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Energy and electron transfer on
titania-silica binary oxides

By

Anisoara Vancea

A Doctoral Thesis

Submitted in partial fulfillment of the requirements for the Award of
Doctor of Philosophy of Loughborough University

August 30th, 2012

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# Table of contents

Abstract ............................................................................................................................. i

Research aims ................................................................................................................... iii

Glossary of terms ............................................................................................................. iv

1. **Introduction and theory** ...................................................................................... 1
   1.1 Principles of photochemistry ........................................................................... 1
       1.1.1 Spin multiplicity ..................................................................................... 5
       1.1.2 Franck-Condon principle ....................................................................... 7
       1.1.3 Energy distribution in the excited molecule.......................................... 8
       1.1.4 Spin-orbit coupling ................................................................................ 14
       1.1.5 Delayed fluorescence ............................................................................. 15
   1.2 Energy transfer ................................................................................................. 18
       1.2.1 Radiative energy transfer ....................................................................... 18
       1.2.2 Collisional (exchange) mechanism........................................................ 19
       1.2.3 Coulombic mechanism ........................................................................... 21
   1.3 Electron transfer ............................................................................................... 22
       1.3.1 Marcus theory ........................................................................................ 24
   1.4 Reflectance spectroscopy ................................................................................. 27
       1.4.1 Kubelka-Munk theory ............................................................................ 30

2. **Techniques and instrumentation** ......................................................................... 33
   2.1 UV-VIS absorption spectroscopy technique .................................................... 33
   2.2 Fluorescence emission technique ..................................................................... 34
   2.3 Ground state diffuse reflectance technique...................................................... 35
   2.4 Laser flash photolysis technique ...................................................................... 36
       2.4.1 Lasers ..................................................................................................... 38
           2.4.1.1 Types of laser systems................................................................. 40
       2.4.2 The optical cavity ................................................................................... 42
       2.4.3 Q-switching ............................................................................................ 44

3. **Photochemistry of and on solid substrates** .......................................................... 48
   3.1 Properties of silica surface ............................................................................... 48
   3.2 Properties of titania-silica surface ................................................................... 52
   3.3 Photochemistry of polycyclic aromatic hydrocarbons ..................................... 59
       3.3.1 Photochemistry of anthracene ................................................................ 59
       3.3.2 Photochemistry of azulene and perylene ............................................... 65
   3.4 Energy and electron transfer on surfaces ......................................................... 69
   3.5 Photocatalytic properties of titania and titania-silica mixed oxides ................. 75

4. **Experimental** ........................................................................................................ 85
   4.1 Materials .......................................................................................................... 85
   4.2 Preparation of silica gel .................................................................................... 85
       4.2.1 “Dropwise” method ............................................................................... 85
   4.2.2 Sol-gel method ............................................................................................ 86
   4.3 Preparation of titania-silica binaries ................................................................. 86
       4.3.1 “Dropwise” method ............................................................................... 86
4.3.2 Sol-gel method....................................................................................... 87
4.4 Calcination....................................................................................................... 87
4.5 Physico-chemical characterization................................................................... 88
  4.5.1 $^{29}$Si solid state NMR spectroscopy........................................................ 88
  4.5.2 Fourier transformation infrared spectroscopy (FTIR)................................... 88
  4.5.3 The Brunauer–Emett–Teller (BET) surface area.................................... 89
4.6 Sample preparation.......................................................................................... 89
  4.6.1 Anthracene adsorbed on silica surface................................................... 89
  4.6.2 Anthracene (9-anthracenecarboxylic acid) co-adsorbed with radical cation quencher on silica sol-gel........................................................ 90
  4.6.3 Anthracene adsorbed on titania-silica surface (TiSi_1 and TiSi_2)............ 90
  4.6.4 Anthracene (9-anthracenecarboxylic acid) co-adsorbed with radical cation quencher on TiSi_2 surface........................................................ 90
  4.6.5 Photocatalytic activity measurements.................................................... 91
4.7 Solution ground state absorption spectra......................................................... 91
4.8 Fluorescence emission spectra......................................................................... 92
4.9 Ground state diffuse reflectance spectra.......................................................... 92
4.10 Laser flash photolysis..................................................................................... 92
4.11 Data analysis.................................................................................................. 93
  4.11.1 Dispersive kinetic model...................................................................... 97
5. Physico-chemical characterization.................................................................... 100
  5.1 $^{29}$Si solid state NMR data................................................................................. 101
  5.2 FTIR spectra.................................................................................................... 104
  5.3 Surface properties (BET surface area)............................................................. 106
6. Results and discussion...................................................................................... 110
  6.1 Anthracene adsorbed on TiSi_1 and TiSi_2 surfaces...................................... 110
    6.1.1 Ground state diffuse reflectance spectra................................................ 110
    6.1.2 Fluorescence emission spectra............................................................... 114
    6.1.3 Transient absorption spectra................................................................. 117
    6.1.4 Kinetics analysis.................................................................................... 123
      6.1.4.1 Triplet state kinetics..................................................................... 124
      6.1.4.2 Radical cation decay kinetics....................................................... 129
    6.1.5 Conclusions............................................................................................ 134
  6.2 Anthracene co-adsorbed with azulene on silica sol-gel and TiSi_2 surfaces.. 135
    6.2.1 Ground state diffuse reflectance spectra................................................ 136
    6.2.2 Fluorescence emission spectra............................................................... 138
    6.2.3 Transient absorption spectra................................................................. 141
    6.2.4 Kinetics of energy and electron transfer................................................ 144
    6.2.5 Activation energies for energy and electron transfer in a bimolecular system on silica sol-gel and TiSi_2 surfaces......................................... 156
  6.3 9-Anthracenecarboxylic acid co-adsorbed with azulene and perylene on silica sol-gel and TiSi_2 surfaces.......................................................... 161
    6.3.1 Ground state diffuse reflectance spectra................................................ 163
    6.3.2 Fluorescence emission spectra............................................................... 166
    6.3.3 Transient absorption spectra................................................................. 170
    6.3.4 Kinetics of energy and electron transfer................................................ 175
    6.3.5 Activation energies for electron transfer in a termolecular system on silica sol-gel and TiSi_2 surfaces.......................................................... 183
Abstract

Steady state reflectance and emission characteristics of anthracene adsorbed on silica gel and titania-silica mixed oxides have been investigated as a function of sample loading. Titania-silica mixed oxides with 1, 3, 5 and 10 wt. % TiO$_2$ were prepared by two different methods: a “dropwise” method and a sol-gel route. Ground state diffuse reflectance and fluorescence emission spectra of anthracene adsorbed on titania-silica surfaces show a dependence on titania content. The absorption peaks of anthracene are difficult to resolve at higher titania content due to the increasing red-shift of the titania absorption edge. The absorption edge of titania is shifted to longer wavelengths and the band gap energy decreases with increasing the titania loading. Diffuse reflectance laser flash photolysis at 355 nm produces both the triplet and radical cation of anthracene and gives relevant information regarding the photochemical transients and the kinetics details of the surface photochemical processes. Energy dependence studies confirm the monophotonic nature of the triplet production, whereas the anthracene radical cation is formed by monophoton or multiphoton ionisation in the mixed titania-silica systems.

Energy and electron transfer reactions of anthracene co-adsorbed with azulene as electron donor on silica sol-gel and titania-silica mixed oxides prepared by the sol-gel method with different titania content have been studied using the time-resolved diffuse reflectance laser flash photolysis technique. The fluorescence of excited anthracene adsorbed on silica sol-gel is quenched by the addition of azulene, while co-adsorption of azulene on titania-silica mixed oxides resulted in a decrease in the fluorescence intensity of the adsorbed anthracene due to the formation, at the same time, of anthracene radical cation and Ti$^{3+}$ species on the titania-silica surface. Triplet-triplet energy transfer from the excited anthracene to ground state azulene and electron transfer from azulene to the anthracene radical cation have been investigated using a time-resolved diffuse reflectance laser flash photolysis technique following laser excitation at 355 nm. Bimolecular rate constants for energy and electron transfer between anthracene and azulene have been obtained. Kinetic analysis of the decay of the anthracene triplet state and radical cation show that the kinetic parameters depend on the titania content of the sample and the azulene concentration. This indicates that the rate of energy and electron transfer reactions increases as a function of azulene concentration and decreases with...
increasing titania content in titania-silica mixed oxides, whereas the observed rate of reaction on silica sol-gel is predominantly governed by the rate of diffusion of azulene.

Electron transfer reactions in a ternary system using azulene for hole transfer between 9-anthracenecarboxylic acid radical cation as electron acceptor and perylene as electron donor were also studied in order to demonstrate the mobility of radical cations on the silica sol-gel and titania-silica surfaces. The co-adsorption of azulene as a molecule shuttle with 9-anthracenecarboxylic acid and perylene on both silica sol-gel and titania-silica systems has been shown to enhance the rate of electron transfer in this ternary system.

Activation energies for energy and electron transfer on photoinduced bimolecular and termolecular processes on silica sol-gel and titania-silica mixed oxides have been measured. In bimolecular anthracene / azulene systems, at higher azulene loadings, the activation energies and the pre-exponential factors on titania-silica surfaces are the same for both energy and electron transfer and are comparable with the parameters extracted for azulene diffusion on silica Davisil suggesting that azulene diffuses across the silica Davisil and titania-silica mixed oxides surfaces, while at lower azulene loadings, ion-electron recombination dominates and the activation energy extracted is for this process. In a ternary 9-anthracenecarboxylic acid / azulene / perylene system, the activation energy for perylene diffusion is higher than that observed for the anthracene / azulene system, reflecting the lower mobility of the perylene molecule.

In this study, a series of titania-silica samples with different loadings of titania (1 – 10 wt. %) prepared by the sol-gel method and also the pure TiO₂ P25 Degussa have been used to study the photocatalytic degradation of 4-chlorophenol in aqueous solution under UV light irradiation. The absorption peak of 4-chlorophenol at 280 nm decreases with increasing titania content and finally disappeared suggesting that titania has a positive influence on the degradation of 4-chlorophenol. The investigated titania-silica mixed oxides prepared by the sol-gel method are less efficient photocatalysts for the degradation of 4-chlorophenol than TiO₂ P25.
Research aims

The photochemistry and photophysics of anthracene adsorbed to the titania-silica mixed oxide surfaces prepared by two different methods: a “dropwise” route and a sol-gel synthesis has been the subject of this work. Steady state absorption and emission characteristics of anthracene adsorbed on titania-silica surface at different titania content have been investigated as a function of anthracene loading. The mobility of adsorbed molecules on the oxide surfaces has been studied through both energy and electron transfer reactions. Photoinduced reactions on titania-silica surface involve energy and electron transfer between the co-adsorbed molecules or between an adsorbate and the surface. Triplet state and radical cation formation of anthracene and 9-anthracenecarboxylic acid adsorbed on titania-silica mixed oxides has been investigated using a nanosecond diffuse reflectance laser flash photolysis technique. Energy and electron transfer reactions of these compounds with co-adsorbed azulene and perylene have been studied. Triplet energy transfer from anthracene and its derivative to azulene and the electron transfer from azulene to the anthracene radical cation or to 9-anthracenecarboxylic acid radical cation have been investigated in order to distinguish between diffusional and energetic control in these systems. Bimolecular rate constants for energy and electron transfer between anthracene (and its derivative) and azulene or perylene have been obtained. Activation energies for energy and electron transfer in bi- or termolecular systems have also been measured in order to demonstrate the diffusion of azulene and its radical cation on the titania-silica surfaces.

Also, a study was undertaken to investigate the photodegradation performance of 4-chlorophenol using titania-silica binaries with 1, 3, 5 and 10 wt. % titania prepared by the sol-gel method and the pure TiO$_2$ P25 Degussa.
Glossary of terms

$E$ = energy of photon

$h$ = Planck’s constant (6.63 x $10^{-34}$ J s)

$\nu$ = frequency of radiation (Hz)

$c$ = velocity of light in a vacuum (2.998 x $10^{8}$ m s$^{-1}$)

$\lambda$ = wavelength of radiation

$A$ = absorbance

$I_o$ = intensity of the incident radiation

$I_t$ = intensity of the transmitted radiation

$\varepsilon$ = molar absorption coefficient (l mol$^{-1}$ cm$^{-1}$)

$c$ = concentration of sample (mol l$^{-1}$)

$l$ = length of the sample cell (cm)

$\sigma$, $\sigma^*$ = sigma bonding and antibonding molecular orbitals, respectively

$\pi$, $\pi^*$ = pi bonding and antibonding molecular orbitals, respectively

HOMO = highest occupied molecular orbital

LUMO = lowest unoccupied molecular orbital

$\Psi$ = wavefunction

$M$ = spin multiplicity

$S$ = spin angular momentum

$S_0$ = singlet ground state

$S_1$, $S_2$,......$S_n$ = excited singlet states

$T_0$ = lowest triplet state
$T_1, T_2, \ldots, T_n = \text{excited triplet states}$

$v'', v' = \text{vibrational levels corresponding to the ground state and excited state, respectively}$

$\text{IC} = \text{internal conversion}$

$\text{ISC} = \text{intersystem crossing}$

$VR = \text{vibrational relaxation}$

$A = \text{photon absorption (Jablonski diagram)}$

$F = \text{fluorescence (emission)}$

$P = \text{phosphorescence}$

$k_F, k_{IC}, k_{ISC}, k_p = \text{first order rate constants for fluorescence, internal conversion, intersystem crossing and phosphorescence (s}^{-1})$

$\tau^0_r = \text{radiative lifetime of a species (s)}$

$\tau_F, \tau_p = \text{fluorescence and phosphorescence lifetimes (s)}$

$\Phi = \text{quantum yield}$

$\Phi_F = \text{fluorescence quantum yield}$

$\Phi_T = \text{triplet quantum yield}$

$^1M^* (S_1), ^3M^*(T_1) = \text{molecule in the excited singlet state and in the triplet state, respectively}$

$D, A = \text{ground state of the donor and acceptor, respectively}$

$D^*, A^* = \text{electronically excited donor and acceptor}$

$E_D^*, E_A^* = \text{energy of the excited donor and acceptor, respectively}$

$\Delta G^{\circ}_{et} = \text{free energy change for electron transfer (J mol}^{-1})$
\[ \Delta G^* = \text{free energy of activation for forward electron transfer} \]

\[ F = \text{Faraday constant (9.6485 x } 10^4 \text{ Coulomb mol}^{-1}) \]

\[ E_{D}^{ox}, E_{A}^{red} = \text{oxidation and reduction potentials of the donor and acceptor (volt)} \]

\[ \Delta \omega = \text{electrostatic work term} \]

\[ k_{et} = \text{rate constant for electron transfer (s}^{-1}) \]

\[ Z = \text{bimolecular collision frequency} \]

\[ R = \text{universal gas constant (8.314472 J } K^{-1} \text{ mol}^{-1}) \]

\[ T = \text{thermodynamic temperature (Kelvin)} \]

\[ n_i, n_r = \text{indices of refraction of the incident medium and the refractive medium, respectively} \]

\[ \theta_i, \theta_r = \text{angle of incidence and refraction, respectively} \]

\[ R_{reg} = \text{regular reflectance at the interface between two media} \]

\[ K = \text{Kubelka-Munk absorption coefficient} \]

\[ S = \text{Kubelka-Munk scattering coefficient} \]

\[ R = \text{reflectance of a homogeneous optically thick sample} \]

\[ F(R) = \text{remission function or Kubelka-Munk function} \]

\[ \text{TEOS = tetraethoxysilicate (tetraethyl orthosilicate)} \]

\[ \text{TMOS = tetramethoxysilicate (tetramethyl orthosilicate)} \]

\[ \text{TIP = titanium isopropoxide (iv)} \]

\[ \text{TMPD = N,N,N’,N’-tetramethyl-1,4-phenylenediamine} \]

\[ \text{TPA = triphenylamine} \]

\[ \text{DMA = N,N-dimethylaniline} \]
2-PrOH = 2-propanol (isopropanol)

4-CP = 4-chlorophenol

An = anthracene

Az = azulene

Pe = perylene

9-AnCA = 9-anthracenecarboxylic acid

Si dropwise = silica gel prepared by the “dropwise” method

Si sol-gel = silica gel prepared by the sol-gel method

TiSi_1 = titania-silica mixed oxides prepared by the “dropwise” method

TiSi_2 = titania-silica mixed oxides prepared by the sol-gel method

CB = conduction band

VB = valence band

$^{29}$Si DP-MAS NMR = direct polarization magic angle spinning nuclear magnetic resonance

$^{29}$Si CP-MAS NMR = cross polarization magic angle spinning nuclear magnetic resonance

FTIR = Fourier transformation infrared spectroscopy

$C, C_0$ = transient concentrations at times $t = t$ and $t = 0$ after laser pulse

$\Delta R, \Delta R_0$ = reflectance changes at times $t = t$ and $t = 0$ (relative to the laser pulse)

Q = quencher molecule

$[Q]$ = concentration of quencher molecule

$\gamma$ = width of the distribution
\( k \) = mean rate constant (s\(^{-1}\))

\( k_o \) = unquenched rate constant (s\(^{-1}\))

\( k_q' \) = bimolecular quenching rate constant (g mol\(^{-1}\) s\(^{-1}\))

An / TiSi\(_1\) = anthracene adsorbed on titania-silica mixed oxides surface prepared by the “dropwise” method

An / TiSi\(_2\) = anthracene adsorbed on titania-silica mixed oxides surface prepared by the sol-gel method

AnAz / Si sol-gel = anthracene co-adsorbed with azulene on silica gel prepared by the sol-gel method

AnAz / TiSi\(_2\) = anthracene co-adsorbed with azulene on titania-silica mixed oxides surface prepared by the sol-gel method

9-AnCAAzPe / Si sol-gel = 9-anthracenecarboxylic acid co-adsorbed with azulene and perylene on silica gel prepared by the sol-gel method

9-AnCAAzPe / TiSi\(_2\) = 9-anthracenecarboxylic acid co-adsorbed with azulene and perylene on titania-silica mixed oxides surface prepared by the sol-gel method

AnT = anthracene triplet state

An.\(^+\) = anthracene radical cation

9-AnCAT = 9-anthracenecarboxylic acid triplet state

9-AnCA.\(^+\) = 9-anthracenecarboxylic acid radical cation

Pe.\(^+\) = perylene radical cation

PTT = pre-treatment temperature (Celsius)

\( A \) = pre-exponential factor in the Arrhenius equation (s\(^{-1}\))

\( E_a \) = activation energy (KJ mol\(^{-1}\))
Chapter 1. Introduction and theory

1. Introduction and theory

1.1 Principles of photochemistry

Photochemistry is the study of chemical changes which occur due to the interaction of ultra violet (UV) or visible light with a molecule. Light is a form of electromagnetic radiation which consists of an oscillating electric field and an oscillating magnetic field, operating in planes perpendicular and traveling in space at right angles to one another. Absorption of light can promote a molecule to a number of electronically excited states, each with its own characteristic properties and electron distribution. As a result, molecules in electronically excited states may have different chemical and physical properties than their electronic ground states and the products of these reactions may be very different from those obtained from thermally activated processes. The major difference is due to the different electronic distribution between the ground state and the excited states of a molecule in a photochemical reaction which may cause an alteration in the chemical behaviour. A second major difference is the thermodynamics; since an electronically excited state of a molecule has a higher internal energy and is a better electron acceptor and a better electron donor than the ground state, there is a much greater choice of reaction pathways for the excited state due to a higher internal energy of the electronically excited state on thermodynamic grounds.

The energy of electromagnetic radiation is quantized. Light of a given energy will be absorbed by a molecule to produce an electronically excited state; the energy of this quantum of light will be equal to the excitation energy of each of the excited molecules. Moreover, each photon has a discrete amount of energy, which can be calculated from the Planck–Einstein equation (1.1):

\[ E = h \nu \]  

(1.1)

where \( E \) is the energy of photon, \( h \) is Planck’s constant \( (6.63 \times 10^{-34} \text{ J s}) \) and \( \nu \) is the frequency of radiation (Hz). Another form to express the equation (1.1) is given by equation (1.2), which can show the relation between the wavelength and the frequency of radiation:

\[ E = h \frac{c}{\lambda} \]  

(1.2)
where \( c \) is the velocity of light in a vacuum (2.998 \( \times \) 10\(^8\) m s\(^{-1}\)) and \( \lambda \) is the wavelength (m).

The bulk absorption of radiation which can promote a molecule from the ground state to an excited state or from the excited state to a higher excited state can be represented by equation (1.3) called the Beer-Lambert law:

\[
A = \log_{10} \frac{I_0}{I_t} = \varepsilon cl
\]

In this equation, the absorbance, which is a measure of the amount of radiation that is absorbed is represented by \( A \), \( I_0 \) is the intensity of the incident monochromatic radiation, \( I_t \) represents the intensity of transmitted radiation, \( c \) is the concentration of sample in mol l\(^{-1}\), \( l \) represents the length of the sample cell in cm and \( \varepsilon \) is the molar absorption coefficient (1 mol\(^{-1}\) cm\(^{-1}\)) and defines how strongly a substance absorbs light at a given wavelength.

The Beer-Lambert law is only true for monochromatic light, which is light of a single wavelength or narrow band. The fraction of radiant energy transmitted by a given thickness of the absorbing medium is independent of the intensity of the incident radiation provided that the radiation does not alter the physical or chemical state of the medium. When monochromatic radiation passes through a homogeneous solution in a cell, the intensity of the emitted radiation depends upon the thickness (\( l \)) and the concentration (\( c \)) of the solution.

A molecular orbital is used to describe the electronic structure of a molecule. Molecular orbitals are obtained by combining the atomic orbitals of the atoms in the molecule. According to Pauli’s principle, the maximum number of electrons in each molecular orbital is two (the spins of electrons are paired). A bonding molecular orbital (\( \sigma \) or \( \pi \)) is more stable and of lower energy than that of the constituent atomic orbitals. The energy of the antibonding orbitals (\( \sigma^* \) or \( \pi^* \)) is higher than the atomic orbitals from which they are formed, whereas a non–bonding orbital (\( n \)) has the same energy as the constituent atomic orbitals. The electrons are placed in the orbitals in the order of increasing energy, in order to form the ground state. An excited state is formed when one or more electrons are displaced to form other orbitals.
The most common electronic transitions characteristics of an organic molecule are: \( \pi \rightarrow \pi^* \), \( n \rightarrow \pi^* \) and \( n \rightarrow \sigma^* \). In \( \pi \rightarrow \pi^* \) transitions, an electron is promoted from \( \pi \) orbital to an antibonding \( \pi^* \) orbital. The transition is denoted \( \pi \rightarrow \pi^* \) and the state is symbolized \( (\pi, \pi^*) \) reflecting the location of the now unpaired electrons. On the same principle, an aliphatic aldehyde or ketone loses an electron from its \( n \) orbital which will then be promoted to a \( \pi^* \) orbital. In this case, the involved transition is \( n \rightarrow \pi^* \) and the excited states arising from this transition are usually labelled according to the transition which form them, e.g. an \( n \rightarrow \pi^* \) transition gives rise to a singlet or a triplet state.

In a \( \pi \rightarrow \pi^* \) transition, the absorption band can usually be seen in the spectral range 200 – 700 nm. For allowed \( \pi \rightarrow \pi^* \) transitions in alkenes, dienes or carbonyl compounds \( \varepsilon_{\text{max}} \) is large \( (10^3 - 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}) \), while for intramolecular charge-transfer transitions \( \varepsilon_{\text{max}} \) is very large \( (10^4 - 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}) \) and the absorption band shows a pronounced red shift as the solvent polarity increases. In conjugated molecules, if the conjugated double bonds increase, the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) decreases and \( (\pi \rightarrow \pi^*) \) transition occurs at longer wavelengths (figure 1.2).
n→π* transitions are characteristic of molecules which have double bonds and contain an heteroatom (e.g C = O, C = N, C = S, N = N, N = O). The absorption intensity is low for these transitions.

n→σ* transitions correspond to compounds with heteroatoms and they depend on the nature and the electronegativity of the heteroatom. The absorption is weak and can be expected in the spectral range 180 – 260 nm.

Wavefunctions Ψ are used to define the probability of the presence of a particle at space coordinates x, y, z through its square Ψ²(x, y, z). The square of the wavefunction shows the distribution density of electrons and nuclei. Wavefunctions describe the energy state and can be separated into electronic and vibrational components denoted by φ and λ respectively.

Figure 1.2: Orbital energies for butadiene.1
1.1.1 Spin multiplicity

The orbitals of an excited state have two unpaired electrons of the same spin (parallel) or of different spin (opposed). The spin quantum number of electrons in a molecule is $\pm 1/2$ and can have two orientations depending on the electrons alignment on the specified axis. The vector sum of all contributions for each electron is called spin angular momentum ($S$) of a molecule. The spin multiplicity which represents the number of possible orientations of the spin angular momentum, is given by the equation (1.4):

$$M = 2S + 1$$  \hspace{1cm} (1.4)

where $M$ represents the spin multiplicity and $S$ is the spin angular momentum.

Molecules of which electrons have paired spins possess $S = 0$ and a spin multiplicity of 1 are termed singlet state. A molecule with $S = 1/2$, according to equation (1.4) will have a spin multiplicity of 2. This means that it will be a doublet. For a molecule with $S = 1$, the spin multiplicity is 3, the resulting state is a triplet state and the electrons have parallel spins.

The symbol used to represent a singlet ground state is $S_0$ and exited singlet states are designated $S_1, S_2, \ldots S_n$, the subscript denoting increasing energy. Accordingly, the lowest triplet state is $T_0$ (if the molecule has a triplet ground state) and the higher excited triplets are $T_1, T_2$, etc. Not many molecules have a triplet ground state, one of the few molecules that does is molecular oxygen ($O_2$) due to the two unpaired electrons in its outer shell.

The electron spin has two orientations: up ($\uparrow$) and down ($\downarrow$). According to the Pauli exclusion principle, an orbital can be occupied only with two electrons of opposite spin. The electrons of a molecule from the ground state will be paired, so, the ground state will typically be a singlet state (exception e.g $O_2$). In a singlet excited state ($S = 0, M = 1$) and respectively, in a triplets state ($S = 1, M = 3$), the electrons reverse the spin orientation as in figure 1.3.
Figure 1.3: Schematic arrangements of singlet and triplet excited states.

The possible configurations of the spin vectors for two electrons are shown in figure 1.4. The singlet state may have only one possible spin vector representation (out of phase), while triplet states have three possible orientations (in phase).

Figure 1.4: Spin multiplicity diagram for singlet and triplet states.

Triplet states are found to have lower electronic energy than corresponding singlet states derived from the same orbital configuration. This is because electrons having the same set of quantum numbers cannot share the same region of space and so in the triplet state, electron motion is correlated in a fashion which minimises electron–electron repulsion. This correlation is not required for singlet states which have a spin paired configuration.

The spin selection rule for all chemical reactions can be expressed as follows: in any allow electronic energy transfer process, the overall spin angular momentum of the system should not change. This statement is known as Wigner’s spin conservation rule.
Chapter 1. Introduction and theory

The rule is applicable whether the transfer occurs between an excited atom or a molecule and another molecule in its ground state or in the excited state.

Wigner’s spin conservation rule requires that there must be a correlation of the spins between the reactants and the products. In particular, a singlet precursor can only form a singlet product in an elementary step that makes or breaks a bond, and a triplet precursor can only form a triplet product in an elementary step that makes or breaks a bond.

The Wigner’s spin rule is used to predict the outcome of photophysical processes such as: allowed electronic states of triplet-triplet annihilation processes, electronic energy transfer by exchange mechanism, etc.

1.1.2 Franck-Condon principle

A molecule can absorb visible or ultraviolet light which may induce an electronic transition from the ground state to an excited state. Moreover, this molecule does not change the geometry during the excitation, and will have the same internuclear distance after light absorption as it has in the ground state. In accordance with figure 1.5, \( v'' \) and \( v' \) represent the vibrational levels corresponding to the ground state and the excited state respectively. The wavefunctions corresponding to each vibrational level are designated by the oscillating curves. Also, the parabolic curves from this figure represent the potential energy for varying internuclear separations. The vertical transition between the ground state and the electronically excited state corresponds to the Franck-Condon transition. The overlap of the wavefunctions between these two states will determine the intensity of the transition. The total transition probability is proportional to the square of the transition moment.

Figure 1.5 illustrates the two different situations that arise in a molecule: a) when the nuclear geometries of the ground and the excited states are very similar and b) when the equilibrium geometry in the excited state is different compared to the ground state. In case (a) it can be seen that (0,0) transitions are the strongest, in both absorption and emission, while in case (b) the most intense transition will occur from the lowest vibrational energy level of the ground state to a vibrational state of higher electronic state. The stronger vibrational transition corresponding to absorption process in this
diagram is expected to be from $v'' = 0$ to $v' = 2$; the same rationale is applied to the emission process.

![Diagram showing transitions between states of similar and different equilibrium nuclear geometry.]

**Figure 1.5**: (a) Transition between states of similar equilibrium nuclear geometry. (b) Transition between states of different equilibrium nuclear geometry.

1.1.3 **Energy distribution in the excited molecule**

There are two types of transitions which can be described as radiative or non-radiative and can be spin allowed or spin forbidden. Selection rules indicate whether a transition between two states is likely to occur. A radiative transition involves the emission of electromagnetic radiation from a molecule to return the ground state; the spin selection rule for this transition is $\Delta S = 0$. The non-radiative transitions occur between states of
either the same or different multiplicity and will take place without emission of electromagnetic radiation.

For a transition to be allowed there must be a good spatial overlap between the orbitals of the state involved. Therefore $\pi \rightarrow \pi^*$ is allowed whereas $n \rightarrow \pi^*$ is forbidden. The transition moment in allowed transitions is non-zero in contrast to forbidden transitions which have small intensities and are observed as weak transitions. The intensity of a forbidden transition is dependent on the degree of spin-orbit coupling which is discussed below in section 1.1.4.

The Jablonski diagram (figure 1.6) can be used to describe the energy distribution and photophysical processes which can occur in the excited molecule. In this figure, the symbols $S_0$, $S_1$ and $S_2$ represent the ground state and first and second excited singlet states (electron spin antiparallel or paired), respectively, $T_1$ and $T_2$ represent the triplet states (electron spins parallel or unpaired). The singlet and triplet states are arranged in order of increasing energy. The lowest triplet ($T_1$) level is placed below the lowest excited singlet level ($S_1$), in according with Hund’s rule. The radiative transitions are designated by straight lines, whereas the non radiative transitions between states of different multiplicity are symbolized by dashed lines. These transitions are described in detail below.
1. $S_0 \rightarrow S_1$ (*Absorption of light*)

This is a spin allowed transition and corresponds to absorption of a photon by the ground state ($S_0$) to produce an excited singlet state ($S_1$) or from an excited singlet state to a higher excited state ($S_2$).

2. $S_1 \rightarrow S_0$ (*Fluorescence emission*)

Fluorescence is a radiative transition which is spin allowed and occurs between states of like multiplicity. There are two types of fluorescence: prompt and delayed. The latter will be discussed in section 1.1.5. The prompt fluorescence occurs when the molecule returns to the electronic ground state ($S_0$), from the excited singlet state ($S_1$), by emission of a quantum of light.
Kasha’s rule states “the emitting electronic energy level of a given spin multiplicity is the lowest excited energy level of that multiplicity”. There are a few exceptions to this rule, fluorescence in both azulene\textsuperscript{2,3} and thioketones\textsuperscript{4} has been shown to occur from the $S_2$ state.

The singlet excited states exist for a finite time ($1 – 10$ ns). The energy of the excited state is partially dissipated. The energy of the emitted photon and the wavelength are lower than the energy and the wavelength corresponding of the excitation photon.

3. $S_2 \rightarrow S_1$, $T_2 \rightarrow T_1$ and $S_1 \rightarrow S_0$ (Internal conversion)

Internal conversion occurs from the lowest vibrational level of the higher state to an isoenergetic vibrational level of the lower state (the transition is horizontal). This is a non radiative transition which involves no change in the spin multiplicity of the excited electron. In this process, the excess of energy is lost as heat by collision with other molecules (e.g. solvent). The $S_1 \rightarrow S_0$ conversion involves larger amount of energy than the $S_2 \rightarrow S_1$ or $T_2 \rightarrow T_1$ conversion because the energy gap between $S_1 \rightarrow S_0$ is larger than of any other states.

4. $S_1 \rightarrow T_1$, $S_2 \rightarrow T_2$ and $T_1 \rightarrow S_0$ (Intersystem crossing)

Intersystem crossing involves the transfer of population between states of different spin multiplicity. This is a forbidden transition and it is less probable to occur than the internal conversion since it involves a spin inversion, but the transition can be possible by the effect of spin orbit coupling (described in section 1.1.4). The energy of the triplet state is less than the energy of the excited singlet state. The most important transitions take place from $S_1$ to $T_1$ and from $T_1$ to $S_0$. The transition from $T_1$ to $S_0$ is more efficient when the energy gap between these two states is small due to more favourable Franck-Condon factors.

5. $T_1 \rightarrow S_0$ (Phosphorescence)

A molecule in the excited triplet state can lose the energy by emission of a photon and it is returned to the ground state. This radiative transition between states of different multiplicity (triplet to singlet) is known as phosphorescence and will take place with change in the total electron spin. Phosphorescence is a spin forbidden process.
The energy of this transition is less than the energy corresponding to the fluorescence transition, and the phosphorescence emission can be observed at longer wavelength than the fluorescence emission band.

For these processes described earlier, some equations can be written below (table 1.1).

<table>
<thead>
<tr>
<th>Transition</th>
<th>Rate constant / sec⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Absorption of light</td>
<td>( I_a )</td>
</tr>
<tr>
<td>( A + h\nu \rightarrow ^1A^* )</td>
<td></td>
</tr>
<tr>
<td>2. Fluorescence emission</td>
<td>( k_f = 10^7 - 10^9 )</td>
</tr>
<tr>
<td>( ^1A^* \rightarrow ^1A + h\nu )</td>
<td></td>
</tr>
<tr>
<td>3. Internal conversion</td>
<td>( k_{ic} = 10^{11} - 10^{14} ) for ( S_2 \rightarrow S_1 ) transition</td>
</tr>
<tr>
<td>( ^1A^* \rightarrow ^1A )</td>
<td>( k_{ic} = 10^5 - 10^8 ) for ( S_1 \rightarrow S_0 ) transition</td>
</tr>
<tr>
<td>4. Intersystem crossing</td>
<td>( k_{isc} = 10^7 - 10^9 )</td>
</tr>
<tr>
<td>( ^1A^* \rightarrow ^3A^* )</td>
<td></td>
</tr>
<tr>
<td>( ^3A^* \rightarrow ^1A )</td>
<td></td>
</tr>
<tr>
<td>5. Phosphorescence</td>
<td>( k_p = 10^{-1} - 10^4 )</td>
</tr>
<tr>
<td>( ^3A^* \rightarrow ^1A + h\nu )</td>
<td></td>
</tr>
</tbody>
</table>

*Table 1.1: Electronic transitions in an excited molecule and the rate constants corresponding to these transitions.*

where: \(^1A^*\) and \(^3A^*\) are the lowest excited singlet and triplet states.

In accordance with the table 1.1, the values of the rate constants for radiative transitions are lower than the rate constants of non radiative transitions. The radiative lifetime of a species \( \tau^0_r \) either fluorescence or phosphorescence can be calculated by using the following equation:

\[
\tau^0_r = \frac{1}{k_r}
\]  

(1.5)
where \( k_r \) is the radiative rate constant for spontaneous emission.

The radiative lifetimes for both fluorescence and phosphorescence are shown in table 1.2.

<table>
<thead>
<tr>
<th>Excited states</th>
<th>Radiative lifetimes / s</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \tau_r^0 (S_i =^1 (\pi, \pi^*)) )</td>
<td>( 10^{-9} )</td>
</tr>
<tr>
<td>( \tau_r^0 (S_i =^1 (n, \pi^*)) )</td>
<td>( 10^{-6} )</td>
</tr>
<tr>
<td>( \tau_r^0 (T_i =^3 (n, \pi^*)) )</td>
<td>( 10^{-2} )</td>
</tr>
<tr>
<td>( \tau_r^0 (T_i =^3 (\pi, \pi^*)) )</td>
<td>( 10 )</td>
</tr>
</tbody>
</table>

*Table 1.2: The radiative lifetimes of fluorescence and phosphorescence.*

The singlet excited state \( ^1 (\pi, \pi^*) \) has the shortest radiative lifetime since the \( \pi \rightarrow \pi^* \) transition is spin allowed and does not involve a change in orbital configuration. The triplet states have a longer lifetime than the singlet states because relaxation to the singlet ground state is spin forbidden and the transition occurs with change in the spin multiplicity.

The fluorescence and phosphorescence lifetimes can be expressed by following equations (1.6 and 1.7):

\[
\tau_F = \frac{1}{(k_F + k_{ISC} + k_{IC})} \tag{1.6}
\]

\[
\tau_P = \frac{1}{(k_P + k_{ISC})} \tag{1.7}
\]

where \( k_F, k_{IC} \) and \( k_{ISC} \) are the first order rate constants for fluorescence, internal conversion and intersystem crossing respectively.

The quantum yield (\( \Phi \)) of a process can be defined in one or two ways:
Equation (1.8) defines the quantum yield as a ratio of the number of molecules undergoing a process per number of photons absorbed, and equation (1.9) expresses it as a ratio of the rates of the process involved. In the absence of any competing photochemical process, the efficiency of the quantum should be unity. If other processes are in competition then the efficiency will be determined by the relative rates of the competing processes.

The quantum yield of fluorescence ($\Phi_F$) and the triplet formation ($\Phi_T$) can be expressed by following equations (1.10 and 1.11):

$$\Phi_F = \frac{k_F}{k_{IC} + k_F + k_{ISC}}$$  \hspace{1cm} (1.10)

$$\Phi_T = \frac{k_{ISC}}{k_{IC} + k_F + k_{ISC}}$$  \hspace{1cm} (1.11)

These expressions represent a fraction of all competing processes and therefore the sum of all quantum yields must be unity i.e. ($\Phi_{IC} + \Phi_F + \Phi_{ISC}$) = 1.

1.1.4 Spin-orbit coupling

Selection rules give information regarding of the possible transitions of a system from one state to another. In a singlet-singlet transition, the electron has only two spin states. The promoted electron does not change its spin state, the transition moment is non-zero and the singlet-singlet transition is fully allowed. The triplet-triplet transition is also fully allowed because the transition occurs with no change in multiplicity and the transition moment is non-zero. In contrast to allowed transitions, the forbidden transitions occur with a change in multiplicity. In a singlet-triplet transition, which is strongly forbidden,
an electron undergoes spin inversion, the transition moment is zero and the transition occurs due to spin-orbit coupling.

Spin-orbit coupling arises when the spin of the electron is affected by the electron’s orbital motion. As a result of the coupling between spin and orbital angular momentum, the singlet states have some triplet character and the triplet states have some singlet character.

The presence of heavy atoms like iodide, bromide or xenon in the molecule or solvent can enhance the probability of singlet-triplet transitions. These atoms with their large nuclear charge generate strong interactions between the spin angular momentum and the orbital angular momentum of the electron, i.e. spin-orbit coupling. This is the internal heavy atom effect. The external heavy atom effect occurs when a heavy atom is added to the molecule to form a weak transient complex. This means that the triplet state acquires some singlet character and conversely the singlet state acquires some triplet character. In light atoms there can be some interactions between spin angular momentum and orbital angular momentum of the electron and the transition between states can occur with a small probability compared with the case when heavier atoms are employed.

1.1.5 Delayed fluorescence

Delayed fluorescence is the process in which the molecules emit the same fluorescence spectra but with much longer decays and often with complex non-exponential kinetics.

Two types of delayed fluorescence are known:

a) **E-type delayed fluorescence** known also as thermally activated delay fluorescence is the process in which the first excited singlet state becomes populated by a thermally activated non radiative transition from the first triplet state. This is shown schematically in figure 1.7.
Chapter 1. Introduction and theory

Figure 1.7: Diagram to illustrate the energy levels for thermally activated delayed fluorescence.

Light absorption followed by intersystem crossing and vibrational relaxation gives triplets which by a thermally activated radiationless transition (reverse intersystem crossing) from T\textsubscript{1} to S\textsubscript{1} state gives excited singlets which then fluoresce. This process only occurs when the S\textsubscript{1} - T\textsubscript{1} gap is small enough for thermal energies to populate S\textsubscript{1} from T\textsubscript{1}.

E-type delay fluorescence can be represented by the following equation:

\[ ^3A^* + \text{heat} \rightarrow ^1A^* \rightarrow ^1A + h\nu \]

In this process in which the population of the singlet and triplet states are in thermal equilibrium, the lifetimes of delayed fluorescence and the concomitant phosphorescence are equal, but longer than the prompt fluorescence. Also, the prompt and delayed fluorescence emission spectra are identical.

b) P-type delayed fluorescence which arises from triplet-triplet annihilation occurs when the first excited singlet state is populated by interaction of two molecules in the triplet state \(^3M^*(T_1)\) producing one molecule in the excited singlet state \(^1M^* (S_1)\) and the other collapses to the ground state \(M(S_0)\). Once back in the excited singlet state \((S_1)\), emission occurs with the same rate constant as prompt fluorescence.

\[ ^3M^*(T_1) + ^3M^*(T_1) \rightarrow ^1M^*(S_1) + M (S_0) \]
In this process, the life time of delayed fluorescence is half the value of the concomitant phosphorescence.

The following scheme describes the pathways leading to triplet-triplet annihilation:

\[
\begin{align*}
S_0 & \xrightarrow{h\nu} S_1 & \text{Absorption} \\
S_1 & \xrightarrow{k_F} S_0 + h\nu_f & \text{Normal fluorescence} \\
S_1 & \xrightarrow{k_{ISC}} T_1 & \text{Intersystem crossing} \\
T_1 & \xrightarrow{k_p} S_0 + h\nu_p & \text{Phosphorescence} \\
T_1 + T_1 & \rightarrow X & \text{Triplet-triplet annihilation} \\
X & \rightarrow S_1 + S_0 & \text{Back intersystem crossing} \\
S_1 & \xrightarrow{k_F} S_0 + h\nu_f & \text{Delayed fluorescence}
\end{align*}
\]

*Figure 1.8: Mechanism of delay fluorescence via triplet-triplet annihilation.*

The intermediate X in the above mechanism can be an excited dimer or excimer. P-type delayed fluorescence can be detected in gases, solution, rigid glasses or crystals.
1.2 Energy transfer

The transfer of energy from a molecule to another molecule can be represented by the following reaction:

\[ \text{D}^* + \text{A} \rightarrow \text{D} + \text{A}^* \]

where D and A represent the ground state of the donor and the acceptor, respectively, D* and A* are the electronically excited donor and acceptor.

In an energy transfer reaction, an excited molecule (e.g. an excited donor) loses its energy by transferring the energy to another molecule (an acceptor) producing the ground state of the donor, and the excited state of the acceptor. This process is also referred to as a photosensitization reaction; the acceptor becoming “sensitized” to a wavelength of radiation absorbed by the donor. The sensitizer deactivates (quenches) an electronically excited state of another molecule to the ground state or lower electronically excited state by energy or electron transfer.

The excitation energy can be transferred via this mechanism, if the energy of the excited acceptor (E_A*) is lower than the energy of the excited donor (E_D*). Two types of energy transfer can occur: a radiative energy transfer and a non radiative energy transfer which includes the collisional and coulombic mechanism.

1.2.1 Radiative energy transfer

The radiative mechanism for energy transfer can be represented by following reactions:

\[ \text{D} + \text{h} \nu \rightarrow \text{D}^* \]
\[ \text{D}^* \rightarrow \text{D} + \text{h} \nu \]
\[ \text{A} + \text{h} \nu \rightarrow \text{A}^* \]

The donor molecule absorbs energy and it is promoted from the ground state to an excited state. The excited donor loses the energy by emission (fluorescence or phosphorescence), the donor is returned to the ground state and the emitted photon is absorbed by the acceptor molecule producing the excited state of the acceptor. For the
radiative energy transfer to occur, the acceptor must absorb in the wavelength region in which the donor emits. The emission of the donor is not influenced by the presence of the acceptor; the emission is a spontaneous process.

1.2.2 Collisional (exchange) mechanism

The collisional mechanism involves an exchange of electrons from an excited donor molecule to an acceptor and vice versa. This exchange mechanism can be seen in figure 1.9. In accordance with this figure, an electron of an excited donor molecule D* from LUMO (the lowest unoccupied molecular orbital) transfers into the LUMO of the acceptor molecule A, simultaneously, an electron of the acceptor molecule from HOMO (the highest occupied molecular orbital) is transferred to the corresponding orbital of the donor D. This exchange of electrons is a concerted mechanism.

![Diagram of collisional energy transfer](image)

*Figure 1.9: Collisional energy transfer schematic representation.*

The efficiency of the exchange mechanism is increased when the energy gap between the ground state and excited state of the donor is equal or greater than the energy gap between the states of the acceptor molecule.
Chapter 1. Introduction and theory

Figure 1.10: Mechanisms for forming D and A* via electron-exchange processes.

There are two different possibilities of electron exchange and can be seen in figure 1.10. The charge transfer mechanism occurs when the electron is transferred from the LUMO of the donor to the LUMO of the acceptor with formation of a radical ion pair.
Chapter 1. Introduction and theory

The transfer of the electron from the HOMO of the acceptor to the HOMO of the donor involves the production (step 1) of a bonded intermediate (such as diradical or zwitterion) and is followed by the formation of the donor and the excited acceptor (step 2) by a transfer of the electron from LUMO of the donor to LUMO of the acceptor.

The rate of energy transfer can be described by the Dexter\textsuperscript{6} equation:

\[
K_{ET\text{(exchange)}} = KJ \exp\left(-\frac{2R_{D,A}}{L}\right)
\]

where \( K \) is related to the specific orbital interaction, \( J \) represents the normalised spectral overlap integral and \( R_{D,A} \) is the donor-acceptor separation relative to the Van der Waal’s radii \( L \).

Triplet-triplet energy transfer occurs via the exchange energy transfer due to the low value of the molar absorption coefficient \( \epsilon_a \) for the \( S_0 \) to \( T_n \) transition. Triplet-triplet annihilation is another example of collisional exchange mechanism where both the donor and the acceptor in a triplet state interact to produce a molecule in an excited singlet state and another in its ground state.

1.2.3 Coulombic mechanism

The coulombic mechanism does not involve an exchange of electrons between the donor and the acceptor; it depends on the electrostatic interactions. The moving of an electron of the excited donor (\( D^\ast \)) from LUMO to HOMO means a change in dipole moment which will produce an electric field. In this way, a dipole-dipole interaction can occur as a result of the motion coupling of the electrons in the excited donor and of the electrons in the acceptor. This interaction causes the electron in the HOMO of the acceptor A to oscillate leading to the excitation of this electron to the LUMO of the acceptor, with corresponding deactivation of the excited electron in the donor molecule, D (figure 1.11). Energy is transferred without emission of a photon.
The rate of energy transfer can be described by the Förster equation:

\[ k_{ET(Coulombic)} = k \frac{\kappa^2 k^0_D}{R_{DA}^6} J(\varepsilon_A) \]  

where \( k \) is a constant determined by experimental conditions such as refractive index of the solvent and concentration, \( \kappa^2 \) represents the dependence of the interaction between two oscillating dipoles on the orientation of the dipoles in space, \( J \) represents the spectral overlap integral and which depends on the molar absorption coefficient \( \varepsilon_A \) of the acceptor and \( R_{DA} \) is the donor-acceptor separation relative to the Van der Waal’s radii.

Fluorescence quenching occurs via Coulombic mechanism due to the large value of the molar absorption coefficient \( \varepsilon_A \) for the allowed singlet-singlet transitions.

1.3 Electron transfer

Electron transfer reactions can occur in both ground and excited states. In the latter case, the donor molecule (D) is excited with light of suitable frequency prior to transferring an electron to the acceptor (A). In an electron transfer reaction, an electron relocates from an atom or molecule to another atom or molecule and will form an ion pair. If one of the molecules is electronically excited, it will be deactivated and the radical cation may
undergo recombination to return to the ground state. This process can be represented by the following mechanism:

\[ e^- \\
A + h\nu \rightarrow A^+ + D \\
A^+ + D \rightarrow A + D^+ \]

where D is the electron donor and A represents the electron acceptor.

The electron transfer reaction between two molecules can be considered a photochemical reaction, but if one of the molecules is electronically excited it will be deactivated and the process may appear as a quenching if the reactants are restored to their initial states.

The free energy change \( \Delta G_{\text{et}}^0 \) (in J mol\(^{-1}\)) for an electron transfer reaction is determined from the redox potentials of the reactants and is given by equation (1.14):

\[
\Delta G_{\text{et}}^0 = F\left( E_{D}^{\text{ox}} - E_{A}^{\text{red}} \right) + \Delta \omega
\]

where \( F \) is the Faraday constant (9.6485 \( \times \) 10\(^4\) C mol\(^{-1}\)), \( E_{D}^{\text{ox}} \) and \( E_{A}^{\text{red}} \) are the oxidation and reduction potentials of the donor and acceptor (in volts) and \( \Delta \omega \) represents the electrostatic work term.

The efficiency of the electron transfer reaction depends on the oxidation potential of the electron donor which must be lower than the reduction potential of the electron acceptor and also, both the donor and the acceptor must be sufficiently close to form an encounter pair.
1.3.1 Marcus theory

In a homogeneous process, the electron is usually transferred intermolecularly from a single molecular donor (excited) state into a single molecular acceptor state. The dynamics of intermolecular electron transfer can be described using Marcus theory\(^8,^9,^{10}\) of electron transfer.

According to Marcus theory, the nuclear potential energy surfaces for both donor and acceptor states are usually treated as classical harmonic oscillators and the electron transfer can occur at the intersection point of two potential energy surfaces. The potential energy of the precursor (D...A) depends on the nuclear configuration which results in a multidimensional potential energy surface. In Marcus theory, the curvature of the reactant and product surfaces is considered to be the same.

The free energy of activation for forward electron transfer \(\Delta G^*\) is given by equation (1.15):

\[
\Delta G^* = W_r + \frac{1}{4} \left( \lambda + \Delta G_{\text{et}}^0 \right)^2
\]  
(1.15)

where \(W_r\) is the electrostatic work required to bring the reactants together, \(\Delta G_{\text{et}}^0\) represent the free energy change for electron transfer and \(\lambda\) is the reorganisation energy and consists of two components: inner sphere and outer sphere. The inner sphere component of \(\lambda\) is the energy associated with the nuclear configuration changes in both donor and acceptor states, while the outer sphere component accounts for the rearrangement of solvent molecules during the course of the electron transfer.

The rate constant of electron transfer \(k_{\text{et}}\) can be represented as equation (1.16):

\[
k_{\text{et}} = Z \exp \left( -\frac{\Delta G^*}{RT} \right)
\]  
(1.16)

where \(Z\) is the bimolecular collision frequency, \(R\) is the gas constant (8.314472 J K\(^{-1}\) mol\(^{-1}\)), and \(T\) is thermodynamic temperature.
Figure 1.12: Schematic diagrams of the potential energy curves for the reactant and product states in Marcus theory: (a) $\Delta G_{et}^0 = 0$; (b) the normal region where $\Delta G_{et}^0 \neq 0$; (c) $\Delta G_{et}^0 = \lambda$; (d) the “inverted region” where $-\Delta G_{et}^0 > \lambda$.

For a reaction of zero $\Delta G_{et}^0$ (figure 1.12 a), the potential energy of the reactant surface ($D\ldots A$) represented by curve R and the potential energy of the product surface ($D^+\ldots A^-$)
(curve P) are symmetrical. This means that the reactant and product states have the same nuclear configuration.

For reactions where $\Delta G_{et}^0 \neq 0$ (figure 1.12 b), the potential energy curve of product state undergoes a slight modification by $\Delta G_{et}^0$. In this case, the free energy for electron transfer is negative ($\Delta G_{et}^0 < 0$) and smaller than the reorganisation energy ($\Delta G_{et}^0 < \lambda$) and the free energy of activation for forward electron transfer ($\Delta G^+_{et}$) decreases and the rate of electron transfer ($k_{et}$) increases as $\Delta G_{et}^0$ falls to negative values.

When the free energy change for electron transfer becomes equal to the reorganization energy of the system ($-\Delta G_{et}^0 = \lambda$) (figure 1.12 c), there is no energetic barrier to electron transfer, the electron transfer becomes essentially activationless ($\Delta G^+ = 0$) and, as a result, the fastest rate of electron transfer can be achieved.

For more negative values of $\Delta G_{et}^0$ than $\lambda$ ($-\Delta G_{et}^0 > \lambda$), the intersection point of the potential energy of reactant and product is shifted more to left (figure 1.12 d) than in figure 1.12 c. This suggests that, the free energy of activation and the solvent reorganisation energy $\lambda$ increase with increasing of the rate constant. This is called the Marcus “inverted region”.

When the electron transfer rate is plotted against the free energy change for electron transfer (figure 1.13), at the point $-\Delta G_{et}^0 = \lambda$, the rate of electron transfer is maximum.

\[
k_{et} = \max \quad -\Delta G_{et}^0 = \lambda
\]

\[\ln k_{et} \quad -\Delta G_{et}^0
\]

---

Figure 1.13: Schematic representation of the dependence of electron transfer rate upon the free energy change for electron transfer in terms of Marcus theory.
1.4 Reflectance spectroscopy

Reflectance spectroscopy is the study of light that has been reflected or scattered from a solid, liquid or gas. Reflectance measurements are made using both specularly and diffuse reflected light.

Specular reflectance occurs when the light reflected from a sample has an angle of reflectance equal to the angle of incidence of the illuminating light. The amount of light reflected depends on the angle of incidence, the reflective index, surface roughness and absorption properties of the sample. Specular reflectance is used for the measurement of samples whose surface reflects light but shows very little scatter, such as surface treated metals, paints and polymers.

![Figure 1.14](image)

\(\text{Figure 1.14: Light reflection from: (a) smooth surface (specular reflection) and (b) rough surface (diffuse reflection). In both cases the angle of incidence equals the angle of reflection at the point that the light ray strikes the surface.}\)

In diffuse reflectance, energy from the incident beam that penetrates the sample is scattered in all directions from the sample. The reflected light can be collected onto an optical detector; the surface reflectance may be measured either at a given wavelength or by performing a scan over a range of wavelengths. Many samples will give diffusely reflected spectra including powders, fibres or mat surfaced samples such as textiles.

When light passes through an interface between two media at an oblique angle and the media have different reflective indices of reflection, both reflected and refracted lights are produced (figure 1.15). Refraction takes place at the interface between two materials due to a change in the speed of light that passes from one medium to another.
Chapter 1. Introduction and theory

Snell’s law\textsuperscript{11,12} describes the relationship between the angles of incidence and refraction and the indices of refraction of the two media as shown in the following equation:

\[ n_i \sin \theta_i = n_r \sin \theta_r \quad (1.17) \]

where: \( n_i \), \( n_r \) are the indices of refraction of the incident medium and the refractive medium respectively, \( \theta_i \) is the angle of incidence and \( \theta_r \) is the angle of refraction.

If light is travelling from a less reflective medium to a more reflective medium (\( n_r > n_i \)), the refracted ray will be bent towards to normal.

According to Fresnel equations\textsuperscript{11,12}, the regular reflectance \( R_{\text{reg}} \) at the interface between two media can be expressed by following equation:

\[ R_{\text{reg}} = \frac{1}{2} \left[ \frac{\sin^2 (\theta_i - \theta_r)}{\sin^2 (\theta_i + \theta_r)} + \frac{\tan^2 (\theta_i - \theta_r)}{\tan^2 (\theta_i + \theta_r)} \right] \quad (1.18) \]

A matt surface does not have regular reflection. The diffuse reflection arises from penetration of the incident flux into the interior of the sample. It is assumed that a portion of this incident flux penetrates a certain distance into the interior of the sample and that
Reflections occur at every point, while a part of the radiation is returned to the surface through multiple scattering.

Diffuse reflection can be explained by the Bouguer-Lambert law which says that the intensity of reflected light decreases exponentially with increasing penetration depth into the sample and is given by equation (1.19):

\[ I = I_0 \exp[-Kx] \]  

(1.19)

where \( I \) is the intensity of light reflected by the medium, \( I_0 \) represents the intensity of the incident light, \( K \) is the absorption coefficient and \( x \) is the mean penetrated layer thickness.

The Lambert cosine law states that the radiant intensity observed from a matt surface at a particular direction is directly proportional to the cosine of the angle between that direction and the surface normal. According to the Lambert cosine law, the radiation strength of a non-absorbing, matt surface is given by:

\[ B = \left( \frac{I_o}{\pi} \right) \cos \alpha \cos \theta \]  

(1.20)

where \( I_o \) is the incident radiation strength, \( \alpha \) is the angle of incidence and \( \theta \) is the angle of observation.

Equation (1.20) requires that the reflected radiation be distributed symmetrically with respect to the surface normal, without regard to the angle of incidence. Diffusion of light in a matt surface occurs by multiple scattering of the small particles within the interior of the sample distributed at all possible angle with respect to the macroscopic surface. Several theories related to diffuse reflectance have been suggested that both regular and diffuse reflection are always present, the relative proportion of each depending on the nature of the reflecting medium\(^{11} \). The simple approach to the problem of multiple scattering of light is the Kubelka-Munk theory where the differential equations were used to obtain expressions for the diffuse reflectance of a powdered sample in order to solve the problem of the behaviour of light in diffusing media.
1.4.1 Kubelka-Munk theory

The theory which describes the behavior of light travelling inside a light-scattering medium, the relationship between incident and scattered light intensity, absorption and concentration was proposed by Kubelka and Munk\textsuperscript{13,14}. The model of Kubelka and Munk describes the propagation through a medium that absorbs, emits and scatters light. The medium is assumed to be uniform, isotropic and homogeneous and the sample has to be illuminated by diffuse, monochromatic light.

The Kubelka-Munk theory is based on a continuum model (figure 1.16) where the reflectance properties are described by following differential equations:

\[
dI(x) = -(K + S)J(x)dx + SJ(x)dx \tag{1.21}
\]

\[
dJ(x) = +(K + S)I(x)dx - SI(x)dx \tag{1.22}
\]

where \( I \) and \( J \) are the intensities of light travelling inside the sample towards its illuminated and unilluminated surfaces respectively, \( dx \) is the thickness of the layer, \( K \) and \( S \) represent Kubelka-Munk absorption and scattering coefficient respectively. The scattering and absorption coefficients are proportional to the intensities and to the thickness of the layer.

When passing through the layer, light that is absorbed is lost, and some part of the light that is scattered change direction from upwards to downwards, or vice versa, and is exchanged between \( I \) and \( J \).
Figure 1.16: Schematic diagram of the light scattering in a medium layer in Kubelka-Munk model.

It is assumed that two light fluxes $I$ and $J$ propagate in opposite directions through the sample and perpendicular to the irradiated sample surface. The downward flux through a layer of thickness $dx$ is decreased by absorption and scattering processes and increased by scattering process of the light travelling upward towards the surface. Radiant fluxes at $x = 0$ are denoted by $I_{(0)}$ and $J_{(0)}$, where $x$ is the penetration depth and $D$ is the layer thickness.

The above equations by integration using the limits $x = 0$ and $x = x$ and with simple substitution $b = \left(\frac{K^2 + 2KS}{S}\right)^{1/2} = \left(\frac{1}{2R} - R\right)$ reduce to the form:

$$I_{(x)} = I_{(0)} \exp(-bS_x) \quad (1.23)$$

$$J_{(x)} = RI_{(0)} \exp(-bS_x) \quad (1.24)$$

where $R$ is the reflectance of an infinitely thick layer at the illuminated surface ($x = 0$).

At $x = 0$, by division of equation (1.24) by equation (1.23), we can define the reflectance factor $R$ as:
Chapter 1. Introduction and theory

\[ R = \frac{J_0}{I_0} \]  

1.25)

In the limiting case of an infinitely thick sample, thickness and sample holder have no influence on the value of reflectance \( R \). In this case, the Kubelka-Munk equation at any wavelength becomes:

\[
F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{K}{S} 
\]

(1.26)

where \( F(R_\infty) \) is the remission or Kubelka-Munk function. \( K \) and \( S \) are the absorption and scattering coefficients respectively, both of which have units cm\(^{-1}\). For a uniform distribution of absorbers, \( F(R_\infty) \) is a linear function of absorber concentration. This equation only applies to optically thick samples for which any further increase of the thickness does not affect the experimentally determined reflectance.

For an ideal diffuse reflector, the absorption coefficient \( K \) can be related to the concentration \( C \) (in mol \( 1^{-1} \)) of a homogeneously distributed absorber by the equation (1.27):

\[
K = 2\varepsilon C 
\]

(1.27)

where \( \varepsilon \) is the molar Naperian absorption coefficient (in l mol\(^{-1}\) cm\(^{-1}\)).

According to equations (1.26) and (1.27), the remission function can be written as:

\[
F(R_\infty) = \frac{2\varepsilon C}{S} 
\]

(1.28)

The scattering coefficient is inverse proportional to the particle size. In other words, if the particle size increases, the scattering coefficient decreases.
2. Techniques and instrumentation

2.1 UV-VIS absorption spectroscopy technique

UV-Vis spectroscopy can be used to determine the concentration of the absorber in a solution and involves the spectroscopy of photons in the UV-Vis region. An experimental measurement of absorbance is provided by the Beer-Lambert law (equation 2.1) and this method is often used to determine the concentration of the absorber in solution:

\[ A = \log_{10} \frac{I_0}{I_t} = \varepsilon cl \]  

where \( A \) is the absorbance, \( I_0 \) is the intensity of the incident monochromatic radiation, \( I_t \) represents the intensity of transmitted radiation, \( \varepsilon \) is the molar absorption coefficient (1 mol\(^{-1}\) cm\(^{-1}\)), \( c \) is the concentration of sample in mol l\(^{-1}\) and \( l \) represents the length of the sample cell in cm.

A UV-Vis spectrophotometer measures the intensity of light which penetrates the sample and compares it to the intensity of light before it penetrated the sample. The liquid samples for UV-Vis spectroscopy are placed in a glass or quartz cuvette with known path length, typically 10 mm. The cuvette must be transparent to the radiation.

A diode array spectrophotometer (figure 2.1) consists of two light sources: a deuterium arc lamp for consistent intensity in the UV range (190 to 380 nm) and a tungsten-halogen lamp for consistent intensity in the visible spectrum (380 to 800 nm). A polychromatic light passes through the sample and is focused on the entrance slit of the polychromator. The light is then dispersed onto the diode array which each diode measuring a portion of the spectrum. An UV-Vis absorption spectrum is a graph representation of light absorbance versus wavelength in a range of ultraviolet or visible regions.
Chapter 2. Techniques and instrumentation

2.2 Fluorescence emission technique

Fluorescence is the radiative emission from an excited state of the same spin multiplicity as the lower state (the ground state) in the transition. Fluorescence is the result of three processes that can occur in molecules. The first stage consists of creating an excited electronic state \( S_1 \), when a molecule absorbs a quantum of light and it is promoted from the ground state to excited singlet state. The excited state exists for a finite time (1-10 nanoseconds). During this time, the energy of excited state is partially dissipated. The third stage involves the emission of a photon and the molecule is returned to its ground state \( S_0 \).

A fluorescence spectrophotometer (figure 2.2) consists of an excitation source of UV-Vis radiation (for example a xenon or a mercury arc lamp) which is passed through a monochromator to select an excitation monitoring wavelength. A sample placed in quartz cuvette of known path length (10 mm) absorbs the exciting radiation and emits fluorescence. The emission monochromator selects the emission wavelength and records the fluorescence emission spectrum. The emission photons will be then registered by a detector. The graph representation of the emission intensity versus wavelength is a fluorescence emission spectrum.
2.3 Ground state diffuse reflectance technique

A diffuse reflectance technique can be used for measuring powdered and crystalline materials in the UV-Vis spectral range. Also, diffuse reflectance spectrometry can be applied in qualitative and quantitative analysis providing an excellent alternative to transmission spectrometry in measuring the infrared spectrum of samples in dark colour or samples which are not suitable for the preparation of a transparent potassium bromide (KBr) disc for analysis.

The apparatus equipped with an integrating sphere contains a low intensity light source. An incident beam passes through the sample, then it is scattered in all directions and transmitted through the sample material. The incident beam which is scattered within a sample and returned to the surface will be collected and transmitted to an optical
detector. In this case, this incident radiation can be considered a diffuse reflection. The surface reflectance may be measured either at a given wavelength or by performing a scan over a range of wavelengths. The ratio of the total amount of light reflected by a surface to the total amount of the incident radiation on the surface is the reflectance.

For a high spectral quality in diffuse reflectance, samples prepared must be uniform and well mixed. Moreover, the particle’s size and sample loading play an important role in diffuse reflectance spectra. The incident radiation can better penetrate smaller particles and diluted samples and also, the quality of spectra is improved. The multiple reflections of the light at the inner surface of the integrating sphere demands the highest possible reflectivity of the inner surface of the sphere to minimise the attenuation of the light reaching the detector. For this reason the inner surface must be constructed from material of the highest reflectivity available (i.e. barium oxide coatings).

2.4 Laser flash photolysis technique

The flash photolysis technique was developed in 1949 by Manfred Eigen, Ronald Norrish and George Porter who won the 1967 Nobel Prize in Chemistry for this invention and used for studying excited state concentrations, triplet states and the rate constants or photo-physical and photochemical processes. This technique is employed for measuring the changes of the sample absorption caused by the excitation of the sample with a short (micro or nanoseconds) pulse of light. A short pulse of exciting light derived from a laser or flash lamp irradiates the sample and generates a transient species. Transients and products that are formed after the generating pulse can be characterized by analysing the time behaviour of the absorption. The concentration of transient species (excited states, radicals, complexes, etc) can be determined by measuring the changes in the amount of light absorbed by the transient as a function of time. The decay can be determined at one particular wavelength and recorded as a function of time.

The difference between transmission flash photolysis and diffuse reflectance flash photolysis is in the geometry of the collection of the analysing light. In transmission mode, the incident light is reflected from the surface with the angle of reflection equal to the angle of incidence, while in diffuse reflectance mode, the sample undergoes
substantial penetration and if the incident beam that penetrated the sample is scattered in all directions from the sample, then its diffuse reflection can be used to monitor the absorption. Transmission flash photolysis is used for liquid or gas sample, while diffuse reflectance flash photolysis is a common technique for opaque samples. In both cases, the transmitted analysing light from the sample and the diffuse analysing light from an opaque sample are monitored as a function of time. Diffuse reflectance laser flash photolysis and its data analysis will be discussed later in the sections 4.10 and 4.11.

The apparatus (figure 2.3) used for nanosecond laser flash photolysis consists of a laser source whose pulse length is measured in nanoseconds. An intense pulse of laser radiation is absorbed by the sample (contained within a 1cm path length quartz or glass cuvette). A xenon arc lamp is used to produce a probe beam perpendicular to the laser excitation beam through the sample. The role of the monochromator is to monitor the beam intensity at a particular wavelength. The photomultiplier converts the light into a voltage and the signal from the photomultiplier is then transferred to a digital oscilloscope. A personal computer records this data for analysis.

Figure 2.3: Schematic representation of nanosecond diffuse reflectance laser flash photolysis apparatus.
2.4.1 Lasers

The term “laser” is an acronym for Light Amplification by Stimulated Emission of Radiation. A laser is a source of high intensity optical, infrared or ultraviolet radiation produced as a result of stimulated emission maintained within a solid, liquid or gaseous medium.

There are three major characteristics of laser light which distinguish it from that produced by other sources:

a) beam width and intensity

A laser emits a narrow, parallel and high intensity beam of light from its output mirror in a well-defined direction with low divergence, allowing the beam to be focused on a specific point.

b) coherence

Coherence is a result of the stimulated emission processes and distinguishes laser light from conventional light sources. This characteristic suggests that there is a correlation in both time and space between the phases of light waves; the emitted photons by the excited laser medium are in phase with those already present in the cavity.

c) monochromaticity

This is the most important property of laser light and result from the fact that all photons are emitted as a result of an induced transition between the same two atoms or molecular energy levels and hence have almost the same frequency.

Spontaneous emission

Spontaneous emission of light is the process by which an atom or molecule in the excited state undergoes a transition to a state with a lower energy (e.g. the ground state via the emission of a photon). The emitted photon has an energy equals to the difference in energy between the two atomic states involved and the direction of the emission is completely random.
Stimulated emission

Stimulated emission is the process by which an incoming photon stimulates an excited atom to give up its stored energy in the form of a new photon. This photon is identical in wavelength, direction polarization and phase to the photons of the incident wave, giving a coherent beam which allows optical amplification to take place.

\[
\Delta E = E_u - E_l \quad \text{where} \quad E_u = \text{higher energy level}, \quad E_l = \text{lower energy level}
\]

Figure 2.4: Diagram of (a) Spontaneous emission and (b) Stimulated emission between two states.
Population inversion

The distributions of the population of molecules among their various energy states will
be biased towards the ground state according to the Boltzmann equation:

\[
\frac{N_u}{N_l} = e^{-(E_u - E_l)/kT}
\]  

(2.5)

where \(N_u\) and \(N_l\) are the populations of molecules in the states with energies \(E_u\) and \(E_l\),
\(k\) denotes the Boltzmann constant (1.38 x 10^{-23} \text{ J K}^{-1}) and \(T\) represents temperature, in K.

For laser action to occur, it is necessary that the atoms in the active medium to be excited
into an energetic state, a population inversion is achieved and if the excited state now
releases a photon, this photon can stimulate another photon to be released causing a
cascade of stimulated emission. However, until a population inversion is achieved,
absorption is dominant over emission.

The process of exciting is called pumping and the excitation source is called the pump.
The medium in which the population inversion occurs is called the active medium and
can be gas, solid or liquid and depends on the type of the output required.

Population inversions can not be achieved in systems with two energy levels. Three and
four level system can achieve inversions much more easily and are used in laser systems.

2.4.1.1 Types of laser systems

Three level laser

In a three level system, the energy level \(E_3\) is populated by excitation of the particle
which then quickly decays via a radiationless transition to populate the energy level \(E_2\).
The transition from \(E_3\) to \(E_2\) must be rapid and from \(E_2\) to \(E_1\) is relatively slow, so, the
population of this level can increase, while that of the ground state is reduced because of
pump transitions to \(E_3\). It is important for the pumped state to have a short lifetime for
spontaneous emission and the energy level \(E_2\) a long lifetime. In these conditions, the
energy level \(E_2\) is necessary to be metastable and the laser emission is slow.
An example of a three level laser illustrated in figure 2.5 is the Ruby laser (crystalline aluminium oxide doped with chromium), with the active medium being Cr\textsubscript{2}O\textsubscript{3}. The chromium ions (Cr\textsuperscript{3+}) are excited from the ground state \(E_1\) to a higher excited level \(E_3\) by an intense flash of light. Because of the energy level \(E_3\) has a short lifetime, a rapid decay will occur to the \(E_2\) state where the atom remains for long periods, before dropping down to the ground state by stimulated emission.

![Figure 2.5: Schematic representation of a three level laser.](image)

**Four level laser**

Four level lasers are quite similar to the three level systems; the only difference is that the lower of the two laser levels (\(E_2\)) involved in the radiative transition lies above the ground state (\(E_1\)) as shown in figure 2.6. This difference makes the four level lasers potentially more efficient than a three level laser.

The Nd:YAG (neodymium yttrium-aluminium garnet) laser operates as a four level system. The atoms in the ground state \(E_1\) are pumped into an intermediate state \(E_4\). Intersystem crossing occurs from this state to a metastable state, \(E_3\), from which the lasing action occurs. The lower laser level \(E_2\) is depopulated by a fast decay process, \(E_2\)
level behaves as the ground state and any population in $E_3$ results in a population inversion.

Figure 2.6: Schematic representation of a four level laser.

2.4.2 The optical cavity

The optical cavity is an arrangement of two parallel mirrors placed around the laser medium which provide feedback of the light. One of the mirrors is totally reflecting, while the other is partially reflecting in order to allow some of the light to leave the cavity to provide optical power. Light from the medium, produced by spontaneous emission is reflected by the mirrors back and across the cavity several times, causing more stimulated emission.

In order to sustain laser action, the light amplification can be increased either by increasing the path length over which the light beam interacts with the medium or by increasing the number of times the light beam passes through the medium.

The optical cavity must be resonant at the wavelength of radiation. In addition to an adequate population inversion, an adequate pathlength is required through the laser.

42
medium. A maximum amplification is achieved only for the light waves which satisfy the so-called standing wave condition:

\[ \lambda = \frac{2d}{n} \]  

(2.6)

where \( d \) is the cavity length and \( n \) is the number of half wavelengths contained within length \( d \).

The modes that satisfy this condition and propagate through the axis of the laser are called axial or longitudinal cavity modes. The modes that propagate of axis are known as transverse modes.

**Axial (longitudinal) modes**

These modes oscillate along the axis of the laser beam and consist of a large number of frequencies given by:

\[ \nu = \frac{nc}{2d} \]

(2.7)

where \( n \) is the number of half wavelengths contained in cavity length \( d \), and \( c \) is the speed of light (3 x 10^8 m s\(^{-1}\)).

The longitudinal cavity modes are the only frequencies of light which are self-regenerating and allowed to oscillate by the resonant cavity; all other frequencies of light are suppressed by destructive interference.

**Transverse modes**

A transverse mode of a beam of electromagnetic radiation is a particular electromagnetic field pattern of radiation measured in a plane perpendicular to the propagation direction of the beam. These modes affect the spatial profile of the beam and are a function of the cavity width. They are defined in term of the Transverse Electromagnetic wave distribution across the cavity, TEM\(_{pq}\), where \( p \) is the number of radial zero fields and \( q \) is the number of longitudinal fields. These two indexes (\( p \) and \( q \)) describe the number of intensity minima across the laser beam in perpendicular direction. The ideal operation
mode is the TEM$_{00}$ which corresponds to a Gaussian intensity profile. Figure 2.7 shows the TEM$_{00}$, TEM$_{10}$ and TEM$_{20}$ transverse mode in a laser cavity.

![TEM modes](image)

*Figure 2.7: Transverse modes in a laser cavity.*

2.4.3 Q-switching

The Q-switching technique is available to increase the peak power and to reduce the length of the pulse in laser sources. The quality factor ($Q$) of the laser cavity can be expressed as:

$$Q = \frac{2\pi\nu}{\text{energy loss per optical cycle}} \left(\text{energy stored in cavity}\right)$$  \hspace{1cm} (2.8)

where the optical cycle is the inverse of the resonant frequency.

In a Q-switched laser, the laser cavity is prevented from allowing radiation density to build up until the population inversion has reached a peak level greater than it would ordinarily attain. When the cavity performance ($Q$) is subsequently restored, all the energy accumulated in the inversion can become released as an intense pulse of very short duration, lasting a few nanoseconds.

There are various methods of Q-switching a laser.

**Mechanical Q-switching**

This method involves replacing one of the end mirrors of the cavity with one which rotates at high speed and lasing could only occur when the mirror is almost perpendicular to the laser axis$^{15}$. 

44
Chapter 2. Techniques and instrumentation

Figure 2.8: Schematic representation of mechanical Q-switching.

Passive Q-switching

A passive Q-switched laser contains a solution of saturable absorber dye placed in a 1 mm cell in the laser cavity, up against the 100% reflecting mirror\textsuperscript{15}. A saturable absorber is an optical device that exhibits an intensity-dependent transmission. This means that the device behaves differently depending on the intensity of the light passing through it. In passive Q-switched laser, the saturable absorber will absorb low intensity light and transmit light which is of sufficiently high intensity.

Figure 2.9: Schematic representation of passive Q-switching.

In the initial stage, the active medium is pumped to give a high degree of population inversion before the photon population begins to build up in the cavity. Once a large population inversion has been achieved in the active medium, the intensity of emission
increases to the point where the dye is bleached, light reaches the cavity mirror, the optical cavity is restored and the Q-factor is rapidly switched from a high value to a low value and stimulated emission resulting from the population inversion generates an intense pulse of laser light.

Dye solutions as Q-switches are simple and cheap, creating pulses of 10–20 nanoseconds, but they can degrade on use and operate better with circulation of the dye (between pulses) using a pump and reservoir.

**Electro-optical Q-switching**

This is a non-mechanical switching method used for Q-switching a laser and is based on the Pockels effect. The polarization state of light can be modified via the electro-optic effect (or Pockels effect) and this can be turned into a modulation of the losses by using a polarizer.

The Pockels cell effect occurs in uniaxial crystals lacking a centre of symmetry, which change their reflective index and thus rotate the plane of light when an electrical field is applied. The change is small, but is sufficient to alter the spatial phase condition of light.

![Figure 3.0: Schematic representation of an electro-optical Q-switching](image)

Both the polarizer and the Pockels cell in the laser cavity act as a switch and without an applied voltage across the cell the photons pass through it. When a voltage is applied, the population inversion builds up and is rapidly depopulated when the voltage is removed. The pulse duration is typically around 5-10 nanoseconds.
Chapter 2. Techniques and instrumentation

**Acousto-optic switching**

An acousto-optic effect is usually employed to give a slower Q-switch than those based on the Pockel effect. Acousto-optic Q-switches are driven by a radio-frequency electric field and generate an acoustic wave which produces off-axis diffraction of the laser beam. When the acoustic wave travels through a medium such as silica, it causes local changes in the material density which gives rise to changes in the reflective index. The acoustic wave is switched off when pumping of the laser is complete and all the light reaches the mirror and a laser pulse builds up rapidly. The most commonly acoustic Q-switch uses fused silica and has an opening time of around 100 nanoseconds.

**Mode-locking**

Another method of producing laser pulses of shorter duration than either cavity dumping or Q-switching is known as mode-locking. The technique of mode-locking consists of creating the phase relationship, which results in completely constructive interference between all the modes at just one point with destructive interference everywhere else\(^\text{15}\). Consequently, a pulse of light is obtained which travels back and forth between the end mirrors, giving a pulse of output each time it is incident upon the semi-transparent output mirror.

Methods for producing mode-locking in a laser may be classified as either active or passive.

**Active methods** typically involve using an external signal (an electro-optic or acousto-optic switch) to induce a modulation of the gain of the laser cavity. The most common active mode-locking technique places a standing wave acousto-optic modulator into the laser cavity. When driven with an electrical signal, this produces a sinusoidal amplitude modulation of the light in the cavity.

**Passive methods** do not use an external signal, but are generally accomplished by placing a saturable absorber cell within the laser cavity which causes self-modulation of the light. The saturable absorber selectively absorbs low intensity light and transmits light of sufficiently high intensity.
3. Photochemistry of and on solid substrates

3.1 Properties of silica surface

Silica gel is a porous material with many applications in industry as a support for catalysts\textsuperscript{16,17} or as an adsorbent in acid-catalyzed reactions\textsuperscript{18,19}. Silica contains siloxane groups (Si—O—Si) and some silanol groups (Si—OH). Both groups (siloxane and silanol) influence the reactivity of the silica. Three types of silanol groups occur on silica gel: \textit{vicinal silanols} where two single silanol groups attached to different silicon atom form hydrogen bonds; \textit{geminal groups} characterized by the presence of two silanol units attached to the same silicon atom and \textit{isolated silanol groups} (figure 3.1).

![Figure 3.1: Schematic presentation of three types of silanol groups on the silica surface.](image)

The silanol groups are formed on the surface during the silica synthesis, in the condensation process of Si(OH)\textsubscript{4}. On the other hand, the silanols appear when the silica reacts with water or aqueous solutions. This reaction involves the breaking of the surface siloxane bonds.

The silanol groups have an important role in the adsorption process of different organic compounds on the silica surface. The mobility of aromatic hydrocarbons depends on the pre-treatment temperature. With heat treatment, the water can be removed from silica surface. The physically adsorbed water is removed from the silica surface\textsuperscript{20} at temperatures below 400 K. At temperatures higher than 400 K, the silanol groups of the silica surface are dehydrated and finally so are the internal silanol groups\textsuperscript{20}. An increase of pre-treatment temperature leads to the reduction in the number of silanol groups and also in the mobility of aromatic hydrocarbons on the surface due to formation of consequent siloxane network. This observation is confirmed by Kelly and co-workers\textsuperscript{21}.
in their studies on the effect of pre-treatment temperature on the mobility of adsorbed pyrene on \( \gamma \)-alumina.

Infrared spectroscopic studies of the surface silanols give relevant information about the structure of silica gel. Moreover, absorption around 3530 cm\(^{-1}\) confirms the presence of a hydrogen-bonded silanol close to another silanol\(^{22}\). A broad absorption around 3750 cm\(^{-1}\) corresponds to an isolated silanol group.

The surface properties of silica gel depend on the presence of silanol groups. The surface area of silica gel, the pore volume or size and the particle size depend on the method and specific parameters of the silica preparation.

**Silica synthesis**

The most commonly used method for the preparation of silica is the sol-gel route. This method consists of the hydrolysis and condensation of the alkoxy group derived from an alkoxy silane (Si(OR)\(_4\)), where R is CH\(_3\) or C\(_2\)H\(_5\). The siloxane networks are formed as a result of the condensation process. It is known that the alkoxy silane is not miscible with water. For this reason, an alcohol is used as a homogenizing agent. An acid or a base may be used as catalyst in order to get a rapid and complete hydrolysis.

Both hydrolysis and condensation may occur by an acid catalyzed bimolecular nucleophilic substitution reaction (SN\(_2\)). The mechanism (scheme 3.1) involves the nucleophilic attack of water to the silicon atom and the alkoxy group is rapidly protonated.

Brinker *et al.*\(^{23}\) suggested that in an acid solution, silica particles aggregate into a three dimensional network and form gels, whereas in a basic solution, the particle size becomes larger and the particle number decreases.
• Hydrolysis reaction:

\[
\text{RO-Si(OH)}_3 + H^+ \xrightarrow{\text{fast}} \text{RO-Si(OH)}_2 + \text{H}_2\text{O}^+
\]

\[
\text{RO-Si(OH)}_2 + \text{RO-Si(OH)}_3 \xrightarrow{\text{slow}} \text{RO-Si-O-Si-OR + H}_2\text{O}^+
\]

• Condensation reaction:

\[
\text{RO-Si(OH)}_3 + \text{RO-Si(OH)}_3 \rightarrow \text{RO-Si-O-Si-OR} + \text{H}_2\text{O}^+
\]

Scheme 3.1: The acid catalyzed hydrolysis and condensation mechanisms of the alkoxy silane.

In the hydrolysis reaction, the alkoxide groups (OR) are replaced with hydroxyl groups (OH), whereas in the condensation reaction, the silanol groups form the siloxane network (Si—O—Si). An acid catalysis is more efficient than a base catalysis\textsuperscript{23}. The contribution of the acid catalyst can influence the rate and extent of the hydrolysis reaction. Moreover, the gelation time will be shorter when the hydrolysis and condensation reactions are catalysed by a strong acid, whereas a weaker acid catalyst requires a longer gelation time.

Another factor which can influence the hydrolysis reaction and also the particle size of silica is the molar ratio TEOS (TMOS) : H\textsubscript{2}O. Pouxvier \textit{et al.}\textsuperscript{24} investigated the acid catalyzed hydrolysis of TEOS at different molar ratios (r) H\textsubscript{2}O : TEOS. They found that at low content of water (r < 10) the hydrolysis reaction is partially finished and some monomers remain unhydrolyzed. The effect of increasing the water content (r > 10) is to accelerate the hydrolysis reaction and also a significant reduction of the silica particle size can be observed.
The role of the solvent is to create a miscible region in the TEOS—H₂O—ROH ternary system and to influence the structure or drying behaviour of the monolithic gel. The most common polar solvents which are used to solvate tetraethoxysilicate (TEOS) or tetramethoxysilicate (TMOS) are water and ethanol.

During the hydrolysis reaction, two processes can be involved: re-esterification and transesterification. The re-esterification process takes place when an alcohol molecule displaces a hydroxyl group producing an alkoxide ligand and water. The bimolecular nucleophilic substitution mechanism (SN₂) is shown below in scheme 3.2:

\[
ROH + Si(OR)₂OH + H⁺ \rightleftharpoons \text{pentacoordinate intermediate} \rightarrow \text{pentacoordinate intermediate} + Si(OR)₄ + HOH + H⁺
\]

**Scheme 3.2: The bimolecular nucleophilic substitution mechanism of the re-esterification reaction.**

The transesterification process occurs when an alcohol molecule is formed as a result of displacing an alkoxide group by an alcohol:

\[
R'OH + Si(OR)₄ \rightarrow Si(OR)₃OR' + ROH
\]

The condensation reaction involves the formation of the siloxane network and also the by-products alcohol and water (scheme 3.3).
• Alcohol condensation (alcoholysis):

\[
\text{Si} - \text{OR} + \text{HO-Si} \rightleftharpoons \text{Si} - \text{O-Si} + \text{ROH}
\]

• Water condensation (hydrolysis):

\[
\text{Si} - \text{OH} + \text{HO-Si} \rightleftharpoons \text{Si} - \text{O-Si} + \text{H}_{2}\text{O}
\]

Scheme 3.3: The formation of the siloxane bonds by an alcohol or water condensation reaction.

Similar to the hydrolysis reaction, the acid catalyzed condensation process can be described as a bimolecular nucleophilic substitution (SN$_2$). According to this mechanism, the silicon atom becomes more electrophilic and more susceptible to nucleophilic attack, as result of protonation of the silanol.

Based on sol-gel kinetics studies, Brinker et al.$^{23}$ suggested that if the hydrolysis rate is much larger than either water or alcohol condensation, the alkoxy functional groups are completely hydrolyzed and the condensation reaction does not take place. If the hydrolysis rate is much smaller than either condensation rate, the alkoxy functional groups are not completely hydrolyzed and in this case, the hydrolysis reaction will be followed by condensation.

### 3.2 Properties of titania-silica surface

Titania anatase is known as a photocatalyst with many applications in the field of environmental protection and energy development.$^{25,26,27}$ It is interesting in catalysis because it can provide active sites on the surface. Silica-titania composites exhibit excellent thermal stability, and larger surface area and a better photocatalytic performance than pure titania$^{28,29,30}$. The photocatalytic activity$^{31-38}$ and photo-induced hydrophilic activity$^{39,40}$ can be enhanced when titania is combined with silica.
Titania-silica mixed oxides which possess high catalytic activity present applications in a number of areas\textsuperscript{41-45} such as photocatalysts in organic synthesis, for example propylene epoxidation reactions\textsuperscript{46,47} or isomerisation of olefins\textsuperscript{48}. Also, titania-silica mixtures can be used as protective coatings on stainless steel to resist oxidation and chemical attack. Titania is often used as a photocatalyst for decolorizing wastewater\textsuperscript{49-52} and also for air oxidation reactions of various organic compounds\textsuperscript{53}.

The structure and surface properties of titania–silica mixed oxides depend on the method of synthesis and the chemical composition of components. The use of base or acid-catalysed hydrolysis of tetraethyl orthosilicate (TEOS) in the preparation of titania-silica mixed oxides allows the production of materials with excellent textural properties with potential for use as a catalytic support. The chemical interaction between the silicon and titanium oxides depends on the degree of dispersion and the thermal treatment. The OH groups from the oxide surface are hydrophilic and act as adsorptive / reactive sites. The dispersion capacity depends on the concentration of OH groups on the silica surface and the method of preparation. In a sol–gel synthesis, the structure of silica supported titania is changed during heat treatment. This is reflected by the silica content which is larger on the surface of silica–supported titania than that of silica–coated titania. In silica-supported titania, Si\textsuperscript{4+} in the core diffuses into the TiO\textsubscript{2} shell and then spreads out of it during heat treatment, whereas in silica–coated titania, both Si\textsuperscript{4+} and Ti\textsuperscript{4+} diffuse less because they themselves are in the shell and core. For this reason, the silica content on the surface of silica–coated titania is slightly lower than that of silica–supported titania.

Titania-silica nanoparticles can be obtained by a sol gel method (hydrolysis and condensation of an alkoxide in aquo-alcoholic media in the presence of an acid) and also, in order to prevent aggregation in organic solvents, a non-hydrolytic\textsuperscript{46} sol-gel route is indicated. Based on this non-hydrolytic sol-gel synthesis, UV-Vis spectroscopy studies demonstrated that the absorption band at 330 nm\textsuperscript{47} does not correspond to anatase. Furthermore, this observation confirms that Ti atoms are homogenously incorporated in titania-silica mixtures. An absorption band at 260 nm corresponds to four-coordinated Ti atoms and the band at 290 nm suggests the presence of higher-coordinated Ti atoms\textsuperscript{47}. 

53
In silica gel, Si atom is tetrahedrally coordinated with each oxygen atom bonding to two silicon atoms. In titania, Ti is octahedrally coordinated with each oxygen bonding to titanium atoms (scheme 3.5). The Ti—O—Si bond is formed by breaking of Ti—O—Ti and Si—O—Si bonds. The formation of this new bond results in the decrease of the coordination number of Ti (IV) on the interface of titania and silica in titania-silica mixed oxides. According to Gao \textit{et al.} \textsuperscript{54} and Kosuge \textit{et al.} \textsuperscript{55}, both the dehydrated and hydrated titania-silica samples at different Ti loadings show a silica IR absorption band shifted to lower wavenumber which suggests that the Si—O—Si bridges are affected by the dispersed titanium oxide. Furthermore, the bands at ~980 cm\textsuperscript{-1} and at ~1080 cm\textsuperscript{-1} confirm the formation of Ti—O—Si bridges\textsuperscript{56-60}. Based on UV-Vis spectroscopy studies, Dutot and co-workers\textsuperscript{56} found that the UV absorption edge shifts to longer wavelengths for titania-silica samples with higher Ti content. Also, the formation of Ti—O—Si linkages was confirmed by diffuse reflectance infrared Fourier transform spectroscopy. It is reported\textsuperscript{54} that, while at a low loading of titania (1 % TiO\textsubscript{2}) the silica surface contains isolated TiO\textsubscript{4} sites, at a medium loading of titania (5 % TiO\textsubscript{2}) the silica surface possesses a large amount of TiO\textsubscript{4} units. Polymerized TiO\textsubscript{4} species are present on the silica surface at higher content of titania (> 10 % TiO\textsubscript{2}). In titania-silica mixed oxides, Ti atoms substitute Si atoms in the silica matrix and form tetrahedral TiO\textsubscript{4} units. These units are considered active sites for epoxidation reactions\textsuperscript{61,62}.

It is known that titania has three types of crystal structures: anatase, rutile and brookite. Anatase and rutile have the same chemistry, TiO\textsubscript{2}, but they have different crystal structures. In anatase, the octahedra shares four edges hence the four fold axis, whereas in rutile the octahedra shares two edges of the octahedron with other octahedra and forms chains. The brookite structure is more complicated and has a larger cell volume than the anatase and rutile. Brookite crystallizes in an orthorhombic system. The anatase phase possesses the strongest photocatalytic activity, while the rutile phase displays poor photocatalytic activity. Rutile is the stable form, whereas the anatase and brookite are metastable at all temperatures. The anatase and brookite phases transfer to rutile when they are heated. The reaction time and pH play an important role in preparation of the brookite phase. It is reported\textsuperscript{60} that the abundance of the brookite phase increases at shorter reaction times and higher basicity, whereas the abundance of the rutile phase decreases. Reyes-Coronado \textit{et al.} \textsuperscript{63} have observed that the anatase phase shows a low
absorption coefficient in the wavelength range 500 – 750 nm and the absorption coefficient of brookite is larger than of anatase at wavelengths smaller than 510 nm. The characteristic bands for brookite are evidenced at 216, 245, 320, 364 and 449 cm\(^{-1}\) with relative stronger intensity than those evidenced for anatase at 144, 197, 399, 519 and 639 cm\(^{-1}\).

Different coordinations of Ti in titania–silica mixtures have been identified by XANES (X-Ray absorption near-edge structure) study. It was reported that Ti is octahedrally coordinated in amorphous material, while in mixed oxides Ti is tetrahedral. Zecchina et al. and Astorino et al. found that a charge transfer of the tetrahedral titanium sites between O\(^{-2}\) and the central Ti (IV) atom is confirmed by the absorption band in the range of 230 – 280 nm, whereas the band at around 260 – 330 nm corresponds to octahedral Ti. The increase in intensity of the absorption band at around 230 – 280 nm indicates the transformation of some of the octahedral titanium framework to the tetrahedral structure during the attachment of silica (scheme 3.4).

\[
\text{Scheme 3.4: The transformation of octahedral titanium to the tetrahedral structure during the attachment of silica.}
\]

Diffuse reflectance spectroscopy used to determine the surface structures involving Ti shows that the band at 210 nm indicates a charge transfer process in isolated Ti(OSi)\(_4\) or Ti(OSi)\(_3\)OH units from the ligand oxygen to an unoccupied orbital of the central Ti ion. This evidence confirms isolated Ti ions in tetrahedral locations in the silica matrix. Titania–silica mixed oxides can also contain Ti ions in other coordination numbers (e.g. six), which can be evidenced by a broad absorption in the region around 270 – 290 nm. Moreover, the anatase particles have an absorption maximum at 330 nm, while the rutile absorbs at 400 nm. The changes in coordination (from 6 to 4) and the presence of
isolated Ti ions in the silica matrix are reflected by the blue shift from 300 nm to 210 nm\textsuperscript{73,74}.

The majority of titania–silica composites contain tetrahedral Ti species, but if the sample is not fully dehydrated or contains a large amount of titania, minor quantities of Ti in 5– and 6– fold coordination can be observed\textsuperscript{75} in addition to the tetracoordinated Ti species. The various spectroscopic techniques have revealed that Ti\textsuperscript{4+} ions in dehydrated titania–silica mixtures are 4– coordinated and are present in two types of structure: tetrapodal Ti(OSi)\textsubscript{4} and tripodal Ti(OSi)\textsubscript{3}OH species. On interaction with water, NH\textsubscript{3} or H\textsubscript{2}O\textsubscript{2}, the Ti ions expand their coordination number to 5 or 6 and will form oxo– or super–oxo complexes with applications in oxidation reactions of organic molecules.

The surface properties of alumina-titania and silica-alumina systems prepared by hydrolysis of metal alkoxides have been studied\textsuperscript{76}. It is reported that anatase from titania-silica mixtures can be seen when the mixtures are heated at 100 °C. The calcination of titania-silica mixtures at higher temperatures (600 – 700 °C) leads to the appearance of the titania rutile form\textsuperscript{77}. Titania-silica samples calcined at 400 °C or 600 °C have reduced catalytic activity. The untreated samples have higher activities for epoxidation reactions\textsuperscript{78}. In the systems with higher content of titania\textsuperscript{77}, the X-ray diffraction analysis of the titania-silica particles shows that the anatase structure can be observed in the calcination range 500 °C – 800 °C. The calcination plays an important role in crystallization of titania on the surface, the surface area decreases\textsuperscript{79,80} and the anatase phase is transformed into the rutile phase at temperatures higher than 650 °C.

Alumina, silica and titania surfaces are covered with hydroxyl groups, which act as primary adsorption sites for polar molecules. The higher acidity of the titania-silica surface is caused by bridging hydroxyl groups (Ti—O(H)—Si) and also for titania (Ti—O(H)—Ti) or silica (Si—O(H)—Si). The mobility\textsuperscript{81} of titania-silica particles depends on the concentration of titania and pH. The contribution of (Si—O—Ti) species increases at a TiO\textsubscript{2} content ≤ 30 wt % and decreases at higher Ti content, whereas the optimum Ti-dispersion is achieved with a content of 20 wt % TiO\textsubscript{2}. The amount of the acid used in the sol-gel preparation procedure influences the catalytic properties of the titania-silica aerogels.
In essence, titania-silica aerogels with a content of 20 wt % TiO₂ and a molar ratio alkoxide : acid of 1 : 0.009 yield optimum textural properties and Ti-dispersion and exhibit the best catalytic performance for the epoxidation of cyclohexene.

The physical and catalytic properties of titania–silica mixed oxides depend on their composition. At low titania content, the proportion of isolated Ti species which interact with Si—O groups increases. The X-ray diffraction studies of titania-silica binaries show that at a titania content greater than 50 mol %, a broad peak due to anatase titania can be detected. On the other hand, the titania content affects the oxidation-reduction properties of the titania-silica composites. If the loading of titania is decreased, the electron-accepting and -donating abilities decrease and the band gap between the valence and conduction bands of titania increases. Imamura et al. and Worrall et al. found using ground state diffuse reflectance spectroscopy studies that the absorption edge of titania in titania-silica mixed oxides with 1, 3, 5 and 8 wt.% of titania ranges from 410 – 415 nm. At low titania content, the absorption edge of titania is shifted to shorter wavelength regions. This shift could be attributed to the size quantization effect arising from the presence of small titania particles in titania-silica mixed oxides or the presence of highly dispersed titania species with low coordination number. It is reported that the band gap of the mesoporous titania is 3.2 eV, while titania-silica mixed oxides have an increased band gap. The band gap energy of brookite has been found to be in the range 3.1 – 3.4 eV.

Yamashita et al. confirmed that titania species are highly dispersed in the silica matrices and exist in a tetrahedral coordination in titania-silica mixed oxides prepared by a sol-gel method. Additionally, in sol-gel samples, titania particles are better dispersed due to the formation of Ti—O—Si bonds and silica particles are well covered by titania. Moreover, titania-silica mixtures with low titania content have weak acid sites due to the low electron-withdrawing ability of its small titania grains. Itoh et al. reported that the catalytic activity could not be attributed to the properties of pure oxides because pure titania has only Lewis acid properties and the silanol groups (Si—OH) of silica are weakly acidic. The catalytic activity of titania-silica mixed oxides was attributed the formation of Brönsted acid sites upon the interaction of titania and silica at the molecular level.
The interaction of Ti with Si—O groups is assumed to be the main factor affecting the physical properties or catalytic function of titania-silica. In order to see this interaction, Imamura et al.\textsuperscript{83} found that the band at 955 cm\textsuperscript{-1} corresponds to titania-silica samples with lower titania content. Based on further investigations, Srinivasan \textit{et al.}\textsuperscript{89} reported that the broad peak ranging from 870 cm\textsuperscript{-1} to 970 cm\textsuperscript{-1} for titania-silica with a low content of titania (TiO\textsubscript{2} < 5 wt\%) can be ascribed to that of segregated titania and not of isolated titania species. The interaction of Ti with Si—O groups produces acid sites. A content of titania greater than 60 mol \% increases the number of acid sites.

Titania-silica mixed oxides and supported oxides at a content of titania below 5 \% possess isolated TiO\textsubscript{4} species. At a titania content greater than 5 \%, polymerized TiO\textsubscript{4} can be observed. Hydration increases the number of Ti—O—Ti bonds of titania-silica supported and mixed oxides. In titania-silica supported oxides, Ti atoms are located on the outer surface of the silica support, while in titania-silica mixed oxides Ti atoms are located on the surface of micro, meso and macro pores. In-situ spectroscopy studies\textsuperscript{54} demonstrated that the surface area of titania-silica decrease with increasing Ti loading. The increase of Ti content in the silicate network leads to microporous titania-silica particles.

To better understand both photocatalytic and catalytic activity\textsuperscript{90,91} of titania–silica mixed oxides, many types of composite structures of titania–silica binaries have been investigated. Liu \textit{et al.}\textsuperscript{31} found that the higher photocatalytic activity of titania–silica oxides can be attributed to quantum size effect of titania, while Cheng and co-workers\textsuperscript{92} suggest that the crystalline structure of titania which might change the electronic field of the surface is the main factor which contributes to an enhanced photocatalytic activity of titania–silica mixtures. A decrease in titania grain size reduces the electron transfer efficiency of the sample and also the redox catalysis ability is decreased. Moreover, the increase of silica content of titania-silica mixed oxides leads to a decrease in the number of anatase crystallites and an increase of both surface area and surface hydroxyl groups\textsuperscript{31}. That means the high surface area facilitates the adsorption of reactants and the photocatalytic activity of the mixed oxides increases.
3.3 Photochemistry of polycyclic aromatic hydrocarbons

The photochemistry of aromatic molecules can be considered analogous to the photochemistry of alkenes due to both aromatic hydrocarbons and alkenes having $S_1(\pi, \pi^*)$ and $T_1(\pi, \pi^*)$ states as reactive states. In a $\pi \rightarrow \pi^*$ transition, the absorption band can be usually seen in the spectral range 200 – 700 nm. Saturated organic compounds (alkanes) are generally “transparent” to light in the region 200 – 700 nm. For these saturated hydrocarbons, an electron from HOMO is promoted by absorption of light to an unoccupied antibonding orbital; this jump corresponds to a $\sigma (\text{HOMO}) \rightarrow \sigma^* (\text{LUMO})$ orbital transition. On the other hand, unsaturated organic molecules (ketones, alkenes, aromatic hydrocarbon, etc) possess several absorption bands in the region 250 – 700 nm of the electromagnetic spectrum. Absorption of light in this region corresponds to $\pi (\text{HOMO}) \rightarrow \pi^* (\text{LUMO})$ transitions for alkenes and aromatic compounds which possess a $\pi^*$ electron in the HOMO, or to $n (\text{HOMO}) \rightarrow \pi^* (\text{LUMO})$ transition for compounds, such as ketones, that have an $n$ electron in the HOMO.

Transitions between states of different multiplicity are strongly forbidden since the transition involves a spin inversion. However, the transitions are made possible due to the phenomenon of spin orbit coupling. As a consequence, a singlet state can be considered to have some triplet character and a triplet state some singlet character. The spin forbidden transition becomes pronounced in aromatic hydrocarbons substituted with heavy atoms, such as iodide or bromide due to spin orbit coupling. In contrast to alkenes where fluorescence is rare, most of the aromatic compounds fluorescence strongly due to their rigid ring structure which does not favour non radiative deactivation. Both alkenes and aromatic hydrocarbons have a low rate of intersystem crossing from $S_1$ to $T_1$. Substitution with heavy atoms on the aromatic framework or use of a heavy atom solvent, such as ethyl iodide, enhances intersystem crossing from $S_1$ to $T_1$ in aromatic molecules.

3.3.1 Photochemistry of anthracene

A photochemical study of an organic molecule involves the measuring of its electronic absorption and emission spectra which provide information concerning the structure,
energetics and dynamics of electronically excited states of the molecule. From measurements of the lifetimes of singlet and triplet states and of the quantum efficiencies of emission, the rate constants of the radiative and non-radiative photophysical pathways available to $S_1$ and $T_1$ can be deduced.

In aromatic hydrocarbons that have many bonding $\pi$ electrons, the absorption of light induces a $\pi \rightarrow \pi^*$ transition, so that the excitation of an $\pi$ electron to a $\pi^*$ orbital does not significantly change the structure of the excited molecule compared to that in ground state. Since the vibrational wavefunctions between the ground state and the excited state are assumed to lie exactly over one another, the most favoured Franck-Condon transition will occur from the minimum of the ground surface ($\nu = 0$) to the minimum of the excited surface ($\nu = 0$).

Figure 3.2 shows both the absorption and fluorescence spectra of anthracene (An) in hexane solution. In this figure, the absorption and fluorescence bands can be seen to be mirror images of one another about the $0 \rightarrow 0$ transition which is relatively intense for this planar molecule since there is little geometric displacement between the ground and excited state. The fluorescence emission spectrum of anthracene is observed at longer wavelengths because the emitted photons possess less energy than those originally absorbed. It can be seen from figure 3.2 that the spectra do not overlap exactly however. This slight difference in the spectral position of the $0 \rightarrow 0$ transition arises as a result of the geometric changes and/or perturbation of the surrounding solvent molecules by the changes in dipole moment between the ground and excited state. The excited states have a different electronic configuration compared to the ground state since excitation involves promotion of an electron to an anti-bonding orbital.
Figure 3.2: (a) Absorption (solid line) and emission (dash line) of anthracene in hexane solution; (b) Energy level diagram showing some of the transitions involved in the IR vibration-rotation spectrum of anthracene.
The anthracene molecule in the ground state $S_0(\pi, \pi)$ may absorb a photon of suitable energy (or wavelength) and undergo promotion to an excited singlet state $S_1(\pi, \pi^*)$ (figure 3.3). The excited anthracene can lose the energy by emission (fluorescence $S_1 \rightarrow S_0$ transition or phosphorescence $T_1 \rightarrow S_0$ transition) and the molecule is returned to the ground state. On the other hand, the excess energy can be lost as heat by collision with other molecules. This transition called internal conversion from $S_1(\pi, \pi^*) \rightarrow S_0(\pi, \pi)$ or from $T_2(\pi, \pi^*) \rightarrow T_1(\pi, \pi^*)$ involves no change in the spin multiplicity of the excited electron. Similar to olefins, the intersystem crossing from $S_1(\pi, \pi^*) \rightarrow T_1(\pi, \pi^*)$ or from $T_1(\pi, \pi^*) \rightarrow S_0(\pi, \pi)$ is a forbidden transition and the rate of this transition is very slow. The transitions from $T_1(\pi, \pi^*)$ can generate reactive intermediates like radical pairs, radical ion pairs or bi-radicals. Because the energy gap between $S_1$ and $T_2$ excited states of anthracene is very small, substitution with heavy atoms such bromide or iodide on the aromatic framework can enhance the quantum yield of fluorescence (the value of the fluorescence quantum yield of anthracene determined in solution$^{96,97,98}$ is 0.30) and the intersystem crossing rate.

![Energy diagram for anthracene.](image-url)

| $A$ | photon absorption |
| $F$ | fluorescence (emission) |
| $P$ | phosphorescence |
| $VR$ | vibrational relaxation |
| $IC$ | internal conversion |
| $ISC$ | intersystem crossing |
| $S$ | singlet state |
| $T$ | triplet state |
For these processes described earlier, some equations can be written below (table 3.1):

<table>
<thead>
<tr>
<th>Process</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Absorption of light</td>
<td>$S_0(\pi, \pi) \rightarrow S_1(\pi^<em>, \pi^</em>)$</td>
</tr>
<tr>
<td>$\text{An} + h\nu \rightarrow \text{1An}^*$</td>
<td></td>
</tr>
<tr>
<td>2. Fluorescence emission</td>
<td>$S_1(\pi, \pi^*) \rightarrow S_0(\pi, \pi)$</td>
</tr>
<tr>
<td>$\text{1An}^* \rightarrow \text{1An} + h\nu$</td>
<td></td>
</tr>
<tr>
<td>3. Internal conversion</td>
<td>$S_1(\pi, \pi^*) \rightarrow S_0(\pi, \pi)$</td>
</tr>
<tr>
<td>$\text{1An}^* \rightarrow \text{1An}$</td>
<td>$T_2(\pi, \pi^<em>) \rightarrow T_1(\pi, \pi^</em>)$</td>
</tr>
<tr>
<td>4. Intersystem crossing</td>
<td>$S_1(\pi, \pi^<em>) \rightarrow T_1(\pi, \pi^</em>)$</td>
</tr>
<tr>
<td>$\text{1An}^* \rightarrow \text{3An}^*$</td>
<td>$T_1(\pi, \pi^*) \rightarrow S_0(\pi, \pi)$</td>
</tr>
<tr>
<td>$\text{3An}^* \rightarrow \text{1An}$</td>
<td></td>
</tr>
<tr>
<td>5. Phosphorescence</td>
<td>$T_1(\pi, \pi^<em>) \rightarrow S_0(\pi, \pi^</em>)$</td>
</tr>
<tr>
<td>$\text{3An}^* \rightarrow \text{1An} + h\nu$</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.1: Electronic transitions in an excited anthracene molecule.

The polynuclear aromatic hydrocarbons which contain a maximum number of $\pi$ electron sextets (benzenoid) are considered to be the most stable molecules. The addition of molecular oxygen to anthracene (scheme 3.5) takes places at the central ring to give 9,10-anthracene endoperoxide which contains two aromatic sextets, whereas the reaction at the 1,4-position does not form another benzene ring and is not observed experimentally. In this case, the 9,10-position is more reactive than 1,4-position and the preference for addition at the 9 and 10 positions can be explained by the fact that aromatic stabilization energy is directly correlated with the number of conjugated $\pi$ bonds in an aromatic system. In other words, 9,10-anthracene endoperoxide contains two aromatic sextets (six conjugated $\pi$ bonds) and the addition of singlet oxygen is favourable to occur at the most stable position, whereas the 1,4-isomer contains a total of five conjugated $\pi$ bonds and is not the thermodynamically favourable product.
Photocycloaddition reactions of anthracene are common for both singlet and triplet excited states. Photoinduced [4+4] cyclodimerization of anthracene occurs across the 9,10-position (scheme 3.6). The preferential [4+4] dimerization at the 9,10-carbons could be attributed to the interactions of the same type of orbitals\textsuperscript{100,101} between anthracene excited state and ground state.

In a [4+4] photodimerization, the singlet excited state anthracene is self quenched by its ground state. The quantum yield of dimerization increases, but the fluorescence quantum yield decreases with increasing anthracene concentration.

Based on the same reasoning, the addition of cyclohexadiene to the excited anthracene will take place across the C\textsubscript{9} and C\textsubscript{10} atoms of anthracene (scheme 3.7). This addition will be controlled by the interactions of the same orbitals (HOMO – HOMO or LUMO – LUMO) between the excited state anthracene and the ground state of the olefin.
Polycyclic aromatic hydrocarbons have been the focus of many works because of their strong fluorescence and interesting photophysical and photochemical properties. A number of fluorescent polycyclic aromatic hydrocarbons have been immobilized on a variety of surfaces, including pyrene, anthracene, azulene, perylene on oxide and metallic substrates.

A large number of organic molecules respect Kasha’s rule and fluorescence is observed only from S\(_1\) state and phosphorescence only from T\(_1\). But there are some “anomalous” emissions from S\(_2\), S\(_3\), etc and from T\(_2\), T\(_3\) states and so on which are not in the accordance to Kasha’s rule. For azulene (Az) (a blue organic molecule) and its derivates fluorescence is found to be from S\(_2\) to S\(_0\) state. The 0,0 band of S\(_0\) → S\(_2\) absorption and the 0,0 band of S\(_2\) → S\(_0\) fluorescence overlap and display a mirror image to one another (figure 3.4). The reason for the observed S\(_2\) → S\(_0\) emission is the large energy gap between S\(_2\) and S\(_1\) leading to a relatively slow internal conversion by decreasing the Franck-Condon factor for radiationless transitions coupled with a fast fluorescence from S\(_2\) state, while the energy gap between S\(_1\) and S\(_0\) is relatively small and leads to a fast internal conversion which can occur in competition with a slow inherent fluorescence. The S\(_1\) → S\(_0\) fluorescence from azulene is extremely weak (\(\Phi_F < 10^{-4}\)) and can be obtained only under special conditions.

\[ \text{Scheme 3.7: The addition of cyclohexadiene to anthracene across the } C_9 \text{ and } C_{10} \text{ atoms of anthracene.} \]
Perylene (Pe) is a five-ring polycyclic aromatic hydrocarbon found in nature whose source can include soil, forest fire or volcano dust, although it also occurs in petroleum products\textsuperscript{122-129}. It has also been identified in products of incomplete combustion such as cigarette smoke and engine exhaust. Perylene is an interesting chromophore not only because of its optical properties and high fluorescence quantum yield, but also because of its spectroscopic properties and reactivity. The oxidation potential of perylene (0.85 V vs SCE)\textsuperscript{97} is low relative to that of anthracene (1.29 V vs SCE)\textsuperscript{97}, leading to electron transfer reactions between the anthracene radical cation and the perylene ground state.

The absorption and emission spectra of perylene in acetonitrile are shown in figure 3.5. The most structured absorption band belongs to the transition from the ground electronic state to the first excited electronic state. This transition shifts to the red as the concentration of perylene is increased. Perylene shows blue fluorescence. In dilute solutions, perylene molecules remain isolated, whereas in concentrated solutions perylene molecules forms excited state dimers (excimers).
The physical and chemical properties of the surface affect the photophysical and photochemical behaviour of adsorbed perylene by producing band broadening and shifts, changes in the lifetimes, changes in the photodegradation rates on the decay kinetics of the perylene radical cation. The absorption and emission spectra of adsorbed perylene on alumina or silica gel are similar to those observed in polar solutions such as, methanol or acetonitrile. The adsorbed perylene shows spectra with broader bands and a small red shift to longer wavelengths relative to solutions due to the formation of aggregates and the interaction of perylene with the solid surface. The absorption and emission spectra of perylene change with surface properties and sample loading\textsuperscript{117,118}.

Perylene degrades faster as the pore size of the surface increases suggesting a significant dependence of the photodegradation rate on the nature of the surface interactions\textsuperscript{117}. A slow degradation rate is observed at higher sample loadings. This decrease can be explained in the term of a deactivation of the triplet state. At higher loadings it is possible that fewer highly active surface sites are available resulting in a decreased stabilization of the polar reactive intermediates. Higher concentration of perylene
generates exciplex in the excited state which is observed in the form of a broad red shifted band.

The electron transfer reactions on silica gel between anthracene radical cations and co-adsorbed molecules with oxidation potential below the reduction potential of the anthracene radical cation (1.09 V vs SCE) such as azulene, perylene and different amines on silica gel have been investigated\textsuperscript{108,110,130,131}. The co-adsorption of an electron donor molecule with anthracene on silica gel accelerates the rate of the decay of the anthracene radical cation. In the case of N,N,N’,N’-tetramethyl–1,4-phenylenediamine (TMPD), triphenylamine (TPA) and N,N-dimethylaniline (DMA), the accelerated radical cation decay is accompanied by the concomitant appearance of the radical cation of the electron donor, whereas the formation of azulene radical cation is not clearly observed\textsuperscript{108} due to the location and the intensity of the azulene radical cation absorption peak which is located at 368 nm, underneath the anthracene ground state absorption.

The energy and electron transfer reactions of anthracene, 9-carboxylic acid anthracene, phenanthrene, naphthalene and its derivates co-adsorbed with azulene on silica gel have been studied\textsuperscript{108,113,114,130,131} by a combination of steady state reflectance and emission spectroscopy and nanosecond laser flash photolysis. Triplet-triplet energy transfer is observed between the excited arenes and the ground state azulene. Photoionisation of the arenes leads to the formation of their radical cations and the electron transfer then occurs from azulene to the arene radical cations. Bimolecular rate constants for energy and electron transfer between anthracene (and its derivative) and azulene have been obtained. It was demonstrated that both the energy and electron transfer between anthracene or 9-carboxylic acid anthracene and azulene proceed at the diffusion controlled rate\textsuperscript{113,114}, whereas for some naphthalene derivates the rate of electron transfer from azulene is considerably lower than the diffusion controlled limit\textsuperscript{113}. This reduction in the rates of both energy and electron transfer can be attributed to a steric effect which may also be influencing them in these systems. Moreover, electron transfer reactions have been studied between 9-anthracene carboxylic acid co-adsorbed with perylene on silica gel surface\textsuperscript{115} employing azulene as a molecular shuttle in order to facilitate hole transfer. The presence of azulene in this ternary system has been shown to enhance the rate of electron transfer proving mobility of the azulene and its radical cation species on the silica surface.
3.4 Energy and electron transfer on surfaces

Photochemical processes in heterogeneous systems have many applications in photography, chemical synthesis and the conversion and storage of solar energy. The photophysics of various organic molecules adsorbed on reactive or non-reactive surfaces have been studied\textsuperscript{108,130,132-134}. Different photochemical and photo physical studies offer information about the nature of the interaction between the surface and the adsorbed molecule, the nature of the adsorption sites and the mobility of the probe.

The mobility of molecules adsorbed on silica gel and also on titania-silica surfaces can be demonstrated by energy and electron transfer studies\textsuperscript{133}. Many studies\textsuperscript{108} have shown that the mobility of different molecules adsorbed on solid substrates depends on the pre-treatment temperature of the substrate.

The surface plays an important role in influencing the course of a photochemical reaction. On a non-reactive surface, such as silica gel\textsuperscript{108,130,133-136}, \(\gamma\)-alumina\textsuperscript{134} or zeolites\textsuperscript{137-143} the electron transfer can occur between two adsorbed molecules. These kinds of surfaces can modify the course of a photochemical reaction by influencing the excited state behaviour of photoactive molecules, whereas a reactive surface, such as titania or titania-silica mixed oxides absorbs the light and transfers the charge to another molecule or can directly quench the excited state of the adsorbed molecule.

In previous works\textsuperscript{110,144-148} some polyaromatic hydrocarbons such as anthracene, substituted anthracene, fluorine, tetracene, naphthalene and substituted naphthalene were studied adsorbed on different solid surfaces. It was observed that at low surface loadings (< 5 wt %), most aromatic hydrocarbons form ground state pairs or aggregates, whereas at higher surface loadings crystallization appeared to dominate. The absorption spectra of polyaromatic hydrocarbons adsorbed on a metal oxide surface show a broadening band (compared to solution) at low surface loadings (<1 % of a monolayer coverage) as a result of the interaction between the surface and the organic molecule. At higher surface loadings the absorption band is shifted to longer wavelengths and indicates the formation of aggregates. Moreover, the fluorescence emission spectra of aromatic hydrocarbons on solid surfaces revealed that the changes in the emission intensity as a result of increasing concentration of these aromatic hydrocarbons can be attributed to the formation of ground state pairs or aggregates.
The hydroxyl groups which cover the metal oxide surfaces have an important role in the adsorption process of organic molecules on these surfaces. The aggregates appear due to an inhomogeneous interaction of the aromatic hydrocarbons with the surface. Absorption and emission studies of adsorbed aromatic hydrocarbons on solid surfaces can give relevant information about the mobility of these molecules on the surface. For example, broadening in the absorption band in the reflectance spectra as a consequence of an increase in dimer formation has been observed when molecules such as pyrene\textsuperscript{149} or anthracene\textsuperscript{109,139,150-153} are adsorbed on silica or alumina surface. Moreover, anthracene-1,5-disulfonate and anthracene-1-sulfonate molecules adsorbed onto alumina-coated silica particles did not dimerize due to the orientational effects which can control the formation of dimer\textsuperscript{154}.

Fluorescence emission techniques and diffuse reflectance laser flash photolysis have been used to study aromatic hydrocarbons adsorbed on silica\textsuperscript{108,135,136}, $\gamma$-alumina\textsuperscript{134}, zeolites\textsuperscript{137-139} or titania-silica surfaces\textsuperscript{84}. The interpretation of emission and reflectance spectra can give relevant information about the properties of different molecules adsorbed on surfaces. Moreover, the absorption and fluorescence emission spectra of aromatic hydrocarbons are influenced by these interactions with silanol groups; the spectra are broader than those spectra obtained in solution\textsuperscript{150-153}. The mobility of aromatic hydrocarbons is reduced when they are adsorbed on a solid surface due to the interaction with the hydroxyl groups. For good mobility of aromatic hydrocarbons on silica surfaces\textsuperscript{150} it is necessary to reduce in the interactions with the silanol groups.

By direct irradiation of titania surface, holes and electrons are produced. Electrons are trapped at Ti\textsuperscript{4+} sites to form Ti\textsuperscript{3+} and holes at subsurface oxide ions to form O\textsuperscript{2-}. The hydroxyl groups at the surface on titania can be considered deep traps for valence band holes. Bahnemann and his co-workers\textsuperscript{155} and Howe et al.\textsuperscript{156} found that the O\textsuperscript{2-} radical anion is the chemical entity which combines with the trapped electrons in the conduction band. According to scheme 3.8, the reaction of holes with the hydroxyl groups at the surface of titania produces hydroxyl radical which then dimerize to form peroxide. The obtained peroxide will trap to further hole to produce O\textsuperscript{2-} species. It was reported\textsuperscript{156} that the formation of peroxide occurs in a temperature range where the hydroxyl radicals are extremely mobile on the anatase surface. By further irradiation at 77 K, loss of O\textsuperscript{2-} is possible due to both oxidation and reduction of adsorbed O\textsuperscript{2-}.
Titania-silica mixed oxides can be often more efficient photocatalysts than pure titania. The efficiency of titania and titania-silica photocatalysts depends on the effective separation of the photoproduced holes and electrons and subsequent charge transfer reactions with adsorbed molecules. Under band gap excitation, semiconductor particles can participate in charge transfer processes with adsorbed molecules (figure 3.6 a). Additionally, an electron can be transferred from the excited state of the adsorbed molecule into the conduction band of the semiconductor. In this case, the reactive surface acts as a quencher by accepting a charge from the excited molecule adsorbed on its surface (figure 3.6 b).
The interaction between metal oxides and a sensitizer molecule, such as anthracene-9-carboxylic acid, Rose Bengal and chlorophyllin has been studied using ground state absorption and emission spectroscopy of the sensitizer. Spectroscopic techniques like emission and nanosecond diffuse reflectance laser flash photolysis have been employed to investigate the interaction between an excited molecule and the metal oxide surface. These techniques were also used to characterize the formation of radical cation of the adsorbed molecules and their subsequent reactions. The fluorescence emission yield and emission lifetime measurements can probe the quenching of the singlet excited sensitizer by a colloidal semiconductor. Kamat studied the absorption of anthracene-9 carboxylic acid on colloidal titania and found that the quenching mechanism involves electron transfer from the excited singlet state of the aromatic hydrocarbon into the conduction band of titania.

The formation of arene radical cations is influenced by the nature of the interactions between the solid substrate and the molecule which is adsorbed. It has been reported that the formation of radical cations from polycyclic aromatic hydrocarbons on silica gel and γ-alumina is via bi- or multiphotonic processes. Moreover, the formation of anthracene or pyrene radical cations within zeolites involves a mono- and bi-photonic mechanism. Verzin et al. studied the adsorption of anthracene molecules into the channels of Al-ZSM-5 zeolites. It was demonstrated that one of the most important property of silicoaluminate porous materials is to generate organic radical cations and to stabilize them over few months at room temperature. Verzin et al. have reported that the stabilization of the radical cations can be attributed to the presence of aluminium atom in the siliceous matrix. On the other hand, the tight fit between the shape of anthracene and the pore size of the straight channels of the zeolite could be the main factor responsible for the stabilization of the anthracene radical cation.

The photophysics of anthracene co-adsorbed with N,N-dimethylaniline (DMA) on titania-silica mixed oxides has been studied. Fluorescence behaviour of anthracene on titania-silica mixtures depends on the titania content. Furthermore, the fluorescence intensity from anthracene on titania-silica mixed oxides decreases with increasing Ti content, whereas the fluorescence of anthracene adsorbed on silica gel is quenched by the addition of DMA. When anthracene is co-adsorbed with DMA, the DMA radical cation is generated from the pre-exciplex (An • DMA) state on the titania-silica surface.
It has been reported\textsuperscript{109} that the anthracene radical anion cannot be observed in the transient absorption spectrum of anthracene co-adsorbed with DMA on a titania-silica surface because of the electron goes spontaneous to the surface. This observation confirms that the electron affinity of silica and also of titania-silica surface is higher than that of anthracene\textsuperscript{170}.

The decay of delayed fluorescence which arises from triplet-triplet annihilation can be used to study the rate of diffusion across the surface. Oelkrug \textit{et al}.\textsuperscript{135} suggested that the decay of delayed fluorescence can be analysed by two models: a two dimensional model and a fractal model. The two dimensional model assumes that the molecules diffuse in two dimensions, on a “flat” surface, while a fractal model is used to describe the diffusion of molecules across the pores of the surface. Using delayed fluorescence measurements, Oelkrug \textit{et al}.\textsuperscript{135,136} have observed the mobility of azaaromatic compounds on silica gel. The decay rate constants for the delayed fluorescence using both models have been reported\textsuperscript{131}. The decay of excited states and radical cations on silica gel has been fitted using the dispersive kinetic model of Albery \textit{et al}.\textsuperscript{171}. Transient decay data has been analysed using this model which assumes a log Gaussian distribution of rate constants.

Nanosecond diffuse reflectance laser flash photolysis\textsuperscript{113-115,172-175} has been used to investigate energy and electron transfer reactions of aromatic hydrocarbons in heterogeneous media (adsorbed on silica gel and titania-silica surfaces). Triplet excited states of different aromatic hydrocarbons adsorbed on oxide surfaces have been characterized using diffuse reflectance laser flash photolysis. Triplet-triplet absorption spectra of some organic molecules such as anthracene\textsuperscript{108,130,133-136}, pyrene\textsuperscript{176} and benzophenone\textsuperscript{177,178,179} adsorbed on a solid surface are different from those observed in solution due to a charge transfer transition between the surface and the adsorbed molecules. In the case of pyrene adsorbed on γ-alumina, Kessler \textit{et al}.\textsuperscript{180} reported a strong triplet-triplet absorption band at 475 nm and a shoulder and a broad band at 500 and 575 nm respectively, whereas the triplet-triplet absorption spectrum of pyrene in ethanol\textsuperscript{181} shows an absorption maximum at 415 nm. The triplet-triplet absorption of anthracene in ethanol\textsuperscript{181} is in the spectral range 390 – 440 nm with an absorption maxima at 430 nm, while the characteristic triplet-triplet absorption peak corresponding to anthracene adsorbed on silica gel\textsuperscript{110,131} can be observed at 420 nm.
Previously electron transfer reactions for system involving anthracene radical cation have been studied. Azulene, N,N-dimethylaniline (DMA) or triphenylamine (TPA) were used as electron donor molecules. The electron transfer kinetics can be characterised by the dispersive model of Albery et al.. Triplet-triplet energy transfer from molecules to azulene offers information regarding of the rate of diffusion on surfaces. Based on millisecond flash photolysis studies, it has been reported that the anthracene radical cation is formed by a multiphoton process following laser excitation at 355 nm and the rates of energy and electron transfer reaction between anthracene and azulene are predominantly governed by the diffusion of azulene on the silica gel surface. Additionally, the rate of radical cation decay increased as result of the addition of an electron donor to the system.

Kamat studied the electron transfer reaction of adsorbed viologen on CdS surface and found that the value of rate constant (5 x 10^10 s^-1) indicates an interfacial electron transfer from the photoexcited CdS surface to the adsorbed viologen.

Laser flash photolysis was used to study the photoinduced electron transfer reactions of the pyrene molecule to titania particles in a titania-silica system and also electron transfer reactions of adsorbed anthracene on titania-silica surfaces. The formation of the pyrene radical cation adsorbed on γ-alumina is observed following laser excitation at 337 nm. The increase in the rate of pyrene radical cation decay is the consequence of the co-adsorption of an electron donor such as N,N’-dimethylaniline on the silica surface. Wilkinson and co-workers and Thomas and co-workers have reported that the production of pyrene and anthracene radical cations on various surfaces, such as, silica gel, alumina and silica-alumina surface is a biphotonic process. Worrall et al. have investigated the photophysics of anthracene adsorbed to binary titania-silica mixed oxide surfaces and have been found that the formation of the anthracene radical cation on titania-silica surface is via both monophoton and multiphoton ionisation.

The reactivity of the surface can control the photochemical behaviour of the adsorbed molecules. The charge transfer process on semiconductor surfaces and the photoionization of adsorbed molecules on silica gel or alumina surface yields the same reaction product (the radical cation of the adsorbed molecule). It was
demonstrated\textsuperscript{84,130,132} that the electron transfer process on a semiconductor surface is monophotonic, whereas the photoionisation is a biphotonic process.

### 3.5 Photocatalytic properties of titania and titania-silica mixed oxides

Titania has been widely used to make products as diverse as paper, plastics, toothpaste and pharmaceutical tablets\textsuperscript{185}. As a promising material, TiO\textsubscript{2} nanoparticles can be used in various applications, such as self-cleaning window glass, antibacterial coatings, solar cells\textsuperscript{186,187} and in the photocatalytic degradation of polluted water and air\textsuperscript{49-53}.

TiO\textsubscript{2} photocatalysts can destroy almost all organic pollutants by generating pairs of electron / positive hole (e\textsuperscript{-} / h\textsuperscript{+}), when the photocatalyst is subjected to UV light. Electron / hole pair formation takes place by the band gap excitation of the titania particles. Positive holes oxidize adsorbed organic substrates or react with water leading to the formation of hydroxyl radicals which are very efficient oxidizing agents.

There are numerous semiconductors which can be used for photocatalysis, such as TiO\textsubscript{2}, WO\textsubscript{3}, Fe\textsubscript{2}O\textsubscript{3}, CeO\textsubscript{2}, ZnO, ZnS, CdS and ZrO\textsubscript{2}. Most of the semiconductors are either photo-corrosive in nature (Fe\textsubscript{2}O\textsubscript{3}, ZnO and CdS) or possess higher band gap energy (ZrO\textsubscript{2}) which can not be useful as efficient photocatalysts. Moreover, ZnO is unstable in water and forms Zn(OH)\textsubscript{2} on the particle surface\textsuperscript{188}. Metal sulfides (ZnS, CdS) are not stable enough for catalysis in aqueous media due to the photoanodic corrosion and they are also toxic.

In this study, the most important purpose is the modification and utilization of titania as an efficient photocatalyst because of its chemical and photocatalytic stability, low cost and lack of toxicity. In order to activate the photocatalysts with higher efficiency it is necessary to couple TiO\textsubscript{2} with other semiconductors with appropriate conduction band and valence band gaps. Photocatalysts such as: SiO\textsubscript{2}-TiO\textsubscript{2}\textsuperscript{37}, CdS-TiO\textsubscript{2}\textsuperscript{189}, ZnO-TiO\textsubscript{2}\textsuperscript{190} and SnO\textsubscript{2}-TiO\textsubscript{2}\textsuperscript{191} have been prepared and used for many reactions.

The TiO\textsubscript{2} photocatalytic reactions can be described by the following equations:
The hydroxyl ions (OH⁻) formed by direct irradiation of TiO₂ surface react with the holes producing hydroxyl radicals which are responsible for the photodegradation of organic molecules to CO₂, H₂O, NO₃⁻ or other oxides, phosphate, halide ion, etc.

In heterogeneous photocatalysis, the free radicals, OH and O₂⁻ super-oxide anion are responsible for the photocatalytic degradation of organic pollutants. The hydroxyl radical mediated photocatalysis reaction depends on the type and amount of catalyst, type and concentration of pollutant, light intensity and operating conditions such as, calcination temperature, pH and irradiation time. The photocatalytic ability of TiO₂ depends on the surface area, particle sizes and on its crystalline nature and phase composition. It is known that the anatase phase is considered to be a more highly active phase for the degradation of organic compounds than the other two forms (rutile and brookite).

The calcination temperature and the amount of catalyst have an important influence on the degradation of organic pollutants for TiO₂ catalysts. Neppalian et al.¹⁹² have demonstrated that TiO₂ calcined at 500 °C possesses a higher photoactivity towards degradation of 4-chlorophenol (4-CP) than TiO₂ calcined at 450 °C. This is due to the fact that in the case of TiO₂ catalyst calcined at 500 °C the anatase phase is highly crystalline, whereas the TiO₂ catalyst calcined at 450 °C is amorphous in nature and may act as a recombination center for the formation of electron / hole pairs. It was found that a loading of 200 mg catalyst / 200 ml of the 4-CP solution is an optimum amount for the degradation reaction of 4-CP. At a loading of catalyst < 200 mg, free radical production rate is limited and the rate of the degradation reaction of 4-CP will be lower, while at higher catalyst loading (> 200 mg) some TiO₂ particles can undergo excitation and more recombination of the photogenerated electrons and holes can take place.

The wavelength of the light sources is another important factor for the heterogeneous photocatalysis reaction. A low energy UV light source (from 315 to 400 nm) may be not

\[
\text{TiO}_2 + h \nu \rightarrow e_{\text{CB}}^- + h^+_{\text{VB}}
\]

\[
h^+_{\text{VB}} + \text{Ti} - \text{OH} \rightarrow \text{Ti} - \text{OH}^*
\]

*Scheme 3.9: Photocatalytic reactions of TiO₂.*
sufficient for the excitation of more electrons from the valence band to the conduction band of TiO$_2$ and will affect the photocatalytic decomposition of 4-CP (low rate of degradation of 4-CP could be obtained). Using a high energy UV light source ($\sim$254 nm), electron / hole pair formation can be generated by the band gap excitation of the TiO$_2$ particles which leads to more recombination of electrons and holes and will reduce the photocatalytic activity of the catalyst showing less degradation of 4-CP. A UV light source which emits light around in the range between 270 – 300 nm was found to be the optimum light source in order to produce a higher rate of degradation of 4-CP than the other two light sources (of low and high energy).

A wide variety of inorganic compounds such as: ammonia, chromium and iron species, nitrates and nitrites, platinum and rhodium species, silver, etc and organic compounds including alkanes, aliphatic alcohols, carboxylic acids, alkenes, aromatic compounds and dyes which are sensitive to photochemical transformation on semiconductor surfaces have been involved in the study of the photocatalytic activity of semiconductors. In recent years, the oxidative transformation of inorganic and organic compounds to HCl, HBr, NO$_3^-$, CO$_2$, H$_2$O, etc via heterogeneous photooxidation on TiO$_2$ has received a great attention for many authors. The effect of TiO$_2$ nanoparticles on the degradation of different pollutants in aqueous solution were studied using electron beam irradiation.

The photoreductive degradation of carbon tetrachloride (CCl$_4$) in the presence of TiO$_2$ proceeds via the following stoichiometry:

$$\text{CCl}_4 + 2 \text{H}_2\text{O} \xrightarrow{h\nu, \text{TiO}_2} \text{CO}_2 + 4 \text{H}^+ + 4 \text{Cl}^-$$

Choi and Hoffmann$^{193}$ have proposed the following mechanism (scheme 3.10) in the absence of oxygen for the photodegradation of carbon tetrachloride on TiO$_2$ in aqueous suspension in the presence of organic electron donors (alcohols, carboxylic acids or benzene derivates). The role of the organic electron donors is to enhance the rate of CCl$_4$ dechlorination. In this mechanism, the dichlorocarbene is formed due to a two electron transfer pathway initiated by conduction band electron transfer.
Chapter 3. Photochemistry of and on solid substrates

Scheme 3.10: Reaction mechanism of the photodegradation of carbon tetrachloride (CCl₄) on TiO₂ in aqueous suspensions.

\[
\begin{align*}
\text{CCl}_4 + e^-_{CB} & \rightarrow \text{CCl}_3^\cdot + \text{Cl}^- \\
\text{CCl}_3^\cdot + e^-_{CB} & \rightarrow :\text{CCl}_2 + \text{Cl}^- \\
\text{CCl}_4 + 2 e^-_{CB} & \rightarrow \text{CCl}_5^- + \text{Cl}^- \\
\text{CCl}_3^- & \rightarrow :\text{CCl}_2 + \text{Cl}^- \\
\end{align*}
\]

R—H₂C—OH + Ti—OH⁺ + h⁺_{VB} \rightarrow R—CH—OH + TiOH₂⁺

R—CH—OH + CCl₄ \rightarrow CCl₃⁺ + HCl + R—CHO

R—CH—OH + CCl₃⁺ \rightarrow :CCl₂ + HCl + R—CHO

CCl₃⁻ + H⁺ \rightarrow HCCl₃

2 CCl₃⁻ \rightarrow Cl₃C—CCl₃

2:CCl₂ \rightarrow Cl₂C—CCl₂

:CCl₂ + H₂O \rightarrow CO + HCl

Ti—OH⁺ + CO \rightarrow TiH⁺ + CO₂

TiH⁺ + CCl₄ \rightarrow TiOH₂⁺ + CCl₃⁺ + HCl

In the presence of oxygen, the following reaction occurs:

\[
\text{CCl}_3^\cdot + \text{O}_2 \rightarrow \text{Cl}_3\text{CO}_2^\cdot + 3 \text{H}^+ \rightarrow \text{CO}_2 + 3 \text{HCl}
\]

Mills et al.¹⁹⁴,¹⁹⁵ have also studied the photocatalytic oxidation of 4-chlorophenol (4-CP) adsorbed on the surface of TiO₂. The reaction intermediates were determined to be hydroquinone (HQ) and 4-chlorocatechol (4-CC). The pathway of 4-CP degradation and the intermediates formed during the reaction are shown in scheme 3.11. The addition of ClO₃⁻ increases the rate of degradation of 4-CP.

78
According to the reaction mechanism shown in scheme 3.11, three reaction pathways proceed in parallel after the initial hydroxylation of 4-CP to form 4-chlorodihydroxycyclohexadienyl radical (4-CD). The formation of the hydroquinone via reduction by a conduction band electron is the main primary degradation step. Abstraction of an H-atom leads to the formation of the unstable intermediate (1) which is hydrolyzed to form a ring opened acid chloride (2). The acid chloride formed hydrolyzes then to a carboxylic acid (3) and releases HCl. Abstraction of an electron from 4-CD yields 4-CD$^+$. This reaction (3) is facilitated by the presence of ClO$_3^-$ anion. Further, 4-CD$^+$ undergoes a back reaction (4) to the 4-CD via reduction by a conduction band electron or deprotonates (5) to form the unstable intermediate (1) and then the products (2) and (3).
The photochemistry of 4-CP was studied on silica and cellulose\textsuperscript{196} and in aqueous solution\textsuperscript{197} using time-resolved reflectance laser flash photolysis. The results have shown that the photochemistry of 4-CP is complex and depends on the support, the pH, concentration of 4-CP and the presence of molecular oxygen.

Da Silva \textit{et al.}\textsuperscript{196} and Durand \textit{et al.}\textsuperscript{197} have reported that the main photoprocess resulted during the photolysis of 4-CP at low concentration in air saturated solution is benzoquinone (BQ), while at higher concentration, benzoquinone results from both molecular and bimolecular reactions. In the absence of oxygen, at low concentrations, hydroquinone (HQ) was detected as the main product, whereas at higher concentrations of 4-CP the formation of 5-chloro-2,4’-dihydroxybiphenyl was reported.

The mechanism of the photodegradation of 4-CP in solution is presented below.
Scheme 3.12: Reaction mechanism for the photodegradation of 4-chlorophenol in solution.

Scheme 3.13 shows the reaction mechanism proposed by Da Silva et al.\textsuperscript{196} for 4-CP adsorbed on silica and cellulose and some differences in the resulted photoproducts on these both surfaces during the degradation of 4-CP were detected.
Scheme 3.13: Reaction mechanism of the photodegradation of 4-chlorophenol on silica and cellulose.

The photooxidation of 4-CP is best described by four reaction pathways. One reaction pathway leads to the formation of the carbene-4-oxocyclohexa-2,5-dienylidene (1) from 4-CP by loss of HCl and it is considered the main primary photodegradation product.
Chapter 3. Photochemistry of and on solid substrates

On silica gel as in aqueous solution\textsuperscript{197}, the carbene (1) reacts with the molecular oxygen and forms 1,4-benzoquinone–O-oxide which subsequently yields 1,4-benzoquinone (2). 1,4-hydroxyquinone (3) is detected as the result of the reaction of the carbene with water. Moreover, in both cases of silica and cellulose, at higher concentrations of 4-CP, the carbene can react with ground state 4-CP molecules and form 5-chloro-2,4’-dihydroxybiphenyl (4).

On cellulose, at lower concentrations of 4-CP, the formation of phenol (5) is possible by abstraction of a hydrogen atom from the carbene (1) and then from the phenoxy radical resulted as intermediary in this reaction pathway. At higher loading of 4-CP, phenoxy radical can couple and form dihydroxybiphenyls (6).

The modification of titania with silica and zirconia\textsuperscript{198} or alumina\textsuperscript{30} has been shown to be a better photocatalyst for the oxidation of ethylene. The photocatalytic activity is improved relative to TiO\textsubscript{2} alone when the mixed oxides prepared by sol-gel are used in the photocatalytic decomposition of different organic compounds. This increase in activity due to the addition of silica or zirconia may be a result of higher surface area. The hydroxyl groups on the surface of mixed oxides accept holes generated by irradiation and oxidize the adsorbed molecules. Hole traps prevent electron-hole recombination and therefore, increase quantum yield.

Anderson et al.\textsuperscript{199} have studied the photodecomposition of rhodamin-6G adsorbed on titania-silica mixed oxides prepared by sol-gel method. It is known that the rhodamine adsorbs on SiO\textsubscript{2}, but not on TiO\textsubscript{2} and it does not undergo photodegradation in aqueous solution. The authors have demonstrated that the rate of decomposition of rhodamine-6G depends on the TiO\textsubscript{2} / SiO\textsubscript{2} ratio and found that the largest rate corresponds to a ratio of 30 / 70 TiO\textsubscript{2} / SiO\textsubscript{2} suggesting that the TiO\textsubscript{2}-SiO\textsubscript{2} catalyst is 3 times more active than Degussa TiO\textsubscript{2} P25. The increase in efficiency can be attributed to a large surface area and to the acidic SiO\textsubscript{2} sites which promote the adsorption of rhodamine-6G. The TiO\textsubscript{2} behaves as a photoactive centre generating hydroxyl radicals under irradiation, while SiO\textsubscript{2} provides better adsorption sites in the vicinity of the TiO\textsubscript{2}.

Anderson et al.\textsuperscript{30} have also studied the photodecomposition of salicylic acid in a mixed TiO\textsubscript{2} / Al\textsubscript{2}O\textsubscript{3} photocatalyst relative to pure TiO\textsubscript{2} and the photocatalytic oxidation of phenol on TiO\textsubscript{2} / SiO\textsubscript{2}, TiO\textsubscript{2} / Al\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2} materials prepared by sol-gel methods.
The measured rates for the decomposition of phenol are reported to be slower for all the mixed oxides than for pure TiO$_2$. This is due to the fact that SiO$_2$ and Al$_2$O$_3$ do not adsorb the phenol and it decreases the activity of the catalysts by reducing the quantity of TiO$_2$ available for photoreactions relative to pure TiO$_2$. The increase in the photocatalytic activity of the TiO$_2$ on TiO$_2$ / SiO$_2$ mixed oxides can be attributed to the presence of a mixed Ti—O—Si phase at the TiO$_2$ / SiO$_2$ interface (situated in the very close proximity to the TiO$_2$ sites) and possessing sites of high Brønsted acidity which activate the oxidation of phenol near the photoactive TiO$_2$ sites.

The photocatalytic activity of TiO$_2$ / Al$_2$O$_3$ mixed oxides is increased relative to the pure TiO$_2$ due to the high surface area of the mixed materials. On the other hand, the enhancement of the photocatalytic efficiency of TiO$_2$ / Al$_2$O$_3$ mixed oxides can be attributed to the adsorption of salicylic acid on the Al$_2$O$_3$ near the TiO$_2$ sites and the loss of catalyst activity by the replacement of the active TiO$_2$ sites with nonphotoactive TiO$_2$ / Al$_2$O$_3$.

The present study was undertaken to investigate the capability of titania-silica mixed oxides prepared by sol-gel method (TiSi$_2$) and also the pure TiO$_2$ P25 Degussa to degrade the 4-chlorophenol molecule. A comparative study of the results obtained for the photodegradation of 4-CP using TiSi$_2$ as catalyst relative to those obtained for pure TiO$_2$ P25 will be presented in section 6.4.
4. Experimental

4.1 Materials

Anthracene (99 %) was purchased from Aldrich.

Azulene (99%) and perylene (≥ 99%) used as radical cation quenchers were purchased from Aldrich.

Acetonitrile spectrophotometric grade ≥ 99.5 % used as solvents for preparation of anthracene samples was obtained from Aldrich.

Ludox As – 40 colloidal silica, 40 % wt. suspension in water SiO₂, pH = 9.1, surface area ~ 135 m² / g was purchased from Aldrich.

Tetraethyl orthosilicate (TEOS), tetramethyl orthosilicate (TMOS) and titanium isopropoxide (TIP) were obtained from Aldrich and used to synthesize the silica and titania-silica mixed oxides.

2-Propanol 99 % ACS reagent was purchased from Aldrich.

2M Hydrochloric acid (HCl) was prepared from hydrochloric acid 32 % (purchased from Fischer) and deionized water.

2M Nitric acid was prepared from nitric acid conc. 1.42 Sp. Gr., purchased from Fischer.

Titanium dioxide P25 (TiO₂ P25) was purchased from Degussa-Hüls and 4-Chlorophenol (99 %) used to study the photocatalytical activity of titania-silica mixed oxide was obtained from Aldrich.

4.2 Preparation of silica gel

4.2.1 “Dropwise” method

Silica gel was obtained by a “dropwise” method from 40 % Ludox (15 ml) purchased from Aldrich in presence of 2M HCl (15 ml). After 4 hours of mixing, the water was removed from system by rotary evaporation and silica was dried in air overnight at 60 °C.
and then calcined in a furnace at 450 °C for 30 minutes. Silica particles prepared by this method were designed silica “dropwise”.

4.2.2 Sol-gel method

Silica gel monolith was synthesized according to the technique reported in literature\textsuperscript{200}. Silica monolith was prepared from tetraethyl orthosilicate (TEOS) or tetramethyl orthosilicate (TMOS), water and 2M nitric acid. The molar ratios were: TEOS (TMOS) : H\textsubscript{2}O : HNO\textsubscript{3} = 1 : 20 : 1.04. Firstly, 2M nitric acid was added to deionized water and stirred for a few minutes. Then, TEOS or TMOS was added under continuously stirring until the solution became transparent. After all chemicals were added, the mixture was stirred for 30 min at room temperature. After this time, the solution was stirred continuously while it was heated at 80 °C for a further 30 min. The water and the alcohol formed during the hydrolysis and condensation process were removed from system by rotary evaporation. The silica monolith was dried in air overnight at 60 °C and then at 130 °C for a further 6 hours. Finally, the silica particles were calcined at 450 °C for 30 min. A large amount of water (20 mol) involves a complete hydrolysis of the alkoxide precursor and it is followed by the condensation process which leads to formation of cross-linked colloidal particles\textsuperscript{47}. Also, an increase in the amount of acid leads to a fast gelation time\textsuperscript{200}. Silica particles prepared by the sol-gel method were designed silica sol-gel.

4.3 Preparation of titania-silica binaries

4.3.1 “Dropwise” method

Titania-silica mixed oxides were prepared by a dropwise addition of titanium isopropoxide (iv) (TIP) to a mixture of 2M HCl and 40 % Ludox under stirring for 4 hours. The water was removed from system by rotary evaporation and the resulting titania-silica solids were dried in air overnight at 60 °C and then calcined in a furnace at 450 °C for 30 minutes. Titania-silica solids prepared by this method are designed TiSi_1.
4.3.2 Sol-gel method

Titania-silica mixed oxides obtained by the sol-gel method were synthesized according to the technique reported in the literature\textsuperscript{200,201}. Titania-silica mixtures with 1, 3, 5 and 10 wt. % of TiO\textsubscript{2} were prepared from tetraethyl orthosilicate (TEOS) or tetramethyl orthosilicate (TMOS), water, 2M nitric acid, titanium isopropoxide (iv) (TIP) and 2-propanol. The molar ratios were: TEOS (TMOS) : H\textsubscript{2}O : HNO\textsubscript{3} : TIP : 2-PrOH = 1 : 20 : 1.04 : 0.05 : 0.2. Firstly, 2M nitric acid was added to deionized water and stirred for a few minutes. Secondly, TEOS or TMOS was added under continuously stirring until the solution became transparent. After that, the mixture was stirred for 30 min at room temperature. After this time, the solution was stirred continuously while it was heated at 80 °C for a further 30 min and cooled down to room temperature. Next the TIP solution (a mixture of TIP and 2-propanol) was added dropwise to the silica solution under vigorous stirring. Titania-silica mixed oxides were then heated at 80 °C for 5 min. The solvents formed during the hydrolysis and condensation process were removed from system by rotary evaporation and the mixture was dried in air overnight at 60 °C and then at 130 °C for a further 6 hours. The resulting titania-silica solids were treated at 450 °C for 30 min to form the anatase crystalline phase. Samples prepared by the sol-gel method are designed TiSi\_2.

4.4 Calcination

Silica gel and titania-silica mixed oxides prepared by both methods (a “dropwise” method and a sol-gel route) were dried in air overnight at 60 °C and then at 130 °C for a further 6 hours. The pre-treatment temperature at < 150 °C corresponds to the removal of adsorbed water. After drying, the resulting solids were calcined in a furnace at 450 °C for 30 min and then ground to white fine powders.

The role of the calcination process is to remove all organic residues. The uncalcined aerogels contain large amounts of carbon which comes from the realkoxylation of surface hydroxyl groups and also the incorporation of both unhydrolyzed alkoxides and solvent\textsuperscript{202}. The thermal treatment in air at 450 °C increases the surface area. Simultaneously, a crystallization of TiO\textsubscript{2} occurs during calcinations.
Chapter 4. Experimental

The calcination process leads to significant particle agglomeration, grain growth and small surface area. The phase transformation from anatase to rutile occurs at calcination temperatures higher than 450 °C and the photocatalytic activity of titania decreases as the result of increasing the calcination temperature\(^8\)\(^{66,203}\).

4.5 Physico-chemical characterization

4.5.1 \(^{29}\)Si solid state NMR spectroscopy

Solid-state \(^{29}\)Si DP-MAS NMR (direct polarization magic angle spinning nuclear magnetic resonance) and \(^{29}\)Si CP-MAS NMR (cross polarization magic angle spinning nuclear magnetic resonance) measurements were recorded on a Bruker Avance 500 MHz NMR spectrometer, equipped with a 4 mm MAS HX probe (MAS up to 15 kHz), 100 W proton amplifier and 500 W amplifier for the X channel. Cross-polarization used a 1H pulse of 2 s (at −5.5 dB), a ramped proton CP pulse of 2 ms (at −4.0 dB) and a carbon CP pulse of 2 ms (at −3.1 dB). Two pulsed phase modulation (TPPM 15) proton decoupling was applied during the 30 ms acquisition time. The free induction decays (FIDs) contain 3k data points which were Fourier transformed into 16k data points; an exponential function of 50 Hz was applied to the FID using Bruker TOPSPIN (1.3) software. Spectra were referenced to external tetramethylsilane (TMS, \(^{29}\)Si) and the magic angle was set up using KBr. Magic angle spinning of 10 kHz was used. CP-MAS \(^{29}\)Si a relaxation delay of 10 s was used between each scan. DP-MAS \(^{29}\)Si a relaxation delay of 300 s was used. Solid-state NMR experiments were conducted with the kind help of Dr. Mark Edgar from Loughborough University.

4.5.2 Fourier transformation infrared spectroscopy (FTIR)

Fourier transformation infrared (FTIR) measurements were performed on an instrument with a dedicated Diamond Attenuated Total Reflectance single bounce accessory in the range 400 - 4000 cm\(^{-1}\). Sample wafers consisted of 100 mg dry KBr and ca. 1 mg sample. For each spectrum, 128 scans were accumulated at a spectral resolution of 8 cm\(^{-1}\). The spectrum of dry KBr was taken for background subtraction. The FTIR measurements were conducted with the kind help of Dr. Pik Leung Tang from the University of Strathclyde.
4.5.3 The Brunauer–Emett–Teller (BET) surface area

The Brunauer-Elmett-Teller (BET) surface area ($S_{BET}$) and desorption pore volume ($V_P$) of calcined titania-silica mixed oxides were determined by N$_2$ adsorption at 77 K using a Micrometrics TriStar 3000 instrument. The BET surface area measurements were conducted with the kind help of Mr. Andrew Lau from Department of Chemical Engineering, Loughborough University.

4.6 Sample preparation

4.6.1 Anthracene adsorbed on silica surface

Silica gel (obtained by 4.2.1 and 4.2.2 methods) was dried under vacuum at 5 x 10$^{-5}$ mbar and 125 °C for 8 hours to remove the physically adsorbed water from the surface and left overnight under vacuum at room temperature. The vessel was re-pressurised with dry nitrogen and the anthracene solution added to the silica gel. Anthracene was added from acetonitrile solution and concentrations were in the range 1.0 μmol g$^{-1}$ to 10 μmol g$^{-1}$ corresponding to less than 5 % of a monolayer coverage. The percentage of monolayer can be determined from the area of the molecule adsorbed on the surface divided by the surface area and expressed by the following equation:

\[
\% \text{ monolayer} = \frac{A_{An} \times N_r \text{ of molecules}}{S_{BET}}
\]

where $A_{An}$ represents the area of anthracene molecule and can be estimated from a molecular modelling package (e.g from HyperChem, $A_{An}$ =364.05 Å$^2$) and $S_{BET}$ is the surface area of silica gel or titania-silica mixed oxides (m$^2$ / g).

After equilibration for 1 hour, the solvent was removed under vacuum and samples of anthracene were dried under vacuum to a pressure of 5 x 10$^{-5}$ mbar for a further 8 hours and sealed into a cylindrical glass or quartz cuvette (22 mm diameter x 10 mm pathlength). Sample loadings were determined from the mass of solution and concentration of dissolved compound added to the surface.
4.6.2 Anthracene (or 9-anthracenecarboxylic acid) co-adsorbed with radical cation quencher on silica sol-gel

Anthracene (or 9-anthracenecarboxylic acid) with radical cation quencher adsorbed on silica sol-gel was prepared by method 4.6.1. Anthracene (9-anthracenecarboxylic acid) with azulene and/or perylene as quenchers were added and dissolved in acetonitrile solution and then adsorbed to the silica sol-gel surface. The concentrations of anthracene (or its derivative) and perylene were kept constant at 1.0 \( \mu \text{mol g}^{-1} \) and 0.5 \( \mu \text{mol g}^{-1} \) respectively and the azulene loadings used for preparation of samples were in the range 0.25 \( \mu \text{mol g}^{-1} \) - 2.0 \( \mu \text{mol g}^{-1} \) on the support surface.

4.6.3 Anthracene adsorbed on titania-silica surface (TiSi_1 and TiSi_2)

TiSi_1 or TiSi_2 mixtures (obtained by methods 4.3.1 or 4.3.2) with different titania content were dried under vacuum at 5 \( \times \) 10^{-5} mbar and 125 °C for 8 hours to remove the physically adsorbed water from oxide surface and left overnight under vacuum at room temperature. The vessel was re-pressurised with dry nitrogen and the anthracene solution added to the titania-silica mixed oxides. Anthracene was added from acetonitrile solution and concentrations were in the range 1.0 \( \mu \text{mol g}^{-1} \) to 10 \( \mu \text{mol g}^{-1} \) corresponding to less than 5 % of a monolayer coverage (calculated as in section 4.6.1). After equilibration for 1 hour, the solvent was removed under vacuum and samples of anthracene adsorbed on TiSi_1 and TiSi_2 surfaces were dried under vacuum to a pressure of 5 \( \times \) 10^{-5} mbar for a further 8 hours and sealed into a cylindrical glass or quartz cuvette (22 mm diameter x 10 mm pathlength). Sample loadings were determined from the mass of solution and concentration of dissolved compound added to the surface.

4.6.4 Anthracene (or 9-anthracenecarboxylic acid) co-adsorbed with radical cation quencher on TiSi_2 surface

Anthracene (or 9-anthracenecarboxylic acid) with radical cation quencher adsorbed on TiSi_2 surface was prepared by method 4.6.3. Anthracene (9-anthracenecarboxylic acid) with azulene and/or perylene as quenchers were added and dissolved in acetonitrile solution and then adsorbed to the titania-silica surface. The concentrations of anthracene (or its derivative) and perylene were kept constant at 1.0 \( \mu \text{mol g}^{-1} \) and 0.5 \( \mu \text{mol g}^{-1} \)
respectively and the azulene loadings used for preparation of samples were in the range
0.25 μmol g$^{-1}$ - 2.0 μmol g$^{-1}$ on the support surface.

4.6.5 Photocatalytic activity measurements

The preparation method for the TiSi$_2$ mixed oxides has been described previously in
section 4.3.2. Titanium dioxide P25 (TiO$_2$ P25) is provided from Degussa-Hüls and used
as a standard photocatalyst. 4-Chlorophenol (99 %) used to study the photocatalytic
activity of TiO$_2$ P25 and TiSi$_2$ mixed oxides at different content of titania (1, 3, 5 and
10 wt. % TiO$_2$) was purchased from Aldrich.

Deionized water was used to prepare the 4-chlorophenol solution with a concentration of
9.6 x 10$^{-5}$ mol l$^{-1}$. 40 mg of photocatalyst (calcined TiSi$_2$ mixed oxides at different
content of titania and TiO$_2$ P25) was suspended in a glass vessel with the aqueous
solution of 4-chlorophenol (10 ml). Prior to UV light irradiation, the suspension was
stirred for 20 minutes under oxygen atmosphere at room temperature. The sample was
then irradiated at 25 °C for 4 hours using UV light from a 275 W xenon arc lamp (Oriel)
with continuous stirring under oxygen atmosphere in the system. At periodic interval of
10 minutes, ~ 5 ml of sample were taken from the system and filtered through a
Millipore filter (Iso-Disc Filter PVDF 254, 25 mm x 0.45 mm) to remove the TiSi$_2$ or
TiO$_2$ P25 particles.

The % degradation of 4-chlorophenol was then analysed and characterized by a UV-Vis
spectrophotometer (Hewlett Packard 8453 diode array spectrophotometer) at 225 nm
(the maximum absorption of 4-chlorophenol) as a function of time. The destruction rates
of photocatalytic oxidation of 4-chlorophenol molecule over irradiated TiSi$_2$ mixed
oxides or TiO$_2$ P25 were determined in order to compare the photocatalytic efficiency of
each catalyst under identical reaction conditions.

4.7 Solution ground state absorption spectra

Solution absorption measurements were carried out using a Hewlett Packard 8453 diode
array spectrophotometer which is provided with a low power light composed from two
lamps: a tungsten and a deuterium lamp. The equipment used in ground state absorption spectroscopy is described in section 2.1. Baseline correction was achieved using a sample of pure solvent. The spectra were recorded between 200 nm and 1100 nm.

4.8 Fluorescence emission spectra

The fluorescence emission spectra of anthracene samples adsorbed on silica and titania-silica surfaces were recorded using a Spex FluoroMax spectrofluorimeter using front surface geometry. The fluorescence emission technique is described in section 2.2.

4.9 Ground state diffuse reflectance spectra

Diffuse reflectance measurements were performed using a Perkin-Elmer Lambda Bio 40 spectrophotometer equipped with a Spectralon integrating sphere. The diffuse reflectance technique is described in section 2.3. The samples were analysed under ambient conditions. The spectra were recorded between 300 nm and 800 nm using barium sulphate as reference. The reflection in percentage was measured and presented using the Kubelka-Munk function.

4.10 Laser flash photolysis

Diffuse reflectance laser flash photolysis studies were carried out exciting with the third harmonic (355 nm, 5 ns fwhm, 110 mJ / pulse) of a Continuum Surelite I Nd:YAG laser. The pulse energy was attenuated using solutions of sodium nitrite in water, to ensure that transient reflectance changes were kept below 10 %, where the change in reflectance is directly proportional to the concentration of transient species\textsuperscript{204,205,206}. Diffusely reflected analysing light from a 275 W xenon arc lamp (Oriel) was collected and focused onto the entrance slit of a f / 3.4 grating monochromator (Applied Photophysics) and detected with a side-on photomultiplier tube (Hamamatsu R928). Signal capture was by a TDS420D (Tektronix) or an LT364 Waverunner digital oscilloscope (LeCroy), interfaced via GPIB to an IBM-compatible PC\textsuperscript{84,109,114,133}. 

92
4.11 Data analysis

Kinetic analysis and spectral interpretation of transient absorption data obtained from diffuse reflectance laser flash photolysis are dependent on the distribution of transients in the scattering medium below the irradiated surface. The concentration of transient species (excited states, radicals) can be determined by measuring the changes in the amount of light absorbed by the transient as a function of time. To analyse transient absorptions in opaque samples, the level of diffusely reflected monitoring light is recorded before and after laser excitation.

In order to obtain a corrected trace for the reflected change $\Delta R_{(t)}$ as a function of time two traces need to be recorded. A representation of the traces is shown in figure 4.1 where TR is the transient absorption produced by simultaneous irradiation of the sample by the laser and the arc lamp (both the arc lamp and laser shutters are open) and results in a decrease in the diffusely reflected monitoring light and EM is the emission induced by laser excitation alone (the laser shutter is open, but the arc lamp shutter is closed).

Figure 4.1: Experimental traces collected from diffuse reflectance laser flash photolysis.

The corrected transient absorption is obtained by using all recorded traces; first, subtracting the emission traces and then the top line (calculated from the emission
pretrigger average) is subtracted from the baseline (calculated from the transient pretrigger average).

\[ \Delta R_{(t)} = \frac{\text{Transient absorption} - \text{Emission}}{\text{Baseline} - \text{Topline}} \]  

(4.2)

The change in diffuse reflectance at the analysing wavelength at time \( t \) can be calculated according to the equation (4.3):

\[ \Delta R_{(t)} = \frac{(R_b - R_{(t)})}{R_b} \]  

(4.3)

where \( R_b \) is the corrected sample reflectance before the laser pulse and \( R_{(t)} \) is the corrected sample reflectance at time \( t \) after laser excitation (TR − EM).

The equation (4.3) can be expressed as:

\[ \%R = \frac{(R_b - R_{(t)})}{R_b} \times 100 \]  

(4.4)

The transient absorption spectrum is plotted as % reflectance change versus wavelength.

The change in diffuse reflectance depends on the decay of the transient species formed by the laser pulse and on the transient concentration profile.

After laser excitation, there are three types of transient concentration profile with respect to sample depth and penetration depth of the analysing light and are shown in figure 4.2.
Figure 4.2: Schematic representation of the three types of transient concentration profile formed by laser excitation of solid sample showing: a) an exponential fall-off profile, b) an intermediate profile and c) a homogeneous plug profile of excited states.

These three limiting cases for the concentration profile as a function of penetration depth are discussed below:

a) An exponential fall-off profile

This arises for samples that have a high molar absorption coefficient at the laser wavelength and low laser fluence. Most of the exciting laser pulse is absorbed by the ground state in the first few layers of sample and little will penetrate deeply into the sample. In this case, the concentration of transient species decreases exponentially with penetration depth into the sample. The Kubelka-Munk equation can not be applied in this case due to the variation of the absorption coefficient with sample penetration depth. For these samples, \( \Delta R \) is directly proportional to the concentration of transient species for changes in reflectance less than 10 \%.

b) An intermediate profile

This occurs when the laser fluence and the absorption coefficient are high. In this case, the first few layers of the sample (the front surface) are saturated and form a region of uniform transient concentration, but the analysing light may also penetrate deeply into the sample if the transient absorption at the analysing wavelength is low.
The concentration of transient species falls off exponentially with penetration depth into the sample. The intermediate case is difficult to analyse due the fact that the analysing light irradiates both of the regions of the sample with consequent effects on the diffusely reflected intensity. The intermediate case is avoided by adjusting the sample concentration or laser fluence to form one of the cases discussed above or below, generally the exponential fall-off profile achieved by attenuation of the laser beam.

c) A homogeneous plug profile

The Kubelka-Munk remission function $F(R_\infty)$ is used to express the linear relationship between concentration and the observed reflectance:

$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{K}{S}$$

(4.5)

where $R_\infty$ is the reflectance of a homogeneous optically thick sample, $K$ is the absorption coefficient and $S$ is the scattering coefficient.

This case arises for samples that have a low molar absorption coefficient at the laser wavelength and a high laser pulse. When high laser fluence is used, each layer of the sample is saturated, a plug of excited states is formed and there is a homogeneous distribution of transient absorbers. In this situation, the Kubelka-Munk relationship can be applied and the difference between the remission function following laser excitation and the remission function before to excitation is proportional to the concentration of the transient species:

$$\Delta F(R) = \frac{(1 - R)^2}{2R} - \frac{(1 - R')^2}{2R'}$$

(4.6)

where $R$ and $R'$ are the observed reflectance before and after laser excitation respectively, and $\Delta F(R)$ is the change in remission function.

The change in remission function can be used to probe the change in excited state concentration.
4.11.1 Dispersive kinetic model

The kinetic decays of homogeneous systems can be explained using the rate laws of first and second order kinetics, whereas in heterogeneous media such as oxide surfaces, semiconductor electrodes, colloidal particles or solid powdered substrates simple photo-induced reaction like unimolecular photoisomerizations do not follow first or second order kinetics.

The solid support can affect or even control the photochemistry and photophysics of an adsorbed probe. The heterogeneous nature of the adsorption sites of solid powdered samples usually leads to complex kinetics. The decay analysis requires a detailed knowledge of the specific physical and chemical interactions of the probe with the solid support sites.

For analysing decays of adsorbed molecules on heterogeneous solid supports, one of the more successful models applied in this context is that developed by Albery et al.\textsuperscript{171}. The Albery model describes kinetic decays using two adjustable parameters: an average rate constant and a parameter determining the width of the rate constant distribution. The derivation of the equations describing this model begins with the assumption that the reaction rate constant \( k \) is proportional to the particle surface area \( r^2 \). The natural logarithm of the particle radius is given as:

\[
\ln r = \ln \bar{r} + \rho x \tag{4.7}
\]

where \( \bar{r} \) is the average particle radius, \( \rho \) is a parameter determining the effective width of the particle size distribution and \( x \) represents the distribution variable and is allowed to take values between plus and minus infinity.

The distribution of the rate constants is then given by:

\[
\ln k = \ln \bar{k} + \gamma x \tag{4.8}
\]

where \( k \) is the rate constant and \( \gamma \) describes the width of the distribution around some average rate constants \( \bar{k} \).
Chapter 4. Experimental

The decays of excited states and radical cations on silica gel and titania-silica surfaces have been characterised using the dispersive kinetic model of Albery et al. using equation (4.9):

$$\frac{C}{C_0} = \frac{\int_{-\infty}^{+\infty} \exp(-t^2) \exp\left[-\tilde{k}t \exp(\gamma t)\right] dt}{\int_{-\infty}^{+\infty} \exp(-t^2) dt}$$  \hspace{1cm} (4.9)

where $C$ and $C_0$ are transient concentrations at times $t = t$ and $t = 0$ after laser pulse, $\tilde{k}$ represents the mean rate constant and $\gamma$ is the width of the distribution.

The replacement of transient concentration $C$ and $C_0$ by the reflectance changes at times $t = t$ and $t = 0$ (relative to the laser pulse) represented by the symbols $\Delta R$ and $\Delta R_0$ can be applied at low sample loadings and smaller reflectance change than 10% (see section 4.11). The transient decay will be then analysed by fitting for $\Delta R_0$, $\gamma$ and $\tilde{k}$ in order to ensure a minimum in the reduced chisquare ($\chi^2$) parameter space.

The parameter $\gamma$ describes the width of the Gaussian distribution (the dispersion of the system). When $\gamma = 0$ there is no dispersion and equation (4.9) reduces to a simple first-order exponential decay:

$$\frac{C}{C_0} = \exp(-\tilde{k}t)$$  \hspace{1cm} (4.10)

The computer program uses the extended Simpson’s rule for a numerical integration of the equation (4.9).

$$\int_{-\infty}^{+\infty} \exp(-t^2) \exp\left[-\tilde{k}t \exp(\gamma t)\right] dt = \int_0^1 g(\lambda) d\lambda$$  \hspace{1cm} (4.11)

$$g(\lambda) = \lambda^{-1} \exp\left[-(\ln \lambda)^2\right] \left\{ \exp\left(-\tilde{k} t \lambda^2\right) + \exp\left(-\tilde{k} t \lambda^{-2}\right) \right\}$$  \hspace{1cm} (4.12)
The advantage of this transformation is that the integration limits are 0 and 1 rather than \( \pm \infty \).

The transient data were analysed by fitting over a range of \( \gamma \) values in order to obtain a global minimum\(^{114} \) in the reduced \( \chi^2 \). From figure 4.3 (a) it can be observed that the minimum value of the reduced \( \chi^2 \) corresponds to the optimum value for \( \gamma \) of 1.1. The 3-dimensional plot of the reduced \( \chi^2 \) versus \( \gamma \) with an additional y-offset axis is represented in figure 4.3 (b).

Figure 4.3: (a) Plot of reduced \( \chi^2 \) versus \( \gamma \) for anthracene co-adsorbed with azulene (0.8 \( \mu \)mol g\(^{-1}\)) on silica gel; (b) 3-Dimensional plot of reduced \( \chi^2 \) versus \( \gamma \) with an additional y-offset axis for anthracene co-adsorbed with azulene (0.8 \( \mu \)mol g\(^{-1}\)).
5. Physico-chemical characterization

A series of silica gel samples and titania-silica mixed oxides were prepared by two different methods; a “dropwise” and a sol-gel route (see sections 4.2 and 4.3), the latter at different titania loadings. The “dropwise” method consists of a dropwise addition of titanium isopropoxide (iv) (TIP) to a mixture of 2M HCl and 40 % Ludox, while the sol-gel route used to synthesize titania-silica mixed oxides involves the hydrolysis and condensation reactions of tetraethyl orthosilicate (TEOS) and titanium isopropoxide (iv).

Titania-silica mixed oxides, whose properties depend on their composition, homogeneity and structure, have attracted considerable interest due to their potential applications as catalysts and supports in a wide variety of reactions. The efficiency of these oxide catalysts is dependent on the molecular scale dispersion of the titanium atoms, high surface area and pore diameter in the mesoporous range (2 – 50 nm) i.e. large enough for the easy accessibility of reactants.

The presence of silanol groups has an important role in the adsorption process of different organic compounds on the oxide surface. Moreover, the hydroxyl groups of silica present a strongly hydrophilic environment limiting the access of organic substrates to the surface. The surface area of silica sol-gel and titania-silica mixed oxides, the pore volume or size and the particle size depend on the method of synthesis and the chemical composition of components. There is a linear relationship between surface area and the adsorption capacity for porous materials, so it is expected that a higher surface area per mass of material should correlate with a higher amount of organic compound adsorbed to the surface. The size distribution is often important to ensure efficient transport of reactants and products to and from the active surface.

Different spectroscopic techniques (solid state $^{29}$Si MAS NMR spectroscopy, FTIR spectroscopy and nitrogen adsorption) have been employed for the physical-chemical characterization of silica gel and titania-silica mixed oxides. The preparation conditions (Ti precursors, content and calcinations temperature) can strongly affect the structure and the surface area of the resulting materials.

Solid state $^{29}$Si MAS NMR spectroscopy has been applied to the study of the structure of silica gel and titania-silica mixed oxides prepared by both methods. $^{29}$Si magic angle
spinning nuclear magnetic resonance investigations indicate that the silica matrix is affected by the substitution of titania. The amount of titania which was substituted depended on the preparation conditions and chemical composition (from TEOS or commercial Ludox). Solid state $^{29}$Si DP-MAS is the best tool for elucidating the connectivity of silicon atoms in solid oxide materials. This is a quantitative technique to determine the structure of titania-silica mixed oxides compared to $^{29}$Si CP-MAS where the energy is transferred from the protons of OHs to the Si, so the silicon surface is favoured. In both materials (TiSi\_1 and TiSi\_2), Ti atoms are shown to substitute Si in the silica matrix to form tetrahedral TiO\_4 units. The results demonstrated the homogeneous incorporation of titania into silica for titania-silica mixed oxides prepared from TEOS (by the sol-gel method).

Fourier transformation infrared spectroscopy (FTIR) is a quantitative technique used to identify the presence of a certain functional groups in a molecule. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present.

The effect of titania addition to silica and the degree of incorporation and dispersion of titanium ions in the silica matrix were evaluated by FTIR spectroscopy of the framework vibrations.

In the present study, we used nitrogen adsorption (BET surface area), $^{29}$Si MAS NMR and FTIR spectroscopy as the characterization tools for determining the nature of the titania species present in the titania-silica mixed oxides. The structural information derived from these spectroscopic studies provides fundamental understanding of surface structure of the molecularly dispersed titania-silica mixed oxides under various conditions.

5.1 $^{29}$Si solid state NMR data

The $^{29}$Si NMR spectra of titania-silica mixed oxides prepared by both methods (TiSi\_1 and TiSi\_2) are given in figure 5.1 and consist of three signals at: -90.6, -102.5 and –111.7 ppm with varying intensities for 10 % TiSi\_1. The -90.6 ppm signal comes from Si sites in a $Q^2$ configuration, and the -102.5 and -111.7 ppm signals come from $Q^3$ and $Q^4$ configurations respectively, where $Q^n$ denotes a SiO\_4 unit with $n$ bridging oxygens.
In 10 % TiSi_2 sample, the peaks at -92.1, -101.2 and -109.9 ppm are also due to silicon atoms occupying Q^2, Q^3 and Q^4 sites respectively. The $^{29}$Si NMR spectra were deconvolved by Gaussian fitting, the percentage of Q^2, Q^3 and Q^4 in both TiSi_1 and TiSi_2 samples was calculated from the integrals of their respective peaks in the spectra of figure 5.1, with the results summarized in table 5.1.

![Figure 5.1: $^{29}$Si DP-MAS NMR spectra of titania-silica mixed oxides: a) 10 % TiSi_2 and b) 10 % TiSi_1.](image)

The corresponding $^{29}$Si NMR spectra of silica sol-gel and silica dropwise samples are given in figure 5.2. For silica sol-gel sample, the chemical shifts are typically -92.4 ppm for Q^2, -101.0 ppm for Q^3 and -109.9 ppm for Q^4. The relative amounts of these different structural sites are derived from the integrated areas of the single pulse peaks in the spectra of figure 6.2 and the results are given in table 5.1. It shown that the chemical shifts in the $^{29}$Si DP-MAS NMR spectra of silica sol-gel and silica dropwise are very similar, even though their preparation is distinctly different. There are structural differences as shown by the different proportions of the various silica environments (table 5.1).
Figure 5.2: $^{29}$Si DP-MAS NMR spectra of silica prepared by two different methods: a) silica sol-gel and b) silica “dropwise”.

Table 5.1: $^{29}$Si DP-MAS NMR data of the investigated titania-silica mixed oxides and silica gel.
The data in table 5.1 indicate that the samples prepared by sol-gel technique are more highly condensed than those prepared by “dropwise” method. There is more bulk silicon (Q⁴ Si(O)₄) than surface silicon (Q² and Q³). ²⁹Si NMR data show that titanium enters the silica network, namely, in “dropwise” samples, there is less Ti in Q⁴ sites than in the case of sol-gel samples were Ti is in bulk (Q⁴ sites preferred).

The Q² and Q³ species result from the presence of a high concentration of terminal –OH and –OTi groups bonded to Si and represent incomplete condensation of the network. SiO₄ units (Q⁴) appear more in the sample prepared by the “dropwise“ method than those synthesized by the sol-gel route. “Dropwise” samples produce a small percentage of Q² and Q³ units and more Q⁴ units than samples prepared by sol-gel. A large Q⁴ percentage indicates a high degree of cross-linking in the silica matrix.

Solid state ²⁹Si DP-MAS NMR spectroscopy allows direct quantitative observations of the structure of titania-silica mixed oxides. The results presented above demonstrate that the synthesis parameters of that two methods influences the structural properties of mixed oxides derived from TEOS and TIP precursors. Chemical shift values (Q² and Q³) obtained from the spectral deconvolution indicate the presence of Si—O—Ti bridges formed during the chemical reactions. Characteristic NMR signals of silica are silanediol groups (Q²), silanol groups (Q³) and siloxane groups (Q⁴). The percentage of Q² and Q³ units is significantly enhanced from the partial hydrolysis of the silicon alkoxide with the acid condition. A fast condensation process and the heat treatement on the mixed oxides increases polymerized Q⁴ species. The Q⁴ sites (SiO₄) are dominant in pure silica, indicating that the condensation of the silicon alkoxide precursor is complete and the samples have a well-developed three-dimensional framework.

5.2 FTIR spectra

To gain information about the formation of Si—O—Ti linkages, or a better understanding of the chemical structure of the composite, the FTIR spectra of pure silica and titania-silica mixed oxides with different titania content calcined in air at 450 °C were measured and presented in figure 5.3. The strong IR absorbance at 1046 cm⁻¹ can be assigned to asymmetric υas (Si—O—Si) stretching vibrations (figure 5.3 (a)).
Figure 5.3: FT-IR absorption spectra of pure silica sol-gel and titania-silica mixed oxides (TiSi₂) at different titania content.

Titania-silica mixed oxides are characterized by a typical band at ~ 953 cm⁻¹, which is associated with the formation of Si—O—Ti bridges. This band is assigned to the
tetrahedrally coordinated Ti\(^{4+}\) ions which should substitute for Si\(^{4+}\) ions in the bulk matrix of titania-silica mixed oxides.

The band at \(\sim 800 \text{ cm}^{-1}\) is attributed to the asymmetric and symmetric Si—C stretching modes, respectively. It shows in figure 5.3 (b) a strong band in the region 3600 – 3000 cm\(^{-1}\) associated to H-bonded OHs of water molecules and of silanol groups. A small amount of silanols free from H-bonding is present and responsible for the residual sharp band at \(\sim 3740 \text{ cm}^{-1}\).

Finally, FTIR surface technique permits the quantitative evaluation of the exposed titanium on the surface. The OH spectral region in the figure 5.3 (b) shows that hydroxyl groups are present in calcined samples. The presence of Si—O—Ti species at \(\sim 953 \text{ cm}^{-1}\) indicates good mixing of Ti and Si at the atomic level has resulted, which is an important factor in catalytic applications.

### 5.3 Surface properties (BET surface area)

The surface area is one of the most important quantities for characterizing porous materials. BET analysis is the standard method for determining surface areas from nitrogen adsorption isotherms. The nitrogen adsorption-desorption isotherms of synthesized TiSi\(_2\) mixed oxides with various titania content and silica sol-gel are presented in figure 5.4. It shows type III and IV adsorption isotherms (IUPAC classification) indicating that mesopores are present in the mixed oxides.

Structural properties of TiSi\(_2\) mixed oxides calcined in air at 450 °C are listed in table 5.2. As it is presented in section 4.3, a high water / alkoxide ratio of 20 : 1 was chosen for the hydrolysis of the precursor and the gel prepared under these conditions is porous with a high surface area. The surface area of the titania-silica mixed oxides decrease as the percentage of titania is increased as evident from table 5.2. The decrease in surface area may be due to the occupation of titania in the pores of the aerogels. Based on earlier studies, Balkis and co-workers\(^{207}\) reported that the decrease in surface area with increasing silver content in silver-silica aerogels is attributed to crystallisation of silver particles in the pores of the aerogel matrix.
Figure 5.4: Nitrogen adsorption isotherms of TiSi$_2$ mixed oxides prepared with different titania content and pure silica sol-gel.

The pore size distributions for titania-silica mixed oxides and silica sol-gel were calculated by applying the Barret-Joyner-Halenda (BJH) method to the adsorption branches of the nitrogen isotherms. These distributions are given in figure 5.5. The mesopore volume changes in the same way as BET surface area. Titania is a low porosity material and from this reason the increase in titania content results in a decrease in the mesopore volume and lower specific surface area. The pore size distribution extends from 2 to 50 nm.
Table 5.2: BET surface areas and pores diameter of TiSi_2 mixed oxides and silica sol-gel.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m²/g)</th>
<th>Pores diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 % TiSi_2</td>
<td>727 ± 2.3</td>
<td>3.8 ± 0.12</td>
</tr>
<tr>
<td>3 % TiSi_2</td>
<td>662 ± 5.1</td>
<td>2.9 ± 0.22</td>
</tr>
<tr>
<td>5 % TiSi_2</td>
<td>585 ± 10.9</td>
<td>2.7 ± 0.24</td>
</tr>
<tr>
<td>10 % TiSi_2</td>
<td>619 ± 7.3</td>
<td>2.8 ± 0.24</td>
</tr>
<tr>
<td>Silica sol-gel</td>
<td>658 ± 6.2</td>
<td>3.0 ± 0.26</td>
</tr>
</tbody>
</table>

Figure 5.5: Pore size distributions of TiSi_2 mixed oxides and pure silica sol-gel prepared by calcination at 450 °C.
All of the TiSi$_2$ samples have a narrow distribution of pore size. Although the average pore size of the synthesized titania-silica mixed oxides is in the range of mesoporous materials, their adsorption/desorption isotherms are similar to one of the mesoporous materials. In conclusion, titania-silica mixed oxides prepared by sol-gel method possess large surface area and mesopore volumes ideal for catalytic applications.
6. Results and discussion

6.1 Anthracene adsorbed on TiSi_1 and TiSi_2 surfaces

6.1.1 Ground state diffuse reflectance spectra

UV spectroscopy has been utilized to characterize the bulk structure of titania-silica mixed oxides. Titania is a semiconductor oxide with an easily measured optical band gap. Ultra-violet diffuse reflectance spectroscopy is used to probe the band structure or molecular energy levels, in the materials since UV excitation creates photogenerated electrons and holes. Spectra of titania-silica mixed oxides (TiSi_1 and TiSi_2) with different titania content are presented in figure 6.1.

![Figure 6.1: Ground state diffuse reflectance spectra of: a) TiSi_1 and b) TiSi_2 mixed oxides at different titania content.](image)

The band gap energy of bulk anatase$^{208,209}$ is 3.2 eV. The band gaps estimated from the absorption spectra are as follows: 1 % TiO_2 – 4 eV; 3 % TiO_2 – 3.8 eV; 5 % TiO_2 – 3.7 eV; 10 % TiO_2 – 3.4 eV. The band gap energy of titania-silica mixed oxides increases with the decrease of the amount of titania. The shift of the band gap to higher energy might be the result of the quantum size effect. With a rise in titania content of the titania-silica mixed oxides, the UV absorption edge shifts to longer wavelengths. This shift in the spectra of titania-silica solids indicates that the Ti domains grow progressively larger with increasing titania content.
Ground state diffuse reflectance absorption spectra for anthracene adsorbed onto TiSi\textsubscript{1} and TiSi\textsubscript{2} surfaces were studied as a function of titania content. Anthracene concentrations were in the range 1.0 \( \mu\text{mol g}^{-1} \) to 10 \( \mu\text{mol g}^{-1} \) corresponding to less than 5\% of a monolayer. Kubelka-Munk remission function spectra of anthracene adsorbed on both titania-silica surfaces at different titania loading are shown in figures 6.2 and 6.3.

**Figure 6.2:** Ground state diffuse reflectance spectra of anthracene: (a) 1.0 \( \mu\text{mol g}^{-1} \), (b) 5.0 \( \mu\text{mol g}^{-1} \) and (c) 10 \( \mu\text{mol g}^{-1} \) adsorbed on TiSi\textsubscript{1} surfaces at different titania content and silica dropwise plotted as remission function spectra.
According to the figures 6.2 and 6.3 anthracene ground state absorption $S_0 \rightarrow S_1$ transition ($\pi - \pi^*$) has absorption in the spectral range 330 – 380 nm. The solution spectra of anthracene (in hexane) and the ground state diffuse reflectance spectrum of anthracene adsorbed on silica sol-gel also present this $\pi - \pi^*$ transition in the UV peaking at approximately the same wavelengths (figure 6.4). The peak positions and shapes of the remission function spectra are similar to those obtained in hexane solution. The slight broadening of the spectrum results from the interaction of anthracene with the solid surface and due to the heterogeneity of the adsorbent surface.
Figure 6.4: A comparison between anthracene in hexane solution plotted as absorbance (dash line) and anthracene on silica sol-gel plotted as remission function (solid line).

The ground state diffuse reflectance spectra of anthracene adsorbed on TiSi\(_1\) surface at different loading of titania (figure 6.2) are similar with the spectra corresponding to anthracene adsorbed on TiSi\(_2\) surface (figure 6.3).

The absorption peaks of anthracene are difficult to observe at higher content of titania due to the titania absorption edge which overlaps significantly with the anthracene absorption as the band gap decreases. The absorption edge of titania in titania-silica mixed oxides is defined at 410 – 415 nm. The absorption peak corresponding to anthracene radical cation can be observed at 715 nm. This small amount of anthracene radical cation is formed after irradiation of the samples with the UV lamp (a low intensity light source) of the spectrophotometer. The samples were not exposed to any laser radiation or an arc lamp before the ground state diffuse reflectance spectra were recorded. That means, this production of anthracene radical cation under these conditions is a monophotonic process\(^{208,209}\). The formation of anthracene radical cation on titania-silica surface is due to the interactions of anthracene molecule with Lewis acid sites present on the surface. There is a charge transfer from the anthracene excited state into the conduction band of titania.
6.1.2 Fluorescence emission spectra

The fluorescence emission spectra of a number of anthracene concentrations adsorbed on both TiSi_1 and TiSi_2 surfaces at different titania content following excitation at 355 nm are shown in figures 6.5 and 6.6. All spectra were recorded using a Spex FluoroMax spectrofluorimeter with a front surface geometry. The fluorescence spectra of anthracene adsorbed on TiSi_1 and TiSi_2 surfaces at different loading of titania show a dependence on titania content.

![Fluorescence emission spectra of anthracene](image)

*Figure 6.5: Fluorescence emission spectra of anthracene: (a) 1.0 µmol g\(^{-1}\), (b) 5.0 µmol g\(^{-1}\) and (c) 10 µmol g\(^{-1}\) adsorbed on TiSi_1 surfaces at different loading of titania and silica dropwise following excitation at 355 nm.*
Figure 6.6: Fluorescence emission spectra of anthracene: (a) 1.0 μmol g⁻¹, (b) 5.0 μmol g⁻¹ and (c) 10 μmol g⁻¹ adsorbed on TiSi₂ surfaces at different loading of titania and silica sol-gel following excitation at 355 nm.

It is clearly observed that the fluorescence quenching of the excited anthracene occurs on both systems (TiSi₁ and TiSi₂) and shows a dependence on titania content; the fluorescence emission intensity of adsorbed anthracene decreases with increasing titania content. The fluorescence observed is from the anthracene molecules adsorbed on silica sites, while the extent of fluorescence quenching observed at low anthracene loading is via an electron transfer mechanism which occurs between anthracene excited state and titania centers demonstrating the preferential adsorption of anthracene molecules at titania sites. Another mechanism responsible for the observed decrease in the fluorescence intensity is the inner filter effect in the region of the spectra where there is overlap between the anthracene absorption and titania absorption edge, as is clearly evident in figures 6.2 and 6.3.
The fluorescence emission spectra confirm the presence of the peaks corresponding to anthracene at 380 nm, 400 nm, 420 nm and a small peak at 450 nm. A large decrease in fluorescence intensity can be observed for samples adsorbed on TiSi$_2$ surface prepared by the sol-gel method compared with the fluorescence intensities corresponding to anthracene samples prepared on TiSi$_1$ surface. This reduction in fluorescence intensity can be attributed to production of anthracene radical cation and Ti$^{3+}$ (excitation of the samples with 355 nm UV radiation produces both anthracene radical cation and Ti$^{3+}$). On the other hand, the sol gel samples contain tetrahedrally coordinated titanium dioxide species which possess high absorption activity and hence dimer formation could be considered as a mechanism for fluorescence quenching$^{210}$. 

Increasing of anthracene loading leads to a narrowing of the spectra at longer wavelengths (figure 6.7). This observation may be explained as an effect of the change in depth of penetration of the exciting light into the sample. The fluorescence intensity depends on the amount of light absorbed. This means that the amount of light absorbed increases with increasing anthracene concentration. An increase of the anthracene concentration leads to a decrease in penetration depth. In other words, if the anthracene concentration increases, there is more absorption at the front face of the sample and the effects of self-absorption and reemission are reduced, effectively reducing the relative intensity at longer wavelengths. Moreover, at anthracene loadings in excess of 3.0 $\mu$mol g$^{-1}$ the fluorescence emission intensities of all three peaks decrease due to the formation of aggregates at higher sample loadings$^{110,211}$. 

116
Figure 6.7: Normalised fluorescence emission spectra of anthracene adsorbed on 1 % TiSi_2 surface plotted as a function of anthracene concentration following excitation at 355 nm.

6.1.3 Transient absorption spectra

Transient absorption spectra of anthracene adsorbed on TiSi_1 and TiSi_2 surfaces at different loading of titania were obtained by the use of diffuse reflectance laser flash photolysis (section 4.10). Anthracene concentrations were in the range 1.0 μmol g⁻¹ to 10 μmol g⁻¹. The transient absorption studies were performed at 355 nm laser excitation and the transient absorption spectra of anthracene adsorbed on both titania-silica surfaces at a loading of 1 % titania are shown in figures 6.8 and 6.9.

Figures 6.8 and 6.9 reveal the presence of two species: the anthracene triplet state and anthracene radical cation. The anthracene triplet state is characterized by triplet-triplet absorption peaking at 420 nm, while the peaks corresponding to the anthracene radical cation are localized at 715 nm and 420 nm. Transient absorption at 715 nm in the titania-silica samples may be attributed to production of the anthracene radical cation and on the
other hand to photoinduced production of trapped electrons (Ti$^{3+}$) which absorb in the region 580 - 630 nm. In titania-silica samples, as in conventional titania photocatalysis, holes and electrons are produced in the titania chains by band gap irradiation; the holes react with the adsorbed anthracene and the electrons are trapped at Ti$^{4+}$ sites to generate Ti$^{3+}$.

Figure 6.8: Transient absorption spectra of anthracene adsorbed on: (a) silica dropwise and (b) 1 % TiSi_1 surface at a loading of 5.0 μmol g$^{-1}$ anthracene following laser excitation at 355 nm, in the absence of oxygen.
Figure 6.9: Transient absorption spectra of anthracene adsorbed on: (a) silica sol-gel and (b) 1 % TiSi$_2$ surface at a loading of 5.0 μmol g$^{-1}$ anthracene following laser excitation at 355 nm, in the absence of oxygen.

The spectral characteristics of the transient absorption spectra are not dependent on the anthracene loading; however an increase in anthracene concentration increases the rate of decay or formation of the transient observed.
Analyzing the transient absorption spectrum of anthracene adsorbed on silica dropwise (figure 6.8 a) and the spectrum of anthracene adsorbed on 1 % TiSi_1 surface (figure 6.8 b) can be seen some differences in the relative intensities of the triplet-triplet and radical cation absorption intensities. Figure 6.8 b reveals that the absorption intensities for both triplet-triplet and radical cation absorption are reduced in contrast to the case of silica system (figure 6.8 a). Similar observations can be made in the transient absorption spectra of anthracene adsorbed on silica sol-gel (figure 6.9 a) and anthracene adsorbed on 1 % TiSi_2 surface (figure 6.9 b). A possible explanation of the decrease in the absorption intensities for the anthracene / titania-silica systems could be the competitive absorption of the laser between the anthracene and titania (figures 6.2 and 6.3). Also, comparing the transient absorption spectrum of anthracene adsorbed on 1 % TiSi_1 surface (figure 6.8 b) with that of anthracene adsorbed on 1 % TiSi_2 surface (figure 6.9 b) it is clearly observed that both the triplet-triplet and radical cation absorption of 1 % TiSi_2 system show an increase in absorption intensity relative to the 1 % TiSi_1 system.

Photoexcitation of the anthracene / TiSi_2 systems leads to electron transfer and formation of the anthracene radical cation absorbance at 715 nm which is significantly higher for anthracene sample adsorbed on TiSi_2 surface compared to that of a sample of anthracene on TiSi_1 system and an increased yield of Ti$^{3+}$. In the case of anthracene / TiSi_2 samples, as is clearly evident from figure 6.6, excited singlet state quenching results in the formation of the anthracene radical cation which persists on timescales of a few hundred nanoseconds or longer. Moreover, in both TiSi_1 and TiSi_2 systems, there is observed a slight decrease in radical cation absorption intensity with increasing loading of titania. At higher titania loading the observed transient absorption can be attributed to Ti$^{3+}$ species.

The absorption at 420 nm corresponding to triplet-triplet absorption of anthracene is higher in the case of TiSi_2 system. This suggests that the absorption at 420 nm contains both species: triplet-triplet absorption and radical cation absorption of anthracene. The radical cation absorption overlaps with the triplet-triplet absorption band; the main absorption peak corresponding to anthracene radical cation is located at 715 nm. The presence of this radical cation absorption can be clearly seen in figure 6.10 as
absorption at 715 nm and a change in the shape of the absorption band at 420 nm during the time evolution of the spectrum.

Figure 6.10: Transient absorption spectrum of anthracene at a loading of 1.0 μmol g\(^{-1}\) adsorbed on TiSi\(_2\) surface at a loading of 1 % titania following laser excitation at 355 nm.

The production of anthracene radical cation has been proved to be monophotonic or multiphotonic by monitoring the intensity of both the triplet-triplet absorption at 420 nm and the radical absorption at 715 nm as a function of laser intensity. The laser energy dependence of the anthracene triplet and radical absorption bands was determined by attenuation of the laser pulse using sodium nitrite filters. Figure 6.11 shows the change in reflectance for the anthracene triplet and anthracene radical cation, at a loading of 5.0 μmol g\(^{-1}\) anthracene adsorbed on both TiSi\(_1\) and TiSi\(_2\) surfaces with a content of 1 % titania, as a function of laser fluence, monitoring at 420 nm and 715 nm respectively. The triplet state data were corrected for the absorption due to the radical cation contribution at the triplet wavelength. The radical cation contribution was subtracted from the triplet state data at 420 nm and shown in figure 6.11.
Chapter 6. Results and discussion

Figure 6.11: Triplet and radical cation intensity of anthracene at a loading of 5.0 μmol g⁻¹ adsorbed on: (a) 1 % TiSi_1 and (b) 1 % TiSi_2 plotted as a function of laser intensity.

For the triplet-triplet absorption, there is a linear correlation between laser fluence and reflectance change with a negative deviation at higher laser intensity, typical of monophotonic absorption, due to competition between photoionisation and intersystem crossing of the first excited singlet state. The shape of the plot of triplet-triplet absorption
versus laser fluence demonstrates that the production of the triplet state is a monophotonic process. The triplet-triplet absorption increases rapidly at low laser fluence and then saturates at higher laser fluence, while the radical cation absorption rises slowly with increasing fluence and does not saturate. The plot shown in figure 6.11 for the triplet production is typical for a monophotonic process, while the concave curve shown for the amount of anthracene radical cation production as a function of laser intensity corresponds to a bi- or multiphoton absorption.

Earlier in this thesis it is clearly observed that the radical cation absorption intensity is higher than the triplet-triplet absorption intensity for both the TiSi_1 and TiSi_2 systems (figures 6.8 and 6.9). Because this is due to laser energy demonstrates the multiphotonic nature of radical cation production. As is it mentioned in section 6.1.1, there is a least some monophotonic production of the anthracene radical cation which is also demonstrated by the straight line portion of the plot in figure 6.11 for the radical cation absorption. Energy dependence studies show that the triplet state of anthracene is populated by a monophotonic process, while the radical cation is formed by monophoton and multiphoton ionisation in the mixed titania-silica systems.

Worrall et al. have demonstrated that the triplet-triplet absorption of anthracene on silica gel is a monophotonic process, while the production of anthracene radical action is bi- or multiphotonic. Similar observation has been reported by Oelkrug et al. for the triplet state and radical cation production of distyrylbenzenes adsorbed on silica gel.

6.1.4 Kinetic analysis

Energy dependence studies show that the triplet state formation is monophotonic in the mixed titania-silica systems, while the radical cation production is via a combination of monophoton (as shown in sections 6.1.1 and 6.1.3) and bi- or multiphoton ionisation. The kinetics of decay of radical ions on titania-silica surfaces is not straightforward since the surface is heterogeneous in nature and rates rarely conform to simple exponential kinetics. The observed triplet state and radical cation decays follow complex kinetics.

The model described by Albery et al. based on the distribution of rate constants was used to characterize the decay of triplet excited state and radical cation. The concentration of
transient species formed by the laser pulse falls off exponentially with the penetration depth into the sample. For such samples, the reflectance change $\Delta R$ is directly proportional to the concentration of transient species for values of $\Delta R \leq 0.1$ and the transient concentrations can be replaced\textsuperscript{204-206} by the reflectance change $\Delta R$.

The triplet state and radical cation decays of anthracene adsorbed on silica gel and titania-silica surfaces at different titania content were observed following 355 nm laser excitation and recorded as a function of time. Anthracene was adsorbed from acetonitrile onto silica gel and titania-silica surfaces with a loading in the range of 1.0 $\mu$mol g$^{-1}$ – 10 $\mu$mol g$^{-1}$.

**6.1.4.1 Triplet state kinetics**

Triplet state absorption of anthracene adsorbed on silica, TiSi_1 and TiSi_2 surfaces at different titania loading was monitored at 420 nm. This absorption at 420 nm contains both triplet and radical cation contributions. At the timescales monitored, the anthracene radical cation does not decay and its contribution in triplet-triplet absorption is negligible. From this reason, the anthracene radical cation contribution does not affect the triplet state kinetics. The measured rate constants ($k$) and the width of the distribution ($\gamma$) have been used to characterize the decay. A typical decay trace of the anthracene triplet state at 420 nm and its dispersive model fit are shown in figure 6.12 as reflectance change versus time.
Figure 6.12: Triplet state decay measured at 420 nm of anthracene at a loading of 5 μmol g⁻¹ adsorbed on 10 % TiSi₂ surface following laser excitation at 355 nm plotted as reflectance change versus time. Residuals to the fit are also shown.

Analysis of the decay curves of anthracene samples adsorbed on TiSi₂ surfaces (figure 6.13) show some variation in the observed decay with titania content. The decay is faster in the case of sol-gel samples. At longer times (up to 4 ms), there is still some decay on the sol-gel samples (figure 6.9), but not on the TiSi₁ system (figure 6.8). This suggests that in the TiSi₂ samples, the triplet can move around and find trapping sites, whereas in TiSi₁ samples clustering of titania means that many of the triplet may be a significant distance from a trapping site at longer times. In the anthracene / TiSi₂ systems, photoejected electrons from anthracene are captured by Ti⁴⁺, giving Ti³⁺. The formation of Ti³⁺ species is predominantly in TiSi₂ samples prepared by the sol-gel method from tetraethyl orthosilicate (TEOS) and titanium isopropoxide (iv) (TIP) (section 4.3.2) and where the titania is in very close contact with / or covalently attached to the silica surface. There is a homogeneous distribution of the titania within the silica matrix proved by the formation of Si—O—Ti linkages (section 5.2) at low titania content, while in the
case of dropwise samples (TiSi_1), there are more titania aggregates at the surface and the anthracene may adsorb preferentially on the clusters on TiSi_1 surface.

In TiSi_1 system, the triplet yield at 1 % TiO_2 (figure 6.8 b) is lower than in the case of the sample with no titania (adsorbed on silica dropwise, figure 6.8 a) and the fast decay component is slower and results in the loss of more triplet. The delayed fluorescence yield is also less. This indicates a less mobility resulting in less delayed fluorescence and the triplet state is quenched by the surface titania groups. There is no observed rise on the radical cation signal showing that triplet state quenching does not result in anthracene radical cation formation. At higher titania loading, the triplet yield is substantially reduced.

In TiSi_2 system (figure 6.9), absorption change at 420 nm is greater than in the case of TiSi_1 system (figure 6.8) as the result of the increased radical cation absorption. If the titania content increases, the amplitude of the triplet-triplet absorption decreases. In terms of kinetics, the higher titania contents result in a greater rate of decay at longer
times although there is less delayed fluorescence. The decay of the triplet state anthracene adsorbed on silica gel is dominated by second order process$^{84}$.

The measured rate constants ($k$) and the width of the distribution ($\gamma$) for triplet-triplet absorption of anthracene adsorbed on both titania-silica surfaces and silica gel are presented in table 6.1. Fitting of the triplet-triplet absorption curve of anthracene adsorbed on titania-silica mixed oxides gives a low value of $k$ for samples containing 1 % TiO$_2$. As the titania content increases from 0 to 10 % and the anthracene loading from 1.0 $\mu$mol g$^{-1}$ to 10 $\mu$mol g$^{-1}$, the rate of triplet state decay increases for both TiSi$_1$ and TiSi$_2$ systems.
Chapter 6. Results and discussion

Table 6.1: The mean rate constants ($\tilde{k}$) and the distribution width ($\gamma$) for triplet-triplet absorption decay kinetics of anthracene adsorbed on TiSi_1 and TiSi_2 surfaces as a function of titania content.

<table>
<thead>
<tr>
<th>Titania content</th>
<th>1.0 $\mu$mol g$^{-1}$ anthracene</th>
<th>5.0 $\mu$mol g$^{-1}$ anthracene</th>
<th>10 $\mu$mol g$^{-1}$ anthracene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>An / TiSi_1</td>
<td>An / TiSi_2</td>
<td>An / TiSi_1</td>
</tr>
<tr>
<td>Titania content</td>
<td>$\tilde{k}/10^3$ s$^{-1}$</td>
<td>$\gamma$</td>
<td>$\tilde{k}/10^3$ s$^{-1}$</td>
</tr>
<tr>
<td>1 % TiO$_2$</td>
<td>3.6</td>
<td>1.5</td>
<td>0.5</td>
</tr>
<tr>
<td>3 % TiO$_2$</td>
<td>4.3</td>
<td>1.1</td>
<td>2.9</td>
</tr>
<tr>
<td>5 % TiO$_2$</td>
<td>4.9</td>
<td>1.1</td>
<td>3.4</td>
</tr>
<tr>
<td>10 % TiO$_2$</td>
<td>5.6</td>
<td>0.9</td>
<td>3.9</td>
</tr>
<tr>
<td>Silica</td>
<td>0.8</td>
<td>1.6</td>
<td>1.7</td>
</tr>
</tbody>
</table>
6.1.4.2 Radical cation decay kinetics

Radical cation absorption is observed at 715 and 420 nm. The transient absorption at 715 nm of anthracene adsorbed on TiSi_1 and TiSi_2 surfaces can be attributed\(^8^4\) to production of anthracene radical cation and also to photoinduced production of trapped electrons (Ti\(^{3+}\)) which absorb across the visible region. A typical decay trace of the anthracene radical cation at 715 nm is shown in figure 6.14, fitted using the dispersive kinetic model and plotted as reflectance change versus time.

![Figure 6.14: Radical cation decay measured at 715 nm of anthracene at a loading of 5 \(\mu\)mol g\(^{-1}\) adsorbed on 10 % TiSi_2 surface following laser excitation at 355 nm plotted as reflectance change versus time. Residuals to the fit are also shown.](image)

Inspection of the transient absorption spectra of anthracene adsorbed on both TiSi_1 and TiSi_2 surfaces (figures 6.8 and 6.9) reveals that the radical cation yield is substantially higher for the TiSi_2 samples prepared by the sol-gel method than in the case of TiSi_1 system. This along with the kinetic observations indicates a greater radical stability on
the TiSi_2 samples than on the TiSi_1 samples. Moreover, in both cases of titania-silica mixed oxides the radical cation absorption intensity decreases with increasing titania loading.

The radical cation decay curves of anthracene adsorbed on silica sol-gel and TiSi_2 systems are shown in figure 6.15.

![Radical cation decay curves](image)

Figure 6.15: Radical cation decays measured at 715 nm of anthracene at a loading of 10 μmol g⁻¹ adsorbed on: (a) silica sol-gel, (b) 1 % TiSi_2 and (c) 3 % TiSi_2 surfaces following laser excitation at 355 nm plotted as reflectance change versus time.

The radical cation kinetics show an increase in rate with increasing titania content for both cases of TiSi_1 and TiSi_2 samples.
Table 6.2: The mean rate constants ($\tilde{k}$) and the distribution width ($\gamma$) for radical cation absorption decay kinetics of anthracene adsorbed on TiSi_1 and TiSi_2 surfaces as a function of titania content.

<table>
<thead>
<tr>
<th>Titania content</th>
<th>Radical cation decay kinetics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.0 µmol g⁻¹ anthracene</td>
</tr>
<tr>
<td></td>
<td>An / TiSi_1</td>
</tr>
<tr>
<td>$\tilde{k}$ / 10³ s⁻¹</td>
<td>$\gamma$</td>
</tr>
<tr>
<td>1 % TiO₂</td>
<td>0.8</td>
</tr>
<tr>
<td>3 % TiO₂</td>
<td>0.9</td>
</tr>
<tr>
<td>5 % TiO₂</td>
<td>1.0</td>
</tr>
<tr>
<td>10 % TiO₂</td>
<td>1.1</td>
</tr>
<tr>
<td>Silica</td>
<td>0.6</td>
</tr>
</tbody>
</table>
Table 6.2 indicates that for samples prepared on TiSi₂ surface, the width of the distribution increases as the titania content is increased suggesting that there are some radical decaying faster as a result of the presence of the titania. The increase in the rate constants with increasing titania content suggests changes in the morphology of the titania-silica crystallites.

As have been shown by Worrall et al., analysis of the decay kinetics of the anthracene radical cation produced after laser excitation at low loading (1.0 μmol g⁻¹) for anthracene samples prepared on both silica systems (dropwise and sol-gel) reveals that the decay of the anthracene radical cation could be predominately by geminate recombination. At higher anthracene loadings (5.0 μmol g⁻¹ and 10 μmol g⁻¹) the geminate recombination is no longer the dominant mechanism responsible for radical cation decay.

For a better understanding, figures 6.16 and 6.17 show the variation of the rate constants with titania content and anthracene loading respectively. The decay rates observed appears largely dependent on the titania loading. For TiSi₁ system (figure 6.16), the rate of triplet state decay is due to the increase of the titania content and anthracene loading. Radical cation decay kinetics show an increase of the rate constants with increasing titania loading from 1 % to 10 % and anthracene concentration from 1.0 μmol g⁻¹ to 5.0 μmol g⁻¹ and a slow decrease as the anthracene concentration is increased. In the case of TiSi₂ system (figure 6.17), the rate constants for both triplet state and radical cation decays increase as the titania content and the anthracene loading are increased. At higher anthracene loading (10 μmol g⁻¹) a slow decrease of the rate constants is observed. The loss of the very fast component at higher loading of titania is due to the formation of titania crystallites. Titania synthesis on porous silica matrix typically leads to the formation of titania crystallites larger than the pore size of the matrix because titania crystallites manly form at the outer surface of silica particles.

The difference in the $k$ of samples prepared on TiSi₁ and TiSi₂ surfaces can be attributed to the properties of these surfaces and the method of oxide synthesis. There is more dispersion in titania-silica mixed oxides prepared by the sol-gel method (TiSi₂), while blocks of titania can take place in TiSi₁ mixed oxides and the anthracene adsorbs preferentially on the clusters on TiSi₁ surface.
Figure 6.16: Variation of the rate constants of anthracene (from a loading of 1.0 \( \mu \text{mol g}^{-1} \) to 10 \( \mu \text{mol g}^{-1} \)) adsorbed on TiSi_1 surface plotted as a function of titania content.

Figure 6.17: Variation of the rate constants of anthracene (from a loading of 1.0 \( \mu \text{mol g}^{-1} \) to 10 \( \mu \text{mol g}^{-1} \)) adsorbed on TiSi_2 surface plotted as a function of titania content.
6.1.5 Conclusions

Photophysical and photochemical studies of anthracene adsorbed on the titania-silica mixed oxide surfaces prepared by two different methods have been demonstrated that the interaction between the surface and adsorbed molecule and the mobility of the probes on the surfaces depend on the properties of titania-silica mixed oxides and on the method of oxides synthesis. Ground state reflectance spectra of anthracene adsorbed on titania-silica surfaces have been shown that the absorption peaks of anthracene are difficult to observe at higher content of titania due to the titania absorption edge which overlaps with the anthracene absorption. The changes in the emission intensity as a result of increasing concentration of anthracene can be attributed to the formation of ground state pairs or aggregates. Wilkinson et al. has been also reported\textsuperscript{110} the formation of aggregates for anthracene samples adsorbed on silica gel at low surface loadings corresponding to a surface coverage of only a few percent of a monolayer. Moreover, the fluorescence emission intensity of anthracene adsorbed on titania-silica mixed oxides depends on the titania content. Transient absorption spectra show the presence of two species: the excited triplet state with $\lambda_{\text{max}}$ at 420 nm and anthracene radical cation with $\lambda_{\text{max}}$ at 715 nm.

The production of anthracene radical cation was shown to be monophotonic or multiphotonic by monitoring the intensity of both the triplet-triplet absorption at 420 nm and the radical absorption at 715 nm as a function of laser intensity. The formation of anthracene radical cation on titania-silica mixed oxides is due to the electron injection from the anthracene excited states to the conduction band of titania particles in the silica matrix.

Nanosecond diffuse reflectance laser flash photolysis was used to study photoinduced electron transfer reactions of anthracene adsorbed on titania-silica surfaces and to determine the role of titania particles in the process of adsorption. Decay rate constants of anthracene triplet state and anthracene radical cation show a dependence on titania content and the method of oxide synthesis. The rates were found to increase with increasing titania content.
6.2 Anthracene co-adsorbed with azulene on silica sol-gel and TiSi_2 surfaces

Energy and electron transfer reactions of anthracene co-adsorbed with azulene on silica sol-gel and TiSi_2 surface at different content of titania have been studied using nanosecond time-resolved diffuse reflectance laser flash photolysis. Anthracene and azulene co-adsorbed from acetonitrile onto silica sol-gel and TiSi_2 surface at different loadings of titania were studied as a function of azulene concentration in the range 0.25 μmol g\(^{-1}\) to 2.0 μmol g\(^{-1}\), with a loading of 1.0 μmol g\(^{-1}\) of anthracene. Both the anthracene triplet state and radical cation are formed following laser excitation of anthracene on silica sol-gel and TiSi_2 surface at 355 nm.

In this system, the azulene molecule with an oxidation potential (0.71 V vs SCE) below the reduction potential of the anthracene radical cation (1.09 V vs SCE)\(^{97}\) acts as electron donor and an electron transfer mechanism occurs between the anthracene radical cation and the azulene ground state as in the following scheme:

![Scheme 6.1: Electron transfer mechanism from azulene molecule to the anthracene radical cation.](image)

The addition of azulene as electron donor causes an increase in the rate of decay of the anthracene radical cation.

Ground state diffuse reflectance and fluorescence emission intensity spectra of anthracene co-adsorbed with azulene on silica sol-gel and TiSi_2 surface, the effect of TiSi_2 mixed oxides on the process of photoinduced electron transfer and the decay
kinetics of the anthracene triplet state and anthracene radical cation in presence of the co-adsorbed azulene as electron donor will be discussed below in this section.

6.2.1 Ground state diffuse reflectance spectra

Ground state diffuse reflectance spectra of anthracene co-adsorbed with azulene on silica sol-gel and 1 % TiSi₂ surface at different loadings of azulene and its corresponding Kubelka-Munk remission function spectra are shown in figure 6.18 and figure 6.19 respectively. Upon inspection of the reflectance spectra of the anthracene / azulene samples, it is clear that the absorption peaks corresponding to the anthracene molecule are in the spectral range 330 – 380 nm. As the azulene loading is increased, the spectra show a broadening and a slight red shift as a result of azulene absorbing in the same spectral region as the anthracene. Also, a deviation from Kubelka-Munk theory can be observed.

![Ground state diffuse reflectance spectra of anthracene (1.0 μmol g⁻¹) co-adsorbed with azulene on silica sol-gel plotted as remission function spectra as a function of azulene loading.](image)

Figure 6.18: Ground state diffuse reflectance spectra of anthracene (1.0 μmol g⁻¹) co-adsorbed with azulene on silica sol-gel plotted as remission function spectra as a function of azulene loading.
Figure 6.19: Ground state diffuse reflectance spectra of anthracene (1.0 μmol g⁻¹) co-adsorbed with azulene on 1 % TiSi₂ surface plotted as remission function spectra as a function of azulene loading.

This deviation from Kubelka-Munk theory can be explained by formation of aggregates which cause a reduction in the expected absorption. This aggregation has been observed previously on silica gel surface¹¹⁰.

The absorption peaks of anthracene are difficult to observe at higher content of titania due to the influence of the absorption edge of the titania. In the spectral range 330 – 380 nm, the overlap between the titania absorption edge and the anthracene absorption can be observed as a result of the increasing titania content of the samples (figure 6.20). The band gap energy decreases with increasing titania loading and the absorption edge of the titania is shifted to longer wavelengths. Similar effects are observed for anthracene samples adsorbed on the titania-silica surfaces at different content of titania in section 6.1.1.
Figure 6.20: Ground state diffuse reflectance spectra of anthracene (1.0 μmol g⁻¹) co-adsorbed with azulene (1.0 μmol g⁻¹) on silica sol-gel and TiSi₂ surfaces plotted as remission function spectra as a function of titania content.

6.2.2 Fluorescence emission spectra

Fluorescence emission spectra of anthracene co-adsorbed with azulene on both silica sol-gel and TiSi₂ surfaces at different content of titania were measured following excitation at 355 nm. Figures 6.21 and 6.22 show spectra measured for anthracene (1.0 μmol g⁻¹) co-adsorbed with various azulene loadings on silica sol-gel and 1 % TiSi₂ surface, respectively. From these figures it is revealed that the emission spectrum appears in the region 400 - 475 nm. The most intense peak corresponding to the anthracene molecule is located at 400 nm. Another two peaks of lower intensity can be seen at 385 nm and 426 nm and a small, poorly resolved peak at 450 nm.

Co-absorption of azulene on silica sol-gel and TiSi₂ mixed oxides resulted in a decrease in the fluorescence intensity of the adsorbed anthracene; the emission intensity of the adsorbed anthracene is greater in the absence of azulene. The fluorescence emission spectra of anthracene co-adsorbed with azulene indicate that the fluorescence emission intensity of the anthracene peaks decreases with increasing azulene loading.
Figure 6.21: Fluorescence emission spectra of anthracene (1.0 \( \mu \text{mol g}^{-1} \)) co-adsorbed with azulene on silica sol-gel following excitation at 355 nm plotted as a function of azulene concentration.

Figure 6.22: Fluorescence emission spectra of anthracene (1.0 \( \mu \text{mol g}^{-1} \)) co-adsorbed with azulene on 1 % TiSi_2 surface following excitation at 355 nm plotted as a function of azulene concentration.
Quenching of the anthracene fluorescence by azulene occurs in both systems (silica sol-gel and TiSi₂). There is the same amount of azulene for both systems, but the extent of quenching by azulene and also by titania for a given bulk of titania loadings is more pronounced for samples prepared on TiSi₂ surfaces than that on silica sol-gel as the effect of the titania which contributes to the reduction in fluorescence emission intensity of the excited anthracene as it was presented in section 6.1.2.

Quenching of the anthracene fluorescence by azulene and also by the titania for samples prepared on TiSi₂ surface it is clearly evident from this data. Figure 6.23 indicates that the fluorescence quenching of the excited anthracene shows a dependence on titania content. The fluorescence intensity of the adsorbed anthracene decreases with increasing titania loading.

![Figure 6.23: Fluorescence emission spectra of anthracene (1.0 μmol g⁻¹) co-adsorbed with azulene (1.0 μmol g⁻¹) on silica sol-gel and TiSi₂ surfaces plotted as a function of titania loading following excitation at 355 nm.](image)

The lowest singlet excited state of anthracene undergoes fluorescence and intersystem crossing. The excited state anthracene interacts with the azulene present in system by energy transfer, charge transfer or by molecular aggregation and an exciplex formation occurs in this case. The decrease in intensity of anthracene indicates the
possibility of energy or electron transfer from excited azulene molecule (electron donor) to ground state anthracene (electron acceptor).

### 6.2.3 Transient absorption spectra

Transient absorption spectra of anthracene co-adsorbed with azulene on silica sol-gel and TiSi₂ surfaces at different titania content were obtained following laser excitation at 355 nm. Anthracene with a loading of 1.0 μmol g⁻¹ and azulene (the concentration of azulene is in the range 0.25 μmol g⁻¹ – 2.0 μmol g⁻¹) were co-adsorbed from acetonitrile onto the solid surface. Figure 6.24 and figure 6.25 show the transient absorption spectra obtained from photolysis of anthracene co-adsorbed with azulene on silica sol-gel and TiSi₂ surface, respectively. Both figures reveal the presence of two species: the anthracene excited triplet state and anthracene radical cation. The wavelength of maximum absorbance of anthracene triplet state is 420 nm and the peaks corresponding to anthracene radical cation are localized at 420 nm and 715 nm as discussed in section 6.1.3.

![Figure 6.24](image.png)

*Figure 6.24: Transient absorption spectrum of anthracene (1.0 μmol g⁻¹) co-adsorbed with azulene (0.25 μmol g⁻¹) on silica sol-gel following laser excitation at 355 nm.*
Analyzing the transient absorption spectrum of anthracene co-adsorbed with azulene on silica sol-gel (figure 6.24) and the spectrum of anthracene co-adsorbed with azulene on 1 % TiSi₂ (figure 6.25) some differences can be observed in the relative intensities of the triplet-triplet and radical cation absorptions. The absorption intensities for both triplet-triplet and radical cation absorption are reduced in contrast to the case of silica sol-gel system. In the case of anthracene / azulene sample adsorbed on TiSi₂ surface at a loading of 1 % titania, as is clearly evident from figure 6.25, the radical cation absorption intensity is higher than the triplet-triplet absorption intensity. Photoionisation at 355 nm of the anthracene sample co-adsorbed with azulene on 1 % TiSi₂ surface produces both the anthracene radical cation and Ti³⁺ species. The anthracene radical cation is located at 715 nm and persists on timescales of a few hundred nanoseconds or longer. Moreover, there is observed a slight decrease in anthracene triplet-triplet absorption and anthracene radical cation absorption intensities as the content of titania is increased (figure 6.26). The decays of both anthracene triplet state and anthracene radical cation are slower for samples containing a higher amount of titania. This observation is also reflected in the rate constants of anthracene triplet state and radical cation decays; the rate constants for both transients decrease with increasing titania content.
Chapter 6. Results and discussion

Figure 6.26: Transient absorption spectrum of anthracene (1.0 μmol g\(^{-1}\)) co-adsorbed with azulene (1.0 μmol g\(^{-1}\)) on 3 % TiSi\(_2\) surface following laser excitation at 355 nm.

The spectral characteristics of the transient absorption spectra are not dependent on the azulene loading; both anthracene excited triplet state and radical cation have an increased rate of decay when azulene is present and acts as electron donor. An increase in azulene concentration increases the rate of decay or formation of the transient observed. Triplet-triplet energy transfer between the excited anthracene (\(E_T = 178\) kJ mol\(^{-1}\)) and ground state azulene (\(E_T = 163\) kJ mol\(^{-1}\)) is responsible for the increased rate of decay of the anthracene triplet\(^{215}\). The azulene triplet at 360 nm\(^{133}\) is not observed as a result of its low molar absorption coefficient (4000 l mol\(^{-1}\) cm\(^{-1}\)) and of overlapping with the anthracene triplet peak. Shida\(^{216}\) reported that the main absorption peak corresponding to azulene radical cation is located at 368 nm and others two peaks of lower intensity were observed at 480 nm and 830 nm. Inspection of the transient absorption spectra of anthracene co-adsorbed with azulene as electron donor on both silica sol-gel and TiSi\(_2\) surface reveals that the formation of the azulene radical cation at 368 nm is not observed. This is due to the low absorption of the azulene radical cation which overlaps with the anthracene ground state absorption. The band at 480 nm corresponding to azulene radical cation is also very weak and also the 830 nm peak is outside of analysing spectra range.
The production of the radical cation is a combination of monophoton and multiphoton ionisation depending on the sample; this is discussed in detail in section 6.1.3. Co-adsorption of azulene into anthracene / silica sol-gel and anthracene / TiSi₂ systems changes the observed electron transfer kinetics. In the presence of azulene as electron donor the anthracene radical cation exhibits decay that is faster than in its absence; all of the observed decay is due to electron transfer from azulene to the anthracene radical cation.

6.2.4 Kinetics of energy and electron transfer

A series of samples was prepared with anthracene co-adsorbed with azulene as a quencher on silica sol-gel and TiSi₂ surfaces at different content of titania. Anthracene and azulene were co-adsorbed from acetonitrile onto the solid surface and studied as a function of azulene concentration in the range 0.25 μmol g⁻¹ to 2.0 μmol g⁻¹ with a loading of 1.0 μmol g⁻¹ anthracene. The kinetics of the decay of excited triplet state and radical cation of anthracene have been studied following 355 nm laser excitation in the presence of co-adsorbed azulene. The transient decay was studied using diffuse reflectance laser flash photolysis.

There is triplet-triplet energy transfer between the excited anthracene and azulene and electron transfer from azulene to the anthracene radical cation. Triplet state decay was analysed at 420 nm, while the electron transfer between the anthracene radical cation and azulene was monitored at 715 nm where interference from triplet state absorption is absent.

The kinetic data for both triplet state and radical cation decay were analysed using the dispersive kinetic model of Albery et al., which assumes a logarithm Gaussian distribution of rate constants for the observed reaction to give a value for the average decay rate constant \( \tilde{k} \) as a function of azulene concentration. This model was described in detail in section 4.11.1 and can be expressed by following equation (6.1):
\[
\frac{C}{C_0} = \frac{\int_{-\infty}^{\infty} \exp(-t^2) \exp(-kt \exp(\gamma t)) dt}{\int_{-\infty}^{\infty} \exp(-t^2) dt}
\]  

(6.1)

where \(C\) and \(C_0\) are transient concentrations at times \(t = t\) and \(t = 0\) after laser pulse, 
\(k\) represents the mean rate constant and \(\gamma\) is the width of the distribution. 

The replacement of transient concentration \(C\) and \(C_0\) by the reflectance changes at times 
\(t = t\) and \(t = 0\) represented by the symbols \(\Delta R\) and \(\Delta R_0\) can be applied at low sample 
loadings and smaller reflectance change than 10 %. The transient decay will be then 
analysed by fixing the parameter \(\gamma\) and fitting for \(\Delta R_0\) and \(k\).

Figure 6.27: Triplet state decay measured at 420 nm of anthracene (1.0 \(\mu\)mol g\(^{-1}\)) 
co-adsorbed with azulene (2.0 \(\mu\)mol g\(^{-1}\)) on 1 % TiSi_2 surface following laser excitation 
at 355 nm plotted as reflectance change versus time. Residuals to the fit are also shown.
Figure 6.28: Radical cation decay measured at 715 nm of anthracene (1.0 \( \mu \text{mol g}^{-1} \)) co-adsorbed with azulene (2.0 \( \mu \text{mol g}^{-1} \)) on 1 \% TiSi\(_2\) surface following laser excitation at 355 nm plotted as reflectance change versus time. Residuals to the fit are also shown.

Two typical decay traces corresponding to anthracene triplet state at 420 nm and anthracene radical cation at 715 nm and their dispersive model fits are shown in figures 6.27 and 6.28 as reflectance change versus time.

Table 6.3 and table 6.4 reflect the results of the fits obtained for constant anthracene concentration (1.0 \( \mu \text{mol g}^{-1} \)) with varying azulene loading (from 0.25 \( \mu \text{mol g}^{-1} \) to 2.0 \( \mu \text{mol g}^{-1} \)) for both the anthracene triplet state and anthracene radical cation.
Table 6.3: The mean rate constants ($\tilde{k}$) and the distribution width ($\gamma$) for triplet state decay kinetics of anthracene co-adsorbed with azulene on silica sol-gel and TiSi$_2$ surfaces at different titania content as a function of azulene concentration.

These tables show that the distribution width ($\gamma$) which varies from 1.0 to 3.0 is independent of the electron donor concentration, whereas the mean rate constants ($\tilde{k}$) for both anthracene triplet state and anthracene radical cation decay increase linearly with increasing azulene concentration and decrease as the titania content is increased.
Table 6.4: The mean rate constants ($\tilde{k}$) and the distribution width ($\gamma$) for radical cation decay kinetics of anthracene co-adsorbed with azulene on silica sol-gel and TiSi$_2$ surfaces at different titania content as a function of azulene concentration.

The variation of the rate constants with the electron donor concentration and titania content is shown in figure 6.29. This figure shows the increase of the rate constants as a function of azulene concentration and the decrease of the rate constants with increasing titania content.
Figure 6.29: Variation of the rate constants of anthracene (1.0 μmol g⁻¹) adsorbed on TiSi_2 surface plotted as a function of electron donor concentration and titania content.

In the analysis of the energy and electron transfer data for anthracene co-adsorbed with azulene on silica sol-gel and TiSi_2 surfaces it is necessary that the experimental results
to be corrected in order to take account of the ground state association between anthracene and azulene which is evidenced by changes in the reflectance spectra and has been observed previously and methodology developed to correct for this\textsuperscript{114}.

Assuming that anthracene and azulene diffuse together and form an association complex as follow:

\[
\text{An} + \text{Az} \rightleftharpoons \text{AnAz}
\]

where \( \text{An} \) and \( \text{Az} \) denote anthracene and azulene respectively, and \( \text{AnAz} \) is an association complex.

The equilibrium constant \( K \) is given by:

\[
K = \frac{[\text{AnAz}]}{[\text{An}][\text{Az}]}
\]  \hspace{1cm} (6.2)

where \([\text{An}]\) and \([\text{Az}]\) are the concentrations of anthracene and azulene respectively, and \([\text{AnAz}]\) is the concentration of the association complex.

Replacing the anthracene and azulene concentrations by the difference between their initial concentrations and the concentration of the association complex, the equation (6.2) can be expressed as follows:

\[
K = \frac{[\text{AnAz}]}{([\text{An}]_0 - [\text{AnAz}])([\text{Az}]_0 - [\text{AnAz}])}
\]  \hspace{1cm} (6.3)

where \([\text{An}]_0\) and \([\text{Az}]_0\) are the initial concentrations of the anthracene and azulene respectively.

By solving the equation (6.3) and rearrangement of terms, the equation (6.3) can be written as:

\[
[\text{AnAz}]^2 - \left( [\text{An}]_0 + [\text{Az}]_0 + \frac{1}{K} \right) [\text{AnAz}] + [\text{An}]_0 [\text{Az}]_0 = 0
\]  \hspace{1cm} (6.4)
According to equation (6.4) and by solving the roots of $[AnAz]$, values of the free azulene loading can be calculated by subtracting the concentration of $[AnAz]$ from the initial azulene loading $[Az_0]$.

In the absence of a quencher:

$$An^* + e^- \xrightarrow{k_0} An$$

where $An^*$ is the excited triplet state of anthracene and $k_0$ represents the rate of decay of the anthracene triplet state in the absence of a quencher molecule. It should be noticed that since the quencher is the same species in both energy and electron transfer in this system, i.e. ground state azulene, the same treatment can be applied to both energy and electron transfer.

The possible deactivation mechanism of the excited state species of anthracene in the presence of a quencher molecule is given by:

$$An^* + Q \xrightarrow{k'_q} \text{Products}$$

where $Q$ is the quencher molecule (in this section azulene) which deactivates the transient species and $k'_q$ is the bimolecular rate constant for quenching.

The rate of decay of the anthracene triplet state in the presence of a quencher molecule is given by:

$$-\frac{d[An^*]}{dt} = \bar{k}_0[An^*] + k'_q[Q][An^*] \quad (6.5)$$

where $[An^*]$ is the concentration of the excited species of anthracene (mol l$^{-1}$) and $[Q]$ is the concentration of quencher molecule (mol l$^{-1}$).

In most cases, we can assume that $[Q] \gg [An^*]$, as $[An^*]$ is in the order of $10^{-6}$ mol l$^{-1}$ and the concentration of quencher molecule $[Q]$ remains unchanged.

$$-\frac{d[An^*]}{dt} = \left(\bar{k}_0 + k'_q[Q]\right)[An^*] \quad (6.6)$$
Chapter 6. Results and discussion

\[ \frac{d[An^*]}{dt} = -k [An^*] \]  
\hspace{1cm} (6.7)

where \( k = k_0 + k'_q [Q] \) and \( k \) is the observed rate constant for the anthracene triplet state decay in the presence of quencher \( Q \) and the units depend on the units of the quencher concentration used.

The rate of energy transfer between anthracene and azulene can be determined by following equation (6.8):

\[ \tilde{k} = \tilde{k}_0 + \tilde{k}'_q [Q] \]  
\hspace{1cm} (6.8)

According to equation (6.8) and from plotting the observed mean rate constants versus quencher concentration, bimolecular rate constants can be obtained. Figure 6.30 and figure 6.31 show a plot of \( \tilde{k} \) versus azulene concentration for the anthracene triplet state and anthracene radical cation for anthracene samples prepared on silica sol-gel and on 1 % TiSi_2 surface respectively. A linear correlation between the decay rates obtained from the dispersive kinetic model and azulene concentration was found and a summary of bimolecular quenching rate constants (the gradients of the plots) of the anthracene triplet state and radical cation decay in the presence of electron donor is provided in table 6.5.

In the case of anthracene radical cation, the intercept of the plot is zero within experimental error. This zero intercept is due to the fact that there is no measurable decay of the anthracene radical cation on the time-scale monitored in the absence of electron donor^{108,110}. 
Figure 6.30: Plots of the average rate constants ($k'$) obtained from the dispersive kinetic analysis for the triplet-triplet energy transfer (black line) and electron transfer (blue line) for anthracene (1.0 μmol g$^{-1}$) co-adsorbed with azulene on silica sol-gel versus azulene concentration.

$k'_q = 3.6 +/- 0.3 \times 10^9$ g mol$^{-1}$ s$^{-1}$

$k'_q = 1.3 +/- 0.3 \times 10^{10}$ g mol$^{-1}$ s$^{-1}$

An triplet state at 420 nm
An radical cation at 715 nm
Chapter 6. Results and discussion

Figure 6.31: Plots of the average rate constants ($\tilde{k}$) obtained from the dispersive kinetic analysis for the triplet-triplet energy transfer (black line) and electron transfer (blue line) for anthracene (1.0 $\mu$mol g$^{-1}$) co-adsorbed with azulene on 1 % TiSi$_2$ surface versus azulene concentration.

<table>
<thead>
<tr>
<th>Anthracene / Azulene samples</th>
<th>Triplet state quenching constant / g mol$^{-1}$ s$^{-1}$ (energy transfer)</th>
<th>Radical cation quenching constant / g mol$^{-1}$ s$^{-1}$ (electron transfer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti content</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 % TiO$_2$</td>
<td>$3.4 \pm 0.4 \times 10^{10}$</td>
<td>$1.2 \pm 0.4 \times 10^{10}$</td>
</tr>
<tr>
<td>3 % TiO$_2$</td>
<td>$7.4 \pm 0.6 \times 10^{9}$</td>
<td>$3.1 \pm 0.3 \times 10^{9}$</td>
</tr>
<tr>
<td>5 % TiO$_2$</td>
<td>$7.8 \pm 0.6 \times 10^{9}$</td>
<td>$2.3 \pm 0.2 \times 10^{9}$</td>
</tr>
<tr>
<td>10 % TiO$_2$</td>
<td>$6.7 \pm 0.5 \times 10^{9}$</td>
<td>$1.6 \pm 0.7 \times 10^{9}$</td>
</tr>
<tr>
<td>Si sol-gel</td>
<td>$1.3 \pm 0.3 \times 10^{10}$</td>
<td>$3.6 \pm 0.3 \times 10^{9}$</td>
</tr>
<tr>
<td>Silica Davisil$^{114}$</td>
<td>$9.5 \pm 0.3 \times 10^{9}$</td>
<td>$10 \pm 0.4 \times 10^{9}$</td>
</tr>
</tbody>
</table>

Table 6.5: Bimolecular quenching rate constants of anthracene (1.0 $\mu$mol g$^{-1}$) co-adsorbed with varying loading of azulene on silica sol-gel and TiSi$_2$ surfaces at different content of titania.
It can be observed a trend in the variation of bimolecular rate constants with titania content, quenching rate constant decreases with increasing titania content. As can clearly be seen, the obtained bimolecular rate constants for energy and electron transfer of anthracene co-adsorbed with azulene on 1 % TiSi_2 surface and also for samples prepared on silica sol-gel yield different values (the rate of energy transfer are higher than the rate of electron transfer) and demonstrate that the rate of reaction is governed by the diffusion of anthracene on the surface of silica sol-gel and TiSi_2 mixed oxides.

Anthracene is mobile on the silica sol-gel and TiSi_2 surfaces. In the binary system and on silica sol-gel, triplet-triplet energy transfer rate is faster than the rate of anthracene radical cation quenching. On the basis that the radical cation is less mobile than the neutral species, in line with observations on silica Davisil¹¹³,¹¹⁴, this would suggest that the anthracene moves faster on both silica sol-gel and TiSi_2 surface than the azulene molecule, possible as a result of the smaller pore size (section 5.3) relative to silica Davisil restricting the parts of the surface explored by the anthracene relative to the azulene.

Pore morphology of silica sol-gel and TiSi_2 surfaces plays an important role in evaluating the energy and electron transfer reactions in this bimolecular system. The pore size of these solid substrates prepared by sol-gel method is smaller than the pore size of silica Davisil. That means a greater number of anthracene molecules can be adsorbed on silica sol-gel and 1 % TiSi_2 mixed oxides per unit of area. This results in greater light absorption by these samples and production of radical cations. The anthracene molecules located in the middle of the pores display a considerable faster dynamics and have lower activation energy. Comparison with silica Davisil diffusion data shows that the anthracene radical cation diffusion on silica sol-gel is lower than for silica Davisil indicating that the average pore size of the sol-gel solid substrates is probably smaller. The pore size is responsible for the slowing down of the mobility of the investigated systems.

The rate of electron transfer is consistently slower than the rate of energy transfer. The observed rate of reaction (energy and electron transfer) is governed by the rate of diffusion of anthracene across the silica sol-gel and titania-silica surfaces. It was found that the azulene molecule is less mobile than the anthracene species on the surface of
silica sol-gel or titania-silica mixed oxides. The rate of the reaction between the anthracene radical cation and azulene is consistent of that of energetic control in these systems.

Worrall et al.\textsuperscript{113,114} have been previously reported that the anthracene radical cation does not decay on silica Davisil and found that the rate of energy and electron transfer reactions of anthracene co-adsorbed with azulene on silica Davisil is governed by the rate of diffusion of azulene. For both the energy and electron transfer processes, bimolecular quenching rate constants yield the same values ($k_q = 9.5 \times 10^9 \pm 0.3 \text{ g mol}^{-1} \text{ s}^{-1}$ for the energy transfer between the excited anthracene and ground state azulene and a value of $k_q = 10.0 \times 10^9 \pm 0.4 \text{ g mol}^{-1} \text{ s}^{-1}$ for electron transfer reaction from azulene to the anthracene radical cation).

\subsection*{6.2.5 Activation energies for energy and electron transfer in a bimolecular system on silica sol-gel and TiSi$_2$ surfaces}

The effects of temperature on energy and electron transfer rates of anthracene / azulene samples prepared on silica sol-gel and TiSi$_2$ surface at a loading of 1 \% titania were investigated. Temperature dependence studies were carried out on two systems: anthracene co-adsorbed with azulene on silica sol-gel (AnAz / Si sol-gel) and anthracene co-adsorbed with azulene as electron donor on 1 \% TiSi$_2$ surface (AnAz / 1 \% TiSi$_2$). Anthracene (1.0 μmol g$^{-1}$) and azulene (with a loading of 0.5 μmol g$^{-1}$ and 2.0 μmol g$^{-1}$) were co-adsorbed from acetonitrile onto the solid surface. Samples were prepared under vacuum to a pressure of 5 x 10$^{-5}$ mbar and pre-treated at 125 °C.

The kinetics of the decay of anthracene excited triplet state and anthracene radical cation were studied following 355 nm laser excitation in the presence of co-adsorbed azulene as electron donor and analysed using the dispersive kinetic model. Triplet state decay of anthracene was analysed at 420 nm, while the anthracene radical cation decay was monitored at 715 nm.

The rate measurements at different temperatures fitted using the dispersive kinetic model demonstrates that the rates increase with increasing temperature. A particular case is
Chapter 6. Results and discussion

illustrated in table 6.6 where the rate constants of anthracene triplet state and radical cation decay for AnAz / 1 % TiSi_2 system are measured at different temperatures and an increase of the rate constants with increasing temperature can be clearly observed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>t / °C</th>
<th>Anthracene triplet state</th>
<th>Anthracene radical cation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\tilde{k}$ / s$^{-1}$</td>
<td>$\gamma$</td>
</tr>
<tr>
<td>AnAz / 1 % TiSi_2 PTT = 125 °C An : Az = 1 : 0.5</td>
<td>21.4</td>
<td>1046</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td>1187</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>28.3</td>
<td>1540</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>32.4</td>
<td>1739</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>37.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>43.3</td>
<td>3337</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>49.5</td>
<td>4481</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>55.8</td>
<td>6038</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>62.1</td>
<td>7429</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>57.0</td>
<td>6736</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>51.6</td>
<td>5270</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>41.7</td>
<td>2822</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>33.7</td>
<td>1777</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Table 6.6: The mean rate constants ($\tilde{k}$) and the distribution width ($\gamma$) for triplet state and radical cation decay kinetics of anthracene (1.0 $\mu$mol g$^{-1}$) co-adsorbed with azulene (0.5 $\mu$mol g$^{-1}$) on 1 % TiSi_2 surface obtained at different temperatures.

The Arrhenius equation (6.9) shows the dependence of the rate constants on temperature:

$$ k = Ae^{-\frac{E_a}{RT}} $$

(6.9)

The equation (6.9) can also be written as:

$$ \ln k = \ln A - \frac{E_a}{RT} $$

(6.10)
where $k$ is the rate constant measured at different temperatures (in s$^{-1}$), $A$ is the pre-exponential factor, $E_a$ represents the activation energy (in kJ mol$^{-1}$), $R$ is the universal gas constant (8.314 J mol$^{-1}$ K$^{-1}$) and $T$ is the absolute temperature (in K).

By measuring the decay of the sample at different temperatures and plotting $\ln k$ versus $(1/T)$, the activation energy for the process can be calculated. An Arrhenius plot for energy and electron transfer constructed using the value of rate constants for the AnAz / 1 % TiSi$_2$ system is shown in figure 6.32.

Figure 6.32: Arrhenius plots for energy transfer (black line) and electron transfer (blue line) between anthracene (1.0 μmol g$^{-1}$) and co-adsorbed azulene (0.5 μmol g$^{-1}$) on TiSi$_2$ surface at a loading of 1 % titania, PTT 125 °C, following laser excitation at 355 nm.
The plot of $\ln k$ versus $(1/T)$ is linear and the slope of the resulting line corresponds to the values of the activation energies. The determined values of activation energy $E_a$ for all analysed samples are presented in table 6.7.

Inspection of the activation energies on TiSi$_2$ (table 6.7) reveals that, at high azulene loadings, the activation energies and pre-exponential factors are the same for both energy and electron transfer, and are comparable with the parameters extracted for azulene diffusion on silica Davisil$^{217}$ suggesting that the azulene diffuses across the silica Davisil and TiSi$_2$ mixed oxides surfaces. At lower azulene loadings, both the activation energy and pre-exponential factors are lower. This, along with the fact that there is appreciable decay of the anthracene radical alone on the surface on relatively short timescales, can be rationalised on the basis of a lower oxidation potential of these surfaces than is seen for silica Davisil, and consequently ion-electron recombination competes with electron transfer from azulene. At lower azulene loadings ion-electron recombination dominates, and the activation energy extracted is then for this process. On the silica sol-gel surface, in the absence of the Ti trapping sites ion-electron recombination can compete efficiently with electron transfer at all azulene loadings studied.

Williams et al.$^{217}$ have found the same activation energies for energy and electron transfer reactions between anthracene or 2-methylantracene and azulene on silica gel. This suggests that the azulene diffuses across the silica surface followed by either energy transfer from the anthracene triplet state or electron transfer to the anthracene radical cation.

The rate constants are dependent on the temperature and an increase of the rate constants with increasing temperature has been observed. The activation energies are found to be strongly dependent on the surface morphology.
Table 6.7: Activation energies and pre-exponential factors for energy and electron transfer between anthracene (An) and azulene (Az) adsorbed on silica sol-gel and 1% TiSi₂ surface where AnT and An⁺ denote the anthracene excited triplet state and radical cation respectively.

<table>
<thead>
<tr>
<th>An : Az</th>
<th>AnAz / 1% TiSi₂</th>
<th>AnAz / Si sol-gel</th>
<th>AnAz / Silica Davisil²¹⁷</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AnT at 420 nm</td>
<td>AnT at 715 nm</td>
<td>AnT at 420 nm</td>
</tr>
<tr>
<td></td>
<td>An.⁺ at 420 nm</td>
<td>An.⁺ at 715 nm</td>
<td>An.⁺ at 715 nm</td>
</tr>
<tr>
<td></td>
<td>Ea / kJ mol⁻¹</td>
<td>A / s⁻¹</td>
<td>Ea / kJ mol⁻¹</td>
</tr>
<tr>
<td></td>
<td>Ea / kJ mol⁻¹</td>
<td>A / s⁻¹</td>
<td>Ea / kJ mol⁻¹</td>
</tr>
<tr>
<td>1 : 0.5</td>
<td>49 ± 1</td>
<td>5 x 10¹¹</td>
<td>51 ± 1</td>
</tr>
<tr>
<td></td>
<td>5 x 10⁻¹¹</td>
<td>25 ± 1</td>
<td>5 x 10¹¹</td>
</tr>
<tr>
<td></td>
<td>4 x 10⁶</td>
<td>4 x 10⁶</td>
<td>36 ± 3</td>
</tr>
<tr>
<td></td>
<td>51 ± 1</td>
<td>5 x 10¹¹</td>
<td>3 x 10⁸</td>
</tr>
<tr>
<td>1 : 2</td>
<td>49 ± 1</td>
<td>5 x 10¹¹</td>
<td>48 ± 2</td>
</tr>
<tr>
<td></td>
<td>50 ± 1</td>
<td>4.8 x 10¹¹</td>
<td>5.3 x 10¹¹</td>
</tr>
<tr>
<td></td>
<td>48 ± 2</td>
<td>5.3 x 10¹¹</td>
<td>28 ± 1</td>
</tr>
<tr>
<td></td>
<td>4.8 x 10¹¹</td>
<td>2.6 x 10⁷</td>
<td>2.6 x 10⁷</td>
</tr>
<tr>
<td></td>
<td>48 ± 2</td>
<td>0.7 x 10¹²</td>
<td>51 ± 2</td>
</tr>
<tr>
<td></td>
<td>5 x 10¹¹</td>
<td>3.2 x 10¹²</td>
<td>3.2 x 10¹²</td>
</tr>
</tbody>
</table>

*Table 6.7: Activation energies and pre-exponential factors for energy and electron transfer between anthracene (An) and azulene (Az) adsorbed on silica sol-gel and 1% TiSi₂ surface where AnT and An⁺ denote the anthracene excited triplet state and radical cation respectively.*
6.3 9-Anthracenecarboxylic acid co-adsorbed with azulene and perylene on silica sol-gel and TiSi_2 surfaces

Energy and electron transfer reactions in a ternary system on silica sol-gel and TiSi_2 surface at a content of 1 % titania have been studied using nanosecond time-resolved diffuse reflectance laser flash photolysis. The system chosen was 9-anthracenecarboxylic acid (9-AnCA) / azulene (Az) / perylene (Pe). 9-Anthracenecarboxylic acid was chosen because it is hydrogen bonded and therefore fixed to the surface of silica sol-gel or titania-silica mixed oxides and does not contribute to the observed diffusional kinetics. 9-Anthracenecarboxylic acid (1.0 $\mu$mol g$^{-1}$) and perylene (0.5 $\mu$mol g$^{-1}$) were co-adsorbed with azulene from acetonitrile onto silica sol-gel and 1 % TiSi_2 surface and studied as a function of azulene concentration in the range 0.5 $\mu$mol g$^{-1}$ to 2.0 $\mu$mol g$^{-1}$. The excited triplet state and radical cation of the 9-anthracenecarboxylic acid (9-AnCA T and 9-AnCA.$^+$) and perylene radical cation (Pe.$^+$) on silica sol-gel and TiSi_2 surface are formed following laser excitation at 355 nm.

In this ternary system, azulene molecule with the oxidation potential (0.71 V vs SCE)$^{97}$ below the reduction potential of the 9-anthracenecarboxylic acid radical cation (1.49 V vs SCE)$^{97}$ acts as a shuttle molecule in order to facilitate electron / hole transfer. Photoionisation of the 9-AnCA leads to the formation of the 9-AnCA radical cation and electron transfer then occurs between the 9-AnCA radical cation and the ground state azulene and from perylene to the azulene radical cation generating the azulene ground state and forming the perylene radical cation. The electron transfer mechanism which occurs in this ternary system can be represented as in the following scheme:

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161
Scheme 6.2: Electron transfer mechanism in a ternary system between the 9-anthracenecarboxylic acid and ground state azulene and from perylene to the azulene radical cation.

Ground state diffuse reflectance and fluorescence emission intensity spectra of 9-anthracenecarboxylic acid co-adsorbed with perylene and azulene on silica sol-gel and 1 % TiSi₂ surface, the effect of TiSi₂ mixed oxides on the process of photoinduced electron transfer and the decay kinetics of the 9-anthracenecarboxylic acid triplet state and radical cation in the presence or absence of the co-adsorbed azulene as electron donor and the rise / decay kinetics of perylene radical cation formed during the electron transfer process between perylene and the azulene radical cation will be discussed below in this section.
6.3.1 Ground state diffuse reflectance spectra

Ground state diffuse reflectance spectra of 9-anthracenecarboxylic acid (9-AnCA) co-adsorbed with azulene and perylene and the spectrum of perylene alone on silica sol-gel and TiSi_2 surface at a loading of 1 % titania have been measured. Figures 6.33 and 6.34 show the change in absorption profile of the 9-AnCA samples co-adsorbed with perylene (0.5 \( \mu \text{mol g}^{-1} \)) in the presence and absence of varying loadings of azulene (from 0.5 \( \mu \text{mol g}^{-1} \) to 2.0 \( \mu \text{mol g}^{-1} \)) on silica sol-gel and 1 % TiSi_2 surface respectively.

Figure 6.33: Ground state diffuse reflectance spectra of 9-AnCA (1.0 \( \mu \text{mol g}^{-1} \)) co-adsorbed with perylene (0.5 \( \mu \text{mol g}^{-1} \)) and azulene on silica sol-gel plotted as remission function spectra as a function of azulene loading. The inset shows expended region of the spectra for 9-AnCA / perylene sample without azulene (black line) between 600 – 800 nm.
Figure 6.34: Ground state diffuse reflectance spectra of 9-AnCA (1.0 μmol g⁻¹) co-adsorbed with perylene (0.5 μmol g⁻¹) and azulene on 1 % TiSi₂ surface plotted as remission function spectra as a function of azulene loading. The inset shows expended region of the spectra for 9-AnCA/ perylene sample without azulene (black line) between 600 – 800 nm.

The absorption peaks corresponding to 9-AnCA molecule are in the spectral range 330 – 450 nm. The absorption maxima of 9-AnCA at 344, 361 and 381 nm in acetonitrile⁵⁷ shifted to 337, 366 and 384 nm in the presence of solid surface. The absorption of 9-AnCA also extended further into the visible region (up to λ ~ 450 nm) when it was adsorbed on the silica sol-gel and titania-silica mixed oxide surface. The bathochromic shift could be attributed to the interaction of 9-AnCA with the active sites of the surface and also due to the heterogeneous nature of the surface. The weak absorbance around 715 nm and 730 nm is due to formation of 9-AnCA radical cation. The inset of figures 6.33 and 6.34 shows the expended region of the spectrum between 600 – 800 nm where 9-AnCA radical cation absorbs. The red shift of the 9-AnCA radical
cation at 730 nm in the UV-Vis absorption spectra is attributed to the adsorption of 9-AnCA onto the surface of the titania nanoparticles.

Figure 6.35 shows the absorption spectra of perylene (0.5 \( \mu \text{mol g}^{-1} \)) adsorbed on silica sol-gel and 1 % TiSi_2 surface. Similar to the absorption spectrum of perylene in acetonitrile solution (blue dot line), the diffuse reflectance spectra of perylene adsorbed on the solid surface of the mixed oxides reveal the absorption bands corresponding to an extended system of conjugated double bonds and assigned to \( \pi-\pi^* \) transition. From figure 6.35 it can be clearly observed that the absorption bands corresponding to perylene are broadened relative to solution due to the interaction of perylene with the oxides surface. The weak band at 530 is attributed to the radical cation of perylene molecule in good agreement with the reported spectrum of perylene on silica-alumina catalyst^{218} and in frozen matrix^{216}.

Figure 6.35: A comparison between perylene (0.5 \( \mu \text{mol g}^{-1} \)) in acetonitrile solution plotted as absorbance (dot line) and perylene (0.5 \( \mu \text{mol g}^{-1} \)) on silica sol-gel (dash line) and 1 % TiSi_2 surface (solid line) plotted as remission function.
These results clearly show that the initial absorption of 9-AnCA and perylene on silica sol-gel and 1 % TiSi₂ surface is accompanied by the formation of a small amount of their corresponding radical cation at the active sites.

### 6.3.2 Fluorescence emission spectra

Fluorescence emission spectra of 9-AnCA co-adsorbed with perylene at a loading of 0.5 μmol g⁻¹ and azulene with various loadings (from 0.5 μmol g⁻¹ to 2.0 μmol g⁻¹) on both silica sol-gel and 1 % TiSi₂ surfaces were measured following excitation at 355 nm and are shown in figures 6.36 and 6.37. From these figures it is revealed that the fluorescence of 9-AnCA is completely quenched by azulene. Increasing the azulene loading induces change in the emission spectra. The emission spectra appear in the region 440 – 500 nm peaking at 443 nm and 465 nm and a shoulder at ~ 500 nm. The decrease in the fluorescence intensity of the adsorbed 9-AnCA with increasing azulene loading is due to concentration quenching effect and indicated the possibility of energy or electron transfer from excited 9-AnCA species to ground state azulene and perylene. The interaction between the excited 9-AnCA and perylene is possible because the excited singlet state energy levels of perylene are lower lying than those of 9-AnCA²¹⁹.
Figure 6.36: Fluorescence emission spectra of 9-AnCA (1.0 μmol g⁻¹) co-adsorbed with perylene (0.5 μmol g⁻¹) and azulene on silica sol-gel following excitation at 355 nm plotted as a function of azulene concentration.
Chapter 6. Results and discussion

Figure 6.37: Fluorescence emission spectra of 9-AnCA (1.0 \( \mu \text{mol g}^{-1} \)) co-adsorbed with perylene (0.5 \( \mu \text{mol g}^{-1} \)) and azulene on 1 % TiSi_2 surface following excitation at 355 nm plotted as a function of azulene concentration.

In this ternary system, azulene acts as a shuttle molecule facilitating electron / hole transfer. The electron transfer will be from azulene to the 9-AnCA radical cation and from perylene to azulene cation producing the 9-AnCA ground state and the perylene radical cation.

The fluorescence emission spectra of perylene adsorbed alone on the surface of silica sol-gel and TiSi_2 mixed oxides are shown in figure 6.38. The silanol groups have an important role in the adsorption process of different organic molecules on the silica sol-gel and titania-silica surfaces. The binding of molecules with \( \pi \)-sytems, such as perylene onto these surfaces is due to hydrogen bonding to the silanols and Ti—OH or to physically adsorbed water molecules from the surface. The interaction with silanol groups can be different depending on the silanol distribution on the surface and the properties of the surface (surface area, pore size, etc). From this reason, perylene
molecules are adsorbed in a variety of local environments on the surface and the adsorbed molecules present broader absorption and emission bands than in solution.

Figure 6.38: A comparison between fluorescence emission spectra of perylene (0.5 µmol g⁻¹) in acetonitrile solution (dot line) and perylene (0.5 µmol g⁻¹) adsorbed on silica sol-gel (dash line) and 1 % TiSi₂ surface (solid line) following excitation at 355 nm.
6.3.3 Transient absorption spectra

All transient absorption spectra were recorded following laser excitation at 355 nm. 9-Anthracenecarboxylic acid with a loading of 1.0 \( \mu \text{mol g}^{-1} \) was co-adsorbed with perylene (0.5 \( \mu \text{mol g}^{-1} \)) from acetonitrile solution onto both silica sol-gel and TiSi_2 surface with a loading of 1 % titania. Azulene with a concentration varying from 0.5 \( \mu \text{mol g}^{-1} \) to 2.0 \( \mu \text{mol g}^{-1} \) was also co-adsorbed from acetonitrile solution into the 9-AnCA / perylene system in order to investigate the mobility of radical cations on the surface of silica sol-gel and titania-silica mixed oxides in this ternary system.

The transient absorption spectra of laser irradiated samples of 9-AnCA co-adsorbed with perylene on silica sol-gel and 1 % TiSi_2 surface using 355 nm photons for excitation are shown in figures 6.39 and 6.40 respectively. From these figures, a very small amount of the 9-AnCA triplet state is observed at 420 nm and the 9-AnCA radical cation bands were assigned at 715 and 730 nm (the main absorptions) and a small absorption at 430 nm. The radical cation absorption spectrum of 9-AnCA exhibited a red shift from 715 nm to 730 nm which was similar in magnitude to the shift in the ground state absorption spectrum. The bathochromic shift at 730 nm could be due to the interaction of 9-AnCA with the active sites of the surface and also the heterogeneous nature of the surface.

While the absorption at 420 nm is due to the triplet-triplet absorption of 9-AnCA adsorbed on silica sol-gel and TiSi_2 surfaces, the absorption around 730 nm can be attributed to the 9-AnCA radical cation which could be formed as a result of excited state annihilation processes as well as the electron injection process. However, as can be seen in figures 6.39 and 6.40 the yield of the 9-AnCA radical cation is small enough so as not interfere with the investigation of the 9-AnCA triplet state.
Figure 6.39: Transient absorption spectrum of 9-anthracenecarboxylic acid (1.0 μmol g⁻¹) co-adsorbed with perylene (0.5 μmol g⁻¹) on silica sol-gel following laser excitation at 355 nm.

Figure 6.40: Transient absorption spectrum of 9-anthracenecarboxylic acid (1.0 μmol g⁻¹) co-adsorbed with perylene (0.5 μmol g⁻¹) on 1 % TiSi₂ surface following laser excitation at 355 nm.
The transient absorption data supports the occurrence of an electron transfer from the LUMO of the 9-AnCA to the conduction band of the titania for all samples prepared on titania-silica mixed oxides. The decay of the 9-AnCA triplet state at 420 nm is accompanied by the rise of the perylene radical cation at 530 nm. The perylene radical cation appears concomitantly with the 9-AnCA radical cation decay at 715 nm.

Co-adsorption of azulene into the 9-AnCA / perylene systems changes the observed electron transfer kinetics and the resulting transient absorption spectra are shown in figures 6.41 and 6.42. The 9-AnCA radical cation has an increased rate of decay when azulene is present and acts as electron donor molecule. An increase in azulene concentration increases the rate of decay or formation of the transient observed.

For all 9-AnCA / azulene / perylene samples prepared on 1 % TiSi₂ surface, the 9-AnCA triplet state is not observed. The absorption bands at 420 nm and 450 can be attributed to the 9-AnCA radical cation. For samples prepared on silica sol-gel, the 9-AnCA triplet state is slightly observed at 420 nm. The absorption band corresponding to perylene radical cation is assigned at 530 nm and decays slowly.

![Figure 6.41: Transient absorption spectrum of 9-anthracenecarboxylic acid (1.0 μmol g⁻¹) co-adsorbed with azulene (0.5 μmol g⁻¹) and perylene (0.5 μmol g⁻¹) on silica sol-gel following laser excitation at 355 nm.](image-url)
Chapter 6. Results and discussion

Figure 6.42: Transient absorption spectrum of 9-anthracenecarboxylic acid (1.0 \( \mu \text{mol g}^{-1} \)) co-adsorbed with azulene (0.5 \( \mu \text{mol g}^{-1} \)) and perylene (0.5 \( \mu \text{mol g}^{-1} \)) on 1 % TiSi_2 surface following laser excitation at 355 nm.

The transient absorption spectra resulting from the 355 nm laser excitation of perylene alone on silica sol-gel and 1 % TiSi_2 surface are shown in figures 6.43 and 6.44. These figures present an intense absorption band with maximum at 530 nm assigned to the perylene radical cation absorption band by analogy to the same characteristic absorption bands observed in solution as well as on surfaces^{220-222}. The small band around 470 nm could have contributions from the absorption of the perylene triplet state. The presence or the absence of the triplet-triplet absorption band at 470 nm in the transient absorption spectra of adsorbed perylene can be rationalized in terms of a reduction in the intersystem crossing quantum yield for adsorbed perylene compared to that in solution^{223}. 

173
Figure 6.43: Transient absorption spectrum of perylene (0.5 μmol g⁻¹) adsorbed on silica sol-gel following laser excitation at 355 nm.

Figure 6.44: Transient absorption spectrum of perylene (0.5 μmol g⁻¹) adsorbed on 1 % TiSi₂ surface following laser excitation at 355 nm.
6.3.4 Kinetics of energy and electron transfer

Energy and electron transfer reactions have been studied between 9-anthracenecarboxylic acid (9-AnCA) co-adsorbed with azulene and perylene on silica sol-gel and TiSi_2 surface at a loading of 1 % titania. Following laser excitation the 9-AnCA is photoionised to its radical cation. After transferring an electron from azulene to the photoproduced 9-AnCA radical cation it will recombine to return to the ground state and form the azulene radical cation which then diffuses across the surface. By adding a third molecule (perylene) to the system, the electron transfer can be demonstrated using azulene molecule for hole transfer between the 9-AnCA radical cation as an electron acceptor and perylene as an electron donor. Perylene transfers an electron to the azulene radical cation forming the azulene ground state and generating the perylene radical cation. In this ternary system, the azulene behaves as a shuttle molecule in order to facilitate electron / hole transfer producing the 9-AnCA ground state and the perylene radical cation.

A series of samples was prepared for 9-AnCA co-adsorbed with perylene on silica sol-gel and 1 % TiSi_2 surface employing azulene as electron donor molecule. 9-AnCA (1.0 μmol g\(^{-1}\)) and perylene (0.5 μmol g\(^{-1}\)) were co-adsorbed with azulene from acetonitrile onto the solid surface and studied as a function of azulene concentration in the range 0.5 μmol g\(^{-1}\) – 2.0 μmol g\(^{-1}\).

The kinetics of the decay of excited triplet state and radical cation of 9-AnCA and the rise or decay of perylene radical cation have been studied following laser excitation at 355 nm in the presence or the absence of co-adsorbed azulene as electron donor. The transient decay was analysed using diffuse reflectance laser flash photolysis.

Energy transfer between the excited 9-AnCA and azulene was analysed at 420 nm, while the electron transfer reactions from azulene to the 9-AnCA radical cation and from perylene to the azulene radical cation were studied at two wavelengths: 715 nm corresponding to the 9-AnCA radical cation and at 530 nm respectively where the perylene radical cation shows a maximum absorption.

The kinetic data was analysed as in previous sections (6.1 and 6.2) using the dispersive kinetic model of Albery et al. which provides analytical parameters with which to
characterise the decay or rise (in the case of perylene) rate constant as a function of concentration. A kinetic trace showing the decay of the 9-AnCA radical cation and the rise of the perylene radical cation is shown in figure 6.45 as reflectance change versus time.

Figure 6.45: (a) Decay of the 9-AnCA radical cation monitored at 715 nm and (b) rise of the perylene radical cation monitored at 530 nm with azulene adsorbed as molecule shuttle on silica sol-gel following laser excitation at 355 nm.
Figure 6.45 shows also the residuals for fitting using the Albery model for both the decay of 9-AnCA radical cation and the rise of the perylene radical cation.

Table 6.8 reflects the result of the fits obtained for constant 9-AnCA (1.0 μmol g⁻¹) and perylene (0.5 μmol g⁻¹) concentrations with varying azulene loading (from 0.5 μmol g⁻¹ to 2.0 μmol g⁻¹) for all analysed transient species (9-AnCA triplet state, 9-AnCA radical cation and perylene radical cation). This table shows that the distribution width (γ) which varies from 0.1 to 3.0 is independent of the azulene concentration. Co-adsorption of azulene into the 9-anthracenecarboxylic acid / perylene systems increases the rates of both 9-AnCA triplet state and radical cation in this ternary system. For the 9-anthracenecarboxylic acid / azulene / perylene system on silica sol-gel, the rate constants for perylene radical cation increase with increasing azulene concentration, while for the 9-anthracenecarboxylic acid / azulene / perylene system on 1 % TiSi₂ surface, the rate constants of perylene radical cation decrease as the azulene concentration is increased suggesting that the perylene radical cation is populated by the formation of azulene radical cation on the surface of titania-silica mixed oxides.
### Table 6.8: The mean rate constants ($\tilde{k}$) and the distribution width ($\gamma$) for triplet state and radical cation decay kinetics of 9-anthracenecarboxylic acid co-adsorbed with perylene and azulene on silica sol-gel and 1 % TiSi_2 surface and the kinetics of the decay or rise of the perylene radical cation as a function of azulene concentration, where 9-AnCAT and 9-AnCA.+ denote the 9-anthracenecarboxylic acid excited triplet state and radical cation respectively and Pe.+ represents the perylene radical cation.

<table>
<thead>
<tr>
<th>System</th>
<th>Kinetic analysis of</th>
<th>9-AnCA Az Pe / 1 % TiSi_2</th>
<th>AnCAAz Pe / Si sol-gel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>9-AnCAT at 420 nm</td>
<td>9-AnCA at 715 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\tilde{k}$ / s$^{-1}$</td>
<td>$\gamma$</td>
</tr>
<tr>
<td>$0 : 0 : 0.5$</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$1 : 0 : 0.5$</td>
<td></td>
<td>185</td>
<td>1.4</td>
</tr>
<tr>
<td>$1 : 0.5 : 0.5$</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$1 : 1 : 0.5$</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$1 : 1.5 : 0.5$</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$1 : 2 : 0.5$</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
By using the extracted mean value for the decay rate constant $\tilde{k}$ and by application of equation (6.11), bimolecular quenching rate constants for the energy and electron transfer processes can be obtained:

$$\tilde{k} = k_0 + k_q' [Q]$$  \hspace{1cm} (6.11)

where $\tilde{k}$ is the observed rate constant for the triplet state or radical cation decay in the presence of quencher (azulene), $k_0$ is the unquenched decay rate constant, $k_q'$ represents the bimolecular quenching constant and $[Q]$ is the concentration of quencher molecule.

In the analysis of the energy and electron transfer data for 9-AnCA co-adsorbed with perylene and azulene on silica sol-gel and 1 % TiSi_2 surface it is not necessary to do any corrections of the experimental results because there is no evidence of the ground state association between 9-AnCA and azulene compared to the case of anthracene / azulene system presented in section 6.2.4 and where significant ground state association between anthracene and azulene was observed and the free concentration of azulene was calculated from the sample loading and the radical cation quenching data.

Bimolecular quenching constants have been measured for two processes involving the 9-anthracenecarboxylic acid, azulene and perylene. These are triplet-triplet energy transfer between the excited 9-AnCA and ground state azulene and electron transfer from azulene to the 9-AnCA radical cation and then from perylene to the azulene radical cation generating the perylene radical cation.

A plot of fitted rate constants ($\tilde{k}$) versus quencher concentration for energy and electron transfer in the 9-anthracenecarboxylic acid / azulene / perylene system on silica sol-gel is shown in figure 6.46. Figure 6.47 shows a typical quenching plot only for electron transfer in the 9-anthracenecarboxylic acid / azulene / perylene system on TiSi_2 surface at a content of 1 % titania. A linear correlation between the decay rates obtained from the dispersive kinetic model and azulene concentration was found.

Bimolecular quenching rate constants (the gradient of the plots) for energy transfer between the excited 9-AnCA and azulene and electron transfer from azulene to the
9-AnCA radical cation and then from perylene to the azulene radical cation are summarised in table 6.9.

Figure 6.46: Plots of the average rate constants ($\tilde{k}$) obtained from the dispersive kinetic analysis for energy transfer (red line) between the excited state of 9-AnCA (1.0 $\mu$mol g$^{-1}$) and azulene and electron transfer from azulene to 9-AnCA radical cation (black line) and perylene (0.5 $\mu$mol g$^{-1}$) to azulene radical cation (blue line) on silica sol-gel following laser excitation at 355 nm as a function of azulene concentration.
Figure 6.47: Plots of the average rate constants ($k$) obtained from the dispersive kinetic analysis for electron transfer from azulene to 9-AnCA radical cation (1.0 $\mu$mol g$^{-1}$, black line) and perylene (0.5 $\mu$mol g$^{-1}$) to azulene radical cation (blue line) on 1 % TiSi$_2$ surface following laser excitation at 355 nm as a function of azulene concentration.

Table 6.9: Bimolecular quenching rate constants for energy transfer between the excited 9-AnCA and azulene and electron transfer between azulene and the 9-AnCA radical cation and perylene and the azulene radical cation, where $x$ denotes the concentration of azulene which is changing.
In the ternary system, the rate of electron transfer from azulene to the 9-AnCA radical cation reflects the relatively slow diffusion of the azulene molecule on the surface of silica sol-gel and TiSi$_2$ mixed oxides. It is known that the 9-AnCA is not mobile on the surface of silica sol-gel or titania-silica mixed oxides. The 9-AnCA molecule is hydrogen bonded and is fixed on the surface and for this reason the rate of electron transfer is governed by the diffusion of the azulene molecule across the silica sol-gel and TiSi$_2$ surface.

A possible explanation of the increased rate of energy and electron transfer of anthracene co-adsorbed with azulene (table 6.7) relative to those obtained for the 9-AnCA in the ternary system (table 6.9) could be the fact that unsubstituted anthracene is able to diffuse freely across the surface and the rate of decay of the triplet and radical cation are greatly dependent on the anthracene loading. The observed lower rates of triplet-triplet energy and electron transfer of 9-AnCA adsorbed on silica sol-gel than those corresponding to silica Davisil system (table 6.9) can be ascribable to some factors such as the geometry and steric hindrance of the substituted anthracene as a result of the smaller average pore size of the surface. Silica sol-gel surface have half the pore size of Davisil silica gel. The carboxylic group (which is an electron withdrawing group) attached to the anthracene ring may cause distortion of the planar hydrocarbon skeleton and hence resonance is reduced. The $\pi$-$\pi$ interaction together with the intermolecular hydrogen bonding via the carboxylic group contributes to a reduction in the possible arrangements of the molecule (less orientation freedom).

The rate of diffusion of azulene is faster than that of perylene (ten times faster for the system prepared on TiSi$_2$ surface and hundred times faster for samples prepared on silica sol-gel). Perylene diffuses slower in both cases (TiSi$_2$ mixed oxides and silica sol-gel) compared to the case of silica Davisil grade 635. In the absence of azulene, the electron transfer rate is governed by the rate of diffusion of the perylene.
6.3.5 Activation energies for electron transfer in a termolecular system on silica sol-gel and TiSi_2 surfaces

Activation energies for electron transfer have been measured in a ternary system on silica sol-gel and TiSi_2 surface with a content of 1 % titania. The systems chosen were 9-anthracenecarboxylic acid (9-AnCA) / azulene (Az) / perylene (Pe) on silica sol-gel and 9-anthracenecarboxylic acid / azulene / perylene on 1 % TiSi_2 surface. The effects of temperature on electron transfer rates of 9-anthracenecarboxylic acid / azulene / perylene samples prepared on silica sol-gel and TiSi_2 surface at a loading of 1 % titania were investigated. 9-Anthracenecarboxylic acid (1.0 μmol g⁻¹) and perylene (0.5 μmol g⁻¹) were co-adsorbed with azulene (with a loading of 0.5 μmol g⁻¹ and 2.0 μmol g⁻¹) from acetonitrile solution onto the solid surface of silica sol-gel and titania-silica mixed oxides. Samples were prepared under vacuum to a pressure of 5 x 10⁻⁵ mbar and pre-treated at 125 °C.

The kinetics of the decay of the 9-AnCA radical cation and perylene decay / rise were studied following 355 nm laser excitation in the presence or the absence of co-adsorbed azulene as a molecule shuttle in order to facilitate electron / hole transfer from the ground state azulene to the 9-AnCA radical cation and then from perylene to the azulene radical cation regenerating the 9-AnCA ground state and producing the perylene radical cation and analysed using the dispersive kinetic model. The electron transfer between the 9-AnCA radical cation and azulene was monitored at the peak of the 9-AnCA radical cation absorption at 715 nm, while the perylene radical cation decay / rise was analysed at 530 nm.

Rate constants for the decay of 9-AnCA radical cation and rates for the decay or rise of perylene radical cation in the presence of 0.5 μmol g⁻¹ and 2.0 μmol g⁻¹ azulene or in the absence of azulene have been measured. The rate measurements at different temperatures fitted using the dispersive kinetic model demonstrates that the rates become faster with increasing temperature. A particular case is illustrated in table 6.10 where the rate constants of 9-AnCA radical cation and perylene radical cation for 9-anthracenecarboxylic acid / perylene system on silica sol-gel are measured at different temperatures and an increase of the rate constants with increasing temperature can be clearly observed.
### Table 6.10: The mean rate constants ($\bar{k}$) and the distribution width ($\gamma$) for perylene rise and radical cation decay kinetics of 9-anthracencarboxylic acid (1.0 $\mu$mol g$^{-1}$) co-adsorbed with perylene (0.5 $\mu$mol g$^{-1}$) on silica sol-gel obtained at different temperatures.

The Arrhenius equation (6.12) shows the dependence of the rate constants on temperature:

$$k = Ae^{-(E_a/RT)}$$  \hspace{1cm} (6.12)

The equation (6.12) can also be written as:

$$\ln k = \ln A - \frac{E_a}{RT}$$  \hspace{1cm} (6.13)
where \( k \) is the rate constant measured at different temperatures (in s\(^{-1}\)), \( A \) is the pre-exponential factor, \( E_a \) represents the activation energy (in kJ mol\(^{-1}\)), \( R \) is the universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)) and \( T \) is the absolute temperature (in K).

By measuring the decay of the 9-AnCA radical cation of sample as a function of temperature and plotting \( \ln k \) versus (1/T), the activation energy for the diffusion of the azulene ground state can be calculated, while monitoring the rise / decay of the perylene radical cation as a function of temperature allows determination of the activation energy for the diffusion of the azulene radical cation. An Arrhenius plot for electron transfer constructed using the value of rate constants of the 9-AnCA radical cation and perylene radical cation for the 9-anthracencarboxylic acid / perylene system on silica sol-gel is shown in figure 6.48.

![Arrhenius plot](image)

**Figure 6.48: Arrhenius plots for electron transfer between 9-anthracencarboxylic acid (1.0 µmol g\(^{-1}\)) and co-adsorbed perylene (0.5 µmol g\(^{-1}\)) on silica sol-gel, PTT 125 °C, following laser excitation at 355 nm.**
The plot of $\ln k$ versus $(1/T)$ is linear and the slope of the resulting line corresponds to the values of the activation energies. The determined values of activation energy $E_a$ for all analysed samples are presented in table 6.11.

It can be seen from table 6.11 that in the ternary system, the activation energy for perylene diffusion is higher than observed for the anthracene / azulene system, reflecting the lower mobility of the perylene molecule. The activation energy for the electron transfer from the azulene radical to perylene in the sol-gel system is comparable to that observed on silica Davisil.

Williams et al.\textsuperscript{217} have found for a ternary anthracene (9-anthracenecarboxylic acid) / azulene / perylene system that the activation energy for the perylene radical cation rise is higher by around 10 kJ mol\textsuperscript{-1} than that for the anthracene decay reflecting the higher activation energy for diffusion of the azulene radical cation. It was demonstrated that azulene and its radical cation diffuse across the silica surface followed by electron transfer to the anthracene or 9-anthracenecarboxylic acid radical cation and from perylene to the azulene radical cation.
### Table 6.11: Activation energies and pre-exponential factors for electron transfer between 9-anthracenecarboxylic acid and azulene and from perylene to the azulene radical cation adsorbed on silica sol-gel and 1 \% TiSi$_2$ surface where 9-AnCA$^+$ and Pe$^+$ denote the 9-anthracenecarboxylic acid radical cation and perylene radical cation respectively.

<table>
<thead>
<tr>
<th>System</th>
<th>9-AnCA:Az:Pe</th>
<th>9-AnCAAzPe / 1 % TiSi$_2$</th>
<th>9-AnCAAzPe / Si sol-gel</th>
<th>9-AnCAAzPe / Silica Davisol$_{217}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>9-AnCA$^+$ at 715 nm</td>
<td>Pe$^+$ at 530 nm</td>
<td>9-AnCA$^+$ at 715 nm</td>
<td>Pe$^+$ at 530 nm</td>
</tr>
<tr>
<td>9-AnCA : Az : Pe</td>
<td>Ea / kJ mol$^{-1}$</td>
<td>A / s$^1$</td>
<td>Ea / kJ mol$^{-1}$</td>
<td>A / s$^1$</td>
</tr>
<tr>
<td>1 : 0 : 0.5</td>
<td>76 ± 4</td>
<td>8 x 10$^{13}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1 : 0.5 : 0.5</td>
<td>-</td>
<td>-</td>
<td>52 ± 2</td>
<td>1.3 x 10$^{10}$</td>
</tr>
<tr>
<td>1 : 2.0 : 0.5</td>
<td>-</td>
<td>-</td>
<td>96 ± 4</td>
<td>6.0 x 10$^{12}$</td>
</tr>
</tbody>
</table>

Table 6.11: Activation energies and pre-exponential factors for electron transfer between 9-anthracenecarboxylic acid and azulene and from perylene to the azulene radical cation adsorbed on silica sol-gel and 1 \% TiSi$_2$ surface where 9-AnCA$^+$ and Pe$^+$ denote the 9-anthracenecarboxylic acid radical cation and perylene radical cation respectively.
6.3.6 Conclusions of energy and electron transfer data

Energy and electron transfer kinetics have been measured for anthracene on silica sol-gel and TiSi₂ surface co-adsorbed with azulene acting as an electron donor molecule. Transient decay data has been analysed using the dispersive kinetic model of Albery et al. which assumes a log Gaussian distribution of rate constants. A linear correlation between the decay rates obtained from the dispersive kinetic model and azulene concentration was observed. The rate of energy and electron quenching is seen to increase as a function of azulene concentration and decrease with increasing the content of titania in titania-silica mixed oxides. In TiSi₂ system, the triplet-triplet energy transfer rate is faster than the rate of anthracene radical cation quenching. On the basis that the radical cation is less mobile than the neutral species, in line with observations on silica Davisil₁¹⁴, this would suggest that anthracene moves faster on both silica sol-gel and TiSi₂ surfaces than the azulene molecule, possible as a result of the smaller pore size relative to Davisil silica gel restricting the parts of the surface explored by the anthracene relative to the azulene. On TiSi₂ surfaces and at higher azulene loadings, the activation energies and the pre-exponential factors are the same for both energy and electron transfer suggesting that the azulene diffuses across the surface of titania-silica mixed oxides. At lower azulene loadings, it was found that both the activation energies and pre-exponential factors are lower. This can be attributed to the ion-electron recombination which dominates and the activation energies extracted are then for this process.

Electron transfer has been also studied in a ternary system using azulene molecule for hole transfer between the 9-anthracenecarboxylic acid radical cation as an electron acceptor and perylene acting as an electron donor. The co-adsorption of azulene as a molecule shuttle with 9-anthracenecarboxylic acid and perylene on silica sol-gel and 1 % TiSi₂ surface causes an increase in the rate of electron transfer. The rate of electron transfer from azulene to the 9-anthracenecarboxylic acid radical cation is governed by the slow diffusion of the azulene molecule across the silica sol-gel and TiSi₂ surfaces; the rate of diffusion of azulene being faster relative to perylene.
6.4 Photocatalytic degradation of 4-chlorophenol

The photocatalytic activity of TiO$_2$ P25 and TiSi$_2$ mixed oxides prepared by sol-gel method were studied by decomposition of 4-chlorophenol (4-CP) aqueous solution under UV light irradiation.

The absorption spectra of $9.6 \times 10^{-5}$ mol l$^{-1}$ 4-CP solutions in the absence of photocatalyst or in the presence of TiO$_2$ P25 and TiSi$_2$ mixed oxides with different titania content are shown in figure 6.49. The most intense peaks corresponding to the absorption of 4-CP in UV area are located at 225 nm and 280 nm. The absorption peaks of 4-CP decrease with increasing TiO$_2$ content from 1 % to 10 % in TiSi$_2$ mixed oxides. It can be observed that the absorption peak at 280 nm decreased and finally disappeared with increasing TiO$_2$ content of the mixtures suggesting that TiO$_2$ has a positive influence on the degradation of 4-CP.

![UV-absorption spectra of 4-chlorophenol aqueous solution in the absence or in the presence of TiO$_2$ P25 and TiSi$_2$ mixed oxides with different titania content as photocatalysts.](image-url)

Figure 6.49: UV-absorption spectra of 4-chlorophenol aqueous solution in the absence or in the presence of TiO$_2$ P25 and TiSi$_2$ mixed oxides with different titania content as photocatalysts.
The peak observed at 255 nm can be attributed\textsuperscript{224} to the formation of carbene-4-oxocyclohexa-2,5-dienylidene which can react with the molecular oxygen forming 1,4-benzoquinone-O-oxide which subsequently yields 1,4-benzoquinone.

The concentration of 4-CP solutions decreases with increasing TiO\textsubscript{2} content (figure 6.50) suggesting that the 4-CP adsorbed on the TiO\textsubscript{2} sites of the photocatalyst. It can be clearly observed that 4-CP concentration decreases rapidly with increasing the irradiation time from 0 to 120 minutes and then decreases slowly while the irradiation time continues to increase.

![Absorbance at 225 nm vs. Irradiation time](image)

**Figure 6.50:** Photocatalytic degradation of 4-chlorophenol with TiSi\textsubscript{2} mixed oxides with different titania content compared with commercial Degussa TiO\textsubscript{2} P25.

The presence of TiO\textsubscript{2} nanoparticles affects the intermediate degradation products during the decomposition of 4-CP. The chloride ion concentration in 4-CP solutions with different TiO\textsubscript{2} content increases along with the irradiation time and TiO\textsubscript{2} content.
A possible mechanism for the degradation of 4-CP aqueous solution can be seen in scheme 6.3.

Scheme 6.3: Possible mechanism for the degradation of 4-chlorophenol aqueous solution under UV light irradiation.

The degradation of 4-CP and the formation of chlorine ions can be attributed to the reduction and oxidation of 4-CP. Under UV irradiation, TiO$_2$ nanoparticles generate electron / hole pairs. Positive holes oxidize the 4-CP adsorbed on the TiO$_2$ P25 and TiSi$_2$ mixed oxides or react with water leading to the formation of hydroxyl radicals on the particle surface which are very strong oxidants.

In order to compare the photocatalytic efficiency of each photocatalyst, it was assumed that the absorption intensities of UV data were linearly proportional to the concentration of 4-CP:

\[
\text{Degradation} \,(\%) = \frac{C_0 - C}{C_0} \times 100
\]  

(6.14)

where $C_0$ is the initial concentration of 4-CP (before irradiation) and $C$ is the concentration of 4-CP after irradiation.

The degradation rates of photocatalytic oxidation of 4-CP follows the Langmuir-Hinshelwood kinetics model$^{44}$:
where \( r \) is the degradation rate of 4-CP, \( C \) is the concentration of 4-CP in solution, \( t \) represents the irradiation time, \( k_r \) is the reaction rate constant and \( K_a \) is the adsorption coefficient of the reactant.

When the initial concentration \( C_0 \) of 4-CP is small, the equation (6.15) can be simplified to a pseudo first-order equation:

\[
\ln \frac{C_0}{C} = kt
\]

where \( k \) is the rate constant and can be used to compare the relative efficiency of the photocatalysts.

The variations of 4-CP concentration as a function of irradiation time are given in figure 6.50 and the rate constants obtained from the experimental data as a function of TiO\(_2\) content of the TiSi\(_2\) mixed oxides and the % degradation of 4-CP are shown in table 6.12. The rate of reaction of the TiO\(_2\) P25 is also shown for comparison.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( k / s^{-1} )</th>
<th>% degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-CP / TiO(_2) P25</td>
<td>2.9 x 10(^{-4})</td>
<td>68.2</td>
</tr>
<tr>
<td>4-CP / 1% TiSi(_2)</td>
<td>1.4 x 10(^{-4})</td>
<td>36.1</td>
</tr>
<tr>
<td>4-CP / 3% TiSi(_2)</td>
<td>1.5 x 10(^{-4})</td>
<td>39.3</td>
</tr>
<tr>
<td>4-CP / 5% TiSi(_2)</td>
<td>1.1 x 10(^{-4})</td>
<td>36.2</td>
</tr>
<tr>
<td>4-CP / 10% TiSi(_2)</td>
<td>9.5 x 10(^{-5})</td>
<td>36.1</td>
</tr>
<tr>
<td>4-CP / Water</td>
<td>3 x 10(^{-5})</td>
<td>23.4</td>
</tr>
</tbody>
</table>

*Table 6.12: The rate constants and the % degradation of 4-chlorophenol for each sample.*

4-Chlorophenol in the absence of TiO\(_2\) P25 or TiSi\(_2\) particles shows negligible photodecomposition. Table 6.12 confirms that the highest value of rate constant (\( k \)) corresponds to TiO\(_2\) P25 compared with TiSi\(_2\) mixed oxides where the rate constant
decreases with increasing titania content. The degradation efficiencies of 4-CP are almost the same in the case of TiSi_2 mixed oxides with different titania content. It can be seen from figure 6.50 that TiO_2 P25 exhibits much higher photocatalytic activity than TiSi_2 mixtures. The highest conversion of 4-CP (68 %) occurs in the presence of TiO_2 P25 and low conversion for TiSi_2 mixtures. There is not a difference between the % of titania, the % degradation of 4-CP on 1 % TiSi_2 mixed oxides is almost the same with those corresponding to higher titania content.

The rate of decomposition of 4-CP depends on the TiO_2 / SiO_2 ratio. It is known that 4-CP does not adsorb onto the silica sites of the TiSi_2 mixed oxides. Titania-silica mixed oxides prepared by sol-gel method (TiSi_2) contain a low loading of titania (from 1% to 10 %) and high loading of silica and exhibit high surface area. As the silica loading is increased, the surface area and the photocatalytic activity of the mixed oxides increase. At higher content of silica than 10 wt. % in the titania-silica mixed oxides, a decrease in the photocatalytic activity was reported. The decrease in the photocatalytic activity of TiSi_2 mixtures with high loading of silica is due to the fact that SiO_2 does not adsorb the 4-CP and it decreases the photoactivity of the catalyst by blocking the active sites of TiO_2 available for the photoreaction relative to TiO_2 P25. In this way, upon irradiation, TiO_2 sites can not generate enough electron / hole pairs and the formation of hydroxyl radicals on the particle surface is limited and the rate of degradation of 4-CP will be lower compared to TiO_2 P25. Raj et al. have found that materials possessing a loading of 7.5 wt. % SiO_2 have high photocatalytic activity and are able to degrade the 4-CP molecules with high rate.

Titania-silica mixed oxides produced by sol-gel method are less efficient photocatalysts for the degradation of 4-CP than TiO_2 P25. The presence of silica increases the surface area and the photocatalytic efficiency of the mixed oxides, but a too high amount of SiO_2 reduces the quantity of TiO_2 sites available for the photodegradation reaction of 4-CP and the photoactivity of the TiSi_2 catalysts decreases.
7. Conclusions

Analysis of ground state absorption and emission spectra of anthracene adsorbed on silica gel and titania-silica mixed oxides at different titania content prepared by two different methods (a “dropwise” method and a sol-gel route) revealed aggregates formation at relative low surface loadings. These loadings correspond to a surface coverage of only a few percent of a monolayer indicating preferential adsorption occurs at some surface sites. The absorption peaks corresponding to the anthracene molecule are difficult to observe at higher titania content due to the titania absorption edge which overlaps significantly with the anthracene absorption. Fluorescence quenching of the excited anthracene occurs on titania-silica surfaces prepared by both methods, and shows a dependence on titania content. The data show that anthracene has to adsorb in close proximity to the titania sites on the silica matrix. This leads to some quenching of the anthracene fluorescence by the titania, but more so by the Ti$^{3+}$ species which are located in the titania. The characteristic anthracene triplet-triplet absorption and radical cation absorption spectra are both observed following laser excitation at 355 nm. Triplet state production was found to be monophotonic, whereas the anthracene radical cation is formed by monophoton or multiphoton ionisation in the mixed titania-silica systems. The decay of the anthracene triplet state and radical cation can be well described by the dispersive kinetic model of Albery which is based on a log Gaussian distribution of rate constants. Kinetic analysis of the decay of the anthracene triplet state and radical cation show that the kinetic parameters depend both on the titania content and the method of oxide synthesis.

The co-adsorption of azulene as electron donor with anthracene on silica sol-gel and titania-silica mixed oxides prepared by the sol-gel method causes an increase in the rate of decay of the anthracene radical cation. Triplet-triplet energy transfer was observed between the excited anthracene and ground state azulene. Photoionisation of the anthracene leads to the formation of anthracene radical cation and electron transfer then occurs from azulene to the anthracene radical cation. Decay rate constants of both the anthracene triplet state and radical cation show a dependence on the titania content and the azulene concentration. The rate of energy and electron transfer was found to decrease with increasing titania content in titania-silica mixed oxides and increase as a function of azulene concentration. The rate of reaction of anthracene on silica sol-gel surface and
titania-silica mixed oxides prepared by the sol-gel method is governed by the diffusion of the anthracene across the surface; azulene molecule was found less mobile on the surface of these solid substrates, possible as a result of the smaller pore size relative to silica Davisil.

Energy and electron transfer reactions were also studied between 9-anthracenecarboxylic acid co-adsorbed with azulene and perylene on silica sol-gel and titania-silica mixed oxides at a content of 1 % titania prepared by the sol-gel method. Azulene was employed as a molecule shuttle in this ternary system in order to facilitate the electron transfer between the 9-anthracenecarboxylic acid radical cation acting as an electron acceptor and perylene acting as an electron donor. The 9-anthracenecarboxylic acid triplet state at 420 nm was not observed for 9-anthracenecarboxylic acid / azulene / perylene samples prepared on 1 % titania-silica surface, while for samples prepared on silica sol-gel surface, the 9-anthracenecarboxylic acid triplet state is weakly observed at 420 nm. The decay of the 9-anthracenecarboxylic acid triplet state at 420 nm is accompanied by the rise of the perylene radical cation at 530 nm. The perylene radical cation appears concomitantly with the 9-anthracenecarboxylic acid radical cation decay at 715 nm. The co-adsorption of azulene with 9-anthracenecarboxylic acid and perylene on both silica sol-gel and 1 % titania-silica systems causes changes in the observed electron transfer kinetics. The rate constants for decay of both the 9-anthracenecarboxylic acid triplet state and radical cation increase with increasing azulene concentration. Bimolecular quenching rate constants for energy transfer between the excited 9-anthracenecarboxylic acid and azulene and electron transfer from azulene to the 9-anthracenecarboxylic acid radical cation and then from perylene to the azulene radical cation were obtained. The rate of reaction on 9-anthracenecarboxylic acid on both silica sol-gel and titania-silica mixed oxides is predominantly governed by the slow diffusion of azulene molecule. It was found that the rate of diffusion of azulene across the silica sol-gel and titania-silica surfaces is faster than that of perylene.

The investigated titania-silica mixed oxides with 1, 3, 5 and 10 wt. % titania prepared by the sol-gel method proved to be efficient photocatalysts for 4-chlorophenol degradation. Photocatalytic activity of the titania-silica mixed oxides is found to decrease with increasing crystallinity. A high silica content reduces the quantity of TiO₂ sites available
for the photodegradation of 4-chlorophenol. Commercial TiO₂ P25 Degussa showed larger rate of degradation of 4-chlorophenol than titania-silica mixed oxides.
8. Further work

- Since the rate of reaction of anthracene co-adsorbed with azulene on silica sol-gel and titania-silica binary oxides prepared by the sol-gel method is governed by the diffusion of the anthracene across the surface of these solid substrates, it would be interesting to investigate the energy and electron transfer reactions of 9-anthracenecarboxylic acid co-adsorbed with azulene on both silica sol-gel and titania-silica surfaces. This study may examine the bimolecular quenching rate constants obtained for energy and electron transfer between the 9-anthracenecarboxylic acid and azulene in order to see if the rate of reaction of 9-anthracenecarboxylic acid on silica sol-gel and titania-silica binary oxides is dominated by the diffusion of azulene. Due to its greater polarity, 9-anthracenecarboxylic acid is much less mobile on the silica gel and titania-silica surfaces than anthracene molecule and it is expected that the azulene molecule is diffusing faster than the 9-anthracenecarboxylic acid across the surface of silica sol-gel and titania-silica mixed oxides.

- It would also be interesting to measure the activation energy for energy and electron transfer reactions of 9-anthracenecarboxylic acid co-adsorbed with azulene on both silica sol-gel and titania-silica mixed oxides prepared by the sol-gel route. On the basis that, for the anthracene / azulene system, at higher azulene loadings, the activation energies and the pre-exponential factors yield the same values for both energy and electron transfer and are comparable with those obtained for azulene diffusion on silica Davisil suggesting that the azulene diffuses across the silica Davisil and titania-silica mixed oxides surface, while at lower azulene loadings ion-electron recombination dominates, it would be necessary to show the activation energies for both energy and electron transfer for the 9-anthracenecarboxylic acid / azulene system on silica sol-gel and titania-silica binary oxides and how the mobility of the investigated system is affected by the increasing azulene loadings and by the surface morphology.

- Since kinetic analysis of the decay of the anthracene triplet state and radical cation have been shown that the kinetic parameters depend on the anthracene loadings (aggregation formation can take place at higher anthracene loadings and due to the heterogeneous nature of the surface) and on the titania content of the sample, Monte Carlo simulations will be carried out in order to give us a better understanding of
the interpretation of the extracted parameters and then to be able to compare results obtained experimentally with those modelled.
9. References


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