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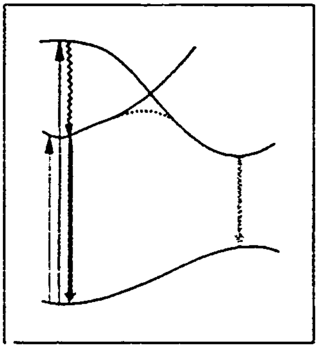
EXPERIMENTAL AND THEORETICAL ASPECTS OF EXCITED STATE ELECTRON TRANSFER AND RELATED PHENOMENA

In honour of Zbigniew R. Grabowski



Pułtusk, Poland

September 27 - October 2, 1992

120pp

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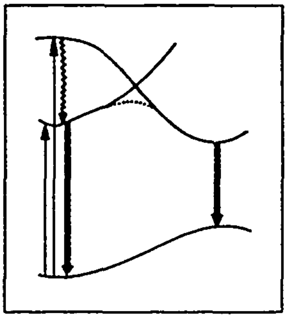


CONFERENCE PROGRAMME

Conference programme

Sunday, Sept. 27

20:00 Welcoming mixer

Monday, Sept. 28

8:00 *Breakfast*

9:00 Opening

9:30 R.A. MARCUS:
Electron Transfers Across Interfaces.
10:00 A. WELLER:
Photoinduced Electron Transfer in Covalently Linked Donor-Acceptor Systems.
10:30 *Coffee*
11:00 N. MATAGA:
Photoinduced Electron Transfer and Multiple States Mechanisms.
11:30 J.H. van der WAALS:
Spin Transfer Versus Charge Transfer in the Excited State of Inorganic Ions.
12:00 J. KROH:
Electron Scavenging Processes in Micellar Solutions.

13:00 Lunch

14:30 POSTER SESSION
16:00 *Coffee*
16:30 K.H. GRELLMANN:
Competition Between Tunnel- and Viscosity-Effects on a Bimolecular Hydrogen-Transfer Reaction.
17:00 M. ITOH:
Picosecond Fluorescence Studies of the Excited-State Proton Transfer in Substituted 3-Hydroxychromones in Supersonic Jet and in Nonpolar Solution.

18:00 Dinner

19:30 J. MICHL:
Electron Delocalization in Saturated Frameworks.
20:00 H. SHIZUKA:
Intramolecular Charge Transfer Emission from Excited Phenyldisilanes without TICT.

Tuesday, Sept. 29

8:00 Breakfast

9:00 M. KASHA:
Solvent Cage Spectroscopy. Viscosity Control of Dissociative, Torsional, and Dielectric Relaxation Potentials.
9:30 J.T. HYNES:
SN1 Ionization in Solution: an Electron Transfer Perspective.
10:00 G. KÖHLER:
Solvent Effects on Excited State Relaxation Phenomena.
10:30 *Coffee*
11:00 KUZMIN:
Exciplex Mechanism of the Fluorescence Quenching in Polar Media.
11:30 E. LIM:
Photoassociation in the Lowest Triplet State of Aromatic Molecules: Triplet Excimers and Exciplexes.
12:00 M. Van der AUWERAER:
Photo-induced Electron Transfer in Polychromophoric Systems.

13:00 Lunch

14:30 POSTER SESSION
16:00 *Coffee*
16:30 K. YOSHIHARA:
Femtosecond Electron Transfer between Dyes and Electron-Donating Solvents.
17:00 P.F. BARBARA:
Ultrafast Experiments on the Role of Solvent Motion in Electron Transfer.

18.00 Dinner

19:30 C. von BORCZYSKOWSKI:
Temperature and Solvent Dependent Charge Transfer in Self-Organized Porphyrin-Quinone Compounds.
20:00 D. BIRCH:
Energy and Electron Transfer in Bilayer Membranes.
20:15 W. ZIEGS:
Ultrafast Ti:Sapphire Lasers and Amplification Approaches. Current States and Outlook.
21:00 Concert at the Polonia Home.

Wednesday, Sept. 30

8:00 Breakfast

9:00 V. BONAČIĆ-KOUTECKÝ:
Role of Biradical- and Exciplex- Minima in Photochemical and Photophysical Processes.
9:30 B.O. ROOS:
Multiconfigurational Second Order Perturbation Theory Applied to the Calculation of Excited States.
10:00 E. HASELBACH:
Examples to the "SDT-Equation".
10:30 *Coffee*
11:00 W. RETTIG:
The Photophysics of Stilbenoid Dye Systems. A Comparison of Experiment and Theory.
11:30 R. LAPOUYADE:
Synthesis of new N-phenylaza-15-crowns-5 for Selective Cations Complexation, in The Ground State, and Dissociation of the Crowned Cations Following Optical Excitation.
12:00 C. RULLIÈRE:
Picosecond Studies of Charge Transfer States in "Push-Pull" Linear Diphenyl-Polyenes.

13:00 Lunch

14:00 TRIP TO WARSAW
15.00 Visit to the Royal Castle
18:00 Concert at the Ostrogski Palace

21:30 *Supper* (in Pultusk)

Thursday, Oct. 1

8:00 *Breakfast*

9:00 M.A. FOX:
Experimental Probes of Excited State Character in Supercritical Fluids.
9:30 J.W. VERHOEVEN:
Conformational Aspects of Intramolecular Electron-Transfer and 'Exciplex' Fluorescence.
10:00 J.M. WARMAN:
Photon-induced Intramolecular Charge Separation Studied by Time-Resolved Microwave Conductivity.
10:30 *Coffee*
11:00 W. BAUMANN:
Photoinduced Charge Transfer as Revealed by Ground and Excited State Dipole Moments.
11:30 R. WORTMANN:
Photoinduced Charge Separation and Broken Symmetry in Franck-Condon Excited $\pi\pi^*$ States of $[4N]\pi$ Cumulenes.
12:00 D. OELKRUG:
Excited-State Deactivation of p-Dimethylaminobenzonitrile and Related Compounds Adsorbed on Solid Surfaces.

13:00 Lunch

14:00 P. SUPPAN:
Solvation of TICT States in Mixtures of Polar and Non-Polar Solvents.
14:30 K.A. ZACHARIASSE:
Intramolecular Charge Transfer in Aminobenzonitriles. Dynamics and Dipole Moments.
15:00 *Coffee*
15:30 Z.R. GRABOWSKI:
Intramolecular Electron Transfer in Flexible Molecules and Molecular Ions.

16:30 Closing remarks

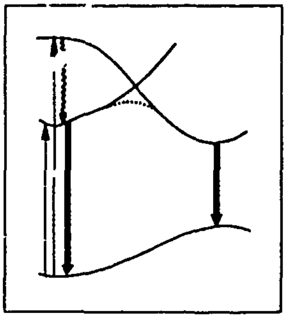
18:00 Reception

Friday, Oct. 2

8:00 *Breakfast*

9:00 Departure by bus to Warsaw

ETC



ABSTRACTS

LECTURES

Electron Transfer Across Interfaces

Rudolph A. Marcus
California Institute of Technology
Division of Chemistry and Chemical Engineering, 127-72 Pasadena,
California 91125, USA

Electron transfer (ET) across interfaces include many topics: ET across metal-liquid, semiconductor-liquid, liquid-liquid, and monolayer bridged interfaces, ET across membranes and at colloidal surfaces; and STM imaging. Several recent theoretical developments are summarized. The STM theory incorporates solid state concepts with ideas used for treating ET across organic and other bridges. ET theory for liquid-liquid or polymer-liquid interfaces and a resultant "cross-relation", together with related topics, are discussed.

PHOTOINDUCED ELECTRON TRANSFER
IN COVALENTLY LINKED DONOR-ACCEPTOR SYSTEMS

Albert Weller
Max-Planck-Institut für biophysikalische Chemie
Abt. Spektroskopie, D-3400 Göttingen, Germany

The investigation of photoinduced electron transfer in covalently linked donor-acceptor systems may be considered as a first step toward supramolecular photochemistry and, by the same token, as a study of primary charge separation in natural photosynthesis.

Model compounds, A-L-D, consisting of A=pyrene, D=dimethylaniline and various covalent linkages, L, such as $(CH_2)_n$ (with n = 1-16), o-, m-, p-Xylene and others have been used to investigate the effect of the linkage on the intramolecular electron transfer process in solution and also the influence of external magnetic fields on the spin dynamics in the radical ion pair, ${}^2A^-$-L-${}^2D^+$, from which the molecular triplet state, ${}^{3*}A$-L-${}^1D$, is formed. This was done using fluorescence lifetime and transient absorption measurements carried out with nano- and picosecond laser flashes.

The results show that the effective diffusion coefficient, D_{eff}, that determines the intramolecular encounter formation between A and D is several orders of magnitude smaller than the relative diffusion coefficient of the unlinked A and D molecules and has an activation energy which is considerably greater than that for free diffusion in the same solvent. This clearly shows that in the linked systems D_{eff} is governed by conformational changes of the linkage group between A and D.

The magnetic field effect can be interpreted quantitatively by assuming that the spin realignment in the radical ion pair leading from the initially-produced overall singlet state to the molecular triplet state is governed by the hyperfine interaction in each radical, by the exchange interaction of the radical spins in the pair (which increases with decreasing distance between ${}^2A^-$ and ${}^2D^+$) and by the Zeeman splitting of the T_{+1}, T_o, T_{-1} energy levels of the radical pair triplet state.

The differences in behaviour with respect to molecular triplet formation in the linked compounds with long, medium and short linkages are discussed.

Photoinduced Electron Transfer and Multiple States Mechanisms

Noboru Mataga
Department of Chemistry, Faculty of Engineering Science,
Osaka University, Toyonaka, Osaka 560, Japan

Results obtained by our ps-fs laser photolysis studies on the interactions between various unlinked donor(D) - acceptor(A) systems in luminescence quenching reactions and dynamics of produced transient CT(charge transfer) or IP(ion pair) states and also on some intramolecular exciplex systems linked by methylene chains such as p-$(CH_3)N$-Ph-$(CH)_n$-(1-pyrenyl) indicate the importance of the multiple states mechanism of the reaction processes. Namely, many of those results can be understood by taking into consideration the formation of multiple CT states or IP's with different structures in the photoinduced CS(charge separation) depending on the solvation of the ET (electron transfer) state, strength D-A interactions, energy gaps for CS,etc. and that the distribution of those states changes in the course of reaction. Similar mechanism may be possible also in the photoinduced CT of some directly linked D-A, with respect to the change of electronic structure by twisting and solvation.

The multiple states mechanism of photoinduced ET(electron transfer) phenomena is of crucial importance for the interpretation of the fact that no inverted region is observed in the photoinduced CS reaction while the CR(charge recombination) of geminate IP's shows rather typical bell-shaped energy gap dependence and also the fact that both weakly fluorscent exciplex and nonfluorescent loose IP's of, for example, pyrene-DMA(N,N-dimethylaniline) system exist even in acetonitrile solutions. Moreover, we have demonstrated recently by means of detailed ps-fs laser photolysis studies that this distribution of multiple IP states depending on the energy gap for CS and strength of the D-A interactions severely affects the reaction mechanism of the benzophenone-amine hydrogen abstraction via IP state.

On the other hand, in view of the rather dominant effects of the multiple states mechanism in the photoinduced ET phenomena, we should avoid to use those systems discussed above for the experimental examinations of the most fundamental factors which are considered theoretically to be regulating the photoinduced ET reactions. We have examined in detail recently the energy gap, temperature, as well as solvet polarity dependences of CS and CR reactions by means of ps-fs laser studies on fixed distance D-spacer-A systems.

SPIN TRANSFER VERSUS CHARGE TRANSFER IN THE EXCITED STATES OF INORGANIC IONS

J.H. van der Waals

Huygens Laboratory, University of Leiden
P.O. Box 9504, 2300 RA Leiden
The Netherlands

In the discussion of the spectroscopic properties of complex molecules and ions by Grabowski and many others, the idea of "charge transfer" has been a very fruitful concept. In simple molecular orbital theory it is directly related to the spatial extent of the orbital form which the electron is excited and the orbital to which it goes.

A classic example of such a charge transfer transition in the domain of inorganic chemistry is provided by the long-wavelength absorption band of the $3d^0$ transition metal oxo-ions, $VO_4^{\equiv}$, $CrO_4^{=}$, MnO_4^{-}. According to molecular orbital theory [1] this band arises from a transition in which an electron is excited from a pure ligand orbital to an orbital that has a high electron density on the central metal. Ab-initio calculations have revealed that the real situation is far more complex. Owing to relaxation of the electrons in closed-shell orbitals, hardly any charge transfer is to be expected, but nevertheless, the transition should involve the transfer of an entire electron spin [2].

In Leiden we are involved in the investigation of the $VO_4^{\equiv}$ and $CrO_4^{=}$ ions, experimentally by electron paramagnetic resonance and optical methods, and theoretically by ab-initio quantum-chemical calculations. Detailed data obtained by Van Tol on the magnetic properties of the metastable triplet states of $VO_4^{\equiv}$ and its modes of luminescent decay will be compared with the theoretical analysis by Chaudron, Van Duijneveldt and Van Hemert of the electronic structure of the singlet and triplet lower excited states of $CrO_4^{=}$. The results confirm that in this type of system the first optical transition involves an electron spin transfer without charge transfer. In addition, there is a remarkable Jahn-Teller effect which will be discussed.

[1] C.J. Ballhausen and A.D. Liehr, J. Molec. Spectrosc. 2 (1958), 342; 4 (1960), 190.
[2] H. Johansen, Chem. Phys. Lett. 156 (1989), 592.

ELECTRON SCAVENGING PROCESSES IN MICELLAR SOLUTIONS

E. Szajdzińska-Piętek, J.L. Gebicki and J. Kroh

Institute of Applied Radiation Chemistry
Technical University of Łódź, POLAND

Micellar solution are regarded as primitive models of cell membranes. Information obtained for these systems may be applicable for elucidation of the processes occuring in more complex biological media. In particular, electron transfer between aqueous and lipoidic phase may be studied by means of pulse radiolysis.

In this contribution a survey of pulse radiolytic investigations on the mechanism of reactions of hydrated electrons (e_{aq}^-) with hydrophobic solutes bound to ionic micelles carried out in the IARC is given.

Various scavengers of different structure and hydrophobic properties were studied in anionic micellar solutions of sodium or lithium dodecylsulfates as well as in cationic micellar solutions of hexadecyltrimethylammonium bromide or dodecyltrimethylammonium bromide and chloride.

The following points are shortly discussed:

(-) Dependence of the rate of e_{aq}^- reaction with a scavenger bound to anionic micelles on its distribution between aqueous and lipoidic phases as well as on its location within aggregates;

(-) Effect of the addition of tetraalkylammonium salts on e_{aq}^- decay in anionic micellar solutions;

(-) Multiexponential e_{aq}^- decay in cationic micellar solutions;

(-) Dependence of e_{aq}^- decay on the scavenger effectiveness in cationic micellar solutions, observed in spite of a strong positive electrostatic effect of micelles;

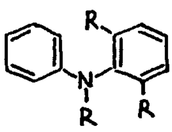
(-) Influence of the nature of cationic surfactant on e_{aq}^- decay.

The presented data demonstrate that pulse radiolysis remains a powerful tool for investigation of micellar systems as it can deliver not only kinetic parameters of fast reactions but also enables to infer about solubilization locus and distribution of a scavenger in micellar systems.

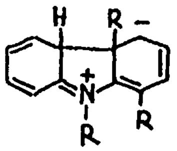
COMPETITION BETWEEN TUNNEL- AND VISCOSITY-EFFECTS ON A BIMOLECULAR HYDROGEN-TRANSFER REACTION

U. Kensy and K. H. Grellmann
Max-Planck-Institut für Biophysikalische Chemie
Göttingen. Germany

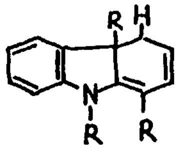
In the triplet state, the diphenylamine derivative **A** converts into the stable dihydrocarbazole **D** via the zwitterionic intermediate **Z**.



A



Z



D

$R = CH_3$

The observation of tunnel effects on the *intra*molecular, singlet ground-state

$$Z \rightarrow D \qquad (1)$$

reaction has been reported ten years ago [1]. If the concentration of the transient Z is high enough, a second-order process

$$2\ Z \rightleftharpoons (ZZ) \rightarrow 2D \qquad (2)$$

competes effectively with the first-order reaction (1). Both reaction branches, (1) and (2), yield *the same* final photoproduct **D**. Reaction (2) is the first example of an *inter*molecular hydrogen-transfer process where it could be shown that tunnel effects determine the reaction rate to a large extent over a wide temperature range. When, at low enough temperatures, the solvent viscosity becomes very high, reaction (2) becomes diffusion-controlled and tunnel effects are no longer rate determining.

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1) K.H. Grellmann, U. Schmitt, H. Weller, Chem. Phys. Letters **1982**, *88*, 40.

PICOSECOND FLUORESCENCE STUDIES OF THE EXCITED-STATE PROTON TRANSFER IN SUBSTITUTED 3-HYDROXYCHROMONES IN SUPERSONIC JET AND IN NONPOLAR SOLUTION

M. Itoh, T. Ohkubo, A. Ito, R. Takasu
H. Mukaihata, and K. Tokumura

Faculty of Pharm. Sciences, Kanazawa University,
Takara-machi, Kanazawa 920, Japan

In spite of numerous investigations on the excited state proton transfer (ESPT) and relaxation in the intramolecular hydrogen bonding systems, some of these studies of 3-hydroxyflavone are in conflict with each other. The points at issue are energy barriers in the ESPT and in the ground state reverse proton transfer.

One of the main emphases is laid on the intramolecular ESPT in jet-cooled 3-hydroxychromone (3-HC), 3-hydroxyflavone (3-HF), and 2-(2-naphthyl)-3-hydroxychromone (2-NHC), and in their water and/or solvent clusters. In the supersonic jet of these compounds, appreciably resolved vibrational structures starting from their respective strong origin bands in the fluorescence excitation spectra suggest a small potential minimum in the excited state of the normal form. The upper limit of rate constant of the tautomer formation was estimated to be $1.77 \times 10^{12} s^{-1}$ for 3-HC, $6.5 \times 10^{11} s^{-1}$, and $1.54 \times 10^{11} s^{-1}$ for 2-NHC from simulation of line widths of the respective origin bands. The order of rate constants of the tautomer formation in the supersonic jet is well consistent with that of the ESPT of these compounds in 3-methylpentane (MP) solution. The fluorescence excitation and dispersed fluorescence spectra demonstrate no ESPT in 1:1 and 1:n ($n \leqq 3$) water and/or alcohol clusters of 3-HF and 2-NHC formed in supersonic expansion.

Another of the emphasis is laid on the slow reverse proton transfer in the ground state in MP solutions of 2-NHC and 2-(1-naphthyl)-3-hydroxychromone (1-NHC). Two-step laser induced fluorescence (TS-LIF) demonstrates that short and long lived tautomers were involved in the relaxation of the ESPT in both compounds. Picosecond fluorescence indicates a very fast (<10 ps) and relatively slow rise of the tautomer fluorescence. Double exponential decay of the tautomer fluorescence was observed in 1-NHC solution, while only single exponential decay was detected in 2-NHC solution. Picosecond fluorescence and TS-LIF were consistent with each other taking account of the envolvement of two types of tautomers both in the ground and excited states. The twisted and less-twisted naphthyl torsional conformers at 2-position of γ-pyrone ring are responsible to two types of tautomers in NHC. No significant contribution of the tautomer triplet state to TS-LIF was confirmed in these compounds.

ELECTRON DELOCALIZATION IN SATURATED FRAMEWORKS

Josef Michl and Harald S. Plitt
Department of Chemistry and Biochemistry
University of Colorado
Boulder, CO 80309-0215

Charge transfer, charge separation, and charge annihilation processes frequently proceed across a formally saturated framework, and their understanding then requires an analysis of electron delocalization in sigma-bonded skeletons. Electronic spectroscopy of such structures offers a sensitive tool for probing the mechanisms of electron delocalization and their dependence on the topology and the three-dimensional geometry of sigma bond arrays.

We have performed a series of UV absorption and emission measurements on saturated oligosilanes, whose spectroscopic properties are dominated by excitations from Si—Si bonding to Si—Si antibonding orbitals. Spectra of individual conformers in matrix isolation reveal striking stereoelectronic effects, which cannot be accounted for by nearest-neighbor interactions (Sandorfy C or McConnell models), but can be understood in terms of ab initio and semiempirical calculations or by using an extended simple model that considers interactions between all hybrid orbitals located on adjacent atoms. This model is closely related to those developed earlier by others for the interpretation of electron transfer through saturated hydrocarbons. It predicts that the mobility of a positive charge on a polysilane chain is severely impeded by one or two adjacent gauche turns, and that such turns also serve as termini of localized chromophoric segments in the chain.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research, the U.S. National Science Foundation, and a Deutsche Forschungsgemeinschaft Fellowship to H.S.P.

Intramolecular Charge Transfer Emission from Excited Phenyldisilanes without TICT

Haruo Shizuka
Gunma University

Dual (local and CT) emission of aromatic disilanes has been observed and it has been found that the intramolecular CT fluorescence has a broad and structureless band with a large Stokes-shift. The CT process in the excited state of phenyldisilanes occurs even in rigid glass at 77K. This finding shows that twisting or internal rotation in the excited state is not necessary for the CT process.

The fluorescence polarization experiments show that the CT band is polarized almost parallel to the $^1L_a \leftarrow {}^1A$ band, i.e. the in-plane long-axis polarization (not out-of-plane). On the basis of fluorescence polarization, in addition to the MCD results, the CT emission of phenyldisilane is ascribed to that from $^1(2p\pi,3d\pi)$CT state produced by the 2pπ* orbital (the phenyl ring) to the vacant 3dπ orbital (the Si-Si bond) intramolecular CT transition.

The intramolecular CT in the excited state of phenyldisilane occurs very rapidly (<10ps) both in MP at 293K and in EPA glass at 77K. At room temperature, a long-lived 425nm transient (which is assigned to the rearranged intermediate silene) is produced with a rise time of 30ps, showing that the transient formation proceeds via the intramolecular CT state. At 77K in rigid glass, the intersystem crossing from singlet CT to $^3(\pi,\pi*)$ ^3L_a takes place effectively.

SOLVENT CAGE SPECTROSCOPY. VISCOSITY CONTROL OF DISSOCIATIVE, TORSIONAL, AND DIELECTRIC RELAXATION POTENTIALS

M. Kasha and A. Sytnik, Institute of Molecular Biophysics and Department
of Chemistry, Florida State University, Tallahassee, Florida 32306-3015.

The Born-Oppenheimer-based theory of the solvent cage which we have developed has been applied thematically to a variety of molecular potentials. Included among these (with the consequence of solvent cage perturbation indicated in parenthesis) are the (1) Morse oscillator potential (vibrational overtones become more harmonic), (2) the dissociative repulsive potential (photodissociation is blocked), (3) the torsional potential (change of Franck-Condon envelope in absorption, but not in emission; intense fluorescence from the trapped torsiomer, instead of isomerization), (4) the TICT potential (twisted intramolecular charge-transfer is blocked), (5) the Jahn-Teller potential (*it is conjectured that* the symmetry-breaking distortion could be blocked), (6) the hydrogen-bonding potential for n,π^* excited states (fluorescence from a forced H-bonded-complex is observed). It is indicated in the summary just given that the solvent cage perturbations on intramolecular motions of a solute can give rise to dramatic changes in observed spectroscopic phenomena.

Applications of the model are given to H-bonded complexes of aza-aromatics illustrating control of photo-dissociation by the solvent cage, Franck-Condon contour perturbations by solvent cages, and dielectric cage effects on the TICT phenomena.

SN1 Ionization in Solution: an Electron Transfer Perspective

James T. Hynes
Department of Chemistry and Biochemistry
University of Colorado
Boulder, CO 80309-215 USA

In this talk, we will discuss our recent theoretical work on the topic of the title, focussing on the tertiary butyl halides (t-BuX, where X = Cl, Br, and I) in solvents over a wide polarity range. An interpretation of the solvent polarity trends of the reaction activation free energy will be given which contradicts the conventional Hughes-Ingold picture. The issue of the appearance of an activated electron transfer barrier in the solvent coordinate will be addressed for t-BuI.

This work was performed in collaboration with H.J.Kim and J.R. Mathis, and was supported by NSF and NIH.

Solvent Effects on Excited State Relaxation Phenomena

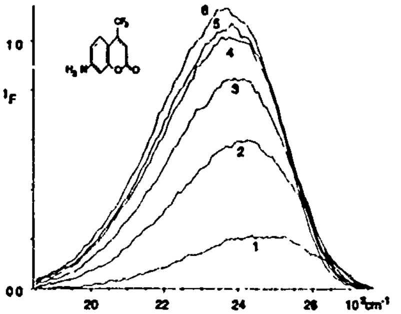
Gottfried Köhler and Karl Rechthaler
Institut für theoretische Chemie und Strahlenchemie, University of Vienna, Währingerstr. 38, A-1090 Vienna, Austria.

Various studies on solvent effects on excited state relaxation phenomena by steady state and time resolved fluorescence spectroscopy are comparatively reviewed. The results obtained for hydroxy- and amino-aryl compounds (e.g. phenols, anilines and other amines, naphthols, hydroxy- and aminocoumarines etc.) are discussed in the frame of:

1) the continuum model for dielectric solute-solvent interactions,
2) preferential solvation effects,
3) statistical distribution of various solvates,
4) ground state solute-solvent complexes,
5) excited state complex formation (exciplexes).

Representative results will be presented for these various types of solute-solvent interactions.

Fig. 1: Fluorescence of coumarin 151 (4.10^{-6} M) in binary hexane-butylether solvent mixtures (1: pure n-hexane, 2-6: plus 0.8, 1.6, 2.4, 3.2 and 4.0 vol-%butyl ether).



Two examples will be given below: 1) 7-amino-4-trifluoromethylcoumarin (coumarin 151) shows exciplex formation by hydrogen bonding in hexane solution after addition of small concentrations of ether (see figure 1). Strongly increased fluorescence efficiency results from exciplex formation.

2) Fluorescence of the respective 7-dimethylamino-4-trifluoromethylcoumarin (coumarin 152) is strongly quenched in alcoholic solution. In a series of pure solvents of increasing polarity quenching sets in at a defined value for the Onsager polarity function and is largely determined by the bulk dielectric properties.

Exciplex Mechanism of the Fluorescence Quenching in Polar Media

Michael G. Kuzmin
Moscow University
Moscow 117234 Russia

The formation of non-emitting exciplexes is proposed as a cause of the deviations of the experimental data from the classical model of excited state electron transfer in polar solvents which supposes the formation of radical-ion pairs as transients. Formation of exciplexes is well-known for non-polar media, but exciplex emission was not observed in polar solvents. Absence of exciplex emission in polar solvents is assumed to be caused by their dissociation to radical-ions. Experimentally measured activation energies of pyrene fluorescence quenching by weak electron acceptors were found to be much less than activation energies, calculated from the experimental values of the quenching rate constants, and in some cases even negative, which is typical for excited state complex formation. Lifetime quenching exhibits negative deviations from a linear law, also typical for complex formation in the excited state. These data give evidence for the formation of long lived (up to 30 ns) exciplexes, which are in equilibrium with excited pyrene molecules. Electronic structure of the exciplex may be close to contact radical-ion pair only at sufficiently negative Gibbs energy of electron transfer, when the rate of quenching is mainly limited by diffusion, but for positive or close to zero Gibbs energy of electron transfer the structure of the exciplex should be much less polar (weak charge transfer complexes). Such exciplexes can decay rather by internal conversion and intersystem crossing processes than by complete electron transfer, which needs relatively high activation energy. The proposed model explains the difference between theoretical and experimental dependencies of quenching rate constants vs. Gibbs energy of electron transfer and other experimental features known for fluorescence quenching by electron donors and acceptors. According to this model the apparent quenching rate constant is determined by two main factors - by the lifetime of the exciplex and by the equilibrium constant for its formation. Experimentally observed dependence of the apparent quenching rate constants on Gibbs energy of electron transfer is caused rather by the dependence of the exciplex formation enthalpy on Gibbs energy of electron transfer, than by the dependence of electron transfer activation energy on Gibbs energy of electron transfer, considered by the other theoretical models. The nature of the excited state electron transfer photoreactions and their relationships according to this model can be quite different from that of the ground state electron transfer reactions. Therefore, fluorescence quenching cannot be used with confidence for the verification of the theories of electron transfer processes and for determination of redox-potentials of quenchers.

References

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PHOTOASSOCIATION IN THE LOWEST TRIPLET STATE OF AROMATIC MOLECULES: TRIPLET EXCIMERS AND EXCIPLEXES

Edward C. Lim
Department of Chemistry, The University of Akron, Akron, OH 44325-3601 USA

Intermolecular and intramolecular photoassociations, leading to the formation of triplet excimers and exciplexes will be discussed for a number of aromatic systems.

Photo-induced Electron Transfer in Polychromophoric Systems

M. Van der Auweraer, G. Verbeek, A. Vaes, N. Helsen, P. Van Haver, F.C. De Schryver, C. Geelen
Laboratory for Molecular Dynamics and Spectroscopy
K.U.Leuven Celestijnenlaan 200-F, B-3001 Heverlee, Belgium.

D. Terrell, S. De Meutter
Agfa-Gevaert N.V. Septestraat 27, B-2650 Mortsel, Belgium.

Combining stationary and time resolved fluorescence spectroscopy with laser-induced opto-acoustic spectroscopy allowed to investigate the influence of molecular structure and solvent polarity on the rate of the radiative and radiationless decay processes of exciplexes of -phenyl-α-N,N-dimethylaminoalkanes. By making intersystem crossing to the locally excited state less exergonic increasing the solvent polarity decreased the rate constant for intersystem crossing. The apparent decrease of the fluorescence rate constant in highly polar solvents was attributed to the direct formation of a solvent separated ion-pair. The formation of solvent separated ion-pairs can also explain why, contradicting the predictions of Marcus theory, the rate constant for internal conversion decreases sometimes in highly polar solvents.

The solvent dependence of the fluorescence spectra of (dialkylamino) and (diarylamino) substituted triphenylbenzene derivatives indicates that in those completely symmetric molecules the emission occurs from a highly polar excited state. The exponential fluorescence decays, obtained with time correlated single photon timing, suggest that equilibration between the different excited species occurs within the time resolution of the experimental set-up. The comparison of compounds with meta- and para-substitution and the comparison of dialkylamino and diarylamino derivatives suggest that either a conjugated intramolecular charge transfer state or a TICT, in which the amino moiety rotates out of the plane of the triphenylbenzene moiety, are formed.

Femtosecond Electron Transfer between Dyes and Electron-Donating Solvents.

K. Yoshihara, A. Yartsev, Y. Nagasawa, H. Kandori, A. Douhal, and K. Kemnitz[1]

Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

[1]Government Industrial Research Institute, Midorigaoka Ikeda, Osaka 563, Japan

Abstract. An ultrafast electron transfer (ET) was found in diffusionless weakly polar contact systems of various electron donors and acceptors, namely, xanthene dyes in aniline. ET was measured as nonexponential when it is determined by mutual displacement of the reactants and by the solvent relaxation. ET process becomes single exponential in a case when ET is determined by electronic interaction between donor and acceptor and nuclear motion in reacting systems.

ULTRAFAST EXPERIMENTS ON THE ROLE OF SOLVENT MOTION IN ELECTRON TRANSFER

Paul F. Barbara
Department of Chemistry
Kolthoff and Smith Halls
207 Pleasant Street S.E.
Minneapolis
Minnesota 55455-0431, USA

The role of vibrational modes in ultrafast photoinduced intramolecular electron transfer reactions is explored. Femtosecond resolved experiments on two chemical classes are described, namely, metal-metal intervalence electron transfer in mixed valence compounds and intramolecular charge recombination/separation in the organic donor/acceptor compound class, and betaines.

The measured dynamics can generally be characterized by two time scales: i) A fast transient bleach and ii) a slower bleach or increased absorption with a decay time that depends on the solvent. The dominant fast response is ascribed to electron transfer. The electron transfer dynamics have been analyzed to reveal the complex interactions of intramolecular and intermolecular modes in electron transfer reactions. Static resonance Raman and absorption spectra of the electron transfer transition provide frequencies and displacements of the vibrational modes coupled to the electron transfer reaction. These molecular parameters have been used to evaluate multimode expressions for the reaction rate with no adjustable parameters. In general, we find good agreement between the calculated and measured electron transfer rates. This analysis elucidates the important pathways for electron transfer and allows a quantitative evaluation of the theoretical treatments to be performed.

The behavior of the slower component varies as a function of the probe wavelength and the peak of the absorption spectrum. The slower component is tentatively attributed to local heating or ground state solvation, i.e., to nuclear motions in the solute and solvent. The recovery of the increased absorption and the additional bleach then correspond to local cooling of the molecule's environment. This interpretation is consistent with the measured temperature and solvent dependence of the static absorption spectrum.

Temperature and Solvent Dependent Charge Transfer in Self-Organized Porphyrin-Quinone Compounds

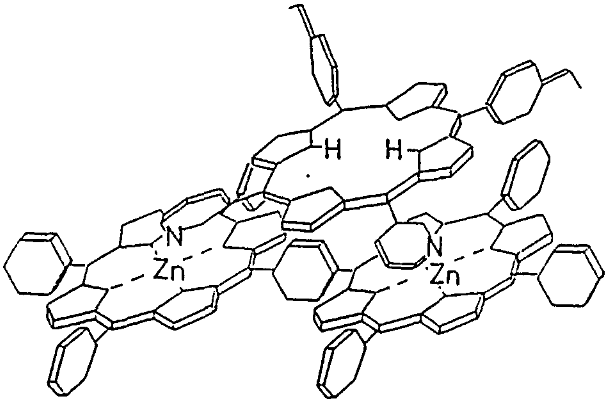
U. Rempel, B. von Maltzan and C. von Borczyskowski

Fachbereich Physik, Freie Universität Berlin, FRG

During the past decade much effort has been directed towards the synthesis of model compounds to mimic dynamic processes in photosynthetic reaction centers. In most cases donor and acceptor molecules have been covalently linked. In order to extend the seize and spatial arrangement of such supermolecules we have chosen an alternative way to form more complex donor-acceptor arrays via self-organization.

Two routes for this process have been chosen. In the first case aggregates are formed via oppositely charged porphyrins and viologens which form together with covalently attached anthraquinone an electron transfer triade. In the second case we make use of the ability of metalloporphyrins (such as zinc) to form complexes with suitable ligands (such as nitrogen and oxygen containing molecules). Also the association with TICT state molecules has been observed. For a twofold complexation extended arrays of more than 10 molecules can be formed. The stability of such complexes depends on solvent polarity and temperature.

In the case of the supramolecular structure shown in Fig. 1 pyridine-substituted free base porphyrin (2HP) has been attached to a zinc porphyrin (ZnP) dimer by tailoring the distance of nitrogen atoms as compared to the zinc interatomic distance. From picosecond time resolved fluorescence spectroscopy we have evidence that fast energy transfer from ZnP to 2HP is followed by charge transfer from 2HP to quinone via a superexchange mechanism. The results from time resolved optical spectroscopy demonstrate the multifunctional properties of such supramolecular structure.



Role of Biradical– and Exciplex–Minima in Photochemical and Photophysical Processes

Vlasta Bonacic–Koutecky
Freie Universität Berlin, Institut für Physikalische und Theoretische Chemie
Takustr. 3, D–1000 Berlin 33, Germany

A knowledge of the geometries at which excited molecules return to the electronic ground state (S_0) is essential for the understanding of the structures of photoproducts. Particularly good candidates are goemetries corresponding to local minima on the S_1 (lowest excited singlet) and T_1 (lowest triplet) surfaces, as well as S_0–S_1 conical intersections (funnels). Since many of these are biradicaloid and exciplex geometries, their properties will be examined first using simple models. It will be shown that these results are supported by ab initio large–scale configuration interaction (CI) calculations. The likely consequences of these results for the detailed description of the mechanisms of cis–trans isomerization, the formation of twisted internal charge–transfer (TICT) states, as well as for the understanding of the regio–specificity of singlet photocycloaddition will be shown.

Multiconfigurational Second Order Perturbation Theory Applied to the Calculation of Excited States

Björn O. Roos
Department of Theoretical Chemistry
Chemical Centre, University of Lund
P.O.B. 124, S-221 00 Lund, Sweden

Abstract

A multiconfigurational second order perturbation theory has been developed and is applied to the calculation of excited states in molecular systems with surprisingly high accuracy in computed excitation energies and transition properties. The approach is a two-step procedure, where the first step consists of a Complete Active Space (CAS) SCF calculation, which determines the molecular orbitals and the reference function for the second order perturbation calculation. All important configurational mixing is included in this step of the calculation, while remaining dynamical correlation effects are treated by perturbation theory.

The approach has been applied to the calculation of singlet and triplet excited states of a large variety of molecules, both of valence and Rydberg type. Calculated excitation energies normally agrees with experimental vertical energies to 0.3 eV (2400 cm^{-1}) or better. A number of new assignments, especially of Rydberg excited states have been proposed. Among the molecules to be discussed in the lecture are: polyenes (ethene to octatetraene), benzene, the azabenzenes, furan, pyrrole, and cyclopentadiene.

EXAMPLES TO THE "SDT-EQUATION"

Edwin Haselbach
Physical Chemistry Institute
University of Fribourg/CH

Some time ago a simple equation was suggested (henceforth named "SDT-equation) which relates the energies of excited singlet (S) and triplet (T) states of alternant systems (M) to those of the excited doublet (D) states of the corresponding radical ions (M^+ or M^-), provided a) the associated electron promotions involve the same MO's which are futhermore "paired ones" (special case: HOMO – > LUMO promotions); b) the "frozen orbital approximation" holds; c) the "ZDO-approximation" holds.

Neglecting interaction between excited configurations (CI) the SDT-equation is

$$D = (S + T)*0.5 \qquad \text{(algebraic mean).}$$

Allowing additionally for (2*2)-CI between S_0 and the doubly excited configurations S_d results in a depression of S_0. After rescaling the SDT-equation takes now the form

$$D = (S * T)^{0.5} \qquad \text{(geometric mean).}$$

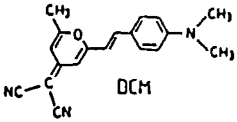
The D-states of M^+/M^- are of so called "non-Koopmans nature" which are not accessible via photoelectron spectroscopy of the parent M. Progress in matrix isolation techniques has brought many of these states to light via UV/VIS-spectroscopy of M^+/M^-. The resulting energies can now be applied to test SDT-equation.

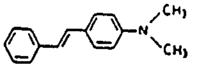
The Photophysics of Stilbenoid dye systems. A Comparison of Experiment and Theory

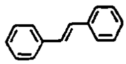
Wolfgang Rettig[a], Bernd Strehmel[a], Wilfried Majenz[a], Ralf Herter[a] and René Lapouyade[b]

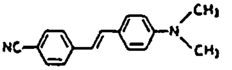
I.N.Stranski-Institute, Techn.Univ.Berlin,
Strasse des 17. Juni 112, D-1000 Berlin 12, FRG[a]
Photophysique et Photochimie Moleculaire, URA du CNRS N° 348,
Univ. de Bordeaux I, 351, cours de la Libération,
F-33405 Talence, France[b],

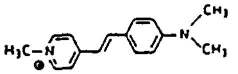
Recent theoretical models including both "TICT" states and "sudden polarization" /1/ allow to predict the nature of the excited states of compounds with flexible single- and/or double bonds. Application to donor-acceptor-substituted stilbene dye systems leads to the expectation, that the so-called "phantom-singlet" state (twisted double bond) changes its dipolar nature from highly polar to weakly polar along the substituent polarity scale. These predictions are confirmed by stationary and time-resolved fluorescence measurements on the series of dye systems I-V, and by semiempirical SCF-CI calculations.





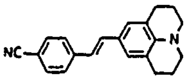




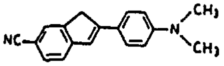


I II III IV V

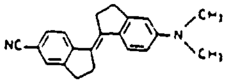
Comparison to the behaviour of partially rigidized stilbenes VI-VIII allows to pinpoint the intramolecular rotation around the single bond connecting the phenyl rings /2/ as a further important photochemical/photophysical relaxation channel.



VI



VII



VIII

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This work has been supported by BMFT (project 05414 FAB)

SYNTHESIS OF NEW N-PHENYLAZA-15-CROWNS-5 FOR SELECTIVE CATIONS COMPLEXATION, IN THE GROUND STATE, AND DISSOCIATION OF THE CROWNED CATIONS FOLLOWING OPTICAL EXCITATION.

J.F. LETARD[a], R. LAPOUYADE[a] and W. RETTIG[b].

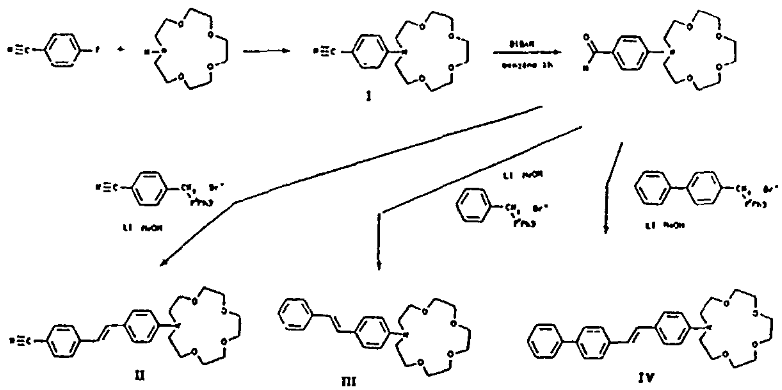
Photophysique et Photochimie Moléculaire, URA 348, Université de BORDEAUX I, 351 cours de la Libération, 33405 Talence (FRANCE)[a]. I.N. Stranski-Institute, Tech. Univ. BERLIN Strasse des 17 Juni, D-1000 Berlin 12 (FRG)[b].

The recognized high sensibility of the absorption and fluorescence spectroscopies led to the design of Chromo- and Fluoroionophores for the study of ions binding by multidentate macrocyclic compounds(1). When one of the heteroatoms of the ionophore is part of the mesomeric system of the chomophore, cations complexation influences the electronic states depending on the size and direction of the dipole moments μ_g and μ_e(1-3).

We report the photophysical properties of the four probes (I-VI) classified according to decreasing capacity of charge localisation on the nitrogen atom, near the complexed cation, in the excited state.

SYNTHESIS:

The 4-N-(monoaza-1-tetraoxa-4,7,10,13-cyclopentadecane)-benzonitrile, **I**, was prepared by nucleophilic aromatic substitution of 4-fluorobenzonitrile (4). Reaction first with DIBAH and then with the relevant phosphonium salts led to **II**, **III** and **IV**.



PHOTOPHYSICAL STUDY:

The cations binding properties (log Ks) of I-IV were determined from spectrophotometric titration in solvents of various polarity (CH_2Cl_2, BuCN, CH_3CN) and cations ejection in the excited state was demonstrated from the dual fluorescence of the IV.$Ca(ClO_4)_2$ complex.

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PICOSECOND STUDIES OF CHARGE TRANSFER STATES IN "PUSH-PULL" LINEAR DIPHENYL-POLYENES

By Claude RULLIERE

Centre de Physique Moléculaire Optique et Hertzienne
Unité Associée au CNRS N° 283 Université de Bordeaux I
351 cours de la Libération 33405 TALENCE Cedex (France)

A series of "push-pull" linear diphenyl-polyenes (trans-stilbene, diphenyl-butadiene and diphenyl-hexatriene derivatives) with different donor and acceptor groups at the 4,4' positions have been studied using time-resolved emission and absorption spectroscopy technics.

Until three emission bands may be observed in these different derivatives depending on solvent polarity, temperature, concentration and excitation conditions.

In non-polar solvents a single emission band is observed corresponding to the normal "locally-excited" (L.E.) state.

In polar solvents, at any concentration, but with weak excitation, a second emission band may appear. Depending on the derivatives and experimental conditions, a clear "successor-precursor" relation-ship occurs between the L.E. emission band and this second emission band which is attributed to a now "classical" TICT state according to the Grabowski model.

When the excitation intensity is increased, and only at high concentration, a third emission band, red-shifted in respect to the TICT emission band, may appear. Its presence depends on the studied derivatives. When , by bridging, the rotation of certain chemical bonds is prevented or hindered this third emission band does not appear. Moreover laser action may be obtained at wavelength corresponding to its emission spectra, as revealed by transient absorption and gain experiments.

On the basis of our different experimental results this third band may be attributed to a new species formed by the association of two electronically excited molecules, the stabilisation of which involving dipolar interaction due to large charge transfer character of the concerned electronic states and solvent polarity. This new species is called a "bicimer".

EXPERIMENTAL PROBES OF EXCITED STATE CHARACTER IN SUPERCRITICAL FLUIDS

Marye Anne Fox* and Ya-Ping Sun
Department of Chemistry and Biochemistry
University of Texas at Austin
Austin, TX 78712 USA

Supercitical fluids provide a unique medium for characterizing condensed phase solute-solute and solute-solvent interactions at a fundamental level. In the highly compressible region near the supercritical point, significant deviations from solvation as predicted dielectric continuum theory can be assigned as indicative of enhanced local solvent density associated with macroscopic clustering. Fluorescence spectroscopy has proven to be particularly useful in characterizing local density, local composition, and solute-solvent interactions. We describe in this paper how spectroscopic and kinetics studies in supercritical fluids and mixtures can provide valuable information on weak, local intermolecular associations and how an appropriate modeling for this clustering can provide a unique corollary description of the excited state polarity of included probe molecules.

Solute-solute and solute-solvent clustering of N,N-dimethylaminobenzonitrile and ethyl N,N-dimethylaminobenzoate in supercritical trifluoromethane and carbon dioxide can be described by quantitatively evaluating the dependence of the relative contributions of the locally excited state and the twisted intramolecular charge transfer (TICT) emissions on supercritical fluid composition and pressure. The density dependence of the local solvation of mixtures of these fluids is similar to that observed in the pure components. The polar CHF_3 clusters perferentially with the solute, with the size of the solute-solvent cluster depending on the total pressure. Both microscopic and macroscopic solvation in these mixtures can be rationalized with an Onsager reaction field model.

With this model of local solvation, it is also possible to employ supercritical fluid mixtures as a chemically invariant probe for excited state character. Picosecond transient absorption spectra and decay kinetics for the twisted excited state of tetraphenylethylene in supercritical fluid - cosolvent mixtures reveal microscopic solvation of a highly polar state. By monitoring the fluorescence of the TICT state of ethyl N,N-dimethylaminobenzoate, it can be shown that the decay rate constant for the tetraphenylethylene $^1p^*$ state correlates well with solvent-induced changes in the excited state - ground state energy gap, as is predicted by radiationless relaxation theories.

CONFORMATIONAL ASPECTS OF INTRAMOLECULAR ELECTRON-TRANSFER AND 'EXCIPLEX' FLUORESCENCE

J.W. Verhoeven, T. Scherer and R. Willemse

Laboratory of Organic Chemistry, The University of Amsterdam,
Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands

Abstract:

Recent investigations of both natural and artificial systems have revealed the possibility of rapid (photoinduced) electron-transfer over distances largely exceeding the sum of the Van der Waals radii of the Donor and Acceptor sites involved. Rigidly bridged systems of the type D-bridge-A , in which the bridge is a saturated hydrocarbon unit, have played a crucial role in these studies since such systems allow unequivocal fixation of the D/A distance and relative orientation.

By variation of the degree of flexibility of the bridge it has now been found that under certain conditions also more flexibly bridged systems, which can in principle adopt 'folded' conformations allowing for direct D/A contact, in fact undergo photoinduced intramolecular electron transfer in 'extended' conformations devoid of such contact. This raises the interesting question from which conformation(s) the 'exciplex' emission originates, that is often observed for such systems. As will be shown the answer to this question depends crucially upon factors such as solvent, temperature and the nature of D and A.

Photon-Induced Intramolecular Charge Separation Studied by Time-Resolved Microwave Conductivity

John M. Warman
IRI, Delft University of Technology, Mekelweg 15, 2629 JB, DELFT,
The Netherlands

The time-resolved microwave conductivity (TRMC) technique for monitoring transient changes in the dielectric loss of solutions resulting from the formation of dipolar excited states on flash photolysis will be briefly described.

The use of the technique will be illustrated by results on donor-spacer-acceptor compounds for which the spacer has a flexible, semi-rigid or rigid sigma-bonded structure, and by results on charge separation in the excited state of molecules which are symmetrical in their ground state.

Photoinduced Charge Transfer as Revealed by Ground and Excited State Dipole Moments

Wolfram Baumann
Institute of Physical Chemistry, University of Mainz, Germany

There are not many experimental methods available to study photoinduced charge transfer directly which means that the electric dipole moment before and after the absorption of a photon has to be measured. Usually, the solvent polarity induced shift of the absorption or fluorescence band is observed quantitatively from which excited state electric dipole moments can be derived. With a non-rigid compound the geometric and electronic structure may depend on the solvent dielectric constant ε and therefore the resultant value for an excited state dipole moment can only be a poorly defined average value.

This drawback is avoided by electro optical absorption measurements (EOAM) [1] and electro optical emission measurements (EOEM) [2] with which the effect of an external electric field on the absorption or fluorescence intensity of solute molecules is studied. Careful evaluation of the effects measured in a single solvent yield excited state dipole moments $\mu_e(S)$ of the solute in this solvent S.

For some compounds which fluoresce from a twisted intramolecular charge transfer (TICT) state $\mu_e(S)$ has been observed to be strongly solvent dependent, e.g.[3] what would be in agreement with a solvent induced change of the electronic (and geometrical) structure. On the other hand it has to be taken into account that the internal electric field in solvents gives rise to induced moments - the observed effective electric dipole moment therefore is increased. As a result, it is impossible to decide from such experiments on non-rigid molecules whether a strong solvent dependence of a measured excited state dipole moment is due to solvent induced changes of the electronic structure, or more simply due to polarizability effects from the solvent's internal electric field.

In order to elucidate this situation better, a series of compounds has been investigated here which contains pretty rigid compounds as well as related less rigid ones. As an example, the effective dipole moment of the fluorescent state of some coumarins is shown in table 1, together with results from [3] for the sterically hindered compound 2,N,N-trimethylcyanoaniline (TriMCA).

Solvent	ε	C152a	C153	C47	C102	TriMCA
cyclohexane	2.02	46.6	47.4	39.1	39.9	38.8
Amylether	2.77	48.8	50.4	40.9	43.6	46.8
iso-propylether	3.88	52.7	53.4	44.4	46.7	51.8
fluorobenzene	5.42	48.1	48.8	42.2	42.2	50.2
dioxane	6*	51.5	51.5	44.1	42.5	50.5
benzotrifluoride	9.04	47.8	48.5	42.2	43.6	50.1

Table 1 Dipole moment of the fluorescent state of some coumarins and of TriMCA, given in units of 10^{-30}Cm. * microscopic dielectric constant

Apart of the different absolute values of the fluorescent excited state dipole moment, the solvent effect is much less with those states which are not TICT states. These and some more results are discussed.

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Photoinduced charge separation and broken symmetry in Franck-Condon excited $\pi\pi'^*$ states of $[4N]\pi$ cumulenes

R. Wortmann, R. Schmittgen, N. Detzer and W. Liptay

Institut für Physikalische Chemie, Universität Mainz, Germany

FC excited state dipole moments and polarizabilities of tetraphenylpentatetraene (TPPT) and tetrakis-(2-methoxyphenyl)-pentatetraene (OMTPPT) have been investigated by means of electrooptical absorption measurements (EOAM) in cyclohexane solution at 298K. The electronic structure of these symmetric $[4N]\pi$ cumulenes is characterized by two equivalent and mutually perpendicular π systems, π and π'. The lowest excited configuration $(e)^3(e)^1$ gives rise to two 'charge resonance' states of type $\pi\pi'^*$, 1^1B_1 and 1^1A_2, and two 'locally excited' states of type $\pi\pi^*$, 1^1B_2 and 2^1A_1. The optical absorption spectrum shows two well separated bands at $\lambda \sim 340$ nm (strong) and $\lambda \sim 420$ nm (weak) which can be ascribed to the $\pi\pi^* 1^1B_2 \leftarrow 1^1A_1$ transition (allowed) and the $\pi\pi'^* 1^1A_2 \leftarrow 1^1A_1$ transition (forbidden). The latter transition gains intensity by static or dynamic b_1 distortions of the cumulenes from ideal D_{2d} symmetry. The two $\pi\pi'^*$ states are near degenerate (Pseudo Jahn-Teller situation) and therefore susceptible to any internal or external perturbations due to different conformations of the terminal phenyl groups or different solvent environments at the two π subsystems. Such perturbations could lead to a directed electron transfer between the two inequivalent π subsystems upon excitation. Actually, the EOA experiment reveals excited state dipole moments of 5 and 7×10^{-30} Cm for TPPT and OMTPPT in their $\pi\pi'^*$ excited states. These dipole moments are parallel to the long molecular axis and to the transition dipole. The long axis polarizability increases by factors of about 2 compared to the ground state. Remarkably, a significant transition hyperpolarizability is observed in the case of TPPT.

The results of this work clearly demonstrate symmetry breaking and charge separation in $\pi\pi'^*$ excited states of $[4N]\pi$ cumulenes. In contrast to the conventional TICT situation these effects are observed for FC excited states and in an apolar solvent.

EXCITED-STATE DEACTIVATION OF p-DIMETHYLAMINOBENZONITRILE AND RELATED COMPOUNDS ADSORBED ON SOLID SURFACES

Dieter Oelkrug[1], Reiner Günther[1] and Wolfgang Rettig[2]
Institute of Physical and Theoretical Chemistry
Universities of Tubingen[1] and Berlin[2], FRG

The deactivation of excited molecules via twisted intramolecular charge treansfer states is controlled by the hights of internal torsional barriers and by the viscosity of the environment. It is not easy to separate these two effects, but we succeeded by fixing molecules of the type of p-dimethylaminobenzonitrile (DMABN) with the acceptor group on polar metal oxide surfaces so that the donor group is not in direct contact with matter and behaves like in vacuum.

Under these conditions we investigated the time-resolved dual fluorescence of the DMABN's as a function of temperature. It is not possible to freeze out the anomalous TICT-fluorescence at T = 77 K, and the TICT-state is formed even at this temperature without any significant rise time. The main deactivation channel at low temperatures leads from the untwisted Franck-Condon-state directly to the TICT-singlet and from here back to the untwisted triplet state that is strongly phosphorescent with a yield of ca. 0.7. All luminescence yields and most of the non-radiative deactivation constants are determined and compared to molecules with very similar electronic states but without the possibility of intramolecular twisting. Finally, the problem of DMABN aggregation in the adsorbed state and the resulting dual fluorescence of the aggregates will be discussed.

SOLVATION OF TICT STATES IN MIXTURES OF POLAR AND NON-POLAR SOLVENTS.

Nagwa GHONEIM and Paul SUPPAN

Institute of Physical Chemistry, University of Fribourg,
Switzerland

Abstract.

The formation of the twisted intramolecular charge transfer state (TICT state) of 4,4'-dimethylaminobenzonitrile (DMABN) depends on solvent relaxation around the giant dipole. In neat polar solvents, this corresponds to the solvent's rotational relaxation. In solvent mixtures, dielectric enrichment of the polar solvent in the solvation shell becomes the limiting kinetic step, in a time-scale of ns at low polar solvent concentrations. The translational and rotational solvent relaxations around DMABN in the course of TICT state formation raise interesting questions concerning the time-scale of the actual electron transfer step in other types of charge transfer reactions, in particular intermolecular processes which involve exciplex formation.

Intramolecular Charge Transfer in Aminobenzonitriles
Dynamics and Dipole Moments

K. A. Zachariasse
Max-Planck-Insitut für biophysikalische Chemie
-Spektroskopie und Photochemische Kinetik -
W-3400 Göttingen, Germany

The dual fluorescence coupled with intramolecular charge transfer (ICT) in N,N-dimethyl-4-aminobenzonitrile (DMABN) and related molecules has attracted unabated attention since its discovery in 1959. A perhaps surprisingly large variety of mechanisms has been presented in the literature to explain this phenomenon. Among these, the model of "Twisted Internal Charge Transfer" (TICT) pioneered by Grabowski [1], has played the most prominent role.

In the present contribution, the dynamics and thermodynamics for a number of aminobenzonitriles undergoing reversible ICT will be discussed [2]. These data are derived from time-correlated single-photon counting measurements in the picosecond time domain.

Dipole moments of the singlet and triplet excited states of a series of meta- and para-substituted aminobenzonitriles were determined by using the time-resolved microwave conductivity (TRMC) technique, combined with fluorescence decay time measurements [3]. It was found that the overall singlet excited state dipole moment of a series of N,N-dialkyl-4-aminobenzonitriles (methyl, ethyl, propyl, decyl), for which ICT occurs even in the nonpolar solvent cyclohexane, increases with the length of the N-alkyl groups as well as with solvent polarity.

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INTRAMOLECULAR ELECTRON TRANSFER
IN FLEXIBLE MOLECULES AND MOLECULAR IONS

Zbigniew R. Grabowski
Institute of Physical Chemistry, Polish Acad. Sci.
Kasprzaka 44, 01-224 Warsaw; Poland

Electron transfer (**ET**) processes occurring *in* or *after* the excitation in flexibly bonded donor (**D**) - acceptor (**A**) molecules will be discussed, along with the accompanying changes in molecular structure. Most deactivation processes, both radiative and radiationless, involve again the ET *(back ET)*. Special emphasis will be laid on the singly bonded **D-A** molecules, often forming the **TICT** excited states. The existing data will be interpreted in terms of orbitals and orbital overlap; of the resulting states and thermodynamics of processes; of the theory of electron transfer rates.

Many aspects of the original TICT model now appear inconsistent with new experimental results, specially those related to more complex molecules. The TICT hypothesis seems to describe adequately the longest known (and structurally the simplest) systems, like dialkylamino-derivatives of substituted benzene or of pyrimidine. It fails to describe well the behaviour of large aromatic systems, including some of the biaryl polar excited states.

Specially interesting is the photophysics of *molecular ions, e.g.*, $A\text{-}D^+$. Most often their fluorescence is strongly quenched just under conditions which suggest a TICT state formation. They differ, however, from the TICT states in the nature of the ET's, which are the *charge shifts* in these cases, as opposed to *charge separations* and *charge recombinations* in the TICT states.

An effort will be presented to systematize the structural and kinetic rules concerning the ET states of the flexible molecules, and of the much less understood molecular ions.

Energy and Electron Transfer in Bilayer Membranes

David Birch

University of Strathclyde, U.K

The mechanisms of quenching perylene fluorescence in small unilamellar vesicies of DPPC have been investigated for cobalt and nickel ions. In the case of cobalt, Förster type energy transfer is observed wheras, in the case of nickel, more complex behaviour is encountered.

POSTERS

FORMATION OF SINGLET AND TRIPLET EXCITED STATES ON CHARGE RECOMBINATION IN TRACKS OF HIGH-ENERGY ELECTRONS IN NONPOLAR LIQUIDS. A COMPUTER SIMULATION STUDY

WITOLD M. BARTCZAK and ANDRIES HUMMEL

(WMB) Institute of Applied Radiation Chemistry, Technical University, Łódź, Poland
(AH) Interfaculty Reactor Institute, Technical University, Delft, The Netherlands

The evolution in time of the recombination of ions in tracks and spurs produced by high-energy electrons was calculated by computer simulation of the diffusion and drift of the ions in each other's Coulomb field. The formation of singlet and triplet excited states on ion recombination was taken into account in the simulation codes.

The time dependent probability $f_S(t)$ of the singlet production and the overall yield of singlets was calculated for different groups of ion pairs and for the ionization tracks of high energy electrons, for wide range of the initial energy of ionizing particle. It was found that the initial geometry of the ionic cluster is of primary importance for the time evolution of the probability $f_S(t)$ and for the overall yield of the singlets. The time dependent probability has been Laplace-transformed to find the influence of the electron scavengers introduced into the system with different concentrations on the singlet contribution to the excited states formed by the ion recombination in the track.

The singlet yield, calculated as a function of the energy of ionizing particle, decreases sharply with the increase of energy on the low energy side and reaches a minimum around one keV, with the singlet probability close to the value of 0.25 for random recombination. At higher energies the singlet yields increases again towards an asymptotic value. Approximately the same behaviour is found for different distributions of the thermalization distance for electrons.

Fock Space Multi-reference Coupled-Cluster Study of Excitation Energies and Dipole Oscilator Strengths of Ozone

Maria Barysz,[*] Magnus Rittby[**] and Rodney J. Bartlett[**]

[*]Silesian University, Institute of Chemistry, 40-006
Katowice, Poland
[**]Texas Christian University, Department of Physics,
Box 32915, Fort Worth, TX 76129, USA
[***]Quantum Theory Project, University of Florida,
Gainesville, Florida 32611-2085, USA

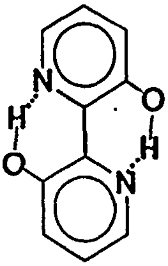
The singlet and triplet excitation energies are investigated by the Fock space multi-reference coupled-cluster method. A procedure for evaluating dipole moments and oscilator strengths is also presented, and applied. Good agreement is achieved for excitation energies and transition moments where experimental data are known

Symmetry and its lack in phototautomerisation reactions of the internally H-bonded bipyridyl-diols and model compounds.

Pawel Borowicz[*], Anna Grabowska[*] and Łukasz Kaczmarek[**]

[*] - Institute of Physical Chemistry, Polish Academy of Sciences
[**] - Intitute of Organic Chemistry, Polish Academy of Sciences
44/52 Kasprzaka, 01-224 Warsaw, Poland

2,2'-bipyridyl-3,3'-diol (I) undergoes a double proton transfer (DPT) in the S_1 state. The phototautomerisation reaction goes adiabatically through the symmetric primary excited species. This was demonstrated by the determination of the dipole moments of the reaction product and of its precursor, both in excited states. For this purpose two electrooptical methods, EOAM and EOEM, were applied [1,2].



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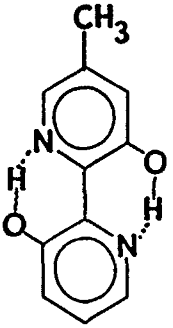

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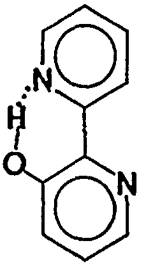

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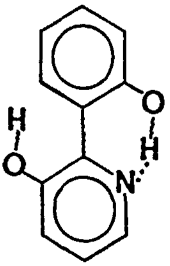

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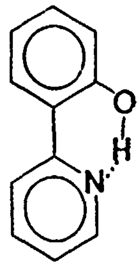

V

In the present work the photophysics of a family of compounds are studied in order to show, how the weak (II) and strong (III-IV) perturbation of the symmetric parent molecule (I) influences the mechanism of the excited state proton transfer reaction.

New compounds IV and V were synthetized by the asymmetric coupling two different aromatic moieties by Grignard palladium catalyzed reaction.

Photophysics and spectroscopy of all compounds will be reported and critically compared. Attention will be focused on the phototautomeric fluorescence and transient absorption spectra. Experimental studies are performed with the assistance of the theoretical treatment involving the Molecular Mechanics and INDO/S methods.

Results will be discussed in terms of cooperativity of the DPT process in the electronically excited molecule.

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Solvent and Substituent Influence on the Hypersurface of TICT-Reactions

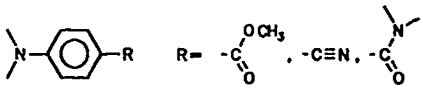
David Braun and Wolfgang Rettig

Iwan-N.-Stranski Institute, Techn. Univ. Berlin, Straße des 17.Juni 112,
1000 Berlin 12, FRG

The TICT-mechanism, which is responsible for the dual fluorescence of Dimethylaminobenzonitrile (DMABN) and its derivatives, is characterized by the charge transfer and the intramolecular twisting motion between the donor and the acceptor part of these compounds. In general, the electron transfer (ET) is not only accompanied by the intramolecular motion, but also by the reorganisation of the dipolar solvent molecules, which occurs after photoexcitation due to the high dipole moment of the TICT-state.

As early as 1975 Grabowski et al. [1] concluded from O_2-quenching experiments in acetonitrile, that the TICT formation process in DMABN is in the picosecond range but significantly slower than the dipolar relaxation of the polar solvent molecules. Thus, the solvent reorganisation cannot be the rate-determing step. But the assumption, that the TICT-reaction is controlled by solvent viscosity alone is insuffient, too. This can be concluded from different TICT-reaction rates (up to a factor 60) of the ester and nitrile compounds (fig.1 Ia, Ib) despite a very similar rotational volume.

This difference can, however, be explained by the presence and absence of a conical intersection along the multi-dimensional hypersurface of the excited state. Fig. 2 schematically shows a one-dimensional cross-section of this multi-dimensional hypersurface and its solvent polarity dependence. The reaction coordinate in figure 2 contains both intramolecular modes and the intermolecular solvent relaxation.



I Ia Ib Ic

Fig.1 model compounds

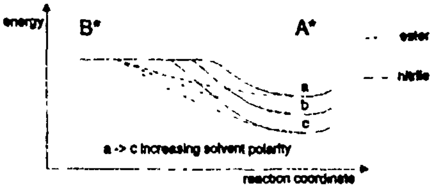


Fig.2 Variation of the "barrier" position - the edge of a flat portion of the potential surface - induced by solvent polarity

The model, which describes ester and nitrile, will be extended to amides Ic TICT-formation rates derived from time-resolved fluorescence at low temperatures will be compared with experimental results of high-pressure measurements at room temperature to allow a seperation of the various factors contributing to the experimental "activation-barrier".

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This work has been supported by BMFT (project 05414 FAB) and DFG (SFB 337)

Electron transfer in three-component electron donor-acceptor systems.

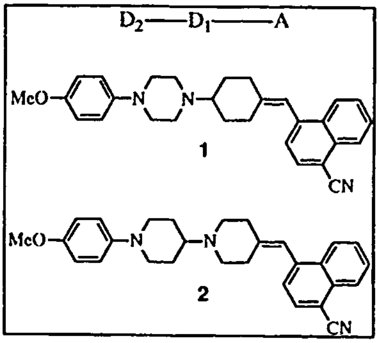
A.M. Brouwer, C. Eijckelhoff, R.J. Willemse, J.W. Verhoeven

Laboratory of Organic Chemistry, Nieuwe Achtergracht 129,
1018 WS Amsterdam, The Netherlands

Natural photosynthetic systems achieve a high quantum yield of light-induced charge separation by an elegant trick : the initial photon-induced electron transfer is followed by rapid consecutive electron transfer steps which take the electron and the hole further apart to prevent charge recombination. Several more or less successful man-made mimicking systems have been constructed, mostly employing nature-like building blocks such as porphyrins and quinones. Our purpose has been to use photoexcitable electron acceptor chromophores to achieve sequential electron transfer as shown in eq. (1), in relatively simple organic systems.

$$D_2\text{-}D_1\text{-}A^* \rightarrow D_2\text{-}D_1{}^{+}\text{-}A^- \rightarrow D_2{}^{+}\text{-}D_1\text{-}A^- \qquad (1)$$

Two of the compounds investigated are trichromophoric systems **1** and **2**, which contain the vinylcyanonaphthalene acceptor and two different amines as donors. It was found [1,2] that a $D_2{}^{+}$-D_1-A^- state is arrived at in **1** in polar and nonpolar solvents, without evidence of an intermediate D_2-$D_1{}^{+}$-A^- state. In **2**, on the other hand, the step D_2-$D_1{}^{+}$-A^- → $D_2{}^{+}$-D_1-A^- could be monitored on a nanosecond timescale using the Charge-Transfer fluorescence of D_2-$D_1{}^{+}$-A^-, which is decreased in intensity as well as in lifetime compared to an appropriate reference system. An interesting aspect of our present research is the interaction within the $(D_2\text{-}D_1)^+$ fragment. Evidence suggests that the positively charged site is stabilized in the piperazines (e.g. **1**), but destabilized in piperidine systems (e.g. **2**).



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MECHANISM AND DYNAMICS OF THE PHOTOISOMERIZATION IN CYANINE DYES. EFFECTS OF THE SOLVENT POLARITY ON THE TICT STATE.

I.Baraldi, A.Carnevali, F.Momicchioli, G.Ponterini
Dipartimento di Chimica, Universita' di Modena, Italy

and G.Berthier
Institut de Biologie Physico-Chimique, Paris, France.

The photochemical cis-trans isomerization of cyanines has a relevant role in some important applications of these dyes (photography, lasers, photopolymerization).
Recently we suggested a theoretical model [1],formulated for simple streptocyanines, according to which the photoreaction proceeds through a Twisted Intramolecular Charge Transfer (TICT) minimum present on the S_1 surface.
In order to determine the relative importance of intramolecular and intermolecular (solute-solvent) interactions in controlling the dynamics of the photoisomerization, we have undertaken a combined, theoretical and experimental, investigation on a series of cyanines sharing the same chromophore (pentamethine) but bearing different end substituents.
The potential energy curves in the S_0, T_1 and S_1 states have been determined by CS-INDO/CI calculations. Then the solvent effect has been evaluated making use of a formula based on the virtual charge model [2].
The comparison between theoretical results and the findings of a kinetic study of excited-state decay, photoisomer formation and ground-state back isomerization in solvents of different polarity, leads to the following observations:
- in keeping with the above mentioned theoretical model [1], a precursor-successor relationship exists between the fluorescent species and the photoisomer;
-unlike simple open-chain cyanines, for complex cyanines the solvent seems to have a determinant role for the TICT state to be the absolute minimum in the S_1 surface;
-the effect of the solvent polarity is negligible on the photoisomer formation kinetics, while it is appreciable as far as the thermal back isomerization kinetics is concerned.

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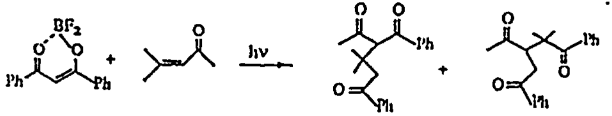
A DEMONSTRATION OF EXCIMER PARTICIPATION IN [2+2] PHOTOCYCLOADDITION.

Shi-Sen Wang, Xianen Cheng, Carl I. Johansson, and Yuan L. Chow.*
Department of Chemistry, Simon Fraser University, Burnaby B. C. V5A 1S6

Dibenzoylmethanatoboron difluoride (DBMBF$_2$) undergoes photoreaction with olefins through a partial electron transfer that leads to cycloaddition or sensitized Diels-Alder reactions. We are surprised to observe that DBMBF$_2$ undergoes similar photocycloaddition efficiently with α,β-unsaturated carbonyl compounds (that are poor electron donors), to give products that may react by secondary thermal reactions. The regioselectivity of the addition begins to lose its integrity when the number of β-methyl groups increases. The fluorescence intensities of both the DBMBF$_2$ monomer and excimer are quenched by these substrates by one of two mechanistic patterns. The first case is that both the monomer and the excimer fluorescence is quenched simultaneously and proportionately. The second is that the excimer fluorescence is quenched, while the monomer peak remains unaffected. The quantum yields of products are dependent on DBMBF$_2$ concentrations owing to dynamics of the excimer formation. Kinetic analysis indicates that cyclohexenone reacts with the excimer, but not the monomer, to afford the product. This new reaction mechanism must involve a triplex as the intermediate.

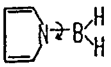


Experimental and Theoretical Results on TICT-forming Aminoboranes

Claudia Cornelissen, Wolfgang Rettig and Vlasta Bonačić-Koutecký,

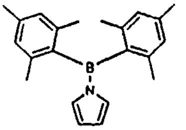
I.N. Stranski Inst., Techn. Univ. Berlin, Strasse d. 17. Juni 112, D-1000 Berlin 12 and
Inst. f. Physikal. u. Theoret. Chemie, Freie Univ. Berlin, Takustr. 3, D-1000 Berlin 33,
FRG

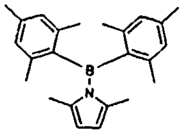
Aminoborane H_2N-BH_2 as the prototype TICT-system lends itself, due to its small size, to large-scale ab initio calculations of the hypersurfaces involved /1/. Large charge separation occurs in the perpendicular, the classical TICT conformation Recently, pyrrole systems derived from dimethylaminobenzonitrile (DMABN) have been studied, where charge separation is present for both planar and perpendicular conformations /2/. Here, we wanted to confront theory and experiment and extended the theoretical study to the corresponding pyrroloboran PB while comparing the experimentally accessible systems I and II with both steady state and time-resolved fluorescence.



PB

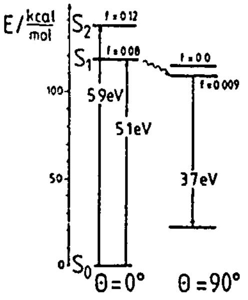
I





II

We could confirm the large Stokes shift and solvatochromism of I previously found by Britelly and Eaton /3/ and indicative of the highly dipolar nature of the emissive state. The Stokes shifts for I and II are very large already in the nonpolar alkane solvents, and an increased value for II is a further manifestation of the CT nature of the emission. The fluorescence lifetimes are long and strongly solvent polarity-dependent consistent with a forbidden radiative transition.



Schematical state diagrams for PB obtained from large scale ab initio CI calculations. The partially optimized ground state geometries were used as input for the excited state calculations.

The theoretical results support a strong redshift for twisting from the planar to the perpendicular conformation (Figure). The calculated S_1-dipole moments, however, are large for both conformations, and the results indicate that a redshift can also be induced by a structural relaxation within the planar conformation.

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This work has been supported by BMFT (project 05414 FAB) and DFG (SFB 337).

ORIENTATION EFFECTS IN EXCIPLEX FORMATION REACTION

I.Deperasinska

Institute of Physics, Polish Academy of Sciences
Al.Lotnikow 32/46, 02-668 Warsaw, Poland

The charge-transfer interaction between electronically-excited and ground-state molecules of the electron donor and the electron acceptor may result in the formation of the molecular exciplex. Recent experiments with van der Waals complexes, generated in the supersonic molecular beam expansions [1-5], have shed a new light on the exciplex formation reaction (because in contrast with the situation in liquid solution the stabilization and spectral properties of the complex and exciplex formation kinetics are not dependent on the solvent).

The results of such experiments have revealed the existence of different isomeric forms of an exciplex. Both, the different spectroscopic and dynamic properties of such isomers, as well as the ability of an electron-donor-acceptor (EDA) system to their formation, are strongly suggesting that the exciplex formation reaction is controlled by the steric orientational factors, inherent for a given EDA pair.

In this paper we discuss the steric barriers which can hinder an electronic overlap in EDA systems and these are employed in the discussion of experimentally observed differences between the anthracene-dimethylaniline and anthracene-diethylaniline systems [3]. The separation distance between donor and acceptor is larger for the anthracene-diethylaniline complex and the relative orientation of this pair is medium between two orientation .orresponding to maximum overlap.

The results of calculations of the potential energy surfaces for the complexes of cyanonaphtalene with aliphatic amines [4] and olefins [5] are also presented and discussed.

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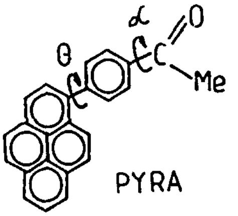
GROUND AND EXCITED STATE GEOMETRY OF 4'-(1-PYRENYL)ACETOPHENONE

J.Dobkowski, W.Rettig, C.Rullière**, J.Waluk, W.Yang***

Institute of Physical Chemistry, Polish Academy of Sciences,
Kasprzaka 44/52, 01-224 Warsaw, Poland.
*Iwan N.Stranski-Institute for Physical and Theoretical Chemistry
Technical University of Berlin, 1000 Berlin, FRG.
**Centre de Physique Moléculaire Optique et Hertzienne, Université de Bordeaux I,
33405 Talence, France.

It is well established that numerous para-substituted aromatic molecules of the type D-Ar-A (where D/A represent Donor/Acceptor subgroups and Ar aromatic ring) in polar solvents undergo relaxation to a highly polar state, and the emission occurs from two different states: primary one and Twisted Intramolecular Charge Transfer (TICT) state. The aim of our studies is to investigate whether in the case of molecules characterized by a donor group with extended π-electron system (PYRA) the relaxation to the TICT state occurs similarly as in the case of carbonyl derivatives of N,N-dimethylaniline.



We present the stationary and picosecond time-resolved fluorescence spectra and nanosecond fluorescence decay curves. The ground state geometry of PYRA has been calculated as a function of two possible angles of twist, θ and α, by molecular mechanics. These results served as input geometry for quantum chemical (INDO/S) calculations of the energies, electronic transitions and oscillator strengths. Two models are discussed: (i) TICT state formation, (ii) inversion of two low lying singlet states.

Charge Separation in Dinaphthylamines

Józef Dresner*, Steven H. Modiano and Edward C. Lim
The University of Akron, Knight Chemical Laboratories, Akron OH 44325, USA
**Instytut Fizyki PAN, Al. Lotników 32/46, 02-668 Warszawa*

The mechanism of charge separation between two aromatic moieties in the symmetric, bichromophoric molecular systems is pertinent to the understanding of the dynamics of charge and electron transfer (CT and ET) processes in general. This is evidenced, for example, by the extensive discussion on the nature of CT in 9,9'-bianthryl.

In the symmetric dinaphthyl systems (Np-X-Np, where X=O, CH_2 or NH_2) only in dinaphthylamines (DNA, Np-NH_2-Np) the formation of the polar CT state was reported [1]. Although our systematic studies of dinaphthylmethanes and dinaphthylethers (DNM and DNE) led to the finding of a new type of intramolecular singlet state association between naphthalene moieties [2], there is no evidence that this new species bears any CT character.

On the contrary, DNA systems exhibit highly polar excited singlet states which possibly involve charge separation between naphthalene chromophores

The crucial role of the bridging amino group in the CT process is demonstrated by the protonation of the group, which leads to the formation of a non - polar excited state characteristic of the excimer - like species, similar to that found in DNM and DNE

In our communication we present the basic characteristics of the formation and decay of the intramolecular CT state in 1,1'- and 2,2'-dinaphthylamines in polar and non-polar solvents.

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Polarized Fluorescence and Photobleaching Spectroscopy of Photoreactive Molecules in Solutions and Ordered Systems

J.J. Fisz

Institute of Physics, N. Copernicus University,
ul. Grudziądzka 5/7, 87-100 Toruń, Poland

There exist several, well documented in the literature, inter- and intramolecular relaxation processes occuring in the excited state of the molecules after their light-induced electronic excitation (e.g., intramolecular geometrical relaxation, solvation effects, photoreactions leading to excited photoproducts, electronic energy transfer etc.). Remarkable advance in picosecond and in femtosecond laser spectroscopy makes possible deeper recognizing the nature of these processes. The fluorescence and absorption state-to-state kinetic relaxation measurements provide the information on the rates of different reversible and irreversible relaxation processes which control the evolution of the excited state of molecules.

In this work we want to demonstrate that the polarized time-resolved fluorescence and absorption spectroscopy represent another set of powerful experimental tools in studies of different inter- and intramolecular processes. Furthermore, we intend to show that the application of ordered systems, such as liquid crystals or oriented polymers, as the molecular matrices for aligning the photoreactive molecules can provide many additional information on the photoreaction channels leading to different photoproducts, and which are not accessible from the studies on solutions and from the traditional kinetic relaxation measurements in particular. We intend to show that from polarized time-resolved fluorescence and absorption spectroscopy the information on the state-dependent rotational motion (solutions and liquid crystals), state-dependent aligning interactions between the probe molecules and the ordered environment (ordered systems) as well as on the photoisomerization processes (solutions, ordered systems) can be extracted.

Excited State behaviour of 2,2'-Bispyridyl-ethene-diol [Pyridoin]

Murthy S. Gudipati

Physikalisch-Chemisches Institut der Universitat zu Koln
Luxemburger Strasse-116, D-5000 KOELN-41, GERMANY

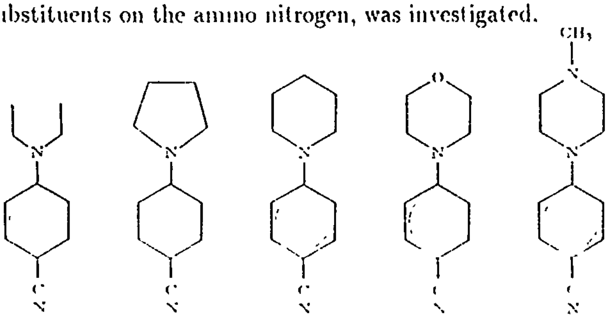
The title molecule has a strong absorption around 380 nm from an intramolecular H-bonded planar conformer. In aprotic, non-polar solvents, the planar conformation is very stable, giving the molecule a golden-yellow colour due to the long wavelength absorption. However, in protic solvents like methanol, at RT, this absorption band diminishes with time (it takes a few days before the colour completely disappears). This behaviour could be attributed to the breakage of intra-molecular H-bonding by the solvent, which could in turn lead to the non-planar conformation of the molecule in the ground state. In planar H-bonded conformation, this molecule is a potential candidate for excited state intramolecular proton transfer (ESIPT). It would also be interesting to see whether the ESIPT would in turn bring TICT state too!

Spectroscopic investigations on the title molecule, in connection with intramolecular H-bonding/H-transfer as well as charge transfer would be presented. comparison of semi-empirical calculations with the experimental results would be discussed.

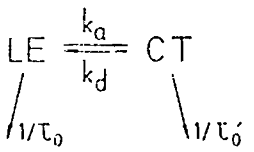
INTRAMOLECULAR CHARGE TRANSFER IN AMINOBENZONITRILES

Th. von der Haar, W. Kühnle, U. Leinhos, and K. A. Zachariasse
Max-Planck-Insitut für biophysikalische Chemie
-Spektroskopie und Photochemische Kinetik-
W-3400 Göttingen, Germany

The intramolecular charge transfer (ICT) in a series of 4-aminobenzonitriles, with different substituents on the amino nitrogen, was investigated.



Double exponential fluorescence decays were obtained over an extended temperature range, using time-correlated single-photon counting with a time resolution down to ten picoseconds. This shows that two species are involved in the reversible ICT reaction: the initially excited *LE* state and a charge transfer state *CT*. The *CT* state is not present at the moment of excitation.



From an analysis of the fluorescence decays, the rate constants k_a, k_d, and the *CT* lifetime τ_0' were determined. In addition, the values for the change in reaction enthalpy ΔH and entropy ΔS were obtained from the temperature dependence of the rate constants.

The meaning of these results for the molecular mechanism of the ICT reaction in the aminobenzonitriles will be discussed.

FLUORESCENCE QUENCHING VIA INTRAMOLECULAR CHARGE TRANSFER WITHOUT TWISTING

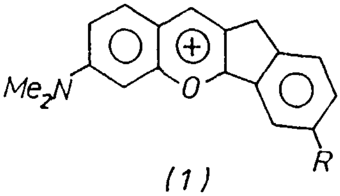
G. Haucke, P. Czerney and D. Steen

Institute of Physical Chemistry, Friedrich Schiller University,
D O-6900 Jena, Germany

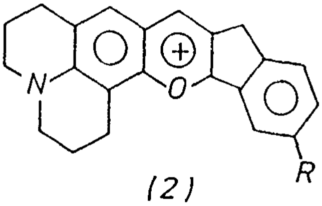
Very often a drastic drop of fluorescence efficiency is associated with the occurrence of a so-called "Twisted Intramolecular Charge Transfer" (TICT) state. The formation of TICT states involves twisting of molecular subunits (the dimethylamino group and the flavylium moiety in (1)) against each other and leads to complete charge separation for the perpendicularly twisted conformation.

Since TICT and ground state are close lying energetically a fast nonradiative deactivation through this funnel occurs.

As these funnels are available only for the twisted geometry, their access can usually be stopped by either chemical bridging of the rotatable groups (substitution of the dimethylamino group by the julolidine group in (2)) or by viscosity effects of the surrounding medium, in particular, frozen solvent matrices at 77K.



(1)



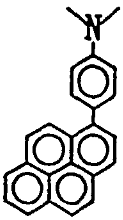
(2)

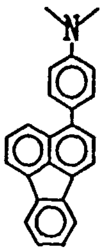
In our contribution we will show that also without the possibility of twisting as in (2) intramolecular fluorescence quenching is observed. A sufficiently large acceptor and/or donor strentgh is prerequisite for this case. In (2) the acceptor strength of the flavylium moiety can be tuned by variation of R (R: H, OMe, NMe_2, F).

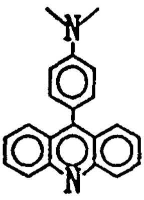
RADIATIVE ELECTRON TRANSFER IN ARYL DERIVATIVES OF AROMATIC AMINES

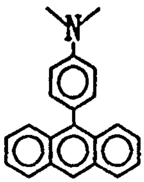
Jerzy Herbich and Andrzej Kapturkiewicz
Institute of Physical Chemistry, Polish Academy of Sciences,
Kasprzaka 44, 01-224 Warsaw, Poland

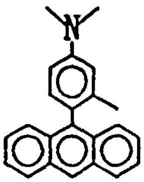
The charge recombination (CR) processes identified with the fluorescence of the intramolecular charge transfer (CT) states have been studied in six members of the series of aryl derivatives of aromatic amines by means of the solvent [1] and temperature effects on fluorescence spectral positions and quantum yields (Φ_f), and excited-state depopulation kinetics (τ_f).

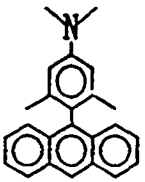

PDMA


FDMA


BDMA


ADMA


ADMT


ATMA

The radiative rate constant ($k_f = \Phi_f/\tau_f$) for all compounds decreases considerably with increasing solvent polarity and, contrary to our expectation [2,3], the fluorescence is not thermally activated. Moreover, k_f values decrease markedly with the increase of the energy of the Franck-Condon (FC) ground state reached upon CT emission. The reduction of the half-width of the CT fluorescence spectra with lowering of temperature, as well as the corresponding solvatochromic effects, allow us to determine the outer (λ_o) and inner (λ_i) reorganization energies in terms of the Marcus theory in the inverted region [4]. The mechanism of the radiative electron transfer will be discussed.

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KINETICS AND MECHANISM OF PHOTOCHEMICAL REACTIONS OF SELECTED TERTIARY AROMATIC AMINES WITH CHLOROMETHANES IN ACETONITRILE

Waldemar IWANEK and Tadeusz LATOWSKI
Institute of Chemistry, Pedagogical University,
25-020 Kielce, Poland

Aromatic amines in the medium of methane polychloroderivatives have been known to be photochemically active. The UV radiation absorbed by an amine has been shown to produce hydrogen chloride and a number of organic compounds resulting from thermal transformations of the primary photochemical reaction products For the primary photochemical reaction in the DMA methane polychloro-derivative system, a mechanism has been proposed based on electron transfer from the first excited singlet state of the amine molecule onto the chloromethane molecule in its ground state This, in conjunction with the rapid heterolytic dissociation of the C–Cl bond produces an active $CH_{3-x}Cl_x$ (x = 1, 2, 3) radical and a thermodynamically stable Cl^- ion. Accordingly, among the products of the primary photochemical reaction, in the solvent cage there are: the amine cation radical, the polychloromethane radical and the chloride ion.

Irradiation with the 313 nm Hg line of the acetonitrile solutions of N,N-dimethylaniline (DMA), N,N,N',N'-tetramethyl-4,4'-diaminophenylmethane $(DMA)_2CH_2$, and N-methyl-N-(4-N,N-dimethylaminobenzyl)aniline (BA), in the presence of chloromethanes results in appearance of a few absorption bands in the visible region of the electromagnetic spectrum.

Interactions have been studied of DMA, $(DMA)_2CH_2$ and BA with chloromethanes in the ground and the first excited singlet states of the amines Stability constants of the complexes of the amines with chloromethanes in acetonitrile have been determined Quenching of the fluorescence of the amines by the chloromethanes has been observed in acetonitrile and the kinetics of the process has been characterized A scheme of the primary and secondary photochemical processes has been suggested, leading to the formation of products responsible for the appearance of the new absorption bands in these systems

MULTIPLE REHM-WELLER PLOTS IN THE SINGLET AND TRIPLET QUENCHING OF 7 METHYL-3 CARBETHOXY THIOXANTHONE (ETX) BY ELECTRON DONORS IN ACETONITRILE

Patrice JACQUES, Dominique BURGET

Laboratoire de Photochimie Moléculaire et Photopolymérisation
Unite de Recherche Associéc au CNRS n°431
Ecole Nationale Supérieure de Chemie
3 rue A. Werner, 68093 Mulhouse Cedex
France

The plots of the logarithm of the rate constants versus the donors ionization potentials show three distincts Rehm-Weller type functions: i) one for the 'π' aromatic donors; ii) one for the 'π' olefinic donors; iii) one for the 'n' donors.

The different quenching efficiencies are tentatively explained according to the role of the electronic interaction term. Moreover in the case of donors exhibiting both 'π' and 'n' properties use of vertical ionization potentials (vIP) for chracterizing the donor ability reveal theemselves to be more useful in the understanding of the quenching rates than adiabatic ones (aIP)or redox potentials ($E_{1/2}$).

P-18

A NOVEL SERS EQUIPMENT AND ITS APPLICATION FOR STUDIES OF ADSORPTION OF Fe(bpy)+2 COMPLEX ON SILVER

J.Jasny and M.Janik-Czachor

Institute of Physical Chemistry, Polish Academy of Sciences

Warsaw, POLAND

ABSTRACT

A novel SERS equipment optimizing the separation from the noise and collection of Raman signals originating from an spectroelectrochemical cell has been built in the laboratory. It has been then used for an investigation of the system: Fe(bpy)+2 +0.1M KCl/Ag.

Specific surface roughness necessary to measure large SERS signals has been successfully modelled by latex spheres covered with a thin Ag overlayer. The results suggest an irreversible adsorption of the complex on Ag and compare with those obtained with a "standard" SERS procedure. The role of a surface morphology in the enhancement process is discussed.

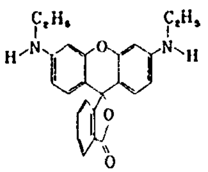
Electron Transfer in Lactone Forms of Some Rhodamines. The Effect of the Donor.

Jerzy Karpiuk+, Zbigniew R. Grabowski+ and Frans C. De Schryver#

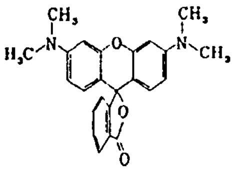
+ Polish Academy of Sciences, Institute of Physical Chemistry
Kasprzaka 44/52, 01-224 Warsaw, POLAND

Catholic University of Leuven, Department of Chemistry
Celestijnenlaan 200F, 3001 Heverlee, BELGIUM

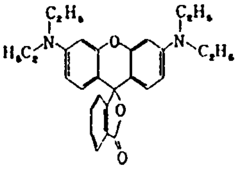
It has been shown that electron transfer plays a key role in the photophysics of lactone form of rhodamine B [1,2]. In the present communication we show the results of our studies on electron transfer reactions in excited state in a series of rhodamines with donors of different electron donating abilities:



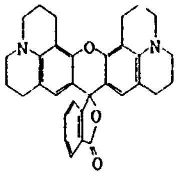
LDR10



LRMet



LRB



LR101

All of the lactones undergo the excited state dissociation of the **C-O** bond in the lactone ring, which is revealed by the fluorescence of the zwitterion form built up after dissociation. The electron-donating properties of the substituents at amino group determine the polarity range in which the dissociation is observed. This seems to be strictly linked to the solvent induced quenching of the zwitterions excited states.

The quenching in LR101 excludes transition to the TICT-state as a mechanism of zwitterion quenching in the case of lactones. The lactone ring closure and the participation of the triplet states are discussed as a possible cause of the accelerated deactivation of the zwitterions.

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Charge recombination processes in the deactivation of singlet excited molecules

T. Kircher and H.-G. Löhmannsröben

Institut für Physikalische und Theoretische Chemie, TU Braunschweig,
Hans-Sommer-Str. 10, D-3300 Braunschweig, F.R.G.

Charge recombination (CR) reactions are important elementary electron transfer -and often energy wasting-processes for the deactivation of photoexcited species. A detailed knowledge of the properties of CR reactions is therefore of fundamental interest for the understanding of luminescence quenching mechanisms and for the optimization of photodriven processes. Due to their high quantum yields of fluorescence (Φ_F), their photostability and photoconductive properties perylene and perylene derivatives are suitable as fluorescent probes in energy and electron transfer processes and are promising materials for laser dyes, solar cells, molecular devices, etc

Extending our earlier studies of photoinduced bimolecular reactions [1] we have investigated the quenching of the fluorescence of perylene and of perylenebis(dicarboximide) dyes (PBI) as energy donors (D^*) by organic quencher molecules (A) in benzene and acetonitrile solutions. From time-resolved measurements after laser excitation the rate constants (k_G^E, k_T^E) for the deactivation of the geminate ion pairs ($D^{\pm} \cdots A^{\mp}$) in acetonitrile by return CR reactions to the ground and triplet state molecules were obtained. The dependence of k_G^E and k_T^E on the free energy change is analyzed within the framework of nonadiabatic electron transfer theory.

For a comprehensive description of the overall deactivation processes of PBI in polar and unpolar solvents the effect of ground state complexation, the temperature dependences of the fluorescence quenching efficiencies and termolecular quenching reactions were also studied. The results indicate the roles of charge transfer (CT) properties, of the heavy atom effect and of the participation of exciplexes in the quenching processes. The investigations in benzene solutions are of particular interest since the deactivation mechanisms in unpolar solvents are hitherto not well understood.

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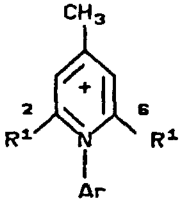
THE ROLE OF ADIABATIC STRUCTURAL CHANGES IN DEACTIVATION OF ELECTRON-EXCITED STATES IN ARYLSUBSTITUTED PYRIDINIUM CATIONS

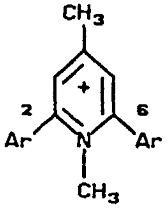
M.I.Knyazhansky, V.A.Kharlanov, N.I.Makarova

Instutute of Physical and Organic Chemistry,
Stachki Str., 194/3, Rostov-on-Don, 344104, Russia

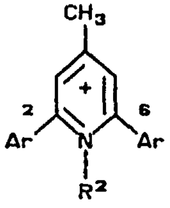
Luminescent and photochemical properties of the arylsubstited pyridinium cations I - III and reference compounds are investugated in solvents having various viscosity (T =77 - 295 K) and in crystall state.



I



II



III

^{1}R : H(a), CH$_3$(b); Ar: Ph, Napht, Anthr; R^2: Ar, NH$_2$, -N=C-Ar;

These properties are connected with the possibility of adiabatic aryl rings rotation due to photoindused electron (or charge) transfer from aryls to pyridinium fragment. In the cations I the fluorescent properties are caused by the N-aryl ring ability for the rotation. E.g., the fluorescence of the cation Ib with bulky N-anthryl substituent is conditioned with its biradicaloid orthogonal structure in the liquid solvent and with local excitement of anthryl fragment in the strong viscous enviroments. In the Ia full fluorescence quenching is observed due to its flat structure formation. In the cations II fluorescence and its quenching are connected with formation of flattened and TICT-structures accordingly due to the 2,6-ring rotation. The flurescence of the cations III is caused by rotation of the substituents in the 2,6- and N-positions and this process is also primary step of competitive cyclization photoreaction.

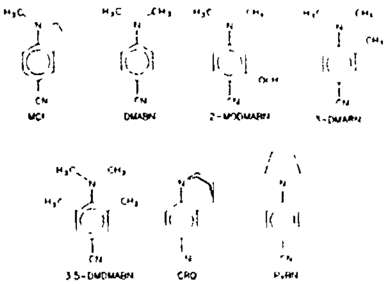
Time Resolved Fluorescence Study of TICT State Relaxation in Binary Mixed Solvents.

Gottfried Köhler[1], **Krystyna Rotkiewicz**[2], **and Wolfgang Rettig**[3]

[1])Institut für Theoretische Chemie und Strahlenchemie, University of Vienna, Austria,
[2])Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland, and
[3])Ivan N.-Stranski-Institut für Physikalische und Theoretische Chemie, Technical University, Berlin, Germany.

Stationary and time resolved fluorescence spectra as well as decay kinetics were investigated for some planar (CMI, 2-MODMABN, PyBN) and non-planar (3-MDMABN, 3,5-DMDMABN, CBQ) derivatives of 4-(dimethylamino)benzonitrile (DMABN, see scheme 1) in various binary mixtures of n-hexane and a polar co-solvent at various temperatures.

All these compounds relax to the TICT-state on excitation. The only exception is CMI, a rigidly co-planar molecule and thus a model for the primarily excited state. This relaxation mechanism depends strongly on the polarity of the molecular environment, as it is primarily promoted by energetic stabilization of the highly dipolar TICT state by electrostatic solute-solvent interactions. In order to discuss the effects of preferential solvation, ground state complexation, and solute-solvent exciplex formation on this intramolecular charge transfer relaxation mechanism, detailed studies were performed in various binary solvent mixtures.



The results can be summarized as follows:

1) **Highly polar co-solvents:** especially hydroxylic solvents cause complex non-exponential decay kinetics allready at low additive concentrations. At low temperatures such a behaviour was also found for the pure polar solvents. There was, however, no evidence for the formation of stoichiometric exciplexes in the excited state. The complex kinetics results rather from a distribution of various ground state solvates and further excited state reorganization and aggregation reactions.

2) **Medium polar co-solvents:** (e.g. ether etc.) a simple mono-exponential decay behaviour was found, the photophysical parameters varying continously over the whole range of mixture. They are thus correlated predominantly to the bulk dielectric properties, although preferential solvation effects dominate in the low concentration range.

Coupling Between Different Kinds of Internal Motions in a Molecule

J Konarski, Faculty of Chemistry, A Mickiewicz University
Grunwaldzka 6, 60-780 Poznań, Poland

The coupling between different kinds of internal motions in a molecule involves intermolecular energy transfer The Coriolis force leading to the Coriolis coupling terms mixes vibrational momentum with an overall rotation of a molecule giving rise to the energy flow betwee vibrational and rotational degrees of freedom

Supposing that a molecule is not rigid but may be described by the soft or deformable body model,[1,2] a new channel of intermolecular energy transfer should be taken into account, namely a coupling between the equilibrium position of an atom in a molecule changed by overall rotation and the electronic structure of this molecule, which leads to a dependence of dissociation energy on the rotational quantum number The application of the mechanism descibed above in the calculation of the Franck-Condon coefficients is discussed

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[1] J Konarski, *J Mol Spectroscop* **124**, 218 (1987)

[2] M Molski, *Acta Phys Polon* **A76**, 877 (1989)

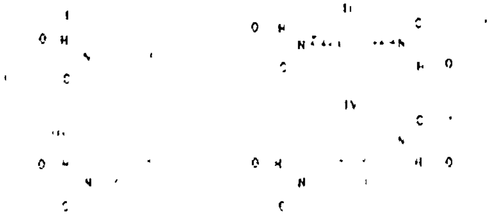
Typeset by $\mathcal{A}_{\mathcal{M}}\mathcal{S}$-TEX

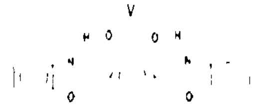
Single vs Double Proton transfer Reactions in the Symmetric Aromatic Schiff Bases and Related Molecules

*K. Kownacki**, *A. Grabowska**, *B. Osińska** *and Ł. Kaczmarek***

***Institute of Physical Chemistry, Polish Academy of Sciences**
****Institute of Organic Chemistry, Polish Academy of Sciences**
44/52, Kasprzaka, 01-224 Warsaw, Poland

Excited state proton transfer reaction of the typical photochromic systems I-IV, known to change their colour upon excitation in the crystalline state [1], are investigated for isolated molecules in solution.





The rotational barrier of the H-bonded sub-system around the single bond was calculated by the PC Model (molecular mechanics method) on the example of II, to be ≈ 4 Kcal/mol. It was shown by calculations and verified experimentally in So state that centrosymmetric molecules, like II, reveal considerable dipole moment because of important contribution of the nonplanar rotamers. Therefore, the determination of the dipole moment of the excited phototautomer cannot be used as a key for distinguishing between the single and double proton transfer in this class of excited molecules. In contrast, molecule V changes its dipole moment exclusively upon excitation and proton transfer process.

In molecules I-IV the PT reaction mechanism can be decoded by the proper choice of the model compounds. Transient absorption spectra [2] and other time resolved photophysical studies will be reported and discussed.

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Bull. Chem. Soc. Jpn. 61 (1988) 4207,
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Bull. Chem. Soc. Jpn. 50 (1977) 1909.

OPTICAL STUDIES OF THERMALLY ACTIVATED PROCESSES IN MIXED STACK CHARGE TRANSFER CRYSTALS

B. Kozankiewicz

Institute of Physics, Polish Academy of Sciences
Al. Lotnikow 32/46, 02-668 Warsaw, POLAND

Recent optical studies of mixed stack charge transfer (CT) molecular crystals, performed within the wide temperature range, have given deeper understanding of many of intriguing properties of these crystals, connected to electron and energy transfer, energy relaxation, lattice dynamics, etc.

A photophysical behaviour of some pure, as well as of intentionally doped CT crystals, has been explained as an interplay between thermal detraping and thermal activation of the (back) intersystem crossing transition, $T_1 \rightsquigarrow S_1$. This later process, detected by a presence of thermal-delayed fluorescence, has been observed only in those CT crystals where S_1-T_1 energetic separation is below 2000 cm^{-1} [1-4]. It has been concluded that delayed fluorescence is either of excitonic or of trap origin and an evolution with temperature of the intensity of both kinds of emission can be easily described with the aid of proper kinetic model These kinetic studies have led to an experimental estimation of the both, $S_1 \rightsquigarrow T_1$ and thermally activated $T_1 \rightsquigarrow S_1$, intersystem crossing rate constants.

Optical properties of CT traps are highly sensitive to their environment. In a case of TCNB-naphthalene crystal doped with pyrene, an intensity and decay time of dopant phosphorescence drastically change in a narrow temperature range, just below the "order-disorder" phase transition of the host crystal, at 73 K [5]. This behaviour has been attributed to thermally activated change of the geometry of TCNB-pyrene trap, induced by the activation of naphthalene librations.

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SUBSTITUENT AND SOLVENT EFFECTS ON THE PHOTOTAUTOMERISM OF ALLOXAZINES

A Koziołowa, H Szymusiak and J Kozioł

Institute of Commodity Science, Poznan University of Economics,
Al Niepodleglosci 10, 60 967 Poznan, Poland

The excited state alloxazine-isoalloxazine phototautomerism is observed in solutions containing molecules able to form with alloxazines hydrogen bonds of proper strength and conformation (e.g. carboxylic and phosphoric acids, water, pyridine) [1]. This reaction classified as excited state concerted double proton transfer (ESCDPT) [2] is promoted by the electron density redistribution on N-1 and N-10 upon excitation. The efficiency of phototautomeric effect depends on: (i) the substituent type and its location site in benzene ring, (ii) polarity of the bulk solvent used.

(i) High phototautomeric efficiency is ascribed to alloxazine, 8-methyl-, 7-cyano- and 8-cyanoalloxazines and a lower efficiency to 6-, 7- and 9-methylalloxazine [3]. Owing to undefined specific reasons the 7- and 8-cyano-derivatives display higher ESCDPT efficiency than the methyl analogues, since in the contrary to the latter, this process is observed also in the presence of methanol and N-methyl formamide. The suggested mechanism of ESCDPT in alloxazines is consistent with the calculated by INDO/S-CI-1 electron density distribution in the ground and in the first $(\pi-\pi^*)$ excited states of alloxazines. Fairly good correlation is found between phototautomeric efficiencies and electron density differences on the N-10 and N-1 nitrogen atoms; in all alloxazines studied upon excitation the N-10 gains electron density whereas the N-1 loses it. The deviation from linearity in the case of 9-methylalloxazine is interpreted as a result of steric effects.

(ii) The kind of bulk solvent of reaction has a pronounced influence upon the phototautomeric efficiency. The decrease of F_{izo}/F_{all} value of 3,7,8-trimethylalloxazine corresponds fairly good with the increase of solvent polarity expressed by Onsager function when correlated for solvent molecules of the same chemical constitution [1]. The excellent correlations between phototautomeric efficiencies and Onsager functions obtained for the wide class of organic compounds are very instructive for further studies and interpretations.

References

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SPECTROSCOPIC STUDY OF BIPHENYL DERIVATIVES

Jan Kukielski
University of Gdansk
Institute of Experimental Physics
Gdansk

Electronic absorption and emission spectra were measured in different nonpolar and polar, as well as aprotic and protic solvents.

The electric dipole moments in the ground and first excited singlet state of 4-pentyl-4'-cyanobiphenyl are $20.4*10^{-30}$ C*m and $38.5*10^{-30}$ C*m , respectively.

The electronic absorpion spectra of these solutions do not display any vibrational structure in different nonpolar and polar solvents, their fluorescence spectra however are structured in nonpolar or less structured in slightly polar solvents, even at room temperature, whereas in polar solvents they are structureless.

It is clearly seen from the emission spectra that their shape strongly depend on the polarity of the solvent.

In the compounds investigated there exists a weak vibrational coupling between the two phenyl rings.

The electron donating effect result from the presence alkyl and cyano group.

In solution the solute molecules interact with the solvent molecules.

The environment effect can influence the twist angle.

P-28

INTRAMOLECULAR ELECTRON TRANSFER IN PERIPHERALLY MOLYBDATED TETRAPHENYL PORPHYRINS

Stefan S. Kurek *Politechnika Krakowska, Krakow, Poland*

Natalie M. Rowley, Christopher J. Jones *School of Chemistry, University of Birmingham, Birmingham, UK*

Stephan M. Hubig *Center for Fast Kinetic Research, University of Texas at Austin, USA*

Paul D. Beer *Inorganic Chemistry Laboratory, University of Oxford, Oxford, UK*

Jon A. McCleverty *School of Chemistry, University of Bristol, Bristol, UK*

There are many well documented examples of intramolecular electron transfer from photoexcited porphyrin to organic acceptors, such as quinones or pyromellitimide. Despite many attempts, examples of similar compounds with transition metal based electron acceptors are very rare.

A series of peripherally molybdated tetraphenyl porphyrins of the type:

$$[\mathrm{Mo(NO)(L^{*})(X)\{-E-C_6H_4-(porphineH_2-Ph_3)\}}]$$

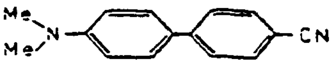
where L^{*} - hydrotris(3,5-dimethylpyrazol-1-yl)borate;
E - *para* -O, *para* - NH; X - Cl, HO-
was synthesised. All the compounds exhibit the same pattern of fluorescence as ordinary tetraphenylporphyrins, but it is quenched. The absorption and nmr spectra indicate no coupling between the porhyrin in the ground state and molybdenum. Redox potentials are only slightly shifted and are characteristic of tetraphenyl porphyrin and similarly substituted molybdenum centres.

Time resolved picosecond spectroscopy results in DMF solutions showed the presence of porphyrin radical cations, thus providing evidence for the electron transfer from photoexcited porphyrin. In all the cases the porphyrin radical cation is formed very fast ($\tau<30$ ps), so only the charge recombination rates could be determined. The rate constants (measured as the rates of decay of the porphyrin radical cation) are essentially the same ($k_R \cong 4 \cdot 10^{9}$ s^{-1}) despite differences in the driving force ($-\Delta G^{o}$ = 1.38 eV in the case of X = Cl, E = ρ-O and $-\Delta G^{o}$ = 1.87 eV if X = HO-).

CHARGE TRANSFER PROPERTIES IN THE EXCITED STATES OF SUBSTITUTED BIARYLS

F.LAHMANI, E.BREHERET, A.ZEHNACKER-RENTIEN
Laboratoire de Photophysique Moléculaire
Bât 213, Université Paris Sud, ORSAY

The photophysical properties of biaryls I-IV have been examined in order toget insight on the photoinduced intramolecular charge transfer in a family of bichromophoric molecules presenting variable twisting angle between the aromatic acceptor and donor subunits.



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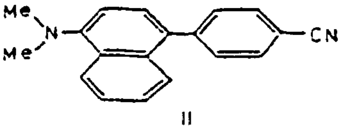

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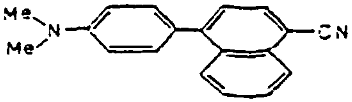
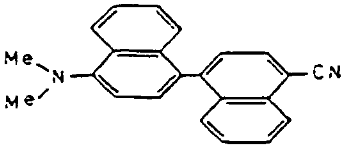


III



IV

The absorption and fluorescence spectra of compounds I-IV in non polar solvents can be related to the change of torsion angle between the ground and excited states with compounds I and III showing strong conjugation between the aromatic moieties in agreement with structure approaching coplanarity.

In solvents of increasing polarity a strong red shift of the fluorescence spectrum is observed indicating a large increase of the excited state dipole moment relative to the ground state. This effect is attributable to the formation of an intramolecular charge transfer state which is stabilized in polar solvents. Analysis of the data as a function of the polarity of the solvent according to the current theories of solvatochromism shows an increase of the dipole moment as high as 17 Debye for I and III in the excited state.

While compounds I,II,III exhibit in all solvents a single emission band, the binaphthyl IV presents a double fluorescence even in non polar solvents. The position and intensity of the blue fluorescence is not sensitive to solvent polarity while the red one undergoes the same strong red shift as that observed for the other compounds in polar solvents. The excitation spectra of the blue and red components of the fluorescence are not identical and allow to decompose the absorption spectrum of IV in two overlapping bands involving two close electronic transitions.

Fluorescence quantum yields and lifetimes measurements in cyclohexane and acetonitrile have been performed in order to compare the radiative and non radiative rate constants of the four biaryls derivatives. The fluorescence characteristics of compounds I-IV will be discussed on the basis of the electronic delocalization and the torsion angle between the electron donor and acceptor moieties.

Acknowledgments.

The authors are grateful to C. Amatore and A. Jutand for the gift of products I-IV. Fluorescence decay times have been measured with the picosecond set up of the Laboratoire de Physicochimie des Rayonnements (Orsay) and we are indebted to J.F. Delouis for his assistance.

STUDIES ON PRODUCTS AND MECHANISM OF THE REACTION OF BROMOBENZENE AND α-BROMONAPHTHALENE IN T_1 STATE WITH N,N-DIMETHYLANILINE IN SOLUTION

Tadeusz LATOWSKI and Ewa MACHOWSKA
Institute of Chemistry, Pedagogical University
25-020 Kielce, Poland

UV radiation, when absorbed by aromatic amines in the presence of an aromatic chloroderivative in solution, initiates a photochemical reaction The mechanism of the primary, photochemical reaction in such systems in connected with the irreversible transfer of electron from the donor molecule (aromatic amine) to the acceptor molecule (aromatic chloroderivative). Reaching by the system: aromatic amine -aromatic chloroderivative, the negative value of free energy of the reaction has a significant meaning for the initiation of that process, and, in case of the considered systems, requires a decrease in ionization potential of the donor or increase in electron affinity of the acceptor. Electron excitation of one of the reagents allows the required changes of the above mentioned potentials The works published on that subject concern mainly reactions, in which a reagent excited to a singlet state participates.

Bromobenzene exhibits, apart from $S_1 \longleftarrow S_0$ band (240-270nm), weak is attributed to the forbidden transition $T_1 \longleftarrow S_0$ (peak 334nm, $\varepsilon_{max} = 0.0827$). Those values for α-bromonaphthalene are respectively: 390-430nm (peak 410nm, $\varepsilon_{max} = 0.025$ nm). The manifestation of the metioned absorption bands is caused by a strong spin - orbit coupling. Photochemical activity of solutions: N,N-dimethylaniline in bromobenzene, and in α-bromonaphthalene, was examined. In both cases the solutions were exposed to the radiation from the range of forbidden absorption of the title-chloroderivatives. The reaction in bromobenzene was accompanied by the appearance of absorption bands: 440 and 610nm. The product, responsible for the appearance of the band at 440nm, is unstable, and after interruption of the exposure slowly decays. Quantum yields of the hydrogen bromide formation were determined Attempts to isolate and identify the products of the reactions were undertaken

ON AN UNEXPECTED COURSE OF THE PHOTOLYSIS OF p-CHLOROANILINE AND ITS N-METHYL DERIVATIVES IN SOLUTIONS

Tadeusz LATOWSKI and Beata SZCZEPANIK
Institute of Chemistry, Pedagogical University,
25-020 Kielce, Poland

Photochemical activity of the title amines has been found to be strongly dependent on the nature of the medium. Quantum yield of photolysis of the carbon - chlorine bond, Φ_{HCl}, for p-chloroaniline ranges from a few per cent in nonpolar aprotic media to 100 per cent in polar protic media (similar variations of the photochemical activity have not been observed with the other haloaniline isomers). In binary aprotic - protic solvent mixtures, Φ_{HCl} approaches 100 per cent just at ca 20 vol.-% concentration of the protic solvent in the mixture (e.g. of water in methanol or 1,4-dioxane). The amine itself may play the role of the protic constituent. Upon raising p-chloroaniline concentration of both the protic component of the binary mixture and the amine in solution can be linearized to give the following expression:

$$\Phi_{HCl}^{-1} = A + B[\text{donor-H}]^{-1}$$

This expression suggests a bimolecular mechanism of the primary photochemical reaction. The essential role played mostly by the proton-donating capacity of the medium in this process is best illustrated by comparison of the rates of photolysis of e.g. p-chloro-N,N-dimethylaniline in methanol and in aprotic medium of equal or higher polarity, such as DMSO or DMF. In these media Φ_{HCl} is 0.93; 0.44 and 0.45 respectively.

Pyridine and its N-methyl derivatives quench the fluorescence of the amines. In aprotic solvents, quenching of the fluorescence of the amines by the mentioned proton acceptors is accompanied by a decrease in the quantum yield of photolysis.

CLTIN CRYSTAL CONFORMATION AND POSSIBILITY OF PROTON TRANSFER REACTION

Aleksandra Lewanowicz

Instytute of Organic and Physical Chemistry,
Technical University of Wrocław, Wybrzeże Wyspiańskiego 27
57-100 Wrocław, Poland

2-(2'-hydroxy-5'-methylphenyl)-5-chlorobenzotriazole molecule (ClTIN) belongs to the class of compounds which are widely used as a substances protecting polymers against the destructiveness of the UV light. The proton transfer reaction plays a crucial role in this mechanism. After excitation, in solid state and in non-polar frozen matrices, ClTIN emits red fluorescence only, typical for the proton transfer form (λ = 630 nm).

Here we discuss a relation between the conformation of ClTIN and ability of proton transfer reaction depending on environment and temperature.

X-ray analysis of ClTIN at room temperature was carried out as well as a least-square analysis of the rigid-body motion and mean square displacement amplitudes of pairs of bonded non-hydrogen atoms were calculated.

It is evident that the ClTIN molecule is almost planar: the angle between benzotriazole and cresol moieties equals 1°, the length of the single bond between these fragments is r (C-N) = 1.433 Å and *cis*-isomer of ClTIN is dominating in the solid state. However, both isomers (rotamers) are prerequisite for the efective conversion into O...H-N tautomeric form. In hydrogen bridge r (O-H) bond length is 1.149 Å; the O...N and H...N interatomic distances are equal 2.62 Å and 1.72 Å, respectively.

A TLS thermal vibration analysis on non-hydrpgen atoms including internal torsion indicate rigid-body behaviour for cresol and benzotriazole fragments of the molecule. This is confirmed by the rigid bond test.

Dynamic Quenching Measurements in Times Shorter than 200ps on the Example of S_2-xanthione-S_0-3,3-diethylpentane System in Perfluoroalkane Solvent

Wł.Augustyniak, M.Fidecka, A.Maciejewski, M.Sikorski,
R.P.Steer[a], *M.Szymański,*
A.Mickiewicz University, Poznan, Poland
and [a]University of Saskatchewan, Saskatoon, Canada

Investigations of excited state quenching processes at short times (<1ns) provide important information on the dynamics of intermolecular interactions. At such short times the quenching rates are time dependent, and the decay of emission in the presence of a quencher is nonexponential.

We have used S_2-xanthione with a lifetime in perfluoroalkanes of 177 ps as a donor, "spherical" 3,3-diethylpentane as a quencher and perfluoroalkanes as solvents. The emission decay measurements were performed with a picosecond laser excitation (MCP-PMT) single photon counting detection system having an instrument response function of ca. 40 ps FWHM.

The decay of the donor emission in the presence of a quencher was described by the "all" function of the Smoluchowski-Collins-Kimbal (SCK) model. The results of dynamic quenching were compared with those from in steady-state measurements. The values of D, R and k_r determined with the SCK model are consistent with the nature of the interactions between S_2-XT and S_0-DEP and the mechanism of S_2-thione quenching. For the system studied we have obtained, for the first time, statistically significant differences (expressed e.g. in the χ^2 values), between the decay predicted by the SCK model and that of a one-exponential function for which the fit was poor.

Acknowledgements
This work has been supported by Polish State Committee for Scientific Research (grant No 2 2617 91 02) and by Natural Science and Engineering Research Council of Canada.

ELECTRON TRANSFER PROCESSES IN THE QUENCHING OF BENZOPHENONE TRIPLET STATE BY SULFUR-CONTAINING AMINOACIDS. LASER FLASH PHOTOLYSIS AND PULSE RADIOLYSIS STUDIES

Bronislaw Marciniak[a], Krzysztof Bobrowski, Gordon L. Hug
Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556, USA

The knowledge of the mechanism for the quenching of excited triplet states of aromatic ketones by sulfur-containing aminoacids is of importance to the understanding of electron transfer processes in more complex systems, e.g. sulfur-containing peptides and proteins. Furthermore, excited carbonyl compounds have been produced "in vivo", and hence their reactions with sulfur-containing aminoacids are particularly relevant due to the role that these reactions may have in the migration of electrons over long distances through the peptides and protein matrix.

In this study the mechanism of benzophenone sensitized photooxidation of sulfur-containing aminoacids with different numbers of terminal functions, COOH and NH_2, and with the varying relative locations of the groups with the respect to the sulfur atom has been examined in aqueous solutions at pH=6.8 using the laser flash photolysis technique. Electron transfer from the sulfur atom to the triplet state of benzophenone, followed by protonation of ketyl radical anion to form ketyl radical (fast component), was shown to be a primary photochemical reaction. This was established by noting the large values of quenching rate constants (k_q $10^8 - 10^9$ M^{-1} s^{-1}, dependent on the nature of the aminoacid), by direct observation of the intermolecular S∴S bonded radical cations, and by correlations of k_q (obtained for particular aminoacids) with $-E_T - E_{red}$ values for various substituted benzophenones. The latter results enabled us to estimate transmission coefficients and intrinsic barrier parameters for the electron transfer process studied.

Secondary reactions following photoinduced electron transfer were analyzed in detail with collaborative evidence supplied by pulse radiolytic generation of appropriate intermediates. A slow process of formation of ketyl radical, occurring on the microsecond time scale, was assigned to the one-electron reduction of benzophenone ground state by the α-aminoalkyl-type of radicals, that were produced as a result of intramolecular electron transfer from the carboxyl group to sulfur-centered radical cation followed by decarboxylation. Further evidence to support this reaction scheme was provided by the observation of a linear dependence of pseudo-first order rate constants for the slow process of ketyl radical formation on benzophenone ground state concentration and by the generation of the appropriate α-aminoalkyl-type radicals and kinetic studies in complementary pulse radiolysis experiments.

This study allow us to present detailed quantitative description of all primary and secondary electron transfer processes occurring in the investigated system.

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[a] Fulbright Scholar, on leave from Faculty of Chemistry, A.Mickiewicz University, Poznan, Poland.

PHOSPHORESCENCE EMISSION AND POLARIZATION OF 3-CARBOXYQUINOLINE

F. Márquez, I. Zabala and F. Tomás

Departament de Quimica Fisica. Universitat de Valencia.
Dr. Moliner 50, 46100- Burjassot, Valencia (Spain)

The purpose of this paper is to investigate the phosphorescence polarization and phosphorescence lifetime of 3-carboxyquinoline in ethanol and methylcyclo hexane glasses at 77 K in order to assign the symmetry of the lowest excited triplet state and to demonstrate the extent to which various optical criteria are affected by the breakdown of the Born-Oppenheimer approximation due to the "proximity effect".

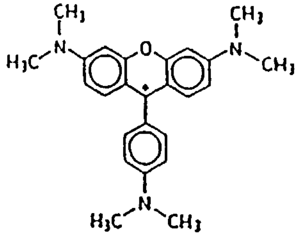
The phosphorescence properties of 3-carboxyquinoline, like those of 3-bromoquinoline fail to conform to eiher a pure $^3\pi\pi^*$ or $^3n\pi^*$ assignment for the lowest excited triplet state according to standard spectroscopic criteria. Although the shift in the phosphorescence spectrum by the solvent effect and the short phosphorescence lifetimes might point to an $^3n\pi^*$ triplet state, the polarization results point to an $^3\pi\pi^*$ state. This visibly contradictory behavior, is very similar those previously observed in 3-bromoquinoline. Normally, the polarization results in the characterizing an excited state are stronger criteria than others (like polarity effect and lifetime emission) and so, possibly, the emitting state of phosphorescence is of $^3\pi\pi^*$ nature. The phosphorescence spectrum of 3-carboxyquinoline shows several features which arise from strong perturbations of the lowest $^3\pi\pi^*$ state by the higher-lying $^3n\pi^*$ state.

Evidence for a TICT-like State in Amino-Rhodamine by Ultrafast Spectroscopy

M. Martin, P. Plaza, N. Dai Hung, Y.H. Meyer *
M. Vogel, W. Rettig **

*Laboratoire de Photophysique Moléculaire du CNRS, Bât 213, Univ. Paris-Sud 91405, Orsay, France
**Iwan-N.-Stranski Inst., Techn. Univ. Berlin, Strasse des 17 Juni 112, 1000 Berlin 12, Germany

Intramolecular relaxation towards a low lying non emissive TICT- like state was invoked to explain the low fluorescence quantum yield of amino-Rhodamine (ARh) in neutral ethanol. The fluorescence yield increases by more than two orders of magnitude in acidic ethanol solutions, where the electron donating property of the anilino group is blocked by protonation [1].



In the present communication, we report a study of the time-resolved absorption and gain spectroscopy of Amino-Rhodamine in neutral and acidic ethanol, by the pump-probe technique with subpicosecond resolution, as well as stationary and time resolved fluorescence measurements. In order to study the rôle of internal charge transfer and conformational relaxation, solvent properties such as viscosity and static dielectric constant are also examined.

The time resolved changes in optical density of a solution of ARh in neutral ethanol, observed in the 380-640 nm range, after excitation with ~ 0.5 ps pulses at 550 nm evidence a fast change in shape of the 380 - 470 nm transient absorption band within 5 ps after excitation simultaneously with a fast decrease in the gain signal above 580 nm. The transient spectra recorded for the fluorescent protonated-ARh under similar conditions do not show these fast changes. In decanol and dioxan the spectral changes occur with slower rates. Streak camera measurements confirm that the ARh fluorescence lifetime is slowed down when the solvent is changed from ethanol to dioxan and from dioxan to decanol.

The results give evidence for the formation of a transient state from the first excited state of the Amino-Rhodamine dye at a solvent viscosity and polarity dependent rate. This transient state is not observed for the corresponding protonated dye, showing that the electron donating property of the aniline-substituent is involved in the process. These results support the interpretation [1] of the formation of a non-emissive TICT-like state to explain the fluorescence quenching of this class of compounds.

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Heterogenous Photocatalysis: Semiconductor Mediated Hydrogen Isotope Exchange Reaction in *o*-Alkyl Substituted Phenyl Ketones

Jacek Michalak and Jerzy Gębicki

Institue of Applied Radiation Chemistry,
Technical University, 90-924 Lodz, Poland

Hydrogen isotope exchange reaction between *o*-alkyl substituted phenyl ketones (*o*-methylacetophenone, *o*-methylbenzophenone and 5,8-dimethyl-1-tetralone) and alcohols (methanol and isopropanol) labelled with deuterium or tritium in the hydroxy group mediated by illuminated semiconductor (CdS, TiO_2 and ZnO) powders has been studied.

Deuterated or tritiated ketones separated from the reaction mixture by thin-layer chromatography have been analyzed by mass spectrometry or liquid scintillation counting, respectively. Mass spectrometric analysis showed incorporation of deuterium atoms exclusively to the *o*-alkyl group of the ketones.

It has been found that the yield of isotope exchange reaction correlates well with the amount of ketone adsorbed on the semiconductor surface. Electron donor (1,3,5-trimetoxybenzene) or electron acceptor (tetrabromomethane) added to the studied system has been found to affect the reaction yield.

Reaction mechanism involving participation of the ketone radical cations spontaneously tautomerizing to the enol radical cations has been proposed.

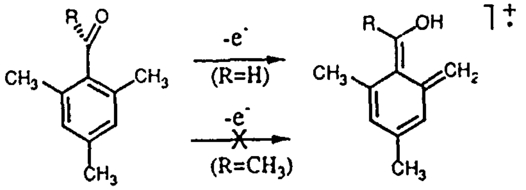
Spectroscopic Properties of Neutral and Ionized Dienols Generated Photochemically and Radiolytically from Matrix-isolated 2,4,6-Trimethylbenzaldehyde

Jacek Michalak[1,2], Jacek Rogowski[1], Thomas Bally[2]
and Jerzy Gębicki[1]

[1] *Institute of Applied Radiation Chemistry,*
Technical University, 90-924 Lodz, Poland
[2] *Institute of Physical Chemistry, University of Fribourg,*
CH-1700 Fribourg, Switzerland

Upon irradiation (λ = 290 or 313 nm) of 2,4,6-trimethylbenzaldehyde (**1**) isolated in nitrogen and argon matrices the corresponding dienol was stabilized and characterized by the UV-VIS-IR absorption spectroscopy. Further irradiation (λ = 365 nm) gave propely substituted benzocyclobutenol along with partial re-formation of the starting material.

Upon radiolytic ionization (X-ray) of **1** isolated in an argon matrix the radical cation in the keto-form was generated which spontaneously tautomerized to form the enol radical cation. On the other hand, 2,4,6-trimethylacetophenone (**2**) showed no enolization upon ionization.



1 R = H
2 R = CH_3

The O-H stretching vibration of the ionized enol of **1** is observed at lower frequency as compared to the O-H stretching of the neutral enol (ν = 110 cm^{-1}). The relative conformer distribution of enol radical cation of **1** could be changed by photolysis with visible light.

Kinetics of enolization process of $1^{\bullet +}$ has been monitored by the low-temperature pulse radiolysis.

Dynamics of Electron-transfer in the Excited CT Complexes of the Fullerenes, C_{60} and C_{70}: A Picosecond Laser Flash Photolysis Study

D.K. Palit, H.N. Ghosh, H. Pal, A.V. Sapre, J.P. Mittal
Chemistry Division, Bhabha Atomic Research Centre
Trombay, Bombay 400 085, India

Ram Seshadri and C.N.R Rao
Solid State & Structural Chemistry Unit and
CSIR Centre of Excellence in Chemistry
Indian Institute of Science
Bangalore 560 012, India

Abstract

Both C_{60} and C_{70} form ground-state charge-transfer complexes in benzene solution with aliphatic and aromatic amines having favourable oxidation potentials. Picosecond time-resolved absorption measurements show that on photoexcitation, the CT complexes undergo charge separation to produce ion-pairs which in turn undergo fast geminate recombination either to produce the triplet state of fullerenes or give back the ground state of the complex, depending on the oxidation potential of the amine. Free-ion yield is found to be generally negligible.

TRIPLET STATES OF ANTHRACENE - ACRIDINE MIXED CRYSTALS

O. Morawski and J. Prochorow

Institute of Physics, Polish Academy of Sciences
Al.Lotników 32/46, 02-668 Warsaw, Poland

In this work the results of investigations of the triplet states of anthracene-acridine mixed crystals are presented as a natural extension of our earlier studies of singlet states of these crystals [1], which have shown that singlet traps form two distinctly different groups: ofshallow (depth to 500 cm^{-1}) and of deep (of ca.1000 cm^{-1}) traps. The first group of traps have been assigned to anthracene X-traps and the second to acridine aggregates.

In the present work, a phosphorescence was observed at low temperatures, with the intensity increasing upon increase of acridine concentration in the crystal. However, in all crystals, phosphorescence spectrum is the same - it is emitted from anthracene traps (in accordance with the fact that T_1 triplet state of anthracene is the lowest triplet state in these mixed crystals, the energy of acridine T_1 state being of ca. 1000 cm^{-1} higher). Furthermore, the phosphorescence excitation spectra, at 1.7 K, reveal that intensity of phosphorescence is one order of magnitude stronger when the excitation is tuned directly to singlet traps, than when it is tuned to the anthracene singlet excitonic band.

This can only be accounted for if one assumes that processes which control a population flow to the lowest triplet state are much stronger within the trap sites. Since, acridine molecules are characterized by a very efficient intersystem crossing [2], this may indicate that, contrary to our previous assignement [1], the acridine monomer levels are located below singlet excitonic band of the host crystal and may form shallow traps together with previously identified anthracene X traps [1].

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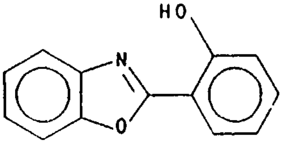
EXCITED STATE PROTON TRANSFER STUDIED BY VIBRATIONAL SPECTROSCOPY

L. Adamowicz[a], F. Langkilde[b], A. Leś[a,c], A. Mordziński[d], R. Wilbrandt[e]

(a) Department of Chemistry, University of Arizona, Tucson, AZ 85721, USA
(b) Department of General Chemistry, Royal Danish School of Pharmacy, 2 Universitetparken, DK-2100, Denmark
(c) Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland
(d) Institute of Physical Chemistry, Polish Academy of Sciences, 44 Kasprzaka, 01-224 Warsaw, Poland
(e) Department of Environmental Science and Technology, Riso National Laboratory, DK-4000 Roskilde, Denmark

Vibrational spectroscopy and quantum chemical calculations were applied for the study of two molecules undergoing the excited state intramolecular proton transfer (PT). Fourier transform (FT) Raman spectra of I and II in the electronic ground state, and the corresponding time resolved resonance Raman (TRRR) spectra in the excited triplet state were obtained. The intensities as well as frequencies of the vibrational transitions are reproduced by the ab-initio calculations at SCF level with the 3-21 G and 6-31 G** basis sets. Theoretical calculations together with experimental data allow us to identify the most stable tautomeric forms in the ground as well as in the excited states. The structural changes following the proton transfer in the excited state are stated and will be discussed.



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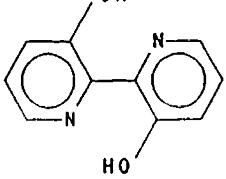

II

TRANSIENT KINETICS OF CHARGE SEPARATION IN SOLUTIONS

Jan Najbar
Faculty of Chemistry, Jagiellonian University
3 Ingardena, 30-060 Kraków, Poland

The photochemical reactions of many dyes and photobiological systems involve both the large amplitude changes in the internal coordinates as well as substantial outer sphere reorganizations of the solvent [1,2]. However, for rigid molecular systems having polar excited states of the CT character in polar solvents the major contribution to the reaction coordinate is connected with the solvation of the reactants and products.

Kinetics of transient populations of the locally excited state and CT states produced due to reversible outer sphere electron transfer processes in asymmetrical multidimensional systems, e.g. Donor(1)-Acceptor-Donor(2), Acceptor(1)-Donor-Acceptor(2) in liquid solutions is presented. Special case of symmetrical three surface problem of the electron transfer kinetics is also considered. The theoretical approach is based on the Zusman type of kinetic equations [3,4] and applies to adiabatic and nonadiabatic electron transfer processes. The solution for the models are given in the Laplace domain and Stehfest algorithm is used for numerical inverse Laplace transformation [4,5]. The calculations demonstrating the influence of the dielectric relaxation properties of the solvent (for Debye and non-Debye solvents) on the transient populations of CT states are presented.

The advantage of the present approach is that it allows for more direct interpretation of the influence of different factors on the electron transfer rates. The comparisons of the time scales for the electron transfer in polar solvents and dynamics of the solvent shifts of fluorescent probes can be carried out conveniently in terms of the wave packet propagation function for the polarization coordinate. The problems of the correlation between electron transfer rates and solvation dynamics for different models are discussed. The differences resulting from the fact that the electron transfer in adiabatic limit is govern by dynamics of the reaction coordinate on two potential energy surfaces whereas solvation shifts are interpreted usually as precesses occuring on the single potential surface are evaluated The dynamics on three surfaces with different force constants is more complex and shows more complicated dependence on the reaction exothermicity. The central quantities in the theory of the multistep electron transfer processes are the solvent time scale functions characterizing the influence of the dielectric friction on the couplings between charge separation and subsequent recombination.

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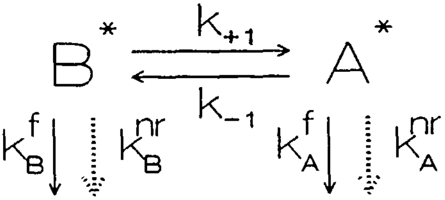
A stochastic model for dual fluorescence of DMABN in polar media.

Pier Luigi Nordio and Antonino Polimeno
Department of Physical Chemistry, University of Padua, via Loredan 2
35131 Padova, Italy

The dual fluorescence of N,N-dimethylaminobenzonitrile (DMABN) and other related aromatic donor-acceptor compounds has been successfully interpreted in its main features by the kinetic scheme first proposed by Grabowski et al. [1]:



The static and dynamic fluorescence emission spectra are strongly affected by polar solvents, due to the influence of electrostatic interactions on the interconversion rates between the two metastable states A^* and B^*.

In this communication we present a stochastic model intended to reproduce the kinetic scheme given above, in terms of the adiabatic potential surface which defines the excited singlet state, and the physical properties of the solvent medium. The dynamics of interconversion between the two metastable states is described as a diffusional process coupled to a solvent coordinate, which is treated as the stochastic equivalent of the static reaction field, according to Onsager-Debye models [2].

The potential surfaces for the ground and excited state are defined as a combination of energy functions calculated *ab initio* [3] for the isolated molecule plus a simple stabilization term generated by the polar solvent. Phenomenological expressions for radiative and non-radiative decay rates [4] are explicitly introduced in the multidimensional diffusion equation, giving rise to a sink term.

The method provides a derivation of the interconversion kinetic constants from first principles, and it is able to predict, by using a reduced number of experimental parameters, the relevant aspects of both static and dynamic fluorescence emission.

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Influence of Steric Effects on the Formation of Charge Transfer States in 4-N,N-dimethylaminobenzonitrile Derivatives. A CS-INDO Study.

Ivan Baraldi and Wieslaw Nowak

Dipartimento di Chimica, Universita di Modena,
Via Campi 183, 41100 Modena, Italy

Instytut Fizyki UMK
ul.Grudziadzka 5
87100 Torun, Poland

Photophysics of the 4-N,N-dimethylaminobenzonitrile (DMABN) has been a subject of numerous studies , the most discussed is the problem of the origin of the dual fluorescence of this molecule [1]. Important arguments, supporting Twisted Molecular Charge Transfer (TICT) model of Grabowski et. al. [2] come from spectral studies of model compounds with hindered rotation of the dimethylamino group. Although electronic transitions in some of these compounds have been recently obtained by INDO/S method [3], the detailed shapes of potential energy curves, crucial in an interpretation of the experiments, are not known

In the paper we present results of calculations by the CS-INDO S-CI and D-CI methods [4] on DMABN and its two sterically hindered derivatives: 3-methyl-4-N,N-dimethylaminobenzonitrile (3-MeDMABN) and 3,5-dimethyl-4-N,N-dimethylaminobenzonitrile (3,5-DiMeDMABN) This approach have been useful in the explanation of steric effects in fluorescence spectra of large organic molecules [5].

For DMABN, in both approximations, potential energy curves of two lowest excited singlet and triplet states exhibit maxima for the perpendicular arrangment of the dimethylamino group. Along the torsional coordinate a crossing of two lowest singlet states is present, and the TICT state is the lowest excited singlet

No such crossing in 3-MeDMABN and 3,5-DiMeDMABN have been found using CS-INDO S-CI method The ground state potential energy of 3-MeDMABN shows the minimum at $\phi = 0$ while for 3,5-DiMeDMABN the minimum is at $\phi = 90$. In the lowest excited states 3-MeDMABN is predicted to be planar, in contrast to 3,5-DiMeDMABN where for S_1 and S_2 twist angles of 50° and 40 have been respectively obtained.

This research was supported by the Polish Ministry of National Education within project CPBP 01.06 2.03. and Consiglio Nazionale delle Ricerche (Roma) and C.I.C.A.I.A. (Universiata di Modena). W N. wishes to acknowledge grant GM1905 and equipment grant RR04884 from the NIH for partial support.

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Picosecond–Femtosecond Dynamics of TICT State Formation of DMABN and Related Compounds in Alkanenitriles and Alcohols

Tadashi Okada
Department of Chemistry, Faculty of Engineering Science and Research Center for Extreme Materials, Osaka University, Toyonaka, Osaka 560, Japan

In order to elucidate the mechanisms of the solvent-induced change of the electronic structure in the excited state of 4-(N,N-dimethylamino)benzonitrile(DMABN) and related compounds, femtosecond laser photolysis studies of solvent effects upon transient absorption spectra and their time dependences at room temperature have been carried out.

The time dependences of the transient absorption spectra of DMABN in acetonitrile have been analyzed as a superposition of the absorption spectrum of the relaxed excited state of DMABN in non-polar solvent (cyclohexane) and that in polar solvent (acetonitrile). The obtained charge transfer (CT) time is about 4ps which is much longer than the longitudinal dielectric relaxation time of solvent, 0.2ps, while the CT time in viscous polar solvents such as 1-pentanol agreed with the solvent relaxation time [1].

According to a theoretical study on the mechanisms of CT state formation of DMABN in an aqueous solution, the shape of free energy curve of S_2 state (TICT state) is far from a parabolic form along the solvation coordinate and the torsional coordinate around the phenyl and dimethylamino groups is required to reach the transition state region of CT state formation reaction [2].

When the intramolecular rotational barrier of the amino group is very small, the torsional motion will be faster than the reorientational motion of the viscous alcoholic solvent. In such a case, the torsional angle between amino and phenyl groups will be adjusted so as to minimize the free energy including the solvent orientation at the moment, leading to give the solvent controlled CT time. When the torsional motion and solvent diffusional motion are comparable, the dynamics of the CT state formation may be complicated because the degree of the charge transfer in the excited DMABN depends directly on the torsional angle.

The mechanisms and dynamics of CT state formation in the excited state of DMABN compared with the results for the more rigid structured compounds such as CBQ and 2-methylDMABN will be presented and discussed in terms of the relation between diffusional motion of the solvent molecules and the rotational diffusion of the amino group.

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MANIFESTATION OF HYDROGEN BONDING IN 1,10-PYRIMIDINOANTHRONE DERIVATIVES

A. Olszowski, W. Grygiel
Institute of Organic and Physical Chemistry, Technical University, Wrocław, Poland

4-hyroxy-1,9-pyrimidinanthrone-10 (4hPA) belongs to the group of organic dyes exhibiting relatively high photochemical stability and the presence of proton donor and proton acceptor groups in the molecule permits the formation of intra- or intermolecular hydrogen bonds. Photophysical properties of 4hPA were investigated in different solvents by absorption and fluorescence spectroscopy at both ambient and lower temperatures (77 K).

The solvent polarity dependence of absorption and fluorescence spectra at room temperature suggests that the emitting state is of the $\pi\pi^*$ type. Small bathochromic and Stokes shifts of measured spectra indicate a minimal change of dipole moment and molecular geometry of 4hPA upon excitation. Fluorescence lifetimes (2.5 ns) and quantum yields (0.01-0.02) were found to be relatively independent of solvent polarity.

The spectral properties of frozen 4hPA at low temperatures were very solvent sensitive. A significant increase in fluorescence intensity was observed only in chloroform at 93 K. Phosphorescence appeared on the red side of fluorescence in hexane, carbon tetrachloride, acetone, methanol and pyridine matrices. Total lack of fluorescence and only orange phosphorescence emission was found for 4hPA frozen in acetonitrile.

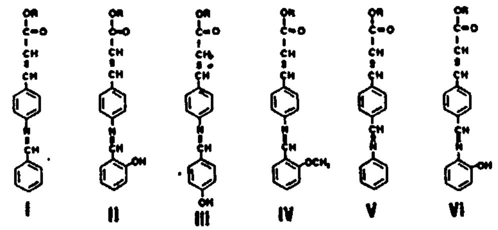
The explanation of the observed phenomena was given in terms of competition between formation of intra- vs. intermolecular hydrogen bonds and the influence of solvent polarity on the mutual location of $n\pi^*$ and $\pi\pi^*$ states in the singlet and triplet manifolds.

Triple Fluorescence in 4-N-(2-hydroxybenzylidene) cinnamate.

Maria Toczek, Jerzy Pączkowski*
Department of Chemistry and Chemical Engineering, Sminaryjna 3, 85-326
Bydgoszcz, Poland
Danuta Jeziorek, Wiesław Woźnicki
Institute of Physics, Nicholas Copernicus University, Gagarina 5, 80-107 Torun,
Poland

A comparative study is presented of the unusual triplet competitive fluorescence in 4-N-(2-hydroxybezylidene) cinnamate. The structures of 4-N-(benzylidene)cinnamates, 4-N-(hydroxybenzylidene)cinnamates and N-(4- acrylbenzylidene)anilines are shown in Fig. 1.

Figure 1



where: R = H or Butyl.

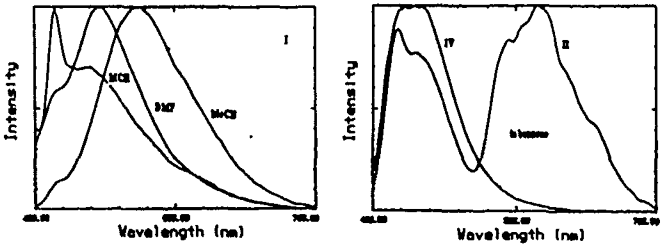
The ground states properties of molecules tested were characterized both by the electronic absorption spectra measurements and quantum mechanical calculations (MNDO method). Results are summarized in Table.

Table I The ground state properties of tested molecules

molecule	abs. λ_{max} [nm]	ε [mol^{-1}l^{-1}] x 10^{-4}	ΔH of form. [kcal·mol^{-1}]	Total enrgy [eV]	μ_g [D]
I	338	3.22	-7.096	-3079.42	2.86
II	357	2.50	-54.86	-3401.94	4.61
III	344	2.98	-54.66	-3401.93	3.46
IV	351	2.98	—	—	—
V	334	8.07	-6.95	-3079.41	2.46
VI	334, 368	0.382, 0.444	-54.66	-3401.93	3.46

The steady-state fluorescence spectra, in contrast to Heldt's and Kasha's results[1,2], gives for II a simple resolution of three distinctive fluorescences originating from three various structures of the singlet excited state (see Fig. 2). The fluorescence observed at the shortest wavelength originates from the normal locally exited state. The second emission band is related to the emission from TICT state formed by the twist of cinnamate residue (Fl. λ_{max} is solvent polarity dependent). The third long-wavelength emission originates from the proton-transfer tautomer emission.

Figure 2



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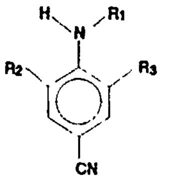
Unusual Hindrance of TICT State Formation in Strongly Alkaline Solutions.

K. Rotkiewicz[1], G. Köhler[2] and Z.R. Grabowski[1]
[1]Institute of Physical Chemistry, Polish Academy of Sciences,
Kasprzaka 44, 01-224 Warsaw, Poland and
[2]Institut für theoretische Chemie und Strahlenchemie, University of Vienna,
Währingerstr. 38, A-1090 Vienna, Austria.

Fluorescence spectra and decay times were measured for some methylated 4-aminobenzonitrile (ABN) derivatives (scheme 1) in strongly alkaline solutions:



Scheme 1:
ABN: R_1, R_2, R_3 = H
3-MMABN: R_1, R_2 = CH_3, R_3 = H
MABN: R_1 = CH_3, R_2, R_3 = H
3,5-DMABN: R_1 = H, R_2, R_3 = CH3

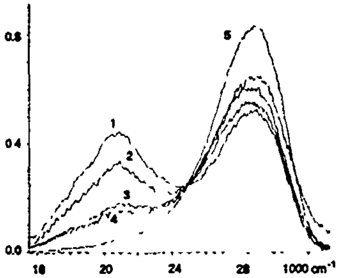


Figure. 1: 3-MMABN in H_2O (1) and plus 0.17, 0.5, 1.0, and 4.1 M NaOH (2 - 5).

Fluorescence quenching was observed for MABN in strongly alkaline solutions (up to 5N NaOH), whereas the emission yield for 3,5-DMABN increases approximately twofold under the same conditions.

Dual fluorescence due to conversion to the TICT state after excitation is only observed for 3-MMABN in polar solvents. This was shown previously[1]. In this case increased NaOH concentration causes:

i) no quenching of primary or TICT state fluorescence,
ii) hindrance of the relaxation from the primarily excited state to the TICT state (appearance of an iso-emissive point in the spectra, fig. 1).

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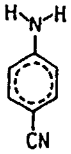
THE TICT EXCITED STATE OF SECONDARY AROMATIC AMINES

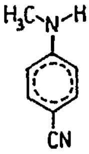
Krystyna Rotkiewicz(1) and Wolfgang Rettig(2)

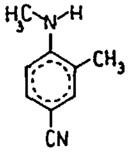
(1)Institute of Physical Chemistry, Polish Academy of Sciences
Kasprzaka 44, 01-224 Warsaw, Poland
(2)Iwan-N.-Stranski-Institute for Physical and Theoretical Chemistry, Technical University of Berlin
Strasse des 17. Juni 112, D-1000 Berlin-12, Germany

The fluorescence spectra, quantum yields and lifetimes of 4-(methylamino)benzonitrile (MABN), its 3-methylated derivative (3-MMABN) and of 4-(amino)benzonitrile (ABN) were measured and disscused. Only 3-MMABN shows dual fluorescence.

On the basis of the analysis of the values of radiative as well as nonradiative rate constants the long wave anomalous band is assigned to the TICT state (this band is of forbidden nature).


ABN


MABN


3-MMABN

The experimental evidence for the TICT state formation in the case of 3-MMABN and the lack of this process in the case of MABN (the energetic conditions for the relaxation to the TICT state are fulfilled for both compounds) is explained. The explanation is based on the considerations of: i)energetic separation of the ^1L_b and ^1L_a states, ii)existence of two sterically hindered ground state conformers for 3-MMABN, iii)results of force field calculations.

PHOTOPHYSICALLY RELEVANT AB INITIO POTENTIAL ENERGY FUNCTIONS OF BENZENE AND PYRAZINE

Andrzej L. Sobolewski
Institute of Physics, Polish Academy of Sciences,
02-668 Warsaw, Poland.

Clemens Woywod and Wolfgang Domcke
Institute of Physical and Theoretical Chemistry,
Technical University of Munich,
8046 Garching, Germany.

The adiabatic potential energy surfaces of the ground and the excited electronic configurations are the most crucial entities in the theoretical description of intramolecular radiationless decay of excited molecules. The non-adiabatic interactions that govern this phenomenon are particularly strong when the potential energy surfaces closely approach or intersect each other.

In this contribution we present the results of ab initio complete-active-space (CAS) self-consistent-field (SCF) and contracted-configuration-interaction (CCI) calculations of the potential energy functions of the lowest (singlet and triplet) valence states of benzene and pyrazine along the reaction path to the biradical prefulvenic form.

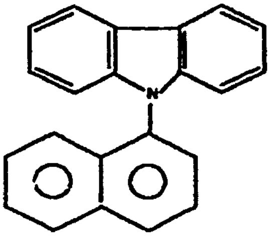
It has been found that the lowest $\pi\pi^*$ singlet states, $S_1(B_{2u})$ of benzene and $S_2(B_{2u})$ of pyrazine, cross with the ground state near saddle point for the isomerization reaction. A similar behavior was also found for the triplet manifold. Here, however, the higher states, $T_2(E_{1u})$ and $T_3(B_{2u})$, in benzene and pyrazine, respectively, are relevant. The orbital nature of the effect and its consequences for intramolecular radiationless dynamics are discussed.

ELECTRON TRANSFER PHOTOCHEMISTRY INITIATED FROM A TWISTED INTRAMOLECULAR CHARGE TRANSFER STATE USED AS AN ELECTRON DONOR AND AS AN ACCEPTOR.

J.L. HABIB JIWAN, J.Ph. SOUMILLION*

Laboratory of Physical Organic Chemistry and Photochemistry, Catholic University Louvain, Place Louis Pasteur, 1, B1348 Louvain-la-Neuve, Belgium.

The photochemical reactivity of N-(α-Naphtyl)-Carbazole (NC) in polar solvent is reported. The photophysical properties of this compound were already studied and the occurence of a TICT state has been shown in the literature (1).



NC

In this work, the feasibility of electron transfer reaction starting from the NC TICT state is demonstrated. This is evidenced on one hand by TICT fluorescence quenching measurements and confirmed on the other hand by photoinduced chemical reactions.
The rate constants obtained by the quenching experiments were correlated with the thermodynamics of the electron transfer by the Marcus theory.
The reactivity of the two moieties of the NC TICT state were tested by two reactions :

- the isomerization of quadricyclane in norbornadiene sensitized by the radical-cation moiety
- the dechlorination of pentachlorobenzene sensitized by the radical-anion moiety.

The ring-closure of norbornadiene in quadricyclane sensitized by a triplet state of NC is also demonstrated.

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EXCITED STATE PROTON TRANSFER IN SOME PYRIDINE DERIVATIVES

A. C. Testa
Department of Chemistry
St. John's University
Jamaica, New York 11439 (U.S.A.)

Abstract

With the aim of elucidating factors controlling molecular luminescence we have undertaken a comparative study of the luminescence of some pyridine derivatives, which exhibit an unexpected solvent behavior. The systems investigated include i) comparison of 2-methoxypyridine with 2-pyridone, and ii) comparison of phenylpyridines with benzylpyridines. Results coupled with semi-empirical CNDO/S calculations indicate the involvement of hydrogen bonded dimers for 2-pyridone and the excited state proton transfer in the case of phenylpyridines. Analysis of the absorption and emission data also provide evidence of geometrical changes in the excited state. CNDO/S predicts the inversion of close lying n,π and π,π states for the molecules investigated. Fluorescence and phosphorescence data will be presented and discussed together with the results of CNDO/S calculations for 2-pyridone and 4-phenylpyridine.

ORIENTATION AND REACTIVITY OF PHOTOCHROMIC PROBES: AZOBENZENE AND STILBENE MOLECULES IN PE.

P. Uznański, M. Kryszewski
Center of Molecular and Macromolecular Studies, Polish Academy of Science, 90-363 Łódź, Sienkiewicza 112, Poland.

We have examined matrix orientational effect on the photoconversion of trans-azobenzene (trans-Ab) and trans-stilbene (trans-St) molecules in anisotropic polyethylene (PE). The linear dichroism (LD) spectroscopic and kinetic studies of the photoisomerization of the title compounds have yielded an information on the alignment and reactivity of reactant and products in stretched PE. The method which uses photochromic molecules can probe the changes that occur to the size and shape of local sites when polymer is stretched.

The main deactivation pathways of excited trans-Ab isomer in PE is trans->cis photoisomerization while for trans-St additionally fluorescence is observed. Excited cis-St isomer forms mostly dihydrophenanthrene (DHP). The UV/VIS and IR LD studies demonstrate high degree of alignment of trans isomers and low degree of alignment of cis products. The trans->cis photoisomerization of Ab and St was measured in polarized light with electric vectors parallel and perpendicular to the uniaxially stretched polyethylene sample. Orientation of PE increases the ability for isomerization of both probes. The results indicate that, although the macroscopic stretching of the PE film alters the distribution of the site size, however the rate of phototransformation is faster in the stretched sample than in unstretched one.

MOLECULAR RELAXATION SPECTROSCOPY OF FLAVINS

A.J.W.G. Visser and N.V. Shcherbatska
Department of Biochemistry
Agricultural University
Wageningen, The Netherlands

In order to understand the exact functional properties of flavoproteins it is important to have knowledge about the dynamical structure of this class of proteins. The flavin prosthetic group is a natural fluorescent reporter group which can probe the dynamical structure of the active site of flavoproteins. As a model compound for studying dynamical behaviour 3-methyllumiflavin in propylene glycol was chosen. In this relatively polar system spectral and dynamical features depending on inhomogeneous broadening can be expected. Steady-state fluorescence spectra as a function of temperature showed a progressive blue-shift of the center of gravity of the emission band at decreasing temperature when excitation was in the main absorption band. From these data and by application of Bakhshiev's theory of solvent relaxation, dipolar relaxation times of the flavin environment were determined in the temperature range of 203-303 K. This dipolar relaxation process was confirmed by time-resolved fluorescence experiments using main-band excitation and detection at the blue-edge of the fluorescence spectrum. Under these conditions a subnanosecond decay component was resolved indicative for the disappearance of the initially prepared, non-equilibrium state. The formation of the solvent-relaxed or equilibrium state could be monitored at the red-edge of the emission band. In agreement with expectations these spectral and kinetic effects disappeared when excitation was at the red-edge of the absorption band. These results may assist in interpreting flavoprotein fluorescence and therefore in elucidating the dynamical structure of the flavin site.

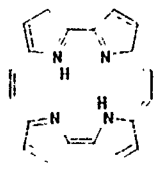
Distance dependence of excited state double proton transfer in porphycenes

Jacek Waluk[a] and Emanuel Vogel[b]

[a]Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44, 01-224 Warsaw, Poland;
[b]Institut für Organische Chemie der Universität Köln, Greinstrasse 4, D-5000 FRG.

Upon excitation, parent porphycene (1) and several of its alkyl derivatives (2-3) undergo fast intramolecular double proton transfer. This "narcissistic" process can be detected by inspecting the polarization of fluorescence excitation: the emission anisotropy remains low and constant upon excitation into differently polarized absorption bands [1].

The rapid rate of phototautomerization may be attributed to a small distance between the hydrogen-bonded nitrogen atoms (2.63 Å in 1, 2.53 Å in 2, 2.62 Å in 3). It may be expected that the elongation of this distance could lead to the reduction of the proton transfer rate. We checked this by studying the spectra of octaethylporphycene (4), in which the N...N distance equals 2.80 Å. Contrary to other porphycenes, fluorescence polarization of 4 varies for excitation to different electronic bands, attaining nearly theoretical values. Thus, excited state double proton transfer in porphycenes seems to be controlled by the N...N distance and cannot occur on a nanosecond time scale when the distance is increased to 2.80 Å.



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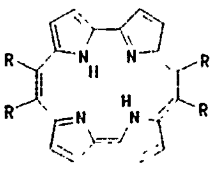
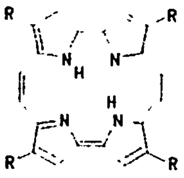
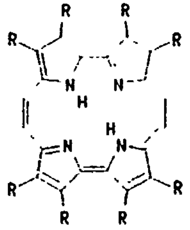


2 R = C_3H_7





3 R = C_3H_7

4 R = C_2H_5

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The Effect of Pressure on Charge Separation in Photosynthetic Bacterial Reaction Centers of *Rhodopseudomonas Viridis*

Neil L. Redline and Maurice Windsor
Department of Chemistry
Washington State University
Pullman, WA 99164-4630, USA

Abstract

Reaction centers of *Rhodopseudomonas Viridis* were studied at ambient pressure (0.1 MPa) and at three higher pressures, 120, 240, and 350 MPa using picosecond difference absorption spectroscopy. High pressure increased the rate of electron transfer from $P^{+}H_{L}^{-}Q_{A}$ to $P^{+}H_{L}Q_{A}^{-}$, measured by the decay of the transient optical absorption of H_{L}^{-} in the 650 - 700 nm wavelength range, from $(181 \pm 17\ \mathrm{ps})^{-1}$ at 0.1 MPa to $(127 \pm 16\ \mathrm{ps})^{-1}$ at 120 MPa. At 240 MPa the decay became biexponential with a fast $(198 \pm 66\mathrm{ps})^{-1}$ component of 33% amplitude and a slow component $(7.8 \pm 1.4\ \mathrm{ns})^{-1}$ of 67% amplitude. At 350 MPa the fast component was undetectable and only a slow exponential decay at $(4.1 \pm 0.3\ \mathrm{ns})^{-1}$ was observed.

The values for the fast component were also confirmed by measurement of the recovery of the absorption of H_L in the 545 - 550 nm region and for the slow components by studying the recovery of the absorption of P in the 851 - 865 nm region. The slow component is attributed to the charge recombination process $P^{+}H_{L}^{-}Q_{A} \rightarrow PH_{L}Q_{A}$.

Comparisons with charge separation in model systems such as bianthryl(1) will be made and the possible influence of the solvent medium and the role of TICT states involving aromatic protein residues(2) in the RC in mediating electron transfer will be discussed.

(1) H. Lueck, M.W. Windsor & W. Rettig. J. Phys. Chem. 94 (1990) 4550.
(2) H. Lueck, M.W. Windsor & W. Rettig. J. Luminescence 48 (1991) 425.

The support of NATO Grant CRG88054 is gratefully acknowledged.

Photoinduced Electron Transfer in
a Rigid Medium

Marian Wolszczak and Jerzy Kroh
Institute of Applied Radiation Chemistry
Technical University of Łódź
Łódź, Wróblewskiego 15, Poland

The quenching of several luminescence probes (tris (2,2'-bipyridine) ruthenium (II) - Ru $(bpy)_3^{2+}$, Ru $(bpy)_2(CN)_2$, pyrene) by electron transfer using ca twenty quenchers have been investigated by steady-state and time-resolved emission/absorption spectroscopy in the temperature range 6-298 K. The excited state of the probes was rapidly deactivated in bimolecular reactions with neutral or positively charged quenchers at room temperature, in both the oxidative and reductive processes, according to Stern-Volmer kinetics. For most of the anionic quenchers, there is evidence for ion-pairing with $Ru(bpy)_3^{2+}$ resulting in deviation of the Stern-Volmer plots.

In contrast, at low temperatures in glassy matrices (ethylene glycol-water, 1,5-pentadiol-water, 12 M LiCl) we failed to observe quenching even by the highly efficient quenchers.
The decay curves of the Ru $(bpy)_3^{2+}$ luminescence were found to deviate significantly from a single exponential decay, only in the presence of $[Fe(CN)_5NO]^{2-}$ and $S_2O_8^{2-}$ anions.
This latter observation was explained by electron-tunneling.

The Difference in the TICT Behaviour of Donor-Accptor-Biphenyls and Phenyl-Anthracenes

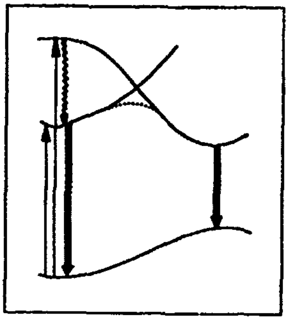
André M. Klock and Wolfgang Rettig

**I.N.Stranski-Institute, Techn. Univ. Berlin, Strasse des 17.
Juni 112, D-1000 Berlin 12, Germany**

Experiments are described which show that a twisting relaxation towards perpendicularity is unlikely for donor-acceptor-biphenyl derivatives in the excited state. This seems to exclude a TICT mechanism for these compounds. For the case of dimethylamino- and cyano-substituents, this behaviour is compared to that of the corresponding phenyl-anthracene derivative (CN-ADMA) which exhibits clear TICT behaviour [1]. Quantum chemical calculations show that there are major differences in the angular dependence of transition and dipole moments. These results serve as a basis for discussion.

[1] W. Baumann, B.Schwager, N. Detzer, T. Okada, and N. Mataga. Bull.Chem. Soc. Jpn., 60, 4245, 1987

ETC



PARTICIPANTS

LIST OF PARTICIPANTS

M.Sc. J. Al-Abbas
Instytut Fizyki PAN
Al. Lotników 32/46
PL-02-668 Warszawa
POLAND

Prof. Aleksander Balter
Instytut Fizyki
Uniwersytetu im. M. Kopernika
ul. Grudziądzka 5
PL-87-100 Toruń
POLAND

Prof. Paul F. Barbara
Department of Chemistry
Kolthoff and Smith Halls
207 Pleasant Street S.E.
Minneapolis, Minnesota 55455-0431
USA

Prof. Witold M. Bartczak
Instytut Techniki Radiacyjnej
Politechnika Łódzka
Wróblewskiego 15
PL-93-590 Łódź
POLAND

Dr. Maria Barysz
Uniwersytet Śląski
Instytut Chemii
PL-40-006 Katowice
POLAND

Prof. Dr. Wolfram Baumann
Institut für Physikalische Chemie
der Universität
Jakob Welder Weg 11
D-6500 Mainz
GERMANY

Dr. David Birch
I.B.H. Ltd.
64 St. Vincent Crescent
Glasgow G 38 NG
SCOTLAND

Prof. Vlasta Bonačić-Koutecký
Freie Universität Berlin
Fachbereich Chemie
Institut für Physikalische
und Theoretische Chemie
Takustrasse 3
D-1000 Berlin 33
GERMANY

Dr. Christian von Borczyskowski
Freie Universität Berlin
Fachbereich Physik
Institut für Experimental Physik
Arnimallee 14
D-1000 Berlin 33
GERMANY

M.Sc. Paweł Borowicz
Instytut Chemii Fizycznej PAN
Kasprzaka 44
PL-01-224 Warszawa
POLAND

M.Sc. David Braun
Technische Universität Berlin
Ivan-N.-Stranski-Institut
Strasse des 17. Juni 112
D-1000 Berlin 12
GERMANY

Dr. Albert M. Brouwer
University of Amsterdam
Laboratory of Organic Chemistry
Nieuwe Achtergracht 129
NL-1018 WS Amsterdam
THE NETHERLANDS

Prof. Annamaria Carnevali
Universita' degli studi di Modena
Dipartimento di Chimica
via Campi 183
I-41100 Modena
ITALY

Mr. Massimo Cattini
ITALY

Ms. Swan Chow
CANADA

Prof. Yuan L. Chow
Department of Chemistry
Simon Fraser University
Burnaby, B. C.
Canada V5A 1S6
CANADA

M.Sc. Claudia Cornelissen
Technische Universität Berlin
Ivan-N.-Stranski-Institut
Strasse des 17. Juni 112
D-1000 Berlin 12
GERMANY

Prof. Barbara Czochralska
Zakład Biofizyki
Instytut Fizyki Doświadczalnej
Uniwersytet Warszawski
Żwirki i Wigury 93
PL-02-089 Warszawa
POLAND

Ms. Anneliese Dahne
GERMANY

Prof. Siegfried Dähne
Bundesanstalt für Materialforschung
und -prüfung (BAM)
Außenstelle Adlershof
Labor 10.14
Rudower Chaussee 5
D(0)-1199 Berlin
GERMANY

Dr. Irena Deperasińska
Instytut Fizyki PAN
Al. Lotników 32/46
PL-02-668 Warszawa
POLAND

Dr. Jacek Dobkowski
Instytut Chemii Fizycznej PAN
Kasprzaka 44
PL-01-224 Warszawa
POLAND

Dr. Józef Dresner
Instytut Fizyki PAN
Al. Lotników 32/46
PL-02-668 Warszawa
POLAND

Dr. Jacek J. Fisz
Instytut Fizyki
Uniwersytetu im. M. Kopernika
ul. Grudziądzka 5
PL-87-100 Toruń
POLAND

Prof. Marye Anne Fox
College of Natural Science
The University of Texas at Austin
Department of Chemistry
Austin, Texas 78712-1167
USA

Prof. Anna Grabowska
Instytut Chemii Fizycznej PAN
Kasprzaka 44
PL-01-224 Warszawa
POLAND

Prof. Zbigniew R. Grabowski
Instytut Chemii Fizycznej PAN
Kasprzaka 44
PL-01-224 Warszawa
POLAND

Prof. Karl H. Grellmann
Max-Planck-Institut
für Biophysikalische Chemie
Am Fassberg, Postfach 2841
D-3400 Göttingen
GERMANY

M.Sc. Paweł Grochowski
Zakład Biofizyki
Instytut Fizyki Doświadczalnej
Uniwersytet Warszawski
Żwirki i Wigury 93
PL-02-089 Warszawa
POLAND

Dr. Murthy S. Gudipati
Institut für Physikalische Chemie
Lehrstuhl II
Universität zu Köln
Luxemburger Str.116
D-5000 Köln-41
GERMANY

M.Sc. Thomas von der Haar
Max-Planck-Institut
für Biophysikalische Chemie
Am Fassberg, Postfach 2841
D-3400 Göttingen
GERMANY

Prof. Edwin Haselbach
Physical Chemical Institute
University of Fribourg
Pérolles, CH-1700 Fribourg
SWITZERLAND

Dr. Günter Haucke
Institute of Physical Chemistry
Friedrich Schiller University
Philosophenweg 14
D-O-6900 Jena
GERMANY

M.Sc. Axel Hebecker
Max-Planck-Institut
für Biophysikalische Chemie
Am Fassberg, Postfach 2841
D-3400 Göttingen
GERMANY

Dr. Hans Heitele
Institut für Physikalische
und Theoretische Chemie
der TU München
Lichtenberg Str. 4
D-8046 Garching
GERMANY

Dr. Jerzy Herbich
Instytut Chemii Fizycznej PAN
Kasprzaka 44
PL-01-224 Warszawa
POLAND

Prof. James T. Hynes
Department of Chemistry
Box 215
University of Colorado
Boulder, CO 80309-0215
USA

Prof. Michiya Itoh
Faculty of Pharmaceutical Sciences
Kanazawa University
Takara-machi
Kanazawa 920
JAPAN

Ms. Yuko Itoh
JAPAN

Dr. Waldemar Iwanek
Instytut Chemii WSP
Chęcińska 5
PL-25-020 Kielce
POLAND

Prof. Patrice Jacques
Université de Haute-Alsace
École Nationale Superieure
de Chimie de Mulhouse
Laboratoire de Photochimie Generale
3 rue Alfred Werner
F-68093 Mulhouse Cedex
FRANCE

Dr. Maria Janik-Czachor
Instytut Chemii Fizycznej PAN
Kasprzaka 44
PL-01-224 Warszawa
POLAND

M.Sc. Jakub Kaniowski
Zakład Biofizyki
Instytut Fizyki Doświadczalnej
Uniwersytet Warszawski
Żwirki i Wigury 93
PL-02-089 Warszawa
POLAND

Dr. Andrzej Kapturkiewicz
Instytut Chemii Fizycznej PAN
Kasprzaka 44
PL-01-224 Warszawa
POLAND

M.Sc. Jerzy Karpiuk
Instytut Chemii Fizycznej PAN
Kasprzaka 44
PL-01-224 Warszawa
POLAND

Ms. Lili Kasha
USA

Prof. Michael Kasha
Institute of Molecular Biophysics and
Department of Chemistry
Florida State University
Tallahassee, Florida 32306-3015
USA

M.Sc. Thomas Kircher
Institut für Physikalische
und Theoretische Chemie
TU Braunschweig
Hans-Sommer-Straße 10
D-3300 Braunschweig
GERMANY

Dr. André M. Klock
Technische Universität Berlin
Ivan-N.-Stranski-Institut
Strasse des 17. Juni 112
D-1000 Berlin 12
GERMANY

Prof. Michael I. Knyazhansky
Institute of Physical
and Organic Chemistry
Stachki Str.194/3
Rostov-on Don 344104
RUSSIA

Prof. Gottfried Köhler
Institut für Theoretische Chemie
und Strahlenchemie
Universität Wien
Währingerstrasse 38
A-1090 Wien
AUSTRIA

M.Sc. Robert Kojer
Instytut Fizyki PAN
Al. Lotników 32/46
PL-02-668 Warszawa
POLAND

Prof. Jerzy Konarski
Wydział Chemii
Uniwersytetu im. A.Mickiewicza
ul. Grunwaldzka 6
PL-60-780 Poznań
POLAND

Dr. Wojciech Korneta
Zakład Fizyki
Wyższa Szkoła Inżynierska
ul. Malczewskiego 29
PL-26-600 Radom
POLAND

Dr. Jean Kossanyi
Photochimie Solaire du C.N.R.S.
2-8 rue H.Dunant, B.P.28
94320-THIAIS
FRANCE

Ms. Małgorzata Kowalewska
Instytut Chemii Fizycznej PAN
Kasprzaka 44
PL-01-224 Warszawa
POLAND

M.Sc. Krzysztof Kownacki
Instytut Chemii Fizycznej PAN
Kasprzaka 44
PL-01-224 Warszawa
POLAND

Dr. Bolesław Kozankiewicz
Instytut Fizyki PAN
Al. Lotników 32/46
PL-02-668 Warszawa
POLAND

Prof. Anna Koziolowa
Instytut Towaroznawstwa
Akademii Ekonomicznej
Al. Niepodległości 10
PL-60-967 Poznań
POLAND

Prof. Jacek Kozioł
Instytut Towaroznawstwa
Akademii Ekonomicznej
Al. Niepodległości 10
PL-60-967 Poznań
POLAND

Prof. Jerzy Kroh
Międzyresortowy Instytut
Chemii Radiacyjnej
Politechnika Łódzka
Wróblewskiego 15
PL-93-590 Łódź
POLAND

Prof. Marian Kryszewski
Centrum Badań Molekularnych
i Makromolekularnych PAN
Polskiej Akademii Nauk
Sienkiewicza 112
PL-90-363 Łódź
POLAND

Dr. Jan Kukielski
Instytut Fizyki Eksperymentalnej
Uniwersytetu Gdańskiego
Wita Stwosza 57
PL-80-952 Gdańsk
POLAND

Dr. Stefan S. Kurek
Instytut Inżynierii Chemicznej
i Chemii Fizycznej
Politechniki Krakowskiej
ul. Warszawska 24
PL-31-155 Kraków
POLAND

Prof. Michael G. Kuzmin
Department of Chemistry
Moscow University
Moscow 117234
RUSSIA

Prof. Francoise Lahmani
Lab. de Photophysique Moléculaire
Bat 213-Université Paris-Sud
F-91405 Orsay, CEDEX
FRANCE

Ms. Paulette Lapouyade
10 rue des Vergers
33170 Gradignan
FRANCE

Dr. René Lapouyade
Lab. de Photochimie Organique
Université de Bordeaux I
351, Cours de la Libération
F-33405 Talence, Cedex
FRANCE

Prof. Tadeusz Latowski
Instytut Chemii WSP
Chęcińska 5
PL-25-020 Kielce
POLAND

Dr. Aleksandra Lewanowicz
Instytut Chemii Organicznej i Fizycznej
Politechniki Wrocławskiej
Wybrzeże Wyspiańskiego 27
PL-50-370 Wrocław
POLAND

Prof. Edward C. Lim
Knight Chemical Laboratory
Akron OH 44325-3601
USA

Prof. Janusz Lipkowski
Instytut Chemii Fizycznej PAN
Kasprzaka 44
PL-01-224 Warszawa
POLAND

Prof. Hans-Gerd Löhmannsroben
Institut für Physikalische
und Theoretische Chemie
TU Braunschweig
Hans-Sommer-Straße 10
D-3300 Braunschweig
GERMANY

M.Sc. Ewa Machowska
Instytut Chemii WSP
Chęcińska 5
PL-25-020 Kielce
POLAND

Dr. Andrzej Maciejewski
Wydział Chemii
Uniwersytetu im. A.Mickiewicza
ul. Grunwaldzka 6
PL-60-780 Poznań
POLAND

Prof. Bronisław Marciniak
Wydział Chemii
Uniwersytetu im. A.Mickiewicza
ul. Grunwaldzka 6
PL-60-780 Poznań
POLAND

Ms. Laura Marcus
USA

Prof. Rudolph A. Marcus
California Institute of Technology
Division of Chemistry
& Chemical Engineering 127-72
Pasadena, California 91125
USA

M.Sc. Jan Marczyk
Instytut Chemii Fizycznej PAN
Kasprzaka 44
PL-01-224 Warszawa
POLAND

M.Sc. Francisco Márquez Linares
Department of Physical Chemistry
University of Valencia
Dr. Moliner 50
E-46100-Bujassot Valencia
SPAIN

Dr. Monique M. Martin
Laboratoire de Photophysique
Moléculaire du CNRS
Bat. 213-Université Paris-Sud
F-91405 Orsay, CEDEX
FRANCE

Prof. Noboru Mataga
Department of Chemistry
Faculty of Engineering Science
Osaka University
Toyonaka, Osaka 560
JAPAN

Dr. Jacek Michalak
Institute of Applied Radiation Chemistry
Technical University of Łódź
ul. Żwirki 36
PL-90-924 Łódź
POLAND

Prof. M. E. Michel-Beyerle
Institut für Physikalische
und Theoretische Chemie
der TU München
Lichtenberg Str. 4
D-8046 Garching
GERMANY

Prof. Josef Michl
Department of Chemistry
and Biochemistry
University of Colorado
Boulder, Colorado 80309-0215
USA

Prof. Jai Pal Mittal
Chemistry Division
Bhabha Atomic Research Centre
Trombay, Bombay 400 085
INDIA

Dr. Olaf Morawski
Instytut Fizyki PAN
Al. Lotników 32/46
PL-02-668 Warszawa
POLAND

Dr. Andrzej Mordziński
Instytut Chemii Fizycznej PAN
Kasprzaka 44
PL-01-224 Warszawa
POLAND

Prof. Jan Najbar
Wydział Chemii
Uniwersytetu Jagiellońskiego
Ingardena 3
PL-30-060 Kraków
POLAND

Prof. Pier Luigi Nordio
Universita' Degli Studi di Padova
Dipartimento di Chimica Fisica
2, Via Loredan
I-35131 Padova
ITALY

Dr. Wiesław Nowak
Instytut Fizyki
Uniwersytetu im.M. Kopernika
Grudziądzka 5
PL-87-100 Toruń
POLAND

Prof. Dieter Oelkrug
Institute of Physical
and Theoretical Chemistry
Tübingen University
Auf der Morgenstelle 8
D-7400 Tübingen
GERMANY

Prof. Tadashi Okada
Department of Chemistry
Faculty of Engineering Science
Osaka University
Toyonaka, Osaka 560
JAPAN

Dr. Maria Amparo Olba-Torrent
Department of Physical Chemistry
University of Valencia
Dr. Moliner 50
E-46100-Bujassot Valencia
SPAIN

Prof. Andrzej Olszowski
Instytut Chemii Organicznej
i Fizycznej Politechniki Wrocławskiej
Wybrzeże Wyspiańskiego 27
PL-50-370 Wrocław
POLAND

M.Sc. Tomasz Oszal
Zakład Biofizyki
Instytut Fizyki Doświadczalnej
Uniwersytet Warszawski
Żwirki i Wigury 93
PL-02-089 Warszawa
POLAND

Dr. Nagnath H. Paike
P.O.Box 103
Khorixas
Namibia-9000.SWA.
NAMIBIA

Prof. Stefan Paszyc
Wydział Chemii
Uniwersytetu im.A. Mickiewicza
ul. Grunwaldzka 6
PL-60-780 Poznań
POLAND

Dr. Jerzy Pączkowski
Instytut Technologii
i Inżynierii Chemicznej
Akademii Techniczno-Rolniczej
Seminaryjna 3
PL-85-326 Bydgoszcz
POLAND

Dr. Antonino Polimeno
Universita' Degli Studi di Padova
Dipartimento di Chimica Fisica
2, Via Loredan
I-35131 Padova
ITALY

Prof. Jerzy Prochorow
Instytut Fizyki PAN
Al. Lotników 32/46
PL-02-668 Warszawa
POLAND

Dr. Anna Psoda
Zakład Biofizyki
Instytut Fizyki Doświadczalnej
Uniwersytet Warszawski
Żwirki i Wigury 93
PL-02-089 Warszawa
POLAND

Prof. Wolfgang Rettig
Technische Universität Berlin
Ivan-N.-Stranski-Institut
Strasse des 17. Juni 112
D-1000 Berlin 12
GERMANY

Prof. Björn O. Roos
Department of Theoretical Chemistry
Chemical Centre
University of Lund
P.O.B.124
S-22100 Lund
SWEDEN

Dr. Krystyna Rotkiewicz
Instytut Chemii Fizycznej PAN
Kasprzaka 44
PL-01-224 Warszawa
POLAND

Dr. Claude Rullière
Centre de Physique Moléculaire
Optique et Hertzienne
Unité Associée au CNRS N283
Université de Bordeaux I
351, Cours de la Liberation
F-33405 TALENCE Cedex
FRANCE

Dr. Jerzy Sepioł
Instytut Chemii Fizycznej PAN
Kasprzaka 44
PL-01-224 Warszawa
POLAND

Dr. Nina V. Shcherbatska
Dept. of Biochemistry
Agricultural University
Dreijenlaan 3
NL-6703 HA Wageningen
THE NETHERLANDS

Prof. Haruo Shizuka
Department of Chemistry
Gunma University
Kiryu
Gunma 376
JAPAN

M.Sc. Marek Sikorski
Wydział Chemii
Uniwersytet im. A.Mickiewicza
ul. Grunwaldzka 6
PL-60-780 Poznań
POLAND

Dr. Andrzej L. Sobolewski
Instytut Fizyki PAN
Al. Lotników 32/46
PL-02-668 Warszawa
POLAND

Prof. Jean Ph. Soumillion
Lab. de Chimie Organique Physique
UCL-UNITE CICO
Place Louis Pasteur, 1
B-1348 LOUVAIN-LA-NEUVE-BELGIQUE
BELGIUM

Prof. Paul Suppan
Physical Chemical Institute
University of Fribourg
Pérolles, CH-1700 Fribourg
SWITZERLAND

M.Sc. Beata Szczepanik
Instytut Chemii WSP
Chęcińska 5
PL-25-020Kielce
POLAND

Dr. Anna W. Szemik
Instytut Chemii
Uniwersytetu Wrocławskiego
ul. Joliot-Curie 14
PL-90-383 Wrocław
POLAND

Dr. Jacek Szubiakowski
ul. Niesiołowskiego 10d m. 44
PL-87-100 Toruń
POLAND

Prof. Marian Szymański
Wydział Chemii
Uniwersytetu im. A.Mickiewicza
ul. Grunwaldzka 6
PL-60-780 Poznań
POLAND

M.Sc. Henryk Szymusiak
Instytut Towaroznastwa
Akademii Ekonomicznej
Al. Niepodległości 10
PL-60-967 Poznań
POLAND

Dr. Anthony C. Testa
St.Johns University
Department of Chemistry
Jamaica
New York 11439
USA

Dr. Paweł Uznański
Centrum Badań Molekularnych
i Makromolekularnych PAN
Sienkiewicza 112
PL-90-363 Łódź
POLAND

Dr. Mark Van der Auweraer
K.U. Leuven
Departement Scheikunde
Celestijnenlaan 200F
B-3001 Heverlee
BELGIUM

Prof. Johan H. van der Waals
Huygens Laboratorium
Rijksuniversiteit te Leiden
P.O.Box 9504
NL-2300 RA Leiden
THE NETHERLANDS

Prof. Jan Verhoeven
Laboratory of Organic Chemistry
University of Amsterdam
Nieuwe Achtergracht 129
NL-1018 WS Amsterdam
THE NETHERLANDS

Prof. A. J. W. G. Visser
Dept. of Biochemistry
Agricultural University
Dreijenlaan 3
NL-6703 HA Wageningen
THE NETHERLANDS

Dr. Jacek Waluk
Instytut Chemii Fizycznej PAN
Kasprzaka 44
PL-01-224 Warszawa
POLAND

Dr. John M. Warman
Radiation Chemistry Department
IRI, Delft University of Technology
Mekelweg 15
NL-2629 JB Delft
THE NETHERLANDS

Prof. Albert Weller
Max-Planck-Institut
für Biophysikalische Chemie
Am Fassberg, Postfach 2841
D-3400 Göttingen
GERMANY

Dr. Grażyna Wenska
Wydział Chemii
Uniwersytetu im. Adama Mickiewicza
Grunwaldzka 6
PL-60-780 Poznań
POLAND

Dr. Wiesław Wiczk
Wydział Chemii
Uniwersytetu Gdańskiego
Sobieskiego 18
PL-80-952 Gdańsk
POLAND

M.Sc. Alexander Wiessner
Max-Planck- Institut
für Biophyskalische Chemie
Postfach 968
D-3400 Göttingen
GERMANY

Dr. Jacek Wierzchowski
Zaklad Chemii Fizycznej
Wydział Farmacji
Akademii Medycznej
Banacha 1
PL-02-097 Warszawa
POLAND

Ms. Charmian M. Windsor
USA

Prof. Maurice W. Windsor
Department of Chemistry
Washington State University
Pullman, WA 99164-4630
USA

Dr. J. Jens Wolff
Organisch-Chemisches Institut
der Universität
Im Neuenheimer Feld 270
D-6900 Heidelberg
GERMANY

Dr. Marian Wolszczak
Międzyresortowy Instytut
Chemii Radiacyjnej
Politechnika Łódzka
Wróblewskiego 15
PL-93-590 Łódź
POLAND

Dr. Rüdiger Wortmann
Institut für Physikalische Chemie
der Universität
Jakob Welder Weg 11
Postfach 3980
D-6500 Mainz
GERMANY

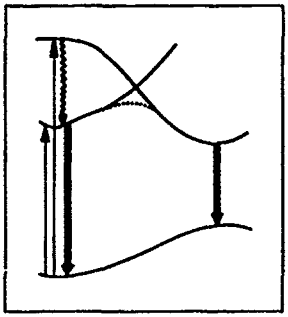
Prof. Keitaro Yoshihara
Institute for Molecular Science
Myodaiji
Okazaki 444
JAPAN

Dr. Isabel Zabala - Sanchez
Department of Physical Chmistry
University of Valencia
Dr. Moliner 50
46100-Bujassot Valencia
SPAIN

Prof. Klaas A. Zachariasse
Max-Planck-Institut
für Biophysikalische Chemie
Am Fassberg, Postfach 2841
D-3400 Göttingen
GERMANY

M.Sc. Zbigniew Zieliński
Instytut Chemii Fizycznej PAN
Kasprzaka 44
PL-01-224 Warszawa
POLAND

ETC



LIST OF AUTHORS