

Solvent effects on excited state relaxation phenomena

Gottfried Köhler and Karl Rechthaler

Institut für Theoretische Chemie und Strahlenchemie, University of Vienna, Vienna, Austria.

Abstract: Solvent effects on excited state relaxation phenomena in binary solvent mixtures, studied by steady state and time-resolved fluorescence spectroscopy, are discussed in the frame of: electrostatic interactions, preferential solvation, weak associations with defined stoichiometry and structure and strongly bonded ground and excited state complex formation. It is shown, that effects of hydrogen bonded complex formation can be discriminated from unspecific interactions in hydrocarbon - hydroxylic binary solvent mixtures. The structure of such complexes and their role in altering excited state processes is discussed for some hydroxy- and amino- compounds (phenols, anilines, aliphatic tertiary amines, and aminocoumarins etc.).

INTRODUCTION

Most of photochemistry is concerned with molecules in the condensed phase, i.e. in liquids or solids, and intermolecular solute - media interactions affects the energy of the electronic states. As the interaction energy depends on the nature and the properties (e.g. the charge distribution or the dipole moment) of the respective state, it will be different for ground and excited state molecules and gives thence rise to spectral shifts, normally referred to as *solvatochromic shifts*. Solvatochromy is thus an excellent measure for variations of the relative energies of the molecular states in different environments (for recent reviews see refs. 1,2).

As solute-solvent interaction energies depend essentially on the nature of the molecular state, the orbital characteristics of the fluorescent state might vary as the solvent is changed. One important example is the reversal of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ states often observed in hydroxylic environment. The lone pair acts as electron donor in a hydrogen bond with a solvent molecule and is, thus, lowered in energy by approximately the energy of this hydrogen bond, causing an increased energy gap to the excited π^* orbital (ref. 3).

The efficiency of excited state decay processes (e.g. fluorescence, intersystem crossing, charge transfer etc.) is widely determined by the relative energies of the excited states involved and their orbital characteristics. Therefore, intermolecular interactions can cause important changes in the excited state decay mechanism. For instance, $n \rightarrow \pi^* - \pi \rightarrow \pi^*$ state reversal can cause a dramatic increase in the fluorescence yield. But also external solvent parameters as the viscosity of the solvent, the dielectric or rotational relaxation times, etc. influence the rate of intramolecular processes, especially in the case efficient charge separation or internal nuclear motions are involved (ref. 4). Although, a wide range of literature exists on solvatochromism, studies on solvent effects on the dynamics or kinetics of excited state decay are much less numerous.

A large variety of different processes are involved in the excited state decay and a general treatment must be performed for every type of processes separately. The most extensive experimental and theoretical treatments are available for the dynamic solvent effect on charge transfer rate (refs. 4-7). Even in this case, the theory is restricted to effects by the bulk dielectric properties of the solvent and specific solute-solvent interactions, as e.g. hydrogen bonding, is not included. Such short range interactions between substrate and medium molecules become often evident in a strongly non-linear dependence of spectral or photophysical properties on the composition of binary solvent mixtures (refs. 8,9,10). Addition of low amounts of a polar, hydroxylic solvent to an inert medium (e.g. adding alcohol to an hydrocarbon) can result in large spectral shifts, which can be attributed to the formation of molecular clusters. Studies of spectroscopic and photophysical properties in such binary mixtures allows to separate effects on the relaxation mechanism caused by solute-solvent complexes from these resulting from long range, electrostatic interactions. Furthermore, information on the stoichiometric structure of such clusters, on the interaction strength, on structural changes upon excitation, etc. can be obtained from such studies.

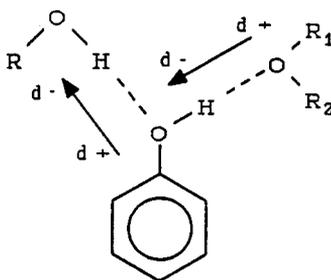
In this paper we will discuss two examples for the influence of specific interactions on photophysical and spectroscopic properties and their dependence on the structure of such complexes. Some general features common to these systems will be summarized.

SOLUTE-SOLVENT INTERACTIONS IN MIXED SOLVENTS

A coarse classification of solute - solvent interactions could be done by the intermolecular interaction energy between the solute molecule and a molecule of the solvent environment. The relative interaction energies are reflected in the observed spectral shifts. Photophysical properties of excited states could either be influenced by the variation of the relative energies of the initial and final electronic state between that the transition occurs, or by some specific influence on the respective rate. As an example, hydrogen bonding decreases the energy of the X-H stretching mode of the proton donating group. In a case where this is the accepting mode in a radiationless transition, its rate could significantly decrease upon hydrogen bonding. However, also relative changes of the state energies influence the magnitude of the vibrational overlap integrals.

Two broad categories of phenomena can be defined: 1) The first category comprises phenomena attributed to physical solute - solvent interactions. These are phenomena, which can be treated as a perturbation of the respective state of the isolated molecule by the electrostatic field generated by the environment. The perturbation potential is thus related to the high and low frequency dielectric constants of the medium, viewed as a continuum (refs. 11,12). 2) In many media shifts can additionally be attributed to specific chemical effects of the solvent on one or both electronic states. Important specific effects are hydrogen bonding, proton or charge transfer, solvent dependent aggregation, etc. Such specific effects have often larger interaction energies and are characterized by defined stoichiometric and structural relationships. A theoretical treatment must involve quantum chemical calculations on *supermolecules* consisting of a molecule of the solute and one or more of the solvent.

Scheme 1



In pure solvents effects of electrostatic forces and of specific short range interactions on the spectral position or photophysical properties are not easily distinguished. Shifts attributed to either of these two categories could add up or cancel dependent on the structure of the solute-solvent cluster and the orbital type of excited states involved. Type 1 interactions causes most generally a redshift of the spectra on increasing solvent polarity, because excited state dipole moments are more often larger than in the ground state. Specific interactions could influence the energy of the initial and final state of an electronic transition in the same or in opposite way, causing thus a red or a blue shift of the spectrum. As an example assume hydrogen bonding of a phenol molecule in an hydroxylic solvent (see Scheme 1). Phenol and the solvent molecule (e.g. an alcohol) could act as proton donors as well as proton acceptors and two types of hydrogen bonds are possible. In the case phenol is the proton donor, electronic charge is transferred from the solvent molecule to the phenolic oxygen. This stabilizes both, ground and excited state, the latter, however, to a larger extent, as this charge cancels partly the negative charge flow from the phenolic oxygen to the ring upon excitation. Therefore, a red-shift of the absorption results (ref. 13). The second type of hydrogen bond, in which phenol is the proton acceptor, transfers charge from the phenol to the solvent molecule. This destabilizes the excited state and causes thus a blue shift of the spectrum. This type of hydrogen bond should be stable only in the ground state, but is strongly weakened when the molecule is excited. Hydrogen bonds of the first type are, however, strengthened. Hence, geometrical rearrangement occurs after excitation and the fluorescence is generally bathochromically shifted (ref. 14).

This example shows, that hydrogen bonding, a general phenomenon in many solvents, has important effects on spectroscopic properties and information about the preferred structure of such aggregates could be obtained from absorption or fluorescence data. Whereas in type 1 interactions, excited state relaxation is due to solvent dipole reorientation according to the dipole moment of the excited solute, differing from this in the ground state, both in amount and direction. Relaxation in such clusters involves therefore breaking up and formation of hydrogen bonds. In a pure solvent this is a fast process, as only adjacent molecules are involved. Relaxation times are thus in the ps time domain. Adding small amounts of hydroxylic or other polar solvents to an inert environment, diffusion processes could become involved in the excited state relaxation mechanism and such processes could then be observed on a ns time scale. Complex formation could also manifest in essential spectral shifts and changes of the photophysical properties observed in a narrow range of low concentrations of added polar cosolvent. Gradual changes at higher concentrations reveals effects of electrostatic interactions as the medium becomes essentially polar (refs. 8,9,13). For the exemplary case of phenol, the fluorescence quantum yield, q_f , is considerably lower in a hydrocarbon solutions than in alcohol or ether as solvent. In a mixed environment this increase is essentially finished at rather low polar cosolvent concentrations. The respective decrease in the efficiency of non-radiative decay in a polar environment can, therefore, be attributed to effects of hydrogen bonding (refs. 9,14). A similar influence of complex

formation, - causing, however, an increase in the non-radiative decay efficiency - was observed for aniline solutions (ref. 15). In this case excited state association kinetics were observed, supporting the conclusion, that excited state complex formation (*solute-solvent exciplexes*) are responsible for the higher deactivation rate. Excited state versus ground state complexation will be discussed for two examples below.

Not only 1:1 but also higher associations were observed in time resolved fluorescence spectroscopy. One example is exciplex formation of triethylamine with ethanol, where, besides a 1:1 complex, also 1:2 exciplexes were characterized spectroscopically and kinetically (refs. 21,22). A geometry for such structures was deduced from *ab initio* model calculations, suggesting a structure the ethanolic oxygens pointing towards the nitrogen lonepair in the excited state (ref. 23).

Studies in mixed solvents could thus give detailed information on ground and excited state aggregation phenomena, relative binding energies, structural relaxation processes in such complexes, the influence of association on the excited state decay, etc. Therefore, studies in mixed solvents became increasingly important (refs. 1,10,16).

As the interaction energy between solute and medium molecules becomes smaller, appreciable association is only observed at higher concentrations of polar cosolvent, i.e. spectroscopic or photophysical properties change gradually over a wide range of mixture composition. Slow excited state complexation could also result from a short fluorescence lifetime. Although the interaction energy is low, a defined stoichiometric structure should be retained and the binding energy is determined by the overlap of electronic orbitals of solute and solvent molecules. The enrichment of polar solvent molecules in the vicinity of the solute dipole, which is governed by electrostatic interactions, i.e. the *preferential solvation effect*, can be understood as a limiting case (ref. 1). Here the characteristics of specific solvent effects, as the defined geometric structure, is lost. This shows that there exists a broad range of phenomena, between strong, well defined complexes and non-specific, long range interactions. Association rates should be essentially diffusion controlled. Therefore, after excitation the solvation equilibrium at this rather high concentrations of polar component is established fastly and the reaction is not observed on a ns time scale. Typical examples for this type of aggregation were observed for tertiary aromatic amines (ref. 15) or for solvent dependent TICT formation of N,N-dimethylaminobenzonitrile in hydrocarbon - chlorocarbon mixed solvents (refs. 17,18). Such a behaviour is also characteristic for mixtures of highly polar solvents (e.g. alcohols plus water) as in this case the difference in the interaction energy is small for both components (refs. 19,20). Generally a plot of the fluorescence properties on the solvent composition is strongly non-linear and association can be modeled by statistical simulations (refs. 10,20).

Summing up, the following categories of solute - solvent interactions in non-polar - polar mixed solvents can be distinguished and determine the spectroscopic and photophysical parameters. They are coarsely dicriminated by the interaction energy between single solute and solvent molecules:

- (1) Long-range electrostatic interactions, present in all solvents.
 - (2) Preferential solvation effects, observed for dipolar solutes in polar solvents.
 - (3) Weak associations with defined stoichiometry and structure. Relaxation is fast.
 - (4) Strong complex formation in the excited state (exciplexes). Kinetics can be observed on a ns time scale.
 - (5) Strong complex formation in the ground state. Excitation causes structural reorganization and is thus fast.
- Some examples are discussed below.

GROUND STATE COMPLEXES: PHENOLS

Compounds with -OH functional groups are both, good proton donors and proton acceptors, and form thus strong hydrogen bonds. Aromatic phenols are typical examples and excited state properties can easily be monitored by their fluorescence. As the fluorescence yield of phenols is considerably lower in hydrocarbons than in hydroxylic solvents, hydrogen bonding could significantly effect excited state decay mechanisms. As an example catechol is presented, as q_f is essentially zero in hexane but increases to 0.18 in alcohols. This is shown in Figure 1. In binary ethanol - hexane mixtures, the quantum yield increases steeply upon addition of only 5 vol-% alcohol to approximately 0.10 and then gradually to reach the value of neat alcohol. The

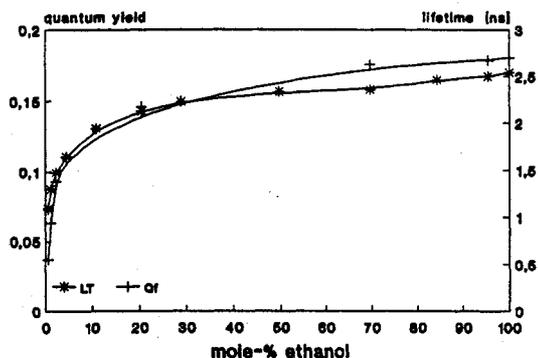


Figure 1: Absolute fluorescence quantum yield, q_f , and fluorescence lifetime of catechol in n-hexane binary mixtures with ethanol.

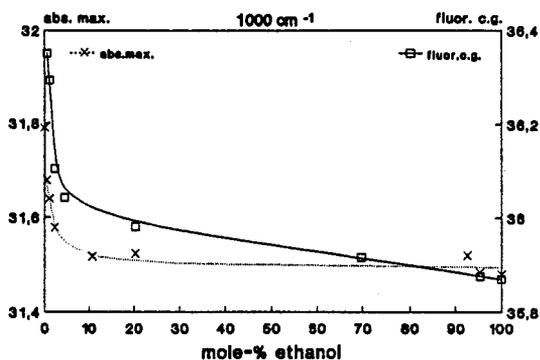


Figure 2: Absorption maximum and the center of gravity of the fluorescence spectrum of catechol in n-hexane binary mixtures with ethanol.

fluorescence lifetime follows this trend (see Figure 1). Calculating the radiative rate, k_{FM} , its value increases at low concentrations but remains constant in a wide high alcohol concentration range. The suppression of the radiationless decay is thus primarily due to complexation.

Figure 2 depicts the spectral shifts of absorption (shown is the absorption maximum, $\bar{\nu}_{abs}^{max}$) and fluorescence (the center of gravity calculated from emission spectra) on the composition of hexane-alcohol mixtures. Both spectra shifts mostly in the same low alcohol concentration range as is observed for the photophysical parameters. This indicates, that the main solvent effects on spectral shifts as well as photophysical parameters are due to ground state complexation. Electrostatic effects of the bulk of the solution influences also slightly both sets of parameters.

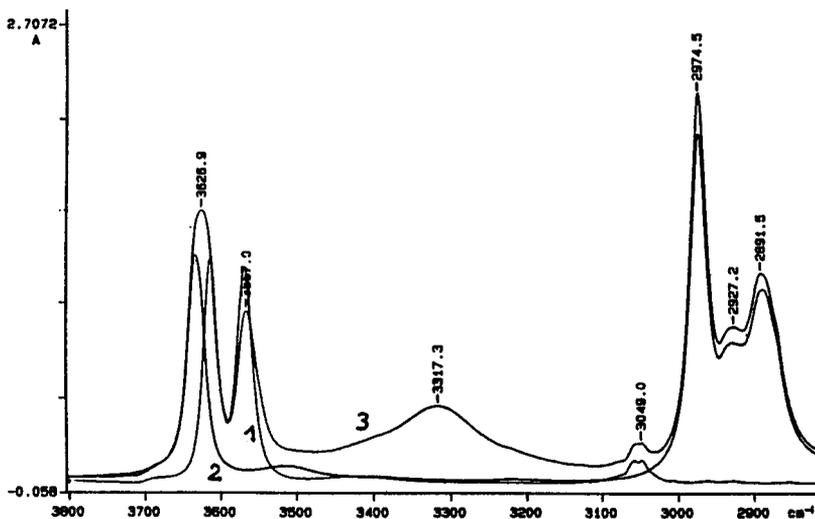


Figure 3: Infrared spectra of catechol in (1), ethanol (2) and of catechol plus ethanol (3) in CCl₄ solution.

To show, that ground state complexation is essentially by hydrogen bonding in this alcohol concentration range, i.r. spectra of catechol in CCl₄ adding 0.14 vol-% ethanol are given in Figure 3. The spectra show clearly the formation of hydrogen bonds between the substrate and ethanol by the increase of the peak at 3317 cm⁻¹, typical for intermolecular hydrogen bonding. Also catechol absorption (peaks at 3614 and 3569 cm⁻¹) decreases. These two peaks indicate intramolecular hydrogen bonding of the two neighbouring -OH groups. From absorption spectral shifts and from the i.r. spectra it is concluded, that the first alcohol adds as acceptor to the free catechol hydrogen atom. At higher alcohol concentrations the intramolecular bond breaks up and additional alcohol molecules could also add as proton donors to the cluster. Alcohols as proton donors should cancel the bathochromic shift caused by the increasing polarity of the medium and this explains the constancy of

$\bar{\nu}_{abs}^{max}$ at high alcohol content. Shifts of the fluorescence should then result from a breaking up of hydrogen bonds, catechol acting as acceptor but strengthening of these, in which the phenol is the donor. This is because of the charge flow from the -OH group to the ring in the excited state. From this a bathochromic shift of the fluorescence results.

Solvent effects on the photophysical parameters should thus be due to this rearrangement of the cluster geometry. It was shown previously, that homolytic OH bond cleavage is an important pathway in the photochemistry of phenol in hexane solution and this process is completely suppressed by hydrogen bonding (refs. 9,24). This could be one reason for the effective decrease of the non-radiative decay rate. An other explanation could be, that the accepting modes for internal conversion are predominantly the OH vibrations, the highest energy modes in the system. Upon hydrogen bonding, their energy decreases considerably and the internal conversion rate decreases thence likewise. OH vibrational modes play, therefore, a dominant role in the decay of phenols.

EXCITED STATE COMPLEXATION: AMINOCOUMARINS

7-Aminocoumarins are important laser dyes and their fluorescence was widely studied (e.g. refs. 25,26). Of special interest is fluorescence quenching observed for flexible 4-trifluoromethyl- (an electron acceptor) and 7-(N,N-dialkyl)- (an electron donor group) substituted derivatives at high solvent polarities. These compounds exhibit q_F -values near to 1 in low polarity solvents but significantly smaller values in alcohols or nitriles. This effect was attributed to internal charge transfer quenching (ref. 26) and the rate is predominantly dependent on electrostatic solvent parameters (ref. 27).

Contrary to these N,N-dialkyl- substituted aminocoumarins, the fluorescence efficiency of the primary 7-amino-4-trifluoromethylcoumarin (Cou151) is small ($q_F = 0.19$) in hydrocarbons, but near to 1 in alcohols or other polar solvents. Also in this case the main increase in binary ether - hexane solvent mixtures is already finished at rather low polar solvent concentrations. For 1.0 vol-% dibutylether $q_F = 0.4$. Absorption spectra change, however, insignificantly in the same concentration range.

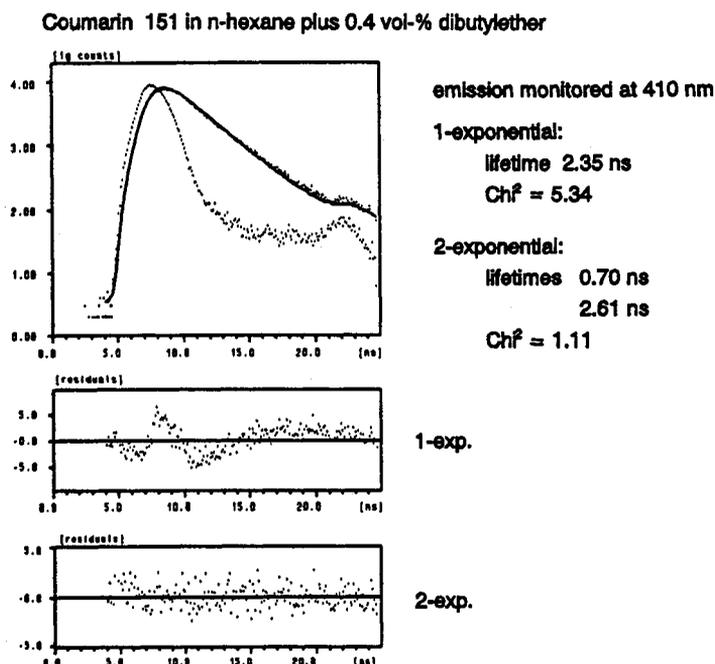


Figure 4: Fluorescence decay curve of 7-amino-4-trifluoromethylcoumarin (Cou151) in hexane plus 0.4 vol-% dibutylether, monitored at 410 nm.

It is seen from Figure 4, that the fluorescence decay of Cou151 at low dibutylether content fits clearly to a double exponential. The short lifetime component decreases with increasing ether concentration. A Stern-Volmer plot for this component is given in Figure 5. An association rate constant $k_a = 1.2 \cdot 10^{10} \text{ mol}^{-1}\text{s}^{-1}$ is obtained which is near to diffusion control in n-hexane. This shows clearly, that also in this case non-radiative decay is suppressed by hydrogen bonding, however, the complexes are formed by a diffusion controlled reaction in the excited state, they can be termed solute-solvent exciplexes. The non-radiative decay observed in hydrocarbons are, however, not primarily suppressed by hydrogen bonding, as also non-polar but highly polarizable solvents like benzene causes likewise an increase of fluorescence quantum yield and lifetime. Therefore, variations in the non-radiative decay rate should be viewed as the result of variations in the relative energies of the states involved.

Conclusively it should be stated, that excited state complexation is characteristic for primary, aromatic amino systems, but ground state associations for aromatic molecules containing an -OH functional group. In diaminoalkyl- substituted compounds complexation reactions are considerably less pronounced and solvent effects in such systems can be widely explained by electrostatic models.

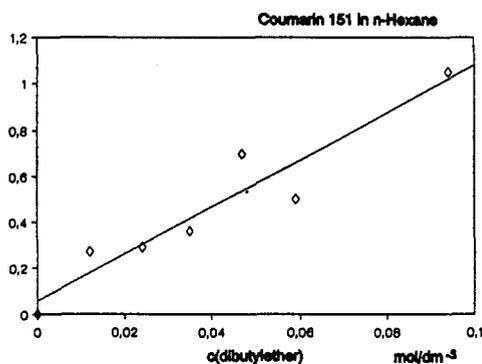


Figure 5: Stern-Volmer plot (versus c) for the short lifetime component observed for 7-amino-4-trifluoromethylcoumarin at low dibutylether concentrations in n-hexane.

EXPERIMENTAL

The fluorescence equipment was described previously (ref. 15,21). Absorption spectra were measured on a Perkin Elmer Lambda 16. Solvents were of highest available purity. Catechol was purified by sublimation in the vacuum and Cou151 (Sigma) was used as received.

REFERENCES

1. P. Suppan, *J. Photochem. Photobiol., Chemistry*, **50**, 293-330 (1990).
2. G. Köhler, P. Wolschann and K. Rotkiewicz, *Proc. Indian Acad. Sci. (Chem. Sci.)*, **104**, 197-207 (1992).
3. H.H. Jaffé and M. Orchin, *Theory and Applications of Ultraviolet Spectroscopy*, p. 187, Wiley, New York (1965).
4. D.F. Calef, *Photoinduced Electron Transfer*, Eds. M.A. Fox and M. Chanon, p. 167, Elsevier, Amsterdam (1988).
5. M.D. Newton and N. Sutin, *Annu. Rev. Phys. Chem.*, **35**, 437-450 (1984).
6. R.A. Marcus and N. Sutin, *Biochim. Biophys. Acta*, **811**, 265 (1985).
7. P. Barbara, G.C. Walker and T.P. Smith, *Science*, **256**, 975-981 (1992).
8. D.A. Chignell and W.B. Gratzler, *J. Phys. Chem.*, **72**, 2934 (1968).
9. J. Zechner, G. Köhler, G. Grabner and N. Getoff, *Canadian J. Chem.*, **58**, 2006-2010 (1980); *ibid.* **59**, 1744 (1981).
10. C. Lerf and P. Suppan, *J. Chem. Soc., Faraday Trans.*, **88**, 963-969 (1992).
11. W. Liptay, *Z. Naturforsch.*, **A20**, 1441 (1965).
12. M.F. Nicol, *Appl. Spectrosc. Rev.*, **8**, 183-227 (1974).
13. G. Nemethy and A. Ray, *J. Phys. Chem.*, **77**, 64-70 (1973).
14. G. Köhler, G. Kittel and N. Getoff, *J. Photochem.*, **18**, 19-27 (1982).
15. G. Köhler, *J. Photochem.*, **38**, 217-238 (1987).
16. S. Meech and D. Phillips, *J. Chem. Soc., Faraday Trans. 2*, **83**, 1941-1956 (1987).
17. G. Köhler and K. Rotkiewicz, *Spectrochim. Acta*, **42A**, 1127-1132 (1986).
18. K. Rotkiewicz and G. Köhler, *J. Luminescence*, **37**, 219-225 (1987).
19. G. Köhler and N. Getoff, *J. Mol. Structure*, **115**, 331-334 (1984).
20. G.W. Robinson, P.J. Thistlethwaite and J. Lee, *J. Phys. Chem.*, **90**, 4224-4233 (1986).
21. G. Köhler, *J. Photochem.*, **35**, 189-207 (1986).
22. G. Köhler, *J. Photochem. Photobiol., A: Chemistry*, **40**, 307-324 (1987).
23. G. Köhler and R. Janoschek, *J. Phys. Chem.*, **91**, 2051-2057 (1987).
24. G. Köhler and N. Getoff, *J. Chem. Soc., Faraday Trans. 1*, **72**, 2101-2107 (1976).
25. G. Jones II, W.R. Jackson, S. Kanoktanaborn and A.M. Halpern, *Optics Comm.*, **33**, 315-320 (1980).
26. G. Jones II, S.F. Griffin, C.-Y. Choi and W.R. Bergmark, *J. Org. Chem.*, **49**, 2705-2708 (1984).
27. K. Rechthaler and G. Köhler, to be published.