

VU Research Portal

High-resolution and time-resolved absorption and fluorescence studies on proton transfer

de Klerk, J.S.

2009

document version

Publisher's PDF, also known as Version of record

[Link to publication in VU Research Portal](#)

citation for published version (APA)

de Klerk, J. S. (2009). *High-resolution and time-resolved absorption and fluorescence studies on proton transfer*. [PhD-Thesis - Research and graduation internal, Vrije Universiteit Amsterdam]. Proefschrift Maken.

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

E-mail address:

vuresearchportal.ub@vu.nl

SUMMARY

The focus of this thesis is on molecules that contain both a proton donating and a proton accepting site. These compounds undergo complicated photochemical and photophysical processes, including excited-state intramolecular proton transfer (ESIPT). They also tend to form dimers or other associates so that intermolecular or double proton transfer may play a role as well.

In order to study these excited-state proton transfer processes, several advanced fluorescence and absorption spectroscopic techniques can be applied, as detailed in the literature study of **Chapter 2**. High-resolution spectra in the fluorescence mode in the wavelength domain can be achieved by using Shpol'skii spectroscopy, fluorescence line-narrowing spectroscopy, supersonic jet spectroscopy and matrix isolation spectroscopy. Furthermore, high-resolution techniques in the time-domain such as transient absorption spectroscopy and time-correlated single photon counting provide complementary information on the proton transfer reactions.

All these high-resolution techniques in the wavelength-domain focus on the reduction of the inhomogeneous broadening of spectral bands. From the resulting spectra and the extent of homogeneous broadening, detailed kinetic information on excited-state proton transfer processes can be extracted, such as ESIPT and back proton transfer rates in the femtosecond range.

By using low-temperature (poly)crystalline matrices, typically at temperatures < 20 K and preferably in combination with narrow-banded laser excitation, one can obtain very sharp molecular electronic spectra. This technique, called Shpol'skii spectroscopy after the Russian scientist E.V. Shpol'skii, is discussed in detail in **Chapter 3**. The approach can be used for fingerprint identification (e.g. isomer-specific determination of pollutants) or for detailed photophysical studies (e.g. intra and intermolecular proton transfer). Shpol'skii spectroscopy was found to be very suitable for non-polar aromatic compounds such as polycyclic aromatic hydrocarbons (PAHs), but also hetero-PAHs, PAH metabolites, dioxins, and proton-transfer compounds such as 3-hydroxyflavone have been studied successfully. So far, Shpol'skii spectroscopy has almost exclusively been used for fluorescence and phosphorescence spectroscopy (emission and excitation), but in order to extend its applicability range, a setup was developed for measurements in absorbance mode. It can be used to characterize the

various chemical species, fluorescent as well as non-fluorescent, involved in the photochemistry/physics.

A main hindrance for Shpol'skii spectroscopy to be accepted as a tool in for example analytical chemistry is a lack of commercially available instrumentation, but significant improvements in design can be noted here. By using optical fibers and simple storage dewars (instead of optical cryostats), experiments can be carried out with minimum cooling time and at lower costs. By combining the technique with direct extraction procedures and time-resolved detection, Shpol'skii spectroscopy can be used to identify and quantitate individual analytes in very complex mixtures, or infer molecular structure information from distinct species.

In **chapter 4** the exceptional photophysics of 2-butylamino-6-methyl-4-nitropyridine-*N*-oxide (2B6M) is described. This compound may undergo excited-state intra- or intermolecular proton transfer reactions in the electronically excited state. The techniques used to study 2B6M are steady-state fluorescence excitation and emission spectroscopy in the liquid state, Shpol'skii spectroscopy in the fluorescence and in the absorption mode, as well as transient absorption spectroscopy in the liquid state.

First of all it is found that in a non-polar solvent 2B6M exists as one single monomeric species; dimers or other associates do not play a role. When the molecule is excited in the first or higher electronic state both normal (N) and tautomeric (T) fluorescence is observed. The steady-state fluorescence results are surprising: there is a substantial difference between the relative band intensities of the excitation and absorption spectra. Furthermore, in emission the relative intensities of the N- and T-bands depend on the excitation wavelength, thus not fully obeying the Kasha-Vavilov rule. A tentative kinetic scheme describing the exceptional excited-state processes is presented in Chapter 4.1 and is refined in Chapter 4.3.

Chapter 4.2 deals with the fact that upon cooling the formation of dimers can no longer be ignored. Under frozen, crystalline matrix conditions (Shpol'skii spectroscopy) more species show up in the spectra. This multi-species system is studied using absorption and fluorescence experiments in *n*-octane at various temperatures between 293 and 5 K. Three species can be discerned: two of these providing high-resolution spectra, the third species gives broad-banded spectra. We tentatively assign the three species to a monomer, a H-bonded dimer and a strongly interacting (π - π -stacked) dimer, respectively. We conclude from the excitation spectra

that (anomalous) intramolecular proton transfer at higher excited states is still operative under cryogenic conditions. Indications for excited-state intermolecular proton transfer in the stacked dimeric species were not found.

In Chapter 4.3, transient absorption measurements on 2B6M are described that resulted in a more complete kinetic scheme that can explain the observed transient absorption results as well as the earlier fluorescence data. In fact, the transient absorption spectra and the associated decay spectra fully support the earlier conclusion that upon short-wavelength excitation ES IPT* can also start at a higher state, and that an additional decay channel must exist that is sufficiently fast to be in competition with vibrational relaxation. Based on the spectra and lifetimes this state is identified as a so called hot state. Furthermore, the data show that a dark state – most probably the triplet state of the normal configuration $T_1(N)$ – plays a main role in the decay pathway.

In **Chapter 5** the complex photochemical behavior of pyrazolo[3,4-*b*]quinoline (PQ) is described. We find that in *n*-alkane solvents it tends to form dimers, but also strong complexes with protic solvent constituents (often present as minor impurities) must be taken into account. Both types of H-bond complexes are studied systematically by temperature-dependent conventional absorption and fluorescence spectroscopy. The effect of protic solvent constituents is mimicked by varying the ethanol concentration in *n*-octane. By lowering the temperature of PQ solutions in *n*-octane, and thus increasing the dimer concentration, the fluorescence is strongly reduced since the dimer is non-fluorescent.

Unexpected results are obtained under crystalline sample conditions: during irradiation a narrow-banded Shpol'skii-type fluorescence spectrum gradually appears. This points at a photochemical reaction, despite the rigid matrix and the low temperature (5 K). To explain this unusual photochemical behavior, PQ and its deuterated analogue are studied using low-temperature absorption and fluorescence spectroscopy. In the case of normal (protonated) PQ, very fast excited-state intermolecular double proton transfer is responsible for the efficient quenching of the PQ dimer fluorescence. Deuteration significantly slows down this proton transfer process (indicating a tunneling mechanism), and in that case the dimer is fluorescent. Photoirradiation under cryogenic conditions leads to a molecular rearrangement of the dimers and the gradual appearance of monomer fluorescence spectra. For both H-PQ and D-PQ this rearrangement is found to be reversible.