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de Klerk, J.S.

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CHAPTER 1

PREFACE AND SCOPE OF THIS THESIS

This thesis focuses on the photochemistry and photophysics of compounds that may undergo proton-transfer reactions in the electronically excited state. Such reactions generally are quite different from those in the electronic ground state because of the change in the distribution of electrons upon excitation – implying a change in chemical and physical properties of the compound concerned. A well-known example to illustrate this difference is 2-hydroxynaphthalene which is a very weak acid in the ground-state (pKa in water 10.0) but a relatively strong acid in the first electronic singlet state (S_1) with a pKa of 2.0. Of course, the excited-state proton transfer is in competition with the fast non-radiative and radiative decay of the S_1 -state which is typically in the 0.1-10 ns range.

Excited-state intramolecular proton transfer (ESIPT) may occur if molecules are provided with both a proton donating and a proton accepting site. Such molecules also tend to form dimers – or other associates – so that additionally excited-state intermolecular or double proton transfer (ESDPT) may play a role. Finally, also the possible interaction with polar solvent molecules has to be taken into account.

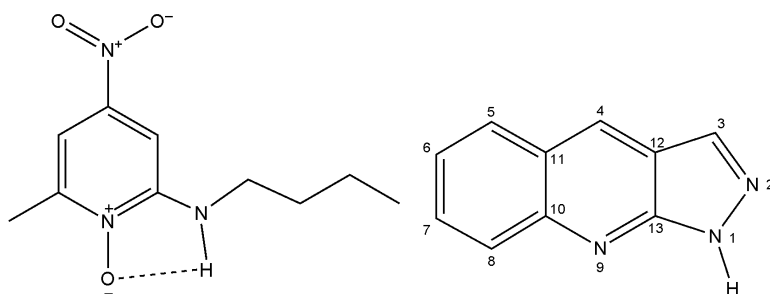
As will be discussed in Chapter 2, both intra- en intramolecular proton transfer reactions receive extensive interest in recent chemical literature: in the 21st century more than 1500 papers in refereed journals have been published. The attention comes from a wide variety of chemical disciplines, including analytical chemistry, biochemistry, physical chemistry and theoretical chemistry, which underlines the relevance of the topic.

In this thesis the focus is on organic molecules in liquid or frozen solutions. It is shown that significant progress in this field can be made – i.e., to elucidate kinetics, and mechanisms as well as to identify chemical species – by combining a variety of electronic spectroscopy modes. The techniques involved to study these processes are not only conventional liquid-state absorption and fluorescence (excitation and emission) spectroscopy. In particular the involvement of high-resolution fluorescence in the wavelength domain recorded under cryogenic sample conditions, a technique well established in our laboratory is quite

informative. Furthermore, for this purpose we developed a high-resolution molecular absorbance technique applicable to snow-like scattering samples over a temperature range from room temperature down to 10 K. Time-resolved fluorescence techniques were involved based on time-correlated single photon counting. Last but not least, we made use of transient absorption measurements in good collaboration with our colleagues from the University of Amsterdam; these measurements provide information about non-fluorescent excited states.

Of course, conventional fluorescence and absorption methods have been amply reviewed in literature and do not need a separate introduction. The high-resolution mode deserves special attention, although for this topic extensive literature is available. Below, a separate chapter is devoted to this topic.

As regards molecules that possibly show excited-state proton transfer, in this thesis we confine our attention to two types of molecules, i.e. an amino substituted pyridine-*N*-oxide which especially in non-polar aprotic solvents behaves extraordinarily and pyrazoloquinoline a molecule that hardly has fluorescence properties in its dimeric form and will be shown to undergo double proton transfer. Their monomer structures are given below:



*Figure 1: Monomer structures of 2-butylamino-6-methyl-4-nitropyridine-*N*-oxide (2B6M, left) and 1H-pyrazoloquinoline (1H-PQ, right)*

In chapter 2 the literature dealing with high-resolution spectroscopy studies on excited-state intra- and intermolecular proton transfer is reviewed. Recent results are shown for four classes of compounds, i.e. hydroxychromones, aza-indoles, pyrazoloquinolines, and amino-substituted pyridine-*N*-oxides which were studied in liquid solutions, polycrystalline matrices and/or a supersonic jet. These species can exist as monomers, dimers, complexes with polar solvent molecules, or mixtures of these. Proton/deuteron exchange, which strongly slows down those transfer reactions

that take place through tunneling, is an important tool for elucidating the reaction mechanisms. In this chapter, emphasis is on spectral information in the wavelength domain, but time-resolved femtosecond studies (for example on the ESDPT in dimers of 7-azaindole) are also included. Cryogenic high-resolution (Shpol'skii) spectroscopy – not only in the fluorescence but also in the absorbance mode – receives special attention. It can be used to characterize the various chemical species involved in the photochemistry/physics of the above compounds, but in favorable cases (in case of hydroxychromones) also to provide detailed kinetic information on excited-state proton transfer processes that can be extracted from the homogeneous spectral linewidths.

High-resolution spectroscopy in low-temperature crystalline matrices is further reviewed in chapter 3. This chapter focuses on obtaining high resolution in crystalline environments according to Shpol'skii, i.e. fluorescence, phosphorescence and absorption spectroscopy of organic molecules in polycrystalline matrices (denoted as Shpol'skii matrices). For most of these applications the use of laser excitation is crucial. The chapter starts with a theoretical description of the Shpol'skii effects followed by experimental parameters and instrumentation of Shpol'skii spectroscopy (SS). We show that over the years, SS has been invoked in a diversity of research topics.

In chapter 4 different spectroscopic fluorescence and absorption techniques are used to study one particular 4-nitropyridine-*N*-oxide compound, namely 2-butylamino-6-methyl-4-nitropyridine-*N*-oxide (2B6M). This molecule may undergo excited-state intra- or intermolecular proton transfer. Three topics are distinguished.

Chapter 4.1 describes the exceptional photophysics of 2B6M studied by conventional fluorescence and absorption spectroscopy. In non-polar solvents, 2B6M exhibits an unusual fluorescence behavior: there is a substantial difference between the relative band intensities of the excitation and absorption spectra. Furthermore, in emission two bands are observed, and their relative intensities depend on the excitation wavelength, pointing to the fact that not only the vibrational ground state of S_1 but also higher states are involved in photophysics, thus violating the Kasha-Vavilov rule. It is the objective of this research to interpret these results.

We noted that under frozen, crystalline matrix conditions more species show up in the spectra. To study this multi-species system in more detail, in chapter 4.2 we present absorption and fluorescence experiments on 2B6M, recorded in *n*-octane at

various temperatures between 293 and 5 K. High-resolution spectra are included, not only in fluorescence but also in absorption.

Finally in chapter 4.3 a transient absorption study in *n*-octane in the liquid state is described for a better understanding of the exceptional photophysics of 2B6M in non-polar solvents.

Pyrazoloquinolines are highly fluorescent, both in liquid solutions and in the solid state, which makes them good candidates for several optical devices. In chapter 5 the photochemical behavior of pyrazolo[3,4-*b*]quinoline (PQ) is described, which is quite complicated since PQ tends to form strong complexes with protic solvent constituents as well as dimers in *n*-alkane solvents. Both types of H-bond complexes were studied systematically by temperature-dependent conventional absorption and fluorescence spectroscopy; the effect of polar solvent constituents was mimicked by varying the ethanol concentration in *n*-octane. Upon lowering the temperature, dimer formation can be observed in pure *n*-alkane. The fluorescence is strongly reduced since the dimer is non-fluorescent. Very fast excited-state proton transfer processes via a tunneling mechanism are responsible for the efficient quenching of PQ dimer fluorescence at low temperatures.