PICOSECOND DYNAMICS OF DOUBLE PROTON TRANSFER IN 7-AZAINDOLE DIMERS

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Fluorescence kinetics indicate that photoexcited dimers of 7-azaindole undergo a double proton transfer in less than 5 ps at room temperature and 77 K. The photoautomerization at 77 K is found to be dependent on the excitation wavelength. A double well excited state potential surface is used to interpret the results.

1. Introduction

Excited state proton transfer is a key step in many energy relaxation and structure changing phenomena. The strong coupling between the proton position and the electronic energies provides important channels for these ultra-fast radiationless processes [1–3]. An unusual system is the 7-azaindole (7AI) dimer which was discovered to undergo a simultaneous double proton transfer process [4–8], thereby generating a tautomer of the original dimeric molecule. Particular interest in the 7AI system derives not only from the double proton transfer phenomenon, but recognition [4] that the dimer of 7AI, similar to the hydrogen bonded base pairs of DNA, could serve as a model for tautomerization and thus possible mutagenic behavior in genetic material.

It was found upon photoexcitation of the ground state hydrogen bonded 7AI dimer that a tautomer in an excited state was produced (see fig. 1). The formation of the tautomer in its excited singlet state is manifested by the appearance of a new fluorescence band (origin at 430 nm) which is red-shifted by 7500 cm^{-1} from the dimer absorption origin at 325 nm (see fig. 1). In the present studies picosecond laser methods have been used to investigate this very rapid double proton transfer process. The kinetics of the tautomer formation, indicative of the transfer step, has been monitored at room temperature and 77 K by measurement of the tautomer fluorescence risetime following photoexcitation with a picosecond light pulse. In addition excitation spectra of the dimer and tautomer at 77 K

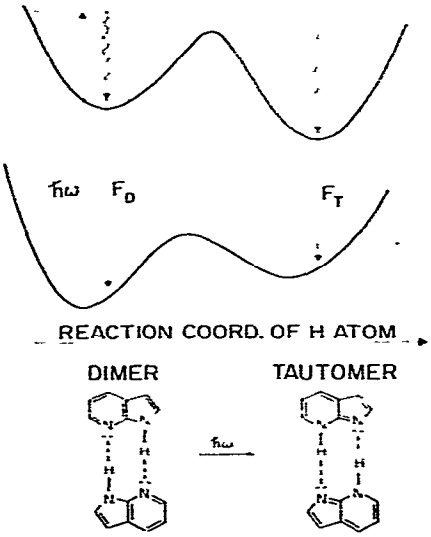

Fig. 1. Potential energy diagram and structural diagram describing excited state double proton transfer in the 7-azaindole H-bonded dimer. $\hbar\omega$ is the excitation energy and Γ_D and Γ_T are the dimer and tautomer fluorescence respectively.

have been used to provide information on the phototautomerization process.

2. Experimental

Time-resolved fluorescence spectra were obtained with a spectroscopic system consisting of a mode lock-

ed Nd^{3+}: phosphate glass laser, a streak camera, an optical multichannel analyzer, and a magnetic tape drive for data storage. A single pulse (0.1 mJ) at the 263.5 nm fourth harmonic of the 1054 nm fundamental was used to excite the dimer. Pulse widths were typically 3–6 ps at the second harmonic (527 nm) and were somewhat shorter after conversion to the fourth harmonic. The tautomer fluorescence was collected through filters passing wavelengths between 450 nm and 560 nm. The fluorescence was displayed as a function of time on the streak camera and recorded through the use of an OMA with an overall time resolution of 5 ps. To provide a time reference for signal averaging and to monitor the excitation pulse width, a 527 nm prepulse was recorded slightly ahead of the fluorescence on each streak camera record.

7-azaindole (Aldrich) was purified by recrystallization from dry cyclohexane and by vacuum sublimation. 3-methylpentane (3MP) was purified, dried and used as the solvent in all experiments. The degassed 8×10^{-3} M 7AI in 3MP solution used in this work exhibited the same fluorescence spectra at 77 K and 296 K as reported in previous studies [4–6]. The time-resolved fluorescence signals were found to be independent of excitation intensity within a pulse energy range of 0.005 to 0.1 mJ. Laser excitation of the solvent alone produced no observable signal.

3. Results and discussion

It is estimated that more than 85% of the 7AI (10^{-2} M) exists in the dimeric form at room temperature [6]. The fluorescence spectrum consists of two well-resolved bands arising from the residual monomer emission peaked at 330 nm and the tautomer emission peaked in the visible at 480 nm. There is no evidence for emission from the dimer at room temperature [6]. The rise-time of the tautomer fluorescence following photoexcitation at 263.5 nm, fig. 2, is so rapid that it cannot be resolved by the laser–streak camera system. The double proton transfer step producing the tautomer is therefore faster than 5 ps at room temperature.

At 77 K a major portion of the tautomer fluorescence rise appears within the excitation pulse width (fig. 3) as was found to be the case at room temperature. The risetime of this major component is therefore 5 ps or less. The slowly rising minor component is

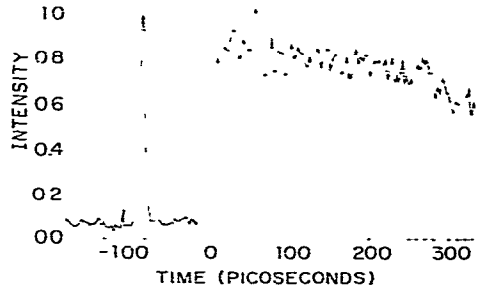

Fig. 2. Streak camera record of the tautomer fluorescence at 296 K for 8×10^{-3} M 7-azaindole in 3-methylpentane. A prepulse used as a time marker precedes the fluorescence and is indicative of the time profile of the excitation pulse. This plot is an average of the results of three laser shots.

responsible for less than 20% of the tautomer emission. Preliminary measurements carried out at slower streak camera speeds indicate that the small slower component must level off in about 1 ns.

The presence of a fast and slow component in the tautomer fluorescence suggests that there are at least two different pathways for the generation of the tautomer. If there were only one pathway for tautomerization, then only the more rapid step would be observed. Support for the idea of different channels for tautomerization is obtained from measurements of the emission spectrum at 77 K. Excitation of the system at 263.5 nm (either with a cw source or a picosecond laser pulse) revealed two well-resolved bands. One

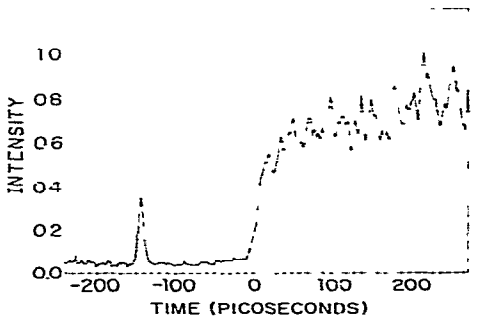

Fig. 3. Streak camera record of the tautomer fluorescence of 8×10^{-3} M 7-azaindole in 3-methylpentane glass at 77 K also showing the prepulse. This is the average of the results of three laser shots.

weak band in the UV corresponds to dimer emission at 360 nm and the stronger band at 480 nm due to the tautomer fluorescence. If there was one channel for tautomerization and it was very rapid, corresponding to the rapid rise observed (< 5 ps), then all of the dimers excited at 263.5 nm should undergo tautomerization. Thus no dimer emission should be observed, contrary to observation.

The time dependent tautomer fluorescence and spectral measurements at 77 K imply that the double proton transfer process leading to the tautomer is energy dependent. To examine this possibility the excitation spectra of both the dimer and tautomer were measured at 77 K. The excitation spectra of the dimer and tautomer were found to be different indicating that the tautomerization is indeed energy dependent. Excitation of the system from 325 nm to 318 nm produced more emission from the dimer than the tautomer, whereas excitation at shorter wavelengths yielded more tautomer than dimer. This wavelength dependence offers an explanation of the relatively slow risetime (4 ns) for the tautomer fluorescence observed in the deuterated 7AI at 77 K [7]. At wavelengths below 318 nm the excitation spectra become identical within our experimental accuracy, thus showing that the rate of formation of tautomer to the rate of formation of the relaxed dimer has become constant, i.e. their ratio is energy independent.

To provide a framework for these various experimental measurements a simple model is employed, namely an excited state potential surface with a barrier separating the dimer and tautomer forms. The height of the barrier can be directly estimated by taking the energy difference between the first peak in the tautomer and dimer excitation spectra at 77 K. In this way an upper limit to the barrier height of approximately 700 cm^{-1} is obtained. This is in good agreement with the 500 cm^{-1} barrier estimated in earlier studies [6]. Excitation at 263.5 nm therefore prepares the system in an excited state which is significantly above the excited surface barrier. The geometric structure of the initially excited molecule corresponds to the ground state dimeric structure (protons on the indolic nitrogens) (see fig. 1). However, at this energy above the barrier the state must be described as some superposition of dimer and tautomer states. Energy relaxation from this initially prepared state can occur down to the zero point excited dimer level, D_0^*, or the zero point excited state tautomer level, T_0^*. Molecules which have decayed to D_0^* can undergo a tautomerization by a thermal process if sufficient energy is available or by tunneling. Both of these processes compete with dimer fluorescence and internal conversion processes. At room temperature a barrier height of 500–700 cm^{-1} and a frequency factor of about 10^{13} yields a thermal tautomerization time from D_0^* to T_0^* of a few picoseconds. Both the direct tautomerization from the initially excited molecule and the indirect tautomerization from D_0^* are sufficiently fast to appear as a single fluorescence risetime of less than 5 ps. However, at 77 K the rate of the indirect thermal tautomerization is in the range of 10^7–10^9 s^{-1}. Thus at this temperature it would be possible to observe both the fast direct and slow indirect tautomerizations with the laser–streak camera system used in these experiments. At this temperature the dimer fluorescence rate becomes competitive with the D_0^* thermal tautomerization and can therefore be observed.

This single surface model is thus seen to be consistent with the experimentally observed time-resolved tautomer fluorescence, the dimer and tautomer excitation spectra, and the temperature dependences of the tautomer and dimer emissions [6]. However, more detailed measurements could require a more complex model based on several excited state potential surfaces. To more fully elucidate double proton transfer further experiments covering a range of temperatures, excitation energies, and the effects of deuteration are in progress.

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References

[1] W. Klöpffer, Advan. Photochem. 10 (1977) 311.
[2] K.K. Smith and K.J. Kaufmann, J. Phys. Chem. 82 (1978) 2286.
[3] H. Shizuka, K. Matsui, T. Okamura and I. Tanaka, J. Phys. Chem. 79 (1975) 2731.

[4] C.A. Taylor, M.A. El-Bayoumi and M. Kasha, Proc. Natl. Acad. Sci. US 63 (1969) 253.
[5] K.C. Ingham, M. Abu-Eigheit and M.A. El-Bayoumi, J. Am. Chem. Soc. 93 (1971) 5023.
[6] K.C. Ingham and M.A. El-Bayoumi, J. Am. Chem Soc. 96 (1974) 1674.
[7] M.A. El-Bayoumi, P. Avouris and W.R. Ware, J. Chem. Phys. 62 (1975) 2499.
[8] V.I. Pechenaya and V.I. Danilov, Chem. Phys. Letters 11 (1971) 539.