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A time-resolved photoelectron study of the double excited-state proton-transfer reaction in 7-azaindole dimer

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Abstract

A study employing picosecond and subpicosecond excitation in a mass and photoelectron spectrometer is reported for the 7-azaindole (7-AI) dimers, reactive and unreactive. The 7-AI photoelectron spectrum is structured and has a sharp ionisation threshold at 8.17 eV above the neutral ground electronic state. The reactive dimer ionisation threshold was measured as 7.19 eV. The excited-state lifetime of the reactive dimer was measured by a technique that monitors the ionisation signal as a function of pulse duration. 1 + 1 resonance ionisation photoelectron spectra were recorded using 0.8 ps and 5 ps pulses. Our results indicate a lifetime substantially less than a picosecond, however, consistent with recent real time studies. Advantages of the method are discussed. © 1997 Elsevier Science B.V.

1. Introduction

Proton transfer reactions represent a prototype for reactions in living systems. In many cases the rates are significantly enhanced in the excited states [1] due to electronic structures that stabilise the anion of the acid (conjugate base). These reactions are also strongly dependent on the solvent, both in the condensed phase and in clusters [2,3], and that the reaction rate is influenced by solvent rearrangement [4]. The case of intermolecular double proton transfer reactions in dimers differs from the more typical case of an acid in a base solvent or cluster, in that a sterically specific geometry is required for the double proton exchange. The reaction then is less dependent on the solvent and can represent a model for proton transfer studies in the gas phase [5].

The 7-azaindole dimer (I) has been studied by Kasha et al. in solutions who was the first to observe a luminescence that was evidence for a reaction product [6], formally identified later as the tautomer (II) [7]. The dimer was chosen by Kasha for its similarity to the hydrogen-bond pairing in nucleic bases where tautomerisation had been considered as a major denaturation process. A rich literature has followed in solution [8]. Kaya and co-workers first observed this system in a supersonic jet in a series of articles and recorded the action spectrum of the dimer [9]. Their spectrum shows evidence of a small barrier, and of the influence of a promoting mode for

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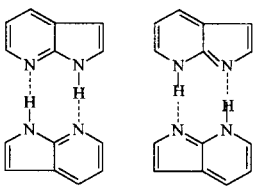
the reaction involving the symmetric N–H · · · N stretch. From excitation spectra monitoring excited-state reactant and product emission, they inferred a lifetime of about a picosecond or less. In another study these investigators spectroscopically characterised the tautomer [10]. The Zewail group have directly observed the subpicosecond time evolution of the reacting dimer by femtosecond mass spectrometry and have shown the presence of a complex evolution, possibly via an intermediate [11].



I II

In this study we have performed picosecond time resolved photoelectron spectroscopy (PES) of the reacting dimer. The recording of the photoelectron energy distribution potentially offers additional information regarding proton transfer reactions compared to total ion yield mass spectrometry measurements, as shown before [4,12]. In particular, PES is sensitive to the change of the ionisation potential along the reaction coordinate. In a pump probe experiment the ionising probe pulse projects the evolving excited-state wavepacket onto the ion ground state. The time-resolved photoelectron spectrum should contain information on the electron dynamics as well on the nuclear dynamics via the overlap with the ground state ion; this latter issue has been considered by Stolow [13]. The 7-azaindole (henceforth 7-AI) dimer is an attractive system as its first excited state can be approximatively characterised by a one-electron configuration [14,19], simplifying a description of the excited-state evolution from the time-resolved photoelectron spectrum.

The principal result reported here is the observation of the time resolved photoelectron spectrum of the dimer with 0.8 and 5.0 ps pulses. The differences in these spectra are interpretable in terms of the lifetime and excited-state properties.

2. Experimental

The dimer was prepared in a pulsed supersonic helium expansion (1.2 atm) with a 300 μm nozzle heated to 80–90°C. The timing of the pulsed valve firing was carefully adjusted to the maximum of the valve opening. However, we also varied this delay to control the extent of clustering in most cases to maximise dimer and minimise other cluster formation. Fig. 1 shows the different extent of clustering that can be achieved; from nearly pure dimer (Fig. 1a) to larger oligomers (Fig. 1b). The dimer abundance in Fig. 1a was also enhanced relative to other species by heating the 7-AI sample to 80°C. On the

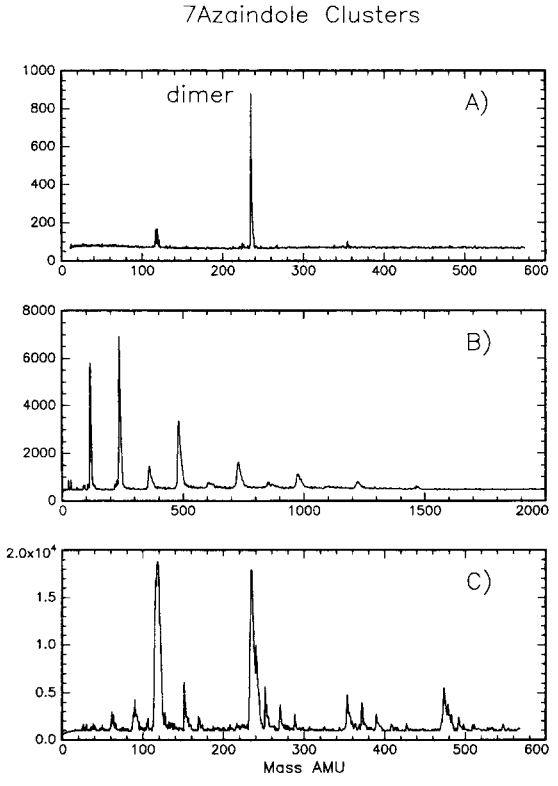


Fig. 1. (A) Time-of-flight mass spectra of 7-AI in 1.2 bar He with 80°C sample temperature and laser excitation early in the gas pulse. (B) 3 bar argon expansion 90°C sample temperature and laser excitation near the peak of the gas pulse density. Ionisation is by one-color 1 + 1 resonance ionisation at 3100 Å. (C) similar conditions with 1% NH_3.

other hand increasing the temperature to 90°C and using argon expansion at 3 bar generated oligomers as recorded in the spectrum of Fig. 1c Fluorescence excitation spectra of the tautomer were recorded from dispersed emission in the free jet region with a frequency doubled nanosecond dye laser.

The free jet is skimmed at 12 cm and the resulting beam passes into a chamber, evacuated by cryopumps, where the photoelectron spectrometer is installed. This spectrometer constructed in the C.E. Saclay by Agostini and co-workers is of paraboloidal time of flight design reflecting the electrons in a 2π sr solid angle, as a telescope for electrons. Its design has been described before [15,16]. The electron energy resolution $\Delta E/E$ is about 0.05 in the 0–1 eV region where the spectra presented here generally lie. The spectrometer can also be operated as a TOF mass spectrometer by changing the polarity of the paraboloidal grid and the detector.

A tuneable ultrashort laser [17] of 0.8 ps pulse duration was used to ionise the dimer. The laser is continuously tuneable with a 1 nm rotating filter setting the spectral resolution; a 30 cm^{-1} resolution is achieved in the UV. Although the laser could be used in the continuously tuning mode we preferred to record point by point spectra.

3. Observation of the dimer

The dimer excitation spectrum was recorded by tuning a nanosecond laser over the absorption range of the dimer and collecting the tautomer fluorescence centred at 5000 Å. The resulting spectrum in Fig. 2 is very similar to the spectrum described by Fuke and Kaya [10]. The main features include a progression of bands with a fundamental frequency of about 117 cm^{-1} that the former authors assign to the symmetric N–H · · · N stretch vibration. Another mode at about 100 cm^{-1} is evident in both the present and the earlier spectra. This mode forms a combination with the 117 cm^{-1} progression. There are other intermolecular modes including the wagging out of plane mode. Calculations by Douhal et al. indicate that the excited state loses the centre of inversion corresponding to two non equal N–H · · · N bonds [12], therefore Franck–Condon excitation could lend some activity onto modes involving the

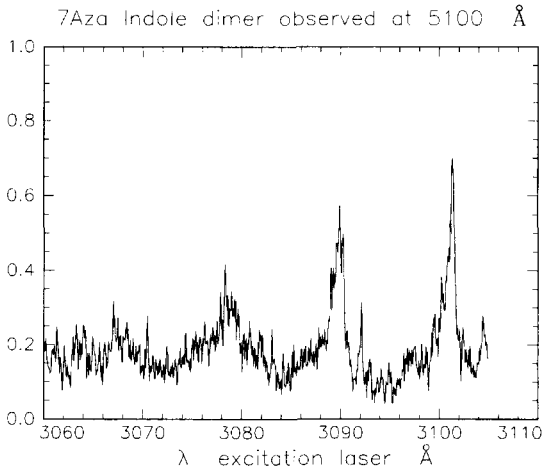


Fig. 2. Fluorescence excitation spectrum of 7-AI dimer recorded by collecting the tautomer fluorescence at 5100 Å.

asymmetric motion of the two N–H · · · N bonds. More recently Guallar [19] performed calculations on the modes of the dimer which indicate the existence of two modes at 80 and 100 cm^{-1} involving the relative torsion of the two azaindole moieties, and also found the symmetric stretch van der Waals mode N–H · · · N, in excellent agreement at 118 cm^{-1}.

The integrated intensity of the 0–0 band relative to the fundamental corresponds to a calculated reduction in the intermolecular N · · · N distance of about 0.1 Å due to excitation assuming a simple one-dimensional displaced harmonic oscillator model. The existence of a well defined progression in the van der Waals mode as first observed by Fuke and Kaya that also exhibits an increasing width with excitation energy is consistent with a small barrier in the initial step of the tautomerisation [10]. This conclusions are consistent with temperature-dependent rates in solutions [20] or with the deuterium effect in the gas phase kinetics [11] and linewidths [10].

4. Structure of the dimer

The dimer can be considered as fully doubly hydrogen bonded, in agreement with calculations. Under intense expansion conditions (3 bar total pressure), large clusters of 7-AI can be formed as shown

in Fig. 1b. One observes a clear alternation in intensity of the even and odd clusters corresponding to a strong propensity for formation of even-sized clusters. This is due to the stability of doubly-hydrogen bonded structure. Oligomers presumably involve an arrangement of dimers, stacked or chained and therefore the even numbered multimers will have the highest stabilisation. The odd numbered multimers will involve a stacked monomer and be at higher energies, as the stacking energy amounts to only ca. 1000 cm^{-1} (no minimum is found in that configuration) as compared to 3950 cm^{-1} for the double hydrogen bond. The double-hydrogen-bonded geometry is further supported by an experiment in which ammonia was added to the expansion to titrate free hydrogen bonds. It is seen in Fig. 1c that the most stable $(7\text{-AI})_n(NH_3)_m$ series of m occur for odd-numbered n. In the odd multimers, NH_3 can bond efficiently to the free pyrrolic hydrogen, whereas in the even multimers, the only free sites for NH_3 to bind to are the less favourable aromatic or heteroaromatic rings.

Kaya and coworkers, reported the existence of an apparent isomer of the dimer, which has the following attributes that differ from the reactive dimer: (1) the isomer is unreactive in so far as not generating red-shifted tautomer-like emission, (2) the excitation spectrum contains a large number of low frequency modes. On the other hand, the spectral red-shift of the isomeric dimer relative to the monomer is large, about 2400 cm^{-1}, and nearly the same as the reactive dimer, suggesting that the isomeric dimer also has a double hydrogen-bonded geometry. Since the pyrrolic Nitrogen atom is conjugated in 7-AI, the pyrrolic hydrogen is expected to lie within the plane hence it can be reasonably expected that the dimer does not deviate too much from planarity. However, if the hydrogen were out-of-plane, corresponding to a pyramidal amino-like nitrogen, then the existence of two isomers of 7-AI dimer can be explained. This situation does not violate the planar structure of the skeletal ring, as determined by X-ray crystallography [21]. An out of plane H atom would correspond to a chiral N site. The dimer may then assume two geometries, a displaced by parallel geometry, and an out-of-plane geometry. The latter structure is consistent with the experimental observation of low-frequency modes. The lower overlap in the non planar form will result in a much lower drop in the ionisation potential consistent with the observation. The lack of reactivity might also arise from the non-parallel overlap of the aromatic systems, which would diminish the orbital overlap of the two aromatic systems.

Another possible explanation of the unreactive dimer was recently reported by Kaya, Miller and coworkers [25] based on high resolution IR spectroscopy of 7-AI monomer, dimer and solvated 7-AI complexes. They speculated that the unreactive dimer may actually contain an H_2O molecule that is unstable in the ion and hence dissociates to give an uncomplexed 7-AI dimer cation in the mass spectra. However, the evidence is scant; hence, the issue of structure is still an open question. We have recorded the photoelectron spectra of the two species with picosecond and nanosecond excitations, which we report next.

5. Photoelectron spectra of the dimer

The photoelectron spectra of the 7-AI dimer were recorded under expansion conditions that minimised larger clusters. The mass spectrum in Fig. 1a consists mostly of the dimer, a small amount of trimer, and essentially no tetramer. A weak monomer signal appears via a 3 photon absorption and this signal is reduced by tuning the focus of the ionising lens as far as possible.

The photoelectron spectrum of the 7-AI monomer has been observed by resonance 1 + 1 ionisation at the S_1 origin transition at 34634 cm^{-1}. The onset to the photoelectron spectrum corresponds to an ionisation threshold of 8.17 eV, in agreement with ZEKE measurements 8.117 eV by Kaya et al. [18]. The sharp onset and peak is consistent with a measurement of an adiabatic ionisation potential. The 7-AI dimer photoelectron spectra in Fig. 3 were recorded at the S_1 origin transition of 32252 cm^{-1} [10]. The onset to the photoelectron spectrum corresponds to an ionisation threshold of 7.19 eV or about 8000 cm^{-1} lower than for the monomer. The dimer spectrum is structureless and the onset relatively broad (about 0.2 eV rise) in contrast to the monomer spectrum. These features are assignable to the general changes in geometry through ionisation of the cluster species.

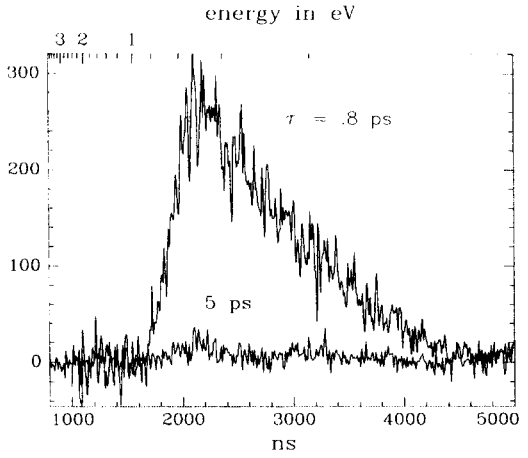


Fig. 3. PES recorded by 1+1 resonance ionisation for two different pulse durations, 0.8 ps and 5.0 ps and 3100 Å excitation.

The unreactive dimer discussed above has the distinguishing property of having considerably more two-photon activity than the reactive dimer [9]. Photoelectron spectra were recorded of the unreactive dimer by 2-photon resonance multiphoton ionisation at 614.0 nm. Expansion conditions were optimised to accentuate the ratio unreactive to reactive dimer, consistent with the conditions used by Fuke and Kaya. The presence of the unreactive dimer was confirmed by recording an excitation spectrum that agreed with that of Fuke and Kaya. The ionisation threshold for the unreactive dimer was measured to be 7.81 eV.

6. Time dependence of the ionisation of the dimer

To probe the time dependence of the tautomerisation reaction, we recorded photoelectron spectra using different pulse durations. In Fig. 3 are PES recorded by 1 + 1 resonance ionisation using 0.8 ps and 5.0 ps pulses of equal energy. The temporal broadening was achieved by substituting a 2 cm long frequency doubling KDP crystal in place of the 0.2 cm thick crystal used to generate the shorter pulse. Fig. 3 shows a dramatic drop in intensity for the long pulse relative to the short pulse. Also, no detectable electron or ion signal is observed for nanosecond resonance ionisation. These results indicate the following properties: (1) the reactant excited state lifetime is significantly less than 5 ps, and (2) the ionisation cross section from the tautomer excited state is considerably less than for the reactant excited state. These properties are consistent with the femtosecond measurements by the Zewail group who showed a lifetime less than 1 ps, and explains why the ion signal decays to nearly the baseline and not to some other level resulting from ionisation of the tautomer excited state.

The ionisation yield for a reacting system is a function of the competition between the up-pumping (ionisation) and other decay channels. For 7-AI dimer excitation, the competition is between the probe pulse ionisation rate and the chemical reaction. We calculated this competition using two models. The first is based on numerical integration of rate equations for the relevant states (ground, excited, and ion) assuming pulses of Gaussian temporal profile. This model, described in more detail previously [23], shows the change in populations before, during, and after the ionising pulse. The second model is an analytical solution of the ion yield following an assumed square-wave pulse. The results from integrating the rate equations are presented in Fig. 4 for ionising pulses of equal energy, but different duration (0.8 ps vs. 5.0 ps; Fig. 4a and 4b, respectively). For a reaction time of 650 fs, the model predicts a 3.2-fold greater signal for the shorter pulse relative to the longer pulse. Experimentally, the relative intensity ratio is greater than 10. A calculated ratio of 10 is obtained for reaction time less than 100 fs, which is much shorter than measured by the Zewail group [11] or indirectly determined by Fuke and Kaya [10].

At present, the model relating reaction rate to relative intensity for different duration ionisation pulses is not rigorous. The ionisation cross section is not known; we have assumed that the excitation and ionisation steps are under non-saturating conditions, although the model handles conditions of saturation. Input parameters to the calculation are given in the caption to Fig. 4.

The method described, though not yet quantitative, has the potential to be very useful in addressing issues relating to state-specific rates or in cases, when pulse duration's are longer than time constants of dynamical interest. The excitation spectrum of 7-AI is relatively rich and structured. Furthermore,

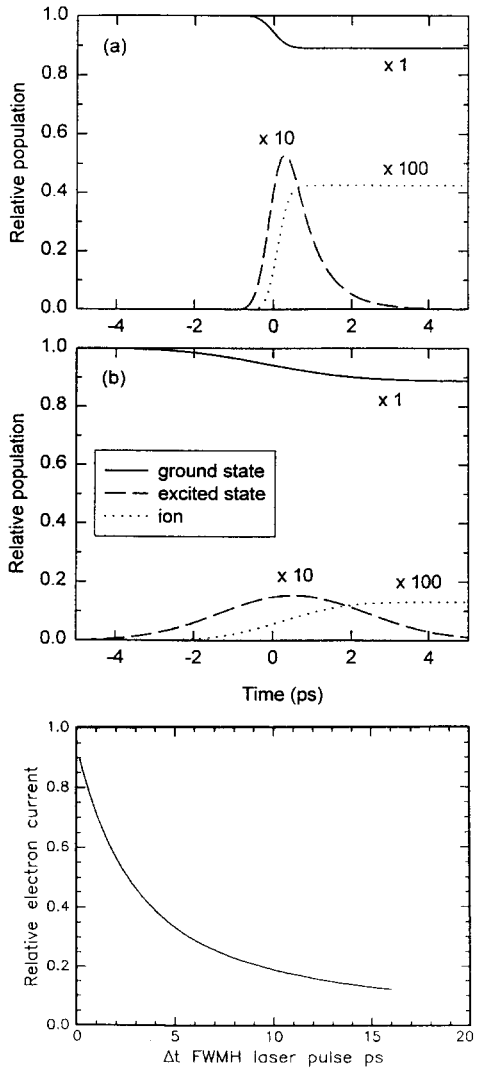


Fig. 4. Calculated time evolution for ground, excited, and ion state of 7-AI dimer for model reported in Ref. [22]. Calculation assumes $1/k = 650$ fs, $\sigma_{12} I_1 = \sigma_{23} I_2 = 0.12$ photons/molecule, where σ_{12} and σ_{23} are the transition cross sections (cm^{-2}) from the ground to excited state and excited state to ion, respectively, and I_1 and I_2 are the pump and probe fluence (photons/cm^2), which are the same in this experiment. a) pulse width (gaussian) 0.5 ps (0.8 FWMH), b) 3 ps (5 FWMH), c) $I(\Delta t)$ as in Eq. (2) for $\tau = 1$ ps, plotted as a function of Δt (FWMH) width of the pulse.

there is intriguing evidence that certain S_1 modes lead to significantly enhanced rates of reaction [9,10]. These results are consistent with predictions of recent proton tunnelling theories in clusters [23]. Single-vibronic level excitation is not possible with ultrashort pulses due to the large frequency bandwidth. In some sense, one needs to use excitation pulse duration's that are matched to the time constants of dynamical interest in order to explore mode-specific processes. The method of varying pulse duration and observing changes in ionisation signal, described above, is one means to achieve this information. Since pump and probe measurements are frequently difficult when pump and probe excitation also gives individual 1-color signal, this method offers a simple alternative for exponential decays and could easily be implemented with the use of stretcher compressor device or with a wedged frequency doubler, where the pulse duration is related to the path length traversed by the beam.

To examine the utility of this method further, we consider some additional issues below and provide an analytical solution relating the ratio of ionisation signal for different resonance ionisation pulse duration's to intermediate state lifetime. We assume that the drop in ionisation efficiency results from the evolution of the excited dimer along the reaction coordinate. The total ion signal induced by a sequential two photon excitation with a delay T, by a pulse of duration Δt (gaussian width) via an intermediate state of lifetime τ is given by the following equation:

$$I(\Delta t) = K/(\Delta t)^2 \int_{-\infty}^{\infty} dT \int_{-\infty}^{\infty} e^{-(t/\Delta t)^2} \times e^{-((t+T)/\Delta t)^2} e^{-(T/\tau)} H(t)\, dt. \quad (1)$$

K is constant and $H(t)$ the unit step function; this can be transformed in the numerical integration of the following expression

$$I(\Delta) := \int_0^{10\cdot\Delta t} \frac{1}{2} \exp\left[\frac{-1}{(2\Delta t^2)} T^2 - \frac{T}{\tau}\right] \frac{\sqrt{\pi \cdot 2}}{\Delta t} dT,$$

which is plotted in Fig. 4c. Intuitively, when the duration of the pulse Δt is greater than the decay rate $k = 1/\tau$ and it can be seen that the ionisation yield decreases with increasing duration of the pulse. For example, the intensity $I(\Delta t)$ decreases by a factor of 3 for $\Delta t = 5$ ps FWMH (3ps gaussian) relative to 0.8 ps FWMH (0.5 ps gaussian). The determination of an exponential decay with a constant τ via a simple correlation $I(\Delta t)$ should pro-

vide a simple measurement with a single pulse. However there are a few considerations to be taken into account: (1) The frequency width of the laser should always match the absorption spectrum, since we have supposed that the integrated absorption remains constant as Δt changes. (2) the pumping rate should be under a non-saturation regime, i.e. the electron current should remain proportional to the square of the laser power. If the intensity of the laser becomes too high the ionic state will be reached by a one step two photon excitation (this corresponds to conditions where the Rabi frequency is much greater than the decay rate). These latter conditions are easily attained with a powerful ultrashort pulse. Therefore we checked carefully the conditions by varying the focus of the laser through the molecular beam diameter. This method is similar in concept, but different in practice from the method by Syage and Steadman of obtaining fast rate measurements from long duration pulses by observing the unusual lineshapes that arise when scanning in a saturation regime [22].

An interesting observation here is the significant decrease in the photoelectron signal for the excited tautomeric 7-AI dimer product. This result is in agreement with the femtosecond measurements by Douhal [11]. The identity of the ionised species was verified by tuning the picosecond laser throughout the dimer absorption range and the total electron yield was plotted as a function of frequency resulting in the action spectrum of Fig. 5. This spectrum can be compared with the tautomer action spectrum in Fig. 2 and, although it does not have the same resolution, it exhibits the characteristic spacing of the dimer vibrations and covers the same domain. In the blue region of the photoelectron action spectrum the intensity decreases relative to the fluorescence action. This has to be related to the shorter lifetime. A similar spectrum was found when monitoring the dimer mass with picosecond laser excitation.

The decrease of the dimer ionisation efficiency observed by Douhal et al. [11] and here, results from several causes: i) the tautomerisation corresponds to ca. 3800 cm^{-1} excess vibrational excitation and ii) the ionisation threshold increases with the tautomerisation. Calculations have shown that the tautomer may have a slightly lower ionisation potential from its ground state However the ionisation limit reached

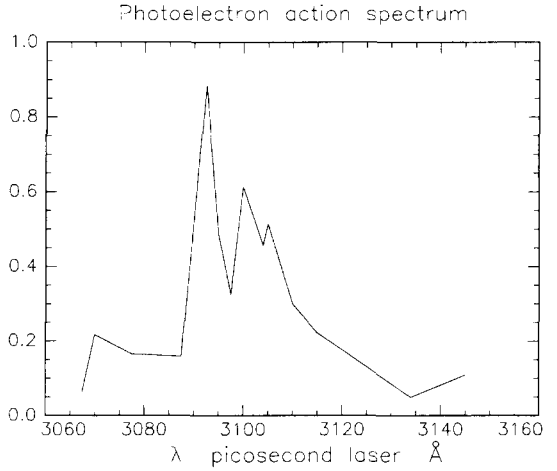


Fig. 5. Excitation spectrum of 7-AI dimer recorded by collecting the photoelectron signal (integrated) while scanning a picosecond laser.

after the reaction should lie above that of the dimer owing to the higher energy of the ground state tautomer. In calculations performed here it was found that the monomeric tautomer in its ground state lied ca. 5800 cm^{-1} above the 7-AI ground state, the same applies in the dimeric form with 8500 cm^{-1} higher energy of the tautomer, as shown in Ref. [12].

7. Conclusion

The ionisation potential has dropped in the dimer by 1 eV and this provides the driving force for the tautomerisation. Indeed the excited proton transfer reactions have long been related to changes in the charge density in the reacting molecule, Weller showing in solutions the presence of Zwitterions. The relation of the excited proton acidity with the calculated electron flow in the excited state of proton transferring systems has been extensively studied and a strong correlation found between this flow and the efficiency of the transfer [24]. For the 7-AI dimer early INDO/S calculations by Waluk [14] indicate that in the second excited state of the monomer, $\frac{1}{2}$ of a negative charge had flown from the pyrrole ring to the pyridine ring. This charge flow is confirmed in the dimer by Douhal et al. [12] and Guallar [19] who found a 0.3 charge unit flow. Hence in the dimer

after the excitation the pyridinic nitrogen will attract the hydrogen of the other moiety while the pyrrolic N–H bond will be weakened. The influence of partially charged species on the tautomerisation is in agreement with the observations of Douhal et al. [11], but the question of the concerted motion of the hydrogens has not been addressed here.

In conclusion the driving force for the reaction is to be found in the flow of charges through the excitation, but the reaction would not proceed if the dimer had not been prepared so precisely in this double hydrogen bond configuration, in difference with the similar 7azacarbazole dimer. We have also observed a drop of 1 eV in the ionisation potential for the 7-AI $(NH_3)_3$ complex but no double proton transfer, presumably because the ammonia are clustered around the pyrrolic nitrogen and not connected with the pyridinic ring, thus precluding the transfer.

Acknowledgements

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