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Ultrafast single and double proton transfer in photo-excited [2,2'-bipyridyl]-3,3'-diol

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Abstract

We report on a subpicosecond fluorescence study of [2,2'-bipyridyl]-3,3'-diol using the fluorescent up-conversion technique with a time resolution of ≈ 300 fs. A new short-living fluorescence band, peaking at 568 nm, is observed, which is attributed to the emissive keto–enol tautomer. This tautomer is discussed to be formed in its excited singlet state in a stepwise proton transfer mechanism; eventually the keto–enol tautomer decays into the double-protonated di-keto product, which alternatively could also have been formed in a direct double proton transfer reaction.

1. Introduction

Excited-state intramolecular proton transfer is characteristic of numerous enol–keto tautomerization reactions in liquid solution (for a review, see Ref. [1]). Photo-induced intramolecular proton transfer is usually very rapid and its time-resolved study has recently advanced into the femtosecond time regime [2–4]. So far these ultra-fast studies involved molecular systems which showed intramolecular transfer of a single proton. In this Letter we report on a femtosecond study of a molecule showing photo-induced intramolecular dual proton transfer. We focus on the proton transfer dynamics of [2,2'-bipyridyl]-3,3'-diol (hereafter referred to as BP(OH)₂, for structure see insert of Fig. 1). The proton transfer mechanism of BP(OH)₂ has attracted great interest in the last decade [5–24]. Based on the almost independence of the absorption and fluorescence band maxima of BP(OH)₂ to the polarity of the solvent and also on the basis of results from semi-empirical calculations, Bulska et al [5,6] concluded that photo-

excitation of the molecule gives rise to a cooperative double proton transfer process. The strong fluorescence at $\lambda_{\max} \approx 510$ nm is due to the formed di-keto form [5] which in part relaxes into a dark, long-living triplet state [8,9]. Kaschke et al. [11] reported on a picosecond study of BP(OH)₂ (with a time resolution of ≈ 5 ps). They found that the initially excited S₁ state is depleted within a few picoseconds, this time being taken as characteristic of the double proton transfer; no evidence for a stepwise transfer of the two protons in BP(OH)₂ was obtained. Additionally, later experiments by Grabowska et al. [12] suggested that proton transfer dynamics might be detectable on a subpicosecond time scale. Recently, electro-optical measurements were performed for a number of bipyridyl-diols to determine the electric dipole moment of the fluorescent state [13]. The relatively small electric dipole moment for BP(OH)₂ in its fluorescent state was taken as further evidence that emission is from the di-keto product formed in an intramolecular double proton transfer reaction. In addition, computational results obtained from INDO

calculations showed that the energy of the excited singlet state of the mono-keto form (i.e. the single-protonated tautomeric form) is in-between that for the first excited singlet states of the di-enol and the di-keto forms, respectively [5,13]. Recent ab initio calculations showed that in the ground state the di-enol form of $\text{BP}(\text{OH})_2$ is by far more stable than the keto-enol or the di-keto tautomeric forms which also show up as minima in the potential energy plotted as a function of the proton transfer reaction coordinate [14].

In this Letter we report on fluorescence up-conversion experiments for $\text{BP}(\text{OH})_2$ with a time resolution of about 300 fs. Our main result is the observation of a new ultrafast fluorescence transient. This fluorescence, with its band maximum near 17.6 kK (568 nm), has a rise time of less than 300 fs and a decay time of about 10 ps. The transient fluorescence will be assigned to the mono-keto tautomeric form of $\text{BP}(\text{OH})_2$. Moreover, our results show that the di-keto tautomer can be formed in either of two ways: in a direct concerted double proton transfer reaction starting from $\text{BP}(\text{OH})_2$ in the di-enol form in the photoexcited singlet state, or in an indirect stepwise process involving a single proton transfer to form first the intermediate mono-keto tautomer, followed by the decay of the latter into the di-keto form in its excited electronic singlet state.

2. Experimental

[2,2'-Bipyridyl]-3,3'-diol ($\text{BP}(\text{OH})_2$) was purchased from Aldrich and dissolved without further purification in cyclohexane (Fluka, Microselect) and acetonitrile (Merck, Uvasol) in a concentration of about 10^{-3} M. Steady-state absorption spectra were monitored by means of a Shimadzu (UV-240) spectrophotometer. The steady-state fluorescence spectrum of $\text{BP}(\text{OH})_2$ was measured using a calibrated emission spectrometer [25]. Femtosecond laser excitation was accomplished using an all-line Ar^+ -laser which pumped a Tsunami Ti:sapphire laser operating at 800 nm and which delivered 60 fs pulses at a repetition rate of 82 MHz. The laser pulses were first amplified in a Quantronix regenerative amplifier laser system to about 500 mW at 1 kHz, and then frequency tripled using the appropriate optics for mix-

ing the fundamental and the frequency doubled waves. The fs laser pulses (267 nm, pulse energy: 1 μJ) were used to photo-excite the 10^{-3} M solution of $\text{BP}(\text{OH})_2$ which was contained in a flow cell at ambient temperature. The ensuing transient fluorescence was time-resolved detected by applying the fluorescence up-conversion detection technique [26]. In the latter experiments, an attenuated part of the fundamental beam pulses (800 nm) was led through a delay line and focussed together with the pump-beam induced fluorescence onto a 1 mm thick BBO crystal (type I phase matching condition). The up-conversion signal (at the sum frequency of the fluorescence and the fundamental of the fs laser) was focussed on the entrance slit of a Zeiss M 20 monochromator and photodetected by means of a photomultiplier (EMI 9863 QB/350) connected to a PAR lock-in amplifier system linked to a personal computer for data storage and analysis. To avoid detection of kinetics due to reorientational motions of the probed $\text{BP}(\text{OH})_2$ molecules, the polarization of the excitation beam was at the magic angle of $54^\circ 44'$ with respect to the vertically polarized gating beam. From the measured cross-correlation function of the excitation and gating pulses at 400 nm and 800 nm, the instrumental time response was estimated to be approximately 300 fs (FWHM). The decay part of the deconvoluted up-conversion transients as obtained at a series of detection wavelengths, was fitted to a bi-exponential function, $I_s(\lambda, t)$. From the $I_s(\lambda, t)$ functions the time-resolved spectra of $\text{BP}(\text{OH})_2$ could be reconstructed following the method described previously [27].

3. Results

The steady-state absorption spectrum as measured for $\text{BP}(\text{OH})_2$ dissolved in cyclohexane is given by the dashed curve in Fig. 1. The band with its maximum at 340 nm coincides with that reported for $\text{BP}(\text{OH})_2$ elsewhere [5]. The steady-state emission spectrum measured for $\text{BP}(\text{OH})_2$ is included in Fig. 1 (solid curve). This spectrum is in agreement with that reported in Refs. [5] and [6]. The results for the absorption and emission spectra measured for $\text{BP}(\text{OH})_2$ dissolved in acetonitrile were similar to those in cyclohexane.

Fig. 1. Steady-state absorption (dashed curve) and emission spectrum (solid curve) of BP(OH)_2 dissolved in cyclohexane. Insert is the molecular structure of BP(OH)_2 .

The excitation wavelength in the fluorescence up-conversion experiments was either at 267 nm or 400 nm. Fig. 2a shows a few representative fluorescence transients of BP(OH)_2 dissolved in cyclohexane in a time window of 67 ps, as detected for a series of different detection wavelengths, when excitation was at 267 nm. Likewise, Fig. 2b shows a few typical fluorescence transients of BP(OH)_2 dissolved in acetonitrile. A few best fit results for $I_s(\lambda, t)$ are displayed by the dashed curves in the figure. Typically, the observed fluorescence transient is very dependent on the wavelength of the emission. When detection is to the red ($\lambda > 550$ nm), the fluorescence shows a sharp (instantaneous) rise within the duration time of the laser pulses followed by a rapid decay on a time scale of about 10 ps. A much slower

Fig. 2. Fluorescence transients of BP(OH)_2 dissolved in (a) cyclohexane and (b) acetonitrile. Dashed curves represent best fittings to a bi-exponential function.

Fig. 3. Time-resolved emission spectra of BP(OH)_2 dissolved in (a) cyclohexane and (b) acetonitrile. Solid curves are the total emission spectra. Dotted curves are the emission spectra of di-keto formed through concerted double proton transfer process. Dashed curves are the transient components.

decay component, corresponding to the steady-state lifetime of the fluorescent state of BP(OH)_2 , was found at longer time windows using a time-correlated single-photon-counting detection system [25] (3.2 ns in cyclohexane and 1.1 ns in acetonitrile). When detection is to the blue ($\lambda < 550$ nm), there is also an instantaneous intensity increase but now followed by another increase on a time scale of again 10 ps. The experimental transients appeared insensitive to the applied excitation wavelength. Using the functions $I_s(\lambda, t)$ in the spectral reconstruction procedure [27], the time-resolved spectra for BP(OH)_2 dissolved in cyclohexane and acetonitrile, as represented by the solid curves in Figs. 3a and b, respectively, were obtained.

4. Discussion

Previously it has been discussed that the BP(OH)_2 absorption near 340 nm primarily excites the excited singlet state of BP(OH)_2 in the di-enol form, this state being considered as the precursor of the di-keto tautomeric form [5,13]. Since the proton transfer process was found to be very rapid (the time constant was estimated to be in the subpicosecond regime), the double proton transfer was thought to involve a concerted dual proton transfer and not a

stepwise reaction involving two sequential single proton transfers. The data presented in this Letter reveal that an additional picosecond fluorescence component can be resolved in the emission of photoexcited BP(OH)_2 . To spectrally resolve this component the following procedure was followed. As seen from Fig. 2, an instantaneous fluorescence component with its emission wavelength near 480 nm, is observed. This component is considered to be the instantaneously produced di-keto tautomer, formed in a direct double proton transfer process within the pulse duration time of the exciting laser pulses. In the reconstructed spectrum at 1.5 ps following the excitation pulse (cf. solid curves of top legends in Figs. 3a and b), the emission at energies larger than 21.5 kK is assigned to completely arise from the instantaneously produced di-keto form. The emission intensity to the lower energy side of the spectrum of this component is obtained by extrapolating the steady-state emission function which fitted the higher energy side (dotted curves in top legends of Fig. 3). By subtracting the emission intensity of the directly formed di-keto product from the total fluorescence intensity (solid curves in Fig. 3), the residual contribution of the transient tautomers, formed at 1.5 ps after excitation, is obtained (cf. dashed curves of top legends of Figs. 3a and b). The progression of these transient tautomeric forms at the later times of 4, 10 and 40 ps is obtained after correcting for the decay on a nanosecond time scale of the di-keto tautomer (see corresponding dotted curves in the lower legends of Figs. 3a and b) and subtracting this di-keto emission intensity from the total emission intensity (solid curves), thus resulting in the emission bands of the transient tautomeric forms (dashed curves in Figs. 3a and b). Finally, the transient emissions (given by the solid spectra in Figs. 4a and b, these spectra being identical to the dashed emission bands of Figs. 3a and b) can be separated into two emission bands. One of them is represented by the emission band observed immediately after the excitation laser pulse. Its shape is represented by the top drawn legends of Figs. 4a and b, for BP(OH)_2 dissolved in cyclohexane and acetonitrile, respectively, with band maxima at 17.6 kK and 18.2 kK. The aforementioned band appears to decay with a characteristic time constant of 10 ps. Another band for which the spectral shape coincides with that of the initially

Fig. 4. Time-resolved emission spectra of BP(OH)_2 dissolved in (a) cyclohexane and (b) acetonitrile arising from the stepwise proton transfer. Solid curves are the transient emission spectra. Dotted curves represent the emission spectra of the intermediate mono-keto tautomer, and dashed curves are the emission spectra of di-keto formed from mono-keto.

formed di-keto tautomer (cf. dotted curves in Fig. 3) appears to increase, also with a time constant of 10 ps. This rise is represented by the dashed curves in Figs. 4a and b. It therefore appears that the total transient spectra (solid curves in Fig. 4) in fact are the superposition of two bands: the first, peaking near 17.6 kK, and decaying (dotted curves in Fig. 4), and the second (dashed curves in Fig. 4), peaking near 19.4 kK and rising at the expense of the first.

The 'new' transient emission band peaking at 17.6 kK (568 nm) most likely originates in an excited state that decays into the emissive excited state of the di-keto tautomer. It is proposed that the 568 nm emission originates in an intermediately formed photo-product (and not in the excited S_1 -state of the di-enol, *vide infra*), which in turn decays within 10 ps into the double protonated di-keto form of BP(OH)_2 . The most likely precursor of the di-keto tautomeric form is of course the mono-protonated tautomer, for which the possible existence has been alluded to in semi-empirical calculations also [5,13]. Furthermore, the peak position of the 'new' transient emission band coincides with that of the model compound BPOH, which shows a single-proton transfer in its excited singlet state, dissolved in non-polar solvents [6]. Thus we assign the short-lived 568 nm band emission to arise from the intermediately

formed enol-keto tautomer. Note that the observed transients of Fig. 2, all show a component reflecting an instantaneous intensity increase. Thus both the single and the double protonated tautomers of BP(OH)_2 are, at least in part, formed synchronously within about 300 fs from the excited singlet state of the di-enol form. The latter singlet state decays therefore very rapidly (within 300 fs) and thus cannot be held responsible at the same time for the slower decaying 568 nm emission.

The proposed decay sequence, di-enol $\rightarrow$ enol-keto tautomer $\rightarrow$ di-keto tautomer, implies that the energies of the corresponding excited singlet states of these species decreases in the same order. On the other hand, the transition energies for the fluorescence of the mono-keto and di-keto forms are approximately 17.6 kK and 19.4 kK, respectively. It follows that the minimum in the potential energy surface of BP(OH)_2 in the electronic ground state corresponding to the enol-keto tautomer is well above that for the di-keto form, in agreement with the calculated AM1 result reported recently [14].

Finally, we briefly comment on the competitive dynamics for the formation of the mono- and di-keto tautomeric forms of BP(OH)_2 . To visualize the reaction scheme of the excited state processes of BP(OH)_2 we consider the excited singlet potential energy in a multi-dimensional representation to be a function of single and double proton transfer reaction coordinates. Once the pulsed vertical excitation to the potential energy surface is accomplished, the excited-state population sinks to the potential energy minima along each of the two reaction pathways. The sink to the energy minima is instantaneous on the time scale of the duration of the laser pulses. The mono-keto tautomer (with a lifetime of 10 ps) eventually decays into the di-keto tautomeric form: in this process the reaction trajectory is thought to develop from the mono-keto potential energy minimum, possibly passing a saddle point in the potential energy surface, to end up in the energy sink of the di-keto form.

In summary, the time-dependence of the fluorescence of BP(OH)_2 has been studied by means of femtosecond fluorescence up-conversion measurements. From our data we conclude two competitive intramolecular proton transfer processes to take place upon pulsed photo-excitation of the BP(OH)_2

molecule: (i) a concerted double proton transfer reaction giving rise to the ultrafast (< 300 fs) formation of the di-keto tautomer; (ii) a step-wise single proton transfer, where the first step is the formation of the enol-keto form (in competition with the di-keto tautomer), and the second step includes the decay of the excited singlet state of the enol-keto form into the more stable singlet state of the di-keto form.

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References

- [1] M. Kasha, *Fest. J. Phys. Chem.* 95 (1991) 10215.
- [2] C. Chudoba, S. Lutgen, T. Jentsch, E. Riedle, M. Woerner and T. Elsaesser, *Chem. Phys. Letters* 240 (1995) 35.
- [3] B.J. Schwarz, L.A. Peteanu and C.B. Harris (Springer Series in Chemical Physics, Vol. 55, 1993) p. 592; *ibid.*, *J. Phys. Chem.* 96 (1992) 3591.
- [4] T. Elsaesser, in *Femtosecond chemistry*, eds. J. Manz and L. Wöste (VCH, Germany, 1995) p. 563.
- [5] H. Bulska, *Chem. Phys. Letters* 98 (1983) 398.
- [6] H. Bulska, A. Grabowska and Z.R. Grabowski, *J. Lum.*, 35 (1986) 189.
- [7] H. Bulska, *J. Lum.* 39 (1988) 293.
- [8] J. Sepiol, A. Grabowska, H. Bulska, A. Mordziński, F. Perez Salgado and R.P.H. Rettschnick, *Chem. Phys. Letters* 163 (1989) 443.
- [9] F.W. Langkilde, A. Mordzinski and R. Wilbrandt, *Chem. Phys. Letters* 190 (1992) 305.
- [10] A. Grabowska, P. Borowicz, D.O. Mártire and S.E. Braslavsky, *Chem. Phys. Letters* 185 (1991) 206.
- [11] M. Kaschke, S. Rentsch, and J. Opfermann, *Laser Chem.* 8 (1988) 377.
- [12] A. Grabowska, A. Mordzinski, N. Tamai and K. Yoshihara, *Chem. Phys. Letters* 169 (1990) 450.
- [13] P. Borowicz, A. Grabowska, R. Wortmann, and W. Liptay, *J. Lum.* 52 (1992) 265.
- [14] V. Barone and C. Adamo, *Chem. Phys. Letters* 241 (1995) 1.
- [15] L.H. Vogt Jr. and J.G. Wirth, *J. Am. Chem. Soc.* 93 (1971) 5402.
- [16] W. Siemanowski and H. Witzel, *Liebigs Ann. Chem.* 1984 (1984) 1731.
- [17] J. Waluk, H. Bulska, A. Grabowska and A. Mordzinski, *New J. Chem.* 10 (1986) 413.

- [18] J. Sepiol, H. Bulska and A. Grabowska, *Chem. Phys. Letters* 140 (1987) 607.
- [19] M. Eyal, R. Reisfeld, V. Chernyak, L. Kaczmarek and A. Grabowska, *Chem. Phys. Letters* 176 (1991) 531.
- [20] L. Kaczmarek, B. Nowak, J. Zukowski, P. Borowicz, J. Sepiol and A. Grabowska, *J. Mol. Struct.* 248 (1991) 189.
- [21] J. Lipkowski, A. Grabowska, J. Waluk, G. Castelani and B.A. Hess Jr., *J. Cryst. Spectry. Res.* 22 (1992) 563.
- [22] R. Wortmann, K. Elich, S. Lebus, W. Liptay, P. Borowicz and A. Grabowska, *J. Phys. Chem.* 96 (1992) 9724.
- [23] A. Mordzinski, K. Kownacki, A. Les, N.A. Oyler, L. Adamowicz, F.W. Langkilde and R. Wilbrandt, *J. Phys. Chem.* 98 (1994) 5212.
- [24] P. Borowicz, A. Grabowska, L. Kaczmarek, A. Les and L. Adamowicz, *Chem. Phys. Letters* 239 (1995) 282.
- [25] E.R. Middelhoek, P. van der Meulen, J.W. Verhoeven and M. Glasbeek, *Chem. Phys.* 198 (1995) 373.
- [26] M. Maroncelli and G.R. Fleming, *J. Chem. Phys.* 86 (1987) 6221.
- [27] H. Zhang, A.M. Jonkman, P. van der Meulen and M. Glasbeek, *Chem. Phys. Letters* 224 (1994) 551.