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Femtosecond laser selective intramolecular double-proton transfer in [2,2′-bipyridyl]-3,3′-diol

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Abstract

We report an excitation energy dependence of the dynamics of the excited-state intramolecular double-proton transfer of [2,2′-bipyridyl]-3,3′-diol in liquid solution. By means of femtosecond fluorescence upconversion experiments it is shown that an increase of the vibrational energy in the excited electronic S_1 state results in an increase of the ratio of the reaction yields of the monoketo and diketo tautomeric products. The dominance of the concerted double-proton transfer process at the lower excitation energies is evidence for an energy barrier in the dienol–monoketo reaction pathway. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Recently, ultrafast excited-state intramolecular proton transfer reactions have attracted much interest [1–16]. In these studies, focus has been on enol–keto tautomerization reactions at femtosecond up to picosecond time scales. For example, for the photoexcited model base pair, 7-azaindole dimer, studied in a supersonic molecular beam [1], a two-step sequential proton tunneling mechanism was inferred, with typical transfer times of several hundreds of femtoseconds for the first step and a few picoseconds for the second step. For 2-(2′-hydroxy-5′-ethylphenyl) benzotriazole (TIN) in liquid solution, the pump–probe study of the single-proton transfer dynamics of the excited state enol–keto reaction dynamics revealed the survival of vibrational coherence during and after the proton transfer up to 700 fs [3]. In the

case of TIN, the proton transfer is thought to be barrierless and along a low-frequency proton transfer coordinate. As the proton transfer progresses, there is a concomitant change in the potential energy surface along another vibrational coordinate with higher frequency. Coupling of the low- and high-frequency modes explains the oscillatory proton transfer dynamics [3]. Finally, in our recent femtosecond fluorescence upconversion studies of the double-proton transfer dynamics of [2,2′-bipyridyl]-3,3′-diol (hereafter referred to as $BP(OH)_2$) in liquid solution, the simultaneous occurrence of a concerted double-proton transfer (one-step process) and a sequential double-proton transfer (two-step process) was found [4]. The concerted reaction and the first step in the sequential process were too fast to be resolved in the experiment (< 100 fs); the mono-to-diketo reaction in the two-step mechanism occurred with a typical time constant of 10 ps (see Scheme 1). In a subsequent study of the double-proton transfer dynamics

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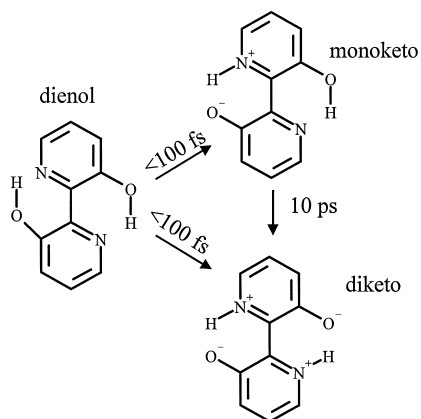
Scheme 1.

of BP(OH)$_2$ and its deuterated counterpart, in aprotic and protic solvents, we showed that the proton transfer is part of a collective atomic motion, involving the assistance of vibrational modes. In particular, stretching and bending modes were considered to promote the one- and two-step double-proton transfer reactions, respectively [5].

In both previous femtosecond fluorescence upconversion studies of the BP(OH)$_2$ system [4,5], photoexcitation was at 267 nm, i.e., the excitation energy was over 10000 cm^{-1} in excess of the initial dienol vibrationless excited S$_1$ state. Under such conditions, any photoselectivity in the subsequent alternative reaction pathways (one-step vs. two-step transfer) might be obscured by additional competitive processes such as ultrafast intramolecular vibrational redistribution (IVR) and energy relaxation. Since for other enol–keto reactions in the excited state, tunneling through a potential energy barrier [1,11,12] as well as barrierless proton transfer [3] had been found, it is of great interest to investigate which mechanism (tunneling, thermal activation or barrierless transfer) applies in the case of BP(OH)$_2$ when excitation is to lower vibronic excess energies. In this Letter, we investigate the role of the amount of vibronic excess energy on the relative yield of the photoproducts in the concerted and the sequential proton transfer reactions in BP(OH)$_2$. We demonstrate that the amount of excess vibrational energy significantly influences this ratio. In fact, the yield of the formed monoketo tautomeric intermediate, in the two-step reaction dienol → monoketo → diketo, is

drastically reduced when photoexcitation is to the lower vibrational levels of the dienol photoexcited S$_1$ state. It is emphasized that the observation of the photoselectivity in the double-proton transfer process relies on the probing of the reaction products on a femtosecond time scale.

2. Experimental

[2,2′-Bipyridyl]-3,3′-diol (BP(OH)$_2$) was purchased from Aldrich and dissolved without further purification in cyclohexane (Fluka, Microselect) in a concentration of $\sim 10^{-3}$ M.

Femtosecond laser excitation was accomplished using a diode-pumped cw Millennia X Nd:YVO$_4$ 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 ~ 400 mW at 1 kHz, and then split into two beams by a beam splitter. One of the beams was led into an OPA system. The fourth harmonic of the signal pulses produced by the OPA (with a energy of ~ 0.1 μJ/pulse and a duration of 100 fs/pulse), was selected by a 2 mm thick optical filter DUG 11 (from 300 to 400 nm). These pulses were used to photoexcite the 10^{-3} M solution of BP(OH)$_2$ which was contained in a flow cell at ambient temperature. The ensuing transient fluorescence was time-resolved detected by applying the fluorescence upconversion detection technique [4,17]. In the latter, an attenuated part of the fundamental beam (800 nm) was led through an optical delay line and focussed together with the pump-pulse induced fluorescence onto a 1 mm thick BBO crystal (type I phase matching condition). The upconversion 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 an SRS lock-in amplifier system linked to a personal computer for data storage and analysis. To avoid the influence of reorientational motions of the BP(OH)$_2$ molecules on the temporal behavior of the fluorescence transients, the polarization of the excitation beam was at the magic

angle of 54°44′ with respect to the vertically polarized gating beam. From the measured cross-correlation function of the excitation and gating pulses at 400 and 800 nm, the instrumental time response was estimated to be ~ 300 fs (FWHM).

3. Results and discussion

The steady-state absorption and emission spectra of $BP(OH)_2$ in cyclohexane are presented in Fig. 1. By means of femtosecond fluorescence upconversion experiments [4], it was previously shown that immediately after the pulsed photoexcitation of $BP(OH)_2$ at 267 nm, the fluorescence spectrum consists of two emission bands, peaking at 510 and 568 nm, respectively. The 568 nm band has a lifetime of 10 ps and has been assigned to the emissive monoketo tautomer intermediate [4]. The band with its maximum at 510 nm is due to $BP(OH)_2$ in the diketo tautomer form [18,19]. The diketo product is formed either instantaneously (within less than 100 fs), or from the decay of the (also instantaneously formed) monoketo intermediate into the diketo form [4]. This latter process was found to occur with a time constant of 10 ps. The lifetime of the emissive diketo state is typically 2–4 ns, depending on the solvents and the temperature [5,20].

Using the OPA system, the excitation wavelength in the fluorescence upconversion measurements was varied from 300 to 380 nm. The fluorescence upconversion measurements were performed with the de-
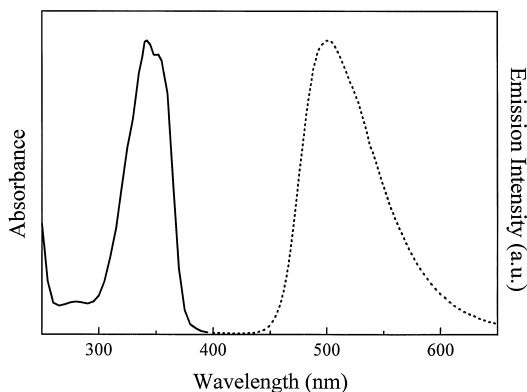

Fig. 1. Steady-state absorption spectrum (solid curve) and emission spectrum (dotted curve) of $BP(OH)_2$ dissolved in cyclohexane at room temperature.
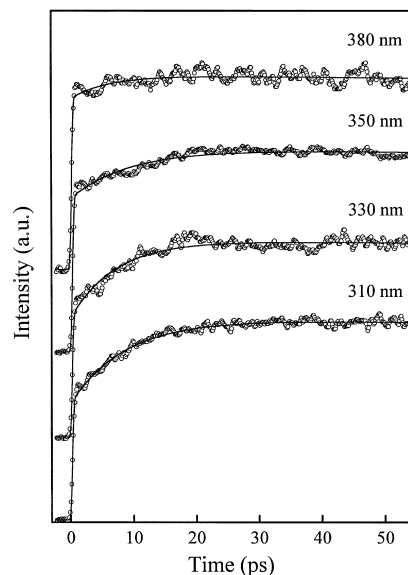

Fig. 2. Fluorescence upconversion transients of $BP(OH)_2$ dissolved in cyclohexane. The detection wavelength is 480 nm. Excitation wavelengths are indicated in the figure. The solid curves represent the best biexponential fits to the experimental data points.

tection wavelength maintained at 480 nm. At this wavelength, the emission is almost exclusively due to the diketo tautomeric form [4].

A few typical fluorescence upconversion transients observed for $BP(OH)_2$ in cyclohexane, for a series of different excitation wavelengths, are presented in Fig. 2. Detected at 480 nm, the amplitude of the instantaneous rise component (for $t \leq 100$ fs) corresponds to the ultrafast formation of a diketo compound. The additional rise, with a time constant of ~ 10 ps, is representative of the monoketo-to-diketo reaction in the two-step process. The amplitude of this 10 ps rise component is characteristic of the amount of the monoketo intermediate formed in the first step of the sequential double-proton transfer process. Thus, by considering the ratio of the amplitudes of the 10 ps rise and instantaneous components as a function of the excitation wavelength, we can follow the ratio of the concentrations of the instantaneously ($t \leq 100$ fs) formed monoketo and diketo products as a function of the excitation energy.

All fluorescence transients following the instantaneous component of the diketo $BP(OH)_2$ emission could be fitted to a biexponential function convo-

luted with the system response function. In the biexponential function,

$$I(\lambda, t) = c_1(\lambda)\{\exp(-t/\tau_2) - \exp(-t/\tau_1)\}$$
$$+ c_2(\lambda)\exp(-t/\tau_2), \qquad (1)$$

the short-time rise component, τ_1, is the characteristic time constant of the mono to diketo transfer (~ 10 ps), the long-time decay component, τ_2, is representative of the lifetime ($\sim$ ns) of the emissive diketo tautomer, $c_1(\lambda)$ is a measure of the amount of diketo formed out of the monoketo intermediate and $c_2(\lambda)$ is representative of the amount of the instantaneous diketo tautomer. The long-time component (τ_2) was measured separately in the picosecond time-correlated single-photon-counting setup described elsewhere [21]. Best fittings to the transients are also displayed in Fig. 2. It is remarked that, whereas the proportionality factors $c_1(\lambda)$ and $c_2(\lambda)$ change with the excitation wavelength (vide infra), the time components τ_1 and τ_2 were found to be excitation wavelength independent. The independence of the monoketo-to-diketo proton transfer rate constant ($1/\tau_1$) of the wavelength in the optical excitation process of the dienol suggests that the monoketo tautomer intermediate has already vibrationally relaxed before it decays into the diketo form.

In Fig. 3, the ratio between the amplitudes of the 10 ps rise component and the instantaneous diketo component, c_1/c_2, 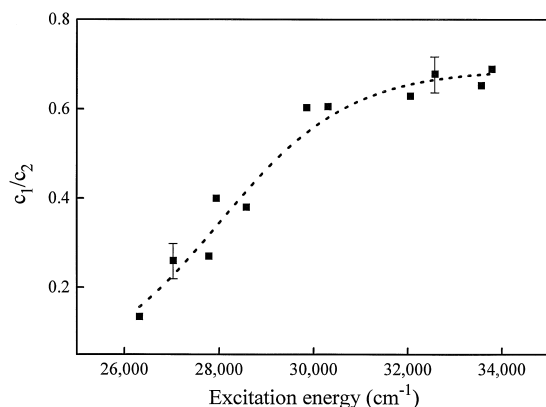is plotted for a series of excitation energies. The figure shows that the ratio decreases as the excitation energy is decreased. The decrease in the c_1/c_2 ratio with decreasing excitation energy reveals that for lower excitation energies the production of the monoketo tautomer is no longer favoured as compared to the diketo tautomer, but instead becomes less likely. This is considered to be evidence for the existence of an energy barrier in the reaction pathway for the dienol to monoketo conversion.

Previously it has been discussed that the concerted double-proton transfer process is vibrationally assisted by a stretching mode involving stretching and compression motions of the carbon–carbon bond linking the two pyridyl rings of the $BP(OH)_2$ molecule [5]. The two-step double-proton transfer process, on the other hand, is thought to be promoted by an asymmetrical bending mode [5]. Since these vibrationally assisted processes involve the motions of many atoms in the molecule, deuteration of the hydroxyl groups is expected to have negligible effect on the effective mass and thus the yield and formation dynamics of the monoketo and diketo bipyridyl–diol tautomers. This could be verified experimentally indeed. For the deuterated samples the fluorescence upconversion results were the same as in Figs. 2 and 3.

We now adopt a simplified picture for tunneling 'through' the barrier. For a parabolically shaped barrier with a shape function, $V = V_0 - \frac{1}{2}Ax^2$, the expression for the permeability, G, becomes [22],

$$G = \left\{1 + \exp\left[2\pi m^{1/2}(V_0 - W)/\hbar A^{1/2}\right]\right\}^{-1}. \qquad (2)$$

In Eq. (2), the permeability G is defined as the ratio between the fluxes of the transmitted and incident particle, i.e., $G = (k_T/k_I)|A_T|^2$, where k_T/k_I is the ratio of the velocities of the transmitted and incident particle and $|A_T|^2$ represents the particle density of the transmitted particle. V_0 is the potential energy corresponding to the maximum of the barrier with $A > 0$, and W is the excitation energy. The plot of a best-fit function, in accordance with Eq. (2), to the experimentally determined values of c_1/c_2 vs. the excitation energy, is included in Fig. 3. The best-fit values of the parameters of Eq. (1) are: $V_0 = 28000$ cm^{-1} and $A/m = 2.6 \times 10^{30}$ s^{-2}.

From ab initio calculations of the $BP(OH)_2$

Fig. 3. Ratio of the yields of the instantaneously formed monoketo (c_1) and diketo tautomers (c_2). Squares represent the ratio as obtained from the analysis of the experimental data. The dashed curve is the best fit using the expression for the tunneling permeability as given in the text.

molecule, the excitation energy of the 0–0 electronic transition is estimated to be at 27400 cm^{-1} [23]. Choosing this value for W, it follows that in our simplified approach the estimated height of the barrier becomes ~ 600 cm^{-1}. It is noted that the angular frequency given by $\omega = (A/m)^{1/2}$ is characteristic of an oscillating particle in a potential with $V = \frac{1}{2}Ax^2$. The parabolic curvature of the latter potential is opposite in sign compared to that for the parabola considered above. For the tunneling particle we can consider therefore the imaginary angular frequency $i\omega_{\ddagger} = (A/m)^{1/2}$. We find for the imaginary mode corresponding to the best-fit plot of Fig. 3 that its period is ~ 5 fs. Experimentally the monoketo tautomer is formed within the laser pulse duration of 100 fs [4]. Thus the estimated period of the imaginary oscillatory mode does at least not exceed the experimental upper limit of the transmittance time, as expected.

If the excited state double-proton transfer of BP(OH)$_2$ would not show any preference for either the one- or two-step process, it would be expected that the probability for the formation of the monoketo tautomer form would be twice that for the diketo form and thus, in this statistical limit, the c_1/c_2 ratio would be equal to 2. This value was actually experimentally verified, when the excitation wavelength was at 267 nm [4]. For the lower excitation energies applied in this work, the maximum value obtained for c_1/c_2, even when applying excitation energies above the barrier top at 28000 cm^{-1}, is only 0.7 (cf. Fig. 3). This result suggests that even if excitation into the S$_1$ level is above the potential energy barrier, the initially excited Franck–Condon state of the BP(OH)$_2$ dienol tautomer does not completely decay into either a monoketo or diketo tautomer form. An additional relaxation channel must therefore be present which is responsible for the reduction of the optimum yield of the monoketo intermediate. A likely candidate for this additional relaxation is intramolecular vibrational relaxation (IVR), which could deactivate the excitation of the bending mode and thus reduce the probability for the dienol-to-monoketo reaction to occur. Since we tentatively conclude that IVR for BP(OH)$_2$, in its dienol S$_1$ state is competitive to the formation of the monoketo intermediate, it should occur on a time scale similar to that of the monoketo formation time, i.e., ≤ 100 fs.

As already found previously [4], when optical excitation of BP(OH)$_2$ is to levels at an energy of 37450 cm^{-1} (which corresponds to an excitation wavelength of 267 nm) or higher, the experimental result for the ratio c_1/c_2 becomes the statistical limit value of 2. It should be added that for these excitation energies a second band is observed in the BP(OH)$_2$ absorption spectrum and possibly excitation is to the excited S$_2$ state. The potential energy surface for this state, in contrast to the case of the S$_1$ state, may lack a potential energy barrier along the dienol–monoketo reaction coordinate. Moreover, radiationless decay out of the S$_2$ state could be less rapid than 100 fs.

In summary, the reaction yield of the monoketo intermediate in the sequential double-proton transfer process for photoexcited BP(OH)$_2$ is significantly influenced when optical excitation is to the lower vibrational levels of the excited S$_1$ state. From this, an energy barrier in the first step of the sequential double-proton transfer has been concluded, with an estimated height of 600 cm^{-1}.

Acknowledgements

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