



# Reaction path dependent coherent wavepacket dynamics in excited state intramolecular double proton transfer

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## ABSTRACT

The primary steps and the wavepacket dynamics of the ultrafast photoinduced double proton transfer in (2,2'-bipyridyl)-3,3'-diol are observed. A two-color pump probe spectrometer with 30 fs time resolution allows the variation of the vibrational excess energy. We find that the first step of the sequential proton transfer and the concerted double proton transfer both proceed in about 50 fs. We observe two types of coherently excited vibrational modes: (i) two symmetric stretching modes are closely associated with the concerted double proton transfer indicating that a simultaneous and symmetric reduction of the donor acceptor distances in both chelate rings takes place during the transfer; (ii) a nonsymmetric in-plane-bending mode is associated with the sequential proton transfer and provides evidence that the transient reduction of the donor acceptor distance occurs only in one chelate ring. This mode is exclusively excited by the reaction and cannot be excited optically according to symmetry selection rules. This constitutes a direct proof that a vibrational wavepacket can be excited by an ultrafast reaction itself.

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## 1. Introduction

Molecules exhibiting excited state intramolecular proton transfer (ESIPT) are excellent model systems for studying ultrafast reactions. Many important aspects like the evolution of an initially prepared wavepacket and the role of skeletal motions in molecular reactions have been investigated using such systems [1–8]. In most cases considered so far the molecules exhibiting wavepacket dynamics proceed only along one distinct reaction channel without any branching. However, systems with parallel and branching reaction channels are highly interesting due to their chemical and biological relevance. The question arises if in this situation coherent wavepacket dynamics can be observed and if so, can it be used to characterize the different channels and get an improved understanding of the reaction mechanisms. Can the different path ways be treated on their own or do we observe a coupling between the branches and interference effects? Such molecules bear the possibility to choose one or the other reaction channel by an appropriate optical excitation similar to recent control experiments [9,10]. A good understanding of the wavepacket dynamics should lead

to a deeper insight in the underlying control mechanisms and to new control concepts. It is well established that ultrafast ESIPT is associated with coherent wavepacket motion and its analysis gives direct insight into the reaction mechanism [2–7,11–14]. Therefore, molecules exhibiting double proton transfer (PT) seem to be well suited model systems to investigate the aforementioned questions.

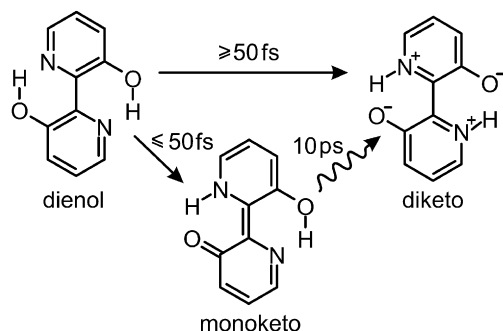
Molecules showing intramolecular as well as intermolecular double PT have been the subject of several experimental and theoretical studies [4,15–26]. In particular the question whether concerted or sequential PT occurs has been discussed for different systems. Since the mechanism of excited state intramolecular PT is now extremely well understood for molecules with a single H-chelate ring [5–8,14] a comparison with double PT will elucidate the typical features of a system with multiple reaction channels.

For our investigations (2,2'-bipyridyl)-3,3'-diol [BP(OH)<sub>2</sub>] is used. It has two H-chelate rings and exhibits intramolecular double PT in the electronically excited state [15,16,27,28]. The dienol ground state and the diketo form adopted after the double PT in the electronically excited state exhibit a centrosymmetric planar geometry [28,29]. This manifests itself in the lack of a detectable dipole moment in the ground state, at the Franck–Condon point, and at the diketo minimum of the electronically excited potential energy surface (PES) [28,30]. The symmetry leads also to strict selection rules for the optical excitation of vibrational modes

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**Scheme 1.** Concerted and sequential double proton transfer of BP(OH)<sub>2</sub> in the electronically excited state.

[31]. From fluorescence up-conversion studies [17,18] it is known that concerted and sequential double PT occur simultaneously (see Scheme 1). After optical excitation, part of the molecules transfer both protons of the chelate rings within a very short time forming directly the diketo tautomer. The other molecules shift in a first step only one proton and form the monoketo intermediate. Subsequently the second proton is transferred with a rate of  $(10 \text{ ps})^{-1}$  leading again to the diketo form [17,18]. The branching ratio depends on the excess energy of the optical excitation, more monoketo is formed at shorter wavelengths [19]. Any significant involvement of triplet states in the PT process has been excluded [32]. Asymmetric substitution [31,33] and deuteration [18,31] have been used to further elucidate the PT. Despite all this work, the very initial steps, i.e., the concerted double PT and the first transfer in the sequential pathway have not yet been temporally resolved and the notion of the transfer mechanisms is still of somewhat hypothetical character.

In this paper we report on transient absorption measurements on BP(OH)<sub>2</sub> with a time resolution of 30 fs. The very initial steps of the process are resolved and pronounced oscillatory signal contributions are found indicating a coherent excitation of vibrational modes involved in the process. We utilize the dependence of the coherent dynamics on the excess energy to attribute the vibrational modes to one or the other channel and give a model for the reaction mechanism.

## 2. Experimental techniques

Transient absorption measurements were performed with two different setups. For the recording of transient spectra a fraction of the output of a home-built Ti:Sa regenerative amplifier (800 nm, 1 kHz repetition rate, 90 fs pulses) is used for third harmonic generation resulting in pulses at 267 nm with 500 nJ pulse energy for the excitation of the sample. With another part a continuum is generated in a CaF<sub>2</sub> disc to probe absorption changes. The beams are focused into the sample with a focus diameter of 200  $\mu\text{m}$  for the pump beam and 80  $\mu\text{m}$  for the probe beam. The sample is a cyclohexane solution of BP(OH)<sub>2</sub> in a fused silica cuvette with 500  $\mu\text{m}$  optical path length. Spectra are recorded with a multichannel detector after dispersing the probe beam with a spectrograph. To avoid effects of orientational relaxation occurring on a time scale of about 10 ps all spectra were measured with the probe beam polarized in magic angle with respect to the pump beam. Further details of the setup are described elsewhere [34–36].

To resolve the wavepacket dynamics a two-color UV/Vis pump-probe spectrometer with a time resolution of 30 fs based on two noncollinearly phase matched optical parametric amplifiers (NOPAs) was used [3,6,37]. One NOPA uses a two stage setup with

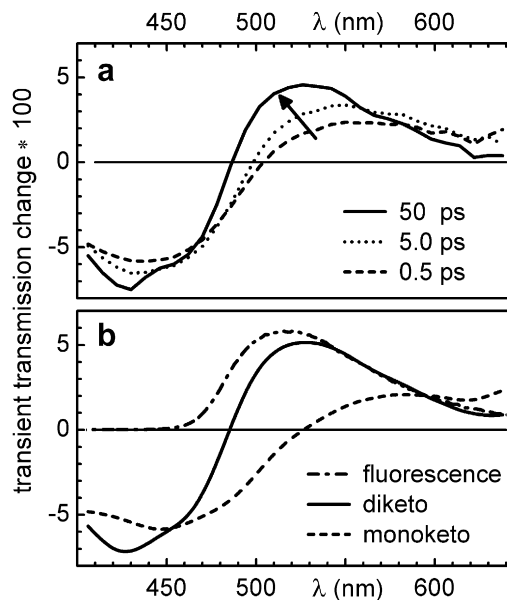
an intermediate white light generation. Its output is frequency doubled in a 100  $\mu\text{m}$  BBO crystal and compressed with a fused silica prism sequence. This allows to access the wavelength region between 310 nm and 380 nm that is required for covering the absorption band of the sample. Pulses (20 fs) in the visible region are generated with a second NOPA and a fused silica prism compressor. A part of this beam is split off and used as reference. Pump and probe beam are focused into the sample and detected by photodiodes. They are polarized parallel to each other.

To exchange the excited volume after each laser pulse the sample is pumped through a home made cell with 200  $\mu\text{m}$  thick fused silica windows and an optical path length of 120  $\mu\text{m}$ . BP(OH)<sub>2</sub> with a stated purity of 98% (Sigma Aldrich) is dissolved in cyclohexane (UVASOL; Merck) at a concentration of  $2 \times 10^{-3} \text{ M}$ . Absorption and fluorescence spectra of the samples used in the femtosecond experiments were taken regularly and compared to spectra measured for a small sample of high purity and also to published spectra [38]. No differences were observed and this was taken as indication for the lack of any relevant impurities. Experiments with neat solvent under the same conditions did not show significant solvent or window contributions to the signal.

To determine the time zero of the pump-probe delay the cross-correlation is measured at the sample position with the same amount of glass in the beam path. As crosscorrelation signal difference frequency mixing in a 100  $\mu\text{m}$  BBO crystal is used. The width of the crosscorrelation was typically 40 fs and the time zero was determined with an accuracy better than 10 fs.

## 3. Results

Transient spectra at various delay times are presented in Fig. 1 for 267 nm excitation. Stimulated emission (SE) and excited state absorption (ESA), which dominates below 480 nm, contribute to the spectra. In the region of the fluorescence of BP(OH)<sub>2</sub> we observe a blue shift of the spectrum with increasing time. Between 400 nm and 460 nm only minor changes occur after the excitation. The ESA seems to be less strongly affected by the PT than the emission similar to the situation in 2-(2'-hydroxyphenyl)benzothiazole (HBT) [5,6] and signal changes due the PT process are dominated



**Fig. 1.** (a) Transient absorption spectra of BP(OH)<sub>2</sub> dissolved in cyclohexane for different time delays. (b) Deduced absorption spectra of the electronically excited monoketo and diketo conformer.

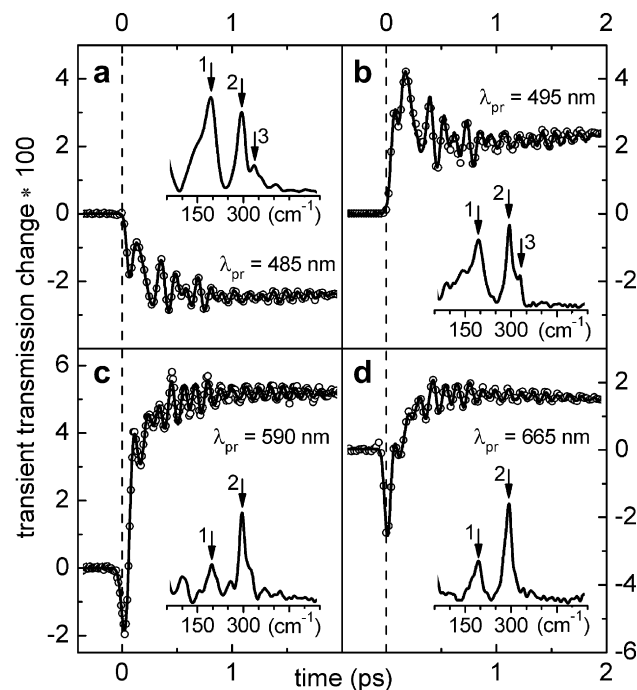
by variations in the emission spectra. The measurements can be fitted by a triexponential function with time constants (for discussion see below) of 200 fs, 10 ps, and about 3–4 ns. The latter two times agree very well with previous reports [17,18] and are attributed to the transition from the monoketo to the diketo form and to the fluorescence lifetime of BP(OH)<sub>2</sub> in cyclohexane. We did not find any indication that a  $n\pi^*$  state contributes significantly to the dynamics as proposed by others [24].

From the total transmission change we can reconstruct the transient absorption spectra for the different tautomers. The spectrum for the diketo tautomer is identical to the transient spectrum at long delay times. Shortly after optical excitation the ratio between monoketo to diketo is equal to 2 for the excitation at 267 nm [17,19] and the spectrum consists of 2/3 of the monoketo spectrum and 1/3 of the diketo. By suitable scaling and subtraction of the diketo spectrum (approximated by the transient spectrum after 200 ps) from the transient spectrum at 0.5 ps, we obtain the spectrum of the monoketo form (see Fig. 1b). The spontaneous emission spectra of both conformers were reconstructed in a similar way from fluorescence up-conversion measurements [17,38]. Our spectra are a combination of ESA and SE and describe the absorption properties of the individual conformers. The emission peaks at  $\sim 530$  nm for the diketo and at  $\sim 580$  nm for the monoketo form are in good agreement with the up-conversion measurements. As the PT reactions proceed, the fractions of monoketo and diketo evolve and the total transient spectrum changes accordingly.

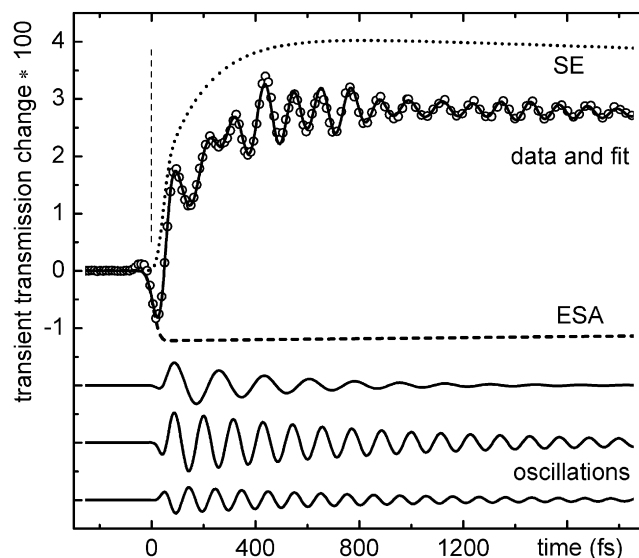
In accord with previous reports [17,19] we can conclude that the diketo tautomer is preferentially detected at short probe wavelengths and the monoketo at longer ones. This does, however, only apply to the total signal. Unfortunately the total transient absorption signal is a poor measure of the state population due to the opposing signal contributions from SE and ESA and the differing SE and ESA spectra for the two tautomers. In this work we are focused on the wavepacket dynamics and the coherent excitation of vibrational modes. A wavepacket oscillating in a vibrational coordinate causes periodic spectral shifts of the transient spectrum [5]. For time traces measured at a fixed probe wavelength this results in oscillatory signal contributions with the frequency of the vibration. Their amplitude scales with the slope of the spectrum [5] and we therefore expect the largest contribution of a wavepacket in the monoketo form in the wavelength region between 470 nm and 560 nm.

Fig. 2 shows transient transmission changes of BP(OH)<sub>2</sub> dissolved in cyclohexane with high temporal resolution at selected probe wavelengths. The center wavelength of the excitation pulses was 350 nm. We probe the transmission changes in the spectral region of the product state fluorescence [17]. The large Stokes shift ensures the observation of dynamics in the electronically excited state without any interference from ground state processes. All signals have contributions from SE and ESA. At a probe wavelength of 485 nm the ESA is dominant (see Fig. 2a) and the signal shows a transient transmission decrease. At the other presented probe wavelengths the SE is dominant resulting in a transmission increase. Note that this emission rise has a small but significant delay with respect to the excitation.

The transients in Fig. 2 show strong oscillations lasting more than 2 ps. These oscillations are due to vibronic wavepackets. Fourier transformation reveals the contributing frequencies (marked by arrows in Fig. 2). Independent of the probe wavelength we observe three oscillations at about 193 cm<sup>-1</sup>, 294 cm<sup>-1</sup> and 331 cm<sup>-1</sup>. These average values will be used below as labels for the three oscillations. The relative strength of the 193 cm<sup>-1</sup> mode decreases as the probe wavelength is tuned to the red. After the emission rise the nonoscillating components change with time constants of 200 fs and 10 ps.



**Fig. 2.** Transient absorption traces of BP(OH)<sub>2</sub> in cyclohexane excited at 350 nm and probed at (a) 485 nm, (b) 495 nm, (c) 590 nm and (d) 665 nm. Positive values indicate stimulated emission. The insets show the Fourier transformation of the time traces. The arrows and labels 1–3 indicate the oscillations termed 193, 294, and 331 cm<sup>-1</sup> (when present). The precise values of the experimental frequencies are given in Table 1.



**Fig. 3.** Transient absorption trace and the corresponding fit for BP(OH)<sub>2</sub> excited at 350 nm and probed at 625 nm. The data (open circles), the complete fit (solid line) and the components of the fit for SE (dotted), ESA (dashed) and the oscillations (solid lines in the lower part) are shown.

For a more detailed analysis a model function is fitted to the data sets analogous to the procedure described in Ref. [5]. Fig. 3 shows the transient at 625 nm together with the fitted model function and the various components. The oscillatory components are taken into account by exponentially damped cosine functions. The ESA occurs instantaneously with the excitation of the molecule to the S<sub>1</sub> state. It is modeled with a drop of the transmission at time

zero convoluted with the crosscorrelation. The SE is attributed to the  $S_1$  keto tautomers and indicates single or double proton transfer. The onset of the SE is modeled with a time delayed step function. The delay of the SE rise corresponds to the time, the wavepacket needs to reach a keto region of the  $S_1$  PES, i.e., the ESIPT to complete. It is therefore taken as a measure for the proton transfer time [14].

After the SE rise the nonoscillating components can be fitted by a biexponential function with a short time constant of about 200 fs and a longer one of  $\sim 10$  ps. The fast component is a decay at short probe wavelengths and a rise in the red. A similar effect has also been observed in HBT [3,5,11], 10-hydroxybenzo[h]quinoline [13,14] and other molecules exhibiting ESIPT [6,39]. It results from a red shift of the emission spectrum and is attributed to internal vibrational redistribution (IVR). Similar time constants of 350 fs and  $\sim 10$  ps were also found in fluorescence up-conversion measurements and the inferred anisotropies [38]. The 10 ps constant was attributed to the monoketo to diketo conversion, which is in good agreement with our findings.

The reported 350 fs time constant was explained as a demixing of the optically excited electronic wavefunction (dienol form) into the monoketo and diketo diabatic wavefunctions [38]. The analysis of our data implies that the initial splitting of the wavefunction into monoketo and diketo takes place within  $\sim 50$  fs. Since both experiments achieved different time resolutions and are of complementary nature, no clear conclusion can be drawn at present. Most likely, both IVR and electronic state demixing contribute to the observed signal kinetics.

The fit function reproduces the data very well (see solid lines in Figs. 2 and 3). The results for the proton transfer time and the oscillation frequencies are summarized in Table 1. We observe a proton transfer of about 50 fs. In the blue probing range there seems to be a tendency toward somewhat larger values while in the red the values are somewhat shorter. This contrasts to observations in HBT where longer times in the red spectral region were observed due to the time the wavepacket motion needs for transversing the observation region [5]. According to Fig. 1 the SE has large contributions from the diketo tautomer in the blue spectral region while in the red region the monoketo contributes stronger. Therefore the longer delay time in the blue could be taken as an indication that the formation of the diketo form is somewhat slower than the formation of the monoketo. A classical rate model would not allow such a distinction, since even differing rates for conversion

to the two keto states would still lead to an equal rise time of the two product signals. The situation is significantly different in the wavepacket picture. The optically prepared wavepacket can split very early in time and the resulting fragments need different times to reach the respective PES minima. These times do not have to correlate.

According to prior investigations [19] the branching ratio between the concerted and the sequential pathway depends on the vibrational excess energy deposited by the excitation. To explore this effect, excitation wavelengths of 375 nm at the low energy onset of the absorption spectrum, 350 nm and 310 nm were used. The results are depicted in Fig. 4. In line with the findings from the transient spectra (see Fig. 1) the net signal of the time traces is a delicate balance between ESA and SE. With the excitation wavelength the monoketo and diketo contributions to the signal change, and thus the net signal changes accordingly. The monoketo to diketo conversion on a 10 ps time scale leads in the blue and green spectral regions to a signal increase for long delay times, and in the red to a signal decrease (data not shown). For 375 and 350 nm excitation we find again pronounced oscillations in the signal with the same frequencies as in Fig. 2. At the highest excess energy only very weak oscillations can be found.

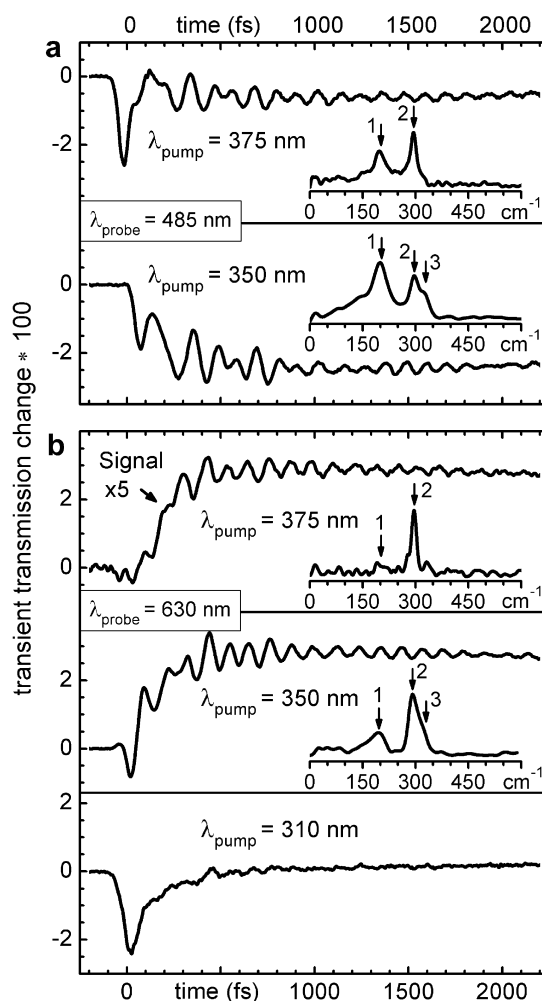
**Table 1**  
Fit results for the delay of the emission rise and for the frequencies of the oscillations at various pump and probe wavelengths

Pump (nm)	Probe (nm)	Delay (fs)	Frequencies ( $\text{cm}^{-1}$ )		
310	485	–	196	289	327
	560	64	180	301	332
	630	64	170	291	–
350	485	–	193	293	332
	495	(48)	194	293	332
	570	65	189	294	331
	590	57	195	295	333
	625	37	192	292	331
	665	40	192	294	330
375	485	59	195	294	330
	635	–	196	295	–
IR <sup>a</sup> /Raman <sup>b</sup> spectroscopy			203 (IR)	316 (Raman)	351 (Raman)
B3LYP/ 6-311+G(d,p)			198	304	343

At a probe wavelength of 485 nm the ESA is dominating and the time of the emission rise cannot be determined. Around 630 nm the contribution of the  $331\text{ cm}^{-1}$  mode is very small and cannot be established for all pump wavelengths.

<sup>a</sup> Ref. [40].

<sup>b</sup> Ref. [31].



**Fig. 4.** Transient absorption of BP(OH)<sub>2</sub> with Fourier transformations at different excitation wavelengths probed at (a) 485 nm and (b) nominally 630 nm. The signal at 375 nm excitation and 630 nm probing is multiplied by a factor of 5. The arrows and labels 1–3 indicate the oscillations termed 193, 294, and  $331\text{ cm}^{-1}$  (when present). The precise values of the experimental frequencies are given in Table 1.



#### 4. Discussion

It has previously been established that BP(OH)<sub>2</sub> exhibits single proton transfer as well as double proton transfer on a sub-100 fs timescale in the first electronically excited state [17,18]. The measurements presented in this work allow us now to give a value of 50 fs or slightly less for the first step of the sequential transfer and 50 fs or slightly more for the concerted transfer. The additional observation of oscillatory signal contributions necessitates that a description of the processes in terms of wavepacket motion is used and a simple rate model does not seem suitable. Still, the principal mechanism for the first steps seems to be similar for both reaction channels. Obviously the presence of a second reaction channel does not significantly affect the process of the proton transfer itself.

The fast time scale for the double proton transfer and the step-like rise of the signal that has also been observed in other ESIPT molecules [8] suggests that the nature of this process is very similar to the single PT. It can be treated as a barrierless process and as motion of a well defined nuclear wavepacket on an excited PES. Due to momentum conservation the molecule performs after the PT oscillatory motions on the PES around the product minimum in normal modes which are correlated to the geometric changes of the molecules during the PT process. It leads to a periodic modulation of the transient spectrum that reflects the vibrational modes which have large projections on the reaction path. As

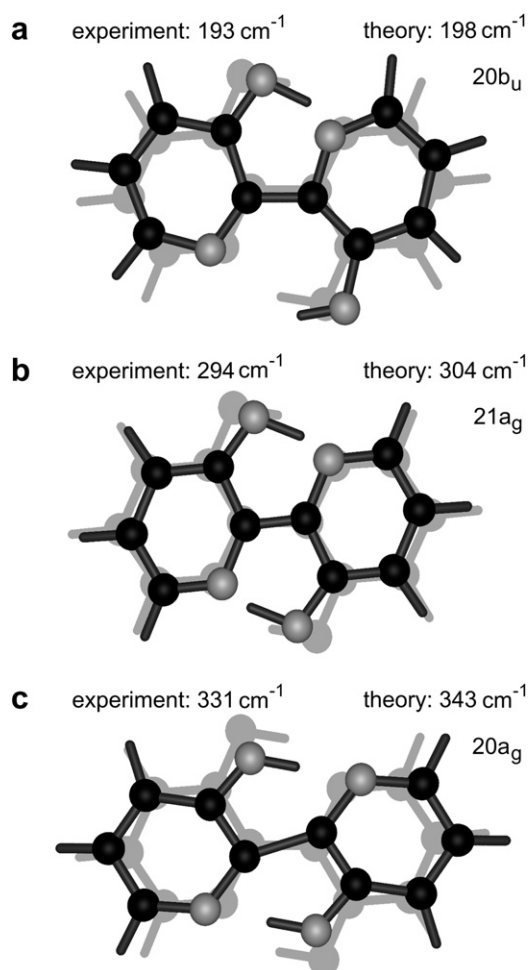
shown in Figs. 2–4 three vibrational modes are observed in our experiment.

To identify the molecular motions involved in the reaction we compare the observed frequencies with results from Raman and IR spectroscopy [31,40] and perform ab-initio calculations (cf. Table 1). The vibrational eigenmodes of BP(OH)<sub>2</sub> in the electronic ground state were calculated at the B3LYP/6-311+G(d,p) level using the GAUSSIAN 03 program package [41] and scaled by 0.9679 [42]. The point group C<sub>2h</sub> is assumed for the planar centrosymmetric BP(OH)<sub>2</sub> both in the ground and the excited state [30]. In the case of the ESIPT molecule HBT it was shown that the low frequency normal modes in the electronically excited state do not deviate much from those in the ground state [7]. This justifies the comparison of the observed S<sub>1</sub> with the ground state data. Fig. 5 shows results of the calculation. The three observed modes match with the calculated ones at 198 cm<sup>-1</sup>, 304 cm<sup>-1</sup> and 343 cm<sup>-1</sup>, all in-plane normal modes, which affect strongly the H-chelate rings of the molecule. The mode at 198 cm<sup>-1</sup> is assigned to the 20b<sub>u</sub> overall bending mode of BP(OH)<sub>2</sub> while the two higher frequencies correspond to symmetric in-plane-bending of the hydroxy groups (21a<sub>g</sub>) and an in-plane-shear deformation (20a<sub>g</sub>) of the molecule. There is no other calculated mode energetically close to the observed 193 cm<sup>-1</sup> vibration and the assignment to the mode 20b<sub>u</sub> is unambiguous. An additional out-of-plane mode 8b<sub>g</sub> is calculated at 304 cm<sup>-1</sup>. A visual inspection of the corresponding molecular deformation shows no change in the chelate rings. We therefore consider it highly unlikely that it is this mode that we observe experimentally.

The overall bending of the molecule by the 20b<sub>u</sub> mode decreases the O–N distance at one side of the molecule while it increases it on the other side (see Fig. 5a). For a number of ESIPT molecules it has been demonstrated that such low frequency bending modes strongly affecting the chelate ring are crucial for the PT since they cause the initial reduction of the donor acceptor distance necessary for the enol to keto change [5–7,12,39]. For BP(OH)<sub>2</sub> this suggests a connection of the bending mode to the first step of the sequential proton transfer. According to the selection rules in the C<sub>2h</sub> point group, only total symmetric (a<sub>g</sub>) modes can be directly excited in the allowed electronic dipole transition. The observation of the 20b<sub>u</sub> mode at 193 cm<sup>-1</sup> is in contradiction to this rule and indicates an excitation by a reactive process, in this case by the ESIPT.

The observed symmetric modes change both O–N distances simultaneously and conserve the C<sub>2h</sub> symmetry of the molecule. This suggests that these molecular vibrations are associated with the concerted proton transfer. Similar proposals can also be found in the literature [18,31,40], however, direct experimental evidence was not yet available.

To verify this claim we analyze the measurements with the same probe wavelength and different excess energies in the excitation (see Fig. 4). The excitation wavelength changes the branching ratio between the generation of the diketo and monoketo tautomer [19]. If there is indeed the proposed coupling between the two reaction pathways and the observed wavepacket dynamics, a change of the branching ratio should affect the observed amplitudes of the modes. In Fig. 4 the Fourier transforms of traces with 350 and 375 nm excitation and probe wavelengths of 485 nm and 630 nm are compared. According to Ref. [19] about 30% of the excited molecules are transferred to the monoketo form after excitation at 350 nm compared to 16% at 375 nm. Because the amount of the monoketo form is changed by a factor of about 2 and the amount of diketo formation only slightly, we expect much larger changes in the oscillation amplitudes assigned to the single proton transfer. The Fourier analysis clearly shows a significantly higher amplitude for the 193 cm<sup>-1</sup>-bending mode at higher excess energy. The observed dependence of the oscillation amplitudes on



**Fig. 5.** Calculated normal modes of BP(OH)<sub>2</sub> [DFT, B3LYP/6-311+G(d,p)] that are assigned to the ones observed in the experiment. The particular modes shown are the 20b<sub>u</sub>, 21a<sub>g</sub> and 20a<sub>g</sub> (top to bottom).

the excitation wavelength corroborates the assignment of the wavepacket dynamics to the different reaction channels.

Excitation at 310 nm results in only weak oscillatory signal components (see Fig. 4b – lower panel). The molecule is prepared with a very high excess energy. A large number of vibronic states is populated and significant coupling between the vibrational modes is expected. This leads to a fast broadening of the wavepacket and a loss of contrast in the signal oscillations as it is observed.

## 5. Summary and conclusions

The nature of the primary steps in the photodynamics of BP(OH)<sub>2</sub> and the associated wavepacket evolution have been revealed by UV–Vis transient absorption spectroscopy with 30 fs time resolution. It is found that both the concerted double proton transfer and the initial step of the sequential transfer proceed in about 50 fs. The former is associated with a symmetric shortening of the donor acceptor distances and the latter with an asymmetric one. The molecular deformations are observed as characteristic wavepacket motions. In all these respects, the double proton transfer is extremely similar to the previously investigated single proton transfers. The two reaction channels seem to evolve independently from each other.

The ultrafast concerted process can well be rationalized by an appropriate gradient of the S<sub>1</sub> PES at the Franck–Condon (FC) point. Pronounced normal modes might not be developed in the dienol excited state due to its rapid decay to the keto tautomers, and hence a normal mode picture is not informative, however a projection of the ground state wavepacket to the FC point should be a suitable description. From the FC point the wavepacket accelerates toward the diketo minimum. An acceleration towards one of the monoketo minima is less obvious as it has to spontaneously break the symmetry of the molecule. We have to keep in mind, however, the thermal excitation of the molecules before the optical excitation. This is equivalent to rapid fluctuations from the symmetric geometry and the ultrafast excitation will catch the molecule in such a deformed geometry. It is therefore placed on the S<sub>1</sub> PES off the symmetric FC point and free to break into an asymmetric reaction. Similarly, solvent fluctuations will contribute to a loss of symmetry. To substantiate these ideas, a PES from high level quantum chemical calculations is dearly needed.

It is worth noting that the experimental observation of the excitation of the 20b<sub>u</sub>-bending mode in the PT product is a direct proof that a wavepacket can be generated by the ultrafast reaction itself. We consider it quite likely that such a mechanism contributes considerably to all vibrations that are active in the PT. We furthermore expect that the reaction induced creation of a wavepacket, i.e., a coherent vibrational excitation in the product, is possible for many ultrafast photochemical processes. It can happen when the reaction time is shorter than the relevant vibrational periods. This situation should occur for processes proceeding on an adiabatic PES without an effective potential barrier.

The observed wavepacket dynamics in BP(OH)<sub>2</sub> is characteristic for each reaction channel and can also be used for the distinction between the two paths. This is not only true for the analysis of the process, but even more interestingly it might provide a unique chance for coherent control experiments [40]. If the symmetric vibrations – that can be accessed optically – are constructively enhanced, more diketo production is expected. If, on the other hand, the symmetric vibrations are destructively superimposed, the monoketo tautomer should be preferentially formed. This scheme could be combined with a suitable choice of the excitation wavelength.

Beyond the present example of BP(OH)<sub>2</sub> the new insight into the mechanism of double proton transfer might also aid the under-

standing of other systems displaying such multidimensional dynamics. The relatively slow progressing double proton transfer in porphycene does show clear vibrational activity [43,44]. For related systems with vanishing barriers, the reactions will most likely proceed on an ultrafast time scale as wavepacket motion. For the well known example of dimers of 7-azaindole it is still an open debate whether only stepwise double proton transfer or also a concerted one occurs [22,25,26]. We expect that an experiment with sufficient temporal resolution should render wavepacket signatures on the experimental curves that can be interpreted similarly to the present work to determine whether there is a symmetric or an asymmetric approach of the two 7-azaindole moieties.

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