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Femtosecond Dynamics of a Simple Merocyanine Dye: Does Deprotonation Compete with Isomerization?

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Abstract: The primary photochemistry of the trans isomer of a simple merocyanine dye of the stilbazolium betaine type 1-methyl-4-(4′-hydroxytyryl)pyridinium betaine (M_{trans}) and its conjugate acid $MH^+{}_{trans}$ in aqueous solution is studied by femtosecond time-resolved pump probe spectroscopy. The measured rate of the primary photodynamics is determined to be $k = 1.1 \times 10^{12}\ s^{-1}$ for M_{trans} at pH 10 and $0.8 \times 10^{12}\ s^{-1}$ for $MH^+{}_{trans}$ at pH 6. This was assigned to either conformational changes or a simple vibrational relaxation before the actual isomerization takes place. Wavelength excitation studies give support for the former assignment. These results are discussed in terms of the recent results found for the primary processes of retinal in bacteriorhodopsin. Time-resolved transient measurements show that *no* excited-state deprotonation of $MH^+{}_{trans}$ occurs in aqueous solutions at pH 6 or pH 0, suggesting that the deprotonation occurs on a longer time scale than the picosecond time domain. This is in agreement with present theories of intermolecular proton-transfer reactions, which require solvent reorganization as well as the time of deprotonation estimated from the pK_a value of this molecule in the excited state. The results of our MO calculations on the electronic structure of these two compounds could account for the fact that, while $MH^+{}_{trans}$ photoisomerizes, its deprotonated form does not.

Introduction

The photoisomerization of C═C double bonds[1−5] is one of the most fundamental reactions, with great significance in diverse fields spanning the range from molecular electronics[6−8] to photobiology.[9,10] It has been extensively studied by time-resolved spectroscopy.[11−17] Substantial theoretical and experimental efforts have been made to understand the photochemistry of stilbenes and their derivatives.[1−19] An interesting class of stilbene derivatives are the merocyanine dyes of the stilbazolium betaine type such as 1-methyl-4-(4′-hydroxystyryl)pyridinium betaine (M).

This class of compounds has been used as sensitizers in color photography,[19] and due to their extreme hyperpolarizability they are used in nonlinear optics[20−25] and in electrochromics.[26−30] Furthermore, they seem to be promising for solar-energy conversion and in imaging technology.[31−33] Therefore, they attracted considerable attention and several studies were carried out in order to elucidate the molecular mechanism of their

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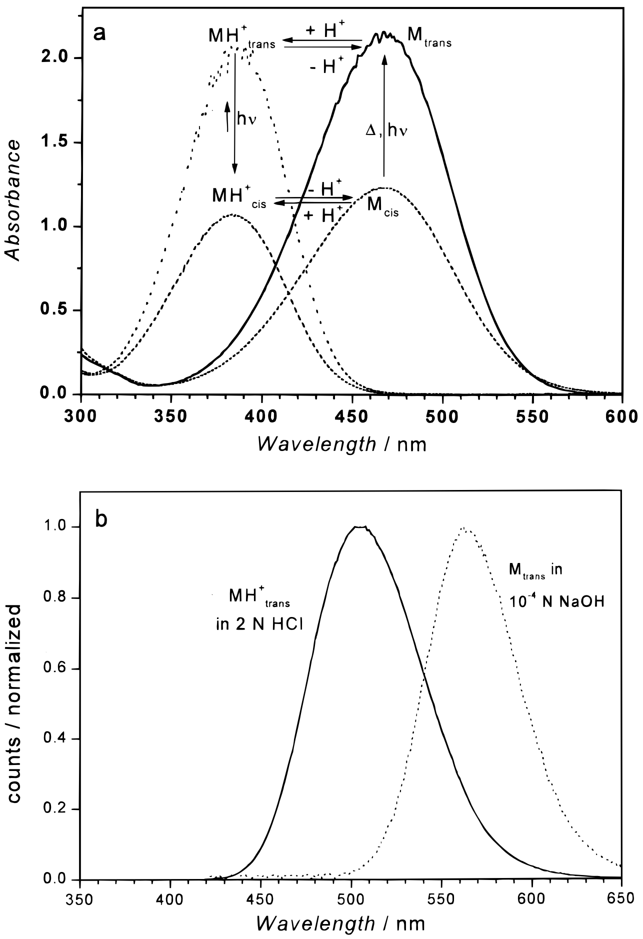
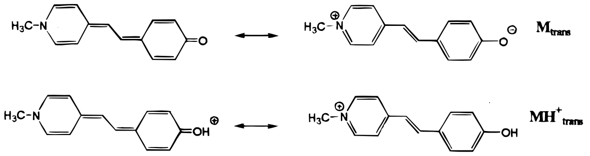


Figure 1. (a) Ground-state absorption spectra of M ($\lambda_{max} = 470$ nm) and MH^+ ($\lambda_{max} = 375$ nm) in aqueous solution. The protonation of M_{trans} leads to a hypsochromic shift of the absorption maximum from 470 to 380 nm. Photoisomerization to MH^+_{cis} leads to reduction of the absorbance but not to a shift in the absorption maximum. Deprotonation of MH^+_{cis} forms M_{cis} which also absorbs at 470 nm but with lower absorption coefficient than the trans isomer.[18] These absorption bands were used for the interpretation of the femtosecond transient absorption spectra. The spectra of the trans conformer are from pure samples measured prior to irradiation with 400 nm laser pulses. The less intense spectra, assigned to M_{cis}, are photostationary spectra of trans−cis mixtures after irradiation for 5 min with a Xenon arc lamp. (b) The corresponding emission spectra of M_{trans} ($\lambda_{max} = 540$ nm) in 10^{-4} N NaOH and MH^+_{trans} ($\lambda_{max} = 505$ nm) in 2 N HCl. The sample concentration was adjusted to an optical density of 0.3 at 400 nm in each case. For clarity, the emission intensities were normalized to a maximum value of one although the emission quantum yield of the protonated sample was 17× higher than that of the deprotonated one.

photochemistry.[9−18,34] Furthermore, due to its structure, the merocyanine dye of the stilbazolium betaine type (M) is regarded as an interesting model compound for the light-absorbing molecules in important photobiological systems such as the proton pump of the halobacterium halobium, the process of vision, and the phototactic properties of yellow protein. Previously,[17] time-resolved experiments on the picosecond time domain concluded that deprotonation might compete with the photoisomerization of MH^+_{trans}, which is not observed in the photobiological systems.

Figure 1a shows the known absorption spectra of M_{trans} and M_{cis} and their conjugate acids together with a scheme representing their experimentally determined photochemical and thermal interconversion.[17,18] A large absorption shift is observed to occur upon deprotonation reactions due to the differences in the acid−base equilibrium constant in the ground and excited states as described by Förster.[35] The absence of a large shift in absorption wavelength during the trans−cis isomerization is explained by the mirror symmetry of the electronic state correlation diagram for the cis−trans photoisomerization of stilbenes calculated by Hohlneicher et al.[5] The relative energies of the states do not change significantly; only the transition moments according to the symmetry change during the isomerization. We base the interpretation of our transient absorption study on the work by Steiner et al.,[18] who determined the photoproducts by means of ^1H NMR spectroscopy. In weakly acidic solution MH^+_{trans} is present. Upon photoexcitation, the cis conformer MH^+_{cis} forms[18] which can be deprotonated with the addition of base. M_{cis} isomerizes to M_{trans} both photochemically and thermally ($k_{iso,th} = 6.4 \times 10^{-5}\ s^{-1}$ at 23 °C).[18] The reaction series $M_{trans} \rightarrow MH^+_{trans} \rightarrow MH^+_{cis} \rightarrow M_{cis} \rightarrow M_{trans}$ completes a full cycle[18] and is regarded as a possible chemical model comparable to the molecular mechanism of important photobiological phenomena such as the light-driven proton-pump of halobacterium halobium or the process of vision. Steiner et al.[18] studied this system in great detail by measuring the photoreaction yields in aqueous solution with various proton concentrations. They showed that M_{trans} is thermodynamically more stable than M_{cis} and could not measure any net photoisomerization of M_{trans}. On the other hand, photoisomerization of MH^+_{trans} yields the cis isomer MH^+_{cis} which is thermally stable (up to 100 °C[18]).

The trans forms have the following resonance structures:



The resonance structures reveal a reduced bond order of the ethylenic C═C double bond leading to the thermal cis/trans isomerization observed for these stilbene derivatives.[18] Furthermore, the resonance structures indicate a polar contribution to the ground state leading to a large ground-state dipole moment. The dipole moment of M_{trans} is significantly reduced in the first excited state.[36,37] The change of dipole moment upon excitation results in a strong negative solvatochromic behavior, as observed in the blue shift in the long-wavelength absorption maximum with increasing solvent polarity.[38,39]

Ikeda et al.[17] used a Nd:YAG laser to study the photochemistry of M_{trans} and MH^+_{trans} with picosecond time resolution. With MH^+_{trans} they measured a transient absorption at 440 nm, which was attributed to the deprotonation of MH^+_{trans} in competition with its isomerization. However, with their laser powers, they observed absorption from solvated electrons due to multiphoton processes. They also concluded that the primary events of the investigated photocycle occur on the subpicosecond time domain, beyond their time resolution. To examine whether deprotonation can actually occur in this system in competition with isomerization, we studied this system with femtosecond time-resolved pump probe spectroscopy. Using low power pump pulses, new data were obtained, which helped to identify the

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primary photoreactions of the stilbazolium betaine (M) and its protonated form (MH^+). From the results of our study, we reached the important conclusion that deprotonation is not a competitive reaction pathway with photoisomerization of the excited state of MH^+_{trans}. Such processes require solvent reorganization, a process that occurs on a time scale of tens or hundreds of picoseconds. Furthermore, for an excited state with a pK_a value of 1.9, the rate of deprotonation is estimated to occur in the 1 ns time regime.

Experiment

The stilbazolium betaine M was taken from the same sample used in the previous study.[18] Solutions of pH 6 and pH 10 in deionized water[17] were used to study the MH^+ and M samples, respectively. The samples were prepared in the dark, to avoid photodegradation prior to the experiment. Steady-state UV−vis absorption spectra were measured with a Beckman DU 650 dual-beam spectrometer in a standard 1 cm quartz cell before and after the experiment. The steady-state emission was recorded with the PTI Quanta Master in a standard 1 cm fluorescence quartz cell. A xenon arc lamp served as the excitation source. The optical density for the steady-state emission was adjusted to 0.3 both in the basic and the acidic solution at an excitation wavelength of 400 nm.

The femtosecond transient absorption experiments were carried out with an amplified Ti−sapphire laser system (Clark MXR CPA 1000). It was pumped by a diode-pumped, frequency-doubled Nd:vanadate laser (Coherent Verdi). This produced laser pulses of 100 fs duration (HWFM) and an excitation energy of 1 mJ at 800 nm. The repetition rate was 1 kHz. A small fraction (4%) of the fundamental laser pulse energy was used to focus in a 2 mm sapphire plate to generate a white light continuum in the 430−780 nm region. The remaining laser light was split into two equal parts in order to pump two identical Optical Parametric Generators (Quantronix TOPAS). Each produced signal and idler waves with a total energy of 100 μJ. Tunable excitation wavelengths in the visible range were then produced by second harmonic generation (400 nm) and sum frequency gGeneration (490−550 nm) of the signal wave. The excitation pulses were modulated by an optical chopper (HMS 221) with a frequency of 500 Hz. The probe light was split into a reference and a signal beam. The samples were irradiated in cylindrical cuvettes of 2 mm optical path length, placed in a spinning sample holder to continuously remove the photochemical products during data collection. The optical density was adjusted to one at the excitation wavelength of 400 nm.

For spectral measurements a CCD camera (Princeton Instruments) attached to a spectrograph (Acton Research) was used. The group velocity dispersion of the white light continuum was compensated. For kinetic measurements both beams were detected by two photodiodes (Thorlab) after passing a monochromator (Acton Research). The kinetic traces were obtained using a sample-and-hold unit and a lock-in-amplifier (Stanford Research Systems). The lifetimes are obtained by using nonlinear least-squares fitting. The error of our femtosecond pump probe kinetics is generally 15%. The typical measured optical density (OD) changes were in the range of 50 mOD. All measurements were carried out at lowest possible laser excitation powers of 500 nJ/pulse.

Results and Discussion

We carried out a series of measurements in basic and slightly acidic solutions, respectively. The steady-state spectral behavior of M upon isomerization was previously described in the literature[17,18,34] From their work, which included photoproduct analysis by NMR spectroscopy,[18] it is known that the protonated system undergoes isomerization upon photoexcitation. As illustrated in Figure 1a, the absorption spectra of M_{trans} ($\lambda_{max} = 470$ nm) and MH^+_{trans} ($\lambda_{max} = 370$ nm) show that protonation of M_{trans} leads to a significant hypsochromic shift, whereas isomerization leads to a change in absorbance but not to a significant shift in the wavelength of the absorption maximum. The spectral positions and intensities of the absorption bands (as shown in Figure 1a) were used in the interpretation of the femtosecond transient absorption spectra. In Figure 1b the normalized steady-state fluorescence bands with maxima at 560 and 506 nm for M_{trans} and MH^+_{trans} are presented. Also the shape and position of these fluorescence bands will be used in the discussion of the transient pump probe spectra.

1. Excited-State Dynamics of the Stilbazolium Betaine M_{trans} in Basic Solution. At pH 10, M_{trans} is the only species present in solution. Only the pure excited-state dynamics of M_{trans} are expected to be observed without interference of the deprotonation process. So far, no time-resolved study has been published on the stilbazolium betaine in basic solution. Steiner et al.[18] reported that according to their reaction yield studies no measurable amount of M_{cis} was formed in basic solution. Nevertheless, by applying femtosecond pump probe spectroscopy we found that upon excitation M_{trans} shows a relatively rich dynamical behavior within the first 6 ps. After laser excitation, a negative transient absorption is monitored between 540 and 580 nm (Figure 2a), which can, due to its spectral shape, be attributed to stimulated emission induced by the probe pulse following the excitation in our pump−probe experiment. That we indeed observe induced emission is concluded from a comparison between the steady-state spectra in Figure 1b and the transient spectra in Figure 2a. The probe pulse is a 100 fs white-light continuum pulse, which simultaneously probes the observation window from 450 to 750 nm. Therefore, emission can be induced at all wavelengths in this spectral range, as long as the emissive state is populated.

Relaxation of the Initially Excited-State M_{trans}*. The maximum of the induced emission shifts from 540 to 580 nm with a time constant of 1.1 ps. The kinetic measurements at different observation wavelengths show that the spectral shift is caused by the rise of a transient absorption at 520 nm. At 520 nm the transient absorption was found to have a rise time of 1.1 ps, as shown in (Figure 2b squares). This matches the decay of the induced emission at 570 nm (Figure 2b, diamonds). Therefore, the transient at 1.1 ps absorbs at 520 nm and is a nonfluorescent intermediate. We assign this transient to either an electronically excited state of M_{trans} in its vibrational ground state or to an excited-state conformer, as illustrated in Figure 3. This suggests that the dominant process of M_{trans}^* is a vibrational relaxation or a change in conformation within the first ps, leading to a spectroscopic minimum M_{con}^* on the excited-state potential energy surface, from which it relaxes to the ground state of M_{trans}.

Recovery of the Ground-State M_{trans}. At 480 nm the transient bleach of ground-state M_{trans} can be monitored without interference from the 520 nm transient absorption. At this wavelength, the bleach of the ground state occurs instantaneously and recovers with a lifetime of 5.8 ps. This indicates that no net-photoisomerization to M_{cis} occurs. This is also in accordance with the continuous wave studies reported by Steiner et al.[18] that concluded that an immeasurably small quantum yield of M_{cis} was formed.[18] More than 99% of the transient absorption

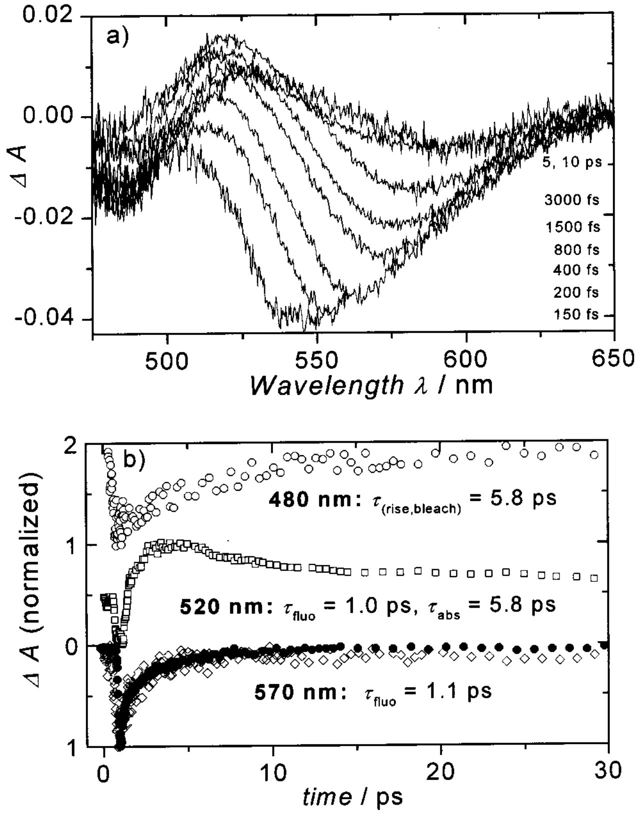

Figure 2. The time dependence of the femtosecond transient spectra after laser ecxitation of M_{trans} in basic solution (pH 10). Figure 2a shows the femtosecond laser-induced emission spectra of M_{trans}* as a function of delay time. In Figure 2b the kinetic traces after 400 nm excitation are shown for different observation wavelengths. At 480 nm the ground-state bleach and its decay are observed, indicating the recovery of the ground-state M_{trans}. At 520 nm the formation of the ground state absorption bleach is initially observed, then an intermediate conformer M_{con}* is formed with a time constant of 1.1 ps. M_{con}* decays within 5.8 ps to form the ground state of M_{trans}. At 570 nm the induced emission of M_{trans}* is monitored. To clarify whether the 1 ps lifetime is due to the internal conversion or due to an activation barrier to another conformer the sample was in addition excited at lower energy (500 nm excitation, black circles). The identical fluorescence lifetime compared to the 400 nm excitation (diamonds) indicates that the red shift of spectrum (a) is due to the crossing of a reaction barrier not due to vibrational relaxation. The induced emission decays during the formation of the intermediate M_{con}*. For clarity each trace is normalized with respect to its intensity. Furthermore, they were displaced in a vertical direction.

at 520 nm decay with a lifetime of 5.8 ps, repopulating the M_{trans} ground state.

Excited-State Dynamics of M_{trans}*: Internal Conversion vs Chemical Dynamics. Two different photoprocesses are possible for M_{trans}* in basic solution, and are summarized in Figure 3. Figure 3a shows that vibrationally excited M_{trans}* internally converts to its ground vibrational levels in 1.1 ps, which relaxes to the ground electronic state in 5.8 ps. In Figure 3b, vibrationally excited M_{trans}* can change into a conformer M_{con}*, which relaxes to M_{trans} ground electronic state in 5.8 ps. To distinguish whether internal conversion (Figure 3a) or transition to a conformer (Figure 3b) takes place on the 1 ps time scale, we carried out experiments with varying excitation wavelengths. With 400 nm wavelength, the excitation had 0.6 eV of excess vibrational energy in the lowest excited singlet state. Therefore, the 1 ps component could simply be the vibrational relaxation within the S_1 state. This would also explain a red-shift in the induced emission. On the other hand, the red shift of the emission is found to be only 0.08 eV. Excitation with 500 nm pulses does not add much vibrational energy to S_1. So, one would expect that not much time-resolved red shift of the emission is observed. However, this is not the case. The same emission with the same lifetime was observed. This shows that neither the red-shift, nor the lifetime of 1.1 ps, is related to the internal conversion process after 400 nm laser excitation. Indeed, 1.1 ps seems to be a rather long relaxation time for such a large organic molecule. Therefore, an activated process over a transition state as indicated in Figure 3b is concluded. M_{con}* undergoes further relaxation and repopulation of the ground-state M_{trans} with a time constant of 5.8 ps.

Solvent Relaxation versus Internal Conversion. Since M_{trans} undergoes a large change in dipole moment upon excitation, we considered the possibility of the observation of a time-resolved Stokes shift. We measured the kinetics at different wavelengths between 480 and 700 nm and did not find a change in the fluorescence rise time at longer observation wavelengths. This suggests that the solvent shell of M_{trans}* undergoes relaxation in less than our time resolution (100 fs). This is in agreement with the known solvent relaxation times in water.[40] As the change in dipole moment is much larger in the basic form (M) than in its conjugate acid, no stokes shift is expected for MH^+.

On the other hand, we observed the shift of the emission maximum from 540 to 580 nm. As we pointed out above, it seems that the initially created Franck−Condon state relaxes internally into a spectroscopic minimum, which is then observed as a transient absorption at 520 nm.

2. Excited-State Dynamics of the Stilbazolium Cation MH^+_{trans}. The protonated stilbazolium betaine MH^+_{trans} in acidic solution has a potentially more complex photochemistry since it is a weak acid[18] in the ground state with $pK_a = 8.54$ and was predicted[41] to be a stronger acid in the excited state with a $pK_a^* = 1.9$. The pK_a* is a thermodynamic equilibrium constant and it immediately raises the interesting question whether this equilibrium ever will be established within the excited-state lifetime, in other words, if for MH^+_{trans}* deprotonation is a competitive relaxation pathway to the isomerization process or if one of the two possibilities dominates the primary photoreactivity.

The femtosecond transient absorption spectra in Figure 4a of MH^+_{trans} in 2 N HCl solution show an induced emission in the range from 480 to 570 nm with a maximum at 540 nm. As in the case of basic solution, the transient induced emission is similar to the emission observed in the steady-state experiments shown in Figure 1b.

Relaxation of the Initially Excited-State MH^+_{trans}*. A fast decay component of 800 fs is observed between 480 and 500 nm (Figure 4b, squares). Its amplitude and decay time are found to be independent of the pH of the solution (between pH 6 and pH 0). Furthermore, the spectral shape of the induced emission did not depend on the pH of the solution. The fast 800 fs decay component at 480 nm was found to be due to a slight red shift of the emission band. Correspondingly, at 530 nm a slightly delayed decay of the induced fluorescence was observed in the first few ps (Figure 4b, diamonds). However, no delayed rise was observed at 570 nm and longer wavelengths. The slight spectral shift of the induced emission within the first picosecond can result from the formation of a new transient MH^+_{con}* (see Figure 5b) or from a vibrationally relaxed state of MH^+_{trans}*

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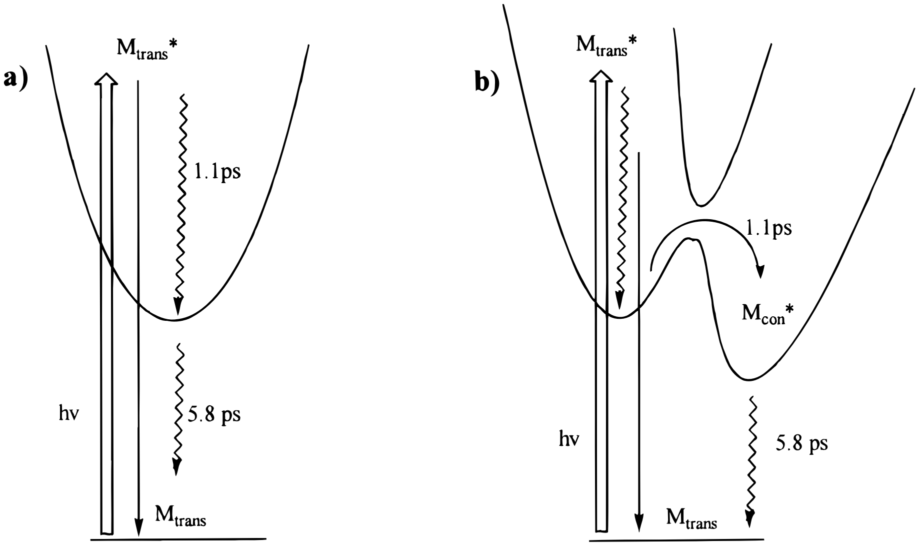

Figure 3. The molecular mechanism for the relaxation dynamics of the photoexcited M_{trans} illustrated by different schemes. In (a) the observed relaxation dynamics with a lifetime of 1.1 ps is interpreted as an internal conversion to the vibrational ground state of the initial Franck−Condon state M_{trans}* within the same electronic state. In (b) the transition to a conformational intermediate on a new potential energy surface is shown. In both processes, a short-lived transient of 1.1 ps lifetime (spectroscopic minimum) is observed and both pathways lead to relaxation to the trans isomer electronic ground state. On grounds of spectroscopic measurements with only a fixed excitation wavelength, it is difficult to estimate whether (a) or (b) is realized. Pump probe experiments with varying excitation energies showed that, even if we excite into low vibrational levels of the excited state (500 nm excitation) the 1.1 ps component does not change. Therefore, it is concluded that it is not due to the internal conversion process, but due to a transition which is rate limited by an activation barrier, as indicated in Figure 3b.

(Figure 5b). The pump probe experiments show that the fast 800 fs component does not change after varying the excitation wavelength. Therefore, we conclude that, like in M_{trans}, the fast component is not the internal conversion but an actual transition into a new potential minimum, as shown in Figure 5b. The recovery of MH^+_{trans}* (and the formation of MH^+_{cis} in comparable quantum yields[18]) occur within 24.6 ps. Because of the very similar fluorescence of MH^+_{con}* and MH^+_{trans}* (spectra at 400 fs and 30 ps in Figure 4a), it is concluded that the relaxation to the MH^+_{con}* involves only minor changes in the structure of the MH^+_{trans}* from its initial Franck−Condon structure.

The assignment of the primary process of MH^+_{trans}* as formation of an intermediate conformer MH^+_{con}* is based on our interpretation of the observed fast dynamics. There are several other possibilities that might account for the fast 800 fs component besides being the formation of MH^+_{con}*. First is the adiabatic deprotonation of MH^+_{trans}. The fact that the M_{trans} absorption was not observed gives strong evidence against the occurrence of this process. As was previously shown,[18] the deprotonated M_{trans}* does not lead to M_{cis}. However, quantum yield measurements showed that 53% of MH^+_{trans}* lead to formation of MH^+_{cis}. Second, the possibility of the direct photoisomerization of MH^+_{trans}* to MH^+_{cis} taking place in 800 fs would make it difficult to explain the shift of the emission from 480 nm to longer than 500 nm during this short time. MH^+_{trans}* emission occurs near 500 nm. The decay time of this emission is observed to be 24.6 ps. We thus assign the longer component of the decay to the isomerization process. A third possibility for the interpretation of the fast component is intramolecular vibrational relaxation. Formation of a vibrationally relaxed state, MH^+_{con}* on the same potential energy surface seems to be plausible. On the basis of transient spectroscopy, by using only one excitation wavelength, it would not be possible to decide whether MH^+_{con}* is formed on a different potential energy surface or simply by internal conversion. Femtosecond experiments, using different excitation wavelength, showed that the first observed dynamics of 800 fs does not change when we excite to lower vibrational levels of the electronically excited-state MH^+_{trans}*. This indicates that the observed dynamics is not due to the internal vibrational relaxation in the S_1 state of MH^+_{trans}.

Isomerization vs Deprotonation of MH^+_{trans}*. The long-lived lifetime component of the emission was measured to be 24.6 ps at $\lambda_{obs} = 530$ nm (Figure 4b, diamonds). The lifetime was found to depend on the pH. It increases from 20 ± 1 ps in 10^{-6} N HCl to 25 ± 1 ps in 2 N HCl solution. This increase in fluorescence lifetime is consistent with the measured increase in the quantum yield of the trans−cis isomerization,[17] which also increases by 20% in 2 N HCl solution.

A careful examination of the transient absorption in the 460 nm region was carried out in the pH range of 0−7. The 460 nm region is the one at which M_{trans} would absorb. The result illustrated in Figure 4 strongly suggests that deprotonation does not occur in competition with isomerization in the excited state of MH^+_{trans}. This conclusion is further confirmed by examining whether any of the kinetics observed slows down in D_2O. The excited-state relaxation time measured for MH^+_{trans}* in H_2O compared to that of MD^+_{trans}* in D_2O is shown in Figure 6, when probing at 530 nm. It is known, that if deprotonation is the occurring process, the rate of the process should decrease by a factor of 2−5 as a result of the kinetic isotope effect.[42] Additionally, it was shown that temperature can change the ratio of the deprotonation rates, but the trend of the kinetic isotope effect is unchanged.[43] As shown in Figure 6, no change in the lifetime was observed in accordance with the fact that no absorption due to deprotonated species was detected. Therefore, we conclude that the isomerization process is much faster than the deprotonation and hence dominates the excited-state dynamics of MH^+_{trans}. Recent investigation show that reorganization is necessary prior to the successful transfer of the proton.[44,45]

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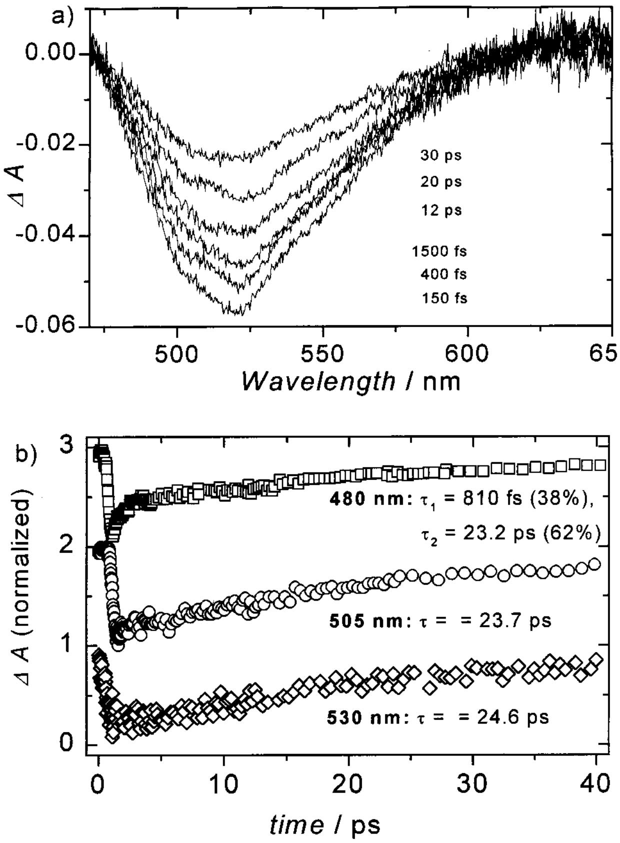

Figure 4. The time dependence of the femtosecond transient absorption spectra of MH^+_{trans} in aqueous solution of 2 N HCl after excitation with 100 fs laser pulses at 400 nm. Figure 4a shows the induced emission as a function of time. In Figure 4b the normalized kinetic traces are shown. The lack of transient absorption at 570 nm, where M_{trans} absorbs, strongly suggests the lack of deprotonation on this fast time scale. The data were fitted to extract the time constants for the different processes. For clarity, the kinetic traces are vertically displaced by one OD unit. At longer monitoring wavelength only the long decay component is observed. At 480 nm an additional fast decay component of 800 fs is measured. The rate and intensity of this fast component was pH independent in the 2−6 pH range, which indicates a fast conformational change on this time scale (see text for the detailed argumentation of this assignment).

This may take several picoseconds, e.g. the rates of proton transfer from 2-naphthol-3,6-disulfonate ($pK_a^* = 0.5 \pm 0.1$) and 8-hydroxy-1,3,6-pyrenetrisulfonate ($pK_a^* = 0.4 \pm 0.1$) to the solvating water molecules were 3.1 ± 10^{10} and 3.2 ± 10^{10} s^{-1}, respectively.[46,47]

MH^+_{con}* might correspond to the proposed J intermediate in the bR photocycle. The assignment of the J intermediate is not yet confirmed. It was believed[48] that all-trans retinal in the J intermediate is already the 13-cis isomer. More recent picosecond time-resolved coherent antistokes Raman shift (PTR-CARS) studies,[49−51] however, suggest that retinal in the J intermediate is not 13-cis but still the all-trans isomer. This suggests that the 500 fs component in bR is not a photoisomerization time but the time required to form adiabatically another conformer in the excited state. Isomerization is believed to take place in the J → K process on the 3 ps time scale. In other words, the formation of the conformer takes place in 500 fs and decays by photoisomerization to form the K intermediate in 3 ps. In K, the Schiff base is still protonated.

In bR, the deprotonation process occurs in 70 μs.[52,53] This is consistent with the pK_a value of the protonated Schiff base. The pK_a value of the excited state of MH^+ is 1.9 i.e.,

$$MH^+_{trans}{}^* + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} M_{trans}{}^* + H_3O^+$$

and $K_a = [M_{trans}{}^*][H_3O^+]/[MH^+_{trans}{}^*] = k_1/k_2 = 10^{-1.9} = 0.013$. Thus, if equilibrium is assumed, the deprotonation rate constant $k_1 = k_2 \times K_a$. If we further assume that the reprotonation is a diffusion-controlled process, this gives the value of $k_1 = k_d \times [H_3O^+] \times K_a = 10^{10} \times 0.01 \times 0.013 \approx 10^6\ s^{-1}$ for the deprotonation rate at pH 2. This places the deprotonation time in the microsecond rather than in the picosecond time scale, as observed for the biological analogue bR.[48,52,53]

Electronic Structure Calculations and the Photoisomerization Rates of M_{trans}* and MH^+_{trans}*. It is interesting to note that MH^+_{trans}* photoisomerizes but M_{trans}* does not. Furthermore, the conformer M_{con}*, formed from M_{trans}*, does not fluoresce while that formed from MH^+_{trans}* does. Both facts together show that the primary excited-state dynamics for the investigated system does not involve deprotonation. However, it needs at least one more reaction coordinate to explain the experimental results. A plausible explanation was recently proposed from the results of the Raman study of the excited state of retinal in bacteriorhodopsin.[48,51] The authors proposed that the central C=C bond stretching and C−C contraction is the primary reaction coordinate after photoexcitation. The measured fast reaction component could indeed be a primary stretching process (this can also be regarded simply as a vibrational relaxation), which precedes the bond twisting. This is consistent with the fact that the excitation process itself involves a $\pi \rightarrow \pi^*$ promotion, which switches the bond order of the central C=C ground state double bond in the conjugated system. Both processes (stretching and twisting) lead to different spectroscopic minima in the case of the protonated MH^+_{trans} and the basic form M_{trans}, respectively. This can be understood in terms of the different dipole moments and solvation of the betaine (M) and the cation (MH^+) in water. In water, the betaine will be, due to its larger dipole moment, better energy-stabilized in the longer trans form than in its cis conformer. Therefore, isomerization is unfavorable in the basic form. On the other hand, the change in free energy for the bond twist around the central C=C bond of the cation MH^+ is small. That might explain the observed 53% isomerization.

The C−C-stretching coordinate will be affected by the binding of a proton on the arylic oxygen. Semiempirical calculations (PM3 including geometry relaxation) on the ground state of M_{trans} show that the ground-state structure of the deprotonated form has a reduced bond order (143 pm bond length) for the central C=C bond and therefore the compound is well described by the quinoide resonance form. This suggests that the order of the central C−C bond is increased upon photoexcitation, which leads, in agreement with our observation, to the conclusion that photoisomerization of M_{trans} is hindered.

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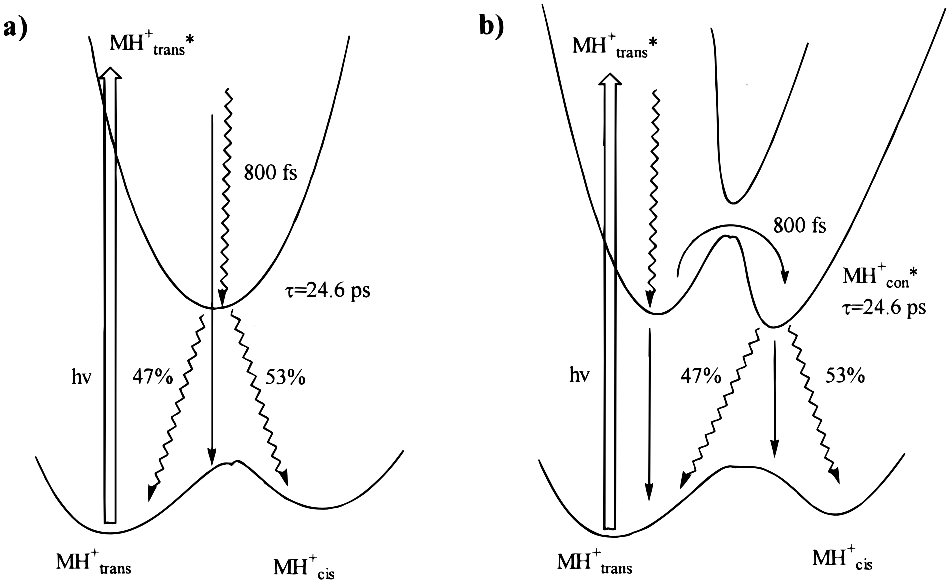

Figure 5. The molecular mechanism for the isomerization dynamics of the photoexcited MH^+_{trans} shown in two different schemes. In (a) the observed initial relaxation dynamics with a lifetime of 800 fs is interpreted as an internal conversion to the vibrational ground state of the initial Franck−Condon state $MH^+_{trans}*$ within the same electronic state. In (b) the transition to a conformational intermediate on a new potential energy surface is shown. In both processes a short-lived transient of 800 fs lifetime (spectroscopic minimum) is observed and both pathways could lead to the measured cis:trans distribution of 53:47%. On grounds of our spectroscopic measurements and the known theory (see text) it is difficult to estimate whether (a) or (b) is occurring. An internal conversion of 800 fs seems to be possible but quiet slow, so that the possibility of (b) is more likely. Moreover, the fast component did not change when we excited into the vibrational ground state of the excited state. This gives additional evidence that the 800 fs component is not due to the observation of the internal conversion process but due to a transition to another conformer $MH^+_{con}*$.

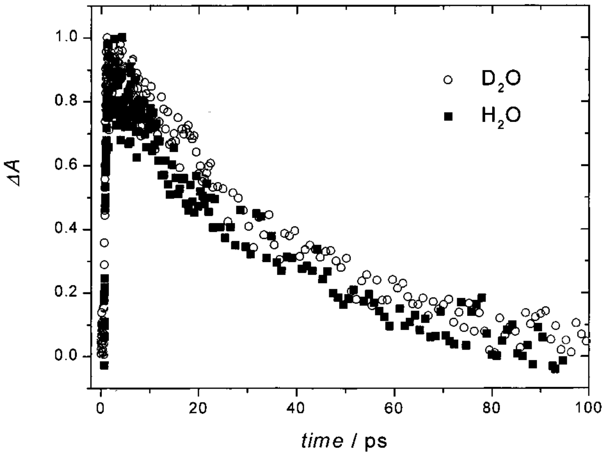

Figure 6. Comparison of the decay time of $MH^+_{trans}*$ and $MD^+_{trans}*$ in H_2O and D_2O, after 400 nm excitation. The dynamics were measured in solutions of pH (pD) = 0 at 530 nm at room temperature. No measurable difference in the dynamics was observed, which excludes proton transfer as an excited-state reaction pathway on this time scale.

The same calculations on MH^+_{trans} give for the central C═C bond a typical double bond length of 135 pm. This explains its thermal stability mentioned above and also suggests a reduced bond order for the excited state in accordance with the observed photoisomerization.

Conclusion

The photoexcitation of MH^+_{trans} does not produce species with the absorption characteristics of M_{trans} on the subpicosecond time scale. This, together with the absence of the isotope effect on the decay of the photoexcited state of MH^+_{trans}, strongly suggests that the deprotonation occurs on a longer time scale than the excited-state lifetime. This is similar to what is observed in the photobiological systems, e.g. bacteriorhodopsin. Using the pK_a value of its excited state, a simple calculation suggests that it should occur on the microsecond time scale.

The excitation of MH^+_{trans} forms a fluorescent conformer $MH^+_{con}*$ within 800 fs. This is proposed to form as a result of ultrafast stretching and twisting of the central C═C bond. While internal conversion might account for the 800 fs process, excitation wavelength-dependent measurements do not support this assignment. Combining our results with the earlier quantum yield data by Steiner et al., suggests that $MH^+_{con}*$ decays with equal probability to give cis and trans MH^+ in 24.6 ps.

The photoexcitation of M_{trans} leads to a conformer $M_{con}*$ with a time constant of 1.1 ps. $M_{con}*$ is nonfluorescent or only weakly fluorescent and decays with a lifetime of 5.8 ps back to the ground state of M_{trans}. Thus, while MH^+_{trans} photoisomerizes, M_{trans} does not. The results of the MO calculations on the structure of these two compounds could account for the difference in their dynamic behavior.

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