Direct versus Indirect H Atom Elimination from Photoexcited Phenol Molecules

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The active role of the optically dark $\pi\sigma^*$ state, following UV absorption, has been implicated in the photochemistry of a number of biomolecules. This work focuses on the role of the $\pi\sigma^*$ state in the photochemistry of phenol upon excitation at 200 nm. By probing the neutral hydrogen following UV excitation, we show that hydrogen elimination along the dissociative $\pi\sigma^*$ potential energy surface occurs within 103 ± 30 fs, indicating efficient coupling at the S_1/S_2 and S_0/S_2 conical intersections, with no identifiable role of statistical unimolecular decay of vibronically excited (S_0) phenol in the timeframe of our measurements.

Introduction

Aromatic amino acids like tyrosine, tryptophan, and phenylalanine have very large UV-absorption cross sections; however, the fluorescence quantum yields of these molecules are very small. This is an indication of efficient nonradiative processes, which effectively quench the fluorescence.[1–3] These nonradiative processes must be very fast in order to compete effectively with and overcome the fluorescence pathway. In such systems as those described above, it seems natural to study the chromophore of the biomolecule itself. Phenol, which is the chromophore of the amino acid tyrosine, shows similar low fluorescence quantum yields.[4]

Recent ab initio calculations by Sobolewski, Domcke and co-workers[5–7] have shown that the low fluorescence quantum yield of phenol following excitation at the wavelength of interest here (200 nm) is primarily due to an excited singlet state of $\pi\sigma^*$ character, which is dissociative with respect to the stretching coordinate of O−H bond. This dissociative state (S_2) bisects both the optically bright $\pi\pi^*$ state (S_1) and the ground state (S_0) through two successive conical intersections (CI, S_1/S_2 and S_0/S_2, respectively), leading to elimination of neutral hydrogen (see Figure 1 in Nix et al.[8]). The absorption of UV photons below 248 nm corresponds to the photoexcitation of phenol above the S_1/S_2 CI. Generally, the optically dark S_2 state cannot be excited directly. Population from optically bright states such as S_1 can be transferred to the S_2 state through the S_1/S_2 CI. Once on the S_2 state, the excited phenol evolves towards the S_0/S_2 CI and can undergo two photochemical fates. The first is to continue its passage through the CI and dissociate directly. Alternatively, highly excited ground-state phenol may be formed which, following energy dissipation into the correct vibronic mode, i.e., O−H, can also lead to dissociation. The former and the latter pathways are referred to as direct dissociation and statistical unimolecular decay.[8]

The dynamics of H atom and proton transfer have been heavily studied in phenol−ammonia clusters.[9–11] Pino et al.[12,13] first suggested that excited state hydrogen transfer could be used to explain the decrease in $[PhOH-(NH_3)_n]^+$ and the concurrent increase in the $[NH_4(NH_3)_{n-1}]^+$ signal. According to Pino et al. and later confirmed by Ishiuchi et al.,[14] when using time-resolved ion-dip experiments, the initially excited optically bright $\pi\pi^*$ (S_1) state couples to the optically dark $\pi\sigma^*$ (S_2) state through a CI. The decay of the phenol cluster can then be explained by tunnelling through a barrier along the O−H coordinate. Unlike in the bare phenol, the reorganization of the electronic levels due to clustering results in the S_2 state not intersecting the ground electronic state (S_0); that is, there is no S_0/S_2 CI.

The direct observation of H atom detachment driven through the S_2 state of phenol was first reported by Tseng et al.,[15–17] and then by Nix et al.,[8,18] by using multimass ion imaging and total kinetic energy release (TKER) measurement, respectively, although so far, no time-resolved measurements probing the absolute timescales of the direct and statistically unimolecular decay pathways of these two processes have been reported. This provides the driving forces for the work presented in this paper. In their work, Nix et al.[8] report how at the highest energies in their excitation, which corresponds to approximately the same region of excitation as that described in this work, they observed two primary peaks in the H atom kinetic energy release. They attributed the peak corresponding to the highest kinetic energy to direct dissociation. They proposed that the low-energy peak could be attributed to statistical unimolecular decay of highly excited phenol (S_0) molecules formed because of coupling at the S_0/S_2 CI. A similar observation was also made by Tseng et al.[15–17]

To the best of our knowledge, the only direct demonstration of time-resolved H atom elimination in such systems has been reported in pyrrole via the excited $\pi\sigma^*$ state by Lippert et al.[19] by using (2+1) resonance-enhanced multiphoton ionization (REMPI) by femtosecond laser pulses at 243.1 nm following photoexcitation at 250 nm in a pump−probe setup. Interestingly, Lippert et al. report two timescales for the dissociation. They attribute the first to direct dissociation, with a measured timescale of 0.11 ps. They measured the second pathway, due to indirect or statistical unimolecular decay, to occur in 1.1 ps.

If indeed highly excited phenol molecules are undergoing a statistical unimolecular decay process, this should manifest itself in a similar two-step process in phenol. This article reports the results of a two-color pump−probe experiment with femtosecond laser pulses. The phenol molecules were excited at 200 nm, and the photoproducts were probed by (2+1) REMPI at 243.1 nm with TOF-MS detection. The results presented strongly implicate that a single pathway to dissociation is operative on the timescale of the experiment. The measured

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dissociation is very fast, suggesting direct dissociation, while no slower component is observed. This implies that if any H is indeed being formed through a statistical unimolecular decay process, this must be occurring at much longer timescales (>200 ps).

To set the scene, we begin by describing the experimental setup including a description of our TOF-MS. We then present time-resolved TOF-MS of H^+ and discuss the implications of the appearance of H^+ in relation to the dynamics of dissociation. Finally, the results of these findings are summarized, and the ramifications of these findings are briefly discussed with reference to other biologically relevant molecules that have been suggested to display similar decay dynamics.

Experimental Section

As the experimental setup is not described elsewhere, what follows is a detailed description of the apparatus used. The femtosecond laser is a commercial Spectra-Physics XP system consisting of a Ti-Sapphire oscillator and a regenerative amplifier. The system delivers 3 mJ pulses centred at 800 nm at 1 kHz repetition rate. The measured pulse duration is 35 fs. The output is split into three beams of equal intensity. 1 mJ/pulse is used to generate approximately 1 μJ/pulse at 200 nm by frequency doubling, tripling, and then quadrupling the fundamental by using a series of type-I, type-II, and type-I BBO crystals, respectively. The remaining two beams are used to pump two optical parametric amplifiers (OPA, TOPAS C, Light Conversion). Only one OPA is used for the experiments described herein, which is set at 243.1 nm to probe the neutral H. The output power is around 7−8 μJ/pulse. The 200 nm and TOPAS output are combined collinearly at a dichroic mirror and sent into the interaction region of a TOF-MS, intercepting a molecular beam of phenol. A pump−probe laser cross-correlation (instrument response function) of approximately 160 fs full width half maximum (FWHM) was measured through nonresonant two-color (200 nm / 243.1 nm) multiphoton ionization of NH_3 and H_2O. The relative delay between the pump and probe is varied by using a motor-controlled delay stage (Physik-Instrumente). The probe is typically varied over 2 ps with a minimum step size of 0.033 ps. A molecular beam of phenol is produced by coexpanding 2−3 psi of He and the vapour pressure of phenol at 70 °C into vacuum by using an Even−Lavie pulsed solenoid valve[20] operating at 500 Hz. The source chamber housing the pulsed valve is separated from the interaction chamber by a 2 mm skimmer. The interaction chamber houses the TOF optics which accelerate the ions, hitting the microchannel plate (MCP) detector located at the terminus of the flight tube (approximately 50 cm). The molecular beam apparatus together with the TOF-MS is shown in Fig. 1. The MCP signal is directed into a multichannel scalar (Stanford, SR430). The ion TOF data accumulated for each 10 000 laser pulses is transferred via general purpose interface bus to a computer running an acquisition program written in LABVIEW. Typical peak counts are kept below 0.1 ion counts per 5 ns TOF bin per laser pulse in order to avoid saturation of the scalar.

Results and Discussion

Figures 2a and 2b shows the TOF-MS of phenol obtained by photoionization by using only the pump (200 nm) and both the pump and probe (200 and 243.1 nm), respectively. In all the measurements described in this paper, the intensity of the 200 nm was carefully adjusted such that minimum fragmentation of the parent was observed, greatly reducing alternative sources of H production through multiphoton effects. A representative

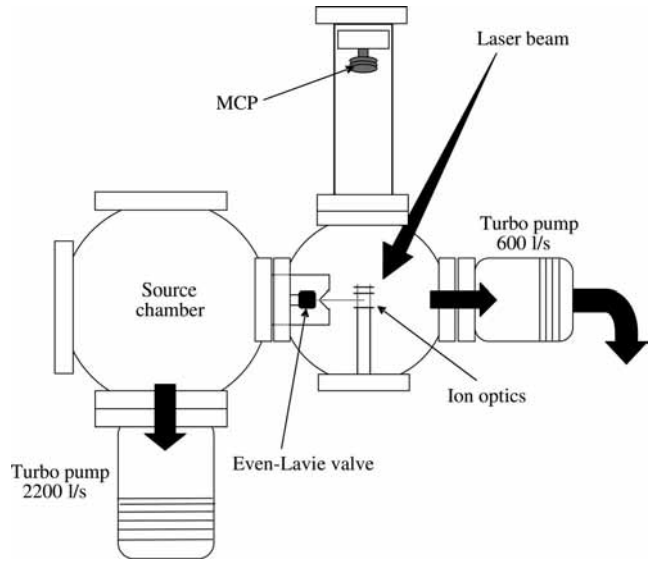

Figure 1. Experimental setup comprises a source chamber and linear time-of-flight mass-spectrometer (TOF-MS). The source chamber houses the solenoid pulsed-valve (Even-Lavie valve) that is separated from the interaction chamber (TOF-MS) by a 2 mm skimmer.

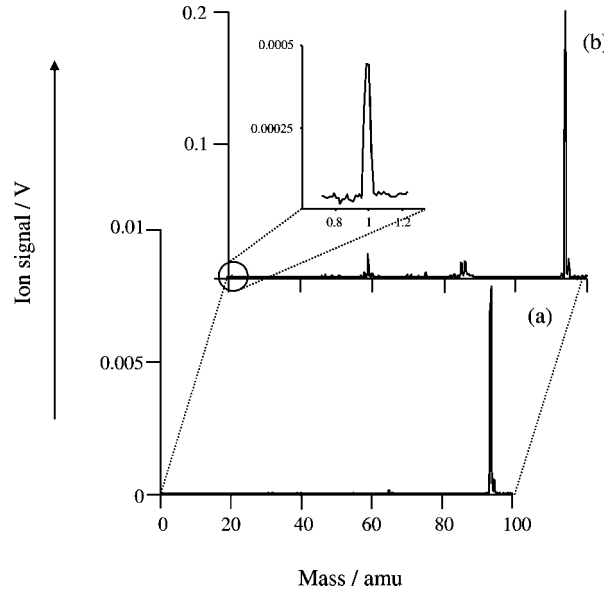

Figure 2. One- and two-color mass spectra recorded with femtosecond laser pulses at 200 nm (a) and 200 + 243.1 nm (b), respectively. The delay between the 200 and 243.1 nm pulses was fixed at 1.5 ps. The intensity of the 200 nm was reduced to avoid other fragmentation pathways.

example of this is shown in Figure 2a, in which a strong signal is observed at 94 amu, corresponding to the parent phenol, in addition to peaks at 65 and 66 amu corresponding to $C_5H_5^+$ and to a lesser extent $C_5H_6^+$, respectively. From Figure 2a, we do not observe a peak at 1 amu. In contrast, when the pump is followed by the probe, as shown in Figure 2b, careful inspection of the TOF-MS reveals a peak at 1 amu, corresponding to the appearance of H^+. This peak can be seen more clearly in the inset which is magnified 100-fold for illustration purposes. Figure 2b was obtained by setting the probe delay to be 1.5 ps after the pump. The relatively small size of the H^+ signal is indicative of the inefficiency of the excitation of a narrow atomic line (2s) with a spectrally broad laser pulse, coupled to the nonlinearity of the process itself (2+1 REMPI).

Ensuring that the 200 nm minimizes the extent of fragmentation through multiphoton ionization is critical to such measure-

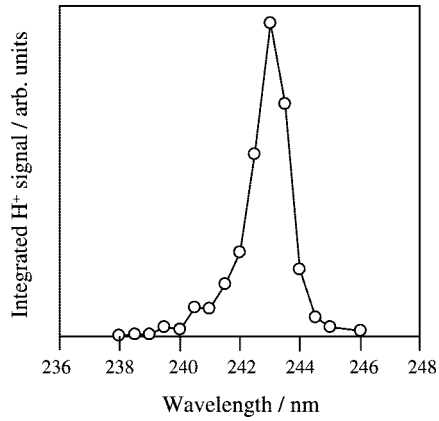

Figure 3. One-color multiphoton ionization of H atoms as a function of wavelength. As the wavelength is tuned on resonance with the 1s → 2s transition ($\lambda \approx 243$ nm), there is a considerable rise in the integrated H^+ signal, as expected.

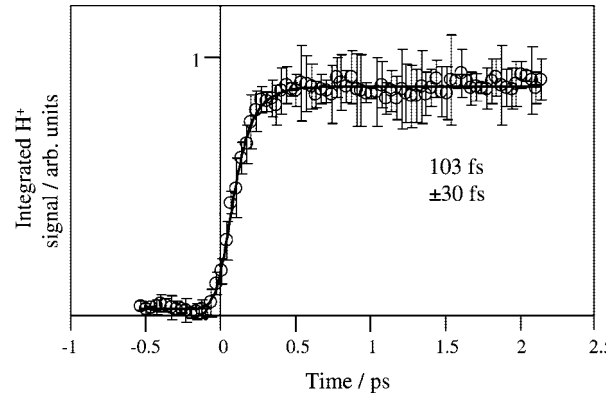

Figure 4. H^+ transient as a function of pump−probe delay. At negative time delays ($t < 0$), there is no appreciable H^+ signal. At positive delays, the H^+ signal rises sharply and plateaus beyond 400 fs. The experimental data was fitted with a step function convolved with a Gaussian of 160 fs FWHM (solid line) to yield a time constant of 103 ± 30 fs. The error bars reported correspond to a 95% confidence limit.

ments because other pathways can lead to the generation of H. For example, appearance energy data[21] show that at 12.96 eV, another exit channel $C_5H_5^+$ (amu = 65) emerges, the other photoproducts being CO + H. It is therefore essential that $C_5H_5^+$ is minimized to avoid any contributions of this pathway to the total H signal, and because 12.96 eV corresponds to at least three photons of 200 nm (~6.2 eV), small adjustments to the intensity of the 200 nm greatly reduces $C_5H_5^+$ and therefore eliminates this pathway.

Further confirmation that we are indeed probing H following excitation above the S_1/S_2 CI is shown in Figure 3. This spectrum represents the variation in the integrated H^+ signal as a function of probe wavelength. This measurement was once again taken by setting the delay between the pump and the probe to 1.5 ps. As is immediately apparent, the peak in the H^+ signal is centred at 243 nm. This is to be expected, because 243.1 nm coincides with the resonance at the two-photon level with the 2s state in H (Lyman-α transition). The FWHM of this peak (approximately 1.5 nm) results from the broad spectral profile of the ultrafast pulses originating from the OPA. Competing pathways such as dissociative ionization which generate H^+ directly can certainly be operative in such large molecular systems and with the high intensities inherent with femtosecond lasers. It is reasonable to assume, however, that dissociative ionization is unlikely to show such a sharp wavelength dependence on the H^+ signal, as that observed in Figure 3, coinciding with the 1s → 2s transition in H. The REMPI signal shown in Figure 3, together with the minimum fragmentation observed in phenol with 200 nm alone (Figure 2a), suggests that the H^+ observed in these measurements originates from neutral H such as those formed through dissociation via the $\pi\sigma^*$ state and not through dissociative ionization to yield H^+ directly.

Figure 4 shows the transient H^+ signal as the delay between the pump and probe is varied as a function of time. Error bars reported correspond to 95% confidence limits, that is, two standard deviations of the mean. As can be seen in Figure 4, when the probe precedes the pump, that is, at $t < 0$, no H^+ is observed. At times corresponding to $t > 0$, we begin to see a sharp rise in the H^+ signal, indicative of very fast dissociation. We have extended these scans up to 200 ps and see no appreciable increase in the H^+, but rather, a plateau appears at 400 fs and persists at such long delays. Fitting the time trace to a convolution of an exponential rise with a Gaussian (instrument response function 160 fs) yields a time constant of 103 ± 30 fs (solid line). Although extracting a time constant shorter than the instrument response function does require well characterized pulses, more critical to our fitting procedure is measuring as accurately as possible the temporal overlap between the pump and probe pulses (time zero) because we need to determine the displacement of the H^+ half maximum from time zero. This, we characterize, once again, through nonresonant two-color multiphoton ionization of NH_3, H_2O, and phenol. The uncertainties in the measured FWHM of the Gaussian and the accuracy of time zero have been incorporated in the error.

The ultrafast H detachment in phenol can be explained by using the PES from Figure 1 in Nix et al.[8] Following excitation above the S_1/S_2 CI at 6.2 eV (200 nm), the optically dark S_2 state is populated. This state, which is repulsive with respect to the stretching coordinate of O−H bond, intersects not only the electronically excited S_1 state but also the electronic ground state. These non-adiabatically coupled PES are responsible for H elimination.[5−7] The minimum of the S_1 state is located at ~4.5 eV, whereas the S_1/S_2 CI is at ~5 eV. As previously reported[4,8] excitation at $\lambda \leq 248$ nm (>5 eV), H detachment is suggested to occur either directly through two successive CI, S_1/S_2 and S_0/S_2, or through statistical unimolecular decay following population of vibronically excited phenol (S_0) molecules from the S_0/S_2. These two pathways should indeed have two distinct timescales (as shown by Lippert et al.[19]), the direct dissociation showing much faster dynamics as compared to the statistical unimolecular decay pathway. The data that we present in Figure 4 shows very clearly that highly efficient decay dynamics are operative, with a single step observed in the H^+ appearance signal, strongly implicating, within the time-window of the experiment, the direct dissociation pathway dominating, with no apparent statistical unimolecular decay contributing to the signal.

The observation of ultrafast elimination of H observed in this work is consistent with the recent time-dependent quantum wave-packet calculations by Lan et al.[7] In this work, the authors show the effects of initial vibronic excitation in the ground electronic state (S_0) of phenol and the population dynamics between the S_2, S_1, and S_0 states. These calculations, although they do not exactly mimic the experiments described here, show that the population dynamics are essentially over in 100 fs which, on a qualitative level, agrees with the observations made here.

As described, the recent TKER measurements by Nix et al.,[8] suggest that the statistical unimolecular decay pathway may be operative. The slow H atom fragments observed in these

experiments show TKER distributions consistent with statistical unimolecular decay of highly vibrationally excited phenol (S_0) molecules such as those that might be formed by the coupling at the S_0/S_2 CI. Unlike the fast H, which show anisotropy in the H atom distribution, consistent with prompt dissociation, the lack of anisotropy in the slower H suggests that this pathway is slower than the rotational period of the molecule itself.

In principle, these highly vibrationally excited phenol (S_0) molecules can decay on the period of a single O−H stretching vibration (and longer). If this pathway is indeed operative here, this should manifest itself in a slower component in the appearance of the H^+ signal, which we do not observe, even up to delays of 200 ps. It is interesting to discuss this result in reference to the recent time-resolved measurements by Lippert et al.[19] in pyrrole, following excitation at 250 nm directly to the $S_1(\pi\sigma^*)$ state. Lippert et al. observed a slower component in their H^+ signal with a time constant of 1.1 ps, which they attributed to indirect dissociation, following population of vibrationally excited pyrrole (S_0) molecules via the $S_0/S_1(\pi\sigma^*)$ CI. It may be that vibrationally excited phenol (S_0) molecules formed via the S_0/S_2 CI do not possess sufficient energy in the O−H vibration to overcome S_0/S_2 barrier. These excited molecules must then remain on the S_0 PES and, as suggested by Nix et al.,[8] through anharmonic mixing, sample a much larger range of vibrational phase space before finding a route to dissociate by loss of an H atom. However, following excitation above the S_1/S_2 CI, both dissociation channels are open in phenol, leading to either the electronic ground or excited phenoxyl fragment, the latter of which has not been observed.[8] Therefore, it is debatable that reflection and subsequent capture of the wavepacket back to the bound state surface of phenol (S_0) will occur, unless the excess energy is absorbed by other degrees of freedom.[7] Alternatively, vibrationally excited phenol (S_0) molecules are formed through an alternative internal conversion pathway which then undergo statistical unimolecular decay. Either process however must be occurring on a timescale that is longer than the duration of our experimental measurements (>200 ps).

Finally, it is important to highlight here that attempts have been made to observe H elimination following excitation with 266 nm. At these wavelengths, we are now below the S_1/S_2 CI which, as noted by Nix et al.,[8] results in the production of only slower H atoms. The lack of pump−probe H^+ transient observed within the time window of these measurements is consistent with the long lived $\pi\pi^*$ state (1−2 ns)[4,22,23] which undergoes internal conversion to yield highly vibrationally excited phenol (S_0) molecules which can then undergo statistical unimolecular decay.

Conclusion

The photochemistry of phenol following excitation at 200 nm and probing of the neutral hydrogen atoms via (2+1) REMP at 243.1 nm shows that H elimination along the dissociative $\pi\sigma^*$ occurs within $t = 103 \pm 30$ fs, indicating efficient coupling of the S_2, S_1, and S_0 PES at the S_1/S_2 and S_0/S_2 CI. This is consistent with the fast H observed in recent TKER measurements. Within the time window of our measurements, however, we do not observe an appreciable second pathway to H elimination as that observed in time-resolved measurements made in pyrrole. This suggests that the slower H observed in the multimass ion imaging and TKER measurements are likely to occur on a much longer timescale (>200 ps).

The work presented here provides further evidence of the active participation of the $\pi\sigma^*$ in the photochemistry of biologically important molecules. Time is ripe for time-resolved experiments which directly probe the timescale for H elimination, given the importance of H elimination following UV excitation of these important molecules. The next step in these experiments will be to begin probing H elimination in more complex molecules such as the nucleobase adenine. The role of the $\pi\sigma^*$ following excitation at 266 nm is under considerable scrutiny in the recent literature,[24–27] and such measurements are currently being actively pursued in our group.

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