Femtosecond Multiphoton Ionization Photoelectron Spectroscopy of the S_2 State of Phenol

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We investigated the short-lived S_2 ($^1A_1$) state of phenol using two-photon resonance-enhanced photoionization coupled with photoelectron spectroscopy. Spectra were obtained by exciting the S_2 state with femtosecond laser pulses at various wavelengths near 207 nm and ionizing with pulses at 207 or 414 nm. The spectra feature a strong transition to the ground electronic state of the ion ($\tilde{X}$) and a very weak transition to the first excited electronic state of the ion ($\tilde{A}$). In comparison, ionization via the longer-lived S_1 state using 275 nm pulses generates slightly more $\tilde{A}$ ions. We interpret the relative intensities of the $\tilde{A}$ state signals as a reflection of configuration interactions in the intermediate S_2 and S_1 states. Time-delayed ionization experiments, as well as experiments with different laser pulse durations, suggest that the S_2 state has a lifetime between 150 and 350 fs. Ionization via S_1 produces a vibrationally resolved photoelectron spectrum, while ionization via S_2 leads to a highly congested spectrum. The envelope of the latter spectrum extends over more than 1 eV and features a long progression, probably in the 6a vibration. This suggests that the S_2 state has a geometrical structure that is displaced from the ground state along the 6a coordinate. No vibrational structure could be resolved in the $\tilde{A}$ ion spectrum obtained by ionization via either S_2 or S_1.

Introduction

Highly excited states of molecules are interesting because of their complicated electronic structure, their importance in natural processes such as those occurring in the atmosphere, their relevance to photochemistry and radiation chemistry, and their importance as energetic materials. Unfortunately, many traditional tools to study excited electronic states are ineffective because of the extremely short lifetime of many high lying excited states. For example, absorption spectra in the near and far ultraviolet often reveal the presence of higher excited electronic states, without being able to resolve vibrational or rotational structure. Fluorescence excitation spectra are often similar to the absorption spectra, while dispersed fluorescence spectra are dominated by the emission from electronic states that are populated by electronic relaxation processes. Resonance-enhanced ionization experiments using short-lived resonances are possible, but for most laser pulses, the rate of relaxation vastly exceeds the rate of ionization, leading to highly congested spectra with little information content. To be sure, there are some techniques that provide limited insights into short-lived states. Among them are photofragment anisotropy, spectral hole burning, coherent four-wave mixing, and resonance Raman depolarization spectroscopy.[1−3] Unfortunately, these techniques are not always applicable, and analyses of the spectra are difficult. Thus, very little is known about high lying electronic states of many molecules, even though their existence and electronic energies are readily observed in absorption spectra. Additional techniques to study such states are highly desirable, especially if their information content is complementary to that of other techniques. Recent developments in the area of photoionization suggest that it may indeed be possible to use resonance enhanced multiphoton ionization (REMPI), combined with photoelectron spectroscopy (PES), to study ultrashort-lived electronic states, provided ultrashort laser pulses are employed.[4−9] Here, we apply this technique to explore the spectroscopy and relaxation dynamics of the S_2 state of phenol (C_6H_5OH).

In a REMPI-PES experiment, a molecule, typically seeded in a molecular beam, is ionized by simultaneous or sequential absorption of two (or more) photons. Figure 1 illustrates REMPI−PES using the example of the phenol molecule investigated in this work. The molecule absorbs a photon, which promotes it to an excited electronic state. During the ionization process, where the molecule absorbs a subsequent photon, the molecule ejects an electron to form a singly positive ion. The photoelectron spectrum is the measurement of the electron current as a function of the electron energy. Since the total energy of the absorbed photons is known (from a measurement of the laser wavelength), the observation of the photoelectron kinetic energy spectrum constitutes an observation of the ion spectrum. Franck−Condon factor arguments are applied to infer the energy level structure of both the ion and the intermediate resonance.[10−17]

In recent years, the traditional REMPI−PES experiment has been adapted to study the dynamics of short-lived excited states.[7−9,18−26] Short duration laser pulses are employed to provide the excitation step followed by the ionization step. By observing the photoelectron spectrum as a function of time delay between the two laser pulses, the dynamics of the intermediate resonance can be mapped onto the electronic and vibrational states of the ion. The time-resolved REMPI−PES technique features excellent time resolution, great sensitivity, and almost universal applicability. However, a careful consideration of the laser pulse bandwidth and the electron configurations of the resonance steps are essential for an interpretation of the time-resolved photoelectron spectra.

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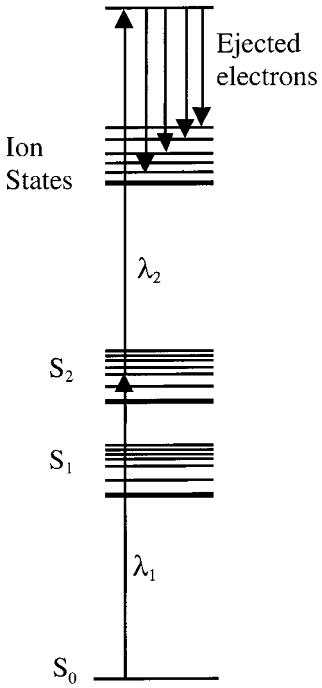

Figure 1. The two-photon ionization photoelectron spectroscopy experiment. Photons with wavelengths λ_1 and λ_2 ionize the molecule via an intermediate molecular resonance. The measurement of the kinetic energy of the ejected electrons determines the final ion energy.

First, in order for the REMPI−PES spectra to provide information about short-lived, highly excited electronic states, the laser pulse duration must be well matched to the homogeneous lifetime of the electronic state. In a series of papers on azulene and phenanthrene, Thantu and Weber have shown that one can obtain resonance-enhanced photoelectron spectra even if the duration of the laser pulse is much longer than the relaxation lifetime of the excited state.[4−6] However, the nonradiative processes that occur during the two-photon ionization place amplitude into the vibrational manifold belonging to the lower electronic state, making the photoelectron spectra a highly congested projection of this lower state onto the ion. To study the spectroscopy of the short-lived resonance, it is important to use a laser pulse with a duration equal to or less than the lifetime of the resonance, even though the ionization could be performed efficiently with such a longer duration pulse. Interestingly, failure of the experiment to meet this condition is apparent in the photoelectron spectrum, since a broad, relaxed peak is observed in a different energy region.

Second, for the interpretation of time-delayed photoelectron spectra the propensity rules governing the projection of excited molecular states onto electronic states of the ion need to be considered.[24] For example, when Kim et al. studied the photoionization out of the S_1 state of aniline, they found that 93% of the ionization proceeds to the ground state ion, $\tilde{X}$, and only 7% of the ions were generated in the first excited state, $\tilde{A}$.[27] This is in stark contrast to the ionization out of the ground state molecule, where the $\tilde{X}$ and $\tilde{A}$ ion states are generated with about equal probability.[28] The propensity of the molecule to ionize into certain ion states can be accounted for by considering the orbital configuration of the S_1 state; the transition from S_0 to S_1 promotes an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), leaving a vacancy in the HOMO. Ionization from S_1 ejects the electron from the LUMO, generating an ion that still has a vacancy in the HOMO. This electron configuration represents the lowest energy ground state ion. Understandably, the excited state ions are not accessed in this way. At closer inspection, Kim's photoelectron spectrum did reveal some signal corresponding to electronically excited ions in the $\tilde{A}$ state. Kim et al. pointed out that this signal might arise from a configuration interaction in the S_1 state, which could make the transition to the $\tilde{A}$ ion one-photon allowed. The important conclusion is that the ionization from an excited electronic state of a molecule onto the manifold of electronic states of the ion is a projection of electronic wave functions. This projection leads to propensity rules in photoionization from excited states, but can also provide an experimental measure of configuration interactions of excited electronic states. In the present paper, we exploit this effect to investigate configuration interactions in the S_1 and S_2 states of phenol.

Extrapolating from these previous investigations, one expects that time-resolved REMPI−PES be ideally suited to study high lying excited states of molecules. Observables are the time scales and pathways for energy redistribution processes, spectroscopic data about vibrational and electronic energies, and configuration interactions in electronic states. To date there have been only a few studies of highly excited electronic states of molecular systems. Beyond the above-mentioned studies on azulene and phenanthrene,[4−6] there has been an elegant investigation of the ultrafast internal conversion (IC) of 1,3,5-hexatriene from the 1^1B_u state to the 2^1A_g state by Hayden and Chandler[7] and Cyr and Hayden,[8] and a study of internal conversion from S_2 to S_1 in benzene by Radloff and co-workers.[9]

Many experimental investigations have dealt with the spectroscopy and dynamics of phenol in the ground electronic state (S_0), the first excited singlet state (S_1), and the ion ground state ($\tilde{X}$).[29−35] There is also an investigation of the highly resolved spectra of the second excited state ($\tilde{B}$) of the phenol ion.[36] Comparatively little is known about the second excited singlet state (S_2) of the molecule in the gas phase. The UV absorption spectrum features an unstructured band stretching from 220 to about 200 nm, with a molecular extinction coefficient of about 7000 L/mol cm.[29] In the solution phase, Grabner et al.,[37] Steen et al.,[38] and Dellonte et al.[39,40] studied the temperature dependence of internal conversion from S_2 to S_1, competing electron solvation processes, and hydrogen abstraction processes by observing fluorescence quantum yields. Dellonte et al.[39] calculated rate constants of $k_{ISC} = 7 \times 10^{11}$ s^{-1} and $k_{IC} = 3 \times 10^{11}$ s^{-1}, where the intersystem crossing (ISC) was to a dissociative triplet state that was evidenced by H atom abstraction. Direct observations of the electronic relaxation in the gas phase have, to our knowledge, not yet been reported. There are also no observations about the pathways for energy relaxation in gas-phase phenol.

Application of the two-photon ionization photoelectron technique allows us to address the following specific topics relating to the spectroscopy and dynamics of the S_2 state of phenol. First, the projection of the S_2 electronic state onto the ion states investigates the extent of configuration interaction in the intermediate state. Second, even though a highly resolved vibrational spectrum should not be expected on account of the femtosecond duration of the ionizing laser pulses, we should be able to obtain partially resolved spectra revealing the Franck−Condon envelope of the photoelectron spectrum, as well as any prominent progressions. This provides some insights into the displacement of the S_2 potential surface with respect to the surfaces of the electronic ground states of the neutral molecule and the ion. Moreover, from the observation of relaxed molecules, we can assess the dominant electronic relaxation pathways. Finally, we can infer the time scale of the relaxation

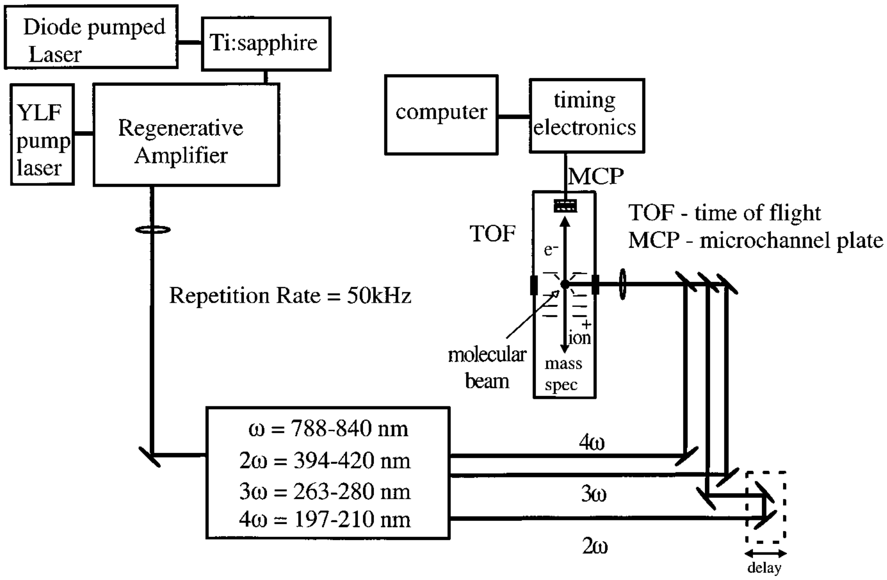

Figure 2. The experimental apparatus.

from the appearance of relaxed signal in spectra taken with longer pulse durations and from time-delayed two-color ionization experiments.

Experimental Setup

Our experimental apparatus consists of a femtosecond pulsed laser system and a molecular beam machine, equipped with a photoelectron spectrometer and a mass spectrometer (Figure 2). The laser system is based on a chirped pulse regenerative amplifier, which is seeded by 80 fs pulses from a Ti:sapphire oscillator. The regenerative amplifier is pumped by a Q-switched YLF laser, while the oscillator is pumped by ~10 W from either a large frame argon ion laser or a diode pumped solid-state laser. The infrared pulses emitted by the regenerative amplifier are tunable over a range of ±40 nm centered at 800 nm, and feature durations as short as 116 fs, as measured by autocorrelation. The laser system operates at a repetition rate of 50 kHz. This high repetition rate allows us to operate the photoelectron detector in a single particle counting mode, while still providing ample power for harmonic generation (about 8 μJ/pulse for the IR output). As a result, the time-of-flight photoelectron spectrometer features good time resolution, very high detection efficiency, and almost complete absence of noise from the detection electronics.

For the photoelectron spectra discussed in this paper, we generate the second harmonic in a 1.0 mm LBO crystal and the third harmonic in a 1.5 mm BBO crystal by sum frequency mixing of the second harmonic and the fundamental. For most experiments, the fourth harmonic is generated by frequency doubling the second harmonic in a 0.1 mm BBO crystal. The cutoff of BBO for harmonic generation limits the tunability of the fourth harmonic below 206 nm. Typical energies for the fourth harmonic are about 10 nJ/pulse. The fourth harmonic pulses generated in the 0.1 mm BBO crystal have a 0.5 nm spectral bandwidth and are hereafter referred to as “short” pulses. To study the effect of the pulse duration on the photoelectron spectra, and to ascertain that the “short” pulses are short in comparison to the time scale of internal conversion from S_2 to S_1, we also generated longer duration fourth harmonic pulses using a 1.0 mm BBO crystal. Those pulses typically have a spectral bandwidth of 0.1 nm and are hereafter referred to as “long” pulses. Autocorrelation of the 206−211 nm radiation was not possible, but we measured the duration of the second harmonic using the short BBO and found the autocorrelation width to be 125 fs. However, a spatial chirp limited the instrument function to about 350 fs when using both the second and fourth harmonics.

The molecular beam machine and the photoelectron spectrometer, including details about the differential pumping scheme and the timing electronics, have been described previously.[41,42] Briefly, a molecular beam is formed by expanding the sample entrained in the carrier gas through a 94 μm nozzle into a source region. The beam is extracted by a 150 μm skimmer and a subsequent 1 mm aperture. All vacuum regions are pumped by turbomolecular pumps. The photoelectron spectrometer operates by the time-of-flight principle, where the start times are given by the arrival of the electrons at the detector and the stop times by laser pulses. This instrument can deliver energy resolutions well below 10 meV for slow (<1 eV) electrons. In the current work, the spectral resolution for slow electrons is limited by the bandwidth of the femtosecond laser pulses that ionize the molecule. The energy resolution for fast electrons (>2 eV) is limited by the time-of-flight spectrometer or the channel resolution in the data acquisition electronics.

The analysis of the time-of-flight data, and their conversion to electron energy spectra, involves the transformation from the time domain to the energy domain and the associated intensity correction, as described previously.[41] The observation of fast electrons reported here requires additional correction terms. First, we obtain a precise stop time for the laser by fitting a Gaussian to the stop signal arising from the scattered laser light. Second, we consider the time correction due to the flight time of the laser pulse to those surfaces of the vacuum apparatus that scatter the laser radiation. Finally, we account for the proper velocity of the electrons in the short acceleration step from the grid that defines the field-free region to the microchannel plate detector. With these corrections, we found that the energy of electrons with velocities up to 5 eV can be measured with an accuracy of 20 meV.

All spectra reported in this paper have been analyzed based on two-photon ionization processes. Some time-of-flight spectra also show a signal corresponding to much faster electrons, arising from a three-photon ionization process. These latter parts

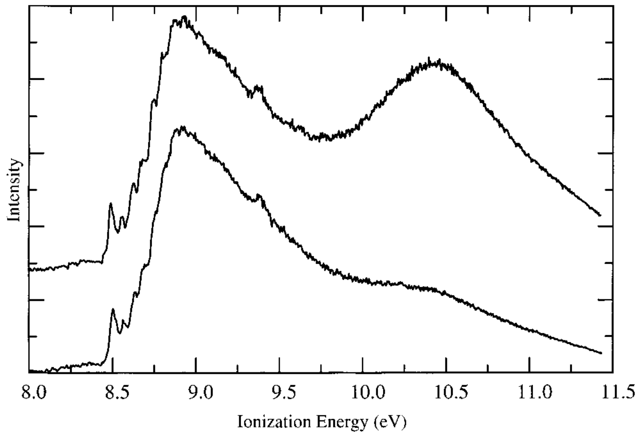

Figure 3. Photoelectron spectra of phenol, taken with 207.3 nm pulses, with different pulse durations: (top trace) long BBO crystal, pulse duration about 900 fs; (bottom trace) short BBO crystal, pulse duration between 150 and 325 fs.

of the spectra fall outside the ranges plotted here and they are discussed in a separate publication.[43]

Phenol was obtained from Aldrich and used without further purification. The helium carrier gas at a pressure of 1.1 bar was bubbled through the phenol at 60 °C to form the seed gas. A time-of-flight mass spectrum, also obtained after two-photon ionization of phenol via the S_2 state, shows almost exclusively the parent ions at mass 94 and a very small amount of phenol fragments only. The mass spectrum is reproduced elsewhere.[44]

Results and Discussion

Ionization via S_2. We first explore the question whether the resonance ionization photoelectron spectra via the S_2 state indeed reflect ionization out of S_2 or if electronic relaxation populates other electronic states prior to the ionization process. Figure 3 shows the photoelectron spectra of phenol, obtained upon ionizing the molecules with two photons with a wavelength of 207.3 nm.

The top trace of Figure 3 is taken with pulses obtained by frequency quadrupling in the long BBO crystal, while the bottom trace is taken with pulses obtained by quadrupling in the short BBO crystal. The duration of the long laser pulses is estimated to be about 900 fs, based on the cross correlation with the much shorter second harmonic using the S_2 state investigated here. The short pulses cannot be shorter than 150 fs, based on their bandwidth, or longer than 325 fs, based again on the cross correlation with the second harmonic.

Several important features stand out in Figure 3. Both spectra have an onset at 8.50 eV, which is the ground vibrational state of the electronic ground state of the ion.[45] Built upon this electronic origin is a broad peak with a maximum at about 8.9 eV. Up to an energy of about 8.8 eV, corresponding to 0.3 eV (2400 cm^{-1}) of vibrational energy, our spectrometer can partially resolve a vibrational progression. Beyond 9 eV, there is no more resolved vibrational structure.

The spectrum taken with the long duration laser pulses, top trace of Figure 3, shows an additional unresolved, broad peak at an ion energy of about 10.4 eV. We attribute this signal to molecules that are ionized after internal conversion from S_2 to S_1 has converted electronic energy to vibrational energy. Evidence for this assignment comes from a consideration of the relevant energies of the molecular states. The S_2 state is excited with laser pulses at 207.3 nm, or 5.98 eV. IC from S_2 to S_1 leaves the molecule in the S_1 state, which is known to have an electronic energy of 4.51 eV.[34] Thus, the relaxation must insert 1.47 eV of energy into the vibrational manifold of S_1. From the photoelectron spectrum taken via the S_1 state, we know that the ionization process $S_1 \rightarrow \tilde{X}$ inserts an average of about 0.3 eV into vibrational coordinates.[33] For the ions that undergo internal conversion during the two-photon ionization, we thus expect to observe an average vibrational energy of $1.47 + 0.3 = 1.77$ eV, that is, ions at a total energy of 10.27 eV. This is in fairly good agreement with our observation of the relaxed peak at 10.4 eV; the remaining small difference may well be due to slightly different curvatures of the potential energy surfaces of the S_1 state and the ion $\tilde{X}$ state. We conclude that the spectra are consistent with a process where an internal conversion process from S_2 to S_1 inserts 1.47 eV of energy into vibrational coordinates on the time scale of the 900 fs laser pulses.

Having established that the broad peak at 10.4 eV in the top trace of Figure 3 arises from molecules undergoing IC during the ionization process, we now return to the consideration of the bottom trace. Using the shorter duration laser pulses, the intensity of the broad feature at 10.4 eV is greatly reduced, to the extent that the spectrum is completely dominated by the first broad peak. Clearly, ionization with the short duration laser pulse effectively competes with IC to the S_1 state.

Dellonte et al. reported two electronic relaxation paths out of the S_2 state: an intersystem crossing with a rate of 7×10^{11} s^{-1} and an internal conversion with a somewhat slower rate of 3×10^{11} s^{-1}. Our spectra show evidence for IC from S_2 to S_1 within the duration of the 900 fs laser pulses but no evidence for a faster intersystem crossing. It is conceivable, however, that the broad and spectrally unresolved part of the spectrum above 8.9 eV arises from an electronic relaxation process. Given that we observe the same structure in the photoelectron spectra obtained with the "short" and the "long" pulses, any such electronic relaxation must be essentially complete within the duration of even the short pulse. Thus, if there were an intersystem crossing from S_2 to a triplet state, it would have to be at least an order of magnitude faster than suggested by Dellonte et al. In addition, it is useful to note that there is a clear transition to the vibrationless level of the ion. It is difficult to reconcile this observation with an ultrafast electronic relaxation process within the duration of the laser pulses; any relaxation should insert a large amount of energy into vibrational coordinates, making a transition to the vibrationless ion highly unfavorable. We conclude that, while we cannot completely rule out an intersystem crossing to a triplet state, such a process appears highly unlikely, and, if it existed, it would have to be 10 times faster than previously thought.

Ionization to $\tilde{X}$ Ions vs $\tilde{A}$ Ions. Photoionization is a projection of the electronic wave function of the excited molecular state onto the electronic states of the ion. Therefore, neglecting configuration interactions in the ion and assuming equal cross sections for ejection of electrons from different orbitals, the intensities of electronic peaks in the photoelectron spectra reflect the electron configurations of the molecular state that is ionized. Figure 4 compares the photoelectron spectra of phenol obtained by ionization with (a) one-color, two-photon ionization via S_2, (b) two-color, two-photon ionization via S_1, and (c) one-photon ionization from the S_0 state with a 21.2 eV photon. The latter spectrum is reproduced from the paper by Kesper et al.[46] All spectra exhibit a prominent transition to the ground electronic state $\tilde{X}$ of the ion. In addition, the one-photon spectrum from S_0 features a strong transition to the first excited

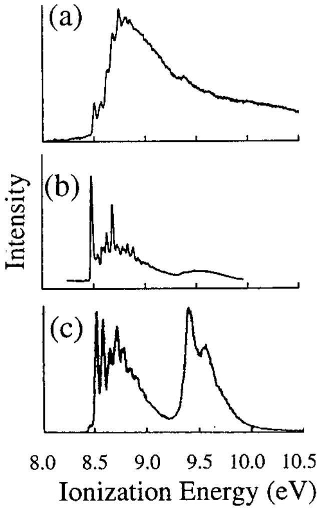

Figure 4. Photoelectron spectra of phenol with ionization from different electronic states. (a) Ionization via S_2, using the two-photon, one-color scheme, with 207 nm laser pulses. (b) Ionization via S_1, using a two-photon, two-color scheme; S_1 is excited to its vibrationless level by a laser pulse at 275 nm and ionized by a subsequent laser pulse at 206 nm. (c) Ionization from the ground state, S_0, using He(I) radiation, 21.2 eV photons. This spectrum is reproduced from the work of Kesper et al.[46] with permission from Elsevier Science.

state of the ion, the Ã state at about 9.39 eV. Kimura et al. have assigned this transition to the ejection of an electron from the orbital directly below the HOMO, i.e., orbital #17.[28]

The excitation of the molecule from its ground electronic state to the S_1 state dramatically changes the photoelectron spectrum of the ion states. As shown in Figure 4b, the photoelectron spectrum from S_1 is dominated by the vibrational progression belonging to the X̃ ions. Between 9.3 and 9.8 eV, it features a broad, unstructured peak similar to the one observed in the He-(I) spectrum, but much weaker (about 12% of the total signal). Based on the similarity between the vibrational envelopes of the two spectra, and in particular the absence of vibrational structure in either spectrum, we assign this feature in the S_1 ionization spectrum to the Ã ions. Note that in a recent publication we reported a three-photon ionization signal in the same energy range.[43] While it is conceivable that the broad peak from 9.3 to 9.9 eV in the S_1 ionization spectrum is the same state as the one accessed in the three-photon spectrum, the vibrational envelopes are so vastly different that we reject this scenario. The present spectrum has a narrow envelope (0.3 eV width) without any discernible vibrational structure, while the three-photon spectrum has prominent progressions in stiff ring modes, stretching over an energy range in excess of 2 eV. Thus, we maintain that the broad feature in the S_1 ionization spectrum arises from the Ã ion state and not from the state accessed by three-photon ionization.

The ionization via the S_2 state (Figure 4a) leads to a broad Franck−Condon envelope belonging to the X̃ ions. A small peak appears to be present at 9.4 eV, close to the origin of the Ã state. While it overlaps too much with the highly vibrationally excited part of the X̃ ion signal to be accurately analyzed, it is clear that only a small part of the ionization leads to Ã ions. We estimate this fraction to be no more than 4%. Again no vibrational structure can be discerned in the Ã state.

We conclude that the electronic components of the photoelectron spectra indicate that the S_1 electronic state has very little configuration interaction, and is largely given by the well-known excitation of an electron from the HOMO to the LUMO. The photoelectron spectrum of the S_2 electronic state shows even less evidence for configuration interactions. Experimentally, we observe that the S_2 state is characterized by a vacancy in orbital #18, with very little admixture of other electron configurations. As already observed in the traditional one-photon ionization spectra with a helium lamp, the Ã state of the ion does not feature a well-resolved vibrational structure. It is possible that the Ã state decays rapidly into the excited ion state that we observed in the three-photon ionization spectra or into the ground state of the ion.

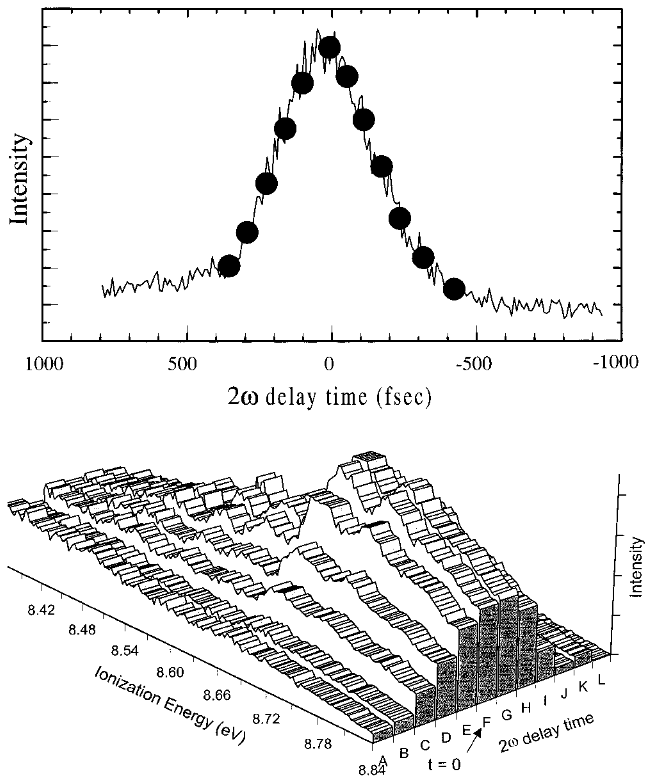

Figure 5. Time-dependent photoelectron spectra obtained upon ionization via S_2 in a $4\omega + 2\omega$ scheme. (top panel) The total photoelectron signal, integrated from 8.38 to 8.84 eV, as a function of the 2ω delay time. (bottom panel) Photoelectron spectra at different delay times. (A → L) from 334 to −400 fs, separated by 66.7 fs. (Positive delay times are for the 4ω photon preceding the 2ω photon).

Decay Kinetics of the S_2 State. A one-color time-resolved observation of the decay of the S_2 state is difficult because the photoelectron spectrum taken with two time-delayed fourth harmonic (4ω) pulses overlaps with the signals from two-photon ionizations from each pulse individually. Spectra with the third harmonic (3ω) of the laser as the ionizing pulse from S_2 are swamped by signal arising from the photoionization via S_1; even given the reverse timing of the pulses, the wings of the $3\omega + 4\omega$ ionization dwarf the signal of the $4\omega + 3\omega$ process. Thus, we resorted to a time-resolved experiment using the fourth and the second harmonic (2ω) pulses. The total photon energy is then only slightly higher than the ionization energy so that only the time dependence of those states that contribute to the low vibrational levels of the ground ion state could be recorded.

Figure 5 displays the time-dependent photoelectron spectra resulting from $4\omega + 2\omega$ ionization. The upper panel shows the time dependence of the total signal covering the range from 8.38 to 8.84 eV. The lower panel displays the photoelectron spectra for various delay times as indicated in the figure caption and by dots in the upper panel. Within the time resolution of our experiment, the time scan shows none of the asymmetry that one would expect if the decay time of the S_2 signal were

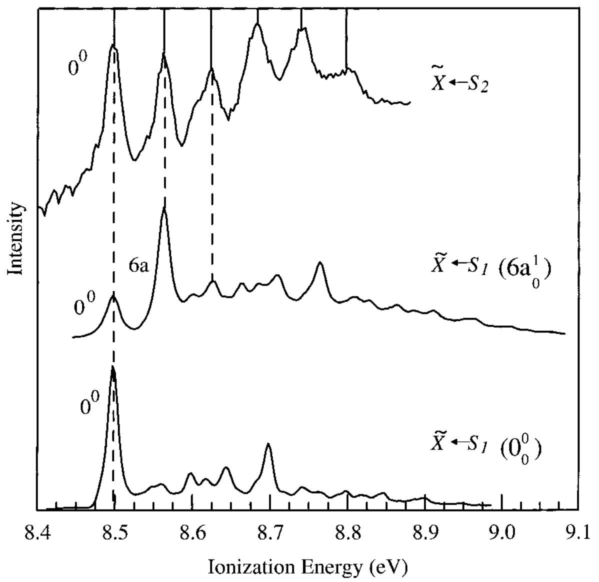

Figure 6. Vibrationally resolved femtosecond two-photon ionization spectra of phenol. (top trace) Ionization via S_2, in the $4\omega + 2\omega$ scheme; the 4ω photon (at 208.5 nm) was polarized perpendicular, and the 2ω photon was polarized parallel to the direction of the photoelectron detector. (center and bottom traces) Ionization via the $6a^1$ level and 0^0 level, respectively, of the S_1 state in a $3\omega + 3\omega$ scheme. Both 3ω photons were polarized along the direction of the photoelectron detector.

longer than the pulse duration. We conclude that those components of the S_2 state that ionize to the ion with little vibrational energy decay within the duration of the cross correlation signal, about 350 fs. Note that the photoelectron spectra show a background that increases toward lower ion energies, that is, faster electron energies. This background stems from the three-photon signal mentioned earlier. It exhibits a decay time of around 5 ps and gives rise to the somewhat elevated baseline at positive delays in the upper panel of Figure 5. At the present time we have no explanation for the time dependence of this signal.

The absence of a relaxed peak in the two-photon ionization photoelectron spectrum with the short laser pulses (Figure 3) was interpreted as indicating that the ionization proceeds on a time scale that is faster than internal conversion. On the other hand, the time-delayed spectra indicate that the decay of the S_2 state is faster than the cross correlation time. The apparent contradiction is reconciled by realizing that the two-color cross correlation measurement is greatly affected by a spatial chirp that originates in the frequency doubling crystals, while the one-color two-photon ionization is not likely affected by this chirp. If this explanation is correct, then the internal conversion of the S_2 state to S_1 must be faster than the 350 fs cross correlation width, but not faster than the duration of the shortest 207 nm pulses. From the spectral bandwidth we estimate a lower bound for the duration of the 207 nm pulses to be about 150 fs. Thus, we loosely bracket the decay time as between 150 and 350 fs. Clearly, experiments with shorter pulses would be desirable to obtain an accurate value.

Vibrational Structure in the $S_2 \rightarrow \tilde{X}$ Spectra

While the ionization of phenol with two 4ω photons produces very fast electrons whose energy is difficult to analyze, ionization with the $4\omega + 2\omega$ scheme generates fairly slow electrons with energies of less than 0.5 eV. The $4\omega + 2\omega$ spectra therefore show well-resolved vibrations, with an energy resolution given by the bandwidth of the laser pulses. Figure 6 shows, in the top trace, the photoelectron spectrum obtained via the S_2 state in the $4\omega + 2\omega$ scheme. This spectrum was taken with orthogonal laser polarizations, which we found to produce a crisper vibrational resolution. The 4ω photon was polarized perpendicular to the direction of the photoelectron detector, while the 2ω photon was parallel to the direction of the detector. In the lower traces of Figure 6, $3\omega + 3\omega$ spectra taken via two vibrational levels of the S_1 resonance are shown. The dominant vibrations in those spectra have been assigned to the 6a vibration at 64 meV, the vibration 1 at 121 meV, and the vibration 8a at 207 meV.[33] Most of the other lines have been assigned as well.

Based on the similarity between the $4\omega + 2\omega$ spectrum and the $3\omega + 3\omega$ spectra, we tentatively assign the vibrations observed in the former spectrum to a progression in the 6a coordinate. Within the approximate C_{2v} symmetry of the molecule, 6a is a totally symmetric mode. Since the $S_2(^1A_1) \leftarrow S_0(^1A_1)$ transition is dipole allowed, transitions to 6a vibrations are vibronically allowed.

A number of $4\omega + 4\omega$ spectra at different wavelengths between 211 and 206 nm, as well as several $4\omega + 2\omega$ spectra, all show vibrational progressions that are almost identical to the one shown in Figure 6. This suggests that excitation to the S_2 state always excites vibronic levels with significant 6a content, and that the ionization out of S_2 is always associated with significant activity in 6a. From the one-photon photoelectron spectrum, and from two-photon ionization spectra via S_1, we know that there is only a small structural difference along the 6a coordinate between the ground state molecule and the ground state ion. We conclude that the activity in the 6a coordinate observed in our ionization spectra via S_2 must relate to a structural displacement of that electronic state along the 6a coordinate.

Finally, we note that the $4\omega + 4\omega$ spectra taken with different pulse durations, as well as the $4\omega + 2\omega$ spectra taken at different delay times, show no variation in the vibrational structure. All these spectra show some intensity in the vibrationless level of the ion. We take this to be an indication that there is no vibrational relaxation process (IVR) within S_2 competing on the time scale of the electronic relaxation.

Summary

The femtosecond two-photon ionization photoelectron experiment provides new insights about the S_2 electronic state of phenol. Like the S_1 state, the S_2 electronic state has an electron configuration with a vacancy in orbital #18, the HOMO of the ground state molecule. Both excited electronic states appear to have very little configuration interaction; the S_1 state has only about 12% admixture from configurations with a vacancy in orbital #17, while the S_2 state has less than 4% of such admixtures. This assignment is based on the interpretation of the broad spectral feature observed around 9.5 eV as the $\tilde{A}$ ion state. In this scenario, the $\tilde{A}$ state of the ion is homogeneously broadened, either by decay to the ground state of the ion or to the ion state observed in the three-photon ionization spectra.

We were not able to cleanly time-resolve the decay of the S_2 state. However, we did establish that the internal conversion of S_2 to S_1 is the dominant pathway for energy relaxation, and that the time scale for this process must be in the range 150−350 fs. Our spectra do not show any evidence for competing processes, such as intersystem crossing to a triplet surface, as previously postulated, or an IVR process within S_2.

An analysis of the vibrational structure of the two-photon ionization spectrum is possible, despite the limits to the energy resolution set by the ultrashort lifetime of the S_2 state. We found significant vibrational activity in the 6a mode, regardless of the excitation wavelength within S_2. This is consistent with a geometrical displacement of the S_2 state along the 6a coordinate in relation to the molecular ground state.

In conclusion, the photoelectron spectra of phenol show that photoionization with femtosecond laser pulses can beat ultrafast internal conversion in medium sized molecules. It is thus possible to perform vibronic spectroscopy of ultrashort-lived, highly excited molecular states.

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