THRESHOLD IONIZATION SPECTROSCOPY OF THE LOW FREQUENCY VIBRATIONAL MODES OF STYRENE AND TRANS-STILBENE CATIONS

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High resolution photoelectron spectra are reported for styrene and stilbene with an emphasis on identifying the low frequency modes which are important in the phenyl–vinyl torsional motion. In the styrene cation three low frequency out-of-plane vibrations are measured, ν_{42} , ν_{41} and ν_{40} as well as a number of higher frequency in plane modes. Generally the low frequency modes do not appear with significant intensity but by pumping the appropriate modes in the S_1 intermediate state the intensity for these modes in the threshold ionization spectrum is quite good. In the stilbene cation the analogous phenyl–vinyl torsion, ν_{37} , is also measured as well as the related mode ν_{36} . The ethylene torsional mode in stilbene is not observed. In both molecules the observed frequencies are used to relate the electronic structure of the cation to the S_1 and S_0 states of the molecule.

KEY WORDS: Photoelectron Spectroscopy, ZEKE, Torsional motion Styrene, Stilbene

I INTRODUCTION

Styrene and stilbene represent model compounds in the investigation of the effect of electronic excitation on conjugation. In each molecular system there are two important out-of-plane torsional motions, the phenyl–vinyl torsion ($C_{\text{eth}}-C_{\text{ph}}$) and the torsion about the ethylene double bond. In styrene^{1–4} the focus of interest has been the phenyl–vinyl torsional coordinate in regards to the equilibrium geometry, the potential about the local minimum and the barrier height for rotation. In stilbene⁵ the largest concern is the torsional barrier between the cis and trans form which is dependent on π bonding in the vinyl group. In the ground state, this barrier at 90° is high, $\approx 16,000 \text{ cm}^{-1}$. However, photoisomerization takes place on this torsional coordinate in the excited state where the potential barrier for isomerization is much lower,⁵ $\sim 1,400 \text{ cm}^{-1}$. The low excited state barrier is due to electronic state interactions. In addition to the isomerization torsional coordinate experiments have also revealed much about the phenyl–vinyl torsion similar to the motion in styrene. It is this torsion which is observed in the photoelectron spectrum and is the focus of this work. In both molecules the low frequency torsional vibrational mode involving the twisting of the ethenyl group about the single bond serves as an excellent probe of

the interaction between the aromatic and ethenyl π electrons and the extent of electronic coupling to the torsional potential. The effect of electronic excitation on conjugation in these compounds can be examined by observing the change in vibrational frequency upon electronic excitation as well as possible mode mixing in the coupled low frequency motions. Such studies, employing S_0 to S_1 excitation have been performed on a number of molecules including styrene¹⁻⁴ and stilbene.⁷⁻¹¹ Herein we extend such studies to the cation ground state. This allows a further probe of the influence of the highest lying molecular orbitals on the torsional potential.

Styrene

The spectroscopy of the ground and first excited singlet state of styrene has been carefully detailed in a number of studies.²⁻⁴ Planar styrene is of C_s symmetry and thus normal modes fall into two groups, a' and a'' . The a' vibrations, ν_1 to ν_{29} , are symmetry allowed for the electronic transitions between the ground state, S_0 ($\tilde{X}^1A'$), and the excited state, S_1 ($\tilde{A}^1A'$), while a'' vibrations, ν_{30} to ν_{42} can appear only as even overtones or in totally symmetric combination bands. The $S_0 \rightarrow S_1$ transition involves excitation of π electrons to a π^* antibonding orbital. The majority of the intense bands that appear in the excitation spectrum are benzene like modes which do not include the vinyl substituent, indicating that the $S_0 \rightarrow S_1$ electronic excitation takes place largely on the ring.

Information about the nature of the cation potential energy surface can provide important details about the ethenyl-benzene system conjugation and the associated molecular orbitals. Dyke et al.¹² performed a ZEKE-PES study on styrene revealing some of the vibrational frequencies in the cation but did not observe the bands associated with the ethenyl torsion. The results reported here include vibrational analysis and assignments using ZEKE-PES of cation vibrational bands which are sensitive to the ethenyl torsional potential and which provide information about the nature of cation potential energy surface.

This study concentrates on the changes in the structure of styrene upon electronic excitation as manifest in the appearance of vibronic bands in the cation spectrum. These changes are apparent in the comparison of vibrational frequencies, couplings, and intensities in different states and have connections to the description of the torsional barrier. Detailed studies have been done on the ground and S_1 state including vibrational analysis²⁻⁴ and calculations.¹³ Cation spectra obtained by ZEKE PES provides information about π bonding in the cation after removal of the HOMO electron.

Stilbene

The low frequency modes of stilbene have received great attention because of the interest in the cis-trans isomerization process in both the ground and excited states. Planar¹⁴ trans-stilbene has C_{2h} symmetry with optically active modes of a_g symmetry. The primary torsional mode under consideration here is ν_{37} , Figure 1, which is of

Figure 1 Schematic representation of the low frequency phenyl-vinyl torsional modes in styrene and stilbene.

a_u symmetry and consists primarily of $C_{eth}-C_{ph}$ torsion, similar to mode 42 in styrene. The S_0 and S_1 frequency of ν_{37} has been positively identified by stimulated emission experiments of Suzuki et al⁹ as 8 and 47 cm^{-1} respectively. The extremely low frequency mode is very anharmonic in the ground state but is much more harmonic in the S_1 state as the frequency increase significantly. Mode 36 is primarily an out-of-plane phenyl bending motion^{9,11} and is not observed in emission from the origin of S_1 . However, it is observed in emission from the 37² excited state indicating significant mode mixing of 36 and 37 upon excitation. This is confirmed by observation of the 36¹37¹ combination band in the excitation spectrum.⁹

Herein we report the ZEKE spectrum of stilbene for the first time and again focus on the nature of the low frequency modes in the cation.

II EXPERIMENT

The threshold ionization photoelectron spectroscopy, also known as pulsed field ionization (PFI) and zero electron kinetic energy (ZEKE) spectroscopy,¹⁵ is performed as described in detail in a previous publication.¹⁶ The spectroscopy is a two color pump-probe process in which the pump laser is tuned to a vibronic resonance in the S_1 electronic state and the probe is then tuned to further excite the molecules to the ionization threshold and above. Just below each cation resonance is a dense manifold of high n Rydberg states. It is these Rydberg states which are the final state in the pulse excitation sequence. The Rydberg states are created in an initially

field free region but are then field ionized by a -30 V/cm pulse which is applied approximately $1\text{ }\mu\text{sec}$ after their creation. The delay time allows all prompt electrons (non-resonant) to leave the focal volume and only the Rydberg derived electrons are then detected. The spectral resolution is $\sim 6\text{--}10\text{ cm}^{-1}$ for our spectra and is determined primarily by the extraction pulse voltage. A number of studies have indicated that the intensity of the observed peaks is primarily determined by Franck-Condon factor although some evidence exists to suggest this is not always the case.

The experiments are performed in a pulsed supersonic beam apparatus which consists of two differentially pumped chambers. The second chamber houses the photoelectron spectrometer which detects the electrons perpendicular to the laser and molecular beam directions. The pulsed valve (General Valve Inc.) is mounted in a heated flange and also contains a separately heated sample reservoir in close proximity to the nozzle. Stilbene was heated to 100°C (~ 10 Torr vapor pressure) and the valve itself was maintained at a slightly greater temperature. Styrene was contained at 0°C (~ 5 Torr vapor pressure) in an external sample container through which the He carrier gas (30 psig) was bubbled.

Two laser systems were used for the studies presented. Most experiments were performed with a 20 Hz frequency doubled ND : YAG laser (Continuum NY-61) pumping two high resolution (0.04 cm^{-1}) grazing incidence dye lasers (Lumonics HD 500). The output of each dye laser is frequency doubled and one is used as the pump and the other the probe. The pump and probe lasers were equipped with autotracking frequency doubling as required. The second laser is a two color pulse amplified picosecond system which has been describe previously.¹⁷ Although the spectral resolution of this system is significantly lower ($3\text{--}5\text{ cm}^{-1}$) it is comparable to the width of the threshold ionization peaks and therefore does not compromise the experimental resolution to a great degree.

For each molecule a series of photoelectron spectra are scanned, each with a different intermediate state resonance. The S_1 to ion transition is generally dominated by a strong $\Delta v = 0$ transition. This strong propensity has two important implications. First, it allows observation of cation features which might be quite weak if only the S_1 origin was used as an intermediate state. Secondly, it makes assignments of bands in the cation spectra quite easy, since the vibronic structure of S_1 state of each of these molecules is almost completely assigned.

III RESULTS AND DISCUSSION

Styrene

As mentioned above the vibrational activity in the ZEKE spectrum is determined by the particular intermediate state accessed and so a number of spectra were recorded with different intermediate states. The possible intermediate states are illustrated in Figure 2 which is the $1 + 1$ MPI spectrum of styrene. The S_1 spectrum is almost completely assigned²⁻⁴ and although the low frequency modes are not prominent in

Figure 2 $S_1 \leftarrow S_0$ 1 + 1 photoionization spectrum of jet cooled styrene. A number of the vibronic states observed were used as intermediate states in ZEKE photoelectron spectroscopy, particularly the low frequency modes. This spectrum is not normalized to the laser intensity.

the spectrum a number of bands are observed. The a'' modes do not show up as fundamentals but totally symmetric combinations of these modes do appear, specifically the transitions 42_0^{2+} , $40_0^1 42_0^1$ and $40_0^1 41_0^1$. These are all weak transitions but each had sufficient intensity to use as an intermediate state. In fact a demonstration of the sensitivity of ZEKE spectroscopy is that a high quality ZEKE spectrum can be obtained by pumping the 42_0^{2+} transition which is only 1% of the intensity of the electronic origin. Figure 3 shows the ZEKE spectra obtained by pumping each of these bands in S_1 . It is expected that the strongest feature in each cation spectrum is the $\Delta v = 0$ transition. This is confirmed by scanning the ZEKE spectrum from the S_1 origin which is dominated by a large peak ($\Delta v = 0$) which appears at the expected adiabatic ionization threshold. Given an S_0 to S_1 transition energy of $34,758 \text{ cm}^{-1}$ the adiabatic ionization potential is determined to be $68,267 \text{ cm}^{-1}$, in close agreement with the reported work of Dyke et al.¹² Once the $\Delta v = 0$ propensity is established the low frequency modes can be assigned by identifying the strongest transitions in each of the above mentioned spectra as 42_2^{2+} , 41_1^{1+} , 42_1^{1+} and 40_1^{1+} , respectively. Table 1 summarizes the S_0 , S_1 and cation energies for these combination bands. Unfortunately the important ν_{38} mode is not observed in the S_1 spectrum and so its value could not be determined in the cation. In addition to the a'' modes a number of higher frequency a' modes were investigated, specifically modes 23, 24, 25, 27, 28 and 29. The frequencies of all the modes measured are summarized in Table 2 including the values for the S_0 , S_1 and cation ground state. Note that mode 42 is attained by assuming the observed cation overtone is harmonic and taking half of the frequency of the 42_2^{2+} band. This is often a poor approximation for low frequency, large amplitude motions but ν_{42} is quite harmonic in S_1 ² and

Figure 3 Styrene ZEKE spectra with a number of different intermediate states as indicated. The energy of the spectra are referenced to the adiabatic ionization potential at $68,267 \text{ cm}^{-1}$. The dotted lines are provided to indicate the energies of the $\Delta v = 0$ transitions from the intermediate state to the cation.

Table 1 Observed low frequency combination bands in styrene emission, fluorescence excitation and ZEKE-PES spectra

Band	$S_0^{(a)}$	$S_1^{(b)}$	Cation ground state
42_0^2	86.5	371	368.2
$41_0^1 42_0^1$	—	282	281
$40_0^1 41_0^1$	—	349	451

^(a) see reference 2

^(b) see reference 3

since the cation frequency is close to that in S_1 it is likely to also be harmonic in the cation. Once ν_{42}^+ is established then ν_{41}^+ and ν_{40}^+ are determined from the observed combination bands.

Table 2 Summary of observed styrene vibrational modes.

<i>Vibrational Mode</i>	$S_0^{(a)}$ (cm^{-1})	$S_1^{(b)}$ (cm^{-1})	<i>Cation</i> (cm^{-1})
42	38	185	184
41	199	97	97
40	399	252	354
29	227	237	229
28	433	395	449
27	548	437	550
25	779	746	780
24	996	948	982
23	1011	959	1008

^(a) see reference 2^(b) see reference 3

The vibrational bands that are most sensitive to the conjugation in the vinyl substituent are the a'' modes ν_{38} and ν_{42} both of which are depicted in Figure 2. Mode 38 is primarily a torsion about the double bond of the vinyl group, $\text{C}_{\text{eth}}-\text{C}_{\text{eth}}$ while mode 42 is primarily a torsion about the single bond, $\text{C}_{\text{eth}}-\text{C}_{\text{ph}}$. Bands with quanta of ν_{38} are unobserved but the second overtone and combination bands with ν_{42} quanta are observed. In the excited state the modes 40, 41, and 42 are found to couple strongly producing observable combination bands between 41 and 42 and between 40 and 41. Hemley et al.¹³ present a complete ground state vibrational analysis using extended PPP-CI calculations. The vibrational analysis details the components of each mode. 75% of mode 42 is found to be $\text{C}_1-\text{C}_\alpha$ torsion while the remaining is 10% ring torsion, 8% ring out of plane, and 7% substituent out of plane. Mode 41 is characterized as 17% $\text{C}_1-\text{C}_\alpha$ torsion, 48% ring torsion and 35% ring out of plane motion. The $\text{C}_1-\text{C}_\alpha$ torsion component explains the strong coupling of this mode to mode 42. Mode 40 is composed of 60% ring torsion and 40% ring out of plane motion. The similarity of mode 40 and 41 explain their strong coupling.

Upon electronic excitation from the ground state the single bond torsion, mode 42, increases from 38 cm^{-1} in the ground state to 185 cm^{-1} in the first excited state. This can be compared with the ν_{38} ground state frequency of 640 cm^{-1} showing that the $\text{C}_1-\text{C}_\alpha$ bond takes on more double bond character in the excited state but is still primarily a single bond.

The ZEKE spectroscopy reveals that the cation frequency of mode 42 is 184 cm^{-1} , representing little change from the excited state frequency of 185 cm^{-1} . Removing the π^* electron appears not to change the bonding between $\text{C}_1-\text{C}_\alpha$ and thus the conjugation through the vinyl group. Mode 41 has a frequency of 97 cm^{-1} in the cation, which is exactly the value in S_1 but significantly less than the 199 cm^{-1} in

the ground state. Again, the S_1 and cation frequencies nearly match. More typical is a correlation between the ground state frequency and that of the ground state of the cation as in the case of 9,10-dihydrophenanthrene.¹⁷ Mode 41 is lower in frequency upon excitation, perhaps related to the increased flexibility in the ring due to the antibonding π electron in S_1 and the removal of this electron in the cation. Mode 40 is found to have a cation frequency of 354 cm^{-1} , which is an increase from the excited state frequency of 252 cm^{-1} . This mode is localized on the benzene ring and, as such, is associated with benzene mode 16a.

The ZEKE spectra arising from totally symmetric vibrations, a' , also are examined. Modes 28, 24, and 18 are related to benzene modes 6a, 12, and 18a respectively. The excited state frequencies of these benzene-like modes in styrene correlate with those of alkylbenzenes upon comparison with work by Hopkins et al.¹⁸ This indicates that the vinyl group represents only a slight perturbation to the ring system. Comparison with stilbene is discussed in a later section. The cation spectra reveal some changes in these frequencies. Mode 27 and 29 both involve substituent bends and should thus be sensitive to the changes in the vinyl group. Both modes decrease in frequency upon excitation and in the cation their frequencies are the same or higher than in S_0 . This data and the fact that mode 40, partially a ring out of plane mode, follows the same trend indicates that the substituent has more flexibility out of plane in S_1 than in the ground and cation ground states.

Electronic structure calculations of Hemley et al.¹³ are particularly useful in assessing the effect of electronic excitation on the low frequency torsional modes. They used PPP-CI and CNDO/S-CI calculations to evaluate the electronic energy, molecular structure and molecular orbital configuration interaction in each electronic state. These calculations show that the effect of S_0 to S_1 excitation is to shorten the $C_{\text{eth}}-C_{\text{ph}}$ bond. This effect is attributed to a mixed molecular orbital excitation which contains a significant contribution from a nonbonding-to-bonding transition and an antibonding-to-nonbonding transition with respect to the $C_{\text{eth}}-C_{\text{ph}}$ bond. This increased $C_{\text{eth}}-C_{\text{ph}}$ bond strength in S_1 is reflected in the increase in frequency of ν_{42} from 38 cm^{-1} in S_0 to 185 cm^{-1} in S_1 . As mentioned above it was also shown that extensive low frequency mode mixing occurs as a result of the S_1 excitation. The cation electronic structure can be evaluated by applying Koopman's theorem and looking at the change in bonding due to removal of an electron in the highest lying molecular orbital. In many aromatic molecules characterized by π to π^* excitations the cation frequencies often are between those of S_0 and S_1 because the antibonding electron is removed upon ionization. In styrene the low frequency modes are quite similar to the S_1 state. This suggests that the highest lying electron is primarily nonbonding with respect to the $C_{\text{eth}}-C_{\text{ph}}$ bond, and thus its removal has little effect on the bond strength and resulting vibrational frequencies. Thus one would expect that the torsional potential of the styrene cation is very similar to the S_1 state of the molecule. The nonbonding nature of the excited state (with respect to $C_{\text{eth}}-C_{\text{ph}}$) is consistent with the leading configuration to S_1 calculated by Hemley et al.¹³

Stilbene

ZEKE spectra were obtained from the following four different S_1 vibronic pump transitions; 0^0 , 36^137^1 , 37^2 , 25^1 , 24^1 . Again, as in the case of styrene, the origin ZEKE spectrum exhibits a strong propensity for the $\Delta v = 0$ transition which should also apply to the other transitions studied. The measured ionization potential is $61,756 \text{ cm}^{-1}$ which is in good agreement with the $61,750 \text{ cm}^{-1}$ value determined by Suzuki et al⁹ using a Rydberg series extrapolation. Several of the ZEKE spectra are shown in Figure 4. The data for stilbene was taken with the picosecond laser system described above and thus the relative and absolute band positions are subject to greater uncertainty. The cation vibrational mode frequencies have a conservative error of $\pm 5 \text{ cm}^{-1}$.

Applying the $\Delta v = 0$ propensity allows the assignment of the low frequency modes in the cation ground state. Using the 37^2 pump transition yields a value for 37^{2+} of 78 cm^{-1} as compared to 95 cm^{-1} for 37^2 in the S_1 state. Since 37^{1+} is not observed

Figure 4 Stilbene ZEKE spectra with a number of different intermediate states as indicated. The largest peaks in the middle two traces appear to consist of at least two overlapping transitions which give an increased uncertainty to the derived frequencies in the cation. The largest peak in the upper trace is saturated. The dotted lines are provided to indicate the energies of the $\Delta v = 0$ transitions from the intermediate state to the cation.

directly in the ion spectrum its frequency is estimated by taking half of the overtone to yield a value of 39 cm^{-1} . This is a reasonable approximation because ν_{37} appears harmonic in S_1 and is not drastically different in frequency in the cation. Once ν_{37} is established the value of ν_{36} can be determined from pumping the S_1 36^137^1 band. The value of 36^{1+} is thus determined to be 42 cm^{-1} in the ion which is the same value as assigned to S_1 so it undergoes no significant shift upon ionization. A summary of the cation frequencies obtained for stilbene is given in Table 3.

Table 3 Summary of observed *trans*-Stilbene vibrational modes.

Vibrational Mode	$S_0^{(a)}$ (cm^{-1})	$S_1^{(a)}$ (cm^{-1})	Cation (cm^{-1})
37^b	8	47	38
36^b	33	42	42
25	204	197.6	182
24	290	280.3	254.3

^(a) see references 8 and 11

^(b) See reference 9

As in the case of styrene the phenyl torsional potential in the stilbene cation, as evidenced by the frequency of ν_{37} , is similar to the S_1 excited state. One can interpret this again as primarily due to a loss of antibonding character in the $C_{\text{ph}}-C_{\text{e}}$ bond on promotion of the HOMO electron from S_0 to S_1 without much bonding contribution in the LUMO. Therefore upon ionization loss of an essentially non-bonding LUMO electron causes little change in the $C_{\text{ph}}-C_{\text{e}}$ bond strength or resulting torsional frequency. In regards to this torsional motion the behavior of styrene and stilbene are actually quite similar. The difference in torsional mode frequency is dominated by the contribution of the change in the reduced moment of inertia between the two molecules. Also the behavior upon electronic excitation is quite similar with the frequencies increasing by a factor of 4.9 in S_1 for styrene and a factor of 5.9 for stilbene. The cation potentials in both molecules are very similar to those in S_1 . Therefore it is clear that the electronic structure of these molecules is quite similar with regards to the $C_{\text{ph}}-C_{\text{e}}$ conjugation.

In stilbene ν_{25} is a prominently observed a_g vibration in the S_0 to S_1 spectrum and consists of an in plane $C_{\text{phenyl}}-C_{\text{eth}}-C_{\text{eth}}$ bend. The vibrational activity is ascribed⁸ to an increase in the bond angle upon excitation of approximately 1.3° . ν_{25} is clearly observed in the cation spectrum when pumping the 25^1 transition and is assigned a frequency of 182 cm^{-1} as compared to 202 cm^{-1} in S_0 and 198 cm^{-1} in S_1 . ν_{25} is also observed prominently in the ZEKE spectrum obtained when pumping the S_1 origin which suggests that the bond angle also changes upon ionization. Although the bond angle may be changing the small frequency change upon electronic excitation indicates that the bending flexibility of the vinyl bridge is changing very little.

IV SUMMARY

ZEKE photoelectron spectroscopy has been used to study the low frequency modes of styrene and stilbene. Although the spectral intensity of these modes is quite low in the $S_0 \rightarrow S_1$ transition it is shown that these states can still be used as intermediate vibrations in the ZEKE process and thus reveal the frequencies of these modes in the cation. The phenyl–vinyl torsional potential in both molecules is observed to change only slightly upon excitation from S_1 to the cation, even though larger changes are observed for the $S_0 \rightarrow S_1$ transition. Particularly in the case of styrene these vibrational changes can be compared to calculations which assess the change in bonding between $C_{\text{eth}}-C_{\text{ph}}$ upon ionization. Since the highest lying electron in the S_1 configuration is non-bonding its removal does not have a great influence on the $C_{\text{eth}}-C_{\text{ph}}$ torsional potential.

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