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, $v_42$, $v_41$ and $v_40$ 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, $v_37$, is also measured as well as the related mode $v_36$. 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 ($C_{eth}$–$C_{ph}$) and the torsion about the ethylene double bond. In styrene 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 stilbene the largest concern is the torsional barrier between the cis and trans form which is dependent on $\pi$ bonding in the vinyl group. In the ground state, this barrier at 90° is high, $\approx$16,000 cm$^{-1}$. However, photoisomerization takes place on this torsional coordinate in the excited state where the potential barrier for isomerization is much lower, $\approx$1,400 cm$^{-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 $\pi$ 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 styrene$^{1-4}$ 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 $C_4$ symmetry and thus normal modes fall into two groups, $a'$ and $a''$. The $a'$ vibrations, $v_1$ to $v_{29}$, 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, $v_{30}$ to $v_{42}$ can appear only as even overtones or in totally symmetric combination bands. The $S_0 \rightarrow S_1$ transition involves excitation of $\pi$ electrons to a $\pi^*$ 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 analysis$^{2-4}$ and calculations.$^{13}$ Cation spectra obtained by ZEKE PES provides information about $\pi$ 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. Planar$^4$ trans-stilbene has $C_{2v}$ symmetry with optically active modes of $a_g$ symmetry. The primary torsional mode under consideration here is $v_{37}$, Figure 1, which is of
Figure 1  Schematic representation of the low frequency phenyl–vinyl torsional modes in styrene and stilbene.

\[ v_{38} \quad v_{42} \]

\[ v_{37} \]

**STYRENE**  
**trans-STILBENE**

a_u symmetry and consists primarily of C_ethylene–C_phenyl torsion, similar to mode 42 in styrene. The S_0 and S_1 frequency of \( v_{37} \) has been positively identified by stimulated emission experiments of Suzuki et al.\(^9\) 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 increases 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 S_1 excited state indicating significant mode mixing of 36 and 37 upon excitation. This is confirmed by observation of the 36\(^1\)37\(^1\) 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 $-30 \text{ V/cm}$ pulse which is applied
approximately $1 \mu\text{sec}$ 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 $\sim 6-10 \text{ cm}^{-1}$ 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 con-
sists 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 $100^\circ\text{C}$ ($\sim 10 \text{ Torr vapor pressure}$)
and the valve itself was maintained at a slightly greater temperature. Styrene was
contained at $0^\circ\text{C}$ ($\sim 5 \text{ Torr vapor pressure}$) 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 $20 \text{ Hz}$ frequency doubled ND: YAG laser (Continuum NY–61)
pumping two high resolution ($0.04 \text{ cm}^{-1}$) 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.\textsuperscript{17} Although the spectral
resolution of this system is significantly lower ($3-5 \text{ cm}^{-1}$) it is comparable to the
width of the threshold ionization peaks and therefore does not compromise the ex-
perimental resolution to a great degree.

For each molecule a series of photoelectron spectra are scanned, each with a dif-
ferent 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 assigned\textsuperscript{2-4} and although the low frequency modes are not prominent in
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 \( 42^2_{0} \), \( 40^1_{0}42^1_{0} \) and \( 40^1_{0}41^1_{0} \). 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 \( 42^2_{0} \) 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 \( S_0 \) 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 cm\(^{-1}\) the adiabatic ionization potential is determined to be 68,267 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 \( v_{38} \) 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 \( v_{42} \) is quite harmonic in \( S_1 \) 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 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\(^2\)_0  | 86.5        | 371         | 368.2               |
| 41\(^1\)42\(^1\)_0 | –          | 282         | 281                 |
| 40\(^1\)41\(^1\)_0 | –          | 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 $v_{42}^+$ is established then $v_{41}^+$ and $v_{40}^+$ are determined from the observed combination bands.
Table 2  Summary of observed styrene vibrational modes.

| Vibrational Mode | S₀⁽ᵃ⁾ (cm⁻¹) | S¹⁽ᵇ⁾ (cm⁻¹) | Cation (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 \( \alpha'' \) modes \( \nu_{38} \) and \( \nu_{42} \) both of which are depicted in Figure 2. Mode 38 is primarily a torsion about the double bond of the vinyl group, \( C_{\text{eth}}-C_{\text{eth}} \) while mode 42 is primarily a torsion about the single bond, \( C_{\text{eth}}-C_{\text{ph}} \). Bands with quanta of \( \nu_{38} \) are unobserved but the second overtone and combination bands with \( \nu_{42} \) 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 \( C_{1}-C_{\alpha} \) 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% \( C_{1}-C_{\alpha} \) torsion, 48% ring torsion and 35% ring out of plane motion. The \( C_{1}-C_{\alpha} \) 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 \( \nu_{38} \) ground state frequency of 640 cm⁻¹ showing that the \( C_{1}-C_{\alpha} \) 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 \( \pi^* \) electron appears not to change the bonding between \( C_{1}-C_{\alpha} \) 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\textsubscript{0} 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\textsuperscript{17}. Mode 41 is lower in frequency upon excitation, perhaps related to the increased flexibility in the ring due to the antibonding \( \pi \) electron in S\textsubscript{1} and the removal of this electron in the cation. Mode 40 is found to have a cation frequency of 354 cm\textsuperscript{-1}, which is an increase from the excited state frequency of 252 cm\textsuperscript{-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, \( \alpha' \), 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.\textsuperscript{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\textsubscript{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\textsubscript{1} than in the ground and cation ground states.  

Electronic structure calculations of Hemley et al\textsuperscript{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\textsubscript{0} to S\textsubscript{1} excitation is to shorten the \( \text{C}_{\text{eth}}-\text{C}_{\text{ph}} \) 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 \( \text{C}_{\text{eth}}-\text{C}_{\text{ph}} \) bond. This increased \( \text{C}_{\text{eth}}-\text{C}_{\text{ph}} \) bond strength in S\textsubscript{1} is reflected in the increase in frequency of \( \nu_{42} \) from 38 cm\textsuperscript{-1} in S\textsubscript{0} to 185 cm\textsuperscript{-1} in S\textsubscript{1}. As mentioned above it was also shown that extensive low frequency mode mixing occurs as a result of the S\textsubscript{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 \( \pi \) to \( \pi^* \) excitations the cation frequencies often are between those of S\textsubscript{0} and S\textsubscript{1} because the antibonding electron is removed upon ionization. In styrene the low frequency modes are quite similar to the S\textsubscript{1} state. This suggests that the highest lying electron is primarily nonbonding with respect to the \( \text{C}_{\text{eth}}-\text{C}_{\text{ph}} \) 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\textsubscript{1} state of the molecule. The nonbonding nature of the excited state (with respect to \( \text{C}_{\text{eth}}-\text{C}_{\text{ph}} \)) is consistent with the leading configuration to S\textsubscript{1} calculated by Hemley et al.\textsuperscript{13}
Stilbene

ZEKE spectra were obtained from the following four different S₁ vibronic pump transitions; 0⁰, 36¹37¹, 37², 25¹, 24¹. Again, as in the case of styrene, the origin ZEKE spectrum exhibits a strong propensity for the Δν = 0 transition which should also apply to the other transitions studied. The measured ionization potential is 61,756 cm⁻¹ which is in good agreement with the 61,750 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 ±5 cm⁻¹.

Applying the Δν = 0 propensity allows the assignment of the low frequency modes in the cation ground state. Using the 37² pump transition yields a value for 37²⁺ of 78 cm⁻¹ as compared to 95 cm⁻¹ for 37² in the S₁ state. Since 37⁺ is not observed

![Figure 4](image)

**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 Δν = 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 \(\nu_{37}\) appears harmonic in \(S_1\) and is not drastically different in frequency in the cation. Once \(\nu_{37}\) is established the value of \(\nu_{36}\) can be determined from pumping the \(S_3 36'\) \(37\) 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.

| 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 \(\nu_{37}\), is similar to the \(S_1\) excited state. One can interpret this again as primarily due to a loss of antibonding character in the \(C_{ph}\)–\(C_e\) 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 \(C_{ph}\)–\(C_e\) 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 \(C_{ph}\)–\(C_e\) conjugation.

In stilbene \(\nu_{25}\) is a prominently observed \(\alpha_g\) vibration in the \(S_0\) to \(S_1\) spectrum and consists of an in plane \(C_{phenyl}\)–\(C_{eth}\)–\(C_{eth}\) bend. The vibrational activity is ascribed\(^8\) to an increase in the bond angle upon excitation of approximately 1.3°. \(\nu_{25}\) 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 \(S_1\). \(\nu_{25}\) 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 $C_{eth}-C_{ph}$ 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 $C_{eth}-C_{ph}$ torsional potential.

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References

1. C. W. Bock, M. Trachtman and P. George. Chem. Phys., 93, 431 (1985).
2. J. M. Hollas and T. Ridley. Chem. Phys. Lett., 75, 94 (1980); J. M. Hollas and T. J. Ridley. J. Mol. Spect., 89, 232 (1981); J. M. Hollas, H. Musa, T. Ridley, P. H. Turner and K. H. Weisenberger. J. Mol. Spect., 94, 437 (1982).
3. J. A. Syage, F. A. Adel and A. H. Zewail. Chem. Phys. Lett., 103, 15 (1983).
4. J. I. Seeman, V. H. Grassian and E. R. Bernstein. J. Am. Chem. Soc., 110, 8542 (1988); V. H. Grassian, E. R. Bernstein, H. V. Secor and J. I. Seeman. J. Chem. Phys., 94, 6691 (1990).
5. D. H. Waldeck. Chem. Rev., 91, 415 (1991).
6. J. Saltiel, G. Srinivasan and C. Werking. J. Phys. Chem., 91, 2755 (1987).
7. T. S. Zwier, E. M. Caracasquillo and D. H. Levy. J. Chem. Phys., 78, 5493 (1983).
8. J. A. Syage, P. M. Felker and A. H. Zewail. J. Chem. Phys., 81, 4706 (1984).
9. T. Suzuki, M. Mikami, Naohiko and M. Ito. J. Phys. Chem., 90, 6431 (1986).
10. L. H. Spangler, W. B. Bosman, R. DD. van Zee and T. S. Zwier. J. Chem. Phys., 88, 6768 (1988).
11. T. Urano, H. Hamaguchi, M. Tasumi, K. Yamiouchi, S. Tsuchiya and T. L. Gustafson. J. Chem. Phys., 91, 3884 (1989).
12. J. M. Dyke, H. Ozeki, M. Takahashi, M. C. R. Cockett and K. Kimura. J. Chem. Phys., 97, 8926 (1992).
13. R. J. Hemley, U. Dinur, V. Vaida and M. Karplus. J. Am. Chem. Soc., 107, 836 (1985). R. J. Hemley, D. G. Leopold, V. Vaida and M. J. Karplus, J. Chem. Phys., 82, 5379 (1985).
14. B. B. Champagne, J. F. Pranstiel, D. F. Plusquello, D. W. Pratt, W. M. van Herpen and W. L. Meerts. J. Phys. Chem., 94, 6 (1990).
15. K. Muller-Dethlefs and E. W. Schlag. Ann. Rev. Phys. Chem., 42, 109 (1991), and references therein.
16. X. Zhang, J. M. Smith and J. L. Kneal. J. Chem. Phys., 97, 2843 (1992).
17. J. M. Smith and J. L. Kneal. J. Chem. Phys., 99, 38(1993).
18. J. B. Hopkins, D. E. Powers and R. E. Smalley. J. Chem. Phys., 72, 5039 (1980).