Spectroscopic characterization on the neutral excited state and cationic ground state of styrene

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ABSTRACT

The spectroscopic properties of styrene have been investigated via resonance-enhanced multiphoton ionization (REMPI) and slow electron velocity-map imaging (SEVI) methods. Vibrational frequencies in the first excited state of neutral (S_1) and ground electronic state of cation (D_0) have been accurately measured. From the one-color REMPI spectrum of styrene, the $S_1 \leftarrow S_0$ electron transition energy is determined as $34729 \pm 3 \text{ cm}^{-1}$. Most low-frequency vibrations of S_1 state are unambiguously identified with the aid of calculated results at TD-B3LYP/6-311++G(d, p) level. Some controversially high-frequency vibrational modes of S_1 state are reassigned in comparison with theoretical results. The SEVI spectra taken via various S_1 intermediate levels provide the detailed vibrational structures of D_0 state and directly yield the accurate adiabatic ionization potential (IP) of $68267 \pm 6 \text{ cm}^{-1}$. The vibrational frequencies of the D_0 state calculated at the B3LYP/6-311++G(d, p) level are in excellent agreement with the experimental results to aid us assigning some high-frequency vibrational modes. In addition, photoelectron angular distributions (PADs) in the two-step transitions are presented, suggesting no apparent threshold shape resonance is investigated in the ionization of styrene without unambiguous drastic changes in PADs.

Key words: Velocity-map imaging, Time-of-flight, REMPI, Styrene

1. Introduction

Styrene, the simplest molecule containing both an aromatic ring and a double bond, is widely used in different areas of industrial, environmental and biological processes [1,2]. It plays an essential role in the atmospheric oxidation reaction and the production of secondary organic aerosols [3,4]. In addition, styrene has been extensively studied as a prototype for ultrafast relaxation in many photochemical and photobiological processes [5]. The study on the structures and vibrations of styrene molecule in the specifically electronic state can help us to understand the molecular properties, and hence has become an increasing active field.

The investigations of neutral ground state (S_0) of styrene have extensively been performed via different spectroscopic [6-12] and theoretical [12-18] methods. The discrepancy about the structure of the S_0 state exists in previous works. These studies, such as Suzuki [6] using electronic absorption spectra, Grassian *et al.* [7] using one-color time-of-flight mass spectrometry (TOFMS), Britton *et al.* [13] and Granadino-Roldán *et al.* [12] using theoretical approaches conclude that the styrene molecule is planar in S_0 state. On the other hand, the results from NMR spectroscopy experiment [8] and theoretical calculations using HF/4-31G, HF/6-31G* and MP2/6-311G** method [14-16] suggest non-planar property of styrene in S_0 state, with a deviating from planarity by $\sim 10.5^\circ$. As for the neutral first excited (S_1) state of styrene, strictly planar structure is investigated by resonant-enhanced multiphoton ionization [19-22] and fluorescence [23-28] spectra as well as semi-empirical [17,18] and *ab initio* [29,30] calculations, indicating a fairly deep well in the torsional degree of freedom. In addition, ionic properties of styrene have also been investigated by zero kinetic energy (ZEKE) spectroscopy [31,32]. Still, a more detailed vibrational structure for the ground and excited states in neutral and the ground state in cation of styrene needs to be investigated to extend spectra far from low-frequency region.

Recently, pump-probe laser photoelectron spectroscopy is one of most potential tool for probing the dynamics of the excited state and locating ion internal structure. In conjunction with slow electron velocity-map imaging (SEVI) technique, they extended the field to medium and large biological and photochemistry related organic molecules by virtue of excellent collection efficiency and high energy resolution [33]. One of merit for this technique is that the information on the photoelectron angular distribution can be extracted from SEVI.

In this work, one-color resonant two-photon ionization (1C-R2PI) spectrum within $\sim 2000\text{ cm}^{-1}$ upon the $S_1 \leftarrow S_0$ electronic transition and the two-color resonant two-photon ionization (2C-R2PI) SEVI spectra of styrene cation have been reported. The precise adiabatic ionization potential (IP) and vibrational frequencies of styrene has been deduced from the spectra. SEVI spectra are obtained by ionizing through the intermediate vibrational level in the S_1 state to obtain more information about the active vibrational modes

in D_0 state. *Ab initio* and density functional theory (DFT) calculations have also been performed to predict the electronic transition energies, vibrational frequencies, to provide a clear-cut assignment of the vibrational spectra of styrene and its cation.

2. Experimental and computational methods

The experimental apparatus used for this study has been previously described [34], and only a brief description is given here. The styrene (98%) purchased from J&K Scientific was used without any purification. The molecular beam was supersonically expanded into vacuum chamber through a pulsed valve of orifice diameter 0.5 mm (Parker, General Valve series 9) running at 10 Hz. The backpressure of the pulse valve was about 4 bar supplied with bubbling argon through a reservoir of styrene at room temperature. After collimation by the skimmer with a 0.5 mm diameter, the styrene beam entered the interaction region midway between the repeller and extractor plates. The excitation laser pulse was generated by frequency doubling of the dye laser output (Sirah) pumped by the third harmonic output of Nd:YAG laser (Spectra-Physics). The ionization laser pulse was generated by frequency-doubling of the output of another dye laser (ND6000, Continuum) pumped by another Nd:YAG laser (Powerlite Precision II, Continuum). Coumarin 153, Rhodamine 590, Pyrromethene 597, and Rhodamine 610 were used to acquire the required dye laser wavelengths. The laser bandwidth was approximately 0.1 cm^{-1} , and the duration of the laser pulse was about 8 ns.

The 1C-R2PI experiment was performed near the $S_1 \leftarrow S_0$ transition of styrene by using a tunable frequency-doubling dye laser (Sirah) pumped by Nd:YAG laser (Spectra-Physics). Energy of $\sim 40\text{ }\mu\text{J/pulse}$ was held without focusing. The produced ions were perpendicularly accelerated by time-of-flight lenses. Ion signals were measured and analyzed by a multichannel scaler (MCS, SRS, SR245). The time-gated mass spectra were accumulated for 100 laser shots for each wavelength. And wavelength was scanned at 0.3 cm^{-1} spacing. In the 2C-R2PI experiment, the pulse energy of the excitation laser was held below $10\text{ }\mu\text{J}$ to prevent the 1C-R2PI process. The photoelectron signal was practically absent when only one of two laser pulses was applied to the system. Both laser pulses were linearly polarized with their E vectors perpendicular to the time-of-flight axis. The delay time between the excitation laser, the ionization laser and the pulse valve was controlled using two digital delay/pulse generators (DG535, SRS). Photoelectrons were accelerated along the time-of-flight axis in the velocity mapping condition and projected onto a home-made position-sensitive detector (50 mm diameter) coupled with a personal computer-interfaced CCD camera (Basler Scott, 782×582 pixels) system in conjunction with the photo-counting mode software interface embedded in LabVIEW code. The SEVI images were taken at low electric field condition (38 V/cm), and reconstructed through the BASEX program [35].

Geometry optimization and harmonic vibrational frequency calculations of styrene in the S_0 , S_1 , and D_0

states were all performed via the NWChem program package [36]. The carbon atoms of styrene around the ring are labeled 1-6 and the substitution is numbered as C₄-C₇=C₈. For S₀ and D₀ states B3LYP/6-311++G(d, p) method was applied [37], whereas the TD-B3LYP/6-311++G(d, p) method was employed for the S₁ state. The stationary points were characterized as the energy minimum by verifying that all the corresponding frequencies were real. The calculated vibrational frequencies were scaled by a certain factor to approximately correct the combined errors stemming from the basis-set incompleteness and vibrational anharmonicity.

3. Results

1. Molecular geometries of styrene in the S₀, S₁, and D₀ states

Optimized structural parameters and frequencies of styrene in the ground states (S₀ and D₀) and the first excited state (S₁) are listed in Table 1, in comparison to the experimental frequencies. Fig. 1 shows the diagram of styrene molecule structure with the CC bond lengths (in Å) of S₀, S₁, and D₀ states in different fonts. The bold, italic, and underline types represent S₀, S₁, and D₀ states, respectively. Most vibrational frequencies predicted at this method agree well with experiment within the range of ± 10 cm⁻¹ except for mode 8 and 9 with a slight deviation of 19 cm⁻¹. The gap in vibrational frequency between theory and experiment is much less than that obtained from the torsional structure in S₀ state of styrene [16].

The S₁←S₀ transition is subjected to the $\pi^*\leftarrow\pi$ excitation of the benzene ring due to the population of antibonding orbital. As expected, the structure of S₁ state is also planar. When it is excited to the S₁ state, the lengths of ring CC bonds are all lengthened, except that the C₂-C₃ and C₅-C₆ bonds are shorten by 0.002 and 0.019 Å. The CH bond lengths are almost unchanged upon excitation. In addition, the C₇=C₈ bond is slightly lengthened and the C₄-C₇ bond is shortened slightly.

The same as S₀ and S₁ states, the D₀ state is also found to be strictly planar. On the D₀←S₁ excitation, the benzene ring is deformed: the C₂-C₃, C₃-C₄ and C₁-C₆ bonds are shortened, while the C₁-C₂ and C₄-C₅ bonds are lengthened. The aromatic character of the ring is considerably expanded in this state in comparison to the CC bond lengths in the neutral ground state. The CH bonds are nearly unchanged upon ionization. The bond lengths of the C₇=C₈ and C₄-C₇ bonds are changed from 1.401 and 1.407 Å in the S₁ state to 1.375 and 1.423 Å in the D₀ state for styrene, respectively.

Fig. 1. Geometries and labeling of the atoms for styrene at neural ground state S_0 , ionic ground state D_0 using the optimized B3LYP/6-311++G(d, p) structure, and first excited state S_1 at the TD-B3LYP/6-311++G(d, p) level. The Bold, italic, and underline types represent S_0 , S_1 , and D_0 states, respectively. Bond distances are given in Å.

2. 1C-R2PI spectrum of styrene

Fig. 2. 1C-R2PI spectrum of styrene within ~ 2000 cm^{-1} upon the $S_1 \leftarrow S_0$ electronic transition. The origin band of styrene is ionized at 34759 cm^{-1} . * denotes unassigned bands.

Fig. 2 shows the 1C-R2PI spectrum of styrene in the range of ~ 2000 cm^{-1} upon the $S_1 \leftarrow S_0$ transition. The band origin of this vibronic spectrum appears at 34759 cm^{-1} in accordance with previous experimental investigations [20,27,28]. In term of reported assignments [19-28], the bands at 395 , 748 and 1149 cm^{-1} are readily identified as vibrational modes 28, 25 and 17, respectively, which mainly involve the in-plane bending and stretching motions of C_4 - C_7 and ring.

Transition 29_0^1 resulting from the characteristic in-plane bending motion of the C_4 - C_7 single bond appears at 238 cm^{-1} . The intense band at 1211 cm^{-1} is recognized as mode 18, which is related to the in-plane C_4 - C_7 single bond stretching vibration. Those peaks at 438 and 524 cm^{-1} are assigned to transitions 27_0^1 and 26_0^1 , corresponding to the in-plane $C=C$ double bond bending and ring deformation vibrations. The combination bands $41_0^1 42_1^0$, $41_0^1 42_0^1$ and $40_0^1 41_0^1$ are relevant to the out-of-plane vibrational modes, which appear at 59 , 283 and 350 cm^{-1} , respectively. The bands at 194 and 506 cm^{-1} are ascribed to the two-quantum transition 41_0^2 and 40_0^2 , respectively. The frequencies of ν_{40} , ν_{41} and ν_{42} modes in S_1 state are thus determined to be 253 , 97 and 186 cm^{-1} . A weak band at 149 cm^{-1} is assigned to the hot band 42_1^1 .

To re-examine above assignments, we performed theoretical calculation at TD-B3LYP /6-311++G(d, p) level for the S_1 state of styrene. The calculated frequencies listed in Table 1 are in reasonable agreement with the above assignments. We suggest a possible reassignment of some of high-frequency modes for S_1 state. The bands appearing at 950 , 961 , 983 , 1031 , 1098 , 1187 and 1357 cm^{-1} are assigned to the 24_0^1 , 23_0^1 , 22_0^1 ,

21_0^1 , 20_0^1 , 19_0^1 and 15_0^1 transitions, respectively, which mainly involve the in-plane ring deformation and CH bond bending. Those at 1271 and 1525 cm^{-1} are identified as modes 16 and 9, corresponding to the in-plane motion of C=C double bond. Transition 14_0^1 resulting from the characteristic in-plane scissoring motion of the CH_2 group appears at 1379 cm^{-1} . The peaks at 1475 and 1492 cm^{-1} correspond to the 12_0^1 and 10_0^1 transitions, which are related to the in-plane $\text{C}_4\text{-C}_7$ stretching vibrations. The bands at 1417 and 1431 cm^{-1} are assigned to the 13_0^1 and 11_0^1 transitions, respectively. These two transitions are involved in the ring stretching motion. All of the observed vibronic bands in the 1C-R2PI spectrum are summarized in Table 2, along with the new possible assignments.

3. SEVI spectra via the $S_1\text{-}S_0$ origin

Fig. 3. 2C-R2PI SEVI images (left column) and corresponding spectra (right column) following the ionization of styrene in the $00\ 0$ level in S_1 , recorded with the probe wavelength set to (a) 294.099 nm, (b) 290.305 nm, (c) 287.422 nm, (d) 284.192 nm. The photoelectron images are reconstructed images after inverse Abel transformation. The double arrow indicates the directions of the laser polarization.

Figs. 3a-d demonstrate SEVI spectra of styrene recorded at four different wavelengths via $S_1\ 0_0^0$ origin. The SEVI bands resulting from the active vibrations of the styrene cation are listed in Table 1, along with the calculated frequencies and possible assignments. In view of reported assignments [31,32], the pronounced features shifted from the 0_0^0 band by 449, 552, 983 and 1236 cm^{-1} corresponds to the 28^1 , 27^1 , 24^1 and 18^1 transitions, respectively. The frequency for the transition 28^2 is measured to be 895 cm^{-1} . The weak peaks appearing at 644 and 779 cm^{-1} are assigned to the modes 26 and 25. Transitions 28^1 , 25^1 and 18^1

mainly involve the in-plane C₄-C₇ motion, whereas mode 27 results from the in-plane C=C double bond bending vibration. Furthermore, modes 24 and 26 are related to the ring deformation.

Theoretical calculation was carried out at B3LYP/6-311++G(d, p) level in D₀ state for vibrational assignment. All calculated vibrational frequencies of D₀ state are listed in Table 1 for comparison. Clearly, most vibrational frequencies agree well with the experimental results except for mode 26 with a deviation from experiment by -68 cm⁻¹. The calculation suggests that the intense bands at 1194, 1410, 1530 and 1618 cm⁻¹ are assigned to the 19¹, 14¹, 10¹ and 9¹ transitions. The weak bands at 1303, 1325 and 1465 cm⁻¹ are identified as vibrational modes 17, 16 and 13, respectively. Transitions 17¹, 14¹ and 10¹ mainly involve the in-plane C₄-C₇ motion, whereas modes 16 and 9 result from the in-plane C=C double bond stretching vibration. And, modes 19 and 13 are related to the ring stretching and CH bond bending vibration.

4. SEVI spectra via the low frequency vibrational transitions

Fig. 4. 2C-R2PI SEVI images (left column) and corresponding spectra (right column) following the ionization of styrene via various intermediate states, recorded with the ionization wavelength set to 294.956 nm, 294.099 nm, 291.139 nm. The photoelectron images are reconstructed images after inverse Abel transformation. The double arrow indicates the directions of the laser polarization.

As seen in Figs. 4a–f, when the low-frequency transitions 41⁰42⁰, 42¹, 41⁰2, 29⁰, 41⁰42⁰, 40⁰41⁰ in S₁ state are used as the intermediate levels, the same transitions to D₀ state of styrene display strong bands based on the Δv=0 propensity rule. An exception is shown in 4g via 28⁰ transition, which suggests a slightly worse Franck-Condon overlap along this vibrationally canonical coordinate.

The strongest peak is observed at the ionic vibrational energy of 67 cm^{-1} via the $41_0^1 42_1^0$ vibrational level in Fig. 4a is obviously recognized as the combination vibration $41^1 42_1^0$. The 508 and 618 cm^{-1} bands are ascribed to combination vibrations $41^1 42_1^0 28^1$ and $41^1 42_1^0 27^1$, respectively. In Fig. 4b, as in the case of pump 42_1^1 transition, three distinct bands observed at 159 , 605 and 713 cm^{-1} are assigned to the 42_1^1 vibration, combination vibrations $42_1^1 28^1$ and $42_1^1 27^1$. Fig. 4e shows the spectra taken via the $41_0^1 42_0^1$ vibrational level in the S_1 state. The highest peak at 289 cm^{-1} corresponds to the combination vibrational band $41^1 42^1$ in the cationic ground state and other two bands at 732 and 842 cm^{-1} are due to the combination vibrations $41^1 42^1 28^1$ and $41^1 42^1 27^1$, respectively.

When the S_1 41_0^2 state is used as the intermediate level shown in Fig 4c, the band at 200 cm^{-1} is assigned to the 41^2 transition. The weak bands located at 381 , 646 and 775 cm^{-1} are ascribed to combination transitions of the $41^2 42^1$, $41^2 28^1$, and $41^2 27^1$, respectively. Since the transition 41^1 is not observed directly in the SEVI spectra, its frequency is estimated by taking half of the overtone to yield a value of 100 cm^{-1} . This is a reasonable approximation because ν_{41} appears harmonic in S_1 (194 cm^{-1}) and is not drastically different in frequency in the cation. Thus the small peak located at 305 cm^{-1} is ascribed to the three-quantum transition 41^3 . The $40^1 41^1$ combination vibration is easily recognized at 816 cm^{-1} in Fig. 4f. The value of ν_{40} and ν_{42} can be determined to be 359 and 189 cm^{-1} due to the established value of ν_{41} and the observed combination bands $40^1 41^1$ and $41^1 42^1$. Therefore the peak located at 359 cm^{-1} is assigned to 40^1 transition. Two weak bands of $40^2 41^1$ and $40^1 41^1 28^1$ are observed at 803 and 901 cm^{-1} , respectively.

The SEVI spectrum obtained through the 29_0^1 vibronic level (238 cm^{-1}) clearly shows that the corresponding 29^1 vibrational band in the D_0 state is located at 254 cm^{-1} , as shown in Fig. 4d. Its first weakly overtone 29^2 vibration is found at 502 cm^{-1} , while the $29^1 28^1$ and $29^1 27^1$ bands can be easily identified at 696 and 816 cm^{-1} , respectively. As shown in Fig. 4g, the frequency of mode 28 is measured to be 449 cm^{-1} , and the two-quantum transition 28^2 is found at 895 cm^{-1} . The peak at 997 cm^{-1} is assigned to the combination band $28^1 27^1$.

Table 1. Vibrational frequencies of styrene in the S₀, S₁ and D₀ states (in cm⁻¹).

Mod e	S ₀		S ₁		D ₀		Approximate description
	Calc.freq. . ^a	Obs.freq. . ^b	Calc.freq. . ^a	Obs.frequ. q.	Calc.freq. . ^a	Obs.frequ. q.	
In plane modes (a' symmetry)							
1	3088	3085	3108		3116		CH ₂ stretch
2	3057	3060	3056		3078		ring CH stretch
3	3049	3055	2995		3073		ring CH stretch
4	3041	3041	3006		3066		ring CH stretch
5	3032	3035	2983		3057		ring CH stretch
6	3025	3027	2977		3053		ring CH stretch
7	3011	3008	2965		3032		CH ₂ stretch
8	2999	2980	2826		3022		vinyl CH stretch
9	1649	1630	1528	1525	1629	1618	C=C stretch; C ₄ -C ₇ bend
10	1606	1601	1473	1492	1539	1530	ring stretch; C ₄ -C ₇ stretch
11	1581	1576	1409	1431	1513		ring stretch
12	1494	1494	1436	1475	1473		C ₄ -C ₇ stretch; ring def.
13	1450	1450	1399	1417	1454	1465	ring stretch; CH bend
14	1422	1412	1352	1379	1421	1410	CH ₂ scissor; C ₄ -C ₇ stretch
15	1334	1334	1341	1357	1368		CH bend
16	1317	1317	1257	1271	1324	1325	ring stretch; C=C bend
17	1290	1296	1138	1149	1281	1303	ring stretch; C ₄ -C ₇ bend
18	1199	1202	1216	1211	1232	1236	C ₄ -C ₇ stretch
19	1179	1182	1149	1187	1194	1194	ring CH bend
20	1157	1156	1129	1098	1163		ring CH bend
21	1087	1083	1033	1031	1103		ring CH bend
22	1033	1033	848	983	1023		ring def.; vinyl CH bend
23	1018	1021	963	961	995		ring def.; vinyl CH bend
24	993	995	922	950	980	983	ring def.
25	770	775	670	748	770	779	C ₄ -C ₇ stretch; ring stretch
26	620	620	562	524	576	644	ring def.

27	549	555	511	438	547	552	C=C bend; ring stretch
28	438	436	393	395	442	449	C ₄ -C ₇ bend; ring stretch
29	229	228 ^d	206	238	237	254	C ₄ -C ₇ bend
Out of plane modes(a'' symmetry)							
30	1007	992 ^c	836		1004		C=C torsion
31	980	985 ^c	937		1009		ring CH bend
32	964	970 ^c	927		995		ring CH bend
33	912	909	749		965		CH ₂ wag
34	910	909 ^c	806		947		ring CH bend
35	832	841	645		805		ring CH bend
36	781	783	711		639		ring CH bend; C ₄ -C ₇ bend
37	694	699	518		793		ring CH bend
38	641	640 ^c	431		513		C ₄ -C ₇ bend; ring CH bend
39	437	433 ^c	383		386		ring puckering
40	402	399 ^d	255	253	367	359	ring def.
41	199	199 ^d	96	97	96	100	C ₄ -C ₇ bend
42	32	38 ^d	191	186	189	188	C ₄ -C ₇ torsion

^a Mode 1-8 frequencies scaled by 0.96, mode 9-42 frequencies scaled by 0.98

^b Reference 12

^c Reference 9

^d Reference 24

Table 2. A possible new assignment of the 1C-R2PI spectrum of styrene

Expt./ cm ⁻¹	Assignment ^a	Assignment ^b	New assignment	Expt./ cm ⁻¹	Assignment ^a	Assignment ^b	New assignment
0	0 ₀ ⁰	0 ₀ ⁰	0 ₀ ⁰	1232			24 ₀ ¹ 41 ₀ ¹ 42 ₀ ¹
59	41 ₀ ¹ 42 ₁ ⁰	42 ₁ ³	41 ₀ ¹ 42 ₁ ⁰	1243			23 ₀ ¹ 41 ₀ ¹ 42 ₀ ¹
149			42 ₁ ¹	1271			16 ₀ ¹
194	41 ₀ ²	42 ₀ ⁶	41 ₀ ²	1289			—
238	29 ₀ ¹	29 ₀ ¹	29 ₀ ¹	1302			24 ₀ ¹ 40 ₀ ¹ 41 ₀ ¹
283	41 ₀ ¹ 42 ₀ ¹	40 ₀ ¹ 42 ₀ ¹	41 ₀ ¹ 42 ₀ ¹	1312			23 ₀ ¹ 40 ₀ ¹ 41 ₀ ¹
350	40 ₀ ¹ 41 ₀ ¹	39 ₀ ¹ 42 ₀ ¹ or 40 ₀ ¹ 42 ₀ ³	40 ₀ ¹ 41 ₀ ¹	1322			24 ₀ ¹ 42 ₀ ²
372	42 ₀ ²	41 ₀ ²	42 ₀ ²	1345			24 ₀ ¹ 28 ₀ ¹
395	28 ₀ ¹	28 ₀ ¹	28 ₀ ¹	1357			15 ₀ ¹

438	27_0^1	$41_0^2 42_0^2$ or $40_0^1 41_0^1$	27_0^1	1379	14_0^1
506	40_0^2	40_0^2	40_0^2	1417	13_0^1
518	$28_0^1 29_0^1$	$29_0^1 40_0^1 41_0^1$	$28_0^1 41_0^1 42_0^1$	1431	11_0^1
524		$28_0^1 42_0^4$	26_0^1	1448	$24_0^1 40_0^1 41_0^1$
529	26_0^1	27_0^1	$38_0^1 41_0^1$	1466	$23_0^1 40_0^2$
538		$38_0^1 42_0^5$	$40_0^1 41_0^1 42_0^2$	1475	12_0^1
549		$28_0^1 42_0^5$	$40_0^1 41_0^3$	1492	10_0^1
565	$41_0^2 42_0^2$	$40_0^2 42_0^2$	$41_0^2 42_0^2$	1525	9_0^1
632	$28_0^1 29_0^1$	$28_0^1 29_0^1$	$28_0^1 29_0^1$	1560	$18_0^1 40_0^1 41_0^1$
681	$28_0^1 40_0^1 41_0^1$	$27_0^1 41_0^1 42_1^0$	$28_0^1 40_0^1 41_0^1$	1569	—
689			$38_0^1 40_0^1$	1583	$18_0^1 42_0^2$ or $19_0^1 28_0^1$
748	25_0^1	25_0^1	25_0^1	1607	$18_0^1 28_0^1$
873			27_0^2	1621	$20_0^1 26_0^1$
921			$26_0^1 28_0^1$	1638	$15_0^1 41_0^1 42_0^1$
943	22_0^1	$37_0^1 39_0^1$	$25_0^1 41_0^2$	1685	$10_0^1 41_0^2$
950	24_0^1	24_0^1	24_0^1	1691	—
961	23_0^1	23_0^1	23_0^1	1697	—
968	20_0^1	$35_0^1 39_0^1$	$36_0^1 40_0^1$	1708	$16_0^1 27_0^1$
974		$37_0^1 38_0^1$	—	1715	$12_0^1 29_0^1$
983	21_0^1	22_0^1	22_0^1	1729	$18_0^1 26_0^1$
998			$25_0^1 29_0^1$	1778	$14_0^1 28_0^1$
1031	$25_0^1 41_0^1 42_0^1$	21_0^1	21_0^1	1813	$13_0^1 28_0^1$
1045			26_0^2	1826	$11_0^1 28_0^1$
1098	$25_0^1 40_0^1 41_0^1$	$25_0^1 39_0^1 42_0^1$	20_0^1	1858	—
1110			$25_0^1 40_0^1 41_0^1$	1868	$12_0^1 28_0^1$
1141	$25_0^1 26_0^1$	$25_0^1 28_0^1$	$25_0^1 28_0^1$	1896	$17_0^1 25_0^1$
1149	17_0^1	20_0^1	17_0^1	1910	24_0^2
1187		19_0^1	19_0^1	1922	23_0^2
1198		$23_0^1 29_0^1$	$23_0^1 29_0^1$	1958	$18_0^1 25_0^1$
1211	18_0^1	18_0^1	18_0^1		

^a Reference 27

^b Reference 16

Table 3. Observed styrene peak locations (in cm^{-1}) in the D_0 state

Assignments	Styrene transition excited							
	0_0^0	$41_0^1 42_1^0$	42_1^1	41_0^2	29_0^1	$41_0^1 42_0^1$	$40_0^1 41_0^1$	28_0^1
0^0	0							
28^1	449							449
27^1	552							
26^1	645							
25^1	779							
28^2	895							892
24^1	983							
19^1	1194							
18^1	1236							
17^1	1303							
16^1	1325							
15^1	1369							
14^1	1410							
10^1	1530							
9^1	1618							
$41^1 42_1^0$		67						
$41^1 42_1^0 28^1$		508						
$41^1 42_1^0 27^1$		618						
42_1^1			159					
$42_1^1 28^1$			605					
$42_1^1 27^1$			713					
41^2				200				
41^3				305				
$41^2 42^1$				381				
$41^2 28^1$				646				
$41^2 27^1$				775				
29^1					254			
29^2					502			
$29^1 28^1$					696			

$29^1 27^1$	816		
$41^1 42^1$		289	
$41^1 42^1 28^1$		732	
$41^1 42^1 27^1$		842	
40^1			359
$40^1 41^1$			451
$40^2 41^1$			803
$40^1 41^1 28^1$			901
28^2			895
$28^1 27^1$			997

4. Discussions

1. Ionization energy

For measurement of the IP of styrene, we utilized a number of different ionization wavelengths via S_1 0_0^0 origin at 34759 cm^{-1} in SEVI spectra. The position of the outmost ring associated with the $D_0 \leftarrow S_1$ origin transition is plotted versus the photon energy to acquire a linear relationship with respect to each other, as shown in Fig. 5. Extrapolation of the linear fit to the center of the image corresponding to the zero-kinetic energy yields the adiabatic IP, which is estimated to be $68267 \pm 6\text{ cm}^{-1}$ ($8.46383 \pm 0.000744\text{ eV}$), in good agreement with the $68267 \pm 5\text{ cm}^{-1}$ value derived from previous ZEKE spectroscopy measurement [31].

Fig. 5. The total photon energy is plotted against the squares of the radial positions corresponding to the 0_0^0 peak of the styrene cation. Data points are marked with empty circles. Several photoelectron images are shown together. A linear regression enables the extrapolation of this peak position to zero radius from which the IP denoted by an arrow is deduced.

2. The vibrational frequencies in the S_1 state

Table 2 shows all observed transitions in the 1C-R2PI spectrum and our new assignments compared with the assignments reported by Zilberg et al.[16] and Syage et al. [27]. The frequencies of ν_{42} and ν_{41} modes in S_1 are experimentally measured to be 186 and 97 cm^{-1} by Syage. However, the frequency of 97 cm^{-1} reported by Zilberg was assigned as 42^3 transition due to their calculation revealing the frequencies of modes 42 and 41 being 33 and 155 cm^{-1} , respectively. There is still a large gap between the experimental values and the calculated ones in S_1 , so some vibrational assignments relevant to the out-of-plane vibrations should be reconsidered.

According to our calculated results, the frequencies of ν_{40} , ν_{41} and ν_{42} modes in S_1 state are determined to be 255 , 96 and 191 cm^{-1} , which are in excellent agreement with the reported experimental values [26,27] and our determined ones. There is every reason to believe that the frequency of 97 cm^{-1} is assigned as mode 41.

According to the vibrational mode analysis provided by Hemley et al. [17], Mode 42 is composed of 75% C_4 - C_7 torsion, 10% ring torsion, 8% ring out of plane bending and 7% substituent out of plane bending. 17% of mode 41 is ascribed to be C_4 - C_7 torsion while the remaining is 48% ring torsion and 35% ring out of plane bending motion. The C_4 - C_7 torsion component of mode 42 and 41 explains their strong coupling.

Mode 40 is characterized as 59% ring torsion, 40% ring out of plane bending vibration and 1% C₄-C₇ torsion. The same vibrational components of mode 40 and 41 explain the strong coupling of both modes.

The peaks at 529, 689 and 968 cm⁻¹ are assigned to the combination bands 38₀¹41₀¹, 38₀¹40₀¹, and 36₀¹40₀¹, respectively. Modes 36 and 38 are related to the out-of-plane C₄-C₇ bending with the ring CH bending. These four modes are strongly coupled because of the motion of C₄-C₇. The frequencies of modes 36, 38, 40 and 41 are determined to be 711, 431, 253 and 97 cm⁻¹, respectively. So the assignments of transitions at 529, 689 and 968 cm⁻¹ to the combination bands 38₀¹41₀¹, 38₀¹40₀¹ and 36₀¹40₀¹ should be reasonable.

The assignments for modes 9-24 of styrene in S₁ state are conflicting with the previous works. For instance, the frequency of ν₂₀ is considered to be 967 [20,27], 959 [24], 1114 [26] or 1146 [16] cm⁻¹. Our calculation at TD-B3LYP/6-311++G(d, p) level suggests a possible reassignment of these modes for S₁ state. According the calculated results, the frequencies of ν₂₄, ν₂₃, ν₂₂, ν₂₁ and ν₁₉ modes in S₁ state, which were assigned to be 960 [20], 940 [26], 948 [24], 959 [24] and 966 [24] cm⁻¹, are now proposed to be 950, 961, 983, 1031 and 1187 cm⁻¹, respectively. These assignments are in accordance with the Zilberg's assignments[16]. Furthermore, the ν₀⁰ + 1098 cm⁻¹ transition may be assigned to mode 20 rather than to the 25₀¹40₀¹41₀¹ [27] and 25₀¹39₀¹42₀¹ combination transitions [16].

The combination transitions 25₀¹28₀¹ and 18₀¹28₀¹ locate at 1141 and 1607 cm⁻¹ with medium intensity. Mode 25 is related to the in-plane C₄-C₇ bending, and mode 28 and 18 are involved in the in-plane C₄-C₇ stretching. The frequencies of modes 18, 25 and 28 are measured to be 1208, 748 and 395 cm⁻¹ in S₁, so it is reasonable that the peak with a frequency of 1141 and 1607 cm⁻¹ is assigned to the combination transitions 25₀¹28₀¹ and 18₀¹28₀¹, respectively.

3. The vibrational frequencies in the D₀ state

Frequencies of transitions 29¹, 28¹, 25¹, and 18¹ relevant to the in-plane C₄-C₇ motion along with ring stretching vibrations are measured to be 254, 449, 779, and 1236 cm⁻¹ for styrene cation in the D₀ state. The corresponding frequencies of these normal modes are measured to be 237, 395, 748, and 1211 cm⁻¹ for the molecule in the neutral vibronic excited S₁ state. Clearly, frequencies of these vibrations of this molecule in the D₀ state are slightly higher than those in the S₁ state. An interpretation is that the molecular geometry of styrene along these canonical coordinates is slightly more rigid in the cationic D₀ state than that in the neutral S₁ state as supported by theoretical prediction.

Mode 27 and 16 are related to the in-plane double bond bending vibration. In the 1C-R2PI spectrum mode 27 and 16 are weak transitions at 438 and 1271 cm⁻¹, whereas in the SEVI spectra, they correspond to the strong transitions at 552 and 1325cm⁻¹. Mode 9 (in-plane double bond stretching with C₄-C₇ bending) is observed as a medium peak at 1525 cm⁻¹ in the 1C-R2PI spectrum, but strongly appears in the SEVI spectra

at 1618 cm⁻¹. The motion of double bond is not obvious in the excited state with the antibonding π electron, nevertheless the Franck-Condon overlap of these three modes become larger due to the removal of π^* electron.

Mode 42 is related to the C₄-C₇ single bond torsion vibration. Mode 42 has a frequency of 188 cm⁻¹ in the cation, which is representing little change from the first excited state of 186 cm⁻¹ but more than 38 cm⁻¹ in the ground state. Removing the π^* electron does not affect the interaction of the vinyl group with the ring. The frequencies of mode 41 corresponding to the C₄-C₇ single bond bending decrease from 213 cm⁻¹ in the S₀ state to 97 cm⁻¹ in S₁. The SEVI spectra reveal that the frequency of cation is 100 cm⁻¹. The frequencies of the S₁ and D₀ state are close but much lower than the S₀ state, indicating that the molecular geometry of styrene is more rigid with the π electron. Mode 40 is involved in the out-of-plane ring deformation. It is found to have a frequency of 359 cm⁻¹ in the ground state of cation, which is between the excited state frequency of 253 cm⁻¹ and the ground state frequency of 422 cm⁻¹. The antibonding π electron makes the ring more flexible.

4. Photoelectron Angular Distribution

The photoelectron angular distribution (PAD) is obtained by integrating the intensity of the Abel-inverted image. The PADs in two-photon ionization with linearly polarized light are generally described by the function: [38,39]

$$I(\theta) = k[I + \beta_2 P_2(\theta) + \beta_4 P_4(\theta)], \quad (1)$$

where θ is the angle between the electron velocity vector and the laser polarization direction in the laboratory frame, k is a normalization constant proportional to the total photoionization cross-section, and P_2 and P_4 are the second-order and fourth-order Legendre polynomials. The angular dependence is completely defined by β , the anisotropy parameter, which can be determined by fitting Eq. (1) to the experimental PAD.

Fig. 6. The photoelectron angular anisotropy parameters (β_2 and β_4) obtained from the images pumping by S₁0₀⁰ level shown in Fig. 2 as a function of PKE. The solid and hollow symbols indicate β_2 and β_4 values, respectively. Different symbols represent the values obtained for different vibronic states in the D₀ state.

The PAD is determined by a photoelectron scattering wave that varies with the photoelectron kinetic

energy (PKE) and the vibronic state of the cation upon ionization. The values of β_2 and β_4 following excitation of S_1 0_0^0 vary with PKE displayed in Fig. 6. The graph shows that the β_2 decreases slowly with the increase of PKE and gently fell into negative value within 1700 cm^{-1} above the ionization threshold; however the β_4 values vacillate near zero. All values of β_2 and β_4 are available in Table S4.

PAD studies of difluorobenzene isomers [40-42] and our previous work for aniline [43] all suggest that the decrease of β_2 parameter is dramatic with the increase of PKE. This behavior is believed to be a near threshold shape resonance taking place in the ionization due to the virtual π^* antibonding orbital mainly concentrated on the benzene ring [41,42]. However the virtual π^* antibonding orbital of styrene extends to the vinyl group under the influence of C-C double bond [5]. Based on above analysis, there is no observable near threshold shape resonance detected in the case of styrene.

5. Conclusion

The energies, geometries, and vibrational frequencies of styrene in S_1 and D_0 states are studied in detail by the R2PI and SEVI techniques in combination with the high-level theoretical calculations. The neural ground state appears to be planar with the B3LYP/6-311++G(d, p) level calculation. The predicted vibrational frequencies agree well with the experiment results. For S_1 state, the planar feature is revealed under the theoretical calculation at TD-B3LYP/6-311++G(d, p) level. With the $\pi^* \leftarrow \pi$ excitation, the benzene ring is expanded unsymmetrically and the double bond is lengthened a bit, whereas the length of C_4 - C_7 bond decreases. The interaction of the vinyl group with the ring is enhanced. The 1C-R2PI spectrum of styrene gives the $S_1 \leftarrow S_0$ electron transition energy, $34729 \pm 3\text{ cm}^{-1}$. Most low-frequency vibrations are unambiguously identified with the aid of calculated results. Some controversially high-frequency vibrational modes are reassigned in comparison of theoretical results. In the 2C-R2PI SEVI spectra, the accurate IP is obtained to be $68267 \pm 6\text{ cm}^{-1}$. The SEVI spectra taken via various S_1 intermediate states provide accurate vibrational frequencies of styrene in cationic ground state. The vibrational frequencies of the D_0 state calculated at the B3LYP/6-311++G(d, p) level are in excellent agreement with the experimental results to aid in assigning some high-frequency modes.

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