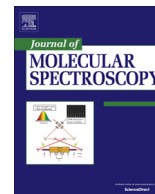




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journal homepage: www.elsevier.com/locate/jmsIonization energy and active cation vibrations of *trans*-2-fluorostyrenePei Ying Wu^{a,b}, Sheng Yuan Tzeng^{a,c}, Ya Chu Hsu^{a,c}, Wen Bih Tzeng^{a,c,*}^a Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-166, 1, Section 4, Roosevelt Road, Taipei 10617, Taiwan^b Department of Chemistry, National Taiwan University, 1, Section 4, Roosevelt Road, Taipei 10617, Taiwan^c Department of Chemistry, National Taiwan Normal University, 88, Section 4, Tingzhou Road, Taipei 11677, Taiwan

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ABSTRACT

We applied the two-color resonant two-photon mass-analyzed threshold ionization (MATI) technique to record the cation spectra of *trans*-2-fluorostyrene by ionizing via six intermediate vibronic levels. The adiabatic ionization energy was determined to be $69304 \pm 5 \text{ cm}^{-1}$. The distinct MATI bands at 67, 124, 242, 355, 737, 806, 833, and 993 cm^{-1} were assigned to the active cation vibrations related to out-of-plane substituent-sensitive bending vibrations and in-plane ring deformation and bending motions. Many combination vibrations were also observed. Our experimental results suggest that the molecular geometry and vibrational coordinates of the *trans*-2-fluorostyrene cation in the D_0 state resemble those of the neutral species in the S_1 state.

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1. Introduction

Because of substituent–ring and substituent–substituent interactions, the geometries, vibrations, and other molecular properties of di-substituted benzenes are different from those of benzene. Gaseous 2-fluorostyrene (or called 1-ethenyl-2-fluorobenzene) has been investigated by radiofrequency microwave double resonance spectroscopy [1]. It is found that the stable configuration of this molecule has a *trans* form with the vinyl group twisted by 13.6° with respect to the plane of aromatic ring. In a similar experiment, *trans*-2-fluorobenzaldehyde appears to be planar owing to formation of a weak H···F bonding [2]. In the case of 2-fluoronitrobenzene, the through-space interaction between the O atoms and the F atom causes the nitro group rotates by about 32° with respect to the ring [3].

The observed molecular vibrations of 2-fluorostyrene in the ground S_0 state have been tabulated on the basis of the results from the IR experiments [4]. Hollas and Hussein [5] recorded the excitation and dispersed laser-induced fluorescence (LIF) spectra of 2-fluorostyrene and reported the active molecular vibrations in the S_0 and electronically excited S_1 states. They proposed that only the *trans* form involved in the $S_1 \leftarrow S_0$ electronic transition. To the best of knowledge, neither the ionization energy (IE) nor the cation spectrum of *trans*-2-fluorostyrene has been reported. Both zero-kinetic energy (ZEKE) photoelectron [6–8] and

mass-analyzed threshold ionization (MATI) [9–12] spectroscopy are powerful methods for recording the vibrationally resolved cation spectra. These experimental results give information about the precise adiabatic IE and active molecular vibrations in the cationic ground D_0 state. In particular, the latter method provides mass information and is useful to confirm the detected molecular species.

In this paper, we report the vibronic, photoionization efficiency (PIE), and cation spectra of *trans*-2-fluorostyrene, recorded by using the two-color resonant two-photon ionization (2C-R2PI) and MATI techniques. The MATI spectra were recorded by ionizing via six intermediate vibronic levels to investigate the molecular geometry and to detect more active vibrations of the cation. We also performed the ab initio and density functional theory (DFT) calculations to support our experimental findings.

2. Experimental and computational methods

We performed these experiments by using a laser based photoionization time-of-flight (TOF) mass spectrometer described elsewhere [13]. 2-Fluorostyrene (98% purity) was purchased from Sigma-Aldrich and used without further purification. The two-color resonant two-photon excitation process was achieved by utilizing two independent tunable UV laser systems controlled by a delay/pulse generator (Stanford Research Systems DG535). The first laser system consists of a Nd:YAG pumped dye laser (Quanta-Ray PRO-190-10/Lambda-Physik, ScanmateUV with BBO-III crystal; R590, and R610 dyes). Its output visible radiation was frequency-doubled to produce UV radiation. The second tunable

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UV laser (Lambda-Physik, ScanmateUV with BBO-III crystal; R575, and R590 dyes) was pumped by a frequency-doubled Nd:YAG laser (Quanta-Ray LAB-150). A laser wavelength meter (Coherent, WaveMaster) was used to calibrate the wavelengths of both lasers. These two counter-propagating laser beams were focused and intersected perpendicularly with the molecular beam at 50 mm downstream from the nozzle orifice.

In the resonant two-photon MATI experiments, both prompt ions and high n Rydberg neutrals were formed simultaneously in the laser-molecular beam interaction zone. A pulsed electric field of -1 V/cm was applied about 32 ns after the occurrence of the laser pulses to remove the prompt ions. About 11.8 μ s later, a second pulsed electric field of $+200$ V/cm was applied to field-ionize the high n Rydberg neutrals in the second TOF lens region. The newly formed threshold ions were directed to fly through a 1.0 m field-free region and detected by a microchannel plate particle detector.

All calculations were performed by using the Gaussian 09 program package [14]. The fully optimized geometries, total energies and vibrational frequencies in the S_0 , S_1 , and D_0 states were obtained. The calculated vibrational frequencies were used as references for spectral assignment. The IE was deduced from the difference in the zero-point energy (ZPE) levels of the cation in the cationic ground D_0 state and the corresponding neutral species in the S_0 state.

3. Results

3.1. Vibronic spectrum

We recorded the vibronic spectrum of 2-fluorostyrene by using the 2C-R2PI technique. This experiment was done by scanning the excitation laser from 280 nm to 292 nm while fixing the wavelength of the ionization laser at 285.00 nm (35088 cm^{-1}). Under this experimental condition, the excess energy is estimated to be no more than 1330 cm^{-1} . No fragment ions were observed in the TOF spectrum. Fig. 1(a) shows the vibronic spectrum of *trans*-2-fluorostyrene, obtained by this 2C-R2PI method. The 0_0^0 band appears at 34342 ± 2 cm^{-1} , which is in excellent agreement with the previously reported value on the basis of the excitation LIF experiment [5]. The excitation LIF experiment only needs one laser and its signal is related to fluorescence quantum yield. However, the 2C-R2PI experiment requires the excitation and ionization lasers. The spatial and temporary overlaps of the two lasers are crucial in addition to the ionization probability of each vibronic state. As seen in Fig. 1(a) and (b), the distinct vibronic bands at 254, 649, and 713 appear in the present 2C-R2PI and previous excitation LIF [5] spectra. However, other spectral features are somewhat different. In particular, Hollas et al. observed several weak combinational bands in their fluorescence excitation spectrum under the experimental conditions with background pressure of about 1.5×10^{-4} Torr. They also stated that the fluorescence intensity was not corrected for the variation of laser power with wavelength. In contrast, the laser-molecular beam interaction region was maintained at a pressure of about 4×10^{-8} Torr during our R2PI experiments [13]. Furthermore, our optical spectra were normalized to the laser power. Fig. 1(c) displays the simulated spectrum, obtained by the B3LYP/6-311++G(d,p) calculations, which involve consideration of both S_0 and S_1 states. The vibronic bands X_0^2 , 4_0^1 , and 1_0^1 observed in the 2C-R2PI and LIF spectra match those predicted by the calculations.

Table 1 lists the vibronic bands of *trans*-2-fluorostyrene appeared in Fig. 1(a). The spectral assignment was done by comparing these data with the experimental values of literature values of 2-fluorophenylacetylene [15] and *trans*-2-fluoroanisole [16] as well as the predicted vibrational frequencies from the time-dependent Becke three-parameter with the Lee–Yang–Parr

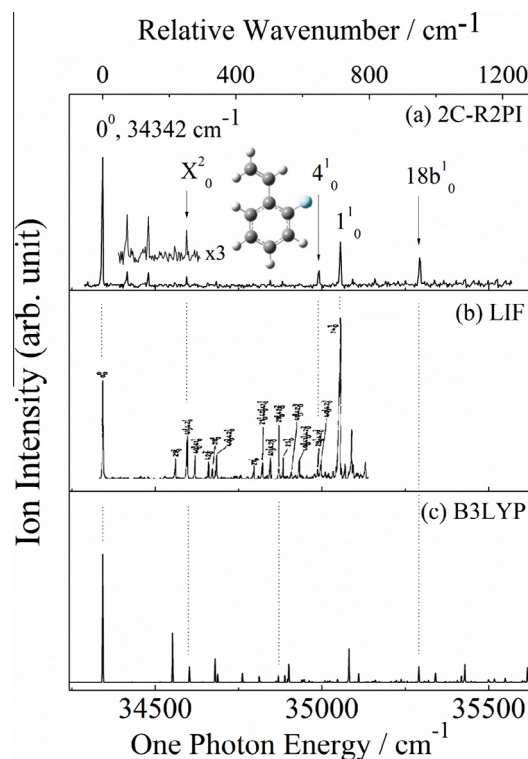


Fig. 1. Vibronic spectrum of *trans*-2-fluorostyrene. (a) The 2C-R2PI spectrum was obtained by scanning the excitation laser while fixing the ionization laser at 285.00 nm (35088 cm^{-1}). (b) The excitation LIF spectrum was obtained from Ref. [5]. (c) The simulated spectrum was calculated at the B3LYP/6-311++G(d,p) level.

functional (TD-B3LYP) calculations with the 6-311++G(d,p) basis set. The numbering system of the normal vibrations follows that used by Varsanyi and Szoke [4,17] for benzene derivatives and is based on Wilson's notations [18]. The normal vibrations can be viewed on a computer screen by using the Gaussview program [19]. The pronounced vibronic bands at 713 and 950 cm^{-1} result from vibronic transitions 1_0^1 and $18b_0^1$, which are related to the breathing and in-plane ring-H bending vibrations of *trans*-2-fluorostyrene in the S_1 state, respectively. The spectral features at 73 and 649 cm^{-1} are assigned to vibronic transitions $10b_0^1$ and 4_0^1 , respectively. Mode 10b involves out-of-plane vinyl-ring bending vibration, whereas mode 4 results from out-of-plane ring deformation. The low-frequency bands at 135 and 254 cm^{-1} in Fig. 1 are assigned to the fundamental and overtone transitions X_1^1 and X_2^2 related to the out-of-plane vinyl C=C bending motions, respectively.

3.2. Cation spectra

We performed both the PIE and MATI experiments to record the cation spectra of *trans*-2-fluorostyrene. The PIE experiment was

Table 1
Observed vibronic bands (in cm^{-1}) of *trans*-2-fluorostyrene in Fig. 1.^a

Ref. [5]	Exp.	Cal.	Assignment and approximate description ^b
	0		0_0^0 band origin
	73	85	$10b_0^1$, γ (ring-vinyl)
	135	165	X_0^1 , γ (vinyl, C=C)
253	254		X_0^2 , γ (vinyl, C=C)
649	649	639	4_0^1 , γ (CCC)
716	713	709	1_0^1 breathing
	950	983	$18b_0^1$, β (ring-H)

^a The experimental values are shifts from the 0_0^0 band at 34342 cm^{-1} , whereas the calculated ones are obtained from the TD-B3LYP/6-311++G(d,p) calculations (scaled by 0.97).

^b β , in-plane bending; γ , out-of-plane bending.

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