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Mass-analyzed Threshold Ionization Spectroscopy of Rotamers of *p*-ethoxyphenol Cations and Configuration Effect[†]Qiu-sha Zheng^{a,b,c}, Teng I Fang^a, Bing Zhang^b, Wen Bih Tzeng^{a*}*a.* Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 106*b.* State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, China*c.* Graduate School of the Chinese Academy of Sciences, Beijing 100049, China

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Two-color resonant two-photon mass-analyzed threshold ionization (MATI) spectroscopy was used to record the vibrationally resolved cation spectra of the selected rotamers of *p*-ethoxyphenol. The adiabatic ionization energies of the *trans* and *cis* rotamers are determined to be 61565 ± 5 and 61670 ± 5 cm^{-1} , which are less than that of *p*-methoxyphenol by 645 and 643 cm^{-1} , respectively. Analysis on the MATI spectra of the selected rotamers of *p*-ethoxyphenol cation shows that the relative orientation of the ethoxy group has little effect on the in-plane ring vibrations. The low-frequency OC_2H_5 bending vibrations appear to be active for both forms of the cation.

Key words: Mass-analyzed threshold ionization spectroscopy, *p*-ethoxyphenol, Cation, Vibration

I. INTRODUCTION

Spectroscopic studies on phenol derivatives help us to have insights into photochemical and photophysical properties of tyrosine, because phenol is the base molecule of an important amino acid tyrosine which is related to UV absorption [1,2]. Among these derivatives, alkoxyphenols have alkoxy and hydroxyl groups which may act as active sites for chemical reactions. As the oxygen atom of the alkoxy group shares its lone-pair electrons with the benzene ring as that of the hydroxyl group, it is believed that both of the two groups may act as active sites for chemical reactions. Patwari *et al.* used laser-induced fluorescence (LIF) and hole-burning spectroscopy to study the intramolecular vibrational relaxation of *p*-alkoxyphenols in the electronically excited S_1 state [3,4]. They found that the *trans* and *cis* rotational conformers (rotamers) coexist in the sample. However, the LIF and hole-burning spectroscopy can not explore ionic properties. Since the ionization energies of various isomers may differ by only a few tens to a few hundreds of wavenumbers, a high-resolution spectroscopic method is needed for probing the ionic properties of the selected rotamers.

Since the well-defined intermediate states can be specified with the first photon, the beam resonance-

enhanced multiphoton ionization (REMPI) technique can be used to select a particular species in a mixture for a variety of spectroscopic experiments. The ionic properties of these rotamer species can be investigated by using zero-kinetic energy (ZEKE) photoelectron or mass analyzed threshold ionization (MATI) spectroscopy with a resonant excitation scheme. Both ZEKE and MATI spectroscopy can give precise ionization energy (IE) and cation spectra of selected conformers [5–9]. In addition to the distinct IE value of each rotamer, the obtained spectra may be used as fingerprints for identifying the specific rotamer of molecular ions.

To our knowledge, the detailed spectroscopic data of the selected rotamers of *p*-ethoxyphenol in the cationic ground D_0 state are not yet available in the literature. Here, we report the MATI spectra of the selected *trans* and *cis* rotamers of *p*-ethoxyphenol. Comparison of these results with those of phenol [10], *p*-hydroquinone [11], and *p*-methoxyphenol [12] gives insights into the substitution effects on the transition energy and molecular vibration. We have also performed *ab initio* and density functional theory (DFT) calculations to provide possible interpretation for our experimental findings.

II. EXPERIMENTS

The experiments were performed with a time-of-flight mass spectrometer described elsewhere [13]. The *p*-ethoxyphenol (Aldrich, 99% purity) sample was heated up to about 94 °C to acquire sufficient vapor pressure. The vapors were seeded into 0.2–0.3 MPa of helium

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and expanded into the vacuum through a pulsed valve with a 0.15 mm diameter orifice. The two-color resonant two-photon excitation process was initiated by utilizing two independent tunable UV laser systems controlled by a delay/pulse generator (Stanford Research Systems DG535). A Fizeau-type wavemeter (New Focus 7711) was used to calibrate the wavelengths of both lasers. These two counter-propagating laser beams were focused on and intersected perpendicularly with the molecular beam at 50 mm downstream from the nozzle orifice. In the MATI experiments, about 70 ns after the occurrence of the laser pulses, a pulsed electric field of -2.0 V/cm was switched on to reject the prompt ions. About 8.8 microseconds later, a second pulsed electric field of 420 V/cm (duration= 10 μ s) was applied to field-ionize the Rydberg neutrals. These threshold ions were then accelerated and passed a 1.0 m field-free region before being detected by a dual-stacked microchannel plate detector. The ion signal from the detector was collected and analyzed by a multichannel scaler (MCS, Stanford Research Systems, SR430). The MCS and the transient digitizer were interfaced to a personal computer.

All *ab initio* and DFT calculations were performed by using the Gaussian 03W program package [14]. The computations give information about the molecular geometries, total energies, and vibrational frequencies of *p*-ethoxyphenol in the S_0 , S_1 , and D_0 states. The IE was obtained as the difference in the zero-point level (ZPL) of the cation and the corresponding neutral in the ground state. Since the frequency calculations are on the basis of the harmonic oscillator model, the obtained frequencies are scaled by an appropriate value to correct approximately for the combined errors stemming from basis set incompleteness, neglecting of electron correlation and vibrational anharmonicity [15].

III. RESULTS AND DISCUSSION

A. 1C-R2PI spectra of *p*-ethoxyphenol

Figure 1 shows the one-color resonant two-photon ionization (1C-R2PI) spectrum of jet-cooled *p*-ethoxyphenol in the energy range near its $S_1 \leftarrow S_0$ electronic transition. The observed vibronic features are in good agreement with those reported in the literature [3]. The pronounced bands at 33550 ± 2 and 33647 ± 2 cm^{-1} are identified as the band origins of the *trans* and *cis* rotamers.

For benzene derivatives, the $S_1 \leftarrow S_0$ transition is mainly subject to the $\pi^* \leftarrow \pi$ electronic excitation, leading to an expansion in the ring. This gives rise to many active vibronic transitions related to the benzene-like vibrations [16]. The observed 1C-R2PI bands and assignments are in good agreement with those reported in the literature [3]. The pronounced bands resulting from the 15_0^1 , $6a_0^1$, 1_0^1 , and $7a_0^1$ transitions appear at 154 , 319 ,

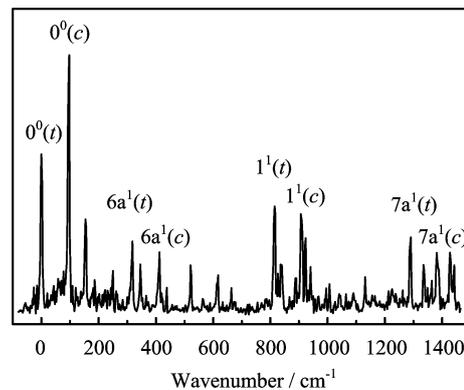


FIG. 1 1C-R2PI spectrum of *p*-ethoxyphenol. The transition origins of the *trans* (*t*) and *cis* (*c*) rotamers appear at 33550 and 33647 cm^{-1} , respectively.

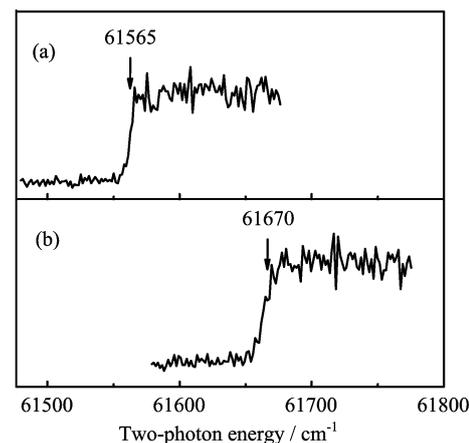


FIG. 2 2C-R2PI spectra of the (a) *trans*, (b) *cis* rotamers of *p*-ethoxyphenol, recorded by ionizing via their $S_1 0^0$ intermediate states.

814 , and 1291 cm^{-1} for the *trans* rotamer and at 153 , 315 , 809 , and 1283 cm^{-1} for the *cis* rotamer, respectively. The present results indicate that different orientation of the OH with respect to the OC_2H_5 group only slightly affects the frequencies of these in-plane ring vibrations.

B. MATI spectra of selected rotamers of *p*-ethoxyphenol

To our knowledge, the IE of *p*-ethoxyphenol is not yet available in the literature. In principle, each value of the rotamers is expected to be unique if it can be measured precisely. We have performed the two-color resonant two-photon ionization (2C-R2PI) and MATI experiments to locate the IEs of the selected rotamers of *p*-ethoxyphenol. Figure 2 shows the 2C-R2PI spectra of the *trans* and *cis* rotamers of *p*-ethoxyphenol recorded by ionizing via their vibrationless $S_1 0^0$ levels at 33550 and 33647 cm^{-1} , respectively. Investigations on the rising steps yield the respective adiabatic IEs of these iso-

TABLE I Observed bands (in cm^{-1}) in the MATI spectra of *p*-ethoxyphenol and possible assignments^a.

<i>Trans</i>				<i>Cis</i>			Assignment and approx. description ^c
$0^{0b}_{\text{Exp.}}$	$6a^{1b}_{\text{Exp.}}$	$1^{1b}_{\text{Exp.}}$	Cal.	$0^{0b}_{\text{Exp.}}$	$6a^{1b}_{\text{Exp.}}$	Cal.	
151		168	136	147		135	15^1 , $\beta(\text{C}-\text{OC}_2\text{H}_5)$
	325		310		312	310	$6a^1$, $\beta(\text{CCC})$
372			367	372		367	$9b^1$, $\beta(\text{C}-\text{O})$
					460	445	$15^1 6a^1$
537		537	546	533		545	$6b^1$, $\beta(\text{CCC})$
		645	630				$6a^2$
					690	677	$6a^1 9b^1$
754			734				$9b^2$
821			832	822		833	1^1 , breathing
897			896	897		896	$19a^1$, $\nu(\text{CC})$
967			970	974		967	$18a^1$, $\nu(\text{CH})$
1149	1149		1157		1142	1157	$6a^1 1^1$
1172			1176	1172	1187	1176	$18b^1$, $\beta(\text{CH})$

^a The *trans* experimental values are shifts from 61565 cm^{-1} , the *cis* experimental values are shifts from 61670 cm^{-1} , whereas the calculated one is obtained from the the UB3PW91 (without scaling) calculations using the 6-311++G basis set.

^b Intermediate level in the S_1 state.

^c ν , stretching; β , in-plane bending.

mers to be 61565 and 61670 cm^{-1} , with an uncertainty of about 10 cm^{-1} .

Since the MATI technique involves detection of threshold ions resulting from pulsed field ionization, it leads to a sharp peak at the ionization threshold. Thus, it yields a more definitive IE value than the two-color R2PI approach. Another advantage of MATI over two-color R2PI spectroscopy is that it provides information about the active vibrations of the cation.

Figure 3 displays the MATI spectra of *trans p*-ethoxyphenol recorded by ionizing via the 0^0 , $6a^1$ (0^0+319 cm^{-1}), and 1^1 (0^0+814 cm^{-1}) levels in the S_1 state. The observed bands are listed in Table I, along with the calculated values and their possible assignments. The MATI features shifted from the 0^0 band by 151 , 821 , and 1172 cm^{-1} result from the 15^1 , 1^1 , and $18b^1$ vibrations of the *trans p*-ethoxyphenol cation, as shown in Fig.3(a). Most of the observed bands are related to the in-plane ring deformation vibrations. As the MATI spectrum was recorded by ionizing via the $S_1 6a^1$ state, one dominant band at 325 cm^{-1} in the MATI spectra corresponds to the $6a^1$ vibration of the *p*-ethoxyphenol cation, as seen in Fig.3(b). When the $S_1 1^1$ state is used as the intermediate level, the pronounced band results from vibration $6b^1$, as shown in Fig.3(c). The assignment to the observed MATI bands was made on the basis of our calculations and conformity with the experimental data of this molecule in the S_1 and S_0 states. Mode 15 mainly involves the in-plane substituent-sensitive $\text{C}-\text{OC}_2\text{H}_5$ bending vibration, and mode 6a is related to the in-plane ring deformation vibration. Mode 1 represents the breathing motion,

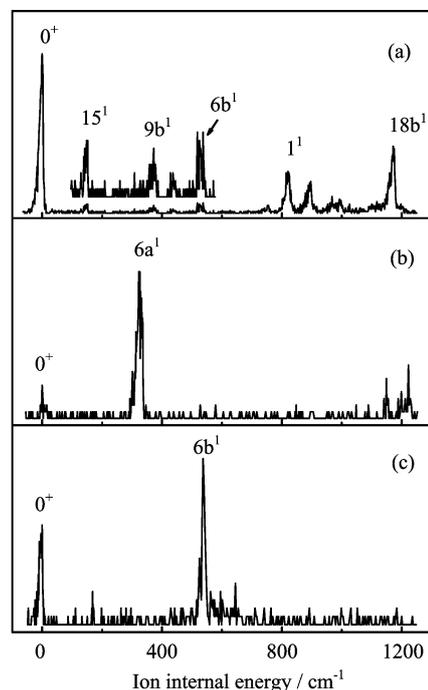


FIG. 3 MATI spectra of *trans p*-ethoxyphenol recorded by ionizing via the (a) 0^0 , (b) $6a^1$, and (c) 1^1 levels in the S_1 state, respectively.

whereas mode 18b is related to the in-plane $\text{C}-\text{H}$ bending vibration. It is noted that mode 1 also appears to be active with respective frequencies of 814 cm^{-1} for this species in the S_1 state. Since vibrational frequency

TABLE II Measured transition energies (in cm^{-1}) of phenol and some of its substituted derivatives^a.

Molecule	$E(S_1 \leftarrow S_0)$	ΔE_1	$E(D_0 \leftarrow S_1)$	ΔE_2	IE	ΔIE
Phenol [10]	36349	0	32276	0	68625	0
<i>p</i> -hydroquinone [11], <i>trans</i>	33500	-2849	30498	-1778	63998	-4627
<i>p</i> -hydroquinone [11], <i>cis</i>	33535	-2814	30516	-1760	64051	-4574
<i>p</i> -methoxyphenol [12], <i>trans</i>	33572	-2777	28638	-3638	62210	-6415
<i>p</i> -methoxyphenol [12], <i>cis</i>	33667	-2682	28646	-3630	62313	-6312
<i>p</i> -ethoxyphenol, <i>trans</i>	33550	-2799	28015	-4261	61565	-7060
<i>p</i> -ethoxyphenol, <i>cis</i>	33647	-2702	28023	-4253	61670	-6955

^a ΔE_1 , ΔE_2 , and ΔIE are shifts of $S_1 \leftarrow S_0$, $D_0 \leftarrow S_1$, and IE with respect to those of phenol.

is proportional to square root of force constant, the observed higher frequency for the cation may result from the slightly stiffer bonds associated with these vibrations.

Figure 4 displays the MATI spectra of *cis p*-ethoxyphenol recorded by ionizing via the 0^0 , $6a^1$ ($0^0 + 315 \text{ cm}^{-1}$), and 1^1 ($0^0 + 809 \text{ cm}^{-1}$) levels in the S_1 state. The frequencies of the observed MATI bands are also listed in Table I, along with the calculated values and their possible assignments. When the $S_1 0^0$ state is used as the intermediate level, the pronounced features corresponding to the 15^1 , 1^1 , and $18b^1$ vibrations appear at 147, 822, and 1172 cm^{-1} , as seen in Fig.4(a). As the MATI spectrum was recorded by ionizing via the $S_1 6a^1$ state, one dominant band at 312 cm^{-1} in the MATI spectra correspond to the $6a^1$ vibration of the *p*-ethoxyphenol cation, as seen in Fig.4(b). When the $S_1 1^1$ state is used as the intermediate level, only one pronounced peak results from transition 0^0 , and no vibration $6b^1$ appears, shown in Fig.4(c).

The excitation energies (EEs) of $S_1 \leftarrow S_0$ electronic transition of phenol [10], *p*-hydroquinone [11], *p*-methoxyphenol [12], and *p*-ethoxyphenol are listed in Table II. It shows that both OH and alkoxy substituents give rise to a red shift in the electronic excitation and ionization energies. The substitution of the *trans* hydroxyl, *cis* hydroxyl, *trans* methoxy, *cis* methoxy, *trans* ethoxy, and *cis* ethoxy group on the para position of phenol causes the EE to be lowered by 2849, 2814, 2777, 2682, 2799, and 2702 cm^{-1} respectively. The substitution also causes the IE to be lowered by 4627, 4574, 6415, 6312, 7060, and 6955 cm^{-1} respectively. These results indicate that the OH group leads to a slightly greater shift in the $S_1 \leftarrow S_0$ excitation energy and a much less red shift in the $D_0 \leftarrow S_1$ transition energy than the alkoxy group. We have also applied various theoretical methods to investigate these findings by calculating the IEs of these molecules. The results show that they all give the same trend in the relative IEs. Since the CH_3 group may donate its electrons through the σ bond, the electron density nearby oxygen is expected to increase. Thus, the alkoxy substitution will cause a less transition energy than the OH substiti-

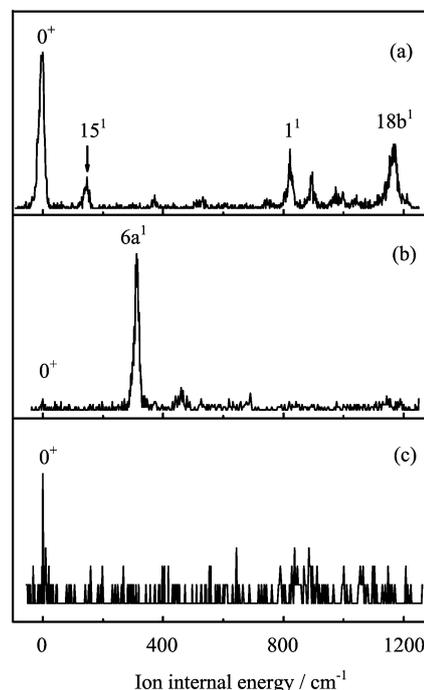


FIG. 4 MATI spectra of *cis p*-ethoxyphenol recorded by ionizing via the (a) 0^0 , (b) $6a^1$, and (c) 1^1 levels in the S_1 state, respectively.

tion. As a result, the alkoxy group causes a greater red shift in the IE than the OH group.

The ethoxy and methoxy substitutions lead to about the same magnitude of red shift in the $S_1 \leftarrow S_0$ excitation energy, the ethoxy substitution gives a greater red shift of 22 cm^{-1} of the *trans* form, 20 cm^{-1} of the *cis* form. Interestingly, the *trans* form gives a greater red shift of 97 cm^{-1} than the *cis* form of *p*-ethoxyphenol in the $S_1 \leftarrow S_0$ excitation energy. In the $D_0 \leftarrow S_1$ transition energy, the ethoxy substitution gives a slightly greater red shift of 623 cm^{-1} of both two forms. It is believed that red shift results from the interaction between the alkoxy group and the aromatic ring. The length of alkoxy chain leads to a slightly smaller red shift for alkoxy group substituent.

Frequencies of vibrations 15^1 , $6a^1$, and 1^1 are measured to be 151, 325, and 821 cm^{-1} for the *trans* and 147, 312, and 822 cm^{-1} for the *cis* conformer of the *p*-ethoxyphenol cation. This indicates that the influence of different orientation of the OH and OCH₃ at the para position on these active in-plane vibrations is negligible.

Comparison of the MATI spectra of phenol, *trans p*-methoxyphenol, *cis p*-methoxyphenol, *trans p*-ethoxyphenol, and *cis p*-ethoxyphenol allows us to investigate the effect of alkoxy group on the vibrations of the phenol cation. It is known that the observed band intensity in the MATI spectra is related to (i) the oscillator strength corresponding to the $S_1 \leftarrow S_0$ transition, (ii) the transition cross section from the S_1 state to the Rydberg state, and (iii) the pulsed field ionization efficiency. In addition, one has to take into consideration of the overlap integral between the molecular coordinates of the neutral and the ion in order to observe more active vibrations of the cation. For instance, the MATI bands related to vibration $6a^1$ of the *trans p*-ethoxyphenol cation are very weak when the $S_1 0^0$ is used as the intermediate level, as shown in Fig.3(a). However, the strongest MATI band results from vibration $6a^1$ when the $S_1 6a^1$ is used as the intermediate level, as seen in Fig.3(b). There are the same features in these MATI spectra of *cis p*-ethoxyphenol, as seen in Fig.4. Therefore, several vibronic states are used as the intermediate levels for recording the MATI spectra in these studies. It is found that most of the MATI spectra demonstrate a propensity of maintaining the vibration of the intermediate level [11,17–19]. The calculated results indicate that the geometries of these molecules in the S_1 state resemble those in the D_0 state. Thus, the theoretical calculations support these experimental findings.

Figure 3(c) shows the MATI spectra of *trans p*-ethoxyphenol recorded by ionizing via the vibrational 1^1 level in the S_1 state, the pronounced band results from vibration $6b^1$, not vibration 1^1 . Figure 4(c) shows the MATI spectra of *cis p*-ethoxyphenol recorded by ionizing via the vibrational 1^1 level in the S_1 state, only one weak peak results from transition 0^0 . It is interesting that the $\Delta\nu=0$ propensity rule does not hold when the $S_1 1^1$ state is used as the intermediate level for recording the MATI spectra of *p*-ethoxyphenol. The calculated results indicate that the geometries of these molecules in the S_1 state resemble those in the D_0 state. Thus, besides the consideration of the changes in molecular geometry and vibrational coordinate there could be other factors leading to the observed breakdown of the $\Delta\nu=0$ propensity rule. Although the MATI spectra here monitor the threshold ions, it is presumed that the intramolecular vibrational relaxation (IVR) dynamics in the excited state maybe play an important role. Patwari *et al.* and Doraiswamy *et al.* [20,21] have studied the IVR dynamics in several *p*-alkyloxylanilines and *p*-alkylanilines by single vibronic level fluorescence spectroscopy. They found that the onset of IVR oc-

curs near 800 cm^{-1} for *p*-alkyloxylanilines and 821 cm^{-1} for *p*-alkylanilines. The observed broad bandwidth in MATI experiments for *p*-propylphenol [22] may imply IVR takes place in the electronically excited $S_1 1^1$ state at 830 cm^{-1} . The onset of IVR in the *p*-ethoxyphenol is set around 800 cm^{-1} referred to the LIF spectroscopy [3]. It is corresponding to the electronically excited $S_1 1^1$ state at 814 cm^{-1} of *trans p*-ethoxyphenol, 809 cm^{-1} of *cis p*-ethoxyphenol.

IV. CONCLUSION

We have applied R2PI and MATI spectroscopy and theoretical calculations to confirm that two rotamers of *p*-ethoxyphenol coexist in the sample. The respective adiabatic IEs of the *trans* and *cis* rotamers of *p*-ethoxyphenol are determined to be 61565 ± 5 and $61670\pm 5\text{ cm}^{-1}$, respectively. Comparison of these values with those of phenol, *p*-hydroquinone, and *p*-methoxyphenol suggests that both OH and alkoxy substituents give rise to a red shift in the electronic excitation and ionization energies, and a longer alkoxy chain causes a greater red shift in the IE. Furthermore, the *cis* form gives a slightly less red shift than the *trans* form. This finding may be attributed to the interaction between the terminal CH₃ of the alkoxy group and the ring in the *cis* rotamers.

Investigations on the MATI spectra of the *trans* and *cis* rotamers of *p*-ethoxyphenol indicate that the general spectral features related to in-plane ring vibrations of the corresponding cations are quite similar. This indicates that the orientation of the OC₂H₅ group with respect to the OH substituent at the para position has little influence on these in-plane ring vibrations. Comparing these values of the cation with the corresponding frequencies suggests that *p*-ethoxyphenol is slightly more rigid in the cationic D_0 state than in the neutral S_1 state.

V. ACKNOWLEDGMENT

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