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Review

Rotamers of aromatic molecules studied by two-color resonant two photon ionization and mass-analyzed threshold ionization spectroscopy

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ABSTRACT

Combination of the molecular beam, two-color resonant two-photon ionization, and mass-analyzed threshold ionization spectroscopic techniques can be used to record the vibrationally resolved spectra of rotational isomers (rotamers) in the electronically excited S_1 and cationic ground D_0 states. These vibronic and cation spectra can be used as the fingerprints for identification of the selected rotamers. Analysis of these experimental data leads us to have better insights into substitution and conformational effects on various molecular properties.

KEYWORDS: resonant two-photon ionization, threshold ionization, vibronic spectra, cation spectra

1. INTRODUCTION

Many biological systems consist of rotational isomers (rotamers) which can be interconverted by rotations about single bonds. It is known that rotamers can possess different reactivity in biological phenomena and processes [1-4]. For these reasons, rotamers of benzene derivatives have become an attractive research subject for spectroscopists who focus on understanding photochemical and photophyscial properties of various selected rotamers.

By nature, different rotamers may coexist in chemical samples at room temperature [5]. Separation and identification of specific rotamers can be quite challenging. The traditional spectroscopic methods, such as IR or Raman spectroscopy, cannot distinguish these rotamers in the condensed phases. Most of the benzene derivatives can absorb UV photons and be excited to the electronically excited states. However, the resulting vibronic spectra can be very complicated at room temperature due to the population of a large number of rovibrational levels in the ground electronic state [6].

Supersonic jet laser spectroscopy can be used to record vibronic spectra with discrete spectral features for each isomeric species [7-10]. It has been demostrated that the combined supersonic jet-cooled resonance-enhanced multiphoton ionization (REMPI) in conjunction with time-of-flight mass spectrometry (TOFMS), hole-burning spectroscopy, and theoretical calculations can confirm the presence of different conformers [11-14]. These methods can provide information about the molecular vibrations of specific conformers in the electronically excited state. Previous experiments show that the origins of electronic transitions and vibrational frequencies of active mode for different rotamers may differ only as small as a few tens of wavenumbers

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[10-14]. As a result, the vibronic features of different isomeric species may overlap in a common spectral region [15, 16]. A spectroscopic method with capability of species selection is needed to confirm the existence of rotamers.

An excellent approach to study molecular conformers is zero-kinetic energy (ZEKE) [17-23] photoelectron or mass-analyzed threshold ionization (MATI) [24-32] spectroscopy with two-color resonant excitation scheme. These methods can provide information on a unique set of precise adiabatic ionization energy (IE) and the active cation vibrations of the selected isomers of the molecular system. In particular, the MATI method can provide mass information and is trouble-free from complications caused by impurities, complexes, and clusters.

In this article, we review the results of the ZEKE and MATI experiments for investigating rotamers of aromatic molecules. Although this survey is by no means complete, the measured data on the first electronic excitation energy (E_1), adiabatic ionization energy, and active vibrations of molecules in the electronically excited S_1 and cationic D_0 states allow us to study the substitution effects on the transition energy and molecular vibration.

2. EXPERIMENTAL METHODS

The apparatus used for these experiments is a TOF mass spectrometer equipped with two tunable UV lasers [33]. Since the benzene derivatives usually have low vapor pressure at room temperature, these chemical samples were heated to 50-120°C to obtain sufficient quantity of vapors. The vapors were seeded into 2-3 bar of helium and expanded into the vacuum through a pulsed valve with a 0.15 mm diameter orifice. The molecular beam was collimated by a skimmer located 15 mm downstream from the nozzle orifice. During the experiments, the gas expansion and the ionization regions were maintained at a pressure of 1×10^{-3} and 1×10^{-5} Pa, respectively.

The two-color resonant two-photon excitation process was initiated by utilizing two independent tunable UV laser systems controlled by a pulse delay generator (Stanford Research Systems, DG 535). The excitation (pump) source is a Nd:YAG (Quanta-Ray GCR-3) pumped dye laser (Lambda-Physik, Scanmate-2 OG with BBO-I crystal) with bandwidth ≤ 0.3 cm^{-1}. The visible radiation is frequency doubled to produce UV radiation. The ionization (probe) UV laser (Lambda-Physik, Scanmate-2 with BBO-III crystal) was pumped by a frequency-doubled Nd:YAG (Quanta-Ray LAB-150). A Fizeau-type wavemeter (New Focus 7711) was used to calibrate the wavelengths of both dye 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 two-color resonant two-photon ionization (2C-R2PI) experiments, the specific rotamer is selected by fixing the excitation laser while scanning the ionization laser. Analysis on the rising step in the photoionization efficiency (PIE) curve yields an IE with an uncertainty of about 10-20 cm^{-1}. In a typical MATI experiment, about 50-2000 ns after the occurrence of the laser pulses, a pulsed electric field of -1.0 V/cm was switched on to reject the prompt ions. About 8-12 microseconds later, a second pulsed electric field of 140-200 V/cm was applied to field-ionize the Rydberg neutrals. These threshold ions were then accelerated and passed through a field-free region before being detected by a dual-stacked microchannel plate detector. The MATI technique leads to a sharp peak at the ionization threshold and thus gives a more precise IE value. In addition, we can apply the state-selective method to record the MATI spectra via different intermediates. It allows us to observe more active vibrations of the cation. The lowest energy band (usually labeled 0^+) in a MATI spectrum corresponds to the signal of the vibrationless cations. Because the threshold ions are formed by pulsed field ionization (PFI) of high n Rydberg neutrals with energy of a few wave numbers below the true ionization threshold, the determination of the adiabatic IE should consider the high-energy side of the 0^+ band [34, 35]. The energy lowering (in cm^{-1}) due to the Stark effect may be estimated by $4.0\ F^{1/2}$ when a pulsed field F (in V/cm) is applied [36]. This method generally leads to an uncertainty of 4-6 cm^{-1} in the determination of the IE.

Ab initio and density functional theory (DFT) calculations were performed to predict the molecular structure, energy, vibrational frequency and other properties using the GAUSSIAN 09 program package [37]. These calculations give a spin multiplicity $<S^2>$ of 0.75 for the cation. The IE was obtained as the difference in the zero-point energies of the cation in the D_0 state and the corresponding neutral in the S_0 state. The calculated results are very helpful in the spectral assignment and provide possible interpretation for the experimental findings.

3. Theoretical calculations for identification of rotamers

One may perform theoretical calculations to predict whether rotamers exist as stable species. Here, we choose *m*-fluoroanisole [38] as a model molecule to show how to incorporate calculated results to support the experimental findings. Previous studies [16, 39] show that the DFT methods give better predictions on the electronic transition and ionization energies than the *ab initio* methods. The Becke three-parameter functional with the restricted Lee-Yang-Parr correlation functional (RB3LYP) calculations with the aug-cc-PVDZ basis set predict that in the S_0 state *m*-fluoroanisole has two stable rotamers. In addition, the zero-point energy level (ZPE level) of the cis rotamer is lower than that of the trans rotamer by 25 cm^{-1}. The theoretical calculations also predict that *m*-fluoroanisole has two stable rotamers in the S_1 and D_0 states.

The E_1's of the cis and trans rotamers have been found to be at 36,662 and 36,819 cm^{-1}, whereas the IEs are 67,867 and 68,304 cm^{-1}, respectively [38]. Therefore, the ZPE levels of the cis rotamer in the S_1 and D_0 states can be deduced to be lower than those of the trans rotamer by 182 and 462 cm^{-1}, respectively, as shown in Figure 1.

The time-dependent B3LYP/aug-cc-PVDZ calculations predict the E_1's of *cis*-*m*-fluoroanisole and *trans*-*m*-fluoroanisole to be at 38,925 and 38,952 cm^{-1}, whereas the unrestricted B3LYP/aug-cc-PVDZ predict the corresponding IEs to be 66,048 and 66,509 cm^{-1}, respectively. Although the calculations overestimate the E_1 by about 6% and underestimate the IE by about 3%, they all predict that the cis has lower values in these two transition energies. These results indicate that the calculated results are consistent with those found in the vibronic and cation spectroscopic experiments

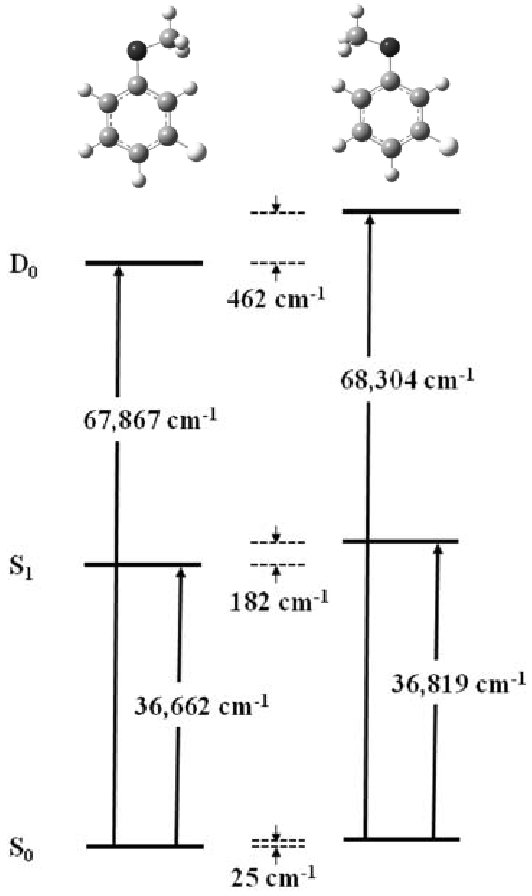


Figure 1. Energy level diagram of the cis and trans rotamers of *m*-fluoroanisole in the S_0, S_1, and D_0 states. The energy is in unit of cm^{-1}. The relative energy of the two rotamers in the S_0 state is obtained from the aug-cc-PVDZ/6-311++G(d,p) calculations, whereas those in the S_1, and D_0 states are deduced from the vibronic and MATI experimental measurements and the predicted value in the S_0 state.

4. Substitution effects on the transition energy

It is known that the functional group of benzene derivatives can interact with ring by the inductive effect through the σ bonds or by the conjugation effect through the π orbitals. The collective effect causes a slight change of the nearby electron density and molecular geometry. It causes a lowering of the ZPE level of the electronic state. When these molecules absorb UV photons, they are usually subject to a $\pi^* \leftarrow \pi$ electronic transition. Many spectroscopists perform the excitation laser-induced fluorescence or REMPI experiments [5, 11, 12] to record the vibronic spectrum which contains information about the electronic excitation energy and active vibrations in the electronically excited state.

The cation spectra of aromatic molecules can be recorded by the ZEKE or MATI experiment in connection with either the one-photon vacuum ultraviolet (VUV) [40-42] or the two-color resonant two-photon UV scheme. Since the two-color resonant two-photon method offers species selection, it is more appropriate for studies of rotamers of aromatic molecules. In the present review, we only collect the data obtained from the two-color resonant two-photon ZEKE and MATI experiments.

Table 1 lists the measured electronic transition and ionization energies of some rotamers of para di-substituted benzenes by the R2PI, ZEKE and MATI experiments. The E_1 and IE of benzene have been reported to be 38,086 and 74,557 cm^{-1}, respectively [43, 44]. It is evident that the E_1's and IEs of these di-substituted benzenes are smaller than those of benzene by 4234-4836 cm^{-1} and 10,506-13,994 cm^{-1}, respectively. These results indicate that the magnitude of lowering of the ZPE level of the upper S_1 or D_0 state is greater than that in the lower S_0 state. In other words, the interaction between the substituent and the aromatic ring in the upper S_1 or D_0 state is greater than that in the lower S_0 state.

5. Influence of transition energy by the nature and relative orientation of the substituent

For di-substituted benzenes, both the substituent-ring and substituent-substituent interactions exist in each electronic state. The collective effect of these two types of interactions is different for each electronic state. Depending on the nature and the relative orientation, each rotamer has a unique E_1 and adiabatic IE.

As seen in Table 1, the E_1's and IEs of the cis rotamers of hydroquinone [16], *p*-methoxyphenol [45], *p*-ethoxyphenol [46], and *p*-dimethoxybenzene [16] are slightly greater than those of the trans rotamers. For para di-substituted benzenes, the two substituents are far apart. As a result, the interaction between the two substituents is minimized. The observation of greater E_1 and IE indicates that the interaction between the subsituent and the aromatic ring in the upper S_1 or D_0 state is slightly smaller than that in the lower S_0 state for the cis rotamer of hydroquinone, *p*-methoxyphenol, *p*-ethoxyphenol, and *p*-dimethoxybenzene.

Table 1. Measured transition and ionization energies (in cm^{-1}) of some rotamers of para di-substituted benzenes by the R2PI, ZEKE and MATI experiments[a].

Molecule	E_1	δE_1	E_2	δE_2	IE	δIE	Ref.
cis-Hydroquinone	33,535	0	30,516	0	64,051	0	16
trans-Hydroquinone	33,500	-35	30,498	-18	63,998	-53	16
cis-*p*-Methoxyphenol	33,667	0	28,646	0	62,313	0	43
trans-*p*-Methoxyphenol	33,572	-95	28,638	-8	62,210	-103	43
cis-*p*-Ethoxyphenol	33,647	0	28,023	0	61,670	0	44
trans-*p*-Ethoxyphenol	33,550	-97	28,015	-8	61,565	-105	44
cis-*p*-Dimethoxybenzene	33,852	0	26,920	0	60,772	0	16
trans-*p*-Dimethoxybenzene	33,631	-221	26,932	12	60,563	-209	16
cis-*p*-Methoxystyrene	33,250	0	29,237	0	62,487	0	51
trans-*p*-Methoxystyrene	33,325	75	29,187	-50	62,512	25	51

[a] The measured origins of $S_1 \leftarrow S_0$ electronic transition and IEs have typical uncertainties of 2 and 5 cm^{-1}, respectively.

In contrast, the E_1 and IE of the cis rotamer of *p*-methoxystyrene are slightly less than those of the trans rotamer. It is noted that *p*-methoxystyrene has a vinyl (ethenyl, $CH=CH_2$) group. As a result of the vinyl-ring interaction, the π-electron delocalization may be enhanced. The observed smaller E_1 and IE suggest that the interaction between the vinyl group and the aromatic ring in the upper S_1 (or D_0) state is slightly greater than that in the lower S_0 state for the cis rotamer of *p*-methoxystyrene.

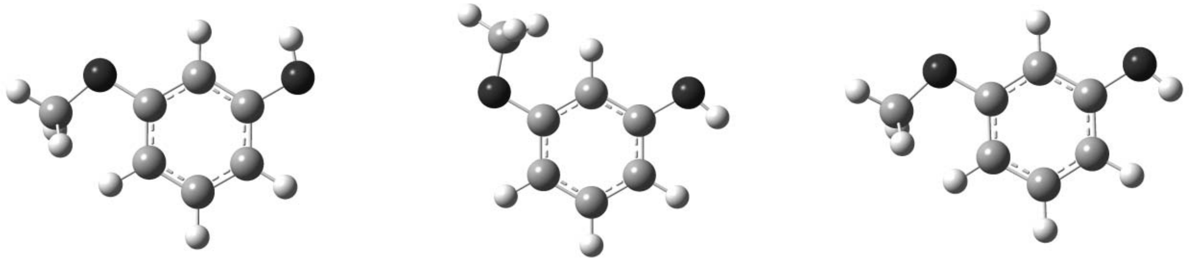
Table 2 lists the measured E_1's and IEs of the rotamers of resorcinol [13], *m*-fluorophenol [5], *m*-cresol [47], *m*-aminophenol [48], *m*-methoxyaniline [49], and *m*-fluoroanisole [38] by the R2PI, ZEKE and MATI experiments. It is clear that the E_1's and IEs of the cis rotamers are slightly smaller than those of the trans rotamers. For these meta di-substituted benzenes possessing OH, OCH_3, NH_2, CH_3, or F substituent, there exists "through-space interaction" between the two substituents. The observed smaller value in the E_1 and IE indicates that "through-space" interaction between the two substituents in the upper S_1 or D_0 state is slightly greater than that in the lower S_0 state for the cis rotamers of these molecular systems.

Previous R2PI and MATI experiments [11, 50] show that three rotamers involve in the photoexcitation and ionization processes of *m*-methoxyphenol and *m*-dimethoxybenzene. The stable structures of these rotamers are shown in Figure 2. As seen in Table 3, the E_1's of the rotamers of *m*-methoxyphenol follow the order: a < b < c, whereas the IEs are b < a < c. For rotamer a of *m*-methoxyphenol, the H atom of the hydroxyl group may interact with the O atom of the methoxyl group by through-space interaction. In the case of rotamer b, the H atom of the methoxyl group may interact with the O atom of the hydroxyl group by through-space interaction. There is no interaction between the hydroxyl and the methoxyl groups in rotamer c. In addition to the interaction between the two substituents, the substituent-ring interaction at different electronic states has to be taken into consideration. The collective effect of the substituent-substituent and substituent-ring cannot be quantified. Therefore,

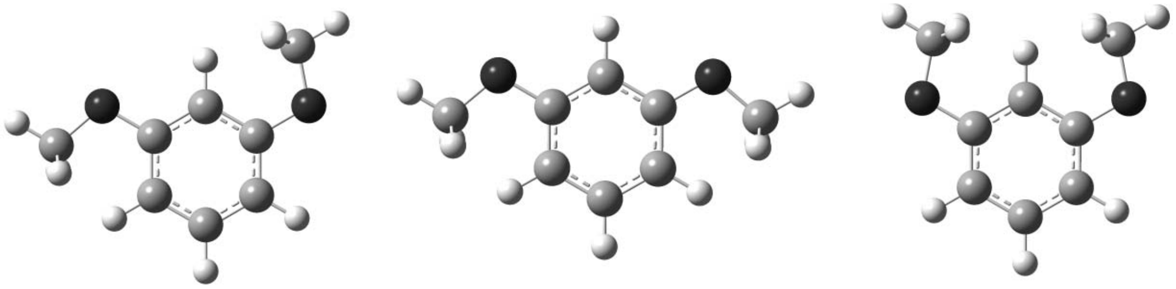
Table 2. Measured transition and ionization energies (in cm^{-1}) of some rotamers of meta di-substituted benzenes by the R2PI, ZEKE and MATI experiments[a].

Molecule	E_1	δE_1	E_2	δE_2	IE	δIE	Ref.
cis-Resorcinol	35,944	0	30,751	0	66,695	0	13
trans-Resorcinol	36,196	252	30,952	201	67,148	453	13
cis-*m*-Fluorophenol	36,623	0	33,565	0	70,188	0	5
trans-*m*-Fluorophenol	36,829	206	33,620	55	70,449	261	5
cis-*m*-Cresol	35,982	0	30,951	0	66,933	0	47
trans-*m*-Cresol	36,098	116	30,986	35	67,084	151	47
cis-*m*-Aminophenol	34,110	0	27,350	0	61,460	0	48
trans-*m*-Aminophenol	34,468	358	27,266	-84	61,734	274	48
cis-*m*-Methoxyaniline	34,308	0	25,675	0	59,983	0	49
trans-*m*-Methoxyaniline	34,495	187	26,384	709	60,879	896	49
cis-*m*-Fluoroanisole	36,662	0	31,205	0	67,867	0	38
trans-*m*-Fluoroanisole	36,819	157	31,485	280	68,304	437	38

[a] The measured origins of $S_1 \leftarrow S_0$ electronic transition and IEs have typical uncertainties of 2 and 5 cm^{-1}, respectively.



m-Methoxyphenol, a *m*-Methoxyphenol, b *m*-Methoxyphenol, c



m-Dimethoxybenzene, a *m*-Dimethoxybenzene, b *m*-Dimethoxybenzene, c

Figure 2. Molecular structures of *m*-Methoxyphenol. and *m*-Dimethoxybenzene.

Table 3. Measured transition and ionization energies (in cm^{-1}) of some rotamers of *m*-Methoxyphenol and *m*-Dimethoxybenzene by the R2PI, ZEKE and MATI experiments[a].

Molecule	E_1	δE_1	E_2	δE_2	IE	δIE	Ref.
m-Methoxyphenol, a	35,974	0	29,254	0	65,228	0	11
m-Methoxyphenol, b	36,034	60	28,707	-547	64,741	-487	11
m-Methoxyphenol, c	36,202	228	29,446	192	65,648	420	11
m-Dimethoxybenzene, a	36,117	0	27,406	0	63,523	0	50
m-Dimethoxybenzene, b	36,185	68	28,306	900	64,491	968	50
m-Dimethoxybenzene, c	36,268	151	27,490	84	63,758	235	50

[a] The measured origins of $S_1 \leftarrow S_0$ electronic transition and IEs have typical uncertainties of 2 and 5 cm^{-1}, respectively.

the determination of the E_1 and IE for each selected rotamers of these molecular systems relies on the results from the vibronic and cation spectroscopic experiments with capability of species selection.

6. Cation vibrations affected by the nature and relative orientation of the substituent

Although di-substituted benzenes have 3n-6 normal vibrations, not all of them can be observed in the electronically vibrational and cationic states. Because the $S_1 \leftarrow S_0$ electronic transition is subject to an $\pi^* \leftarrow \pi$ excitation, it usually gives rise to a vibronic coupling. As a result, many in-plane ring deformation vibrations of these molecules in the S_1 state can be seen in the vibronic spectrum. In particular, modes 1, 6a, and 12 are commonly seen in the vibronic spectra of di-substituted benzenes. Active vibrations of the cation are not easily observed by conventional spectroscopic methods which detect non-energy-selected ions. In contrast, the ZEKE and MATI techniques which detect zero-kenetic threshold ions can give information about the active cation vibrations.

For a 2C-R2PI-MATI process, the intensity of the observed MATI band is related to (1) the oscillator strength of the $S_1 \leftarrow S_0$ transition, (2) the transition probability from the S_1 state to the Rydberg state, (3) the pulsed field ionization efficiency, (4) the overlap integral between the vibrational coordinates of the neutral in the S_1 state and the cation in the D_0 state, (5) the fluctuation of the laser intensity, and (6) the relative abundance of each isomeric species. Therefore, not all cation vibrations of each species can be observed in the spectrum. To observe more active vibrations of the cation, one may record the MATI spectra by ionizing through different intermediate levels in the S_1 state. This procedure is also called the state selection method, mentioned previously.

Table 4 lists the measured frequencies of the active in-plane ring vibrations 6a, 1, and 12 of the rotamers of hydroquinone [16], *p*-methoxyphenol [45], *p*-ethoxyphenol [46], *p*-dimethoxybenzene [16], and *p*-methoxystyrene [51] cations. As mentioned previously, for these para di-substituted benzenes, the interaction between the two substituents is negligible. The difference in vibrational frequency of each mode may only result from the difference in the interaction between the substituent and the ring. In other words, the difference in the vibrational frequency of each mode reflects the nature of the substituent of these molecules. The totally symmetric normal vibration 1 is often referred to as the breathing vibration. Vibrational frequency of this mode is nearly the same for the cis and trans rotamer for each molecular system, as seen in Tables 4 and 5.

For normal mode 6a, the ring atoms C1, C4, and the two substituents in the long axis move

Table 4. Frequencies (in cm^{-1}) of the observed in-plane ring vibrations 6a, 1, and 12 of meta di-substituted benzenes.

Molecule	Vibrational modes			
	6a	1	12	Ref.
cis-Resorcinol	522	736		13
trans-Resorcinol	526	733		13
cis-*m*-Fluorophenol	517	736		5
trans-*m*-Fluorophenol	516	725		5
cis-*m*-Cresol	528	704		47
trans-*m*-Cresol	520	696	979	47
cis-*m*-Aminophenol		744		48
trans-*m*-Aminophenol	527	737	976	48
m-Dimethoxybenzene, a	572	715	961	50
m-Dimethoxybenzene, b	538	707	960	50
m-Dimethoxybenzene, c		716	965	50
cis-*m*-Methoxyaniline		726		49
trans-*m*-Methoxyaniline		709	961	49
cis-*m*-Fluoroanisole	549	714	955	38
trans-*m*-Fluoroanisole	565	716	964	38

Table 5. Frequencies (in cm^{-1}) of the observed in-plane ring vibrations 6a, 1, and 12 of para di-substituted benzenes.

Molecule	Vibrational modes			
	6a	1	12	Ref.
cis-Hydroquinone	454	838	724	16
trans-Hydroquinone	460	837		16
cis-*p*-Methoxyphenol	519	830		45
trans-*p*-Methoxyphenol	517	831	757	45
cis-*p*-Ethoxyphenol	312	822		46
trans-*p*-Ethoxyphenol	325	821		46
cis-*p*-Dimethoxybenzene	523	818		16
trans-*p*-Dimethoxybenzene	396	815		16
cis-*p*-Methoxystyrene	373	810		51
trans-*p*-Methoxystyrene	395	809		51

outwards while other atoms move inwards. The frequency difference between the cis and trans rotamers is no more than 22 cm^{-1} for the hydroquinone, *p*-methoxyphenol, *p*-ethoxyphenol, and *p*-methoxystyrene cations. In the case of *p*-dimethoxybenzene, there is a distinct difference in vibrational frequency in this mode. The frequencies of mode 6a for the *cis* and *trans* rotamers of *p*-dimethoxybenzene are 523 and 396 cm^{-1}, respectively [16], as listed in Table 5. Detailed plots of the atomic displacements on the basis of *ab initio* calculations show that mode 6a of *trans*-*p*-dimethoxybenzene involves the in-plane ring deformation and the O–CH_3 bending vibrations. Nevertheless, the involvement of OCH_3 group in mode 6a of *cis*-*p*-dimethoxybenzene is not significant. Therefore, investigations on the frequencies of different rotamers can be used as a measure for the extent of the substitutents involved in the overall normal vibration. In addition, the relative orientation of the substituent may affect the frequency of some normal vibration.

Table 4 lists the measured frequencies of the active in-plane ring vibrations 6a, 1, and 12 of the rotamers of resorcinol [13], *m*-fluorophenol [5], *m*-cresol [47], *m*-aminophenol [48], *m*-methoxyaniline [49], *m*-fluoroanisole [38], and *m*-dimethoxybenzene [50] cations. As mentioned previously, for these meta di-substituted benzenes possessing OH, OCH_3, NH_2, CH_3, or F substituent, there exists a through-space interaction between the two substituents. Concerning the frequency difference of the rotamers, other factors need to be taken into consideration. These factors include (1) the interaction between the substituent and the aromatic ring, (2) the nature and relative orientation of the substituent, (3) the overall normal vibration, and (4) the molecular symmetry. The measured frequency reflects the collective effect of all of these factors.

CONCLUDING REMARKS

Possible rotamers can be predicted by theoretical calculations. One may apply the 2C-R2PI and MATI techniques to identify the existence of rotamers. In addition, the obtained vibronic and cation spectra can be used as the fingerprints for identification of the selected rotamers.

For para di-substituted benzenes, the two substituents are far apart. Consequntly, the interaction between the two substituents is small. It is found that the E_1's and IEs of the cis rotamers of hydroquinone, *p*-methoxyphenol, *p*-ethoxyphenol, and *p*-dimethoxybenzene are slightly greater than those of the trans rotamers. However, in the case of *p*-methoxystyrene which has a vinyl (ethenyl, $CH=CH_2$) group, the π-electron delocalization is enhanced. As a result, the E_1 and IE of the cis rotamer of *p*-methoxystyrene are slightly less than those of the trans rotamer.

In contrast, the meta di-substituted benzenes possessing OH, OCH_3, NH_2, CH_3, or F substituent, have "through-space interaction" between the two substituents. The experimental results show that the E_1's and IEs of the cis rotamers of resorcinol, *m*-fluorophenol, *m*-cresol, *m*-aminophenol, *m*-methoxyaniline, and *m*-fluoroanisole are slightly smaller than those of the trans rotamers.

Previous experimental results show that both *m*-methoxyphenol and *m*-dimethoxybenzene have three rotamers involved in their photoexcitation and ionization processes. Both the substituent-ring and substituent-substituent interactions exist in each electronic state. Because they cannot be quantified, the determination of the order of the E_1 and IE for each selected rotamers of these molecular systems relies on the experimental measurements.

Concerning the frequency difference of the rotamers, many factors such as, substituent-ring, substituent-substituent interactions and vibrational pattern, need to be taken into consideration. Unfortunately, all of these factors are not easy to be quantified. The Nature, location on the ring, and relative orientation of the substituent can influence the electronic transition and molecular vibration. The obtained experimental data and theoretical calculations can help us have a better understanding about the substitution and conformational effects on various molecular properties.

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