Resonant two-photon ionization and mass-analyzed threshold ionization spectroscopy of the selected rotamers of \textit{m}-methoxyaniline and \textit{o}-methoxyaniline

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Abstract

We report the resonant two-photon ionization and mass-analyzed threshold ionization (MATI) spectra of \textit{m}-methoxyaniline and \textit{o}-methoxyaniline. The vibronic features of \textit{m}-methoxyaniline are built on 34308 ± 2 and 34495 ± 2 cm\(^{-1}\) corresponding to the origins of the \(S_1 \leftrightarrow S_0\) electronic transition (\(E_1's\)) of the \textit{cis} and \textit{trans} rotamers. Analysis of the MATI spectra gives the adiabatic ionization energies (IEs) of 59983 ± 5 and 60879 ± 5 cm\(^{-1}\) for these two species. \textit{o}-Methoxyaniline is found to have only one stable structure whose \(E_1\) and IE are 33875 ± 2 and 58678 ± 5 cm\(^{-1}\), respectively. Most of the active vibrations of \textit{m}- and \textit{o}-methoxyaniline in the electronically excited \(S_1\) and cationic ground \(D_0\) states result from the in-plane ring vibrations. Comparing these data with those of \textit{p}-methoxyaniline allows us to learn about the vicinal substitution effects resulting from the relative locations of the NH\(_2\) and OCH\(_3\) substituents.

Keywords: Resonant two-photon ionization; Threshold ionization; Vibronic spectra; Cation spectra; \textit{m}-Methoxyaniline; \textit{o}-Methoxyaniline

1. Introduction

Investigations on molecular conformers are essential for understanding many biochemical phenomena and processes [1]. \textit{m}-Methoxyaniline can form a conducting copolymer with diphenylamine and may be used in many industrial applications [2]. The ionization energy (IE) of \textit{m}-methoxyaniline has been reported on the basis of the electron impact ionization experiments [3]. However, the conformation of this species is not specified. Up to date, the detailed spectroscopic data of \textit{m}-methoxyaniline in the electronically excited \(S_1\) and cationic ground \(D_0\) states are still not available in the literature. Previous studies [4,5] show that many \textit{meta} di-substituted benzenes may possess \textit{cis} and \textit{trans} rotational conformers (rotamers). These rotamers may coexist in a chemical sample. Since the origins of the electronic transitions of these rotamers may only differ by a few tens to a few hundreds of wavenumbers, the resulting vibronic features may overlap in a common spectral region. To study the selected rotamers, it requires a high-resolution spectroscopic method. Supersonic jet-cooled resonance-enhanced multiphoton ionization (REMPI) in conjunction with time-of-flight mass spectrometry (TOFMS) and hole-burning spectroscopy are useful techniques to confirm the presence of different conformers [5,6]. These methods can provide information about the molecular vibrations of specific conformers in the electronically excited state.

An alternative approach to study molecular conformers is to utilize zero-kinetic energy (ZEKE) photoelectron or mass-analyzed threshold ionization (MATI) spectroscopy with two-color resonant excitation scheme. Both methods can give precise adiabatic IEs of the selected conformers as well as the active vibrations of the corresponding cations.

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[4,7]. Since the MATI technique detects ZEKE ions, it has an additional advantage of providing mass information, it has an additional advantage of providing mass information. Thus, it is suitable for the spectroscopic studies of systems containing radicals [8], isotopomers [9], complexes [10], and impurities [11].

When the two substituents of a di-substituted benzene locate in ortho position, existence of possible rotamers can be related to the nature, intra-molecular interaction and steric hindrance of the substituents. Previous studies indicate that only one stable structure exists for catechol [12], o-fluorophenol [13], and o-methoxyphenol [13]. Intuitively, one would expect that o-methoxyaniline also has only one stable structure. However, experimental and theoretical evidences are needed. The IE of this molecule has been determined by the charge transfer experiments [14]. To the best of our knowledge, little is known about the spectroscopic properties of o-methoxyaniline in the S₂ and D₀ states.

In this paper, we report the one-color, two-color resonant two-photon ionization (1C, 2C-R2PI) and MATI spectra of m-methoxyaniline and o-methoxyaniline. These new experimental data provide information about the origins of the S₁ → S₀ electronic transition (E₁'s), IEs, and vibrations of the selected rotamers in the electronically excited S₁ and cationic ground D₀ states. We have also performed ab initio and density functional theory (DFT) calculations to support our experimental findings. The computed vibrational frequencies are used to assign the obtained vibrionic and MATI spectra. Comparing these data with those of p-methoxyaniline [15,16] helps us to gain knowledge about the vicinal substitution effect on substituted anilines.

### 2. Experimental and computational methods

The experiments were performed with a TOF mass spectrometer described elsewhere [7]. Both m-methoxyaniline (99% purity) and o-methoxyaniline (99% purity) were purchased from Sigma–Aldrich and used without further purification. The vapor of these liquid samples was seeded into 2–3 bar of helium 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). The excitation source is a Nd:YAG pumped dye laser (Quanta-Ray PRO-190-10/Lambda-Physik, ScanmateUV with BBO-III crystal; Rhodamine 575, 590, 610, and 640 dyes) with bandwidth ≤ 0.3 cm⁻¹. The visible radiation is frequency doubled to produce UV radiation. The ionization UV laser (Lambda-Physik, ScanmateUV with BBO-III crystal; LDS 765, and 821 dyes) was pumped by a frequency-doubled Nd:YAG laser (Continuum Surelite I-10). A Fizeau-type wavemeter (New Focus 7711) 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 MATI experiments, the pump laser was used to excite the selected molecular species to a specific vibronic level in the S₁ state. The probe laser was scanned to bring the electronically excited molecule to high n Rydberg states lying a few wavenumbers below the ionization limit. Under this condition, both prompt ions and Rydberg neutrals were formed simultaneously in the laser and molecular beam interaction zone. A pulsed electric field of -1.0 V/cm was switched on about 190 ns after the occurrence of the laser pulses to reject the prompt ions. About 9.60 μs later, a second pulsed electric field of +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.

We have also performed ab initio and density functional theory (DFT) calculations to support our experimental findings. All calculations were performed by using the GAUSSIAN 03 program package [17]. The restricted Hartree–Fock (RHF), configuration interaction singles (CIS), and unrestricted HF (UHF) calculations with the 6-311++G** basis set were applied to predict the molecular properties including the vibrational frequencies of these molecules in the S₀, S₁, and D₀ states, respectively. The IE was obtained as the difference in the zero-point level (ZPL) energies of the molecules in the S₀ and D₀ states. The computed vibrational frequencies are used to assign the obtained vibrionic and MATI spectra.

### 3. Results

#### 3.1. m-Methoxyaniline

3.1.1. 1C-R2PI spectrum of m-methoxyaniline

The E₁'s of p-aminophenol, cis m-aminophenol, and trans m-aminophenol, and p-methoxyaniline have been reported to be 31,393, 34,110, 34,468, and 31,581 cm⁻¹, respectively [4,15,16,18–20]. This information helps us to set a proper range for scanning our laser to locate the E₁'s of m-methoxyaniline. Fig. 1 shows the 1C-R2PI spectrum of m-methoxyaniline in the energy range near its S₁ ← S₀ electronic transition. Similar to that reported previously for cis and trans m-aminophenol [18–20], the vibronic bands appear in two series which are built on 34,308 ± 2 and 34,495 ± 2 cm⁻¹ corresponding to the transition origins of the cis and trans rotamers of m-methoxyaniline, respectively. We have applied both ab initio and DFT calculations to predict the E₁'s of these two rotamers. The ZPLs in the S₀, S₁, and D₀ states were calculated by using the RHF and CIS methods with the 6-311+G** basis set, respectively. The E₁'s of cis and trans m-methoxyaniline are estimated to be 40,605 and 41,800 cm⁻¹, respectively.

With the same basis set, the time-dependent Becke three-parameter functional with the PW91 correlation functional (TD-B3PW91) method gives 33,612 and 35,371 cm⁻¹ for
Table 1
Observed bands in the 1C-R2PI spectrum of \( m \)-methoxyaniline and possible assignments

<table>
<thead>
<tr>
<th>Energy (cm(^{-1}))</th>
<th>Relative intensity</th>
<th>Shift (cm(^{-1}))</th>
<th>Cal. (cm(^{-1}))</th>
<th>Assignment (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( c = \text{cis} )</td>
<td>( t = \text{trans} )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>34495</td>
<td>100</td>
<td>0</td>
<td>12 ( ^1 \sigma )</td>
<td>( \beta ), in-plane bending</td>
</tr>
<tr>
<td>34744</td>
<td>10</td>
<td>249</td>
<td>249</td>
<td>( \gamma ), out-of-plane bending</td>
</tr>
<tr>
<td>34963</td>
<td>52</td>
<td>468</td>
<td>503</td>
<td>( \beta ) (CCC)</td>
</tr>
<tr>
<td>35120</td>
<td>42</td>
<td>625</td>
<td>649</td>
<td>( \delta ), ( \gamma ) (CCC)</td>
</tr>
<tr>
<td>35204</td>
<td>117</td>
<td>709</td>
<td>702</td>
<td>( \delta ), breathing</td>
</tr>
<tr>
<td>35443</td>
<td>45</td>
<td>948</td>
<td>948</td>
<td>( \delta ), breathing</td>
</tr>
<tr>
<td>35456</td>
<td>45</td>
<td>961</td>
<td>948</td>
<td>( \delta ), breathing</td>
</tr>
<tr>
<td>35674</td>
<td>18</td>
<td>117</td>
<td>119</td>
<td>( \sigma ), ( \delta )</td>
</tr>
<tr>
<td>35983</td>
<td>12</td>
<td>1671</td>
<td>1671</td>
<td>( \sigma ), ( \delta )</td>
</tr>
</tbody>
</table>

\( ^a \) Obtained from the CIS/6-311++G** calculations (scaled by 0.9).

\( ^b \) \( \beta \), in-plane bending. \( \gamma \), out-of-plane bending.

3.1.2. 2C-R2PI and MATI spectra of \( c = \text{cis} \) \( m \)-methoxyaniline

The IE of \( m \)-methoxyaniline is reported to be 7.8 ± 0.1 eV on the basis of the electron impact ionization measurement [3]. Since this technique typically utilizes electron energy of about 70 eV, it may give information about the vertical IE rather than the adiabatic IE. Due to lack of energy resolution, it does not provide information about molecular conformation. Here, we performed the 2C-R2PI and MATI experiments to determine the adiabatic IEs of the selected species with high precision. Fig. 2a displays the photoionization efficiency (PIE) curve of \( c = \text{cis} \) \( m \)-methoxyaniline recorded by ionizing via its \( S_1 \) intermediate level at 34308 cm\(^{-1}\). Investigation on the rising step gives an IE of 59991 ± 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 and yields a more definitive IE value, as seen in Fig. 2b. Analysis on the 0\(^{+}\) band gives the field-corrected IE to be 59983 ± 5 cm\(^{-1}\) (7.4369 ± 0.0006 eV). The distinctive MATI feature shifted from the 0\(^{+}\) band by 726 cm\(^{-1}\) results from the 1\(^{+}\) vibration of the \( c = \text{cis} \) \( m \)-methoxyaniline cation in
the D₃ state. It is noted that the frequency of this breathing vibration of the cis m-aminophenol cation was found to be 744 cm⁻¹ [19].

3.1.3. 2C-R2PI and MATI spectra of trans m-methoxyaniline

Fig. 3a shows the PIE curve of trans m-methoxyaniline obtained by ionizing via the S₀⁰ intermediate state at 34495 cm⁻¹, giving an IE value of 60880 ± 10 cm⁻¹. Fig. 3b–d show the MATI spectra of trans m-methoxyaniline recorded by ionizing via the 0⁰, 6b¹(0⁰ + 468 cm⁻¹), and 1¹(0⁰ + 709 cm⁻¹) levels in the S₁ state. These yield the field-corrected IE of 60879 ± 5 cm⁻¹ (7.5480 ± 0.0006 eV). The pronounced bands at 507, 724, and 974 cm⁻¹ result from the in-plane ring deformations 6b², 1, and 12 of the trans m-methoxyaniline cation. The respective frequencies of these in-plane vibrations are measured to be 479, 735, and 985 cm⁻¹ for the trans m-methoxyaniline cation [19]. The band at 696 cm⁻¹ in Fig. 3d is tentatively assigned to the combination of the 6b¹ vibration and the O–CH₃ torsion of the trans m-methoxyaniline cation. The weak band at 1449 cm⁻¹ results from the overtone vibration 1².

3.2. o-Methoxyaniline

3.2.1. 1C-R2PI spectrum of o-methoxyaniline

Fig. 4 displays the 1C-R2PI spectrum of o-methoxyaniline in the energy range near its S₁ ← S₀ electronic transition. The band origin appears at 33875 ± 2 cm⁻¹. Similar to o-fluorophenol and o-methoxyphenol [13], only one stable structure is found for o-methoxyaniline. Table 2 lists the observed vibronic bands and their possible assignments. The strong vibronic bands at 118 and 648 cm⁻¹ are related to the out-of-plane O–CH₃ bending (designated as γ(O–CH₃)) and its combination with the in-plane ring deformation 6a⁰. The moderately intense bands at 482, 529, 729, and 838 cm⁻¹ result from the 6a², 12, 0, 1⁰ transitions of o-methoxyaniline. The corresponding frequencies of vibrations 6a₂, 1, and 12 of o-methoxyphenol in the S₁ state are reported to be 526, 726, and 814 cm⁻¹, respectively [13].

Table 2 Observed bands in the 1C-R2PI spectrum of o-methoxyaniline and possible assignments

<table>
<thead>
<tr>
<th>Energy (cm⁻¹)</th>
<th>Relative intensity</th>
<th>Shift (cm⁻¹)</th>
<th>Cal.a (cm⁻¹)</th>
<th>Assignmentb</th>
</tr>
</thead>
<tbody>
<tr>
<td>33875</td>
<td>100</td>
<td>0</td>
<td>0⁰, band origin</td>
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</tr>
<tr>
<td>33993</td>
<td>39</td>
<td>118</td>
<td>98</td>
<td>γ(O–CH₃)</td>
</tr>
<tr>
<td>34109</td>
<td>10</td>
<td>234</td>
<td>210</td>
<td>τ, CH₃ torsion</td>
</tr>
<tr>
<td>34144</td>
<td>10</td>
<td>269</td>
<td>282</td>
<td>10a, γ(C-OCH₃, C–NH₂)</td>
</tr>
<tr>
<td>34204</td>
<td>22</td>
<td>329</td>
<td>329</td>
<td>9b, γ(CCC)</td>
</tr>
<tr>
<td>34343</td>
<td>21</td>
<td>468</td>
<td>462</td>
<td>16b, γ(CCC)</td>
</tr>
<tr>
<td>34357</td>
<td>24</td>
<td>482</td>
<td>463</td>
<td>6b⁰, γ(CCC)</td>
</tr>
<tr>
<td>34404</td>
<td>26</td>
<td>529</td>
<td>561</td>
<td>6b², γ(CCC)</td>
</tr>
<tr>
<td>34471</td>
<td>18</td>
<td>596</td>
<td>98</td>
<td>10a, γ(C–OCH₃)</td>
</tr>
<tr>
<td>34523</td>
<td>58</td>
<td>648</td>
<td>6a⁰, γ(C–OCH₃)</td>
<td></td>
</tr>
<tr>
<td>34593</td>
<td>26</td>
<td>718</td>
<td>6a², γ</td>
<td></td>
</tr>
<tr>
<td>34604</td>
<td>34</td>
<td>729</td>
<td>737</td>
<td>1⁰, breathing</td>
</tr>
<tr>
<td>34614</td>
<td>24</td>
<td>739</td>
<td>1⁰, 10a</td>
<td></td>
</tr>
<tr>
<td>34713</td>
<td>29</td>
<td>838</td>
<td>817</td>
<td>12, γ(C–C)</td>
</tr>
<tr>
<td>34841</td>
<td>47</td>
<td>966</td>
<td>11b, γ</td>
<td></td>
</tr>
<tr>
<td>34958</td>
<td>13</td>
<td>1083</td>
<td>12a, γ</td>
<td></td>
</tr>
</tbody>
</table>

a Obtained from the CIS/6-311++G** calculations (scaled by 0.9).
b β, in-plane bending. γ, out-of-plane bending.
Fig. 5. (a) 2C-R2PI spectrum via the 000, (b and c) MATI spectra of o-methoxyaniline recorded by ionizing via the 000 and c(O–CH3) levels in the S1 state, respectively.

Table 3: Observed bands (in cm⁻¹) in the MATI spectra of o-methoxyaniline and possible assignments.

<table>
<thead>
<tr>
<th>Intermediate level</th>
<th>Cal. Assignment</th>
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<tr>
<td>S00+ S100</td>
<td>S1t</td>
</tr>
<tr>
<td>217</td>
<td>224</td>
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<tr>
<td>260</td>
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<tr>
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</tr>
<tr>
<td>988</td>
<td>988</td>
</tr>
<tr>
<td>1164</td>
<td>1164</td>
</tr>
</tbody>
</table>

Fig. 6 shows the one-dimensional potential energy surfaces of m-methoxyaniline along the dihedral angle of C2C3OC(H3). This result predicts that the energy barrier for the cis-trans isomerization of m-methoxyaniline in the S0 state is in the range of 1051–1100 cm⁻¹. It has been reported that the energy barrier to the O–CH3 torsion of p-dimethoxybenzene is 712 cm⁻¹ at the B3PW91/6-31G* level of calculation [7]. This shows that the NH₂ group in the meta position causes a slightly greater the energy barrier to the O–CH3 torsion than the OCH₃ group in the para position.
The respective $E_1$'s of the cis and trans rotamers of $m$-methoxyaniline are found to be 34,308 and 34,495 cm$^{-1}$ on the basis of our 1C-R2PI experiments. Taking into account this energy difference and calculated energies for the two rotamers in the $S_0$ state, the ZPL in the $S_1$ state of the trans rotamer is expected to be higher than that of the cis one by 82 cm$^{-1}$. This indicates that in the $S_1$ state the interaction between the NH$_2$ and OCH$_3$ groups of the cis rotamer is stronger than that of the trans rotamer.

The adiabatic IEs of the cis and trans rotamers of $m$-methoxyaniline are determined to be 59,983 ± 5 cm$^{-1}$ and 60,879 ± 5 cm$^{-1}$, respectively, with our MATI experiments. With these measured IE values and the calculated energies in the neutral $S_0$ state, the ZPL in the cationic $D_0$ state of the trans rotamer is deduced to be higher than that of the cis rotamer by 791 cm$^{-1}$. Similar to the argument stated previously for the $S_1$ state, the interaction between the NH$_2$ and OH groups of cis $m$-methoxyaniline is stronger than that of trans $m$-methoxyaniline in the cationic $D_0$ state. Our unrestricted B3PW91/6-311+G** calculations predict that the ZPL of the trans rotamer lies higher than that of the cis rotamer by 856 cm$^{-1}$. Although the magnitude is slightly different, the general trend predicted by the theoretical calculations is consistent with the experimental findings. The calculated results shown in Fig. 6 also show that the energy barrier for the cis–trans isomerization of $m$-methoxyaniline in the $D_0$ state is 3132 cm$^{-1}$, which is greater than the value of 1051–1100 cm$^{-1}$ in the $S_0$ state. Our B3PW91/6-311+G** calculations predict that the C3–OCH$_3$ bond of $m$-methoxyaniline is about 1.360 Å in the $S_0$ state and becomes 1.322 Å in the $D_0$ state. The shortening of this C3–OCH$_3$ bond implies a stronger chemical bond and hence a greater isomerization energy barrier in the cationic $D_0$ state. Therefore, the theoretical calculations support our experimental findings. A similar argument has been reported for $m$-aminophenol [19].

Table 4 lists the measured frequencies of in-plane vibrations 6$^a_A$, 1, and 12 of the cis and trans rotamers of $m$-methoxyaniline in the $S_1$ and $D_0$ states. Frequencies of mode 6$^a_A$ are measured to be 465 and 537 cm$^{-1}$ for the cis, and 468 and 507 cm$^{-1}$ for the trans rotamer in the $S_1$ and $D_0$ states, respectively. Evidently, the vibrational frequency of the electronically excited $S_1$ state is less than that of the cationic ground $D_0$ state. A plausible interpretation is that the molecular geometry is less rigid in the $S_1$ state than that in the $D_0$ state. A similar observation has been reported for $p$-methoxyphenol [20] and $p$-methylanisole [23]. Another interesting finding is that frequency of vibration 6$^a_A$ of the cis is slightly less than that of the trans rotamer in the $S_1$. However, it is greater than that of the trans in the $D_0$ state. This indicates that different orientation of the OCH$_3$ group with respect to the NH$_2$ group as well as the electronic structures can influence the degree of both substituents involved in overall motion. The above argument can also be applied to interpret the observed frequencies of vibrations 1 and 12, as listed in Table 4.

When the $S_16^a_A$ and $S_11$ states were used as the intermediate levels for recording the MATI spectra of trans $m$-methoxyaniline, the results show that all the bands related to the same vibrational pattern exhibit strong intensities, as seen in Fig. 3c and d. This indicates that the geometry and the vibrational coordinates of vibrations $6^a_A$ and 1 of the cation resemble those of the neutral species in the $S_1$ state. A similar finding has been reported for trans $m$-aminophenol [19].

4.2. o-Methoxyaniline

To search for possible conformers of o-methoxyaniline, we have performed many ab initio and DFT calculations in the $S_0$, $S_1$, and $D_0$ states. The initial molecular geometries have configurations with different orientation of the O–CH$_3$ with respect to the O–H group. As a result, only one stable structure with the N–H···O–CH$_3$ configuration (see the inserted figure in Fig. 4.) is found. This result is similar to that of o-methoxyphenol [13], whose only stable structure has the O–H···O–CH$_3$ configuration. The general spectral features of o-methoxyaniline in Fig. 4 are somewhat similar to those of o-methoxyphenol [13]. One expects that the active vibrations of these two species in the $S_1$ state are alike. The 0$^1$ bands of the MATI spectra recorded by ionizing through the 0$^0$ and (0$^0 + 118$ cm$^{-1}$) intermediate levels give the same IE value, as seen in Fig. 5b and c. This indicates that both cation spectra of o-methoxyaniline result from the same form. Therefore, our experimental results also imply that there is only one stable structure for o-methoxyaniline in the $D_0$ state.

Analysis on the vibronic and cation spectra of o-methoxyaniline shows that frequency of the breathing motion (mode 1) is 729 cm$^{-1}$ in the $S_1$ and 756 cm$^{-1}$ in the $D_0$ state. This indicates that the molecular geometry of o-methoxyaniline is less rigid in the neutral $S_1$ state than that in the cationic $D_0$ state, as in the cases of the cis and trans rotamers of $m$-methoxyaniline stated previously.

4.3. Substitution effects

The $S_1$ ← $S_0$ transition of benzene derivatives is known to undergo an $\pi\pi^*$ electronic excitation, leading to an expansion in the ring [24]. A substituent can interact with the aromatic ring by the inductive effect through the $\sigma$ bond or by the resonance effect through the $\pi$ orbitals. The collective effect gives rise to a slight change in the neighboring electron density and molecular geometry. Consequently, the ZPL is lowered by a small extent. If

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the degree of the lowering of the ZPL in the upper electronic state is greater than that of the lower one, it causes a red shift in the transition energy. Oppositely, it yields a blue shift.

Table 5 lists the measured $E_1$’s and IEs of o-methoxyaniline, m-methoxyaniline, and p-methoxyaniline, and several substituted anilines [16,19,20,25–29]. These species have a general formula of $XC_6H_4NH_2$, where $X$ is H, OH, OCH$_3$, CH$_3$, or F at the ortho, meta, or para position with respect to the NH$_2$ group. In consideration of the conductive effect, the OH, OCH$_3$ and CH$_3$ are classified as electron-donating groups whereas the F atom is an electron-withdrawing substituent. Previous R2PI and MATI experimental studies [25,26] show that the $S_1 \leftarrow S_0$ excitation mainly occurs around the ring whereas the transition from the $S_1$ to the $D_0$ state corresponds to the removal of one of the lone-pair electrons of nitrogen. Huang and Lombardi [30] performed Stark effect measurements and showed that the $para$ substituted anilines in the $S_1$ state can be viewed as a quinoid-like (dipolar) resonance structure, resulting from the prominent resonance effect. When the OH, OCH$_3$, CH$_3$, or F locate at the $para$ position, they lead to a red shift in the $E_1$ due to the enhanced interaction between the substituents and the ring, as seen in Table 5. As for the $ortho$ and $meta$ positions, the observed shift in the $E_1$ results from the collective effect of the conductive and resonance factors.

As stated previously, the $D_0 \leftarrow S_1$ transition process involves the removal of one of the lone-pair electrons of the nitrogen or oxygen atoms of the substituents of aniline derivatives. Because the OH, OCH$_3$ and CH$_3$ can increase the electron density nearby the atom with lone-pair electrons, the $D_0 \leftarrow S_1$ transition energies ($E_1$’s) of aminophenol, methoxyaniline, and methylaniline are lower than that of aniline. In contrast, the F atom can decrease the electron density and give rise to a higher $E_2$ for fluoroaniline. As the ionization process includes both $S_1 \leftarrow S_0$ and $D_0 \leftarrow S_1$ transitions, the $IE$ is red-shifted for $X =$ OH, OCH$_3$, and CH$_3$ and is blue-shifted for $X =$ F, as seen in Table 5. In addition, the IEs of these o-, m-, p-substituted anilines follow the order: $para < ortho < meta$. These results suggest that both the nature and relative location of substituents can influence the adiabatic ionization energy.

5. Conclusion

We have applied the R2PI and MATI techniques to record the vibrational spectra of m-methoxyaniline and o-methoxyaniline in the $S_1$ and $D_0$ states. Analysis of these new data shows that the $E_1$ and adiabatic IE of cis m-methoxyaniline are determined to be 34 308 ± 2 349 and 59 983 ± 5 cm$^{-1}$, whereas those of its trans rotamer are 34 495 ± 2 and 60 879 ± 5 cm$^{-1}$, respectively. Most of the observed active vibrations of these isomeric species are related to the in-plane ring deformations. The frequencies of vibrations 469 and 1 are measured to be 465 and 706 cm$^{-1}$ for the cis and 468 and 709 cm$^{-1}$ for the trans rotamer in the $S_1$ state; 537 and 726 cm$^{-1}$ for the cis and 507 and 724 cm$^{-1}$ for the trans rotamer in the $D_0$ state, respectively. This indicates that the molecular geometry is less rigid in the $S_1$ state than that in the $D_0$ state. In addition, different orientation of the OCH$_3$ group with respect to the NH$_2$ group as well as the electronic structures can influence the degree of both substituents involved in overall motion.

Similar to the cases of o-fluorophenol and o-methoxyphenol, only one stable structure of o-methoxyaniline is...
found. The \( E_1 \) and IE of \( o \)-methoxyaniline are measured to be \( 33.875 \pm 2 \) and \( 58.678 \pm 5 \) cm\(^{-1} \), respectively. Comparison of the experimental data shows that the \( E_1 \)'s and IEs of \( o-, m-, \) and \( p \)-methoxyanilines follow the order: \( \text{para} < \text{ortho} < \text{meta} \). The relatively low electronic transition and ionization energy of the \( \text{para} \) structural isomer may be attributed to the formation of the quinoid-like structure in the \( S_1 \) and \( D_0 \) states.

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References


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