I. INTRODUCTION

Zero kinetic-energy (ZEKE) photoelectron spectroscopy\(^1\) and mass-analyzed threshold ionization (MATI) spectroscopy\(^6\)\(^-\)\(^8\) are useful techniques to measure accurate ionization energies of neutrals and high-resolution vibration-rotation spectra of cations. In these techniques, a neutral is excited to a Rydberg state lying close to the ionization limit. It is thought that some of the neutrals in Rydberg states (high \(n\), low \(l\)) undergo radiationless transition to high \(n,l,|m_l|\) states, which are generically called ZEKE states and are thought to have lifetimes in microsecond range. Neutrals in ZEKE states are ionized by pulsed electric field. ZEKE and MATI spectra are obtained by recording the electron and ion currents, respectively, as a function of the excitation energy. ZEKE has better resolution than MATI, while the mass selectivity and capability to generate state-selected ions\(^9\) are the advantages of the latter.

Excitation to a Rydberg state via an intermediate state, or two-photon (1+1) scheme, was almost exclusively used in early works on ZEKE and MATI.\(^10\)\(^-\)\(^11\) The fact that powerful monochromatic radiation in the vacuum ultraviolet (VUV) region was not routinely available must have been one of the reasons for the popularity of this scheme. It is to be acknowledged, however, that selection of a particular vibrational state of the intermediate electronic state aids the vibrational assignment of the spectra.\(^12\) More often than not, the first excited electronic state of a molecule cannot be accessed by outputs from commercial dye lasers displays a diffuse spectrum,\(^13\) or has hardly been investigated ever before. The two-photon scheme is impossible or difficult to use in such cases.

The one-photon scheme\(^14\) utilizing coherent VUV generated by four-wave mixing\(^15\)\(^-\)\(^17\) can overcome the above difficulties, enabling ZEKE or MATI spectroscopy for almost any volatile molecule. Compared to the two-photon scheme, its main drawback is that the vibrational state information available through the intermediate state selection in the former is absent, which may cause some difficulties for the vibrational assignment. In this laboratory, investigations were carried out to see if the results from quantum chemical calculations for open-shell cations, both the vibrational frequencies and the intensities of peaks in one-photon MATI spectra, could provide adequate information for spectral assignment. It turned out that the quantum chemical results, especially those from the calculations at the density-functional theory (DFT) level using the B3LYP functionals, were excellent guidelines for spectral assignment as demonstrated in our recent papers.\(^18\)\(^-\)\(^19\) In one case reported, MATI of CH\(_2\)ClI,\(^20\) the results from simple DFT/B3LYP calculations for the cation were not quite adequate. Better, but still not quite satisfactory, agreement between the experimental and calculated results was achieved via rather extensive DFT/B3LYP calculations including the relativistic effects.

One of the molecules investigated with the above perspective was 2-bromopropene, 2-C\(_3\)H\(_5\)Br.\(^19\) Peaks in its MATI spectrum could be assigned readily by utilizing the vibrational frequencies and the Franck-Condon factors obtained at the DFT/B3LYP and BP86 levels. In particular, dramatic lowering of the methyl torsional barrier observed in the calculated results was found to be compatible with the

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\(^{11}\)Author to whom correspondence should be addressed. Electronic mail: myungsso@snu.ac.kr
experimental results. Namely, the spectral pattern could be reproduced remarkably well through quantum-mechanical calculations.

The results from MATI spectroscopic investigation of 2-C₃H₅Cl are reported in this paper. In addition to the fact that photochemistry and ionization of aliphatic halides are important in the upper atmosphere, the incentive for the present work is to confirm that the overall scheme developed to analyze one-photon MATI spectra leads to reliable spectral assignments even for the complicated torsional peaks.

II. EXPERIMENT

2-C₃H₅Cl was purchased from Aldrich and used without further purification. Gaseous sample at 0 °C was seeded in He at the stagnation pressure of 2 atm, supersonically expanded through a pulsed nozzle (diameter: 500 μm, General Valve) and introduced to the ionization chamber through a skimmer (diameter: 1 mm, Beam Dynamics) placed about 3-cm downstream from the nozzle orifice. Typical background pressure in the ionization chamber was 2 × 10⁻⁸ torr.

The method to generate a VUV pulse by four-wave difference frequency mixing in Kr was explained in detail previously and will not be repeated here. The VUV laser pulse was collinearly overlapped with the molecular beam in a counterpropagation manner and slit electrodes along the beam path were used to maximize ion collection efficiency. To achieve pulsed-field ionization of neutrals in the ZEKE state, an electric field of 15–90 V/cm was applied at 10–20-μs delay time after the VUV pulse. Ions were then accelerated, flew through a field-free region, and were detected. Scrambling field was applied at the laser irradiation time, which significantly lengthened the lifetime of the ZEKE states. Photoelectric current from a thin gold plate placed in the VUV beam path was used to calibrate the VUV intensity.

III. THEORY AND COMPUTATION

A. Vibrational selection rule

The selection rule that affects the vibrational peak intensity pattern of a ZEKE or MATI spectrum has been investigated over the years. Under Born-Oppenheimer approximation, the vibrational selection rule determining the ZEKE/MATI spectral pattern becomes equivalent to the rule governing the electronic transitions in neutrals. Almost all the neutrals in the ground electronic state are in the ground vibrational state under the beam condition, which is totally symmetric (a' in the case of 2-C₃H₅Cl). Hence, fundamentals and overtones of totally symmetric modes can appear in the spectrum while only the even number overtones are allowed for nontotally symmetric modes (a'' in the present case). Relative intensities of these electric dipole-allowed transitions are determined by Franck-Condon factors. It is known that the fundamentals of nontotally symmetric modes also appear, even though weakly, via vibronic mechanism.

2-C₃H₅Cl becomes a nonrigid molecule due to the torsional motion of the methyl group. Then, the molecular symmetry group rather than the usual point group must be used. The neutral and the cation of 2-C₃H₅Cl with planar molecular framework belong to the G₅ molecular symmetry group which possesses three irreducible representations, a₁, a₂, and e. Symmetry of a torsional state is classified into one of these depending on the transformation properties of its wave function. In an electric dipole-allowed transition, the vibrational selection rule is determined by the vibrational overlap integral as before, leading to a₁ ↔ a₁, a₂ ↔ a₂, and e ↔ e. Since the ground torsional state of 2-C₃H₅Cl in the ground electronic state consists of the nearly degenerate a₁ and e states, the transitions to the a₁ and e torsional states are electric dipole allowed while those to the a₂ states are forbidden.

B. Energy levels and eigenfunctions of torsional states

The methods to treat the methyl torsional motion were reported previously. A brief outline is as follows. The semirigid model in which a molecule is assumed to consist of rigid methyl group and rigid remainder has been adopted and hence coupling between the torsional motion and other vibrations has been ignored. Since 2-C₃H₅Cl was cooled by supersonic expansion, overall rotation has been ignored (J = 0) and hence torsion-rotation coupling also. Then, the torsional Hamiltonian operator becomes

\[ \hat{H} = -\frac{\hbar^2}{2I_a} \frac{\partial^2}{\partial \phi^2} + V(\phi). \]  

Here \( \phi \) is the torsional angle referred to the framework and \( B \) is the reduced internal rotational constant of the methyl rotor around the methyl top axis given by

\[ B = (2I_a)^{-1} \]

with

\[ r = 1 - I_a(\lambda_a^2I_a + \lambda_b^2I_b) \]

Here \( I_a \) is the moment of inertia of the methyl top, \( I_a, I_b \), and \( I_c \) are the principal moments of inertia, and \( \lambda \) are the direction cosines between the principal axes and the methyl top axis. \( V(\phi) \) is the one-dimensional torsional potential which is usually modeled by symmetry-adapted Fourier expansion.

The first term in the expansion was found to be adequate as in the previous case of 2-C₃H₅Br.

\[ V(\phi) = (V/2)(1 - \cos(3\phi)). \]

The eigenfunctions of the one-dimensional free rotor, \( \cos(m\phi) \) and \( \sin(m\phi) \), were used to construct the Hamiltonian matrix, which was diagonalized to obtain the eigenvalues and the eigenfunctions. The size of the basis set was increased until the truncation error became insignificant, which was achieved at around \( m = 100 \).

C. Franck-Condon factors

The method of Sharpe and Rosenstock was used to calculate the Franck-Condon factors for the electric dipole-allowed vibrational transitions including those for the torsional mode. Properties of the cation were assumed to approximate those of the ion core of a high Rydberg state. Harmonic wave functions were used for vibrations other than...
Quantum chemical calculations were done for the 2-C3H5Cl neutral and cation in the ground states at the DFT/B3LYP and BP86 levels using the GAUSSIAN 98 suite of programs.28 The size of the basis set was systematically increased until the basis-set dependence became insignificant. Equilibrium geometries, transition structures for the methyl torsional motion, and Hessians were obtained for the neutral and the cation. The potential-energy curves for the torsional motion were calculated also by rotating the methyl group and calculating the optimized energy.

IV. RESULTS AND DISCUSSION

A. One-photon MATI spectrum and ionization energy

One-photon MATI spectrum of 2-C3H5Cl recorded by monitoring C3H535Cl+ generated in the ground state is shown in Fig. 2. The spectrum recorded by monitoring C3H537Cl+ looks quite similar except for small isotope shifts and is not shown. The spectrum magnified along the y direction is shown as an inset as an aid for peak identification. The most intense peak at around 76 941 cm−1 in Fig. 2 corresponds to the 0-0 band. Its position in one-photon MATI spectrum is equivalent to the ionization energy. In practice, it is lower than the correct ionization energy because neutrals in ZEKE states lying some cm−1 below the threshold can also be ionized when a high pulsed-field ionization (PFI) field is used. To correct for this effect, the 0-0 position was measured using various PFI fields and the results were extrapolated to the zero-field limit. Spoil field was not applied in such measurements. The ionization energies thus obtained were 9.5395±0.0006 and 9.5394±0.0006 eV for 2-C3H535Cl and 2-C3H537Cl, respectively, as listed in Table I. To our knowledge, this is the first time that the ionization energy for this molecule is reported.

B. Quantum chemical calculations

Optimized geometries and vibrational frequencies of the neutral and the cation and the Franck-Condon factors were

FIG. 1. Atomic numbering for 2-C3H5Cl.
calculated at the Hartree-Fock, the second-order Möller-
Plesset perturbation theory, and DFT levels using various
basis sets. Even though the results obtained at these levels
agreed with one another reasonably well, including the
prediction of $C_s$ symmetry for the neutral and the cation.
The DFT results obtained at the B3LYP and BP86 levels
displayed better agreement with the experimental data than
others. The results obtained at the B3LYP/6-311+
+G(3df, 3pd) level will be presented. Similar results obtained
at the BP86/6-311+ +G(3df, 3pd) level are available through
the journal’s EPAPS service.\(^\text{26}\)

Considering the valence orbital only, the ground-state
electron configuration of the neutral is 
\[ \cdot \cdot \cdot (2a')^2 (9a')^2 (3a')^2, \]
resulting in $\tilde{X}^1A'$. Here \(3a'\) is a $\sigma$ orbital with \(C(1)=C(2)\)
bonding and \(C(2)=Cl\) antibonding characters. \(9a'\) and \(2a'\) are the
chlorine 3$p$ nonbonding orbitals parallel and perpendicular
to the molecular plane, \(n(Cl3p_x)\) and \(n(Cl3p_y)\), respectively.
The ground state of the cation, $\tilde{X}^2A''$, is formed by
removal of an electron from \(3a'\).

The optimized geometries of the neutral and the cation
obtained at the B3LYP/6-311++G(3df, 3pd) level are listed
in Table II together with the experimental data\(^\text{30}\) for the
neutral. It is seen that the calculated geometry agrees with
the experimental data quite well for the neutral. Geometry
changes upon ionization are also listed in the table. As
expected from the character of the orbital losing an electron,
the \(C(1)C(2)\) bond length is lengthened and the \(C(2)Cl\) bond
length is shortened upon ionization. In addition, the
$\angle C(1)C(2)Cl$ and $\angle C(1)C(2)C(3)$ bond angles decrease with
the concomitant increase of $\angle C(3)C(2)Cl$. The results lead
one to expect strong fundamentals and overtones for the
\(C(1)C(2)\) and \(C(2)Cl\) stretchings and the bending modes
including \(C(2)\). Stretchings and bendings including hydrogen
atoms are expected to be very weak or difficult to observe in
the MATI spectrum.

\(2C_2H_3Cl\) has 21 nondegenerate normal modes, 14 of
which belong to $a'$ and 7 to $a''$. Calculated vibrational
frequencies of the neutral and the cation are listed in Table III.
The Mulliken notation has been used to designate the normal
modes. It turned out that the modes designated 2 and 3
exchange their characters upon ionization. The same were
the cases for the pair 19 and 20. The mode designations for the
cation will be used throughout the paper. Among the $a'$
modes, $v_1\sim v_4$ are mostly due to CH stretching, $v_5$ to \(C=C\)
stretching, $v_6, v_8, \text{and} v_10$ to \(CH_3\) deformation, $v_7, v_9, \text{and}
v_{11}$ to combined in-plane bending and skeletal vibration, $v_{12}$
to CCl stretching, and $v_{13}$ to CCCI bending. Among the $a''$
 modes, $v_{15}$ is asymmetric CH stretching in \(CH_3\), $v_{16}\sim v_{20}$
are out-of-plane bending, and $v_{21}$ is \(CH_3\) torsion. Calculated
Franck-Condon factors for the fundamentals in electric
dipole-allowed transition normalized to that of the 0-0 band
are listed in the same table. The results predict strong funda-
mentals of $v_5, v_7, v_8, v_9, v_{11}, v_{12}$, and $v_{13}$ in agreement with
the qualitative prediction based on the geometry changes
upon ionization. The numbers in parentheses show the iso-
tope shifts upon substitution of $^{33}Cl$ by $^{35}Cl$.

The torsional barriers and the reduced rotational con-
stants for the neutral and the cation calculated at the B3LYP
and BP86 levels using the 6-311++G(3df,3pd) basis set are
listed in Table IV. For the neutral, the barriers calculated at
the two levels underestimate the experimental barrier a little.
More importantly, the barrier (925 cm\(^{-1}\)) (Ref. 31) is high
enough to provide vibrational character to several low-lying
torsional states. For the cation, however, the calculated bar-
riers are dramatically lower than that of the neutral. Except
for a few low-lying states, torsional states would have rotational
character. It is to be noted that the methyl torsional barrier for the
cation at the BP86 level is significantly lower than that at the
B3LYP level. The harmonic frequency at the BP86 level is also smaller than that at B3LYP, 12 versus 36 cm\(^{-1}\).

### C. Vibrational assignment

Assuming that the spoil field affects positions of all the
peaks appearing in the MATI spectrum similarly, the vibra-
tional frequency of the cation corresponding to each peak
can be estimated simply by taking the difference of its posi-
tion from that of the 0-0 band. Vibrational frequency scale
with the origin at the 0-0 band position is also shown in Fig.
2. Vibrational frequencies for the fundamentals measured
from the spectrum are listed in Table III together with mode
assignment which will be explained below. Peak intensities

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**TABLE I. Ionization energy (IE) to the ground electronic state of 2-C\(_2\)H\(_3\)Cl cation, in eV.**

<table>
<thead>
<tr>
<th>IE((\tilde{X}^1))</th>
<th>2-C(_2)H(_3)^{36}\text{Cl}</th>
<th>9.5395±0.0006</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2-C(_2)H(_3)^{35}\text{Cl}</td>
<td>9.5394±0.0006</td>
</tr>
</tbody>
</table>

**TABLE II. Geometries of the 2-C\(_2\)H\(_3\)Cl neutral and cation in the ground electronic states calculated at the B3LYP level using the 6-311+ +G(3df,3pd) basis set.**

<table>
<thead>
<tr>
<th>C(_i)</th>
<th>Neutral ((\tilde{X}^1A'))</th>
<th>Cation ((\tilde{X}^2A''))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Expt(^a)</td>
<td>B3LYP</td>
</tr>
<tr>
<td>C(1)(-C(2))</td>
<td>1.338</td>
<td>1.324</td>
</tr>
<tr>
<td>C(2)(-C(3))</td>
<td>1.495</td>
<td>1.493</td>
</tr>
<tr>
<td>C(2)(-Cl)</td>
<td>1.744</td>
<td>1.758</td>
</tr>
<tr>
<td>C(1)(-H(1))</td>
<td>1.089</td>
<td>1.079</td>
</tr>
<tr>
<td>C(1)(-H(2))</td>
<td>1.089</td>
<td>1.081</td>
</tr>
<tr>
<td>C(3)(-H(3))</td>
<td>1.089</td>
<td>1.089</td>
</tr>
<tr>
<td>C(3)(-H(4))</td>
<td>1.089</td>
<td>1.091</td>
</tr>
<tr>
<td>C(3)(-H(5))</td>
<td>1.089</td>
<td>1.091</td>
</tr>
</tbody>
</table>

\(^a\)The experimental values by combined analysis of electron diffraction and microwave spectroscopic data in Ref. 30.\(^b\)Numbers in the parentheses show the geometrical changes upon ionization.
normalized to that of the 0-0 band are also listed and will be compared with the calculated Franck-Condon factors normalized similarly. Isotope shifts are also listed for peaks displaying measurable difference and are compared with the calculated shifts to check the assignment.

It has been mentioned earlier that the calculated Franck-Condon factors predict prominent 5, 7, 8, 9, 11, 12, and 13 peaks. In agreement with this prediction, the MATI spectrum is dominated by strong peaks at 1482, 1366, 1330, 1245, 960, 711, and 384 cm⁻¹ which can be correlated with the observed fundamentals at 1512, 1376, 1347, 1247, 943, 711, and 397 cm⁻¹, respectively. It is to be noted that the isotope shifts observed for these peaks are compatible with the calculated shifts. Other strong peaks appear near the 0-0 band. These are the torsional peaks which will be dealt with later. Other peaks that can be assigned to a' fundamentals are the weak peak at 1012 cm⁻¹ and the shoulder peaks at 370 and 1466 cm⁻¹ which can be correlated with the calculated frequencies at 1006 (10¹), 373 (14¹), and 1478 (6¹) cm⁻¹, respectively. Even though there are very weak peaks at around 3000 cm⁻¹, we are reluctant to assign them to 1¹, 2¹, 3¹, and 4¹ because the calculated Franck-Condon factors for these fundamentals are very small. These features can be due to overtones and combinations of vibrations showing strong fundamentals. Some a'' fundamentals appear weakly in the spectrum presumably via vibronic mechanism. These are the peaks at 1425, 459, and 330 cm⁻¹ which can be assigned to 16¹, 19¹, and 20¹, respectively. Overtones and combinations also appear, which will be described after assigning the torsional peaks.

Several peaks appear prominently in the vicinity of the 0-0 band in the one-photon MATI spectrum such as those at 63, 89, 137, and 193 cm⁻¹. It is to be recalled that the lowest-frequency fundamental other than the torsional vibration is 20¹ which has been assigned to the peak at 330 cm⁻¹ already. A few possibilities were checked before assigning these peaks to the torsional progression. The first was the possibility that some of these were due to hot bands. This possibility was eliminated by observing variation in the relative intensities.

### Table III: Experimental and calculated [B3LYP/6-311+ +G(3df, 3pd)] vibrational frequencies (in cm⁻¹) for the 2-C₃H₅Cl neutral and cation in the ground electronic states, calculated Franck-Condon factors, and peak intensities in MATI.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Symm.</th>
<th>Expt.³</th>
<th>B3LYP</th>
<th>MATI ⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Freq.</td>
<td>Freq.</td>
<td>Freq.</td>
</tr>
<tr>
<td>1</td>
<td>a'</td>
<td>3121</td>
<td>3248</td>
<td>3264</td>
</tr>
<tr>
<td>2</td>
<td>a'</td>
<td>2992</td>
<td>3115</td>
<td>3151</td>
</tr>
<tr>
<td>3</td>
<td>a'</td>
<td>3025</td>
<td>3156</td>
<td>3147</td>
</tr>
<tr>
<td>4</td>
<td>a'</td>
<td>2940</td>
<td>3032</td>
<td>3005</td>
</tr>
<tr>
<td>5</td>
<td>a'</td>
<td>1645</td>
<td>1699</td>
<td>1512</td>
</tr>
<tr>
<td>6</td>
<td>a'</td>
<td>1450</td>
<td>1490</td>
<td>1478</td>
</tr>
<tr>
<td>7</td>
<td>a'</td>
<td>1424</td>
<td>1435</td>
<td>1376</td>
</tr>
<tr>
<td>8</td>
<td>a'</td>
<td>1382</td>
<td>1412</td>
<td>1347</td>
</tr>
<tr>
<td>9</td>
<td>a'</td>
<td>1184</td>
<td>1193</td>
<td>1247</td>
</tr>
<tr>
<td>10</td>
<td>a'</td>
<td>999</td>
<td>1021</td>
<td>1006</td>
</tr>
<tr>
<td>11</td>
<td>a'</td>
<td>926</td>
<td>930</td>
<td>943</td>
</tr>
<tr>
<td>12</td>
<td>a'</td>
<td>641</td>
<td>629</td>
<td>711(-5)</td>
</tr>
<tr>
<td>13</td>
<td>a'</td>
<td>396</td>
<td>403</td>
<td>397(-2)</td>
</tr>
<tr>
<td>14</td>
<td>a'</td>
<td>343</td>
<td>348</td>
<td>373(-2)</td>
</tr>
<tr>
<td>15</td>
<td>a''</td>
<td>2973</td>
<td>3087</td>
<td>3044</td>
</tr>
<tr>
<td>16</td>
<td>a''</td>
<td>1450</td>
<td>1471</td>
<td>1428</td>
</tr>
<tr>
<td>17</td>
<td>a''</td>
<td>1046</td>
<td>1073</td>
<td>1020</td>
</tr>
<tr>
<td>18</td>
<td>a''</td>
<td>879</td>
<td>918</td>
<td>941</td>
</tr>
<tr>
<td>19</td>
<td>a''</td>
<td>434</td>
<td>451</td>
<td>466</td>
</tr>
<tr>
<td>20</td>
<td>a''</td>
<td>692</td>
<td>712</td>
<td>329</td>
</tr>
<tr>
<td>21</td>
<td>a''</td>
<td>195</td>
<td>210</td>
<td>36</td>
</tr>
</tbody>
</table>

³Infrared absorption spectroscopic data in Ref. 31.
⁴Numbers in the parentheses are isotope shifts. Symbols designate the torsional fundamentals.
⁵Franck-Condon factors normalized to that of the 0-0 transition.
⁶Peak intensities (in area) normalized to that of the 0-0 band.

### Table IV: Internal rotational parameters for the 2-C₃H₅Cl neutral and cation, in cm⁻¹, obtained by experiments and quantum chemical calculations. 6-311++G(3df, 3pd) basis set was used.

<table>
<thead>
<tr>
<th></th>
<th>Neutral (X₁A')</th>
<th>Cation (X₂A⁺)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Expt.³ B3LYP BP86</td>
<td>Expt.³ B3LYP BP86</td>
</tr>
<tr>
<td>V₁</td>
<td>925 686.4 711.7</td>
<td>53.6 46.8 19.8</td>
</tr>
<tr>
<td>B</td>
<td>5.50 5.35 5.27</td>
<td>5.20 5.32 5.29</td>
</tr>
</tbody>
</table>

³Determined in this work.
sities of these peaks under relaxed beam expansion condition. The second possibility was that some of these were MATI peaks of other C$_3$H$_5$Cl isomers such as cis-1- and trans-1-C$_3$H$_5$Cl, 3-C$_3$H$_5$Cl, and cyclic-C$_3$H$_5$Cl. Among these compounds, 3-C$_3$H$_5$Cl can be eliminated because its ionization energy, 10.05 eV$^{32}$ is much higher than that of 2-C$_3$H$_5$Cl. There are no literature data on the ionization energies of other compounds and purified samples of these compounds are not commercially available. In the case of bromides, 3-C$_3$H$_5$Br and cyclic-C$_3$H$_5$Br have ionization energies much higher than that of 2-C$_3$H$_5$Br and could be neglected in the assignment of the MATI spectrum of 2-C$_3$H$_5$Br. On the other hand, the ionization energies of cis-1- and trans-1-C$_3$H$_5$Br were lower than that of 2-C$_3$H$_5$Br by around 1000 cm$^{-1}$. Possibility of contamination by MATI peaks from these compounds had been neglected because hardly any signal was present at the 0-0 band positions expected for these compounds. Since ionization of C$_3$H$_5$Br and C$_3$H$_5$Cl removes an electron from the C==C π orbitals, one may assume similar situation for the corresponding chlorine compounds. Accordingly, search was made for the presence of the 0-0 bands of cis-1- and trans-1-C$_3$H$_5$Br by recording the spectrum as low as 1000 cm$^{-1}$ below the 0-0 band position of 2-C$_3$H$_5$Cl, which eliminated the second possibility.

Assuming that the peaks mentioned above were the torsional progression, quantum-mechanical calculations were performed to estimate the positions and the intensities of the torsional peaks. The ground torsional level in the neutral split into 0$_{a_1}$ and 1$e$ states which are nearly degenerate. Since these are the states with different nuclear spin wave functions, both of these will have populations even under the most extreme molecular-beam expansion condition. Hence one expects to observe na$_1$ ← 0a$_1$ and ne ← 1$e$ torsional transitions in the MATI spectrum. The torsional energy levels of the cation calculated by using the torsional parameters obtained at the B3LYP/6-311++G(3df, 3pd) level were very useful to identify these transitions. Namely, the na$_1$ and ne states were found at 31, 57, 91, 139, 197, and 266 cm$^{-1}$ above the ground vibrational state of the cation in good agreement with the experimental data. Then, we attempted to further improve the parameters via regression. The torsional parameters thus obtained and the torsional energy levels calculated therefrom are listed in Tables IV and V, respectively. It is to be noted that even the weak shoulder peak at 52 cm$^{-1}$ can be correlated with the forbidden transition to the 3a$_2$ state even though the mechanism for its appearance is not clear.

It is known that a$_1$ or a$_2$ torsional states must have a$_1$ nuclear spin states while $e$ states must have $e$ nuclear spin states$^{33,34}$ and that the statistical weights$^{35,36}$ of a$_1$, a$_2$, and $e$ nuclear spin states are 4, 4, and 2, respectively. Considering also the vibrational degeneracy, all the allowed torsional transitions will have the equal statistical weights, rendering the Franck-Condon factors the direct measures of the torsional peak intensities. The calculated Franck-Condon factors normalized to that of the 0-0 band (a$_1$ ← a$_1$ plus $e$ ← $e$) are compared with the experimental data in Table V. Good qualitative agreement between the experimental and calculated results can be seen. As a visual demonstration of the agreement, the spectrum in the torsional region was simulated using the data in Table V and the bandwidth measured in the spectrum. The result is shown in Fig. 3. The MATI spectrum recorded under a higher-resolution condition than that for Fig. 2 is also shown in Fig. 3 to demonstrate the remarkable agreement achieved.

With the assignments for the torsional progression and the fundamentals of other vibrations completed, the remaining weak peaks in the MATI spectrum can be assigned to overtones and combinations. In particular, participation of v$_8$, v$_9$, p$_{12}$, and v$_{13}$ in these types of peaks is expected because their fundamentals are strong in the MATI spectrum. Participation of the transitions to the 3a$_1$, 4$e$, 5$e$, and 6a$_1$ torsional states in combinations is also expected for the same reason. Calculated Franck-Condon factors and isotope shifts are also useful to check the assignments made. Following these guidelines, most of the remaining peaks could be assigned. The results are available through the journal’s EPAPS service.$^{20}$ Some distinct peaks are left unassigned. These are peaks at 668, 1041, 1146, 1807, 2135, and 2275 cm$^{-1}$.

![FIG. 3. (a) One-photon MATI spectrum of 2-C$_3$H$_5$Cl in the vicinity of the 0-0 band. Ar carrier gas and relatively low PFI field (20 V/cm) were used to improve the spectral resolution. (b) A spectrum simulated with the calculated frequencies and Franck-Condon factors for the torsional transitions.](http://jcp.aip.org/jcp/copyright.jsp)
D. Torsional barrier

At the equilibrium geometries of the neutral and cation of 2-C\textsubscript{3}H\textsubscript{5}Cl, two hydrogen atoms of CH\textsubscript{3} are at the staggered positions with respect to the chlorine atom as shown in Fig. 1 while one of the hydrogen atoms is at the eclipsed position in the transitional structures. Energy difference between these structures is the torsional barrier, which is 925 and 53.6 cm\textsuperscript{-1} for the neutral and the cation, respectively, as listed in Table IV. Dramatic decrease in the torsional barrier upon ionization was also observed in our previous study of 2-C\textsubscript{3}H\textsubscript{4}Br\textsuperscript{19}, from 928.7 cm\textsuperscript{-1} in the neutral to 80.0 cm\textsuperscript{-1} in the cation. Decrease in the torsional barrier is a little more dramatic in the case of 2-C\textsubscript{3}H\textsubscript{4}Cl.

Methyl torsional motion in the related molecule, propene, was investigated over the years. Durig and Gürgis\textsuperscript{37} reported \(V_3\) of 693.7 cm\textsuperscript{-1} as determined by fitting four peaks in the far-infrared spectrum of the propene neutral. \(V_3\) of 649.4 cm\textsuperscript{-1} calculated at the self-consistent-field (SCF) level was reported by the same investigators. For the torsional barrier in the cation, Burrill and Johnson\textsuperscript{38} reported 429 cm\textsuperscript{-1} calculated at the MP2/6-311G(2d,p) level with some modifications. We calculated the barriers for propene in this work at the same level adopted for 2-C\textsubscript{3}H\textsubscript{5}Cl, B3LYP/6-311+\(+\)G(3df,3pd). These were 684.7 and 395.3 cm\textsuperscript{-1} for the neutral and the cation, respectively. It is to be noted that calculations at the DFT level result in agreement with the experimental data for the neutral than those at the SCF level. More important is that a substantial decrease of the torsional barrier upon ionization also occurs for propene, from around 700 to around 400 cm\textsuperscript{-1}. It was suggested that loss of an electron from the C=C double bond in propene decreases the \(\pi\) electron density on the carbon adjacent to the methyl group which, in turn, allows the methyl group to rotate more easily.

Since the main character of the orbital in 2-C\textsubscript{3}H\textsubscript{5}Cl or 2-C\textsubscript{3}H\textsubscript{4}Br\textsuperscript{19} which loses an electron upon ionization is the same as that in propene, lowering of the torsional barriers of these molecules upon ionization is not surprising itself. What is surprising is that the degree of lowering is dramatically higher in the halides than in propene. Since the results from B3LYP/6-311++\(+\)G(3df,3pd) calculations were in excellent agreement with the experimental data for 2-C\textsubscript{3}H\textsubscript{4}Cl\textsuperscript{18}, we attempted to account for the barrier lowering based on the molecular orbital picture obtained at this level. The highest occupied molecular orbital (HOMO) of 2-C\textsubscript{3}H\textsubscript{4}Cl has contributions from the C=C \(\pi\) orbital, the 3\(p_z\) nonbonding orbital of Cl, and the \(\pi\) orbital of the methyl group, or \(\pi-n-n\)\(\pi_{CH_3}\). Its energy in the staggered form of the neutral is lower than that of the eclipsed form by 731 cm\textsuperscript{-1}. The same difference in the cation is comparable, 773 cm\textsuperscript{-1}. Then, considering the HOMO only, loss of an electron destabilizes the staggered form relative to the eclipsed form, resulting in the barrier lowering by 731 cm\textsuperscript{-1}, seemingly in fair agreement with 871 cm\textsuperscript{-1} barrier lowering observed in the present experiment. The above argument is overly simplistic because energies of other orbitals also change upon ionization. Hence we checked the energies of several molecular orbitals below HOMO in the staggered and eclipsed forms of the neutral and the cation. By far the largest contribution to the barrier lowering was found to be due to the destabilization of the staggered form relative to the eclipsed form caused by the removal of an electron from HOMO. It is thought, however, that extensive quantum chemical investigation is needed to elucidate the nature of the torsional barrier lowering upon ionization, which is beyond the scope of the present work.

V. CONCLUSION

The one-photon ZEKE/MATI scheme is free from several experimental limitations encountered in the two-photon scheme and can be used to measure the ionization energy and the cation vibrational frequencies. Its main drawback in the vibrational assignment for the open-shell cation is the fact that the vibrational information obtained via intermediate state selection in the two-photon scheme is not available. We have demonstrated in this work, and in previous works also, that such a drawback can be essentially overcome by utilizing frequencies and Franck-Condon factors obtained by quantum chemical calculations. The calculations at the DFT/B3LYP level using basis sets with sufficient size has been found to be especially useful for the purpose. In the present case, the low-frequency torsional progression could be reproduced almost exactly by quantum-mechanical calculations using molecular parameters obtained at the B3LYP/6-311++\(+\)G(3df,3pd) level. The results from the calculations at the BP86 level with the same basis set were not as adequate. This means that the B3LYP results can be used to investigate detailed nature of the barrier lowering upon ionization of 2-C\textsubscript{3}H\textsubscript{4}Cl.

ACKNOWLEDGMENTS

This work was financially supported by CRI, Ministry of Science and Technology, Republic of Korea. Two of the authors (Y.J.B. and M. L.) thank the Ministry of Education for the Brain Korea 21 fellowship.

See EPAPS Document No. E-JCPSA6-123-028526 for calculated results obtained at B3LYP and BP86/6-311++G(3df,3pd) and expanded list of the assignments including the fundamentals, overtones, and combinations. This document can be reached via a direct link in the online article’s HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).