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Citation: J. Chem. Phys. 136, 034304 (2012); doi: 10.1063/1.3676411
View online: http://dx.doi.org/10.1063/1.3676411
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v136/i3
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Dissociative photoionization of methyl chloride studied with threshold photoelectron-phoion coincidence velocity imaging

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(Received 4 November 2011; accepted 22 December 2011; published online 17 January 2012)

I. INTRODUCTION

As an important chemical reagent with a high symmetry of C3v, spectroscopy and molecular structures of methyl chloride (CH3Cl), and its ion have been widely studied in the past decades. The electron configuration of the ground state of CH3Cl molecule is (1a1)2(2a1)2(1e)4(3a1)2(2e)4(X1A1).1–3 Removing an electron from outer orbitals, e.g., 2e, 3a1, or 1e, can generate CH3Cl+ ion in the X2E, A2A1, or B2E states, respectively. An early high resolution photoelectron spectrum of CH3Cl in the excitation energy range of 11–20 eV was recorded using He I ionization source,5 where the lower lying electronic states of CH3Cl+ were assigned. Vibrational structure was observed for the X2E ground ionic state, while the A2A1 and B2E states of CH3Cl+ ions overlapped without any vibrational structure. Vertical ionization energies for the X2E3/2(2E1/2), A2A1, and B2E3/2(2E1/2) ionic states were measured to be 11.289 (11.316), 14.4, and 15.4 (16.0) eV, respectively. Using synchrotron radiation (SR) as light source, Olney et al.2 and Locht et al.4 measured absorption spectrum and threshold photoelectron spectrum (TPES) of CH3Cl. Angular distributions of electron in photoionization of CH3Cl were measured as well, and their anisotropic parameters were obtained.5–7

Combining electron impact ionization and time-of-flight (TOF) mass spectrometer, Tsuda et al.8,9 recorded the ionization efficiency curves of CH3+, CH2Cl+, and CH2+ fragment ions and obtained their appearance potentials (AP). By improving the energy resolution of electron, Lossing10 and Werner et al.11 observed ionization efficiency curves of CH2Cl+ and CH3+, and suggested their adiabatic appearance potentials at 13.02 eV for CH2Cl+ and 13.38 eV for CH3+. Subsequently, Brunetti et al. measured the cross section and branching ratios of CH2Cl+ and CH3+ fragment ions using penning ionization,12,13 where CH2Cl+ fragment ions appeared at adiabatic onset (13.02 eV) with a low branching ratio. However, CH2Cl+ was not observed at the excitation energy of lower than 15 eV in photoelectron-phoion coincidence (PEPICO) experiments,14,15 although the energy was higher than its AP(CH2Cl+, 13.02 eV). A similar phenomenon was also obtained in the photofragmentation of CH3Cl at 366 nm, where CH3Cl+ ions were produced by 13.5 eV electron impact.16 Thus a potential explanation for this inconsistency is needed.

For the dissociation dynamics of state-selected CH3Cl+ ions, several experimental and theoretical investigations have been performed. Using mass-analyzed ion kinetic spectrometry, Won et al.17 obtained kinetic energy released distributions (KED) for different dissociation pathways of CH2Cl+ and proposed that CH3+ dissociated from CH3Cl+ (A2A1) ion was produced via a direct dissociation whereas the dissociation of CH2Cl+(B2E) ion was statistical. Using complete active space self-consistent-field (CASSCF) and multiconfiguration second-order perturbation theory (CASPT2), Xi et al.18 calculated the Cl-loss and H-loss potential energy curves for

\[ \text{Cl}^+ + \text{CH}_3\text{Cl} \rightarrow \text{CH}_2\text{Cl} + \text{Cl} \]

Utilizing threshold photoelectron-phoion coincidence (TPEPICO) velocity imaging, dissociation of state-selected CH2Cl+ ions was investigated in the excitation energy range of 11.0–18.5 eV. TPEPICO time-of-flight mass spectra and three-dimensional time-sliced velocity images of CH3+ dissociated from CH3Cl+(A2A1 and B2E) ions were recorded. CH3+ was kept as the most dominant fragment ion in the present energy range, while the branching ratio of CH2Cl+ fragment was very low. For dissociation of CH3Cl+(A2A1) ions, a series of homocentric rings was clearly observed in the CH3+ image, which was assigned as the excitation of umbrella vibration of CH3+ ions. Moreover, a dependence of anisotropic parameters on the vibrational states of CH3+(1A’1) provided a direct experimental evidence of a shallow potential well along the C–Cl bond rupture. For CH3Cl+(B2E) ions, total kinetic energy released distribution for CH3+ fragmentation showed a near Maxwell-Boltzmann profile, indicating that the Cl-loss pathway from the B2E state was statistical predissociation. With the aid of calculated Cl-loss potential energy curves of CH3Cl+, CH3+ formation from CH3Cl+(A2A1) ions was a rapid direct fragmentation, while CH3Cl+(B2E) ions statistically dissociated to CH3+ + Cl via internal conversion to the high vibrational states of X2E. © 2012 American Institute of Physics. [doi:10.1063/1.3676411]
the lower lying electronic states of CH$_3$Cl$^+$, and suggested brief dissociative mechanisms of CH$_3$Cl$^+$(A$^2A_1$ and B$^2E$). In addition, ion-pair dissociation of CH$_3$Cl was studied by Liu et al.$^{19}$

Although many experimental and theoretical studies have been performed on the dissociation of CH$_3$Cl$^+$, dissociation mechanism, kinetic energy and internal state distributions of fragments, in addition to the angular distributions of CH$_3$ are still not clarified. Especially, resolution of kinetic energy released during dissociation obtained in Won et al.’s experiment$^{17}$ is not high enough to determine the vibrational state distribution of CH$_3$+, and thereby the detailed information of dissociation dynamics may be buried.

In this work, a recently developed TPEPICO velocity map imaging$^{20}$ technique has been applied for investigation of dissociation dynamics of state-selected CH$_3$Cl$^+$ ions. Due to the high energy resolution of ion velocity imaging,$^{21-23}$ velocity distribution of CH$_3$+ is measured and its corresponding vibrational distributions are identified. Moreover, angular distributions of CH$_3$+ dissociated from specific state-selected CH$_3$Cl$^+$ ion are obtained directly from its TPEPICO images as well. Therefore, the overall dissociative mechanism of state-selected CH$_3$Cl$^+$(A$^2A_1$ and B$^2E$) ions will be proposed.

II. EXPERIMENTAL

The present TPEPICO measurements were performed at U14-A beamline of National Synchrotron Radiation Laboratory, Hefei, China. Details of the beamline$^{24}$ and the TPEPICO velocity map imaging spectrometer$^{20}$ were described previously, and thus only a brief introduction was presented here.

Synchrotron radiation from an undulator was dispersed with a 6 m monochromator equipped with a 370 grooves mm$^{-1}$ spherical grating, and covered the photon energy range of 7.5–22.5 eV. The absolute photon energy scale of the grating was calibrated using the well-known ionization energies of 7.5–22.5 eV. The absolute photon energy scale of the grating was determined by measuring contributions of residual hot electrons.

FIG. 1. Threshold photoelectron spectrum of CH$_3$Cl in the energy range of 11.0–18.5 eV

With an extraction electric field of 15 V cm$^{-1}$, TPES of CH$_3$Cl in the excitation energy range of 11.0–18.5 eV was recorded, where energy increment was 15 meV. As resolution of the present threshold photoelectron energy was about 9 meV (full width at half magnitude, FWHM),$^{20}$ main vibrational structures of the electronic states of CH$_3$Cl$^+$ could be discerned. Figure 1 shows the modified TPES after subtracting contributions of residual hot electrons.

The lower energy band in Fig. 1 covers an energy range of 11.2–12.2 eV and exhibits a series of resonance peaks,
which can be assigned to the vibrational structures of the ground state, $X^2E_{3/2}$ and $X^2E_{1/2}$, of CH$_3$Cl$^+$. Both intensities and resonance energies of these vibrational bands agree very well with previous measurements.\(^1,^3\) In the energy range of 12.2–18.5 eV, a double-peak band is observed in TPES and no vibrational structure can be discerned, which is very similar to previous TPES (Ref. 1) and high resolution photoelectron spectrum.\(^3\) However, relative intensities of two peaks are much different between the present and previous TPES.\(^1\) In the previous TPES,\(^1\) relative intensity of the double-peak band is close to that of $X^2E$ state, which was quite different with the present observation. It is well known that a major disadvantage in previous TPES measurement is contamination of collected threshold electron by energetic electrons. However, our spectrometer has an excellent ability to suppress hot electrons with application of a decelerating ion lens,\(^20\) and thus the most contaminations of energetic electrons are not involved in TPES. Therefore, the present intensities of all bands in Fig. 1 are believed to be more reliable.

According to the previous spectral assignments,\(^1,^3\) both the $A^2A_1$ and $B^2E$ states of CH$_3$Cl$^+$ ions are assigned to the double-peak band, and the intensity of $A^2A_1$ state is slightly higher than that of $B^2E$. Due to such a small energy gap between these two excited ionic states, the $A^2A_1$ and $B^2E$ bands are overlapped in some extent. Thus in the energy range of 14.8–15.6 eV, both the $B^2E$ band and the high-excited vibronic levels of the $A^2A_1$ state can be excited simultaneously, and hence the corresponding dissociation of CH$_3$Cl$^+$ are expected along two dynamic processes from the $A^2A_1$ state or the $B^2E$ state, which will be discussed in Sec. III F.

B. TPEPICO time-of-flight mass spectra

In the present excitation energy range, many dissociation channels of CH$_3$Cl$^+$ ions are possible in thermodynamics, and CH$_2$Cl$^+$, CH$_3$+, Cl$^+$, and HCl$^+$ fragment ions are expected to be produced. Thus, three TPEPICO TOF mass spectra were measured at photon energies of 11.290, 14.530, and 15.480 eV, respectively, which correspond to the $X^2E_{3/2}$, $A^2A_1$, and $B^2E$ bands. Only CH$_3$+ and CH$_2$Cl$^+$ fragment ions were observed among all possible thermodynamic ionic products, and therefore the two most dominant dissociation pathways were investigated in the present work as follows:

\[
\text{CH}_3\text{Cl}^+ \rightarrow \text{CH}_2\text{Cl}^+(1^1A') + \text{H},
\]

\[
\rightarrow \text{CH}_3\text{Cl}^+(1^1A_1) + \text{Cl}.
\]

In addition, both of them are two lowest channels for dissociation of CH$_3$Cl$^+$ ions, and the corresponding dissociation limits are 13.02 eV and 13.38 eV, respectively.\(^1\)

TPEPICO TOF mass spectra measured with an extraction electric field of 15 V cm$^{-1}$ are shown in Fig. 2, where (a) was recorded at 11.290 eV, (b) and (c) were obtained at 14.530 and 15.480 eV, respectively. At 11.290 eV, CH$_3$Cl$^+$ ions were generated at the lowest vibronic level of $X^2E_{3/2}$ state. Since the excitation energy was lower than any dissociation limits, only two molecular ions with TOF of 14.55 $\mu$s and 14.84 $\mu$s were observed, which corresponded to CH$_3$Cl$^+$($m/z = 50$) and CH$_3$Cl$^+$($m/z = 52$) ions, respectively. Both isotopes of CH$_3$Cl$^+$ ion were clearly observed with intensities of their nature abundance. Moreover, the TOF profile of CH$_3$Cl$^+$ ions showed a wide wing in Fig. 2(a), which was contributed by amounts of thermal background in the beam of pure CH$_3$Cl gas. Thus, a diluted MB of CH$_3$Cl/Ne (1:9) was used in order to reduce the thermal background as much as possible during measurement of TPEPICO velocity map imaging.

When the excitation energy was higher than dissociation limits of the channels (1) and (2), both CH$_2$Cl$^+$ ($m/z = 49$) and CH$_3$+ ($m/z = 15$) fragment ions were clearly observed as shown in Figs. 2(b) and 2(c), while no CH$_3$Cl$^+$ ($m/z = 50, 52$) ions existed. Thus, the $A^2A_1$ and $B^2E$ states of CH$_3$Cl$^+$ are unstable and completely dissociative. CH$_3$+ fragment ions were kept dominant in the excitation energy range of 13.4–18.5 eV, while the branching ratio of CH$_2$Cl$^+$ ions was very low. Compared with the $A^2A_1$ state, less CH$_3$Cl$^+$ ions were produced from CH$_3$Cl$^+$($B^2E$) ions, which are consistent with the previous results of mass spectra using SR photoionization.\(^1\) However, in the PEPICO investigations using He I light source, no CH$_3$Cl$^+$ ions were observed at an excitation energy of lower than 15 eV.\(^14,15\) Similar conclusions were also obtained in photodissociation of CH$_3$Cl$^+$ at 366 nm.\(^16,17\) In order to explain the inconsistency, Baer\(^27\) suggested that a dark electronic state of CH$_3$Cl$^+$ near $A^2A_1$ caused C–H bond cleavage, but it was rejected by conclusions of \textit{ab initio} calculation.\(^18\) Only the ground $X^2E$ state adiabatically correlated to the CH$_3$Cl$^+$(1$^1A'$) + H dissociation limit among three low-lying electronic states.\(^18\) Therefore, the inconsistency between the present and previous results is believed original from contribution of autoionization process. In SR-based photoionization, molecular ions could be prepared from direct ionization and/or autoionization processes. Thus in the energy range of $A^2A_1$ state, parts of CH$_3$Cl$^+$ ions were also produced at the high vibrational level of $X^2E$ state via autoionization process, and then dissociated to CH$_2$Cl$^+$ and H atom along the potential energy surface of $X^2E$. On the contrary, the autoionization cross section is probably very low at the energy of He I light source, and thus all CH$_3$Cl$^+$ ions were generated at the ionic excited electronic state from direct.
ionization in PEPICO experiments.\textsuperscript{14,15} For CH$_3$Cl$^+(A^2A_1)$ ions, the adiabatic C–H bond cleavage will produce the excited CH$_2$Cl$^+(^1A^\prime\prime)$ ion and the corresponding dissociation limit is higher than the present excitation energy as calculated in Ref. \textsuperscript{18}, and hence no CH$_2$Cl$^+$ fragments were observed.

As shown in Figs. 2(b) and 2(c), the widths of two TOF peaks of CH$_2$Cl$^+$ and CH$_3^+$ were broadened due to released kinetic energy in dissociation. As the signal-to-noise ratio of CH$_2$Cl$^+$ fragment ion was poor, we did not measure its TPEPICO velocity image. For CH$_3^+$ fragment ion, its TOF profile in Fig. 2(b) was recorded with a nearly rectangular contour and a FWHM of 500 ns at 14.530 eV, implying that dissociation along the channel (2) is fast. It was very interesting that the TOF profile of CH$_3^+$ changed its contour to a nearly triangle when the excitation energy was increased to 15.480 eV, as shown in Fig. 2(c). Moreover, its FWHM decreased to 320 ns although the available energy for the dissociation channel (2) was increased much. Since CH$_3$Cl$^+(A^2A_1)$ and CH$_2$Cl$^+(B^2E)$ ions were mostly prepared at 14.530 eV and 15.480 eV, respectively, dissociative mechanisms of CH$_3$Cl$^+$ ions along the channel (2) are expected to be entirely different for the $A^2A_1$ and $B^2E$ states.

C. TPEPICO velocity image of CH$_3$Cl$^+$ in the X$^2E_{3/2}$ state

Kinetic energy resolution of the present ion velocity imaging is better than 3% of $\Delta E/E$,\textsuperscript{20} and hence vibrational state population of fragment can be discerned. Therefore, we performed TPEPICO velocity imaging measurements for the X$^2E$, $A^2A_1$, and $B^2E$ electronic states of CH$_3$Cl$^+$ ions, respectively.

At 11.290 eV, no fragmentation process of CH$_3$Cl$^+$ happened. Thus, only image of CH$_3^{35}$Cl$^+$ was recorded and presented in Fig. 3(a), where SR propagated along the direction of x axis, and electric vector $\varepsilon$ of photon was along y axis. Since MB flew along y axis from top to bottom and the TOF axis was perpendicular to MB, the image of CH$_3^{35}$Cl$^+$ was eccentric from the center of CCD along the beam direction as shown in Fig. 3(a).

Due to a perpendicular geometry of MB direction and the TOF axis, the velocity spread of beam inevitably causes recorded images broadened along MB direction (y axis)\textsuperscript{20,21,28}. On the contrary, the image along x axis is scarcely affected due to collimation of the skimmer. As Figs. 3(b) and 3(c) shown, intensity distributions of the image along x axis and y axis have Gaussian profiles, where the FWHMs are 9 and 27 pixels, respectively. Thus, the recorded image presents an elliptical contour in Fig. 3(a). In this case, the real ion images need to be handled prior to extracting speed and angular distributions through a multi-step data reduction scheme including quadrant symmetrization and deconvolution. Its details have been described in the supplementary material of Ref.\textsuperscript{28}. From the intensity distribution in Fig. 3(c), the parallel translational temperature of MB can be estimated as 18 K,\textsuperscript{29}, which will be used in deconvolution of CH$_3^+$ images in Secs. III D–III E.

D. TPEPICO 3D time-sliced velocity image of CH$_3^+$ in the $A^2A_1$ state

Figure 4(a) shows the recorded TPEPICO 3D time-sliced image of CH$_3^+$ dissociated from CH$_3$Cl$^+(A^2A_1)$ ions at 14.530 eV, where a mass gate of 60 ns was applied. Besides a major structure of multi-ring, there is a bright off-centered spot, which is composed by CH$_3$Cl$^+$ ions from false coincidence events. The pure image of CH$_3^+$ fragment can be obtained through subtracting a false coincidence image as described in Ref.\textsuperscript{30}. Subsequently, the data reduction process of deconvolution and quadrant symmetrization is necessary to obtain the real ion images, in order to subtract contamination in the raw images from velocity spread of MB. Thus the modified image of CH$_3^+$ fragment ions at 14.530 eV is presented in Fig. 4(b), where the direction of MB and electric vector $\varepsilon$ of photon are fixed as the same as Fig. 3(a).
A series of homocentric rings are clearly observed in Fig. 4(b), which is contributed by CH$_3^+$ ions with different velocities. By accumulating intensity of the image over angles, speed distribution of CH$_3^+$ fragment ions is acquired directly. From the conservation of linear momentum, total KERD in dissociation of CH$_3$Cl$^+(A^2A_1)$ ions can be obtained and shown in Fig. 4(c). Benefit from high energy resolution of velocity imaging, the present KERD shows more clear internal energy distributions than previous results,$^{15,17}$ that five distinct peaks corresponding to vibrational excitation of fragment are observed in the total KERD. Based on the energy conservation in dissociation, assignment of these peaks in terms of the vibrational states of CH$_3^+$ can be obtained and shown in Fig. 4(c). Relation between the internal energy of CH$_3^+$ fragment ion, $E_{\text{int}}$, and the total released kinetic energy, $E_T$, can be expressed as the following formula:

$$hv - D_0 = E_{\text{avail}} = E_{\text{int}} + E_T,$$

where $hv$ is photon energy, $E_{\text{avail}}$ is available energy after dissociation and $D_0$ is the dissociation limit for a specific channel.

In the dissociation process to form CH$_3^+$, the C–Cl bond of CH$_3$Cl$^+$ ions is broken and carbon atom moves towards the plane of three H atoms under the action of the recoil momentum of the leaving chloride atom. As such a movement is very similar to the umbrella vibration (v$_2^+$) of CH$_3^+$, the v$_2^+$ mode is expected to be dominantly excited during the fast dissociation. In fact, the energy intervals between the adjacent peaks in Fig. 4(c) are very close to the v$_2^+$(CH$_3^+$) vibrational frequency, 1380 cm$^{-1}$. Taking the dissociation limit $D_0 = 13.38$ eV for the CH$_3$Cl$^+(1^1A_1)+$Cl channel,$^{11}$ the maximal v$_2^+$ quantum number of CH$_3^+$ is equal to 6. Therefore, the possible vibrational state population of CH$_3^+$ dissociated from CH$_3$Cl$^+(A^2A_1)$ ions can be assigned and shown in Fig. 4(c) as well. Moreover, relative intensities of every vibrational state can be estimated through fitting the total KERD with six Gaussian profiles, and summarized in Table I.Obviously, an occurrence of vibrational population reversion is happened for CH$_3$Cl$^+(1^1A_1)$ fragment ions. As the assignments shown, the maximum vibrational population of CH$_3$Cl$^+(1^1A_1)$ is located at v$_2^+ = 3$. In addition, no other vibration modes of CH$_3^+$ are observed in the total KERD, indicating that the C$_{3v}$ geometry of CH$_3^+$ moiety is kept during dissociation and no distinct intermolecular vibrational redistribution happens.

From the image of Fig. 4(b), angular distributions of CH$_3^+$ fragment ions can be derived by integrating the image over a proper range of speed at each angle. Consequently, anisotropic parameters $\beta$ for dissociation pathways to form CH$_3^+$(1$^1A_1$) in a special vibrational state can be calculated by fitting the angular distribution, $I(\theta)$, with the following formula:\textsuperscript{32}

$$I(\theta) = \frac{1}{4\pi} [1 + \beta \cdot P_2(\cos \theta)],$$

where $\theta$ is the angle between the recoil velocity of fragment and the electric field vector $\mathbf{e}$ of photon, and $P_2(\cos \theta)$ is the second-order Legendre polynomial. Thus the anisotropic parameters $\beta$ for CH$_3$Cl$^+(1^1A_1)$ ions in the vibrational states of v$_2^+ = 2, 3,$ and 4 are obtained to be 0.44, 0.37, and 0.22, which are listed in Table I as well. For CH$_3$Cl$^+(1^1A_1)$ at the other vibrational states, e.g., v$_2^+ = 1$ and 5, the $\beta$ values are estimated to be 0.5 and 0.1, respectively, but relative large uncertainties exist due to their poor signal-to-noise ratios in images. Thus we do not summarize them in Table I. Obviously, all $\beta$ values are positive, indicating that dissociation of CH$_3$Cl$^+(A^2A_1)$ ions has a character of parallel transition. In addition, a dependence of $\beta$ on the vibrational states of CH$_3^+$(1$^1A_1$) ions is shown, which will be discussed in Sec. III F.

<table>
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<tr>
<th>Vibratic level of CH$_3$(1$^1A_1$)</th>
<th>Relative intensity</th>
<th>FWHM of profile (eV)</th>
<th>Anisotropic parameter, $\beta$</th>
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</thead>
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<td>v$_2^+$ = 0</td>
<td>&lt; 0.01</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>v$_2^+$ = 1</td>
<td>0.17</td>
<td>0.09</td>
<td>...</td>
</tr>
<tr>
<td>v$_2^+$ = 2</td>
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<td>0.07</td>
<td>0.44 ± 0.07</td>
</tr>
<tr>
<td>v$_2^+$ = 3</td>
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<td>0.37 ± 0.07</td>
</tr>
<tr>
<td>v$_2^+$ = 4</td>
<td>0.64</td>
<td>0.06</td>
<td>0.22 ± 0.09</td>
</tr>
<tr>
<td>v$_2^+$ = 5</td>
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<td>0.08</td>
<td>...</td>
</tr>
<tr>
<td>v$_2^+$ = 6</td>
<td>0.07</td>
<td>0.11</td>
<td>...</td>
</tr>
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</table>
E. TPEPICO 3D time-sliced velocity image of CH$_3^+$ in the B$^2$E state

Fixed photon energy at 15.480 eV, CH$_3$Cl$^+$($B^2$E) ions were mainly generated and subsequently dissociated. The modified TPEPICO 3D time-sliced image of CH$_3^+$ fragment ions was shown in Fig. 5(a). Different from the structure of homocentric rings in Fig. 4(b), only a pancake was observed in Fig. 5(a), where the brightest part was located at the center.

Through the data reduction process of subtraction, deconvolution, and quadrant symmetrization as described in Ref. 28, total KERD in dissociation of CH$_3$Cl$^+$ ions at 15.480 eV was obtained and presented in Fig. 5(b). The average released kinetic energy in dissociation is obviously smaller than that of CH$_3$Cl$^+$($A^2A_1$) ions, which is consistent with that suggested by the FWHM of TOF profiles in Fig. 2. Moreover, the total KERD curve shows a near Maxwell-Boltzmann profile as the red line in Fig. 5(b), indicating that the CH$_3^+$ formation pathway of CH$_3$Cl$^+$($B^2E$) ions is slow via a statistical dissociation. These speculations were also suggested by previous experimental studies.  

Interestingly, several peaks superimpose over a broadened background in the total KERD curve of Fig. 5(b), and energy intervals between these peaks look very close to those in Fig. 4(c). Thus the umbrella vibration ($v_2^+$) of CH$_3^+$ seems to be prominently excited during dissociation, which is inconsistent with the statistical dissociation of CH$_3$Cl$^+$(B$^2$E) ions. However, as shown in TPES of Fig. 1, CH$_3$Cl$^+$ ions can be prepared in both the B$^2$E state and the high-excited vibronic levels of the A$^2A_1$ state at 15.480 eV, although the most part of CH$_3$Cl$^+$ ions were certainly in the B$^2$E state. Therefore, dissociation from the minority CH$_3$Cl$^+$ ions at the high-excited vibronic levels of A$^2A_1$ contributes the peaks in total KERD curve of Fig. 5(b).

From the image of Fig. 5(a), the angular distribution of CH$_3^+$ was plotted as shown in Fig. 6. The angular distributions were very similar for all released kinetic energies. Using the formula (4), the anisotropic parameter $\beta$ is obtained to be $-0.32$. Therefore, dissociation of CH$_3$Cl$^+$(B$^2$E) has a character of perpendicular transition and is entirely different from the parallel dissociation of CH$_3$Cl$^+$(A$^2A_1$).

F. Dissociative mechanism of CH$_3$Cl$^+$ ions

From the images and total KERD curves in Figs. 4 and 5, the energy distributions of CH$_3^+$ dissociated from CH$_3$Cl$^+$ ions at 14.530 and 15.480 eV can be estimated. The average total released kinetic energies, $\langle E_T \rangle$, as well as the average vibrational energy $\langle E_{vib} \rangle$ and rotational energy $\langle E_{rot} \rangle$ of CH$_3^+$, are summarized in Table II.

In the A$^2A_1$ state, CH$_3$Cl$^+$ dissociates fast along the C–Cl bond rupture with C$_3$V geometry. “Impulsive model” is expected to describe its dissociative mechanism, in which the proportion of average total kinetic energy $\langle E_T \rangle$ and available energy $E_{avail}$ can be calculated as the following formula:

$$f_T = \frac{\langle E_T \rangle}{E_{avail}} = \frac{\mu_{C-CI}}{\mu_{CH3-Cl}} = 0.85,$$

where $\mu_{C-CI}$ and $\mu_{CH3-Cl}$ are the reduced masses of C–Cl and CH$_3$–Cl, respectively.
where μ is reduced mass. In this case, the geometry of methyl group is initially kept during the fast dissociation until separation of Cl atom and CH₃. The final umbrella vibration energy of CH₃ will be distributed from its initial kinetic energy. However, only 53% of available energy is taken by the translation of CH₃⁺ ion and Cl atom at 14.530 eV as shown in Table II. Therefore, the partial relaxation of methyl group happens to change from the tetrahedral structure to planar during the impulsive period of the dissociation process.

As shown in Table I, a dependence of β on the vibrational states of CH₃⁺(11A₁) is observed, which does not agree with a usual conclusion of fast dissociation along a repulsive potential energy surface. Thus, details of potential energy surface of CH₃Cl⁺(A²A₁) need to be carefully examined. The CI-loss potential energy curves of the low-lying electronic states of CH₃Cl⁺ are shown in Fig. 7, which are obtained by plotting the calculated energies of electronic states at different C–Cl bond length in Table III of Ref. 18. As the slight energy shifts exist between experimental and calculated dissociation limits, we vertically shifted the calculated curves in Fig. 7 in order to match the experimental dissociation limits. It needs to be noted that the X²E and B²E states should be divided to 2A’ and 2A” states when taking into account Jahn-Teller distortion, however, only a little difference was observed between the CI-loss potential energy curves of the 2A’ and 2A” states. Therefore, we did not involve this effect in discussing the dissociative mechanism of CH₃Cl⁺ ions, as shown in Fig. 7.

### IV. CONCLUSIONS

For the A²A₁ state, it adiabatically correlates to the CH₃⁺(1³A₀) + Cl dissociation limit. In the Frank-Condon area, the steep repulsive potential initially pushes Cl atom far away quickly, and methyl group is almost kept the original tetrahedral geometry. However, a shallow potential well exists along the C–Cl bond rupture as shown in Fig. 7, although it is not a true minimum in the CASSCF full geometry optimization calculation. Thus, the binding interaction of the potential well is stronger with the v₂⁺ quantum number increasing, and hence the dissociation time scale of CH₃Cl⁺(A²A₁) to produce the CH₃⁺(1³A₀,v₂⁺) fragment ion is expected increasing. Consequently, the CH₃⁺ formation process from CH₃Cl⁺(A²A₁) ions tends to be isotropic as the v₂⁺ quantum number increases.

As shown in Fig. 7, the B²E state is typical bound and adiabatically correlates to the 1³A” excited electronic state of CH₃⁺. Because the present excitation energy is lower than the adiabatically dissociation limit, the probable C–Cl cleavage of CH₃Cl⁺(B²E) ions is through internal conversions to the lower electronic states, A²A₁ or X²E. According to the perpendicular dissociation of CH₃Cl⁺(B²E) with the β value of −0.32, the unique potential mechanism is via internal conversion to the high vibrational state of X²E and subsequently statistical dissociation.

### TABLE II. Energy distribution of CH₃⁺ dissociated from CH₃Cl⁺ ions.

<table>
<thead>
<tr>
<th>hv (eV)</th>
<th>E avail (eV)</th>
<th>⟨ET⟩ (eV)</th>
<th>⟨Evib⟩ (eV)</th>
<th>⟨ET⟩/E avail</th>
<th>(E avail)</th>
<th>⟨ET⟩</th>
<th>(E avail)</th>
<th>⟨ET⟩</th>
<th>(E avail)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A²A₁</td>
<td>14.530</td>
<td>1.15</td>
<td>0.612</td>
<td>0.532</td>
<td>0.52</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B²E</td>
<td>15.480</td>
<td>2.20</td>
<td>0.508</td>
<td>0.231</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a(⟨ET⟩) is the average total kinetic energy released in dissociation.

*b(⟨ET⟩) is the average vibrational energy of CH₃⁺.

*c(⟨ET⟩) is the average rotational energy of CH₃⁺. (E avail) = (⟨ET⟩)/⟨ET⟩ = (⟨ET⟩)*(⟨ET⟩).
CH₃⁺(1A₁) ions is clearly observed, which provides a direct experimental evidence of a shallow potential well along the C–Cl bond rupture.

Different from the rapid dissociation, the total KERD of CH₃⁺ fragmentation from CH₃Cl⁺(B²E) ions did exhibit a near Maxwell-Boltzmann profile. Besides CH₃Cl⁺(B²E) ions, the minority CH₃Cl⁺ ions at the high-excited vibronic levels of the A²A₁ state were simultaneously produced at 15.480 eV, which contributed the small peaks superimposed over a broadened background in the total KERD curve.

With the aid of previous calculated potential energy curves of CH₃Cl⁺ along the C–Cl ruptures, the dissociative mechanisms of CH₃Cl⁺ in the A²A₁ and B²E states are obtained. CH₃⁺(A¹A') fragment ions can be produced from CH₃Cl⁺(A²A₁) via a rapid direct dissociation, while CH₃Cl⁺(B²E) ions can dissociate via internal conversion to the high vibrational states of X²E and subsequently statistical dissociation.

ACKNOWLEDGMENTS

Financial supports from the National Natural Science Foundation of China (NSFC, Nos. 10979042 and 21073173) and National Key Basic Research Special Foundation (NKBRSF, Nos. 2007CB815204 and 2010CB923300) are appreciated. X. Zhou also thanks the Fundamental Research Funds for the Central Universities (No. WK2060030006) and USTC-NSRL Association funding (No. KY2060030007) for supports.