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Fragmentation of methyl chloride studied by partial positive and negative ion-yield spectroscopy

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The authors present partial-ion-yield experiments on the methyl chloride molecule excited in the vicinity of the Cl2p and C1s inner shells. A large number of fragments, cations produced by dissociation or recombination processes, as well as anionic species, have been detected. Although the spectra exhibit different intensity distributions depending on the core-excited atom, general observations include strong site-selective fragmentation along the C–Cl bond axis and a strong intensity dependence of transitions involving Rydberg series on fragment size. © 2007 American Institute of Physics. [DOI: 10.1063/1.2464093]

I. INTRODUCTION

Resonant excitation or ionization of a core electron by a photon in the soft-x-ray regime promotes a molecule to a rather unstable potential energy surface. The excited system relaxes on a very short time scale, typically tens of femtoseconds or less, most likely by emitting an electron(s), then adopting a different geometry and/or breaking one or several chemical bonds. Below the core-level ionization limits, electronic relaxation processes lead generally to singly charged ions, produced either by participator or spectator resonant Auger decay. Above the core-level ionization limits, the intermediate state is itself singly charged and relaxes preferentially by normal Auger decay, leading to doubly charged species. In rarer situations, emission of several electrons during the (resonant or not) Auger decay is possible. In each case, ion fragmentation is dependent on internal energy, i.e., upon the electronic and vibrational energies stored in the system: the more energy stored, the more the ion is likely to dissociate. These phenomena can be highlighted by detection of one or several emitted particles. High-resolution electron spectroscopy is a suitable tool to study the ultrafast processes of electronic and nuclear rearrangements, whereas ion spectroscopy typically monitors processes taking place on longer time scales. However, one can obtain a wealth of information on dynamics of core-excited species by analysis of partial-ion-yield spectra, as demonstrated in experiments showing unusual fragmentation products formed by recombination processes. For example, in the case of H2O excited along the resonance O1s → 2b2, Piancastelli et al.1 measured the production of the H+2 ion dependent on the way the intermediate state is prepared. The maximum intensity for H+2 production is detected following the decay of higher vibrational levels of the intermediate state, i.e., when the molecule undergoes large-amplitude bending and stretching vibrations. This recombination process probed by ion spectroscopy is an illustration of a fast nuclear motion occurring on the same time scale as electronic relaxation. Monitoring one particular ion fragment over a large photon-energy range allows one to emphasize transitions usually hidden (when ions are not selected by mass and charge) by one or several electronic states with higher absorption cross section. The most striking example is the observation by anion spectroscopy of doubly excited states usually concealed by shape resonances above the ionization thresholds of the C1s and O1s core orbitals of CO2 of the two nonequivalent N1s orbitals of N2O,3 and of the O1s orbital of CO2.4

We report here a partial-ion-yield study of CH3Cl excited around the C1s and Cl2p thresholds. Fragmentation of methyl chloride excited around the Cl2p edge has been investigated previously using charge-separation mass spectrometry and photoelectron-photeoin coincidence,5 yielding accurate information at four distinct photon energies. A general overview of the different transitions around the C1s edge has been described in Refs. 6 and 7 by inner-shell electron-energy-loss studies, without giving details on disso-
cation of the molecule. In our measurements, we have taken advantage of the tunability of synchrotron radiation over a wide energy range, and of partial-ion-yield measurements, to follow the production of each charged species—positive or negative—with an excitation resolution less than the core-hole-lifetime broadening.

A key experimental finding from this study is the confirmation of the observations of Piancastelli et al. of high fragmentation efficiency when exciting ethylene and acetylene compounds along core-to-Rydberg series. Such excited molecular species with one electron in an orbital far from the ionic core relaxes preferentially by spectator-Auger decay, and the singly charged ion, with two valence holes and one electron in a diffuse outer orbital, remains in a highly excited state more susceptible to dissociation. These results have been established at both the Cl2p and Cl1s edges. A second finding is the strong selective fragmentation along the C–Cl bond after promotion of a carbon K-shell electron to the first empty orbital, as particularly seen along the CH bond after promotion of a carbon electron multiplier. The potentials of the analyzer electrodes can be tuned and/or switched in polarity to select fragments with a specific mass and charge. The working pressure in the target chamber was set to 1 × 10−5 Torr, and the chamber was isolated from the beamline vacuum by differential pumping. Due to the relative natural abundance of 35Cl and 37Cl isotopes in a 3:1 ratio, some pairs of ionic fragments are not discernible in the measurements, namely, CH3Cl+ and CH37Cl+, CH35Cl+ and C37Cl+, as well as their doubly charged counterparts.

II. EXPERIMENT

Experiments were performed on beamline 8.0.1.3 at the Advanced Light Source, Lawrence Berkeley National Laboratory. The monochromator resolution achieved at 204 eV photon energy was estimated at 30 meV, using previous measurements of the 4s(1D)2D5/2 atomic chlorine transition at 204.31 eV with a theoretical lifetime broadening of 5.3 meV. The resolution at hν=300 eV was estimated as 70 meV based on previous measurements of CO2 ion mass and charge characterization was done with a 180° hemispherical analyzer with a resolution of 1 mass in 50. Briefly, the fragments are created by interaction with the light beam at the exit of an effusive gas jet. Ions are extracted from the gas cell by an electric field and focused on the entrance slit of the analyzer by an electrostatic lens. They are then deflected between the plates of the analyzer and focused onto the exit slit before being detected by a channel electron multiplier. The potentials of the analyzer electrodes can be tuned and/or switched in polarity to select fragments with a specific mass and charge. The working pressure in the target chamber was set to 1 × 10−5 Torr, and the chamber was isolated from the beamline vacuum by differential pumping. Due to the relative natural abundance of 35Cl and 37Cl isotopes in a 3:1 ratio, some pairs of ionic fragments are not discernible in the measurements, namely, CH35Cl+ and CH37Cl+, CH35Cl+ and C37Cl+, as well as their doubly charged counterparts.

III. RESULTS AND DISCUSSION

We present in Fig. 1 the partial ion yields of the Cl+ and C+ ions recorded over a photon-energy range large enough to cover both the Cl2p and Cl1s edges. The intensity of the transitions located below (above) the Cl2p ionization threshold is weak (strong) compared to the ones located just below (above) the Cl1s threshold, quasi-independently of the fragment. In the vicinity of the carbon K edge, the large background is attributed mainly to contributions of ions coming from relaxation of Cl2p core holes.

A. Cl2p edge

Excitation of methyl chloride around the Cl2p edges leads to a large number of cations: CH3Cl+ and CH3Cl++ for both 35Cl+ and 37Cl+ isotopes, CH with i=0–3, C++, CH2++, 35Cl+, 37Cl+, 35Cl++, 37Cl++, H+, H2, H+, H35Cl+, H37Cl+, and two anions 35Cl− and C−. Table I provides the peak assignments in the 198–280 eV photon-energy range. The energy position of the 8a1 transition given in Ref. 5 was used for energy calibration.

In Fig. 2, we present the partial ion yields for the CH3Cl+ series. Assignments for the five resonant features are as follows. The lowest-lying resonance (A) is attributed to the Cl2p3/2→8a1 transition and its large width (870 meV full width at half maximum) is due to its strong repulsive character. In addition to elongation of the C–Cl bond, this transition is due to its strong repulsive character. In addition to elongation of the C–Cl bond, this transition is due to its strong repulsive character.

TABLE I. Energy positions and assignments of lines observed in the region of the Cl2p and Cl2s ionization thresholds. Peak labels refer to Fig. 2.

<table>
<thead>
<tr>
<th>Label</th>
<th>Energy (eV)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>200.70</td>
<td>Cl2p3/2→8a1</td>
</tr>
<tr>
<td>B</td>
<td>202.35</td>
<td>...</td>
</tr>
<tr>
<td>C</td>
<td>204.25</td>
<td>4p</td>
</tr>
<tr>
<td>D</td>
<td>205.25</td>
<td>5s</td>
</tr>
<tr>
<td>E</td>
<td>206</td>
<td>4p</td>
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<td>F</td>
<td>206.90</td>
<td>IP</td>
</tr>
<tr>
<td>...</td>
<td>207.96</td>
<td>IP</td>
</tr>
</tbody>
</table>

Energy positions and assignments of lines observed in the region of the Cl2p and Cl2s ionization thresholds. Peak labels refer to Fig. 2.

<table>
<thead>
<tr>
<th>Extra peaksa</th>
<th>Energy (eV)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>...</td>
<td>272.60</td>
<td>8a1</td>
</tr>
<tr>
<td>...</td>
<td>276.60</td>
<td>Rydberg</td>
</tr>
</tbody>
</table>

TABLE II. Energy positions and assignments of lines observed in the region of the Cl2p and Cl2s ionization thresholds. Peak labels refer to Fig. 2.

<table>
<thead>
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<tr>
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<td>276.60</td>
<td>Rydberg</td>
</tr>
</tbody>
</table>

aDeduced from the spin-orbit splitting value.

bCf. Fig. 1.
C13Cl+ ions are much more abundant around the Cl2−H2O849 region;2,4 such an overlap could be the origin of these intensities.2,4

Above threshold, a large structure dominates the maxima positions are 216.6, 218.85, 222.8, and 225 eV. We speculate that as the photon energy increases above threshold, more vibrational and/or electronic energy is stored in the singly charged ion. After Auger decay, this energy stays in the system as internal energy, supporting subsequent dissociation.

In Fig. 4, we compare the ion production for the CH3Cl+ series. The Cl2p3/2,3/2−8a1 resonances and the Rydberg series have very weak intensities and sit on a low background. Of course, the production of doubly charged species in the below-threshold region is not expected, and their formation must be due to many-electron processes. The CH3Cl++, CH2Cl++, and CHCl++ spectra are very similar in shape, with a strong intensity increase above the Cl2p edges due to the opening of electronic relaxation by Auger effect. With the exception of the CCI++ spectrum, the lighter the fragment, the more abundant its production. Also, the higher production of CHCl+ relative to the three other dications supports the work of Wong et al.,13 who predicted its stability in a linear geometry. We also note that the spectral shapes for CHCI+ and CHCI++ are very similar above threshold. One
which is repulsive along the C–Ar bond. The fragmentation with the results in Figs. 2 and 4, where the intensity of the multielectron processes. These observations are consistent molecular orbital leads to the core-equivalent system CH_3Ar, an electron from the Cl_2 ultrafast process is supported by the fact that a transition of chlorine atoms produced after ultrafast dissociation. An gested the possibility of electronic relaxation in core-excited range can occur via several processes. Thissen et al. sug-

| 8a_1 resonance is weak across both the singly charged and doubly charged CH_3Cl series. However, we note that shake-off processes can accompany Auger decay, also leading to doubly charged ions below threshold likely to dissociate. Some possible pathways for formation of doubly charged chlorine are

\[
\text{CH}_3\text{Cl} + h\nu \rightarrow \text{CH}_3\text{Cl}^+, \quad \text{CH}_3\text{Cl}^+ \rightarrow \text{CH}_3\text{Cl}^{++} + e^- \quad \text{(resonant Auger decay)}
\]

\[
\text{(CH}_3)^+ + \text{Cl}^{++} + e^- \quad \text{(dissociation)}
\]

\[
\text{(CH}_3)^+ + \text{Cl}^{++} + 2e^- \quad \text{(second-step electronic relaxation)},
\]

\[
\rightarrow \text{CH}_3\text{Cl}^{++} + 2e^- \quad \text{(resonant Auger decay + shake off)}
\]

\[
\text{(CH}_3)^+ + \text{Cl}^{++} + 2e^- \quad \text{(and dissociation)},
\]

\[
\rightarrow (\text{CH}_3)^+ + \text{Cl}^- \quad \text{(ultrafast dissociation)}
\]

\[
\text{(CH}_3)^+ + \text{Cl}^{++} + 2e^- \quad \text{(resonant Auger decay and shake off)}.
\]

Brackets for the CH_3 groups indicate a possible dissociation process, before, after, or on a time scale comparable to electronic relaxation. The notation “*” corresponds to a true, or, with brackets, to a possible electronic excitation. At variance with the observation of Thissen et al., production of Cl^{++} increases slightly above threshold with the opening of Auger decay.

Production of Cl^{+++} ion is negligible below threshold. In Fig. 6, we show measurements at higher photon energies for the cations Cl^{++}, Cl^{+++}, C^{++}, and CH_2^{++}. The production threshold of Cl^{+++} does not coincide with that of Cl^{++} and is shifted to higher energy (above \( h\nu = 215.6 \) eV). One explanation could be that the formation of the triply charged ion requires a shake-up process during Cl_2p ionization. This double-electron process (one core ionization + one valence-electron excitation) must lead, after normal Auger decay, to a molecule or chlorine atom (in the case of ultrafast fragmentation) in an unstable highly excited electronic state that autoionizes to form a triply charged ion. If the shake-up process does not produce intermediate states energetic enough, only doubly charged species will be formed, as seen below.
This explanation is supported by the presence of a bump around 220 eV photon energy in Fig. 6, the region delimited by dotted lines for several fragments [Cl^{++}, Cl^{+}, CH_{i}^{+} (i=0–3), or CH_{i}^{++} (i=0 or 2)] and can be assigned to fragmentation of doubly excited states that may lead to triply charged species. In the doubly charged chlorine-ion spectrum, this bump is attributed to the opening of dissociation paths leading to CH_{3}^{**}+Cl^{++}, in competition with the paths CH_{3}Cl+h\nu \rightarrow CH_{3}^{+}+Cl^{+}, with the methyl groups in both cases susceptible to dissociation. Similarly, the path CH_{3}Cl+h\nu \rightarrow CH_{i}^{++}+Cl^{+} must be open as well, but the only relevant doubly charged species we are able to detect are C^{++} and CH_{2}^{++}. In the C^{++}, CH_{2}^{++}, and Cl^{+} spectra, the bump around 220 eV photon energy (also seen in the CH_{i}^{+} series in Fig. 3) is present but weaker than for the couples Cl^{++}/CH_{i} and Cl^{+}/CH_{i}.

In Fig. 7, we show the H^{+}, H_{2}^{+}, and H_{3}^{+} ion yields. Below threshold, the formation of H^{+} and H_{2}^{+} on the 8a_{1} resonance is relatively important, whereas it is virtually nonexistent for H_{3}^{+}. However, the production of the latter is slightly visible over the Rydberg series, where the two other ions are clearly present. Above threshold, production of all three ions increases and reaches maxima around 220 eV. The maximum peak positions of the 8a_{1} and Rydberg resonances do not differ with photon energy for all three ions, in contrast to the observations in H_{2}O excited along the O1s\rightarrow 2b_{2} resonance, where maximum production of H_{2}^{+} shifted slightly towards the high-energy side of the resonance, i.e., towards higher vibrational levels presumably inducing formation of molecular hydrogen. In the current results, no narrowing of the H_{2}^{+} or H_{3}^{+} resonance peaks compared to H^{+} has been found either, also in contrast to the observations of Piancastelli et al. on acetylene, where the explanation was that the intermediate core-excited state leads to production of recombination fragments only when higher vibrational levels are excited.

Figure 8 displays the measured HCl^{+} and HCl^{++} ion yields. The observation of these two ions is surprising because their formation requires three distinct steps: breaking of a H–C bond, creation of a H–Cl bond, and breaking of the Cl–C bond. Though we cannot determine the order of these processes from our measurements (the formation mechanisms of these species will be described in a forthcoming paper), it is worth noting that the HCl^{+} and HCl^{++} spectra show different behaviors compared to the Cl^{+} and Cl^{++} yields, respectively. The main difference between Cl^{+} and HCl^{+} is an intensity decrease of the latter above the Cl_{2}p ionization limit compared with the resonant region. In contrast, the HCl^{++} mimics perfectly the Cl^{++} yield. Thus, HCl^{+} and HCl^{++} seem to arise from two distinct processes, or chains of processes.

In Fig. 9, we show the partial ion yields of the two detectable anions, Cl^{−} and C^{−}, in the region of the Cl_{2}p ionization thresholds. For clarity an offset is used on the vertical axis for Cl^{−}.

In Fig. 8, we show the partial ion yields of the two detectable anions. Both Cl^{−} and C^{−} are present below and above thresholds, but no clear structure which could be related to doubly excited states, as described by Stolte et al. in other molecules, is evident. Comparison with anions collected after excitation around the C K edge is given in the next section.
The first intense transition is attributed to the promotion of an orbital, to specific atomiclike orbital symmetries peak energies relative to the ionization potential of the core in Refs. 6 and 7. This method correlates the term values, i.e., intermolecular correlation method of Robin 15,16 is presented.

K the C ground due to Cl2 10. A large number of features are observed on a high back to the carbon K edge in Fig. 11 are quite different from the CH3Cl+ series in Fig. 10. The intensity of the 8a1 resonance is comparable to the intensities in the Rydberg series; this is most significant for CH3+. As for other series, the lighter the fragment, the higher the intensity of the Rydberg peaks. For C+ and CH+, the peak progression extends more clearly to higher photon energy than for CH3+ and the methyl parent ion. The strong intensity of the lowest-energy resonance for these ions is evidence of the C–Cl bond rupture following decay to final states with electron vacancies localized near the C–Cl bond.

In Fig. 12, the spectra represent production of doubly charged CH3Cl+ ions (i=0–3). The main observation is the near-total suppression of the 8a1 resonance in all the spectra, again clear evidence that promotion of a core electron to the 8a1 orbital leads to an unstable species likely to dissociate along the C–Cl bond. In addition, due to Coulomb repulsion, dications fragment more easily than singly charged ions, lowering the intensity of the entire Rydberg series. We note also an intensity increase for CCl++ at the C1s threshold, corresponding to opening of electronic relaxation via Auger decay. The different spectral shapes of CH3Cl+ and CH3Cl++ show that the formation of the dications cannot be consid-

![FIG. 10. Partial ion yields of the CH3Cl+ fragments (i =0–3) around the C1s ionization threshold. Spectra are normalized to the intensity of the first peak (C1s→8a1). Scaling factors and offsets on the vertical axis are shown. Labels refer to Table II.](image)

### TABLE II. Energy positions and assignments of peaks observed after excitation around the C1s orbital of methyl chloride. Notations are from Refs. 6 and 7, where the Rydberg levels are treated as extensions of the halogen atomic orbitals. According to these last two references, nomenclature reflecting molecular symmetries a1 and e in the C3v group has been retained for some Rydberg states, contrary to assignments presented in Table I.

<table>
<thead>
<tr>
<th>Label</th>
<th>This work</th>
<th>Refs. 6 and 7</th>
<th>Attribution C1s →</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>287.34</td>
<td>287.34</td>
<td>8a1(C–Cl)</td>
</tr>
<tr>
<td>B</td>
<td>288.45</td>
<td>288.34</td>
<td>4xα1</td>
</tr>
<tr>
<td>C</td>
<td>288.79</td>
<td>288.54</td>
<td>8a1(C–H)/4a1 + νCH</td>
</tr>
<tr>
<td>D</td>
<td>289.50</td>
<td>289.39</td>
<td>4pe</td>
</tr>
<tr>
<td>E</td>
<td>289.95</td>
<td>289.78</td>
<td>4pe + νCH</td>
</tr>
<tr>
<td>F</td>
<td>290.37</td>
<td>290.19</td>
<td>4pα1/4pe + 2νCH</td>
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<tr>
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<td>290.56</td>
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</tr>
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<td>H</td>
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<td>291.08</td>
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<td>291.34</td>
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<td>M</td>
<td>292.01</td>
<td>...</td>
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</tr>
<tr>
<td>...</td>
<td>292.40</td>
<td>...</td>
<td>IP C1s</td>
</tr>
</tbody>
</table>

![FIG. 11. Partial ion yields of the CH3Cl+ fragments (i =0–3) around the C1s ionization threshold. Spectra are normalized to the intensity of the first peak (C1s→8a1). Scaling factors and offsets on the vertical axis are shown.](image)
tered as a second step following formation of the singly charged ions. Rather, doubly charged species can be formed directly when the energy content of the core-excited intermediate state is high enough for it to decay to final states with two valence holes, i.e., above the double-ionization threshold. The subsequent fragmentation probabilities seem to be essentially the same in the Rydberg region for all doubly charged species, at variance with the relative intensity increase of the Rydberg series for lighter fragments observed in the singly charged series (see Figs. 2, 3, 10, and 11).

As seen in Fig. 13, the intensity distribution of the $\text{H}_2^+$ and $\text{H}_3^+$ fragments following $\text{Cl}_1s$ core excitation is quite similar to the one for $\text{H}^*$. Below threshold, the $8a_1$ orbital and the Rydberg series are clearly resolved in the case of $\text{H}_2^+$ formation, whereas for $\text{H}_3^+$, due to a lower yield, only the most intense peaks are well resolved. As observed around the $\text{Cl}_2p$ threshold, no shift in energy or narrowing of peaks is observed for the two recombination fragments, as compared with $\text{H}^*$. This means that the vibrational population of the intermediate state does not affect production of these ions (see discussion of Fig. 7). One interesting point is the suppression of the $\text{H}_2^+$ and $\text{H}_3^+$ formations above the $\text{Cl}_1s$ threshold; the opposite behavior was observed for the $\text{Cl}_2p$ threshold.

The fragments $\text{H}^{35}\text{Cl}^+$ and $\text{H}^{35}\text{Cl}^{++}$ were also observed (not shown), mainly below the $\text{Cl}_1s$ threshold. However, the associated spectra mimic the ones of $^{35}\text{Cl}^+$ and $^{35}\text{Cl}^{++}$, strongly suggesting that their formation is due to the post-

photodissociation collision between atomic or ionic chlorine and hydrogen rather than a direct combination process induced by core excitation.

In Fig. 14, we show the partial ion yields for the anions detected near the $\text{Cl}_1s$ threshold, namely, $\text{C}^-,^{35}\text{Cl}^-$, and $\text{H}^-$. As in the case of $\text{Cl}_2p$ excitation/ionization, the $8a_1$ resonance and the Rydberg series show somewhat different spectral intensities compared to the cation of the same mass. The main difference between the anion yields around the $\text{Cl}_1s$ and $\text{Cl}_2p$ thresholds (Fig. 9) is their relatively strong intensity above the $\text{Cl}_2p$ threshold. A possible explanation for above-threshold anion production would be the presence of doubly excited states, as observed in several other systems;\textsuperscript{2–4} but in the present case there is no clear resonant structure, just a relatively broad distribution of intensity. To explain this observation, we suggest that above threshold the dominant process is normal Auger decay following core-level ionization. Although anion production due to fragmentation of dications generated by Auger decay is probably very weak, it can oc-

![FIG. 12. Partial ion yields of the CH$_3$Cl$^{++}$ fragments (i=0–3) around the Cl$_1s$ ionization threshold. Spectra are normalized to the intensity of the first peak (Cl$_1s \rightarrow 8a_1$). Scaling factors and offsets on the vertical axis are shown.](image1)

![FIG. 13. Partial ion yields of the H$^+$, H$_2^+$, and H$_3^+$ fragments in the region of the Cl$_1s$ ionization threshold. Scaling factors and offsets on the vertical axis are shown.](image2)

![FIG. 14. Partial ion yields of the detectable anions C$^-$, $^{35}\text{Cl}^-$, and H$^-$ fragments around the Cl$_1s$ ionization threshold. These spectra are compared to partial ion yields of C$^+$, $^{35}\text{Cl}^+$, and H$^+$ normalized to the intensity of the Cl$_1s \rightarrow 8a_1$ resonance and calibrated in energy at the first Rydberg component. As described in the text, the arrow indicates the zone corresponding to shorter C–Cl bond distances.](image3)
cur for a polyatomic system such as CH₃Cl, if three positive charges can be accommodated in the fragmentation process, such as

\[ \text{CH}_3\text{Cl}^+ \rightarrow \text{C}^+ + 2\text{H}^+ + \text{H} + \text{Cl}^- . \]

At variance with this, anion production from a molecular trication is extremely unlikely, because it would be necessary to distribute four positive charges over a relatively small number of fragments. Therefore, a possible explanation for the different anion behaviors around the two edges is that deeper C₁s core holes are more likely to undergo Auger-cascade or double-Auger processes leading to triply or multiply charged species relative to shallower Cl₂ edges. This can be compared with results on SF₆ with results on SF₆ (Ref. 17) and CH₃OH (Ref. 18) for which the number of different anions is larger for the case of inner-shell excitation of the central sulfur or carbon atoms, respectively, than for the case of inner-shell excitation of the peripheral fluorine or oxygen atoms. In sulfur hexafluoride, this behavior is attributed to the presence of a potential barrier due to the electronegativity difference between the central and peripheral atoms temporarily trapping the emitted electron. The explanation for site-specific production of H⁻ in methanol, or methyl chloride, is less straightforward. One possibility could be related to proximity or steric hindrance; the ejected electron may have a higher probability to be captured by free hydrogen in the cases of emission from the carbon rather than from the oxygen or chlorine atoms. Also, comparison of the intensity distribution of anion spectra after C₁s ionization with spectra of the same mass cations shows a lower intensity on the left side of the C₁s → 8σ₂ resonance for Cl⁻, in contrast to the other anions (see Fig. 14). This could mean that core-level photoexcitation preferentially reaches the Franck-Condon region corresponding to longer (shorter) C–Cl bond distances at lower (higher) photon energies along the profile of this strongly antibonding resonance, suggesting a possible bond-length dependence in the formation of an anionic species.

IV. CONCLUSION

We have measured the partial ion yields following excitation of the CH₃Cl molecule in the region of the Cl₂p and C₁s core-level thresholds. We confirm the role of Rydberg transitions in the formation of lighter fragment species and the strong localization of the electron vacancies in the final state along the C–Cl bond after promotion of a carbon K-shell electron to the first empty orbital. Furthermore, some remarkable effects have been observed, such as anion production, dependent on the environment of the initially excited atom, namely, whether its location in the molecule is central or peripheral, as well as a possible bond-length dependence on the formation of Cl⁻.

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