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

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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 H2+ ion dependent on the way the intermediate state is prepared. The maximum intensity for H2+ 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-photoion 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-
ication 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.\(^8\) 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 C1s 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\(^{i}\) bond after promotion of a carbon \(\text{Cl}^{+}\) with two anions 35Cl\(^{-}\) and C 37Cl\(^{-}\). Table I provides the peak assignments in the 198–280 eV photon-energy range. The energy position of the 8\(\bar{a}\) transition given in Ref. 5 was used for energy calibration.

In Fig. 2, we present the partial ion yields for the CH\(^{i}\)Cl\(^{+}\) series. Assignments for the five resonant features are as follows. The lowest-lying resonance (A) is attributed to the Cl2p\(3\bar{a}_1\) 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 weak (strong) compared to the ones located just below (above) the C1s 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.

**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 as 30 meV, using previous measurements of the 4s(1D)\(^2\)D\(_{5/2}\) atomic chlorine transition at 204.31 eV with a theoretical lifetime broadening of 5.3 meV.\(^9\) The resolution at \(h\nu=300\) eV was estimated as 70 meV based on previous measurements of CO.\(^2\) Ion mass and charge characterization was done with a 180° hemispherical analyzer with a resolution of 1 mass in 50.\(^10\) 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 refocused 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 \(\times 10^{-5}\) 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, CH\(^{i}\)35Cl\(^{+}\) 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 C1s 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 C1s 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: CH\(^{i}\)Cl\(^{+}\) and CH3Cl\(^{++}\) for both 35Cl\(^{+}\) and 37Cl\(^{+}\) isotopes, Cl\(^{+}\) with \(i=0–3\), C\(^{3+}\), CH\(^{2+}\), 35Cl\(^{+}\), 37Cl\(^{+}\), 35Cl\(^{++}\), 37Cl\(^{++}\), H\(^{+}\), H\(^{2+}\), H\(^{3+}\), 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 8\(\bar{a}\) transition given in Ref. 5 was used for energy calibration.

In Fig. 2, we present the partial ion yields for the CH\(^{i}\)Cl\(^{+}\) series. Assignments for the five resonant features are as follows. The lowest-lying resonance (A) is attributed to the Cl2p\(3\bar{a}_1\) 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 weak (strong) compared to the ones located just below (above) the C1s 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.

**TABLE I. Energy positions and assignments of lines observed in the region of the Cl2p and C1s ionization thresholds.**

<table>
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<tr>
<th>Label</th>
<th>This work</th>
<th>Ref. 5</th>
<th>Cl2p(3\bar{a}_2)</th>
<th>Cl2p(3\bar{a}_1)</th>
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<tr>
<td>A</td>
<td>200.70</td>
<td>200.70</td>
<td>8(\bar{a}_1)</td>
<td>8(\bar{a}_1)</td>
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<tr>
<td>···</td>
<td>202.35</td>
<td>···</td>
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<td>8(\bar{a}_1)</td>
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<td>202.50</td>
<td>4(s)</td>
<td>4(s)</td>
</tr>
<tr>
<td>C</td>
<td>204.25</td>
<td>204.10</td>
<td>4(p)</td>
<td>4(p)</td>
</tr>
<tr>
<td>D</td>
<td>205.25</td>
<td>···</td>
<td>5(s)</td>
<td>5(s)</td>
</tr>
<tr>
<td>E</td>
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<td>206.26</td>
<td>IP</td>
<td>IP</td>
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<td>···</td>
<td>206.90</td>
<td>···</td>
<td>5(s)</td>
<td>5(s)</td>
</tr>
<tr>
<td></td>
<td>207.96</td>
<td>207.90</td>
<td>IP(^a)</td>
<td>IP(^a)</td>
</tr>
</tbody>
</table>

**TABLE I. Energy positions and assignments of lines observed in the region of the Cl2p and C1s ionization thresholds.**

<table>
<thead>
<tr>
<th>Position (eV)</th>
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<th>Ref. 6</th>
<th>Cl2s→</th>
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<td>Extra peaks(^b)</td>
<td>272.60</td>
<td>271.70</td>
<td>8(\bar{a}_1)</td>
</tr>
<tr>
<td></td>
<td>276.60</td>
<td>···</td>
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</table>

\(^a\)Deduced from the spin-orbit splitting value.

\(^b\)Cf. Fig. 1.
sition to a core-excited state may have influence on the population of vibrational levels corresponding to stretching and bending motions in the methyl group. With photoelectron photoion coincidence measurements, Thissen et al.\textsuperscript{5} assigned unresolved structures on this resonance to a population of excited vibrational states separated by 250 meV and corresponding to the C–H stretching mode. We also observe cited vibrational states separated by 250 meV and CCl+, and CH\textsuperscript{35}Cl+, respectively. For the first two, weak features at resonance, one resolved peak

\[ \text{Cl}_2^+ \rightarrow \text{H}_2 \] to empty orbitals of 4s, 4p, 5s, and 5p atomic characters.

In Fig. 2, curves 1 and 2 are associated with the CH\textsuperscript{35}Cl+/C\textsuperscript{37}Cl+ and CH\textsuperscript{35}Cl+/CH\textsuperscript{37}Cl+ fragments, respectively, whereas curves 3 and 4 correspond to CH\textsuperscript{35}Cl+ and C\textsuperscript{35}Cl+, respectively. For the first two, weak features at resonances A–C sit on a high decreasing background attributed to direct valence photoemission. In contrast, the CH\textsuperscript{35}Cl+ and C\textsuperscript{35}Cl+ ions are much more abundant around the Cl2p edges. For these latter fragments, the Cl2p→8a\textsubscript{1} transition and transitions to the first two Rydberg orbitals are clearly resolved. In addition, for Cl\textsuperscript{2} only, three additional transitions, one resolved peak (E) and two shoulders (D and F), are also visible. Above threshold, a large structure dominates curves 3 and 4, with two distinct maxima depending on the ion. Precise assignment remains difficult because doubly excited states generally overlap the shape resonances in this region;\textsuperscript{2,4} such an overlap could be the origin of these intensity variations above threshold.

Figure 3 shows partial ion yields for the CH\textsuperscript{3} ions (i=0–3). With the exception of the methyl ion, the Cl2p→4s, 4p, and 5s Rydberg excitations are well resolved. Weak production of CH\textsuperscript{3} following excitation to the lower Rydberg components allows us to assign the two lowest-lying spectral features to the Cl2p\textsubscript{3/2}→8a\textsubscript{1} and Cl2p\textsubscript{1/2}→8a\textsubscript{1} transitions, with an intensity ratio of 2:1 in the absence of exchange effects. With an experimental resolution of 30 meV, we measured a spin-orbit splitting of 1.65 eV, in very good agreement with the value of 1.64 eV obtained in x-ray photoelectron spectroscopy studies by Aitken et al.\textsuperscript{11}

Below threshold, the main experimental finding for both the CH\textsuperscript{3}Cl+ and the CH\textsuperscript{3}+ series is the relative intensity enhancement of the spectral structures corresponding to Rydberg transitions as the fragments become lighter, as already observed by Piancastelli et al.\textsuperscript{5} for ethylene/acyetylene compounds\textsuperscript{3} and by Stolte et al.\textsuperscript{12} for water.\textsuperscript{12} The explanation is that a core-to-Rydberg excited molecule is more likely to relax by spectator-Auger decay: the excited electron is far from the nucleus and the system relaxes preferentially by emitting an electron from an orbital having strong overlap with the core hole, i.e., a valence orbital, while the initially excited electron remains as a “spectator.” The resulting ion is still in an excited state and is energetically more likely to dissociate. Above threshold, we observe an equivalent tendency: the lighter the fragment, the larger the relative intensity. The position of the maxima above threshold, however, depends on the fragment mass in the CH\textsuperscript{3}+ series: for lighter fragments, the maximum is shifted towards higher energies (the maxima positions are 216.6, 218.85, 222.8, and 225 eV for CH\textsuperscript{3}, CH\textsuperscript{2}, CH\textsuperscript{+}, and C\textsuperscript{+}, respectively). We speculate that as the photon energy increases above threshold, more vibrational and/or electronic energy is stored in the singly charged intermediate state. 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 CH\textsubscript{3}Cl++ series. The Cl2p\textsubscript{1/2,3/2}→8a\textsubscript{1} 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 CH\textsubscript{3}Cl+++, CH\textsubscript{2}Cl++, 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 CCl++ 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.,\textsuperscript{13} who predicted its stability in a linear geometry. We also note that the spectral shapes for CHCl++ and CHCl+++ are very similar above threshold. One
leads to a neutral CH$_3$ and an excited chlorine atom that 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 with the possibility of electronic relaxation in core-excited anions. An ultrafast process is supported by the fact that a transition of chlorine atoms produced after ultrafast dissociation. An explanation could be an equivalence of how they are produced, with the location of the positive charges at the time of the dissociation being the only difference,

$$\text{CH}_3\text{Cl} + h\nu \rightarrow \text{CH}_3\text{Cl}^* + e^-,$$

$$\text{CH}_3\text{Cl}^* \rightarrow \text{CHCl} + \text{H}^+ + \text{H} \text{ or } \text{CHCl}^* + 2\text{H} + e^-.$$

In contrast, the CCl$^{++}$ spectrum differs completely from CCl$^+$, both above and below thresholds. We attribute this behavior to an instability of the CCl$^{++}$ dication due to Coulombic repulsion.

For the Cl$^{++}$ spectrum shown in Fig. 5, there is a large contribution from below-threshold resonances that cannot be explained by anion-cation pair production: the only detected anions are C$^-$ and Cl$^-$, and C$^-$ intensity is much too weak. The production of Cl$^{++}$ in the 199–206 eV photon-energy range can occur via several processes. Thissen et al.$^5$ suggested the possibility of electronic relaxation in core-excited chlorine atoms produced after ultrafast dissociation. An ultrafast process is supported by the fact that a transition of an electron from the Cl2p orbital to the lowest unoccupied molecular orbital leads to the core-equivalent system CH$_3$Ar, which is repulsive along the C–Ar bond. The fragmentation leads to a neutral CH$_3$ and an excited chlorine atom that relaxes primarily to Cl$^+$, with minority production of Cl$^{++}$ via multielectron processes. These observations are consistent with the results in Figs. 2 and 4, where the intensity of the $8\alpha_1$ resonance is weak across both the singly charged and doubly charged CH$_3$Cl 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

$$\text{CH}_3\text{Cl} + h\nu \rightarrow \text{CH}_3\text{Cl}^+,$$

$$\text{CH}_3\text{Cl}^+ \rightarrow \text{CH}_2\text{Cl}^+ + e^- \text{ (resonant Auger decay)}$$

$$(\text{CH}_3)^* + \text{Cl}^{++} + e^- \text{ (dissociation)}$$

$$(\text{CH}_3)^* + \text{Cl}^{++} + 2e^- \text{ (second-step electronic relaxation)},$$

$$\rightarrow \text{CH}_2\text{Cl}^+ + 2e^- \text{ (resonant Auger decay + shake off)}$$

$$(\text{CH}_3)^* + \text{Cl}^{++} + 2e^- \text{ (and dissociation)},$$

$$\rightarrow (\text{CH}_3)^* + \text{Cl}^- \text{ (ultrafast dissociation)}$$

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

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$_3^a$. 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 Cl2p 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.

---

**FIG. 4.** Partial ion yields of the CHCl$^{+++}$ fragments ($i=0–3$) around the Cl2p ionization thresholds. A scaling factor and offsets on the vertical axis are shown.

**FIG. 5.** Qualitative comparison of partial ion yields of the $^{35}$Cl$^-$, $^{35}$Cl$^+$, $^{35}$Cl$^{++}$, and $^{35}$Cl$^{+++}$ fragments below the Cl2p ionization thresholds. Scaling factors are used to normalize the spectra to the intensity of the first transition.

**FIG. 6.** Comparison of $^{35}$Cl$^{+++}$, $^{35}$Cl$^{++}$, C$^{++}$, and CH$_3^+$ ions yields. The dotted lines delimit a zone corresponding to the opening of dissociation pathways involving triply charged species. Scaling factors and offsets on the vertical axis are shown.
hν=215.6 eV. This explanation is supported by the presence around 220 eV photon energy 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$\rightarrow$CH$_3$*+Cl++,$\rightarrow$CH$_2$+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$_3$+ series in Fig. 3) is present but weaker than for the couples Cl++/CH$_3$+ and Cl+/CH$_3$+.

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$_2$ 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. 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.
Excitation of methyl chloride around the carbon K edge leads to a large number of cations: CH$_3$Cl$^+$, CH$_2$Cl$^{++}$, and CH$_i$(i=0–3), H$^+$, H$_2^+$, H$_3^+$, Cl$^+$, Cl$^{++}$, Cl$^{+++}$, HCl$, HCl^{++}$, and C$^{++}$, as well as three anions: Cl$^-$, C$^-$, and H$^-$.

The partial ion yields for the series CH$_i$Cl$^+$(i=0–3) in the region of the C1s ionization threshold are shown in Fig. 10. A large number of features are observed on a high background due to CI$_2p$ ionization (see Fig. 1). Assignments of the C$K$-edge peaks by Hitchcock and Brion, based on the intermolecular correlation method of Robin [15,16], is presented in Ref. 6 and 7. This method correlates the term values, i.e., peak energies relative to the ionization potential of the core orbital, to specific atomiclike orbital symmetries (s, p, d, ...). The first intense transition is attributed to the promotion of a C1s electron to the 8a$_1$ antibonding orbital. The narrower peaks at higher energy are attributed to a Rydberg progression, with vibrational substructures for some states (see Table II). Spectra 1 and 2 in Fig. 10 correspond to a 1:3 mixture of the ions CH$^{35}$Cl$^+$/CH$^{37}$Cl$^+$ and C$^{37}$Cl$^+$/CH$^{35}$Cl$^+$, respectively, whereas spectra 3 and 4 correspond only to the fragments CH$^{35}$Cl$^+$ and C$^{37}$Cl$^+$, respectively. By normalizing to the intensity of the 8a$_1$ resonance, we observe very similar spectra, contrary to results in the CI$_2p$ region (see Fig. 2); formation of the ions in this series appears to ensue from very similar dissociation processes.

The shapes of the ion-yield spectra for the CH$^+_i$ series in Fig. 11 are quite different from the CH$_i$Cl$^+$ series in Fig. 10. The intensity of the 8a$_1$ resonance is comparable to the intensities in the Rydberg series; this is most significant for CH$_2^+$. 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 CH$_2^+$ 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 CH$_i$Cl ions (i=0–3). The main observation is the near-total suppression of the 8a$_1$ resonance in all the spectra, again clear evidence that promotion of a core electron to the 8a$_1$ 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 CH$_i$Cl$^+$ and CH$_i$Cl$^{++}$ show that the formation of the dications cannot be consid-

**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 $a_1$ and $e$ in the C$_{3v}$ group has been retained for some Rydberg states, contrary to assignments presented in Table I.

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<th>Label</th>
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<tr>
<td>⋮</td>
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**FIG. 10.** Partial ion yields of the CH$_i$Cl$^+$ fragments (i=0–3) around the C1s ionization threshold. Spectra are normalized to the intensity of the first peak (C1s→8a$_1$). Scaling factors and offsets on the vertical axis are shown. Labels refer to Table II.

**FIG. 11.** Partial ion yields of the CH$_i^+$ fragments (i=0–3) around the C1s ionization threshold. Spectra are normalized to the intensity of the first peak (C1s→8a$_1$). Scaling factors and offsets on the vertical axis are shown.
considered 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 H$_2^+$ and H$_3^+$ fragments following C1s core excitation is quite similar to the one for H$^+$. Below threshold, the 8a$_1$ orbital and the Rydberg series are clearly resolved in the case of H$_2^+$ formation, whereas for H$_3^+$, due to a lower yield, only the most intense peaks are well resolved. As observed around the Cl$_2p$ threshold, no shift in energy or narrowing of peaks is observed for the two recombination fragments, as compared with 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 H$_2^+$ and H$_3^+$ formations above the C1s threshold; the opposite behavior was observed for the Cl$_2p$ threshold.

The fragments H$^{35}$Cl$^+$ and H$^{35}$Cl$^{++}$ were also observed (not shown), mainly below the C1s threshold. However, the associated spectra mimic the ones of $^{35}$Cl$^+$ and $^{35}$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 C1s threshold, namely, C$^-$, $^{35}$Cl$^-$, and H$^-$. As in the case of 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 C1s and Cl$_2p$ thresholds (Fig. 9) is their relatively strong intensity above the 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; 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 C1s ionization threshold. Spectra are normalized to the intensity of the first peak (C1s → 8a$_1$). Scaling factors and offsets on the vertical axis are shown.

FIG. 13. Partial ion yields of the H$^+$, H$_2^+$, and H$_3^+$ fragments in the region of the C1s ionization threshold. Scaling factors and offsets on the vertical axis are shown.

FIG. 14. Partial ion yields of the detectable anions C$^-$, $^{35}$Cl$^-$, and H$^-$ fragments around the C1s ionization threshold. These spectra are compared to partial ion yields of C$^+$, $^{35}$Cl$^+$, and H$^+$ normalized to the intensity of the C1s → 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.
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 Cl₁s core holes are more likely to undergo Auger-cascade or double-Auger processes leading to triply or multiply charged species relative to shallower Cl₂p holes, implying a negligible probability for anion formation.

Finally, H⁻ is formed after photoexcitation in the C₁s region, but not near the Cl₂p edge. This can be compared with results on SF₆ (Ref. 17) and CH₂OH (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 → 8d₁ 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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