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Role of ultrafast dissociation in the fragmentation of chlorinated methanes

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Photon-induced fragmentation of a full set of chlorinated methanes (CH_3Cl , CH_2Cl_2 , CHCl_3 , CCl_4) has been investigated both experimentally and computationally. Using synchrotron radiation and electron-ion coincidence measurements, the dissociation processes were studied after chlorine $2p$ electron excitation. Experimental evidence for CH_3Cl and CH_2Cl_2 contains unique features suggesting that fast dissociation processes take place. By contrast, CHCl_3 and CCl_4 molecules do not contain the same features, hinting that they experience alternative mechanisms for dissociation and charge migration. Computational work indicates differing rates of charge movement after the core-excitation, which can be used to explain the differences observed experimentally. *Published by AIP Publishing.*
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I. INTRODUCTION

Excitation of an inner-shell electron in molecules often results in a distinctive fragmentation pattern governed by the resulting electronic relaxation pathways as well as nuclear dynamics. In the context of chlorinated methanes, fragmentation following an inner-shell excitation can be an effective way of releasing chlorine from the molecules. In atmospheric sciences, the depletion of ozone has been linked to reactions with chlorine atoms and radicals.¹ Collisions between ozone molecules and atomic chlorine are highly efficient at producing chlorine monoxide and oxygen.¹ Chlorine monoxide can react further producing atomic chlorine, leading to a cycle where ozone is destroyed into molecular oxygen but no chlorine atoms are consumed.¹ Here we report several mechanisms related to atomic chlorine production from chlorinated methanes via core-electron excitation.

In industrial applications, chlorinated methanes are used mainly as precursors. The processing of silicones, various solvents, new hydrochlorofluorocarbons, and chlorofluorocarbons all have different chlorinated methanes incorporated in their manufacture. As the global consumption of these compounds is increasing, the impact on atmosphere demands further study.^{2–4} It has been found that the atmospheric concentrations of some chlorinated methanes have been rising in the 21st century,⁵ and all of them have natural and anthropogenic sources.⁶

Ultrafast dissociation (UFD) has been shown to be an effective way of releasing the molecular internal energy after electronic core excitation into an unoccupied molecular orbital with a strong antibonding character.⁷ In this paper,

dissociation is discussed as proceeding by two-steps, i.e., occurring before or after the emission of an Auger electron. This distinction is an approximation, as in reality the system is only truly explained by a one-step process once the wave-packet dynamics and scattering times are on a similar time frame.⁸

The time scale of molecular dissociation is rather sensitive to the masses of the constituent particles involved in the process. For example, in the case of increasing the mass of the neutral fragment by a factor of 15 (e.g., when moving from HCl to CH_3Cl) and assuming rigid motion of fragments, dissociation is expected to slow down considerably,^{8,9} which in turn promotes competing molecular decay (i.e., electronic relaxation that takes place before the nuclear rearrangement).

Chlorinated methanes have been studied intensively by numerous X-ray based techniques. The fragmentation has been widely studied using electron-ion coincidence techniques.^{10–17} The electronic structure of the valence region and its relationship to fragmentation has been investigated by various UV and vacuum ultraviolet (VUV) excitation studies.^{18–23} The dissociation dynamics and fragment production have been investigated in the vicinity of the Cl $2p$ absorption edge in gaseous and condensed CH_2Cl_2 ,^{24,25} CHCl_3 ,²⁶ and CCl_4 ²⁷ using partial ion yield techniques. Resonant inelastic X-ray scattering (RIXS) is also a common method for probing dissociation and nuclear dynamics. For chlorinated methanes, RIXS has often been used in conjunction with carbon $1s$ excitation.^{28–32}

In the present experiment, we investigate the dissociation of four chlorinated methanes (CH_3Cl , CH_2Cl_2 , CHCl_3 , and CCl_4) by exciting a chlorine $2p$ core electron into an unoccupied σ^* type orbital with a strong antibonding character. The potential fragmentation pathways are studied using

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Auger-electron fragment-ion coincidence spectroscopy. Special interest is given to whether UFD is a prominent process in the different systems. These four similar molecules provide an excellent test case for studying the details of the dissociation pathways initiated by an identical resonance excitation. In all four molecules, the detected electrons were from the spectator decay of the L-VV Auger decay process. All created positive ions were subsequently detected. Fragmentation of CH_3Cl and CH_2Cl_2 has been studied by Miron *et al.*³³ and recently by Alcantara *et al.*,²⁵ respectively, using similar methods. We complement these studies with a systematic study of these four molecules under similar experimental conditions.

II. EXPERIMENTS

The experiments were conducted on the I411 beamline^{34,35} of the MAX IV Laboratory in Lund, Sweden. A Scienta SES-200 type hemispherical deflection analyzer (HDA)³⁶ was used to measure the kinetic energies of the emitted photo and Auger electrons and a two-field Wiley-McLaren type time-of-flight mass spectrometer (TOFMS)³⁷ for the measurements of the mass-to-charge ratios of the ions. The two spectrometers were operated in the coincidence mode where the successful electron detection initiates the TOFMS to record the masses of the produced ions.

The TOFMS consists of an extraction, acceleration, and drift regions, each with lengths of approximately 15 mm, 100 mm, and 660 mm. The extraction region has two circular meshes on the either side to ensure a homogeneous electric field as well as to allow the passage of electrons and ions to the opposite directions. The acceleration region houses a series of aluminium rings with resistors in series to distribute the voltage for each ring in order to further enhance the homogeneity of the accelerating field. To get a good mass resolution, the TOFMS is equipped with a long drift tube allowing the different mass-to-charge particles to be differentiated.

The voltages that create the extraction and acceleration fields are optimized according to the Wiley-McLaren conditions for spatial focusing.³⁷ The voltage ratio between the acceleration (U_{acc}) and extraction (U_{ext}) regions in these experiments was found to be about $U_{\text{acc}}/U_{\text{ext}} = 7.40$. Here, acceleration voltages of about 2 kV were used, which yielded electric field strengths of 16 V/mm and 20 V/mm for the extraction and acceleration regions, respectively.

The detector of the TOFMS consists of three Z-stacked multichannel plates (MCPs) of 75 mm diameter active area. The detector is equipped with a delay line type position sensitive detector manufactured by Roentdek Handels GmbH. The delay lines create a hexagonal anode structure for optimal particle detection.³⁸ In the results provided in this paper, however, the position information of the ions was not used.

The SES-200 electron spectrometer is otherwise unmodified with the exception of the detector, which instead of a CCD camera based detection system houses three MCPs and a resistive anode manufactured by Quantar Technology Inc. The resistive anode allows for a fast electron detection, which

is essential for coincidence operation (similar setup has been described previously^{39,40}). In all measurements here, the HDA was operated with a constant pass energy mode, with a pass energy of 100 eV. A curved entrance slit (width 0.8 mm) was also used, yielding an approximate analyser broadening of 0.2 eV. All measurements were done with the analyser at the so-called “magic angle” of 54.7° with respect to the linearly polarized synchrotron light. The electron energies were calibrated using the known resonant Auger (RA) spectra of the chlorinated methane samples.

The coincidence logic follows the schemes utilized earlier,^{17,39,41–45} where the electron detection from the HDA sends a signal to the pulsed voltage source (Directed Energy, Inc. model PVX-4450) which raises the voltages in the extraction region for a specified time interval, allowing the measurement of the ion flight times. Due to the inherent differences between the transmissions of the HDA and the TOFMS, there exists a high likelihood of producing false coincidences between electrons and ions that in reality have no correlation. To subtract false coincidence events from the data, the measurement process includes a random triggering sequence.⁴⁶ An external pulse generator provides pulses with a fixed frequency which is interjected between the electron detections. The externally pulsed events are labeled accordingly in the data storage. In the data handling, it is then possible to subtract the randomly triggered events from the electron triggered events so that one is able to only see the real correlations between the electrons and ions.

The coincidence measurement was run at a trigger rate of approximately 100 Hz from both the electron and random sources (i.e., about 200 Hz trigger rate in total). This enabled us to do measurements which so-far have been impractical due to the time limitations of a typical synchrotron beamtime. For example, a particular coincidence ion can be monitored as a function of incident photon energy, as was demonstrated by Kokkonen *et al.*¹⁷ A similar measurement scheme was later utilized by Sann *et al.*, where they performed photon energy scanned coincidence measurements while also measuring other parameters, such as the electron emission angle dependency.⁴⁷

All samples were introduced to the vacuum chamber via a hypodermic needle inlet in order to increase the pressure in the interaction region. CH_3Cl gas was used without any further purification while CH_2Cl_2 , CHCl_3 , and CCl_4 (all purities >99.5%) which are in liquid form in normal temperature and pressure (NTP) conditions were introduced to the vacuum via several freeze-pump-thaw cycles.

III. RESULTS

Figure 1 contains the total ion yield (TIY) spectra of all four molecules recorded in the vicinity of the chlorine $2p$ absorption edge. These spectra have been used to locate the energies of the $\text{Cl } 2p_{3/2} \rightarrow \sigma^*$ resonances. The energy of the resonance is observed to decrease in larger chlorinated methanes. For different chloromethanes, the experimental resonance energies are gathered in Table I together with the lowest unoccupied molecular orbital type (LUMO). The $2p$ ionization thresholds for all four molecules are at approximately 206 eV

FIG. 1. Total ion yield spectra of CH_3Cl , CH_2Cl_2 , CHCl_3 , and CCl_4 . The arrows indicate the photon energies used to excite the σ^* resonance. The CCl_4 spectrum was measured separately on the same beamline using similar experimental arrangements.

(for $2p_{3/2}$) and 208 eV (for $2p_{1/2}$).^{10,24,26,27} The LUMO orbitals are labeled according to Refs. 11, 24, 26, and 27.

The resonant Auger electron spectra at the $2p_{3/2} \rightarrow \sigma^*$ resonance were measured in the same kinetic energy region for all molecules. The spectra are shown in Fig. 2, and they are also divided into three different regions. The regions were chosen based on the RA electron spectrum of CH_3Cl so that each region contains one of the atomic chlorine spectral lines leading to three $2S+1L\ 3p^{-2}$ final states: region A is centered around 1S , region B around 1D line, and region C around 3P line.

The electron-ion coincidence data in this work are presented in the form of *coincident ion yields* (CIYs), which are composed by summing the amount of coincident ions in each electron energy separately for each fragment ion. Figure 3 contains the CIY spectra of all four chlorinated methanes as well as the RA electron spectra at the top. All spectra are recorded with the photon energy tuned to the selected $2p_{3/2} \rightarrow \sigma^*$ resonance, with energies given in Table I.

The kinetic energies of the resonant Auger electrons (for 1S , 1D , and 3P final states) were determined from the Cl^+ CIY from CH_3Cl and were found to be approximately 177.3 eV, 179.3 eV, and 180.7 eV, which are in good agreement with the values reported earlier.^{8,48,49}

To clarify further the relative abundance of each observed cation, we have modified the CIY spectra to display the relative yields at each energy step via

$$I_i^{\text{rel}}(E) = \frac{I_i^{\text{abs}}(E)}{\sum_j I_j^{\text{abs}}(E)}, \quad (1)$$

where $I_i^{\text{abs}}(E)$ and $I_i^{\text{rel}}(E)$ are the absolute and relative CIY for ion i at energy E with the denominator containing the sum of all

TABLE I. Photon energies used for LUMO σ^* resonance excitation in the different chlorinated methanes.

Molecule	$h\nu$ (eV)	LUMO
CH_3Cl	201.0	$8a_1$
CH_2Cl_2	200.9	$10a_1$
CHCl_3	200.8	$10a_1$
CCl_4	200.4	$7a_1$

FIG. 2. RA spectra of the four molecules and the three different regions where numerical values for the CIYs have been tabulated. The dashed line indicates the position of the atomic 1S , 1D , and 3P states according to Ref. 48.

absolute CIYs (index j running through all observed cations). The spectra are shown in Fig. 4 for CH_3Cl , CH_2Cl_2 , CHCl_3 and CCl_4 . Additionally, the relative CIYs in each molecule have been stacked on top of each other to make the relative contribution of each ion visually clearer.

The electron intensity weighted averages for the CIY for each fragment ion are then tabulated in Table II for the three regions A, B, and C.

In all measurements, no doubly or higher order ionized products were seen in coincidence with RA electrons. Apart from hydrogen, all detected cations were recorded with similar detection efficiency. The sum of all detected coincident ions is plotted together with the electron spectrum on the top of each case in Fig. 3. Since the sum spectra and the electron spectra align quite well, it is reasonable to assume that our experiment captures all the main σ^* fragmentation channels.

A. Chloromethane (CH_3Cl)

In previous studies, chloromethane has been classified as an example where UFD is a likely consequence of the $\text{Cl}\ 2p_{3/2} \rightarrow \sigma^*$ excitation.^{10,33,50,51} The dissociation process has been explained to happen while the molecule is still in the core-excited state. The distance between the carbon and the Cl atom containing the core-hole can reportedly increase so fast that when the Auger decay occurs, the Cl atom is relatively far from the methyl group. The energies of the resonant Auger electrons are consequently modified by this process so that the spectrum does not contain broad molecular Auger peaks but sharper atomic-like features instead. For CH_3Cl , this is seen in the Cl^+ CIY in Fig. 3(a) as three sharp lines at the energies corresponding to atomic chlorine resonant Auger final states.

From the CIY results, we can conclude that the most prominent fragmentations subsequent to the RA process (or during the RA process) are

FIG. 3. CIY spectra from CH_3Cl , CH_2Cl_2 , CHCl_3 , and CCl_4 molecules taken at the σ^* resonance indicated in Table I. Each cation is indicated with a different colour and labeled to the left of each panel. The RA electron spectra in each molecule are displayed on the top of each molecule in black. The sum of all detected ions is plotted in red along the RA spectrum. The energies of the atomic chlorine final states are indicated with dashed lines.⁴⁸ Only the most intense CIY spectra are plotted here.

since the cations CH_3^+ , CH_2^+ , and Cl^+ account for about 70% of all the detected coincidence ions. The reaction leading to the release of Cl^+ is most likely the result of a case where the C–Cl distance has grown large enough so that no charge-transfer interaction can occur. The configuration after the Auger decay therefore leaves the excited charge (coming from the Cl 2p orbital) in the chlorine atom. This is evidenced by the Cl^+ CIY, which, with the current statistical quality, does not show structures originating from the molecular decay. The second reaction leading to a release of CH_3^+ always belongs to the molecular Auger decay regime, i.e., the dissociation occurs after the Auger decay since the excited charge is transferred to the CH_3^+ from the chlorine.

The high amount of CH_2^+ cation seen in coincidence is partially due to direct valence photodissociation. As the inner valence orbital $2a_1$ has a binding energy of approximately 22 eV, there is a non-zero probability that direct photoionization of that orbital occurs, even at the photon energy of 201 eV. Reaction leading to the emission of CH_2^+ is then

where the chlorine and hydrogen can also be bound together as HCl . The appearance of CH_2^+ from direct valence photodissociation is confirmed by an off resonance measurement in Fig. 5(a), where the photon energy is 199 eV and therefore below the σ^* resonance.

CH_3^+ is created at similar final state energies as HCl^+ , where both require breaking of the C–Cl bond. In the creation of HCl^+ though, there is an additional hydrogen movement from the methyl group toward the chlorine atom. The appearance of HCl^+ subsequent to the Auger decay in CH_3Cl has been investigated before and has been attributed to a specific rotation of the methyl group that occurs in one of the Auger final states.^{17,33}

The relative CIYs [calculated using Eq. (1)] for all detected cations from CH_3Cl are shown in Fig. 4(a). There are some changes in the respective final Auger states in the measured energy window. It appears that around the ^3P

FIG. 4. Relative CIYs from all four molecules and the corresponding Auger spectrum on the top. The relative CIYs are stacked on top of each other to visualize the changes in the fragmentation behavior as a function of electron energy.

TABLE II. Percentages of detected fragment ions in coincidence with electrons in three different regions. See text and Fig. 2 on how the regions are chosen.

	Region A				Region B				Region C			
	CH ₃ Cl	CH ₂ Cl ₂	CHCl ₃	CCl ₄	CH ₃ Cl	CH ₂ Cl ₂	CHCl ₃	CCl ₄	CH ₃ Cl	CH ₂ Cl ₂	CHCl ₃	CCl ₄
C ⁺	...	4	3	...	...	1	1	...	...	1	-1	...
CH ⁺	12	11	26	...	6	3	0	...	3	2	1	...
CH ₂ ⁺	36	33	...	...	39	55	...	...	19	56	...	...
CH ₃ ⁺	3	...	...	...	15	...	...	...	25	...	...	...
Cl ⁺	32	31	13	17	24	33	19	19	34	31	16	13
HCl ⁺	4	...	...	...	7	...	...	...	13	...	...	...
CCl ⁺	5	12	49	68	4	3	38	71	2	5	19	65
CHCl ⁺	...	9	6	...	...	6	38	...	...	5	63	...
CH ₃ Cl ⁺	8	...	...	...	6	...	...	...	5	...	...	...
CCl ₂ ⁺	...	...	...	7	...	...	...	5	...	...	...	18
CHCl ₂ ⁺	...	...	3	...	...	...	3	...	...	...	1	...
CCl ₃ ⁺	...	...	...	8	...	...	...	4	...	...	...	5

states the dissociation favours cleaving the C–Cl bond and leaving the charge in either fragment, which is then seen as Cl⁺ or CH₃⁺. These two cations together account for 57% of all detected cations in region C.

When moving to lower kinetic energies (higher binding energies) in region A, the dominant cation changes to CH₂⁺ and Cl⁺, which account for 64% of all ions. This is most likely due to a high probability of direct valence photodissociation to create CH₂⁺.²¹

Region B is in intermediate state between these two cases. Across the whole energy window, it appears that breaking the C–Cl bond is the dominant form of fragmentation.

B. Dichloromethane (CH₂Cl₂)

Fragmentation of dichloromethane in the σ^* resonance is similar to chloromethane. In CH₂Cl₂, it appears that UFD is also a possible dissociation pathway since the CIY of Cl⁺ has three distinctive peaks which match the atomic chlorine final state energies well, as seen from Fig. 3(b). Broadening of the peaks is also small. By a fitting procedure, we can find that the

energies of the ¹S and ¹D states remain constant (within fitting errors) with respect to the same states in the chloromethane case. States ³P, however, experiences a shift of approximately -0.2 eV.

Fragmentation of CH₂Cl₂ subsequent to Cl 2p_{3/2} excitation to the σ^* has been reported previously,^{24,25} and it was postulated that ultrafast dissociation is a possible pathway for producing Cl⁺.

From Fig. 3(b), it is seen that the two most prominent fragmentation pathways are

as these two cations account for about 70% of all the detected ions. The present experiment does not reveal whether the neutral chlorine released together with CH₂⁺ fragment is Cl₂ or two Cl atoms. In the same manner as with chloromethane, since the spectra contain sharp peaks at the atomic chlorine energies, it is possible for the reaction that produces Cl⁺ to proceed in an ultrafast manner. The competing reaction producing CH₂⁺ has to always happen in the molecular region.

The inner valence states 2a₁ at binding energy 21.1 eV⁵² produce some CH₂⁺. We thus note that direct photoionization of 2a₁ orbital and subsequent fragmentation

is also contributing to the total amount of CH₂⁺ that is observed. The appearance of CH₂⁺ was confirmed with a coincidence measurement at photon energy below the σ^* resonance. This is shown in Fig. 5(b).

From the relative CIY results in Fig. 1, we can say that fragments which require breaking of the C–Cl bond is the most dominant reaction in all regions A, B, and C. The amount of Cl⁺ remains constant across the whole window at about 32%. CH₂⁺ is found least in region A with about 33%, whereas it rises to about 56% in regions B and C, which is most likely due to the valence levels that are found in those energies. From the smaller fragments, CH⁺ is slightly more prominent in region A with its 11% yield, but it falls to negligible amounts in regions

FIG. 5. The electron and CIY spectra for CH₃Cl, CH₂Cl₂, and CHCl₃ measured with the photon energy tuned well below the σ^* resonance ($h\nu = 199$ eV for CH₃Cl, 196 eV for CH₂Cl₂, and 197 eV for CHCl₃).

B and C. Overall trends in CH_2Cl_2 CIY are similar with CH_3Cl CIY.

C. Trichloromethane (CHCl_3)

The RA spectrum of trichloromethane recorded at the $2p_{3/2} \rightarrow \sigma^*$ resonance plotted at the top of Fig. 3(c) shows a structure with a narrow linewidth in region B, similar to other chlorinated methanes. However, it does not appear that the chlorine CIY is straightforwardly responsible for the sharp feature. The largest contribution originates from the CHCl^+ fragment which features a peak that appears to form the structure seen in the RA spectrum. CCl^+ contributes as the second largest intensity, but most of its intensity is in the lower kinetic energies, around region A.

In contrast to CH_3Cl and CH_2Cl_2 molecules, in CHCl_3 , chlorine is one of the weakest detected cations. The Cl^+ CIY only peaks slightly at the same energy as the atomic chlorine ^1D state. Based on this, it seems that a similar process leading to Cl^+ release as in CH_3Cl , for instance, is not favorable.

The inner valence of CHCl_3 has orbital $2a_1$ at a binding energy of 20.8 eV completely in the measured window and orbital $1e$ at a binding energy 24.6 eV only partially.⁵² Ionization from orbital $2a_1$ seems to produce CCl^+ due to direct photodissociation, as is evidenced by an off-resonance measurement shown in Fig. 5(c). The fragmentation for the direct photodissociation would therefore be

For the trichloromethane case, it appears that the most probable fragmentation pathway, after the resonant Auger decay, leaves at least one C–Cl bond intact, while breaking the other two. This is supported by the fact that in all regions the CCl^+ and CHCl^+ fragments are the dominant ones (55% in region A, 76% in B, and 82% in C). The dominant fragmentations are therefore

where the composition of the neutral particles is unknown (i.e., the neutral chlorine and hydrogen might also be bound together).

D. Carbon tetrachloride (CCl_4)

The resonant Auger spectrum of carbon tetrachloride at the $2p_{3/2} \rightarrow \sigma^*$ resonance is shown on the top of Fig. 3(d). The spectrum is similar to the trichloromethane spectrum, and it contains at least one relatively sharp peak. In the same way as in trichloromethane, the peak is mostly connected to final states that produce the CCl^+ fragment. The contribution of Cl^+ is small across the whole measured electron energy range, and there are no indications of peak structure in the energies of the atomic ^1S or ^3P states. This indicates that UFD is not the process that creates the chlorine signal in the case of CCl_4 .

Some of the CCl^+ observed here does not originate from the resonant Auger process but is instead created in direct photodissociation of the inner valence orbitals, which appear at

these binding energies.⁵³ The fragmentation producing CCl^+ in the inner valence would be

CCl_2^+ is found to be in coincidence with the spectator Auger states at roughly 182 eV kinetic energy.

Cl^+ and CCl_3^+ are the least detected cations, with CCl_3^+ exhibiting no discernible structure due to low statistics. Cl^+ might be forming a peak at approximately 179 eV kinetic energy, but quantitative information cannot be extracted from it. The most probable fragmentation subsequent to the σ^* resonant Auger decay is then

Similarly as with trichloromethane, carbon tetrachloride also seems to favour breaking two or three C–Cl bonds in the measured energy region. Regions A, B, and C all have roughly the same amount of CCl^+ (approximately 65%–71%).

IV. DISCUSSION

In the present work, we show that the fragmentation pathways that produce Cl^+ are drastically different for the four chlorinated methanes that were investigated. One phenomenological way of explaining the results is with the UFD process. In CH_3Cl and CH_2Cl_2 , promotion of a chlorine $2p$ electron into an antibonding orbital causes dissociation of the molecule while retaining the excited state in the Cl atom. The excited state then subsequently relaxes in the atom which has a relatively large distance to the other fragment. In CHCl_3 and CCl_4 , this same excitation and similar RA final states do not appear to produce chlorine cation signals of the same intensity.

The evidence to support the likelihood of UFD in CH_3Cl and CH_2Cl_2 is found in the chlorine contributions to the ion yields, i.e., the Cl^+ CIY spectra in each molecule (see Fig. 6). In the case of CH_3Cl and CH_2Cl_2 , their similarity indicates that at least a large portion of RA decays producing Cl^+ take place in a chlorine atom that is sufficiently far from the rest of the molecule to have an atomic character. The three clearly distinguishable peaks in Cl^+ CIYs of CH_3Cl and CH_2Cl_2 match energetically very well with RA final states of HCl, in which UFD is well-known.

With the two heavier chlorinated methanes, CHCl_3 and CCl_4 , we cannot get any definitive answers regarding UFD simply from the experimental spectra. Due to the fact that in both cases the Cl^+ yield is rather low in coincidence with the recorded RA final states, we can only tentatively conclude that even if UFD resulting in Cl^+ would be viable, it is not a preferred mechanism.

Regardless of the method of fragmentation, an interesting trend is seen in the total amount of chlorine cations observed in coincidence with the RA final states. As the amount of chlorine atoms increases in the molecule, the total amount of coincident Cl^+ ions seems to decrease (see Table III). Similar trends were seen by Lu *et al.*, who also found that the $\text{Cl } 2p_{3/2} \rightarrow \sigma^*$ excitation only causes small amounts of chlorine cation production in CHCl_3 ²⁶ and CCl_4 ²⁷ when compared to the lighter

FIG. 6. Cl^+ CIY from the four different chlorinated molecules and the RA spectrum of HCl for comparison (HCl spectrum from Ref. 49).

chlorinated methanes. While their experiments were not done in coincidence with any particular electronic states, the same trend is still observed.

To obtain a better view on the nuclear dynamics and C–Cl elongation in the $\text{Cl } 2p$ core-excited state, we performed quantum chemical calculations for all four molecules. The calculations were done using the Orca software (version 4.0.0).⁵⁴ The shapes of the potential energy curves of the $2p \rightarrow \sigma^*$ excited states were obtained by complete active space self-consistent field [CASSCF(7,6)] calculations using the so-called equivalent core model (ECM) (see, e.g., Refs. 55–57 and references therein), where the effect of the $2p$ hole is approximated by replacing one of the Cl atoms with an Ar atom. The “Z+1 approximation” was checked by comparing the derivative of the potential energy curve calculated in multireference configuration interaction (MRCI) method to the ECM in the CHCl_3 case, for which the MRCI calculation was possible to perform. All calculations were done using def2-TZVP basis sets.⁵⁸ One-dimensional nuclear dynamics along the C–Cl distance were then obtained from classical equations of motion, assuming a pseudodiatomic model where the two fragments were approximated as point masses. Here in cases with multiple chlorine atoms, the C–Cl coordinate refers to the distance between the core-excited chlorine and the central carbon atom.

TABLE III. Relative amount of observed coincident Cl^+ cations in each molecule.

Molecule	Cl^+ (%)
CH_3Cl	32.3
CH_2Cl_2	25.8
CHCl_3	12.2
CCl_4	15.9

Despite rigorous attempts, the nuclear dynamics calculations were unable to reproduce satisfactory results that would explain the experimental results. The reason is that the calculated excited state potential energy curves were very similar in all four molecules, and by using the lifetime of the $\text{Cl } 2p$ shell (~ 6.5 fs), classical motion along the slopes of the potential energy curves indicates a movement of less than 0.4 Å in the course of the $2p$ lifetime for all four molecules. At this distance, it is expected that the resonant Auger decay still happens in the molecular regime, which is in disagreement with the experimental results. To explain the fact that the ejected Auger electron would feel an “atomic like” potential from the Cl fragment, the orbital overlap between the atoms needs to be negligible, which would require a distance of 1 Å or more.

Recently Alcantara *et al.* calculated potential energy curves for the $\text{Cl } 2p \rightarrow \sigma^*$ excited state in the case of CH_2Cl_2 as a function of C–Cl distance.²⁵ From the calculations they concluded that UFD exists in CH_2Cl_2 . Their calculated curves agree with ours. However, their conclusion seems to have been primarily made on the basis that the potential energy curve is strongly repulsive. While the strongly repulsive nature of the core-excited state is a necessary requirement for the nuclear rearrangement before Auger decay, it is not a sufficient condition alone because the masses of the fragments and lifetimes of the excited states have to be considered as well. According to our calculations, the slopes of the potential energy curves in all four cases are highly similar which would indicate that all four molecules should fragment roughly in the same manner. This appears not to happen, at least according to the experimental results as seen in Figs. 3 and 6.

Table IV contains the reduced masses and masses of the neutral counterparts of various fragmentation reactions involving the chlorinated methanes investigated in this paper as well as other molecules, such as HCl and DCl, both of which experience UFD. Included in the table is also the reduced mass for the fragmentation Cl_2 molecule, which is known to not show UFD signatures.⁵⁹ Clearly the reduced mass alone is a not a sufficient indicator for the likelihood of UFD, since the reduced mass for $\text{Cl} + \text{Cl}^+$ reaction is less than the $\text{CH}_2\text{Cl} + \text{Cl}^+$ reaction, which does show some indication of fast dissociation and/or charge movement. Moreover, we note that the reduced masses tabulated in Table IV assume that the neutral counterpart in the dissociation process can be reduced to a point-like source, which naturally is not well defined in cases where there are several atoms in the neutral fragment.

TABLE IV. Reduced masses of various fragmentation processes containing an emitted chlorine cation.

Fragmentation reaction	Mass of neutral (u)	Reduced mass (u)
$\text{H} + \text{Cl}^+$	1.00	0.98
$\text{D} + \text{Cl}^+$	2.01	1.91
$\text{Cl} + \text{Cl}^+$	35.45	17.73
$\text{CH}_3 + \text{Cl}^+$	15.02	10.55
$\text{CH}_2\text{Cl} + \text{Cl}^+$	49.47	20.65
$\text{CHCl}_2 + \text{Cl}^+$	83.91	24.92
$\text{CCl}_3 + \text{Cl}^+$	118.36	27.28

To obtain more information on the charge distribution in the chlorinated methanes upon core-excitation, we carried out Mulliken population analysis, identifying the atomic charges on each nucleus as a function of the C–Cl distance (distance between the carbon and the core-excited Cl atom). The calculations were performed using the StoBeDeMon⁶⁰ software. The orbitals were calculated using a variational approach, combined with the transition potential method where both Cl $2p$ and σ^* orbitals are occupied by half an electron, which describes the excitation process well.⁶¹ The basis sets were (5211/411/1) for carbon, (3111/111) for hydrogen, and (iii_iglo) for chlorine atoms. The comparison of results obtained by different basis sets shows little differences in electronic charges assigned to different atoms in the molecule.

The results of the Mulliken analysis for all four molecules at the core-excited state as a function of C–Cl distance are shown in Fig. 7. The calculated charge deficit is defined as a difference of the charge assigned to the particular atom (in our case, the core-excited chlorine atom) with respect to the neutral atom. For comparison, the percentage of population decayed by RA is presented on the same graph as a function of C–Cl distance. A single curve is plotted for all four molecules, given by

$$1 - \exp\left(-\sqrt{\frac{2d}{a_0\tau^2}}\right), \quad (10)$$

where d is the C–Cl distance (0 being the ground state bond length), τ is the lifetime of the core-excited state (6.5 fs) and $a_0 = 0.0095 \text{ \AA/fs}^2$ is the acceleration, assumed to be constant across the considered range of C–Cl distance.

FIG. 7. Results of the Mulliken analysis on the core-excited chlorine atom within each molecule (solid lines). The percentage of population decayed by RA is shown as the dotted yellow line. Using the assumed dissociation acceleration $a_0 = 0.0095 \text{ \AA/fs}^2$, the time versus the elongated C–Cl distance is shown as the dashed red line.

Acceleration a_0 was calculated from the slope of the core-excited state's potential energy curve using reduced masses determined in previous work.²⁹ It was also found that a_0 is similar for all four chlorinated methanes.²⁹ Finally, the curve in Fig. 7 shows the elapsed time during the dissociation process.

Previous studies have concluded that the initial dissociation dynamics of chlorinated molecules after the $1s \rightarrow \sigma^*$ excitation are mostly determined by the core-excited chlorine and the atom it is connected to (in our case this is always a carbon atom).^{29,31,32,62} The full set of vibrational normal modes were also decomposed, and it was shown that the symmetric and antisymmetric C–Cl stretching are the major constituents of the initial movement upon $1s \rightarrow \sigma^*$ photoexcitation. According to Bohinc *et al.*, in the initial phases of the dissociation, only the C–Cl bond elongates, while the other atoms remain stationary. After the C–Cl distance has increased considerably beyond the Franck–Condon (FC) region, the other atoms start to move as well. This point is called the reconnection point and from there on all the CX_3 group members ($X = H, Cl$ or their combination) are set in the movement. The results obtained from previous study are directly applicable here since $1s^{-1}\sigma^*$ and $2p_{3/2}^{-1}\sigma^*$ states have parallel potential energy curves. The reconnection point of molecules studied here is reached at $d \approx 0.5 \text{ \AA}$ and it is marked on Fig. 7 as a vertical line. At the reconnection point, reached about 10 fs after the photoexcitation, about 80% of excited population has decayed through RA. After 6.5 fs (the assumed RA lifetime), approximately 65% of population has decayed by electronic transition. Since the nuclear dynamics change drastically after the reconnection point, our approximation, based on simple initial C–Cl distancing, must be abandoned at distances larger than $0.5 \text{ \AA}$.

The Mulliken population analysis shows that after core-excitation of CH_3Cl , the chlorine atom with the $2p_{3/2}$ hole has about 0.23 electron charges less than a neutral atom (i.e., the atom has become more positive). As the C–Cl bond length increases, there is little change in the charge deficit on the chlorine atom.

The heavier chlorinated methanes exhibit a slight contrast to the CH_3Cl case. In CCl_4 , for example, we initially see a slightly larger charge deficit of about -0.32 electron charges. However, unlike in CH_3Cl , the analysis here shows that the consequent negative charge is distributed among the carbon and the rest of the (non-excited) chlorine atoms. As the C–Cl distance grows in CCl_4 , the core-excited chlorine gains electron density, i.e., its charge deficit becomes less at about -0.23 electron charges. The results show that in heavier chlorinated methanes, larger amount of charge is exchanged with the rest of the molecule while the initial dissociation dynamics unfold.

However, these changes in the charge distribution are relatively small, making it difficult to estimate their impact on the final fragmentation channels. What should also be taken in account is the Auger decay, which occurs at some point during the dissociation and redistributes the charges again. The extent of the redistribution depends on the C–Cl distance and on the nature of the final electronic state, possibly changing the fragmentation pattern.

Our simulations indicate that the nuclear movement before the Auger decay (first phase of dissociation) is similar in all four chlorinated methanes. The observed difference in the coincident chlorine contribution must then originate from the second phase of dissociation occurring after the Auger decay. We suggest that this difference is due to the Auger decay, which can or cannot redistribute the initially created vacancy in the molecule, depending on the molecular type and on time passed before the decay that allowed the molecule to reach a certain C–Cl distance. As seen in Fig. 7, initially CHCl_3 and CCl_4 experience a larger charge deficit on the core-excited chlorine. As the C–Cl distance increases, they interact with the rest of the molecule and draw the negative charge from the other atoms. This indicates that the system is able to interact more strongly, or interact until much later times than is possible for the CH_3Cl and CH_2Cl_2 cases, so that the Auger decay might be able to redistribute larger amount of charge.

After 6.5 fs, approximately 65% of the population has decayed by resonant Auger. This is plotted in Fig. 7 with a vertical line. We consider this distance to be an estimate for the distance at which there no longer would be any major vacancy transfers in the CH_3Cl molecule despite Auger decay happening at later times. According to the total Cl^+ CIY (see Table III), about 32% of cases end up in a situation where the charge is located in the chlorine atom which supports the fact that alternatively there are vacancy transfers in 68% of cases. This percentage is very close to the population that has decayed by RA after 6.5 fs. According to our observations, the corresponding distances in CH_3Cl and CCl_4 would be much larger, well beyond the reconnection point, where the nuclear movements become more complicated.

V. CONCLUSIONS

We have performed electron-ion coincidence experiments on four different chlorinated methanes at the $\text{Cl } 2p_{3/2} \rightarrow \sigma^*$ resonance and observe varying fragmentation pathways for similar products. Special interest was given to the Cl^+ fragment. It was discovered that in the lightest chlorinated methanes, CH_3Cl and CH_2Cl_2 , the chlorine cation is observed to appear in coincidence with the RA final states that are similar to atomic chlorine. Previously, this behavior has been attributed to the ultrafast nuclear motion in the molecule, where the Auger decay occurs in the core-excited chlorine atom that has a considerable distance to the rest of the molecule. Our computational results indicate that there indeed is a strongly repulsive potential energy surface that can induce fast nuclear motion. Curiously, however, our results indicate that in the CHCl_3 and CCl_4 molecules there exists a similar, equally repulsive potential energy surface in the core-excited state. The experimental results for the CH_3Cl and CCl_4 cases, however, differ considerably, as the Cl^+ signal is one of the weakest detected ions in coincidence with the same resonant Auger final states.

We can tentatively explain the great difference in the Cl^+ ion appearance as the difference in the most probable Auger final state that might redistribute the vacancy in the core-excited chlorine. It is possible that in CH_3Cl and CH_2Cl_2

cases, vacancy in the valence shells created by the resonant Auger decay might be located in the vicinity of the Cl atom for long enough and that the charge-interaction between the chlorine and the rest of the molecule is inefficient. Therefore what we can observe is the Cl^+ ion. In the CHCl_3 and CCl_4 cases, this same charge interaction must either take place more efficiently when the C–Cl distance is still relatively small, or the interaction is still possible for a longer time than in the lighter chlorinated methane cases. To verify this, detailed Auger decay rate calculations would be needed for molecular excited states evolving along the dissociation potential energy curve.

It is therefore evident that to properly attribute ultrafast dissociation to a particular resonance excitation in a molecule, detailed information on the nuclear dynamic and Auger decay rate calculations is needed. Knowledge of the potential energy surfaces is required and extremely useful, but they alone cannot be combined with the atomic Auger lifetimes to be able to deduce whether UFD is an efficient process, as we have demonstrated here.

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