Molecular ionization of chloromethane in strong fields: nearest neighbor gateway to highly charged ions

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Abstract
The strong and ultrastrong field-molecule interaction is a complex, many-body process involving multiple ionization processes. We present ion yields and molecular fragment energies for the ionization of chloromethane (CH$_3$Cl) in a laser field with intensities spanning from 10$^{14}$ to 10$^{17}$ W cm$^{-2}$. As the laser intensity increases, ionization of CH$_3$Cl is observed to pass from molecular tunneling, to enhanced ionization (EI), to an atomic-like response. The energy spectra of the ions show no dependence on the intensity and has its source in dissociative molecular ionization. A classical model of an aligned C–Cl ion is used to model the interaction. Following an initial molecular ionization process, our results show EI is a driving influence in the formation of low charge states until ionization becomes atomic-like and involves tightly bound ion states whose ionization is unaffected by nearest neighbor ions of similar ion charge.

Keywords: strong field, molecular ionization, ultrafast laser, highly charged ions, chloromethane

(Some figures may appear in colour only in the online journal)

1. Introduction

Strong field light–matter interactions encompass topics across atomic and molecular physics [1–4], high harmonic generation [5–7], fusion science [8], quantum control [9], and molecular imaging [10]. One prominent strong field process is ionization, which includes x-ray ionization [11], multi-photon ionization [12–14], tunneling ionization [15, 16], and classical over the barrier ionization [17].

Much of strong field atomic ionization is well understood; however, the molecular response is more complex. Processes that occur include molecular alignment [18], stabilization [19], pendular states [20], dissociative ionization [21], enhanced ionization (EI) [22], frustrated double ionization [23], and Coulomb explosion [24]. Much of the work on molecular systems has focused on diatomic homo- and hetero-nuclear molecules in the strong field [25, 26] and lower charge state dissociative ionization channels in polyatomic molecules [27–29]. For molecules in ultrahigh intensities, highly charged fragment ionization has been observed to be like that of the atomic ion [30].

In this study we investigate the production of highly charged carbon atoms and ions from chloromethane. Recent intense field studies of chloromethane [31] have focused on the molecular fragmentation processes and have used recoil-momentum spectroscopy to identify the mechanisms of proton migration and the ionization of the first and second electron from chloromethane fragments. This detailed work identified the strong field analog of fragmentation observed with electron impact [32–34] and single photon ionization [35, 36] in chloromethane. Earlier research concluded the ionization response for CH$_3$-X species such as chloromethane proceed by an initial one-electron tunneling ionization followed by dissociation and fragmentation [37]. The work we present here on chloromethane extends strong field molecular
ionization into the formation of high charge states and clarifies the role of nearest neighbor effects during dissociation. We show the ion fragment energy is driven by Coulomb explosion and the internuclear separation at which ionization occurs during the dissociation of the molecule. At first multiple effects such as alignment [38], multiple fragmentation channels [31], wavepacket dynamics on multiple electronic states [39], rescattering [40], nonsequential double ionization [41], and other effects could seem to give a complex, if not interpretable spectra. Despite this, we show there is a clear and analytical predictability. The interaction proceeds across three different regimes (figure 1) as a function of increasing laser field strength: an initial field ionization of the neutral molecule, nearest neighbor EI, and the ‘isolated’ atomic ion response.

2. Experiment

2.1. Apparatus

The experiments use a TEM00, terawatt CPA laser system [42] consisting of a Ti:Sapphire oscillator seeding a ring-type regenerative amplifier and 5 pass bow-tie multipass amplifier with a final output of 150 mJ at 790 nm in a 40 fs pulse operating at 10 Hz. These laser pulses enter an ultrahigh vacuum time-of-flight (TOF) ion spectrometer where they interact with the sample. Just before the spectrometer, a zero-order λ/4 or λ/2 wave plate adjusts the polarization. In the spectrometer, the beam is focused to a spot size of 2 μm by an off axis f/2 parabolic gold coated mirror into an effusive room temperature sample gas jet.

The ion spectrometer uses single-stage field extraction to accelerate ions from the focus into a field free drift tube. Between the acceleration and drift regions we use a 250 μm circular aperture to obtain high angular resolution of the ion momentum and for isotropic (no angular selection) collections we switch to a rectangular aperture of 250 μm along the laser propagation direction (k) and 10 mm perpendicular to the field free drift axis and k to allow ions with a momentum perpendicular to the flight tube axis into the spectrometer. Ions are detected by chevron micro-channel plates (MCP). Signals from the MCP are sent to a preamplifier (Ortec VT 120), voltage discriminator (Ortec 9307), and finally a picosecond time analyzer (Ortec PTA 9308) where the signal is digitized and downloaded to a computer to generate TOF histograms and correlation maps.

The sample gas manifold pressure, which feeds a leak valve, is kept at roughly 5 psi above atmosphere. The base pressure in our chamber is 9 × 10−10 Torr. During collection the working pressure is kept below 10−6 Torr. To eliminate degeneracy (e.g. 12C4+, 13C4+), we use 13C in addition to 12C. Intensity and saturation calibrations for the terawatt laser system are done by comparing to previous experimental ion yields for argon and methane [30]. The spectrometer calibration has shown yields saturate above count rates of 3 × 106 ions/(shot-Torr). The theory curves we show, which are spatially and temporally integrated, are adjusted by a common multiplier (i.e. a vertical scaling) to the spectrometer saturation.

2.2. TOF spectra

Figure 2 shows example methane and chloromethane ion spectra. A few ions are identified for the reader including multiply charged carbon, chlorine, and contaminant oxygen from water in the chamber background. For chlorine we see the expected 3:1 isotope ratio of 35Cl:37Cl and charge states up to Cl7+, indicating ionization of the valence shell. Chlorine L shell ionization is more difficult and it was not quantified in this study. The ionization potentials (Ip) for atomic Cl13+ and Cl15+ are 314 eV and 400 eV, respectively. This is comparable to the 392 eV Ip for C5+, the highest charge state observed in this study at 1018 W cm−2.

Closer inspection of the TOF for carbon ions is shown in figure 3. Each spectrum is taken at the saturation intensity for the respective carbon ion. Individual ion hits are resolved in
midway between the acceleration plates and 6.5 instrumentally limited to the laser focus the spectra. The width of the carbon peaks from methane are

Figure 3.

High resolution TOF spectra for C$^+$ (a), C$^{2+}$ (b), C$^{3+}$ (c), and C$^{4+}$ (d) for chloromethane (red) and methane (black) at the saturation intensities for methane: 4.4 $\times$ 10$^{14}$ W cm$^{-2}$ for C$^+$ (a), 5.7 $\times$ 10$^{14}$ W cm$^{-2}$ for C$^{2+}$ (b), 1.3 $\times$ 10$^{15}$ W cm$^{-2}$ for C$^{3+}$ (c), and 6.5 $\times$ 10$^{15}$ W cm$^{-2}$ for C$^{4+}$ (d). Chloromethane spectra are offset for easier distinction. Blue shaded times fall outside the window used in the ion energy analysis. Contaminates of known ion species in this study. The carbon ion peaks from chloromethane have a

Figure 4.

Mass spectrometer schematic diagram (a) with the extraction voltage $V_1$, plate separation $l$, $V = 0$ grounded flight tube length $D$, and acceleration length $d$ to the MCP voltage $V_2$. Difference between $t_{\text{exp}}$ and predicted $t_{\text{calc}}$ flight times for known $m/q$ ions (b). The optimized values are: $l = 1.016$ cm, $D =$ 11.95 cm, $y_0 = -0.05$ cm, $d = 0.325$ cm, $t_0 =$ 142.5 ns, $V_1 =$ 2995 V and $V_2 =$ -1750 V.

is the time the ion takes to traverse a region of length $d$, close to the detector where a negative potential, $\Delta V_2$, is placed, and $t_0$ is the electronic time offset.

By assuming an initial velocity of $v_0 = 0$, the time for known ions can be calculated and compared with measured times, $t_{\text{exp}}$. Varying the parameters, $\Delta V_1$, $D$, $d$, and $t_0$, we minimize the residual $S = \left(\frac{m_{\text{exp}} - m_{\text{calc}}}{m_{\text{exp}}}\right)^2$ and can calculate an ion TOF within typically 0.5 ns. For comparison, the full width at half maximum for a C$^{2+}$ peak from methane is ~2.5 ns. Figure 4 shows the difference between $t_{\text{exp}}$ and $t_{\text{calc}}$ for optimized chamber parameters as a function of mass to charge ratio. We also use these parameters to convert the TOF for ions with non-zero velocities into an ion energy spectrum.

2.3. Ion fragment energy

Coulomb explosion, where atoms within a molecule become highly charged and repel one another [25], can release a large amount of kinetic energy to dissociating ions. Methane has
been shown to have little or no Coulomb explosion in experimental [43] and theoretical work [44] since the EI process [45] takes place for all C–H bonds simultaneously. For chloromethane, the carbon and chlorine ion momenta are predominantly directed along the laser electric field; for C$^{3+}$ and Cl$^{+}$ we measure 90% of the momentum is along the electric field in agreement with related studies on CH$_3$I [46]. When this momentum is aligned along the flight tube there is a peak splitting in the TOF due to ion momentum pointed toward the detector (‘forward’, ‘fast’ peak) or away from the detector (‘backward’, ‘slow’ peak). The kinetic energy ($E_{KE}$) [45] of the ions is often calculated [47] from the TOF using $E_{KE} \approx \frac{1}{2m}(qF\Delta t)^2$ where $\Delta t$ is the TOF difference of the fast and slow peaks, $q$ is the ion charge, $m$ is the mass, and $F$ is the extraction field. When fast and slow peaks are not resolved, peak broadening beyond the instrumental temporal resolution is used to estimate this energy. Table 1 gives $E_{KE}$ for carbon and chlorine ion kinetic energies.

Figure 5 shows the energy spectrum for C$^+$, C$^{2+}$, C$^{3+}$ and C$^{4+}$ calculated from the TOF. The data is presented up to the fragment energy limit of the spectrometer (~100 eV) over three orders of magnitude. The calculations show ion energies have a significant breadth that extends up to 30 eV for C$^+$, 50 eV for C$^{2+}$, and near the spectrometer limit of 100 eV for C$^{3+}$ and C$^{4+}$. The energy distributions do not vary as the intensity is changed between 4.4 x 10$^{14}$ and 6.5 x 10$^{15}$ W cm$^{-2}$; the broad energy distributions are inherent to the laser-molecule mechanism and are not due to spatial intensity averaging across the laser focus. There are multiple fragmentation pathways to create carbon ions from the dissociation of chloromethane [48], e.g. CH$_3$Cl + CH$_3$ + n $\rightarrow$ CH$_4$, CH$_2$Cl and CHCl followed by the further ionization of carbon to give the carbon ion, i.e. C + $\rightarrow$ C$^+$ + 2H$^-$. We will quantify the role of multiple pathways shortly when we present intermediate molecular fragment yields, such as CH$_2$Cl$^+$. The most probable energy ($E = \Sigma E \cdot counts/\Sigma counts$) for C$^+$ is 3.3 eV, C$^{2+}$ is 12.4 eV, C$^{3+}$ is 22.6 eV, and C$^{4+}$ is 30.7 eV. One can see in Table 1 the $E$ values are surprisingly consistent with $E_{KE}$.

Figure 6 shows the Cl$^{+}$ energy spectra at the saturation intensities for the carbon ions (see figure 6 caption). Here again even though the intensities for the collections vary by an order of magnitude from 4.4 x 10$^{14}$ to 6.5 x 10$^{15}$ W cm$^{-2}$, the fragment energy does not change. For Cl$^{+}$, even at the lowest intensity of 4.4 x 10$^{14}$ W cm$^{-2}$, there are still some ions detected with an energy distribution that is arguably consistent with the energy spectra at 6.5 x 10$^{15}$ W cm$^{-2}$. Such an intensity dependence confirms the finding with carbon ion fragment energies. There is a correspondence between the experimentally measured energy of the carbon ions and chlorine ions that is in agreement with the conservation of momentum accounting for only the C and Cl ions; our data indicate that hydrogen atoms have little influence on the final momentum of either C or Cl ions.

### 2.4. Coincidence measurements

Insight into the ionization process can be gained by determining the correlation between arriving ions. The auto-variance function for a TOF spectrum is given by [49, 50]

$$C(x, y) = \frac{1}{N} \sum_{i=1}^{N} \text{TOF}(x) \cdot \text{TOF}(y) - \left( \frac{1}{N} \sum_{i=1}^{N} \text{TOF}(x) \right) \left( \frac{1}{N} \sum_{i=1}^{N} \text{TOF}(y) \right),$$

where $N$ is the number of shots, TOF(x) and TOF(y) are the 'horizontal' and 'vertical' TOF spectra.

Figure 7 shows the covariance map for chloromethane taken at the C$^{+}$ saturation intensity of 5.7 x 10$^{14}$ W cm$^{-2}$. Once a peak is identified, it can be traced along the map to determine any correlated ions. Based on conservation of momentum, faster arrival ‘forward’ peaks should be correlated with another ion having a longer arrival ‘backward’ peak.
We begin by focusing on carbon ions in the covariance map. Knowing the TOF for a carbon ion we can take a selection of the map and look for positive auto-variance correlations. Figure 8 shows the slice of the correlation map slice corresponding to $C^+$ and $C^{2+}$. From the figure, we can see the later vertical TOF $C^+$ (toward the top of the correlation map slice) has a correlation with earlier horizontal $Cl^+$ (toward the left of the correlation map slice), i.e. a characteristic backward $C^+$ peak and forward $Cl^+$ peak and vice versa. This correlated $Cl^+$ is circled in figure 8(a). For $C^+$, there is a second, weaker correlated $Cl^{2+}$ ion, also circled in figure 8. For $Cl^{2+}$ there are two correlated chlorine ions, $Cl^{2+}$ and $Cl^{3+}$ (figure 8(b)).

It can be beneficial to reduce a portion of the covariance map to a line-out, effectively giving a TOF ion spectrum correlated with the ion at the line-out time. This is done in figure 9, where the line-out is taken at the $C^+$, $C^{2+}$, and $C^{3+}$ portion of the covariance map and plotted as a function of time. The correlation that we saw in figure 8(a) is now clearly present in the line-out at $C^+$ in figure 9(a). We undertake the same process for the $C^{2+}$ and $C^{3+}$ ions in figures 9(b), (c) but at different intensities than those shown for figure 8 or 9(a).

The $C^{2+}$ correlated TOF spectrum at an intensity of $1 \times 10^{16}$ W cm$^{-2}$ shows a correlation with $Cl^{2+}$ while the correlation with $Cl^{3+}$ present at $5.7 \times 10^{14}$ W cm$^{-2}$ is absent. At a slightly higher intensity of $2 \times 10^{16}$ W cm$^{-2}$ in figure 9(c) the sum is taken over the $C^{3+}$, and again we see a small positive correlation at the time of $Cl^{3+}$. These findings show correlations change as a function of intensity.

### 2.5. Ion yields

Ion yields for molecular fragments from chloromethane as a function of laser intensity are shown in figure 10. Figures 11 and 12 show the yields for carbon and chlorine, respectively. Figure 12 does not show $Cl^{5+}$ because of $^{35}Cl^{5+}:N^{2+}$.
degeneracy issue and lack of a clearly resolved background free $^{37}\text{Cl}^{5+}$ peak. Ion yields for $\text{Cl}^{6+}$ are accurately quantified, however, low level background events off the $\text{Cl}^{6+}$ main peak prevent a full energy resolved TOF for $\text{Cl}^{6+}$. Ion yields above saturation scale as $I^2$ [51] as expected for a Gaussian spatial distribution. At saturation we can get an indication of whether ions go through a sequential ionization processes or are correlated and share a saturation intensity feature with another ion.

The first ion to appear in our studies is the singly charged parent ion [CH$_3$Cl]$^+$ with a saturation intensity measured to be $1.2 \times 10^{14}$ W cm$^{-2}$. This saturation intensity is in agreement with the calculated molecular tunneling ionization [52] also shown in figure 10, which predicts an exp($-1$) ionization probability at a peak intensity $9.8 \times 10^{13}$ W cm$^{-2}$. Prominent fragments that also appear at $10^{14}$ W cm$^{-2}$ include [CH$_2$Cl]$^+$, [CH$_2$]$^+$, [CH]$^+$, and [CCl]$^+$. Additional, small yield fragments (yields less than 0.01 of the parent ion) correlated with the parent ion are shown in gray: [CHCl]$^+$, [CCl]$^+$, [CH$_3$Cl]$^{2+}$, [CH$_2$Cl]$^{2+}$, and [CHCl]$^{2+}$, [CCl]$^{2+}$. 

Figure 9. Comparison between the normal TOF (gray) and covariance TOF spectrum line-out (red) at the $\text{C}^+$ peak for an intensity of $6 \times 10^{14}$ W cm$^{-2}$ (a), the $\text{C}_2^+$ peak for an intensity of $1 \times 10^{16}$ W cm$^{-2}$ (b), and the $\text{C}_3^+$ peak for an intensity of $2 \times 10^{16}$ W cm$^{-2}$ (c). Correlated chlorine and carbon peaks are indicated.

Figure 10. Experimental (symbols) and calculated ion yields (solid lines) for molecular fragments from chloromethane as a function of intensity. The indicated fragments are the parent ion [CH$_3$Cl]$^+$, [CH$_2$Cl]$^+$, [CH$_2$]$^+$, [CH]$^+$. Additional, small yield fragments (less than 0.01 of the parent ion) correlated with the parent ion are shown in gray: [CHCl]$^+$, [CCl]$^+$, [CH$_3$Cl]$^{2+}$, [CH$_2$Cl]$^{2+}$, and [CHCl]$^{2+}$, [CCl]$^{2+}$.

Figure 11. Experimental (symbols) and calculated tunneling ion yields (dashed lines) for $\text{C}^+$, $\text{C}_2^+$, $\text{C}_3^+$, and $\text{C}_4^+$ from chloromethane as a function of intensity.

Figure 12. Experimental (symbols) and calculated ADK tunneling ion yields (solid lines) for $\text{Cl}^+$, $\text{Cl}_2^+$, $\text{Cl}_3^+$, $\text{Cl}_4^+$, $\text{Cl}_6^+$, and $\text{Cl}_7^+$ from chloromethane as a function of intensity.
Table 2. Ionization sequence with molecular $I_P$ [32–34] or atomic $I_P$ shifted to include the nearest neighbor ion (indicated by *). The shift $\Delta I_P$ from atomic values are given where appropriate. Weighting contributions to $E$ are determined from the ion yields. Since several $n, m$ channels contribute to the observed ion energy integrated over the laser focus in the experiment, we weight the calculated $n, m$ ion energies in the table according to the contributions measured in ion yields for the laser focus to give $E$.

| Ion | $I_P$ (eV) | $\Delta I_P$ (eV) | $E$ |
|-----|------------|------------------|-----|
| CH$_3$Cl$^+$ | 11.26 | 0.7 $E_{C1,01} + 0.3 E_{C1,11}$ | |
| CH$_3$Cl$^+$ | 13.0 | 0.6 $E_{C1,11} + 0.4 E_{C1,12}$ | |
| Cl$^+$ | 16.6 | 0.8 $E_{C1,12} + 0.2 E_{C1,22}$ | |
| C$^+$ | 26.3 | 0.7 $E_{C1,22} + 0.3 E_{C1,23}$ | |
| Cl$_2^+$ | 27.7 | 7.7 | 0.9 $E_{C1,23} + 0.1 E_{C1,33}$ |
| C$_2^+$ | 32.7 | 7.7 | 0.8 $E_{C1,33} + 0.2 E_{C1,34}$ |
| Cl$_3^+$ | 47.5 | 11.3 | 1.0 $E_{C1,34} + 0.0 E_{C1,44}$ |
| C$_3^+$ | 59.2 | 11.3 | 0.8 $E_{C1,44} + 0.1 E_{C1,45} + 0.05 E_{C1,46} + 0.05 E_{C1,47}$ |
| Cl$_4^+$ | 64.5 | 13.2 | $E_{C1,47}$ |
| C$_4^+$ | 77.2 | 13.2 | $E_{C1,47}$ |
| Cl$_5^+$ | 80.9 | 13.2 | $E_{C1,45}$ |
| C$_5^+$ | 110.1 | 13.2 | $E_{C1,46}$ |
| Cl$_6^+$ | 127.4 | 13.2 | $E_{C1,47}$ |

the fragment. Molecular fragment yields do not exhibit two components or characteristic ‘knee’ as might be expected with multiple mechanisms for ionization, e.g. nonsequential and sequential ionization [3].

After the molecular parent ion, Cl$^+$ is the first atomic ion to appear and has a yield close to that of [CH$_3$Cl]$^+$. The ionization of Cl$^+$ is followed in quick succession by C$^+$, Cl$_2^+$, C$_2^+$, C$_3^+$, Cl$_4^+$, C$_4^+$, Cl$_5^+$, and Cl$_6^+$. This sequence is consistent with our covariance map observations. Correlation measurements merged with the ionization order give a consistent picture of ionization that is a sequence of ‘tightly’ spaced steps summarized in table 2.

Inspection of figure 11 or 12 show C$^+$ and Cl$^+$ yields are strongly suppressed compared to the calculated atomic tunneling yield [15, 16], also shown in the figures. In the case of C$^+$ this can be attributed to hydrogen since we measure the identical ion yields for C$^+$ from methane and chloromethane. Experimental results [53] from different molecules show production of C$^+$, N$^+$, and O$^+$ is reduced in the case when a hydrogen atom is part of the molecule. In fact, none of the ion yields simply follow the atomic intensity dependence and only the highest charge states appear to agree consistently with the predicted atomic ionization yield at saturation.

3. Theory

The experimental fragment momenta, energies, field dependent ionization yield, and saturation sequence allow us to construct a model of the high charge state molecular ionization process. Briefly, the first ionization step (figure 13(a)) is the production of the parent ion CH$_3$Cl$^+$ ($I_P$ of 11.27 eV) [32]. Dissociation is assumed to begin immediately after the parent ion is formed. The molecule then localizes the positive charge on the chlorine as it dissociates and ‘sheds’ hydrogen. This step of the model is consistent with the ion yields for [CH$_3$Cl]$^+$ and Cl$^+$, which are the most prominent yields after the parent [CH$_3$Cl]$^+$. This step of the model is consistent with the ion yields for [CH$_3$Cl]$^+$ and Cl$^+$, which are the most prominent yields after the parent [CH$_3$Cl]$^+$. Following CH$_n$Cl$^+$ is the ionization of carbon to form C$^+$–Cl$^+$ and higher charge states. We assume hydrogen has no influence on the interaction at this point in the model and use a 1D classical model of carbon and chlorine ions aligned in the field.

The C$^0$–Cl$^m$ potential (approximated as a C$^{0.5+}$–Cl$^{0.5+}$) is shown figure 14 with the external field close to the saturation intensity. In the model, the ions begin to dissociate from an internuclear separation distance equal to the equilibrium bond distance of the parent molecule, $R_{eq} = 178.1$ pm. The initial momentum of the ions is determined by assuming that the total energy, at infinite separation, of C$^+$–Cl$^+$ called the 0–1 channel, has a value of 1 eV. We have varied this initial dissociation energy from 0.1 to 4 eV and determine it has little influence on the values of $\beta_{01}$ in C. This energy is also consistent with our measured CH$_3$ fragment $E$ of 3 eV and fragment energies measured by Ma et al [31].

Integration of the equations of motion for the ions driven by the Coulomb force between C and Cl proceeds from these initial conditions. Ionization is considered instantaneous at an integration process. Brie...
The purpose of this study is to clarify the high charge state formation from strong field interaction with a molecule. The interaction proceeds from ionization of molecular states, to a ‘nearest neighbor’ regime where the influence of the original molecular structure is reduced to a nearest neighbor energy shift of atomic states, to a final isolated atomic ion interaction. This last ‘atomic-like’ interaction is reached when the extent of the ionizing bound state is much less than the intramolecular bond distances; deeply bound states are unaffected by adjacent atoms in a molecule.

The role of the nearest neighbor field to enhance the external laser can be seen in the effective potential for the ionizing electron. Figure 15 shows the effective potentials from the parent ion, nearest neighbor and external laser field for the ionization of carbon. The ionization potential used is the atomic ionization potential adjusted for the presence of the nearest neighbor ion by ΔI_p. The atomic ionization energy shift by ΔI_p can be reasonably approximated for a charged nearest neighbor by considering the amount of work required to remove an electron (e) from an ion in the field of the nearest neighbor E_NN. Figure 16 shows the effective potentials for ionizing chlorine with the similar adjustments to I_p for the chlorine ions

\[ \Delta I_p = \int_{\infty}^{\infty} eE_{NN} \cdot d\vec{r}'. \]

The change in energy will depend on the charge of the nearest neighbor ion q_{NN} and is estimated here as a nearest neighbor Coulomb field correction,

\[ \Delta I_p = -\frac{1}{4\pi\varepsilon_0} \frac{e^2 q_{NN}}{\infty r_e}. \]

One observation that can be made between figures 15 and 16 is that I_p from the nearest neighbor field becomes less pronounced as the ion charge is increased. The EI mechanism is clearly preferred (lower blue barrier in figure 15) due to the direction assisted by the CI^2+ nearest neighbor field. However by figure 15(c) one can see the nearest neighbor field only slightly lowers the barrier for ionization at the CI^{4+} I_p (blue versus red potential comparison in the figure). In figure 16 for CI^{6+} and CI^{7+}, the influence of the nearest neighbor CI^{4+} is almost non-existent and the ionization is best represented as an atomic-like response.

One may pose a more general question, ‘When does the molecular response to a laser field approach an atomic-like response?’ The orbital structure of the atom can give some insight into other light–matter interactions. For a carbon atom the ground state is [He]2s^22p^3 and for chlorine it is [Ne]3s^23p^5. Based on the experimental trend, one may
8.3 chlorine ion location is used as the origin. Ionization of Cl

1.2 field and perturbing nearest neighbor carbon. The chlorine ion location is used as the origin. Ionization of Cl

2.5\text{pm}\) to expect when a shell gap is reached in the production of higher charge states for an ion in a strong field molecular ionization process, an atomic response may be used to describe the ionization.

5. Conclusion

We have investigated how highly charged states are formed for the CH$_3$Cl molecule in strong fields. Our measurements show the first charge state has a molecular type response. From the ionization sequence, fragment energies, correlation measurements, and model we determine that EI plays a dominant role in the production of C$^+$ through C$^{4+}$ as well as for Cl$^{3+}$ through Cl$^{7+}$. As we get to high charge states, the Cl$^{6+}$ and Cl$^{7+}$ response becomes consistent with atomic ionization at saturation. Going forward it would be reasonable to expect when a shell gap is reached in the production of higher charge states for an ion in a strong field molecular ionization process, an atomic response may be used to describe the ionization.

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Figure 16. Effective potentials for ionizing chlorine ions with the external strong field and perturbing nearest neighbor carbon. The chlorine ion location is used as the origin. Ionization of Cl$^+$ (a) at 1.2 $\times$ 10$^{14}$ W cm$^{-2}$, $r_{12} = 2.0 R_{eq}$, and Cl$^{2+}$ $I_P$ (gray line). Ionization of Cl$^{2+}$ (b) at 3.3 $\times$ 10$^{14}$ W cm$^{-2}$, $r_{23} = 2.2 R_{eq}$, and Cl$^{3+}$ $I_P$ (gray line). Ionization of Cl$^{3+}$ (c) at 1.3 $\times$ 10$^{15}$ W cm$^{-2}$, $r_{34} = 2.5 R_{eq}$, and Cl$^{4+}$ $I_P$ (gray line). Ionization of Cl$^{4+}$ (d) at 8.3 $\times$ 10$^{15}$ W cm$^{-2}$, $r_{45} = 2.5 R_{eq}$, and Cl$^{5+}$ $I_P$ (gray line). Ionization of Cl$^{5+}$ (e) at 1.2 $\times$ 10$^{16}$ W cm$^{-2}$, $r_{56} = 2.5 R_{eq}$, and Cl$^{6+}$ $I_P$ (gray line). Shading is added to aid the eye for the extent of the carbon (gray) and chlorine (green) atoms. Approximate descriptions (nearest neighbor enhanced ionization, or atomic) are indicated.

conclude that when a shell gap is reached in the ionization process, the next ionizing electron may be modeled as an atomic ion. Different pulse durations for the interaction, whether long or instantaneous relative to the dissociation time scale, will alter details of when this approximation can be invoked. However, all molecular bond distances measure $\sim$180 ± 50 pm so one can argue that atomic states with a radial extent of one-tenth of this, or less than 18 pm, will respond as independent ions unaffected by an equally charged ‘distant’ nearest neighbor within a molecule, independent of the ionization pulse. Even for ultrahigh intensity (10$^{20}$ W cm$^{-2}$) laser pulses with durations of a femtosecond, the principle quantum number $n = 1$ states of atoms within a molecule should ionize as independent ions.

There is a related impact of our findings on ultrahigh intensity studies. It is often challenging to identify which processes originate from lower fields and which are unique to the interaction with the ultrastrong field. Current investigations are often limited to the noble gases Ne, Ar, and Xe for samples. The findings from this study, that atoms such as chlorine within a molecular species can be treated as atomic ions, make it possible for molecules to serve as an important tool by delivering new elemental species to the ultrahigh intensity focus. Experiments are under way to measure the Cl$^{6+}$, Cl$^{7+}$, Cl$^{8+}$ photoelectron energy spectrum from chloromethane to determine if it agrees with atomic predictions.
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