Velocity Map Imaging and Theoretical Study of the Coulomb Explosion of CH$_3$I under Intense Femtosecond IR Pulses

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**ABSTRACT:** The Coulomb explosion of CH$_3$I in an intense (10–100 TW cm$^{-2}$), ultrashort (50 fs) and nonresonant (804 nm) laser field has been studied experimentally and justified theoretically. Ion images have been recorded using the velocity map imaging (VMI) technique for different singly and multiply charged ion fragments, CH$_3$I$^+$ ($p = 1$) and P$^q$ ($q ≤ 3$), arising from different Coulomb explosion channels. The fragment kinetic energy distributions obtained from the measured images for these ion fragments show significantly lower energies than those expected considering only Coulomb repulsion forces. The experimental results have been rationalized in terms of one-dimensional wave packet calculations on ab initio potential energy curves of the different multiply charged species. The calculations reveal the existence of a potential energy barrier due to a bound minimum in the potential energy curve of the CH$_3$I$^{2+}$ species and a strong stabilization with respect to the pure Coulombic repulsion for the higher charged CH$_3$I$^{n+}$ ($n = 3, 4$) species.

I. INTRODUCTION

The interaction of molecules with strong laser fields has become an attractive field of research in molecular sciences over the last decades, especially because ultrashort lasers have been routinely available. Several ionization phenomena are possible when a molecule is under a strong laser field. At low enough field intensities, molecules can undergo multiphoton ionization, in which the molecular ion is produced after multiphoton absorption. If the ion is either unstable or produced with sufficient available energy, it can break apart, yielding an ion fragment, a neutral fragment, and an electron. This process is known as dissociative ionization. However, at higher intensities, new phenomena can occur, becoming more important than dissociative ionization as intensity increases, such as Coulomb explosion. Coulomb explosion typically occurs when the intensity of the laser field is above a given threshold such that several electrons are removed from the molecule, generating Coulombic repulsion inside the molecule. When the repulsive energy of the charged parts of the molecule overcomes the total cohesive energy, the molecule breaks apart into multiple charged fragments in an explosive way. Several ionization mechanisms, such as multiphoton ionization, tunneling ionization, and over the barrier ionization, have been proposed to explain the phenomena that appear at high laser intensities. In general, the Keldysh parameter $\gamma$ (ref 4) is used to classify nonlinear multiphoton processes in atoms and molecules into two regimes: the multiphoton regime and the tunneling regime. This parameter is defined as follows:

$$\gamma = \sqrt{\frac{I_p}{2U_p}}$$

where $U_p$ is the ponderomotive energy representing the cycle-averaged quiver energy that a free electron acquires in the electric field of the laser pulse and $I_p$ is the ionization potential of the atom or molecule. The relationship between $U_p$ and the intensity of the laser field for an electron irradiated with infrared photons (804 nm) is given by

$$U_p = \frac{e^2}{2m_e \varepsilon_0 c^2 \omega_L^2} \approx 6 \times 10^{-14} I$$

where $e$ and $m_e$ are the charge and mass of the electron, respectively, $c$ is the speed of light, $\varepsilon_0$ is the vacuum permittivity, $I$ is the intensity of the laser field in W cm$^{-2}$, and $\omega_L$, the angular frequency of the laser radiation.

When $\gamma \gg 1$, multiphoton effects, described by perturbation theory, prevail. The number of photons, $n$, required to reach the ion is given by $n \Delta \omega_L > I_p$. When $\gamma \sim 1$, the internal electric field of the atomic or molecular species is comparable with the electric field of the laser. The electronic states of the species are Stark shifted to lower energies and the $I_p$ decreases. The lowering of the ionization barrier is not sufficient to allow direct ionization, although there is a probability that the atom or molecule will ionize through the tunneling effect. When $\gamma \ll 1$, barrier suppression ionization becomes the dominant process and the ionization potential becomes lower than the highest occupied orbital, so the species is readily ionized.

Special Issue: Femto10: The Madrid Conference on Femtochemistry

Received: August 2, 2011
Revised: October 5, 2011
Published: November 21, 2011
A note of caution must be added when the Keldysh parameter for polyatomic molecules is considered. First, there are problems in polyatomic molecules with the single electron approximation, and second, molecular orbitals are spread out and the adiabatic approximation by which it is considered that the electron always follows the external electric field is not so valid. In any case, according to eq 1, for CH₃I and 804 nm, the threshold intensity between the two limiting regimes would correspond to approximately 80 TW cm⁻². However, typical phenomena corresponding to field ionization processes, like Coulomb explosion, have been observed at considerably lower intensities, as will be shown for CH₃I in this paper.

Some theoretical models have been proposed to explain Coulomb explosion in molecules by ultrashort and ultraintense laser pulses. The most employed models are the coherent electron motion model (CEMM), the ionization ignition mechanism (IIM), and the charge-resonance-enhanced ionization (CREI) model. In all the models, barrier suppression plays an important role. In the CEMM, the laser pulse first ionizes the molecule and the removed electrons start to move coherently around the charged molecule producing inelastic collisions. The collisions cause ionization again and another electron is ejected in a similar way as in electron impact ionization, but with a well-defined coherence. In the IIM model, the nuclei of the atoms are first considered frozen whereas the ionized electrons are quickly removed by the laser field. Thus, an asymmetric molecule ion core develops. The asymmetry along the laser polarization suppresses the barrier further and ionization begins. If the molecule reaches a high ionization state, Coulomb explosion takes place. In the IIM model, tunneling is not considered, and ionization is assumed to take place only through barrier suppression. The CREI model suggests that after the neutral molecule becomes singly ionized at the equilibrium distance, Rₑ, the fragments begin to separate from each other. When the distance between the nuclei approaches a certain value (Rₐ), the characteristic oscillatory frequency of the electron coincides with the frequency of the laser radiation, so a quasiresonance process can bring the electron energy to the level where it can overcome the electrostatic barrier and leave the molecule.

No other polyatomic molecule has been so extensively studied as CH₃I when exposed to laser radiation (see refs 12–14 for recent reviews on the real-time photodissociation of this molecule). With respect to processes that occur in the presence of strong laser fields, Graham et al. measured the angular distributions of multiply charged fragment ions generated by Coulomb explosion of CH₃I with a 50 fs intense laser pulse (10 PW cm⁻²) using time-of-flight mass spectrometry (TOFMS). They detected multiply charged fragment ions (up to I⁺⁶) and measured the angular distribution of the I⁺ⁿ as a function of the angle between the laser polarization vector and the TOF axis, to determine the preferred direction of ejection of the fragment ions with respect to the laser field, showing that all of them are peaked in the direction where the polarization vector and TOF axis are collinear. They postulated that the molecule, which is initially tetrahedral, changes from an open to a closed umbrella structure and that the H–C and C–I bonds tend to align along the field direction. Under those conditions, the I ions resulting from the Coulomb explosion are detected more efficiently, producing a maximum in the distribution.

Siozos et al. compared the results of the Coulomb explosion of CH₃I produced with strong femtosecond and picosecond laser pulses using the TOFMS technique. They observed that the kinetic energies of the I⁺ⁿ formed with femtosecond pulses were lower than those obtained with picosecond pulses. They suggested that the high charged ions I⁺ⁿ (q ≥ 3) in the picosecond laser field were produced from the further ionization of low charged I⁺ ions formed at the rising edge of the laser pulse, so the Coulomb explosion happened at longer internuclear distance and, as a consequence, the formed fragments have less kinetic energy.

More recently, Liu et al. reported a study on the ionization—dissociation of CH₃I in an intense laser field using 180 fs pulses at 798 nm, intensities ≤660 TW cm⁻² and high-resolution reflect TOFMS. They measured the kinetic energy distributions (KER) of fragment ions, such as I⁺⁺ (q = 1–6) and CH₃I⁺⁺ (p = 0–3), and the possible Coulomb explosion channels were assigned. They found that the KERs are independent of the laser intensity and concluded that there must be a bound potential near the equilibrium C–I distance for CH₃I because the KERs of CH₃⁺ and I⁺ are much smaller than those calculated considering only Coulomb repulsion forces. With respect to the Coulomb explosion of CH₃I⁺⁺ (n > 2), they proposed that there should be a significant distance between the CH₃I⁺⁺ and I⁺⁺ (n = p + q) at which enhanced ionization of CH₃ occurs. By the measurements of the KER of the fragments, this distance was estimated to be around 3.7 Å.

Zhang and co-workers reported measurements of dissociative ionization and Coulomb explosion for CH₃I using the velocity map imaging technique and 35 fs, 800 nm laser pulses with intensities in the range 40–600 TW cm⁻². They obtained the angular and speed distributions of the I⁺ (q ≤ 3) ions and several channels were assigned. All the measured fragment angular distributions were found to be anisotropic and peaked along the laser polarization direction.

In the present work, we report an extensive study of the Coulomb explosion of CH₃I in an intense laser field produced by pulses of 50 fs centered at 804 nm and intensities in the range 10–100 TW cm⁻². Ion detection is performed with the velocity map imaging technique. Ion images for CH₃I⁺⁺ (p = 1) and I⁺⁺ (q ≤ 3) have been measured and assigned to different Coulomb explosion channels. The experimental results have been rationalized through wavepacket calculations on ab initio potential energy curves of the multiply charged parent molecule.

II. EXPERIMENTAL SETUP

The experimental setup has been described in detail elsewhere. Briefly, it consists of a femtosecond laser system and a molecular beam setup to record fragment ion images using the velocity map imaging technique. The laser is an amplified Ti:sapphire system delivering 50 fs, 3.5 mJ pulses centered at 804 nm with 1 kHz repetition rate. The output beam of the laser system is focused into the molecular beam using a 25 cm focal length lens. To estimate laser pulse intensities, we have followed the procedure described in ref 22. Briefly, the beam radius at the focus, r₀, necessary to evaluate the laser pulse intensity, has been measured carrying out ablation experiments on a Si surface. If the laser fluence exceeds a certain threshold, φ₀, the Si surface suffers an irreversible change, which is characterized by the diameter D of the modified area. For laser pulses with a Gaussian spatial beam profile, the laser fluence,
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The mixture is made of about 5% of CH$_3$I. To avoid the presence of 

tion (kinetic energy and angular distribution) using the 

phosphorescence emitted by phosphor screen as a 2D image.

applying a gating voltage to the front MCP plate. A Peltier-cooled 
detector. Mass selection of the ionized species was carried out by 
generating in the interaction region were extracted perpendicu-
larly and accelerated by the electrostatic lens system working in 

the source chamber from the ionization chamber. The ions 
molecular beam passes through a 1 mm skimmer that separates 
the source chamber from the ionization chamber. The ions 
generated in the interaction region were extracted perpendicu-
larly and accelerated by the electrostatic lens system working in 

velocity map imaging configuration and, at the end of a 30 cm 
time-of-flight tube, were projected onto a 2D detector composed 
of two microchannel plates (MCP) in Chevron configuration 
coupled to a phosphor screen. Typical repeller voltages were 
5.2 kV, with optimum velocity mapping conditions found for 
$V_{\text{extractor}}/V_{\text{repeller}} = 0.75$. In these conditions all ions with 
the same velocity vector are mapped on the same point on the 
detector. Mass selection of the ionized species was carried out by 
applying a gating voltage to the front MCP plate. A Peltier-cooled 
12 bit charge-coupled device (CCD) camera recorded the 
phosphorescence emitted by phosphor screen as a 2D image. 
The raw images are Abel inverted to extract the desired informa-
tion (kinetic energy and angular distribution) using the p-BASEX 
method. The polarization of the laser beam was set parallel to 
the detector face to provide the cylindrical symmetry required for 
the procedure of Abel inversion of the ion images. Typical 
acquisition times for each image were 40 s corresponding to 
40 000 laser shots. The calibration of the apparatus was done 
measuring the CH$_3$I image upon 268 nm photodissociation of 
CH$_3$I and resonant CH$_3$(v=0) ionization and using the known 
kinetic energy release of the CH$_3$(v=0) + I$^\cdot$($^2$P$_{1/2}$) and 
CH$_3$(v=0) + I$^+$($^2$P$_{3/2}$) channels. In these conditions, the kinetic 
energy resolution of the apparatus is better than 50–140 meV at 
0.5–4.6 eV kinetic energy release.

III. THEORETICAL MODEL

To provide some physical insight into the photofragmentation of 
CH$_3$I in the Coulomb explosion regime, wavepacket propagations 
in reduced dimensionality were performed for the different 
possible channels using ab initio potential energy curves.

One dimensional potential energy curves of several electronic 
states were calculated for CH$_3$I$^{n+}$ (2 ≤ n ≤ 4) in the C–I 
distance (maintaining the rest of degrees of freedom of the 
molecule frozen to the equilibrium values of the neutral 
molecule) using the complete active space procedure in its state 
average formalism (SA-CASSCF)$^{24,27}$ with the ANO-RCC 
basis set$^{28}$ with no symmetry constraints. The basis set was 
contracted as (22s19p13d5f3g)/[10s9p8d5f3g], (14s9p4d3f)/ 
[8s7p4d3f], and (8s4p3d)/[6s4p3d] for the iodine, carbon, and 
hydrogen atoms, respectively. Spin–orbit couplings were evaluated 
by using the relativistic Douglas–Kroll Hamiltonian$^{29,30}$ and 
the atomic mean field integrals approximation. The em-
ployed active space includes the two iodine lone pair orbitals and 
the two σ, bonding and antibonding, orbitals of the C–I bond. 
These orbitals correlate in the dissociation limit with the three 
σ orbitals of the iodine atom and the n orbital of the CH$_3$I radical. 
This last orbital is empty at the end of the Coulomb explosion, so 
it becomes unoccupied at large C–I distances. This is important 
in the description of the σ bond at the Franck–Condon geometry. To 
maintain the same active space along the whole 
one-dimensional cut, the neutral dissociation channel, 4 singlets 
and 3 triplets where the n at the CH$_3$I has at least one electron 
during the dissociation, was also included in the averaging of the 
different cationic channels, avoiding the rotation of the n orbital. 
In the Coulomb explosion channels, the number of states was 
chosen to cover all the possible electronic terms of the iodine 
cation, so we consider 6 singlets and 3 triplets (15 states) in 
$I^+$ + CH$_3$ and I$^{3+}$ + CH$_3$ and 8 doublets and 1 quadruplet 
(20 states) in I$^{5+}$ + CH$_3$. The ab initio calculations were carried 
out with the MOLPRO package$^{31}$ using the CI procedure$^{32,33}$ 
with no excitations for the different channels.

The total kinetic energy of the ionic products obtained by 
Coulomb explosion of CH$_3$I was evaluated by propagating the 
ground state wavepacket of the neutral molecule, previously 
calculated using the Fourier grid Hamiltonian method,$^{34}$ on the 
different CH$_3$I$^{n+}$ adiabatic potential energy curves, considering a 
vertical (Franck–Condon) transition from the minimum of the 
ground potential energy curve. This approach assumes that IMM 
is the main contribution to the ionization and neglects the 
possibility of different ionization efficiencies in the different 
channels. In these simulations, the time-dependent Schrödinger 
equation for the nuclei was solved using the split-operator 
method,$^{35}$ and the exit energy was evaluated as the Fourier 
Transform of the time evolution of the wave function at the 
asymptotic region.

IV. RESULTS AND DISCUSSION

As has been observed before,$^{18,19}$ Coulomb explosion in CH$_3$I 
proceeds through the channels described by 

CH$_3$I$^{n+} \rightarrow$ CH$_3$$^{p+}$ + I$^+$ ($n = p + q$) (5)

In this work, three channels corresponding to $p = 1, q = 1–3$, 
have been observed, and will be referred to as (p, q). As expected, 
higher charged states of the iodine atom are found for larger 
intensities. In a relatively weak laser field of about 10 TW cm$^{-2}$, 
the (p, q) channels with $p < 2, q < 2$ dominate. In a stronger laser 
field of about 100 TW cm$^{-2}$, additional multiply ionized frag-
mion fragments of I$^{n+}$ (q > 3) are observed. In the present work, three 
distinct laser intensity regions, 10, 30, and 60 TW cm$^{-2}$, have 
been selected to study the (1, 1), (1, 2), and (1, 3) channels, 
respectively.
The intensity of the peak corresponding to the CH$_3$I$_2^+$ species is similar to those reported in refs 18 and 19. However, in their case mass spectra and their evolution with laser intensity are very distinct. This allows us to rule out alternative dissociative ionization and fragmentation processes. In the insets, the oscillations in the signal baseline are due to the presence of the intense near peak corresponding to the I$_2^+$ species.

Time-of-flight (TOF) mass spectra were acquired at the different intensities and are depicted in Figure 1. At 10 TW cm$^{-2}$, only three strong peaks corresponding to CH$_3$I$^+$, I$^+$, and CH$_3$I$^+$ were found. At higher intensities, peaks corresponding to the multiply charged CH$_3$I$^{2+}$, I$^{2+}$, and I$^{3+}$ species appear, which reveals that Coulomb explosion processes are necessarily taking place. It is worth mentioning that no ions such as CH$_2$I$^+$, CH$_2$I$^{2+}$, CH$I^+$, or CH$I^{2+}$ were detected in the intensity regimes that were explored, which allows us to rule out alternative dissociative ionization and sequential two-body charge separation channels. The present mass spectra and their evolution with laser intensity are very similar to those reported in refs 18 and 19. However, in these images the intensity of the peak corresponding to the CH$_3$I$^{2+}$ species is largest, probably due to the higher laser intensities employed in those cases.

For a purely Coulombic situation, where the repulsion is assumed to be due to point charges located in each of the fragments at their neutral equilibrium distance, the total kinetic energy of CH$_3$I$^{2+}$ in the ($p$, $q$) channel, $E_{(p,q)}$, can be calculated as

$$E_{(p,q)} = \frac{q_pp_q e^2}{4\pi \epsilon_0 R_e}$$

where $q_p$ and $q_q$ are the charges of the two fragments, $R_e$ is the equilibrium C–I internuclear distance of CH$_3$I ($R_e = 2.14 \, \text{Å}$), $\epsilon_0$ is the permittivity of vacuum, and $e$ is the electron charge. This energy is shared between the fragments as

$$E_{\text{Coul}}(\text{CH}_3I^{2+}) = \frac{m_t}{m_{\text{CH}_3I} + m_t} E_{(p,q)}$$

$$E_{\text{Coul}}(I^{2+}) = \frac{m_{\text{CH}_3I}}{m_{\text{CH}_3I} + m_t} E_{(p,q)}$$

where $m_t$ are the masses of the different fragment ions. It follows that the kinetic energy release (KER) of the two fragments CH$_3$I$^{2+}$ and I$^{2+}$ produced by the two-body fragmentation channels has a relationship given by

$$\frac{\text{KER}(I^{2+})}{\text{KER}(\text{CH}_3I^{2+})} = \frac{m_{\text{CH}_3I^{2+}}}{m_{I^{2+}}}$$

A. Channel (1, 1). In this section, we present the results of the Coulomb explosion of CH$_3$I resulting from the interaction of the molecule with a relatively weak laser field (10 TW cm$^{-2}$). In these conditions, channel (1, 1) is clearly dominant. Figure 2 shows the Abel-inverted images corresponding to the CH$_3$I$^+$ and I$^+$ ions. In the CH$_3$I$^+$ image two features can be clearly distinguished. First, a near-zero recoil energy contribution, in the center of the image, which contains a strongly anisotropic distribution. This is believed to be related to dissociative ionization processes and will not be treated in the present work. The main feature of interest consists of two outer rings, which can be assigned to Coulomb explosion events. The fact that two rings appear is an indication of more than one channel occurring in these conditions. A similar structure, with a contribution near the center of the image and two outer well-defined rings, is present in the I$^+$ image in the lower panel. These rings, both for CH$_3$I$^+$ and for I$^+$, show marked parallel anisotropy.

The center-of-mass (CM) total kinetic energy distribution of each fragment can be extracted from the angular integration of the images. The results are also shown in Figure 2c,d, which correspond to the images shown in Figure 2a,b, respectively. As can be seen in the figure, the high kinetic energy region for the CH$_3$I$^+$ ions contains two well-defined peaks corresponding to the Coulomb explosion rings described above, centered around 4.41 and 5.23 eV. The KER of I$^+$ also presents two peaks, although resolving them is harder in this energy region, centered at 4.54 and 5.39 eV, respectively. The relation between the kinetic energies of CH$_3$I$^+$ and I$^+$ satisfies eq 9 rather well, so that it can be assumed that the same two Coulomb explosion contributions can be seen through Coulomb explosion processes. In the case under study the kinetic energy of CH$_3$I$^+$ is the major contribution, and it can be attributed to the existence of some space charge effects, especially for the larger I$^+$ fragment. In any case, the measured KERs of the fragments CH$_3$I$^+$ and I$^+$ are significantly lower than the calculated energies considering only Coulomb explosion repulsive forces of point charges at the neutral molecule internuclear distance (eq 6). This value has been indicated in Figure 2c,d with a vertical line.

This discrepancy between the expected kinetic energy release and the measured values has been reported repeatedly in the literature (see, for instance, refs 6 and 18). As has been described above, it is common to assume that Coulomb explosion does not take place at the internuclear distance of the neutral molecule, but rather at an elongated distance, thus reducing the available energy. Little effort has been devoted to the detailed study of the potential energy surfaces of the multiply charged molecular ion and the consequences of this on the available fragment energies through Coulomb explosion processes. In the case under study here, the fact that the CH$_3$I$^{2+}$ species is visible in the mass spectrum indicates that at least a bound potential for CH$_3$I$^{2+}$ must exist. For more highly charged ions, it becomes less and less likely that this is the case, but even when all states are repulsive, an important stabilization with respect to the Coulomb potential is expected, especially in the Franck–Condon region, and this is

Figure 1. Time-of-flight mass spectra of CH$_3$I irradiated by 804 nm, 50 fs laser pulses at intensities of (a) 10 TW cm$^{-2}$, (b) 30 TW cm$^{-2}$, and (c) 60 TW cm$^{-2}$. The different parent and fragment ions are labeled. The insets correspond to a magnification of the part of the spectrum where the CH$_3$I$^{2+}$ species appear. In the insets, the osculations in the signal baseline are due to the presence of the intense near peak corresponding to the I$_2^+$ species.
To provide a basis to discuss the importance of stabilization vs explosion at elongated distances, ab initio calculations of the potential energy curves (PECs) for the CH$_3$I$_2^+$ species have been performed using the SA-CASSCF methodology. In Figure 3, all possible PECs for CH$_3$I$_2^+$ that correlate with different electronic states of I$^+$ (3P$_2$, 3P$_1$, 3P$_0$, 1D$_2$, and 1S$_0$) are presented (assuming CH$_3^+$ to be in its ground electronic state). The PECs, subtracted from the Coulomb energy, are presented in the inset.

Most of the calculated PECs show a purely repulsive character, so a fast fragmentation, i.e., explosion, is expected to occur. However, for some potential energy curves correlating with the I$^+$ (3P$_2$) fragment, the attractive covalence forces in the Franck-Condon region are comparable with the Coulomb force. This causes the appearance of a potential well that can contain metastable states. In those, tunneling to the continuum is always possible, but on a very long time scale. We believe that this type of state is responsible for the stability of the CH$_3$I$_2^+$ ion, whose lifetime is long enough so that the species appears in the TOF spectra (microsecond time scale).

The time evolution of the 1D wave packet on the bound PECs of the CH$_3$I$_2^+$ correlating with I$^+$ (3P$_2$) is shown in Figure 4a. As can be seen, the wave packet is bound and does not exhibit dissociation on the picosecond time scale. However, when the wave packet is prepared on a purely repulsive PEC, then it evolves toward the asymptotic region, giving rise to rapid dissociation. Figure 4b shows an example of this behavior corresponding to a repulsive PEC correlating with I$^+$ (3P$_2$) (Figure 3).

Figure 5 shows the comparison between the experimental and theoretical center-of-mass total kinetic energy distributions for CH$_3$I$^+$. The theoretical distribution has been obtained from the 1D wave packet calculations carried out on the potential energy curves shown above as described in the Theoretical Model section. It must be pointed out that the intensity of the different peaks in the theoretical KER is arbitrary because we have not calculated the transition dipole moments to the different electronic states. Moreover, the total kinetic energy for a given channel...
is related with the deepness of the potential energy curve once the Coulomb repulsion has been subtracted. The width of the peaks in the KER distribution are related with the shape of the PEC; a broader peak in the KER is related with a flatter potential well and vice versa.

Considering the present calculations, the peak at 4.41 eV in the experimental KER shown in Figure 5 can be assigned to the (1, 1) Coulomb explosion channel yielding electronic ground state CH$_3$I$^+$ and I+(1D$_2$). However, the experimental peak at 5.23 eV cannot be assigned to a single (1, 1) Coulomb explosion channel because, according to theory, at this kinetic energy there are several channels contributing.

The discrepancies observed in the position of the peaks (<0.2 eV) when theory and experiment are compared may be due to inaccuracies in the ab initio potential energy curves. As commented on above, the observed total kinetic energies for the different (1, 1) Coulomb explosion channels are lower than those calculated considering only Coulomb repulsion forces. However, these energy differences are in agreement with the calculated deviations from pure Coulomb interactions of the PECs represented in the inset of Figure 3.

**B. Channel (1, 2).** As the intensity of the laser increases, a higher degree of ionization of CH$_3$I is attained. In this section we will focus on the (1, 2) Coulomb explosion channel leading to CH$_3$I$^+$ and I$_2^+$ ions, which appears at laser intensities of about 30 TW cm$^{-2}$. Figure 6a shows the Abel-inverted image corresponding to the I$_2^+$ ion. A single, broad, structureless ring with a pronounced anisotropy along the direction of polarization of the laser is observed. The corresponding KER is shown in Figure 6b, where the broad peak centered at 10.2 eV corresponds to the ring described above. The corresponding I$_2^+$ CM kinetic energy is 1.06 eV.
According to eq 9, the CH$_3^+$ CM kinetic energy which correlates with I$_2^+$ is 8.96 eV. This CH$_3^+$ recoil energy is, however, too large to be detected in our velocity map imaging setup. The fwhm of the peak shown in Figure 6b is about 2 eV. Because the resolution in the zone of 10 eV is estimated to be $\approx$0.9 eV, the broad peak observed in the I$_2^+$ KER has to be explained as the sum of several contributions.

As for the CH$_3$I$^{+3}$ species, we have carried out ab initio SA-CASSCF calculations of the ground and excited electronic states of CH$_3$I$^{+3}$, which should be responsible for the (1, 2) Coulomb explosion channel. The PECs for CH$_3$I$^{+3}$ that correlate with different electronic states of I$_2^+$ ($^2\Pi_{3/2}, ^2\Pi_{1/2}, ^2\Delta_{5/2}, ^2\Delta_{3/2}, ^4\Sigma_{3/2}$) are shown in Figure 7. The PECs, subtracted from the Coulomb energy, are presented in the inset. As can be seen, at variance with CH$_3$I$^{+3}$, all PECs for CH$_3$I$^{+3}$ are repulsive; i.e., the attractive covalence forces in the Franck-Condon region are always significantly smaller than the Coulomb forces. This can explain the absence of a peak in the TOF mass spectrum corresponding to the CH$_3$I$^{+3}$ species.

We have carried out 1D wavepacket calculations on the PECs shown in Figure 7 and the corresponding KERs obtained from the calculations are depicted in the lower panel of Figure 6b. As can be seen, the calculated KER is in reasonable agreement with experiment, although the calculations predict a narrower distribution. As evidenced by the comparison between theory and experiment, the experimental KER is the result of the combination of several different channels within the (1, 2) Coulomb explosion process. The left part of the experimental peak, in the range of kinetic energies 8–10 eV, can be attributed to excited vibrational states of the CH$_3^+$ fragment ion. The right tail of the KER extending beyond the expected maximum kinetic energy could be related with higher Coulomb explosion channels, yielding I$_2^+$ fragments.

Again, the difference between the expected kinetic energy considering only Coulomb repulsive forces and the observed KER for the (1, 2) Coulomb explosion channel is related to the deviations from a pure Coulomb interaction found in the ab initio PECs of the CH$_3$I$^{+3}$ ion. This interpretation is at variance with the sequential ionization mechanism proposed by Liu et al.$^{18}$

They suggested that, if the laser pulse is sufficiently long, during the ionization of CH$_3$I$^{+3}$ to CH$_3$I$^{+3}$, the C–I distance increases up to some critical value. Thus, the Coulomb repulsion energy has to be calculated according to this elongated distance of the two point charges before explosion ($R_c$), instead of the equilibrium distance ($R_e$) in eq 6. Using their measured total KER (7.78 eV) and eq 6, they were able to estimate a $R_c$ value of 3.7 Å for the (1, 2) Coulomb explosion channel. In the present work, however, the energy difference finds a natural explanation considering the theoretical PECs for the CH$_3$I$^{+3}$ and CH$_3$I$^{+3}$ species.

C. Channel (1, 3), When the laser intensity is further increased, the (1, 3) Coulomb explosion channel is opened. This fact is evidenced by the presence in the TOF mass spectrum of the I$_3^+$ species that appears at laser intensities around 60 TW cm$^{-2}$. Figure 8a shows the Abel-inverted image corresponding to the I$_3^+$ ion. In this case, the ion image displays a main broad structureless and anisotropic ring and a weaker ring with the same...
Figure 9. SA-CASSCF adiabatic potential energy curves along the C–I bond for the electronic ground and excited states of the CH₃I⁺⁺ cation. The potential energy curves that correlate with the same electronic state of I₃⁺ have been represented with the same color. In the potential energy curves shown in the inset, the Coulomb repulsion has been subtracted.

The peak centered at 15.80 eV in the I₃⁺ KER is compatible with the (1, 3) Coulomb explosion channel. In this case, there is an almost perfect agreement between the position of the experimental peak and the theoretical prediction based on 1D wavepacket calculations on the ab initio PECs of the CH₃I⁺⁺ species depicted in Figure 9. As for the (1, 2) Coulomb explosion channel, the energy difference between the vertical line at 20.19 eV for the (1, 3) Coulomb explosion channel and the observed and calculated peaks in the KER is also compatible with the minima depicted in the inset of Figure 9 for the CH₃I⁺⁺ PECs.

V. CONCLUSIONS

The combination of femtosecond intense IR laser pulses and the velocity map imaging technique has allowed us to study several \( (p, q) = (1, 1), (1, 2), \) and \( (1, 3) \) Coulomb explosion channels for CH₃I. Ion images measured for CH₃⁺ and I⁺⁺ \( (q \leq 3) \) fragments and the corresponding total kinetic energy distributions are in good agreement with reduced dimensionality wavepacket calculations carried out on ab initio potential energy curves for CH₃I⁺⁺, CH₃I⁺⁺, and CH₃I⁺⁺ assuming the Ionization Ignition mechanism. The appearance of the CH₃I⁺⁺ species in the time-of-flight mass spectrum and the general observation that the measured kinetic energy release for CH₃⁺ and I⁺⁺ \( (q \leq 3) \) is lower than that calculated considering only Coulomb repulsion forces have been rationalized by means of theoretical calculations, both of ab initio potential energy curves and 1D wavepackets, which reveal the existence of bound potentials in the Franck–Condon region of CH₃I⁺⁺ once the Coulomb repulsion forces are subtracted.

REFERENCES