Valence double ionization electron spectra of CH$_3$F, CH$_3$Cl and CH$_3$I

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A B S T R A C T
Valence double ionization electron spectra of the methyl fluoride, methyl chloride, and methyl iodide molecules have been recorded using a time-of-flight photoelectron-photon coincidence technique. The spectra are interpreted by comparison with existing ionization data, Auger spectra, and theoretical calculations. The lowest double ionization energies have been found to be around 35.0 eV, 30.6 eV, and 26.67 eV for CH$_3$F, CH$_3$Cl and CH$_3$I, respectively. These energies are also compared with the predictions and implications of an empirical rule for the lowest double ionization energy in molecules.

1. Introduction

Double ionization of gas-phase molecules by single photons at energies below the opening of inner shells provides valuable tests of both electronic structure theory and of ionization dynamics. Where Auger processes are energetically impossible the process of double photoionization is forbidden in the simple frozen-orbital model, and depends for its intensity on electronic and dynamic mechanisms which can be described in a general way as electron correlation. Double ionization of molecules is significant as a mechanism by which molecules are destroyed in high-energy environments including astrophysical and atmospheric environments, plasma etching and mass spectrometry. The minimum energy at which molecular double ionization can occur, the double ionization potential (DIP), is the most basic parameter determining the occurrence of the process, while the double ionization spectra are vital for interpretation of its details and mechanisms.

In the present double ionization study, measurements were performed by means of a versatile time-of-flight photoelectron-photoelectron coincidence (TOF-PEPECO) spectrometer. The TOF-PEPECO technique has the advantage that it provides a complete picture of the energy distribution for electrons emitted in multi-ionization processes. The coincidence data can be presented in two dimensional maps, where the correlation between the electron kinetic energies will give information on the underlying ionization processes. Information on both direct and indirect ionization processes such as autoionization and Auger decay may be present as features in the two dimensional maps.

A TOF-PEPECO study [1] on CH$_3$I has previously been carried out at 30.38 nm, which corresponds to a photon energy of 40.8 eV. In this study by Pilcher-Clayton and Eland, the double valence photoionization spectrum of HI was compared to the DIP spectra of CH$_3$I and CF$_3$I. They assigned the lowest double ionization states, as well as some vibrational energies, to the obtained DIP spectra for these molecules. They did also find evidence for atomic autoionization of I$^+$ fragments as an indirect double photoionization pathway in the three molecules. More recently, the double photoionization spectrum of CH$_3$I has been investigated theoretically by Pernpointner et al. [2].

An early empirical rule of thumb [3] states that the lowest double ionization potential is approximately 2.7 times the lowest single ionization potential. This approximation gives surprisingly good agreement with the experimentally known ionization energies of many atoms. For molecules, the Coulomb interaction between the two vacancies created by the photoelectrons becomes a significant extra variable and needs to be considered as a separate term, suggesting an expanded form of the rule [4] as

$$\varepsilon_{\text{DIP}} \approx 2.2 \cdot \varepsilon_{\text{IP}} + \frac{11.5}{r_{\text{BH}}}$$

where $\varepsilon_{\text{IP}}$ and $\varepsilon_{\text{DIP}}$ are the lowest double and single ionization potentials, respectively, $r_{\text{BH}}$ is a notional distance (Å) between the electron vacancies in the molecule and 11.5 eV is a parameter empirically found to provide a fit to data for several molecules. This form of rule gives satisfactory agreement [4] for experimental results on diatomic linear, non-linear polyatomic and some cyclic molecules on the basis that the charges are as far apart as possible within the known molecular structures. The expanded rule was proposed as an improved means to estimate double ionisation energies empirically, where they are not experimentally known. Here we examine...
whether the notional distances $r_{nh}$ deduced from the rule can be sensibly interpreted as real interchange distances in molecular dications.

In this study, we report a systematic investigation of the double photoionization of the methyl halides, CH$_3$X (X = I, Cl, F) up to a photon energy of 130 eV for methyl fluoride, and up to 48.37 eV for methyl chloride and methyl iodide. The double photoionization spectra are compared to existing ionization data, Auger spectra and theoretical investigations of the methyl halides where available. The lowest double ionization potentials are used for further investigation of the rule of thumb for the molecules presented above.

2. Experimental

The basic principle of the TOF-PEPECO spectrometer has been described in detail in previous works [5,6] by Eland et al. The spectrometer originally operated with a helium lamp [7], producing UV light pulses at a repetition rate of a few kHz and a pulse width of 5–10 ns. The light is produced by discharges in a coaxial hollow cathode filled with helium gas. A toroidal grating monochromator is used to select individual wavelengths and to guide the light into the interaction region. Photoionization by the light pulses is followed by the detection of electron pairs in coincidence after they pass through a 2.2 m long magnetic bottle flight tube.

The magnetic bottle is created by a cylindrical neodymium permanent magnet closing the magnetic field at the beginning of the flight tube in the interaction region. The magnetic field is extended through the flight tube by a solenoid wound around the tube, forming a uniform magnetic field for the electrons in the flight tube transit. The shape of the magnetic field is enhanced in the interaction region by a conical soft iron pole cap mounted on the magnet, resulting in a magnetic field of about 0.5 T in the interaction region. The magnetic bottle allows a collection of almost all electrons emitted into the solid angle of 4π in the interaction region. The electrons are shielded from external fields during their flight by a μ-metal shield around the flight tube. The detection of the electron pairs is done by a microchannel plate detector at the end of the flight tube, and the flight time for the electron pairs is registered relative to the start signal, i.e. relative to each lamp pulse.

The samples CH$_3$F, CH$_3$Cl, CH$_3$I were commercially obtained. The purity of the samples were checked by the single photoionization spectra, using the He(I$\lambda$) emission line with a wavelength of 58.43 nm, corresponding to a photon energy of 21.22 eV.

The double photoionization spectra were measured using the He(I$\lambda$) and the He(II$\beta$) emission lines with the wavelength of 30.38 nm and 25.63 nm, corresponding to photon energies 40.81 eV and 48.37 eV, respectively. Calibration of the spectrometer (see e.g. Refs. [5,6]) was performed before and after each measurement by the single ionization spectra of O$_2$, measured at 58.43 nm (21.22 eV). The methyl fluoride spectra measured at 100 eV and 130 eV were obtained at beam line U49/2 PGM-1 of the BESSY-II storage ring at the Helmholtz Zentrum Berlin operated in single bunch mode. The energy resolution of the spectrometer ranges from about 30 meV at low electron kinetic energy up to a few 100 meV for electrons of higher kinetic energies, such as those emitted in the 100 eV and 130 eV measurements on methyl fluoride (resolution about 500 meV).

3. Results and discussion

The methyl halides CH$_3$F, CH$_3$Cl, CH$_3$I all have the same spatial structure and symmetry belonging to the C$_3v$ point group. The molecular orbital structure of the methyl halides can be written as a common ground state electron configuration (inner atomic orbitals)$1\alpha_{1}^{2}2\alpha_{1}^{2}1e^{2}3\alpha_{1}^{2}2e^{4}$ ($^{1}A_1$)

The character of the valence orbitals is essentially the same for all the molecules, where the highest occupied molecular orbital (HOMO) has more dominant lone-pair character and shows stronger spin–orbit splitting as we go to the heavier halogen atoms. The orbital character of CH$_3$F is slightly different from the other methyl halogens because the F2p atomic orbital has higher binding energy than the C2p atomic orbital, whereas in the other molecules the outermost halogen p-orbital is less strongly bound than the C2p orbital. This results in a stronger CH$_3$ character for the outermost orbitals in CH$_3$F.

3.1. Methyl fluoride

The double ionization spectrum of CH$_3$F at 48.37 eV is presented in Fig. 1, and the double photoionization spectra for CH$_3$F at 100 eV and 130 eV are presented in Fig. 2. In these figures the coincidence signal intensity is plotted against the double ionization energy given by the photon energy minus the sum of the kinetic energies of the fast and slow photoelectrons. The DIP spectrum of CH$_3$F, measured at 48.37 eV, is less structured than those of the other methyl halides measured at the same photon energy, which is expected because of the lack of the lone-pair character of the HOMO. This is in accord with the single ionization spectrum (cf. Ref. [8]) where the lowest ionization energies consist of two broad bands. Methyl fluoride has no bound or metastable doubly charged states accessible to photoionization of the neutral molecule, as evident from the lack of doubly charged parent ions in its mass spectrum [9] and there is no resolved vibrational structure.

![Image](https://via.placeholder.com/150)  
**Fig. 1.** Double photoionization TOF-PEPECO spectrum of CH$_3$F at 48.37 eV photon energy.

![Image](https://via.placeholder.com/150)  
**Fig. 2.** Double photoionization TOF-PEPECO spectrum of CH$_3$F at 100 eV (blue) and 130 eV (red) photon energy. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
either in the double ionization spectrum. The spectra in Fig. 2 illustrate a phenomenon which may be found in many photoionization spectra; the relative intensities of the band structures change as the photon energy changes. The band structures at higher ionization energy become more intense as the photon energy is increased, which may mainly be attributed to an increased relative cross-section for deeper lying orbitals.

From Fig. 1 the lowest double ionization energy can be estimated to be around 35.0 eV by interpolation of a slope to the spectrum at 35.5 eV down to the base level of the background coincidence counts, and the maximum for the first broad peak is at about 36.4 eV. In the Auger study of CH₃F by Moddeman [10] the onset of the lowest double ionization was estimated to 35.2 eV. In the carbon and fluoride K-LL Auger spectra presented and analysed by Moddeman [10] and Liegener [11], respectively, many features with some resemblance to Fig. 2 can be seen. Unfortunately, very few peaks occur at the same energies in the two K-LL Auger spectra, and a close enough match to the broad features in Figs. 1 and 2 could not be found for a clear identification of the states. According to the theoretical calculations, by Liegener, all the states have mixed configurations, but single configurations are dominant at the lower double ionization energies. The states from 45 eV and upwards have heavily mixed configurations, with the exception of the weak broad peak that can be seen in Fig. 2 at about 98 eV, which is formed by almost pure F2s electron pair loss [12].

With this in mind, the electron configuration of the neutral molecule is used for the discussion of the doubly ionized states in methyl fluoride. The dicationic states located around 36 eV can be attributed to the loss of two electrons from the outermost e orbital. Using the crude rule of thumb for molecules and the value for the lowest vertical ionization energy of 13.04 eV (cf. Ref. [13]), an interatomic distance of about 1.57 Å is obtained. This value can be compared to the interatomic distance between the carbon and fluorine atom which is about 1.39 Å [15]. The configuration e², in C₃ᵥ symmetry, formally produces the states ³A₂, ¹E, and ¹A₁. The two singlet states are calculated by Liegener to lie at 35.8 and at 36.3 eV, which is in line with Fig. 1. The triplet state will also be close to these values and probably lowest in energy. The broad peak at around 41 eV (cf. Fig. 1) may arise from the configuration 5a¹2e² or/and from 1e¹2e¹, calculated by Liegener to lie at 39.7 and at 41.4 eV, respectively. Because of the lack of structure at higher energies and because of heavily mixed configurations, it is not possible to make an identification of the states at higher energies.

<table>
<thead>
<tr>
<th>Table I</th>
<th>Values for the double ionization of CH₃F.</th>
</tr>
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<tbody>
<tr>
<td>State</td>
<td>Energy (eV)</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>Onset</td>
<td>35.0 ± 0.19</td>
</tr>
<tr>
<td>³A₂, ¹E, ¹A₁</td>
<td>36.0</td>
</tr>
<tr>
<td></td>
<td>40.7</td>
</tr>
</tbody>
</table>

The second feature in Fig. 3 is a broad peak between 33.5 and 36.5 eV, with a maximum at 35.1 eV. In this energy region, Grant et al. could identify at least four doubly ionised states, ¹A₂ at 33.6 eV, ³E at 34.1 eV, ¹E at 35.4 eV, and ³A₂ at 35.5 eV. The theoretical results in Ref. [14] show that the ionization processes contributing to this peak mainly correspond to a leading electron configuration where at least one of the ionized electrons is ejected from the 2e orbital and the second electron from either the 3n or the 1e orbital.

The higher energy region (> 37.5 eV) shows diffuse features where a good classification of final states is hard to make. The first feature centred around 39 eV, has an energy that lies in the range that corresponds to a ¹E (38.5 eV) state [14]. Two more states with an energy close to 39.0 eV (³E and ¹A₂) may also be assigned to this feature. The second feature with maximum around 41 eV may be in the lower energy region of the spectra. This peak can be identified provisionally from previous work by Grant et al. in Ref. [14]. They studied the double ionization spectrum of CH₃Cl with double-charge-transfer spectroscopy and theoretical calculations. They could identify the states ¹E (32.2 eV) and ³A₂ (31.5 eV), with energies within the energy range of this first peak. The leading electron configuration of these two states is 2e². Using the rule of thumb for molecules and the value for the lowest vertical ionization energy of 11.29 eV (see Ref. [13]) and 31.5 eV as the vertical double ionization energy, an intercharge distance of about 1.7 Å is obtained. This value can be compared to the interatomic distance between the carbon and chlorine atom in the neutral molecule, which is about 1.78 Å [15].

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assigned to a $^1$E state at 40.4 eV and a $^3$E state at 41.0 eV. In this energy region the amount of mixed states start to increase. Table III lists the double ionization energies and the identified states for CH$_3$Cl.

### 3.3. Methyl iodide

The direct double ionization spectra of CH$_3$I at 40.81 eV and at 48.37 eV are presented in Fig. 4. The spectrum has three distinct peaks with maxima at 26.67 eV, 27.68 eV and at 28.68 eV. These can be identified from the previous work [1] by Pilcher-Clayton and Eland, where they recorded spectra of CH$_3$I at photon energies of 40.8 eV and 32.7 eV. Compared to the spectra recorded at lower photon energies, the spectrum recorded at 48.37 eV shows a larger relative intensity for the higher energy (> 29 eV) region relative to the lower energy region. Using the rule of thumb for molecules and the value for the lowest vertical ionization energy of 9.54 eV [13] and 26.67 eV as the vertical double ionization energy, an interatomic distance of about 2.0 Å is obtained. This value can be compared to the interatomic distance between the carbon and iodine atom in the neutral molecule, which is about 2.14 Å [15].

In the lower energy region (26–29 eV) in Fig. 4, features can be seen as distinct peaks. The sharp features in the lower energy region (26–29 eV) are best interpreted using the spectrum of Pilcher-Clayton and Eland recorded at 32.7 eV, which has sufficiently high resolution to separate them. The first peak (26.67 eV) in Fig. 4 was assigned as an $^3$A$_2$ state, with spin–orbit splitting into A$_1$ (26.664 eV) and E (26.846 eV). The E state shows some vibrational structure ($\nu = 0, 1$), where $\nu = 1$ has an energy of 26.998 eV. The peak at 27.68 eV was identified as a $^1$E state, with two vibrational levels ($\nu = 0, 1$) at 27.656 and 27.778 eV. The spectrum recorded at 32.7 eV shows an unassigned peak at approximately 27.9 eV. According to Pernpointner et al. (Ref. [2]), this peak may not correspond to an electronic state, but to a higher vibrational state (E, $\nu = 2$). The peak at 28.68 eV was identified in Ref. [1] as a $^3$A$_2$ state with an energy of 28.679 eV. An additional peak at 29.05 eV may be associated with two close lying E states calculated at 28.27 eV and 28.42 eV, respectively [2]. When the calculated spectrum is shifted by 0.84 eV, so the first peak in the experimental spectrum and the calculated spectrum have the same energy, these two E states end up at 29.11 eV and 29.26 eV, respectively.

For comparison with the experimental data measured at 48.37 eV, the calculated double ionization spectrum by Pernpointner et al. is plotted in purple in Fig. 4. The spectrum is a convolution of the discrete spectrum in Ref. [2] with Gaussians of varying full width half maximum (FWHM) as a function of electron energy. The varying FWHM is chosen to match our instrumental resolution of E/ΔE = 50, where E is the electron energy, for the TOF spectrometer at 48.37 eV. This gives us a FWHM that ranges from about 10 meV at high double ionization energies up to about 200 meV at a double ionization energy of 20 eV. The calculated spectrum has been shifted to a higher energy by 0.84 eV, so the first peak in the experimental spectra and the calculated spectrum have the same energy. Comparing the calculated spectrum, which can be seen in further detail in Ref. [2], to the experimental spectra, it can be seen that there is a good match up to about 29 eV.

At double ionization energies above 29 eV, the calculated and experimental spectra have a similar shape although the peak intensities and apparent band widths are different. The lack of discrete structures in the experimental spectra at the energies above 29 eV is presumably due to the highly dissociative nature of the doubly ionized states in this region, which is especially noticeable at the higher energies. There is also considerable overlap of many close-lying states. Despite these difficulties some deductions can be made concerning the bands above 29 eV with help from the calculated spectrum. According to the calculated spectrum, the main contribution to the band with maximum at about 30.0 eV is from orbitals with mainly iodine character. As the double ionization energy increases the iodine character of the orbitals will decrease and the contributions from orbitals with a more CH$_3$ character will increase. By comparing the experimental and calculated spectra this might be seen in the fact that the band with maximum at about 31.2 eV may have an equal contribution of orbitals with both iodine and methyl character. At higher energy, the band with maximum at about 34.8 eV may have a main contribution from orbitals with mainly CH$_3$ character. Above a double ionization energy of 36 eV there are heavily mixed states and the bands are too diffuse for a classification of final states. Table IV lists the double ionization energies and the identified states for CH$_3$I.

### 3.4. Coulomb repulsion between the double vacancies

Table V shows the effective hole distance ($r_{\text{hh}}$) between the two vacancies calculated from the expanded rule of thumb using the lowest single and double ionization potentials of each molecule. Table V also includes the experimental double ionization energies determined here as vertical values and as onsets, and values for the lowest single ionization energies obtained from Ref. [13]. The values for $r_{\text{hh}}$ derived from these lowest ionization energies are listed, and in Table V we can see that the calculated hole distances $r_{\text{hh}}$ are

<table>
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<th>State</th>
<th>Energy (eV)</th>
<th>Leading configuration</th>
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<tbody>
<tr>
<td>Onset</td>
<td>Others$^b$</td>
<td>This work</td>
</tr>
<tr>
<td>$^3$A$_2$</td>
<td>31.5 ± 0.2</td>
<td>31.8$^c$ 2e$^2$</td>
</tr>
<tr>
<td>$^3$E</td>
<td>33.6 ± 0.3</td>
<td>$^1$e$^2$2e$^3$</td>
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<td>$^3$A$_2$</td>
<td>34.1 ± 0.2</td>
<td>$^3$A$^2$2e$^6$</td>
</tr>
<tr>
<td>$^1$E</td>
<td>35.4 ± 0.3</td>
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<tr>
<td>$^3$A$_2$</td>
<td>35.5 ± 0.3</td>
<td>$^3$e$^2$2e$^3$</td>
</tr>
<tr>
<td>$^3$E</td>
<td>38.5 ± 0.3</td>
<td>$^1$E $^2$2e$^3$</td>
</tr>
<tr>
<td>$^3$A$_2$</td>
<td>39.0 ± 0.3</td>
<td>$^3$E $^2$3a$^1$</td>
</tr>
<tr>
<td>$^3$E</td>
<td>40.4 ± 0.3</td>
<td>$^1$E $^2$2e$^3$</td>
</tr>
<tr>
<td>$^3$E</td>
<td>41.0 ± 0.3</td>
<td>2a$^1$2e$^3$</td>
</tr>
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close to the interatomic distance between the carbon and halogen atoms in all three methyl halides. But because of the large spin-orbit splitting in methyl iodide, calculation on the basis of the first peaks in the ionisation spectra is not really appropriate. In single ionisation the band for the first electron configuration has two peaks in the ionisation spectra is not really appropriate. In single ionisation the band for the first electron configuration has two

<table>
<thead>
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<th>Table IV</th>
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<tbody>
<tr>
<td>Values for the double ionization of CH₃I.</td>
</tr>
<tr>
<td>State</td>
</tr>
<tr>
<td>Term</td>
</tr>
<tr>
<td>³A₂</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>E</td>
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<tr>
<td></td>
</tr>
<tr>
<td>¹E</td>
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<tr>
<td>¹A₁</td>
</tr>
</tbody>
</table>

Mainly CH₃ character

I and CH₃ character

Mainly CH₃ character

a Vertical values for the lowest ionization energy. CH₃I: Ref. [13], CH₃Cl: Ref. [13], CH₃F: Ref. [13].

b Interatomic distances from Ref. [15], rounded to two decimals.

cules are reasonable, slightly longer than the bond distance in the methyl fluoride and shortest in proportion to the bond length in the iodide, as might have been expected because of the lone-pair character in the methyl iodide.

It is interesting to note that the ratio DIP/IP is almost equal, about 2.8, for the three methyl halides. Further studies are needed to see if this relationship is valid for a wider group of halide molecules. Also, theoretical investigations are needed to see whether the electron density of the lowest doubly ionized states reflect the hole distributions in terms of one hole being on the carbon atom and the other hole on the halides.

4. Conclusions

Valence double photoionization has been studied for three methyl halide molecules, methyl fluoride, methyl chloride, and methyl iodide, by means of the TOF-PEPECO technique. The double ionization spectra have been interpreted using previous experimental works and theoretical calculations when available for these systems. The lowest onset and vertical double ionization energies for the methyl halides have been measured, and used to investigate the application of a proposed rule of thumb for double ionisation energies to these species. Apparent interchange distances derived by application of the rule are in line with known molecular structures for this group of molecules.

Acknowledgement

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