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Electronically Excited States of the CH_3I^{2+} Ion

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A double-charge-transfer spectroscopy study has provided evidence for the existence of four low-lying electronic states of the CH_3I^{2+} ion, the double-ionization energies to which are 27.0 ± 0.3, 29.6 ± 0.3, 31.3 ± 0.5 and 36.5 ± 0.5 eV. Three of these energies agree, within experimental error, with those determined previously in a dissociative double photoionization study of CH_3I. The present investigation reveals for the first time the state at 29.6 eV. The value of the double-ionization energy to the ground triplet state, calculated in the present investigation using the single-determinant Hartree–Fock approximation to the many-electron wavefunction with corrections of second-order Møller–Plesset perturbation theory for correlation effects, is 25.80 eV, somewhat lower than the measured value of 27.0 eV.

A powerful experimental technique for studying the dissociation and properties of doubly charged cations is that involving photoion–photoion coincidence (PIPICO) in which the corresponding molecule is photoionized and the dissociation of the resulting doubly charged ion investigated by measuring the time difference in the arrival of the fragment ions at a detector. In the first PIPICO study of CH_3I,[1] five ion-pair processes were distinguished. A subsequent study[2] identified six processes and, in a modified technique in which an electron and the two ions from the dissociative double-ionization event are detected,[3] 12 fragmentation pathways of the CH_3I^{2+} ion were differentiated. In two of these investigations[1,3] He(II)α light at 30.4 nm was used, which probably had mixed with it some He(II)β (25.6 nm) and He(II)γ (24.3 nm) lines. In the PIPICO experiment carried out by Dujardin *et al.*,[2] however, synchrotron radiation was used as a continuously tunable light source from 20 to 40 nm. This had the great advantage that the appearance energies for the various dissociation channels could be measured. The authors deduced that at least four electronic states of CH_2I^{2+}, the energies of which are 28.5, 31.0, 34.0 and 35.5 eV, are involved in the dissociation processes observed.

In the present investigation, double-charge-transfer (DCT) spectroscopy, originally developed by Fournier and his co-workers,[4] has been used to investigate CH_3I. This technique gives information about the energies of low-lying electronic states of the doubly charged ion which is complementary to, and may be compared with, that obtained by the PIPICO technique.

Experimental

In DCT spectroscopy, the translational-energy losses associated with double-electron-capture (DEC) reactions of high-velocity, singly charged projectile ions, denoted by A^+, in collisions with molecules of the substance under investigation are measured. In the present study, OH^+ and F^+ projectile ions have been used and the investigations carried out on two spectrometers. The first is a ZAB-2F spectrometer[5] which has been used in most of the previous DCT spectroscopy experiments carried out at Swansea.[6–13] The projectile ions, having a translational energy of 6 keV, were mass-selected by the magnet and interacted with CH_3I molecules contained in a collision-gas cell at the intermediate focal point. The translational-energy spectrum of the A^- ions formed in DEC reactions was recorded by scanning the voltages applied to the electric sector of the spectrometer. The energy losses associated with the peaks were determined by running similar experiments with argon or xenon atoms in the collision-gas cell for which the relevant ionization energies are known.

The second spectrometer used is an MS9,† which is a double-focussing mass spectrometer in which the electric sector precedes the magnetic sector. This has recently been modified[14] for DCT spectroscopy. In it, the translational energy of the A^+ ions entering a collision-gas cell in the intermediate region between the electric sector and magnet was varied, and the transmission energy through the magnet of A^- ions, formed by DEC reactions of A^+ with CH_3I molecules in the cell, was kept constant. The A^- ion current at the final detector was recorded as a function of the translational energy of A^+ and the energy scale was calibrated by carrying out similar experiments with argon or xenon atoms in the cell.

Although the experimental procedures are different with the two spectrometers, both gave double-ionization energies to the ground and excited states of CH_3I^{2+} which agree within experimental error.

At the *low* CH_3I pressures set in the collision-gas cells, the DEC reaction in a single collision, *i.e.*

$$A^+ + CH_3I \rightarrow A^- + CH_3I^{2+} \tag{1}$$

was far more important in generating A^- ions than the two sequential reactions

$$A^+ + CH_3I \rightarrow A + CH_3I^+ \tag{2}$$

$$A + CH_3I \rightarrow A^- + CH_3I^+ \tag{3}$$

which necessitated the involvement of two CH_3I molecules. Reaction (1) has associated with it a translational energy loss, ΔE, given by

$$\Delta E = E_{i,\,2}(CH_3I) - E_{i,\,1}(A) - E_{ea}(A) \tag{4}$$

in which $E_{i,\,2}(CH_3I)$ represents the double-ionization energy of CH_3I, and $E_{i,\,1}(A)$ and $E_{ea}(A)$ the single-ionization energy

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† Manufactured by GEC-AEI (Electronics) Ltd, now Kratos Analytical Ltd.

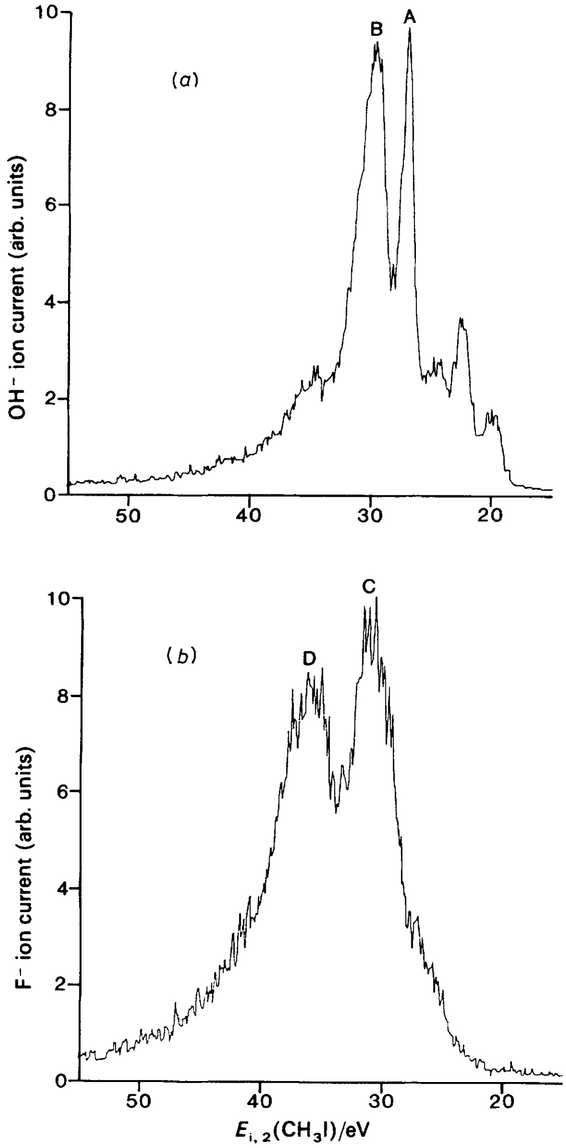

Fig. 1. Negative-ion spectra resulting from double-electron-capture reactions of (*a*) 6 keV OH^+ ions and (*b*) 6 keV F^+ ions with CH_3I molecules.

and electron affinity of A, respectively. The equivalent translational-energy loss ΔE_c with the calibrant gas (say xenon) in the cell is

$$\Delta E_c = E_{i,2}(Xe) - E_{i,1}(A) - E_{ea}(A) \qquad (5)$$

so that

$$\Delta E - \Delta E_c = E_{i,2}(CH_3I) - E_{i,2}(Xe). \qquad (6)$$

Any systematic errors inherent in measuring ΔE and ΔE_c cancel out, and $E_{i,2}(CH_3I)$ is readily calculated from eqn (6) since $E_{i,2}(Xe)$ is accurately known.[15] Peaks in the spectra corresponding to the formation of excited states of CH_3I^{2+} have measured values of energy loss $\Delta E'$, $\Delta E''$ *etc.* associated with them which, when inserted for ΔE in eqn (6), give values of $E'_{i,2}(CH_3I)$, $E''_{i,2}(CH_3I)$ *etc.*, *i.e.* the double-ionization energies to the excited states.

In numerous experiments carried out in this Unit,[6,8–13] the use of the OH^+ projectile ion in DCT spectroscopy has readily allowed the double-ionization energies of organic molecules to be determined. Employing F^+ as a projectile ion is more recent[16] and it allows excited states of the doubly charged molecular ion to be more readily populated. It has been predicted theoretically,[17,18] and confirmed experimentally,[19] that the cross-sections for double-electron capture fall within a reaction window, the position of which depends strongly on the endoergicity of the reaction. By examining eqn (4), it is seen that, if $[E_{i,1}(A) + E_{ea}(A)]$ is increased by changing A^+ (this sum is 14.84 eV for OH and 20.9 eV for F), and ΔE must reside within certain limits for a DEC reaction to take place, then $E_{i,2}(CH_3I)$ must increase, *i.e.* the probability of populating excited states of CH_3I^{2+} is increased. The present results will demonstrate that low-lying states of CH_3I^{2+} are populated using OH^+ in the DCT spectroscopy experiments, and states of higher energy are populated using F^+.

Results

Typical spectra obtained using OH^+ and F^+ projectile ions are shown in fig. 1. Along the abscissa are plotted values of $E_{i,2}(CH_3I)$ derived through eqn (6) from ΔE values. The spectra were obtained using the ZAB-2F spectrometer. Although equivalent spectra obtained using the MS9 spectrometer are at somewhat lower energy resolution, they have all the main features of those of fig. 1. From the variation of peak heights with CH_3I pressure, it was readily established that the peaks to the right of A in spectrum (*a*) were due to double-collision reactions (2) and (3), *i.e.* heights were quadratically dependent on the pressure. These peaks are not of interest in the present investigation. Peaks marked A, B, C and D were found to be linearly dependent on pressure and are the result of double-electron transfer in one collision *i.e.* reaction (1). These spectra strikingly illustrate the advantages of the use of two projectile ions to explore low- and higher-lying states of CH_3I^{2+}. The tailing on the higher-energy side of peak B in spectrum (*a*) is resolved into two well defined peaks when F^+ is the projectile ion [spectrum (*b*)], thus giving information about two higher-lying electronic states of CH_3I^{2+}.

Spectra similar to those of fig. 1 were obtained many times using both spectrometers, and the mean results for the double-ionization energies, and their standard deviations, determined. These are 27.0 ± 0.3, 29.6 ± 0.3, 31.3 ± 0.5 and 36.5 ± 0.5 eV for peaks A, B, C and D, respectively.

Discussion

Dujardin *et al.*[2] measured the threshold energy for the reaction

$$CH_3I + h\nu \rightarrow CH_3I^{2+} \rightarrow CH_3^+ + I^+ \qquad (7)$$

to be 28.5 ± 0.5 eV, which is higher than the lowest energy measured in the present work. However, the minimum threshold energy [deduced by them by adding the measured total kinetic energy, E_{kin}, of the fragment ions (4.65 ± 0.5 eV) to the thermodynamic energy for the formation of the fragment ions[15,20]] is 27.3 ± 0.5 eV which agrees, within the combined experimental errors, with the present lowest energy of 27.0 ± 0.3 eV. The minimum threshold energy corresponds to the formation of the fragment ions in their ground electronic states. Fragmentation of CH_3I^{2+} into CH_3^+ and I^+ was also observed by Curtis and Eland,[1] who measured E_{kin} to be 5.1 ± 0.1 eV and deduced that the minimum threshold energy is 27.8 eV, *i.e.* somewhat higher than that determined by Dujardin *et al.*,[2] and the lowest energy of the present study.

In a previous DCT spectroscopy experiment,[12] in which OH^+ projectile ions interacted with CO_2 and OCS molecules, it was shown that triplet states of CO_2^{2+} and OCS^{2+}

were populated. This is a consequence of the Wigner spin-conservation rule,[21] which requires that the total electron spin angular momentum of a pair of atoms or molecules does not change in the course of a collision. The ground state of OH^+ is $^3\Sigma^-$ while that of OH^- is $^1\Sigma^-$. If the molecule under investigation is in a singlet state, it follows that triplet states of the doubly charged molecular ions are populated in DEC reactions with OH^+. It follows that, in the present work, the vertical double-ionization energy of 27.0 eV is probably that to the ground triplet state of CH_3I^{2+}. This energy has been calculated in the present study using the GAUSSIAN 86 molecular orbital program package[22] on the Amdahl 5980E computer at the University of Manchester Computing Centre. Since the transfer of the two electrons in a DEC reaction takes place rapidly (typically within 10^{-14} s) when a projectile ion having several keV of translational energy is used, it is reasonable to assume that no change in the geometry of the molecule occurs during the reaction. Thus, the total ground-state energies of the neutral molecule and its triplet dication were calculated in the present study for the experimental ground-state geometry of CH_3I.[23] Given the relatively large number of electrons in CH_3I, a balance was struck in the LCAOMO calculation between computational economy and the variational flexibility required for a good description of the change in sizes of the atomic valence shells expected in the ionization process by using the compact split-valence 3-21G$^{(*)}$ basis of atomic orbitals for first-row[24] and fourth-row[25] atoms.

Calculations were performed in the single-determinant Hartree–Fock (HF) approximation to the many-electron wavefunction without and with the corrections of second-order Møller–Plesset (MP2) perturbation theory for correlation effects. For the open-shell dication, the unrestricted HF method does not guarantee that the lowest-energy single-determinant wavefunction will have an integer expectation value of spin quantum number. However, the value obtained, $\langle S^2 \rangle = 2.018$, indicates that any unphysical component in that approximate triplet wavefunction is acceptably small.

The HF prediction of $E_{i,2}(CH_3I)$ in the above basis is 24.60 eV. Our recent experience in calculating double-ionization energies for a variety of small molecules indicates that this is typical of a HF calculation in underestimating the experimental value. Although an expansion of the basis set used would lower the energy of each state calculated, the energy difference between them is not likely to be significantly affected. The origin of the discrepancy is much more likely to be the neglect of correlation effects in the HF calculation. Because the neutral molecule has two more electrons than its dication, the correlation energy is likely to be somewhat greater in the former, consistent with the HF energy difference being less than the experimental one. Further evidence for this is offered by the MP2 calculation in which a significant, but unquantifiable, fraction of each correlation energy is accounted for: the frozen-core MP2 prediction of $E_{i,2}(CH_3I)$ is 25.80 eV. The experimental $E_{i,2}(CH_3I)$ of 27.0 eV, therefore, is quite consistent with the trend exhibited by these two theoretical predictions.

In the PIPICO experiment,[2] the next dissociation reaction observed as the photon energy was increased was

$$CH_3I + h\nu \rightarrow CH_3I^{2+} \rightarrow CH_2I^+ + H^+ \qquad (8)$$

for which the measured threshold energy is 31.0 ± 0.5 eV. The value of E_{kin} measured in that experiment is 5.0 ± 0.5 eV; in the earlier experiment[1] for the same reaction it is 5.4 ± 0.4 eV. Since the thermodynamic energy for the formation of the fragments is 25.7 eV[26] it follows that the minimum threshold energy is 30.7 ± 0.5[2] and 31.1 ± 0.4 eV.[1] Both correlate best with the energy (31.3 ± 0.5 eV) determined in the present investigation. Thus, although there is a distinct peak (peak B of fig. 1) observed in the present investigation corresponding to an energy of 29.6 eV, there appears to be no unique dissociation reaction in the PIPICO experiment which corresponds to it.

From their dissociation results, Dujardin *et al.*[2] deduce that an electronic state of CH_3I^{2+} exists at 34.0 eV. However, no evidence was obtained in the present work of a state existing between 31.6 and 36.5 eV. These energies were determined from the positions of peaks in spectra obtained using F^+ as the projectile ion. The spin-conservation rule predicts that, with F^+ also, triplet states of CH_3I^{2+} would be populated. It is possible that the state observed at 34.0 eV in the PIPICO work is a singlet and thus, because of spin conservation, is not clearly evident in the present work with F^+.

For the reaction

$$CH_3I + h\nu \rightarrow CH_3I^{2+} \rightarrow CH_2^+ + H^+ + I \qquad (9)$$

the threshold energy observed in the PIPICO study[2] is 35.5 ± 0.5 eV. The minimum threshold energy deduced using the measured kinetic energies of the fragments is 35.9 ± 1[2] and 35.1 ± 0.3 eV.[1] The former value is in agreement with the double-ionization energy of 36.5 ± 0.5 eV measured in the present investigation.

Conclusions

Dujardin *et al.*[2] deduced that at least four electronic states were evident in their experimental study of the photodissociative double ionization of CH_3I. The energies of these states listed in their paper are appearance energies and there is a possibility that the fragmentation products could, to some extent, be internally excited. The corresponding minimum threshold energies, calculated using their measured translational energies of fragment ions and known thermodynamic energies for the formation of the fragments, represent, on the other hand, the energies to generate CH_3I^{2+} ions which dissociate into fragmentation products which are not internally excited. These values are 27.3 ± 0.5, 30.7 ± 0.5, 33.5 ± 0.5 and 35.9 ± 1 eV. In the DCT spectra of the present investigation, four peaks were observed corresponding to double-ionization energies of 27.0 ± 0.3, 29.6 ± 0.3, 31.3 ± 0.5 and 36.5 ± 0.5. The first, third and last of these agree with three of the minimum threshold energies determined by Dujardin *et al.*[2] There is no evidence of a dissociative reaction in the PIPICO work corresponding to an excited state having an energy of 29.6 ± 0.3 eV, as measured in the present investigation. In the present work, no evidence was obtained of a state having an energy between 31.3 and 36.5 eV yet Dujardin *et al.*[2] observed a distinct dissociation at 33.5 eV giving rise to H^+ and I^+ fragment ions. The state at this energy may be a singlet and this may not have been apparent in the present study using the F^+ projectile ion because of the spin-conservation rule.

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