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Triple ionisation of methane by double Auger and related pathways

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Abstract

Triple ionisation of methane by decay of the singly charged ion with a 1s vacancy produces a trication spectrum starting near 70 eV binding energy. Vibrational excitation in the initial hole state broadens and shifts the triple ionisation bands. Ionisation through core-valence doubly ionised states gives lower triple ionisation onsets and changes the spectral intensity pattern in accordance with retention of the initial valence holes in course of the double Auger effect. The double Auger effects occurs both directly and as cascades, the different pathways producing different electron distributions and final state spectra.

INTRODUCTION

As the most basic organic molecule, methane forms a system with properties that serve as an exemplar for the whole of organic chemistry. The molecule plays a vital role in the atmospheres of the earth, the gas-giant-planets and Saturn’s moon Titan. In these contexts the mechanisms for destruction of methane is practically important as, for example, on Mars where it is being destroyed 600 times faster than expected [1]. One important pathway is photodissociation, which can be dissociative photoionisation at high photon energy. To understand these processes we have to understand the spectra of methane in various ionisation forms.

The valence single and double ionisation spectra of the methane molecule are by now well known, and the mechanisms of decay of these ions have been studied extensively (see e.g. Refs. [2–4] and references therein). The spectra [5–15] and dissociations [16–18] of singly and doubly ionised methane following 1s (K-shell) hole formation have also been studied in some detail. Triple ionisation of this vitally important molecule also occurs to a considerable extent after creation of a core-hole vacancy in the 1s orbital, but neither the electron spectra nor the ion fragmentation spectra from this triple ionisation have been examined before. In this work we report coincidence studies of the electronic spectrum of triply ionised methane created by Auger effects from states with a 1s vacancy, and on the mechanism of the Auger effects involved.

No stable triply-charged methane ions have ever been observed, so it can be concluded that all accessible triply-charged states are dissociative. For this reason we do not expect any vibrational structure to exist in the spectra, but even if it did exist it would not be resolvable in the present experiments because of limited instrumental resolution.

The basic orbital structure of methane can be written; $1s^2 2a_1^2 1t_2^6$. All triply-charged states with vacancies in the valence orbitals must have at least one vacancy in $1t_2$ and so be subject to Jahn-Teller splitting. This will undoubtedly complicate the manifold of states.

EXPERIMENTAL DETAILS

As light source for the experiments we used monochromatised synchrotron radiation from the storage ring BESSY II, Berlin, at beamline U49/2-PGM-2 [19]. The storage ring was operating in single bunch mode, providing 30 ps lightpulses at approximately every 800.5 nanosecond [20]. The electrons were analysed using a magnetic bottle time-of-flight electron spectrometer, based

on a design by Kruit and Read [21], which has a multi-hit detection capability as described in detail previously [22]. Briefly, target gas is introduced to the interaction region as an effusive jet intersecting the light beam. When photoionisation occurs electrons ejected in nearly any direction are guided by the divergent field of a strong permanent magnet into a solenoid, whose field lines they follow to a multi-channel-plate detector, at a distance of approximately 2.2 m. Arrival times of the electrons are recorded relative to the storage ring cycle by a multi-hit time-to-digital converter connected to an online computer. Because electron flight times can be longer than the period between light pulses, selecting which ring cycle the electron arrival times refer to cannot, in general, be done unambiguously. For the triple ionisation data recorded in this experiment, however, the presence of a fast Auger electron and/or identification of the 1s photoline ensures a correct time reference. The energy resolution of the spectrometer, determined from the ionization linewidths for He and Kr at different photon energies, can be approximated as a fixed numerical resolution of $E/\Delta E = 50$ for energies above 1 eV. The energy scale is calibrated using known photoelectron lines from the rare gases and from the Auger spectrum of Xenon [23]. The energy bandwidth of the wavelength selected light was always narrower in these experiments than the energy resolution of the electron spectrometer. The electron count rate in each run was kept at about 2000 s^{-1} , and in a typical 1 h runtime about 5×10^6 events were accumulated as single electrons, 2×10^6 events as coincident pairs and 5×10^5 events as coincident triples. The target gas was purchased commercially with a stated purity of better than 99%.

RESULTS

Photoelectron spectrum

The photoelectron spectrum for ejection of a 1s electron from methane at 296 eV photon energy is shown in Fig. 1(a) to put the experiments in context. The same spectrum has been measured at high resolution before (see e.g. Ref. [13]) and the present spectrum agrees well with the previous one at a similar photon energy. Vibrational structure is clearly resolved despite the lifetime broadening (ca. 95 meV [13]) and line distortion by PCI (post collision interaction). In analysis of the coincidence data we can therefore select events which involve initial formation of the $\nu=0$ level alone, or formation of the $\nu=1$ or $\nu=2$ levels with more or less admixture of lower vibrational levels in each case. The vibrational mode excited is the symmetric stretch ν_1 , as the

measured interval of 0.39 eV (3150 cm^{-1}) is comparable with 2916 cm^{-1} in the neutral molecule, and because this mode is the only one whose excitation is symmetry-allowed. Recent theoretical work has shown, however, that a Fermi resonance mixes the $\nu_1=1$ level with a doubly excited bending mode [24], so the nuclear motions in this vibronic manifold may be highly complex. In the core-ionised state T_d geometry is retained and the equilibrium bond length is actually shorter and the frequency is higher than in the neutral molecule [14].

The simple 1s hole state is not the only intermediate whose creation can lead to triple ionisation. In Fig. 1(b), part of the core-valence double ionisation spectrum [25] is also shown; the main peak corresponds to removal of one 1s electron and one electron from the outermost orbital of methane, $1t_2$, composed of C2p and H1s atomic orbitals. The smaller peak is attributed to removal of one core electron and one from the $2a_1$ valence orbital. Doubly charged ions in these core-valence states decay by a simple Auger effect, ejecting one electron and leaving a triply charged ion. The main band is wide and shows some structure, presumably arising from the expected Jahn-Teller splitting of the degenerate parent state.

Triple ionisation spectra

Fig. 2 shows triple ionisation spectra selected from the complete dataset by choosing double Auger events starting from the separable vibration levels $\nu=0, 1, 2$ of the hole state in Fig. 1 and from the whole 1s ionisation band. The three peaks, seen most clearly when initial $1s^{-1}$ ($\nu=0$) is chosen, can be assigned immediately on a simple orbital basis as the ionisations $1t_2^{-3}$ with centroid at 76.40.2 eV, $1t_2^{-2} 2a_1^{-1}$ at 86.80.2 eV and $1t_2^{-1} 2a_1^{-2}$ at 96.80.4 eV. These designations are crude, of course, because the triply charged ion would undergo Jahn-Teller distortions even if it were stable, and will presumably distort forming multiple electronic states on its way to fragmentation.

Notable observations from these spectra are that as the initial vibrational excitation increases, the spectra become less resolved and the peaks move to higher ionisation energy. In the spectrum starting from $1s^{-1}$ ($\nu=1$), for example, the first two peak centroids are 77.5 ± 0.3 eV and 87.4 ± 0.3 eV. These differences must be due to the wider nuclear excursions in the higher levels affecting the Franck-Condon transitions to final states of a mainly repulsive character. No theoretical calculations to quantify these effects have yet been undertaken, however. Because there is no stable triply charged methane ion, no meaningful triple ionisation energy can be deduced from the figures; the most that can be said is that triple ionisation from the core-hole state sets in at

an energy near 70 eV. Triple ionisation direct from the neutral molecule would presumably give a different (lower) ionisation energy because of the longer initial bond length. Triple ionisation via the core-valence doubly ionised states of CH_4^{2+} does lead to triply ionised states of lower energy, as we shall see later.

Electron distributions and the mechanism of triple ionisation

In decay of a doubly-ionised core-valence state the Auger effect is emission of a single electron, whose energy is fixed as the difference between the quantised energies of the initial and final states. In the double Auger effect from a simple hole state, by contrast, two electrons are ejected and this can happen in two distinct ways. The two electrons can be ejected simultaneously in a single step, sharing the available energy between them as a continuous distribution, or one electron can be emitted to form a real intermediate, which then emits a second electron on the way to the final state. The two-step pathway is often called an Auger cascade, and its defining characteristic is a structured energy spectrum for each of the two Auger electrons.

To investigate the double Auger mechanisms, we show in Fig. 3 low energy parts of the Auger electron distributions for formation of the three main nascent state bands of CH_4^{3+} seen in Fig. 2, namely $1t_2^{-3}$ at 76.4 eV, $1t_2^{-2} 2a_1^{-1}$ at 86.8 eV and the highest band, $1t_2^{-1} 2a_1^{-2}$ at 96.8 eV. None of the distributions show any structure at higher energies. All slope down gently towards higher energy, but the main contrast is that distribution (a), for formation of the $1t_2^{-3}$ states has a strong intensity peak near zero energy. Distribution (b) has a weak low energy peak and distribution (c), for formation of the highest final state, has essentially none. A simple explanation of this contrast is that intermediate doubly-charged ion states involved in Auger cascades exist in the region of the triply ionised states and can populate the lowest states most easily. There are always candidate intermediates consisting of Rydberg states based on the excited triply-ionised states as their cores. All such states can autoionise to the lowest final state, some to the second state but none to the third state as there is no strong band at higher energy. The electrons from these autoionisations automatically have low energies because the gaps between the final states are narrow, and Rydberg states of low principal quantum number, and so of the lowest energy, are often populated most strongly and have the strongest overlap with the continua.

Because of the different shapes of the low energy electron distributions for formation of the different final states, relative intensities in the triple ionisation spectrum change significantly if

constraints are placed on the energies of Auger electrons allowed to contribute. If the lowest energy Auger electrons are excluded, for instance, the first band in the triple ionisation spectrum is relatively weakened and the second band becomes the most intense.

If intermediate dication states are created in the cascade Auger effects, they may also dissociate to doubly ionised fragments instead of ejecting a third electron. If this happens they contribute to the double, not triple ionisation spectrum and the quantum yield of triple ionisation by double Auger is low. The definition and derivation of the quantum yield in this case are identical to those in two-electron ejection by photoionisation [26]. Figure 4 shows the double ionisation spectrum from single Auger, the triple ionisation spectrum and the estimated quantum yields, starting from the $1s^{-1}$ ($\nu=0$) initial state. Determination of the absolute quantum yields requires knowledge of the overall collection efficiency for electrons, which is not well known for the high energy electrons involved. It also depends critically on the subtraction of background counts, which is a rather subjective procedure at present. The absolute yields are therefore uncertain, but the form of the yield curve is certainly correct in showing a low yield at the onset of triple ionisation and in the range immediately above it. Apart from dissociation, the only other possible decay mechanism to explain a low quantum yield would be optical emission; as this is extremely unlikely to compete on the timescale for ejection of a proton, we ascribe the low quantum yield entirely to rapid dissociation.

The overall relative intensities of double and triple ionisation from the formation of a $1s$ vacancy are approximately 1:0.035 at both 296 eV and 350 eV. There is also some quadruple ionisation, which is detectable in the present data with an onset around 116 eV, but it is not properly quantifiable because of contamination by background. At 350 eV, the core-valence ionisation has about 10% of the intensity of the main photoline.

DISCUSSION

Triple ionisation by the double Auger effect after ejection of an electron from the $1s$ shell can occur both directly, by simultaneous ejection of two electrons with a broad and smooth distribution, or by cascade through intermediate doubly charged states lying within the energy range of the observed triply charged states. We interpret these intermediate states as 3-hole 1-particle states based on excited triply charged cores, where the excited electrons (particles) may be in a valence-like or Rydberg-like orbitals. Their formation can be either ejection of one electron

with shake-up of a second, or nascent ejection of two with recapture of one of them. The second possibility is related to the post collision interaction, whose importance for low energy electrons is clearly visible in the photoelectron spectrum. Once formed, the intermediates seem to dissociate to doubly charged fragments in strong competition with ejection of a second Auger electron. As in the related double ionisation of methane [4], the low mass of the proton presumably contributes to rapid dissociation of the triply charged molecular species, whether or not a Rydberg electron is present.

By choosing events where both Auger electron energies are above 10 eV, we can effectively eliminate the Auger cascades as contributors to the final spectrum, leaving only the spectrum from direct double Auger. The result is shown as Fig. 5(a), where the same three bands are present (identified in Fig. 4), but with different relative intensities. The first band, assigned as $1t_2^{-3}$ ionisation, is now no more intense than the second, for $1t_2^{-2} 1a_1^{-1}$. If the propensity to engage in the direct double Auger process were the same for all electrons, the $1t_2^{-3}$ band would always be the most intense because of its larger number of electrons (6 as against 2). Thus the spectral intensities suggest that the $2a_1$ orbital (basically C2s) has a greater intrinsic tendency to provide the Auger electrons than does $1t_2$ (C2p + H1s).

Even greater changes are effected in the triple ionisation spectrum when the initial state is chosen from the doubly charged core-valence spectrum. Spectra from the main core-valence band at 317 eV in Fig. 1 and from the weaker band at 325 eV are shown as Fig. 5(b) and (c), respectively. When the main core-valence band, assigned as $1s^{-1} 1t_2^{-1}$ is selected, the triple ionisation spectrum moves significantly to lower ionisation energy and retains maximum intensity in its low energy peak. When the second core valence band, $1s^{-1} 2a_1^{-1}$ is chosen there is less shift but considerable intensity redistribution. The changes are entirely comprehensible on the basis of the intuitive idea that selection of an initial state with a vacancy in a particular orbital favours final states where the same vacancy persists. The lesser shift when starting from the weaker core-valence band is also reasonable, since $2a_1$ electron removal in the initial core valence state will retain T_d symmetry, whereas $1t_2$ removal will cause symmetry breaking along a path leading to facile dissociation. The magnitude of the shift of the low energy peak between Fig. 5 (b) and 5(c) is easily understood on the same basis, as an extension of just $1\text{\AA}$ along the $H^+ - CH_3^{++}$ coordinate will produce a drop of more than 10 eV in the final state potential energy.

CONCLUSIONS

Within the rather new field of triple ionisation spectroscopy by double Auger, the present case provides a useful model because of the very simple orbital structure of methane. The orbital identifications given in Fig. 4, for instance, and comparison with the one-electron photoelectron spectrum [2, 3], show how little the effective orbital energies change between different degrees of ionisation. The comparison of double Auger spectra with simple Auger spectra from core-valence states of the dications, typified so clearly in this case, may also help in other cases to identify orbital character of triply ionised states.

Because it has no stable triply charged ion, we cannot claim to have measured the spectrum of CH_4^{3+} , but we have obtained spectra for formation of the nascent species by various pathways. The spectra have been measured at a resolution of about 4 eV, which can reveal only the gross orbital occupancies. Additional details such as the expected Jahn-Teller splittings may be discovered by higher resolution measurements or, if dissociation is very rapid, may be accessible primarily to theoretical investigation.

Three distinct pathways to triple ionisation have been characterised. Direct double Auger emission from the initial vacancy gives a continuous electron distribution with broad cusps at the extremities. Cascade Auger via Rydberg states in the energy range below the populated triply ionised levels gives near zero energy peaks in the distributions. At high enough photon energy, core-valence doubly ionised intermediate states are formed and decay by single Auger emission from their different and evolving nuclear geometries.

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FIG. 1: (a) Photoelectron spectrum for creating a $1s$ hole in methane at 296 eV photon energy. The very small peaks on the right of the main structure are artefacts. (b) Double photoelectron spectrum showing core-valence ionisation bands at 350 eV photon energy. The first band includes several states, all based on $1s^{-1} 1t_2^{-1}$ ionisation and the weaker band represents $1s^{-1} 2a_1^{-1}$ ionisation.

FIG. 2: Triple ionisation spectra of CH_4 from the double Auger effect after ejection of a $1s$ electron: (a) Taking the whole $1s^{-1}$ band as initial state; (b) taking $\nu=0$ only; (c) taking mainly $\nu=1$ and (d) taking mainly $\nu=2$. The 2σ error bars show the number of triple coincidences at each energy defined as $h\nu - (E1 + E2 + E3)$.

FIG. 3: Low energy parts of the electron pair distributions from the double Auger effect starting with CH_4^+ ($1s^{-1}$, $\nu=0$): (a) forming the lowest energy band in the triple ionisation spectrum; (b) forming the central band and (c) forming the highest energy band. The gaps between 4.5 and 5.5 eV are the range assumed to be photoelectrons, where the zero level of each trace is seen.

FIG. 4: Consequences of $1s^{-1}$ ionisation in CH_4 : (a) the double ionisation spectrum with orbital designations following Kukkk et al. [17]; (b) the triple ionisation spectrum and (c) estimated quantum yield of triple ionisation from doubly ionised real or virtual intermediates.

FIG. 5: Triple ionisation spectra of CH₄: (a) from $1s^{-1}$ ionisation at 296 eV excluding all Auger electrons with less than 10 eV energy; (b) from initial formation of the core-valence doubly ionised state at 317 eV and (c) from initial formation of the core-valence doubly ionised state at 325 eV.