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Spectra of the triply charged ion CS_2^{3+} and selectivity in molecular Auger effects

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Spectra of triply charged carbon disulphide have been obtained by measuring, in coincidence, all three electrons ejected in its formation by photoionization. Measurements of the CS_2^{3+} ion in coincidence with the three electrons identify the energy range where stable trications are formed. A sharp peak in this energy range is identified as the $^2\Pi$ ground state at 53.1 ± 0.1 eV, which is the lowest electronic state according to *ab initio* molecular orbital calculations. Triple ionization by the double Auger effect is provisionally divided, on the basis of the pattern of energy sharing between the two Auger electrons into contributions from *direct* and *cascade* Auger processes. The spectra from the direct double Auger effect via S $2p$, S $2s$, and C $1s$ hole states contain several resolved features and show selectivity based on the initial charge localization and on the identity of the initial state. Triple ionization spectra from single Auger decay of S $2p$ -based core-valence states CS_2^{2+} show retention of the valence holes in this Auger process. Related ion-electron coincidence measurements give the triple ionization yields and the breakdown patterns in triple photoionization at selected photon energies from 90 eV to above the inner shell edges. © 2010 American Institute of Physics. [doi:10.1063/1.3352549]

I. INTRODUCTION

While the spectra of doubly charged ions have been known in some measure for many years from Auger spectra, no spectra of triply charged ions have been reported before. Although the double Auger effect is well known, the summed energies of two Auger electrons could not be determined until the advent of modern coincidence methods. This paper reports the spectrum of triply charged CS_2 determined by direct detection of three electrons both in the double Auger effect via the S $2p$ and C $1s$ shells and at photon energies below those of the inner shells.

Triply charged molecular ions are seldom encountered, except in the mass spectra of metal clusters and of large molecules such as the polynuclear aromatic hydrocarbons. Among diatomic and triatomic molecules, there are no more than a dozen long-lived triply charged ions whose existence is reliably attested. CS_2^{3+} and OCS^{3+} were reported early from electron-impact mass spectra¹ and reports of the related CSe_2^{3+} (cf. Ref. 2), S_2^{3+} (cf. Ref. 2), and CS^{3+} (cf. Ref. 3) followed later. Triply charged diatomic halogens can be formed by femtosecond multiphoton ionization⁴ and other known species are SF^{3+} (cf. Ref. 5), B_2^{3+} (cf. Ref. 6),

and the exotic MoHe^{3+} (cf. Ref. 7) and theoretical YHe^{3+} (cf. Ref. 8). The only reported tetra-atomic trication is $(\text{CN})_2^{3+}$ from cyanogen.¹

The CS_2^{3+} ion can also be formed by short pulse multiphoton ionization and by impact of highly charged ions.⁹ The appearance energy of the stable CS_2^{3+} ion was measured using thermionic electrons by Newton as 53.6 ± 0.5 eV,¹ and later by Mathur's group using monoenergetic electrons as 54.18 ± 0.16 eV.¹⁰ Singh *et al.*¹¹ determined the stable ion's lifetime to be long, up to 15 μs .

The essential experimental requirements for a measurement of the spectrum of CS_2^{3+} (or another triply charged ion) produced by photoionization are a means of analyzing three electrons in coincidence, and a light source with photon energy of 60 eV and above. An ideal means of such detection and analysis is provided by the magnetic bottle time-of-flight (TOF) analyzer,^{12,13} whose very high detection efficiency permits high-order coincidence experiments. This analyzer calls for a pulsed (ns or narrower) light source, and the only suitable source available at present is synchrotron radiation from a large storage ring operating in single bunch mode. For this work we have been able to use the electron storage ring BESSY II in Berlin. Because the interpulse period of storage ring light is shorter than the electron flight times, special strategies must be adopted to identify the light pulse

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actually causing ionization in each detected event. We have used three strategies in this work: insertion of a fast mechanical chopper to extend the interpulse period,^{14,15} detection of photoions in coincidence with the electrons,^{16,17} and recognition of photoelectrons of known energy initiating the double Auger effect.¹⁸

II. EXPERIMENTAL METHODS

The two magnetic bottle TOF electron spectrometers used in this work operate on precisely the same principles, which are based on the original theory of Kruit and Read.¹⁹ Ionization occurs where an effusive jet of target molecules intersects the pulsed monochromatic light beam. Almost all the electrons produced are guided by the divergent magnetic field (ca. 0.5 T) of a powerful permanent magnet into a long solenoid (ca. 10^{-3} T), whose fieldlines they follow on almost parallel paths to a distant (ca. 2 m) detector. The arrival times of electrons, whether singly or in bunches, are registered relative to the light pulses by multihit time-to-digital converters and stored in online computers.

One magnetic bottle was mounted on beamline UE 56/2 PGM-2,²⁰ where the available photon energy range extends upwards from 63 eV. On this line, the interval between light pulses was extended from the ring period of 800.5 ns in single bunch mode to about 12 μ s by insertion of a fast mechanical chopper^{14,15} into the light path. The chopper allows one pulse in 15 to pass, and electronic circuits based on a light detector veto the rare events where two adjacent pulses are transmitted, some by reflection from the slit edges. Because the flight time for the slowest electrons (zero initial kinetic energy) can be made shorter than 12 μ s by application of a small negative potential in the ionization region, this arrangement provides unambiguous identification of the light pulse causing each ionization event.

The second magnetic bottle, mounted on beamline U 49/2 PGM-2 (Ref. 21) with energy range of 85 eV and above, received light pulses at the 800.5 ns ring period. This bottle can be used to detect electrons alone, in which case the ionizing light pulse can be identified unambiguously only if one electron in a bunch of two or more was of known energy, e.g., a photoelectron from an inner shell.¹⁸ It can also be equipped to detect photoions in coincidence with the electrons, by extracting them in the opposite direction through a ring-shaped permanent magnet to a TOF mass spectrometer.¹⁶ With a weak (7 V cm⁻¹) extraction field in the ionization region and stronger subsequent acceleration, the flight times of undissociated ions of any charge can be distinguished modulo the ring period. Because the true ion flight times are also known, the ionizing light pulses could then be identified unambiguously for all ionizations of atoms¹⁷ and for ionization of molecules not causing fragmentation. In this technique the quality of the light beam focus is important because the width of the beam d along the spectrometer axis produces an energy broadening of the electrons by Ed in an extraction field E , and also produces broadening in the TOF mass spectrum when, as here, time focusing is

not used. By adjusting baffles in the light path with a small consequent light loss, the beamwidth at focus was restricted to about 250 μ m.

The resolving power of both sets of apparatus for single electrons, when operated in pure electron mode, can be expressed as a fixed numerical resolution $E/\Delta E$ of about 50 for electron energies above 1 eV, and a fixed width ΔE of about 20 meV at lower energies. With the setup to detect ions, the numerical resolution was about 20 and the limiting width was about 200 meV because of the extraction field. The extraction field also accelerates all electrons to half the full extraction potential of 10 eV, but the 5 eV energy gain was removed by retardation before the electrons entered their 2 m flight path within the long solenoid. In multiple ionization the resolution also depends upon the distribution of energy between the ejected electrons; in n -fold photoionization with one fast and $n-1$ slow electrons, the resolution should equate approximately to that in single ionization at the maximum electron energy.

To avoid accidental coincidences, electron count rates were restricted to a small fraction of the ionizing light pulse rate (80 kHz with the chopper, 1.2 MHz without). Because of the high detection efficiency of the magnetic bottles (ca. 50%), the necessary low count rates were achieved by closing the monochromator slits; as a consequence, the energy resolution of the light was better than the electron energy resolution, and so not a limiting factor in any of the experiments.

In related preliminary experiments, the ion detection apparatus was operated with high ion extraction field under time-focus conditions²² to assess the abundance of CS₂³⁺ ions and of overall triple ionization at different photon energies. Because the strongly accelerated electrons could be used as a start-time reference, these experiments, which include all the standard multi-ion techniques such as photoelectron-photoion-photoion coincidence (PEPIPICO) and its congeners, could also be carried out under multibunch operating conditions of the light source. Complementary information on the decay pathways in dissociative triple photoionization was obtained by these techniques.

III. RESULTS

A. PEPIPICO experiments

Distributions of single ions, ion pairs, and ion triplets were measured at several photon energies from 90 to 298 eV, with observations concentrated on the highly structured pre-edge resonances below the S 2*p*⁻¹ edges.²³ It was initially hoped that stable triply charged ions might be unusually abundant at some particular resonance, but while no such enhancement was found, the spectra showed one interesting characteristic. The S₂⁺ fragment ion, whose formation requires a rearrangement, is formed with strongly enhanced abundance following excitation of most of the resonances.

The relative intensities of triple ionization and stable triply charged ions at five broadly different photon energies are collected in Table I. Because ion pairs and ion triples as well as singles are recorded individually, the relative intensities of double and triple ionization could be determined as fractions

TABLE I. Relative intensities and branching ratios of triple ionization and stable triply charged ions at five different photon energies; 164.6 eV is the peak position of a representative pre-edge resonance; 180 eV is just above the S 2*p* ionization edges (169.934 and 171.075 eV); 236 eV is above the S 2*s* edge (231 eV). There is no great change at the C 1*s* edge (293.1 eV). ΣI represents the number of absorptions producing ionization, while ΣDI and ΣTI are the numbers of double and triple ionization events, both dissociative and nondissociative.

Photon energy	100 eV	150 eV	164.6 eV	180 eV	236 eV
Relative yields					
CS ₂ ³⁺ /CS ₂ ²⁺	0.01	0.025	0.05	0.04	0.07
CS ₂ ³⁺ /ΣTI	0.04	0.045	0.05	0.05	0.04
ΣTI/ΣI	0.011	0.037	0.053	0.12	0.24
ΣDI/ΣI	0.18	0.31	0.43	0.65	0.76
Branching ratios in triple ionization					
CS ₂ ³⁺	4%	5%	3.1%	4.7%	4.3%
S ⁺ +CS ₂ ²⁺	20%	6%	3.5%	5%	6.5%
S ²⁺ +CS ⁺	...	5%	7.5%	6.9%	5.7%
S ²⁺ +S ⁺	35%	32%	37%	29%	34.5%
C ⁺ +S ²⁺	...	27%	6%	24%	46.5%
C ⁺ +2S ⁺	41%	30%	47%	27%	4.2%

of the total absorption (neglecting neutral dissociation and photon emission), not just as fractions of the total number of ions produced. In other words, we can allow for the fact that each dissociative double ionization, for instance, adds two ions to the total mass spectrum rather than one. This is a major factor at all energies above the inner shell edges, where double ionization by the Auger effect dominates.

Data reduction to obtain the figures in Table I requires knowledge of the overall collection efficiency for ions, *f_i*. This parameter can be estimated from the spectra themselves, by examination of the intensities recorded for any ion which is formed only as a component of ion pairs. The intensity recorded for such an ion in pairs is *N⁺⁺f_i²*, while its intensity as a single ion is *N⁺⁺f_i(1–f_i)* where *N⁺⁺* is the true number of the specific dissociative double ionization events. The ratio of the two measured intensities thus leads to determination of *f_i*. In the mass spectrum of CS₂, the C⁺ ion is formed so much more abundantly from double than from single ionization, particularly at high photon energy, that it fulfils this function admirably. The collection efficiency was found to lie between 10% and 13%, with slight variation between runs. It is a serious approximation, however, to assume that it is independent of mass and of the initial kinetic energy of fragment ions. Because of this uncertainty, the figures in Table I should be taken as indicative of trends rather than as absolute determinations; we estimate that systematic errors should not exceed about one quarter of the quantities given.

The figures show that the overall abundance of triple ionization increases with photon energy, from about 1% at 100 eV to over 20% above the S 2*p* and C 1*s* edges. Within the overall triple ionization, formation of stable CS₂³⁺ is a remarkably constant fraction, at 5% of the total triple ionization, at all energies. The major dissociation pathways in triple photoionization are atomizations, to S⁺+C⁺+S⁺, to S⁺+S²⁺+C and to C⁺+S²⁺+S. None of the present measurements can determine, however, whether the dissociations

happen directly from nascent triply ionized molecules, or through dissociation of superexcited singly or doubly ionized intermediates.

B. Double Auger spectra via S 2*p*

The data in Table I show significantly increased abundance of triple ionization at all energies where ionization can happen through the double Auger effect. The first inner shell where this is possible is the S 2*p* shell, with edges at 169.934 and 171.075 eV;²⁴ the photoline spectrum is shown as Fig. 1(a). Spectra of nascent CS₂³⁺ were acquired from measurements at photon energies above the edges, where the initial

FIG. 1. Photoelectron spectra at the inner shell edges in CS₂. (a) at 175 eV showing S 2*p*, (b) at 243 eV showing S 2*s*, and (c) at 300 eV showing C 1*s*. The weak sharp features at low electron energy in (a) and (c) are mostly artifacts, but the two that occur at the same kinetic energies in the two curves (asterisks) are due to autoionization from superexcited atomic S.

FIG. 2. Spectra of triply ionized CS_2 produced by the double Auger effect via the $S\ 2p$ hole states at a photon energy of 175 eV. Spectrum (a) includes all Auger pairs; spectrum (b) is from pairs with one electron of energy below 4 eV and spectrum (c) is from pairs where all the Auger electrons have at least 10 eV energy. Error bars in this and other figures represent two standard deviations from the counting statistics. The ionization energies are determined throughout the paper as $h\nu - (E_1 + E_2 + E_3)$ using measured energies of all three electrons.

photoelectrons can be identified by their energy, so removing ambiguity over the ionizing light pulse. Measurements of electrons only (Fig. 2), without ions in coincidence, have the best energy resolution, and show structured spectra; the lowest energy feature in all spectra is a small peak near 53 eV. The resolution of structure in the double Auger spectra depends very strongly on selection of the form of energy sharing between the two Auger electrons. When all electron energies are accepted without selectivity, several bands are visible, but with low contrast [Fig. 2(a)]. If the most asymmetric sharing is chosen, i.e., one electron with near maximum energy and one of very low energy (<4 eV), a much less structured spectrum emerges [Fig. 2(b)]. If highly asymmetric sharing is rejected, taking no Auger electrons of less than 5 to 10 eV, a structured spectrum appears, with distinct peaks at 53.3, 57.7, 61.4, and 65.4 eV, and a weak shoulder at 56.7 eV [Fig. 2(c)]. The spacing of the first four features is very similar to the spacing of bands in the valence photoelectron spectrum.²⁵ Following similar observations on triple ionization of other molecules^{26,27} we attribute the differences in contrast between Figs. 2(b) and 2(c) partly to instrumental resolution effects, but mainly to the occurrence of cascade Auger pathways via superexcited CS_2^{2+} states which autoionize with predominant emission of low energy electrons. Thus we interpret the structured spectrum as characteristic of the direct double Auger process.

The photoelectron spectrum from $S\ 2p$ ionization, shown in Fig. 1(a), has partially resolved structure from both molecular electronic and vibrational effects. The vibration mode giving visible peaks (most clearly on $^2P_{1/2}$) is ν_3 , the asymmetric stretching vibration, excited because the core hole is located specifically on one S atom, breaking the inversion symmetry. The other structure is due to splitting of the $^2P_{3/2}$ atomic term by the molecular field into $\Omega=3/2(\Pi)$ and $\Omega=1/2(\Sigma)$ components. In reduction of the

FIG. 3. Spectra of CS_2^{3+} produced by the double Auger effect from different components of the 2P hole manifold populated by $S\ 2p$ ionization. (a) From the $\Omega=3/2(\nu=0)$ component of $^2P_{3/2}$; (b) from the $\Omega=1/2(\nu=0)$ peak of $^2P_{3/2}$, and (c) from the whole $^2P_{1/2}$ band.

triple coincidence data we can select any part of the photo-lines, also applying the restriction to Auger electrons of more than 10 eV energy, in order to obtain structured triple ionization spectra characteristic of the different initial hole states. Selection of different vibration levels has little visible effect, but spectra from the $\Omega=3/2(\Pi)$ and $\Omega=1/2(\Sigma)$ differ in intensity pattern, as illustrated in Fig. 3; the differences are interpreted below.

Using the apparatus allowing ion detection, we were able to measure the double Auger spectrum from $S\ 2p$ hole creation in coincidence with undissociated parent ions, CS_2^{3+} . The resulting spectrum is shown in Fig. 4(b), where it is apparent, despite the poor electron energy resolution, that only the band with its peak near 53 eV represents states of the trication that remain stable.

FIG. 4. Triple ionization spectra taken using the apparatus configured for ion detection, in coincidence with stable CS_2^{3+} ions: (a) from triple photoionization at 100 eV photon energy, (b) from the double Auger effect via $S\ 2p$ at $h\nu=180$ eV. Bars above the spectra show the expected instrumental resolution.

FIG. 5. Spectrum of CS_2^{3+} taken at 63 eV photon energy.

C. Triple photoionization below the inner shells

Use of the light chopper on beamline UE 56/2 PGM-2 made it possible to record triple photoionization with unambiguous determination of each electron energy at several photon energies, including the lowest available one, 63 eV. At this energy the ejected electrons all have energies of 10 eV or less, so resolution of the order of 200 meV can be expected. The resulting spectrum, Fig. 5, indeed shows a sharp peak, with center at 53.1 ± 0.1 eV, which we take to be the true adiabatic triple ionization energy of the molecule. The width of the peak is about 200 meV, in line with the expected instrumental resolution, so it seems possible that the peak represents a single vibrational level in the ground electronic state. The absence of more extended vibration structure would imply that the bond distance in CS_2^{3+} is not very different from that in neutral CS_2 . Molecular orbital calculations at the MP2/6-311+G(3df) level, performed within the framework of this work using the GAUSSIAN 98 package,²⁸ confirm that the ground state is $^2\Pi_g$, where all three electrons have been removed from the outermost orbital. The bond length is calculated to be slightly longer (1.58 Å) than in the neutral molecule (1.55 Å) and the symmetric stretching frequency is calculated to be lower (586 versus 658 cm^{-1}). The calculated triple ionization energy of 53.04 eV is in excellent but probably accidental agreement with experiment.

Although the spectrum taken at 63 eV shows no additional structure apart from the ground state, some more structures can be seen in triple photoionization at higher photon energy. These are superimposed on an unresolved broad band at high ionization energies. The strong background signal may be caused by spurious low energy electrons from surface scattering, and the weak contrast of the high energy structure may be related to a contribution from cascade processes at these photon energies.

A spectrum was also obtained at 100 eV photon energy, using the apparatus for ion and electron detection. With CS_2^{3+}

FIG. 6. Formation of CS_2^{3+} by Auger decay via selected core-valence states of CS_2^{2+} (left panel) produced by double photoionization at 230 eV photon energy. The selected energy ranges within the core-valence spectrum are shown to the right of the curve in the left hand panel, while the proposed valence orbital hole identities are shown to the left. Right panel: triple ionization spectrum (a) from $S\ 2p^{-1}\pi_g^{-1}$, (b) from $S\ 2p^{-1}\pi_u^{-1}$ and $S\ 2p^{-1}\sigma_u^{-1}$, and (c) from $S\ 2p^{-1}\sigma_g^{-1}$.

ions in coincidence, ambiguity about the initiating light pulse is removed and again it is only the band around 53 eV that persists in the spectrum [Fig. 4(a)].

D. Triple ionization via core-valence doubly ionized states

At photon energies of 200 eV and above new structures appear in the double ionization spectrum corresponding to removal of one $S\ 2p$ core electron and one valence electron. The bands in this core-valence spectrum can be assigned very clearly by comparison with the regular valence photoelectron spectrum²⁵ with which it is almost congruent (apart from peak doubling by the 2P spin-orbit splitting), as will be discussed in a separate work.²⁹ Briefly, it seems that either singlet-triplet splittings in the core-valence states are very small, or only the singlets are appreciably populated. All the core-valence states undergo Auger decay to achieve final triple (or higher) ionization, and it is natural to suppose that the valence shell vacancies already present will persist in the process. This is borne out by the trication spectra shown in Fig. 6, which are compared with simulations from a highly simplified model. The model assumes that each electron configuration of the triply charged ion produces a single contributing state at an energy above the ground state equal to the sum of the participating orbital energies taken from the photoelectron spectrum. The energies used were 0.0 for π_g , 3.0 eV for π_u , 4.6 eV for σ_u , and 6.2 eV for σ_g . The weight of each configuration was taken to be a product of the number of ways of choosing the electrons to be removed with a factor reflecting the extent of electron localization on one S atom, 1/2 for π_g , 1/4 for π_u and 1/3 for both σ_u and σ_g . This crude model, folded with a Gaussian of 3 eV full width at half maximum, correctly reproduces the main features of the experimental spectra in Fig. 6. In particular it shows the progressive shift to higher energies and the absence of the first (π_g^{-3}) band when a core-valence state with any other valence hole is selected.

FIG. 7. Triple ionization spectra of CS_2 by the double Auger effect via the C $1s$ hole, at 300 eV photon energy. (a) shows Auger pairs with all electron energies above 10 eV, (b) from Auger pairs with one energy below 4 eV.

E. Double Auger spectra via S $2s$ and C $1s$

The location of the S $2s$ photoline is given by Wang *et al.*²⁴ as 237 eV, but in our measurements made independently on the two sets of apparatus at photon energies of 240, 243, 300, and 310 eV it appears consistently at 234.7 ± 0.2 eV as a weak and broad but distinct peak (Fig. 1). Its width agrees well with the determination by Wang *et al.*,²⁴ but the discrepancy in its position is puzzling. Not unexpectedly, the main decay route from the initial S $2s$ hole state is the rapid Coster–Kronig transition in which the S $2s$ hole is filled by a S $2p$ electron and a valence electron is ejected. This process populates exactly the same core-valence doubly ionized states discussed above, which then decay by the same Auger emissions.

In order to resolve the puzzle with the seemingly inconsistent energy of Ref. 24, we have consulted the original data of this study carried out at the MAX-laboratory, Sweden. A new energy calibration has been made based on the well-defined energies of the sharp lines of the outer valence photoelectron spectrum²⁵ associated with the B and C states. In this analysis we have found that the energy scale in Fig. 4 of Ref. 24 is shifted by 2.2 eV. Taking this shift into account, we find that the energy of the peak maximum of the S $2s$ line is 234.8 eV, in good agreement with the energy obtained in the present investigation. The centroid energy, 237.05 ± 0.15 eV, given explicitly in Ref. 24, is thus incorrect. The proper value is found to be 234.85 ± 0.15 eV.

At photon energies above 300 eV the photoline corresponding to K -shell ionization from carbon appears, but it is less intense, at all energies, than the line from S $2p$ ionization. Triple ionization spectra from C $1s$ double Auger emission are correspondingly weaker, and also have poor resolution in our experiments because of the high energy, up to 250 eV, of the Auger electrons. The resulting triple ionization spectra are shown in Fig. 7.

IV. DISCUSSION

The overall triple photoionization spectrum from S $2p$ hole creation is in agreement with the mass spectral data, in the sense that the area of the 53 eV peak relative to the whole triple ionization band is 4.5% (Fig. 2), to be compared with the 5% stable CS_2^{3+} out of the total triple ionization at all energies (Table I). The lowest triple ionization energy, 53.1 eV, is consistent with the early threshold determination by Newton.¹ The energies of dissociative triply ionized states can be estimated from the most probable total kinetic energy release in formation of the atomization products $\text{S}^+ + \text{C}^+ + \text{S}^+$ (Ref. 30) as 61 eV, with a wide spread, in good agreement with our spectra.

The observation of a structured triple ionization spectrum from the double Auger effect, when the most asymmetric energy sharing between the Auger electrons is rejected in the data reduction was initially unexpected. The same phenomenon has now also been discovered in triple ionization of other molecules such as OCS (Ref. 26) and CH_4 (Ref. 27) by double Auger, and the structured spectra have been attributed to direct double Auger processes, in contrast mainly to cascade double Auger effects which contribute very low energy Auger electrons. Low energy electrons may also be emitted in dissociative processes, with or without cascade pathways, where part of the excess energy becomes kinetic energy of the fragments. Intermediate CS_2^{2+*} states involved in cascade processes, or partially dissociated states will have their own geometric and electronic structures leading to a wide range of branchings and Franck–Condon factors, resulting in more congested triple ionization spectra, as seen in Fig. 2. The involvement of these additional pathways may also explain the relative lack of structure, apart from the stable ground state, in our triple ionization spectra at the lowest photon energies. In view of the high density of electronic states and rapid dissociations expected in the triply charged ions, it is less clear why the direct process gives such relatively simple structured spectra. Some selectivity is apparently at work in the direct double Auger effect. To investigate its nature we must first attempt to identify the features seen in the spectrum.

The identity of the first resolved band, near 53 eV, is not in dispute, because the calculations of the present work, using the GAUSSIAN 98 package,²⁸ and others³¹ of the electronic structure agree in identifying the ground state of the trication as the $^2\Pi_g$ state from the outer valence configuration $\sigma_g^2\sigma_u^2\pi_u^4\pi_g$. For the higher bands we rely on the form of the observed spectrum compared with the known single and double ionization spectra as interpreted in terms of molecular orbitals in the spirit of Koopmans' theorem.

Because of the open-shell nature of the trication, a great number of electronic states arise from configurations where electrons are extracted from orbitals other than π_g . The lowest quartet state, as calculated in this work and earlier,³¹ comes from the $\sigma_g^2\sigma_u^2\pi_u^3\pi_g^2$ configuration and lies about 3 eV higher in energy. This energy gap also matches excitation to the first excited state in the valence photoelectron spectrum (π_u^{-1}),²⁵ and fits the shoulder in the triple ionization spectrum at 56.7 eV. The peak which follows at 57.8 eV happens to fit

in the same way with the band for σ_u^{-1} in the photoelectron spectrum, and could be loosely ascribed to the configuration $\sigma_g^2\sigma_u\pi_u^4\pi_g^2$. The two remaining bands in the triple ionization spectrum can be matched in a similar way with configurations where at least one electron is removed from π_g , and two from other valence orbitals, with energies estimated by simple addition of orbital energies taken from the photoelectron spectrum. The broad band about 61 eV encompasses five different configurations, while the highest strong band at 65.8 eV is associated with two. This extremely crude attribution, which ignores the expected splitting of configurations into terms and states, corresponds surprisingly well with the real spectrum. It is supported by the observed changes in the spectrum in response to selection of the initial hole state, seen in Fig. 3. When initial photoionization to the $\Omega=3/2$ component of $^2P_{3/2}$ is selected, the intensity of the 65.8 eV band is low. When the $\Omega=1/2$ component is selected, by contrast, the 65.8 band is enhanced. This is exactly the behavior expected on the basis of related observations in double ionization of HCl (Ref. 32) and HBr,^{33,34} and triple ionization of OCS (Ref. 27) if the 65.8 eV band is based mainly on removal from σ orbitals. The two configurations ascribed as contributing to it are indeed so based, $\sigma_g^{-1}\sigma_u^{-1}\pi_g^{-1}$ and $\sigma_g^{-2}\pi_g^{-1}$. It is, of course, in accordance with the well-known inner shell charge localization effects in Auger spectra that all the ionizations following S 2*p* hole creation make at least one vacancy in the π_g orbital, as this is the valence orbital with by far the greatest density at the S atom site.

Because of the importance of initial hole localization, we should expect and indeed find a different triple ionization spectrum when a hole is first created in the C 1*s* orbital [Fig. 7(a)]. The whole spectrum is shifted toward higher ionization energy and shows no sign of the trication ground state. This is exactly what should be expected if electrons are removed from the orbital π_u , σ_u , and σ_g which have significant density at the C atom, and not at all from π_g . There is a marked contrast in intensity distribution between the spectrum where extreme asymmetric energy sharing is excluded [Fig. 7(a)] and the spectrum where it is selected [Fig. 7(b)]. The contrast may again be explicable as a difference between direct and cascade double Auger effects, but in the absence of detailed structure this conclusion remains speculative.

Full understanding of these phenomena will require detailed theoretical input, but it is perhaps relevant to note that relatively equal energy sharing is characteristic of the knockout mechanism in double photoionization, and this property may also be applicable in double Auger.^{35,36} This mechanism is closely akin to electron impact ionization and may share some of its character, particularly any selectivity in the production of final states. But other theoretical mechanisms, akin to those involved in double photoionization³⁵ may also need to be considered.

V. CONCLUSIONS

The most recent coincidence techniques, combined with storage ring synchrotron radiation are shown to be capable of revealing spectra of triply ionized molecules. Nothing fundamental prevents the study of even higher stages of ionization.

Triple ionization spectra of CS₂ from the direct double Auger effect show electronic state selectivity, at least partly due to the initial charge localization.

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- ¹A. S. Newton, *J. Chem. Phys.* **40**, 607 (1964).
- ²L. Morvay and I. Cornides, *Int. J. Mass Spectrom. Ion Process.* **62**, 263 (1984).
- ³C. P. Safvan and D. Mathur, *J. Phys. B* **27**, 4073 (1994).
- ⁴H. Sakai, H. Stapelfeldt, E. Constant, M. Yu. Ivanov, D. Matussek, J. S. Wright, and P. B. Corkum, *Phys. Rev. Lett.* **81**, 2217 (1998).
- ⁵K. Nagesha, V. R. Marathe, and D. Mathur, *Chem. Phys.* **154**, 125 (1991).
- ⁶D. L. Weathers, F. D. McDaniel, S. Matteson, J. L. Duggan, J. M. Anthony, and M. A. Douglas, *Nucl. Instrum. Methods Phys. Res. B* **56–57**, 889 (1991).
- ⁷T. T. Tsong and T. J. Kinkus, *Phys. Scr.* **T4**, 201 (1983).
- ⁸R. Wesendrup, M. Pernpointner, and P. Schwedtfeger, *Phys. Rev. A* **60**, R3347 (1999).
- ⁹D. Mathur, A. K. Dharmadhikari, F. A. Rajgara, and J. A. Dharmadhikari, *Phys. Rev. A* **78**, 013405 (2008).
- ¹⁰D. Mathur and F. M. Harris, *Mass Spectrom. Rev.* **8**, 269 (1989).
- ¹¹S. Singh, R. K. Boyd, F. M. Harris, and J. H. Beynon, *Int. J. Mass Spectrom. Ion Process.* **66**, 167 (1985).
- ¹²J. H. D. Eland, O. Vieuxmaire, T. Kinugawa, P. Lablanquie, R. I. Hall, and F. Penet, *Phys. Rev. Lett.* **90**, 053003 (2003).
- ¹³Y. Hikosaka, T. Aoto, P. Lablanquie, F. Penet, E. Shigemasa, and K. Ito, *J. Phys. B* **39**, 3457 (2006).
- ¹⁴K. Ito, F. Penet, Y. Hikosaka, E. Shigemasa, I. H. Suzuki, J. H. D. Eland, and P. Lablanquie, *Rev. Sci. Instrum.* **80**, 123101 (2009).
- ¹⁵Y. Hikosaka, P. Lablanquie, F. Penet, T. Kaneyasu, E. Shigemasa, R. Feifel, J. H. D. Eland, and K. Ito, *Phys. Rev. Lett.* **102**, 013002 (2009).
- ¹⁶J. H. D. Eland and R. Feifel, *Chem. Phys.* **327**, 85 (2006).
- ¹⁷J. H. D. Eland, P. Linusson, L. Hedin, E. Andersson, J.-E. Rubensson, and R. Feifel, *Phys. Rev. A* **78**, 063423 (2008).
- ¹⁸F. Penet, J. Paladoux, P. Lablanquie, L. Andric, R. Feifel, and J. H. D. Eland, *Phys. Rev. Lett.* **95**, 083002 (2005).
- ¹⁹P. Kruit and F. H. Read, *J. Phys. E* **16**, 313 (1983).
- ²⁰K. J. S. Sawhney, F. Senf, M. Scheer, F. Schäfers, J. Bahrdrdt, A. Gaupp, and W. Gudat, *Nucl. Instrum. Methods Phys. Res. A* **390**, 395 (1997).
- ²¹D. R. Batchelor, R. Follath, and D. Schmeißer, *Nucl. Instrum. Methods Phys. Res. A* **467**, 470 (2001).
- ²²W. C. Wiley and I. H. McLaren, *Rev. Sci. Instrum.* **26**, 1150 (1955).
- ²³L. Hedin, J. H. D. Eland, L. Karlsson, and R. Feifel, *J. Phys. B* **42**, 085102 (2009).
- ²⁴H. Wang, M. Bässler, I. Hjelte, F. Burmeister, and L. Karlsson, *J. Phys. B* **34**, 1745 (2001).
- ²⁵P. Baltzer, B. Wannberg, M. Lundqvist, L. Karlsson, D. M. P. Holland, M. A. MacDonald, M. A. Hayes, P. Tomasello, and W. von Niessen, *Chem. Phys.* **202**, 185 (1996).
- ²⁶J. H. D. Eland, P. Linusson, L. Hedin, E. Andersson, J.-E. Rubensson, and R. Feifel, *Chem. Phys. Lett.* **485**, 21 (2010).
- ²⁷J. H. D. Eland, M. Hochlaf, P. Linusson, E. Andersson, L. Hedin, J.-E. Rubensson, and R. Feifel, *J. Chem. Phys.* **132**, 014311 (2010).
- ²⁸M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 98, Revision A.9, Gaussian, Inc., Pittsburgh, PA, 1998.

- ²⁹E. Andersson, J. Niskanen, L. Hedin, J. H. D. Eland, P. Linusson, L. Karlsson, J.-E. Rubensson, V. Carravetta, H. Ågren, and R. Feifel (unpublished).
- ³⁰M. Gisselbrecht, L.E. Ramanantsoa, F. Lahatra Razafindramisa, and M. Lavollée (submitted for publication).
- ³¹D. Mathur, *Phys. Rep.* **391**, 1 (2004).
- ³²R. F. Fink, M. Kivilompolo, H. Aksela, and S. Aksela, *Phys. Rev. A* **58**, 1988 (1998).
- ³³R. Püttner, Y. F. Hu, G. M. Bancroft, H. Aksela, E. Nömmiste, J. Karvonen, A. Kivimäki, and S. Aksela, *Phys. Rev. A* **59**, 4438 (1999).
- ³⁴P. Lablanquie *et al.* (unpublished).
- ³⁵T. N. Chang and R. T. Poe, *Phys. Rev. A* **12**, 1432 (1975).
- ³⁶Y. Hikosaka, P. Lablanquie, F. Penent, P. Selles, T. Kaneyasu, E. Shigemasa, J. H. D. Eland, and K. Ito, *Phys. Rev. A* **80**, 031404(R) (2009).