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Triple ionization of CO₂ by valence and inner shell photoionization

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Spectra of triply ionized CO₂ have been obtained from photoionization of the molecule using soft x-ray synchrotron light and an efficient multi-electron coincidence technique. Although all states of the CO₂⁺⁺⁺ trication are unstable, the ionization energy for formation of molecular ions at a geometry similar to that of the neutral molecule is determined as 74 ± 0.5 eV. © 2011 American Institute of Physics. [doi:10.1063/1.3643121]

I. INTRODUCTION

Triple ionization of molecules and atoms can be caused by all sorts of high energy collisions, but occurs with particular abundance after creation of a vacancy in an inner electron shell. The creation of CO₂⁺ ions with vacancies in the C1s or O1s shells produces vibrational excitation in the molecule¹ and is followed within a few femtoseconds (fs) by Auger decay. Single (non-resonant) Auger decay from singly charged inner shell ionized states has been studied extensively^{2–5} and produces doubly charged species; the same species have also been examined at higher resolution by coincidence methods applied to valence shell photoionization.^{6,7} Some of the doubly charged species are stable CO₂⁺⁺ molecules, while others dissociate into singly and doubly charged fragments.^{7–9} By contrast, the double Auger effect, in which two electrons are ejected after the photoelectron creating a triply charged nascent ion, has been less studied. No long-lived CO₂⁺⁺⁺ molecules are known, so only the dissociations caused by triple ionization have been examined.^{10–13} Triply charged nascent CO₂ can also be formed by triple Auger decay from neutral core-excited states, and angular distributions in the subsequent dissociations of these species have been examined.¹⁴ Other less abundant routes to triple ionization of the molecule include direct photoionization, a channel which is open below the inner shells, and single Auger decay from core-valence doubly ionized states; these routes have not been explored hitherto. At distinct photon energies above the inner shell edges, shape resonances and shake-up satellites are also formed^{15,16} and may complicate the observation of simple hole states.

In this paper, we report experimental studies of triple ionization of CO₂ by simple photoionization and by double Auger and related routes involving inner shell hole creation, using soft x-ray synchrotron radiation and multi-electron coincidence detection. Because three electrons are emitted,

coincidence techniques are indispensable and the raw data are inherently multi-dimensional distributions. We show that a substantial fraction of the double Auger process is indirect, involving doubly charged intermediate states which may also decompose before the final electron is emitted. No detailed theoretical calculations of the states or potential surfaces of [CO₂]⁺⁺⁺ are available to us at this time, but we suggest that the main features of the spectra can be interpreted by simple calculations and empirical reasoning.

II. EXPERIMENT

One set of experiments was carried out at the BESSY-II storage ring synchrotron radiation source of the Helmholtz Zentrum, Berlin, on line U49/2-PGM-2 (Ref. 17) when the ring was operated in single bunch mode giving light packets with 800.5 ns spacing. A second group of experiments was done at the SOLEIL storage ring at Saclay, Paris, using the TEMPO (Ref. 18) undulator beamline also in single bunch mode, with a light packet separation of 1184 ns. The two sets of apparatus have both been described before.^{19,20} In both sets of experiments, monochromatised light crosses an effusive beam of target gas at one end of a ~2 m long magnetic bottle formed by the strong (~0.5 T) divergent magnetic field of a conical permanent magnet and the weak (~10⁻³ T) uniform field of a long solenoid. Essentially all electrons created in the ionization zone are constrained by the fields to follow the solenoid field lines to a microchannel plate electron detector at the distant end of the bottle. Electron arrival times at the detector are measured relative to the time of a light pulse and the electron flight times are later translated, after calibration against photolines and Auger lines of known energy from the rare gases, into electron energies. Because the single-bunch interpulse periods are shorter than the flight times for slow electrons, strategies are needed to identify the light pulse actually causing each ionization event. In measurements above the inner shell thresholds, this can always be achieved by the

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identification of the inner shell photoelectron peaks, which are of known energy and electron flight time. For measurements at energies below the inner shells, which were carried out at BESSY, we used a newly developed synchronous chopper²¹ locked to the ring frequency which extended the dark time between pulses up to 12 μ s. All electrons were accelerated by a few tenths of an eV so that even those formed with initial zero energy arrived at the detector in about 5 μ s.

III. RESULTS

A. Triple ionization by inner shell hole formation

The C1s and O1s regions of the photoelectron spectrum of CO₂ are shown in Fig. 1 from measurements at 303 and 546 eV photon energy, where there are no prominent resonant structures in the excitation spectra.^{15,16} The structures are in excellent agreement with the better resolved spectra of Hatamoto *et al.*,¹ but the energies of the peaks agree rather with those of Püttner *et al.*² It is notable that in the spectrum at 546 eV the molecular symmetry is reduced from D_{∞v} to C_{∞v} by localisation of the O1s hole on one atom on the time scale of photoelectron emission, with the consequence that the vibration excited by O1s ionization is the antisymmetric stretch ν_3 . At 303 eV, ionization from the central C1s orbital excites only the symmetric stretch ν_1 .

Figure 2 shows the major part of the double Auger decay following creation of an O1s hole in CO₂, as a map of intensity against the energies of the two Auger electrons coincident with a photoelectron from creation of the hole. The broad diagonal stripes represent fixed energy sums for the electron pair and thus define final energy states of the final triply charged species. A notable feature is the concentration

FIG. 1. Photoelectron spectra for creation of (a) a C1s hole at $h\nu = 303$ eV and (b) an O1s hole at $h\nu = 546$ eV in CO₂. Some of the small features at low electron energy are artefacts, but those common to the two curves are real and come from autoionization of atomic O*. The structure, on top of the main peaks, shows vibrational excitation in the core-ionized states. The small separation between the peak and shoulder in (a) corresponds to excitation of one quantum of the symmetric stretching vibration ν_1 , whereas the wider separation between the two peaks in (b) represents one quantum of the antisymmetric stretch ν_3 .

FIG. 2. Intensity distribution for the two Auger electrons from creation of an O1s hole in CO₂ at 546 eV photon energy. Crossed bars indicate the estimated energy resolution at the centre of the map. The blank horizontal line near the bottom of the map is the zone where all slow electrons are identified as photoelectrons, not Auger electrons. Diffuse diagonal bars represent final triply ionized states and their enhanced intensity for low energies of the slower Auger electron is attributed largely to cascade double Auger decay.

of intensity, mainly for the uppermost diagonal, at the lowest energies of the slower Auger electron. Such a concentration is typical of indirect or cascade Auger decay. The equivalent map for Auger decay following creation of a C1s hole (not shown) has exactly the same general features and differs only slightly in intensity distribution.

Finer detail of the low energy part of the distribution, this time after C1s hole creation, is shown in Fig. 3. Because of the difference in scales, the broad bars for fixed final state creation are almost vertical in this figure. The evident horizontal intensity concentrations, representing fixed energies of the

FIG. 3. Part of the intensity distribution of the two Auger electrons from creation of a C1s hole in CO₂ at 303 eV photon energy. Crossed bars indicate the estimated energy resolution at the centre of the map. The horizontal intensity concentrations show atomic autoionizations, mainly from superexcited O*.

FIG. 4. Triple ionization spectra of CO₂ from the double Auger effect after creation of a C1s vacancy: (a) taking all Auger electron pairs and (b) accepting only pairs with both energies above 10 eV. The error bars in this and following figures are 2σ long and represent uncertainty from the counting statistics only.

slow electron, are characteristic of autoionization by excited atomic dissociation products from nascent doubly charged precursors. Such atomic autoionizations have been observed widely in association with double photoionization⁶ and also with triple ionization,²² particularly from small molecules with terminal O atoms. Again, the equivalent low energy Auger pair distribution from O1s hole formation is very similar.

To quantify the deductions to be made from the distributions, we show one-dimensional projections of the data in the remaining figures. Figure 4 shows the energies of the final triply charged states populated after C1s hole formation, with different selections from the Auger electron pair distribution. When all Auger electrons are included, the final state spectrum, which is the complete energy deposition function in this triple ionization, is dominated by a partially resolved band of states between 70 and 100 eV ionization energy. The selection of Auger pairs restricted to high energy Auger electrons reveals three broad bands with peaks near 85, 110, and 130 eV and of comparable intensities. This spectrum from high energy electrons may be considered as representative of a direct double Auger process, in contrast to cascade double Auger decay through intermediate doubly ionized states. In cascade Auger decay substantial nuclear displacement may occur before the final electron ejection, whereas in direct Auger decay the transition time is so short (typically a few fs) that the nascent multiply charged ions are formed at or close to the molecular geometry.

When the initial hole is made in an O1s orbital instead of in C1s, the resulting spectra, shown in Fig. 5, are very similar in form. The main differences are that the relative intensity of the band near 110 eV is considerably greater and the resolution is worse because of the higher energies of the Auger electrons.

As illustrated in Fig. 3, electron distributions in the double Auger spectra of CO₂ contain fine structure at the lowest electron energies. Spectra of these low energy electrons are shown in Fig. 6 where the sharp peaks clearly occur at the same energies and with roughly the same intensity pattern whether the initial hole is on the carbon or on an oxygen atom. All the intense peaks can be attributed to well-known autoionizations of neutral atomic oxygen,^{23,24} of which the

FIG. 5. Triple ionization spectra of CO₂ from the double Auger effect after creation of an O1s vacancy at $h\nu = 546$ eV: (a) taking all Auger electron pairs and (b) accepting only pairs with both energies above 20 eV.

doublet near 0.5 eV is particularly characteristic. It is apparent from Fig. 3 that some ionization processes involving autoionizing states (reflected by the intense horizontal lines) involve higher energy deposition (lower triple ionization energies) than the more direct or molecular process. Figure 3 also shows that the spectrum of intermediate dissociative [CO₂]⁺⁺ states from which the most intense autoionizations occur is a broad band of states without resolvable structure in a range of ionization energies ($E(1s^{-1}) - E_2$) from 70 to 100 eV and with its peak at about 82.5 eV.

Although the spectral patterns of O* autoionization from initial C1s and O1s core holes are very similar, the overall intensities are very different. The ~ 0.5 eV doublet lines constitute about 1% of the total ionization after C1s core hole production, but the same lines contribute only 0.25% in the case of the O1s core hole. This is consistent with the requirement for production of neutral superexcited O* atoms from an intermediate doubly charged dissociative state, where the double charge must reside on the C-containing moiety, not on the O. This is clearly less easy if one O atom already bears the initial charge. Since dissociation is essential to produce

FIG. 6. Parts of the electron pair distributions from the double Auger decay of C1s (lower curve) and O1s (upper curve) initial vacancies in CO₂. The peaks near 0.5 eV, 0.8 eV, 1.8 eV, and 2.5 eV are autoionizations of neutral atomic oxygen.

FIG. 7. Photoelectron spectrum for production of an O1s hole in CO₂ (upper curve, right-hand intensity scale) and spectra of the photoelectrons in coincidence with O* autoionization electrons of the 0.5 eV doublet (error bars, left-hand scale) and in coincidence with low energy electrons outside the sharp lines (lower line).

free O* atoms, it might also be expected that excitation of the asymmetric stretching vibration ν_3 in the initial O1s core hole state (cf. Fig. 1) would favour this decay route. This is indeed observed. The profile of the photoelectron line is the same, within the statistical accuracy of our data, for production of the 0.5 eV O* autoionization doublet and for other low energy electrons in the range shown in Fig. 6, but is different from the profile for core hole production and overall Auger decay, as shown in Fig. 7. In double Auger decay with low energy electron production, the higher vibration levels are significantly more intense relative to $\nu = 0$ than in the overall photoelectron line profile. Two conclusions follow: first, the majority of low energy electrons must originate from dissociations in an intermediate, that is, from cascade double Auger. This confirms the deductions from Figs. 4 and 5. Second, the direction of the effect suggests that in the O1s core-hole state the C–O bond is lengthened relative to the C–O⁺ bond rather than vice versa.

Another route to triple ionization is intermediate formation of a core-valence doubly ionized state, which then emits a third electron in Auger decay. The formation of triply charged states by this route is often informative because the valence orbital hole in the intermediate states, whose identity can frequently be deduced by comparison with the regular photoelectron spectrum, tends to be retained in the final state,^{25,26} limiting the range of final configurations. Molecules in the core-valence ionized states have short lifetimes before Auger decay, so are unlikely to undergo extended nuclear motion before the final electron emission. Figures 8(c) and 8(d) show core-valence ionization spectra of CO₂ above the C1s and O1s edges, respectively. These spectra will be analysed in detail in a later paper, but it is sufficient for the present purpose that the bands representing core ionization plus ionization from the outermost π_g orbital can be recognised unambiguously in both cases. The lower sections (a) and (b) of Fig. 8 show the triple ionization spectra produced by Auger decay from the π_g core-valence doubly ionized intermediate states above the

FIG. 8. Triple ionization spectra produced by Auger decay from core-valence ionized states of CO₂⁺. Spectra above the C1s and O1s edges were taken at 360 eV and 603 eV photon energy, respectively. (a) and (b) are triple ionization spectra taken in coincidence with electron pairs forming the lowest energy core-valence states, as indicated by bars below the upper spectra (c) and (d), respectively. Triple ionization spectra in coincidence with the other core-valence bands (not shown) are broader and show less structure.

two edges. Bars above the principal bands indicate the estimated electron energy resolution in each case. Both spectra show a band of states near 80 eV which we interpret as outer valence electron ejection, presumably including the molecular trication ground state where a single π_g electron remains outside the closed shells. The major part of the band can be attributed to the nine other triply ionized configurations with at least one π_g electron missing from the outer valence orbitals. The spectrum from the C1s⁻¹ π_g^{-1} ionization, Fig. 8(a), resembles the triple ionization spectrum from direct double Auger decay of the simple hole state (Fig. 4(b)) quite closely, but is better defined. As in our interpretation of Fig. 4, the higher energy bands in Figs. 8(a) and 8(b) (discussed further below) probably involve inner valence ejection. Although the C1s inner shell hole is located on the central atom and the π_g orbital is located only on the outer O atoms, the lowest triple ionization band for Auger decay is the strongest in both the C1s and O1s spectra. This may simply reflect the large number of available electrons in the outer valence orbitals. That in the spectrum from Auger decay after O1s⁻¹ π_g^{-1} ionization the valence band is more dominant relative to the higher bands is entirely consistent with the location of the π_g orbital on the O atoms.

Another possible route to triple ionization by inner shell hole creation would involve initial formation of a double core hole (DCH) state where two core electrons are missing from the neutral configuration. The O1s⁻² DCH state of CO₂ where two 1s electrons have been ejected from one O atom is well represented in our data at 1250 eV and 1300 eV, as recently reported.²⁷ It has been pointed out that a concerted process should exist in which double core holes are filled by two outer shell electrons, but only a single high energy electron

is ejected.²⁸ We have searched our data for evidence of such a process without success and estimate a provisional limit of 1% on its intensity relative to the main decay route of the DCH, which is sequential emission of two Auger electrons.

B. Triple ionization below the inner shells

Triple ionization below the inner shells can allow better resolution in the present technique because of the lower electron energies, but this advantage is offset by the very much lower cross section for the process and possibly also by increased spectral congestion. Double ionization of closed-shell molecules by Auger processes populates singlet states preferentially,^{4,29} whereas simple photoionization populates both singlets and triplets.^{6,30} It can be expected on the basis of the atomic localisation and has been proposed on the basis of measured spectra³¹ that double Auger processes favour doublet triply charged final states, whereas direct photoionization below inner shells may populate doublet and quartet states equally. It has not yet been possible to check this idea by examining atomic spectra because of the complicating presence of autoionizations, which always populate low energy states most strongly.

We have examined the ionizations of CO₂ at 150 eV where we find a weak triple ionization signal, almost obscured by background noise. To extract a useful spectrum, it was necessary to filter the raw data by rejecting all electron triples where the slowest electron has less than 5 eV or more than 15 eV energy. This filtering is found from examination of the coincidence maps to correspond to a region of minimum background interference by secondary electrons. The spectrum so extracted is still dominated by noise, but a distinct structured spectrum can be seen on top of a smooth background. The filtered data are shown in Fig. 9. The spectrum contains a weak but clear peak at 74 eV followed by broader structures of greater area, the first centred at about 80 eV; the spectrum resembles that of CS₂⁺⁺⁺ acquired recently by the same technique.³² The width of the 74 eV peak com-

pared with the estimated instrumental resolution of 1.5 eV is consistent with population of a single vibrational level in a quasi-stable state.

IV. DISCUSSION AND CONCLUSIONS

The orbital configuration of neutral CO₂ can be written as O1s⁴C1s²O2s⁴σ_g²σ_u²π_u⁴π_g⁴, where the delocalisation and *g/u* splitting of the inner shells have been neglected. From the photoelectron spectrum, we can identify the orbital binding energies, starting from the outermost in the spirit of Koopmans' theorem as 14, 17, 18, 19, and 40 eV. The lowest state of molecular [CO₂]⁺⁺⁺ can be safely assumed to be the ²Π state attained by removing three electrons from the outermost and non-bonding π_g orbital. Because only non-bonding electrons have been removed, this state may retain some stability, or at least a relatively shallow potential energy surface. The analogous state in CS₂⁺⁺⁺, which is metastable, has been observed directly.³² The lowest energy triple ionization for formation of the nascent [CO₂]⁺⁺⁺ ion, presumably at about the neutral molecule geometry, is seen in the spectrum of Fig. 9 as a sharp peak at 74 ± 0.5 eV, and in Figs. 2–8 as part of the broad bands with maxima near 80 eV and onsets in the range 72–75 eV. Indirect triple ionization pathways, which involve dissociations, show onsets down to 70 eV. The 74 eV peak is in good agreement with theoretical estimates at the B3LYP/6-311G(3*df*) level of theory as 74.7 eV and at the higher CCD(T)/CC-PVTZ level as 74.2 eV (Ref. 33) for the trication ground state. The triple ionization energies for different final configurations can be modelled crudely as a sum of three bonding energies for the electrons removed, the Coulomb repulsion of three charges (~31 eV for the lowest energy arrangement at the bond distance of 1.16 Å) and additional terms including relaxation energy. If we assume that the Coulomb repulsion energy and additional terms are roughly independent of the exact configuration, the excitation spectrum of the nascent triply charged ion can be estimated from the orbital binding energies. If the lowest triple ionization energy, 74 eV, arises from the valence configuration O2s⁴σ_g²σ_u²π_u⁴π_g, excitations where one or two of the other valence electrons are removed, can increase the ionization energy by up to 15 eV, but not much more. Thus the first band in Fig. 4(b) or Fig. 5(b) can be attributed to electron removal from the valence orbitals only. If one electron is removed from the inner valence O2s shell and two from the valence orbitals, the estimated ionization energies run from 108 eV to about 120 eV, accounting well for the second band in the same spectra. The great increase in relative intensity of this second band when the O1s hole is created supports its attribution to the ejection of an O2s electron. The third band in Fig. 5(c) is also much stronger relative to the first band than in Fig. 4(c), suggesting that here again the O2s orbitals are involved; from its energy, the simplest interpretation is that it represents states with a large contribution from configurations where two O2s electrons are missing. This discussion of the spectrum of nascent [CO₂]⁺⁺⁺ is very crude, but it is commensurate with the unresolved spectra that we have measured. Many individual states of different configurations and multiplicities must really be involved, but apart from the ground

FIG. 9. Triple ionization spectrum of CO₂ from photoionization at 150 eV after filtering on the energy of the slowest electron (see text).

state, it is doubtful if any experiment can separate them into more than the present broad bands.

Of the different routes to triple ionization of CO₂ explored by the present technique, triple ionization below all inner shells gives the best resolution and should be implemented in improved coincidence apparatus with lower background noise. Triple ionization by Auger decay from selected core-valence doubly ionized states is helpfully selective and can be widely applied. The triple ionization routes involving dissociation in intermediate doubly ionized states close to the triple ionization limits have now been observed in many contexts. The electrons so produced have spectra dominated by low energies, with sharp structure where atomic autoionization occurs, as is prominent with O atoms. Final triply ionized states of the dissociated products are often at lower binding energy relative to the neutral molecule than the nascent molecular triply charged ions, and complicate the determination and even the definition of triple ionization energies.

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