This is the published version of a paper published in *Journal of Chemical Physics*.

Citation for the original published paper (version of record):

http://dx.doi.org/10.1063/1.3643121

Access to the published version may require subscription.

N.B. When citing this work, cite the original published paper.

Permanent link to this version:
http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-160719
Triple ionization of CO2 by valence and inner shell photoionization


Citation: The Journal of Chemical Physics 135, 134309 (2011); doi: 10.1063/1.3643121
View online: http://dx.doi.org/10.1063/1.3643121
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/135/13?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Inner-shell photoionization and core-hole decay of Xe and XeF2

Carbon dioxide ion dissociations after inner shell excitation and ionization: The origin of site-specific effects

Valence and inner-valence shell dissociative photoionization of CO in the 26–33 eV range. II. Molecular-frame and recoil-frame photoelectron angular distributions

Inner-shell single and double ionization potentials of aminophenol isomers

Core-valence double photoionization of the CS 2 molecule
Triple ionization of CO\(_2\) by valence and inner shell photoionization

J. H. D. Eland,\(^1,2\) L. Andric,\(^3,4,5\) P. Linusson,\(^6\) L. Hedin,\(^2\) S. Plogmaker,\(^2\) J. Palaudoux,\(^3,4\) F. Penent,\(^3,4\) P. Lablanquie,\(^3,4\) and R. Feifel\(^2,4\)\(^a)\)

\(^1\)Department of Chemistry, Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ, United Kingdom
\(^2\)Department of Physics and Astronomy, Uppsala University, Box 516, SE-751 20 Uppsala, Sweden
\(^3\)UPMC, Université Paris 06, LCPMR, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France
\(^4\)CNRS, LCPMR (UMR 7614), 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France
\(^5\)Université Paris-Est, 5 Boulevard Descartes, 77454 Marne-la-Vallée Cedex 2, France
\(^6\)Department of Physics, Stockholm University, AlbaNova University Centre, SE-106 91 Stockholm, Sweden

(Received 18 August 2011; accepted 3 September 2011; published online 5 October 2011)

Spectra of triply ionized CO\(_2\) 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 CO\(_2\)\(^{3+}\) ionization 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 CO\(_2^+\) ions with vacancies in the C1s or O1s shells produces vibrational excitation in the molecule\(^1\) 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 CO\(_2^{++}\) 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 CO\(_2^{3+}\) molecules are known, so only the dissociations caused by triple ionization have been examined.\(^10-13\) Triply charged nascent CO\(_2\) can also be formed by triple Auger decay from neutral core-exited 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 ionization thresholds, this can always be achieved by the 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 [CO\(_2\)]\(^{3+}\) 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

\(^{a}\)Electronic mail: raimund.feifel@physics.uu.se.

0021-9606/2011/135(13)/134309/$30.00 135, 134309-1 © 2011 American Institute of Physics
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 chopper\textsuperscript{21} locked to the ring frequency which extended the dark time between pulses up to 12 μs. 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 μs.

III. RESULTS

A. Triple ionization by inner shell hole formation

The C1\textsubscript{s} and O1\textsubscript{s} regions of the photoelectron spectrum of CO\textsubscript{2} 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.\textsuperscript{15,16} The structures are in excellent agreement with the better resolved spectra of Hatamoto \textit{et al.},\textsuperscript{1} but the energies of the peaks agree rather with those of Pütter \textit{et al.}\textsuperscript{2} It is notable that in the spectrum at 546 eV the molecular symmetry is reduced from D\textsubscript{∞\textnu} to C\textsubscript{∞\textnu} by localisation of the O1\textsubscript{s} hole on one atom on the time scale of photoelectron emission, with the consequence that the vibration excited by O1\textsubscript{s} ionization is the antisymmetric stretch \( \nu_3 \). At 303 eV, ionization from the central C1\textsubscript{s} orbital excites only the symmetric stretch \( \nu_1 \).

Figure 2 shows the major part of the double Auger decay following creation of an O1\textsubscript{s} hole in CO\textsubscript{2}, 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 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 C1\textsubscript{s} 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 C1\textsubscript{s} 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. 4. Triple ionization spectra of CO$_2$ 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 photoionization and also with triple ionization, 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 CO$_2$ 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, of which the 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 [CO$_2$]$^{++}$ 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
free O* atoms, it might also be expected that excitation of the asymmetric stretching vibration $\nu_3$ 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 $\pi_g$ 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 $\pi_g$ core-valence doubly ionized intermediate states above the 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 $\pi_g$ 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 $\pi_g$ electron missing from the outer valence orbitals. The spectrum from the C1s$^{-1}\pi_g^{-1}$ 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 $\pi_g$ 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$^{-1}\pi_g^{-1}$ ionization the valence band is more dominant relative to the higher bands is entirely consistent with the location of the $\pi_g$ 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
FIG. 9. Triple ionization spectrum of CO$_2$ from photoionization at 150 eV after filtering on the energy of the slowest electron (see text).

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, whereas simple photoionization populates both singlets and triplets. It can be expected on the basis of the atomic localisation and has been proposed on the basis of measured spectra that double Auger processes favour doubletriply 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 CO$_2$ 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 CS$_2^{++}$ acquired recently by the same technique. The width of the 74 eV peak compared 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 CO$_2$ can be written as O1s$^2$C1s$^2$O2s$^4$O2p$_g^2$O2p$_u^2$O2p$_g^2$, 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 [CO$_2$]$^{+++}$ can be safely assumed to be the $^2I_I$ state attained by removing three electrons from the outermost and non-bonding $\pi_g$ 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 CS$_2^{+++}$, which is metastable, has been observed directly. The lowest energy triple ionization for formation of the nascent [CO$_2$]$^{+++}$ 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(3df) 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 O2s$^4$O2p$_g^2$O2p$_u^2$O2p$_g^2$, 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 [CO$_2$]$^{+++}$ 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
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 CO$_2$ 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.

ACKNOWLEDGMENTS

This work has been financially supported by the Swedish Research Council (VR), the Göran Gustafsson Foundation (UU/KTH), and the Knut and Alice Wallenberg Foundation, Sweden. This work was also supported by the European Community – Research Infrastructure Action under the FP6 “Structuring the European Research Area” Programme (through the Integrated Infrastructure Initiative “Integrating Activity on Synchrotron and Free Electron Laser Science” – Contract No. R II 3-CT-2004-506008).

33M. J. Frisch, G. W. Trucks, H. B. Schlegel et al., GAUSSIAN 98, Revision A9, Gaussian Inc., Pittsburgh, PA, 1998.