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Core-valence double photoionization of the CS₂ molecule

E. Andersson,¹ J. Niskanen,^{2,3} L. Hedin,¹ J. H. D. Eland,^{1,4} P. Linusson,⁵
L. Karlsson,¹ J.-E. Rubensson,¹ V. Carravetta,⁶ H. Ågren,³ and R. Feifel¹

¹Department of Physics and Astronomy, Uppsala University, Box 516, SE-751 20 Uppsala, Sweden

²Department of Physics, University of Oulu, Box 3000, 90014 Oulu, Finland

³Department of Theoretical Chemistry, School of Biotechnology, Royal Institute of Technology, SE-106 91 Stockholm, Sweden

⁴Department of Chemistry, Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ, United Kingdom

⁵Department of Physics, Stockholm University, AlbaNova University Centre, SE-106 91 Stockholm, Sweden

⁶Institute of Chemical Physical Processes, CNR, via Moruzzi 1, 56124 Pisa, Italy

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Double photoionization spectra of the CS₂ molecule have been recorded using the TOF-PEPECO technique in combination with synchrotron radiation at the photon energies $h\nu=220, 230, 240, 243$, and 362.7 eV. The spectra were recorded in the S 2p and C 1s inner-shell ionization regions and reflect dicationic states formed out of one inner-shell vacancy and one vacancy in the valence region. MCSCF calculations were performed to model the energies of the dicationic states. The spectra associated with a S 2p vacancy are well structured and have been interpreted in some detail by comparison to conventional S 2p and valence photoelectron spectra. The lowest inner-shell-valence dicationic state is observed at the vertical double ionization energy 188.45 eV and is associated with a $(2p_{3/2})^{-1}(2\pi_g)^{-1}$ double vacancy. The spectrum connected to the C 1s vacancy shows a distinct line at 310.8 eV, accompanied by additional broad features at higher double ionization energies. This line is associated with a $(C\ 1s)^{-1}(2\pi_g)^{-1}$ double vacancy. © 2010 American Institute of Physics. [doi:10.1063/1.3469812]

I. INTRODUCTION

Double ionization photoelectron spectroscopy (DIPES) is a powerful method for obtaining information about both the dicationic states themselves and the probability with respect to different available response channels for emission of two electrons from a system by the absorption of a single incident photon. DIPES is based on detection in coincidence of two electrons that are created in the same process, and the method used in the present investigation is called time-of-flight photoelectron-photoelectron coincidence (TOF-PEPECO) spectroscopy. Since it was introduced in 2003 (Ref. 1) this method has been applied to a number of atoms and molecules, and much new data have been acquired (cf. Refs. 2–9 and references therein). Coincidence detection is necessary in order to identify outgoing electrons from the same ionization event, since they can share the available energy arbitrarily.

If the orbitals of the CS₂ molecule are subdivided into inner-shell orbitals (io) and valence orbitals (vo), three types of fundamental characteristic final state electron configurations associated with very different energies can be envisioned: $(io)^{-2}$, $(io)^{-1}(vo)^{-1}$, and $(vo)^{-2}$. For assignments of spectra using qualitative arguments, rather different methods apply to the states derived from these three types of configurations. In the present case, we have obtained spectra associated with $(io)^{-1}(vo)^{-1}$ final state configurations and the analysis will be made using the generally accepted ground state valence electron configuration of CS₂, which is^{10,11}

$$\cdots(5\sigma_g)^2(4\sigma_u)^2(6\sigma_g)^2(5\sigma_u)^2(2\pi_u)^4(2\pi_g)^4.$$

We will presume that the C 1s and S 1s, 2s, and 2p inner-shell orbitals are primarily atomic-like, as has been found to be a good approximation in previous investigations.^{12–14} This study of the CS₂ molecule is a part of a series of investigations aiming at a better characterization of the electronic structure and interaction with radiation of this molecule and of sulfur containing molecules in general. The systematic investigation involves inner shells and valence shells as well as different charge states and different types of ionization processes including also resonant processes.¹⁵ The present study focuses on the S 2p and C 1s states (io) and the valence states (vo), which have all been investigated separately in previous studies by photoelectron spectroscopy using both line sources and synchrotron radiation.^{10,11,14–16}

II. EXPERIMENTAL DETAILS

The experiments were performed at beamline U49/2-PGM-2 (Ref. 17) at BESSY-II, Berlin, using a magnetic bottle time-of-flight electron spectrometer designed for coincidence measurements. The spectrometer has a flight tube with a length of 2.2 m, and it can detect electrons emitted with kinetic energies from zero to several hundred eV over essentially the whole solid angle. More detailed descriptions of the multielectron coincidence technique and the present instrument are given in Refs. 1 and 18–20 and Refs. 20–22, respectively. In the present investigation, the flight times of

two electrons originating from the same ionization process were measured with a time reference set by the ionizing photon pulse of the ring.^{18–20}

The storage ring was operated in single bunch mode, which provides 30 ps light pulses at an interpulse period of 800.5 ns.²³ Data were recorded at the photon energies 220, 230, 240, 243, and 362.7 eV, which are well above the thresholds for creation of the S 2p hole and, the latter one, above the threshold for the C 1s hole along with a vacancy in a valence shell. The stated photon energies may deviate by at most 300 meV from the true values due to some uncertainty in the monochromator energy. The monochromator was set to a resolution of 0.3 eV or better.

The energy resolution of the instrument goes from approximately 20 meV at the lowest kinetic energies to a nearly constant numerical resolution of about 50 at high kinetic energies. The time-to-energy conversion was calibrated using Kr 3d photoelectron lines²⁴ recorded at various photon energies. CS₂ gas was obtained from a commercially available liquid sample with a stated purity of >99.5%. It was introduced to the interaction region of the spectrometer after degassing by repeated freeze-thaw cycles, and its purity was verified by the recording of valence photoelectron spectra.

III. THEORETICAL DETAILS

As for single core hole states, there are some particularities associated with core-valence double hole states which have implications for their calculations and which set strong restrictions on the choice of the computational procedure with respect to normal (multiple) valence hole states. One such particularity is variational collapse, another is that although in a finite basis representation the number (index) for the core-valence hole state is finite, it is unpredictable *a priori*. For wave functions parametrized in terms of orbitals (orbital rotations) and electronic configurations (determinants) the problem of variational collapse can be divided into an orbital part and a configurational part. We apply a two-step, second order, optimization procedure for the core-valence states that solves the orbital part of the collapse problem as given in Ref. 25 (see also applications for single core hole states in Ref. 26). It consists of an intermediate optimization step with the core orbital frozen that brings the wave function to the local, quadratically convergent region. This intermediate frozen-core optimization step takes the expansion point down to the local region in the full (all orbital) variational space. It is followed by a second optimization step taken by a straight Newton–Raphson minimization toward the stationary point including relaxation also of the core orbital. This second optimization step finds in all normal cases the proper Δ MCSCF (multiconfiguration self-consistent field) solution including the open core orbital without variational collapse (see Refs. 25 and 26). In the configurational space the variational collapse is avoided by imposing single occupancy restrictions for the core orbital as the interaction between empty, single and double core occupation states are negligible by virtue of their huge energy separations. This can be accomplished using the restricted active space (RAS) technology,^{27,28} where, in the present

case, the RAS1 space encompasses one orbital, the core orbital, with one and only one electron, while RAS2 is used for complete electron distributions among valence levels except for the ionized valence orbital that forms the RAS3 space with one and only one electron. The RAS2 space is governed by occupation number criteria given by perturbation theory.²⁹ For symmetry delocalized core orbitals we apply symmetry broken solutions, as these solutions are energetically preferential using CAS or RAS wave functions.³⁰ The localization of the core orbital is made in a precalculation, followed by the freeze-relax procedure in the RAS calculations, maintaining localization in the two steps. We note that physical localization and symmetry breaking in the S 2p case is not an electronic effect (the full symmetry is always restored in a full electron correlation calculation of the core hole state),³⁰ but rather the effect of electrovibrational coupling—a pseudo-Renner–Teller effect—which is the general rule for core hole states in species with the possibility of coupling over antisymmetrical modes (here the antisymmetric C–S stretch). CS₂ is in this respect fully compatible with the well-known CO₂ case.^{31,32} For a very recent study on this subject, please see Ref. 33.

The multiconfiguration self-consistent field (MCSCF) calculations were performed to model the double ionization thresholds of each spatial symmetry in molecular CS₂. The molecular symmetry was utilized using D_{2h} and C_{2v} point groups for C 1s and S 2p vacancies, respectively. To obtain proper core hole localization, inversion symmetry was not applied in the calculations of the (S 2p)^{−1} states. Thus the gerade-ungerade states appear as lowest and first excited states in Σ and Π symmetries. The neutral ground state, singly core ionized states, and the core-valence doubly ionized states were optimized with active spaces (2,2,2,1,2,2,1) and (4,4,4,2) where inactive cores (5,1,1,0,4,1,1,0) and (9,2,2,0) corresponding C 1s, C 2s and S 1s, S 2s, S 2p, and S 3s orbitals were assumed. In case of ionized states the RAS method²⁸ was used to model the core hole vacancy where the core hole orbital formed RAS1, the valence hole orbital formed RAS3, whereas RAS2 was the active valence space as before. We have also designed an “independent particle,” open-shell Hartree–Fock wave function as reference, with the same RAS division as above but with an empty RAS2 space (all valence electrons, except the one ionized is in the inactive space). This space thus generates one configuration state function for the singlet and one for the triplet.

The rearrangement of the molecular core after photoionization was taken into account by allowing core relaxation for the core and core-valence ionized states. In case of S 2p core vacancy, the spin-orbit splitting was taken from Ref. 14. In this case we have neglected the coupling of core and valence holes as the exchange integrals were small causing a typical singlet-triplet split of 0.1–0.15 eV except for the σ_g hole state (1.84 eV). The triplet states were always the lower ones and have been used to generate the given energies for the states. The larger value of the singlet-triplet splitting of the σ_g valence vacancy may be due to convergence problems associated with the calculation of the σ_g singlet state.³⁴ All calculations were performed by DALTON, a molecular electronic structure program [Release 2.0 (2005); see <http://>

FIG. 1. S 2p-valence double photoionization spectra of the CS₂ molecule obtained at the photon energies $h\nu=220, 230, 240$, and 243 eV. The onset of the spectra is 187.8 eV. The spectra have been aligned with the first peak maximum at 188.45 eV.

www.daltonprogram.org]. The calculations were performed utilizing two double zeta and triple zeta augmented correlation consistent basis sets with polarizing functions to study the goodness of the one electron basis;³⁵ first the aug-cc-pCVDZ^{36,37} and finally the aug-cc-pCVTZ^{36,37} basis sets were used. Improving the basis set caused changes in double ionization energies of less than 0.3 eV.

IV. RESULTS AND DISCUSSION

A. S 2p-valence DIPES

Figure 1 shows overall double ionization photoelectron spectra of the CS₂ molecule associated with final state configurations of the type $(S\ 2p)^{-1}(\text{vo})^{-1}$. The photon energies used were $220, 230, 240$, and 243 eV, for which the measured individual electron kinetic energies are around $0\text{--}40$ eV. The electrons emitted in the double ionization process are found to preferentially share the available energy in an unequal manner, one carrying a high and the other a low kinetic energy. Over the energy interval chosen, the spectra show many lines or structures as well as a more or less continuous, slightly structured intensity distribution at double ionization energies higher than 198 eV. For these spectra, double ionization energies of the two emitted elec-

TABLE I. Double ionization energies (eV), relative intensities, line widths (FWHM), and assignments of the lines observed in the S 2p-outer-valence double photoionization spectrum measured at the photon energy of 220 eV.

Energy (eV)	Relative intensity (peak height)	Line width (eV)	Dicationic state
188.45	1.0	0.80	$(S\ 2p_{3/2})^{-1}(2\pi_g)^{-1}$
189.72	0.8	0.64	$(S\ 2p_{1/2})^{-1}(2\pi_g)^{-1}$
191.3	0.6	1.1	$(S\ 2p_{3/2})^{-1}(2\pi_u)^{-1}$
~ 192.5	~ 0.5		$(S\ 2p_{1/2})^{-1}(2\pi_u)^{-1}$?
192.9	0.8		$(S\ 2p_{3/2})^{-1}(5\sigma_u)^{-1}$
193.6	0.5		$(S\ 2p_{1/2})^{-1}(5\sigma_u)^{-1}$
193.9	0.4		$(S\ 2p_{3/2})^{-1}(6\sigma_g)^{-1}$
195.4	0.6		$(S\ 2p_{3/2})^{-1}(\text{PES sat } 2)$
196.9	0.4		$(S\ 2p_{1/2})^{-1}(\text{PES sat } 2)$

trons have been determined based on the conservation of the total energy, i.e., the measured total kinetic energy subtracted from the photon energy. Table I gives the energies, relative intensities (peak heights) and widths that have been determined along with assignments according to the following discussions.

The S 2p core-valence spectrum recorded at 220 eV photon energy is shown in Fig. 2 along with the $(S\ 2p)^{-1}(\text{vo})^{-1}$ DIPES energies obtained by calculations. The MCSCF energies were obtained as the difference between the dicationic MCSCF energy and the ground state energy. When the lowest π^{-1} states from the calculations are compared to the experiment, the MCSCF DIPs are seen to be shifted notably, 1.69 eV, down in energy. This underestimation of the appearance energy for core-valence ionization can, to a large extent, be ascribed to core-core correlation in the ground state. We obtained MP2 correlation energies related to the ground state core orbitals by a stepwise procedure of increasing the num-

FIG. 2. The S 2p-valence double photoionization spectrum (labeled "DIPES") of the CS₂ molecule obtained using the photon energy $h\nu = 220$ eV. The interpretation given in the figure is based on the S 2p hole being either $3/2$ or $1/2$ coupled. A simulated spectrum (labeled "valence") based on the UV photoelectron spectrum (narrow lines) constructed as described in the text is also included. The first line of this spectrum is adjusted to the same energy as the corresponding line of the experimental spectrum. Calculated MP2 core-core correlation corrected MCSCF energies (see text and Table II) and their assignments are shown above the experimental spectrum (for details, see text).

TABLE II. Calculated $(S\ 2p)^{-1}(vo)^{-1}$ double ionization energies. A spin-orbit splitting of 1.27 eV has been applied. The first excited states are marked with an asterisk (*), which is understood as ionization from the second highest orbital of the symmetry under consideration. The values with ground state core-core correlation energy from MP2 calculations are shown in parentheses. Coupling of the core hole to the valence vacancy is neglected (for details, see text).

Configuration	Energy (eV)	
	$(S\ 2p_{3/2})^{-1}$	$(S\ 2p_{1/2})^{-1}$
$(S\ 2p)^{-1}\ \pi^{-1}$	186.76 (188.55)	188.03 (189.82)
$(S\ 2p)^{-1}\ \pi^{*-1}$	189.88 (191.67)	191.15 (192.94)
$(S\ 2p)^{-1}\ \sigma^{-1}$	191.30 (193.09)	192.57 (194.36)
$(S\ 2p)^{-1}\ \sigma^{*-1}$	193.86 (195.65)	195.13 (196.92)

ber of orbitals subject to MP2 perturbation in the uncontracted cc-pCVTZ basis.^{36,37} The change related to each orbital was taken as correction to the ground state core correlation energy and its absolute value as a correction to the DIP for the core orbital. For the S 2p orbitals a value of 1.78 eV was obtained, and the correction covers the previously mentioned shift, actually overestimating it a little. The calculated MCSCF energies are listed in Table II where the MP2 core-core correlation corrected MCSCF energies are presented within parentheses.

After applying the MP2 correction and the spin-orbit splitting, the agreement between the calculated and experimental line positions improves considerably (cf. Fig. 2). The $(S\ 2p)^{-1}(vo)^{-1}$ DIPES can be qualitatively considered as a superposition of two similar spectra separated by the energy of the spin-orbit splitting of 1.27 eV of the S 2p hole states¹⁴ and with an expected relative intensity ratio of 2:1.

The lower part of Fig. 2 (labeled valence) shows a simulated spectrum obtained as a sum of two ordinary photoelectron spectra, recorded at a photon energy of 67 eV (cf. Ref. 15), shifted by 178.34 and 179.61 eV, respectively (i.e., they are separated by 1.27 eV), and with an intensity ratio of 2:1. This spectrum was broadened by a Gaussian function with full-width-at-half-maximum (FWHM) of 0.65 eV each, and an intensity ratio of 2:1. Apparently, there is a good correspondence with the experimental spectrum although the latter seems to become reduced in intensity with increasing double ionization energy. This behavior is possibly related to a decrease in cross-section for the double ionization with lower excess energy. Differences from the ordinary valence photoelectron spectrum as concerns the relative intensities of the bands may generally arise both due to the complexity of the double ionization process and the particular localization of the valence orbital involved in each final dicationic state.

The observation of a similarly good agreement between such a simulated spectrum and the core-valence spectrum has been reported before for the O₂ case,²⁰ where it was interpreted in the sense that the core-valence interaction is principally of Coulombic origin, and that details of the hole-hole coupling, e.g., related to localization, are of secondary importance in such small molecules. Since the binding energy of the S 2p_{3/2} electron is approximately 169.87 eV (here we use the arithmetic mean value of the two molecular field

components of the $(S\ 2p_{3/2})^{-1}\ ^2P_{3/2}$ state;¹⁴ see also below) the corresponding core-valence interaction energy is of the order of 8.5 eV.

The first line in the $(S\ 2p)^{-1}(vo)^{-1}$ spectrum of Fig. 2, appearing at 188.45 eV, is the strongest single line of the spectrum. On energetic grounds it can be readily associated with a $(S\ 2p_{3/2})^{-1}(2\pi_g)^{-1}$ double vacancy, which is verified by the calculations. The singlet-triplet splitting in the calculations neglecting spin-orbit interaction is small, indicating a small exchange integral and a weak correlation between the core hole and the valence vacancy. The high intensity could possibly be explained by the double degeneracy of the orbital and also by the localization of the orbital on the sulfur atoms,¹⁴ which gives a favorable transition probability in a single center approximation. The FWHM of this line is 0.80 eV, which does not allow resolution of any vibrational fine structure, such as has been observed in the conventional photoelectron spectra for both the $(S\ 2p_{3/2})^{-1}$ (cf. Ref. 14) and $(2\pi_g)^{-1}$ (cf. Ref. 10) cationic states. This comparatively large width can, to some extent, be due to instrumental broadening. However, a width of this size is observed also in the $(vo)^{-2}$ Auger electron spectrum recorded at photon energies slightly above the S 2p ionization threshold,¹⁵ despite the fact that the dicationic states associated with the $(2\pi_g)^{-2}$ configuration support vibrational levels, as has been shown previously using the original 5.6 m TOF-PEPECO instrument³ but at much lower photon energies. Since also the S 2p photolines are narrow enough to show vibrational structure, the increased width cannot be explained by lifetime limitations but could be ascribed to the increase in kinetic energy in the present spectra as well as in the Auger electron spectra. Alternatively, since both the ν_1 and ν_3 modes could be excited, vibrational congestion may give a possible explanation for the observed line width, and molecular field interaction could also be important in the present context.

According to the above, the second line observed at the double ionization energy 189.72 eV is due to the $(S\ 2p_{1/2})^{-1}(2\pi_g)^{-1}$ double vacancy. The width (FWHM) of the line is about 0.64 eV, which is 0.16 eV smaller than that of the lowest lying line. This difference can be explained by the molecular field, which is known to split the $(S\ 2p_{3/2})^{-1}\ ^2P_{3/2}$ cationic state into two molecular states, $^2E_{3/2}$ and $^2E_{1/2}$, by about 0.13 eV,¹⁴ whereas the $(S\ 2p_{1/2})^{-1}\ ^2P_{1/2}$ cationic state, of course, is a single $^2E_{1/2}$ molecular state. It should be noted that the molecular field splitting of the 2p states refer to the fact that z and x,y components of these levels experience differently the anisotropy of the molecular fields.

The third line of the spectrum appears at 191.3 eV, which is 2.8 eV above the $(S\ 2p)^{-1}(vo)^{-1}$ double ionization threshold. This energy difference is the same as the splitting observed between the X $^2\Pi_g$ and A $^2\Pi_u$ states of the valence photoelectron spectrum,^{10,11} which supports an interpretation in terms of a $(S\ 2p_{3/2})^{-1}(2\pi_u)^{-1}$ final dicationic state. The calculated energies of the next lowest $(S\ 2p_{3/2})^{-1}\ \pi^{-1}$ states are in good agreement with this assignment. The estimated line width is 1.1 eV, which is 0.3 eV larger than for the $(S\ 2p_{3/2})^{-1}(2\pi_g)^{-1}$ line. An increased linewidth is expected

FIG. 3. The C 1s-valence double photoionization spectrum (labeled DIPES) of the CS₂ molecule obtained using the photon energy $h\nu=362.7$ eV. A simulated spectrum (labeled valence) based on the UV photoelectron spectrum (narrow lines) constructed as described in the text is also included. The first line of this spectrum is adjusted to the same energy as the corresponding line of the experimental spectrum. Calculated MP2 core-core correlation corrected MCSCF energies (see text and Table IV) and assignments are shown above the experimental spectrum. Triplet states are indicated by dashed lines and singlet states with solid lines (for details, see text).

considering the comparatively large width of the A ²Π_u state photoelectron band due to substantial vibrational excitations.

The fourth line of the spectrum in Fig. 2 is centered at 192.5 eV. At this energy states associated with the (S 2p_{1/2})⁻¹ (1π_u)⁻¹ and (S 2p_{3/2})⁻¹ (5σ_u)⁻¹ configurations are expected as indicated in Fig. 2. A non-negligible intensity could also be due to states connected to (S 2p_{3/2})⁻¹ and satellite 1 at 14.09 eV of the photoelectron spectrum. The (5σ_u)⁻¹ valence hole state is reflected in the conventional photoelectron spectrum by a narrow line at 14.47 (Ref. 11) and could be expected to appear as a comparatively narrow line also in the present spectrum, as indeed observed using the photon energies 220, 230, and 243 eV.

Transitions to (S 2p_{1/2})⁻¹ (5σ_u)⁻¹ state are expected to appear in the range of the next peak with a maximum at 193.9 eV. In this double ionization energy region, but at slightly higher energy, also the (S 2p_{3/2})⁻¹ (6σ_g)⁻¹ transition should give rise to some intensity. The calculated lowest (S 2p_{1/2})⁻¹ (σ)⁻¹ state appears at this energy with a small shift, confirming the assignment.

The broad double peak structure between 194 and 198 eV obviously acquires some intensity from transitions to the (6σ_g)⁻¹ dicationic states and probably states connected to (S 2p)⁻¹ and satellite 2 configurations of the photoelectron spectrum. The two peaks observed are produced by the calculations as the spin-orbit components of the first excited σ⁻¹ state.

B. C 1s-valence DIPES

Figure 3 shows the DIPES measured for a C 1s hole along with a vacancy among the valence orbitals. In the spectrum, a single well defined peak is observed at 310.8 eV followed by two maxima at 315.9 and 317.8 eV ionization energies. There are also indications of weak maxima at 313.3

TABLE III. Double ionization energies (eV), relative intensities, line widths (FWHM), and tentative assignments of the lines observed in the C 1s-outer-valence double photoionization spectrum of the present study.

Energy (eV)	Relative intensity (peak height)	Line width (eV)	Dicationic state
310.8	1.0	0.80	(C 1s) ⁻¹ (2π _g) ⁻¹
313.3	0.2		
314.8	0.5		
315.9	0.7		(C 1s) ⁻¹ (2π _u) ⁻¹
317.8	0.7		(C 1s) ⁻¹ (5σ _u) ⁻¹
319.9	0.3		

and 314.8 eV, but the statistics are insufficient for definite conclusions. The double ionization energies and peak heights are listed in Table III. In the figure, the MP2 core-core correlation corrected MCSCF energies are indicated above the experimental spectrum. These energies (cf. Table IV) were obtained by calculating the energy difference between the MCSCF energies of the doubly ionized states and the ground state, adding the MP2 correlation correction for the C 1s core orbital, as described in Sec. IV A. The single ionization threshold of 292.9 eV for C 1s was obtained by ordinary MCSCF, the experimental C 1s ionization energy being 293.1 eV.³⁸ The MCSCF double ionization energies involving the π_g (singlet and triplet) states lie approximately 1.2 eV below the first peak in the DIPES, and the obtained MP2 correction for C 1s core, 1.28 eV, recovers the shift seen in the MCSCF (C 1s)⁻¹ (2π_g)⁻¹ energy. The MP2 corrected MCSCF energies are given in parentheses in Table IV.

We note that the MCSCF transition energies are considerably lower than the open-shell Hartree-Fock values (cf. Table IV), by 2 to 3 eV, indicating that a considerable part of the difference in correlation energy between the ground and final states are caught by the MCSCF wave function. In our model we also neglected zero point vibrational corrections amounting perhaps to a few tenths of an eV.

Akin to Fig. 2, a simulated spectrum (labeled valence) is included in the lower part of the figure, obtained by shifting the ordinary photoelectron spectrum, recorded at a photon energy of 67 eV (cf. Ref. 15), by 300.69 eV, and using otherwise the same parameters as for the S 2p case. The peak width is approximately 0.8 eV, which is the same as for the peak associated with the (S 2p_{3/2})⁻¹ (2π_g)⁻¹ state in the S 2p related spectrum.

TABLE IV. Calculated (C 1s)⁻¹(vo)⁻¹ double ionization energies using the MCSCF and the independent particle (single configuration) methods. The core-core correlation (MP2) corrected MCSCF energies are shown in parentheses (for details, see text).

Configuration	Energy (eV)			
	MCSCF		Independent particle	
	Singlet	Triplet	Singlet	Triplet
(C 1s) ⁻¹ π _g ⁻¹	309.30 (310.58)	309.82 (311.10)	311.99	311.98
(C 1s) ⁻¹ π _u ⁻¹	315.79 (317.07)	313.80 (315.08)	318.13	316.81
(C 1s) ⁻¹ σ _u ⁻¹	317.20 (318.48)	317.06 (318.34)	319.88	319.15
(C 1s) ⁻¹ σ _g ⁻¹	320.40 (321.68)	319.77 (321.05)	322.65	321.99

The first line in the spectrum is associated with the $(C\ 1s)^{-1}(2\pi_g)^{-1}$ configuration. The calculated singlet-triplet splitting of these states is 0.52 eV. Using the experimental binding energy of the C 1s electron, which is approximately 293.1 eV,³⁹ we find the corresponding core-valence interaction energy to be of the order of 7.6 eV, which is somewhat smaller compared to the situation at the S 2p edge.

It is noteworthy that the intensity in the DIPES does not form a well-defined peak in the range 312–314 eV and that the total intensity seems to be very low. This behavior could be due to the effect of electronic relaxation that is stronger for the C 1s hole in comparison to the S 2p hole and makes a direct comparison of a valence-simulated double ionization spectrum and DIPES more questionable. The structures between 314 and 318 eV are, according to the MP2 corrected MCSCF calculations, due to the states formed from the $(C\ 1s)^{-1}(2\pi_u)^{-1}$ and $(C\ 1s)^{-1}(5\sigma_u)^{-1}$ configurations.

The computed MCSCF C 1s and S 2p core-valence spectra are somewhat too wide, starting with a lower offset and extending a bit on the high-energy side of the main upper structures. According to MP2 core correlation corrections, we associate the former feature, at least partly, to the dynamical electron correlation of the core electrons in the ground state. At the upper core-valence hole states, static correlation and MO breakdown effects may operate, making the final state less stabilized with respect to the ground state. Unfortunately, highly correlating methods, like methods based on complete active space perturbation theory or coupled cluster theory, are currently not applicable to core-valence states. Another salient feature is the small singlet-triplet splitting, only a few tenths of an eV, computed for the $(C\ 1s)^{-1}(2\pi_g)^{-1}$ states, something that reflects the fact that valence-core penetration and exchange interaction is much smaller than, for instance, valence-valence exchange that is visible by the singlet-triplet splittings in molecular valence Auger spectra.¹³ $(C\ 1s)^{-1}(2\pi_u)^{-1}$ seems to be an exception to this, with a singlet-triplet splitting of 2 eV, indicating that the carbon localized $2\pi_u$ orbital collapses into the core upon C 1s ionization, generating large singlet-triplet splitting. This could be parallel to the well-known CO $(C\ 1s)^{-1}(\pi^*)$ case with large singlet-triplet splitting.⁴⁰

V. SUMMARY

The double ionization spectra of the CS₂ molecule connected to final dicationic states where one vacancy is in an inner-shell orbital (S 2p or C 1s) and the other vacancy is in a valence shell were recorded using synchrotron radiation at various energies between 220 and 362.7 eV. The spectrum connected to the S 2p vacancy is richly structured whereas the spectrum connected to the C 1s vacancy shows only one distinct band along with some additional features at higher double ionization energies. Both spectra have been compared to the conventional UV valence photoelectron spectrum. It is found that the spectrum connected to the S 2p vacancy can be viewed primarily as a superposition of two normal UV photoelectron spectra, associated with the S 2p_{1/2} and S 2p_{3/2} states. In the carbon spectrum the stronger $(C\ 1s)^{-1}$ electronic relaxation makes the comparison of DIPES to the

normal photoelectron spectrum less direct, as supported by MCSCF calculations. They also show, that, differently from $(C\ 1s)^{-1}(2\pi_g)^{-1}$ and $(C\ 1s)^{-1}(5\sigma_u)^{-1}$, the $(C\ 1s)^{-1}(2\pi_u)^{-1}$ singlet and triplet states are substantially separated in energy. A similar behavior is seen also in the corresponding core-valence coincidence spectra of CO₂ and OCS.⁴¹ This observation may be related to different localization at the C atom of the three valence orbitals.

We have applied a computational procedure based on the complete/restricted active space self-consistent field principle that uniquely can address core-valence hole states. It is shown that although the procedure gives a too wide spectrum, it is capable to make a state-by-state assignment of the spectra. Ground state core correlation, estimated by MP2 theory, was found to recover the shifts seen in the onset of the calculated DIPES. Another salient feature is that the singlet-triplet splitting is strongly dependent on the penetration of the valence cloud into the core, leading to a quite different exchange energy for different pairs of core and valence holes.

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