

Symmetry-resolved measurements of the core-excited CS₂ molecule

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Core-excited states of the CS₂ molecule have been studied in high-resolution angular-resolved experiment. The total ion yield and the angular resolved electron-ion coincidence (PEPICO) spectra of the S(2*p*) and C(1*s*) excited molecule have been measured. Bending vibrations are excited at the S(2*p*⁻¹)π_{*j*}^{*} state, while the linear geometry is preserved at the S(2*p*⁻¹)σ_{*j*}^{*} state and at the S(2*p*⁻¹)*nl* Rydberg states. The occurrence of strong vibrational coupling is observed at the S(2*p*) excited Rydberg states, which gives rise to excitations of asymmetric stretching modes. Additionally, we show that transitions to the valence S(2*p*⁻¹)π_{*j*}^{*} and S(2*p*⁻¹)σ_{*j*}^{*} states exhibit a strong atomic character, while transitions to the Rydberg states are of molecular type. At the carbon edge the measurements reveal excitations of the nonzero symmetric stretching vibrations at the C(1*s*⁻¹)π^{*} and the Rydberg levels. Above the C(1*s*⁻¹) threshold doubly excited states have been observed and their assignment is proposed. [S1050-2947(98)01707-7]

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I. INTRODUCTION

The dynamics of core electron excitation processes can efficiently be studied in symmetry-resolved experiments [1–9] in which high-resolution absorption-type measurements are combined with angular-resolved mass spectroscopy techniques. Since the orientation of excited molecules relative to the polarization plane of the synchrotron radiation reflects the change of the total angular momentum Λ occurring during the transition, symmetry-resolved measurements probe the angular momentum of the involved states [10–14]. Originally, this technique has been applied in the analysis of the core-excited states in diatomic molecules ([1–3] and references given therein), and later interest has also been extended to larger systems [4–9].

In linear triatomic molecule fragmentation following a core electron excitation occurs collinearly with the molecular axis, thus the angular distribution of the ejected fragments should directly correspond to the orientation of the excited molecules. It may, however, occur that vibrational bending modes are excited or a molecule is bent in the final state. In this case the direction of recoil depends on a momentarily bent angle that affects the angular distribution of the ejected fragments [15]. This is a clear disadvantage if the goal of the experiment is to measure the symmetry of the excited state. However, if the latter is known, the angular-resolved measurements may be applied to investigate nonaxial recoil processes viewing, for example, the geometry of the core-excited levels [5,9].

Obviously, the vibrational motion, especially bending oscillations, may strongly influence apparent angular distributions. Degenerate excited states are perturbed by the Renner-Teller effect due to which transitions to the bending modes

become allowed. Close-lying core-excited states may interact via vibronic coupling allowing transitions to asymmetric stretching modes. This effect has been theoretically predicted [16] and experimentally observed [18] for ionization of a core electron of a terminal atom in the $D_{\infty h}$ symmetry molecule. The vibronic coupling has also been discussed for excitations to neutral core-excited states [17] but very little experimental data has been presented in the literature so far [19].

To date several studies have been published on angular-resolved measurements of triatomic molecules [4–9]. It has been shown that excitations of core electrons to the degenerate valence-type orbitals (π^{*} states) are often associated with change of a molecular geometry from linear to bent. The technique has also been applied in studies of excitations of bending vibrations induced by the Renner-Teller effect [6–8]. For the CS₂ molecule the only reported angular-resolved measurements have been focused on a study of the Renner-Teller effect at the C(1*s*⁻¹)π^{*} resonance [8]. Recently, we have performed high-resolution total ion yield and angular-resolved ion yield measurements at the S(2*p*) and C(1*s*) edges. We analyze in detail the structure and properties of neutral core-excited states. Much attention is paid to dynamics of vibrational excitations. We experimentally reveal conditions in which the vibrational excitations are governed by vibronic coupling and occur with a total breakdown of the Born-Oppenheimer approximation.

II. EXPERIMENT

The experiment was performed on beamline 51 at the Swedish National Synchrotron Facility MAX in Lund and the details of the apparatus have been published elsewhere [9]. The undulator radiation was monochromatized by an SX700 monochromator (resolution ≥ 5000) and focused into the experimental chamber by a refocusing mirror. The size of the light spot was smaller than 0.1 mm. In the experimental chamber the light beam crossed an effusive gas jet. An am-

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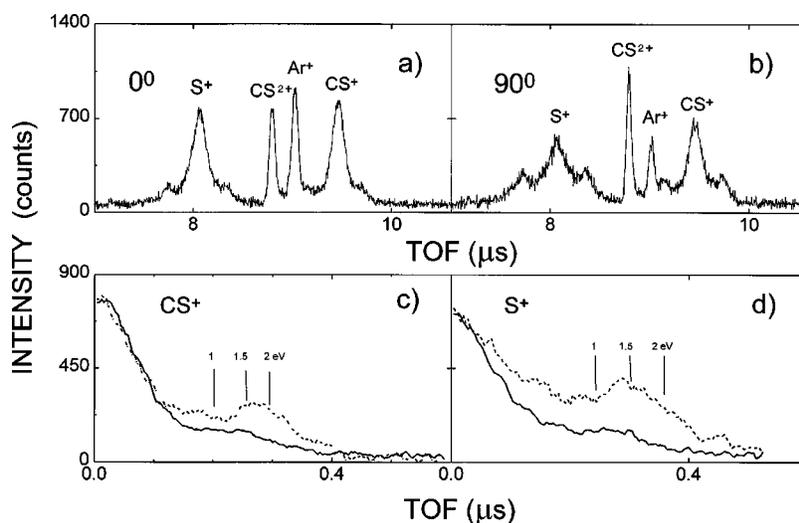


FIG. 1. PEPICO spectra acquired at the excitation to the $S(2p^{-1})\sigma_{3/2}^*$ state (low extraction fields) in the 0° (a) and 90° geometry (b). In (c) and (d) the PEPICO spectra acquired at 0° (solid line) and 90° geometry are superimposed for the S^+ and CS^+ fragments, respectively. The spectra are scaled to obtain equal intensities of the low (zero) kinetic energy ions. Angular anisotropy is clearly observed for the higher kinetic energy ions.

bient pressure better than 1×10^{-5} mbar was maintained during the experiment.

The total ion yield and coincidence measurements were performed using a 210-mm Wiley-McLaren-type time-of-flight spectrometer. Signals from the microchannel plate detectors were amplified by ORTEC VT120 preamplifiers. Coincidence events were acquired with a fast (0.5 ns resolution) multihit PC card.

The total ion yield spectra were measured at the magic angle geometry using strong (40 V/mm) extraction fields. Under these conditions only ions ejected with large velocity components perpendicular to the observation axis may escape observation. For example, for the S^+ and CS^+ ions this velocity corresponds to a kinetic energy of about 4 eV. The bandwidth of the synchrotron light was adjusted to 30 meV and 80 meV for the measurements at the $S(2p)$ and $C(1s)$ edges, respectively, with the exception of PEPICO measurements at weak Rydberg and doubly excited states at the carbon edge, which were performed with substantially lower resolution (300 meV).

The PEPICO spectra were acquired at 4–6 different angles. Low extraction fields (4 V/mm) were applied in order to obtain a good angular selectivity of the ion detection. On the other hand, the acceptance angle for electrons was large and almost no anisotropy was observed in the signal of the emitted electrons produced in ionization of the CS_2 molecules. From these coincidence spectra the signal corresponding to energetic S^+ and CS^+ ions ($KE \geq 1.2$ – 1.6 eV) was extracted and used for derivation of the molecular orientation (see Fig. 1).

The analysis of the β parameters was performed using a Monte-Carlo simulation program in which the geometry of the experiment [strength of the extraction fields, kinetic energies of the ions, dimensions of the time-of-flight (TOF) spectrometer] was fully taken into account. The β parameters were obtained in the best-fit procedure by comparing the shapes of the calculated angular distributions with the

experimental data (see Fig. 2) and the error due to statistical scattering of the experimental points was typically ± 0.1 . Corrections for changes of experimental conditions (variations of the synchrotron light intensity or the gas pressure) were provided by the Ar^{2+} ion signal from Ar gas that was mixed with the CS_2 gas prior to injection into the chamber. The small anisotropy of the PEPICO signal of Ar^{2+} was separately measured. Alternatively, the spectra were analyzed assuming that low kinetic energy S^+ and CS^+ fragments ($KE \leq 200$ meV) are isotropically ejected, which is commonly observed in fragmentation of both diatomic and triatomic molecules [5,9]. Actually, within the experimental errors both methods have yielded identical results.

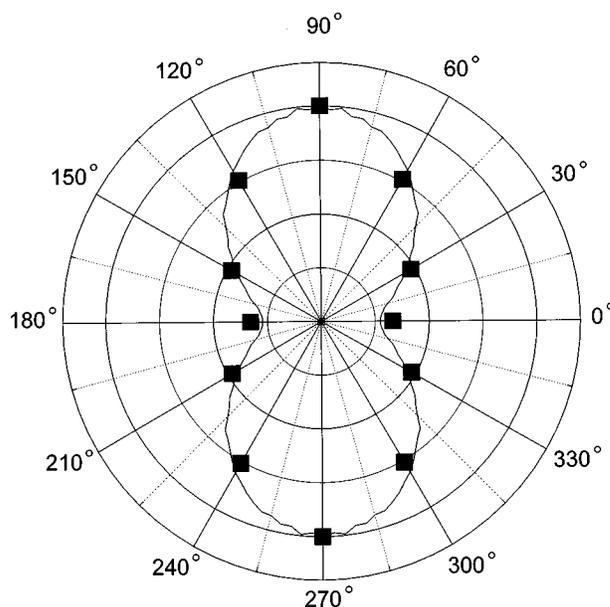


FIG. 2. Angular distribution for the $\beta = -0.65$ simulated for the S^+ ions using a Monte Carlo routine (solid curve). Squares represent experimental data measured at the $C(1s^{-1})\pi^*$ state.

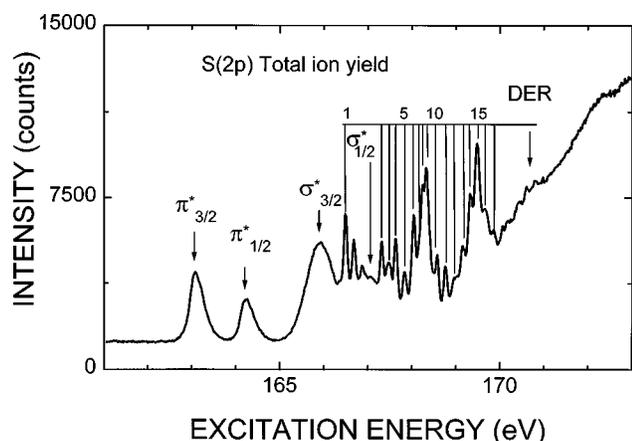


FIG. 3. Total ion yield spectrum acquired at the sulfur edge with a resolution 30 meV. The width of the vibrationally resolved resonances has been established to about 85 meV. For assignment of the structure see Fig. 4 and Table I.

III. RESULTS AND DISCUSSION

A. Sulfur S(2p) edge

1. Total ion yield spectra

The total ion yield spectrum acquired at the sulfur edge is shown in Fig. 3. Since *ab initio* calculations of the core excited states of the CS₂ molecule have not been published, the presented assignment of the Rydberg levels is based on analysis of the quantum defects and results are given in Table I. The energy of the $\sigma_{1/2}^*$ state has been approximately established assuming similar splitting of the $\pi_{1/2}^*$ and $\sigma_{1/2}^*$, and the $\pi_{3/2}^*$ and $\sigma_{3/2}^*$ states.

Noticeably, the shapes of the valence and Rydberg S(2p) resonances in Fig. 3 are very different. In spite of the good instrumental resolution (30 meV) no vibrational structure has been resolved in $\pi_{1/2,3/2}^*$ and $\sigma_{1/2,3/2}^*$ states (this short-hand notation $nl_{j,j'}$ denotes two states nl_j and $nl_{j'}$, respectively). In contrast, the spectra of the Rydberg states show distinct vibrational structures separated by about 190 meV, which corresponds to the energy of the asymmetric stretching mode. No splitting of the vibrational levels due to a molecular field has been observed. The good quality of the total ion yield spectrum permits a vibrational analysis of the Rydberg states in the region 166–168.9 eV, which has been performed by fitting a multipeak Gaussian function to the experimental data. The fit is shown in Fig. 4. Values of energies, quantum defects, and relative intensities of the core-excited states derived from the fit are tabulated in Table I. For all the considered Rydberg states the separation of vibrational progressions (~ 190 meV) indicates excitations of the asymmetric stretching mode. Actually, no other type of vibration has been revealed. Deconvolution of the vibrational structure of the Rydberg states for the excitation energies above 169 eV leads to rather uncertain results due to a large number of overlapping resonances and is therefore not included in Table I.

Two observations follow from the analysis of the vibrational structure. Firstly, the spectra of the $\pi_{1/2,3/2}^*$ and $\sigma_{1/2,3/2}^*$ resonances recorded in the total ion yield spectrum either indicate an extensive excitation of the bending modes, or a

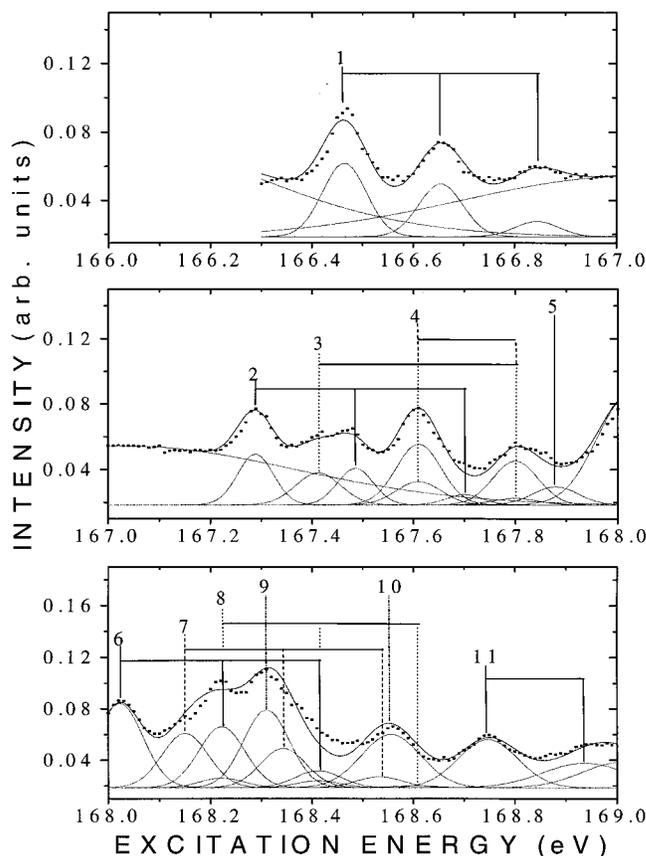


FIG. 4. Analysis of the resonant structure recorded in the energy region 166–169 eV. The results of the fit are tabulated in Table I.

repulsive character of these states. Secondly, excitations to the Rydberg states occur with a change of the vibrational mode from symmetric stretching to asymmetric stretching, a process that is forbidden in the Born-Oppenheimer model.

The excitation of the core electron to the degenerate π states occurs with a change of the molecular geometry due to a Renner-Teller effect. The degeneracy is removed as the state splits into two close-lying levels in which the molecules exhibit bending oscillations. In the case of strong Renner-Teller coupling the molecule may be bent permanently and excitation occurs to states of a_1 and b_1 symmetry whose splitting is typically much larger than the natural width of these states. The occurrence of the Renner-Teller perturbation readily explains the dense vibrational structure of the S(2p) $\pi_{1/2,3/2}^*$ resonances and relatively small value of the β parameter (see Table I). On the other hand, the Renner-Teller effect does not occur in excitation to the nondegenerate $\sigma_{1/2,3/2}^*$ orbitals, thus a change of the molecular geometry is rather unexpected. Also the large negative values of the associated β parameters (especially the $\beta = -0.85$ obtained for the S⁺ fragment at the $\sigma_{3/2}^*$ state, see Table I) would be difficult to understand in the case of nonlinear recoil. The observed diffuse shapes of the $\sigma_{1/2,3/2}^*$ resonances should then be attributed to a repulsive character of these states. Since the dynamical change of the molecular geometry may be better understood in view of the angular-resolved measurements this problem is discussed in the next section of this paper.

In this discussion the coupling of the angular momentum of the core and the valence electrons has been neglected assuming that the molecular symmetry is entirely defined by the excited valence orbital. Although the experimental results seem to justify this approach, such a picture is, strictly speaking, incorrect. In the ground state the $S(2p)$ electrons occupy the $3\sigma_g$, $2\sigma_u$, $1\pi_u$, and $1\pi_g$ orbitals. When the $S(2p^{-1})$ vacancy is formed the coupling of the angular momenta of the $S(2p^5)$ electrons are only weakly affected by a molecular field. The resulting total angular momentum J is not quantized along the molecular axis. Consequently, the core σ and π orbitals are totally mixed perturbing the symmetry of the final nl_j state. In the configuration interaction picture each of the nl_j states is composed of several nearly degenerated states of Σ and Π symmetry that are populated from the ground state of the molecule.

During excitations to the Rydberg states the geometry of the molecule remains linear but the mode of vibrations changes. Cederbaum and Domcke [16] have shown theoretically that ionization of the core electron of the terminal molecule of the $D_{\infty h}$ symmetry from the nearly degenerated states leads to the appearance of a strong vibronic coupling and consequently to excitation of the asymmetric stretching modes. Although the theory has been extended to the general case of excitations of short-lived neutral states, the attention has mainly been paid to the cross section calculations in the original work [17]. Our present results clearly reveal the occurrence of vibronic coupling in excitations to neutral Rydberg states. Importantly, transitions to the asymmetric stretching mode have been observed at the $nl\sigma$ and $nl\pi$ Rydberg states indicating that the symmetry of the excited state play a minor role. Thus, the effect should be understood in terms of the symmetry breaking induced due to formation of a core vacancy analogously to what is observed in core-ionization transitions [16]. Actually, assuming that the wave function of the Rydberg electron may be factorized from the total wave function of the core-excited state, the formalism given in [16] is directly applicable to the case of core-excited Rydberg electrons. In this approximation nearly degenerate electronic levels of the g and u symmetry, which constitute an nl_j state, are coupled via the asymmetric mode. Due to their small energy separations the matrix elements of these states, coupled by an antisymmetric mode, become large permitting strong transitions to this mode. In a kinematical picture, since the symmetry of the molecule is dynamically broken by the creation of the core vacancy, the equilibrium positions of the sulfur atoms shift. This accounts for an appearance of asymmetric forces acting upon the nuclei that change the vibrational motion and almost totally quench the symmetric vibrations. It should be noted that, although the symmetry is locally broken, the total symmetry of the vibrational wave function does not change, since both sulfur atoms are simultaneously excited to the asymmetric modes. A very high efficiency of this process should be noticed, a situation which has also been observed in ionization of the CO_2 molecule [18].

2. β -parameter measurements

The angular distributions of the CS^+ and S^+ fragments have been measured for excitations to the $\pi_{1/2,3/2}^*$, $\sigma_{1/2,3/2}^*$, and $4s\sigma_{1/2,3/2}$ states and for the excitation energies $h\nu$

TABLE I. Neutral $S(2p^{-1})nl_{1/2}$ excited states observed at the sulfur edge. Intensities of the Rydberg states are normalized to the intensity of the $4s\sigma_{g,3/2}, \nu_3=0$ resonance. For the overlapping resonances (for example, $4p\sigma_{u3/2}, \nu_3=1$ and $4s\sigma_{u1/2}, \nu_3=0$) the intensities were approximately established by assuming that Franck-Condon factors are very similar for the states belonging to the one Rydberg progression.

No	State	Energy (eV)	δ_i	Intensity	$\beta(CS^+)$	$\beta(S^+)$
	$\pi_{3/2}^*$	163.1			0.25	0.25
	$\pi_{1/2}^*$	164.26			0.15	0.2
	$\sigma_{3/2}^*$	165.91			-0.6	-0.85
	$\sigma_{1/2}^*$	167.08			-0.5	-0.65
1	$4s\sigma_{g3/2}, \nu_3=0$	166.46	1.90	1	0.6	0.7
	$\nu_3=1$	166.65		0.75		
	$\nu_3=2$	166.84		0.21		
2	$4p\pi_{u3/2}, \nu_3=0$	167.29	1.55	0.58		
	$\nu_3=1$	167.48		0.42		
	$\nu_3=2$	167.7		0.12		
3	$4p\sigma_{u3/2}, \nu_3=0$	167.41	1.48	0.47		
	$\nu_3=1$	167.61		0.35		
	$\nu_3=2$	167.80		0.10		
4	$4s\sigma_{g1/2}, \nu_3=0$	167.61	1.92	0.86	0.5	0.55
	$\nu_3=1$	167.80		0.62		
5	$3d\sigma_{g3/2}, \nu_3=0$	167.88	0.16	0.29		
6	$3d\pi_{g3/2}, \nu_3=0$	168.02	0.03	1.63		
	$\nu_3=1$	168.22		1.18		
	$\nu_3=2$	168.41		0.33		
7	$5s\sigma_{g3/2}, \nu_3=0$	168.15	1.61	1.05		
	$\nu_3=1$	168.34		0.76		
	$\nu_3=2$	168.53		0.21		
8	$5p\pi_{u3/2}, \nu_3=0$	168.22		0.18		
	$\nu_3=1$	168.41		0.13		
	$\nu_3=2$	168.60		0.04		
9	$3d\delta_{g3/2}, \nu_3=0$	168.31	-0.28	1.50	0.5	0.9
10	$4p\pi_{u1/2}$ and $5p\sigma_{u3/2}$	168.55	1.61	1.33		
11	$4p\sigma_{u1/2}, \nu_3=0$	168.74	1.40	1.20		
	$\nu_3=1$	168.93		0.87		
12	$3d\sigma_{g1/2}, \nu_3=0$	169.01	0.22			
13	$3d\pi_{g1/2}, \nu_3=0$	169.14	0.10			
14	$5s\sigma_{g1/2}, \nu_3=0$	169.31	1.94			
15	$3d\delta_{g1/2}, \nu_3=0$	169.46	-0.24		0.35	0.3
16	$5p\sigma_{u1/2}, \nu_3=0$	169.63				
17	$4d\pi_{g1/2}, \nu_3=0$	169.85	0.14			

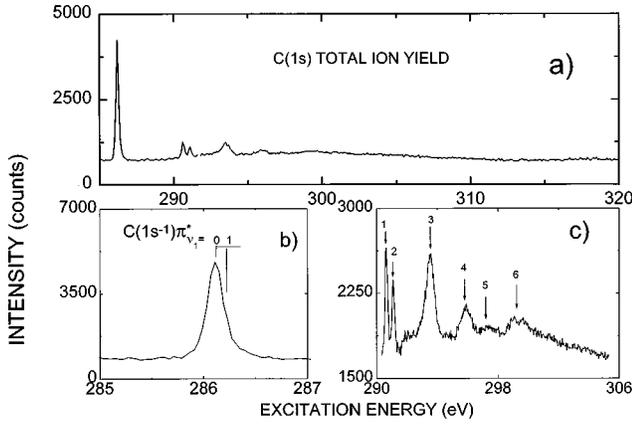


FIG. 5. Total ion yield spectrum acquired at the carbon edge. (a) The spectrum measured in the energy region 285–320 eV. (b) The spectrum of the π^* resonance measured with a resolution of 80 meV. (c) Details of the resonant structure observed in the energy range 290–306 eV (for assignments see Table II).

=168.31 eV and $h\nu=169.46$ eV. Results are given in Table I. Noticeably, β parameters measured for the S^+ ions are systematically larger than obtained for the heavier CS^+ fragments. This is partially due to larger kinetic energy (and thus smaller acceptance angles) of the S^+ ions. Thus, the molecular alignment is best represented by the β parameters obtained for the S^+ ions. Additionally, we have studied the angular distributions of the C^+ ions, but within the experimental uncertainty no anisotropy has been observed.

For the CS^+ and S^+ fragments the measured β parameters are negative for the $\sigma_{1/2,3/2}^*$ states and positive for the remaining studied resonances. The values obtained for the $\sigma_{1/2}^*$ state are lowered by the closely lying $4s\sigma_{g,3/2}$ state. We note that upon excitations to the $\sigma_{1/2,3/2}^*$ and $4s\sigma_{1/2,3/2}^*$ states the molecules are aligned in opposite directions showing occurrence of $\Delta\Lambda = \pm 1$ and $\Delta\Lambda = 0$ transitions, respectively. At excitation energies of $h\nu=168.31$ eV and $h\nu=169.46$ eV transitions occur to several overlapping resonances and for this reason these data may only be considered qualitatively.

Without detailed theoretical calculations only very crude models may be considered in order to explain the experimental values of the β parameters. Assume that the localized valence-state excitations of the $S(2p)$ electron may be regarded as a pure atomic process with a quantization direction along the molecular axis. In this simple picture the induced molecular orientation is due to different transition probabilities from $2pm_l, (m_l = \pm 1, 0)$ to an excited $(nlm_l)'$ state that can be calculated using respective Clebsch-Gordon coefficients. The β parameters expected for transitions to $3p, m=0$ ($\sigma_{1/2,3/2}^*$) and $3p, m=\pm 1$ (π^*) states are $\beta=0.5$ and $\beta=-1$, respectively.

However, if the final state is delocalized over the entire molecule it may no longer be approximated by an atomiclike orbital and the transitions to these states should rather exhibit a molecular character. As discussed in the previous section the final $S(2p^{-1})nl\delta_l$ state should be considered as a mixture of Σ and Π symmetry states due to a nonzero angular momentum of the core vacancy. Therefore, the molecular orientation solely depends on the relative strengths of the Σ - Σ and Σ - Π transitions.

TABLE II. $C(1s)$ excited states observed in the energy region 285–300 eV. Symbol V denotes excitation to $3\pi_g, 3\pi_u, 6\sigma_u, 7\sigma_g$ levels. Labels given in the first column refer to assignment in Fig. 5. The energy scale has been adjusted to match the data of Harrison and King, Ref. [20].

No.	State	Energy
	$\pi^* \nu_1 = 0$	286.10
	$\pi^* \nu_1 = 1$	286.18
1	$3s$	290.5
2	$3p$	291.0
3	$C(1s) \rightarrow \pi^*$	293.5
	$2\pi_g \rightarrow (V)$	
4	$C(1s) \rightarrow \pi^*$	295.8
	$2\pi_u \rightarrow (V)$	
5	$C(1s) \rightarrow \pi^*$	297.3
	$5\sigma_u \rightarrow (V)$	
6	$C(1s) \rightarrow \pi^*$	299.2
	$6\sigma_g \rightarrow (V)$	

The β parameters measured for the valence $\pi_{1/2,3/2}^*$ and $\sigma_{1/2,3/2}^*$ states (see Table I) are close to the expected values in the atomic model of $S(2p)$ electron excitations and indicate a strong atomiclike character of the respective transitions. This is primarily due to a weak participation of the carbon orbitals in formation of these states. It should also be remembered that the values of β parameters measured for the $\pi_{1/2,3/2}^*$ states are lowered due to the nonaxial recoil processes while a high value measured for the $\sigma_{3/2}^*$ state (-0.85 for the S^+ ions) supports the assignment of this resonance to a linear state. Presently, since no *ab initio* computations of the β parameters have been published, only a qualitative discussion concerning the molecular geometry of these states is possible. Assuming that the discrepancy between the expected (~ 0.5) and measured β value (0.2 ± 0.1) is entirely due to the bent geometry of the molecule (neglecting for example the dynamical bending oscillations) the bent angle may be derived using the classical theory [9,15]. In this approach the β parameter is given as a Legendre polynomial of the angle between the recoil direction and the dipole moment {see formula (3.4) in [9]}. Comparing calculated angles for theoretical and experimental values of the β parameters the bent angle of the molecule may be estimated. For the π_j^* states such analysis shows that the angle between the molecular bonds is rather large ($\sim 170^\circ$), which actually suggest that the molecule does not change the geometry permanently and the low anisotropy is entirely due to the occurring bending oscillations. Certainly this conclusion may be changed if the anisotropy, induced during excitation to these states, is higher than expected on the ground of the considered model, which may only be verified by theoretical computations of the β parameters.

In contrast to what is observed at the valence states, the transitions to the $4ns\sigma_{g,1/2,3/2}$ Rydberg levels exhibit a molecular character. Apparently, since the β parameters are positive the Σ - Σ transitions are substantially stronger than Σ - Π transitions. Thus, the symmetry of the $S(2p)$ excited

Rydberg state is, at least in a first approximation, defined by the symmetry of the Rydberg orbital. However, due to other effects like a coupling of the angular momentum of the core vacancy to the total molecular angular momentum the Σ - Π transitions are also excited, which lowers the values of the β parameters.

B. Carbon 1s edge

The total ion yield spectrum acquired in the energy region 284–310 eV is shown in Fig. 5(a). The energies of the observed resonances and their tentative assignments are given in Table II.

Excitations to the $C(1s^{-1})\pi^*$ state have recently been studied in a symmetry-resolved experiment [8]. These results have shown that the Renner-Teller splitting is fairly small and transitions only occur to the lowest vibrational state. The spectrum of the π^* state [Fig. 5(b)] has additionally revealed an underlying resonance separated from the (0,0,0) peak by about 80 meV which originates from transition to the (1,0,0) state. We note that the transitions to the asymmetric stretching mode for excitations of the central atom are not expected [16,17] and they are indeed not observed in the present experiment.

A value $\beta = -0.65$ has been obtained for the S^+ fragment for the $C(1s^{-1})\pi^*$ state. This value is close to the result of Adachi *et al.* [8] and noticeably differs from the value expected for pure Σ - Π transition. However, if the π^* state is perturbed by the Renner-Teller effect [8] the molecule would exhibit bending oscillations around an equilibrium position. It is natural to expect that such zero-point vibrations lower the molecular alignment and consequently affect the β value.

In the energy region 290–301 eV several features have been recorded in the total ion yield spectrum [see Fig. 5(c)]. The resonances at $h\nu = 290.5$ eV and $h\nu = 291.0$ eV have been assigned to the $3s$ and $3p$ Rydberg states [20], respectively. Both peaks are asymmetric and their widths are about 280 meV and 200 meV, respectively, indicating that up to three vibrational levels of the symmetric stretching mode are excited. The angular-resolved measurements performed at both excitation energies show the excess of ions emitted in the 0° direction ($\beta > 0$). This, however, does not reflect the alignment induced in the transition to Rydberg states but should primarily be ascribed to nonresonant ionization processes [note the small intensities of the resonant signals in comparison to the background level, see Fig. 5(c)]. Also, the bandwidth of the synchrotron light adjusted for these measurements (300 meV) make the signal-to-background ratio additionally unfavorable (approximately 1:6). This also explains the almost identical anisotropies observed for the $3s$ and $3p$ states. We conclude that in the considered energy region the direct ionization processes lead to a weak orientation of the molecule preferably along the direction of the polarization vector.

Above the threshold (established at 293.1 eV [21]) four broad features are observed in Fig. 5(c). So far no theoretical

analysis of the excitation of the $C(1s)$ electron has been published, thus the origin of these features is not known. Possibly, the resonances are formed by transitions to the π^* state associated with the shake-up of the $2\pi_g$, $2\pi_u$, $5\sigma_u$, and $6\sigma_g$ electrons to closely lying $3\pi_g$, $3\pi_u$, $6\sigma_u$, $7\sigma_g$ levels. The extreme separation of the four latter states is about 1.8 eV [21] which matches closely to the observed width of the resonances 3–6 in Fig. 5(c). Also the energy separation between the $2\pi_g$, $2\pi_u$, $5\sigma_u$, and $6\sigma_g$ closely matches the spacing of the features 3–6 in Fig. 5(c). For the strongest resonance observed at 293.5 eV [feature 3 in Fig. 5(c)] our angular-resolved measurements reveal the excess of ions emitted perpendicularly to the polarization plane (90°) ($\beta < 0$), which clearly differs from what is observed in the region of the $3s$ and $3p$ resonances. Actually, a large width of this resonance makes the signal-to-background ratio substantially higher than for the narrow $3s, 3p$ resonances (approximately 1:2.5). Although, it is usually misleading to view double excitation processes using an independent electron approximation, we shall presently note that the molecular orientation is mainly determined by the core electron [$C(1s) \rightarrow \pi^*$] transition ($\beta < 0$).

Finally we note an enhancement of the total ion intensity in the region 290–310 eV indicating the transition to the σ^* -type shape resonance.

IV. CONCLUSIONS

We present high-resolution symmetry-resolved measurements of the $S(2p)$ and $C(1s)$ excited CS_2 molecule. The resonant structure observed at the sulfur and carbon edges has been recorded with vibrational resolution and the dynamics of the excitation processes to these states has been analyzed. We show that bending oscillations are excited at the $S(2p^{-1})\pi_{1/2,3/2}^*$ states, while the linear geometry is maintained at the $S(2p^{-1})\sigma_{1/2,3/2}^*$ and at the Rydberg states. Also excitations to the Rydberg levels are associated with transitions to asymmetric stretching modes that are induced by vibronic coupling. The transitions to the $S(2p)$ excited valence states are atomiclike, while excitations to the Rydberg levels are molecularlike. The analysis of the Renner-Teller splitted $C(1s^{-1})\pi^*$ state reveals quenching of the angular anisotropy due to zero-point bending vibrations. Also, only transitions to symmetric stretching mode vibrational levels have been recorded, which confirms the origin of the vibrational coupling mechanism observed at the sulfur edge. Above the $C(1s^{-1})$ threshold four strong features have been revealed and tentatively assigned to doubly excited states. An anisotropy induced in the transitions to the doubly excited states has been observed.

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