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Experimental and theoretical study of S 2p and C 1s spectroscopy in CS_2

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Abstract

Electron energy loss spectra of gas phase carbon disulfide have been recorded under dipole and strongly non-dipole conditions in the region of S 2p, and C 1s excitation. Inner-shell triplet states have also been observed by measuring near threshold C 1s energy loss spectra using a wide range of angles (4–20°) and impact energies (130–1300 eV). The optical oscillator strength (OOS) and generalized oscillator strength profiles (GOS) have been calculated for vertical excitation from the ground $X^1\Sigma_g^+$ electronic state to several C(1s) and S(2p) inner-shell electronic excited states of CS_2 molecule, using high level ab initio (HF-CI) calculations.

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1. Introduction

Inner-shell excitation can be induced either by photoabsorption or charged particle impact. In the present work, electron energy loss spectroscopy (EELS) has been used to study inner-shell excited states of carbon disulfide, CS_2.

Carbon disulfide is produced naturally by several types of soil, sediment and aquatic microorganisms, vegetation, forest and grass fires and volcanoes. Worldwide, at least 40% and possibly as much as 80% of releases are a result of natural or biogenic activity. Carbon disulfide is rapidly metabolized by organisms and does not bioconcentrate or biomagnify. As carbon disulfide is mainly released to and detected in air, this is a critical compartment in the assessment of risk to the environment and its gas phase study is very important. The experimental study of the interaction of electrons with CS_2 can be directly applied to the solar wind electrons interaction with the molecules present in comets. Therefore, the electronic structure and excited states of carbon disulfide, as well as its electronic transitions probabilities and absolute photoabsorption oscillator strengths are useful to analyze observed data from atmosphere.

Under small momentum transfer conditions electron scattering is dominated by electric dipole transitions and therefore simulates photoabsorption. Conversely, at large momentum transfer optically forbidden quadrupole and higher order electric multipole transitions can be excited [1–10]. When the incident electron energy is near the inner-shell excitation threshold, spin-exchange transitions can be excited by the exchange interaction of bound and incident electrons. Spin-forbidden inner-shell transitions have been observed in N_2 [11], CO [12,13], CO_2 [14], N_2O [15], COS, CS_2 and C_2H_2 [16].

The molecules CO_2, N_2O, COS and CS_2 are closely related triatomic linear molecules. This paper presents results for the inner-shell electron energy loss spectroscopy (ISEELS) of CS_2 molecule in the C 1s and S 2p regions. In addition to observations of quadrupole transitions, singlet–triplet transitions have been observed and used to aid spectral assignment.

The literature on the core excitation spectra of CS_2 [17–20] contains inconsistencies in both spectral shapes and interpretation. In particular the positions of the core → σ^* excitations are not well established. One goal of this study is to provide a consistent spectral interpretation of the core excitation spectra of CS_2.

2. Experimental

Electron energy loss spectra of CS_2 in the regions of C 1s, and S 2p excitations were acquired with a variable impact energy, variable scattering angle and electron energy loss spec-

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trometer. A detailed description of the apparatus, its operating procedures and data analysis methods has been published elsewhere [1,3]. Freeze–pump–thaw iterations were performed on CS_2 (stated boiling point range of 46.1–46.6 °C), which was otherwise used as received from the commercial supplier (Aldrich, 99.9% purity). The pressure of the differentially pumped region connected to the gas cell was 5×10^{-6} torr during data acquisition. The energy scales of all spectra were calibrated internally using previously published assignments [21].

3. Theory

We have calculated the optical (OOS) and generalized oscillator strength (GOS) for the vertical excitation from the ground $X^1\Sigma_g^+$ electronic state to several C 1s and S 2p inner-shell electronic excited states of CS_2 molecule. The electronic wave functions for the ground and C 1s excited states were determined with the configuration interaction (CI) method expanded on a C: (12s, 6p, 1d)/[10s, 4p, 1d] and S: (15s, 9p, 1d)/[11s,5p, 1d] Gaussian basis sets. The employed Gaussian basis sets for the C and S atoms were chosen bearing in mind a good description of: (1) the core molecular orbitals and (2) the external single occupied orbital after excitation of one electron from the core. Hence, we have used very uncompressed basis sets with several basis functions for the core region and several diffuse functions for the external region.

The molecular geometry has been determined using the above described basis set at second-order Møller–Plesset level of theory presenting the $D_{\infty h}$ point group with 1.538 Å as the CS-distance. The occupied and improved virtual orbitals (IVO) were determined independently for the ground and each excited state and, as a consequence, they are not orthogonal. This means that the molecular basis for the CI calculation was optimized for each molecular state and includes, for the excited states, the strong relaxation that takes place in the formation of an inner-shell excited state.

Configuration interaction calculations were performed for each molecular state, allowing single and double excitations (SDCI) for the reference configuration to a virtual space composed of 25 virtual orbitals ($6\sigma_g^+$, $6\pi_g$, $1\sigma_g^-$, $5\sigma_u^+$, $6\pi_u$, $1\sigma_u^-$). In each state, the SDCI calculation was performed for about 6000 configurations.

The second-order CI does not balance adequately the fundamental and excited states. This produces errors in the transition energies of about 2 eV. The fourth-order excitations in the CI eliminate these deviations [22]. In our case, computational limitations did not allow to extend the calculation to SDTQ CI level. However, we note that although the absolute values of transition energies were not in good agreement with experimental ones, the relative values show a good agreement, as may be seen in Table 1.

For the excitation from the S 2p orbitals, generalized multistructural (GMS) wave functions [23,24] were used in order to take into account core hole localization effects without breaking the full molecular symmetry. The GMS wave function is defined as

$$\Psi_{\mathrm{GMS}} = \sum_{l=1}^{N_{\mathrm{STRUCT}}} \sum_{i=1}^{N_{\mathrm{SEF}}} c_i^l \Phi_i^l, \tag{1}$$

Table 1
Energies, line shapes, widths and assignments of features of the C 1s spectra of CS_2

Peak	Energy (eV)			Term value	Line type[a] (width)	Assignment	
	This work (experiment)	This work (theory)	Literature				
1	285.2[b]	286.6 (285.0)[c]	285.2[d]	7.9	*G* (0.85)	$3\pi_u^*(^3\Pi)$	$[3\pi_u]$[e]
2	286.1	287.7 (286.1)	286.1[f]	7.0	*G* (0.70)	$3\pi_u^*(^1\Pi)$	$[3\pi_u]$
3	289.4	291.2 (289.6)	288.9[d]	3.7		$3s\sigma_g^*(^3\Sigma_g)$[d]	$[7\sigma_g^+]$
4	289.5	291.3 (289.7)	289.6[d]	3.6	*G* (0.91)	$3s\sigma_g^*(^1\Sigma_g)$	$[7\sigma_g^+]$
5	290.7	292.3 (290.7)	290.6[d]	2.4	*G* (1.25)	$3p\sigma_u$	$[6\sigma_u^+]$
		295.4 (290.9)				$3p\pi_u$	$[4\pi_u]$
6	292.4	296.6 (292.1)	292.4[d]	0.7	*G* (1.46)	$7\sigma_g^*(^1\Sigma_g)$	$[8\sigma_g^+]$
		294.1 (292.4)					$[3\pi_g]$
		294.2 (292.6)	293.1[g]		*E* (5.23)	IP	
7	293.3	298.0 (293.5)	293.4[d]	−0.2	*G* (0.93)	$6\sigma_u^*$	$[7\sigma_u^+]$
8	295.8		295.8[d]	−2.7	*G* (0.78)	$2e^-$	
			297.3[d]			$2e^-$	
9	299.6		299.4[h]	−6.3	*G* (2.53)	$2e^-$	

[a] *G* is the Gaussian profile and *E* the error function edge shape.

[b] Value obtained from fitting for the spectrum acquired with final energy of 130 eV above threshold at 4°.

[c] The values in parentheses are E_{theo} multiplied by a normalization factor *f*. For the first CI root in each symmetry, $f = 286.1/287.7$ and for the second CI roots, $f = 292.1/296.6$.

[d] Ref. [16].

[e] In the square brackets are shown the theoretical molecular orbital for which one electron from the C $1s2\sigma_g^+$ orbital was promoted.

[f] All energies were established by calibrating the C 1s → $3\pi_u^*$ transition to this value [20].

[g] Ref. [27].

[h] Ref. [20].

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