

# ULTRASOFT X-RAY ABSORPTION SPECTRA OF SULFUR IN MOLECULAR COMPOUNDS

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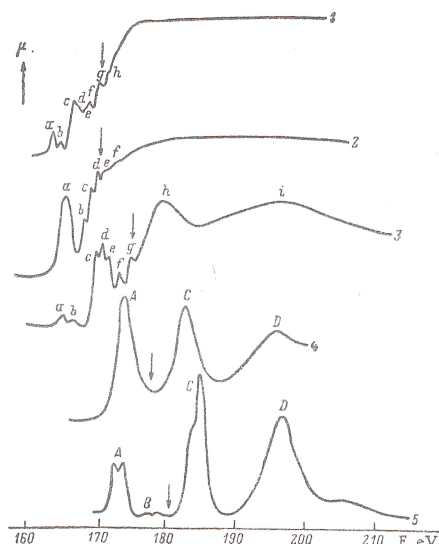
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In the quantum energy region 160-210 eV we have investigated the fine structure of the  $L_{II,III}$  (2p)-absorption spectra of sulfur in  $SO_2$ ,  $H_2S$ , and  $CS_2$  molecules. We have obtained spectra that are markedly different from the previously known  $L_{II,III}$ -spectra of sulfur in the compounds  $K_2SO_4$  and  $SF_6$ , with differences being observed in the absorption structure up to the ionization threshold and beyond. Qualitative analysis of all spectra shows the important role played by the strongly electronegative atoms of fluorine and oxygen in the occurrence of these differences.

Previous investigations [1-3] have considered the characteristics of x-ray photoionization of the molecules  $SF_6$  and  $SiF_4$ . Qualitative analysis of these characteristics has shown that they are associated with the existence of symmetrical configurations of the fluorine atoms in the  $SF_6$  and  $SiF_4$  molecules. In this connection we have been interested in the experimental detection of changes in the nature of the photoionization absorption as a function of the symmetry of the atomic positions within the molecule. For this reason we have investigated the  $L_{II,III}$  (2p)-absorption spectrum for sulfur in the simple molecular compounds  $SO_2$ ,  $H_2S$ , and  $CS_2$ , rather than the spectrum of sulfur in the compounds  $SO_4^{2-}$  [4] and  $SF_6$  [5].

The  $L_{II,III}$ -absorption spectrum of sulfur was determined using an x-ray spectrometer with a diffraction grating [6]. The x-radiation was detected by the use of a proportional counter filled with methylal. The source of a continuous spectrum was bremsstrahlung from the tungsten anode of an x-ray tube. A similar method of investigating the fine structure of the x-ray absorption spectra of gases has previously been described [7, 8] and consequently we will merely note some characteristics of its use in studying the  $L_{II,III}$ -absorption spectra of sulfur ( $\lambda \approx 60-80 \text{ \AA}$ ). To prevent the possibility of overlapping of the investigated spectral region by short wavelength radiation of higher orders of diffraction we used a focusing mirror covered with polystyrene and placed at a grazing angle of  $3^\circ 10'$  to the incident x-radiation. In such a case practically no radiation of  $\lambda < 50 \text{ \AA}$  enters the spectrometer. The structure of the absorption spectrum was determined with an instrumental energy resolution of  $\Delta E \approx 0.4 \text{ eV}$ . The spectra were recorded at several different pressures of the gas in question, and the differences in spectral absorption coefficients did not exceed 5%. The final averaging of the various measurements is shown in the figure as a graph of absorption coefficient  $\mu$  in arbitrary relative units as a function of the energy of the absorbed quanta  $E$  (in eV). The table shows the energy location of the individual components of the fine structure in the investigated absorption spectra. The precision of these locations is estimated to be  $\pm 0.1 \text{ eV}$ . The energies of the x-ray emission lines used to calibrate the spectrometer were taken from published values [10]. The figure also presents data from additional investigations of  $L_{II,III}$ -spectra of sulfur in the  $SO_4^{2-}$  ion of  $K_2SO_4$  [4] and in the  $SF_6$  molecule [5].

The absorption spectra of sulfur obtained in this investigation exhibit a clearly defined fine structure, in addition to which there is a pronounced increase in the continuous absorption. The appearance of the spectrum indicated that this increase should be considered as due to the  $L_{II,III}$ -edge absorption of sulfur, corresponding to the beginning of photoionization of the 2p-orbital of sulfur in the molecules  $SO_2$ ,  $H_2S$ , and  $CS_2$ . The energy location of these edges is in good agreement with electron spectroscopic measurements of ionization potentials for the 2p-electrons of sulfur in the molecules in question [11]. This can be seen directly from the figure, where the energy location of the  $L_{III}$  (2p  $3/2$ )-ionization threshold of sulfur according to the



$L_{II,III}$ -absorption spectra of sulfur in molecular compounds. Vertical arrows show the ionization threshold of the  $L_{III}$ -orbital of the sulfur atom in these compounds [11]. 1- $CS_2$  ( $D_{\infty h}$ ), 2- $H_2S$  ( $C_{2v}$ ), 3- $SO_2$  ( $C_{2v}$ ), 4- $SO_4^{2-}$  ( $T_d$ ), 5- $SF_6$  ( $O_h$ ).

results of these measurements is indicated by vertical arrows.\* [The  $L_{II}$  (2p  $1/2$ )-ionization threshold of sulfur is located approximately 1.2 eV higher than the  $L_{III}$ -threshold.] The maxima in the fine structure of the investigated absorption spectra of the molecules  $SO_2$ ,  $H_2S$ , and  $CS_2$  occur lower than the previously mentioned ionization thresholds, and consequently they may be regarded as the result of transitions of 2p-electrons of sulfur into a bound excited molecular state. At this time we are unable to elaborate on the nature of these excited states (this will be done in another publication), but we merely note the following interesting experimental fact, which it seems to us has a direct bearing on our further discussions. The spin-doublet splitting of the  $L_{II,III}$ -levels of sulfur, previously given [11, 12] as 1.2 eV is most clearly obtained for the first absorption bands a and b in the spectra

\* We know of no experimental values for the ionization potential of the 2p-electrons of sulfur in  $K_2SO_4$  and consequently as approximate values we chose the average of the values for the ionization potential of 2p-electrons of sulfur in  $SO_2$  and in  $SF_6$ , as previously determined [11].

Table. Energy Location (in eV) of Individual Components in the Fine Structure of  $L_{II, III}$ -Absorption Spectra of Sulfur in the Molecules  $SO_2$ ,  $H_2S$ , and  $CS_2$

| Molecules | Energy location (eV) |       |       |       |       |       |       |       |       |
|-----------|----------------------|-------|-------|-------|-------|-------|-------|-------|-------|
|           | a                    | b     | c     | d     | e     | f     | g     | h     | i     |
| $SO_2$    | 164.9                | 166.1 | 169.5 | 170.4 | 171.5 | 172.9 | 174.3 | 179.0 | 196.2 |
| $H_2S$    | 165.3                | 167.8 | 168.8 | 169.7 | 170.7 | 172.3 | —     | —     | —     |
| $CS_2$    | 163.5                | 164.6 | 166.4 | 167.0 | 167.7 | 168.6 | 169.9 | 171.1 | —     |

of  $SO_2$  (1.2 eV) and  $CS_2$  (1.1 eV). According to the statistical weights of the  $L_{III}$ - and  $L_{II}$ -levels of sulfur, the low energy  $L_{III}$ -component of the spin-doublet should be twice as intense as the high energy  $L_{II}$ -component. In the absorption spectra of the molecules  $SO_2$  and  $CS_2$ , the intensities of the components of the spin-doublet have ratios of the order of 1.5:1, which is close to the theoretical ratio of 2:1, although in the case of  $SF_6$  there is an anomalous intensity ratio: the low energy component of the spin-doublet is less intense than that at high energy. (In the figure this is very clear in the example of the doublet absorption bands A and C [5]. It is of interest that the absorption bands a and A in the spectra of  $H_2S$  and  $SO_2^{2-}$ , respectively, do not exhibit spin-doublet splitting, although these spectra were investigated with an energy resolution sufficient to distinguish the components of the spin-doublet.

Let us now consider simultaneously all the  $L_{II, III}$ -absorption spectra of sulfur shown in the figure for the series of compounds  $SF_6 \rightarrow CS_2$  having various symmetries. (In the figure the symmetry group of each compound is shown in parentheses.) Let us give special attention to the appreciable differences among the structures of the absorption spectra of the compounds in this series. Thus, in  $SF_6$  and  $SO_4^{2-}$  the absorption is in the form of broad bands A-D, which are located at energies up to the ionization threshold of the  $L_{II, III}$ -orbital of the sulfur atom and beyond it. Furthermore, in these spectra in the region of the ionization threshold the ordinary jump in the continuous absorption corresponding to the onset of photoionization of the  $L_{II, III}$ -orbital of the sulfur atom does not occur. In contrast to  $SF_6$  and  $SO_4^{2-}$ , the absorption spectra of the molecules  $H_2S$  and  $CS_2$  show clearly the  $L_{II, III}$ -absorption edge with the subsequent smooth continuum. Discrete absorption, occurring in these molecules only below the ionization threshold, is negligible compared to the background of the continuous  $L_{II, III}$ -absorption of sulfur. The absorption spectrum of the  $SO_2$  molecule is a somewhat intermediate link in this series of spectra under discussion, since it contains simultaneously some of the characteristics of the  $H_2S$  and  $CS_2$  spectra (edge and fine structure before the edge) and of the  $SF_6$  and  $SO_4^{2-}$  spectra (broad absorption bands h and i in the continuum).

At the present time it is difficult to give an exhaustive explanation of the differences observed in the structure of  $L_{II, III}$ -absorption spectra of sulfur, except for a few qualitative ideas. First, it should be noted that the special nature of photoionization absorption in  $SF_6$  and  $SO_4^{2-}$  is not associated with the individual properties of the sulfur atom, since the  $L_{II, III}$ -continuum of sulfur in the  $H_2S$  and  $CS_2$  exhibit no special features. In [1, 3] we came to the same conclusion on the basis of the experimental similarity in the structure of the photoionization absorption of sulfur and fluorine atoms in  $SF_6$ . Thus, an explanation of the characteristics of x-ray photoionization of the sulfur and fluorine atoms in  $SF_6$  requires a search for the special properties of this molecule as compared with  $H_2S$  and  $CS_2$ . It should be noted at once that the differences in symmetry among these molecules are apparently not the basis for the fundamental changes in absorption structure. This is confirmed by the experimental fact that there is an appreciable difference in the structure of the absorption spectra of sulfur in the mole-

cules  $H_2S$  and  $SO_2$ , which have the same symmetry ( $C_{2v}$ ). It is obvious that the nature of the  $L_{II, III}$ -photoabsorption of the sulfur atom is considerably affected by the nature of the other atoms in the molecule. Apparently, discrete absorption in the continuum is observed only for those compounds of sulfur having a strongly electronegative atom like fluorine or oxygen, since the larger these atoms are in the molecule, the more intense is the discrete absorption compared to the background of the continuum ( $SO_2 \rightarrow SF_6$ ). The occurrence in the continuum of intense absorption bands causes a decrease of the continuous absorption in those regions adjacent to these bands. In the case of  $SF_6$  such a redistribution of oscillator strengths in the spectrum leads to a practically complete repression of the continuous absorption in the region of the ionization threshold, i.e., to the absence of any significant absorption edge [2]. We have previously [3] indicated that the observed characteristics of the cross section for photoionization of  $SF_6$  are apparently associated with the resonance phenomena that are possible in the second stage of the photoionization process (the stage of photoelectron ejection from the molecule). If the structure of the continuum is actually caused by the scattering of the photoelectrons by the electronegative atoms, an increase in the number of these atoms must lead to an increased contrast of the absorption bands above the ionization threshold. As stated above, this result was observed in the absorption spectra of sulfur in the series of compounds  $SO_2 \rightarrow SF_6$ .

It is of interest that the absorption of  $SF_6$  at energies up to the ionization threshold, which is markedly different from the absorption of the simple molecules  $SO_2$ ,  $H_2S$ , and  $CS_2$ , in its general character (over-all appearance, large values for the absorption by comparison with the continuous absorption [1], and the anomalous spin-doublet intensity ratio) is quite similar to the  $SF_6$  absorption beyond the ionization threshold. Analogous similarities are also observed in the K-absorption spectra of fluorine in  $SF_6$  [1]. This result indicates, apparently, that the structures of the absorption in  $SF_6$  up to the ionization threshold and that beyond it have a very similar nature, and theoretically both should be explained by a single model based on the observed presence of symmetrical configurations of fluorine atoms in molecules of the  $SF_6$  type.

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