

CROSS SECTIONS OF SULFUR HEXAFLUORIDE PHOTOABSORPTION IN THE SOFT AND ULTRASOFT X-RAY RANGE

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The absorption coefficients of the molecular gas SF_6 were measured in the quantal energy range 60-1800 eV over twenty-five X-ray emission lines. From these results we obtain the photoabsorption cross sections of a single molecule. The results obtained were compared with those of measurements in the vacuum uv and in the region of hard X-rays. It was found that the experimentally obtained total oscillator strength is close to the total number of electrons in the SF_6 molecule in agreement with one of the quantum mechanical summation rules. The properties of the continuous $\text{L}_{II}, \text{III}$ (2p) absorption of sulfur in SF_6 in the ionization threshold region of a given shell are discussed.

The unusual nature of the photoionization absorption near the ionization thresholds of the internal electron shells of atoms in the SF_6 molecule has been pointed out previously [1-3]. In [3] we gave a detailed discussion of the observed characteristics of the photoionization. Since the bonding energies of the $\text{K}(1s)$ -, $\text{L}(2s, 2p)$ -electrons of sulfur and the $\text{K}(1s)$ -electrons of fluorine in the SF_6 molecule are substantially different, we thought it worthwhile to measure the photoabsorption cross sections in the intermediate regions and thus obtain a view of the spectral dependence of the cross section over a large energy interval.

Two x-ray spectrometers, possessing a high effectiveness in various spectral regions ($\lambda = 7-50 \text{ \AA}$ and $20-400 \text{ \AA}$), were used to perform the measurements [4, 5]. The detectors employed were either a proportional counter filled with methylal (dimethoxymethane) or a secondary electronic photomultiplier with a LiF photocathode. The absorption coefficients of SF_6 were measured over twenty-five emission lines and bands in the quantal energy region from 60 eV to 1800 eV and then calculated as photoabsorption cross sections. The methodology of these measurements has been described in detail earlier [6, 7]. The relative precision of the results judging from their reproducibility was about 5% and 10% in the regions of large and small energies of the quanta of radiation absorbed, respectively.

Figure 1 presents a logarithmic plot of the photoabsorption cross section (in Mb) of the SF_6 molecule as a function of the quantal energy of the absorbed radiation (in eV). The results of measurements of the photoabsorption cross sections over the x-ray lines are indicated by circles in the figure and are presented in the table. The interpolation between the circles is indicated by dashed lines while the regions of the fine structure of the L absorption spectrum of sulfur and the K absorption spectrum of fluorine investigated by means of the continuous spectrum of a tungsten anode are shown by the solid lines. In constructing the spectral dependence of the photoabsorption cross sections we also used the results of earlier work [1, 8], which provided the results of photoabsorption in the regions of hard x-rays ($E = 2480-2900 \text{ eV}$) and vacuum uv ($E = 10-32 \text{ eV}$).^{*} The vertical arrows in the figure indicate the positions of the ionization thresholds (absorption edges) of the internal electron shells of the sulfur and fluorine atoms. (The problem of the energy positions of these thresholds was discussed earlier [3]).

It is seen from Fig. 1 that there exist three energy regions where the points representing the spectral dependence of the cross sections of SF_6 photoabsorption fall very well on straight line sections in the logarithmic plot. This allows us to use the following analytical expressions for the energy

dependence of the SF_6 photoabsorption cross section in these energy intervals.^{**}

$$\begin{aligned} \sigma &= 6.1 \cdot 10^3 E^{-1.82} & \text{for } 60 \text{ eV} < E < 170 \text{ eV}, \\ \sigma &= 1.9 \cdot 10^5 E^{-1.33} & \text{for } 280 \text{ eV} < E < 690 \text{ eV}, \\ \sigma &= 1.3 \cdot 10^7 E^{-2.66} & \text{for } 770 \text{ eV} < E < 1800 \text{ eV}. \end{aligned}$$

Let us note that all these functions are substantially different from the E^{-3} dependence characteristic of the spectral dependence of our photoabsorption cross sections in the hard x-ray region [9].

The dotted line in Fig. 1 shows the straight-line extrapolation of our measurements of photoabsorption cross sections into the region of large quantal energies. It can be seen that our results are in good agreement with the results of [1] on the photoabsorption in the K-edge region of the sulfur absorption. Because of the absence of experimental data for SF_6 on the absorption of radiation possessing quantal energies 30-60 eV we use two approximations for this region represented by a straight and broken dotted lines.

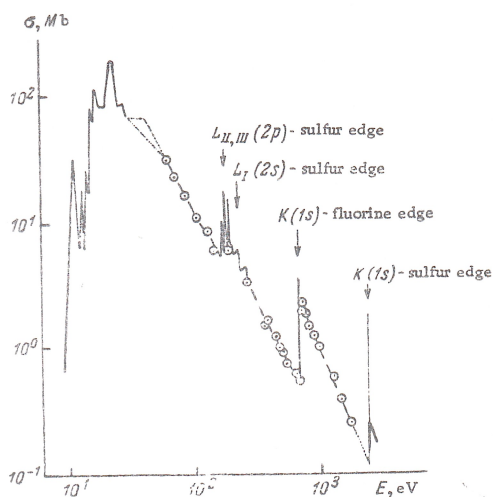
It is known that the photoabsorption cross section is simply related to the spectral density of oscillator strengths ($109.8 \text{ Mb} = 1 \text{ unit of oscillator strength/eV}$) [10]. Hence it is easy to calculate the total oscillator strengths of the SF_6 molecule by determining the area under the curve $\sigma(E)$ over the interval of quantal energies ranging from zero to infinity. According to one of the quantum mechanical summation rules [10], the total strength of the oscillators is equal to the number of electrons of the system absorbing the electromagnetic radiation. (In the SF_6 molecule the total number of electrons is seventy.) Comparison of the experimentally determined total oscillator strength with the theoretical value can be used as a criterion of the precision of photoabsorption measurements over a broad spectral interval. As shown above, the photoabsorption cross section of SF_6 has been measured so far only over the quantal energy interval from 0 eV to 2900 eV. The contribution to the total oscillator strength of the quantal energy region above 2900 eV was estimated by extrapolating the results of 1 to infinity using the E^{-3} dependence. On changing α from 2.5 to 3.5 the oscillator strength corresponding to this spectral interval changed from 3.7 units to 2.3 units of oscillator strength. In calculating the total oscillator strength we assumed the contribution of this interval to be three units of oscillator strength. This value is close to that obtained by extrapolation using the E^{-3} dependence that holds for the hard x-ray region. The total oscillator strength was found to be 64 and 66.5 using two different methods of connecting (straight and broken line, respectively) our results to the uv absorption spectra [8]. Both values are close to the total number of electrons in SF_6 . Taking into consideration the low precision (20%) of photoabsorption cross-section measurements in the vacuum uv, whose contribution to the total oscillator strength is large, we can consider the agreement between the two values to be satisfactory. This at least serves to indicate the sufficient reliability of the experimentally obtained photoabsorption cross sections over a large spectral interval.

^{*}The photoabsorption cross sections of the SF_6 molecule in the vacuum uv region were obtained in [8] as the result of a recalculation of the energy spectrum of inelastically scattered electrons.

^{**} σ is expressed in Mb and E in eV.

Photoabsorption Cross Sections (in Mb) of the SF₆ Molecule

Line	Cs-Nv-OIII	Ba-Nv-OIII	Rb-M _α	Sr-M _α	Y-M _α	Zr-M _α	Mo-M _α	C-K _α	N-K _α	Ti-L _α	Ti-L _β	Cr-L _α	O-K _α	C-L _α	Mn-L _α	Co-L _α	Fe-L _α	Ni-L _α	Co-L _β	Ni-L _β	Cu-L _α	Zn-L _α	Mg-K _α	Al-K _α	W-M _α
Energy, eV	65.2	75.3	96.4	114.3	132.8	151.1	192.6	277.0	392.4	395.3	452.2	500.3	524.9	572.8	637.4	677.8	705.0	742.7	776.2	851.5	929.7	1011.7	1253.6	1486.5	1774.0
Photoabsorption Cross section, Mb	31	24	16	11	8.3	6.0	5.9	3.3	1.6	1.6	1.2	0.98	0.91	0.74	0.60	0.53	1.8	2.1	1.8	1.4	1.2	1.0	0.57	0.38	0.25

Fig. 1. A logarithmic plot of the spectral dependence of the photoabsorption cross section σ of SF₆.

The circles represent the results of our measurements over the x-ray lines. The vertical arrows indicate the positions of the ionization thresholds (absorption edges) of the internal electron shells of the sulfur and fluorine atoms in SF₆.

Figure 2 shows the fine structure of the SF₆ absorption in the L_{II,III}-ionization threshold region (full line) of the sulfur atom according to the results of [2]. In this spectral region, the total photoabsorption cross section of the molecule consists of two parts, corresponding to the photoionization absorption of the outer electron shells of the molecule and the L_{II,III} shell of the sulfur atom. According to our measurements the energy dependence of the photoabsorption cross-section of the outer electron shells of the SF₆ molecule in the spectral region before the L_{II,III} absorption edge of sulfur can be well approximated by the analytical expression $\sigma = 6 \cdot 10^4 E^{-1.82}$. The extrapolation of our results in the region of the L_{II,III} absorption edge of sulfur shown in Fig. 2 by the dashed line allows us to extract from the total photoabsorption cross section of the molecule, the contribution of the L_{II,III} shell of the sulfur atom (area between the full and dashed lines). Let us now remark on some of the peculiarities of the L_{II,III} absorption of sulfur in the SF₆ molecule discussed earlier in [2, 3]. Experimentally [11] the ionization threshold of the L_{III} shell of the sulfur atom in SF₆ occurs at the energy $E_{L_{III}} = 180.4$ eV (the position is indicated by an arrow in Fig. 2).^{*} It is interesting to note that in the region of the foregoing ionization threshold there occur, instead of a characteristic jump of continuous absorption

^{*}The L_{II} threshold of sulfur atom ionization in SF₆ occurs at 1.2 eV higher than the L_{III} threshold [11].

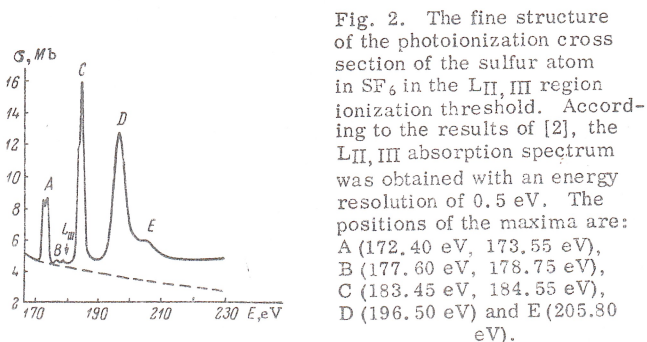


Fig. 2. The fine structure of the photoionization cross section of the sulfur atom in SF₆ in the L_{II,III} region ionization threshold. According to the results of [2], the L_{II,III} absorption spectrum was obtained with an energy resolution of 0.5 eV. The positions of the maxima are: A (172.40 eV, 173.55 eV), B (177.60 eV, 178.75 eV), C (183.45 eV, 184.55 eV), D (196.50 eV) and E (205.80 eV).

corresponding to the beginning of photoionization of the L_{II,III} shell of the sulfur atom, two relatively narrow absorption bands C and D. ** The continuous L_{II,III} absorption of sulfur is small in the region of the ionization threshold and becomes appreciable only at a distance of 30 eV higher than the threshold. Furthermore, the maximum level of the continuous absorption (above the fine structure region) is considerably weaker than the C and D bands.

One of the possible reasons for the appearance of discrete absorption in the L_{II,III} continuum of the sulfur atom are two-electron transitions. In this case it would be natural to relate the C, D, and E absorption bands in the L_{II,III} spectrum of the sulfur atom to the processes of simultaneous photoexcitation of 2p electrons of the sulfur atom and the valence electrons of the SF₆ molecule. However, the experimental results do not provide evidence in favor of such a mechanism. Indeed, the C and D resonance maxima in the L_{II,III} absorption spectrum of sulfur are much more intense than the A and B peaks that can be naturally considered to be the result of photoexcitation only of the 2p electrons of sulfur, in opposition to the results of [12, 13], where it was found that two-electron transitions were considerably less intense than one-electron transitions in the case of x-ray photoionization of rare gas atoms.

At present the reason for the peculiarities in the L_{II,III} absorption of the sulfur atom in the SF₆ molecule noted above has not been clarified. However, our new experimental results that will be published soon indicate that the resonance absorption in the L_{II,III} continuum of the sulfur atom is determined by the scattering of x-ray photoelectrons by the electronegative fluorine atoms that form in SF₆ a highly symmetrical configuration.

**In considering the L_{II,III} absorption spectrum of sulfur it must be kept in mind that each band is the result of two overlapping bands corresponding to the L_{III} (2p_{3/2}) and L_{II} (2p_{1/2}) absorptions of the sulfur atom. The spin-doublet splitting of the L_{III} and L_{II} levels of sulfur are clearly manifest in the first three absorption bands A, B, and C.

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REFERENCES

1. R.E. LaVilla and R.D. Deslattes, *J. Chem. Phys.* **44**, 4399 (1966).
2. T.M. Zimkina and V.A. Fomichev, *Dokl. Akad. Nauk SSSR* **169**, 1304 (1966) [*Sov. Phys. Dokl.* **11**, 726 (1967)].
3. A.S. Vinogradov, T.M. Zimkina and V.A. Fomichev, *Zh. Strukt. Kim.* **12**, 899 (1971).
4. A.P. Lukirskii, N.A. Brytov and N.I. Komyak, in *Instrumentation and Methods of X-ray Analysis* (Special Design Office for Radio Activity, Leningrad, 1967), No. 2, p. 4.
5. A.P. Lukirskii, *Izv. Akad. Nauk SSSR, ser. fiz.* **25**, 913 (1963).
6. A.P. Lukirskii and T.M. Zimkina, *Izv. Akad. Nauk SSSR* **27**, 817 (1963).
7. A.P. Lukirskii, I.A. Brytov and T.M. Zimkina, *Opt. Spektrosk.* **17**, 438 (1964) [*Opt. Spectrosc.* **17**, 234 (1964)].
8. T.A. Simpson, C.E. Kuyatt and S.R. Mielczarek, *J. Chem. Phys.* **44**, 4403 (1966).
9. M.A. Blokhin, *The Physics of X-Rays* (State Press for Theoretical-Technical Literature, Moscow, 1957), p. 154.
10. U. Fano and J.W. Cooper, *Rev. Mod. Phys.* **40**, 441 (1968).
11. K. Siegbahn, C. Nordling, et al., *ESCA Applied to Free Molecules* (North-Holland, Amsterdam, 1969).
12. H.W. Schnopper, *Phys. Rev.* **131**, 2558 (1963).
13. C. Bonnelle and F. Willeumier, *Compt. Rend.* **B256**, 5106 (1963); F. Willeumier, *Compt. Rend.* **B263**, 450 (1966).

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INTRAMOLECULAR INTERACTIONS AND VIBRONIC SPECTRA OF POLYATOMIC MOLECULES. I: ELECTRONIC REARRANGEMENTS AND THE FOUR LEVEL SCHEME OF ELECTRONIC STATES

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The electronic relaxations that connect the Franck-Condon and stationary states of a polyatomic molecule and that have been called electronic rearrangements have been examined. The competition between electronic rearrangements and other types of electronic relaxation: Kasha conversion from higher excited states, internal and intercombination conversions, and also dissociation and ionization of the molecules, has been noted. The suggestions previously put forward by the author regarding the relaxation spectra and the four-level scheme of electronic states necessary for the description of a number of polyatomic molecules have been confirmed. The need to use a four-level scheme has been demonstrated in an examination of work carried out by a number of authors in recent years.

1. We previously showed [1] that the properties of the electronic states of a polyatomic molecule, in particular the positions of its electronic levels, should in the most general case depend on the excitation state of the molecule. This is illustrated in Fig. 1a which gives the systems of levels M_I for a molecule in the ground electronic state (I) and M_{II} for the molecule in the first excited state (II^*). Highly excited states (I^{**} , I^{***} , II^{**} , etc.) are usually not realized as stationary states (relative to the probabilities of optical transitions) but are usually transformed into luminescent molecules in the first excited states (I^* , II^*) or into non-luminescent molecules in the normal states (I, II), with conversion of the electronic excitation energy, partly or completely, respectively, into vibrational energy.¹ This fact, which for luminescent molecules is known as Kasha's rule [2], was studied [3] not only from the spectra but also from other processes associated with the transformation of the vibrational energy of the excited molecule.

For fluorescent molecules these features lead to the scheme of four-electron levels in Fig. 1a in contrast to the usually adopted two-level scheme in Fig. 1b that is borrowed from the theory of the spectra of diatomic molecules and that

represents a particular case of the four-level scheme, realized under certain conditions.

According to [1], for the four-level scheme in Fig. 1a, the absorption of a quantum ($I \rightarrow I^*$) transfers the molecule from the stationary ground state (I) to the Franck-Condon excited electronic state I^* , which is nonstationary as a consequence of the lack of correspondence between the structure of the valence electron shell resulting from the electronic transition and the preserved nuclear configuration of the molecule. This is followed by relaxation of the molecule,

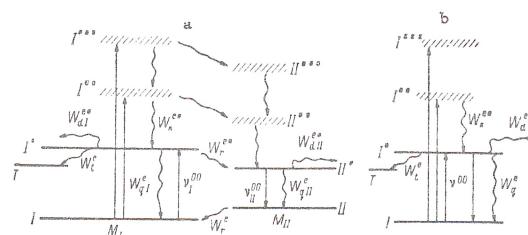


Fig. 1. Four-level (a) and two-level (b) schemes for the electronic levels of molecules.

The wavy arrows in (a) show the possible electronic relaxations associated with the state I^* .

¹It has recently been possible, as a consequence of an increase in the sensitivity of the apparatus, to observe optical transitions with emission from higher electronic excited states, competing with rapid nonradiative transitions.