ABSORPTION SPECTRUM OF SULFUR HEXAFLUORIDE IN THE ULTRASOFT X-RAY REGION

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Abstract

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T. M. ZIMKINA, V. A. FOMICHEV

ABSORPTION SPECTRUM OF SULFUR HEXAFLUORIDE IN THE ULTRASOFT X-RAY REGION

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In this work the absorption spectrum of SF_6 gas has been obtained in the region of the sulfur L_{II-III} absorption edge. The experimental results are of interest, on the one hand, for elucidating the nature of the selective maxima in the edge region and their relation to the energy structure of the molecule, and, on the other hand, from the standpoint of the theory of photoionization absorption and the applicability of the x-ray absorption laws in the ultrasoft x-ray region. The work employed the method for studying gas absorption coefficients described in earlier papers ([1,2]). The gas pressure in the chamber was chosen to be (4.5 ± 0.5) mm Hg, which ensured a maximum transmission of about 30%. The entire spectral region from 41 to 73 Å was investigated with an instrumental broadening $\Delta\lambda = 0.2$ Å; the fine-structure region was obtained with $\Delta\lambda = 0.1$ Å. In the first case the energy resolution of the instrument was 0.5 eV in the region of the first maximum, and in the second case, correspondingly, 0.25 eV. The error in the absolute values of the absorption coefficients is estimated at 10%. The absorption coefficients are given in inverse centimeters and reduced to normal pressure and a temperature of 0°.

The results are presented in Fig. 1 as a curve of the dependence of the absorption coefficients of SF_6 on energy in the range from 170 to 300 eV.

The first three absorption bands, obtained with the best energy resolution, are shown in Fig. 2 on an enlarged energy scale.

According to Skinner' s data ([3]), the sulfur L_{II}- and L_{III}-levels have energies of 164.8 and 163.6 eV, respectively; therefore the absorption spectrum of SF_6 was studied beginning at 150 eV. However, in the region from 150 to 170 eV a monotonic dependence of the absorption coefficient on energy is observed, and therefore this region is not shown in Fig. 1.

As can be seen from Fig. 1, the absorption spectrum of SF_6 has a form unusual for an x-ray absorption edge. It consists of four distinct absorption bands, the first two bands having a doublet structure. Between the first and second

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

intense absorption bands one can distinguish two additional weak maxima C and D, as well as a maximum H on the high-energy side of the third band. The fine-structure region has an anomalously large extent of 70 eV and cannot be represented as a Rydberg series of excited states, either in intensity, in shape, or in the mutual energy positions of the bands. There is also no clearly expressed absorption edge, which is usually the limit of a Rydberg series.

The absence of experimental data on the ultraviolet absorption spectrum of SF_6 (the ionization potential of the molecule is 19.3 eV ([4])) and of theoretical calculations of the electronic structure of the molecule limits the possibility of interpreting the results obtained. At the same time, from the experimental curves in Fig. 2 it is easy to see that the distances between the maxima A and B, C and D, E and F are respectively 1.15, 1.15, and 1.10 eV, which

very close to the spin-doublet splitting of the sulfur L_{II}- and L_{III}-levels, which is equal to 1.2 eV according to the data of Ref. ([3]).

Consequently, the doublet character of the maxima is caused by electron transitions from the sulfur L_{II}- and L_{III}-levels. The first absorption band is well

Fig. 1. Absorption spectrum of SF_6 in the wavelength region from 41 to 73 Å. Three points on the curve correspond to the values of μ measured on the characteristic lines B (67.6 Å), Mo (64.4 Å), and C (44.7 Å).

resolved into two Gaussian curves (in Fig. 2 they are shown as thin lines), whose width at half height is 0.9 eV for maximum A and 1.2 eV for maximum B. The shape of the second absorption band does not correspond to the superposition of two Gaussian curves; it is possible only approximately to resolve this band into two Gaussian curves, and their width proves

Fig. 2. Region of the fine structure of the SF_6 absorption spectrum on an enlarged energy scale. Thin lines show the curves into which the first and second bands are resolved; on the horizontal lines the widths of these curves at half height and the energy positions of the maxima are indicated. E_{ap} denotes the quantities of the instrumental resolution on the scale of the curve.

to be the same as in the case of the first band. Hence it may be assumed that the first and second electronic levels of the excited SF_6 molecule have the same width.

It is important to note the anomalous ratio of the intensities of maxima A and B and of maxima E and F, if one assumes that

maxima A and E are due to absorption by electrons of the L_{III} level, and B and F by electrons of the L_{II} level. Since the statistical weight of the $L_{III}(2p_{3/2})$ level is twice the statistical weight of $L_{II}(2p_{1/2})$, the maxima A and E should be twice as intense as the maxima B and F. Experimentally, the ratios $I_B/I_A = 1.25$ and $I_F/I_E = 1.6$ were found.

The third intense absorption band G differs from the first two. It is considerably broader and has an asymmetric, unsplit form. From its energy position, the fourth band K could be associated with ionization of the sulfur $L_I(2s^2)$ level, which is separated from the L_{III} level by approximately 60 eV ([3]). It is very likely that the peculiar nature of the absorption spectrum obtained for SF_6 is explained not only by the energy structure of the molecule, which has octahedral symmetry, but also by the character of photoionization absorption, since in the ultrasoft X-ray region the X-ray absorption laws derived on the basis of hydrogen-like wave functions are violated ([5-7]).

Leningrad State University
named after A. A. Zhdanov

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Note: Figure translations are in progress. See original paper for figures.