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FEATURES OF INNER ATOMIC SHELL PHOTOIONIZATION IN MOLECULES

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Résumé. — Les caractéristiques expérimentales suivantes des spectres d'absorption moléculaires dans le domaine des rayons X ultra mous [1], [2] sont discutées :

1. Existence de maximums d'absorption intenses dans le continuum, du côté des hautes énergies par rapport aux limites d'ionisation des couches internes des atomes dans les molécules.
2. Similitude de la structure fine du spectre K (1 s) du fluor et du spectre L (2 p) du soufre en ce qui concerne le nombre de maximums et leur position en énergie par rapport à la limite d'ionisation dans la molécule SF_6 .
3. Absence d'augmentation rapide du coefficient d'absorption à la limite d'ionisation des couches internes de l'atome central entouré d'atomes électronégatifs dans des molécules hautement symétriques (SF_6 , SiF_4 , etc...).

[1] ZIMKINA (T. M.), FOMICHEV (V. A.), *Dokladi ANSSSR*, 1966, **169**, 1304.

[2] ZIMKINA (T. M.), VINOGRADOV (A. S.), « X-ray spectra and electronic structure of matter » II, I. M. F. AN USSR, Kiev, 1969.

Abstract. — The following experimental features of ultra-soft X-ray absorption molecular spectra [1], [2] are discussed :

1. Existence of strong absorption maxima on the high energy side of ionization thresholds (in continuum) of inner shells of atoms in molecules.
2. Similarity of the fine structure of K (1 s) spectrum of fluorine and L (2 p) spectrum of sulphur in the number of maxima and their energy position with respect to ionization threshold in molecule SF_6 .
3. Absence of sharp rise in absorption coefficient at the ionization threshold of inner shells of the central atom surrounded by electronegative atoms in high symmetrical molecules (SF_6 , SiF_4 and others).

[1] ZIMKINA (T. M.), FOMICHEV (V. A.), *Dokladi ANSSSR*, 1966, **169**, 1304.

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At present we have studied the ultrasoft X-ray absorption spectra of several complex inorganic molecules (SF_6 , SiF_4 , $SiCl_4$, BF_3 , BCl_3 , NF_3 and the others). All these spectra show a large difference of the fine structure near the absorption edges of the inner atomic shells from the well known fine structure of X-ray spectra of atoms and simple molecules. The latter consists of several discrete lines lying before the absorption edge and their intensity and energy separation decrease rapidly with approach to the edge. The appearance of these lines in X-ray absorption spectra is attributed to the exciton mechanism. If the electron ejected from the inner shell moves in a Coulomb field the lines of the fine structure can be represented as a Rydberg series of absorption lines.

One of the specific feature of the ultrasoft X-ray absorption spectra of molecules consists in existence of several strong absorption lines extending over 10-20 eV. Some of these discrete lines were found to be behind the absorption edge in continuum. The fine structure in these spectra cannot be attributed to transition of inner atomic electrons to a Rydberg series of excited states neither in intensity nor in the

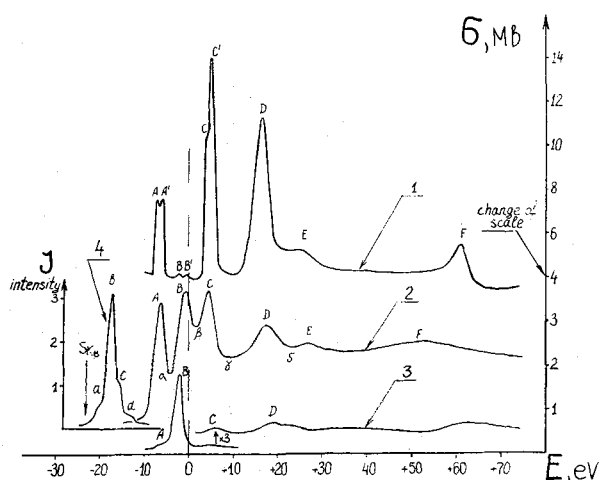
energy position before the ionization threshold. Therefore the hydrogenic model cannot be used to interpret the ultrasoft molecular spectra.

The second feature consists of absence of any detectable jump ratio at the ionization thresholds of the inner electrons of central atom in symmetrical molecules (SF_6 , SiF_4 , $SiCl_4$, BF_3 , NF_3 , BCl_3). Let's consider for a example the ultrasoft X-ray absorption spectra of SF_6 molecule.

It is known, the X-ray absorption spectra of sulphur in SF_6 have unusual fine structure near the K and the $L_{II,III}$ absorption edges [1], [2]. Recently the K fluorine absorption spectrum in this molecule has been studied [3].

Besides, the energy of 1 s fluorine and 2 p sulphur atomic levels in SF_6 molecule have been measured by photoelectron spectrometry [4]. Using these data we can compare the sulphur and fluorine spectra in the same energy scale and receive the additional information about the nature of the fine structure of SF_6 absorption spectra.

The X-ray absorption spectra of SF_6 are shown in figure 1. The first curve is the $L_{II,III}$ -sulphur spectrum,

FIG. 1. — X-ray spectra of SF₆.

- 1 $L_{II,III}$ -absorption spectrum of S [2].
- 2 K -absorption spectrum of F.
- 3 K -absorption spectrum of S [1].
- 4 K -emission spectrum of F [5].

the second one is the K -fluorine spectrum, the third is the K sulphur spectrum. Besides the K emission spectrum of fluorine [5] is shown.

The sulphur absorption spectra were matched using the energy of K_{α_1} emission line (2 309,4 eV) and to match the K fluorine absorption spectrum with them we use the energy difference between the K fluorine and L_{III} sulphur energy levels which were measured in Sweden (694,6 and 180,4 eV accordingly). The position of the ionization threshold was obtained by adding the ionization potential of π -fluorine electrons to the position of the maximum of K emission band of fluorine in SF₆. This position is shown by dotted line in figure 1 and it is used as a zero at the energy scale.

An important feature of these spectra is the similarity of K fluorine and $L_{II,III}$ sulphur fine structure. They have the same number of maxima and the same energy intervals between them. It should be noticed that F maximum on the first curve corresponds to the L_I absorption edge of sulphur.

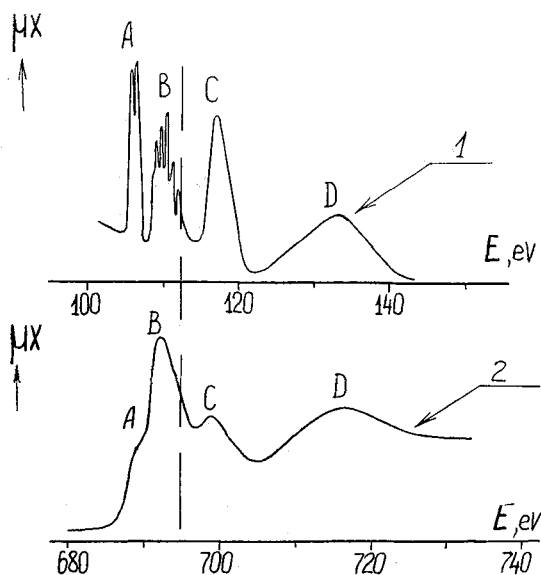
All features of the fine structure are present also in the K absorption spectrum of sulphur, but only B maximum has considerable intensity. The others maxima look rather like weak fluctuations.

From observed similarity of the spectra it can be concluded that discrete structure in these spectra are due to transitions of electrons from inner atomic levels of sulphur and fluorine to some common system of excited states. The experimental fact is that the energy position of excited states with respect to ionization potentials are independent of the vacancy position to within about 1 eV. It seems reasonable that such common system of excited states can be treated as unoccupied molecular orbitals of SF₆ molecule. In accordance with MO model SF₆ molecule has four unoccupied orbitals $a_{1g}^{(3s)}$, $t_{1u}^{(3p)}$, $e_g^{(3d)}$ and $t_{2g}^{(3d)}$. Baranovsky [6] and Nefedov [7] gave the inter-

pretation of the $L_{II,III}$ sulphur spectrum of SF₆ in the framework of idea of transition of 2 p sulphur electrons to unoccupied molecular orbitals.

On the base of experimental data and rough estimation Nefedov has shown that three maxima A, B and C correspond to transitions of 2 p sulphur electrons to a_{1g} , t_{1u} and $e_g + t_{2g}$ free molecular orbitals accordingly. (The energy separation of e_g and t_{2g} orbitals is found to be small). He was unable to explain the nature of two other maxima D and E in this spectrum. Similar interpretation we can attribute them to transition of 1 s fluorine electrons to the above mentioned molecular orbitals. Difference in relative intensity of these maxima in the sulphur and fluorine spectrum may be related to the change of the selection rules for the electron transitions from fluorine atoms. It may be due to the reduction of local symmetry for fluorine atoms (C_{4v}) in SF₆ molecule in comparison with that for sulphur atom in SF₆ (Oh). Let's note, however, that in this spectrum there are also two lines D and E which remain unexplained. So we can conclude, that MO method does not suffice to account for all the observed structure of X-ray absorption spectra of SF₆. This will be especially clear when we consider the second interesting feature of these spectra, the existence of strong discrete absorption lines in continuum. We can see three lines behind the ionization threshold in figure 1. Nefedov has assumed [8] that there was a potential barrier for the electrons ejected from sulphur atom. The absence of any detectable jump ratio at the threshold for 2 p sulphur electrons and existence of discrete lines in continuum in $L_{II,III}$ sulphur spectrum may be ascribed to the effect of the positive barrier in effective potential. However, new results show that the same absorption maxima in continuum are observed in K spectrum of fluorine atoms. Besides in K fluorine spectrum there is a noticeable increase of absorption in the region of ionization threshold. It means that the inner shell 1 s (K) threshold in fluorine spectrum has a jump ratio larger than 1. These new results can not be explained by the effect of the potential barrier acting on the electron after the absorption process. Thus the calculation of photoionization cross sections will be required to give a proper interpretation of the spectra near the inner atomic shell thresholds. In this connection, it was interesting to study the X-ray absorption spectra of the other similar molecules.

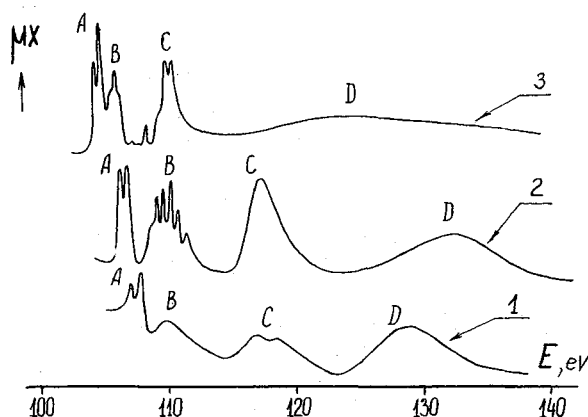
The $L_{II,III}$ silicon and K fluorine absorption spectra of SiF₄ have been investigated. They are shown in figure 2. Absorption coefficients are given in arbitrary units. The both spectra consist of four main lines and energy intervals between them are almost the same. On the base of the above analysis of absorption spectra of SF₆ we match two spectra of SiF₄, so that the position of the four lines in the $L_{II,III}$ silicon and K fluorine spectrum would coincide. Unfortunately, we don't know the 2 p silicon and 1 s fluorine ionization potentials to match these spectra without ambiguity.

FIG. 2. — X-ray absorption spectra of SiF_4 .

- 1 $L_{\text{II,III}}$ -spectrum of Si.
- 2 K-spectrum of F.

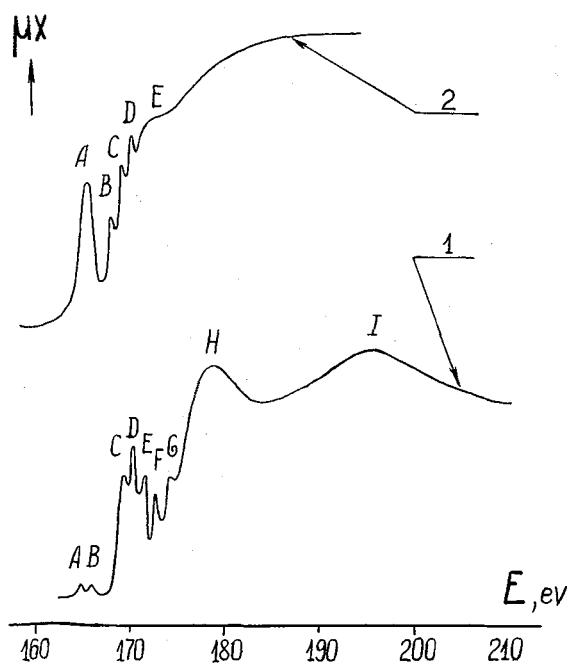
The rough estimation of the 1 s (K) fluorine ionization potential has been done using the energy position of K fluorine emission band maxima in several molecular compounds [5] and the ionization potentials of the valence molecular orbitals of SiF_4 [10]. The position of the threshold according to this estimation is shown in figure 2 by a vertical line. If the maxima in silicon and fluorine spectra are due to the electron transitions to some common excited states we can conclude that this line marks the position of the 2 p ($L_{\text{II,III}}$) silicon ionization potential too. As we can see, there is essential difference in the shape of maxima lying before and beyond the ionization threshold in the $L_{\text{II,III}}$ silicon spectrum. This fact confirms the shown position of the threshold. From comparison of the SF_6 spectra and SiF_4 spectra it can be found that there are common features in spectral behaviour of inner atomic shell photo-ionization cross sections in SF_6 and SiF_4 . One of such common features consists in the fact that both the central atom and the atom from the surrounding show the same picture of the absorption spectrum with several discrete lines in the continuum.

The second one consists of absence of any detectable jump ratio at the threshold for ionization of the inner electrons of central atom in symmetrical molecules. In figure 3 the $L_{\text{II,III}}$ silicon absorption spectra of SiCl_4 , SiF_4 and $[\text{SiF}_6]^{-2}$ are shown. It can be seen that in spite of different symmetry of molecules the $L_{\text{II,III}}$ silicon spectra of SiF_4 and $[\text{SiF}_6]^{-2}$ are similar in a number of maxima and their energy position. On the other side, the $L_{\text{II,III}}$ silicon spectra of SiCl_4 and SiF_4 molecules with the same symmetry but different kind of surrounding atoms show the large difference in the energy extension of the fine structure and in the shape and width of the maxima. It is clear that the first difference arises from smaller value of effective

FIG. 3. — $L_{\text{II,III}}$ -absorption spectra of Si in $(\text{SiF}_6)^{-2}$ /curve 1 [7], SiF_4 /curve 2/, SiCl_4 /curve 3[9].

charge of silicon atom in SiCl_4 than that in SiF_4 . But it is difficult to understand the difference in the shape of the second line in these spectra, because the second line in $L_{\text{II,III}}$ silicon spectrum of SiF_4 has a complex structure and it may be formed from three close doublet lines. The consideration of the fine structure on the base of MO model applies also to the SiF_4 spectra but in this case the MO model can not account for all the features of these spectra.

It is necessary to analyse theoretically the absorption process in symmetrical molecule and estimate the role of neighbouring atoms and symmetry of molecule. From experimental results it follows that, these factors may be very important. Indeed, let's consider the $L_{\text{II,III}}$ sulphur spectra in the simple molecules of H_2S and SO_2 . In figure 4 the first curve is the $L_{\text{II,III}}$ sulphur spectrum of SO_2 and the second is the same spectrum of H_2S . As we can see, the fine structure of these

FIG. 4. — $L_{\text{II,III}}$ -absorption spectra of S in SO_2 /curve 1, H_2S /curve 2.

spectra differs strongly from the structure of the $L_{II,III}$ sulphur spectrum of SF_6 . In these spectra there is clear absorption edge and the oscillator strength of the continuum is many times as large as the oscillator strength of the discrete states. It is interesting to note, that in continuum of SO_2 two broad maxima are observed, but the continuum of H_2S is the smooth curve.

A possible explanation of these maxima is the influence of oxygen atoms on the behaviour of sulphur photoelectrons.

We have studied the other molecular absorption spectra in the ultra-soft X-ray region, for example NF_3 , BF_3 , BCl_3 and the others. They show also some specific features which can not be explained using the hydrogenlike exciton or MO model.

In conclusion we would like to express the hope that new experiments in investigation of the ultrasoft X-ray absorption spectra will attract the attention of the theorists and that they will add to the progress in this field.

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