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THE FEATURES OF PHOTOIONIZATION ABSORPTION IN THE ULTRASOFT X-RAY REGION

T. M. ZIMKINA and S. A. GRIBOVSKII
Leningrad State University

Abstract. — The following results of the experimental and theoretical investigations of the spectral behavior of the photoionization cross sections in the ultrasoft X-ray region are discussed:

1. The notable departure from hydrogen-like behaviour of the atomic photoionization cross sections of the inert gases Ar, Kr and Xe;
2. Similarity of the gross features of absorption spectra both gases and solids;
3. Spectral behavior of absorption coefficients of Au and Bi, rare-earth metals, transition metals from Zr to Pd, and from Ti to Ni and from Ta to Au.

For the past 10 years a great progress has been achieved in the ultrasoft X-ray absorption spectroscopy due to essential development of experimental techniques and especially due to extensive application of synchrotron radiation for the study of absorption spectra.

The absolute cross sections for the photoionization process are very important parameters in many fields of physics. However until recently there was no data on absorption cross sections in the intermediate range of energies between ultra-violet and X-ray regions of spectrum. Semiempirical determination of absorption coefficients in this ultrasoft X-ray region was based on extrapolation to lower photon energies of the hydrogen-like behavior observed in the X-ray region. On the other hand there was no evidence that the hydrogen-like model of photoionization was adequate in the ultrasoft X-ray region. Therefore the experimental and theoretical studies of photoionization cross sections in this region of spectrum attracted the attention of many physicists in different countries and caused great interest among them.

First of the ultrasoft X-ray absorption spectra of the five noble gases He, Ne, Ar, Kr and Xe have been investigated systematically. Review of the measured and calculated cross sections of the atomic gases from the ionization onset to the X-ray region was made by Lukirskii, Brytov and Zimkina [6]. Instead of monotonic decreasing behavior above the 3-d ionization threshold we can observe the increase of the absorption cross section beyond the threshold. The cross section reaches the maximum at 100 eV from the absorption edge.

In the spectrum of Xe, which is shown in figure 2, two maxima were observed in the photon energy range of 50-500 eV [6]. The first striking maximum is very strong and comparatively narrow (above 50 eV). It lies at 33 eV above the 4-d threshold. The second maximum is very broad and low. It lies at about 250 eV above the threshold.

Such unusual behavior of photoionization cross sections of the inert gases has shown distinctly that hydrogen-like model of photoionization breaks down in the intermediate range of energies. As Fano [2] has indicated this was not unexpected because the photons with low energies are absorbed by electrons in the outer portions of the atom where the average field...
differs strongly from the Coulomb field in the hydrogen atom and the effects of the electron correlation are of importance in absorption.

Several theoretical studies have been undertaken to explain the experimental results, each using different assumptions and approximations. Cooper and Manson used the single-electron model with the realistic Herman-Skillman potential for calculation of the photoionization cross sections of a number of atomic shells [7]-[9].

The main features in the spectral shape of the cross sections were correctly predicted by this model. It was shown, that the large maxima in the ultrasoft X-ray absorption spectra are due to the spectral behavior of the partial cross sections. According to the calculation the broad maximum in the spectrum of Kr is due to the $\,^3\!d_{-\epsilon},\,^\text{ef}$ transition $(*),$ and both maxima in the spectrum of Xe arise from the $\,^4\!d_{-\epsilon},\,^\text{af}$ transition.

The notable departure of the spectral behavior of the partial cross sections from hydrogen-like one appears owing to non-Coulomb character of the effective potentials, especially due to the centrifugal potential acting on the electron after the absorption process. As Fano and Cooper have shown [2] the principal effects are the depression of absorption near the threshold and the occurrence of quasi-resonances near the threshold.

In the spectrum of Kr we can see so called by Fano and Cooper «delayed edge» arising above the $\,^3\!d$ threshold, when the energy increases to the value that permits the escaping electron to pass over the potential barrier. In the spectrum of Xe we can see the «resonance near threshold» which reveals in the strong narrow maximum near the $\,^4\!d$ threshold.

The detailed analysis of the spectral behavior of the partial cross sections for different atomic subshells will be given in the next report by Combat Farnoux.

Therefore the independent electron theory based on the Herman-Skillman local potential gives a reasonable estimate of the spectral behavior of the atomic cross sections. At the same time there is a considerable quantitative disagreement between the experimental and calculated data. This disagreement downgrades the significance of the calculations based on this theory.

In figure 3 the calculated cross section for the $\,^4\!d$ subshell of Xe [8] is compared with the cross sections of Xe measured by Ederer [3]. The dash line is the calculated curve and the black points are the experimental data. The amplitude, width and energy position of the maximum in the theoretical curve differ from the experimental one significantly.

Detailed discussion of such disagreement has been given by Fano and Cooper [2]. They have indicated, that the effects of electron-electron correlation should be taken into account to explain the experimental cross sections.

Starting from the single-electron model with Herman-Skillman potential Fano and Cooper have
shown qualitatively that the correlations among the electrons of the absorbing shell (intrachannel interaction) have a major influence on the gross spectral shape of the cross sections [2]. Quite recently we have learned that Starace [10] has calculated the cross sections for the 3p shell of Ar and the 4d shell of Xe using the method, suggested by Fano and Cooper. As far as we know the calculation of the cross sections with inclusion of intrachannel interaction improves significantly the quantitative agreement between the calculated and experimental data.

The contemporary apparatus of many-body theory has been used by Brandt, Eder and Lundqvist [11] and by Amusia, Cherepkov and Sheftel [13] for the calculation of the photoionization atomic cross sections. They proceed from the assumption that the behaviour of all shells of atoms with \( Z \geq 1 \) is similar to the behaviour of high density electron gas in the sense that in both cases the leading correlation terms are the same. Using this plasma-like theory Brandt et al. [11] have obtained a very good agreement between the experimental and theoretical results for the 4d subshell cross section of Xe. As we can see in figure 3 their calculated curve (solid line) coincides with measured cross sections. At the same time this good agreement has been achieved by specially fitted parameters.

The first work of Amusia et al. [12] on the calculation of the 4d cross sections of Xe gave qualitative picture because of a rough assumption about the many electron interaction and a determination of coupling constant through a fitting procedure. However this was only the beginning of research being carried out at A. F. Ioffe Physico-Technical Institute in Leningrad by Amusia and his co-workers. Now they have achieved a great progress in the calculation of the atomic cross sections by using the high density gas theory. They start with calculations in the Hartree-Fock approximation and take many-electron correlations into account by a random phase approximation with exchange (RPAE) [13]. We can’t discuss their method of calculation in detail but we can demonstrate the results of the calculation of the photoabsorption cross sections for the noble gases Ar and Xe by this method.

In figure 4 (courtesy of Amusia) the calculated and experimental data for Ar are shown. It may be seen that within the range of 10% the experimental and theoretical cross sections coincide everywhere except at the region of 5 eV near the threshold. Agreement of theory and experiment was obtained for all gases.

In figure 5 (courtesy of Amusia) the calculated cross sections for Xe are compared with experimental data of Ederer [3]. In this case also the experimental and calculated cross sections coincide everywhere except at the region near the threshold.

Such excellent agreement between the theory and experiment (without a fitting procedure) is a striking result. Now Amusia requires the experimentalists to increase the experimental accuracy in the measurement of the cross sections for the noble gases. From the theoretical investigation into the photoionization process at low energies Amusia has suggested the following conclusion: the photoionization process is entirely collective. All electrons of at least the ionized subshell take part in it. Therefore, Fano and Amusia proceeding from different points of view have proved that the electron-electron interaction among the electrons of the absorbing shell must be included into the calculation of the atomic cross sections.

Besides the mentioned above theoretical studies we should draw your attention to the work of McGuire [14], who has calculated the absorption cross section for all subshells of atoms from He to Xe. He has developed the exact solution to the Schrödinger equation with a central potential more complicated than that in the hydrogen-like model. Using some parameters for the approximation of the poten-
tial McGuire has succeeded in receiving a rather good agreement between calculated and measured cross sections.

![Graph of Xe cross sections](image)

**Fig. 5.** Cross sections for Xe
- experimental data [3],
- the calculated curve by RPAE [13].

Thus, the significance of the studies of photoionization cross sections in the ultrasoft X-ray range for the atomic gases lies not only in the fact that they give very important physical parameters in this range of spectra, but they also stimulate the development of the theory of atomic spectra.

Atomic absorption cross sections in the ultrasoft X-ray region have been measured only for noble gases. The majority of other elements of the periodical table have been studied in the form of thin films and the absorption cross sections have been obtained for solid-state materials.

The most complete investigation into the photoionization cross sections of elements with high atomic number have been made in the Laboratory of Professor Y. Cauchois (Laboratoire de chimie Physique de la Faculté des Sciences de Paris) together with the Laboratory of Physics of the Institute Superiore di Sanita of Roma. The continuum radiation of the Frascati synchrotron has been used to determine the absorption coefficients in the 20-130 Å range. At present the absorption coefficients have been measured for Au, Bi, Pt and Ta by P. Jaegle et al. [15-17].

The spectral behavior of the absorption coefficients of these heavy elements in the ultrasoft X-ray region differs strongly from the hydrogen-like behavior and from the above mentioned ultrasoft X-ray absorption spectra of the noble goses.

In figure 6 the absorption spectra of Au and Bi are shown. When the photon energy increases the absorption cross section passes through the minimum and then reaches the maximum followed by a slow decrease. Such a complex form of the spectra has been interpreted by Combet Farnoux [17], [18]. She has calculated the photoionization cross sections of the 4d, 4f, 5s, 5p and 5d subshells using the nonhydrogenic atomic model with the Herman-Skillman potential just as Cooper and Manson [9] have used. The comparison of experimental and theoretical results has shown that the main features of these spectra can be explained by the combined effects of the 4d, 4f, 5s, 5p and 5d subshells. It turned out that the most important contributions to the total cross sections are made by 5d and 4f subshells. Overlapping of the maxima of these partial cross sections produce the minimum in the absorption spectra. However, the atomic single-electron model explains only the spectral shape of absorption cross sections of the heavy elements but it does not allow to receive the quantitative agreement between experimental and theoretical cross sections. In this case one can expect the effect of solid state, but the main discrepancy is probably due to inadequacy of this model to the photoionization in the heavy elements.

What is more, the importance of these calculations lies in the fact, that they indicate the little influence of solid-state effects in the gross spectral behavior of the absorption cross sections in the ultrasoft X-ray region. This conclusion is confirmed by the ultrasoft X-ray absorption spectra of the Alkali Halidis which was studied by Lukirskii and Zimkina in 1964 [19] and quite recently by Cardona, Haensel, Lynch and Sonntag at DESY synchrotron [20]. It is remarkable, that in the spectra of the Rb- and Cs-Halidis all features of the Kr and Xe spectra are observed respectively. As we can see from the figure 7 the general behavior of the cross sections of Xe and Cs J is very similar.

The most direct information on the influence of the solid state was received by Haensel and his Co-workers at DESY synchrotron [21]. They have studied the continuum absorption of Xe in both the solid and the gaseous state in the region of the resonance maximum.
Both spectra are shown in figure 8. The overall shape of these spectra is the same for the solid and the gas. Therefore, the influence of the atomic cross section behavior on the shape of the ultrasoft X-ray absorption spectra exceeds considerably the solid state effects.

From this point of view the some interesting results have been obtained at the Leningrad State University by Zimkina and Co-workers [22-25]. They have studied the absorption spectra of a number of elements with atomic numbers between 50 and 71 in the 50-500 eV-range. The experimental results demonstrate the behavior of the resonance near the 4d threshold as a function of Z. They reveal its systematic variation in the height, width and distance from the threshold with a gradual filling of the 4f subshell by electrons in the rare-earth elements.

Fano, Cooper and Manson [2], [9] have theoretically considered the problem of resonance disappearance near the threshold in the spectra due to the nl → ef, l + 1 transitions as the bound-state subshell (n, l + 1) becomes gradually occupied. It is proved that the disappearance of the resonant structure in the spectrum occurs approximately at the values of Z when the subshell (n, l + 1) has just become occupied. In the rare-earth spectra we should observe a similar pattern since the resonance is associated with the 4d → ef transition, and the 4f subshell becomes occupied with electrons.

As we can see from figure 9, where the resonance maxima in the spectra of a majority of the rare-earth elements are shown, the clearly pronounced resonance peak disappears with increasing of atomic number. In the spectra of the last three elements Er, Tm and Yb only weak maxima are observed. The spectrum of lutecium (Z = 71) whose 4f subshell is occupied completely does not reveal any maxima, and near the 4d absorption edge the spectral curve is monotonic in shape. In figure 10 these four spectra are shown.

Therefore, the disappearance of the resonance near the 4d threshold in the spectra of the rare-earth elements corresponds to the atomic theory in common features. At the same time, the detailed changes in the shape of the maxima are very complex and can not be interpreted now.
THE FEATURES OF PHOTOIONIZATION ABSORPTION IN THE ULTRASOFT

TABLE I in atoms of the rare-earth metals, which is localized spatially inside the 5s and 5p occupied subshells.

<table>
<thead>
<tr>
<th>Metal</th>
<th>$E_{\text{ev}}$</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
<th>Gd</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Yb</th>
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<td>1.6</td>
<td>2.1</td>
<td>2.9</td>
<td>3.4</td>
<td>3.1</td>
<td>1.6</td>
<td>1.5</td>
<td>1.9</td>
<td>2.1</td>
<td>2.7</td>
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<td>1.8</td>
<td>-1.1</td>
<td>1.3</td>
<td>1.6</td>
<td>2.0</td>
<td>2.1</td>
<td>2.3</td>
<td>2.7</td>
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<tr>
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<td>2.3</td>
<td>1.4</td>
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<td>2.2</td>
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<td>2.1</td>
<td>1.4</td>
<td>1.9</td>
<td>2.0</td>
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<td>Ho</td>
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<td>—</td>
<td>—</td>
<td>—</td>
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<tr>
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<td>6.1</td>
<td>7.6</td>
<td>7.4</td>
<td>13.5</td>
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<td>8.2</td>
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<td>11.3</td>
<td>21.6</td>
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<td>Nb</td>
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<td>21.7</td>
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<td>4.4</td>
<td>5.0</td>
<td>5.0</td>
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<tr>
<td>Mo</td>
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<td>21.2</td>
<td>4.6</td>
<td>4.4</td>
<td>3.3</td>
<td>5.6</td>
<td>4.1</td>
<td>5.4</td>
<td>5.5</td>
<td>5.7</td>
<td>7.6</td>
</tr>
<tr>
<td>Ru</td>
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<td>6.1</td>
<td>5.8</td>
<td>2.7</td>
<td>3.8</td>
<td>5.0</td>
<td>6.0</td>
<td>6.6</td>
<td>6.4</td>
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<td>9.0</td>
<td>3.0</td>
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<td>6.1</td>
<td>7.2</td>
<td>8.5</td>
<td>6.5</td>
<td>9.5</td>
<td>9.4</td>
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<tr>
<td>Cs</td>
<td>65.5</td>
<td>12.0</td>
<td>4.9</td>
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<td>7.2</td>
<td>9.0</td>
<td>10.6</td>
<td>7.8</td>
<td>11.6</td>
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</tbody>
</table>

$\sigma_{\text{hump}}$ 44.5 41.6 25.2 20.1 27.1 31.1 16.7 13.5 11.2 9.3

Existence of a group of weak narrow selective absorption lines on the low-energy side of the resonances presents certain difficulties in the interpretation of the resonances in the spectra of rare-earths. We cannot indicate the element in whose spectrum the resonance maximum actually disappears since in the spectra of the last elements all maxima of the fine structure have the same order of intensity. The nature of these discrete lines observed near the threshold is not clear now. But it is obvious that the fine structure is connected with the unoccupied 4f subshell in atoms of the rare-earth metals, which is localized spatially inside the 5s and 5p occupied subshells.

We have managed to measure the absolute cross sections for 10 rare-earth metals with an accuracy of about 20%. The data in Mb are shown in the table I. The peak value of the cross section in the La spectrum is markedly larger than one in the spectrum of Xe contrary to calculation [9].

Another series of studies carried out in our Laboratory has been denoted to the investigation of the second nonhydrogenic feature of the ultrasoft X-ray spectra, namely, the absence of jumps at the absorption edges and the appearance of «delayed edges» beyond the ionization threshold. We have studied the absorption spectra of Zr, Nb, Mo, Pd and Ag within a broad energy range including the $M_{IV,Y}$ (3d) absorption edge [25].

Figure 11 shows the absorption spectra of Zr, Nb, Mo and Ag. It is easily seen that there is no jump in the absorption cross section near the edge. A gradual increase of absorption beyond the edge, according to the theory of Fano and Cooper [2], is due to a transition on the 3d electrons into the f-states of the continuum, whose intensity becomes noticeable only at a few eV from the edge. This results in the appearance of the «delayed edge» with a considerable increase of the absorption cross section.

The most systematical studies of the spectral behavior of absorption as a function of Z have been made recently by Haensel and his group at DESY synchrotron. They have measured the absolute absorption coefficients for 7 transition elements of the third period (Ti, V, Cr, Mn, Fe, Co and Ni) in the range of energies between 40-300 eV and for the heavy transition elements Ta, W, Re, Pt and Au in the energy region 30-600 eV [26, 27].

The spectra of these elements were investigated in the region of 3p and 5p electron transitions respectively. According to a prediction of the single-electron theory of Fano and Cooper [2] the behavior of absorption cross sections for the 3p and the 5p subshells must have resonance features owing to the 3p $\rightarrow$ ed and the 5p $\rightarrow$ ed transitions. Indeed, the strong maxima have been found in all spectra at the onset of the 3p $\rightarrow$ ed and the 5p $\rightarrow$ ed transitions. In figure 12 the absorption spectra of the transition metals from Ti to Ni are shown. When going from Ti to Ni the 3d subshell becomes occupied and the changes in the shape of the maxima with increasing of the atomic number should be connected with disappearance of the resonance in accordance with the atomic theory. On the other hand, in the absorption spectra of these metals the transition from 3p subshell to unoccupied part of the 3d band may give a rise of absorption at the threshold. In the first three spectra the maximum is too broad to be explained by solid state theory, but the shape of the maximum in the last...
three spectra resembles rather an absorption edge, than a resonance near threshold.

It should be noted, that there is a similarity in the spectral behavior of absorption for the transition metals and for the rare-earth metals. In both cases the maximum near the threshold gets weaker with increasing atomic number and the shape of this maximum changes almost in the same way.

According to Fano and Cooper [2] the effects of electron correlation should be taken into account to explain the spectral shape of the absorption maxima in these spectra. However, this is very difficult problem. In the absorption spectra of the heavy transition metals Ta, W, Re and Pt, the broad maxima at the onset of 5 p transitions were observed too (Fig. 13). The shape of these maxima is more complicated than that found at the onset of the 3 p absorption in the metals from Ti to Ni. At the same time there are common features in the shape of the maxima in these spectra.

Therefore, the behavior of the photoionization cross sections in the intermediate range of photon energies has been studied now for a majority of elements with middle and heavy atomic numbers. These data provide the main basis for theoretical analysis of photoionization process in the ultrasoft X-ray region. Besides they demonstrate the important role of electron-electron interactions in many electron atoms.

In spite of calculational difficulties a substantial work was performed to take into account electron correlations and great success has been achieved in the calculation of atomic cross sections for the noble gases. However, the results of the calculation for other elements are not satisfactory.

Measurements of atomic cross sections for elements in vapor form are of great interest for the theory of photoionization. However considerable technical difficulties present obstacles for such measurements. As far as we known, at NBS synchrotron work is in progress to measure the atomic cross sections of alkali metals in the ultrasoft X-ray region.

The ultrasoft X-ray absorption spectra of solids and molecular gases have been studied extensively in the region of absorption edges. The interest has focused on the discrete structure near absorption edges, because it provides information on the electronic structure of solids and molecules. We have not

![Fig. 12. — Absorption spectra of Ti, V, Cr, Mn, Fe, Co and Ni [26].](image)

![Fig. 13. — Absorption spectra of Ta, W, Re, Pt and Au [27].](image)
considered the results of these studies since they provide little information on the spectral shape of absorption cross sections.

Unfortunately we have no time to consider the very interesting studies of discrete structure within the photo-ionization continuum performed by Samson, these resonance should be the topic of one more paper.

References


DISCUSSION

C. Kunz. — How do you see the relation between the 3 p → 3d transitions in Ti to Cu and the d → e transitions in the rare earth metals?

T. M. Zimkina. — There is a similarity in the change of the shape of the maximum above the threshold with increasing atomic number in the transition elements and in the rare-earth metals. I think that in both cases this maximum is due to the spectral behavior of atomic cross sections. However, in the spectra of rare-earth elements we have observed the fine structure before the large maximum, which has not been observed in the spectra of the transition metals. This fine structure is associated to the transition of 4d electrons to the empty states in the unoccupied 4f subshell which is localized inside of 5p6 5s2 subshells. The absence of such fine structure in the spectra of the transition elements is due to perhaps the fact that the 3d subshell in this metals is not strongly localized as 4f subshell in the rare-earth metals.

M. O. Krause. — Has the theoretical work of Amusia been published yet?

T. M. Zimkina. — The theoretical results of Amusia will be published in the materials of the Oxford symposium in this year. They were reported at London this summer.