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Experimental and Theoretical Study of the Absorption of Ultrasoft X Rays in Some Heavy Elements

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The orbital radiation of the Frascati synchrotron has been used to determine the mass absorption coefficients of some heavy elements in the 20 and 130 Å range. Results have been obtained for tantalum, platinum, gold, and bismuth. The photoionization cross sections of the $4d$, $4f$, and $5p$ electron shells have been calculated from a free nonhydrogenic atomic model. A comparison of the experimental and theoretical results shows that the photoionization in the $4f$ and $5d$ shells plays a fundamental role, and that the combined effects of these shells explain the variations of the absorption coefficient in the range examined. Moreover, certain details in the spectra tend to indicate the existence of multiple excitation mechanisms.

INTRODUCTION

Detailed data on atomic photoionization in the ultrasoft x-ray region has been difficult to obtain until a few years ago, mainly because of the difficulty in constructing convenient sources. Discontinuous-spectra source radiation such as spark discharge under vacuum has been used mainly for the study of light elements. Their absorption is a function of wavelength as in the classical x-ray absorption spectra, and a universal function deriving from an hydrogenic atom model can be used for a semiempirical determination of their absorption coefficients between 5 Å and 50 Å.[1]

The first study of a relatively heavy element in an extended range of wavelengths was, as far as we know, that of tellurium ($Z = 52$) and dates from 1955.[2] It revealed an apparently anomalous behavior. The observation of a large absorption maximum some tens of eV from the N_{IV} and N_{V} edge could not be explained in a satisfactory way. Several years later Ederer[3] compared this result with that obtained for xenon ($Z = 54$), whose spectrum shows a similar absorption maximum. Using Cooper's[4] method of calculation, this author proposed that these maxima were characteristic of $4d$-shell photoionization. At present, several studies point out the necessity of using nonhydrogenic models if the experimental observations on absorption radiation are to be explained over a range extending from about 10 to a few hundred eV.

The use of synchrotron radiation has made this type of research easier by providing an intense source of radiation with a continuous spectral distribution.[5-19]

The Laboratoire de Chimie Physique de la Faculté des Sciences of Paris and the Laboratori di Fisica dell'Istituto Superiore di Sanita of Rome have prepared a program mainly concerned with the determination of photoionization cross sections of elements with a high atomic number, using the Frascati Synchrotron. The results reveal that their spectra is more complex in form than that of tellurium and xenon mentioned above. By taking into consideration the combined effect of a number of electron subshells, it is possible to interpret the experimental results by using of the same nonhydrogenic atomic model employed for Te and Xe.[20,21]

EXPERIMENTAL RESULTS

So far, absorption coefficient measurements for gold,[11] bismuth,[12] platinum, and tantalum[13] have been obtained with the Frascati synchrotron.

The experimental apparatus consists of a grazing-incidence grating spectrograph connected to the synchrotron chamber by a tube which has a compartment in which the specimen can be placed. The spectrograph uses a Siebahn glass grating with a radius of curvature of 2 m and 576 lines. The glancing angle on the grating is 3°. The rotation of the spectrograph round the axis of its entrance slit and its horizontal translation can be remotely controlled for beam alignment. This operation is performed by searching for the maximum intensity of the visible part of the spectrum falling on a photomultiplier placed in the spectrograph. Spectra are recorded photographically on calibrated Kodak SC 5 films.

Relative values of the amount of visible radiation received during each exposure can be determined by a photomultiplier placed outside the spectrograph. As the spectral distribution of the synchrotron radiation is constant for a given working energy, the ratio between the incident and transmitted flux can be calculated for a given specimen from optical density measurements of the films with respect to the photomultiplier output. The specimens are unsupported thin films. They are obtained by vacuum deposition (at 10^{-8} Torr) on a NaCl support which is subsequently dissolved in water. Controls by electron diffraction have failed to show any influence of the support on the formation of the films in the cases so far studied.

Evaporation by electron bombardment was used for the platinum and tantalum samples. Gold and bismuth were evaporated by heating in a crucible. The thickness of the specimens was calculated to within about 5% by weighing.

Six specimens of different thicknesses, expressed in 10^{-6} g/cm^2, vary between 120 and 230 for tantalum, 180 and 240 for platinum, 230 and 570 for gold, and 270 and 640 for bismuth. The value of the absorption coefficient at each point is obtained from the average of about 40 measurements carried out on several photographs for each specimen. The calculation by the method of least squares gives a margin of error of less than 5%. However, taking into account the possible errors due to the overlapping of interference orders, especially towards longer wavelengths, have led us to believe that the accuracy is of the order of 8%. Moreover, any discrepancy in the response of the photographic emulsion (i.e., if the blackening is not quite proportional to the total energy received, independent of the exposure time) may increase the uncertainty slightly. The wavelength is determined to within 1 Å.

The absorption spectra obtained experimentally for tantalum ($Z = 73$), platinum ($Z = 78$), gold ($Z = 79$), and bismuth ($Z = 83$) are shown in Fig. 1. Numerical values of mass absorption coefficients (μ/ρ) are given for 5 Å intervals in Table I. The figure after the decimal place is significant for variations in μ/ρ, but not for absolute values. Figure 4 compares these results with those obtained for gold and bismuth by other authors. Some other results[22] are in satisfactory agreement with ours.

The variation in the absorption coefficient was found to differ in two ways from that observed for higher-energy x rays. Firstly, μ/ρ does not increase rapidly with the atomic number (for a given wavelength); in fact the element with the highest atomic number has the lowest absorption coefficient in the range studied. Secondly, the spectrum of each element shows large variations in μ/ρ – well away from the absorption edges. When the energy of incident quanta decreases, μ/ρ first passes through a minimum (pronounced in the case of bismuth, gold, and platinum, less so in the case of tantalum); it then passes through a maximum followed by a slow decrease, which may contain oscillations.

COMPARISON WITH CALCULATED CROSS SECTIONS

The theoretical study of the photoionization cross sections from a nonhydrogenic free-atom model has made it possible to show[20,21] that the above-mentioned variations can be interpreted by adding the contributions due to $4d$, $4f$, $5s$, $5p$, and $5d$ subshells. The most important contributions to the total cross sections are made by $5d$ and $4f$ subshells. The overlapping of the maxima of the cross sections relative to these subshells provides an interpretation of the existence of an absorption minimum, well removed from the discontinuity positions found experimentally.

These calculations were first begun for gold and bismuth and were subsequently extended in the same way to tantalum and platinum.[13] This formed part of a program concerned with a general study[23,24] of the variations of the different subshell cross sections as a function of the energy of the incident photons and the atomic number. The importance of such a study, apart from its comparison with experimental results, is to be able to predict changes in the role played by the various subshells as they become filled and as they are changed from outer subshells into deeper and deeper inner subshells.

The variations in the form cross sections according to the values of the quantum numbers n and l of the subshell considered, and the changes in amplitude of the maxima as a function of the atomic number, are caused by the changes in the potential in which the electron moves as a function of Z and the distance from the nucleus.

In the calculations performed at the Laboratoire de Chimie Physique, as in those carried out by Manson and Cooper,[21] the potential employed to describe the electron before and after ionization, is the same as that tabulated for all the neutral atoms by Herman and Skillman.[25]

The cross section σ_{nl} describing the ionization of the subshell (nl) occupied by N_{nl} electrons depends very strongly on the overlapping of the function of the initial state with the function of the continuum relative to the energy of the electron considered, as expressed by the integrals:

$$R_{nl,\,l\pm1}(\epsilon)=\int_0^\infty P_{nl}(r)\,r\,P_{\epsilon,\,l\pm1}(r)\,dr \ .$$

The formula expressing σ_{nl} in cm^2 is:

$$\sigma_{nl}(\epsilon)=8.55\times10^{-19}(\epsilon+I_{nl})N_{nl}\times\left[\frac{l}{2l+1}R^2_{nl,\,l-1}(\epsilon)+\frac{l+1}{2l+1}R^2_{nl,\,l+1}(\epsilon)\right],$$

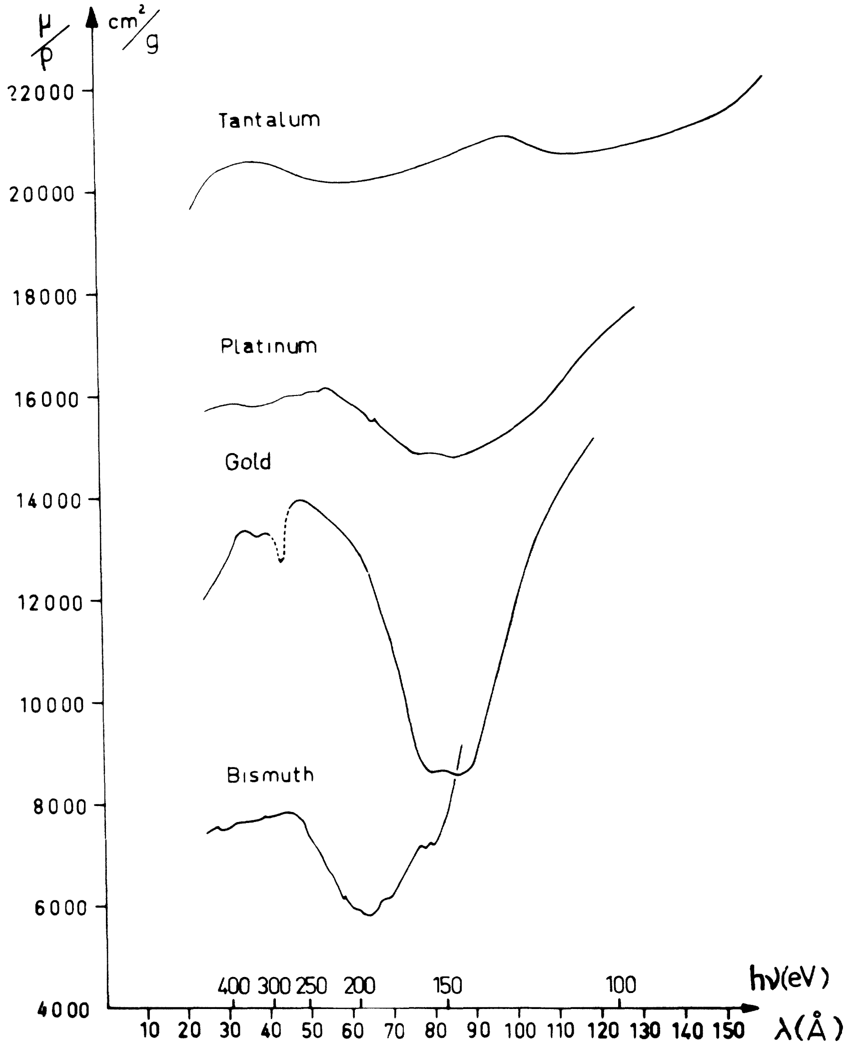

FIG. 1. Mass absorption coefficients measurements for tantalum, platinum, gold, and bismuth.

TABLE I. Mass absorption coefficients of tantalum, platinum, gold, and bismuth.

				$(\mu/\rho) \times 10^{-3}$ (cm^2/g)					
λ (Å)	Ta	Pt	Au	Bi	λ (Å)	Ta	Pt	Au	Bi
25	20.0	15.6	12.0	7.4	80	20.4	14.8	8.6	7.2
30	20.4	15.8	12.6	7.5	85	20.6	14.7	8.5	8.3
35	20.5	15.8	13.4	7.6	90	20.7	14.8	8.7	
40	20.5	15.8	13.3	7.7	95	20.9	15.0	10.3	
45	20.4	15.9	13.2	7.8	100	20.9	15.2	11.8	
50	20.2	16.0	13.9	7.3	105	20.8	15.6	13.1	
55	20.1	16.1	13.6	6.6	110	20.6	15.9	13.8	
60	20.1	15.9	13.2	6.0	115	20.6	16.4	14.5	
65	20.1	15.6	12.5	5.8	120	20.6	16.9	15.1	
70	20.2	15.3	11.2	6.2	125	20.7	17.3		
75	20.3	14.9	9.5	6.9	130	20.8	17.6		

where I_{nl} is the value of the ionization edge.

As an example, we give in Fig. 2 the curves σ_{nl}, as a function of the energy, for every subshell involved in the bismuth absorption for the spectral range considered here. Similar curves concerning gold have been published previously.[20,21] These curves show that: (a) σ_{5p} decreases after a maximum has been reached at the ionization edge. (b) σ_{4f} shows only one maximum, M_{4f}, which is spread out and far from the edge. After the maximum has been reached, the decrease has a hydrogenic behavior. This rather flat maximum can be explained in the following way: For low values of ϵ, the ϵ_g wave belonging to the continuum overlaps weakly only with the $4f$ function of the initial state, since it is held far out from the atomic core by a strong centrifugal barrier. When ϵ increases, the ϵ_g wave penetrates deeper and deeper, but the increasing number of its nodes prevents the overlapping from increasing beyond a certain value of the energy. (c) σ_{5d} has two maxima. The sharper one, M_{5d}, is quite near the edge. It is caused by the negative minimum of the matrix element $R_{5d,f} \times (\epsilon)$. The second one, $M_{2,\,5d}$ which is very weak, corresponds to a slightly positive maximum of $R_{5d,f}(\epsilon)$.

Similar variations are found for the partial cross sections of the atoms whose atomic numbers lie between 73 and 83. It must be emphasized that the behavior of σ_{5d} for $Z \geq 73$ is similar to that of σ_{4d} for $40 \leq Z \leq 71$.[23] On the other hand, σ_{4d} varies in a different way for the elements with which we are concerned here. In fact the negative minimum of $R_{4d,f}(\epsilon)$ no longer exists (the subshell $4f$ is filled and the $5d$ subshell starts filling up), and this agrees with the results obtained by Fano and Cooper[26] who indicate that the matrix element $R_{nl,\,l+1}(\epsilon)$ will become positive at the edge for values of Z which correspond to the complete filling of the subshell $(n, l+1)$. The cross section σ_{4d}, as well as $R_{4d,f}(\epsilon)$ shows only a slight maximum, and the disappearance of the first very-sharp maximum certainly corresponds to the transfer of the oscillator strength from the $4d$ to the $4f$ subshell. This point will be explained in more detail below.[24]

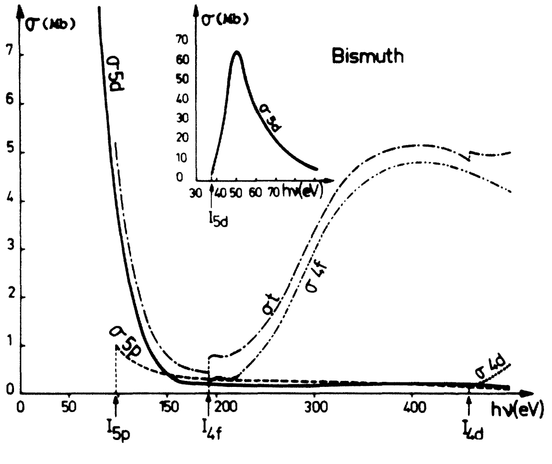

FIG. 2. Partial (σ_{nl}) and total (σ_t) calculated photoionization cross sections for bismuth.

Table II gives the values of the amplitudes M_{nl} (in Mb) and the energy E_{nl} (in eV) above the ionization edge of the maxima corresponding to the $5d$ and $4f$ subshells of tantalum $(Z=73)$, platinum $(Z=78)$, gold $(Z=79)$, and bismuth $(Z=83)$.

The curves which are given in Fig. 3 show the total cross sections σ_t calculated for these elements in the energy range corresponding to the experimental results represented in Fig. 1. The region includes the maximum of σ_{4f} and the minimum produced by the overlapping of the maxima σ_{4f} and σ_{5d}. These curves have been obtained from theoretical values of the ionization levels.[25] In a previous calculation for tantalum,[13] we used experimental values obtained from the x-ray discontinuities.

Table II and Fig. 3 show that the amplitudes of the maxima decrease with increasing Z. This is in keeping with experimental results, but the decrease in experimental values is for more marked than those calculated theoretically. As the region of the σ_{5d} maxima is outside the experimental range studied, it was not possible to determine whether the amplitudes of these maxima increased with Z, as suggested by the theory.

The shift of the maxima, as Z increases produces a shift of the absorption minimum towards the higher energies and a reduction of this minimum. These variations shown in Fig. 3 can also be seen in the experimental curves. The calculated and experimental absorption curves are compared in Fig. 4 for each element. In the case of gold and bismuth the experimental and calculated positions of the minima are in close agreement. In the case of platinum and tantalum the

TABLE II. Calculated maxima for $4f$ and $5d$ subshells in tantalum, platinum, gold, and bismuth (amplitudes M_{nl} in Mb, energy E_{nl} above the ionization edge in eV).

Z	73	78	79	83
$M_{1,\,5d}$	19.3	42.6	46	66.3
$M_{2,\,5d}$	0.025	0.10	0.12	0.185
$E_{1,\,5d}$	10.9	20.4	20.4	13.6
$E_{2,\,5d}$	268.4	340	340	312.8
M_{4f}	6.55	5.5	5.3	4.8
E_{4f}	149.6	204	210.8	217.6

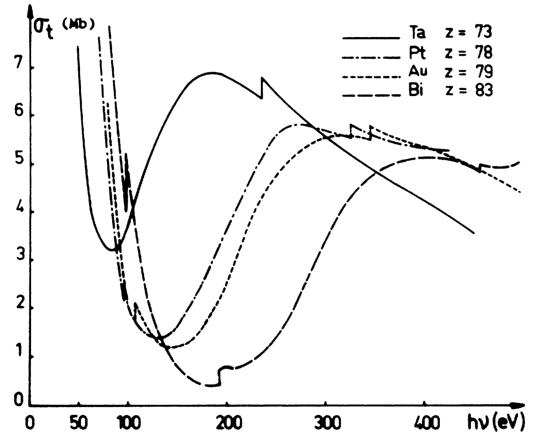

FIG. 3. Total calculated photoionization cross sections for tantalum, platinum, gold, and bismuth.

calculated positions are displaced towards the lower energies with respect to the observed positions. On the other hand, in the four elements studied, the calculated value of σ_t at the absorption minimum is decidedly lower than the experimental value, whereas the maximum corresponding to the $4f$ shell is higher.

The atomic model adopted for the mathematical analysis explains the experimental observations in a general way. It is remarkable that a free-atom model should have proved suitable for the interpretation of results obtained for a specimen in the solid state. The existing quantitative discrepancies may derive, in part, from the crystalline structure of the specimens.

However, it must be remembered that the same model applied in the case of xenon showed an important discrepancy between the experimental and theoretical values of the amplitude and position

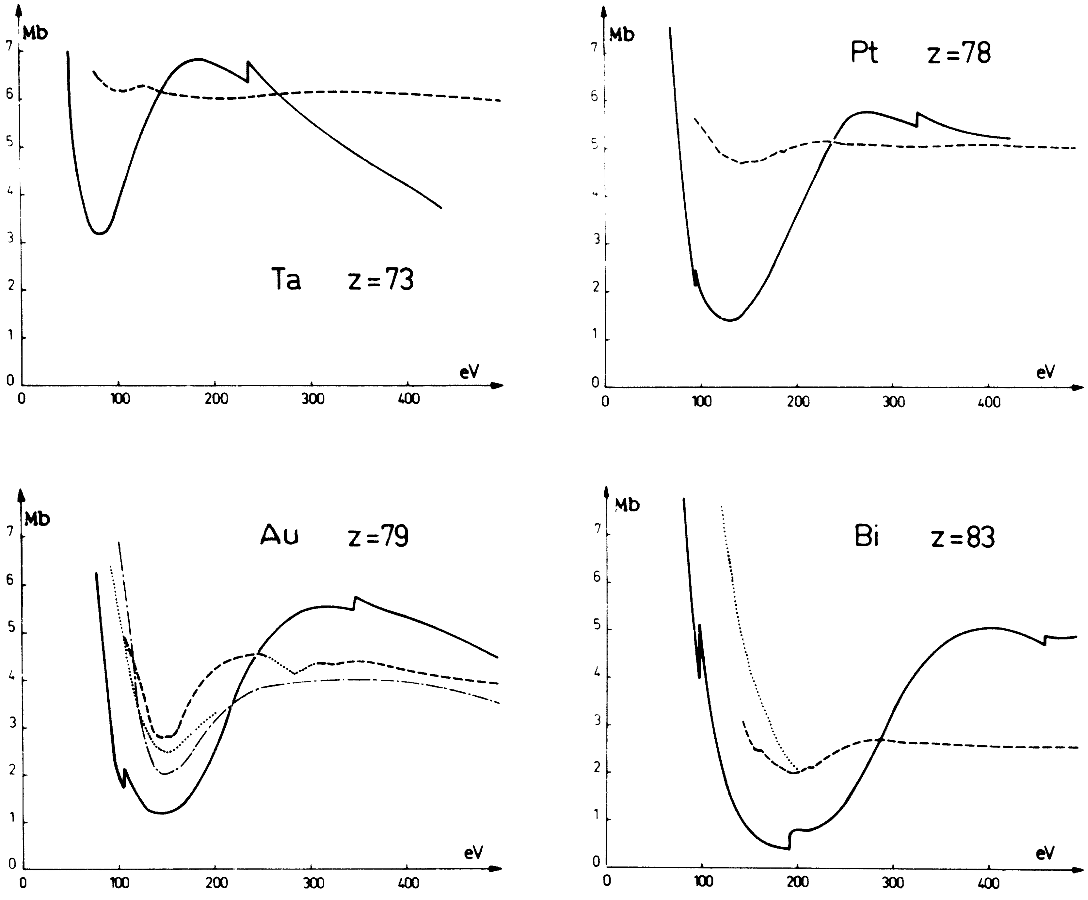

FIG. 4. Calculated photoionization cross sections as compared with experimental results. The full curves are calculated. The dotted curves are experimental {dashed line represents this work; dotted line is from Haensel *et al.* (Ref. 19); and dot-dash line is from O. A. Ershov, Opt. i Spektroskopiya 22, 468 (1967) [English transl.: Opt. Spectry. (USSR) 22, 252 (1967)]}. The ordinates are expressed in Mb.

of the absorption maximum of the 4*d* subshell.

Besides these remarks on the general aspect of the spectra studied, it is important to note the presence of a number of other factors. Two narrow absorption peaks are present in the bismuth spectrum at 158 and 152 eV. These energy values suggest that they are due to the N_{IV} and N_{VII} ionization edges. Other small peaks are observed at 214 eV in bismuth, at 194 eV in gold[11] and at 185 eV in platinum.

These energies are approximately what can be expected in 4*p*-4*d* transitions between the N_{III} and N_{IV} levels of these atoms. These transitions between normally filled internal levels would involve a double-excitation mechanism able to create a preexisting vacancy in the superior N_{IV} level.

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