

Jones for making the Van de Graaff available, and to my colleagues at Harwell and Brookhaven for many useful discussions.

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PHOTOIONIZATION OF THE $4d$ ELECTRONS IN XENON*

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Photoionization in the outer electrons of the rare gases has received a great deal of attention in the past few years with the advent of improved technology in the vacuum ultraviolet. In particular the photoionization of the outer electrons in xenon has been studied extensively.¹ On the other hand, comparatively little is known about the absorption characteristics of inner electrons of high orbital angular momentum. The measurements we are about to describe are a study of the photoionization properties of the $4d$ electrons in xenon. In this note we want to emphasize a feature of the photoionization cross section that is unusual. Instead of the orthodox hydrogenic form one assumes for inner-shell photoionization² in elements of large Z , we find that the photoionization cross section of the $4d$ electrons in xenon rises to a prominent peak about 32 eV above threshold and drops rapidly thereafter. The cross section at the peak is almost a full order of magnitude greater than the cross section at threshold (the $N_{4,5}$ edges are the ionization threshold for the $4d$ electrons).

The measurements were carried out on a grazing-incidence spectrograph in a wavelength region extending from 80 to 275 Å. The apparatus has been described elsewhere³ in some detail, but some of the more important features will be noted here. Several combinations of detectors and sources were utilized. In the first case the source was a condensed spark

discharge in a glass capillary and the detector was Ilford Q-1 photographic plates. This source consisted of discrete lines from highly ionized atoms, superimposed on a weak continuum. In the second case the source consisted of the characteristic radiation from the beryllium K emission band and the aluminum $L_{2,3}$ emission band. The wavelengths of Be K and Al $L_{2,3}$ band heads fall at 110 and 170 Å, respectively. The Geiger counter detector was used in the scan mode in this case but was not located on the Rowland circle. The definition of images suffered in this mounting. This defect and the presence of wide slits on the counter were responsible for our inability to use the $L_{2,3}$ emission band to investigate the discrete structure in the vicinity of the $N_{4,5}$ edge of xenon.

The key to the experiment lay in a cell in which the gas was confined. A detailed description of the cell and gas-handling techniques can be found in reference 3. The light path was about one centimeter and the gas pressure in the cell ranged from 2.0 Torr to 15 Torr.

The results obtained by the photographic technique represent an average of 18 runs. However, because of the large change in cross section, only a small spectral range could be covered in each run so that the cross section at each spectral line was observed an average of four times.

By observing the deviations from a smooth

curve drawn through the data points, the random error is estimated to be $\pm 10\%$. There are regions where the scatter in the data exceeds the assigned error of $\pm 10\%$. It is impossible to say whether or not the data indicate structure in the photoionization cross sections because the cross sections determined by this group of plates reflected the intensity variations of the source to some extent.

Figure 1 is a plot of $\log \sigma$ vs $h\nu$, where the average photoionization cross section σ is expressed in Mb ($1 \text{ Mb} = 10^{-18} \text{ cm}^2$), and the photon energy $h\nu$ is expressed in eV. The dots and the open circles represent the cross section determined by the photographic and counter technique, respectively. The statistical error in the counter measurements is denoted by the vertical bars.

The discrete d -to- p transitions observed by Codling and Madden⁴ and the ${}^2D_{5/2}$ and ${}^2D_{3/2}$ series limits are also shown. The termination of these series coincide with the N_5 and N_4 absorption edges. The $4p$ -to- ns transitions that have been observed by Lukirskii, Zimika, and Britov⁵ are shown along with the ${}^2P_{3/2}$ series limit determined by them. This corresponds to the N_3 edge in x-ray nomenclature. Lukirskii, Zimika, and Britov made no comment about the N_2 edge which lies about 5 eV above the N_3 edge, nor did they give magnitudes for the absorption cross section in the region of the edge.¹⁰ Their value of 1.6 for the $N_{4,5}$ jump ratio is consistent with the present data. Because of the paucity of lines in the 150-eV region we do not observe the edges associated with the $4p$ electrons. From the data it is possible to set an upper limit of about 1 Mb for the N_3 discontinuity, consistent with the value of 1.2 which Lukirskii, Zimika, and Britov gave for the jump ratio.

Samson's results¹ for photon energies greater than 40 eV are shown in Fig. 1 as solid squares and join smoothly with the present measurements. The data of Rustgi, Fisher, and Fuller¹ also overlap the present measurements. Although these data are somewhat lower than the present results, they are in agreement with in the total experimental error.

On the basis of a one-electron model Cooper⁶ has calculated the photoionization cross section of the $4d$ electrons in xenon, and has interpreted the following features in the data: first, a shift in the maximum in the photoionization cross section from threshold to an en-

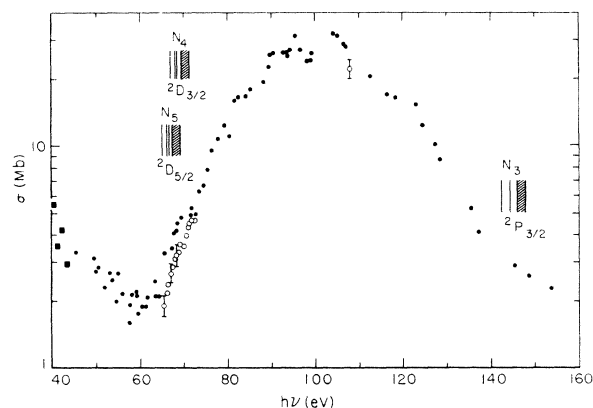


FIG. 1. Photoionization cross section of xenon extending from 40 eV to 150 eV. The $N_{4,5}$ and N_3 edges studied by Codling and Madden⁴ and Lukirskii, Zimkina, and Britov⁵ are shown. The cross sections determined photographically are represented by solid circles. The measurements made with the use of a Geiger-Müller counter are denoted by open circles, where the vertical bars indicate the statistical error in the measurements. Samson's data are shown as solid squares.

ergy of the order of 2 Ry above it; secondly, the range of 4 Ry over which the oscillator strength is distributed (this range would be about 10 times larger in a hydrogenic model); and finally, the large ratio (about a factor of 10) between the peak cross section and the cross section at the absorption edge.

The experimental results have also been corroborated independently by Geiger,⁷ who has studied the rare gases using the technique of electron energy loss. He has observed an increase in the electron current for energy losses greater than 70 eV corresponding to the excitation of the inner d electrons. The current increases to a broad maximum at about 90 eV, which corresponds to the peak we observe in the optical data.

The behavior of the photoionization cross section should not be unique to xenon but should characterize absorption cross sections involving inner $4d$ electrons. This characteristic behavior is subject to the condition that the potential and centrifugal energy of the electron in the final f state be approximately equal at the radius of the $4d$ electron. Theoretical studies have shown that the centrifugal-energy term is responsible for the prominent maximum in the cross section. This maximum should be observable even in the case of solids since the perturbations due to the crystal fields are small

compared to the centrifugal barrier. A prominent peak at 150 Å has been observed in the soft x-ray absorption spectrum of tellurium by Woodruff and Givens.⁸ They suggest that this peak is due to an interband transition from the 4*p* state to the conduction band. In our opinion this peak reflects the characteristic absorption of the 4*d* electron of the atom irrespective of crystal structure, for two reasons. The half-width of the maximum is two Rydbergs, greatly exceeding the width of any solid-state band. Secondly, the oscillator strength⁹ associated with this peak is about 12, where typical interband transitions have oscillator strengths less than one.

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INTERACTION OF MAXIMA IN THE ABSORPTION OF SOFT X RAYS

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Maxima have recently been detected in the photoabsorption cross sections of Ar^{1,2} and Xe³ which do not lie at or near any known absorption edge. These maxima, which are much too broad (~40-50 eV) to be interpreted as due to the excitation of autoionizing discrete states, represent a departure from the familiar hydrogenlike behavior of photoabsorption cross sections in the x-ray range where the cross sections increase sharply at absorption edges and then decrease monotonically and smoothly with increasing energy. This behavior follows from Stobbe's treatment⁴ which utilizes a screened hydrogenic approximation for the wave functions of initial and final states, and provides an ex-

cellent description of the energy dependence of the photoeffect at excitation energies >10 keV.

The purpose of this note is to point out that the observed maxima are predictable by a one-electron nonhydrogenic central-field model. In fact the observations on Ar may be regarded as verifications of a result reported previously.⁵ In order to explore the situation in Xe, further calculations utilizing the method of reference 5 have been performed for the 4*d* shell of Xe. The result shows a peak in the cross section even sharper and higher than that observed by Ederer.³

First consider the case of argon. In refer-