PHYSICAL REVIEW
LETTERS

VOLUME 31 26 NOVEMBER 1973 NUMBER 22

Resonances in the Angular Distribution of Xenon Photoelectrons*

James A. R. Samson and J. L. Gardner
Behlen Laboratory of Physics, University of Nebraska, Lincoln, Nebraska 68508
(Received 19 September 1973)

Measurements are reported of the resonant structure, caused by autoionization, in the angular distribution of xenon photoelectrons. The measurements were made within the autoionizing structure lying between the $^2P_{3/2}$ and $^2P_{1/2}$ ionization thresholds for the wavelength range 956 to 1015 Å. The results show a periodic variation in the asymmetry parameter β with maximum excursions of about +0.9 to −0.9. The overall variation and magnitude of β is in accord with the recent theoretical predictions of Dill.

We report the first measurements of resonant structure, caused by autoionization, in photoelectron angular distributions. Although a number of experimental determinations of photoelectron angular distributions have been reported,[1-12] no measurements exist of the variation of the angular distribution with energy across autoionization resonances. A recent paper by Dill[13] considered, theoretically, the influence of autoionization on the angular distribution parameter β.[14] This paper gave the important general prediction that β should fluctuate rapidly within the allowed range of +2 and −1 across any autoionizing resonance, atomic or molecular. In particular, β was calculated for xenon across the first autoionizing resonance between the $^2P_{3/2}$ and $^2P_{1/2}$ ionization thresholds. The current experiment was designed to measure the xenon photoelectron angular distributions as a function of wavelength between the $^2P_{3/2}$ and $^2P_{1/2}$ thresholds to compare with the predictions of Dill. The importance of measuring β across a resonant structure was emphasized by Dill as a new and independent method to probe atomic and molecular dynamics.

The experimental technique employed was to measure the angular modulation of the photoelectron count rate within a 6° cone of acceptance in the plane normal to the beam of partially plane-polarized radiation emerging from the exit slit of a $\frac{1}{2}$-m Seya-Namioka monochromator. This method has not been previously used. From an expression for the general angular dependence of the photoelectron signal when using partially plane-polarized light,[15] it is readily shown that

$$\left.\frac{d\sigma}{d\Omega}\right|_{x\text{-}z\ \text{plane}} = \frac{\sigma}{4\pi}\left\{1-\frac{\beta}{2}+\frac{3\beta}{2(g+1)}\left[(g-1)\sin^2\theta+1\right]\right\},$$

where the photon beam is traveling along the $+y$ axis, σ is the integrated cross section, θ is the angle of emission measured in the x-z plane from the z axis, and g is the degree of polarization given by I_x/I_z, the ratio of the radiation intensity components in the x and z directions, respectively.

The apparatus is shown schematically in Fig. 1. Electrons formed within the ionization region were allowed to drift in a field-free region through a series of five baffles to a Spiraltron detector, and the resultant pulses were integrated with a rate meter. Since angular distributions were to be determined for xenon in the wavelength range below the $^2P_{1/2}$ ionization threshold, no energy

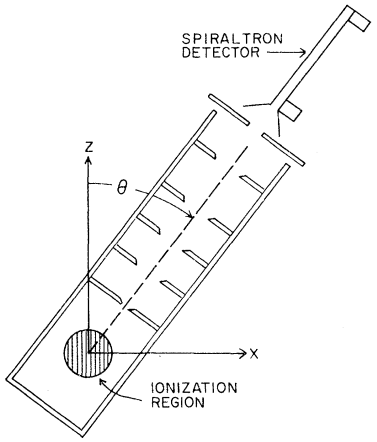

FIG. 1. Cylindrical ionization chamber with defining baffles to provide a 6° field of view. The photon beam is directed along the y axis. The ion chamber is rotated about the y axis. Electrons passing through the series of baffles are detected by the Spiraltron electron multiplier. The ion chamber and the baffles were constructed from Conetic AA magnetic shielding material.

analysis was necessary. The ionization chamber, constructed of Conetic AA and annealed in a hydrogen furnace after fabrication, and the rotatable vacuum chamber that housed the apparatus were placed at the center of a pair of Helmholtz coils positioned to annul the earth's magnetic field. Field penetration, both electric and magnetic, into the ionization region was judged to be negligible from studies on 0.6-eV argon photoelectrons produced by 736-Å radiation.

The expression given for the angular modulation in the x-z plane shows that a functional dependence of the form $A+B\sin^2\theta$ is expected, where both A and B depend on the angular distribution parameter β and the degree of polarization g. Hence g must be measured in an independent experiment if β is to be determined. The polarization of the monochromator used in the current experiment was measured over the wavelength range of interest by the method of Rabinovitch, Canfield, and Madden.[16] The monochromator, fitted with a Pt-coated grating blazed for 700 Å in the first order, was found to polarize the radiation predominantly in the direction of the rulings with an intensity ratio ($1/g$) of 2:1 at wavelengths near 1000 Å, rising to 5:1 at 584 Å.

Preliminary measurements of the asymmetry parameter indicated that an appreciable background of electrons scattered from the walls surrounding the ionization region was being counted along with the true signal at each angle. To determine a correction factor for these scattered electrons, the variation of the photoelectron count rate with angle in the x-z plane was measured for 584- and 736-Å radiation incident on Xe, Kr, and Ar for which the angular distribution parameters have been determined.[9] The background signal, which comes from multiple electron scattering on the walls (and thus should be isotropic), was assumed to be a constant fraction of the total signal. The angular distribution parameter for each gas at each wavelength was taken as the mean of the $^2P_{3/2}$ and $^2P_{1/2}$ values, weighted by the relative intensities of the transitions (these were determined with an electron energy analyzer which produces true intensity ratios independently of the degree of polarization of the radiation or the angular distributions of the electrons[17]). The measured angular distributions were then corrected to give the known values of β and the correction factor was plotted as a function of the electron energy (again the mean of the $^2P_{3/2}$ and $^2P_{1/2}$ values weighted by the experimental intensity ratios). The result was well represented by a gently sloping straight line with the background increasing as the electron energy increased. The linearity of the plot gave confidence to the extrapolation of the background correction factor to the lower electron energies produced between the $^2P_{3/2}$ and $^2P_{1/2}$ thresholds in Xe.

The count rate of photoelectrons from xenon at a pressure of about 1 mTorr was recorded as a function of wavelength (956 to 1015 Å) and angle in the plane normal to the beam direction of the dispersed radiation from a dc discharge in hydrogen, producing the many-lined molecular spectrum. Typical count rates with the monochromator set for a 1-Å bandpass were from 2 to 50 counts/sec. At each wavelength, the count rate was recorded at eight 45° steps around one revolution. Since the angular modulation is the same in the four quadrants, the eight measured count rates were averaged to give mean 0°, 45°, and 90° signals in the first quadrant. The assumed isotropic background was removed using the correction factor explained above, and the ratios of the 0° to 45° and 0° to 90° signals were both used to generate a mean value for β at each wavelength. Results were taken at 1-Å increments and the means of a number of runs were computed to produce the data shown in Fig. 2(a).

The experimental results for β as a function of wavelength are shown in Fig. 2(a) superimposed with the experimental total photoionization cross sections of Xe.[18] This figure illustrates the vari-

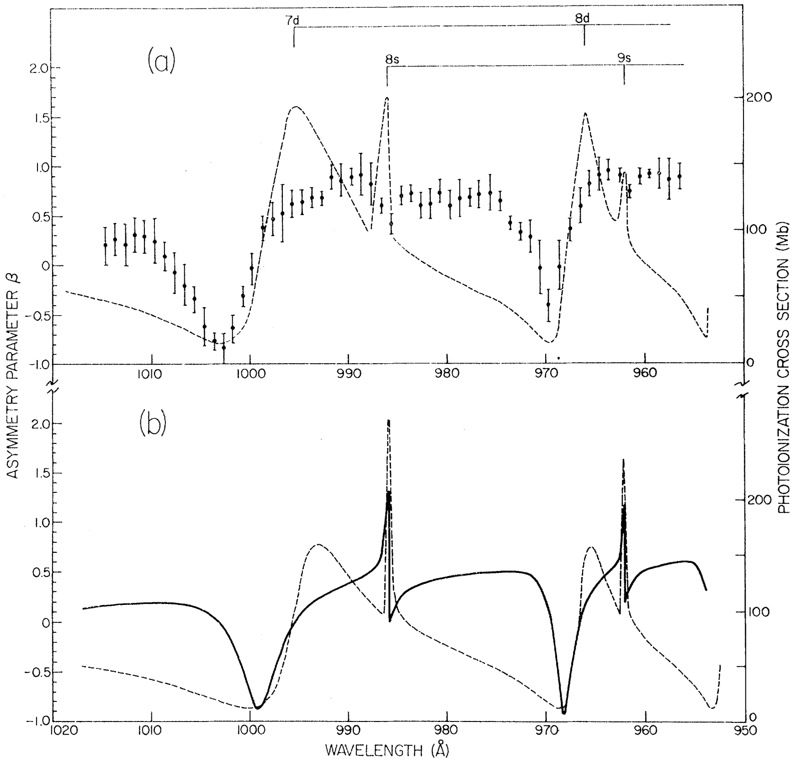

FIG. 2. Asymmetry parameter β as a function of wavelength. (a) Experimental β value shown in relation to the experimental autoionizing resonances (dashed curve). (b) Theoretical β values (solid-line curve) shown in relation to the theoretical photoionization cross sections (dashed curve).

ation of β across the autoionizing structure. The error bars represent the rms average of the detector counts only. Systematic errors in the determination of the degree of polarization and in the correction factor for the scattered background are estimated to give an uncertainty in β of about ±9%. The *s* resonances are extremely narrow[19] (≤ 0.04 Å) and it was not possible to obtain data within these resonances. The widths of the *s* resonances shown in the cross-section curve of Fig. 2(a) reflect the resolution of the original measurements. However, a variation of β is observed in passing through the *s* resonances. To compare the experimental results with theory, the theoretical values for β and the theoretical photoionization cross sections of Dill[19,20] are reproduced in Fig. 2(b).

The overall agreement in the structure and in the absolute values of β between theory and experiment is excellent. The calculation of Ref. 13 utilizes interaction parameters determined by application of multichannel quantum-defect theory to analyze semiempirically the Xe photoabsorption spectrum near the ionization threshold. As such, the significant point of comparison between theory and experiment is that the theoretical σ and β curves show essentially the *same relationship to each other* as do the measured σ and β curves.

The small shift *between* the two sets of curves arises from the inability of the theoretical parameters to fit accurately the position of the minimum and broad *d* maximum of σ. This is aggravated by the fact that the minimum is not a very sharp spectral feature. The corresponding minimum in β, however, is a much sharper spectral feature and can therefore possibly aid in refining the theoretical fit. Note that theory and experiment do agree in absolute position very well at the sharp *s* resonance. This is more clearly shown in Fig. 3 where the experimental and theoretical β values are plotted. The *s*-resonance minima for both experimental and theoretical β values coincide. However, the *d*-resonance minima for the experimental β values lie between 1 and 3 Å to longer wavelengths than the theoretical results. As mentioned above this is an artifact of the theory. Hence a direct comparison of the

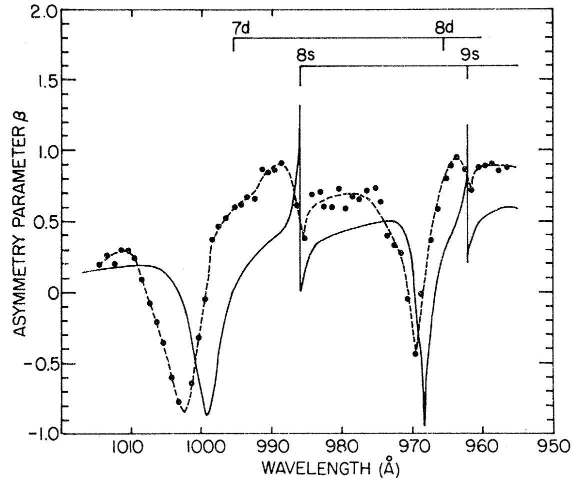

FIG. 3. Asymmetry parameter β as a function of wavelength. The solid line represents the theoretical values. The closed circles and dashed line represent the experimental data. The error bars are omitted for clarity but are shown in Fig. 2(a).

magnitude of β at a given wavelength is not too meaningful.

Unlike the integrated cross section, β is predicted to be only approximately periodic along the Rydberg series of combined (s,d) resonances. This is caused by the energy dependence of the Coulomb phase-shift difference between the outgoing s and d waves. This effect is predicted to be largest for the first resonance, which corresponds to the largest change in photoelectron kinetic energy, and should decrease rapidly in importance for successive resonances. This is verified in the present results where $\Delta\beta = 0.4$ across the $(8s, 7d)$ resonance, whereas $\Delta\beta = 0.2$ across the $(9s, 8d)$ resonance.

The minimum experimental value for β at 970 Å is not as low as it should be, partly because of the 1-Å wavelength resolution used and partly because an emission line may not fall exactly on the minimum.

We are grateful to Dr. Dill for his permission to use unpublished data and for his helpful comments on this work.

---

*Research supported by the National Aeronautics and Space Administration under Grant No. NGR 28-004-021.

[1] J. Berkowitz, H. Ehrhardt, and T. Tekaat, Z. Phys. 200, 69 (1967).

[2] J. W. McGowan, D. A. Vroom, and A. R. Comeaux, J. Chem. Phys. 51, 5626 (1969).

[3] J. A. R. Samson, Phil. Trans. Roy. Soc. London, Ser. A 268, 141 (1970).

[4] T. A. Carlson and A. E. Jonas, J. Chem. Phys. 55, 4913 (1971).

[5] T. A. Carlson, G. E. McGuire, A. E. Jonas, K. L. Cheng, C. P. Anderson, C. C. Lu, and B. P. Pullen, in *Electron Spectroscopy*, edited by D. A. Shirley (North-Holland, Amsterdam, 1972), p. 207.

[6] T. A. Carlson, Chem. Phys. Lett. 9, 23 (1971).

[7] P. Mitchel and K. Codling, Phys. Lett. 38A, 31 (1972).

[8] M. J. Lynch, A. B. Gardner, and K. Codling, Phys. Lett. 40A, 349 (1972).

[9] A. Niehaus and M. W. Ruf, Z. Phys. 252, 84 (1972).

[10] A. Niehaus and M. W. Ruf, Chem. Phys. Lett. 11, 55 (1971).

[11] J. A. Kinsinger and J. W. Taylor, Int. J. Mass Spectrom. Ion Phys. 10, 445 (1972).

[12] M. O. Krause, Phys. Rev. 177, 151 (1969).

[13] D. Dill, Phys. Rev. A 7, 1976 (1973).

[14] The angular distribution parameter β has been discussed theoretically by a number of authors for direct transitions into the ionization continuum. For example, J. Cooper and R. N. Zare, J. Chem. Phys. 48, 942 (1968); J. W. Cooper and S. T. Manson, Phys. Rev. 177, 157 (1969); J. Tulley, R. J. Berry, and B. J. Dalton, Phys. Rev. 176, 95 (1968); A. D. Buckingham, J. B. Orr, and J. M. Sichel, Phil. Trans. Roy. Soc. London, Ser. A 268, 147 (1970); D. Dill, Phys. Rev. A 6, 160 (1972).

[15] J. A. R. Samson and J. L. Gardner, J. Opt. Soc. Amer. 62, 856 (1972).

[16] K. Rabinovitch, L. R. Canfield, and R. P. Madden, Appl. Opt. 4, 1005 (1965).

[17] J. L. Gardner and J. A. R. Samson, unpublished.

[18] R. E. Huffman, Y. Tanaka, and J. C. Larrabee, J. Chem. Phys. 39, 902 (1963).

[19] V. L. Carter and R. D. Hudson, J. Opt. Soc. Amer. 63, 733 (1973).

[20] D. Dill, private communication.