Reprinted from The Journal of Chemical Physics, Vol. 46, No. 12, 4995–4996, 15 June 1967
Printed in U. S. A.

# Measurement of Threshold Electrons in the Photoionization of Ar, Kr, and Xe*

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(Received 16 February 1967)

RECENT studies of electrons produced in photoionization of gases have consisted of measurements of photoelectron energy spectra using discrete photon energies.[1] Alternatively, one can vary the photon energy and observe electrons with kinetic energy $T$ only. Such electrons are produced at photon energies approximately equal to $I_j+T$, where $I_j$ is the energy of the $j$th ionization limit. This Note reports results obtained with $T=0$. In this case the number of electrons produced at photon energy $I_j$ is proportional to the photoionization cross section for that threshold.

Dispersed Hopfield-continuum radiation from a 1-m vacuum monochromator[2] bombards the target gas. Photoelectrons produced in the ionization zone are accelerated and then analyzed with a cylindrical energy analyzer.[3] The analysis energy is chosen to equal the acceleration energy. An electron-multiplier–scalar counts the photoelectrons while the photon flux is monitored as described previously.[4] The experimental conditions were: monochromator bandpass, 2.8 Å; sample pressure, $\sim 10^{-5}$ torr; acceleration energy, 6 eV; and count rate, $10^3$/min. The ratio of photoelectron count rate to incident photon flux is measured as a function of wavelength on a point-by-point basis. Surface-effect photoelectrons produced in the ionization zone determines the limiting-background count rate.

Figure 1 shows data for Xe, Kr, and Ar. These results may be compared with conventional photoionization data and photoelectrically recorded absorption spectra.[5–9] In all three gases, the autoionization structure found at energies between the $^2P_{3/2}$ and $^2P_{1/2}$ ion levels is substantially suppressed, demonstrating the discrimination of the system against electrons with initial kinetic energy. For Xe, two peaks are observed, corresponding to the $Xe^+\ ^2P_{3/2}$ and $Xe^+\ ^2P_{1/2}$ levels. The Kr data shows an additional peak centered at 880.4 Å attributed to autoionization. The initial kinetic energy of the autoionized electron is sufficiently small in this case that a partially attenuated peak is observed. Further support for this interpretation is presented in the figure. Using 3 eV acceleration energy, this autoionizing peak is further suppressed owing to the smaller energy-analyzer bandpass at the lower electron energy. In Ar, the $^2P_{1/2}$ ion level is resolved, but the $^2P_{3/2}$ level is believed to be obscured by autoionization. Convolution of the instrumental resolution function with a step-function photoionization cross section shows that the peak positions are slightly shifted to higher

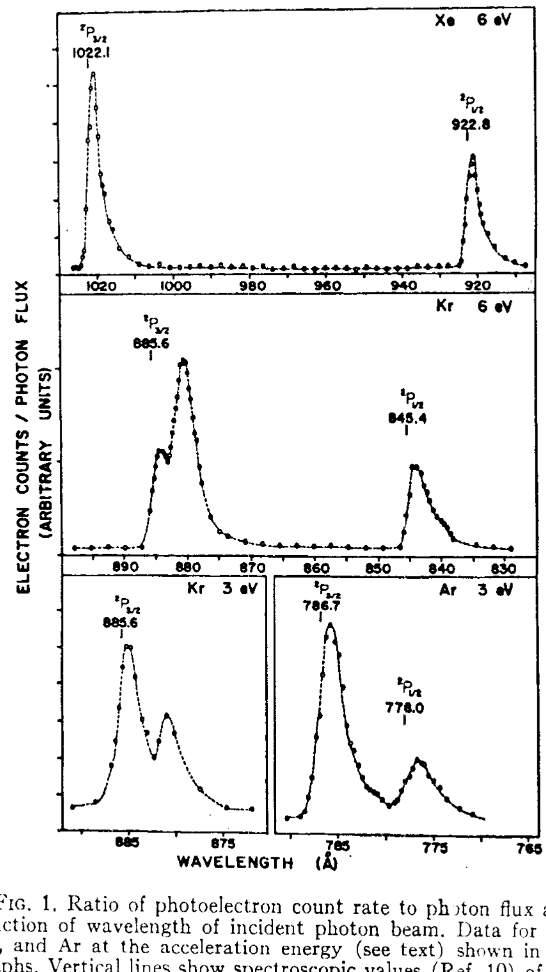


Fig. 1. Ratio of photoelectron count rate to photon flux as a function of wavelength of incident photon beam. Data for Xe, Kr, and Ar at the acceleration energy (see text) shown in the graphs. Vertical lines show spectroscopic values (Ref. 10) of the ionization energies, in wavelength units, for the states indicated. The wavelength scale is accurate to better than 0.5 Å.

energies with respect to the true ionization energy. In the 800–1000 Å region this shift is calculated to be 1.5 Å for 6 eV acceleration energy. Taking this into account, the experimental values for the $^2P_{3/2}$ and $^2P_{1/2}$ ion levels are in good agreement with more accurate spectroscopic determinations.[10]

Since all electrical potentials in the instrument are fixed and only the photon energy is varied, the electron collection efficiency is essentially constant. Thus, comparison of relative peak amplitudes is meaningful. In a separate set of experiments the ratio of photoelectron count rate to incident photon flux was measured in Xe and in Kr at the observed wavelengths of the $^2P_{3/2}$ and $^2P_{1/2}$ peaks only. For Xe, using 6 eV acceleration energy, the observed ratio of $^2P_{3/2}$ amplitude to $^2P_{1/2}$ amplitude was $1.65\pm0.18$ while in Kr, using 3 eV acceleration energy, the ratio was $1.08\pm0.12$. The absorption spectra of both gases show appreciable absorption cross-section variation to the short-wavelength side of the $^2P_{3/2}$ ionization onset but not at the $^2P_{1/2}$ threshold.[8] Hence, the amplitude measured at the $^2P_{3/2}$ onset is an average value weighted by the resolution function of the instrument. The amplitude at the $^2P_{1/2}$ onset should be unaffected. Deconvolution shows that the above ratios must be increased to $1.81\pm0.20$ for Xe and $1.85\pm0.22$ for Kr. These corrected values may be compared with theory.

The photoionization cross section is proportional to both the photon energy and the square of the dipole matrix element.[11] Applied to the present case and assuming that the radial integrals are identical for the two members of the ion doublet, we expect the ratio of amplitudes to be $2I_{3/2}/I_{1/2}$, where $I_{3/2}$ and $I_{1/2}$ are the respective ionization energies. The factor of 2 is the ratio of the statistical weights of the levels. This theory predicts that for Xe and Kr the amplitude ratios should be 1.806 and 1.909, respectively, in good agreement with the corrected experimental values. These results are also consistent with previous determinations using other methods.[1b,d] The accuracy is not sufficient to determine departures from this simple theory due to configuration-interaction effects at threshold.

The authors thank R. Stockbauer for his assistance in this work.

* Work supported in part by the National Science Foundation and in part by the Advanced Research Projects Agency.

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