# PHYSICAL REVIEW LETTERS

## Multiple Photoionization of the Rare Gases*

James A. R. Samson and G. N. Haddad

*Behlen Laboratory of Physics, University of Nebraska, Lincoln, Nebraska 68508*

(Received 24 June 1974)

The photoionization yield or average charge produced per photon absorbed by Ne, Ar, Kr, and Xe has been measured from the threshold of double photoionization to 107 eV. The probability of double ionization is zero at threshold for the rare gases. For Ar, Kr, and Xe double ionization increases rapidly giving an abundance of 16 to 30% at 20 eV beyond the double-ionization threshold. In this region double ionization is constant or increasing slowly. At the threshold for triple ionization the average charge per photon increases rapidly.

There has been considerable interest recently in the process of multiple photoionization. Detailed calculations of the double ionization of He have been made, taking into account ground-state correlations between the electrons.[1,2] There is good agreement between theory and x-ray photoionization.[3] However, agreement is poor with electron-impact experiments.[4-7] For atoms heavier than He there are no detailed calculations of double ionization. Calculations based on the sudden-approximation theory using single-electron wave functions fail to predict the magnitude of double ionization of the rare gases, especially near threshold. Chang, Ishihara, and Poe[8] improved the theoretical agreement for Ne ionized by photons of energy about 200 eV above the double-ionization threshold. The improvement was achieved by considering the contribution of several processes, namely, core rearrangement, virtual Auger transitions, and initial-state electron correlations. However, with the exception of He no results have been published predicting the expected threshold behavior of double ionization in the rare gases. Amusia[9-12] has pointed out the importance of knowing the probabilities of multiple-electron processes in understanding the interaction of the removed electron with those remaining.

There are very few experimental results near the threshold of double ionization. (See Cairns, Harrison, and Schoen.[13]) We present here for the first time detailed experimental results of the threshold behavior of multiple photoionization of the rare gases Ne, Ar, Kr, and Xe.

Previous work on multiple photoionization of gases has used either the technique of mass spectroscopy or photoelectron spectroscopy.[14-16] The present work uses a new technique which simply measures the average charge produced per photon absorbed by the gas. This allows absolute determinations of the number of singly and doubly charged ions produced as a function of photon energy until the triple-ionization threshold is reached. Beyond that point the abundances of the separate ions cannot be distinguished without the use of a mass spectrometer.

Two types of apparatus were used. The first consisted of a single ion chamber (length $L$) terminated with a fluorescent screen of sodium salicylate. The fluorescent screen was used simply to monitor the photon flux emerging from a grazing-incidence vacuum-ultraviolet monochromator. The photoionization yield $Y$, defined as the number of charges produced divided by the number

of photons absorbed in the length $L$, is given by

$$Y = \frac{i/e}{I_0[1 - \exp(-\sigma n L)]}, \qquad (1)$$

where $i$ is the ion current, $I_0$ is the number of photons incident per second, $\sigma$ is the total absorption cross section, and $n$ is the number density of the gas. Because $\sigma$, $n$, and $L$ are constant and known for a given gas, the method consists simply of measuring the ion current and the photon flux as a function of wavelength. Although the cross sections had been measured previously,[17] they were remeasured in the present work to a higher degree of accuracy ($\sim 3\%$). The technique for measuring the absolute photon flux at wavelengths shorter than 300 Å has been reported recently.[18] Briefly, it requires the ion current from the gas under investigation to be compared to that of another rare gas whose photoionization yield is known. The yields of all the rare gases are unity from the first ionization potential to the threshold for double ionization.[19] Helium was used to determine the yield of Ne for photon energies greater than 60 eV because the yield of He is unity for photon energies up to 79 eV. For energies up to 107 eV the yield of He was taken from the results of Carlson.[3] Neon was then used as the standard to determine the multiple ionization of the other rare gases.

In the second apparatus, in order to obtain maximum sensitivity the ion chamber was replaced by a gas jet and electron multiplier. The pressure around the multiplier was $10^{-5}$ Torr. The ions were accelerated through 2.4 kV onto the first dynode of the multiplier. The incident radiation was monitored with a photomultiplier sensitized with sodium salicylate. Equation (1) still applies. However, with the low gas density in the jet and short path length $L$, $\sigma n L \ll 1$ and Eq. (1) becomes

$$Y \propto \frac{i/e}{I \sigma n L}, \qquad (2)$$

where $i$, in this case, is the electron multiplier signal and $I$ is the photomultiplier signal, which is proportional to the absolute photon flux. The experimental procedure was similar to the first method where the test gas was compared with a standard (e.g., Ne). That is,

$$\frac{Y}{Y_0} = \frac{i/I}{i_0/I_0} \frac{\sigma_0 n_0}{\sigma n}, \qquad (3)$$

where the subscript zeros indicate the standard conditions. The unknown path length in the jet

and the electronic charge cancel out in Eq. (3). Because the gas pressure in the jet is unknown the results are relative. However, they are easily normalized if the wavelength range studied covers the region where both gases have a yield of unity.

The yield of Ne was measured with the ionchamber method using He as the standard gas. Xenon was studied with both systems. Similar results were obtained within experimental error. It was assumed, therefore, that the sensitivity of the multiplier under the present conditions was constant for all the rare-gas ions. Because of the higher sensitivity of the gas-jet system it was used to measure the yields of Ar and Kr.

The light source was a high-voltage condensed spark discharge in a low-pressure gas.[20] The source produced a large number of discrete emission lines characteristic of the gas used in the discharge. The short-wavelength limit was imposed by the efficiency of the monochromator. In the present work a useful limit was 116 Å (107 eV).

The spectral resolution of the monochromator was 0.5 Å. With this resolution no discrete resonant structure was observed in the total cross section measurements. Thus, the values of $\sigma$ used in Eqs. (1) and (2) are expected to fall within our error limits of $\pm 3\%$.

The photoionization yields or average charge produced per photon absorbed for Ne, Ar, Kr, and Xe are shown in Figs. 1–4, respectively, as a function of photon energy. The overall accura-
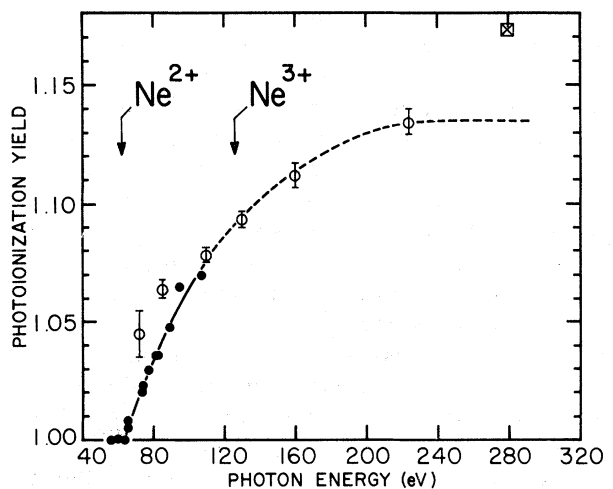


FIG. 1. Photoionization yield of neon as a function of photon energy. Present data, closed circles; Carlson (Ref. 3), open circles; Lightner, Van Brunt, and Whitehead (Ref. 14), cross in square.
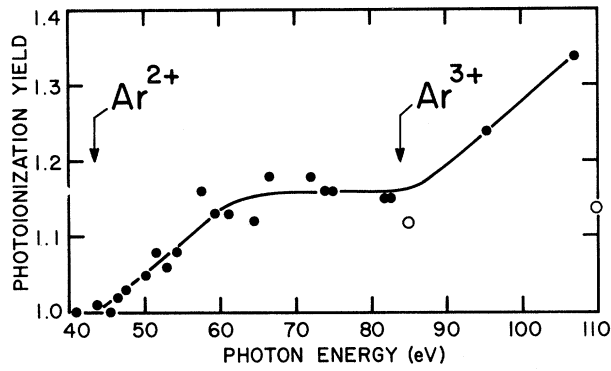
FIG. 2. Photoionization yield of argon as a function of photon energy. Present data, closed circles; Carlson, open circles (for double ionization only).



FIG. 3. Photoionization yield of krypton as a function of photon energy.

cy of the data points is estimated to be ± 6%.

The data of other authors have been expressed either as a ratio $R^{n+}$ of the number of $n$-times charged ions to the number of singly charged ions, or as an abundance $A^{n+}$ equal to the number of $n$-times charged ions divided by the total number of ions of all charges. With these definitions the data can be converted to yields. Thus, in Figs. 1–4 the abundance of doubly charged ions is simply equal to $Y - 1$ for photon energies less than the triple-ionization threshold.

In Fig. 1 the results for Ne are shown along with those of Carlson[3] and of Lightner, Van Brunt, and Whitehead.[14] In the region where the data overlap with that of Carlson's there is reasonable agreement. Excellent agreement is obtained with the electron-impact work of Van der Wiel and Wiebes.[7]

Multiple ionization of Ar, like that for Ne and He, shows a zero probability at threshold (Fig. 2). The yield rises to a plateau giving a constant *abundance* of 16% of doubly ionized argon. This represents a *ratio* $R^{2+}$ of doubly to singly charged ions of 19%. This is to be compared with 13% to 16% obtained by Carlson.[3] Although Carlson's data at 110 eV are plotted on our yield curve they apply to double ionization only as there is no report of the abundance of $Ar^{3+}$. However, in light of the constancy of the double-ionization abundance out to 110 eV the rise in the curve at the triple-ionization threshold is presumably caused by $Ar^{3+}$.

The double-ionization threshold closely follows the electron-impact data[6] up to a photon energy of 65 eV. Beyond this energy the electron-impact data continue to increase in disagreement with the present results.
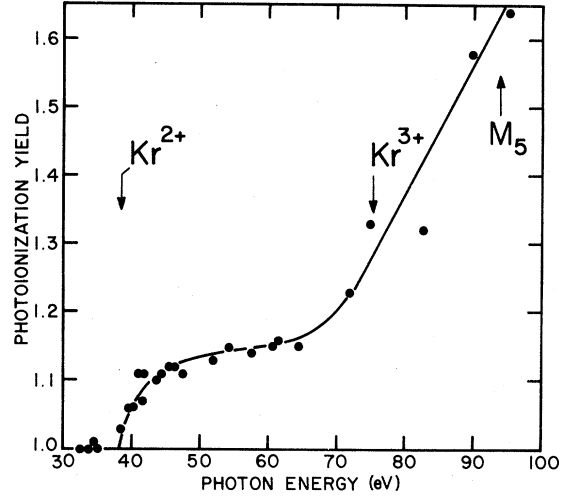
The results for multiple ionization of Kr are shown in Fig. 3. No other experimental data exist for Kr. At the threshold for double ionization krypton shows the characteristic rise from a yield of unity to a plateau giving an abundance of $Kr^{2+}$ of about 14 to 15%. However, the abundance of doubly charged krypton continues to rise rapidly at higher photon energies just before the threshold for triple ionization. Presumably, the increase in double ionization continues beyond the triple-ionization threshold. Thus, no estimate of the abundance of triply ionized Kr can be made.

Figure 4 shows the results for multiple ionization of Xe. The solid data points represent the average of the yields obtained by both the ion-
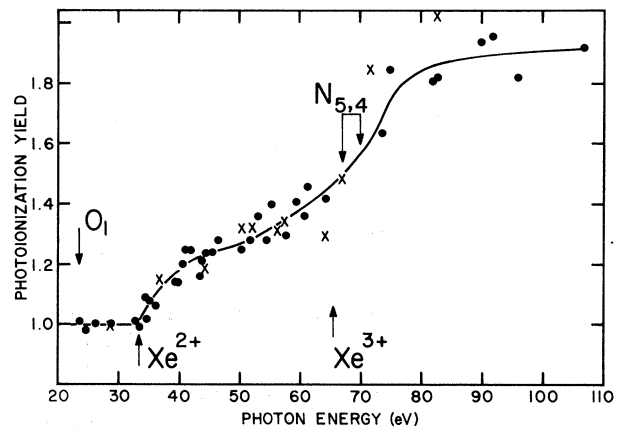


FIG. 4. Photoionization yield of xenon as a function of photon energy. Present data, circles; Cairns, Harrison, and Schoen, crosses.

chamber technique and the gas-jet–electron-multiplier combination. Included in the figure for comparison are the data points of Cairns, Harrison, Schoen.[13] The characteristic plateau that appears in the Ar and Kr data is less distinct. However, the rapid rise in double ionization before the triple-ionization threshold is more pronounced than in the Kr data. This increase may be caused by an interference between competing processes, one or more of which involve the $d^{10}$ shell ($N_{5,4}$ level). In krypton the effect is less pronounced, and in argon, which has no $d$ shell, the effect is absent.

The data of Cairns, Harrison, and Schoen are in good agreement with the present data. Beyond the $N_{5,4}$ edge Auger transitions are energetically possible, but according to the data of Cairns, Harrison, and Schoen the actual abundance (64%) of doubly charged ions peaks at 72 eV and then starts to decrease. At 83 eV they find an abundance of 59%.

The magnitude of multiple photoionization of the rare gases is surprisingly large. Further, double and triple ionization takes place at energies less than the threshold for Auger transitions. These present a challenge for theoretical consideration. The recent successes of the random-phase approximation with exchange in describing single ionization in the rare gases would suggest that this technique should be developed further and applied to multiple ionization.

---

[1] F. W. Byron, Jr., and C. J. Joachain, Phys. Rev. 164, 1 (1967).

[2] R. L. Brown, Phys. Rev. A 1, 587 (1970).

[3] T. A. Carlson, Phys. Rev. 156, 142 (1967).

[4] M. J. Van der Wiel, Th. M. El-Sherbini, and L. Vriens, Physica (Utrecht) 42, 411 (1969); Th. M. El-Sherbini, M. J. Van der Wiel, and F. J. De Heer, Physica (Utrecht) 48, 157 (1970).

[5] M. J. Van der Wiel, Physica (Utrecht) 49, 411 (1970).

[6] M. J. Van der Wiel and G. Wiebes, Physica (Utrecht) 53, 225 (1971).

[7] M. J. Van der Wiel and G. Wiebes, Physica (Utrecht) 54, 411 (1971).

[8] T. N. Chang, T. Ishihara, and R. T. Poe, Phys. Rev. Lett. 27, 838 (1971).

[9] M. Ya. Amusia, in Atomic Physics 2, edited by P. G. H. Sanders (Plenum, New York, 1971), p. 249.

[10] M. Ya. Amusia and M. P. Kazachkov, Phys. Lett. 28A, 27 (1968).

[11] M. Ya Amusia, M. P. Kazachkov, N. A. Cherepkov, and L. V. Chernysheva, in Proceedings of the Sixth International Conference on the Physics of Electronic and Atomic Collisions, Cambridge, Massachusetts, 1969. Abstracts (MIT Press, Cambridge, Mass., 1969), p. 130.

[12] M. Ya Amusia, in Proceedings of the Eighth International Conference on the Physics of Electronic and Atomic Collisions, Belgrade, Yugoslavia, 1973. Invited Lectures and Progress Reports (Institute of Physics, Belgrade, 1973), p. 171.

[13] R. B. Cairns, H. Harrison, and R. I. Schoen, Phys. Rev. 183, 52 (1969).

[14] G. S. Lightner, R. J. Van Brunt, and W. D. Whitehead, Phys. Rev. A 4, 602 (1971).

[15] T. A. Carlson, W. E. Hunt, and M. O. Krause, Phys. Rev. 151, 41 (1966).

[16] M. O. Krause, T. A. Carlson, and R. D. Dismukes, Phys. Rev. 170, 37 (1968).

[17] J. A. R. Samson, in Advances in Atomic and Molecular Physics, edited by D. R. Bates and I. Estermann (Academic, New York, 1966), Vol. 2, p. 177.

[18] J. A. R. Samson and G. N. Haddad, J. Opt. Soc. Amer. 64, 47 (1974).

[19] J. A. R. Samson, J. Opt. Soc. Amer. 54, 6 (1964).

[20] J. A. R. Samson, Techniques of Vacuum Ultraviolet Spectroscopy (Wiley, New York, 1967), p. 166.

---

# Observation of Macroscopic Heat Transfer by a Nuclear Spin System and Measurement of the Spin Diffusion Constant

J. V. Gates, II, and W. H. Potter
Department of Physics, University of California, Davis, California 95616
(Received 13 May 1974)

Experiments are reported which measure directly the macroscopic transfer of energy from the surface of small crystallites to the interior via nuclear spins. The hydrogen nuclei in $Y(C_2H_5SO_4)_3 \cdot 9H_2O$ constitute the nuclear spin system that transports the energy. We directly determine the value $5 \times 10^{-12}$ cm$^2$/sec ($\pm 20\%$) for the spin diffusion constant, which does not depend on the correctness of any theory of nuclear spin-lattice relaxation.

We report what we believe to be the first observation of macroscopic energy transport by a nuclear spin system. From our measurements we obtain directly the value $5.25 \times 10^{-12}$ cm$^2$/sec