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X-RAY SPECTRA FROM ARGON-ARGON COLLISIONS*

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Spectral measurements have been made of L-shell x rays produced by 50- to 330-keV Ar ions incident on Ar gas targets. The data are considered within the framework of the level-crossing model of Fano and Lichten, and the observed lines are consistent with Hartree-Slater calculations for highly excited configurations.

The detailed nature of inner-shell vacancy production in ion-atom collisions has been the subject of active investigation by several authors.[1-3] A useful model for inner-shell excitation has been proposed by Fano and Lichten.[4] According to their model, inner-shell vacancies are produced as a result of level crossings in the pseudomolecule formed during the collisions.

In this paper x-ray spectroscopic measurements for argon ion-atom collisions are reported. These measurements lead to new and more specific information concerning the excitation mechanism. Rudd, Jorgensen, and Volz[1] have investigated details of the process by observing the Auger electron distribution from argon-argon collisions. The analysis of the Auger electron data, however, is complicated by the large number of lines. The existence of stronger selection rules governing x-ray emission leads to relatively simple spectra with correspondingly simple interpretations.

In the present work a beam of argon ions from a duo-plasmatron source was introduced into a chamber containing argon gas at a pressure of approximately 50 μ (between 5 and 70 μ the spectra were not pressure-sensitive). The effective energy of the ion beam was varied from 50 to 330 keV, and the path length for the beam in the gas to the region of observation was 3 cm. X rays produced as a result of collisions were observed with a diffraction spectrometer at 90° to the incident ion beam. The diffracting element was a 1-μ thick lead stearate film mounted on a mica substrate, and the detector was a flow-mode proportional counter with a 90 $\mu g/cm^2$ Formvar window. The window transmission for x rays between 150 and 284 eV ranged from 15 to 65%, and was negligible above 284 eV (the carbon K edge). The counter gas was helium isobutane at atmospheric pressure. The resolution of the spectrometer at 277 eV was 14 eV full width at half-maximum.

Figure 1 shows the x-ray spectra observed for several ion bombarding energies. No correction has been made for background or window absorption. For 50-keV bombarding energy two x-ray lines were detected, at 224± 4 and at 264± 4 eV, respectively [see Fig. 1(a)]. As the bombarding

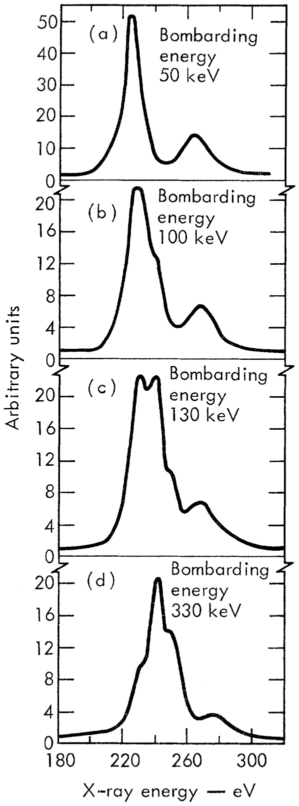

FIG. 1. X-ray spectra observed for several bombarding energies in argon ion-atom collisions.

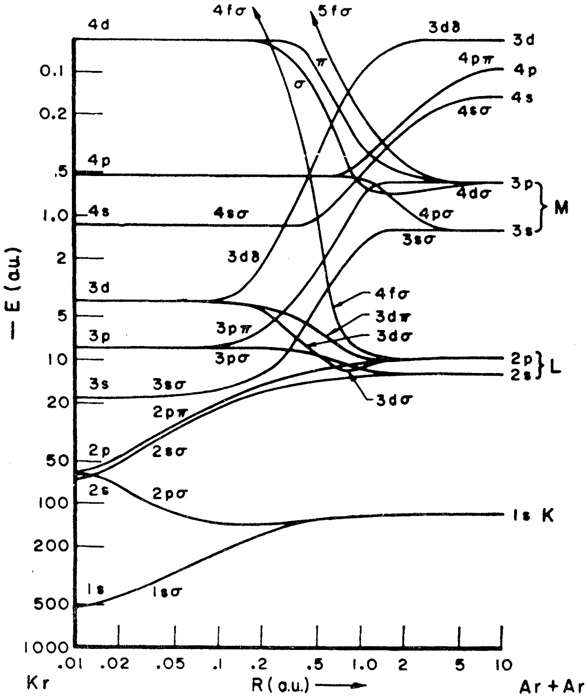

FIG. 2. Electronic energy levels of Ar_2^+ molecule, as given by the Fano-Lichten model of $Ar^+ \rightarrow Ar$ collision (from Ref. 5).

energy was increased to 80 keV, new lines appeared in the spectra close to the 224-eV line. Figure 1(b) shows the data for a bombarding energy of 100 keV; an additional line appears at approximately 240 eV. When the bombarding energy was increased to 130 keV [Fig. 1(c)], the 240-eV peak became relatively more prominent than at lower energies and another new line began to appear at about 250 eV. A further increase in bombarding energy to the maximum available energy of 330 keV [Fig. 1(d)] caused further changes in the relative heights of the peaks, but no other new lines appeared.

These spectra can be understood within the framework of the Fano and Lichten model,[4] with x-ray line emission assumed to occur in the separated atoms. According to Fano and Lichten, a $2p$ vacancy results from a level crossing involving the $4f\ \sigma$ molecular level. In Fig. 2 the electronic energy-level diagram of the Ar_2^+ molecule is plotted as a function of the ion-atom distance of separation. At larger ion-atom separations there are many level crossings which may result in excitation of the outer shells prior to the $2p$ excitation. In section A of Table I we present the results of a Hartree-Slater calculation[6] of electronic energy levels in excited argon atoms. Column 1 shows configurations of the excited atoms prior to the removal of a $2p$ electron. These configurations were chosen because they are consistent with the average 45-eV loss per atom measured for outer shell excitations only by Kessel and Everhart.[2] Column 2 shows the energies required to produce these configurations, column 3 gives the $2p$ binding energies, and columns 4, 5, and 6 give the promotion energies (equal in magnitude to x-ray energies) for $2p \rightarrow 3s$, $2p \rightarrow 3d$, and $2p \rightarrow 4s$ excitations, respectively.

These configurations are representative of the infinite set of outer-shell arrangements consistent with an average 45-eV loss. The promotion energies (x-ray energies) are insensitive, within a few eV, to the exact configuration of outer-shell electrons. The origin of the two x-ray lines seen for the 50-keV bombarding energy is clear. The 224-eV line represents a $3s \rightarrow 2p$ transition, while the 264 eV line is a $4s \rightarrow 2p$ and $3d \rightarrow 2p$ transition. For the 264-eV line, calculated transition rates favor the $3d$ rather than the $4s$ transition. Recent scattering experiments of Afrosimov et al.[3] yield L-shell promotion energies of 258 ± 8 and 272 ± 6 eV. These values are consistent with $2p$ excitations to $3p$, $4s$, $4p$, $3d$, or oth-

Table I. Results of Hartree-Slater calculations of argon energy levels.[a]

	Configuration	Configuration energy (eV)	$2p_{3/2}$ binding energy[b] (eV)	$3s \to 2p_{3/2}$ transition energy[c]	$3d \to 2p_{3/2}$ transition energy[c]	$4s \to 2p_{3/2}$ transition energy[c]
A	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6$	0	247	218	—	—
	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^4(3d)^1(4s)^1$	29	260	222	257	256
	$(1s)^2(2s)^2(2p)^6(3s)^1(3p)^5(3d)^1(4p)^1$	44	262	222	258	—
	$(1s)^2(2s)^2(2p)^6(3s)^1(3p)^4(3d)^1(4s)^1(4p)^1$	63	269	224	262	264
B	$(1s)^2(2s)^2(2p)^5(3s)^2(3p)^4(3d)^1(4s)^1(4p)^1$	286	295	247	286	289
	$(1s)^2(2s)^2(2p)^5(3s)^1(3p)^5(3d)^1$	315	310	248	287	—
	$(1s)^2(2s)^2(2p)^5(3s)^1(3p)^4(3d)^1(4s)^1(4p)^1$	334	311	250	291	298

[a] Calculations performed by J. H. Scofield (private communication).

[b] The $2p_{1/2}$ binding energy is ~2 eV greater than the $2p_{3/2}$ value over the range of the table.

[c] The $2p_{1/2}$ transition energy is ~2 eV greater than the $2p_{3/2}$ value over the range of the table.

er states of lesser binding energy. It has been proposed[7] that the observed excitations are associated with $2s$ vacancy production. However, Hartree-Slater calculations show that the promotion energy required to excite a $2s$ electron is at least 300 eV.

It is important to note that the observed 264-eV x ray attributed to a $4s \to 2p$ or $3d \to 2p$ transition has an energy greater than the binding energy of the ground-state argon $2p$ level. There has been some confusion in the literature over the fact that energy-loss measurements yield excitation energies greater than the ground-state binding energies for the promoted electron. The reason for this is, of course, that the screening effects of the outer-shell electrons strongly affect inner-shell binding energies. The large excitation energies measured reflect the increase in the binding energy of the promoted electron due to multiple excitations.

We observe the effects of double L-shell excitations for bombarding energies above 80 keV. Our x-ray measurements show the two new lines at 240 and 250 eV. As the bombarding energy is increased these lines grow in size relative to the two lines seen at 50 keV, and are consistent with calculations of $3s \to 2p$ transition energies for double vacancies in the argon $2p$ level (see section B of Table I). The $4s \to 2p$ and $3d \to 2p$ transitions for double L-shell vacancies result in x-ray energies above 284 eV. These x rays would not be observed with our present detector.

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[1] M. E. Rudd, T. Jorgensen, Jr., and D. J. Volz, Phys. Rev. 151, 28 (1966).

[2] Q. C. Kessel and E. Everhart, Phys. Rev. 146, 16 (1966).

[3] V. V. Afrosimov, Yu. S. Gordeev, A. M. Polyansky, and A. P. Shergin, in *Proceedings of the Sixth International Conference on the Physics of Electronic and Atomic Collisions, Cambridge, Massachusetts, 27 July-2 August 1969* (Massachusetts Institute of Technology, Cambridge, Mass., 1969), pp. 744-746.

[4] U. Fano and W. Lichten, Phys. Rev. Letters 14, 627 (1965).

[5] Illustration reproduced from Fig. 4 of W. Lichten, Phys. Rev. 164, 131 (1967).

[6] For details of the calculations used to obtain the information in Table I, see J. H. Scofield, Phys. Rev. 179, 9 (1969).

[7] D. Picca, Nuovo Cimento, 64B, 1, 1969.