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INITIAL-STATE CONFIGURATION-INTERACTION SATELLITES
IN THE PHOTOEMISSION SPECTRUM OF Cd^+

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The photoemission spectrum of atomic cadmium ($4d^{10}5s^2;^1S$) should show three peaks, at binding energies¹ of 8.99 eV, 7.58 eV, and 18.28 eV, arising respectively from transitions to the ($d^{10}s;^2S$), ($d^9s^2;^2D_{5/2}$) and ($d^9s^2;^2D_{3/2}$) final states in Cd^+ . In addition to these three lines, we have also observed two weaker peaks at 14.44(3) eV and 14.79(3) eV in high-temperature ultraviolet photoemission studies on atomic Cd. These latter peaks are assigned to the ($d^{10}p;^2P_{1/2}$) and ($d^{10}p;^2P_{3/2}$) states, respectively. Their presence in the spectrum is attributed to photoemission of an np ($n \geq 5$) electron from ($d^{10}5pnp;^1S$) components that are mixed into the nominal ($d^{10}s^2;^1S$) ground state by configuration interaction, forming the eigenstate

$$\Psi(^1S) = a|d^{10}s^2;^1S\rangle + \sum_{n \geq 5} b_n |d^{10}5pnp;^1S\rangle + \dots$$

The largest configuration mixing coefficient b_n should be that of the ($5p^2;^1S$) configuration, due to its being "quasi-degenerate" with ($5s^2;^1S$).³ Berkowitz, et al.² have recently observed similar lines in the photoemission spectrum of Hg. It seems probable that such "CI lines" will be observable in many atomic systems, and that they can provide useful information about electron correlation in these systems.

The experiments were carried out with 21.2 eV HeI radiation at 633°K, using the high-temperature probe in a Perkin-Elmer P.S. 18 Ultraviolet Photoelectron Spectrometer. A typical spectrum is shown in Fig. 1. Derived parameters, based on average values from three separate runs, are given in Table I. Energy calibrations were carried out by introducing Xe and Ar gases with the sample. The spectrometer resolution was 30 meV FWHM. Because the spectrometer efficiency decreases with increasing ionization potential, the observed intensities in Table I have only qualitative significance.

Configuration-interaction satellite lines in photoemission spectra have been observed as "shake-up" peaks in gases⁴ and solids⁵ and as satellites in multiplet spectra.⁶ Such satellites are usually interpreted as arising from final-state configuration interaction. They therefore have the same symmetry as the main final-state peak (this result is also discussed as an "E0" selection rule for shake-up "transitions"). The Cd⁺ satellites are strictly forbidden by this selection rule. They arise instead from initial-state configuration interaction. The selection rule for such transitions is much less restrictive: any state is eligible that may be reached by a one-electron transition from configurations mixed into the ground state. A preliminary search for the other allowed lines (e.g., the $4d^{10}6s; ^2S_{1/2}$ line at 19.28 eV)¹ has yielded negative results, presumably because the small admixtures of their parent configurations into the ground states could not yield intensities observable with our present sensitivity.

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- * Work performed under the auspices of the U. S. Atomic Energy Commission.
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Table I. States of Cd^+ observed in photoemission from Cd vapor.

Final state	Apparent relative intensity(a)	Binding energy, eV(a)	Energy from optical data(b)
$4d^{10}5s^2S$	(1)	8.98(2)	8.991
$4d^{10}5p^2P_{1/2}$	0.03(1)	14.44(3)	14.463
$4d^{10}5p^2P_{3/2}$	0.06(1)	14.79(3)	14.771
$4d^95s^2^2D_{5/2}$	2.5(2)	17.57(2)	17.578
$^2D_{3/2}$	1.3(2)	18.28(2)	18.276

(a) This work. Values given are averages of three runs. Errors in last place are given parenthetically. The Xe lines at 12.130 eV and 13.436 eV and the argon lines at 15.759 eV and 15.937 eV were used for calibration.

(b) Ref. 1.

Figure Caption

Fig. 1. Photoemission spectrum of Cd vapor at 633°K using 21.2 eV HeI radiation.

The whole spectrum took 2.5 hrs. to scan. Lines marked "s" arise from the HeI 23.08 eV radiation (i.e., $1s3p(^1P^o) \rightarrow 1s^2$).

Fig. 1

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