Effects of Autoionization on the Alignment of $Cd^+(4d^95s^2\,^2D_{5/2})$ in the Range 680–710 Å

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The alignment of the $4d^95s^2\,^2D_{5/2}$ state of Cd^+ is obtained from fluorescence polarization measurements using dispersed synchrotron radiation in the spectral region 680 to 710 Å. This region is dominated by strong autoionization features associated with the $nf(^1P_1)$ and $np(^3P_1,^3D_1)$ Rydberg states converging to the $4d^95s^2\,^2D_{3/2}$ fine-structure threshold. The polarization and alignment data show marked variations across the resonance profiles and are compared with recent calculations in the relativistic random-phase approximation in conjunction with multichannel quantum-defect theory.

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The benchmark process for studying photoionization-induced alignment in atoms has been the fluorescence decay of the excited "*d*-hole" states of Cd^+. Fluorescence polarization measurements, from which alignment is derived, have been made at the He I[1,2] and Ne II[2] rare-gas resonance lines and calculations using both single particle[1-4] and many-body models[5,6] have been reported. The effects of nearby autoionizing resonances, however, were not considered. More recently, Kronast, Huster, and Mehlhorn[7] have extended the measurements to cover the region from threshold to 400 Å with dispersed synchrotron radiation. In the range 600 to 400 Å, their polarization data clearly show resonance features which can be attributed to autoionization. From photoabsorption data[8] it is known that this spectral region contains many overlapping lines, most of which have been assigned to doubly excited states of neutral Cd with general configuration $4d^95s(^{1,3}D)nln'l'$ $(J=1)$.

In this Letter we report the results of a photoionization study of Cd in which the effects of autoionization on alignment are examined in more detail. Specifically, fluroescence polarization measurements were made for the $4d^95s^2(^2D_{5/2})$ excited state of Cd^+ at excitation energies encompassing the $4d^95s^2(^2D_{3/2})np\,^3P_1$, $^3D_1$ $(n\geq 8)$ and $4d^95s^2(^2D_{3/2})nf\,^1P_1$ $(n\geq 5)$ autoionizing Rydberg series, first observed and assigned by Beutler.[9] The process under study can be written

$$\mathrm{Cd}(4d^{10}5s^2\,^1S_0)+\gamma(\lambda\leq 706\ \text{Å}) \rightarrow \begin{cases} \mathrm{Cd}^*[4d^95s^2(^2D_{3/2})nl;J=1] \\ \quad\downarrow \\ \mathrm{Cd}^+(4d^95s^2\,^2D_{5/2})+e^- \end{cases}$$
$$\downarrow$$
$$\mathrm{Cd}^+(4d^{10}5p\,^2P_{3/2})+\gamma'(\lambda=4416\ \text{Å})$$

and the alignment of the excited Cd^+ ion is obtained by measuring the linear polarization (P) of the fluorescence γ' at 4416 Å. The *np* and *nf* Rydberg states form well characterized series converging on the $^2D_{3/2}$ limit[9,10] and are, therefore, ideal for study. Furthermore, multichannel quantum-defect theory calculations[11] for the photoionization of Cd in this energy region have just recently become available, making a detailed comparison between theory and experiment possible.

The experimental apparatus was of the crossed-beam type with fluorescence detection at right angles to the intersection of a Cd effusive beam and vacuum-ultraviolet photon beam.[12] The Cd vapor was produced by a two-chamber stainless-steel oven operating at ~400 °C (~2 Torr Cd). Tunable monochromatic radiation from the 4-m normal-incidence monochromator on the U-11 beam line on the vacuum-ultraviolet storage ring at the National Synchrotron Light Source was used as the photoexcitation source. Typical photon fluxes were $5\times 10^{10}\,\mathrm{sec}^{-1}$ (at 100-mA circulating current) with a wavelength resolution of 0.5–1.0 Å.

Fluorescence from the ions, which had been polarization- and wavelength-selected by a rotatable,

thin-film polarizer and narrow-bandpass interference filter, was detected by a photomultiplier tube. Standard single-photon counting techniques were used to generate fluorescence spectra. The polarization of the fluorescence was calculated from $P=(I_{\parallel}-I_{\perp})/(I_{\parallel}-I_{\perp})$, where $I_{\parallel}$ and $I_{\perp}$ are the measured intensities polarized parallel and perpendicular to the axis of quantization, taken to be along the direction of the linear polarization of the synchrotron radiation.

The results of the fluorescence measurements are shown in Fig. 1. The upper curve is an excitation spectrum (total 4416-Å fluorescence intensity as a function of wavelength) which has been corrected for background and normalized to the intensity of ionizing radiation. This spectrum represents the relative partial cross section for producing the $^2D_{5/2}$ ionic state and is derived from the fluorescence excitation spectrum at 90° and the energy-dependent polarization curve (see Fig. 2).[13] The positions and relative intensities of the observed autoionization series are in excellent agreement with previous photoabsorption measurements.[8–10] Although not clearly resolved, the presence of the $5f$ and $6f$ resonances is observed as small shoulders on the high-energy tails of the $8p$ and $9p$ peaks, respectively. Also shown in Fig. 1 (lower curve) is the $^2D_{5/2}$ partial cross section recently calculated by Johnson, Parpia, and Radojevic[11] using the relativistic random-phase approximation (RRPA) in conjunction with multichannel quantum-defect theory (MQDT), which has been convoluted with a 1.0-Å Gaussian slit function to simulate the finite bandwidth of the monochromator. The overall good correspondence between theory and experiment indicates that the incorporation of MQDT into the RRPA method permits a realistic treatment of the bound-continuum coupling responsible for autoionization. Close comparison of the two curves, however, reveals that the calculation underestimates the autoionization strength of the $5f$ and $6f$ resonances into the $^2D_{5/2}$ channel, the consequences of which are very prominent in the polarization data.

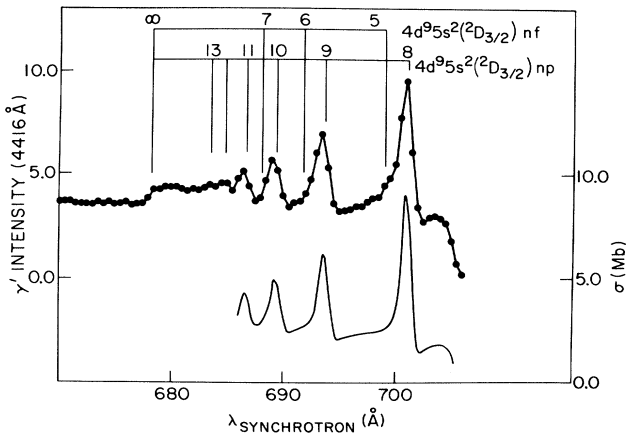

FIG. 1. Partial photoinization cross section of the $^2D_{5/2}$ state of Cd^+ from threshold to 670 Å. Circles, experimental relative cross section (left vertical scale) obtained from fluorescence measurements; solid line, theoretical absolute cross section (right vertical scale) from Ref. 11 convoluted with a Gaussian slit function of 1.0-Å half-width. The $np\,^3P_1$ and $^3D_1$ final-state multiplets cannot be resolved with the present monochromator resolution although the theoretical calculations (Ref. 11) predict that the $^3P_1$ multiplet dominates the cross section.

Figure 2 gives the energy-dependent polarization and the experimentally determined $^2D_{5/2}$ cross section curve for comparison of the excitation and polarization profiles. The connected points are derived from series of excitation spectra in which the linear polarizer is fixed to pass $I_{\parallel}$ or $I_{\perp}$. The heavy points in the figure

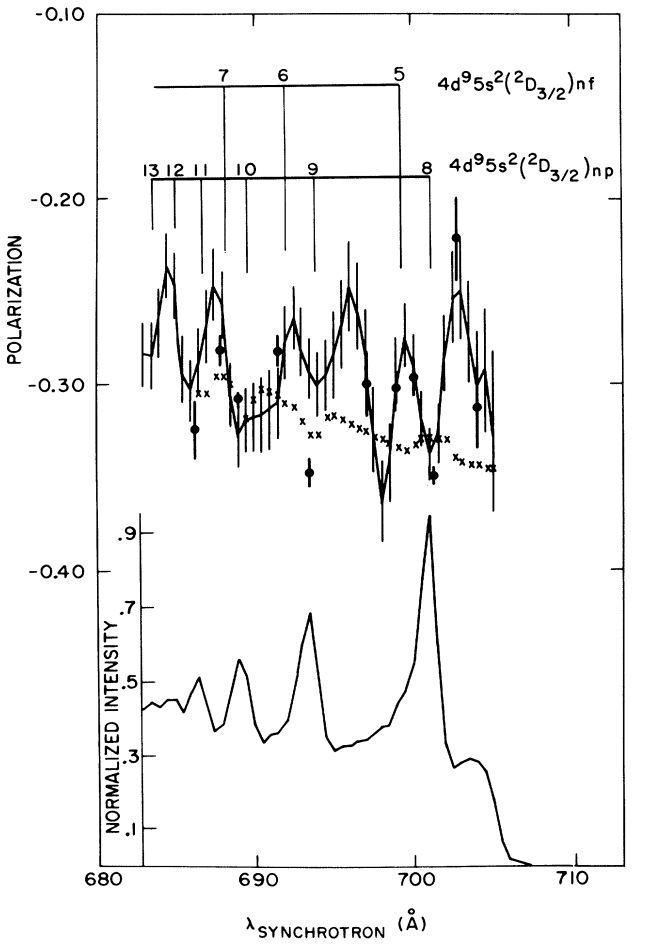

FIG. 2. Linear polarization of the fluorescence for the process $Cd^+(^2D_{5/2}) \rightarrow Cd^+(^2P_{3/2})+\gamma'(4416\ \text{Å})$ from the threshold to 680 Å. Circles, experiment; crosses, theoretical results from Ref. 11, convoluted to reflect 1.0-Å excitation bandwidth. Bottom curve is the experimental $^2D_{5/2}$ partial cross section reproduced from Fig. 1.

are the result of fluorescence intensity measurements at a fixed wavelength having the polarizer oriented successively parallel and perpendicular to the quantization axis. The data shown have been corrected for birefringence in the detection optics, detection solid angle, and magnetic field depolarization.[1] Unresolved hyperfine structure is taken into account by use of formulas developed by Greene and Zare.[5] Finally, a correction for the elliptical polarization of the synchrotron radiation is made based on an analysis by Klar.[14]

It is apparent from Fig. 2 that cross-section minima in the *np* series resonance profiles are associated with marked decreases ($|P| \rightarrow 0$) in the polarization of the emitted radiation. Furthermore, it is at the resonance peak positions in the $^2D_{5/2}$ cross section that the polarization tends to its most negative values. Although rigorously it may not be possible to ascribe spectral regions in this wavelength range which are unaffected by the presence of the resonances, it would appear from the survey polarization results of Kronast, Huster, and Mehlhorn,[7] and the RRPA-MQDT theoretical results[11] that the most negative value of the polarization primarily reflects the direct ionization contribution. Another striking feature of the measured polarization data is the perturbing effect of the *nf* series. These transitions are only weakly visible in the $^2D_{5/2}$ partial cross section, whereas the influence of the lower members of the *nf* series on the polarization is comparable to that of the *np* series.

Also shown in Fig. 2 are the theoretical RRA-MQDT polarization results which have been convoluted by the same finite excitation bandwidth ($\Delta\lambda = 1.0$ Å) as found appropriate for the $^2D_{5/2}$ partial cross section. The comparison between experiment and the convoluted RRPA-MQDT results is quite poor, with the theoretical polarization curve showing much smaller variations across the autoionization resonances. This result is insensitive to the choice of other experimentally feasible excitation bandwidths (0.5–1.0 Å). Qualitatively, the theoretical polarization profiles for the *np* resonances with $n > 8$ show similar behavior as that observed experimentally, i.e., a decrease in the Cd^+ polarization near the autoionization cross-section minima. The polarization profile for the $8p$ resonance, however, shows the opposite behavior. Furthermore, the theoretical polarization results are essentially unaffected by the presence of the $5f$ and $6f$ resonances, in stark contrast to experiment. The source of the large discrepancy between theory and experiment for the polarization is not clear at this time. It should be noted, however, that measurements such as fluorescence polarization and photoelectron angular distributions are in general more sensitive to accurate descriptions of the photoionization dynamics than are the partial or integrated cross sections.

The physically interpretable quantity to be derived from the present experiment is the alignment of the residual Cd^+ following the interfering photoionization-autoionization event. Alignment refers to the asymmetry of the $|m|$ sublevel population of the excited j state of the ion and is defined in the collision frame for a cylindrically symmetric system by[13]

$$A_0^{\mathrm{coll}}(j) = \sum_m \sigma(j,m) \frac{3m^2 - j(j+1)}{j(j+1)} \left[\sum_m \sigma(j,m) \right]^{-1},$$

where $\sigma(j,m)$ is the probability of producing the state j with projection m. The relationship between the fluorescence linear polarization and the alignment of the emitting state is given elsewhere [Eq. (12), Ref. 5].

The alignment parameter over the spectral region of interest is shown in Fig. 3. The variation of the alignment across the autoionizing resonance follows the variation of the linear polarization but is much more pronounced. This is a consequence of the effect of the final state on the polarization, which in general

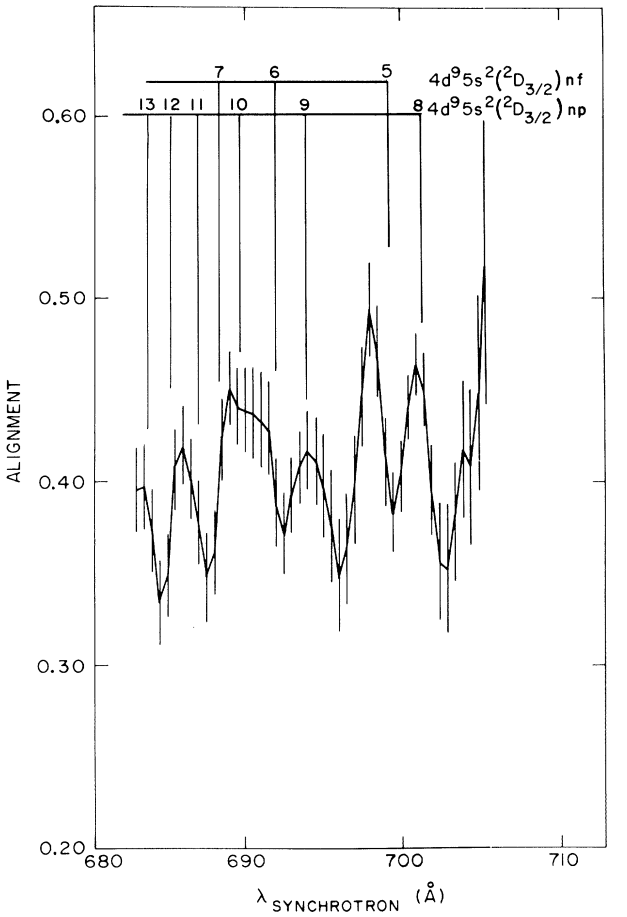

FIG. 3. Alignment of the $^2D_{5/2}$ excited state of Cd^+ from threshold to 680 Å.

reduces the value of P for a given value of A_0^{coll}.[5] For the $^2D_{5/2}$ state, the one alignment parameter does not provide adequate information to extract individual $\sigma(j,m)$ partial cross sections. The fact that the alignment is positive over the entire spectral region, however, indicates that there is enhanced population in the $|m| = \frac{5}{2}$ levels [see Eq. (1)]. Hence, one effect of the autoionizing resonances is to decrease the alignment or, equivalently, the $|m| = \frac{5}{2}$ population at their cross section minima.

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