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Excited state production in collisions between rare gas ion and cadmium atoms has been studied in a crossed beam apparatus at kinetic energies as low as 2 eV. It was found that charge transfer excitation cross sections resulting from impact of metastable argon ions were considerably larger than those with other rare gas ion reactants, either ground or excited state. The selective population of CdII ($6s\ ^2S$) in these low energy Ar^+/Cd interactions suggests that, under the proper conditions, laser action at 257.3 and/or 274.9 nm might be possible.

I. INTRODUCTION

One of the most commonly used methods for producing a population inversion in a laser cavity is by creation of an electrical discharge in a He/metal vapor mixture in the cavity. Many of the laser transitions produced in this way occur between excited levels of the atomic metal ion; these excited ions are usually formed by Penning ionization:

$$He^* + M \rightarrow (M^+)^* + He + e \ , \qquad (1)$$

or by charge transfer excitation (CTE):

$$He^+ + M \rightarrow (M^+)^* + He \ . \qquad (2)$$

In the above equations M represents a metal atom, the asterisks indicate electronic excitation, and He^* represents a metastable helium atom. Because the ionization potential of helium is high (24.6 eV), as are the energies of the metastable states (~ 19–20 eV), a variety of excited ionic states of the metal atom are energetically allowed in a thermal discharge. Although neon has only a slightly lower ionization potential and slightly lower-lying metastable levels than helium, little work has been reported on Ne/metal atom systems. The relatively low ionization potentials of the other rare gases makes it possible to form only a few excited ionic states in processes analogous to (1) and (2). However, while virtually all the He^+ or Ne^+ ions formed in electrical discharges or by simple electron impact are in the ground state, it has been shown that discharges in argon or krypton produce a variety of high-lying metastable ionic states.[1–3] In fact, the electronic recombination energies of these metastable rare gas ions to ground state atoms exceeds the ionization potential of helium by 4–8 eV. Thus, under the proper conditions it might be possible to produce a population inversion by CTE processes utilizing metastable reactant Ar^+ or Kr^+ formed in an Ar/metal vapor or Kr/metal vapor discharge. However, because the fractional concentration of the metastable Ar^+ or Kr^+ is usually quite low[1] the success of such a scheme depends on the cross sections for specific CTE processes. Furthermore, unless the internal energy partitioning among the final product states offers the possibility of producing laser action at a wavelength that has not been achieved with He/metal vapor discharges no advantage is to be gained by using a different rare gas.

One of the most abundant sources of laser transitions in He/metal vapor mixtures is excited, singly ionized cadmium atoms. Both Penning and CTE processes are known to occur in these electrical discharges, and both produce inverted state populations.[4] In fact, He/Cd lasers operating at either 441.6 or 325.0 nm are commercially available. Because He^+/Cd reactions have been extensively studied,[4–6] and because a number of laser transitions have been produced in such reactions, we chose to study reactions between other rare gas ions and Cd, and to compare the results to those for the He^+/Cd system. In this paper we present the results of crossed beam experiments in which the energy partitioning among available quantum states of the product species is diagnosed by dispersal and detection of radiation emitted by decaying excited products. Emission cross sections for the most prominent spectral features are presented and compared to those for the He^+/Cd system. The results show that the cross sections for some specific $(Ar^+)^*/Cd$ CTE channels are large enough to suggest that these reactions could be used to achieve laser action at ultraviolet wavelengths.

II. APPARATUS

The experiments were performed in a computer controlled crossed beam apparatus equipped with an optical system for spectral analysis of radiation from excited product states.[7] Ions were produced by electron impact in an emission regulated source, focused into a beam by a set of cylindrical electrostatic lenses and magnetically mass selected; a second set of electrostatic lenses was used to focus the beam into a collision cell at the desired energy; ions were collected on a Faraday cup located behind the collision cell, and the current monitored with an electrometer. For most of the work reported here the electron energy in the source was set at 50 eV and the gas pressure maintained at ~ 10^{-5} Torr; earlier work has shown that these conditions produce ~ 1–1.5% metastable argon or krypton ions,[1–3] designed $(Ar^+)^*$ and $(Kr^+)^*$, respectively. The states of these ions of Ar^+, that have been shown to be present in the beam after extraction from the source, are listed in Table I together with the corresponding states of Kr^+. Also included in this table are the energies of these states above the ground state of the neutral atom. Neither the Ne^+ nor the He^+ beams contained

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TABLE I. Metastable states present in $(Ar^+)^*$ and $(Kr^+)^*$ beams[a] produced by 50 eV electron impact.

Ion	State	Energy[b] (eV)
Ar^+ $[3p^4(^3P)3d]$	$^4D_{7/2}$	32.16
	$^4F_{9/2}$	33.38
	$^4F_{7/2}$	33.45
	$^2F_{7/2}$	33.25
Kr^+ $[4p^4(^3P)4d]$	$^4D_{7/2}$	28.90
	$^4F_{9/2}$	29.62
	$^4F_{7/2}$	29.86
	$^2F_{7/2}$	30.32

[a]Reference 1.
[b]Zero energy is taken to be $Ar(3p^5\,^1S_0)$ and $Kr(4p^6\,^1S_0)$.

significant populations of metastable excited states.[1] Ar^+ beams free of significant concentrations of metastable states were produced by lowering the electron energy to a value below the energy of the lowest metastable state. Different Ar^+/Cd collision-produced spectra were obtained for the two different sets of ion source conditions (at the same ion kinetic energy) confirming the presence and absence of metastable argon ions in the beam. Although previous work, from other laboratories,[1,3] indicates that the excited state composition of the Kr^+ beam should be similar to that of the Ar^+ beam, no differences in the Kr^+/Cd data were observed for the different ion source conditions. Nevertheless, even in the absence of such unequivocal evidence that metastable states of Kr^+ were present, we retain the Kr^+ and $(Kr^+)^*$ notation to indicate the source conditions under which the ions were produced.

An oven beneath the collision cell produced an effusive beam of cadmium atoms which crossed the ion beam at a right angle in the center of the cell. Photons emanating from the intersection of the two beams were spectrally analyzed with an optical system consisting of focusing lenses, a 0.25 m monochromator, and a cooled photomultiplier tube used in the counting mode. The spectral response of this optical system was determined with standard lamps.

Two methods of data acquisition were employed. In the first, collision-produced spectra were obtained at a fixed ion kinetic energy by stepping the monochromator through the desired range of wavelengths and accumulating photon counts at each setting; multiple scans were taken for signal averaging. This mode of operation yielded collision-produced spectra, at a given kinetic energy, from which the energy partitioning among product quantum states could be deduced. In the second mode of operation the monochromator was fixed at the wavelength of a given atomic transition and the collision energy varied to obtain the energy dependence of a particular emission cross section.

Since the density of cadmium atoms in the effusive beam could not be accurately determined our measurements have been normalized to the absolute emission cross sections for 441.6 nm CdII emissions from 100 eV He^+/Cd collisions reported by Soskida and Shivera.[5] The beam energy was switched between 2 and 100 eV (center-of-mass energy) several times during a run to obtain the relative cross sections at those energies. The same procedure was followed for beams of Ne^+ and $(Ar^+)^*$. In a separate experiment at 100 eV (c.m.) the ion beam was alternated between He^+ and Ne^+, and between He^+ and $(Ar^+)^*$ to obtain Ne^+/Cd and $(Ar^+)^*$/Cd cross sections. While the relative cross sections reported here are considered accurate to 25–30%, the absolute measurements depend on the cross section measurements of Soskida and Shivera.[5]

III. RESULTS

The CdII emissions observed from 2 eV (c.m.) collisions of rare gas ions with cadmium atoms are indicated in the partial term diagram shown in Fig. 1. Collision-produced spectra taken at 2 eV are shown in Fig. 2; the He^+/Cd spectrum is identical to that contained in our earlier report.[6] For impact of ground state ions, only CdII emissions were observed, however $(Ar^+)^*$/Cd collisions produced weak emission from ArII. These weak emissions are probably due to collisional de-excitation of metastable states of Ar^+ to radiating states of Ar^+.

The apparent broadening of the 214.4 nm line in the He^+, Ne^+, and $(Ar^+)^*$ spectra is due to the unresolved 219.5 nm line, similarly the 226.5 nm line is broadened by the 231.3 line. Higher resolution spectra over the wavelength range 210 to 235 nm shows the lines resolved. The 219.5 and 231.3 nm lines are not present in the $(Kr^+)^*$/Cd spectrum as discussed below.

Although there are minor differences, the Ne^+/Cd spectrum is quite similar to that for He^+/Cd. However, the $(Ar^+)^*$/Cd and $(Kr^+)^*$/Cd spectra differ significantly from each other, and from the He^+/Cd and Ne^+/Cd collision-produced spectra. Impact of $(Ar^+)^*$ results in a large increase in the size of the 274.9 and 257.3 nm peaks relative to the other features of the spectrum as compared to the He^+/Cd and Ne^+/Cd cases. The presence of the 274.9, 257.3, 219.5, and 231.3 nm lines in the $(Ar^+)^*$/Cd spectrum confirms the presence of metastable states in the argon ion beam since production of the upper states of these transitions is energetically forbidden in 2 eV collisions with ground state Ar^+.

Figure 3 shows collision-produced Ar^+/Cd spectra at several ion kinetic energies. The electron energy in the ion source was 30 eV, which is below the threshold for production of the metastable states. These spectra are not corrected for relative response of the optical system since the noise at the short wavelength end would be amplified to values that would obscure the changing features in the spectra. At 2 eV (c.m.), where only $5p\,^2P^0$ excited CdII states can be formed in collisions with ground state Ar^+ ions, no emissions were observed, indicating that the CdII emissions observed in the 2 eV $(Ar^+)^*$/Cd spectrum are due exclusively to metastable states of Ar^+.

As the collision energy is increased so that endothermic processes are permitted, the Ar^+/Cd spectrum that emerges is substantially different from that produced by impact of $(Ar^+)^*$. Although the $6s\,^2S$ state,

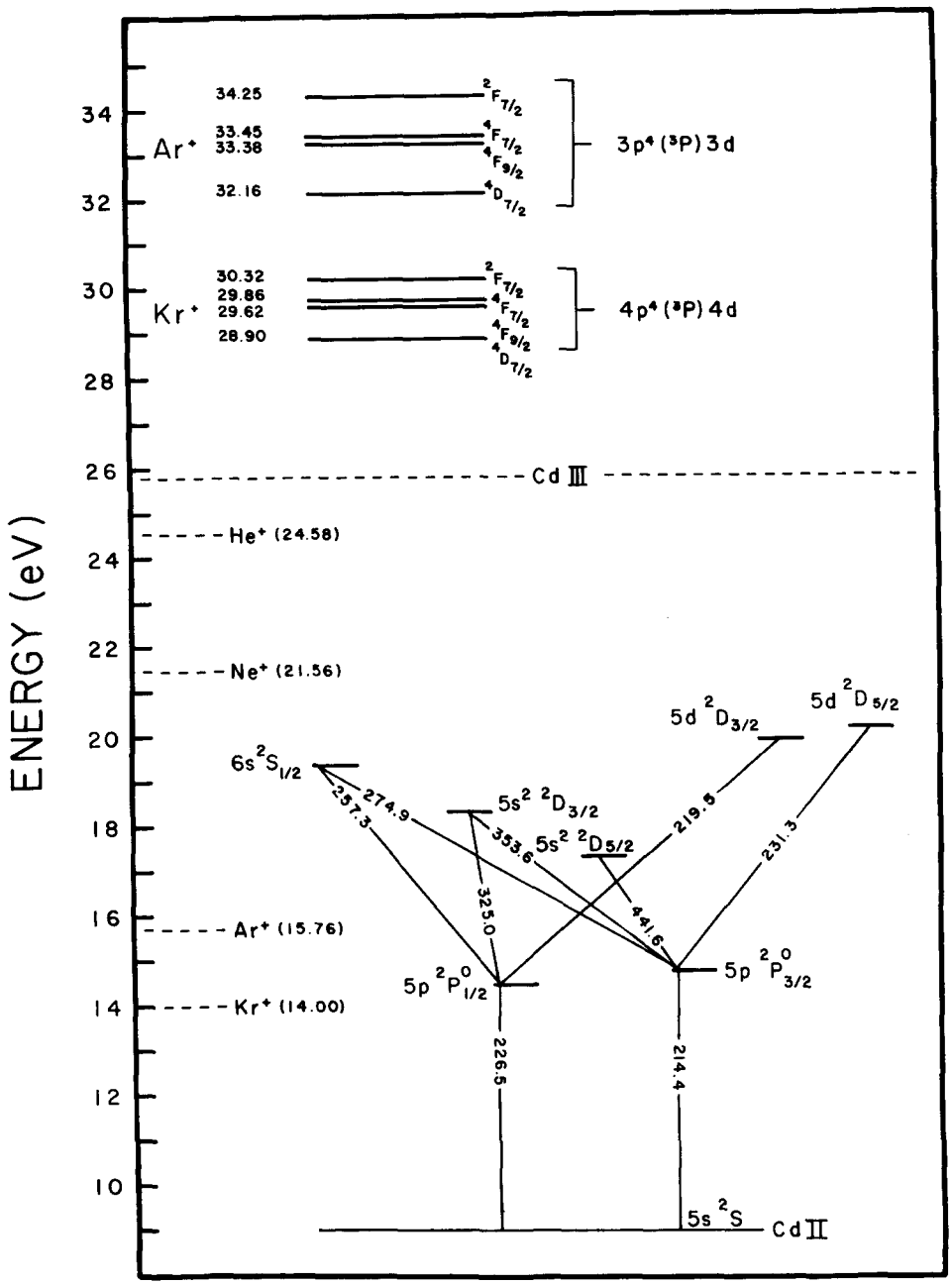

FIG. 1. Partial energy level diagram for Cd II showing the transitions from 2 eV rare gas ion/Cd collisions observed in this work. Energies are relative to the ground state of Cd I and wavelengths are in nanometers (nm). Also shown are the pertinent energy levels of the rare gas ions.

that radiates at 274.9 and 257.3 nm, are formed, as they are for low energy $(Ar^+)^*$/Cd collisions, the 441.6 and 325.0 nm lines, indicative of production of the $5s^2\ ^2D$ states, are not prominent. In fact, 441.6 nm is absent over the entire 2–100 eV ion kinetic energy range, and 325.0 nm appears only weakly at 8 and 20 eV.

For 2 eV $(Kr^+)^*$/Cd collisions (Fig. 2) there are only two peaks in the collision-produced spectrum (plus the second order of 214.4 nm). The upper states for these transitions are members of the lowest-lying excited multiplet of Cd II, and, although production of higher-lying states is energetically possible if metastable states are present in the ion beam, the $5p\ ^2P$ states are the only excited states produced. These low-lying states are the only ones energetically permitted in collisions with ground state Kr^+. The fact that the $(Kr^+)^*$/Cd and Kr^+/Cd 2 eV collision-produced spectra are virtually identical makes it impossible to either confirm or disprove the presence of metastable Kr^+ states in the ion beam.

Using the results of Soskida and Shivera[5] and our spectral calibration it is possible to extract absolute emission cross sections from our data. Table II is a listing of these cross sections for several of the lines observed in this work. The values listed for $(Ar^+)^*$ are based on total measured ion current, only about 1%–1.5% of which[1] is excited Ar^+. Thus the $(Ar^+)^*$/Cd cross sections in the table are "effective" values; actual $(Ar^+)^*$/Cd emission cross sections are roughly one hundred times those listed.

IV. DISCUSSION

The spectrum from 2 eV He^+/Cd collisions that is shown in Fig. 2 is the same as that contained in our earlier report. In that work it was shown that charge transfer excitation contributes to the pumping of the 325.0 and 441.6 nm laser transitions in the He/Cd laser. These laser transitions are however pumped primarily by He($2s\,^3S$)/Cd Penning ionization.[8] The collision-produced spectrum from 2 eV Ne^+/Cd collisions is similar to that for He^+/Cd. All features result from charge transfer processes, and aside from the 214.4 and 226.2 nm lines which result primarily from cascading, the 441.6 nm $5s^2\,^2D_{5/2} \rightarrow 5p\,^2P^0_{3/2}$ transition is strongest. In fact, laser action on the 441.6 nm transition has been observed in a Ne/Cd discharge.[9,10] In this system, Penning ionization using the lowest-lying metastable levels of neon is energetically excluded so that Ne^+/Cd charge exchange may play a major role. In addition, since the emission cross section for the 274.9 nm line is comparable to that for 441.6 nm (see Table II), and, since the lifetime of the $6s\,^2S$ CdII state is comparable to that of the $5p\,^2P^0$ states,[11,12] it might also be possible to produce laser action on this ultraviolet transition (see Fig. 1).

As discussed in Sec. III of this paper, both Ar^+/Cd and $(Ar^+)^*$/Cd collision-produced spectra differ significantly from those produced by impact of He^+ and Ne^+. The 15.7 eV recombination energy of Ar^+ is considerably lower than that of either He^+ or Ne^+ so that, without conversion of kinetic energy to internal energy, only the $5p\,^2P^0$ states may be populated in Ar^+/Cd charge transfer. Conversion of the 2 eV relative energy would permit only the addition of the $5s^2\,^2D_{5/2}$ state, but none of these states are detected from Ar^+/Cd collisions. However, the $(Ar^+)^*$/Cd collision-produced spectrum is quite rich showing that the metastable species present in the beam are highly reactive with neutral cadmium atoms.

Although previous work has shown that the krypton ion beam that is produced under source conditions[1] identical to those for production of the $(Ar^+)^*$ beam should also

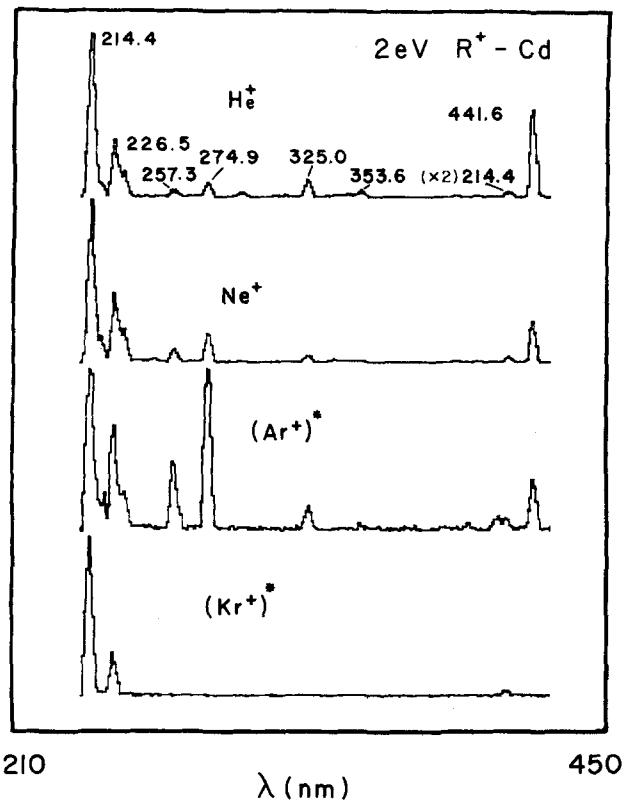

FIG. 2. Emission spectra (210–450 nm) of 2 eV (c.m.) rare gas ion/Cd collisions. The emissions are from excited states of CdII. The signal has been corrected for relative spectral response; resolution is 1.0 nm FWHM. The spectra are normalized to the same amplitude. The argon and krypton spectra were taken with source conditions which produce metastable states in the beam.

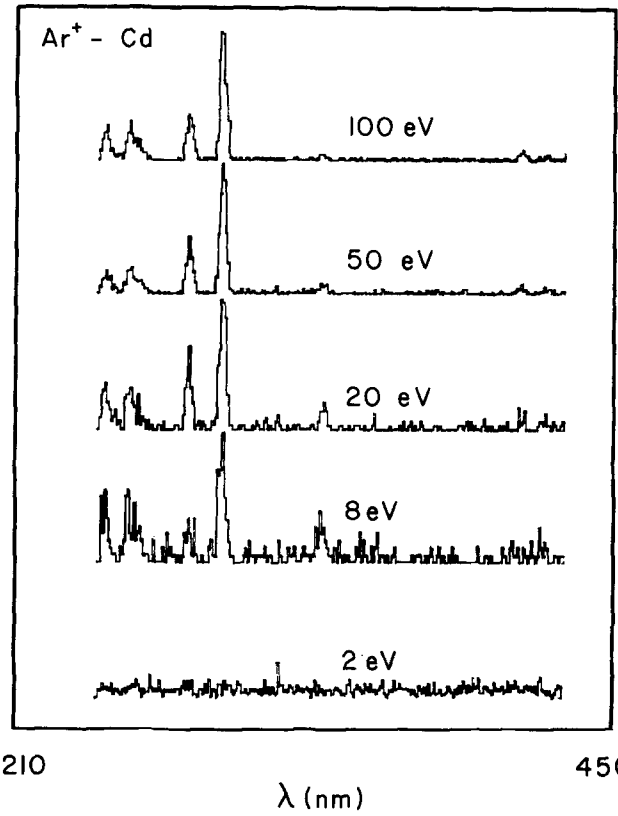

FIG. 3. Emission spectra (210–450 nm) from Ar^+/Cd collisions at various kinetic energies. The argon beam is obtained from source conditions which produce only ground state ions. Resolution is 1.0 nm FWHM; these spectra are not corrected for relative response of the optical system since the noise at the short wavelength end would be amplified to values that would obscure the changing features of the spectra.

TABLE II. Cross sections[a] for the indicated emission at 2 eV (c.m.) collision energy (A^2).

	λ(mn)			
Ion	214.4	226.2	274.9	441.6
He^+	11.0	3.64	0.90	5.60
Ne^+	10.1	3.83	1.74	2.72
$(Ar^+)^*$	1.32	0.79	1.30	0.39

[a]Based on measured ion signal.

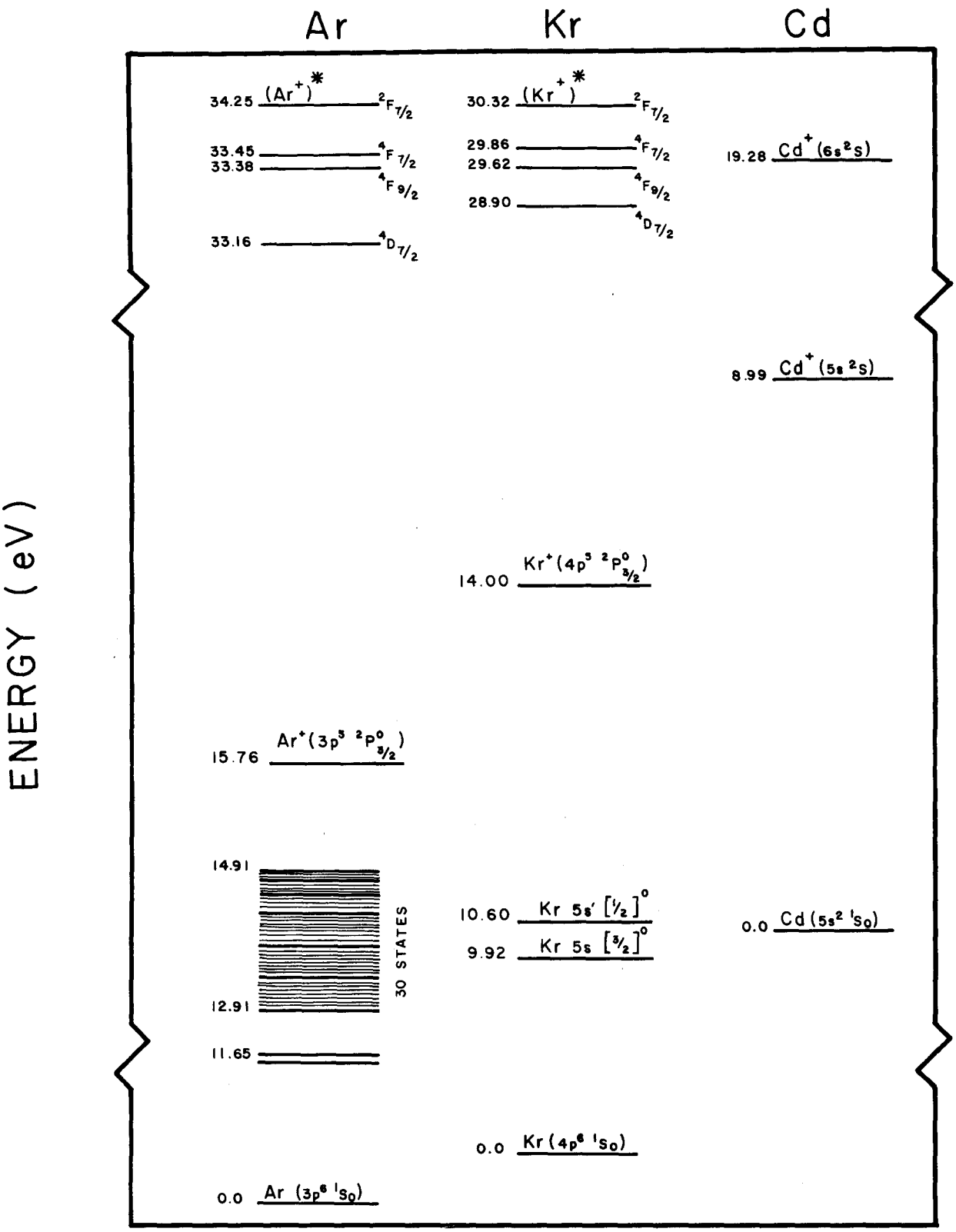

FIG. 4. Partial energy level diagram for argon, krypton, and cadmium. The $6s\,^2S$ state of CdII is aligned with the energy centers of the metastable states of Ar^+ and Kr^+.

contain metastable ions, we have not detected any difference in the 2 eV Kr^+/Cd collision-produced spectrum as compared to the $(Kr^+)^*/Cd$ spectrum at the same kinetic energy. Since there is no reason for metastable krypton ions not to be present, our data suggest that these species are not as reactive with cadmium atoms as are the metastable argon ions. A possible explanation of this difference in reactivity may be found by examining Fig. 4. This combined Cd^+, Ar^+, and Kr^+ energy level diagram is plotted with the $6s\,^2S$ level of CdII,

which is preferentially populated in $(Ar^+)^*/Cd$ collisions, coinciding with the mean energy of the Ar^+ and Kr^+ metastables states. Clearly CTE to Cd II $6s\ ^2S$ with product ground state neutral argon or krypton atoms is highly exothermic. However, as may be seen in Fig. 4 there is a dense grouping of excited argon states that may be formed in $(Ar^+)^*/Cd$ collisions for which CTE will be essentially thermoneutral when accompanied by production of the $6s\ ^2S$ state of Cd II. Krypton on the other hand has only two states in proximity to the ground state of neutral cadmium. Unfortunately this hypothesis cannot be tested in our experimental setup because only two of the states in the argon grouping radiate in our detectable wavelength range,[13] and both of these states are too long lived[14] to observe with our apparatus.

While the above explanation of the observed differences between $(Ar^+)^*/Cd$ and $(Kr^+)^*/Cd$ collisions is attractive, the analogous He^+/Cd and Ne^+/Cd systems do not fit this hypothesis. Neither He nor Ne have quantum states that are located such that the recombination energy of He^+ or Ne^+ coincides with the excitation energy of the upper states of the strongest transitions. Although some of the observed signal at these wavelengths arises from cascading from higher Cd II states, states that are more nearly resonant with the He^+ or Ne^+ recombination energies, it is clear that these states are also directly populated. Thus, we are observing processes in these systems that are exothermic by as much as 7 eV.

An alternate explanation for the difference in reactivity of the argon metastable ions from that of the krypton metastable ions involves the possible formation of doubly excited Cd II states lying in the Cd III continuum. If such a state radiates to the $6s\ ^2S$ or $5d\ ^2D$ (singly excited) states of Cd II, then subsequent emissions from these states would produce the observed spectrum. That is, relatively high yields of 274.9, 257.3, and 219.5 nm radiation would be observed. Under this hypothesis the metastable argon ions would possess enough energy to form this doubly excited Cd II state, but krypton metastable ions would not. Although discrete Cd II states lying in the Cd III continuum have not been observed previously, examination of Hartree–Fock energies for the various atomic orbitals[15] of Cd I suggests that states with configuration $4d^9\ 5p\ 6s$ would have roughly the energies of the argon metastables. Thus the observed increase in the production of the $6s\ ^2P$ and $5d\ ^2D$ states would result from a nearly resonant process. In addition, allowed radiative transitions from the doublet states formed from the $4d^9\ 5p\ 6s$ configuration would lead to the observed $6s\ ^2S$ and $5d\ ^2D$ states. This radiation would occur at roughly 800–950 Å in the vacuum ultraviolet. Further, the one electron $\Delta l = -1$ $5p - 4d$ transition leading to the $6s\ ^2S$ state would be expected to be stronger than the two electron jump leading to the $5d\ ^2D$ states. (It should be pointed out that a two electron jump in an atom such as cadmium can, and does, occur. The strong 325.0 and 441.6 nm lines result from just such a transition.) Thus the 274.9 and 257.3 nm transitions would be expected to be stronger than the 219.5 and 231.3 nm transitions (see Fig. 1). This is observed to be the case.

As discussed in the previous section of this paper the effective emission cross section for 274.9 nm radiation from $(Ar^+)^*/Cd$ collision is 1.3 $Å^2$. Since the fractional population of Ar^+ metastables is only 1%–1.5%, the actual cross section for metastables is the order of 100 $Å^2$. Since the lifetime of the $6s\ ^2S$ state of Cd II is comparable to that of the $5p\ ^2P^0$ states,[11,12] cw laser operation at 274.9 nm might be achievable. Such a possibility would of course be enhanced if the population of metastable argon ions in our Ar/Cd discharge could be increased.

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[1] H. D. Hagstrum, Phys. Rev. **104**, 309 (1956).
[2] H. L. Rothwell, Jr., R. C. Amme, and B. Van Zyl, Phys. Rev. Lett. **36**, 785 (1976).
[3] D. Brandt and C. Ottinger, Phys. Rev. A **19**, 219 (1979).
[4] G. C. Willet, *Introduction to Gas Lasers: Population Inversion Mechanisms* (Pergamon, New York, 1974).
[5] M. -T. I. Soskida and V. S. Shevera, JETP Lett. **22**, 269 (1975).
[6] F. Ranjbar, H. H. Harris, and J. J. Leventhal, Appl. Phys. Lett. **31**, 385 (1977).
[7] J. L. Barrett and J. J. Leventhal, J. Chem. Phys. **71**, 4015 (1979).
[8] L. D. Schearer and F. A. Padovani, J. Chem. Phys. **52**, 1618 (1970).
[9] L. Csillag, V. V. Itagi, M. Janossy, and K. Rosza, Phys. Lett. A **34**, 110 (1971).
[10] S. C. Wang and A. E. Siegman, Appl. Phys. **2**, 143 (1973).
[11] D. A. Shaw, A. Adams, and G. C. King, J. Phys. B **8**, 2436 (1975).
[12] T. Anderson, O. Paulsen, and P. S. Ramanujam, J. Quant. Spectrosc. Radiat. Transfer **16**, 521 (1976).
[13] A. R. Striganov and N. S. Sventitskii, *Tables of Spectral Lines of Neutral and Ionized Atoms* (IFI/Plenum, New York, 1968).
[14] W. L. Wiese, M. W. Smith, and B. M. Miles, *Atomic Transition Probabilities–Sodium Through Calcium*, Natl. Stand. Ref. Data Ser. Natl. Bur. Stand. **22**, 306 pages (1969).
[15] S. Fraga, J. Karwowski, and K. M. S. Saxena, *Handbook of Atomic Data* (Elsevier, New York, 1976).