

## Penning Ionization of Zn and Cd by Noble-Gas Metastable Atoms\*

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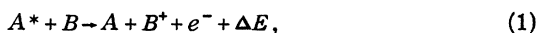
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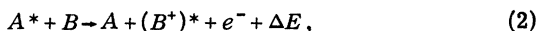
The Penning-ionization cross sections for He, Ne, Ar, and Kr metastable atoms with Zn and Cd have been measured in a pulsed afterglow. Within the framework of existing theories we have determined those parameters which are of importance in collisions of this type. We find that our data are internally consistent if the cross sections are proportional to the cube of the "hard-sphere" radii and the effects of selection rules are included. A theoretical basis for this dependence is suggested.

### I. INTRODUCTION

A great deal of attention has been directed to the study of Penning-ionization processes between atoms and/or molecules in gases. Such a process can be written symbolically as



whereby an excited species  $A^*$  collides with a target species  $B$ , the energy of  $A^*$  being taken up by the ionization of  $B$  and the kinetic energy of the ejected electron. If sufficient energy is available, the following variation to (1) is possible:



where some of the energy of  $A^*$  is taken up in leaving  $B^+$  in an excited state.

Until recently measurements of the Penning cross sections have been for He ( $2^1S_0$ ) or He ( $2^1S_1$ ) metastable atoms with a variety of other gases. Static afterglow measurements, such as those of Benton *et al.*,<sup>1</sup> provided the earliest cross-section measurements for these systems. Subsequently, the beam experiments of Muschlitz and co-workers,<sup>2,3</sup> Cermak,<sup>4,5</sup> and Hotop and co-workers<sup>6-9</sup> were applied to the measurement of these cross sections. Most recently, the flowing afterglow was used by Schmeltekopf and Fehsenfeld<sup>10</sup> and by Shaw<sup>11</sup> to measure the cross sections for collisions by metastable He atoms with a wide variety of gaseous reactants.

Theoretical treatments have also been limited for the most part to these systems, both because of their relative simplicity and because of a lack of understanding of the basic nature of Penning ionization. The earliest treatment by Ferguson<sup>12</sup> employed the momentum transfer cross sections for a van der Waals interaction, but did not treat in detail the transition probability, assigning it as an empirical "efficiency" factor by which this

cross section is multiplied.

Recently, a number of workers<sup>13-17</sup> have carried out detailed calculations of transition probabilities, with varying degrees of success. It is apparent that there is still a great lack of understanding of the Penning-ionization mechanism.

The development of the family of He-metal vapor lasers has indicated that there is an important new family of Penning-ionizing collisions involving rare-gas metastable atoms with atoms of a metal vapor. Of particular interest is the Group-II system, since reactions involving this group can excite levels of the ion from which well-characterized experimentally accessible optical emission takes place. It is these systems in which experiments on polarization transfer and rf spectroscopy of excited ions have been carried out.<sup>18</sup> A further property of the noble-gas-metal-vapor systems is the similarity of a large number of collision pairs. This permits the determination of the dependence of the cross section on particular atomic parameters. Until recently, only the He-Hg and He-Na have been studied experimentally.

In this paper we report in detail the measurement in a pulsed afterglow of the Penning-ionization cross sections of He, Ne, Ar, and Kr metastable atoms with Cd and Zn.<sup>19</sup> The systematic behavior of the total cross sections indicates those parameters which should be important in any theoretical approach.

### II. THEORY

In the semiclassical theory the Penning-ionization cross section has the general form

$$\sigma(E) = 2\pi \int_0^\infty b(1 - e^{-P(b,E)}) db, \quad (3)$$

where  $P(b, E)$  is the probability that the reaction occurs for the trajectory labeled by the relative kinetic energy  $E$  and the impact parameter  $b$ . In

this approximation this probability is given by

$$P(b, E) = 2 \int_{R_M}^{\infty} \left( \frac{W(R)}{v(R, E, b)} \right) dR, \quad (4)$$

with  $W(R)$  the transition rate at the interatomic distance  $R$ ,  $v(R, E, b)$  the relative radial speed of the atoms, and  $R_M$  the distance of closest approach on the trajectory ( $b, E$ ).

For  $P(b, E) \ll 1$  the ionization cross section is approximated by

$$\sigma(E) \approx 2\pi \int_0^{\infty} b P(b, E) db. \quad (5)$$

The integrations over the impact parameter and the interatomic separation [occurring in the definition of  $P(b, E)$ ] can be interchanged in Eq. (5). For a potential such as the 6-12 potential,

$$V(R) = \epsilon \left[ \left( \frac{R_0}{R} \right)^{12} - \left( \frac{R_0}{R} \right)^6 \right], \quad \epsilon > 0 \quad (6)$$

the integration over the impact parameter can be carried out. The effective potential, i.e., the potential energy plus the angular kinetic energy, has an attractive region for  $E < \frac{1}{5}\epsilon$  but is purely repulsive for  $E > \frac{1}{5}\epsilon$ . This leads to a change in the energy dependence of the cross section at  $E = \frac{1}{5}\epsilon$ . For  $E > \frac{1}{5}\epsilon$  we obtain

$$\sigma(E) = Q_0(E), \quad (7a)$$

with

$$Q_0(E) = 4\pi \left( \frac{\mu}{2E} \right)^{1/2} \int_{R_0(E)}^{\infty} R^2 W(R) \times \left( 1 - \frac{V(R)}{E} \right)^{1/2} dR, \quad (7b)$$

where  $\mu$  is the reduced mass of the colliding atoms and  $R_0(E)$  their distance of closest approach for a zero impact parameter. When  $E < \frac{1}{5}\epsilon$ ,

$$\sigma(E) = Q_0(E) - 4\pi \left( \frac{\mu}{2E} \right)^{1/2} \int_{R_1}^{R_2} R^2 W(R) \times \left[ 1 - \left( \frac{b_c}{R} \right)^2 - \frac{V(R)}{E} \right]^{1/2} dR, \quad (8)$$

the limits of integration,  $R_1 < R_2$ , are the zeros of the radial kinetic energy at the critical impact parameter  $b_c$  for a close approach. If  $R^2 W(R)$  decreases rapidly for increasing  $R$ , Eq. (7a) is expected to give a good approximation to the cross section for all energies of interest. In this case, the form does not appear to be potential dependent, indicating that Eq. (7a) would hold for more general potentials than that assumed.

Two parametrizations of the Penning cross section have been suggested. The first, by Bell, Dalgarno, and Kingston,<sup>20</sup> considers the cross section for a "close collision," the critical parameter.

A close collision is defined as one in which the atoms overcome the "centrifugal repulsion." In this case the Penning cross sections should be proportional to  $\pi b_c^2$ , where  $b_c$  is the critical impact parameter. This form would be justified if  $W(R)$  does not decrease sufficiently rapidly with increasing  $R$ . The other, due to Hotop and Niehaus,<sup>7</sup> takes the Penning cross sections proportional to the "hard-core" cross sections  $\pi R_0^2$ . This would follow from Eqs. (7a) and (7b) if  $W(R)$  decreases rapidly with increasing  $R$ .

We consider at this point a possible extension of the Hotop-Niehaus analysis.  $R_0$ , the "hard-core radius," is a characteristic length associated with the interaction of a pair of atoms.  $W(R)$  is obtained from matrix elements similar to those which yield the interaction. If  $W(R)$  has a characteristic length then we expect that this length will be proportional to  $R_0$ . In this case for a given class of reaction pairs and reactions, e.g., the collisions of metastable Ne, Ar, and Kr with Zn or Cd which result in a ground state  $Zn^+$  or  $Cd^+$ ,

$$W(R) = F(R/R_0). \quad (9)$$

The entire dependence on the reaction pair is given in the first approximation, by  $R_0$ . This predicts a Penning cross section which is, from Eqs. (7a) and (7b), proportional to  $R_0^3$ .

The Penning cross sections we consider involve the He ( $^3S_1$ ) and the metastable Ne, Ar, and Kr ( $^3P_2$ ). To facilitate the comparisons we first investigate what effect might occur due to the difference in their electronic angular momentum. The matrix element required for  $W(R)$  can be thought of as the interaction between two charge distributions. In the first approximation, the individual "charge densities" are

$$\rho_{if}^{(\alpha)}(\vec{r}_\alpha) = -e\psi_f^{(\alpha)*}(\vec{r}_\alpha)\psi_i^{(\alpha)}(\vec{r}_\alpha), \quad \alpha = 1, 2 \quad (10)$$

where  $\psi_i^{(\alpha)}(r_\alpha)$  and  $\psi_f^{(\alpha)}(r_\alpha)$  would be the initial- and final-state wave functions for each electron. Franzen's rule<sup>21</sup>—that the electronic orbital angular momentum about the collision axis (defined by the relative positions of the atoms at closest approach) is conserved—is obtained when the "interaction" decreases rapidly for increasing interatomic distances. The orbital angular momentum about the collision axis of the ejected electron will be such as to satisfy this conservation rule. The projection of electronic angular momentum on the collision axis should also determine to some degree the strength of this interaction and therefore the magnitude of  $W(R)$ . Let the metastable atom be in a  $P$  state and the target atom in an  $S$  state, e.g.,  $Kr(^3P_2) + Cd(^1S_0)$ . There are three molecular states for this system, two are  $\Pi$  states, and one is a  $\Sigma$  state. In calculating  $W(R)$

for the  $\Pi$  states the angular integration about the collision axis results in cancellations in the "interaction between the charge distributions." This does not occur for the  $\Sigma$  state. In addition the charge distributions will tend to be further apart in the  $\Pi$  states than in the  $\Sigma$  states. Let  $\sigma(\Pi)$  and  $\sigma(\Sigma)$  be the Penning cross sections for the  $\Pi$  and  $\Sigma$  states. The argument indicates that  $\sigma(\Pi) < \sigma(\Sigma)$ . The observed cross section for the  $^3P$  metastable atoms is

$$\sigma_{\text{obs}} = \frac{1}{3}[\sigma(\Sigma) + 2\sigma(\Pi)], \quad (11)$$

which is, if the above argument is correct, less than  $\sigma(\Sigma)$ . In the case of the metastable He state only the  $\Sigma$  molecular state occurs. One might expect then that the Penning cross sections for forming ground-state ions divided by the appropriate power of  $R_0$  would be larger for the He metastable atoms than for the other noble-gas metastable atoms.

As a final remark we note that in the Hotop-Niehaus analysis and our extension the cross sections will be proportional to the square root of the reduced mass of the colliding atoms<sup>16</sup> [see Eq. (4)].

### III. EXPERIMENTAL TECHNIQUE

#### A. Afterglow Decay Measurements

The technique of spectroscopic study of a pulsed afterglow to determine carrier decay characteristics was first introduced by Phelps and Molnar<sup>22</sup> to investigate He metastable diffusion in a helium afterglow. We consider the helium case, which is in general analogous with the rest of the noble-gas systems we shall be discussing.

In this type of experiment, a cell containing the He gas or gas mixture is subjected to an rf pulse, which excites a weakly ionized glow discharge. After a time of the order of microseconds the electrons thermalize and the short-lived discharge products decay, leaving ground-state helium atoms, ground-state helium ions, and He  $2^3S_1$  metastable atoms.

Consider the decay of helium metastables in the afterglow (in the general sense, noble-gas metastables) in the presence of an impurity. The decay rate per unit time of the metastable density  $N_m$  is given by two terms

$$-\frac{1}{N_m} \frac{dN_m}{dt} = \frac{D}{p\Lambda^2} + N\sigma v, \quad (12)$$

in which the first term represents the loss due to diffusion to the walls of the container, where the diffusion is assumed to occur in the fundamental mode, with diffusion constant  $D$  and diffusion length  $\Lambda$  at the pressure  $p$ . Fundamental-mode diffusion is a reasonable description for the less-

than-1-torr pressure at which we are working. The second term represents the loss of metastables by Penning-ionizing collisions with a second component of density  $N$  and relative velocity  $v$ , where  $\sigma$  is the cross section for the collision.

Therefore, the metastables in a helium afterglow decay by the law

$$N_m = N_m^0 e^{-\gamma t}, \quad (13)$$

where

$$\gamma = \frac{D}{p\Lambda^2} + N\sigma v. \quad (14)$$

The number of metastables can be monitored via the absorption of a resonance line from a helium lamp. The  $2^3S_1 \rightarrow 2^3P$  transition at  $1.08 \mu\text{m}$  and the  $2^3S_1 \rightarrow 3^3P$  transition at  $3889 \text{ \AA}$  are equally convenient. The exponential decay of the resonance absorption yields the decay constant  $\gamma$ . Now the rate constant  $\sigma v$  can be determined from a plot of  $\gamma$  versus  $N$ . In the case of the Group-II metal vapors, the impurity vapor pressure and therefore density can be readily varied by variation of the temperature. The vapor pressure at a given temperature is obtained from the relations<sup>23,24</sup>

$$\text{Zn: } \log_{10} P_{\text{torr}} = 8.741 - (6630 \text{ }^\circ\text{K})/T, \quad (15)$$

$$\text{Cd: } \log_{10} P_{\text{torr}} = 8.818 - (5808 \text{ }^\circ\text{K})/T. \quad (16)$$

A small range of temperature corresponds to a substantial change in vapor pressure, and thus the velocity that enters can be taken as a thermal average without introducing significant errors. The zero-temperature intercept of the  $\gamma$ -versus- $N$  curve will indicate the diffusion time. This parameter, however, is sensitive to the exact He pressure and cell size. No particular care was taken to ensure uniformity of these parameters, and therefore the measurements of diffusion time, though roughly consistent with calculated values, were not exceptionally accurate. These features do not affect, however, the Penning cross-section measurements since the  $\gamma$ -versus- $N$  slope is independent of He pressure and any geometric parameters.

A particular feature of the He-Cd and He-Zn collisions is the fact that the energy of the helium metastable is adequate to excite levels of the metal ion which fluoresce in the visible. This is shown by the energy-level diagram, Fig. 1. Since the radiative lifetimes of these levels are fast ( $< 1 \mu\text{s}$ ) compared with  $\gamma$  ( $\sim 10^4 \text{ s}^{-1}$  at  $10^{-3}$  torr of the metal vapor), it is also possible to monitor the fluorescence of the ion, which reflects the decay time  $\gamma$ , and to distinguish between excitations of these ions resulting from collisions with other long-lived species in the afterglow. In the

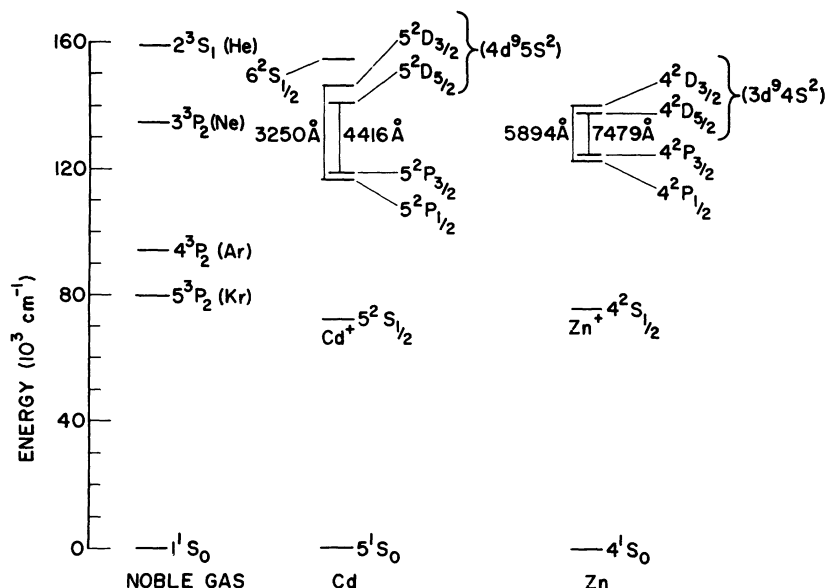


FIG. 1. Energy-level diagram for  $\text{Cd}^+$  and  $\text{Zn}^+$  relative to the energies of the metastable atoms of He, Ne, Ar, and Kr.

case of Ne, only the first excited states of the Zn and Cd ions, the  $4^2P$  and  $5^2P$  levels, respectively, are energetically accessible to the metastable (see Fig. 1). These levels fluoresce in the ultraviolet and were not experimentally observed with our equipment. In the case of Ar and Kr, only the ground-ion level is populated.

In all cases, the decay was monitored via absorption of resonance radiation from the metastable to a higher-lying level. The levels involved and the wavelengths are listed in Table I.

Figures 2 and 3 are indicative of the typical results of the measurement of the metastables Ne, Ar, and Kr decay rates as a function of the metal-vapor pressures. A standard deviation of  $\pm 10\%$  was characteristic of the measurements.

#### B. Cell Preparation

The cells were fabricated of Pyrex glass and were cylinders approximately 2 in. long by 1.5 in. in diameter with optical windows sealed onto the

TABLE I. Resonant transitions used to monitor the density of metastable atoms.

Atom	Metastable level	Resonance transition	Wavelength
He	$2^3S_1$	$2^3S_1 \rightarrow 2^3P_{0,1,2}$	$1.08 \mu\text{m}$
		$2^3S_1 \rightarrow 3^3P_{0,1,2}$	$3889 \text{ \AA}$
Ne	$3^3P_2$	$3^3P_2 \rightarrow 3^3D_3$	$6402 \text{ \AA}$
Ar	$4^3P_2$	$4^3P_2 \rightarrow 5^3D_3$	$8115 \text{ \AA}$
Kr	$5^3P_2$	$5^3P_2 \rightarrow 5^3D_2$	$8106 \text{ \AA}$

ends. These were baked out under vacuum at  $10^{-7}$  torr at  $350^\circ\text{C}$  to remove all impurities with significant vapor pressures in the temperature range in which the experiments were carried out (up to about  $300^\circ\text{C}$  for Zn).

An ampule containing a charge of metal was included between the cell and the pumping manifold, and metal vapor was forced into the cell with a torch and permitted to collect on the cold walls of the cell. The final step was to fill the cell with the appropriate prepurified noble gas to the desired pressure (generally 0.5–1 torr).

Failure to exercise care in cell fabrication, particularly in the case of Zn, where the  $300^\circ\text{C}$  operation was carried out, could have resulted in the introduction of impurities into the system during the course of the experiment. No evidence for such behavior was observed in these cells.

#### C. Temperature Control

The cell was placed in the center of a 12-in.-long cylindrical resistance-heated oven, with the optical axis along the axis of the cylinder (and cell). The inside of the cylinder was sheathed in copper for additional uniformity, and three stages of heat shielding down the exceptionally long oven ensured that there were no thermal gradients along the dimensions of the cell.

Thermocouples were placed in contact with both end windows and the side of the cell, yielding three temperature readings for comparison. A Leeds and Northrup potentiometer determined the thermal emf referenced to a  $0^\circ$  junction. A feedback-stabilized temperature controller eliminated thermal drift. With this system, temperature was uniform, constant, and measurable to within  $1^\circ\text{C}$ .

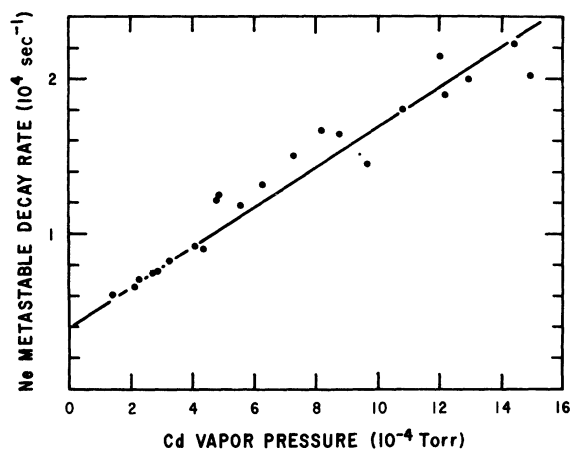


FIG. 2. Decay rate of Ne ( $^2P_2$ ) atoms due to collisional quenching by Cd ( $^1S_0$ ) atoms as a function of Cd vapor pressure.

#### D. Measurement Apparatus

An Arenberg rf pulser was used to excite a repetitive discharge in the cell. A 50-MHz pulse of about 2- $\mu$ s duration was generally employed. A delay of approximately 100  $\mu$ s between the rf pulse and triggering of the detection electronics ensured that the discharge was well into the after-glow region.

rf-excited cw noble-gas lamps<sup>25</sup> provided the resonance radiation for monitoring the metastable-level population. Detection was provided by a 0.5-m Jarrell-Ash spectrometer fitted with a photomultiplier. An ITT FW 130 S-20 was used in the case of the visible transitions and an ITT FW 118 S-1 photomultiplier was used for the near-infrared transitions. A Princeton Applied Research TDH-9 waveform eductor was used for

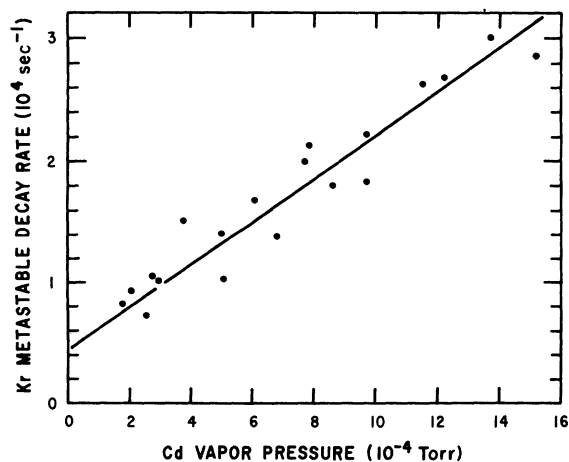


FIG. 3. Decay rate of Kr ( $^3P_2$ ) atoms due to collisional quenching by Cd ( $^1S_0$ ) atoms as a function of Cd vapor pressure.

TABLE II. Penning-collision cross sections (velocity averaged) for noble-gas metastable atoms with Zn and Cd. Velocity averages are at 270 °C (Zn) and 210 °C (Cd). Units are  $10^{-15}$  cm<sup>2</sup>.

	He	Ne	Ar	Kr
Zn	2.91	4.18	5.28	9.28
Cd	4.50 (2.6 <sup>a</sup> )	4.61 (~2.3 <sup>a</sup> )	6.54	10.8

<sup>a</sup> Cross section for the formation of the ground-state ion, Ref. 5.

signal averaging. The lifetime measurements were generally accurate to approximately  $\pm 10\%$ .

Experiments were carried out such that the temperature was recycled several times to determine the reproducibility of the data, which in all cases was satisfactory.

#### IV. RESULTS AND DISCUSSION

In Table II the velocity-averaged Penning cross sections are given. The Cd cross sections were obtained for temperatures in the neighborhood of 210 °C and the Zn cross sections around 270 °C. The temperature difference does not appear to be significant, in agreement with the results of Jones and Robertson.<sup>26</sup> Tables III-V give the ratio of the experimental cross sections to  $\pi b_c^2(E)$ ,  $\mu^{1/2}\pi R_0^2$ , and  $\mu^{1/2}\pi R_0^3$ , respectively. The atomic parameters were approximated according to Hirschfelder *et al.*<sup>27</sup>

There is a significant difference between the Penning reactions with the various metastable atoms. As seen in Fig. 1, the Ar and Kr metastable atoms leave the ions in their ground state. The Ne metastable atom has sufficient energy to produce ions in the  $^2P$  states, while the energy of the He metastable atom allows the formation of the  $^2D$  states and the  $6^2S$  state of Cd<sup>+</sup>. Given the similarity of the Ar and Kr reactions, the difference between the ratios of the cross sections to  $\pi b_c^2(E)$  for Ar and Kr (Table III) indicates that these Penning cross sections are not proportional to the close-collision cross sections.

The Ar and Kr cross sections do not discriminate between the possibilities that the cross sections are proportional to  $\mu^{1/2}\pi R_0^2$  (Table IV) or that they are proportional to  $\mu^{1/2}\pi R_0^3$  (Table V). With Ne, however, there are a number of states of the

TABLE III. Experimental Penning cross sections divided by the close-collision cross sections.

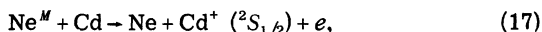
	He	Ne	Ar	Kr
Zn	0.25	0.24	0.20	0.29
Cd	0.29	0.21	0.19	0.25

TABLE IV. Experimental Penning cross sections divided by the hard-sphere cross sections and the square root of the reduced mass of the colliding atoms. Units are  $10^{-1} (\text{amu})^{-1/2}$ .

	He	Ne	Ar	Kr
Zn	2.4	1.1	0.88	1.0
Cd	3.2 (1.8 <sup>a</sup> )	1.0 (~0.5 <sup>a</sup> )	0.91	1.0

<sup>a</sup> Contribution due to the formation of the ion ground state, Ref. 5.

ions formed: the  $^2S$  ground state and the  $^2P$  excited states. It is consistent with the Hotop-Niehaus<sup>7</sup> analysis and with our extension of their analysis to consider the cross sections to be a sum of the cross sections for the formation of the individual states. We expect, therefore, that in Tables IV and V the ratios for the Ne reactions should be greater than those for the Ar and Kr reactions. As seen in Table IV, this is not true if we take the cross sections proportional to  $\mu^{1/2}\pi R_0^2$ . As a check we have included in the analysis the cross section for reaction



which was obtained by Cermak.<sup>5</sup> The agreement between the ratios of the cross section for forming the  $\text{Cd}^+ (^2S_{1/2})$  state and  $\mu^{1/2}\pi R_0^3$  for the Ne, Ar, and Kr metastable atoms supports our proposal that the transition probability  $W(R)$  is given by

$$W(R) = F(R/R_0), \quad (9)$$

where  $F$  is a function which depends only on the general type of atoms involved in the Penning reaction and the particular states which are connected by  $W(R)$ .

In Sec. II it was suggested that those reactions in which the atoms were in a  $\Pi$  molecular state would have a smaller cross section,  $\sigma(\Pi)$ , than those for which the atoms were in a  $\Sigma$  state,  $\sigma(\Sigma)$ . Table V shows, in parentheses, the ratio of the cross section for

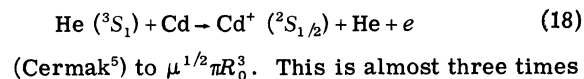


TABLE V. Parameters of Table IV divided by the hard-core radii. Units are  $10^{-2} (\text{amu})^{-1/2} \text{\AA}^{-1}$ .

	He	Ne	Ar	Kr
Zn	5.2	2.9	1.4	1.5
Cd	6.6 (3.8 <sup>a</sup> )	2.5 (~1.3 <sup>a</sup> )	1.4	1.3

<sup>a</sup> Contribution due to the formation of the ion ground state, Ref. 5.

as large as those for the formation of a ground-state ion in a collision with  $\text{Ne}^M$ ,  $\text{Ar}^M$ , or  $\text{Kr}^M$ . Although the interatomic potentials and the functional form of  $W(R)$  will differ between, say, the  $\text{He}^M + \text{Cd}$  system and the  $\text{Ne}^M + \text{Cd}$  system, it seems reasonable to speculate that some part of this difference is due to  $\sigma(\Pi)$  being smaller than  $\sigma(\Sigma)$ . If  $\sigma(\Pi)$  were less than 5% of  $\sigma(\Sigma)$  the factor of 3 would be obtained.

Although we have dealt here with only a limited set of reactions, their similarities gave encouragement to the attempt to relate their cross sections for occurrence. The proposal that the dependence of the transition probability  $W(R)$  on the interatomic separation "scales" with characteristic length  $R_0$  of the interatomic interaction along with that of a "partial selection" rule due to  $\sigma(\Sigma) > \sigma(\Pi)$  seems reasonable. Of course, at this point both proposals are speculative; however, they do indicate some possible directions for future experimental and theoretical research on Penning reactions.

In summary we have found that the Penning cross sections for  $\text{He}^M$ ,  $\text{Ne}^M$ ,  $\text{Ar}^M$ , and  $\text{Kr}^M$  on Zn and Cd are consistent with the following postulates: (i) The cross section for formation of the ground state of the ion is proportional to  $R_0^3$ , with  $R_0$  the hard-core radius; (ii) the reaction cross section for  $\Pi$  molecular states is small compared to that for the  $\Sigma$  molecular states.

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