Photoemission and Electron Detachment in Low-Energy Collisions of Metastable Atoms with Negative Ions

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Cross sections for Penning detachment, $X^* + Y^- \rightarrow X + Y + e$, and collision-induced photon emission, $X^* + Y^- \rightarrow X + Y^- + h\nu$, have been calculated for collisions of metastable neutral atoms and negative ions at low energies ($E \sim 1$ eV). A semiclassical treatment based on the impact parameter method and adiabatic electronic interactions was employed. Collisions involving H* (2^1S), Ca* (3^1D), and He* (2^1S) with H^-, O^-, Cl^-, and C^- were investigated. In all collisions not involving H* (2^1S), Penning detachment predominates and exhibits cross sections on the order of 10^{-14} cm^2.

I. INTRODUCTION

Processes involving electronic energy transfer between neutral atoms which collide at low (kinetic) velocities have been studied theoretically.[1] In particular, energy transfer causing ionization of one of the species $X^* + Y \rightarrow X + Y^+ + e$ (where X and Y, X^* and Y^+ represent atoms in ground, excited, and ionic states, respectively) has been studied both in theory and experiment[2] and has been called Penning ionization. An analogous process involves the detachment of an electron from a negative ion by energy transfer $X^* + Y^- \rightarrow X + Y + e$. Of particular interest are detachment collisions in which the neutral atom is initially in a metastable excited state; we denote such an atom by X_m^*. We call this process Penning detachment. One must keep in mind, however, that another channel exists for deexcitation of X_m^* which competes with Penning detachment, namely spontaneous photon emission $X_m^* + Y^- \rightarrow X + Y^- + h\nu$. In this paper we calculate the cross sections for these two processes in order to predict which will be the dominant feature of a reaction system.

An impact parameter approach is used and throughout the discussion X is assumed to be initially in a metastable excited state. We deal with systems for which the energy of the metastable $E(X_m^*) > A(Y)$, the electron affinity of Y, and the relative collision velocities are small. The latter assumption allows us to treat the collision interactions adiabatically. [Collisions of ions with metastable hydrogen atoms are an exception; the diabatic and adiabatic contributions are comparable for collisions of H(2s) with ions, as we shall see. Furthermore, again anticipating ourselves, H(2s) is the one metastable for which nondegenerate perturbation theory is inadequate.] One may think of the collision as proceeding as follows. The electric field of the negative ion Y^- induces Stark mixing of $|X_m^*\rangle$, the metastable electronic state of X_m^*, with a nearby excited state which may be coupled to the metastable state by an appreciable electric dipole transition moment. If this nearby state (denoted $|X_r^*\rangle$) can decay rapidly enough to the ground electronic state $|X\rangle$ of the atom, then we shall find that both Penning detachment and photoemission have high probabilities of occurring during the collision of X_m^* and Y^-. We shall show that Penning detachment occurs as a result of dipole-dipole interactions of the electrons on the two atoms. We also find that, while the proposed theory applies quite generally when the above conditions are met, the detailed calculations of the cross sections depend on the energy difference $\Delta E_{rm} = |E(X_m^*) - E(X_r^*)|$ at infinite internuclear distance. For this reason we treat several specific collision systems including H* (2^1S), H^- (ΔE_{rm} small), and Ca* (3^1D), H^- (ΔE_{rm} large).

II. GENERAL THEORY

We have assumed classical straight-line trajectories for the interaction paths. A trajectory diagram for the process is shown in Fig. 1. We let μ be the reduced mass of the two colliding particles, R be their internuclear distance, and b be the impact parameter for the trajectory. The diameter r_0 is a hard-core interaction range, the distance of closest approach of the nuclei for collisions in which $b < r_0$. There are two possible collision paths, as is seen in this figure, depending on whether the repulsive forces come into play.

A. Perturbation of Metastable State

Let the wave function for the metastable electronic state of X be denoted by $|X_m^*\rangle$ and that of the neighboring excited state by $|X_r^*\rangle$. These are members of a complete set of orthonormal basis functions for the electronic states. Let $|T(t)\rangle$ be the wave function for the excited electron at any time t:

$$|T(t)\rangle = \mathcal{C}_m |X_m^*\rangle + \mathcal{C}_r |X_r^*\rangle .$$

The coefficients $\mathcal{C}_m$ and $\mathcal{C}_r$ are time dependent and

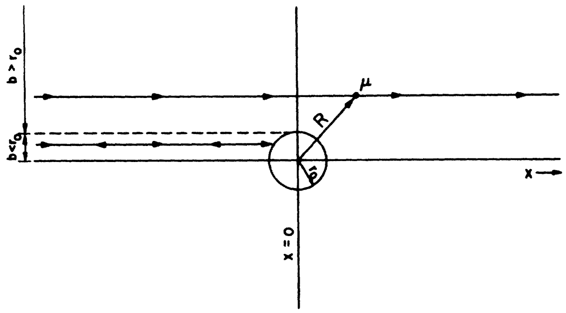

FIG. 1. Center of mass trajectory diagram.

must obey the initial condition for the process: $|\mathcal{C}_m|^2=1$, $|\mathcal{C}_r|^2=0$ at $t=t_0$, effectively $-\infty$. At some later time $t>t_0$, the probability that the electron on X be found in a state $|X_r^*\rangle$ is given by $|\mathcal{C}_r(t)|^2$. The interaction potential V responsible for this perturbation is just that of an atom in an electric field $\vec{\mathcal{E}}(R)$, where the argument R reminds us that the electric field strength depends on the neutral-ion separation. The z axis of the atom is defined at all times by the direction of the electric field vector at its nucleus (rotating atom approximation[3]). Thus

$$V=\vec{d}\cdot\vec{\mathcal{E}}(R)=-e\mathfrak{z}\mathcal{E}(R),$$

where $\vec{d}=-e\vec{r}$.

Having determined the probability $|\mathcal{C}_r(R)|^2$ that the atom is in a state $|X_r^*\rangle$ at some neutral-ion internuclear distance R, we neglect $X_m^*\to X$ transitions and consider only transitions from X_r^* and their effect on Y^-. The use of the separate-particle approximation will be justified later on by the long-range dependence of the interaction cross section and of its large size. Our neutral-ion system is, then, in a state $|X_r^*Y^-\rangle=|X_r^*\rangle|Y^-\rangle$. We proceed to study separately the probability per unit time for transition to a final state $|eXY\rangle$ or $|XY^-\rangle$. These transitions represent Penning detachment and photon emission, respectively.

B. Penning Detachment Cross Section

We first consider the electron-electron interactions between the two atoms which lead to Penning detachment. The probability per unit time P_d that the reaction $X_r^*+Y^-\to X+Y+e$ will occur is, according to Wentzel's Golden Rule,

$$P_d=(2\pi/\hbar)|\langle X_r^*Y^-|\hat{W}|eXY\rangle|^2\rho(E_f)\ , \tag{1}$$

where $\hat{W}$ is the electron-electron interaction operator and $\rho(E_f)$ is the density of final states. Katsuura[1] has treated the Penning ionization problem in cases for which the two-center expansion is valid, so that

$$\hat{W}=-\frac{2e^2}{3R^3}\vec{r}_1\vec{r}_2\ , \tag{2}$$

where $\vec{r}_1$ and $\vec{r}_2$ are the position vectors for the "active" electrons on atoms 1 and 2, respectively. We may use the same expansion for the $X_r^*+Y^-$ process, letting $\vec{r}_1$ and $\vec{r}_2$ refer to X_r^* and Y^-, respectively. Substituting in (1), expanding the matrix element in terms of a set of intermediate states $|X_nY^-\rangle$ and defining $\vec{d}_1=e\vec{r}_1$ and $\vec{d}_2=e\vec{r}_2$, we have

$$P_d=\frac{2\pi}{\hbar}\sum_n|\langle X_r^*Y^-|-\frac{2\vec{d}_1}{3R^3}|X_nY^-\rangle\langle X_nY^-|\vec{d}_2|eXY\rangle|^2\rho(E_f)\ . \tag{3}$$

Because we choose $\langle X_n|X_m\rangle=\delta_{mn}$ and $\langle Y^-|Y^-\rangle=1$ and because of our assumption of the separability of the collision partners, it follows that

$$P_d=\frac{2\pi}{\hbar}|\langle X_r^*|-\frac{2\vec{d}_1}{3R^3}|X\rangle\langle Y^-|\vec{d}_2|eY\rangle|^2\rho(E_f) \tag{4}$$

or

$$P_d=\frac{2\pi}{\hbar}\left(\frac{4}{9R^6}\right)|\vec{\mathfrak{D}}_1|^2|\vec{\mathfrak{D}}_2|^2\rho(E_f)\ . \tag{5}$$

Note that $\vec{\mathfrak{D}}_1$ and $\vec{\mathfrak{D}}_2$ are the dipole matrix elements for the atomic transitions $X_r^*\to X$ and $Y^-\to Y+e$, respectively.

We assume that the electron carries off all the excess energy, i.e., $E(e)=E(X^*)-E(X)+E(Y^-)-E(Y)$. Thus $\vec{\mathfrak{D}}_2$ is related to the cross section for photodetachment of Y^- by the Golden rule. For, upon averaging over the direction of polarization of the incident photon, one obtains an expression for the probability per second for photodetachment,

$$(2\pi/\hbar)(\pi h\nu)|\vec{\mathfrak{D}}_2|^2\rho(E_f)\ , \tag{6}$$

where ν is frequency of the impinging photon and $E_f=E(Y^-)+h\nu=A(Y)+E(e)$. It follows that the cross section for photodetachment $\sigma(h\nu)$ is

$$\sigma(h\nu)=(\pi\nu/c)|\vec{\mathfrak{D}}_2|^2\rho(E_f)\ . \tag{7}$$

Substitution of this quantity into (5) yields

$$P_d=\tfrac{4}{9}\,|\vec{\mathfrak{D}}_1|^2c\sigma(h\nu)/\pi h\nu R^6\ . \tag{8}$$

The total probability per second P_t that perturbation of X_m^* results in Penning detachment is then

$$P_t=4c|\vec{\mathfrak{D}}_1|^2\sigma(h\nu)|\mathcal{C}_r(R)|^2/9\pi h\nu R^6\ , \tag{9}$$

where both $|\mathcal{C}_r(R)|^2$ and R^{-6} will vary with time. The probability for Penning detachment per collision of impact parameter b, $P_c(b)$, is obtained by integrating P_t over all time

$$P_c(b)=\int_{-\infty}^{\infty}P_t dt=\mathrm{M} \tag{10}$$

The cross section for the Penning detachment process is then

$$\sigma_d=\int_{-\infty}^{\infty}2\pi bP_c(b)db \tag{11}$$

or

$$\sigma_d = \frac{4c\,|\vec{\mathfrak{D}}_1|^2\sigma(h\nu)}{9\pi h\nu}\int_0^\infty 2\pi b\,db\int_{-\infty}^{\infty}\frac{|C_r(R)|^2}{R^6}\,dt\,. \tag{12}$$

C. Photon Emission

Once the mixing of $|X_r^*\rangle$ with $|X_m^*\rangle$ has occurred, there is also the possibility that X will spontaneously decay to its ground state with the emission of a photon. Neutral-ion interactions are neglected in this process although it may, of course, be followed by the absorption of the photon by Y^-. The probability of this second step is very small and will be neglected.

The cross section for photon emission is calculated in a manner similar to that in Sec. II B. Again $|\mathfrak{C}_r(R)|^2$ is the probability that the metastable has been perturbed to $|X_r^*\rangle$. This quantity, multiplied by the Einstein coefficient A_r for spontaneous emission to the ground state, $X_r^* \to X + h\nu$, yields the probability for photon emission per unit time when X^* and Y^- are at a distance R apart. Performing the steps indicated by (10) and (11) and substituting for A_r, we find the cross section for photon emission σ_e is

$$\sigma_e = \frac{4\omega^3|\vec{\mathfrak{D}}_1|^2}{3hc^3}\int_0^\infty 2\pi b\,db\int_{-\infty}^{\infty}|\mathfrak{C}_r(R)|^2dt\,. \tag{13}$$

III. CALCULATIONS AND RESULTS

Obtaining numerical results for our cross sections now depends on evaluating the integrals in Eqs. (12) and (13). In determining an expression for the integrand in the integration over the trajectory, it is necessary to consider two different cases, one in which $|\mathfrak{C}_r(R)|^2$ may be approximated as a function of R all along the trajectory by using first-order perturbation theory and one in which perturbation theory breaks down when R becomes too small. To understand this distinction, recall that first-order perturbation theory gives

$$|\mathfrak{C}_r(R)|^2 \cong |V_{rm}|^2/\Delta E_{rm}^2\,, \tag{14}$$

where

$$|V_{rm}|^2 = |\langle X_r^*|\,-e\mathfrak{z}\mathcal{E}(R)\,|X_m^*\rangle|^2$$

and

TABLE I. Minimum separation D of neutral and ion for which perturbation theory is applicable to calculation of Stark mixing of states $|X_r^*\rangle$ and $|X_m^*\rangle$. $[\Delta E_{rm} = |E(X_r^*) - E(X_m^*)|.]$

X_m^*	X_r^*	D (cm)	$\Delta E_{rm}/hc\,(\mathrm{cm}^{-1})$
$H(2^1S)$	$H(2^1P)$	4.0×10^{-5}	~ 0.1
$Ca(3^1D)$	$Ca(4^1P)$	2.0×10^{-8}	1803

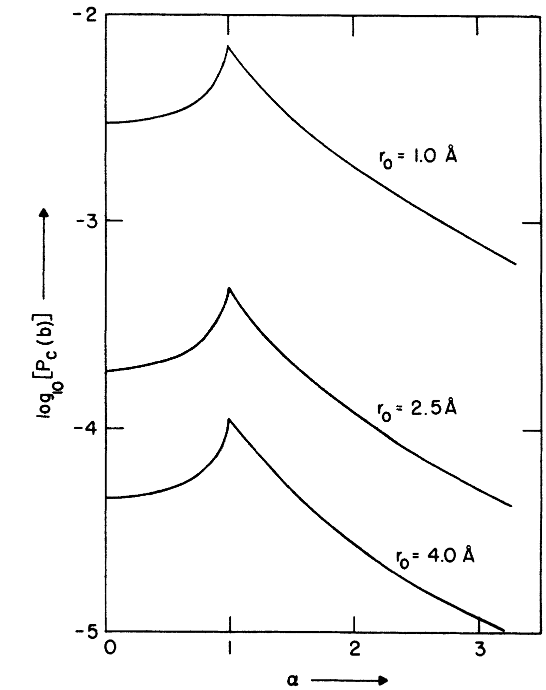

FIG. 2. Probability per collision $P_c(b)$ for photon emission as a function of $\alpha = b/r_0$ for different values of distance of minimum approach r_0. Curves were calculated for Ca*, H⁻ collision of 1-eV collisional energy.

$$\Delta E_{rm} = |E(X_r^*) - E(X_m^*)|\,.$$

Equation (14) is applicable only for $|V_{rm}|^2 \ll \Delta E_{rm}^2$ however. We can estimate the distance D, at which its use becomes inappropriate by calculating the distance R at which $|V_{rm}|^2 = 0.1\Delta E_{rm}^2$. Table I indicates the results. Since the distance of minimum approach of the two atoms r_0 is about 2 Å, it is evident that first-order perturbation theory is applicable for any value of R for the Ca*, H^- system but not for the H*, H^- system. We will determine the cross sections for each system by separate methods.

In general, the probability $P_c(b)$ as calculated from (10) has its maximum value for impact parameter r_0, where it also has a discontinuous slope. Figure 2 shows $P_c(b)$ for photon emission for different values of $r_0 = b/\alpha$ in the case of Ca*, H^- collisions. One finds that $P_c(b)$ is much larger in the Penning detachment cases. Since $P_c(b)$ can never be greater than 1, however, we will set it equal to unity for impact parameters for which Eq. (10) gives a value greater than 1. If s is the impact parameter for which Eq. (10) yields $P_c(b) = 1$, and if $r_0 < s$, then the cross section for the process will be

$$\sigma = \pi s^2 + \int_s^\infty 2\pi b P_c(b)\,db \tag{15}$$

if the backcoupling between initial and final states is negligible.[4] It will be found that this "saturation" of reaction probability leads to a maximum value of σ_d for small values of r_0.

A. Ca*, H⁻ Collision

The Penning detachment process

$$\mathrm{Ca}^*(3^1D)+\mathrm{H}^- \to \mathrm{Ca}(4^1S)+\mathrm{H}+e$$

is considered first. Here $\Delta E_{rm}/h_c = 1803\ \mathrm{cm}^{-1}$. $|\mathcal{C}_r(R)|^2$ is determined from (14) and $\mathcal{E}(R) = -e/R^2$. Employing the relations $x = vt$ and $R^2 = x^2 + b^2$ and integrating over the appropriate path as indicated in Fig. 1, we find

$$\int_{-\infty}^{\infty} \frac{|\mathcal{C}_r(R)|^2}{R^6}\, dt = \frac{35\pi}{128} \frac{e^4 |\mathfrak{z}_{rm}|^2}{v \Delta E_{rm}^2 b^9}, \quad b \geq r_0 \tag{16a}$$

and

$$\int_{-\infty}^{\infty} \frac{|\mathcal{C}_r(R)|^2 dt}{R^6} = \frac{2e^4 |\mathfrak{z}_{rm}|^2}{v \Delta E_{rm}^2} \times \left[\frac{105}{384 b^9}\left(\frac{\pi}{2} - \tan^{-1}\frac{(r_0^2 - b^2)^{1/2}}{b}\right) - \frac{(r_0^2-b^2)^{1/2}}{9 r_0^{10}} \sum_{n=1}^{4}\left(\prod_{m=n}^{4} \frac{(2m+1) r_0^2}{2mb^2}\right)\right], \quad 0 < b < r_0 \tag{16b}$$

where $\mathfrak{z}_{rm}$ is the z component of the transition moment between X_r^* and X_m^*. The probability per collision for Penning detachment is taken to be unity for $b < s = 7.0$ Å.

One then integrates over impact parameter (numerically in the region $0 < b < r_0$) and obtains

$$\sigma_d = \begin{cases} \pi s^2 + (3.5\times 10^{-2}) \dfrac{ce^4 |\vec{\mathfrak{D}}_1|^2 |\mathfrak{z}_{rm}|^2 \sigma(h\nu)}{h\nu \Delta E_{rm}^2 v s^7}, & r_0 < s \quad (17a) \\[2ex] (0.14) \dfrac{ce^4 |\vec{\mathfrak{D}}_1|^2 |\mathfrak{z}_{rm}|^2 \sigma(h\nu)}{h\nu \Delta E_{rm}^2 v r_0^7}, & r_0 > s. \quad (17b) \end{cases}$$

We note that in (17b) σ_d is critically dependent on r_0, the distance of minimum approach, and is inversely dependent on the relative velocities of the two particles.

The photon-emission cross section is calculated from Eqs. (13) and (14). Integration over impact parameter in the region $0 < b < r_0$ was done numerically. $P_c(b)$ is much less than one for all b. The resulting cross section is

$$\sigma_e = (1.4\times 10^1) \frac{e^4}{c^3 h} \frac{\omega^3 |\vec{\mathfrak{D}}_1|^2 |\mathfrak{z}_{rm}|^2}{\Delta E_{rm}^2 v r_0}, \tag{18}$$

where $\omega = 2\pi\nu$. Here the cross section is only inversely proportional to distance of minimum approach.

To obtain quantitative results for σ_e and σ_d, we assume the wave functions of the electron states associated with the neutral atom are hydrogenic. The transition moments are then determined. $\sigma(h\nu)$ is obtained from the photodetachment spectrum of H^- as determined theoretically by Doughty *et al.*[5] using a dipole velocity expression. If r_0 is taken to be 2.5 Å and the relative collision energy is 1 eV, one finds

$$\sigma_d = 1.9\times 10^{-14}\ \mathrm{cm}^2, \quad \sigma_e = 3.6\times 10^{-18}\ \mathrm{cm}^2.$$

We have shown the dependence of σ_d and σ_e on r_0 in Fig. 3. Note that σ_d, especially, is sensitive to r_0, but is very large even for rather large values of r_0.

B. H*, H⁻ Collision

The two processes to be considered are

$$\mathrm{H}^*(2s)+\mathrm{H}^- \to 2\mathrm{H}(1s)+e,$$

$$\mathrm{H}^*(2s)+\mathrm{H}^- \to \mathrm{H}(1s)+\mathrm{H}^- + h\nu.$$

Because of the near-degenerate nature of the 2^1P-2^1S levels in H($\tilde{\nu} \sim 0.1\ \mathrm{cm}^{-1}$), $|\mathcal{C}_r(R)|^2$ cannot be determined by the simple perturbative equation (14). In principle, there could be a region outside a sphere of radius D for which Eq. (14) is applicable, and whose contribution to σ_d or σ_e might be significant. Inside the sphere of radius D, $|\mathcal{C}_r(R)|^2 \cong \frac{1}{2}$. It can be shown that the contributions to the cross sections outside the sphere of radius D are negligible. The important contributions to the probability

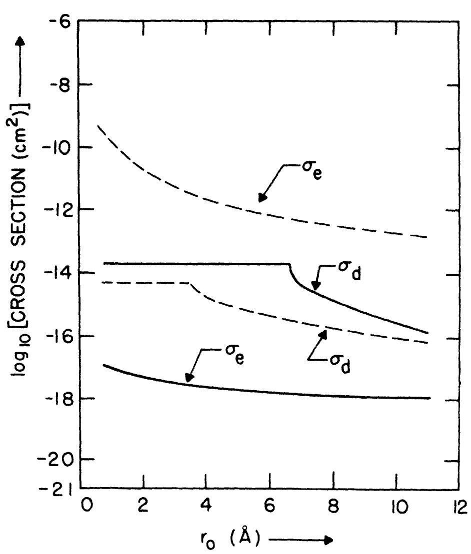

FIG. 3. Dependence of cross sections for Penning detachment σ_d and photon emission σ_e on r_0. Systems represented are Ca*, H⁻ (solid line) and H*, H⁻ (dashed line).

per collision $P_c(b)$ come from

$$P_c(0<b<r_0) \propto 2\int_{(r_0^2-b^2)^{1/2}/v}^{(D^2-b^2)^{1/2}/v} |\mathcal{C}_r(R)|^2 R^{-6} dt \equiv B_1(b) \tag{19a}$$

and

$$P_c(r_0<b<D) \propto 2\int_0^{(D^2-b^2)^{1/2}/v} |\mathcal{C}_r(R)|^2 R^{-6} dt \equiv B_2(b), \tag{19b}$$

which, upon integration and setting $|\mathcal{C}_r(R)|^2 = \frac{1}{2}$ in this region, yield

$$B_1(b) = \frac{(D^2-b^2)^{1/2}}{4vb^2D^2}\left(\frac{1}{D^2}+\frac{3}{2b^2}\right) - \frac{(r_0^2-b^2)^{1/2}}{4vb^2r_0^2}\left(\frac{1}{r_0^2}+\frac{3}{2b^2}\right) + \frac{3}{8b^5v}\left(\tan^{-1}\frac{(D^2-b^2)^{1/2}}{b} - \tan^{-1}\frac{(r_0^2-b^2)^{1/2}}{b}\right), \quad 0<b<r_0 \ ,$$

$$B_2(b) = \frac{(D^2-b^2)^{1/2}}{4vb^2D^2}\left(\frac{1}{D^2}+\frac{3}{2b^2}\right) + \frac{3}{8b^5v}\tan^{-1}\frac{(D^2-b^2)^{1/2}}{b}, \quad r_0<b<D \ . \tag{20}$$

In this instance $s = 4.1$ Å. For $r_0 < s$,

$$\sigma_d = \pi s^2 + (0.35)\frac{c|\vec{\mathfrak{D}}_1|^2\sigma(h\nu)}{h\nu v s^2 D}, \quad r_0 < s \ . \tag{21}$$

In the case of $r_0 > s$, numerical integration was used to solve integrals involving $B_1(b)$. One finds

$$\int_0^{r_0} 2\pi b B_1(b)\, db = (0.28)\pi/vr_0^3 \ . \tag{22}$$

The second contribution to integration over impact parameter gives directly (realizing only $D \gg r_0$)

$$\int_{r_0}^{D} 2\pi b B_2(b)\, db = \pi^2/4vDr_0^2 \ . \tag{23}$$

Comparing (22) and (23), we realize that the principal contribution to σ_d comes from the region where $0<b<r_0$ and $R<D$. This indicates that our neglect of the other reaction regions was justified. Thus

$$\sigma_d = (0.12)c|\vec{\mathfrak{D}}_1|^2\sigma(h\nu)/h\nu v r_0^3 \ , \quad r_0 > s \ . \tag{24}$$

We also investigate the probability for photon emission during an H(2s), H^- collision. The cross section is given by the general equation (13) and $P_c(b) \ll 1$, always. Unlike the case of Penning detachment, however, all portions of the trajectories contribute to the cross section. Integration is carried out over the trajectories indicated in Fig. 1 with the appropriate values for $|\mathcal{C}_r(R)|^2$ as discussed above. Numerical integration was employed in the region $0<b<D$, $R>D$ when integrating over impact parameter. Otherwise, the calculations are straightforward. If one remembers that $D \gg r_0$, it is found that

$$\sigma_e = (2\pi A_r/3v)(D^3 - r_0^3) + A_r(e^4|\mathfrak{z}_{rm}|^2\pi/v\Delta E_{rm}^2 D)(3.75) \ . \tag{25}$$

On substituting for A_r and letting $D \to r_0$, we see that σ_e is, to within a factor of 1.2, just the same as (18), as should be the case.

For a collision energy of 1 eV and a minimum distance of approach $r_0 = 1.0$ Å, we obtain $\sigma_d = 1.7$

TABLE II. Cross sections for Penning detachment σ_d and photon emission σ_e for different collision systems. E(collision) = 1 eV. In the case of H(2s) only adiabatic contributions to the cross sections are given.

Collision system	r_0(Å)[a]	$\sigma(h\nu)$ (10^{18} cm^2)	σ_d(cm^2)	σ_e(cm^2)
H(2s), H^-	1.0	7[b]	1.7×10^{-15}	1.5×10^{-10}
Ca(3^1D), O^-	2.8	6.4[c]	1.9×10^{-14}	1.1×10^{-17}
Ca(3^1D), C^-	2.6	13[d]	2.0×10^{-14}	1.1×10^{-17}
Ca(3^1D), H^-	2.5	23[b]	1.9×10^{-14}	3.6×10^{-18}
He(2^1S), H^-	1.5	1.8[b]	2.7×10^{-15}	3.2×10^{-16}
He(2^1S), O^-	1.6	≥5.5[e]	$\geq 4.0\times10^{-15}$	5.0×10^{-16}
He(2^1S), C^-	1.4	8[f]	4.5×10^{-15}	2.3×10^{-16}
He(2^1S), Cl^-	1.8	10[f]	4.9×10^{-15}	6.2×10^{-16}

[a] $r_0 = r_{max}(X) + r_{max}(Y)$, where r_{max} is radius of maximum radial electron-distribution function calculated by Slater's method of screening constants [J. C. Slater, Phys. Rev. 36, 57 (1930)] except in the case of $Y = Cl$ where a value of 1 Å is used.

[b] Doughty *et al.* (Ref. 5).

[c] L. M. Branscomb, S. J. Smith, and G. Tisone, J. Chem. Phys. 43, 2906 (1965).

[d] M. L. Seman and L. M. Branscomb, Phys. Rev. 125, 1602 (1962).

[e] S. J. Smith, in *Proceedings of the Fourth International Conference on Ionization Phenomena in Gases*, edited by N. R. Nillson (North-Holland, Amsterdam, 1960), p. 219. Smith calculated the photodetachment cross section only for $O^-(^3P) + h\nu \to O(^2P) + e$, thus neglecting formation of excited states. His cross section is therefore taken as a minimum value.

[f] J. W. Cooper and J. B. Martin, Phys. Rev. 126, 1482 (1962).

$\times 10^{-15}$ cm^2 while $\sigma_e = 1.5 \times 10^{-10}$ cm^2.

C. Other Collision Systems

In Table II we present values for σ_d and σ_e for collision systems involving several negative ions and metastables. The energy gap $\Delta E_{rm}/hc = 4857$ cm^{-1} for He$(2^1S) \rightarrow$ He(2^1P) is large enough that the interactions involved may be treated by first-order perturbation theory throughout the collision process. Photodetachment cross sections of negative ions have only been investigated in detail for H^-, C^-, and O^-.[6] Systems involving Cl^- ion have been included since more work is now being done with negative halogen ions.[7] In all cases Penning detachment is seen to dominate over photon emission by factors of 10^1 to 10^4.

IV. APPROXIMATIONS

We have employed a number of approximations in the above calculations and will now discuss their validity and the restrictions they may place on collision processes to be studied. In specifying the relative positions and orientations of the colliding particles, we used the impact parameter and rotating atom approximations. The impact parameter method is applicable if the wave packet of relative motion does not broaden much during the collision. This leads to the requirement[8] that the collisional angular momentum $l \cong \mu b v/\hbar \gg 1$ or that $b \gg \hbar/\mu v$. In addition, if the mass μ is to be approximated by a point, then the dimension of its wave packet $\sim k^{-1} = \hbar/\mu v$ must be small compared to the interaction distance. For $v > 10^5$ cm sec^{-1} and $\mu > \frac{1}{2}$ $\times$(mass hydrogen), $\hbar/\mu v < 0.3$ Å, and both conditions for the applicability of the impact parameter method are satisfied. Any actual deviation from linear trajectory during the collision will be small and will effect the absolute magnitudes of σ_e and σ_d about equally thus having little effect on the relative sizes of these two cross sections. Katsuura[1] has employed the rotating atom approximation to study Penning ionization processes. He points out that doing so increases the true collision cross section by a factor of ~ 2.5. Since similar electron-electron interactions are involved in Penning detachment, as noted above, we expect σ_d to be in excess by the same amount.

We assumed also that the Y^- interacts X_m^* in an adiabatic manner to produce Stark mixing. For ΔE_{rm} large enough that first-order perturbation theory is valid throughout the process, the requirement for adiabaticity is that the interaction takes place over an interval of time larger than the Bohr period of the transition, or

$$(\Delta E_{rm}/\hbar)(a/v) \gg 1 \ , \tag{26}$$

where a is the dimension of the interaction region. For $\Delta E_{rm}/hc \cong 10^3$ cm^{-1} as is the case for both Ca* and He*, one finds that v must be less than about 10^7 cm sec^{-1}.

When first-order perturbation theory is not applicable, appreciable spreading of the energy levels occurs during the collision and it is better to investigate the requirement for adiabaticity[9]:

$$\left| \frac{1}{\omega} \frac{dV_{rm}}{dt} \right| \ll \left| \Delta E_{rm} \right| \ . \tag{27}$$

For velocities of interest, condition (27) is fulfilled except in the region $10^{-5} < R < 5 \times 10^{-15}$ cm. Purcell[10] and Seaton[11] have shown that the *diabatic* contributions from this region lead to cross sections on the order of 10^{-10} cm^2 for the transition H$(2^1S) \rightarrow$ H(2^1P) induced by passing ions. Thus in the limit of very small ΔE_{rm} our theory becomes incomplete because of an onset of a region where interactions are no longer adiabatic. It can be shown using (27) that the interactions will be adiabatic for $\Delta E_{rm}/hc > 1$ cm^{-1}. For energy separations that are at least this large, the theory as applied to Ca*(3^1D), H^- should be quite generally applicable.

We have also assumed the $|\mathfrak{C}_r(R)|^2 + |\mathfrak{C}_m(R)|^2 \cong 1$ at any time during the collision; the probability that the transition $X_r^* \rightarrow X$ occurs during the reaction time $\tau = a/v$ is small. For spontaneous photon emission, A_r^{-1} is a measure of the lifetime of the state X_r^*, thus we require $\tau \ll A_r^{-1}$. At a collision velocity of 10^6 cm sec^{-1}, $\tau \cong 10^{-13}$ sec and 10^{-10} sec for Ca*, H^- and H*, H^- systems, respectively. Since A_r^{-1} is on the order of 10^{-9} seconds or longer our assumption is justified. In the case of Penning detachment it is no longer true that $|\mathfrak{C}_r|^2 + |\mathfrak{C}_m|^2 = 1$ for impact parameters up to several angstroms and we have set $P_c(b) = 1$ in this region.

V. DISCUSSION

The absolute magnitude of σ_d is considerably larger than gas kinetic cross sections. This is to be expected due to the long-range potentials which induce the Stark mixing. For cases where ΔE_{rm} is not small, σ_e is only on the order of gas kinetic cross sections due to the short interaction time during the collision.

The method of calculating σ_d and σ_e which is presented in this report should also be valid for atoms in metastable states whose spin quantum numbers S_m differ from that of the ground state (S_g) [i.e., He(2^3S): $S_m = 1$, $S_g = 0$]. In such a case, however, both σ_d and σ_e are expected to be greatly reduced if we assume that only Stark mixing with an excited state $|X_r^*\rangle$ of spin S_g will result in either photon emission or Penning detachment. In fact, the probability for either process occurring during a collision will probably be reduced considerably. This suggests that electron detachment will occur *via* a mechanism similar to that of Penning *ionization* and that the resulting cross section σ_d will be less than gas kinetic cross sections.

In our calculation, r_0 represents a hard-core interaction range, analogous to the classical distance of closest approach for two colliding particles. While a determination of r_0 from cross sections obtained in monoenergetic collision experiments would, in theory, be possible using the equations presented above, in practice it would be difficult since σ_d and σ_e vary within at most only one order of magnitude over the range of expected values of r_0. In the case of Ca*, H^- collisions, for instance, one expects r_0 to be in the neighborhood of 2–3 Å.

From the restrictions placed upon the theory by the approximations employed, it is evident that our method of calculating Penning detachment and photon-emission cross sections will be useful in gaining an order of magnitude estimate of the relative importance of these two processes when negative ions and metastable atoms collide. The cross sections associated with the H*, H^- system indicate that quenching of $H(2^1S)$ by ions, even H^-, is far more important than Penning detachment in regions such as the solar chromosphere where H^- is known to be abundant. In any neutral-ion collision system for which ΔE_{rm} is so small that *diabatic* contributions become dominant, quenching of the metastable state will dominate over Penning detachment even if adiabatic approximation indicates that $\sigma_d > \sigma_e$. On the other hand, interaction of H^- or other negative ion with atoms in metastable excited states associated with large ΔE_{rm} will result in Penning detachment (see Table II) and may be an important channel for deexcitation of such metastables.

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Unitarity in Coulomb Scattering*

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It is demonstrated that the pure-Coulomb t matrix satisfies a modified unitarity condition and that its discontinuity is not zero, as has been asserted elsewhere.

Recently several attempts[1] have been made to evaluate the scattering amplitude for three charged particles via the impulse approximation applied to the Faddeev equations. All of these approaches rely on a result due to Nutt,[2] who contends that the discontinuity of the off-shell–Coulomb t matrix along the unitarity axis is zero. We will demonstrate here that this result is, in fact, wrong, so that those results based upon it are probably also incorrect.

To formulate the problem precisely, we follow Nutt and define the Coulomb t matrix by the integral representation derived by Schwinger[3]:

$$\langle \vec{K}_2 | T(K^2) | \vec{K}_1 \rangle = -\frac{e^2}{2\pi^2} \frac{1}{|\vec{K}_2 - \vec{K}_1|^2}$$