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Publication Date

1977-07-01

Submitted to Journal of Chemical
Physics

UC-34a
LBL-6653
Preprint 31

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July 1977

Prepared for the U. S. Department of Energy
under Contract W-7405-ENG-48

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A Unified Treatment of Penning Ionization
and Excitation Transfer^{*}

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Abstract

It is shown how Penning ionization ($A^* + B \rightarrow A + B^+ + e^-$) and excitation transfer ($A^* + B \rightarrow A + B^{**}$, B^{**} = Rydberg state) can be described by essentially the same theoretical model. The physical basis of this is that in both cases the final state of species B consists of an ion core B^+ with a highly excited electron, and whether the electron is slightly bound (B^{**}) or slightly unbound ($B^+ + e^-$) matters little to the collision dynamics. The system $He^*(2^3S) + F$ is analyzed as an example of this theory.

I. Introduction

The two reactions

are usually considered to be quite different in nature. This point of view is enhanced by the fact that the experimental techniques for detection of the products of (1.1a) and (1.1b) are entirely different. Process (1.1a), known as Penning ionization, has been investigated by measurement of the ions¹ and electrons,² whereas the excited states B^{**} from process (1.1b) are usually detected by optical spectroscopy.³

For some purposes, however, it may be useful to look at these processes by stressing their common features rather than their differences. This is done in this paper, and it is hoped that from this treatment a better understanding of both reactions arises.

In both cases one has the following physical picture of the collision process: the atom A^* is de-excited to its ground state while one electron is promoted to an excited orbital in the Coulomb field of the ion B^+ . The electronic transition matrix element may be formally written as

$$V_{f \leftarrow i} = \langle f | V | i \rangle \quad , \quad (2)$$

where $|i\rangle$ describes the initial state $A^* + B$ which has the character of a bound state in both cases, so that only a limited range of configuration space contributes to the matrix element. From this it is evident that the final

state $|f\rangle$ ($A + B^+ + e^-$, or $A + B^{**}$, respectively) is of importance only in a finite region around nucleus B. The state $|f\rangle$ contains the orbital of the excited electron, which is a free Coulomb-wave for (1.1a) or a Rydberg state for (1.1b), and in a finite range both of these orbitals are essentially the same except for normalization. From this consideration we draw the conclusion that it should be possible to describe processes (1.1a) and (1.1b) by the same theoretical model.

A further motivation for this uniform treatment can be taken from experimental results. Cross sections have been measured^{2,3} as a function of collision energy for the following reactions:

As shown in Figure 1, the cross sections for all systems are remarkably similar in the thermal energy range. Figure 2 shows schematically the relevant potential curves. For (1.3a,b,c) the potential curve $V[X^* - \text{Hg}]$ of the initial state is embedded in the continuum of $X + \text{Hg}^+ + e^-$. Once ionization has occurred, the nuclei continue their path in the potential $V[X + \text{Hg}^+]$. The picture for $\text{Kr}^* - \text{Hg}$ is different since the excitation energy of Kr^* is below the ionization potential of Hg. The potential $V[\text{Kr}^* - \text{Hg}]$ is, however, embedded in a family of Rydberg state potentials $V[\text{Kr} + \text{Hg}^{**}]$. Thus, compared to reactions (1.3a,b,c), the continuum

$X + \text{Hg}^+ + e^-(\epsilon)$ is simply replaced by the quasi-continuum $\text{Kr} + \text{Hg}^{**}(n)$, where n denotes the principal quantum number of the Rydberg states and ϵ the energy of the emitted electron. After separation of Kr and Hg^{**} many of the Rydberg states thus formed then cascade down to $\text{Hg}^*(^3\text{P}_1)$ which in turn is detected by the 254 nm line that it emits. In this picture the state $\text{Hg}^*(^3\text{P}_1)$ serves as monitor for the formation of all (energetically accessible) Rydberg states during the collision.

Section II summarizes more completely the essential physical ideas of our theoretical approach. It is shown in Section III that the auto-ionization width Γ is indeed continuous at $\epsilon = 0$, the transition between processes (1.1a) and (1.1b), and a simple model for evaluating Γ approximately is described in Section IV. Sections V-VII then apply the approach to the $\text{He}^* - \text{F}$ system.

II. Basic Ideas

We approach the unified treatment of reactions (1.1a,b) by considering a system $A^* + B$ which can react in both ways:

This is possible if the entrance potential curve $V_* = V[A^* + B]$ is asymptotically in the continuum of $A + B^+ + e^-(\epsilon)$ but has a strongly attractive well which falls below the ionization limit (see Figure 3). The crossing point between V_* and $V_+ = V[A + B^+]$ is denoted as R_+ . For distances $R > R_+$ Penning ionization occurs, whereas in the range $R < R_+$ transitions into the states $A + B^{**}$ take place since V_* crosses through a quasi continuum of potential curves which dissociate to A and Rydberg states B^{**} . The crossing points of V_* with Rydberg state potentials are R_n (thus $R_\infty = R_+$) and the potentials are denoted as $V_n = V[A + B^{**}(n)]$.

We consider first the expression for the probability that system $A^* + B$ is elastically scattered, i.e., without undergoing ionization or transition into a Rydberg state. The probability for reaching the turning point R_0 is:

$$P(\infty, R_0) = P(\infty, R_+) P(R_+, R_0) \quad , \quad (2.2)$$

where $P(\infty, R_+)$, the probability that the system does not autoionize for R in the interval $R_+ < R < \infty$, is familiar from Penning ionization⁴

$$P(\infty, R_+) = \exp \left[- \int_{R_+}^{\infty} dR \frac{\Gamma(R)}{\hbar v_b(R)} \right] , \quad (2.3)$$

where $\Gamma(R)$ is the autoionization width (units of energy) and $v_b(R)$ is the radial velocity for impact parameter b . $P(R_+, R_0)$, the probability that the system does not undergo transition into any of the Rydberg states for R in the interval $R_0 < R < R_+$, is given by a product of Landau-Zener probabilities:

$$P(R_+, R_0) = \prod_n P_n , \quad (2.4)$$

with

$$P_n = \exp \left[- \frac{2\pi |V_{*,n}|^2}{\hbar v_b(R_n) \left| \frac{d}{dR} (V_* - V_n) \right|, R=R_n} \right] ; \quad (2.5)$$

i.e., the probability of not transferring into any Rydberg state is the product of the probabilities of surviving each crossing elastically.

Combining Eqs. (2.4) and (2.5) gives

$$P(R_+, R_0) = \exp \left[- \sum_n \frac{2\pi |V_{*,n}|^2}{\hbar v_b(R_n) \left| \frac{d}{dR} (V_* - V_n) \right|, R=R_n} \right] . \quad (2.6)$$

In Eqs. (2.5) and (2.6) $V_{*,n}$ is the coupling between the initial state, A^*-B , and the n^{th} Rydberg state, $A-B^{**}(n)$, evaluated at the crossing point R_n .

We now wish to re-write Eq. (2.6) so that it looks as much as possible like Eq. (2.3), i.e., so that the probabilities of not autoionizing and of

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not undergoing transition into the Rydberg states are treated in a unified manner. To do this one considers the Rydberg states as a continuum and n as a continuous variable. In Eq. (2.6) one thus has

$$\sum_n \rightarrow \int dn = \int_{R_0}^{R_+} dR \left(\frac{dn}{dR} \right), \quad (2.7)$$

where $n(R)$ is the inverse function of $R(n)$ ($R(n)$ is the crossing point R_n for continuous n). Eq. (2.6) then takes the same form of Eq. (2.3),

$$P(R_+, R_0) = \exp \left[- \int_{R_0}^{R_+} dR \frac{\Gamma(R)}{\hbar v_b(R)} \right] \quad (2.8)$$

if for $R < R_+$ one defines $\Gamma(R)$ as

$$\Gamma(R) = \frac{2\pi |V_{*,n}|^2}{\left| \frac{d}{dR} (V_{*,n} - V_n) \right|} \left| \frac{dn}{dR} \right|. \quad (2.9)$$

To see that Eq. (2.9) is the same definition of Γ as for Penning ionization, we assume (as usual) that the Rydberg potential curve $V_n(R)$ is the same shape as $V_+(R)$, simply shifted by the energy of the Rydberg electron:

$$V_n(R) = V_+(R) + \epsilon_n. \quad (2.10)$$

The crossing point $R(n)$ is defined by

$$V_*(R) = V_n(R) = V_+(R) + \epsilon_n, \quad (2.11)$$

or

$$\epsilon_n = V_*(R) - V_+(R) \quad . \quad (2.12)$$

Defining $\epsilon(R)$ by

$$\epsilon(R) = V_*(R) - V_+(R) \quad , \quad (2.13)$$

which is the same definition as in Penning ionization,⁴ one has

$$\left| \frac{d}{dR} (V_* - V_n) \right| = |\epsilon'(R)| \quad , \quad (2.14)$$

so that

$$\frac{\left| \frac{dn}{dR} \right|}{\left| \frac{d}{dR} (V_* - V_n) \right|} = \frac{\left| \frac{dn}{dR} \right|}{\left| \frac{d\epsilon}{dR} \right|} = \left| \frac{dn}{d\epsilon} \right| \equiv \rho(\epsilon) \quad . \quad (2.15)$$

Eq. (2.9) thus takes the following form for $R < R_+$,

$$\Gamma(R) = 2\pi |V_{*,n}|^2 \rho(\epsilon) \quad , \quad (2.16)$$

where $\rho(\epsilon)$ is the density of states per unit energy. This definition of $\Gamma(R)$ for $R < R_+$, Eq. (2.16), is also recognized as the familiar "golden rule" expression⁵ for $\Gamma(R)$ that is found in treating Penning ionization⁴ for $R > R_+$. It will be shown in the next section that the definition of the density of states in Eq. (2.16) is the same as that for $R > R_+$, so that $\Gamma(R)$ is indeed continuous at $R = R_+$.

We have thus shown that the probability of transitions into the true continuum (Penning ionization) and into the quasi-continuum of Rydberg states is given by the same theoretical expression, and this is the basis of the unified treatment of all inelastic processes which occur during

the $A^* - B$ collision. All of the formulae previously derived for Penning ionization⁴ can thus be applied directly to the entire problem:

$$A^* + B \rightarrow A + B^+ + e^- , \quad \epsilon > 0 \quad (2.17a)$$

$$\rightarrow A + B^{**} , \quad \epsilon < 0 \quad (2.17b)$$

If, for example, the total inelastic probability is small, then the energy distribution of the electron is⁴

$$\sigma(\epsilon) = \int_0^\infty db \, 2\pi b \, \frac{2\Gamma(R)}{\hbar v_b(R)} \frac{1}{|\epsilon'(R)|} , \quad R = R(\epsilon) , \quad (2.18)$$

$R(\epsilon)$ being the inverse function of $\epsilon(R)$. The integral over impact parameter can be evaluated, so that Eq. (2.18) simplifies to

$$\sigma(\epsilon) = \frac{4\pi R^2}{|\epsilon'(R)|} \frac{\Gamma(R)}{\hbar v} \sqrt{1 - \frac{V_*(R)}{E}} , \quad R = R(\epsilon) , \quad (2.19)$$

where $v = \sqrt{2E/\mu}$. The interpretation of $\sigma(\epsilon)$ for $\epsilon > 0$ is that $\sigma(\epsilon)d\epsilon$ is the cross section for the ionized electron to have an energy in the increment $(\epsilon, \epsilon+d\epsilon)$. For $\epsilon < 0$ the quantity $\sigma(\epsilon)\Delta\epsilon$ is the cross section for formation of the Rydberg state B^{**} whose energy lies in the interval $(\epsilon, \epsilon+\Delta\epsilon)$.

III. Behavior of $\Gamma(R(\epsilon))$ Near $\epsilon = 0$

From the previous section it is seen that the width function $\Gamma(R)$ is given by⁵

$$\Gamma(R) = 2\pi \rho(\epsilon) |V_{*,\epsilon}|^2, \quad (3.1)$$

with $\epsilon = \epsilon(R)$, and where

$$V_{*,\epsilon} = \langle \chi_{\epsilon} \phi_{N-1} | V | \psi_N \rangle; \quad (3.2)$$

ψ_N is the (Born-Oppenheimer) electronic wavefunction of A^*-B , ϕ_{N-1} the wavefunction of $A-B^+$, χ_{ϵ} is the one-electron orbital for the N^{th} electron in the final state, and V is the operator (actually the total electronic Hamiltonian) which couples the states.

In this section we show that $\Gamma(R)$ is a smooth, continuous function at $R = R_+$, i.e., at $\epsilon = 0$. This is intuitively clear, since for purposes of evaluating the matrix element in Eq. (3.2) there seems little difference between an electron that is "just bound", or "just unbound", in the attractive Coulomb potential.

To facilitate the analysis we define

$$\psi_{\epsilon} = \sqrt{\rho(\epsilon)} \chi_{\epsilon} \quad (3.3)$$

and

$$\bar{V}_{*,\epsilon} = \langle \psi_{\epsilon} \phi_{N-1} | V | \psi_N \rangle, \quad (3.4)$$

in terms of which Γ is given by

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$$\Gamma(R) = 2\pi |\bar{V}_{*,\epsilon}|^2 \quad (3.5)$$

The ϵ dependence is now all contained in the function ψ_ϵ , and it is thus necessary only to consider it in the vicinity of $\epsilon = 0$. Furthermore, since Ψ_N is a bound state function, one is only interested in $\psi_\epsilon(r)$ for r in a finite region about the origin, for this is the only region which contributes to the matrix element.

We thus consider the WKB approximation for $\psi_\epsilon(r)$. First, for $\epsilon > 0$, one has

$$\chi_\epsilon(r) = \sin\left[\frac{\pi}{4} + \int_{r_<}^r dr' k(r')\right] / k(r)^{1/2}, \quad (3.6)$$

where

$$k(r) = \sqrt{2\epsilon + \frac{2}{r} - \frac{\ell(\ell+1)}{r^2}}, \quad (3.7)$$

and where atomic units are being used. ℓ is the orbital angular momentum of the electron, and $r_<$ is the inner turning point,

$$r_< = \frac{-1 + \sqrt{1 + 2\epsilon \ell(\ell+1)}}{2\epsilon}.$$

For χ_ϵ normalized this way one has $\rho(\epsilon) = 2/\pi$, so that

$$\psi_\epsilon(r) \approx \sqrt{\frac{2}{\pi}} \frac{\sin[\frac{\pi}{4} + \int_{r_<}^r dr' k(r')]}{\sqrt{k(r)}}. \quad (3.8)$$

For $\epsilon < 0$ the WKB approximation for the normalized orbital $\chi_n(r)$ is

$$\chi_n(r) = C \frac{\sin[\frac{\pi}{4} + \int_{r_<}^r dr' k(r')]}{\sqrt{k(r)}} \quad (3.9)$$

The normalization constant C is determined in the usual fashion:

$$\begin{aligned} 1 &= C^2 \int_{r_<}^{r_>} dr \frac{\sin^2[\frac{\pi}{4} + \int_{r_<}^r dr' k(r')]}{k(r)} \\ &\approx C^2 \left(\frac{1}{2}\right) \int_{r_<}^{r_>} dr \frac{1}{k(r)} \quad ; \end{aligned} \quad (3.10)$$

differentiation of the WKB eigenvalue relation

$$(n + \frac{1}{2})\pi = \int_{r_<}^{r_>} dr \sqrt{2\varepsilon + \frac{2}{r} - \frac{\ell(\ell+1)}{r^2}} \quad (3.11)$$

gives,

$$\frac{dn}{d\varepsilon} \pi = \int_{r_<}^{r_>} dr \frac{1}{k(r)} \quad , \quad (3.12)$$

and together with Eq. (3.10) this gives C as

$$C = \sqrt{\frac{2}{\pi} \frac{d\varepsilon}{dn}} \quad (3.13)$$

According to Eq. (2.15), $\rho(\varepsilon) = \frac{dn}{d\varepsilon}$ for $\varepsilon < 0$, and with this Eqs. (3.9)

and (3.13) give

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$$\begin{aligned}
\psi_{\epsilon}(r) &\equiv \sqrt{\rho(\epsilon)} \chi_n(r) \\
&= \sqrt{\frac{dn}{d\epsilon}} \sqrt{\frac{2}{\pi} \frac{d\epsilon}{dn}} \frac{\sin[\frac{\pi}{4} + \int_{r_<}^r dr' k(r')] }{\sqrt{k(r)}} \\
&= \sqrt{\frac{2}{\pi}} \frac{\sin[\frac{\pi}{4} + \int_{r_<}^r dr' k(r')] }{\sqrt{k(r)}} , \tag{3.14}
\end{aligned}$$

which is identical to Eq. (3.8) for $\epsilon > 0$ and establishes our principle assertion.

The above analysis has employed WKB radial functions for the coulomb orbital, but this is not an essential limitation of the result. The WKB wavefunctions could, for example, be replaced by uniform approximations valid also in the vicinity of the inner turning point $r_<$. The cases $\epsilon > 0$ and $\epsilon < 0$ differ then only in that there is no outer turning point for $\epsilon > 0$, while there is for $\epsilon < 0$. Since this region of r contributes negligibly to the matrix element, this difference has negligible effect.

IV. A Primitive Approximation to the Function $\Gamma(R)$

The process

can basically be understood as the rearrangement of two electrons (cf. Figure 4). One electron from B falls into the empty orbital of A^* while the second electron is excited to energy ϵ which might be positive or negative with respect to the ionization limit of B. In the initial state $A^* + B$ the two orbitals involved are denoted as ϕ_x and ψ , where ϕ_x represents the excited orbital. In the final state $A + B^+ + e^-(\epsilon)$ the two orbitals are χ_ϵ and ξ , where χ_ϵ describes the continuum or Rydberg state. From the fact that the two electrons are indistinguishable it follows that the matrix element $V_{*\epsilon}$ in Eq. (3.2) consists of two terms,

$$\begin{aligned} V_{*\epsilon} = & \langle \chi_\epsilon(2) \xi(1) | V | \phi_x(1) \psi(2) \rangle \\ & - \langle \chi_\epsilon(1) \xi(2) | V | \phi_x(1) \psi(2) \rangle, \end{aligned} \quad (4.2)$$

where 1 and 2 denote the electrons. As long as the two atoms are sufficiently far apart that the molecular orbitals may be described by atomic orbitals, ξ belongs to A and ψ to B. From this point of view the second term has been called the exchange matrix element⁶. In the case of weak interaction between A^* and B the orbital ϕ_x is mainly located near nucleus A. Therefore the first term in Eq. (4.2) describes a process which can be thought of as the de-excitation $A^* \rightarrow A$ and the emission of a virtual photon which then excites B to B^{**} or $B^+ + e^-$. From this aspect

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the first term is called the nonexchange, or radiative matrix element. In the case of strong interaction between $A^* + B$ it might well be that for small distances the configuration looks more like $A^+ + B^-$ than like $A^* + B$. Obviously the orbital ϕ_x is then located near the nucleus B and the first term also involves an electron exchange between A and B. Hotop and Niehaus⁶ have given some experimental evidence that only the exchange matrix element is of importance if A^* is a metastable, i.e.,

$$V_{*E} \approx - \langle \chi_E(1) \xi(2) | V | \phi_x(1) \psi(2) \rangle \quad (4.3)$$

Figure 4 illustrates this matrix element for weak ($A^* + B$) and strong ($A^+ + B^-$) interaction.

- Our primitive approximation of V_{*E} is constructed as follows: guided by physical intuition rather than by a rigorous derivation we assume that the exchange matrix element can be approximated as

$$V_{*E} \approx - \langle \chi_E(1) | \phi_x(1) \rangle \langle \xi(2) | H' | \psi(2) \rangle \quad (4.4)$$

where $\langle \xi(2) | H' | \psi(2) \rangle$ is the probability amplitude of a one electron jump from B to A. We regard electron 2 as "hard" to move compared to electron 1, so in order to get the order of magnitude and the R-dependence of V_{*E} right, one should take care that this matrix element is evaluated realistically. A semi-empirical formula for one electron exchange between atoms has been given by Olson et al.,⁷ which in our case yields

$$\begin{aligned} H_{AB} &\equiv \langle \xi(2) | H' | \psi(2) \rangle \\ &= D \cdot R \exp(-R/C) \quad , \end{aligned} \quad (4.5)$$

where

$$\frac{1}{C} = (I_A^{1/2} + I_B^{1/2})/2^{1/2} \quad (4.6a)$$

$$D = \sqrt{I_A I_B}/C, \quad (4.6b)$$

I_A = ionization potential of orbital ξ in atom A

I_B = ionization potential of orbital ψ in atom B.

This formula has been applied by Olson et al.,⁷ to a large number of one electron transfer systems and found to yield the correct results within a factor of 2-3.

Since χ_ϵ and ϕ_x are thought of as atomic orbitals, the R-dependence of $V_{*\epsilon}(R)$ in Eq. (4.4) is contained entirely in the second factor, whereas, the overlap $\langle \chi_\epsilon | \phi_x \rangle$ describes the ϵ -dependence of $V_{*\epsilon}(R)$. To check these assumptions we have compared the known $\Gamma(R)$ of the Penning ionizing systems $\text{He}(2^3\text{S})\text{-H}$, H_2 ,⁸ Ar ⁹ with the quantity $|H_{AB}(R)|^2$. We found the slope to be in almost perfect agreement. This does not hold for the systems $\text{He}(2^1\text{S})\text{-H}_2$,¹⁰ Ar .¹¹ It is interesting to note that these latter cases are possible candidates for systems where the radiative matrix element of Eq. (4.2) might play an important role via mixing to the $\text{He}(2^1\text{P})$ state.

Thus, as long as we deal only with the exchange matrix element, we believe the factor $|H_{AB}(R)|^2$ describes the R-dependence of $\Gamma(R)$ reasonably well. The factor $2\pi\rho(\epsilon) |\langle \chi_\epsilon | \phi_x \rangle|^2$ then serves as a scaling factor. Application to the systems $\text{He}(2^3\text{S})\text{-H}$, Ar shows that this scaling factor is the right order of magnitude. Our heuristic formula for $\Gamma(R)$ is then

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$$\Gamma(R) = 2\pi\rho(\epsilon) |\langle \chi_\epsilon | \phi_x \rangle|^2 |H_{AB}(R)|^2, \quad (4.7)$$

which we believe to be reliable to within a factor of 5 or so. Even though not of great accuracy this expression is useful in a case where one wishes to predict whether an unknown total cross section is in a measurable range for today's experimental techniques. All relative differential cross sections which are calculated with the aid of Eq. (4.7) are believed to be even more reliable since the slope of $\Gamma(R)$ is described quite well.

V. $^2\Sigma$ - Potential Curves for System Helium-Fluorine

The remainder of the paper describes application of the above theoretical model to the $\text{He}^* + \text{F}$ system. The potential curves for the system of He, F ($^2\Sigma$ -states only) are shown in Figure 5, and one sees that a potential curve V_* exists which crosses both ranges, the continuum states $\text{He} + \text{F}^+(^3\text{P}) + e^-(\epsilon)$ and the Rydberg states $\text{He} + \text{F}^{**}$. Diabatically, V_* dissociates to $\text{He}^+ + \text{F}^-$, adiabatically to $\text{He}^*(2^3\text{S}) - \text{F}$.

The following method has been used to estimate the potential V_* . $\text{He}(2^3\text{S})$ and Li are quite similar chemically because in both species the outer 2s-electron sees an +1 nuclear charge and is excluded from the inner shell by the Pauli principle. The adiabatic potential $V[\text{He}(2^3\text{S})-\text{F}]$ is therefore assumed to have a similar equilibrium distance r_e , well depth D_e , and curvature $V''(r_e)$ as $V[\text{Li}-\text{F}]$. A slight adjustment has been made to take into account the difference between the ionization potentials of $\text{He}(2^3\text{S})$ and Li (see Table 1). The long range part of the $\text{He}(2^3\text{S})-\text{F}$ potential is assumed to be well described by $V[\text{He}^+ + \text{F}^-]$.

The crossing between the diabatic potentials $V[\text{He}(2^3\text{S})-\text{F}]$ and $V[\text{He}^+ + \text{F}^-]$ is at $R_c = 20.6 a_0$. From Eq. (4.5) one computes that this crossing is only weakly avoided; the separation of the adiabatic potentials is $\sim 4 \times 10^{-5}$ hartree. For comparison, the crossing point for $\text{Li}-\text{F}$ is at $R_c = 13.99 a_0$, and the adiabatic potentials are separated by $\sim 9 \times 10^{-4}$ hartree. From this fact a striking difference between the systems $\text{He}(2^3\text{S})-\text{F}$ and $\text{Li}-\text{F}$ arises: In a thermal collision the system $\text{Li}-\text{F}$ follows the adiabatic potential curve whereas the system $\text{He}(2^3\text{S})-\text{F}$ remains in its original configuration with a probability of 99.99% even at a collision

energy as low as 10 meV. Therefore, in order to reach the attractive part of the potential curve V_* which crosses $V[\text{He-F}^+]$, it is necessary to start experimentally with the system $\text{He}^+ + \text{F}^-$. It is for this reason that we will treat the collision of $\text{He}^+ + \text{F}^-$ instead of $\text{He}(2^3\text{S})-\text{F}$:

with $\epsilon > 0$ or < 0 .

The potential $V[\text{He}^+-\text{F}^-]$, which will be denoted as V_* from now on, has the symmetry $^2\Sigma$. Since total spin is conserved and the collision energies we consider are too low to allow for rotational coupling, the final states $\text{He} + \text{F}^+ + e^-(\epsilon)$ must have the same symmetry. Therefore we take into account only $^2\Sigma$ -potentials. After separation of the particles F^{**} must thus be in a doublet state, and its electronic angular momentum must be perpendicular to the internuclear axis.

Further, since the crossing R_+ occurs in a region where neither potential curve shows strong chemical interaction, we assume that the atomic orbitals of both reaction partners are only slightly perturbed so that a description of the process in atomic orbitals is quite good. Regarding our approximate formula for $\Gamma(R)$ in Eq. (4.7), we thus take ϕ_x to be the 2p orbital of F^- ; χ_e must then also be a p orbital centered on nucleus B.

The potential $V[\text{He-F}^+(^3\text{P})]$ in Figure 5 is the one calculated by Liebman and Allen,¹³ and the potentials $V[\text{He-F}^{**}]$ were constructed in the following manner. From Kraus, Maldonado, and Wahl¹⁴ we took the potential curves calculated for He-Na^+ and $\text{He-Na}(X,A,B)$, which dissociate as

All four potentials were normalized to zero for $R \rightarrow \infty$ and the following differences computed:

$$\Delta V(3s\sigma) = V[\text{He Na}(\text{X}^2\Sigma^+)] - V[\text{He Na}^+] \quad (5.2a)$$

$$\Delta V(3p\pi) = V[\text{He Na}(\text{A}^2\Pi)] - V[\text{He Na}^+] \quad (5.2b)$$

$$\Delta V(3p\sigma) = V[\text{He Na}(\text{B}^2\Sigma^+)] - V[\text{He Na}^+] \quad (5.2c)$$

We then assumed that adding a $3s\sigma$, $3p\pi$ or $3p\sigma$ electron to the system He-F^+ would change the potential $V[\text{HeF}^+]$ in the same way as it changes $V[\text{HeNa}^+]$. Neglecting the symmetry of the core $\text{F}^+(^3P)$, we characterize the Rydberg states F^{**} with $n = 3$ by the outer electron only:

$$\text{He-F}^{**}(n=3) = \begin{cases} \text{He F}^{**}(2p^4(^3P); s\sigma) \\ \text{He F}^{**}(2p^4(^3P); p\pi) \\ \text{He F}^{**}(2p^4(^3P); p\sigma) \end{cases}$$

The desired $\text{He-F}^{**}(n=3)$ -potential curves are then

$$V[\text{He-F}^{**}(2p^4(^3P); 3s\sigma)] = V[\text{HeF}^+] + \Delta V(3s\sigma) \quad (5.3a)$$

$$V[\text{He-F}^{**}(2p^4(^3P); 3p\pi)] = V[\text{HeF}^+] + \Delta V(3p\pi) \quad (5.3b)$$

$$V[\text{He-F}^{**}(2p^4(^3P); 3p\sigma)] = V[\text{HeF}^+] + \Delta V(3p\sigma) \quad (5.3c)$$

with $V[\text{HeF}^+]$ that of ref. 13 and ΔV defined by Eq. (5.2) with the He-Na potentials of ref. 14.

The higher potential curves, $\text{He-F}^*(2p^4(^3P)np)$ $n > 3$, are taken to be the same shape as that of He-F^+ , shifted to the asymptotic value of the atom F^* . Since the atomic energy levels of $\text{F}(2p^4(^3P)np)$, $n > 3$, are not given in Moore's tables,¹³ they were calculated in a simple manner by means of an n -dependent effective charge $Z(n)$, with $Z(n) \rightarrow 1$ as $n \rightarrow \infty$.

So far we have considered only the ground ionic state of F, $\text{F}^+(^3P)$ [the fine structure is neglected throughout this paper]. The first excited level of F^+ is $\text{F}^+(^1D)$ with an excitation energy of 2.588 eV. This ionic state gives rise to a second family of Rydberg states. Since $V[\text{He-F}^+(^3P)]$ and $V[\text{He-F}^+(^1D)]$ are very nearly parallel,¹³ this family of Rydberg potential curves can be assumed to be the same as those belonging to $\text{F}^+(^3P)$ except for an upward shift of 2.588 eV.

VI. $\Gamma(R)$ for System $\text{He}^+ + \text{F}^-$

The width function $\Gamma(R)$ for the collision system $\text{He}^+ + \text{F}^-$ is determined via Eq. (4.7). Application of Eq. (4.6) yields the following expression (all quantities in atomic units)

$$H_{AB}(R) = 0.313 \cdot R \cdot \exp(-0.924 \cdot R) \quad (6.1)$$

For the energy dependent factor $2\pi\rho(\epsilon) |\chi_\epsilon | \phi_x \rangle|^2$ we chose ϕ_x to be the Hartree-Fock¹⁶ 2p orbital of F^- and χ_ϵ to be bound or free hydrogenic p orbital. The overlap was evaluated analytically for $\chi_\epsilon = 3p, 4p, 5p$ -hydrogen wave function and numerically for $\chi_\epsilon =$ free Coulomb wave. In the first case there is of course an ambiguity in the proper choice of $\rho(\epsilon)$; we simply used $\rho(\epsilon = E_n) = 1/(E_{n+1} - E_n)$.

The quantity $2\pi\rho(\epsilon) |\langle \chi_\epsilon | \phi_x \rangle|^2$ is shown in Figure 6. For $\epsilon > 0$ it is a smooth function and for the three calculated levels np ($n = 3, 4, 5$) it is drawn as a histogram.

A logarithmic plot of $\Gamma(R)$ is shown in Figure 7. The values $\Gamma(R_n)$, $n = 3, 4, 5$ are computed from the appropriate terms in Figure 6.

For $R > R_+$ $\Gamma(R)$ is well described by the analytic expression $\Gamma(R) = 2.085 R \exp(-1.764 \cdot R)$. This analytic form is extrapolated into the region $R < R_+$ where $\epsilon < 0$. In this range of negative energies ϵ there are two ways of looking at the process

Either one regards the spectrum of Rydberg states F^{**} as continuous and uses the smooth function $\Gamma(R)$ for $R < R_+$ as well as for $R > R_+$, or one

regards the formation of a certain F^{**} as the result of an isolated curve crossing. In this latter picture one requires the Landau-Zener exponent u_n ,

$$u_n = \frac{2\pi}{\hbar} \frac{|V_{*n}|^2}{\left| \frac{d}{dR} (V_* - V_+) \right|}, \quad R = R_n,$$

which is related to $\Gamma(R)$ by [cf. Eq. (2.9)]

$$u_n = \frac{1}{\hbar} \int_{R_n}^{R_{n+1}} dR \quad \Gamma(R) \quad ;$$

i.e., the exponent of the Landau-Zener transition probability is an integral over $\Gamma(R)$.

VII. Cross Sections

This section presents cross sections for the reaction

as calculated from the potential curves and the function Γ described in the two previous sections. Figure 8 shows several total cross sections as a function of collision energy. The cross sections σ_n for the formation of F^{**} ($n = 3, 4, 5$) are calculated with the aid of the Landau-Zener-formula. For comparison the cross section for reaching the corresponding curve crossing, i.e., πb_{max}^2 , is given as well. Finally the ionization cross section is shown. It is calculated using the formula given by Miller et al.,¹⁷

$$\sigma_{\text{ion}} = \int_{R_+}^{\infty} dR \, 4\pi R^2 \frac{\Gamma(R)}{\hbar v} \sqrt{1 - \frac{V_*(R)}{E}} \quad . \quad (7.2)$$

For the collision energy of 1 hartree we have calculated the energy distribution of the emitted (or excited) electrons (see Figure 9) using Eq. (2.19). The meaning of this quantity is quite clear for $\epsilon > 0$. It is experimentally accessible by means of electron spectroscopy.² For $\epsilon < 0$ the interpretation is that $\sigma(\epsilon)\Delta\epsilon$ is the sum over cross sections for the formation of Rydberg states F^{**} whose energy lies within the interval $\Delta\epsilon$. The energy distribution $\sigma(\epsilon)$ cannot be measured directly for $\epsilon < 0$, of course. It could be probed, however, by optical spectroscopy, i.e., by observing the light emitted from the decaying F^{**} .

In addition we have computed the values $\sigma_n / (E_{n+1} - E_n)$ for the F^{**} states with $n = 3, 4, 5$ where the σ_n are the Landau-Zener cross sections

shown in Figure 9. The agreement for $n = 4, 5$ is quite acceptable. This fact should not be over-interpreted, however. It simply displays two things: extrapolation of $\Gamma(R)$ from $R > R_+$ to $R < R_+$ yields reasonable results and the Landau-Zener cross section is quite compatible with the quantity $\sigma(\epsilon)\Delta\epsilon$ as computed from Eq. (2.19).

So far we have considered only the ground state of the fluorine ion, $F^+(^3P)$. The first excited state of F^+ is the 1D state whose excitation energy is $2.588 \text{ eV} = 0.095 \text{ a.u.}$ All potential curves that arise from $F^+(^1D)$ have crossing points with the entrance potential $V[\text{He}^+ + F^-]$ which are at much larger distances than the corresponding crossings in Figure 5. Since $\Gamma(R)$ decreases strongly with increasing R , the importance of the final states $\text{He} + F^+(^1D) + e^-(\epsilon)$ is very small compared to the states $\text{He} + F^+(^3P) + e^-(\epsilon)$ as long as one compares them at the same value of ϵ . Thus the electron energy distribution $\sigma(\epsilon)$ is not affected much by the existence of $F^+(^1D)$. If, however, one investigates the region $\epsilon < 0$ by optical spectroscopy, it might well be that the states $F^{**}(2p^4(^1D), np)$ do play an important role. This is because when measuring the light from the F^{**} states the energy of reference for both Rydberg families is the ground state of F rather than the two ionizations limits $F^+(^3P)$ and $F^+(^1D)$. Thus, one cannot compare the relative influence of the two Rydberg series at the same ϵ (as is done in electron spectroscopy) but at ϵ for the $F^+(^3P)$ -core and $\epsilon + 0.095 \text{ a.u.}$ for the $F^+(^1D)$ -core.

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- * Supported by the U.S. Energy Research and Development Administration.
- † Camille and Henry Dreyfus Teacher-Scholar.
- ‡‡ Deutsche Forschungsgemeinschaft, postdoctoral fellow.
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Table I. Comparison of Potential Parameters for Li-F and He(2^3S)-F.

<u>System (A-F)</u>	<u>IP(A)(eV)</u>	<u>Reduced Mass</u>	<u>ω_e (eV)</u>	<u>$V''(r_e)$ (eV/a₀²)</u>	<u>D_0 (eV)</u>	<u>D_e (eV)</u>	<u>r_e (a₀)</u>
Li-F	5.392	4.560	0.1995 ^a	4.40	5.889 ± 0.087 ^a	5.946 ± 0.087	2.956 ^a
He(2^3S)-F	4.768	3.304		4.40 ^b		6.5 ^b	3.0 ^b

a) Reference 18.

b) Estimated values.

Figure Captions

1. Reactive cross sections as a function of collision energy for the reactions given by Eq.(1.3). Cases 1,2,3 are from reference 2, and case 4 is from reference 3.
2. Schematic potential energy curves for the reactions in Eq. (1.3). upper curve is appropriate to reactions (1.3a), (1.3b), and (1.3c) and the lower one to reach (1.3d).
3. Sketch of the potential curve for A^*-B . For $R > R_+$ it is embedded in a continuum of curves of the type $A - B^+, + e^-$, and for $R < R_+$ it crosses the infinite family of curves of the type $A - B^{**}$, B^{**} being a Rydberg state of B.
4. Pictorial description of the matrix element $V_{*,\epsilon}$ of Eq. (4.3) as discussed in Section IV of the text.
5. Semiquantitative potential energy curves for $^2\Sigma$ states of He-F, and for the ground state of He-F $^+$ (reference 13).
6. The energy-dependent overlap factor $2\pi\rho(\epsilon)|\langle\chi_\epsilon|\phi_x\rangle|^2$ as a function of ϵ , the energy of the ionized (or Rydberg) electron.
7. The width function $\Gamma(R)$ (in hartrees) as determined from Eq. (4.7).
8. Total cross sections for the reactions $He^+ + F^- \rightarrow He + F^{**}(n)$, $He + F^+ + e^-$, as a function of collision energy.
9. Energy distribution of the ionized (or excited) electron for the same reactions as for Figure 8. The crosses are the values of $\sigma_n/(E_{n+1}-E_n)$, for $n = 3,4,5$, where σ_n is the Landau-Zener cross section and E_n the Rydberg energy.

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Fig. 1

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Fig. 2

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Fig. 3

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Fig. 4

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Fig. 5

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Fig. 6

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Fig. 7

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Fig. 8

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Fig. 9

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This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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