Theory of Penning Ionization. I. Atoms

WILLIAM H. MILLER

Department of Chemistry, University of California, Berkeley, California 94720
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The theory of Penning ionization (PI) and related associative ionization (AI) is developed and examined in a classical, semiclassical, and quantum mechanical framework, the correspondence between the several descriptions being explicitly deduced; formulas for total cross sections for PI and AI, angular distributions for PI, and the distribution of energies of the ionized electron are presented. The possibility of anomalous structure is seen to appear in the energy distribution of the ejected electrons if the difference between the A*+B and A-B' potential curves has a local extremum as a function of internuclear distance. Classically, this appears as an infinity in the distribution of electron energies, but the quantum mechanical expressions are reduced to obtain a uniformly valid approximation; the transition region through the classical infinity is characterized by an Airy function.

I. INTRODUCTION

If A* denotes an excited electronic state of atom A and B the ground electronic state of another atom (or molecule), then the process

$$A^* + B \rightarrow A^+ + B^+ + e^-$$

(1a)

is known as Penning ionization (PI), and the related process

$$A^* + B \rightarrow (AB)^+ + e^-$$

(1b)

is called associative ionization (AI). Reactions of this type have long been considered by workers dealing with ionized plasmas,3,3 where order-of-magnitude estimates of rate coefficients have been sufficient for these purposes. If A* is metastable (cannot decay by optically allowed spontaneous emission), however, it may live long enough to be studied by molecular beam techniques.4 As these experiments produce more detailed results, greater sophistication will be required to describe the dynamics of the collision process.

Of previous theoretical treatments of PI,5,3,5-9 our point of view is most akin to that of Nakamura,5 although we aim to develop the semiclassical analysis further, to see how AI fits into the theory, and to look in more detail at the relation between the classical, semiclassical, and quantum theories. Section II presents the classical theory and shows how cross sections for PI and AI may be obtained; the distribution in energy of the ionized electron is also obtained within the classical theory. Section III considers refinements of the classical theory whereby certain interference features previously absent are obtained. The exact (within the Born-Oppenheimer approximation) quantum mechanical formulas are presented in Sec. IV and analyzed to see in what level of approximation the classical and semiclassical expressions are recovered.

PI falls into that large class of physical processes which are characterized by a discrete state embedded in a continuum of states to which it is coupled; other processes in this general class are autoionization of atoms and predissociation of diatomic molecules. Dissociative attachment (DA)10-12 of electrons to neutral diatomic molecules [AB+e^-→A+B^-] may be thought of as the inverse reaction of AI with one less electron in the system. PI and AI are simpler, in one sense, than DA because there is no free electron in the initial channel; thus, the electronic aspect of the problem can be more easily eliminated.

II. CLASSICAL THEORY

Figure 1 depicts the Born-Oppenheimer-like potential13,14 \( V_0(R) \) of the A-B system which dissociates to the states A* and B, where A* is an electronically excited state of atom A and B is the ground electronic state of atom B. Also sketched is the potential \( V_+(R) \) of the (AB)^+ system which dissociates to the ground electronic species A and B+. If the excitation energy of A to A* is greater than the ionization potential of B (as indicated in Fig. 1), then the (AB)^+ curve is the lower boundary for a continuum of potential curves of the system (AB)^+ + e^-; to a good approximation this continuum of potentials is \( V_+(R) + \epsilon \), \( \epsilon \) being the continuously variable energy of the ionized electron. For any fixed internuclear distance, therefore, the electronic state corresponding to the A*-B curve is embedded in a continuum of states of the (AB)^+ + e^- type. Consequently, for each internuclear distance \( R \) there is a width \( \Gamma(R) \) (units of energy) associated with \( V_0(R) \) for decay of the discrete electronic state into the continuum electronic state degenerate with it. This autoionization process is an example of the familiar “golden rule.”15 At infinite separation the width vanishes \([\Gamma(R) \to 0 \text{ as } R \to \infty]\) since the coupling between discrete and continuum electronic states vanishes. PI, therefore, is the leakage of the discrete state into the continuum state degenerate with it, complicated by the fact that there is simultaneous relative translational motion of the two nuclei.16 The potentials \( V_0(R), \ V_+(R), \) and the width \( \Gamma(R) \) are obtainable by fairly standard (but not trivial) electronic structure calculations,13,14,17 and we shall assume that they are known (or are to be determined by comparing theory with experiment). It is also assumed that these quantities depend only on \( R = |R| \).
Since the potentials are spherically symmetric, we may consider separately the problem of radial motion for each value of orbital angular momentum ℏl. In terms of $V_o(R)$ and $\Gamma(R)$ we wish to find the probability density $P_l(R)$, defined such that $P_l(R)$ $dR$ is the probability that leakage into the continuum occurs when the internuclear distance is between $R$ and $R + dR$. The function $P_l(R)$ will be different depending on whether the trajectories are approaching each other $[P_{l^{\text{in}}}(R)]$ or separating $[P_{l^{\text{out}}}(R)]$ when the internuclear distance has the value $R$. From the above physical definition it is clear that $P_{l^{\text{in}}}(R)$ must satisfy the integral equation

$$P_{l^{\text{in}}}(R) dR = \left[ 1 - \int_{R}^{\infty} dR' P_{l^{\text{in}}}(R') \right] \frac{\Gamma(R)}{\hbar v_l(R)} dR.$$  (2)

The quantity in brackets is the probability that leakage has not occurred previously in the interval $\infty \rightarrow R$, and has been referred to as a survival factor; it is present because transitions into a continuum are irreversible. The other factor is the rate of leakage $[\Gamma(R)/\hbar]$ at internuclear distance $R$ times the time spent in the interval $(R, R + dR)[dR/v_l(R)]$; $v_l(R)$ is the radial velocity and is given by

$$v_l(R) = \sqrt{\frac{2(E - V_o(R) - (\hbar^2 l^2/2mR^2))}{\mu}},$$  (3)

$\mu$ being the reduced mass of the A-B system; in later sections we shall see that a somewhat more accurate choice for $v_l(R)$ is possible.

Equation (2) can be solved (by converting it into a differential equation) to give

$$P_{l^{\text{in}}}(R) = \frac{\Gamma(R)}{\hbar v_l(R)} \exp \left( - \int_{R}^{\infty} dR' \frac{\Gamma(R')}{\hbar v_l(R')} \right),$$  (4)

the exponential being the survival factor. For future reference we note that

$$\int_{R_0}^{\infty} dR P_{l^{\text{in}}}(R) = 1 - \exp \left( - \int_{R_0}^{\infty} dR \frac{\Gamma(R)}{\hbar v_l(R)} \right),$$  (5)

$R_0$ being the classical turning point $[v_l(R_0) = 0]$; the quantity in Eq. (5) gives the probability of leakage into a continuum state at any point on the inward trajectory $R = \infty$ to $R = R_0$.

For the outward part of the trajectory one may similarly write the following integral equation for $P_{l^{\text{out}}}(R)$:

$$P_{l^{\text{out}}}(R) dR = \left[ 1 - \int_{R_0}^{\infty} dR' P_{l^{\text{in}}}(R') - \int_{R_0}^{R} dR' P_{l^{\text{out}}}(R') \right] \times \frac{\Gamma(R)}{\hbar v_l(R)},$$  (6)

where the quantity in brackets is the probability that leakage has not occurred on the inward path $R = \infty$ to $R = R_0$, nor on the outward path from $R_0$ to $R$. Solution of this equation gives

$$P_{l^{\text{out}}}(R) = \frac{\Gamma(R)}{\hbar v_l(R)} \exp \left( - \int_{R_0}^{\infty} dR' \frac{\Gamma(R')}{\hbar v_l(R')} \right) - \int_{R_0}^{R} dR' \frac{\Gamma(R')}{\hbar v_l(R')},$$  (7)

and we see that

$$\int_{R_0}^{\infty} dR P_{l^{\text{out}}}(R) = \exp \left( - \int_{R_0}^{\infty} dR \frac{\Gamma(R)}{\hbar v_l(R)} \right) \times \left[ 1 - \exp \left( - \int_{R_0}^{\infty} dR \frac{\Gamma(R)}{\hbar v_l(R)} \right) \right].$$  (8)

Equations (4) and (7) are the basic results of this classical analysis.

The probability density $P_l(R)$,

$$P_l(R) = P_{l^{\text{in}}}(R) + P_{l^{\text{out}}}(R),$$  (9)

is the probability density that the transition occurs at $R$ whether on the inward or outward part of the trajectory. The probability of a transition during the entire collision, $P_t$, is given by

$$P_t = \int_{R_0}^{\infty} dR P_l(R),$$

or with Eqs. (5), (8), and (9) this gives

$$P_t = 1 - \exp \left( - 2 \int_{R_0}^{\infty} dR \frac{\Gamma(R)}{\hbar v_l(R)} \right);$$  (10)

the total cross section for these inelastic transitions is

$$\sigma_{t^{\text{inel}}} = (\pi/\hbar^2) \sum \int dP_t,$$  (11)

where $\hbar = (2\mu[E - V_o(\infty)]/\hbar^2)^{1/2}$. Equations (10) and (11) are the results usually obtained.4,6,9

We now ask for the probability distribution $P_t(\epsilon)$ which gives the distribution of energy $\epsilon$ of the ionized electron; i.e., $P_t(\epsilon) d\epsilon$ is the probability that the energy of the ejected electron lies in the interval $(\epsilon, \epsilon + d\epsilon)$. If the transition occurs at internuclear distance $R$, then it is clear that the energy of the ejected electron must be $[V_o(R) - V_+(R)]$ since the transition is to an electronic state degenerate with the initial one; i.e.,

$$\epsilon(R) = V_o(R) - V_+(R).$$  (12)

Therefore, the probabilities $P_t(\epsilon)$ and $P_t(R)$ are related.
by

$$P_1(\epsilon) \, d\epsilon = P_1(R) \, dR,$$

or

$$P_1(\epsilon) = P_1(R)/|\epsilon'(R)|, \quad R = R(\epsilon),$$  (13)

where \(R(\epsilon)\) is the inverse function of \(\epsilon(R)\) defined by Eq. (12). Since

$$\epsilon'(R) = V_0'(R) - V_+(R),$$

Eq. (13) becomes

$$P_1(\epsilon) = P_1(R)/|V_0'(R) - V_+(R)|, \quad R = R(\epsilon),$$  (14)

with \(P_1(R)\) given above by Eqs. (4), (7), and (9). If the function \(\epsilon(R)\) is not monotonic, then there may be several values of \(R\), \{\(R_i(\epsilon)\)\} say, which satisfy the equation

$$\epsilon = V_0(R) - V_+(R),$$  (12')

to within the accuracy of \(R\) at which the transition produces electrons at energy \(\epsilon\). In this case Eq. (14) becomes

$$P_1(\epsilon) = \sum_i P_1(R)/|V_0'(R) - V_+(R)|, \quad R = R_i(\epsilon).$$  (14')

At this point an interesting effect becomes apparent: If \(\epsilon(R)\) is not monotonic, then there must be some value of \(R\), \(R_\ast\) say, at which \(\epsilon'(R) = V_0'(R) - V_+(R) = 0\); i.e., \(\epsilon_\ast = \epsilon(R_\ast)\) is a local extremum of \(\epsilon(R)\). Figure 2(a) illustrates this situation, where \(\epsilon_\ast\) is the minimum of \(\epsilon(R)\); the case that \(\epsilon_\ast\) is a local maximum of \(\epsilon(R)\) is similar. For \(\epsilon > \epsilon_\ast\) there are two terms in Eq. (14'), but for \(\epsilon < \epsilon_\ast\) there is no root to Eq. (12'); moreover, \(P_1(\epsilon) \to \infty\) as \(\epsilon \to \epsilon_\ast\) from above. This behavior is illustrated in Fig. 2(b). Since the equations which determine \(\epsilon_\ast\) do not involve \(l\), this "edge effect" is not washed out in the over-all distribution \(P(\epsilon)\), which is obtained by summing (or integrating) over partial waves:

$$P(\epsilon) = \sum_l (2l+1) P_l(\epsilon).$$  (15)

Likewise, the Jacobian factor \(|dR/d\epsilon|\), which is responsible for the anomalous structure in \(P(\epsilon)\), does not depend on the initial collision energy, so that thermal averaging should not obscure this effect. It is clear, of course, that the present classical treatment breaks down for this situation, but we expect the more exact treatments to give a peak in the distribution near \(\epsilon_\ast\) provided that there is a classically accessible value \(R_\ast\) at which \(V_0'(R_\ast) = V_+(R_\ast)\).

Another anomaly which appears in \(P_1(\epsilon)\) within the classical treatment arises when the value \(R(\epsilon)\) is close to the classical turning point \(R_0\). Referring to Eq. (14), say, \(P_1(\epsilon)\) is zero if \(R(\epsilon) < R_0\) [because \(\epsilon(R)\) is not classically accessible] but finite if \(R(\epsilon) > R_0\); moreover, \(P_1(\epsilon) \to \infty\) as \(\epsilon \to R_0\) from above. This infinity arises solely because the classical velocity \(v_1(R_0) = 0\) at the turning point and will disappear with a more accurate choice for \(v_1(R)\) (see Sec. IV); nevertheless, one expects a peak in \(P_1(\epsilon)\). Since the position of the peak depends on \(l\) and \(E\), however, it may be that it will be obscured in the sum over \(l\) and any averaging over \(E\).

We now turn to the question of associative ionization (AI). This can arise only if the potential \(V_+(R)\) possesses a well deep enough to support bound vibrational states, as sketched in Fig. 3(a). Since \(\epsilon\) is the energy carried away by the ionized electron, the final relative translational energy in the potential \(V_+\) is \(E - \epsilon\). If \(E - \epsilon < 0\), therefore, the final relative motion in the \(V_+\) potential must be that of a bound state of \((AB)^+\); this is AI.

There is one complicating feature yet unmentioned, however, and this is due to the fact that the relevant potentials for radial motion are actually \(V_0(R)\) and \(V_+(R)\) plus the centrifugal term \(\hbar^2/2lR^2\), as sketched in Fig. 3(b). [Note that this has no effect on the discussion leading to \(P(\epsilon)\) above since the difference of potentials was involved.] A transition at the value of \(R\) indicated in Fig. 3(b) leads to a final relative translational energy which is, classically, a bound vibrational-rotational state of \((AB)^+\), but quantum mechanically it is a metastable state and will dissociate to \(A+B^+\) with
a characteristic lifetime. Does one call this PI or AI? The answer to this question clearly depends on experimental conditions, namely how soon after the collision the species are detected. Since we are now using classical notions, we shall treat this case as a true bound state, i.e., that tunneling through the barrier is slower than the time scale of the detection process. Thus we say of a transition occurring at internuclear distance $R$: It is AI if $E - \epsilon(R) < \max V_+^t$ and $R < R_{\max}^t$ ($R_{\max}^t$ being the position of $\max V_+^t$), and it is PI otherwise. The probabilities of PI and AI, therefore, are given by

$$P_{P1} = \int_{R_0}^{\infty} dR P_1(R) \left[ 1 - h(R_{\max}^t - R) h[\max V_+^t - E + V_0(R) - V_+(R)] \right],$$  \hspace{1cm} (16a)

$$P_{A1} = \int_{R_{\max}^t}^{R_0} dR P_1(R) \times h[\max V_+^t - E + V_0(R) - V_+(R)],$$  \hspace{1cm} (16b)

where $P_1(R)$ is as above, and $h(x)$ is the usual step function:

$$h(x) = \begin{cases} 1, & x > 0 \\ 0, & x < 0. \end{cases}$$

The total transition probability $P_t$ of Eq. (10) is the sum of $P_{P1}$ and $P_{A1}$; cross sections for PI and AI are obtained by summing over partial waves:

$$\sigma_{P1} = (\pi/\hbar^2) \sum_i (2l+1) P_{P1},$$  \hspace{1cm} (17a)

$$\sigma_{A1} = (\pi/\hbar^2) \sum_i (2l+1) P_{A1}.$$  \hspace{1cm} (17b)

Finally, in this section, we wish to consider the probability of AI into a particular vibrational–rotational state of $(AB)^+$; this probability we call $P_{n,I}$, $(n,I)$ being the quantum numbers of the state. It is clear that

$$P_{A1} = \sum_n P_{n,I},$$

and under classical conditions the sum over $n$ is actually an integral. Since loss of energy $\epsilon$ to the ionized electron corresponds to final translational energy $E - \epsilon$, the probability $P_t(\epsilon)$ of Eqs. (13)–(14) and $P_{n,I}$ must be related by

$$P_{n,I} = \frac{E - \epsilon}{W_{n,I}} P_t(\epsilon),$$  \hspace{1cm} (18)

with $E - \epsilon = W_{n,I}$. Using the WKB eigenvalue relation

$$(n + \frac{1}{2}) \pi = \int dR \left[ (2\mu/\hbar^2) [W_{n,I} - V_+(R)] \right]^{1/2},$$

one finds that the Jacobian factor in Eq. (18) is

$$\left| \frac{\partial W_{n,I}}{\partial \epsilon} \right| = \frac{\pi \hbar^2}{\mu} \int dR \left( \frac{2\mu}{\hbar^2} [W_{n,I} - V_+(R)] \right)^{-1/2}.$$

Using Eq. (14'), $P_{n,I}$ may be expressed as

$$P_{n,I} = \left| \frac{\partial W_{n,I}}{\partial \epsilon} \right| \left| \sum_i P_i(R) / V_0(R) - V_+(R) \right|_{R = R_i(n,I)},$$

where $R_i(n,I)$ are all of the classically accessible values of $R$ satisfying

$$E - W_{n,I} = V_0(R) - V_+(R).$$  \hspace{1cm} (20)

If there is no classically accessible value of $R$ which satisfies Eq. (20), then there is no possibility of forming the state $(n,I)$ by AI in this classical treatment.

**III. SEMICLASSICAL THEORY**

In the previous section we have manipulated probabilities for various processes, whereas quantum mechanics requires that one manipulate the corresponding probability amplitudes, the square modulus of which yields the probability. For systems pertaining to the motion of heavy particles, it is usually possible to proceed semiclassically, by which one means that essentially classical quantities are used but combined according to the principle of superposition of probability amplitudes.

In constructing the probability amplitude, or $S$-matrix element, for a process, one requires a phase as well as a probability—the $S$ matrix having the form

$$S_{f\rightarrow i} = [P_{f\rightarrow i}]^{1/2} \exp(i\phi_{f\rightarrow i}),$$  \hspace{1cm} (21)

where $\phi_{f\rightarrow i}$ is the phase, or phase shift, associated with the $i\rightarrow f$ transition.

It is now necessary to treat transitions on the incoming and outgoing part of the trajectory separately since the phases associated with these two processes are different. If the transition occurs at internuclear distance $R$ on the inward part of the trajectory, then the associated phase is

$$\phi_{i\rightarrow f}(R) = \frac{3}{2} \pi(I' + \frac{1}{2}) + \left[ \int_R^R dR' k_{i,0}(R') - k_0 R \right]$$

$$+ \left[ \int_R^R dR' k_{i,s}(R') \right]^{1/2} + \frac{3}{2} \pi(I' + \frac{1}{2})$$

$$+ \left[ \int_R^R dR' k_{i,s}(R') - k s R \right],$$  \hspace{1cm} (22)

where $\hat{R} \rightarrow \infty$, and

$$k_{i,0}(R) = [2\mu(E - V_0(R')]^{1/2},$$

$$k_{i,s}(R) = [2\mu(E - V_+(R')]}^{1/2},$$

$$k_0 = k_{i,0}(\infty),$$

$$k_s = k_{i,s}(\infty),$$

$$\epsilon = \epsilon(R) = V_0(R) - V_+(R),$$

$$\epsilon = \epsilon(R) = V_0(R) - V_+(R).$$
and the undesignated lower limits in Eq. (22) are the zeros of the integrand (the classical turning points). It should be clear to the reader how the three successive terms in brackets in Eq. (22) are the phases associated with radial motion inward from \( R \) to \( R_0 \) outward from \( R \) to the turning point on \( V_0 \), and outward from the turning point to \( \infty \) on \( V_+ \), respectively. Similarly, the phase associated with a transition at internuclear distance \( R \) on the outward part of the trajectory is

\[
\phi^{\text{out}}(R) = \frac{1}{2} \pi (l + \frac{1}{2}) + \left[ \int_R^\infty dR' k_{1,0}(R') - k_0 R \right] \\
+ \frac{1}{2} \pi (l + \frac{1}{2}) + \left[ \int_R^\infty dR' k_{1,0}(R') \right] \\
+ \left[ \int_R^\infty dR' k_{1,0}(R') - k_0 R \right],
\]

(23)

where \( R \to \infty \), and the three terms in brackets have the obvious physical interpretation.

Having seen how to construct the phases of the \( S \) matrix, let us first obtain the \( S \) matrix for PI to the final state in which the ionized electron has energy \( \epsilon \). Equation (14') gives the probability, but it is composed of several terms which all have different phases associated with them. The superposition principle of probability amplitudes yields

\[
S_{\epsilon \cdot 0'} = \sum_l \left\{ |P_{l}^{\text{in}}(R)| / |V_0'(R) - V_+'(R)| \right\}^{1/2} \\
\times \exp \left[ i \phi_{l}^{\text{in}}(R) \right] + \left\{ |P_{l}^{\text{out}}(R)| / |V_0'(R) - V_+'(R)| \right\}^{1/2} \\
\times \exp \left[ i \phi_{l}^{\text{out}}(R) \right] \quad |R = R_i(\epsilon)|,
\]

(24)

\{ \( R_i(\epsilon) \), \( P_{l}^{\text{in}}(R) \), and \( P_{l}^{\text{out}}(R) \} \) all being the same quantities as in Sec. II. From this \( S \) matrix the differential and total cross sections for this PI process can be constructed:

\[
f_{\epsilon \cdot 0}(\theta) = (2i\hbar)^{-1} \sum_l (2l + 1) S_{\epsilon \cdot 0'} P_l(\cos \theta),
\]

(25a)

\[
\sigma_{\epsilon \cdot 0}(\theta) = |f_{\epsilon \cdot 0}(\theta)|^2;
\]

(25b)

\[
\sigma_{\epsilon \cdot 0} = 2\pi \int_0^\pi d\theta \sin \theta \sigma_{\epsilon \cdot 0}(\theta) = (\pi / \hbar v_i) \sum_l (2l + 1) S_{\epsilon \cdot 0'}^2;
\]

(26)

\( \sigma_{\epsilon \cdot 0}(\theta) \) is the angular distribution of \( A \) and \( B^+ \) in their center-of-mass coordinate system. The "refined" transition probability \( |S_{\epsilon \cdot 0'}|^2 \) differs from the classical result, Eq. (14'), by interference terms only. One sees that there is interference between transitions on the inward and outward part of the trajectory at the same value of \( R \), as well as between the terms associated with different \( R_i(\epsilon) \) terms.

In a similar manner one can synthesize the \( S \) matrix for AI into a particular vibrational-rotational state of \( \text{AB}^+ \). In terms of \( S_{\epsilon \cdot 0'} \), Eq. (24'), one finds that

\[
S_{\epsilon \cdot 0'} = \left( \int d\theta' \Gamma'(R') / \hbar v_i(R') \right) / |V_0'(R) - V_+'(R)| \\
\times \left[ \frac{2\pi}{(\partial / \partial \theta')(\phi_{l}^{\text{in}}(R') - \phi_{l}^{\text{out}}(R'))} \right]^{1/2} \\
\times \cos \left[ \frac{1}{2} \pi + \phi_{l}^{\text{in}}(R) - \phi_{l}^{\text{out}}(R) \right].
\]

(27)

where \( \epsilon = E - W_{n,1} \) is the \( S \) matrix for AI into state \( (n, l) \), \( W_{n,1} \) being the eigenvalue.

Let us first consider the effect of interference terms on the transition probability \( |S_{\epsilon \cdot 0'}|^2 \) as would appear in the cross section of Eq. (26). For simplicity we assume that there is only one value of \( R \) which satisfies the resonance condition Eq. (12'), so that the only interference is that between the incoming and outgoing terms in Eq. (24):

\[
|S_{\epsilon \cdot 0'}|^2 = \left[ |P_{l}^{\text{in}}(R)| + |P_{l}^{\text{out}}(R)| \right] / |V_0'(R) - V_+'(R)| \\
\times \left[ 2 \left[ |P_{l}^{\text{in}}(R)| |P_{l}^{\text{out}}(R)| \right]^{1/2} / |V_0'(R) - V_+'(R)| \right] \\
\times \cos \left[ \phi_{l}^{\text{in}}(R) - \phi_{l}^{\text{out}}(R) \right],
\]

(28)

where \( R = R_i(\epsilon) \). The first term is the classical result, and from Eqs. (4) and (7) it is easy to see that the amplitude of the interference term is

\[
\left[ |P_{l}^{\text{in}}(R)| |P_{l}^{\text{out}}(R)| \right]^{1/2} = \frac{\Gamma(R_i)}{\hbar v_i(R)} \\
\times \left[ - \int dR' \frac{\Gamma(R')}{\hbar v_i(R')} \right],
\]

(29)

and the phase difference

\[
\phi_{l}^{\text{in}}(R) - \phi_{l}^{\text{out}}(R) = 2 \left( \int dR' k_{1,0}(R') - \int dR' k_{1,0}(R') \right).
\]

(30)

Since the cross section \( \sigma_{\epsilon \cdot 0} \) is an integral over \( l \), the oscillatory interference term in Eq. (28) will tend to average to zero, only giving a significant contribution if there is some value of \( l \) for which

\[
(\partial / \partial l) \phi_{l}^{\text{in}}(R) = (\partial / \partial l) \phi_{l}^{\text{out}}(R),
\]

(31)

i.e., a point of stationary phase. If there is such a value of \( l_0(R) \) say, then the cross section of Eq. (26) is

\[
\sigma_{\epsilon \cdot 0} = \sigma_{\epsilon \cdot 0 \parallel} + \Delta \sigma_{\epsilon \cdot 0},
\]

(32)

where \( \sigma_{\epsilon \cdot 0 \parallel} \) is the classical value, and the nonclassical contribution is

\[
\Delta \sigma_{\epsilon \cdot 0} = \left[ \frac{\Gamma(R_i)}{\hbar v_i(R)} \right] \left[ \int dR' \frac{\Gamma(R')}{\hbar v_i(R')} \right] / |V_0'(R) - V_+'(R)| \\
\times \left[ \frac{2\pi}{(\partial / \partial \theta')(\phi_{l}^{\text{in}}(R') - \phi_{l}^{\text{out}}(R'))} \right]^{1/2} \\
\times \cos \left[ \frac{1}{2} \pi + \phi_{l}^{\text{in}}(R) - \phi_{l}^{\text{out}}(R) \right].
\]

(33)
with $R = R(e)$, $l = l_0[R(e)]$; the frequency of the oscillations in $\Delta \phi_{\epsilon,\epsilon_0}$ with varying $\epsilon$ is

$$\frac{\partial}{\partial \epsilon} \left[ \phi_{\epsilon_0}^{\text{in}}(R) - \phi_{\epsilon_0}^{\text{out}}(R) \right] = \frac{\mu}{\hbar^2} \int dR' \left[ \epsilon_{\epsilon_0,l_0}(R') \right]^{-1},$$

with $l = l_0(R)$, $R = R(e)$.

With regard to the differential cross section, Eqs. (25), one can proceed in the usual semiclassical fashion; Equation (24) is substituted into Eq. (25a), and the integral over $l$ is evaluated by stationary phase for each term in Eq. (24), yielding

$$f_{\epsilon_0}(\theta) = \sum_i f_{\epsilon_0}^{\text{in}}(\theta_i) + f_{\epsilon_0}^{\text{out}}(\theta),$$

(34)

$$f_{\epsilon_0}(\theta) = \left( \frac{P_{\epsilon_0}^{\text{in}}(R)}{|V'_{\epsilon_0} - V'_+|} \right)^{1/2} \left| \frac{l + \frac{1}{2}}{P_{\epsilon_0}^{\text{out}}(R)} \right|^{1/2} \frac{\exp i \left[ \phi_{\epsilon_0}^{\text{in}}(R) - (l + \frac{1}{2}) \theta \right]}{i \hbar} \biggr|_{l = l_{\text{in}}}

\left[ \frac{l + \frac{1}{2}}{P_{\epsilon_0}^{\text{out}}(R)} \right]^{1/2} \frac{\exp i \left[ \phi_{\epsilon_0}^{\text{out}}(R) - (l + \frac{1}{2}) \theta \right]}{i \hbar} \biggr|_{l = l_{\text{out}}},$$

(35)

where $l_{\text{in}}(\theta)$ and $l_{\text{out}}(\theta)$ are defined by

$$\theta = \left( \frac{\partial}{\partial \epsilon} \phi_{\epsilon_0}^{\text{in}} \right) l_{\text{in}}(\theta),$$

$$\theta = \left( \frac{\partial}{\partial \epsilon} \phi_{\epsilon_0}^{\text{out}} \right) l_{\text{out}}(\theta),$$

and $R = R(e)$. The interference term resulting from $f_{\epsilon_0}(\theta)$ has the relative phase

$$\phi_{\epsilon_0}^{\text{in}} - \phi_{\epsilon_0}^{\text{out}} = (l_{\text{in}} - l_{\text{out}}) \theta,$$

and the frequency of the interference can be shown to be $|l_{\text{in}}(\theta) - l_{\text{out}}(\theta)|$; this relation can be used to obtain information about the potentials $V_0$ and $V_+$. From the experimentally observed interferences, it may be noted that the condition for a stationary phase in the integral over $l$ to obtain $\sigma_{\epsilon_0}$ [Eq. (31)] is equivalent to the relation $l_{\text{in}}(\theta) = l_{\text{out}}(\theta)$; i.e., if the frequency of an interference term in $\sigma_{\epsilon_0}(\theta)$ goes to zero at some finite angle, then there is a nonclassical contribution to $\sigma_{\epsilon_0}(\theta)$ [given by Eq. (33)] associated with this angle and impact parameter. Similar interference features will result if there are other terms present in Eq. (34).

IV. QUANTUM MECHANICAL THEORY

Here we examine the exact (within the Born–Oppenheimer approximation) quantum mechanical expressions for the $S$ matrix elements to see in what degree of approximation the semiclassical results of the previous section are recovered. This will also provide the correct expressions from which it may be possible to derive “extended semiclassical” results which have a wider range of validity.

The quantum mechanical formulas are obtained by applying Feshbach’s formalism to the electronic problem and then the Born–Oppenheimer approximation to the relative motion of the nuclei. The derivation closely parallels that of O’Malley’s for DA, and one can extract the correct expressions from this work. The appropriate $S$ matrix elements are

$$S_{\epsilon_0} = -2i(2\mu / \hbar^2) \exp (i\eta_{1,0} + i\eta_{1,1}) \langle u_{1,0} | V_0, \epsilon_0 | u_{1,1} \rangle,$$

(36)

where $u_{1,\epsilon}(R)$ is the radial wavefunction of the potential $V_+(R)$ (at energy $E - \epsilon$) with asymptotic form

$$u_{1,\epsilon}(R) \sim \sin \left[ k_0 R - \frac{1}{2} (\pi l + \eta_{1,\epsilon}) \right] / k_0^{1/2};$$

$u_{1,0}(R)$ is the radial wavefunction of the potential $V_0(R) - \frac{1}{2} \Gamma(R)$ [at energy $E - V_0(\infty)$] with asymptotic form

$$u_{1,0}(R) \sim \sin \left[ k_0 R - \frac{1}{2} (\pi l + \eta_{1,0}) \right] / k_0^{1/2}.$$ (Note that $\eta_{1,0}$ is complex.) The function $V_{\epsilon_0}(R)$ is the coupling between the two electronic states at internuclear distance $R$:

$$V_{\epsilon_0}(R) = \int dr \chi_{0}(r; R)(H - E) \chi_{\epsilon}(r; R),$$

where $r$ denotes all electronic coordinates, $\chi_{0}(r; R)$ is the discrete electronic state which dissociates to $A^* + B$, and $\chi_{\epsilon}(r; R)$ is the continuum electronic state (normalized to unity on the energy scale) which dissociates to $A + B^* + e^-(\epsilon)$. The width $\Gamma(R)$, discussed throughout this paper, is given in terms of $V_{\epsilon_0}(R)$ by

$$\Gamma(R) = 2\pi | V_{\epsilon_0}(R) |^2,$$

with $\epsilon = V_0(R) - V_+(R)$. The $S$ matrix for AI into the $(\nu, l)$ vibrational–rotational state of $(AB)^+$ is given by a similar expression

$$S_{\nu, l} = -2i(2\mu / \hbar^2)^{1/2} \exp (i\eta_{1,0}) \langle u_{1,0} | V_{\epsilon_0}, \epsilon_0 | u_{\nu, l} \rangle,$$

(37)

where $\epsilon = E - W_{\nu, l}$ and $u_{\nu, l}(R)$ is the eigenfunction of
$V_+(R)$ with eigenvalue $W_{n,1}$ normalized to unity:

$$dR \left| u_{n,1}(R) \right|^2 = 1.$$ 

To see how the semiclassical expressions of Sec. III can be obtained, the WKB approximation is employed for the radial functions and phase shifts in Eq. (36), and the matrix element of $V_{0,e}(R)$ is evaluated by stationary phase. Thus,

$$u_{l,0}(R) = \sin \left( \frac{\pi}{4} + \int_0^R dR' k_{l,0}(R') \right) / \kappa_{l,0}(R)^{1/2},$$

$$I = \langle u_{l,0} | V_{0,e} | u_{l,e} \rangle$$

$$\simeq \int dR \left[ V_{0,e}(R) \cos \left( \int_0^R dR' k_{l,0}(R') - \int_0^R dR' k_{l,e}(R') \right) - \frac{\kappa_{l,0}(R) \kappa_{l,e}(R)}{2} \right],$$

where we have used the relation

$$\sin x \sin y = \frac{1}{4} [\cos(x-y) + \cos(x+y)]$$

discarded the second term. This integral over $R$ is to be evaluated by stationary phase; thus, the principal contribution to the integral comes from the region about $R(e)$, which satisfies the equation

$$\frac{d}{dR} \left( \int_0^R dR' k_{l,0}(R') - \int_0^R dR' k_{l,e}(R') \right) = 0,$$

or

$$\epsilon = V_0(R) - V_+(R).$$

This is exactly the relation between $\epsilon$ and $R$ used earlier in Secs. II and III. Classically, transitions to the final state with electron energy $\epsilon$ must take place at an internuclear distance $R$ which satisfies Eq. (12'); quantum mechanically, all values of $R$ contribute to the $0 \to \epsilon$ transition—but the stationary phase relation says that the dominant contribution comes from the region of $R$ about the classical value.

The remaining details of the stationary phase integration are fairly standard, and one obtains the following result:

$$I = \frac{V_{0,e}(R)}{2\kappa} \left( \frac{2\pi \hbar^2 / \mu}{\left[ V_0'(R) - V_{0,e}'(R) \right]} \right)^{1/2} \cos \left( \frac{\pi}{4} + \tau \right) \tau,$$

where $R = R(e)$, and $\kappa = \kappa_{l,0}(R) = \kappa_{l,e}(R)$,

$$\tau = i \int_0^R dR' \frac{\Gamma(R')}{\hbar v_i(R')} + \int_0^R dR' k_{l,0}(R')$$

$$- \int_0^R dR' k_{l,e}(R').$$

Using this approximation for the integral $I$ in Eq. (36) gives the semiclassical expression for $S_{ee'}$ in Eq. (24)

where $R \to \infty$, the lower limit of the integrals is the zero of the integrand, and

$$\kappa_{l,0}(R) = \left( 2\mu \left[ E - V_0'(R) + \frac{1}{2} \Gamma(R) \right] / \hbar^2 \right)^{1/2}.$$ (38)

If $\Gamma(R)$ is not too large,

$$\kappa_{l,0}(R) = k_{l,0}(R) + \left[ i \Gamma(R) / 2\hbar v_i(R) \right],$$ (39)

where $k_{l,0}(R)$ and $v_i(R)$ are as in previous sections. The other radial function and phase shift are given by similar expressions.

The principal task is to evaluate the matrix element of $V_{0,e}$ in Eq. (36). With the above WKB radial functions this becomes

(except for a constant phase); the two terms in the cosine (positive and negative exponentials) correspond to the incoming and outgoing terms in Eq. (24).

If there are two points of stationary phase in the $R$ integral [i.e., two roots of Eq. (12')], then one obtains

$$I = I_1 + I_2,$$ (42)

where $I_i$ is just as in Eq. (41), with $R = R_i(e)$. Equation (42) is valid, however, only if $| R_1(e) - R_2(e) |$ is not too small; otherwise the two points of stationary phase interfere with one another and cannot be treated independently. $| R_1(e) - R_3(e) | > 0$, however, corresponds to $e \to \epsilon_*$ and is just the “edge effect” discussed in Sec. II. By using techniques designed to handle two possibly coalescing points of stationary phase, one may obtain an expression for the integral $I$ which is valid uniformly for all values of $| R_1(e) - R_3(e) |$. Proceeding along the lines of Ref. 25, one finds the integral to be given by Eq. (42), but where

$$I_i = \frac{V_{0,e}(R)}{2\kappa} \left( \frac{2\pi \hbar^2 / \mu}{\left[ V_0'(R) - V_{0,e}'(R) \right]} \right)^{1/2}$$

$$\times \left[ \exp \left[ -i \tau - i \phi + \frac{1}{2} (i \pi) \right] \right] \left[ \sin \phi \right] \left( \frac{\mu}{\pi} \right)^{1/2} H_{1/2}^{(1)}(\phi)$$

$$+ \exp \left[ +i \tau + i \phi - \frac{1}{2} (i \pi) \right] \left[ \sin \phi \right] \left( \frac{\mu}{\pi} \right)^{1/2} H_{1/2}^{(1)}(\phi),$$ (43)

with

$$\phi = \phi_i$$

$$= \left( \mu / 3 \hbar^2 \kappa \right) \left[ V_0'(R) - V_{0,e}'(R) \right] / \left[ V_0''(R) - V_{0,e}''(R) \right],$$ (44)

and $R = R_i(e)$ in Eqs. (43) and (44); the Bessel functions $H_{1/2}^{(1)}$ and $H_{1/2}^{(2)}$ are closely related to Airy functions. For large $\phi$ it is easy to see (by using the asymptotic form for the Bessel functions) that the
expression in curly brackets in Eq. (43) reduces to \( \cos(\Delta \pi + \tau) \) and therefore, Eq. (41) is recovered for \( I_1 \). Since the first (second) term in Eq. (43) corresponds to the incoming (outgoing) term in Eq. (24), one may think of the uniform expression in Eq. (43) as providing a correction factor of the form

\[
2 \exp(\pm i\pi/6) \left( \frac{1}{2} \pi \phi \right)^{1/2} \Pi_{1/0}^{1/2}(\phi)
\]

to each term in Eq. (24).

For \( \epsilon \) near the minimum value \( \epsilon_\ast \) [the procedure is analogous if \( \epsilon_\ast \) is a relative maximum of \( \epsilon(R) \)] one has

\[
\phi_1 = \left( \mu / \hbar k \right)^2 \left[ \left( \frac{(1/\sqrt{2})}{\sqrt{2}} \right) \frac{1}{\sqrt{2}} / \left( V_0''(R_\ast) - V_\ast''(R_\ast) \right) \right]^{1/2},
\]

\[
\phi_2 = -\phi_1,
\]

so that the two terms of Eq. (42), each given by Eq. (43), combine to give

\[
I = \left[ V_{0,\ast}(R_\ast) / 2k_\ast \right] \left( 2\hbar^2 k_\ast / \mu \right)^{1/6}
\times 2\pi \cos \theta \sin \theta \sin(\pi - \epsilon) / \sqrt{a},
\]

where

\[
a = \left[ \left( V_0''(R_\ast) - V_\ast''(R_\ast) \right) \hbar^2 k_\ast / \mu \right]^{2},
\]

and the asterisked quantities are evaluated at \( R_\ast \), the root of \( V_0'(R) = V_\ast'(R) \).

Equation (45), when inserted into Eq. (36), correctly describes the “edge effect” observed earlier, the transition region between \( \epsilon < \epsilon_\ast \) and \( \epsilon > \epsilon_\ast \) being characterized by the Airy function. This behavior is very reminiscent of the rainbow in the angular distribution for potential scattering,\(^{30,31}\) where the transition from the dark to bright side of the rainbow angle is characterized by the Airy function. In the oscillatory region \( \epsilon < \epsilon_\ast \) the oscillations will be rapidly damped because the probability factors associated with \( I_1 \) and \( I_2 \) are different. Also one should note the higher frequency oscillations arising from the \( \cos \theta \ast \) factor in Eq. (45), or more generally, the \( \exp(\pm i\tau) \) factors in Eq. (43); these interferences come from the incoming–outgoing phase difference.

With regard to \( A_1 \), it is easy to see that Eq. (37) also reduces to the semiclassical expression of Sec. III by noting that the normalized WKB bound-state wavefunction is

\[
u_{n,1}(R) = N_{n,1} \sin \left( \frac{1}{2} \pi R' h_{n,1}(R) \right) / h_{n,1}(R)^{1/2},
\]

with

\[
N_{n,1} = (2\mu / \pi \hbar^2) \left| \partial W_{n,1} / \partial n \right|.
\]

All of the discussion in the preceding paragraphs concerning the evaluation of the integral \( I \) also applied to \( A_1 \).

There are other refinements that are possible, the most obvious of which is not to make the small \( \Gamma \) approximation of Eq. (39). The exact expression for \( \tilde{C}_{1,0}(R) \) can still be written as in Eq. (39):

\[
\tilde{C}_{1,0}(R) = \tilde{C}_{1,0}(R) + i \mu / 2\hbar k_{1,0}(R) \Gamma(R),
\]

but here

\[
k_{1,0}(R) \rightarrow \left( \frac{1}{2} k_{1,0}(R)^2 + \frac{1}{2} k_{1,0}(R)^4 + \frac{\mu \Gamma(R)}{\hbar^2 \mu} \right)^{1/2},
\]

i.e., \( k_{1,0}(R) \) and \( \Gamma(R) = \hbar k_{1,0}(R) / \mu \) now depend on \( \Gamma(R) \) as well as \( V_0(R) \). This has most effect near the classical turning point, which is to be expected since here the motion is least classical. Nevertheless, it will still be true that \( \Gamma(R) \hbar k_{1,0}(R) \) is peaked near the classical turning point (though never infinite), as was discussed in Sec. II. Aside from a possible value \( R_\ast \) (the “edge effect”), therefore, the most probable internuclear distance at which transitions occur is near the classical turning point. In terms of the quantum expression, Eq. (36), this is a statement of the familiar Franck–Condon principal.

V. CONCLUDING REMARKS

Given the potentials \( V_0(R) \) and \( V_\ast(R) \) and the width \( \Gamma(R) \), the classical and semiclassical expressions of Secs. II and III, respectively, can be evaluated, even if the more accurate expression for the velocity \[ \text{Eq. (47)} \] is used. The quantum mechanical expression in Eq. (36), however, cannot be evaluated from these quantities alone, because of the coupling function \( V_{0,\ast}(R) \). One needs \( V_{0,\ast}(R) \) for all \( \epsilon \) and all \( R \) in Eq. (36), whereas \( \Gamma(R) \) determines \( V_{0,\ast}(R) \) only for \( \epsilon = V_0(R) - V_\ast(R) \). Evaluation of the matrix element of \( V_{0,\ast} \) by stationary phase, however, only requires \( V_{0,\ast}(R) \) to be known at values of \( R \) which satisfy the above relation, and therefore only \( \Gamma(R) \) is needed. Even the uniformly valid expression for the matrix element, Eqs. (42)–(44), involves only \( \Gamma(R) \), although the second derivatives of \( V_0 \) and \( V_\ast \) are required. It would be extremely important to explore the question more fully, perhaps by numerical examples, of under what conditions the matrix element of \( V_{0,\ast} \) can be accurately evaluated by any method which involves only \( V_0, V_\ast, \) and \( \Gamma \).

There is also a need for accurate ab initio electronic calculations of \( V_0, V_\ast, \) and \( \Gamma \). From the analysis presented in this paper, it is clear that many of the salient features of PI and AI are apparent by a casual inspection of these quantities, and it is expected that quantitative cross sections are available by relatively simple calculations involving only these quantities. From \( V_0 \) and \( V_\ast \) one can easily see if the “edge effect” is possible, and also the position of the “edge” (\( \epsilon_\ast \)).

Finally, more detailed experimental measurements of collision phenomena involving electronically excited species are necessary, not only to test our theoretical understanding of the processes, but to infer information about the basic potentials and lifetimes involved.
APPENDIX: WEAK TRANSITIONS AND THE ISOTYPE EFFECT

Equations (10) and (11) give the total ionization cross section as

$$\sigma_{\text{tot}} = \frac{\pi}{k_0^2} \int_0^\infty d\Omega (2l+1) \left[ 1 - \exp[-2\xi(l)] \right], \quad (A1)$$

where

$$\xi(l) = \int_0^l d\Omega \frac{\Gamma(R)}{h \omega_1(R)}. \quad (A2)$$

Since one expects $\Gamma(R)$ to be decreasing with $R$, the quantity $\xi(l)$ should be a decreasing function of $l$. If

$$2\xi(l) < 1 \quad (A3)$$

for all $l$, we refer to the ionization as a “weak transition.”

For a weak transition, therefore,

$$1 - \exp[-2\xi(l)] \sim 2\xi(l),$$

so that Eq. (A1) becomes

$$\sigma_{\text{tot}} = \frac{\pi}{k_0^2} \int_0^\infty d\Omega (2l+1) 2\xi(l). \quad (A4)$$

Substituting Eq. (A2) into (A4), one can interchange the order of integration and evaluate the integral over $l$, obtaining

$$\sigma_{\text{tot}} = 2\pi \left( \frac{2\mu}{\hbar^2 E_0} \right)^{1/2} \int_0^\infty dR \left[ \Gamma(R) \left( 1 - \frac{V_0(R)}{E_0} \right)^{1/2} \right] \Gamma(R). \quad (A5)$$

One important feature of Eq. (A5) is that

$$\sigma_{\text{tot}} = \mu^{1/2} \times \text{function} \left( E_0 \right),$$

so that the isotope effect\textsuperscript{28} for a weak transition is immediately obvious:

$$\sigma(\mu_2) / \sigma(\mu_1) = (\mu_2 / \mu_1)^{1/2}, \quad (A6)$$

$\mu$ being the reduced mass of the collision partners. Equation (A6) seems to fit the data of Penton and Muschlis\textsuperscript{29} on He$^+ +$H$_2$, D$_2$, DH within experimental error. Hotop and Niehaus\textsuperscript{30} have obtained this same mass dependence in a model they have proposed for PI. Here we see that Eq. (A6) is independent of any dynamical considerations other than the requirement that the transition be weak.

If the transition is not weak, then there will be some value of $l$, $L$ say, at which

$$2\xi(L) = 1. \quad (A7)$$

In the spirit of the Massey–Mohr approximation for elastic scattering\textsuperscript{31} we take

$$1 - \exp[-2\xi(l)] = \begin{cases} 1 & \text{if } l < L \\ 2\xi(l) & \text{if } l > L, \end{cases} \quad (A7)$$

and from this one finds the total cross section to be

$$\sigma_{\text{tot}} = \pi B^2 + 2\pi \left( \frac{2\mu}{\hbar^2 E_0} \right)^{1/2} \int_0^\infty dR \Gamma(R) \left[ 1 - \frac{V_0(R)}{E_0} - \frac{B^2}{R^2} \right], \quad (A8)$$

where $B = L/k_0$ is defined by

$$1 = \left( \frac{2\mu}{\hbar^2 E_0} \right)^{1/2} \int_0^\infty dR \Gamma(R) \left( 1 - \frac{V_0(R)}{E_0} - \frac{B^2}{R^2} \right). \quad (A9)$$

By virtue of Eq. (A9) one can show that

$$(\partial \sigma_{\text{tot}} / \partial B)_n = 0. \quad (A10)$$

For the mass dependence, therefore, one finds

$$d\sigma_{\text{tot}} / d\mu = (\partial \sigma_{\text{tot}} / \partial \mu)_n + (\partial \sigma / \partial B)_n (dB / d\mu),$$

or with Eq. (A10) this becomes

$$d\sigma_{\text{tot}} / d\mu = (\partial \sigma_{\text{tot}} / \partial \mu)_n. \quad (A11)$$

Combined with Eq. (A8) one sees finally that

$$d\sigma_{\text{tot}} / d\mu = (\sigma_{\text{tot}} - \pi B^2) / 2\mu. \quad (A12)$$

In general, therefore,

$$d\sigma_{\text{tot}} / d\mu \leq \sigma_{\text{tot}} / 2\mu,$$

the equality holding for a weak transition ($B = 0$); i.e., the isotope effect is maximum for a weak transition. If $|\mu_2 - \mu_1|$ is not too large, Eq. (A12) is equivalent to

$$|\sigma(\mu_2) - \sigma(\mu_1)| / [\sigma(\mu_2) + \sigma(\mu_1)] \leq |\mu_2 - \mu_1| / 2(\mu_2 + \mu_1).$$

\textsuperscript{1} For a recent review of collision processes involving electronically excited species, see E. E. Muschlis, Jr., Advan. Chem. Phys. 10, 171 (1966).
\textsuperscript{2} E. E. Ferguson, Phys. Rev. 128, 210 (1962).
\textsuperscript{9} For treatments of the similar processes A$^+ +$B$^+$ to A$^+$B$^+$, see A. Herzenberg, Phys. Rev. 160, 80 (1967) and J. C. Y. Chen, Phys. Rev. 156, 12 (1967).
\textsuperscript{13} The fact that these are not true Born–Oppenheimer states has been discussed in Ref. 10; see also T. F. O’Malley, J. Chem. Phys. 81, 322 (1969) and Ref. 14.
\textsuperscript{14} H. S. Taylor, Advan. Chem. Phys. (to be published).
\textsuperscript{15} For example, see R. Messiah, Quantum Mechanics (John Wiley & Sons, Inc., New York, 1962), pp. 732–736.
\textsuperscript{16} D. R. Bates and H. S. W. Massey, Phil. Mag. 45, 111 (1954).
Stark Spectroscopy of NH$_2$ $\nu_2$ Band by 10-$\mu$ CO$_2$ and N$_2$O Lasers*

FUDIO SHIMIZU

Gordon McKay Laboratory, Harvard University, Cambridge, Massachusetts 02138

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The Stark spectrum of the $\nu_2$ band of $^{14}$NH$_2$ is studied using CO$_2$ and N$_2$O lasers equipped with a grating for the laser line selection. About 100 coincidences between NH$_2$ lines of $J \leq 7$ and the laser lines are obtained. The NH$_2$ line positions relative to the laser lines are calculated using the data for the dipole moment obtained by the same experiment.

I. INTRODUCTION

Stark modulation has been a useful technique for the microwave spectroscopy. In the infrared region, however, the value of this technique was rather limited because of the poor resolution of the conventional spectrometers compared to the magnitude of the Stark shifts. Since the invention of the infrared lasers, several authors studied Stark spectroscopy by lasers mostly in 3-$\mu$ region, and demonstrated the usefulness of the technique for the study of the vibrational band of molecules.$^{1-4}$

We report in this paper the Stark spectroscopy of $^{14}$NH$_2$ $\nu_2$ band by 10-$\mu$ CO$_2$ and N$_2$O lasers. These two lasers have special advantage for the study of the vibrational spectrum, because they have an oscillating line in every 1 or 2 wavenumbers covering most of the 9- and 10-$\mu$ region.$^{5,6}$ Therefore vibrational bands of many molecules are covered entirely with these lasers. In this paper the main efforts were concentrated on picking up as many coincidences as possible for NH$_2$ lines $J \leq 7$ with electric field up to 150 esu. The accurate relative position between the laser lines and NH$_2$ lines were calculated using the data of the dipole moment obtained by the same experiment.

II. EXPERIMENTAL

The type of the laser used in this experiment was a 2-m flowing system with a cavity length of 2.6 m. The laser was equipped with a grating in place of one of the reflectors composing the cavity.$^6$ The selection of the transition was done by changing the angle of the grating. In most cases it oscillated in single rotational transition. The laser beam was coupled through a 6-mm hole of the gold coated mirror on the other end of the cavity. The laser was linearly polarized to the direction determined by the Brewster windows of the discharge tube. The laser components were mounted on an aluminum H beam. No attempt was made to stabilize it. With this laser we could obtain oscillation of all lines between $P_50$ and $R_50$ of the $\nu_2-\nu_1$ band of CO$_2$ and the lines from $P_42$ to $P_5$ and from $R_5$ to $R_39$ of the $\nu_2-\nu_1$ band of N$_2$O.

The signal was detected by the standard phase sensitive method with sinusoidal modulation of the Stark field.$^7$ The sample cell was 40 cm long with parallel aluminum electrodes. The spacers of the electrodes were glass with thickness of 2.17 mm. The NH$_2$ pressure was kept at $\sim 10^{-3}$--$10^{-4}$ torr. This is considerably lower than the pressure used by other authors. But the high electric field of up to 150 esu was easily applied. Sensitivity was also found sufficient. Potential across the electrodes was measured by a DIGITEC 211 digital voltmeter and a voltage divider in an accuracy of $\pm 30$ V. The modulation voltage was usually about 40 V peak to peak with frequency of 5 kHz. But the voltage was increased for some weaker lines in order to obtain better sensitivity. The laser beam after passing through the absorption cell was detected by a Ge:Au photocoductive detector. The laser power used was much less than the available...