PHYSICAL REVIEW A VOLUME 28, NUMBER 3 SEPTEMBER 1983

Theory of laser-induced chemi-ionization. I. Quantal formulation

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(Received 7 September 1982)

The quantal theory of field-free associative ionization and Penning ionization, due to O'Malley, Bieniek, and others, is generalized to include the closely analogous laser-induced chemi-ionization processes $A+B+\hbar\omega \rightarrow AB^{+}+e^{-}$, $A+B^{+}+e^{-}$. The principal limitations of the theory are its reliance upon the two-state approximation and its neglect of Born-Oppenheimer terms. Formulas are derived for several scattering cross sections descriptive of the energy spectra and angular distributions of the reaction products. These cross sections vary with the direction of polarization of the laser radiation. The polarization dependences of the heavy-particle $(A+B^{+})$ energy-angle double-differential cross section and of the associated heavy-particle (or photoelectron) energy distribution assume simple cosine-squared forms provided that there is a large number of contributing partial waves. Numerical calculations of these cross sections should be no more difficult to perform than for comparable field-free processes.

I. INTRODUCTION

We recently constructed a classical path theory of *laser-induced* (LI) chemi-ionization processes,[1] which closely paralleled earlier classical path theories[2] of *free-field* (FF) associative ionization and Penning ionization. Here further connections are established between the theories of LI and FF collisional events and, in particular, it is demonstrated that the *quantal* formalism appropriate to LI processes differs in no essential way from that for comparable FF events. However, in place of the electronic energy operator which plays the central role in theories of FF chemi-ionization, it is the electric-dipole-moment operator (and the associated transition amplitude for photoionization) that dominates the stage in LI chemi-ionization.

The theory presented here can be extended to many other situations, including LI nonionizing collisional transitions. However, our present considerations will be limited to photoionization processes with the schematic representation

$$A+B \rightarrow [(A\cdots B) \xrightarrow{\hbar\omega} (A\cdots B)^{+}+e^{-}] \rightarrow \left\{ \begin{matrix} A+B^{+}+e^{-},\ \text{LIPI} \\ AB^{+}+e^{-},\ \text{LIAI} \end{matrix} \right\} \tag{1.1}$$

and which are exemplified by the two cases depicted in Fig. 1. Events corresponding to the two different final states indicated in (1.1) will be called laser-induced Penning ionization (LIPI) and laser-induced associative ionization (LIAI), respectively. Weiner and his co-workers[3] have conducted crossed-beam experiments with alkali-metal atoms that involved laser-induced processes such as these. The laser frequency ω is chosen to lie below the ionization limits of both A and B and is not resonant with any electronic transitions of these two atoms. However, when the value of the internuclear separation falls below a critical value $R^{*}(\omega)$, photoionization of the composite, two-atom system can occur. This is illustrated in Fig. 1 by the curves labeled $A+B+\hbar\omega$; these are plots of $E_d(R)+\hbar\omega$, the sum of the adiabatic (diabatic) electronic energy of the initial AB state and the energy of a single laser photon. Photoionization is energetically possible at internuclear separations for which the value of $E_d(R)+\hbar\omega$ exceeds the electronic energy $E_c(R)$ of the AB^{+} molecular ion.

A qualitative grasp of the situation can be extracted from simple energetic considerations. These establish that the energy of the ejected electron and the postcollisional heavy-particle motions depend not only upon the (experimentally controllable) laser frequency and relative kinetic energy of the colliding atoms, but on the internuclear separation at which photoionization occurs. Figures 1(a) and 1(b) are drawn for fixed values of the first and second of these three variables. The function $\epsilon(R)$ is the energy of the electron that is ejected when photoionization takes place at the separation $R<R^{*}(\omega)$. $E_f(R)$ is the corresponding value of the heavy-particle energy, that is, the sum of the relative kinetic energy

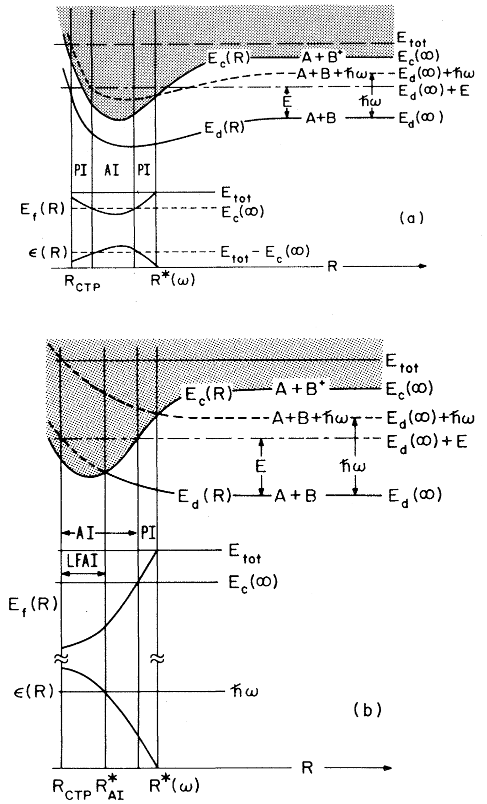

FIG. 1. Two examples of situations where LI chemi-ionization can occur. The major difference between the model systems of Figs. 1(a) and 1(b) is that in the latter case FF chemi-ionization also is a possibility provided that $R < R^*_{\mathrm{AI}}$. $E_d(R)$ and $E_c(R)$ are the energies of the adiabatic (diabatic) electronic states of the initial AB configuration and of the final AB^+ molecular ion. The curves labeled $A+B+\hbar\omega$ are plots of $E_d(R)+\hbar\omega$. R_{CTP} refers to the classical turning point associated with the electronic initial state; it is dependent on the initial values of the relative kinetic energy E and angular momentum L, the latter of which has been set equal to zero in these drawings. Finally, $\epsilon(R)$ and $E_f(R)$, respectively, are the energies of the ejected electron and the residual heavy-particle subsystem when photoionization occurs at the internuclear separation R.

and the potential energy $E_c(R)$ of the diatomic ion that remains after the electron has been ejected. If $E_f(R) > E_c(\infty)$, this molecular ion will be unbound and the ultimate products of reaction will be the three widely separated fragments, $A+B^+ + e^-$. However, when $E_f(R) < E_c(\infty)$, the process is LIAI and the reaction products are an electron and a bound diatomic ion. As the figures reveal, there are ranges of internuclear separations (which shift with changes of ω and E) within which the ionizing events either are exclusively LIAI or LIPI.

The curves shown in Fig. 1 are consequences of energy conservation and the Franck-Condon principle. The first of these requires that the total energy E_{tot} be equal both to the initial energy

$$E_i = E + E_d(\infty) + N\hbar\omega$$

and to the final energy

$$E_f = E' + E_c(\infty) + (N-1)\hbar\omega \ .$$

Here E is the relative kinetic energy of the two atoms prior to collision, and E' denotes the relative kinetic energy of the A and B^+ products of LIPI. (When $E' < 0$ the process is LIAI.) According to the Franck-Condon principle, the nuclear momenta are unaffected by the occurrence of photoionization. This condition together with energy conservation leads to the conclusions that

$$\epsilon(R) = \hbar\omega - [E_c(R) - E_d(R)]$$

and

$$\epsilon(R) + E_f(R) = E + E_d(\infty) + \hbar\omega \ .$$

These essentially classical considerations do, of course, ignore the quantized character of the bound states of the AB^+ ion, but they nevertheless provide a simple, qualitatively correct energetic analysis of LIAI and LIPI.

In the sections which follow, formulas are derived for several scattering cross sections descriptive of the energy spectra and angular distributions of the reaction products. Special attention is given to the dependences of these cross sections on the polarization of the laser photons. So far as we have been able to determine, ours is the first theoretical investigation to concern itself with this polarization dependence. In fact, we also have failed to find any reports of experimental observations of this effect.

The projection operator formalism is used to separate, as nearly as is possible, the treatment of the nuclear motions associated with the discrete initial AB electronic state from those connected with the continuum electronic state of the final $AB^+ + e^-$ configuration. As is usual in theories of this sort, a two-state approximation is introduced by neglecting the effects connected with all electronic states other than the two that have been mentioned specifically. A more comprehensive many-channel theory has been formulated by Bellum and George.[4] This theory and ours share a number of common features, but direct comparisons between the two are difficult to draw. This difficulty is due, at least in part, to differences between the objectives and emphases of the two investigations. Thus while we are intent upon deriving cross-section formulas and establishing connections between these quantities and the rate of photoionization, Bellum and George were more concerned with questions of how to formulate and solve close-coupled equations that involve continuum electronic states.

We began this study by extending O'Malley's[5] theory of laser-free dissociative attachment to LIPI and LIAI, but then shortly thereafter discovered a more recent paper by Bieniek[6] which dealt thoroughly and in great detail with the theory of *laser-free* AI and PI. Both of these very excellent papers, especially the second, have aided us immensely in conducting the present investigation. In recognition of this we have patterned our presentation after Bieniek's and, whenever feasible, have adopted his notation.

II. FORMAL THEORY

The theory presented here is specific to a steady state, crossed-beam experiment in which a single mode laser is focused on the region where the two beams intersect. Our analysis of the dynamic events that occur under these conditions is formulated in the Schrödinger picture. The radiation field is treated in the Coulomb gauge with the static interactions among the charged particles taken as a part V of the electronic energy operator

$$\begin{aligned} H_{\mathrm{el}} &= T_{\mathrm{el}} + V \\ &\equiv \sum_{1}^{n} \left[\frac{\vec{p}_i^{\,2}}{2m_e} - \frac{Z_A e^2}{r_{Ai}} - \frac{Z_B e^2}{r_{Bi}} \right] + \sum_{i>j}^{n} \frac{e^2}{r_{ij}} \\ &\quad + \frac{Z_A Z_B e^2}{|\vec{r}_B - \vec{r}_A|} . \end{aligned} \tag{2.1}$$

The Hamiltonian of the combined system of material particles (m) and radiation (r) can be written (in the nuclear center of mass frame) as the sum

$$H = H_m + H_r + H_{\mathrm{int}} \tag{2.2}$$

with $H_m = T_n + H_{\mathrm{el}}$, and where $T_n \equiv \vec{p}_n^{\,2}/2\mu$ denotes the relative kinetic energy of the two atomic nuclei [reduced mass $\mu = m_A m_B/(m_A + m_B)$]. H_{int} is the energy of interaction between the charged particles and the laser field; its explicit form is given in the Appendix. The Hamiltonian of the free radiation field is

$$H_r = \hbar\omega a^\dagger a . \tag{2.3}$$

Here $a^\dagger$ and a denote creation and annihilation operators of photons, each with polarization $\hat{\alpha}$, momentum $\hbar\vec{\kappa}$, and energy $\hbar\omega = \hbar c\kappa$. The states of the pure, single mode laser field are indicated by the symbols $|N\rangle$ with

$$\langle N | a^\dagger a | N' \rangle = N \delta_{N,N'}$$

and

$$\langle N | a^\dagger | N' \rangle = \sqrt{N} \delta_{N,N'+1} .$$

The electronic state of the initial AB configuration is denoted by the ket $|\phi_d\rangle = |\phi_{AB}\rangle$. Associated with this state is the wave function $\phi_d(\vec{r}\,|\vec{R})$. Here $\vec{r}$ indicates the aggregate of electronic (position and spin) coordinates and $\vec{R} = \vec{r}_B - \vec{r}_A$ is the vector extending from nucleus A to nucleus B. The electronic energy of this initial state is given by the expectation value

$$E_d(R) = \int d\vec{r}\, \phi_d^*(\vec{r}\,|\vec{R}) H_{\mathrm{el}} \phi_d(\vec{r}\,|\vec{R}) \tag{2.4}$$

of the operator

$$H_{\mathrm{el}} = -\frac{\hbar^2}{2m_e} \sum_{1}^{n} \nabla_i^2 + V(\vec{r},\vec{R}) . \tag{2.5}$$

In the case depicted in Fig. 1(a) ϕ_d is a variational, configuration-interaction (CI) wave function appropriate to the initial state of the neutral AB system. In the case of Fig. 1(b) it is (for $R < R^*$) the wave function of a resonance for which a CI approximation can be constructed by the stabilization method.[7]

Because H_{el} and $\vec{R}^{\mathrm{op}}$ (the operator associated with the classical variable $\vec{R}$) commute, there is a ket $|\phi_d,\vec{R}\rangle\rangle$ which simultaneously satisfies the two eigenvalue equations

$$H_{\mathrm{el}} | \phi_d,\vec{R} \rangle\rangle = E_d(R) | \phi_d,\vec{R} \rangle\rangle$$

and

$$\vec{R}^{\mathrm{op}} | \phi_d,\vec{R} \rangle\rangle = \vec{R} | \phi_d,\vec{R} \rangle\rangle .$$

We choose for this ket the normalization

$$\langle\langle \phi_d,\vec{R} | \phi_d,\vec{R}\,' \rangle\rangle = \delta(\vec{R} - \vec{R}\,') .$$

Associated with $|\phi_d,\vec{R}\rangle\rangle$ is the wave function

$$\begin{aligned} \langle\langle \vec{r}\,',\vec{R}\,' | \phi_d,\vec{R} \rangle\rangle &= \langle \vec{R}\,' | \langle \vec{r}\,' | \phi_d,\vec{R} \rangle \rangle \\ &= \phi_d(\vec{r}\,|\vec{R}) \delta(\vec{R} - \vec{R}\,') , \end{aligned} \tag{2.6}$$

and so

$$\begin{aligned} |\phi_d,\vec{R}\rangle\rangle &= \int d\vec{r}\,' d\vec{R}\,' \, | \vec{r}\,',\vec{R}\,' \rangle\rangle \langle\langle \vec{r}\,',\vec{R}\,' | \phi_d,\vec{R} \rangle\rangle \\ &= |\vec{R}\rangle \int d\vec{r}\, |\vec{r}\rangle \phi_d(\vec{r}\,|\vec{R}) = |\vec{R}\rangle\, |\phi_d(\vec{R})\rangle \end{aligned} \tag{2.7}$$

with

$$|\phi_d(\vec{R})\rangle = \int d\vec{r}\, |\vec{r}\rangle \phi_d(\vec{r}\,|\vec{R}) \tag{2.8}$$

and

$$\phi_d(\vec{r}\,|\vec{R}) = \langle \vec{r} | \phi_d(\vec{R}) \rangle . \tag{2.9}$$

Here and henceforth we adopt Bieniek's[6] notation, using a double bra, $\langle\langle\Psi|$, or ket, $|\Psi\rangle\rangle$ to denote states that include a complete nuclear and electronic configuration. Single bras, $\langle\Psi|$, and kets, $|\Psi\rangle$, indicate states that either are nuclear or electronic, but not both.

Analogous to $|\phi_d\rangle = |\phi_{AB}\rangle$ is the electronic ket

$$|\phi_{\vec{\epsilon}}\rangle = |\phi_{AB^+}, e^-(\epsilon,\hat{\epsilon})\rangle$$

associated with an ionized continuum state, $AB^+ + e^-$. ϵ and $\hat{\epsilon}$ appearing here denote the kinetic energy and direction of motion of the unbound electron. These electronic continuum states are orthogonal to $|\phi_d\rangle$. They are so normalized that

$$\langle \phi_{\vec{\epsilon}} | \phi_{\vec{\epsilon}'} \rangle = \rho(\vec{\epsilon})^{-1} \delta(\vec{\epsilon} - \vec{\epsilon}') , \tag{2.10}$$

and

$$\langle \phi_{\vec{\epsilon}} | H_{\mathrm{el}} | \phi_{\vec{\epsilon}'} \rangle = (\epsilon + E_c) \rho(\vec{\epsilon})^{-1} \delta(\vec{\epsilon} - \vec{\epsilon}') . \tag{2.11}$$

Here $\rho(\vec{\epsilon})$ is the density of electronic continuum states

$$\delta(\vec{\epsilon} - \vec{\epsilon}') \equiv \delta(\epsilon - \epsilon') \delta(\hat{\epsilon} - \hat{\epsilon}) ,$$

and E_c is the $(n-1)$-electron analog of E_d.

Our objective is to derive cross-section formulas for the ionizing events

$$A + B \xrightarrow{\hbar\omega} AB^+ + e^- , A + B^+ + e^- .$$

These involve transitions from the initial electronic state $|\phi_d\rangle$ to a final state $|\phi_{\vec{\epsilon}}\rangle$. Depending upon a variety of conditions (see Fig. 1), these events either may or may not involve simultaneous absorption (or emission) of laser photons. Thus the processes of interest are characterized more completely as transitions between the initial state

$$|\phi_d N\rangle \equiv |\phi_d\rangle |N\rangle$$

and one of the final states

$$|\phi_{\vec{\epsilon}} N'\rangle \equiv |\phi_{\vec{\epsilon}}\rangle |N'\rangle$$

with $N' = 0, 1, \ldots, N-1, N, N+1, \ldots$. (In the cases that concern us most directly the only accessible final states are those with $N' = N$ and $N' = N-1$.) Henceforth we neglect the influence upon these transitions of all other electronic states and, in so doing, restrict our attention to the space which is spanned by the basis set $\{ |\phi_d N\rangle ; |\phi_{\vec{\epsilon}} N'\rangle, N' = 0, 1, \ldots, N, N+1, \ldots \}$. The ionizing events are transitions from the part of this space (a two-state approximation to the Hilbert space of electronic states) associated with the projection operator

$$Q = |\phi_d N\rangle \langle \phi_d N| \tag{2.12}$$

to that associated with the (approximately) complementary, orthogonal projection operator

$$P = \sum_{N'} \int d\vec{\epsilon}' \, |\phi_{\vec{\epsilon}'} N'\rangle \rho(\vec{\epsilon}') \langle \phi_{\vec{\epsilon}'} N'| . \tag{2.13}$$

These operators satisfy the conditions $P^2 = P$, $Q^2 = Q$, $PQ = QP = 0$, and $P + Q \approx 1$.

The time-independent Schrödinger equation

$$(H - E_T) |\Psi\rangle\rangle = 0 \tag{2.14}$$

is to be solved for a value of the total energy $E_T \equiv E_{\mathrm{tot}}$ equal to $E + N\hbar\omega + E_d(\infty)$. Here E denotes the initial relative kinetic energy of the two colliding atoms and $N\hbar\omega$ is the energy of N laser photons. The energy of the matter system is equal to $E_d(\infty)$ when (i) the electrons occupy the state $|\phi_d\rangle$, and (ii) the two nuclei are infinitely separated and at rest.

The projections of $|\Psi\rangle\rangle$ upon the P and Q subspaces approximately satisfy the pair of coupled equations

$$(H_{PP} - E_T) P |\Psi\rangle\rangle = -H_{PQ} Q |\Psi\rangle\rangle , \tag{2.15a}$$

$$(H_{QQ} - E_T) Q |\Psi\rangle\rangle = -H_{QP} P |\Psi\rangle\rangle \tag{2.15b}$$

with $H_{PP} = PHP$, $H_{QQ} = QHQ$, $H_{PQ} = PHQ$, and $H_{QP} = QHP$. Associated with these is the corresponding pair of homogeneous equations,

$$(H_{PP} - E_T) P |\Psi_P\rangle\rangle = 0 , \tag{2.16a}$$

$$(H_{QQ} - E_T) Q |\Psi_Q\rangle\rangle = 0 , \tag{2.16b}$$

descriptive of the uncoupled dynamics specific to the ionized and bound electronic states, respectively. By multiplying (2.16b) with $\langle \phi_d N|$ one obtains for

$$|\Psi_{dN}\rangle \equiv \langle \phi_d N | \Psi_Q \rangle\rangle$$

the wave equation

$$(T_n + T_{dd}^{\mathrm{BO}} + V_d - E) |\Psi_{dN}\rangle = 0 \tag{2.17}$$

with

$$V_d \equiv \langle \phi_d | H_{\mathrm{el}} | \phi_d \rangle - E_d(\infty) , \tag{2.18}$$

and where T_{dd}^{BO} is a diagonal element of the matrix of Born-Oppenheimer coupling terms,

$$T_{ij}^{\mathrm{BO}} = \frac{1}{2\mu} \big(\langle \phi_i | \vec{\mathrm{p}}_n^{\,2} | \phi_j \rangle + 2 \langle \phi_i | \vec{\mathrm{p}}_n | \phi_j \rangle \cdot \vec{\mathrm{p}}_n \big) . \tag{2.19}$$

The $\vec{\mathrm{R}}$ representative of the nuclear ket $|\Psi_{dN}\rangle$ is the wave function $\Psi_d(\vec{\mathrm{E}}, N | \vec{\mathrm{R}}) \equiv \langle \vec{\mathrm{R}} | \Psi_{dN} \rangle$. The symbol $\vec{\mathrm{E}} = (E, \hat{K})$ appearing here includes the channel energy E and a unit vector $\hat{K}$ which gives the asymptotic value of the direction of relative motion of the A and B fragments. $\Psi_d(\vec{\mathrm{E}}, N | \vec{\mathrm{R}})$ satisfies the wave equation

$$[T_{\vec{\mathrm{R}}} + T_{dd}^{\mathrm{BO}}(\vec{\mathrm{R}}) + V_d(R) - E] \Psi_d(\vec{\mathrm{E}}, N | \vec{\mathrm{R}}) = 0 , \tag{2.20}$$

wherein

$$T_{\vec{\mathrm{R}}} = -\frac{\hbar^2}{2\mu} \nabla_R^2 , \tag{2.21a}$$

$$T_{ij}^{\mathrm{BO}}(\vec{\mathrm{R}})=-\frac{\hbar^2}{2\mu}(\langle\phi_i\,|\,\nabla_R^2\,|\,\phi_j\rangle$$
$$+2\langle\phi_i\,|\,\vec{\nabla}_R\,|\,\phi_j\rangle\cdot\vec{\nabla}_R)\,, \tag{2.21b}$$

$$V_d(R)=E_d(R)-E_d(\infty)\,, \tag{2.21c}$$

and

$$E_d(R)=\langle\vec{\mathrm{R}}\,|\,\langle\phi_d\,|\,H_{\mathrm{el}}\,|\,\phi_d\rangle\,|\,\vec{\mathrm{R}}\rangle$$
$$=\int d\vec{\mathrm{r}}\,\phi_d^*(\vec{\mathrm{r}}\,|\,\vec{\mathrm{R}})H_{\mathrm{el}}\phi_d(\vec{\mathrm{r}}\,|\,\vec{\mathrm{R}})\,. \tag{2.21d}$$

Analogously, we find from (2.16a) that the nuclear ket

$$|\,\Psi_P(\vec{\mathrm{E}}\,',N')\rangle\equiv\langle\phi_{\vec{\epsilon}}N'\,|\,\Psi_P\rangle\rangle$$

satisfies the equation

$$(T_n+T^{\mathrm{BO}}_{\vec{\epsilon}\,',\vec{\epsilon}\,'}+V_c-E')\,|\,\Psi_P(\vec{\mathrm{E}}\,',N')\rangle=0 \tag{2.22}$$

with $V_c=E_c-E_c(\infty)$. The $\vec{\mathrm{R}}$ representative of this ket is the wave function $\Psi_P(\vec{\mathrm{E}}\,',N'\,|\,\vec{\mathrm{R}})$, with $\vec{\mathrm{E}}\,'\equiv(E',\hat{K}\,')$ and

$$E'\equiv E-\epsilon+(N-N')\hbar\omega-[E_c(\infty)-E_d(\infty)]\,.$$

It is a solution of the wave equation

$$[T_{\vec{\mathrm{R}}}+T^{\mathrm{BO}}_{\vec{\epsilon}\,',\vec{\epsilon}\,'}(\vec{\mathrm{R}})+V_c(R)-E']\Psi_P(\vec{\mathrm{E}}\,',N'\,|\,\vec{\mathrm{R}})=0\,. \tag{2.23}$$

When E' is positive valued (Penning ionization), the nuclear motion governed by this equation is unbounded. However, when E' is negative (associative ionization), solutions of the wave equation (2.23) exist only for the discrete energy eigenvalues, $E'=E_{n'}^{L'}$, of the AB^+ square-integrable eigenfunctions $\Psi_P^{M'}(E_{n'}^{L'},N'\,|\,\vec{\mathrm{R}})$;

$$\langle\Psi_P^{M}(E_n^L,N')\,|\,\Psi_P^{M'}(E_{n'}^{L'},N')\rangle=\delta_{nn'}\delta_{LL'}\delta_{MM'}\,.$$

Here n', L', and M' are the conventional vibrational and rotational angular momentum quantum numbers that characterize these states.

The collection of functions $\{\Psi_P(\vec{\mathrm{E}}\,',N'\,|\,\vec{\mathrm{R}});\ \Psi_P^{M'}(E_{n'}^{L'},N'\,|\,\vec{\mathrm{R}})\}$ is a complete set for the nuclear motions associated with the ionized $AB^+ + e^-$ electronic state. The density of these states is $\rho(\vec{\mathrm{E}}\,')$; for $E'<0$,

$$\rho(\vec{\mathrm{E}}\,')=(4\pi)^{-1}\delta(E-E_{n'}^{L'})\,.$$

Throughout the remainder of this section we shall use the single symbol Ψ_P (or $\Psi_P^{\pm}$) to denote one of these AB^+ states, regardless of whether it is descriptive of bounded or unbounded nuclear motions.

The cross sections which we wish to compute are directly related to the T matrix[6]

$$T=\langle\langle\Psi_P^-\,|\,PHQ\,|\,\Psi^+\rangle\rangle \tag{2.24}$$

for transitions to ionized final states. The superscripts $(+)$ and $(-)$ in (2.24) refer to states which conform to the conventionally defined "out" and "in" boundary conditions of scattering theory. Thus $|\,\Psi^+\rangle\rangle$ and $|\,\Psi_P^-\rangle\rangle$ are solutions of (2.14) and (2.16a) whose asymptotic forms include outgoing and incoming scattered waves, respectively.

We shall be concerned primarily with ionizing collisional events which require absorption of a *single* photon. The T matrix for events of this sort is given by the formula

$$T=\int d\vec{\epsilon}\langle\langle\Psi_P^-\,|\,\phi^-_{\vec{\epsilon}}N-1\rangle\rho(\vec{\epsilon})\langle\phi^-_{\vec{\epsilon}}N-1\,|\,H\,|\,\phi_dN\rangle\langle\phi_dN\,|\,\Psi^+\rangle\rangle$$
$$=\int d\vec{\epsilon}\rho(\vec{\epsilon})T(\vec{\mathrm{E}}\,',\vec{\epsilon}\,|\,\vec{\mathrm{E}})\,, \tag{2.25}$$

where

$$T(\vec{\mathrm{E}}\,',\vec{\epsilon}\,|\,\vec{\mathrm{E}})=\int d\vec{\mathrm{R}}\,\Psi_P^-(\vec{\mathrm{E}}\,',N-1\,|\,\vec{\mathrm{R}})^*\langle\vec{\epsilon}^{\,-},N-1\,|\,\vec{\mathrm{R}},N\rangle X_d^+(\vec{\mathrm{E}},N\,|\,\vec{\mathrm{R}}) \tag{2.26}$$

is the T matrix for production of an ionized electron in the state $\vec{\epsilon}=(\epsilon,\hat{\epsilon})$ together with a heavy-particle state characterized by $\vec{\mathrm{E}}\,'=(E',\hat{K}\,')$. The quantity

$$\langle\vec{\epsilon}^{\,-},N-1\,|\,\vec{\mathrm{R}},N\rangle=\langle\langle\phi^-_{\vec{\epsilon}}N-1,\vec{\mathrm{R}}\,|\,H\,|\,\phi_dN,\vec{\mathrm{R}}\rangle\rangle$$
$$=\langle\langle\phi^-_{\vec{\epsilon}},\vec{\mathrm{R}}\,|\,\langle N-1\,|\,H_{\mathrm{int}}\,|\,N\rangle\,|\,\phi_d,\vec{\mathrm{R}}\rangle\rangle \tag{2.27}$$

that occurs in (2.26) is the photoionization transition amplitude specific to the internuclear separation $\vec{\mathrm{R}}$. $X_d^+(\vec{\mathrm{E}},N\,|\,\vec{\mathrm{R}})\equiv\langle\langle\phi_dN,\vec{\mathrm{R}}\,|\,\Psi^+\rangle\rangle$ and $\Psi_P^-(\vec{\mathrm{E}}\,',N-1\,|\,\vec{\mathrm{R}})\equiv\langle\langle\phi^-_{\vec{\epsilon}}N-1,\vec{\mathrm{R}}\,|\,\Psi_P^-\rangle\rangle$ are nuclear wave functions, the latter of which is a solution of (2.23).

What now must be derived is the wave equation satisfied by

$$X_d^+(\vec{\mathrm{E}},N\,|\,\vec{\mathrm{R}})=\langle\vec{\mathrm{R}}\,|\,X_{dN}^+\rangle\,.$$

To accomplish this we write the "out" solution of (2.15b) in the form

$$Q\,|\Psi^{+}\rangle\rangle = Q\,|\Psi_Q^{+}\rangle\rangle + G_Q^{+} QHP\,|\Psi^{+}\rangle\rangle$$

with $G_Q^{+}=[Q(E_T+i0-H)Q]^{-1}$, and the corresponding solution of (2.15a) as

$$P\,|\Psi^{+}\rangle\rangle = G_P^{+} PHQ\,|\Psi^{+}\rangle\rangle \ .$$

These are then combined to yield the formula

$$Q\,|\Psi^{+}\rangle\rangle = (1-G_Q^{+} QHPG_P^{+} PHQ)^{-1} Q\,|\Psi_Q^{+}\rangle\rangle \tag{2.28}$$

for $Q\,|\Psi^{+}\rangle\rangle$. Next, by using the definition of Q, we transform (2.28) into the expression

$$|X_{dN}^{+}\rangle = (1-g_d^{+}F^{+})^{-1}\,|\Psi_{dN}^{+}\rangle \ ,$$

wherein $g_d^{+}\equiv\langle\phi_d N\,|\,G_Q^{+}\,|\,\phi_d N\rangle$ and $F^{+}\equiv\langle\phi_d N\,|\,HPG_P^{+}PH\,|\,\phi_d N\rangle$. Finally, this in turn can be rewritten as the wave equation

$$(T_n + T_{dd}^{\mathrm{BO}} + V_d + F^{+} - E)\,|X_{dN}^{+}\rangle = 0 \ , \tag{2.29}$$

the $\vec{\mathrm{R}}$ representation of which is

$$[T_{\vec{\mathrm{R}}} + T_{dd}^{\mathrm{BO}}(\vec{\mathrm{R}}) + V_d(R) - E]X_d^{+}(\vec{\mathrm{E}},N\,|\,\vec{\mathrm{R}}) = -\int d\vec{\mathrm{R}}'\langle\vec{\mathrm{R}}\,|\,F^{+}\,|\,\vec{\mathrm{R}}'\rangle X_d^{+}(\vec{\mathrm{E}},N\,|\,\vec{\mathrm{R}}') \ . \tag{2.30}$$

The nonlocal interaction $\langle\vec{\mathrm{R}}\,|\,F^{+}\,|\,\vec{\mathrm{R}}'\rangle$ couples the incident, AB channel to those associated with the ionized, $AB^{+}+e^{-}$ electronic configuration. By substituting the projection operator definitions, (2.12) and (2.13), into the formula

$$F^{+} = \langle\phi_d N\,|\,HPG_P^{+}PH\,|\,\phi_d N\rangle$$

we obtain the expression

$$F^{+} = \sum_{N',N''}\int d\vec{\epsilon}\,'d\vec{\epsilon}\,''\langle\phi_d N\,|\,H\,|\,\phi^{+}_{\vec{\epsilon}\,'}N'\rangle\rho(\vec{\epsilon}\,')\langle\phi^{+}_{\vec{\epsilon}\,'}N'\,|\,(E_T+i0-H)^{-1}\,|\,\phi^{+}_{\vec{\epsilon}\,''}N''\rangle$$
$$\times\rho(\vec{\epsilon}\,'')\langle\phi^{+}_{\vec{\epsilon}\,''}N''\,|\,H\,|\,\phi_d N\rangle \ , \tag{2.31}$$

wherein

$$\langle\phi_d N\,|\,H\,|\,\phi_{\vec{\epsilon}\,'}N'\rangle = \delta_{NN'}T^{\mathrm{BO}}_{d\vec{\epsilon}\,'} + \langle\phi_d N\,|\,H_{\mathrm{int}}\,|\,\phi_{\vec{\epsilon}\,'}N'\rangle \ . \tag{2.32}$$

To this point the analysis has been essentially exact. However, in order to obtain relatively simple, computationally tractable results we now shall introduce a number of approximations. The first of these is to neglect Born-Oppenheimer (BO) terms whenever they occur, namely, the diagonal elements appearing on the left-hand sides of the wave equations (2.20), (2.23), and (2.30) and the (electronic) off-diagonal contributions to the matrix elements of H that appear in the formula (2.31) for F^{+}. In each case the argument in support of this approximation is that the terms retained are expected to produce significantly greater contributions to the transition rate under consideration than do the BO terms which are being discarded. To this approximation the $\vec{\mathrm{R}}$ representative of the coupling operator F^{+} becomes

$$\langle\vec{\mathrm{R}}\,|\,F^{+}\,|\,\vec{\mathrm{R}}'\rangle = \sum_{N',N''}\int d\vec{\epsilon}\,'d\vec{\epsilon}\,''\rho(\vec{\epsilon}\,')\rho(\vec{\epsilon}\,'')\langle\vec{\epsilon}^{\,+\prime},N'\,|\,\vec{\mathrm{R}},N\rangle^{*}\langle\vec{\epsilon}^{\,+\prime\prime},N''\,|\,\vec{\mathrm{R}}',N\rangle$$
$$\times\langle\langle\phi^{+}_{\vec{\epsilon}\,'},\vec{\mathrm{R}}\,|\,\langle N'\,|\,(E_T+i0-H)^{-1}\,|\,N''\rangle\,|\,\phi^{+}_{\vec{\epsilon}\,''},\vec{\mathrm{R}}'\rangle\rangle \ . \tag{2.33}$$

Our second approximation is to neglect *both* the BO and $\mathrm{H}_{\mathrm{int}}$ contributions to the P-space propagator occurring in this expression, viz.,

$$\langle N'\,|\,(E_T+i0-H)^{-1}\,|\,N''\rangle \doteq \delta_{N'N''}(E_T+i0-T_n-H_{\mathrm{el}}-N'\hbar\omega)^{-1} \ .$$

The consequence of this is that $\langle\langle\phi^{+}_{\vec{\epsilon}\,'},\vec{\mathrm{R}}\,|\,\langle N'\,|\,(E_T+i0-H)^{-1}\,|\,N''\rangle\,|\,\phi^{+}_{\vec{\epsilon}\,''},\vec{\mathrm{R}}'\rangle\rangle$ reduces to the product of $\delta_{N'N''}\delta(\vec{\epsilon}\,'-\vec{\epsilon}\,'')\rho(\vec{\epsilon}\,')^{-1}$ with the factor

$$\begin{aligned}
\langle\vec{\mathrm{R}}\,|\,[E+N\hbar\omega+E_d(\infty)+i0-T_n-V_c-\epsilon'-N'\hbar\omega]^{-1}\,|\,\vec{\mathrm{R}}\,'\rangle
&=\int d\vec{\mathrm{E}}\,'d\vec{\mathrm{E}}\,''\langle\vec{\mathrm{R}}\,|\,\Psi_P^+(\vec{\mathrm{E}}\,',N')\rangle\rho(\vec{\mathrm{E}}\,')\\
&\quad\times\langle\Psi_P^+(\vec{\mathrm{E}}\,',N')\,|\,\{E-\epsilon'+(N-N')\hbar\omega-[E_c(\infty)-E_d(\infty)]-T_n-V_c+i0\}^{-1}\,|\,\Psi_P^+(\vec{\mathrm{E}}\,'',N')\rangle\\
&\quad\times\rho(\vec{\mathrm{E}}\,'')\langle\Psi_P^+(\vec{\mathrm{E}}\,'',N')\,|\,\vec{\mathrm{R}}\,'\rangle\\
&=\int d\vec{\mathrm{E}}\,'\rho(\vec{\mathrm{E}}\,')\Psi_P^+(\vec{\mathrm{E}}\,',N'\,|\,\vec{\mathrm{R}}\,')^*\Psi_P^+(\vec{\mathrm{E}}\,',N'\,|\,\vec{\mathrm{R}})\{E-\epsilon'+(N-N')\hbar\omega-[E_c(\infty)-E_d(\infty)]-E'+i0\}^{-1}\,.
\end{aligned}$$

Here it is to be understood that the set $\{\Psi_P^+(\vec{\mathrm{E}}\,',N'\,|\,\vec{\mathrm{R}})\}$ includes the discrete AB^+ molecular ion eigenfunctions of Eq. (2.23) as well as the continuum, $A+B^+$ scattering states. From this result we obtain in place of (2.23) the approximation

$$\begin{aligned}
\langle\vec{\mathrm{R}}\,|\,F^+\,|\,\vec{\mathrm{R}}\,'\rangle=\sum_{N'}\int d\vec{\epsilon}\,'\rho(\vec{\epsilon}\,')\langle\vec{\epsilon}\,^{+\prime},N'\,|\,\vec{\mathrm{R}},N\rangle^*\langle\vec{\epsilon}\,^{+\prime},N'\,|\,\vec{\mathrm{R}}\,',N\rangle
&\times\Bigg[\mathscr{P}\int d\vec{\mathrm{E}}\,'\rho(\vec{\mathrm{E}}\,')\Psi_P^+(\vec{\mathrm{E}}\,',N'\,|\,\vec{\mathrm{R}}\,')^*\Psi_P^+(\vec{\mathrm{E}}\,',N'\,|\,\vec{\mathrm{R}})\\
&\qquad\times\{E-\epsilon'+(N-N')\hbar\omega-[E_c(\infty)-E_d(\infty)]-E'\}^{-1}\\
&\quad-i\pi\int d\hat{K}\,'\rho(\vec{\mathrm{E}}_0')\Psi_P^+(\vec{\mathrm{E}}_0',N'\,|\,\vec{\mathrm{R}}\,')^*\Psi_P^+(\vec{\mathrm{E}}_0',N'\,|\,\vec{\mathrm{R}})\Bigg]\,,
\end{aligned}\qquad(2.34)$$

where $\vec{\mathrm{E}}_0'=(E_0',\hat{K}\,')$ and $E_0'=E-\epsilon'+(N-N')\hbar\omega-[E_c(\infty)-E_d(\infty)]$. The operator $\mathscr{P}$ extracts the principal part of the integral upon which it acts.

One could proceed, without further approximation, using this simplified form of the nonlocal coupling between the initial- and final-state channels. However, we ultimately are interested in establishing connections between the quantal and classical path theories of LI chemi-ionization processes, the latter of which is limited intrinsically to the localized description of autoionizing and photoabsorptive events. Furthermore, there is an abundance of evidence that supports the accuracy of the local approximation, especially for photoexcitation and photoionization.

The procedure for constructing this approximation has been given by Bardsley[8] and later elaborated upon by Bieniek.[6] We illustrate it here by considering the contribution $\langle\vec{\mathrm{R}}\,|\,F^+\,|\,\vec{\mathrm{R}}\,'\rangle_2$ which arises from the second term in the large parentheses, ( ), of (2.34). The first step is to replace the variable of integration ϵ' with E_0' so that

$$\int d\hat{K}\,'d\vec{\epsilon}\,'(\cdots)=\int d\hat{K}\,'d\epsilon'd\hat{\epsilon}\,'(\cdots)=\int d\hat{K}\,'dE_0'd\hat{\epsilon}\,'(\cdots)=\int d\hat{\epsilon}\,'d\vec{\mathrm{E}}_0'(\cdots)\,.$$

Next comes the crucial assumption that the function $\rho(\vec{\epsilon}\,')\langle\vec{\epsilon}\,^{+\prime},N'\,|\,\vec{\mathrm{R}},N\rangle^*\langle\vec{\epsilon}\,^{+\prime},N'\,|\,\vec{\mathrm{R}}\,',N\rangle$ varies so slowly with ϵ' that its dependence on E_0' can be ignored. Then, because the collection of functions $\Psi_P^+(\vec{\mathrm{E}}\,',N'\,|\,\vec{\mathrm{R}})$ forms a complete set for the nuclear motions, it follows that

$$\langle\vec{\mathrm{R}}\,|\,F^+\,|\,\vec{\mathrm{R}}\,'\rangle_2\doteq-i\pi\delta(\vec{\mathrm{R}}-\vec{\mathrm{R}}\,')\sum_{N'}\int d\hat{\epsilon}\,'\{\rho(\vec{\epsilon}\,')\,|\,\langle\vec{\epsilon}\,^{+\prime},N'\,|\,\vec{\mathrm{R}},N\rangle\,|^2\}_{\mathrm{av}}\,.\qquad(2.35\mathrm{a})$$

Finally, for the average $\{\,\}_{\mathrm{av}}$ we use the value of the function evaluated with ϵ' set equal to $\epsilon(R)=(N-N')\hbar\omega-[E_c(R)-E_d(R)]$ which, according to the Franck-Condon principle, is the same as

$$E-E'+(N-N')\hbar\omega-[(E_c(\infty)-E_d(\infty)]\,.$$

The implication attendant to this last approximation is that the angular momentum associated with the motion of the heavy particles is unaffected by the occurrence of photoionization (and/or autoionization).

Using this same approximation we replace E' with $E-\epsilon(R)+(N-N')\hbar\omega-[E_c(\infty)-E_d(\infty)]$ in the denominator factor of the first term in (2.34) and so obtain

$$\begin{aligned}
\langle\vec{\mathrm{R}}\,|\,F^+\,|\,\vec{\mathrm{R}}\,'\rangle_1&\doteq\delta(\vec{\mathrm{R}}-\vec{\mathrm{R}}\,')\mathscr{P}\sum_{N'}\int d\vec{\epsilon}\,'\rho(\vec{\epsilon}\,')\frac{|\langle\vec{\epsilon}\,^{+\prime},N'\,|\,\vec{\mathrm{R}},N\rangle|^2}{\epsilon(R)-\epsilon'}\\
&=\delta(\vec{\mathrm{R}}-\vec{\mathrm{R}}\,')\frac{1}{2\pi}\mathscr{P}\sum_{N'}\int d\epsilon'\frac{\Gamma(\epsilon',N'\,|\,\vec{\mathrm{R}},N)}{\epsilon(R)-\epsilon'}\,.
\end{aligned}\qquad(2.35\mathrm{b})$$

The function

$$\Gamma(\epsilon',N'\,|\,\vec{\mathrm{R}},N)\equiv 2\pi\int d\hat{\epsilon}'\rho(\vec{\epsilon}\,')\,|\,\langle\vec{\epsilon}^{\,+\prime},N'\,|\,\vec{\mathrm{R}},N\rangle\,|^2 \tag{2.36}$$

appearing here is the width of the state $|\phi_d\rangle$, associated with an ionizing electronic transition which is accompanied by the change $N\rightarrow N'$ in the number of laser photons. For the case depicted in Fig. 1(a) this is the photoionization width of the AB electronic configuration. We shall see in the following section that this width depends on the angle $\cos^{-1}(\hat{\alpha}\cdot\hat{R})$ between the internuclear axis and the photon polarization. In the case illustrated by Fig. 1(b) there are two contributing widths, one for photoionization and another for laser-free autoionization. The latter of these is independent of the orientation of the internuclear axis.

Combination of (2.35) and (2.36) produces the formula

$$\langle\vec{\mathrm{R}}\,|\,F^+\,|\,\vec{\mathrm{R}}\,'\rangle=\delta(\vec{\mathrm{R}}-\vec{\mathrm{R}}\,')\sum_{N'}\left[\frac{1}{2\pi}\mathscr{P}\int d\epsilon'\frac{\Gamma(\epsilon',N'\,|\,\vec{\mathrm{R}},N)}{\epsilon(R)-\epsilon'}-\frac{i}{2}\Gamma(\epsilon(R),N'\,|\,\vec{\mathrm{R}},N)\right] \tag{2.37}$$

for the local approximation to the channel coupling operator. And finally, if it is assumed as before that the function $\rho(\vec{\epsilon}\,')\,|\,\langle\vec{\epsilon}^{\,+\prime},N'\,|\,\vec{\mathrm{R}},N\rangle\,|^2$ in (2.36) has only a very weak dependence on the energy ϵ' of the ejected electron, the level shift [first term in (2.37)] then vanishes and the wave equation (2.30) reduces to

$$[T_{\vec{\mathrm{R}}}+\bar{V}_d(\vec{\mathrm{R}},\vec{\omega})-E]X_d^+(\vec{\mathrm{E}},N\,|\,\vec{\mathrm{R}})=0\ . \tag{2.38}$$

Here $\bar{V}_d(\vec{\mathrm{R}},\vec{\omega})$ denotes the complex valued potential function

$$\bar{V}_d(\vec{\mathrm{R}},\vec{\omega})=V_d(R)-\tfrac{1}{2}i\Gamma(\vec{\mathrm{R}},\vec{\omega})\ , \tag{2.39}$$

and

$$\Gamma(\vec{\mathrm{R}},\vec{\omega})=\sum_{N'}\Gamma(\epsilon(R),N'\,|\,\vec{\mathrm{R}},N) \tag{2.40}$$

with $\vec{\omega}=(\omega,\hat{\alpha})$, is the total width of the initial electronic state.

The objective of this section has now been achieved. Thus the task of computing the T matrix of Eq. (2.26) has been reduced to that of evaluating the electronic matrix elements E_d,E_c and $\langle\vec{\epsilon}\,',N'\,|\,\vec{\mathrm{R}},N\rangle$ and constructing scattering solutions of the two wave equations (2.23) and (2.38).

III. PHOTOIONIZATION TRANSITION AMPLITUDE

The quantity upon which the theory of the preceding section depends most crucially is the photoionization transition amplitude [cf. (2.27)]

$$\langle\vec{\epsilon}^{\,-},N-1\,|\,\vec{\mathrm{R}},N\rangle=\int d\vec{\mathrm{r}}\,\phi_{\vec{\epsilon}}^{-}(\vec{\mathrm{r}}\,|\,\vec{\mathrm{R}})^*\langle\!\langle\vec{\mathrm{r}},\vec{\mathrm{R}}\,|\,\langle N-1\,|\,H_{\mathrm{int}}\,|\,N\rangle\,|\,\vec{\mathrm{r}},\vec{\mathrm{R}}\rangle\!\rangle\phi_d(\vec{\mathrm{r}}\,|\,\vec{\mathrm{R}})\ . \tag{3.1}$$

It is shown in the Appendix that

$$\langle\!\langle\vec{\mathrm{r}},\vec{\mathrm{R}}\,|\,\langle N-1\,|\,H_{\mathrm{int}}\,|\,N\rangle\,|\,\vec{\mathrm{r}},\vec{\mathrm{R}}\rangle\!\rangle=i(2\pi I\hbar\omega/c)^{1/2}\hat{\alpha}\cdot\vec{\mathrm{d}}\ , \tag{3.2}$$

where $\vec{\mathrm{d}}\equiv-\sum_i e\vec{\mathrm{r}}_i$ denotes the contribution from the electrons to the electronic-dipole-moment operator and I is the incident flux of laser photons. This flux is given by $I=c(N/\Omega)$ with c the velocity of light and Ω the volume of the region to which the radiation field is confined.

The object $\phi_d(\vec{\mathrm{r}}\,|\,\vec{\mathrm{R}})$ appearing in (3.1) is the BO approximation to the wave function for the initial AB electronic state. This BO state is an eigenfunction, with eigenvalue Λ_i, of the operator $L_{\hat{R}}\equiv\hat{R}\cdot\sum_i^n\vec{\mathrm{r}}_i\times\vec{\mathrm{p}}_i$ for the component of electronic orbital angular momentum parallel to the internuclear axis. $\phi_{\vec{\epsilon}}^{\pm}$ is the corresponding BO wave function for the ionized, AB^++e^- electronic state. It is conventional[4,7,9] to use for this an n-electron CI wave function with Slater determinants composed of $n-1$ bound molecular orbitals, taken from the same set used to construct the CI approximation to $\phi_d(\vec{\mathrm{r}}\,|\,\vec{\mathrm{R}})$, plus a single continuum orbital with the partial-wave representation

$$\phi^{\pm}(\vec{\epsilon},\vec{\mathrm{r}}_i\,|\,\vec{\mathrm{R}})=\sum_{\lambda\mu}Y_{\lambda\mu}^*(\hat{\epsilon})_{\hat{R}}Y_{\lambda\mu}(\hat{r}_i)_{\hat{R}}i^{\lambda}e^{\pm i\sigma^{\lambda}}\mathscr{F}^{\lambda}(\epsilon,r_i\,|\,R)\ . \tag{3.3}$$

The subscripts $\hat{R}$ of the angular variables indicate the direction of the polar axis to which the spherical harmonics are referred. The absence of such a subscript implies reference to the (nonrotating) center-of-mass frame. The radial function $\mathscr{F}^{\lambda}(\epsilon,r_i\,|\,R)$ behaves asymptotically as a Coulomb wave function centered on nucleus B, i.e.,

$$\mathscr{F}^{\lambda}(\epsilon,r_i\,|\,R)\sim a(\epsilon)r_{iB}^{-1}\sin[kr_{iB}+k^{-1}\ln(2kr_{iB})-\tfrac{1}{2}\lambda\pi+\sigma^{\lambda}]$$

with $r_{iB} = |\vec{r}_i - \vec{R}_B|$ and $k = (2m_e\epsilon/\hbar^2)^{1/2}$ and where σ^λ is the Coulomb phase shift.

As a consequence of (3.2) and (3.3) the photoionization amplitude can be written as the sum of terms

$$\langle \vec{\epsilon}^{\,-}, N-1 \,|\, \vec{R}, N \rangle = i(2\pi I \hbar\omega/c)^{1/2} \sum_{\lambda\mu} i^{-\lambda} e^{i\sigma^\lambda} Y_{\lambda\mu}(\hat{\epsilon})_{\hat{R}} \langle \phi_{\epsilon\lambda\mu} \,|\, \hat{\alpha}\cdot\vec{d} \,|\, \phi_d \rangle \tag{3.4}$$

with $\phi_{\epsilon\lambda\mu}(\vec{r}\,|\,\vec{R})$ denoting a CI wave function constructed from $n-1$ bound orbitals and $Y_{\lambda\mu}(\hat{r}_i)_{\hat{R}}\mathscr{F}^\lambda(\epsilon, r_i\,|\,R)$. The state described by this function consists of an ejected electron with the projection quantum number μ and an $(n-1)$-electron "core" with an angular momentum projection quantum number Λ_f equal to that of the product AB^+ diatomic ion. The nuclear motion in this final state may, of course, be either bounded or unbounded. The photoionization amplitude of (3.4) is defined for states with prescribed values of $\Lambda_i(AB)$ and $\Lambda_f(AB^+)$ and so is specific to a transition for which $\mu_0 \equiv \Lambda_i - \Lambda_f$ has some definite numerical value.

The matrix elements appearing in (3.4) may be written more explicitly as

$$\langle \phi_{\epsilon\lambda\mu} \,|\, \hat{\alpha}\cdot\vec{d} \,|\, \phi_d \rangle = \sum_{m=0,\pm 1} (4\pi/3)^{1/2} Y^*_{1m}(\hat{\alpha})_{\hat{R}} \langle \phi_{\epsilon\lambda\mu} \,|\, d_m \,|\, \phi_d \rangle \;, \tag{3.5}$$

where the quantities $d_m \equiv \hat{e}_m \cdot \vec{d}$ are the spherical components $[\hat{e}_0 = \hat{R},\ \hat{e}_\pm = 2^{-1/2}(\hat{X} \pm i\hat{Y})]$ of the operator $\vec{d}$, referred to the rotating frame of reference with the orthonormal Cartesian basis $(\hat{X}, \hat{Y}, \hat{Z} = \hat{R})$. The selection rule for the matrix element $\langle \phi_{\epsilon\lambda\mu} \,|\, d_m \,|\, \phi_d \rangle$ is

$$\Lambda_f + \mu = m + \Lambda_i$$

or $\mu = \mu_0 + m$. Thus (3.4) becomes

$$\langle \vec{\epsilon}^{\,-}, N-1 \,|\, \vec{R}, N \rangle = (4\pi/3)^{1/2} \sum_{\lambda m} Y_{\lambda,\mu_0+m}(\hat{\epsilon})_{\hat{R}} Y^*_{1m}(\hat{\alpha})_{\hat{R}} V_{\epsilon\lambda,\mu_0+m}(R,\omega) \tag{3.6}$$

with

$$V_{\epsilon\lambda,\mu_0+m}(R,\omega) = i(2\pi I \hbar\omega/c)^{1/2} i^{-\lambda} e^{i\sigma^\lambda} \langle \phi_{\epsilon\lambda,\mu_0+m} \,|\, d_m \,|\, \phi_d \rangle \;. \tag{3.7}$$

The angular arguments of the spherical harmonics occurring in (3.6) are referred to a coordinate frame whose polar axis coincides with the direction of the internuclear axis. This expression for $\langle \vec{\epsilon}^{\,-}, N-1 \,|\, \vec{R}, N \rangle$ can be rewritten in the form

$$\langle \vec{\epsilon}^{\,-}, N-1 \,|\, \vec{R}, N \rangle = (4\pi/3)^{1/2} \sum_{\lambda,m} \sum_{\mu',m'} Y_{\lambda\mu'}(\hat{\epsilon}) Y_{1m'}(\hat{\alpha}) \mathscr{R}^{(\lambda)}_{\mu',\mu_0+m}(\hat{R}) \mathscr{R}^{(1)}_{m',-m}(\hat{R}) (-1)^m V_{\epsilon\lambda,\mu_0+m}(R,\omega) \;, \tag{3.8}$$

where the angular arguments of the spherical harmonics now are referred to the center-of-mass frame. The functions

$$\mathscr{R}^{(j)}_{mm'}(\hat{R}) \equiv \mathscr{R}^{(j)}_{mm'}(\phi,\theta,0)$$

are representation coefficients of the three-dimensional rotation group, as defined by Messiah.[10] Their arguments θ and ϕ are the polar spherical coordinates of the unit vector $\hat{R}$, measured in the center-of-mass frame. These representation coefficients are related in the manner

$$\mathscr{R}^{(j)}_{mm'}(\hat{R}) = r^{(j)}_{mm'}(\theta)\exp(-im\phi)$$

to functions $r^{(j)}_{mm'}(\theta)$ which are proportional to Jacobi polynomials.

Corresponding to (3.1), (3.6), and (3.8), respectively, are the three expressions[6]

$$\begin{aligned} \langle \vec{\epsilon}^{\,-}, N \,|\, \vec{R}, N \rangle &= \int d\vec{r}\, \phi^-_{\vec{\epsilon}}(\vec{r}\,|\,\vec{R})^* H_{\text{el}} \phi_d(\vec{r}\,|\,\vec{R}) \;, \\ &= \sum_\lambda Y_{\lambda\mu_0}(\hat{\epsilon})_{\hat{R}} V_{\epsilon\lambda\mu_0}(R) \;, \\ &= \sum_\lambda \sum_{\mu'} Y_{\lambda\mu'}(\hat{\epsilon}) \mathscr{R}^{(\lambda)}_{\mu'\mu_0}(\hat{R}) V_{\epsilon\lambda\mu_0}(R) \end{aligned} \tag{3.9}$$

for the transition amplitude for *laser-free* autoionization. Here

$$V_{\epsilon\lambda\mu_0}(R) = i^{-\lambda} e^{i\sigma^\lambda} \langle \phi_{\epsilon\lambda\mu_0} \,|\, H_{\text{el}} \,|\, \phi_d \rangle \tag{3.10}$$

is a matrix element of the electronic energy operator H_{el}. The significant difference between the formulas for the photoionization and autoionization amplitudes is due, of course, to the different tensor ranks of the associated vector and scalar operators $\vec{d}$ and H_{el}, respectively. Dipole absorption of a laser photon may leave unaltered the projection quantum number of the total electronic orbital angular momentum or it may change it by one. Only the first of these is possible in laser-free autoionization.

The expressions (3.6) and (3.9) lead from the definition (2.36) to the two formulas

$$\Gamma(\epsilon,N\,|\,\vec{\mathrm{R}},N)=2\pi\rho(\epsilon)\sum_{\lambda}|\,V_{\epsilon\lambda\mu_0}(R)\,|^2\,, \tag{3.11}$$

and

$$\Gamma(\epsilon,N-1\,|\,\vec{\mathrm{R}},N)=2\pi\rho(\epsilon)\sum_{m}\big|(4\pi/3)^{1/2}Y_{1m}(\hat{\alpha})_{\hat{R}}\,\big|^2\sum_{\lambda}|\,V_{\epsilon\lambda,\mu_0+m}(R,\omega)\,\big|^2 \tag{3.12}$$

for the widths specific to autoionization and photoionization, respectively. The second of these can be written in the alternative form

$$\Gamma(\epsilon,N-1\,|\,\vec{\mathrm{R}},N)=\tfrac{1}{2}(\Gamma_1+\Gamma_{-1})+\tfrac{1}{2}(2\Gamma_0-\Gamma_1-\Gamma_{-1})(\hat{\alpha}\cdot\hat{R})^2 \tag{3.13}$$

with

$$\begin{aligned}\Gamma_m(\epsilon,\omega\,|\,R)&\equiv 2\pi\rho(\epsilon)\sum_{\lambda}|\,V_{\epsilon\lambda,\mu_0+m}(R,\omega)\,|^2\\ &=\hbar[4\pi^2\rho(\epsilon)I\hbar\omega\alpha]\sum_{\lambda}|\,\langle\phi_{\epsilon\lambda,\mu_0+m}\,|\,(d_m/e)\,|\,\phi_d\rangle\,|^2\,,\end{aligned} \tag{3.14}$$

and where $\alpha\equiv e^2/\hbar c$ is the fine-structure constant.

It is readily verified that $\hbar^{-1}\Gamma(\epsilon,N-1\,|\,\vec{\mathrm{R}},N)$ equals the absorption rate of polarized ($\hat{\alpha}$) photons by an AB "molecule" with fixed internuclear separation and orientation; $\hbar^{-1}\Gamma_m(\epsilon,\omega\,|\,R)$ is the rate of absorption by the $\hat{e}_m$ component of the electric dipole moment, a process which changes by $m\hbar$ the component of total electronic orbital angular momentum along the internuclear axis. Finally, the orientation average of the absorption rate given by (3.13) is

$$\begin{aligned}\hbar^{-1}\Gamma(\epsilon,N-1\,|\,R,N)&\equiv(4\pi)^{-1}\int d\hat{R}\,\hbar^{-1}\Gamma(\epsilon,N-1\,|\,\vec{\mathrm{R}}N)=\tfrac{1}{3}\sum_{m}\hbar^{-1}\Gamma_m(\epsilon,\omega\,|\,R)\\ &=\frac{4\pi^2}{3}\rho(\epsilon)I\hbar\omega\alpha\sum_{\lambda}\sum_{m}|\,\langle\phi_{\epsilon\lambda,\mu_0+m}\,|\,(d_m/e)\,|\,\phi_d\rangle\,|^2\,.\end{aligned} \tag{3.15}$$

In the particular case considered here these photoabsorption rates are, of course, rates of photoionization as well.

IV. CROSS SECTIONS

The analysis now will be carried a step further by resolving the solutions of the various wave equations into partial waves and thereby replacing them with ordinary differential equations for the radial components of the channel amplitudes. The relevant differential and integral cross sections then will be expressed in terms of the solutions of these equations.

Because the imaginary part of the complex potential $\bar{V}_d(\vec{\mathrm{R}},\vec{\omega})$ is noncentral, the radial wave functions associated with the partial-wave expansion of $X_d^+(\vec{\mathrm{E}},N\,|\,\vec{\mathrm{R}})$ depend not only upon the orbital angular momentum numbers L, but on the corresponding projection quantum numbers M as well. Furthermore, $\Gamma(\epsilon,N-1\,|\,\vec{\mathrm{R}},N)$ given by (3.12) couples each partial wave to four others; thus the L wave is coupled to those with the orbital angular momentum quantum numbers $L\pm1$ and $L\pm2$. There is, of course, nothing to prevent us from conducting a partial-wave analysis of X_d^+ which would incorporate these effects of the noncentral complex potential. However, the inclusion of these effects produces cross-section formulas which are quite complex and, in our opinion, unnecessarily so. Indeed, if it were our intention to determine only the lowest-order (first) dependence of the cross sections on the laser intensity, we could completely neglect the orientation (and laser intensity) dependent photoionization contribution to $\Gamma(\vec{\mathrm{R}},\vec{\omega})$. The somewhat less restrictive approximation that we actually shall adopt is to replace $\Gamma(\vec{\mathrm{R}},\vec{\omega})$ with its angle average $\Gamma(R,\omega)$, i.e., the factor $(\hat{\alpha}\cdot\hat{R})^2$ in (3.12a) is replaced with

$$(4\pi)^{-1}\int d\hat{R}(\hat{\alpha}\cdot\hat{R})^2=\tfrac{1}{3}\,.$$

To this approximation $\bar{V}_d(\vec{\mathrm{R}},\vec{\omega})$ becomes

$$\bar{V}_d(R,\omega)\equiv V_d(R)-\tfrac{1}{2}i\Gamma(R,\omega)$$

and the partial-wave expansion of the initial (i) state wave function can be written in the conventional form[6]

$$X_d^{+}(\vec{\mathrm{E}},N\,|\,\vec{\mathrm{R}})=\sum_{L,M} Y_{LM}^{*}(\hat{K}_i)Y_{LM}(\hat{R})i^{L}e^{i\bar{\eta}_i^{L}} \times R^{-1}\bar{F}_i^{L}(E,N\,|\,R)\;. \tag{4.1}$$

The bars over the phase shift $\bar{\eta}_i^{L}$ and the radial amplitude $\bar{F}_i^{L}$ indicate that these functions are complex valued. We adopt for X_d^{+} the energy delta-function normalization

$$\langle X_d^{+}(\vec{\mathrm{E}},N)\,|\,X_d^{+}(\vec{\mathrm{E}}\,',N)\rangle=\delta(\vec{\mathrm{E}}-\vec{\mathrm{E}}\,')$$
$$\equiv\delta(E-E')\delta(\hat{K}_i-\hat{K}_i')\;.$$

The radial wave functions $\bar{F}_i^{L}$ are the solutions of the ordinary differential equations [gotten from (2.38) and (4.1)]

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2}+\frac{\hbar^2L(L+1)}{2\mu R^2}+V_d(R)-\tfrac{1}{2}i\Gamma(R,\omega)-E\right]\bar{F}_i^{L}(E,N\,|\,R)=0\;, \tag{4.2}$$

which behave regularly at the origin and have the asymptotic forms

$$\bar{F}_i^{L}(E,N\,|\,R)\sim(2\mu/\pi\hbar^2K_i)^{1/2}\sin(K_iR-\tfrac{1}{2}\pi L+\bar{\eta}_i^{L})\;. \tag{4.3}$$

Here $K_i=(2\mu E/\hbar^2)^{1/2}$ is the magnitude of the propagation vector $\vec{\mathrm{K}}_i\equiv K_i\hat{K}_i$ associated with the initial relative motion of the two colliding atoms.

A. Laser-induced Penning ionization

The wave functions $\Psi_{\vec{F}}^{\pm}$ for unbound ($E'>0$) final (f) states of the AB^{+} molecular ion can be written in the form

$$\Psi_{\vec{F}}^{\pm}(\vec{\mathrm{E}}\,',N'\,|\,\vec{\mathrm{R}})=\sum_{L'M'} Y_{L'M'}^{*}(\hat{K}_f)Y_{L'M'}(\hat{R})i^{L'}e^{\pm i\eta_f^{L'}}R^{-1}F_f^{L'}(E',N'\,|\,R)\;. \tag{4.4}$$

These functions are normalized to energy delta functions. The channel amplitudes $F_f^{L'}$ are real valued functions which satisfy the differential equations [from (2.23) to (4.4)]

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2}+\frac{\hbar^2L'(L'+1)}{2\mu R^2}+V_c(R)-E'\right]F_f^{L'}(E',N'\,|\,R)=0\;, \tag{4.5}$$

are regular at the origin, and have the asymptotic forms

$$F_f^{L'}(E',N'\,|\,R)\sim(2\mu/\pi\hbar^2K_f)^{1/2}\sin(K_fR-\tfrac{1}{2}\pi L'+\eta_f^{L'})\;, \tag{4.6}$$

wherein $K_f=(2\mu E'/\hbar^2)^{1/2}$.

By substituting (3.8), (4.1), and (4.4) into the defining formula (2.26) we obtain for $T(\vec{\mathrm{E}}\,',\vec{\epsilon}\,|\,\vec{\mathrm{E}})$ the expression

$$T(\vec{\mathrm{E}}\,',\vec{\epsilon}\,|\,\vec{\mathrm{E}})=\sum_{\substack{LM\\L'M'}}\;\sum_{\substack{\lambda\\ \mu'm'}} Y_{LM}^{*}(\hat{K}_i)Y_{L'M'}(\hat{K}_f)Y_{\lambda\mu'}(\hat{\epsilon})Y_{1m'}(\hat{\alpha})[4\pi(2L+1)(2L'+1)/3]^{1/2} \times(-1)^{M'}i^{L-L'}e^{i(\bar{\eta}_i^{L}+\eta_f^{L'})}\bar{T}_{\mu'm'}(E'L'M',ELM,\epsilon\lambda;\omega) \tag{4.7}$$

with

$$\bar{T}_{\mu'm'}(E'L'M',ELM,\epsilon\lambda;\omega)=\sum_{m}A_m(LL'\lambda 1\,|\,MM'\mu'm')\bar{T}(E'L',EL,\epsilon\lambda m;\omega)\;, \tag{4.8}$$

and where

$$\bar{T}(E'L',EL,\epsilon\lambda m;\omega)=(-1)^{m}\langle F_f^{L'}(E',N-1\,|\,R)\,|\,V_{\epsilon\lambda,\mu_0+m}(R,\omega)\,|\,\bar{F}_i^{L}(E,N\,|\,R)\rangle \tag{4.9}$$

$$A_m(LL'\lambda 1\,|\,MM'\mu'm')=\sum_{J'\Omega}(2J'+1)\begin{pmatrix}1 & \lambda & J'\\ m' & \mu' & -\Omega\end{pmatrix}\begin{pmatrix}1 & \lambda & J'\\ -m & \mu_0+m & -\mu_0\end{pmatrix} \times\sum_{J}\frac{2J+1}{4\pi}\begin{pmatrix}L & L' & J\\ -M & M' & \Omega\end{pmatrix}\begin{pmatrix}L & L' & J\\ 0 & 0 & 0\end{pmatrix}\left[\int d\hat{R}\,\mathscr{R}^{(J')*}_{-\Omega,-\mu_0}(\hat{R})\mathscr{R}^{(J)}_{-\Omega,0}(\hat{R})\right]\;. \tag{4.10}$$

The polar axis of the center-of-mass frame will now be chosen to coincide with the initial direction of the relative *A*-*B* motion, that is,

$$\hat{K}_i=(\theta_i,\phi_i)=(0,0)\ .$$

This reduces (4.7) to the form

$$T(\vec{\mathrm{E}}',\vec{\epsilon}\,|\,\vec{\mathrm{E}})=\sum_{L'M'}\sum_{\lambda\mu'm'}Y_{L'M'}(\hat{K}_f)Y_{\lambda\mu'}(\hat{\epsilon})Y_{1m'}(\hat{\alpha})[(2L'+1)/3]^{1/2} \times(-1)^{M'}\sum_{L}(2L+1)i^{L-L'}e^{i(\bar{\eta}_i^L+\eta_f^{L'})}\bar{T}_{\mu'm'}(E'L'M',EL\,0,\epsilon\lambda;\omega)\ , \tag{4.11}$$

where it is here and henceforth to be understood that the angular coordinates of $\hat{K}_f$, $\hat{\epsilon}$, and $\hat{\alpha}$ are measured from the initial direction of the relative nuclear motion $\hat{K}_i$.

The generalized differential cross section[6]

$$\frac{d^4\sigma}{d\epsilon\, d\hat{\epsilon}\, dE'd\hat{K}_f}=\frac{g_i}{f}\frac{d^4W}{d\vec{\epsilon}\,d\vec{\mathrm{E}}'}=g_i\frac{(2\pi)^3\hbar}{K_i^2}\frac{2\pi}{\hbar}\,|\,T(\vec{\mathrm{E}}',\vec{\epsilon}\,|\,\vec{\mathrm{E}})\,|^2\delta(E_i-E_f)\rho(E)\rho(\vec{\mathrm{E}}')\rho(\vec{\epsilon}) \tag{4.12}$$

is the product of g_i, the statistical weight of the initial state, and the $i\rightarrow f$ transition rate $d^4W/d\vec{\epsilon}\,d\vec{\mathrm{E}}'$, divided by the incident flux,

$$f\equiv|\,X_d^{+}(\vec{\mathrm{E}},N\mid\infty)\,|^2(\hbar K_i/\mu)\rho(E)^{-1}=[K_i^2/(2\pi)^3\hbar\rho(E)]\ .$$

The energies of the initial and final states are

$$E_i=E+N\hbar\omega+E_d(\infty)$$

and

$$E_f=E'+\epsilon+(N-1)\hbar\omega+E_c(\infty)\ ,$$

respectively. From this general expression we immediately obtain the two triple-differential cross sections

$$\frac{d^3\sigma}{d\epsilon\, d\hat{\epsilon}\, d\hat{K}_f}(E,\epsilon)=g_i\frac{(2\pi)^4}{K_i^2}\,|\,T(\vec{\mathrm{E}}_0',\vec{\epsilon}\,|\,\vec{\mathrm{E}})\,|^2\rho(E)\rho(\vec{\mathrm{E}}_0')\rho(\vec{\epsilon})\ , \tag{4.13a}$$

and

$$\frac{d^3\sigma}{d\hat{\epsilon}\, dE'd\hat{K}_f}(E,E')=g_i\frac{(2\pi)^4}{K_i^2}\,|\,T(\vec{\mathrm{E}}',\vec{\epsilon}_0\,|\,\vec{\mathrm{E}})\,|^2\rho(E)\rho(\vec{\mathrm{E}}')\rho(\vec{\epsilon}_0) \tag{4.13b}$$

with $E_0'=E-\epsilon+\hbar\omega-[E_c(\infty)-E_d(\infty)]$ and $\epsilon_0=E-E'+\hbar\omega-[E_c(\infty)-E_d(\infty)]$. For convenience, we now select

$$\rho(E)=\rho(\vec{\mathrm{E}}')=\rho(\vec{\epsilon})=1\ .$$

To the best of our knowledge, the angular coincidence measurements for which the cross sections (4.13) are descriptive have not yet been made. More closely related to current experimental studies are the two angle-energy double-differential cross sections

$$\frac{d^2\sigma}{d\epsilon\, d\hat{\epsilon}}(E,\epsilon)=g_i\frac{(2\pi)^4}{3K_i^2}\sum_{L'M'}(2L'+1)\left|\sum_{\lambda\mu'm'}Y_{\lambda\mu'}(\hat{\epsilon})Y_{1m'}(\hat{\alpha}) \times\sum_{L}(2L+1)i^{L}e^{i\bar{\eta}_i^L}\bar{T}_{\mu'm'}(E_0'L'M',EL\,0,\epsilon\lambda;\omega)\right|^2 , \tag{4.14}$$

and

$$\frac{d^2\sigma}{d\epsilon\, d\hat{K}_f}(E,\epsilon)=g_i\frac{(2\pi)^4}{3K_i^2}\sum_{\lambda\mu'}\left|\sum_{L'M'm'}Y_{L'M'}(\hat{K}_f)Y_{1m'}(\hat{\alpha})(2L'+1)^{1/2} \times(-1)^{M'}\sum_{L}(2L+1)i^{L-L'}e^{i(\bar{\eta}_i^L+\eta_f^{L'})}\bar{T}_{\mu'm'}(E_0'L'M',EL\,0,\epsilon\lambda;\omega)\right|^2 , \tag{4.15}$$

gotten by integrating (4.13a). Both of these have as their integrals the electron energy differential cross section

$$\frac{d\sigma}{d\epsilon}(E,\epsilon)=g_i\frac{(2\pi)^4}{3K_i^2}\sum_{L'M'}(2L'+1)\sum_{\lambda\mu'}\left|\sum_{m'}Y_{1m'}(\hat{\alpha})\sum_{L}(2L+1)i^L e^{i\bar{\eta}_i^L}\bar{T}_{\mu'm'}(E_0'L'M',EL\,0,\epsilon\lambda;\omega)\right|^2 . \tag{4.16}$$

The three analogous cross-section formulas that can be obtained from (4.13b) are trivially related to those given by equations (4.14), (4.15), and (4.16). Thus as a consequence of energy conservation, the only differences between the formulas for $d^2\sigma/dE'd\hat{\epsilon}$, $d^2\sigma/dE'd\hat{K}_f$, and $d\sigma/dE'$ and their respective analogs $d^2\sigma/d\epsilon\, d\hat{\epsilon}$, $d^2\sigma/d\epsilon\, d\hat{K}_f$, and $d\sigma/d\epsilon$ is that in each case $\bar{T}_{\mu'm'}(E'L'M',EL\,0,\epsilon_0\lambda;\omega)$ appears in place of $\bar{T}_{\mu'm'}(E_0'L'M',EL\,0,\epsilon\lambda;\omega)$.

The cross-section formulas (4.13)—(4.16) are the results we have been seeking. However, they are somewhat too complex to be readily interpreted. To aid in this interpretation we introduce the approximation

$$i^L e^{i\bar{\eta}_i^L}\bar{T}(E'L',EL,\epsilon\lambda m;\omega)\approx i^{L'}e^{i\bar{\eta}_i^{L'}}\bar{T}(E'L',EL',\epsilon\lambda m;\omega) , \tag{4.17}$$

which should be of little numerical consequence provided that a large number of partial waves contribute to the cross sections. Equation (4.17) is virtually identical to one of the approximations that Hickman and Morgner[11] used to reduce a general formula for the cross section for *laser-free* Penning ionization to Miller's[2] much simpler expression. This approximation is particularly valid provided that $\bar{T}$ is appreciable only for small values of λ, as usually will be the case.

The approximation to the T matrix that results from substituting (4.17) into (4.11) is

$$T(\vec{\mathrm{E}}',\vec{\epsilon}\,|\,\vec{\mathrm{E}})=\sum_{L'}\sum_{\lambda m'}Y_{L'0}(\hat{K}_f)Y_{\lambda,-m'}(\hat{\epsilon})Y_{1m'}(\hat{\alpha})[(2L'+1)/3]^{1/2}e^{i(\bar{\eta}_i^{L'}+\eta_f^{L'})}\bar{T}_{m'}(E'L',EL',\epsilon\lambda;\omega) \tag{4.18}$$

with

$$\bar{T}_{m'}(E'L',EL',\epsilon\lambda;\omega)=\sum_{m}A_m(\lambda\,|\,m')\bar{T}(E'L',EL',\epsilon\lambda m;\omega) , \tag{4.19}$$

and where

$$A_m(\lambda\,|\,m')=\sum_{J'}(2J'+1)\begin{pmatrix}1 & \lambda & J'\\ m' & -m' & 0\end{pmatrix}\begin{pmatrix}1 & \lambda & J'\\ -m & \mu_0+m & -\mu_0\end{pmatrix}\sum_{J}\frac{2J+1}{4\pi}\left[\int d\hat{R}\,\mathscr{R}_{0,-\mu_0}^{(J')*}(\hat{R})\mathscr{R}_{0,0}^{(J)}(\hat{R})\right] . \tag{4.20}$$

In the special case of $\mu_0=0$, $A_m(\lambda,m')=\delta_{m,-m'}$, and $\bar{T}_{m'}(E'L',EL',\epsilon\lambda;\omega)=\bar{T}(E'L',EL',\epsilon\lambda-m';\omega)$. The corresponding approximations to the cross-section formulas (4.14), (4.15), and (4.16) are

$$\frac{d^2\sigma}{d\epsilon\,d\hat{\epsilon}}(E,\epsilon)=g_i\frac{(2\pi)^4}{3K_i^2}\sum_{L'}(2L'+1)e^{-2Im\bar{\eta}_i^{L'}}\left|\sum_{\lambda m'}Y_{\lambda,-m'}(\hat{\epsilon})Y_{1m'}(\hat{\alpha})\bar{T}_{m'}(E_0'L',EL',\epsilon\lambda;\omega)\right|^2 , \tag{4.14$'$}$$

$$\begin{aligned}\frac{d^2\sigma}{d\epsilon\,d\hat{K}_f}(E,\epsilon)&=g_i\frac{(2\pi)^4}{3K_i^2}\sum_{m'}|\,Y_{1m'}(\hat{\alpha})\,|^2\left[\sum_{\lambda}\left|\sum_{L'}Y_{L'0}(\hat{K}_f)(2L'+1)^{1/2}e^{i(\bar{\eta}_i^{L'}+\eta_f^{L'})}\bar{T}_{m'}(E_0'L',EL',\epsilon\lambda;\omega)\right|^2\right]\\ &=[B_1^{\mathrm{PI}}(\theta_f)+B_{-1}^{\mathrm{PI}}(\theta_f)]+[2B_0^{\mathrm{PI}}(\theta_f)-B_1^{\mathrm{PI}}(\theta_f)-B_{-1}^{\mathrm{PI}}(\theta_f)]\cos^2\theta_\alpha ,\end{aligned} \tag{4.15$'$}$$

and

$$\begin{aligned}\frac{d\sigma}{d\epsilon}(E,\epsilon)&=g_i\frac{(2\pi)^4}{3K_i^2}\sum_{m'}|\,Y_{1m'}(\hat{\alpha})\,|^2\left[\sum_{L'}(2L'+1)e^{-2Im\bar{\eta}_i^{L'}}\sum_{\lambda}|\,\bar{T}_{m'}(E_0'L',EL',\epsilon\lambda;\omega)\,|^2\right]\\ &=(B_1^{\mathrm{PI}}+B_{-1}^{\mathrm{PI}})+(2B_0^{\mathrm{PI}}-B_1^{\mathrm{PI}}-B_{-1}^{\mathrm{PI}})\cos^2\theta_\alpha ,\end{aligned} \tag{4.16$'$}$$

wherein

$$B_{m'}^{\mathrm{PI}}(\theta_f\,|\,E,\epsilon)=g_i\frac{\pi^2}{2K_i^2}\sum_{\lambda}\left|\sum_{L'}(2L'+1)P_{L'}(\cos\theta_f)e^{i(\bar{\eta}_i^{L'}+\eta_f^{L'})}\bar{T}_{m'}(E_0'L',EL',\epsilon\lambda;\omega)\right|^2 , \tag{4.21a}$$

and

$$B^{\mathrm{PI}}_{m'}(E,\epsilon)=\int d\hat{K}_f B^{\mathrm{PI}}_{m'}(\theta_f\,|\,E,\epsilon)$$

$$=g_i\frac{2\pi^3}{K_i^2}\sum_{L'}(2L'+1)e^{-2Im\bar{\eta}_i^{L'}}\sum_{\lambda}|\,\bar{T}_{m'}(E'_0L',EL',\epsilon\lambda;\omega)\,|^2\,. \tag{4.21b}$$

The variables θ_α and θ_f appearing in these formulas are the angles between the initial direction of relative motion, $\hat{K}_i$, and the unit vectors $\hat{\alpha}$ and $\hat{K}_f$, respectively.

B. Laser-induced associative ionization

In the case of associative ionization ($E'<0$) the final state of the AB^+ molecular ion can be labeled with the three quantum numbers n' (vibrational), L', and M' and represented by the square-integrable wave function (cf. Sec. II)

$$\Psi_P^{M'}(E_{n'}^{L'},N'\,|\,\vec{\mathrm{R}})=Y_{L'M'}(\hat{R})R^{-1}F_f^{L'}(E_{n'}^{L'},N'\,|\,R)\,. \tag{4.22}$$

Here $F_f^{L'}$ is the eigenfunction associated with the ordinary differential equation

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2}+\frac{\hbar^2L'(L'+1)}{2\mu R^2}+V_c(R)-E_{n'}^{L'}\right]F_f^{L'}(E_{n'}^{L'},N'\,|\,R)=0\,. \tag{4.23}$$

Corresponding to (4.11) is the formula

$$T(E_{n'}^{L'},\vec{\epsilon}\,|\,\vec{\mathrm{E}})=\sum_{\lambda\mu'm'}Y_{\lambda\mu'}(\hat{\epsilon})Y_{1m'}(\hat{\alpha})[(2L'+1)/3]^{1/2}(-1)^{M'}\sum_L(2L+1)i^Le^{i\bar{\eta}_i^L}\bar{T}_{\mu'm'}(E_{n'}^{L'}L'M',EL\,0,\epsilon\lambda;\omega) \tag{4.24}$$

with $\bar{T}_{\mu'm'}(E_{n'}^{L'}L'M',ELM,\epsilon\lambda;\omega)$ related to

$$\bar{T}(E_{n'}^{L'}L',EL,\epsilon\lambda m\,;\omega)\equiv(-1)^m\langle F_f^{L'}(E_{n'}^{L'},N-1\,|\,R)\,|\,V_{\epsilon\lambda,\mu_0+m}(R,\omega)\,|\,\bar{F}_i^L(E,N\,|\,R)\rangle \tag{4.25}$$

by Eq. (4.8). $T(E_{n'}^{L'},\vec{\epsilon}\,|\,\vec{\mathrm{E}})$ given by (4.24) is the T matrix specific to a laser-induced associative ionization event which deposits the molecular ion in the state labeled $n'L'M'$. The energy of the electron produced by this event is

$$\epsilon_{\mathrm{AI}}=\epsilon(E,E_{n'}^{L'},\omega)\equiv E-E_{n'}^{L'}+\hbar\omega-[E_c(\infty)-E_d(\infty)]\,. \tag{4.26}$$

Analogous to $d^2\sigma/d\epsilon\,d\hat{\epsilon}$ of (4.14) is the angular differential cross section

$$\frac{d\sigma_{n'L'M'}}{d\hat{\epsilon}}(E)=g_i\frac{(2\pi)^4}{3K_i^2}(2L'+1)\left|\sum_{\lambda\mu'm'}Y_{\lambda\mu'}(\hat{\epsilon})Y_{1m'}(\hat{\alpha})\sum_L(2L+1)i^Le^{i\bar{\eta}_i^L}\bar{T}_{\mu'm'}(E_{n'}^{L'}L'M',EL\,0,\epsilon_{\mathrm{AI}}\lambda;\omega)\right|^2 \tag{4.27}$$

for the electrons ejected in transitions to a particular vibronic state of the product diatomic ion. The corresponding analog to $d\sigma/d\epsilon$ of (4.16) is the integral cross section

$$\sigma_{n'L'M'}(E)=g_i\frac{(2\pi)^4}{3K_i^2}(2L'+1)\sum_{\lambda\mu'}\left|\sum_{m'}Y_{1m'}(\hat{\alpha})\sum_L(2L+1)i^Le^{i\bar{\eta}_i^L}\bar{T}_{\mu'm'}(E_{n'}^{L'}L'M',EL\,0,\epsilon_{\mathrm{AI}}\lambda;\omega)\right|^2\,. \tag{4.28}$$

The approximation (4.17) reduces the T matrix of (4.24) to

$$T(E_{n'}^{L'},\vec{\epsilon}\,|\,\vec{\mathrm{E}})=\delta_{M'0}\sum_{\lambda m'}Y_{\lambda,-m'}(\hat{\epsilon})Y_{1m'}(\hat{\alpha})[(2L'+1)/3]^{1/2}i^{L'}e^{i\bar{\eta}_i^{L'}}\bar{T}_{m'}(E_{n'}^{L'}L',EL',\epsilon\lambda;\omega) \tag{4.29}$$

with $\bar{T}_{m'}(E_{n'}^{L'}L',EL',\epsilon\lambda;\omega)$ defined analogously to $\bar{T}_{m'}(E'L',EL,\epsilon\lambda;\omega)$ of (4.19). The counterparts to the cross-section formulas (4.27) and (4.28) are

$$\frac{d\sigma_{n'L'M'}}{d\hat{\epsilon}}(E)=\delta_{M'0}\left[g_i\frac{(2\pi)^4}{3K_i^2}(2L'+1)e^{-2Im\bar{\eta}_i^{L'}}\left|\sum_{\lambda m'}Y_{\lambda,-m'}(\hat{\epsilon})Y_{1m'}(\hat{\alpha})\overline{T}_{m'}(E_{n'}^{L'}L',EL',\epsilon_{\rm AI}\lambda;\omega)\right|^2\right], \tag{4.30}$$

and

$$\begin{aligned}\sigma_{n'L'M'}(E)&=\delta_{M'0}\left[g_i\frac{(2\pi)^4}{3K_i^2}(2L'+1)e^{-2Im\bar{\eta}_i^{L'}}\sum_{m'}|Y_{1m'}(\hat{\alpha})|^2\sum_{\lambda}|\overline{T}_{m'}(E_{n'}^{L'}L',EL',\epsilon_{\rm AI}\lambda;\omega)|^2\right]\\&=\delta_{m'0}[(B_1^{\rm AI}+B_{-1}^{\rm AI})+(2B_0^{\rm AI}-B_1^{\rm AI}-B_{-1}^{\rm AI})\cos^2\theta_\alpha]\,,\end{aligned} \tag{4.31}$$

respectively. And finally, the coefficients

$$B_{m'}^{\rm AI}(E)\equiv g_i\frac{2\pi^3}{K_i^2}(2L'+1)e^{-2Im\bar{\eta}_i^{L'}}\times\sum_{\lambda}|\overline{T}_{m'}(E_{n'}^{L'}L',EL',\epsilon_{\rm AI}\lambda;\omega)|^2 \tag{4.32}$$

appearing in (4.31) are the AI analogs to the PI functions defined by (4.21b).

It is not our intention to deal here with the computational aspects of this theory. Nevertheless, it is worth noting that these appear to be no more difficult nor, indeed, even much different from those encountered in the comparable theory of FF chemi-ionization. The latter already have been treated in considerable detail by Hickman and Morgner[11] and, even more thoroughly, by Bieniek.[6] The sole—but not insignificant—difference between the two is that one involves amplitudes for FF autoionization while the other requires a computation of the photoionization transition amplitudes, as functions of internuclear separation and laser polarization.

It is natural to attempt to simplify the task of solving the wave equations (2.38) and/or (4.2) by neglecting the imaginary part of the complex potential which determines the initial-state wave function X_d^+ and the associated set of complex valued channel amplitudes $\bar{F}_i^L$. The solutions of the resulting equations are real valued functions F_i^L. One obvious and possibly significant consequence of this approximation is that it sets equal to unity all of the "survival factors" $\exp(-2Im\bar{\eta}_i^L)$. A clever way of correcting for this deficiency has been proposed by Bieniek,[6] who constructed Born-type estimates of the functions $Im\bar{\eta}_i^L$ from the approximate channel amplitude F_i^L. He then showed (for one special system) that the cross sections obtained from this approximate theory differed by only a few percent from those gotten by computing the complex valued amplitudes $\bar{F}_i^L$.

V. CLOSING REMARKS

The photon polarization dependence of the cross-section formulas derived in the preceding section is a direct consequence of the familiar polarization dependence of the photoabsorption (photoionization) amplitude characteristic of electric dipole transitions. The cross-section dependence is on the orientation of the polarization vector $\hat{\alpha}$, relative to a center-of-mass frame whose polar axis is parallel to $\hat{K}_i$, the initial direction of relative motion of the colliding *AB* pair. The direction of this experimentally controllable vector is essentially coincident with that of the internuclear axis and so the theoretical prediction is completely in accordance with what one would expect intuitively. This dependence is not at all unique to the LI chemi-ionization processes studied here. To the contrary, it is a behavior common to all laser modified processes involving collisions between atomic or ionic species. And indeed, similar but more subtle effects are to be expected in laser modified *molecular* collisions as well, especially those involving oriented molecules.

This polarization dependence of the cross sections was not evident in our recent classical path theory[1] because we inadvertently ignored the dependence of the photoionization and photoexcitation rates on the relative orientation of the internuclear axis and the photon polarization. However, now that this dependence has been recognized it easily can be incorporated into the classical path theory.

The semiclassical limit of the theory presented here already has been constructed and will be presented in subsequent communications. Exploratory numerical studies based on this and on the corresponding classical path theories are in progress. Finally, a number of extensions of the theory are being developed.

ACKNOWLEDGMENT

This research was supported by grants from the National Science Foundation and NATO.

APPENDIX

The interaction between the charged particles and the electromagnetic field is given by the expression[12]

$$H_{\rm int}=\sum_{i=1}^{n}\left[-\frac{e}{m_e c}\vec{p}_i\cdot\vec{A}(\vec{r}_i)+\frac{e^2}{2m_e c^2}\vec{A}(\vec{r}_i)\cdot\vec{A}(\vec{r}_i)\right]+\sum_{\alpha=A,B}\left[\frac{Z_\alpha e}{M_\alpha c}\vec{p}_\alpha\cdot\vec{A}(\vec{r}_\alpha)+\frac{Z_\alpha^2 e^2}{2M_\alpha c^2}\vec{A}(\vec{r}_\alpha)\cdot\vec{A}(\vec{r}_\alpha)\right]. \tag{A1}$$

Here, $\vec{r}_i$ and $\vec{p}_i$ ($\vec{r}_\alpha$ and $\vec{p}_\alpha$) denote the position and momentum operators of electron i (nucleus α) whose mass and charge are m_e and $-e$ (M_α and $Z_\alpha e$), respectively. $\vec{A}(\vec{r})$ is the vector potential of the transverse (div $\vec{A}=0$) field. This potential is related by the formula[12]

$$\vec{A}(\vec{r})=\left[\frac{2\pi\hbar c^2}{\Omega\omega}\right]^{1/2}\sum_{\hat{\kappa},\mu}\hat{\alpha}_\mu(a_{\vec{\kappa}\mu}e^{i\vec{\kappa}\cdot\vec{r}}+a^{\dagger}_{\vec{\kappa}\mu}e^{-i\vec{\kappa}\cdot\vec{r}}) \tag{A2}$$

to the creation and annihilation operators $a^{\dagger}_{\vec{\kappa}\mu}$ and $a_{\vec{\kappa}\mu}$ for photons with momenta $\hbar\vec{\kappa}$, energy $\hbar\omega=\hbar\kappa c$, and polarization $\hat{\alpha}_\mu$ ($\mu=1,2$). The sums over $\hat{\kappa}=\vec{\kappa}/\kappa$ and μ contract to a single term for the plane polarized, single mode laser to which our theory applies.

Since we only shall be concerned with electric dipole transitions, the factors of $\exp(\pm i\vec{\kappa}\cdot\vec{r})$ can be replaced with unity. Furthermore, we ignore the terms of $H_{\rm int}$ which depend quadratically on $\vec{A}$ because they are descriptive of two-photon events. Finally, the first term on the second line of (A1) will be neglected because the nuclear velocities $\vec{p}_\alpha/M_\alpha$ invariably are much smaller than the electron velocities $\vec{p}_i/m_e$. The consequence of these restrictions and approximations is to replace $H_{\rm int}$ given by Eq. (A1) with the far simpler expression

$$H_{\rm int}\simeq-\frac{e}{m_e c}\left[\frac{2\pi\hbar c^2}{\Omega\omega}\right]^{1/2}\sum_{i=1}^{n}\vec{p}_i\cdot\hat{\alpha}_\mu(a_{\vec{\kappa}\mu}+a^{\dagger}_{\vec{\kappa}\mu}). \tag{A3}$$

From this and the properties of the creation and annihilation operators it follows that the relevant electronic-photon ($|\phi N\rangle=|\phi\rangle|N\rangle$) matrix elements of $H_{\rm int}$ are

$$\langle\phi_f N-1|H_{\rm int}|\phi_i N\rangle=-\frac{e}{m_e c}\left[\frac{2\pi\hbar N c^2}{\Omega\omega}\right]^{1/2}\langle\phi_f|\sum_i\vec{p}_i\cdot\hat{\alpha}_\mu|\phi_i\rangle. \tag{A4}$$

The electronic matrix elements appearing in this expression can be rewritten in more conventional forms by invoking the operator identities

$$\vec{p}_i=(-2i\hbar)^{-1}[\vec{p}_i^{\,2},\vec{r}_i]=(-2i\hbar)^{-1}2m_e[H_{\rm el},\vec{r}_i].$$

Thus

$$\langle\phi_f|\vec{p}_i|\phi_i\rangle=i\frac{m_e}{\hbar}\langle\phi_f|[H_{\rm el},\vec{r}_i]|\phi_i\rangle$$
$$=im_e\omega\langle\phi_f|\vec{r}_i|\phi_i\rangle,$$

where $\omega=\hbar^{-1}(E_f-E_i)$. Combining this with (A4) we obtain the desired result

$$\langle\phi_f N-1|H_{\rm int}|\phi_i N\rangle=i\left[\frac{2\pi N\hbar\omega}{\Omega}\right]^{1/2}\langle\phi_f|\hat{\alpha}_\mu\cdot\vec{d}|\phi_i\rangle \tag{A5}$$

with $\vec{d}\equiv-\sum_i e\vec{r}_i$.

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