Theory of laser-induced chemi-ionization. II. Semiclassical limit

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This is an extension of a recently developed quantal theory of laser-induced Penning and associative ionization. Its purpose is to construct cross-section formulas which are specific to a semiclassical description of the heavy-particle motions. The photoionization transition amplitudes occurring in these formulas involve electric dipole matrix elements which connect the initial electronic state of two colliding atoms to the final, ionized state. Which matrix elements appear in the cross-section formulas is dependent upon how the state of the ejected photoelectron has been specified. In our previous theory this specification included both the energy and momentum (direction of motion) of the photoelectron. Here we include the cross-section formulas and collision theory which are appropriate when the direction of motion of the photoelectron is left unspecified.

I. INTRODUCTION

The dynamic events with which this study is concerned may be considered either as collision-induced photoionization or as laser-induced chemi-ionization (LICI). They can be represented schematically as follows:

$$A+B\rightarrow[(A\cdots B)\underset{\hbar\omega}{\rightarrow}(A\cdots B)^{+}+e^{-}]\rightarrow\begin{bmatrix}A+B^{+}+e^{-}, & \text{LIPI}\\ AB^{+}+e^{-}, & \text{LIAI}\end{bmatrix} \tag{1.1}$$

with A and B indicating two atoms and $\hbar\omega$ the energy of a photon produced by a single-mode linearly polarized laser. The frequency of this laser is less than the ionization limits of both A and B and is not resonant with any electronic transitions of the two atoms.

When the products of reaction are the three widely separated species $A+B^{+}+e^{-}$, we shall call the process laser-induced Penning ionization (LIPI). The photoabsorptive process which produces the diatomic AB^{+} ion will be called laser-induced associative ionization (LIAI). As indicated in Fig. 1, neither of these events is energetically possible unless, in the course of a collision, the internuclear separation becomes less than the critical value $R^{*}(\omega)$. Which, (if either) takes place during a given collision is determined by the laser frequency, the initial relative kinetic energy of the two colliding atoms, and the value of the internuclear separation at the instant when photoionization occurs.

We[1] recently presented a quantal theory of these processes in a paper which henceforth will be identified as I. The cross-section formulas generated by this theory involve solutions of heavy-particle scattering equations as well as (internuclear) separation-dependent amplitudes for photoionization. The nature of the information which is available about photoionization depends upon its source. That which is semiempirical often is expressed in terms of photoionization rates rather than amplitudes. Furthermore, some theoretical studies provide more detailed information than do others about the relevant electric dipole matrix elements. Thus, the *first objective* of this paper is to present (in Sec. II) LIPI and LIAI cross-section formulas adapted to the different types of photoionization information which are apt to be available. One of these adaptations requires a modification of our earlier theory which is presented in the Appendix.

Our *second objective,* to which Sec. III is devoted, is to eliminate the need for solving the heavy-particle scattering equations of the "exact" quantal theory by replacing the associated wave functions and phase shifts with suitable semiclassical (JWKB) approximations. There is little reason to doubt the adequacy of numerical predictions

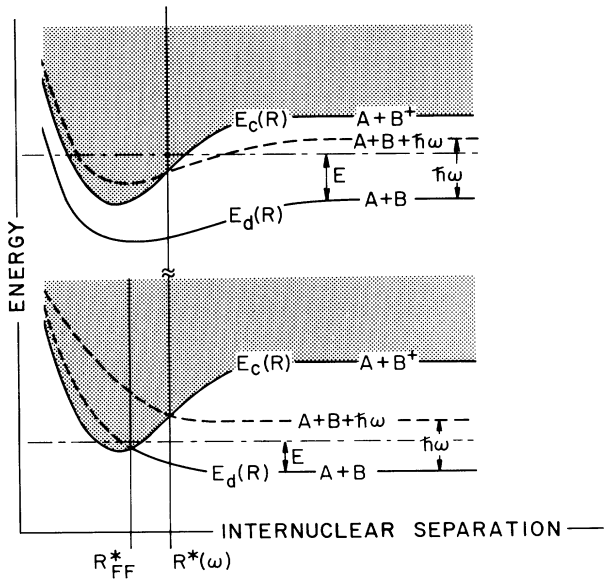

FIG. 1. Examples of situations where LICI can take place. Curves labeled $E_d(R)$ and $E_c(R)$, respectively, show the variations with internuclear separation of the energies of the adiabatic (diabatic) electronic states of the initial AB configuration and of the final AB^{+} molecular ion. Curves labeled $A+B+\hbar\omega$ are plots of $E_d(R)+\hbar\omega$. E is the initial relative kinetic energy of the colliding atoms. LICI can occur only if $R<R^{*}(\omega)$. *FF* chemi-ionization is possible in the lower panel provided that $R<R^{*}_{FF}$.

based on the resulting semiclassical theory. Furthermore, in addition to significantly reducing the computational task, the relatively simple expressions of the semiclassical approximation permit useful insights to be gained into the physical mechanisms underlying the experimentally observable cross sections.

II. QUANTAL CROSS-SECTION FORMULAS

The theory of I and the modification of it (needed in Sec. II C) which is outlined in the Appendix of the present paper, incorporates a number of approximations. One of these, the Born-Oppenheimer (BO) separation, is essential to the entire development. However, the other approximations are less fundamental and could be discarded or at least significantly weakened provided that one were willing to tolerate a more complex formalism and to perform more difficult computations. These additional approximations include the neglect of all channels other than that associated with the initial state and those which are specific to the ionized configurations $AB^+ + e^-$ and/or $A + B^+ + e^-$.

The wave equation descriptive of the nuclear motions associated with the initial electronic state involves an operator which couples to the ionized final state. It is assumed that this coupling can be adequately represented by the local approximation. Furthermore, we replace the imaginary part of this complex-valued local potential with its average over all internuclear orientations. Finally, the complexity of the cross-section formulas and the number of matrix elements that must be computed are greatly reduced by assuming that the (magnitude of) relative angular momentum of the two nuclei is collisionally invariant.

Our attention will be limited to cross sections that do not involve the angular distribution of the ejected photoelectron. This restriction is discussed more fully in Sec. IV.

A. Formulas based on partial-wave expansion

In paper I the wave function of the ejected photoelectron was represented by the partial-wave expansion

$$\phi^{\pm}(\vec{\epsilon},\vec{r}_i \mid \vec{R}) = \sum_{\lambda,\mu} Y^*_{\lambda\mu}(\hat{\epsilon})_{\hat{R}}\, i^{\lambda} e^{\pm i\sigma^{\lambda}} \mathcal{F}_{\lambda\mu}(\epsilon,\vec{r}_i \mid \vec{R}) \tag{2.1}$$

with ϵ and $\hat{\epsilon}$, respectively, denoting the energy and direction of motion of the electron. The subscripts $\hat{R}$ indicate that the polar axis to which the angular variables of $\hat{\epsilon}$ and $\hat{r}_i$ ($\equiv \vec{r}_i/r_i$) are referred coincides with the direction $\hat{R}$ of the internuclear axis. The radial amplitudes $\mathcal{F}_{\lambda\mu}(\epsilon,\vec{r}_i \mid \vec{R})$ behave asymptotically as Coulomb wave functions and the σ^{λ} are the associated Coulomb phase shifts.

The photoionization amplitudes and cross sections of this theory are conveniently expressed in terms of the quantities

$$V_{\epsilon\lambda,\mu_0+m}(R,\omega) = i(2\pi I\hbar\omega/c)^{1/2} i^{-\lambda} \times e^{i\sigma^{\lambda}} \langle \phi_{\epsilon\lambda,\mu_0+m} \mid d_m \mid \phi_d \rangle \tag{2.2}$$

with ω the laser frequency and I the incident photon flux. ϕ_d is the BO wave function of the initial AB electronic state and $\phi_{\epsilon\lambda\mu}$ is a corresponding n-electron configuration-interaction (CI) approximation to the ionized $AB^+ + e^-$ state, with Slater determinants composed of $n-1$ bound molecular orbitals taken from the same set used to construct ϕ_d plus the single continuum orbital $\mathcal{F}_{\lambda\mu}(\epsilon,\vec{r}_i \mid \vec{R})$. $\mu_0 \equiv \Lambda_i - \Lambda_f$ equals the difference between the (electronic orbital angular momentum) projection quantum numbers $\Lambda_i(AB)$ and $\Lambda_f(AB^+)$ specific to the initial and final states of AB and AB^+, respectively. Finally, $d_m = -\hat{e}_m \cdot \sum_{i=1}^{n} e\vec{r}_i$ is a spherical component ($m = 0, \pm 1$) of the electric dipole operator of the n-electron system.

According to Eqs. (4.15′) and (4.16′) of I the angle-energy double differential and the electron-energy differential cross section for LIPI are given by

$$\frac{d^2\sigma^{\mathrm{PI}}}{d\epsilon\, d\hat{K}_f}(E,\epsilon) = [B_1^{\mathrm{PI}}(\theta_f) + B_{-1}^{\mathrm{PI}}(\theta_f)] + [2B_0^{\mathrm{PI}}(\theta_f) - B_1^{\mathrm{PI}}(\theta_f) - B_{-1}^{\mathrm{PI}}(\theta_f)]\cos^2\theta_{\alpha} \tag{2.3}$$

and

$$\frac{d\sigma^{\mathrm{PI}}}{d\epsilon}(E,\epsilon) = (B_1^{\mathrm{PI}} + B_{-1}^{\mathrm{PI}}) + (2B_0^{\mathrm{PI}} - B_1^{\mathrm{PI}} - B_1^{\mathrm{PI}})\cos^2\theta_{\alpha}\,, \tag{2.4}$$

respectively. Here $\theta_{\alpha} \equiv \cos^{-1}(\hat{\alpha}\cdot\hat{K}_i)$ and $\theta_f = \cos^{-1}(\hat{K}_f \cdot \hat{K}_i)$ are the angles between the initial direction of relative motion $\hat{K}_i$ and the unit vectors $\hat{\alpha}$ and $\hat{K}_f$, the first of which is the laser polarization and the second the direction of relative motion of the A and B^+ fragments. The functions $B_{m'}^{\mathrm{PI}}(\theta_f)$ and $B_{m'}^{\mathrm{PI}}$ are given by the formulas

$$B_{m'}^{\mathrm{PI}}(\theta_f \mid E,\epsilon) = g_i \frac{\pi^2}{2K_i^2} \sum_{\lambda} \left| \sum_{L'} (2L'+1) P_{L'}(\cos\theta_f) e^{i(\bar{\eta}_i^{L'} + \eta_f^{L'})} \bar{T}_{m'}(E_0'L', EL', \epsilon\lambda; \omega) \right|^2 \tag{2.5}$$

and

$$B_{m'}^{\mathrm{PI}}(E,\epsilon) = \int d\hat{K}_f B_{m'}^{\mathrm{PI}}(\theta_f \mid E,\epsilon) = g_i \frac{2\pi^3}{K_i^2} \sum_{L'} (2L'+1) e^{-2\,\mathrm{Im}\bar{\eta}_i^{L'}} \sum_{\lambda} |\, \bar{T}_{m'}(E_0'L', EL', \epsilon\lambda; \omega)\,|^2\,, \tag{2.6}$$

wherein

$$\bar{T}_{m'}(E'_0L',EL',\epsilon\lambda;\omega)=\sum_m A_m(\lambda,m')(-1)^m\langle F_f^{L'}(E'_0,N-1\,|\,R)\,|\,V_{\epsilon\lambda,\mu_0+m}(R,\omega)\,|\,\bar{F}_i^{L'}(E,N\,|\,R)\rangle \tag{2.7}$$

and

$$A_m(\lambda,m')=\sum_{J'}(2J'+1)\begin{pmatrix}1 & \lambda & J'\\ m' & -m' & 0\end{pmatrix}\begin{pmatrix}1 & \lambda & J'\\ -m & \mu_0+m & -\mu_0\end{pmatrix}\sum_J\frac{2J+1}{4\pi}\left[\int d\hat{R}\,\mathscr{R}^{(J')*}_{0,-\mu_0}(\hat{R})\mathscr{R}^{(J)}_{0,0}(\hat{R})\right]. \tag{2.8}$$

Here, g_i denotes the statistical weight of the initial electronic state, $K_i=(2\mu E/\hbar^2)^{1/2}$ the magnitude of the propagation vector associated with the initial relative motion of the two colliding atoms, and $E'_0=E'_0(E,\epsilon,\omega)$ the relative kinetic energy of the heavy particle (A,B^+) products of reaction. Finally, the functions $\mathscr{R}^{(j)}_{mm'}(\hat{R})=\mathscr{R}^{(j)}_{mm'}(\theta,\phi,0)$ are representation coefficients of the three-dimensional rotation group, as defined by Messiah,[2] $\bar{F}_i^L$ and $F_f^{L'}$ are heavy-particle channel amplitudes associated with the initial and final states of motions, and $\bar{\eta}_i^L$ and $\eta_f^{L'}$ are the corresponding phase shifts. The symbols with bars above them indicate complex-valued quantities.

Corresponding to (2.4) is the integral cross section

$$\sigma^{\mathrm{AI}}_{n'L'M'}(E)=\delta_{M'0}[(B_1^{\mathrm{AI}}+B_{-1}^{\mathrm{AI}})+(2B_0^{\mathrm{AI}}-B_1^{\mathrm{AI}}-B_1^{\mathrm{AI}})\cos^2\theta_\alpha] \tag{2.9}$$

specific to a laser-induced associative ionization event which produces an AB^+ molecular ion in the vibronic state $(n',L'M')$ with energy $E_{n'}^{L'}$. The coefficients

$$B^{\mathrm{AI}}_{m'}(E)=g_i\frac{2\pi^3}{k_i^2}(2L'+1)\times e^{-2\,\mathrm{Im}\bar{\eta}_i^{L'}}\sum_\lambda|\,\bar{T}_{m'}(E_{n'}^{L'}L',EL',\epsilon_{\mathrm{AI}}\lambda;\omega)\,|^2 \tag{2.10}$$

appearing in (2.9) are the LIAI analogs of the LIPI functions defined by (2.6) and $\epsilon_{\mathrm{AI}}=\epsilon(E,E_{n'}^{L'},\omega)$ is the energy of the photoelectron ejected in this process.

B. Formulas involving photoionization partial widths

It may happen that the only data available (either from empirical sources or theoretical computations) about the electronic transitions are the photoionization partial widths

$$\Gamma_m(\epsilon,\omega\,|\,R)=2\pi\sum_\lambda|\,V_{\epsilon\lambda,\mu_0+m}(R,\omega)\,|^2. \tag{2.11}$$

These widths are related by the formula

$$\Gamma(\epsilon,N-1\,|\,\vec{\mathbf{R}},N)=\tfrac{1}{2}(\Gamma_1+\Gamma_{-1})+\tfrac{1}{2}(2\Gamma_0-\Gamma_1-\Gamma_2)(\hat{\alpha}\cdot\hat{R})^2 \tag{2.12}$$

to $\hbar^{-1}\Gamma(\epsilon,N-1\,|\,\vec{\mathbf{R}},N)$, the absorption rate of $\hat{\alpha}$-polarized photons by an AB "molecule" with internuclear separation R and orientation $\hat{R}$. [The orientation average of this absorption rate is $\hbar^{-1}\Gamma(\epsilon,N-1\,|\,R,N)=\hbar^{-1}\sum_m\frac{1}{3}\Gamma_m(\epsilon,\omega\,|\,R)$.]

In order to express the cross sections of Sec. II A in terms of these partial widths we introduce the analog appropriate to the photoionization matrix elements $V_{\epsilon\lambda,\mu_0+m}(R,\omega)$ of an approximation which Hickman and Morgner[3] applied to the autoionization matrix elements that arise in the theory of laser-free AI and PI. Namely, we assume that

$$V_{\epsilon\lambda,\mu_0+m}(R,\omega)\cong\alpha^{(\mu_0)}_{\lambda m}(R,\omega)[\Gamma_m(\epsilon,\omega\,|\,R)/2\pi]^{1/2}, \tag{2.13}$$

where, in order for (2.10) to be satisfied, the proportionality factors $\alpha^{(\mu_0)}_{\lambda m}(R,\omega)$ must satisfy the condition $\sum_\lambda|\,\alpha^{(\mu_0)}_{\lambda m}(R,\omega)\,|^2=1$. Each of these factors is set equal to its value at the point of stationary phase R_ϵ so that the matrix element appearing in $\bar{T}_{m'}$ [given by (2.7)] is replaced with the product of $\alpha^{(\mu_0)}_{\lambda m}(R_\epsilon,\omega)$ and

$$\bar{\tau}_{-m}(E'_0L',EL',\epsilon;\omega)=\langle F_f^{L'}(E'_0,N-1\,|\,R)\,|\,[\Gamma_m(\epsilon,\omega\,|\,R)/2\pi]^{1/2}\,|\,\bar{F}_i^{L'}(E,N\,|\,R)\rangle. \tag{2.14}$$

(Application of the mean-value theorem would accomplish the same end.) We dodge the issue of how the factors $\alpha^{(\mu_0)}_{\lambda m}(R_\epsilon,\omega)$ are to be evaluated by limiting our attention to those special cases where they can be eliminated from the cross-section formula by the condition $\sum_\lambda|\,\alpha^{(\mu_0)}_{\lambda m}\,|^2=1$. The criterion for this to happen is that $\mu_0=0$, i.e., that the (electronic orbital angular momentum) projection quantum number of the product diatomic ion equals that of the initial A-B state. $A_m(\lambda,m')$ given by (2.8) is equal to $\delta_{m,-m'}$ when $\mu_0=0$. Consequently, $\bar{T}_{m'}(E'_0L',EL',\epsilon\lambda;\omega)$ is replaced with the approximation $(-1)^{m'}\alpha^{(0)}_{\lambda,-m'}(R_\epsilon,\omega)\bar{\tau}_{m'}(E'_0L',EL',\epsilon;\omega)$ and the quantities $B^{\mathrm{PI}}_{m'}(\theta_f)$, $B^{\mathrm{PI}}_{m'}$, and $B^{\mathrm{AI}}_{m'}$ given by (2.5), (2.6), and (2.10) reduce to

$$\mathscr{B}^{\mathrm{PI}}_{m'}(\theta_f\,|\,E,\epsilon)=g_i\frac{\pi^2}{2K_i^2}\left|\sum_{L'}(2L'+1)P'_L(\cos\theta_f)e^{i(\bar{\eta}_i^{L'}+\eta_f^{L'})}\bar{\tau}_{m'}(E'_0L',EL',\epsilon\lambda;\omega)\right|^2, \tag{2.15}$$

$$\mathscr{B}^{\mathrm{PI}}_{m'}(E,\epsilon)=g_i\frac{2\pi^3}{K_i^2}\sum_{L'}(2L'+1)e^{-2\,\mathrm{Im}\bar{\eta}_i^{L'}}\,|\,\bar{\tau}_{m'}(E'_0L',EL',\epsilon\lambda;\omega)\,|^2, \tag{2.16}$$

and

$$\mathscr{B}_{m'}^{\mathrm{AI}}(E)=g_i\frac{2\pi^3}{K_i^2}(2L'+1)e^{-2\,\mathrm{Im}\bar{\eta}_i^{L'}}\,|\,\bar{\tau}_{m'}(E_n^{L'}L',EL',\epsilon_{\mathrm{AI}}\lambda;\omega)\,|^2\,, \tag{2.17}$$

respectively.

These formulas, specific to $\Lambda_i=\Lambda_f$, are unique in that they do not contain the proportionality factors $\alpha_{\lambda m}^{(0)}(R_\epsilon,\omega)$ and are expressed solely in terms of matrix elements involving the photoionization partial widths $\Gamma_m(\epsilon,\omega\,|\,R)$. They are the analogs for LIPI and LIAI of formulas that Hickman and Morgner[3] proposed for the corresponding laser-free processes.

C. Formulas based on eigenchannel representation

A third possibility is that instead of the matrix elements $\langle\phi_{\lambda\epsilon,\mu_0+m}\,|\,d_m\,|\,\phi_d\rangle$ or partial widths $\Gamma_m(\epsilon,\omega\,|\,R)$, electric dipole matrix elements involving states $\phi_{\epsilon\mu}$ for which the linear momentum of the photoelectron is unspecified, are available. Dipole matrix elements of this sort are the outputs of photoionization theories which use (either explicitly or implicitly) the "eigenchannel representation"

$$\phi(\epsilon,\vec{r}_i\,|\,R)=\sum_{\lambda,\mu}Y_{\lambda\mu}(\hat{r}_i)_{\hat{R}}\mathscr{F}_\mu^\lambda(\epsilon,r_i\,|\,R) \tag{2.18}$$

for the wave function of the ejected electron.

According to this model, photoabsorption deposits the ejected electron in a continuum energy state ($\epsilon>0$) with an unspecified direction of motion. A theory of laser induced chemi-ionization that incorporates this model is outlined in the Appendix. The resulting cross-section formulas are identical in form to Eqs. (2.3), (2.4), and (2.9) but the three functions $B_{m'}^{\mathrm{PI}}(\theta_f)$, $B_{m'}^{\mathrm{PI}}$, and $B_{m'}^{\mathrm{AI}}$ [defined by (2.5), (2.6), and (2.10)] are replaced with

$$\tilde{B}_{m'}^{\mathrm{PI}}(\theta_f\,|\,E,\epsilon)=\delta_{m',0}\left[g_i\frac{\pi^2}{2K_i^2}\left|\sum_{L'}(2L'+1)P_{L'}(\cos\theta_f)e^{i(\bar{\eta}_i^{L'}+\eta_f^{L'})}\bar{T}(E_0'L',EL',\epsilon;\omega)\right|^2\right], \tag{2.19}$$

$$\tilde{B}_{m'}^{\mathrm{PI}}(E,\epsilon)=\delta_{m',0}\left[g_i\frac{2\pi^3}{K_i^2}\sum_{L'}(2L'+1)e^{-2\,\mathrm{Im}\bar{\eta}_i^{L'}}\,|\,\bar{T}(E_0'L',EL',\epsilon;\omega)\,|^2\right], \tag{2.20}$$

and

$$\tilde{B}_{m'}^{\mathrm{AI}}(E,\epsilon)=\delta_{m',0}\left[g_i\frac{2\pi^3}{K_i^2}(2L'+1)e^{-2\,\mathrm{Im}\bar{\eta}_i^{L'}}\,|\,\bar{T}(E_0'L',EL',\epsilon;\omega)\,|^2\right], \tag{2.21}$$

respectively. Here, in analogy to (2.7), (2.8), and (2.2)

$$\bar{T}(E_0'L',EL',\epsilon;\omega)=\sum_m A_m\langle F_f^{L'}(E_0',N-1\,|\,R)\,|\,V_{\epsilon,\mu_0+m}(R,\omega)\,|\,\bar{F}_i^{L'}(E,N\,|\,R)\rangle\,, \tag{2.22}$$

$$A_m=\sum_J\frac{2J+1}{4\pi}\int d\hat{R}\,\mathscr{R}_{0,m}^{(1)*}(\hat{R})\mathscr{R}_{0,0}^{(J)}(\hat{R})\,, \tag{2.23}$$

and

$$V_{\epsilon,\mu_0+m}(R,\omega)=i(2\pi I\hbar\omega/c)^{1/2}\langle\phi_{\epsilon,\mu_0+m}\,|\,d_m\,|\,\phi_d\rangle\,, \tag{2.24}$$

where $\phi_{\epsilon\mu}=\sum_\lambda\phi_{\epsilon\lambda\mu}$ is a sum of CI wave functions of the type involved in the dipole matrix elements of $V_{\epsilon\lambda,\mu_0+m}(R,\omega)$, defined by (2.2).

A qualitative distinction between the cross sections of the "partial-wave" and eigenchannel representations of Secs. II A and II C is that the latter are directly proportional to $\cos^2\theta_\alpha$ whereas the former exhibit polarization dependencies of the type $a+b\cos^2\theta_\alpha$. The degree to which the factor a differs from zero is a measure of the inadequacy of the eigenchannel model which, as explained in the Appendix and Sec. IV, is less rigorous than the corresponding partial-wave theory.

In principle, it is possible to construct the partial-wave photoelectron function $\phi^{\pm}(\vec{\epsilon},\vec{r}\,|\,\vec{R})$ from a knowledge of the corresponding eigenchannel wave function $\phi(\epsilon,\vec{r}\,|\,\vec{R})$. Thus, the "components" $\mathscr{F}_{\lambda\mu}$ can be extracted from the latter by the projection operation

$$P_{\lambda\mu}\phi(\epsilon,\vec{r}\,|\,\vec{R})=\int d\hat{r}'Q_{\lambda\mu}(\hat{r})_{\hat{R}}Q_{\lambda\mu}^*(\hat{r}')_{\hat{R}}\phi(\epsilon,r\hat{r}'\,|\,\vec{R}) \tag{2.25}$$

with $Q_{\lambda\mu}(\hat{r})$ a unit-normalized spheroidal harmonic, and then recomposed to form

$$\phi^{\pm}(\vec{\epsilon},\vec{r}\,|\,\vec{R})=\sum_{\lambda\mu}[Y_{\lambda\mu}^*(\hat{\epsilon})_{\hat{R}}i^\lambda e^{\pm i\sigma^\lambda}]\mathscr{F}_{\lambda\mu}(\epsilon,\vec{r}\,|\,\vec{R})\,. \tag{2.26}$$

III. SEMICLASSICAL APPROXIMATION

In this section we briefly summarize the procedure for constructing semiclassical estimates of the heavy-particle matrix elements that occur in the cross-section formulas for laser-induced chemi-ionization. This procedure leads to the three formulas (3.11), (3.13), and (3.15) for the matrix elements specific to LIPI and to analogous formulas for the LIAI matrix elements. The corresponding semiclassical approximations to the cross sections then are obtained by substituting these matrix elements and the associated semiclassical (JWKB) phase shifts given by (3.7) and (3.9) into the formulas of Sec. II.

A. Laser-induced Penning ionization

In each of the three situations considered in the preceding section, the cross-section formulas for LIPI involve matrix elements of the form

$$X^{\mathrm{PI}}=X^{\mathrm{PI}}(E_0'L',EL',\epsilon\omega) \equiv\langle F_f^{L'}(E_0',N-1\mid R)\mid U(R)\mid \bar{F}_i^{L'}(E,N\mid R)\rangle \quad (3.1)$$

with $U(R)$ equal to one of $V_{\epsilon\lambda,\mu_0+m}(R,\omega)$, $V_{\epsilon,\mu_0+m}(R,\omega)$, or $[\Gamma_m(\epsilon,\omega\mid R)/2\pi]^{1/2}$. The F's are heavy-particle radial wave functions. Specifically, $F_f^{L'}(E',N'\mid R)$ is the solution of a one-dimensional Schrödinger equation containing the effective potential

$$V_c(R,L')=V_c(R)+\hbar^2L'(L'+1)/2\mu R^2 . \quad (3.2)$$

This radial wave function is regular at the origin and satisfies the asymptotic boundary condition

$$F_f^{L'}(E',N'\mid R)\sim(2\mu/\pi\hbar^2K_f)^{1/2}\sin(K_fR-\tfrac{1}{2}\pi L'+\eta_f^{L'}) , \quad (3.3)$$

wherein $\eta_f^{L'}$ denotes a real-valued phase shift and $K_f\equiv(2\mu E'/\hbar^2)^{1/2}$. $\bar{F}_i^{L'}(E,N\mid R)$ is a similarly defined function, the radial dependence of which is governed by the complex-valued potential $V_d(R,L')-\frac{1}{2}i\Gamma(R,\omega)$. Here

$$V_d(R,L')=V_d(R)+\hbar^2L'(L'+1)/2\mu R^2 \quad (3.4)$$

and $\Gamma(R,\omega)$ denotes the orientation average of the photoionization level width. The complex-valued amplitude $\bar{F}_i^{L'}$ is regular at the origin and has the asymptotic form

$$\bar{F}_i^{L'}(E,N\mid R)\sim(2\mu/\pi\hbar^2K_i)^{1/2}\sin(K_iR-\tfrac{1}{2}\pi L'+\bar{\eta}_i^{L'}) \quad (3.5)$$

with $K_i=(2\mu E/\hbar^2)^{1/2}$.

Our objective is to construct a semiclassical estimate of X^{PI}. The procedure we use for this purpose is patterned after that of Miller.[4] The first step is to replace the two radial wave functions and the corresponding pair of phase shifts with the appropriate JWKB approximations,

$$F_f^{L'}(E',N-1\mid R)\cong[2\mu/\pi\hbar^2K_f(R;E'L')]^{1/2}\sin\left[\tfrac{1}{4}\pi+\int_{R_f}^{R_F}dR'K_f(R';E'L')\right] , \quad (3.6)$$

$$\eta_f^{L'}(E')\cong\tfrac{1}{2}\pi(L'+\tfrac{1}{2})-K_f\bar{R}+\int_{R_f}^{\bar{R}}dR'K_f(R';E'L') , \quad (3.7)$$

$$\bar{F}_i^{L'}(E,N\mid R)\cong[2\mu/\pi\hbar^2\bar{K}_i(R;EL')]^{1/2}\sin\left[\tfrac{1}{4}\pi+\int_{R_i}^{R}dR'\bar{K}_i(R';EL')\right] , \quad (3.8)$$

$$\bar{\eta}_i^{L'}(E,\omega)\cong\tfrac{1}{2}\pi(L'+\tfrac{1}{2})-K_i\bar{R}+\int_{R_i}^{\bar{R}}dR'\bar{K}_i(R';EL') , \quad (3.9)$$

wherein $\bar{R}\to\infty$. Here $K_f(R;E'L')=\{(2\mu/\hbar^2)[E'-V_c(R,L')]\}^{1/2}$ and $R_f=R_f(E',L')$ is the corresponding classical turning point so defined that $E'-V_c(R_f,L')=0$. Similarly,

$$\bar{K}_i(R;EL')=\{(2\mu/\hbar^2)[E-V_d(R,L')+\tfrac{1}{2}i\Gamma(R,\omega)]\}^{1/2}$$

and $R_i=R_i(E,L')$ is the largest positive root of $E-V_d(R,L')=0$. The result of substituting (3.6)–(3.9) into (3.1) is that X^{PI} can be written as the sum of X_+^{PI} and X_-^{PI} with

$$X_\pm^{\mathrm{PI}}\cong(2\mu/\pi\hbar^2)\int dR\{U(R)/2[\bar{K}_i(R;EL')K_f(R;E'L')]^{1/2}\} \times\cos\left[\int_{R_i}^{R}dR'\bar{K}_i(R';EL')\pm\int_{R_f}^{R}dR'K_f(R';E'L')\right] . \quad (3.10)$$

Since it is expected that $|X_+^{\mathrm{PI}}|\ll|X_-^{\mathrm{PI}}|$, we henceforth identify X^{PI} with X_-^{PI}. The latter is then evaluated in the stationary-phase approximation, the point of stationary phase R^S being the solution of the equation $\epsilon=\hbar\omega+\Delta E(R)$, wherein $\Delta E(R)\equiv E_d(R)-E_c(R)$. To simplify the calculation it is assumed that Γ is so small that $\bar{K}_i(R;EL')$ can be replaced with $K_i(R;EL')+\mu\Gamma(R,\omega)/2\hbar^2K_i(R;EL')$, where $K_i(R;EL')=\{(2\mu/\hbar^2)[E-V_d(R,L')]\}^{1/2}$. The result of these manipulations is the formula

$$X^{\mathrm{PI}}\cong(2\mu/\pi\hbar^2)[(U/2K)(2\pi\hbar^2K/\mu\mid V'\mid)^{1/2}\cos(\tau+\tfrac{1}{4}\pi)]_{R=R^S} \quad (3.11)$$

with $V'\equiv dV/dR$, $K\equiv K_i(R^S;EL')=K_f(R^S;E'L')$, and

$$\tau(R)=\int_{R_i}^{R}dR'\bar{K}_i(R';EL')-\int_{R_f}^{R}dR'K_f(R';E'L') . \quad (3.12)$$

When there are two well-separated points of stationary phase the JWKB approximation to X^{PI} equals the sum of their individual contributions, each of which is of the form given by (3.11). However, two closely neighboring points of stationary phase interfere with one another and cannot be treated independently. An approximation to X^{PI}, which is uniformly valid for all values of the separation $|R_1^S-R_2^S|$, can be obtained using techniques that have been developed to

handle the special case $|R_1^S - R_2^S| \to 0$, of two coalescing points of stationary phase. Thus, following Carrier,[5] we find that $X^{\rm PI} \cong X_1^{\rm PI} + X_2^{\rm PI}$ with

$$X_m^{\rm PI} = (2\mu/\pi\hbar^2)[(U/2K)(2\pi\hbar^2 K/\mu\,|\,V'\,|\,)^{1/2}]_{R=R_m^S}(\pi\beta_m/8)^{1/2}\{\exp[i(\tau_m+\beta_m-\tfrac{1}{6}\pi)]H_{1/3}^{(2)}(\beta_m) + \exp[-i(\tau_m+\beta_m-\tfrac{1}{6}\pi)]H_{1/3}^{(1)}(\beta_m)\}\ . \tag{3.13}$$

Here, $H_{1/3}^{(1)}$ and $H_{1/3}^{(2)}$ are Hankel functions,[6] τ_m is the value of $\tau(R)$ evaluated at $R = R_m^s$, and

$$\beta_m = \{(\mu/3\hbar^2 K)[V'(R)]^3/[V''(R)]\}_{R=R_m^S}\ . \tag{3.14}$$

When the value of β_m is large, $X_m^{\rm PI}$ reduces to $X^{\rm PI}$ given by (3.11) and one recovers from (3.13) the previously stated result appropriate to widely separated points of stationary phase. However, when these points draw close together, $V'(R_1^S)$ and $V'(R_2^S)$ approach the common value of $V'(R^*)=0$,

$$\beta_1 \to (\mu/3\hbar^2 K)\{2[V(R_1^S)-V(R^*)]\}^{3/2}/[V''(R^*)]^{1/2}\ ,$$

and $\beta_2 \to -\beta_1$. Near this point of coalescence the two contributions $X_1^{\rm PI}$ and $X_2^{\rm PI}$ combine to give the expression

$$X^{\rm PI} = (2\mu/\pi\hbar^2)[(U/2K)(2\hbar^2 K/\mu V'')^{1/3}2\pi\cos\tau]_{R=R^*}{\rm Ai}(-z) \tag{3.15}$$

with ${\rm Ai}(-z)$ the Airy function[6] and

$$z = 2^{1/3}(\mu/\hbar^2 K)^{2/3}[V(R_1^S)-V(R^*)]/[V''(R^*)]^{1/3}\ .$$

The Airy function occurring in this formula describes the behavior of $X^{\rm PI}$ within the transition region between $V(R_1^S) < V(R^*)$ and $V(R_1^S) > V(R^*)$. [${\rm Ai}(|z|)$ rises monotonically to a value of ${\rm Ai}(0) \simeq 0.355$ as $|z|$ falls to zero, whereas ${\rm Ai}(-|z|)$ oscillates with an amplitude that rapidly diminishes with increasing $|z|$.]

B. Laser-induced associative ionization

Corresponding to $X^{\rm PI}$ of (3.1) are the matrix elements

$$X^{\rm AI} = X^{\rm AI}(E_{n'}^{L'}L', EL'; \epsilon_{\rm AI}\omega) = \langle F_f^{L'}(E_{n'}^{L'}, N-1\,|\,R)\,|\,U(R)\,|\,\bar{F}_i^{L'}(E,N\,|\,R)\rangle\ , \tag{3.16}$$

which appear in the LIAI cross-section formulas of Sec. II. Here $F_f^{L'}(E_{n'}^{L'}, N-1\,|\,R)$ is a unit-normalized bound-state radial wave function with a vibronic energy equal to $W(n',L') = E_{n'}^{L'}$. The JWKB approximation to this eigenfunction is

$$F_f^{L'}(E_{n'}^{L'}, N-1\,|\,R) \cong N(n',L')K_f^{-1/2}(R;E_{n'}^{L'}L') \times \sin\left[\tfrac{1}{4}\pi + \int_{R_f}^{R} dR' K_f(R';E_{n'}^{L'}L')\right]\ . \tag{3.17}$$

By invoking the JWKB eigenvalue relationship

$$\int dR\,\{(2\mu/\hbar^2)[W - V_c(R,L')]\}^{1/2} = \pi(n'+\tfrac{1}{2}) \tag{3.18}$$

one can show that the normalization constant appearing in (3.17) is given by $N(n',L') = [(2\mu/\pi\hbar^2)\,|\,\partial W/\partial n'\,|\,]^{1/2}$.

$X^{\rm AI}$ is then evaluated by the same approximation procedure as that which was used for $X^{\rm PI}$. The only formal differences that occur are that (i) additional multiplicative factors of $|\,\partial W/\partial n'\,|^{1/2}$ should appear in the LIAI counterparts of formulas (3.11), (3.13), and (3.15) and (ii) $K_f(R';E'L')$ in (3.12) is to be replaced with $K_f(R';E_{n'}^{L'}L')$.

IV. CLOSING REMARKS

Formulas have been presented in Sec. III for the semiclassical approximations to the phase shifts and heavy-particle matrix elements encountered in the theories of LIPI and LIAI. The operators (functions of internuclear separation) occurring in these matrix elements are the R representatives of electronic transition amplitudes for photoionization (or the closely related photoabsorptive level widths). These transition amplitudes are proportional to electric dipole matrix elements connecting the bound electronic state of the initial $A\cdots B$ configuration with electronic continuum states associated with the configuration $(A\cdots B)^+ + e^-$.

The theory which we presented in I was an extension to laser-induced chemi-ioniziation of Bieniek's[7] theory of field-free chemi-ionization (FFCI) and, as such, treated the ejected electron as a free particle with a specified energy $\epsilon > 0$ *and* a linear momentum $\vec{p} = (2m_e\epsilon)^{1/2}\hat{\epsilon}$. However, as we have explained in Sec. II C, the dipole matrix elements which occur in the LICI cross-section formulas based on this theory differ from those occurring in theories of the photoionization process which do not specify the direction of motion ($\hat{\epsilon}$) of the ejected electron. In theories of this second type the ejected electron is treated as if it were in a sort of positive-energy Rydberg state. Now one might argue that if there is no interest in the angular distribution of ejected electrons, their directions of motion then could be ignored from the very beginning. But this is not the way quantum mechanics works: Averages over uninteresting (or difficult to measure) quantum numbers are performed on probabilities, not on probability amplitudes or (the linearly related) wave functions. Thus, it seems to us that a "truly rigorous" theory of photoionization must be based on a final-state representation which includes a specification of the direction of motion (momentum) of the ejected electron. On the other hand, it also seems quite likely on intuitive grounds that in many situations the consequences of using the less rigorous representation will be very slight. Therefore, we have constructed (and presented in the Appendix of this paper) a theory of LICI which is based on a model of the final ionized state, which leaves unspecified the direction of

motion of the ejected electron. This theory produces several interesting results, e.g., (i) it predicts that the LICI cross sections will be proportional to $\cos^2\theta_\alpha$, whereas those generated by the theory of I vary as $a+b\cos^2\theta_\alpha$ with $a\neq 0$; (ii) it is the analog of Miller's[4] adaptation to FFCI of O'Malley's[8] very elegant theory of dissociative attachment. It is obvious that a theory based on this model of the final state cannot generate predictions about the angular distribution of the ejected electrons. However, this particular shortcoming of the model is of no direct concern to us here because we have chosen to limit our considerations to cross sections which are independent of this distribution. There is, of course, no difficulty whatsoever in accounting for the angular distribution of ejected electrons, provided that one uses a theory of the type described in Sec. II A. Indeed, formulas for the LICI electronic energy-angle double-differential cross sections were derived in I and formulas appropriate to the corresponding field-free events have been reported by Miller, Slocomb, and Schaefer.[9]

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APPENDIX: SCATTERING THEORY BASED ON EIGENCHANNEL MODEL

Our purpose here is to present a quantal theory of LICI in which the direction of motion (momentum) of the ejected photoelectron is left unspecified. A theory of this type can be constructed by altering in a few critical ways our previous theory which was based on the partial-wave representation (2.1) of the wave function of the photoelectron. Instead of presenting this modified theory in its entirety we shall, whenever possible, use the space-saving device of indicating how equations and formulas from the previous paper can be suitably modified.

The Hamiltonian of the composite system of material particles (m) and radiation (r) can be written (in the center-of-mass frame) as the sum $H=H_m+H_r+H_{\rm int}$. Here $H_m=T_n+H_{\rm el}$ is the sum of relative kinetic energy of the two atomic nuclei and the electronic energy operator $H_{\rm el}$. H_r is the Hamiltonian of the linearly polarized single-mode laser field and $H_{\rm int}$ is the energy of interaction between the charged particles and the laser field. The eigenstates of H_r are denoted by the symbols $|N\rangle$, with N indicating the number of photons with energy $\hbar\omega$ and polarization $\hat{\alpha}$. We denote by the ket $|\phi_d\rangle=|\phi_{AB}\rangle$ a variational CI approximation to the initial electronic state of the bound A-B state. Associated with this state is the electronic energy $E_d(R)=\langle\vec{R}\,|\,\langle\phi_d\,|\,H_{\rm el}\,|\,\phi_d\rangle\,|\,\vec{R}\rangle$ and the corresponding potential $V_d(R)=E_d(R)-E_d(\infty)$. The symbol $|\phi_\epsilon\rangle=|\phi_{AB^+},e^-(\epsilon)\rangle$ will be used to indicate an ionized state with an unbound electron of energy ϵ. Because the direction of motion of this electron is unspecified, one can think of $|\phi_\epsilon\rangle$ as a positive-energy analog of a molecular Rydberg state. It is assumed that these electronic continuum states are orthogonal to $|\phi_d\rangle$ and so normalized that

$$\langle\phi_\epsilon\,|\,\phi_{\epsilon'}\rangle=\rho(\epsilon)^{-1}\delta(\epsilon-\epsilon')\,, \tag{A1}$$

$$\langle\phi_\epsilon\,|\,H_{\rm el}\,|\,\phi_{\epsilon'}\rangle=(\epsilon+E_c)\rho(\epsilon)^{-1}\delta(\epsilon-\epsilon') \tag{A2}$$

with $\rho(\epsilon)$ denoting the density of states. Analogous to $E_d(R)$ and $V_d(R)$ are the two functions $E_c(R)$ and $V_c(R)$, specific to the AB^+ molecular ion. The principal distinction between this and our previous theory is that the final-state basis functions $|\phi_{\vec{\epsilon}}\rangle$ of I included specifications of *both* the energy (ϵ) and the direction of motion ($\hat{\epsilon}$) of the ejected electron whereas the $|\phi_\epsilon\rangle$ used here contain no reference whatsoever to $\hat{\epsilon}$.

LICI is a collisionally induced photoabsorptive transition from the initial state $|\phi_d N\rangle\equiv|\phi_d\rangle\,|N\rangle$ to a final state $|\phi_\epsilon N-1\rangle\equiv|\phi_\epsilon\rangle\,|N-1\rangle$. As in I, we restrict our attention to the two orthogonal subspaces spanned by these states and completely disregard all others. Associated with this two-state model is the pair of approximately complementary projection operators

$$Q=|\phi_d N\rangle\langle\phi_d N\,|\,, \tag{A3}$$

$$P=\int d\epsilon'\,|\,\phi_{\epsilon'}N-1\rangle[\rho(\epsilon')]^{-1}\langle\phi_{\epsilon'}N-1\,|\,. \tag{A4}$$

The T matrix for LIPI can be written in the form

$$T^{\rm PI}(\vec{E}',\epsilon\,|\,\vec{E})=\int d\vec{R}[\Psi_P^-(\vec{E}',N-1\,|\,\vec{R})]^*\times\langle\epsilon^-,N-1\,|\,\vec{R},N\rangle X_d^+(\vec{E},N\,|\,\vec{R}) \tag{A5}$$

with $\vec{E}=(E,\hat{K}_i)$ indicating the kinetic energy (E) and direction ($\hat{K}_i$) of relative motion of the two colliding particles A and B and $\vec{E}'=(E',\hat{K}_f)$ providing an analogous characterization of the postcollisional motion of the A-B^+ pair. The quantity [cf. (3.1) and (3.2) of I]

$$\langle\epsilon',N-1\,|\,\vec{R},N\rangle=\int d\vec{r}\,\phi_\epsilon(\vec{r}\,|\,R)^*[i(2\pi I\hbar\omega/c)^{1/2}\hat{\alpha}\cdot\vec{d}]\phi_d(\vec{r}\,|\,\vec{R}) \tag{A6}$$

appearing in this expression, is the photoionization transition amplitude specific to the internuclear separation $\vec{R}$. Here, I is the incident flux of laser photons and $\vec{d}\equiv-\sum_i e\vec{r}_i$ denotes the electronic contribution to the electric dipole moment operator. $\phi_\epsilon(\vec{r}\,|\,\vec{R})$ and $\phi_d(\vec{r}\,|\,\vec{R})$ are the coordinate representatives of the two kets $|\phi_\epsilon\rangle$ and $|\phi_d\rangle$, respectively.

The wave function $\Psi_P^-(\vec{E}',N-1\,|\,\vec{R})$, occurring in (A5), is descriptive of the A-B^+ heavy-particle motions subsequent to ionization. $X_d^+(\vec{E},N\,|\,\vec{R})$ is specific to the internuclear motions associated with the initial electronic state $|\phi_d\rangle$. The wave equations for these functions which we derived in I are applicable here as well, provided that the electronic basis elements $|\phi_{\vec{\epsilon}}\rangle$ are everywhere replaced with $|\phi_\epsilon\rangle$. Thus, the width of the discrete state $|\phi_d\rangle$, which contributes to the equation satisifed by X_d^+, is to be identified here with

$$\Gamma(\epsilon',N'\,|\,\vec{R},N)=2\pi\rho(\epsilon')\,|\,\langle\epsilon',N'\,|\,\vec{R},N\rangle\,|^2\,. \tag{A7}$$

With the wave function of the ejected electron given by the expression (2.18) of the text, the many-electron wave function $\phi_\epsilon(\vec{r}\,|\,\vec{R})$ becomes a sum $\sum_\mu\phi_{\epsilon\mu}(\vec{r}\,|\,\vec{R})$, each term of which is a CI wave function constructed from

$n-1$ bound orbitals and a single continuum orbital $\sum_\lambda \mathcal{F}_{\lambda\mu}(\epsilon,\vec{r}\,|\,\vec{R})$. Consequently, the transition amplitude can be written as

$$\langle \epsilon', N-1\,|\,\vec{R},N\rangle = i(2\pi I\hbar\omega/c)^{1/2}\sum_\mu \langle \phi_{\epsilon\mu}\,|\,\hat{\alpha}\cdot\vec{d}\,|\,\phi_d\rangle \tag{A8}$$

with

$$\langle \phi_{\epsilon\mu}\,|\,\hat{\alpha}\cdot\vec{d}\,|\,\phi_d\rangle = (\tfrac{4}{3}\pi)^{1/2}\sum_m Y^*_{1m}(\hat{\alpha})_{\hat{R}}\langle \phi_{\epsilon\mu}\,|\,d_m\,|\,\phi_d\rangle\ , \tag{A9}$$

and where the d_m (with $m=0,\pm1$) are spherical components of $\vec{d}$. We assume that the (orbital electronic angular momentum) projection quantum number of the initial AB electronic state is Λ_i and that of the product ion is Λ_f. The selection rule for the matrix element $\langle \phi_{\epsilon\mu}\,|\,d_m\,|\,\phi_d\rangle$ is then $\mu=\mu_0+m$ with $\mu_0\equiv\Lambda_i-\Lambda_f$ and so

$$\langle \epsilon', N-1\,|\,\vec{R},N\rangle = (\tfrac{4}{3}\pi)^{1/2}\sum_m Y^*_{1m}(\hat{\alpha})_{\hat{R}}V_{\epsilon,\mu_0+m}(R,\omega) = (\tfrac{4}{3}\pi)^{1/2}\sum_{m,m'} Y_{1m'}(\hat{\alpha})\mathscr{R}^{(1)}_{m',-m}(\hat{R})(-1)^m V_{\epsilon,\mu_0+m}(R,\omega)\ . \tag{A10}$$

Here $V_{\epsilon,\mu_0+m}(R,\omega)$ is given by Eq. (2.24) of the text and $\mathscr{R}^{(j)}_{m,m'}(\hat{R})$ denotes a representation coefficient of the three-dimensional rotation group.

We use for X_d^+ and Ψ_p^- the partial-wave expansions (4.1) and (4.4) of I. These, combined with (A10), lead from (A5) to the formula

$$T^{\rm PI}(\vec{E}',\epsilon\,|\,\vec{E}) = \sum_{L,L',M'} Y_{1,-M'}(\hat{\alpha})Y_{L'M'}(\hat{K}_f)[(2L'+1)/3]^{1/2}(2L+1)i^{L-L'}e^{i(\bar{\eta}_i^L+\eta_f^{L'})}T(E'L'M',EL\,0,\epsilon;\omega)\ , \tag{A11}$$

where

$$T(E'L'M',EL\,0,\epsilon;\omega) = \sum_m A_m(LL'1\,|\,0M')\bar{T}(E'L',EL,\epsilon m;\omega)\ , \tag{A12}$$

$$\bar{T}(E'L',EL,\epsilon m;\omega) = \langle F_f^{L'}(E',N-1\,|\,R)\,|\,V_{\epsilon,\mu_0+m}(R,\omega)\,|\,\bar{F}_i^{L}(E,N\,|\,R)\rangle\ , \tag{A13}$$

and

$$A_m(LL'1\,|\,0M') = \sum_J \frac{2J+1}{4\pi}\begin{bmatrix} L & L' & J \\ 0 & M' & -M'\end{bmatrix}\begin{bmatrix} L & L' & J \\ 0 & 0 & 0\end{bmatrix}\int d\hat{R}\,\mathscr{R}^{(1)*}_{M',m}(\hat{R})\mathscr{R}^{(J)}_{M',0}(\hat{R})\ . \tag{A14}$$

This expression has been simplified by choosing the polar axis of the center-of-mass frame to coincide with the initial direction of relative motion $\hat{K}_i$. It can be further simplified by the approximation

$$i^L e^{i\bar{\eta}_i^L}\bar{T}(E'L',EL,\epsilon m;\omega) \simeq i^{L'}e^{i\bar{\eta}_i^{L'}}\bar{T}(E'L,EL',\epsilon m;\omega)\ , \tag{A15}$$

which should have a negligible numerical effect provided that a large number of partial waves contribute to the cross sections. As a consequence of (A15) the T-matrix formula (A11) reduces to

$$T^{\rm PI}(\vec{E}',\epsilon\,|\,\vec{E}) = Y_{10}(\hat{\alpha})\sum_{L'} Y_{L'0}(\hat{K}_f)[(2L'+1)/3]^{1/2}e^{i(\bar{\eta}_i^{L'}+\eta_f^{L'})}\bar{T}(E'L',\epsilon L',\epsilon;\omega) \tag{A16}$$

with $\bar{T}(E'L',EL,\epsilon;\omega)$ given by (2.22) of the text.

Analogous expressions appropriate to LIAI are obtained by the replacement of the scattering function Ψ_p^- in (A5) with a square-integrable eigenfunction $\Psi_P^{M'}(E_{n'}^{L'},N-1\,|\,\vec{R})$ descriptive of the vibronic final state of the AB^+ molecular ion. Then, corresponding to (A11) and (A16) one obtains the two formulas

$$T^{\rm AI}(E_{n'}^{L'},\epsilon\,|\,\vec{E}) = Y_{1,-M'}(\hat{\alpha})[(2L'+1)/3]^{1/2}\sum_L (2L+1)i^L e^{i\bar{\eta}_i^L}T(E_{n'}^{L'}L'M',EL\,0,\epsilon;\omega) \tag{A17}$$

and

$$T^{\rm AI}(E_{n'}^{L'},\epsilon\,|\,\vec{E}) = \delta_{M'0}\{Y_{10}(\hat{\alpha})[(2L'+1)/3]^{1/2}i^{L'}e^{i\bar{\eta}_i^{L'}}\bar{T}_0(E_{n'}^{L'}L',EL',\epsilon;\omega)\}\ , \tag{A18}$$

respectively.

From (A16) and the definition[1,7] $d^2\sigma/d\epsilon\,d\hat{K}_f = g_i(2\pi)^4\,|\,T^{\rm PI}(\vec{E}'_0,\epsilon\,|\,\vec{E})\,|^2/K_i^2$, we obtain the LIPI cross-section formulas

$$\frac{d^2\sigma^{\rm PI}}{d\epsilon\,d\hat{K}_f}(E,\epsilon) = \frac{g_i}{4K_i^2}\left|\sum_L (2L+1)S_\epsilon^L(\omega)P_L(\cos\theta_f)\right|^2\cos^2\theta_\alpha\ , \tag{A19}$$

$$\frac{d\sigma^{\rm PI}}{d\epsilon}(E,\epsilon) = \left[\frac{\pi g_i}{K_i^2}\sum_L (2L+1)\,|\,S_\epsilon^L(\omega)\,|^2\right]\cos^2\theta_\alpha\ . \tag{A20}$$

The quantity

$$S_{\epsilon}^{L}(\omega)=-2\pi i e^{i(\bar{\eta}_i^L+\eta_f^L)}\sum_m A_m\langle F_f^L(E_0',N-1\,|\,R)\,|\,V_{\epsilon,\mu_0+m}(R,\omega)\,|\,\bar{F}_i^L(E,N\,|\,R)\rangle \tag{A21}$$

appearing here is an S-matrix element associated with the T matrix of (A16). Corresponding to (A20) is the formula

$$\sigma_{n'L'M'}^{\mathrm{AI}}(E)=\delta_{M'0}\left[\frac{\pi g_i}{K_i^2}(2L'+1)\,|\,S_{\epsilon}^{L'}(\omega)\,|^2\right]\cos^2\theta_{\alpha} \tag{A22}$$

for the integral cross section for LIAI. The S-matrix element appearing here is similar in form to $S_{\epsilon}^{L}(\omega)$ defined by (A21) but with η_f^L set equal to zero and $F_f^L(E_0',N-1\,|\,R)$ replaced with the bound-state wave function $F_f^L(E_n^L,N-1\,|\,R)$.

The three cross-section formulas (A19), (A20), and (A22) can be written in the forms (2.3), (2.4), and (2.9) of the text, with the functions $B_m^{\mathrm{PI}}(\theta_f)$, B_m^{PI}, and B_m^{AI} replaced with $\tilde{B}_m^{\mathrm{PI}}(\theta_f)$, $\tilde{B}_m^{\mathrm{PI}}$, and $\tilde{B}_m^{\mathrm{AI}}$ of (2.19)—(2.21), respectively. However, we have presented them here in terms of S-matrix elements in order to make a comparison with previously derived formulas for field-free (FF) chemi-ionization. Thus, when the photoionization transition amplitude of (A6) is replaced with the FF autoionization amplitude

$$\langle\epsilon,N\,|\,R,N\rangle\equiv\int d\vec{r}\,[\phi_{\epsilon}(\vec{r}\,|\,\vec{R})]^{*}H_{\mathrm{el}}\phi_d(\vec{r}\,|\,R)=\sum_{\mu}\langle\phi_{\epsilon\mu}\,|\,H_{\mathrm{el}}\,|\,\phi_d\rangle \tag{A23}$$

one obtains in place of (A19) and (A20) and FFPI cross-section expressions

$$\frac{d^2\sigma^{\mathrm{PI}}}{d\epsilon\,d\hat{K}_f}(E,\epsilon)=\frac{g_i}{4K_i^2}\left|\sum_L(2L+1)S_{\epsilon}^{L}P_L(\cos\theta_f)\right|^2, \tag{A24}$$

$$\frac{d\sigma^{\mathrm{PI}}}{d\epsilon}(E,\epsilon)=\frac{\pi g_i}{K_i^2}\sum_L(2L+1)\,|\,S_{\epsilon}^{L}\,|^2 \tag{A25}$$

with

$$S_{\epsilon}^{L}=-2\pi i e^{i(\bar{\eta}_i^L+\eta_f^L)}\langle F_f^L(E_0',N\,|\,R)\,|\,\langle\epsilon,N\,|\,R,N\rangle\,|\,\bar{F}_i^L(E,N\,|\,R)\rangle\,, \tag{A26}$$

These formulas (and the corresponding one for FFAI) are the same as results which Miller[4] reported that he had obtained using a theory by O'Malley.[8] What the present analysis reveals is that these are the cross-section expressions appropriate to the eigenchannel model for the wave function of the ejected electron.

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