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Multiple resonances in non-Franck-Condon transitions due to nonlocal effects in laser-induced associative ionization

Kai-Shue Lam
Department of Physics, California State Polytechnic University, Pomona, California 91768

Thomas F. George
Department of Chemistry, University of Rochester, Rochester, New York 14627

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The laser-induced associative ionization process $A^* + B + \hbar\omega \rightarrow AB^+ + e^-$ is investigated using a nonlocal scattering potential. It is found that for each vibrational level of the ion complex AB^+ multiple resonances for association can occur as the laser frequency is varied, provided the laser intensity is beyond a certain critical value, estimated to be on the order of 10^7 W/cm^2 for alkali diatomic systems. The locations of the resonances also depend crucially on the laser intensity. These results are contrary to the Franck-Condon assumption of localized electronic transitions, which predicts a single resonance for each vibrational level.

I. INTRODUCTION

Recent experiments[1-5] have demonstrated the feasibility of laser-controlled associative ionization processes of the type

$$A^* + B + \hbar\omega \rightarrow AB^+ + e^- \ . \tag{1}$$

While such experiments have generated exciting new results which contribute to the understanding of laser-induced molecular dynamics, much uncertainty remains as to the exact nature of the electronic transitions involved and the interpretation of the ionic or emitted-electron spectrum, especially in experiments where the laser is detuned from the atomic resonances of either collision partner.[2,3] This is in large part due to the fact that, under these circumstances, the photon absorption and the molecular collision cannot be treated as distinct processes. However, apart from the complications introduced by photon absorption, the collision dynamics involved in (1) is distinctly different from other electronically nonadiabatic processes characterized only by transitions between discrete electronic states. In any collisional ionization process, a bound-continuum transition is always involved, because the exit channel of the collision system includes an electronic continuum (due to the presence of the free electron). Such bound-continuum collision processes necessarily entail, at least in principle, a nonlocal scattering potential.[6-9]

For the related process of Penning ionization, we have shown previously that the nonlocal potential can be approximated by a local complex one under conditions of high-collision energy.[9] This approximation has enjoyed wide application and often produced excellent agreement between theory and experiment.[8,10-16] There is, however, one important class of experimental results which cannot be readily explained on the basis of the local theory: the presence of non-Franck-Condon distributions in the emission spectra of Penning-ionization optical spectroscopy (PIOS) studies.[17,18] Although the explanation of these experimental results remains controversial,[19] it appears that a possible cause for non-Franck-Condon behavior in electronic transitions is due to the presence of a nonlocal potential. This has been corroborated theoretically by a numerical study of associative detachment by Bieniek,[20] and more recently, by our model study of Penning ionization based on a semiclassical approach.[21]

While the local potential is at best an approximation in the treatment of Penning ionization, the nonlocal potential plays a dominant role in associative ionization.[9] It is thus expected that non-Franck-Condon effects will be even more pronounced in associative ionization, and these effects should in principle be increasingly more observable as the collision energy is reduced. Rather than varying the collision energy with respect to fixed potential curves on the energy scale, one can fine-tune the laser frequency and change the relative positions of the potential curves instead and thus the effective collision energy on the entrance channel. This is most easily seen by using the electronic field representation for the field-dressed electronic states of the collision system.[22] The laser can in this way be used to "energy-select" the collision partners and probe the nonlocal properties of the potential. In particular, it can be used to "pick out" an arbitrary number of vibrational levels supported by the ionization-threshold potential curve which contribute significantly towards associative ionization.

In this paper, we shall make use of a nonlocal-potential formalism developed in our previous work[9] to analyze the effects of nonlocality in laser-induced associative ionization within the context of a simple model system. The following qualitative predictions are made. Even in the simplest dynamical situation, when only one vibrational level contributes to ionization, there is a critical laser intensity above which multiple resonances for AB^+ can occur when the laser frequency is varied. Moreover, the exact locations of these resonances depend on the strength of the laser intensity. As will be apparent from Sec. V, this is in direct contradiction to conclusions drawn on the basis of the Franck-Condon sudden localized electronic transitions.

Section II specifies our model and establishes the nonlocal Schrödinger equation [Eq. (2)] required for its description. It also presents a physical interpretation for the nonlocal potential appearing in that equation. Section III details the mathematics of the solution for a simplified version of the nonlocal equation, and in Sec. IV the qualitative predictions mentioned in the previous paragraph are made as direct consequences to the solution. Section V closes this work with a discussion of the physical meaning of these predictions and a review of the assumptions and approximations that have been used.

II. THE NONLOCAL SCHRÖDINGER EQUATION FOR ASSOCIATIVE IONIZATION

Throughout this paper we will use the two-state model for the collision dynamics as shown in Fig. 1. The entrance channel is specified by the potential curve $W_d(R)$ with collision energy E_c, and the exit one by $W_+(R)$, with $W_d(\infty)$ taken to be the zero of the energy scale. $W_d(R)$ results from the electronic configuration of the A^*+B complex and is assumed not to support any vibrational levels, while $W_+(R)$ results from that of the ion-core complex $A+B^+$ or AB^+. We assume there is a wide energy gap between the bottom of the potential well in W_+ and the flat region in W_d, so that field-free ionization will not take place. The introduction of a laser field with frequency ω such that $\hbar\omega < E_c$ may then induce the formation of the bound-ion complex AB^+ and the liberation of an electron. The requirement of $\hbar\omega < E_c$ is purely dictated by the energetics of the present model: In the presence of the laser, the entrance channel becomes $W_d(R)+\hbar\omega$ with collision energy $E_c-\hbar\omega$ [see Fig. 1 and Eq. (3) below]. Such a scheme may be of relevance, for example, in the diatomic collision process

$$\mathrm{Na}^*(3p)+\mathrm{Na}(3s)+\hbar\omega \rightarrow \mathrm{Na}_2{}^+ + e^- , \qquad (2)$$

which has been suggested as an important mechanism for the formation of sodium-dimer ions when sodium vapor is subjected to intense nonresonant optical radiation.[2] Another possible mechanism is multiphoton ionization of the neutral sodium dimer.[23,24] This latter mechanism, however, is not directly related to the present work.

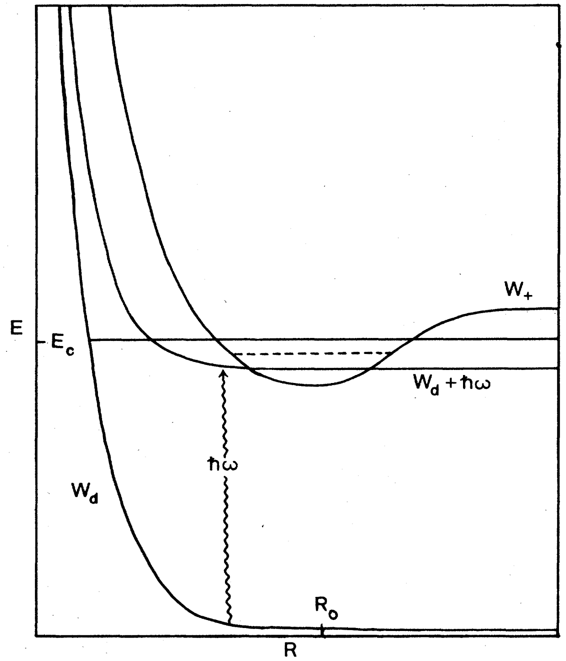

FIG. 1. Schematic diagram of the potential curves for the model of laser-induced associative ionization used in the present study. The zero of energy is taken to be $W_d(\infty)$. E_c is the collision energy in the entrance channel, $W_d(R)$, and ω is the laser frequency. The dashed line represents the ground vibrational level supported by W_+, and R_0 is the equilibrium position of the W_+ well.

The dynamical configuration in Fig. 1 can be well described by the low-energy-limit formalism developed in our previous work.[9] It was shown there that, using the Feshbach projection-operator method, the partial-wave Schrödinger equation in the present context can be written as

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2}+W_d(R)+\hbar\omega+\frac{\hbar^2}{2\mu}\frac{J(J+1)}{R^2}-E_c\right]\chi_J(E_c,R)=i\pi\sum_{l,J',v}(2J'+1)\begin{bmatrix} l & J' & J \\ 0 & 0 & 0\end{bmatrix}^2[\mathscr{V}^{+}_{l0}(R)]^*F_{J'}(E^v_{J'},R)$$
$$\times\int_0^\infty dR'\,\mathscr{V}^{+}_{l0}(R')F_{J'}(E^v_{J'},R')\chi^+_J(E_c,R') , \qquad (3)$$

where $\chi^+_J(E_c,R)$ is the outgoing radial wave function for the Jth partial wave of the diatomic collision system and $F_J(E^v_J,R)$ is the radial wave function for the (J,v) rotational-vibrational state supported by the potential curve $W_+(R)$. $\mathscr{V}^{+}_{l0}(R)$ is the radial part of the bound-continuum coupling calculated with an outgoing continuum lth-partial-wave electron wave function corresponding to the emitted electron.[9] (The z component of the angular momentum for this electron has been set equal to zero for simplicity.) This coupling in the present case is radiatively induced by the laser and is proportional to the laser field strength. It is also assumed to be independent of the emitted-electron energy.

A few points are to be noted about this equation. First, if the right-hand side were set equal to zero, it reduces to the Jth-partial-wave equation for the potential-scattering problem specified by the potential $W_d(R)+\hbar\omega$. Hence, the right-hand side represents the entire effect of the bound-continuum coupling leading to associative ionization. Second, the allowed J' values of the partial waves for the exit channel are related to J and l by the triangle inequality, a consequence of the conservation of electronic angular momentum expressed through the presence of the 3-j symbol. Third, the summation over v only includes those vibrational states such that $E_J^v < E_c$. Thus the interaction potential is energy dependent. Finally, this potential is also nonlocal, with the kernel equal to a sum of separable kernels.

The nonlocality can quite readily be interpreted physically as follows, using semiclassical language. A trajectory of the collision system eventually to be propagated on the discrete-state potential curve $W_d(R)+\hbar\omega$ will contain as part of its "history" a segment that is propagated on the continuum threshold curve $W_+(R)$. If R is the coordinate of the final "upward" transition from W_+ back to $W_d+\hbar\omega$, the initial "downward" transition from $W_d+\hbar\omega$ to W_+ can take place at arbitrary R'. Consequently, one must integrate over this latter coordinate. The strength of the $d\rightarrow+$ transition at R' is given by $\mathscr{V}^{+}_{l0}(R')$, while that of the $+\rightarrow d$ transition at R is given by $[\mathscr{V}^{+}_{l0}(R)]^*$. Since the energetics dictate that, while on $W_+(R)$, the system can only exist as bound states, the propagation between R' and R on the curve W_+ is described by the correlation of the bound-state amplitudes $F_J(E_J^v,R')F_{J'}(E_{J'}^v,R)$. This nonlocal nature of the bound-continuum transition differs essentially from the vertical (local) character of the transitions implied by the Frank-Condon principle.

III. SOLUTION OF THE NONLOCAL SCHRÖDINGER EQUATION

The separability of the kernel in Eq. (3) greatly facilitates the construction of the solution. We shall, however, further simplify the equation by examining the simplest case of the low-energy limit, namely, when the parameters E_c and ω are such that only the $\chi_0^+(E_c,R)$ wave need be considered, and only the ground vibrational state of $W_+(R)$ with energy E_0^0 contributes towards the nonlocal potential. In this case, Eq. (3) reduces to

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2}+W_d(R)-E_\omega\right]\chi_0^+(E_\omega,R)=i\pi\mathscr{V}^*(R)F_0(E_0^0,R)\int_0^\infty dR'\,\mathscr{V}(R')F_0(E_0^0,R')\chi_0^+(E_\omega,R')\ , \tag{4}$$

where

$$\mathscr{V}(R)\equiv\mathscr{V}^{+}_{00}(R) \tag{5}$$

and

$$E_\omega\equiv E_c-\hbar\omega \tag{6}$$

is the effective collision energy.

The first step towards the solution of the integrodifferential equation (4) is to convert it to an integral equation using an outgoing-wave Green's function $G^+(E_\omega;R,R')$ corresponding to the differential operator

$$-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2}+W_d(R)-E_\omega\ ,$$

such that

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2}+W_d(R)-E_\omega\right]G^+(E_\omega;R,R')=\delta(R-R')\ . \tag{7}$$

$\chi_0^+(E_\omega,R)$ then satisfies the integral equation

$$\chi_0^+(E_\omega,R)=\phi_0^+(E_\omega,R)+i\pi\int_0^\infty dR'\,G^+(E_\omega;R,R')\mathscr{V}^*(R')F_0(E_0^0,R')\int_0^\infty dR''\mathscr{V}(R'')F_0(E_0^0,R'')\chi_0^+(E_\omega,R'')\ , \tag{8}$$

where $\phi_0^+(E_\omega,R)$ is the outgoing solution for the homogeneous part of Eq. (4), i.e.,

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2}+W_d(R)-E_\omega\right]\phi_0^+(E_\omega,R)=0\ . \tag{9}$$

We now introduce the following linear functional:

$$\mathscr{F}[\chi_0^+]\equiv\int_0^\infty dR\,\mathscr{V}(R)F_0(E_0^0,R)\chi_0^+(E_\omega,R)\ . \tag{10}$$

With this quantity, Eq. (8) can be rewritten as

$$\chi_0^+(E_\omega,R)=\phi_0^+(E_\omega,R)+i\pi\mathscr{F}[\chi_0^+]\times\int_0^\infty dR'\,G^+(E_\omega;R,R')U^*(R')\ , \tag{11}$$

where

$$U(R)\equiv\mathscr{V}(R)F_0(E_0^0,R)\ . \tag{12}$$

The last definition is consistent with Eq. (8) since the vibrational wave function $F_0(E_0^0,R)$ is always real.[9] Operating on both sides of Eq. (11) with $\mathscr{F}$, we obtain

$$\mathscr{F}[\chi_0]=\mathscr{F}[\phi_0^+]+i\pi\mathscr{F}[\chi_0^+]\times\int_0^\infty dR\int_0^\infty dR'\,U(R)G^+(E_\omega;R,R')U^*(R')\ . \tag{13}$$

This equation then allows us to obtain an explicit form for $\mathscr{F}[\chi_0^+]$, which can eventually be inserted back into the right-hand side of Eq. (11) to yield the solution for $\chi_0^+(E_\omega,R)$.

The double integral in Eq. (13) can be evaluated with the help of the explicit form for $G^+(E;R,R')$:

$$G^+(E;R,R')=\int_0^\infty dE'\frac{\phi_0^+(E',R)[\phi_0^+(E',R')]^*}{E-E'+i\eta}\ , \tag{14}$$

which is valid when the discrete electronic state $W_d(R)$ does not support any vibrational levels, as is the case assumed in this work (see Fig. 1). Now making use of the completeness property of the homogeneous solutions $\phi_0^+(E,R)$,

$$\int_0^\infty dE\,\phi_0^+(E,R)[\phi_0^+(E,R')]^*=\delta(R-R')\ , \tag{15}$$

we can introduce the transform pair

$$Z(E)\equiv\int_0^\infty dR\,\phi_0^+(E,R)U(R)\ , \tag{16a}$$

$$U(R)=\int_0^\infty dE[\phi_0^+(E,R)]^*Z(E),\ \ R\geq 0 \tag{16b}$$

where $U(R)$ has been defined in Eq. (12). Using Eqs. (14) and (16b) in the double integral I in Eq. (13), we thus obtain

$$\begin{aligned}I=&\int_0^\infty dR\int_0^\infty dR'\int_0^\infty dE[\phi^+(E,R)]^*Z(E)\int_0^\infty dE'\frac{\phi_0^+(E',R)[\phi_0^+(E',R')]^*}{E_\omega-E'+i\eta}\int_0^\infty dE''\,\phi^+(E'',R')Z^*(E'')\\ =&\int_0^\infty dE\frac{|Z(E)|^2}{E_\omega-E+i\eta}\equiv Y^+(E_\omega)\ ,\end{aligned}\tag{17}$$

where we have made use of the orthonormality property of the homogeneous solutions,

$$\int_0^\infty dR[\phi_0^+(E,R)]^*\phi_0^+(E',R)=\delta(E-E')\ , \tag{18}$$

to perform the integrals over R and R'. Equation (13) then leads directly to

$$\mathscr{T}[\chi_0^+]=\frac{\mathscr{T}[\phi^+]}{1-i\pi Y^+(E_\omega)}\ , \tag{19}$$

which when substituted into the right-hand side of Eq. (11) finally yields the desired solution to Eq. (4):

$$\chi_0^+(E_\omega,R)=\phi_0^+(E_\omega,R)+\frac{i\pi\mathscr{T}[\phi^+]}{1-i\pi Y^+(E_\omega)}\times\int_0^\infty dR'\,G^+(E_\omega;R,R')U^*(R')\ . \tag{20}$$

Note that when the bound-continuum interaction $\mathscr{V}(R)$ approaches zero, so does $U(R)$ [Eq. (12)], and $\chi_0^+(E,R)$ approaches $\phi_0^+(E,R)$, as expected.

IV. THE RESONANCES FOR ASSOCIATIVE IONIZATION

As revealed by Eq. (20), the properties of the resonances for associative ionization are determined by the zeros of the factor $1-i\pi Y^+(E_\omega)$. Since, according to Eq. (17),

$$\begin{aligned}Y^+(E_\omega)&=\mathscr{P}\int_0^\infty dE\frac{|Z(E)|^2}{E_\omega-E}-i\pi|Z(E_\omega)|^2\\ &\equiv P(E_\omega)-i\pi|Z(E_\omega)|^2\ ,\end{aligned}\tag{21}$$

where $\mathscr{P}$ denotes the principal value of the integral, we have the following equation determining the structure of the resonances:

$$1-\pi^2|Z(E_\omega)|^2-i\pi P(E_\omega)=0\ . \tag{22}$$

In particular, as $P(E_\omega)$ is real, the locations of the resonances are given by the solutions of the equation

$$1-\pi^2|Z(E_\omega)|^2=0\ , \tag{23}$$

where $Z(E)$ is defined in Eq. (16a). We now use our model for the collision process (cf. Fig. 1 and the discussion at the beginning of Sec. II) to give a qualitative calculation for $|Z(E_\omega)|^2$.

Referring to Fig. 1, we make the following assumptions. First, the bound well of W_+ only overlaps appreciably the relatively flat region of $W_d+\hbar\omega$. Then, since only the overlap of the wave functions $\phi_0^+(E_\omega,R)$ and $F_0(E_0^0,R)$ is of importance in the integral of Eq. (16a) [see also Eq. (12)], we can approximate $\phi_0^+(E_\omega,R)$ there by its asymptotic form,

$$\phi_0^+(E_\omega,R)\sim\left[\frac{2\mu}{\pi\hbar^2}\right]^{1/2}\frac{e^{i\delta_0}}{\sqrt{k}}\sin(kR+\delta_0)\ , \tag{24}$$

where μ is the reduced mass of the $A+B$ system, δ_0 is the s-wave scattering phase shift for the potential $W_d(R)$, and the wave number k is defined by $\hbar^2k^2/2\mu\equiv E_\omega$. Next, we approximate the bound-state wave function $F_0(E_0^0,R)$ by a ground-state harmonic oscillator wave function,

$$F_0(E_0^0,R)\sim\left[\frac{\mu\omega_0}{\pi\hbar}\right]^{1/4}\exp\left[-\frac{\mu\omega_0}{2\hbar}(R-R_0)^2\right]\ , \tag{25}$$

where ω_0 is the natural frequency of the oscillator, and R_0 is its equilibrium position (see Fig. 1). Finally, we assume that over the region of R where the overlap between $\phi_0^+(E_\omega,R)$ and $F_0(E_0^0,R)$ is appreciable, $\mathscr{V}(R)$ is effectively constant. Thus, for the purposes of computing the integral in Eq. (16a),

$$\mathscr{V}(R)=V=\text{const}\ .$$

With the above approximation we have

$$Z(E_\omega)=\int_0^\infty dR\,\phi_0^+(E_\omega,R)\mathscr{V}(R)F_0(E_0,R)$$
$$\sim\frac{AVe^{i\delta_0}}{\pi^{3/4}}\left[\frac{2}{k}\right]^{1/2}\int_0^\infty dR\,e^{-\alpha^2(R-R_0)^2/2}$$
$$\times\sin(kR+\delta_0)\ , \tag{26}$$

where

$$A\equiv\frac{\mu^{3/4}\omega_0^{1/4}}{\hbar^{5/4}} \tag{27}$$

and

$$\alpha^2\equiv\frac{\mu\omega_0}{\hbar}\ . \tag{28}$$

R_0 (>0) is assumed to be far enough from zero so that the lower integration limit in Eq. (26) can be extended to $-\infty$. Using the explicit evaluation of the integral,

$$\int_{-\infty}^{\infty} dR\,e^{-\alpha^2(R-R_0)^2/2}\sin(kR+\delta_0)$$
$$=\left[\frac{\pi}{2}\right]^{1/2}\frac{e^{-k^2/2\alpha^2}}{\alpha}\sin(\delta_0-kR_0)\ , \tag{29}$$

we obtain

$$Z(E_\omega)\sim\left[\frac{1}{2\pi\hbar\omega_0}\right]^{1/4}Ve^{i\delta_0}$$
$$\times\frac{\sin\left[\delta_0-R_0\left[\dfrac{2\mu E_\omega}{\hbar^2}\right]^{1/2}\right]}{E_\omega^{1/4}}e^{-E_\omega/\hbar\omega_0}\ . \tag{30}$$

To simplify the formula, we scale all energies in terms of $\hbar\omega_0$ and introduce the following dimensionless parameters:

$$\epsilon\equiv\frac{E_\omega}{\hbar\omega_0}=\frac{E_c-\hbar\omega}{\hbar\omega_0}\equiv\epsilon_c-\varpi\ , \tag{31}$$

$$\epsilon_c\equiv\frac{E_c}{\hbar\omega_0}\ , \tag{32}$$

$$\varpi\equiv\omega/\omega_0\ , \tag{33}$$

$$\bar{V}^2\equiv V^2/\hbar\omega_0\ . \tag{34}$$

It is noted that V has dimensions of the square root of energy, so that $\bar{V}^2$ is a dimensionless "coupling strength" for the radiatively induced bound-continuum coupling and is thus proportional to the intensity of the laser field. We further assume a low effective collision energy (E_ω, $k\rightarrow 0$) so that $\delta_0\rightarrow ka$, where a is the effective range of the potential $W_d(R)$. The final result is that Eq. (23) is equivalent to

$$\left[\frac{\sqrt{2}}{\pi^{3/2}}\right]\left[\frac{1}{\bar{V}^2}\right]=\frac{e^{-2(\epsilon_c-\varpi)}}{\sqrt{(\epsilon_c-\varpi)}}$$
$$\times\sin^2\left[\left[\frac{(\epsilon_c-\varpi)}{\epsilon_0}\right]^{1/2}\right]\equiv f(\varpi)\ , \tag{35}$$

where the dimensionless constant ϵ_0 is defined by

$$\epsilon_0\equiv\frac{\hbar}{2\mu\omega_0(R_0-a)^2}\ . \tag{36}$$

Equation (35) allows the solutions of Eq. (23), i.e., the locations of the resonances, to be directly given in terms of the tunable laser frequency ϖ. The important range of ϖ is given by

$$\varpi_{\min}=\frac{W_+(R_0)-W_d(\infty)}{\hbar\omega_0}<\varpi<\epsilon_c\ . \tag{37}$$

In our model calculation, the following numerical values for the system dependent parameters are chosen: $\epsilon_c-\varpi_{\min}=1$ and $\epsilon_0=1/4\pi^2$. The first choice was adopted since the harmonic oscillator approximation for the bound well of W_+ implies that the ground vibrational state E_0^0 and the first excited state E_0^1 are $\frac{1}{2}$ and $\frac{3}{2}$ scaled energy units above $W_+(R_0)$, respectively, and it is assumed that only the ground state is accessible in the collision, i.e.,

$$E_c-E_0^0<E_0^1-E_0^0\ . \tag{38}$$

Equation (37) thus implies that $\varpi-\varpi_{\min}$ falls in the range between zero and one.

Figure 2 shows the graphical solutions ϖ_R for Eq. (35)

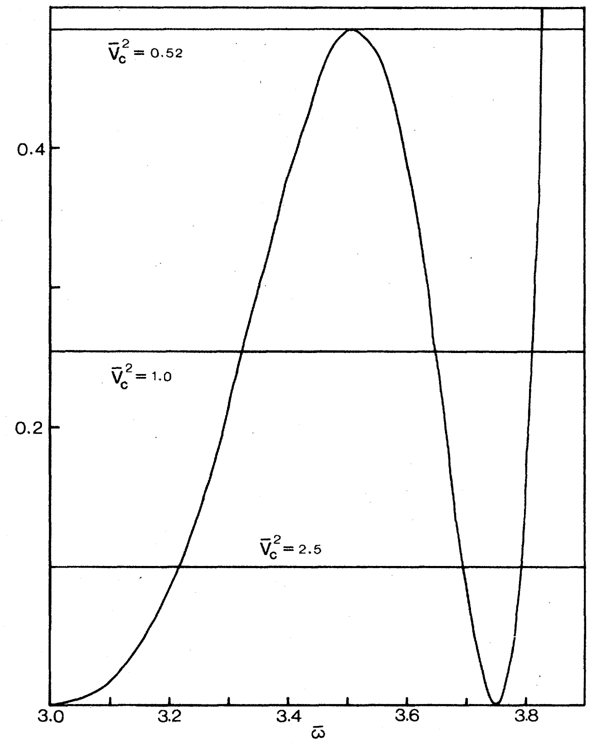

FIG. 2. Graphical solutions for Eq. (35). The curve represents the right-hand side of this equation as a function of ϖ, and the indicated values for $\bar{V}^2$ (proportional to the laser intensity) correspond to the positions of the horizontal lines as given by the left-hand side of the same equation. $\bar{V}_c^2=0.52$ is the critical value for the coupling strength at which multiple resonances begin to occur.

with the above numerical choice of the system parameters and a few typical values for the coupling strength $\bar{V}^2$. The ground vibrational level coincides with $\bar{\omega}=\bar{\omega}_0\equiv\bar{\omega}_{\min}+0.5$. It is thus seen that only for one critical value of the coupling strength $\bar{V}=\bar{V}_c$, will resonance occur exactly at this vibrational level: $\bar{\omega}_{R1}=\bar{\omega}_0$. For this value of the coupling, there is in addition a second resonance $\bar{\omega}_{R2}>\bar{\omega}_0$. For $\bar{V}<\bar{V}_c$, there is only one resonance $\bar{\omega}_R>\bar{\omega}_0$, while for $V_c<\bar{V}<\infty$, three resonances are possible: $\bar{\omega}_{R1}<\bar{\omega}_0$ and $\bar{\omega}_{R3}>\bar{\omega}_{R2}>\bar{\omega}_0$. The threshold for multiple-resonance formation is thus $\bar{V}_c$. From Fig. 2, $\bar{V}_c^2=0.52$. If we assume that the bound-continuum coupling V is due to electric dipole coupling such that $V\sim\mu_0\mathscr{E}/\sqrt{\epsilon_e}\sim\mu_0\mathscr{E}/\sqrt{\hbar\omega_0}$, where μ_0 is the electric dipole moment of the $A+B$ system, $\mathscr{E}$ is the electric field strength of the laser, and ϵ_e is the energy of the liberated electron, we can estimate the critical laser power for multiple-resonance formation to be on the order of $I_c\sim 5\times 10^7$ W/cm^2, where the values $\mu_0\sim 10$ a.u. and $\omega_0\sim 120$ cm^{-1} have been used. This level of laser intensity is well within the range of that employed in many experimental studies of associative ionization.[1,2]

V. DISCUSSION

The possible formation of multiple resonances for associative ionization demonstrated in the last section is clearly an effect due to the nonlocality of the scattered potential in Eq. (3). A local complex potential would at best lead to a single resonance in our model, with an associated width. The reason is that when a local potential is used, the Franck-Condon principle of local vertical transitions is assumed, and the resonances are obtained from the energies E leading to the maximum overlap of the wave functions $\phi_0^+(E,R)$ and $F_0(E_0^0,R)$,[25] i.e., the maximum of the quantity $Z(E)$ [Eqs. (16a) and (12)] in our formulation [$\mathscr{V}(R)$ being assumed to be R independent]. Figure 2 shows that there is only one such Franck-Condon resonance in our model, and it occurs, as expected, when $\bar{\omega}=\bar{\omega}_0$, i.e., when $W_d(\infty)+\hbar\omega$ coincides with the vibrational energy E_0^0 (see Fig. 1). The width associated with this resonance is then simply given by V^2. On the other hand, as a consequence of Eq. (22) derived from the present nonlocal theory, the number of resonances may be larger than one and the widths at the energies E_ω are proportional to the principal-value integral $P(E_\omega)$ [Eq. (21)], instead of to V^2.

The mathematical consequence of nonlocality is that the resonances cannot be simply determined by the maximum overlap of the bound and continuous wave functions. Physically this means that the electronic transition is no longer localized around the bottom of the bound well of W_+. Instead, the "most likely" coordinates for the transition are redistributed around this point, the amount of redistribution depending on the strength of the bound-continuum coupling. Indeed, for a given resonance energy E_ω, one can assign a "most likely" transition coordinate R_t by requiring the local wave numbers of nuclear motion on the two potential curves W_+ and $W_d+\hbar\omega$ be equal,

$$k^2=\frac{2\mu}{\hbar^2}[E_\omega-W_+(R_t)]=\frac{2\mu}{\hbar^2}\{E_\omega-[W_d(R_t)+\hbar\omega]\}\ , \tag{39}$$

or equivalently, the nuclear kinetic energies be conserved in the electronic transition. When $\bar{\omega}_R>\bar{\omega}_0$, this requirement can be fulfilled by two transition coordinates, $R_{t1}>R_0$ and $R_{t2}<R_0$. Figure 3 depicts the relationship between these coordinates and the relevant potential energy curves. The same figure also shows, however, that when $\bar{\omega}_R<\bar{\omega}_0$, no R_t is possible, because the nuclear kinetic energy in the entrance channel, $E_c-[W_d(R)+\hbar\omega_{R2}]$, is always larger than the maximum vibrational energy in the exit channel, $E_0^0-W_+(R_0)$.

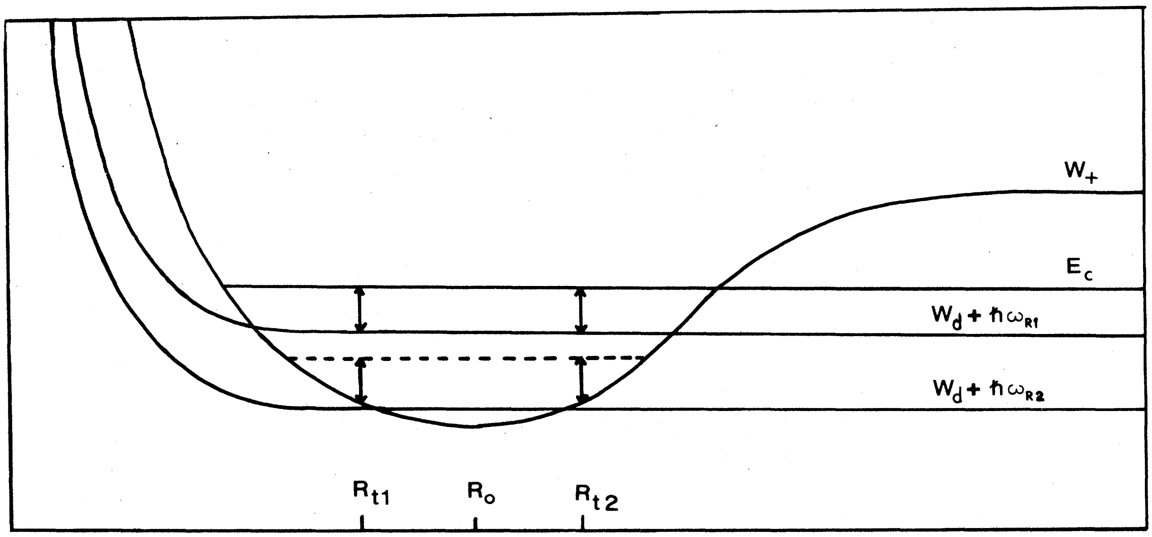

FIG. 3. Schematic diagram illustrating the coordinates R_{t1} and R_{t2}, redistributed around the equilibrium position R_0, of the non-Franck-Condon local electronic transitions in associative ionization for the resonant laser frequency ω_{R1}. These are the coordinates at which the nuclear kinetic energy, represented by double-pointed arrows, is conserved. For the resonant laser frequency ω_{R2}, the transitions, besides being non-Franck-Condon, are also truly nonlocal since nuclear kinetic energy cannot be conserved.

Hence, nuclear kinetic energy is always depleted in the electronic transition, and the energy lost must go into the kinetic energy of the free electron produced by associative ionization. We have thus arrived at a situation in which the energy of the emitted electron, ϵ_e, is not necessarily related to the difference in energy between the electronic potential curves as dictated by the Franck-Condon approximation,

$$\epsilon_e = W_d(R) + \hbar\omega_R - W_+(R) \ . \tag{40}$$

In fact, we have $\epsilon_e > W_d(R) + \hbar\omega_R - W_+(R)$ (see Fig. 3). This state of affairs illustrates most poignantly the effects of the nonlocal potential. Obviously, these effects will also have most interesting consequences on the emitted-electron energy spectrum. However, further investigation of this problem will require a detailed treatment of the widths of the resonances and their overlap.

We recapitulate here the main approximations leading to the present qualitative results. First, the bound-continuum coupling $\mathscr{V}(R)$ has been assumed to be both R and ϵ_e independent. As demonstrated previously, any ϵ_e dependence will alter the nature of the nonlocality of the scattering potential, while an R dependence will decidedly influence the exact locations of the resonances. Of these two approximations, the ϵ_e independence will merit more careful consideration in further work, since it is expected that a radiatively induced bound-continuum coupling is more likely to be ϵ_e dependent. Concerning the available channels for associative ionization, we have only treated the case of the $J=0$ wave with a single vibrational level in the bound well of the ionization-threshold curve. The situation involving higher waves and more vibrational levels is not fundamentally different, although a detailed quantitative picture of the resonance spectrum will involve considerably more substantial computational work. It is expected that higher (J,v) values may lead to a profusion of multiple resonances lying in close proximity to each other, and thus manifesting themselves as continuous bands. This is due to the fact that the resonance widths, being proportional to the quantity $P(E_\omega)$ in Eq. (21), are directly proportional to the laser power, and it is for high laser powers that multiple resonances become important. Finally, laser characteristics such as bandwidth, polarization and pulse duration have been neglected in the present treatment. Inclusion of these effects is expected to further complicate the multiple-resonance structure of the associative ionization spectrum.

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[25] See, for example, G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1950), Chap. 7.