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Laser-induced molecular predissociation without absorption or emission of laser photons*

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Quantum theory and selection rules of laser-induced predissociation of diatomic molecules without actual absorption or emission of laser photons are given. The rate of induced predissociation is a function of the externally controllable laser-field parameters: intensity, frequency, and polarization. Both perturbative and nonperturbative theories are used in the analysis, providing treatment for both low and high laser intensities. The region of validity of perturbative results is determined by comparison with the exact results and is given by a simple criterion. An approximate expression is given for the convenient calculation of the induced predissociation rate. Laser-induced predissociation without absorption or emission of laser photons also occurs in polyatomic molecules, and the analysis is similar.

INTRODUCTION

A stable electronic state of a molecule may be crossed or closely approached by an unstable or less-stable electronic state (see Fig. 1). Various interactions between the two electronic states may cause transition from the stable state to the less-stable state leading to dissociation of the molecule without reaching the dissociation limit of the stable state. Such a phenomenon, called predissociation, is well known in molecular physics.[1,2] Some known interactions leading to predissociation are nonadiabatic interaction (spontaneous predissociation[3]), hyperfine interaction (hyperfine predissociation[4]), dc magnetic or dc electric interaction.[5]

Recently, Lau and Rhodes have predicted and analyzed a new mechanism of predissociation due to applied laser fields.[6,7] In this so-called nonresonant laser-induced predissociation, the coherent electromagnetic field interaction introduces a direct (e.g., electric dipole) coupling between the two electronic states[6] or an effective (via other electronic states) coupling between the two states.[7] Thus molecules in the stable electronic state have a certain probability of transition to the less-stable state, leading to predissociation if the energy of the molecule in the stable state exceeds the dissociative asymptote of the latter state. This transition probability depends on the externally controlled laser intensity, frequency, and polarization.

As distinguished from resonant processes,[8-12] which require actual single or multiphoton absorption or emission of laser photons, the nonresonant laser-induced predissociation does not require actual absorption or emission of photons.[13] The same laser-induced nonresonant effect producing the predissociation can manifest itself in the context of other molecular processes such as atomic and molecular collisions, dissociation, and association.[6,7] These nonresonant effects have the advantage of *not* requiring resonant frequency match, which can be rather stringent for a given transition of interest. From energy consideration, the nonresonant effects of the laser are interesting because physical or chemical changes can be induced without requiring the expense of photon energy.[7] From the viewpoint of chemistry, the laser photons can also be viewed as acting like *catalysts* to effect these changes.[14]

The purpose of this paper is to give a fully quantum theory of and general results for the rates of nonresonant laser-induced predissociation for *any* configurations of the molecular potential curves (see Fig. 1), although the physical idea and a simple formula applicable to some limited configurations were given in Ref. 7. *In addition,* the treatment given here differs from Ref. 7 in the following aspects: First, the quantum rotational motion is explicitly treated and evaluated here whereas in Ref. 7 it was neglected except by

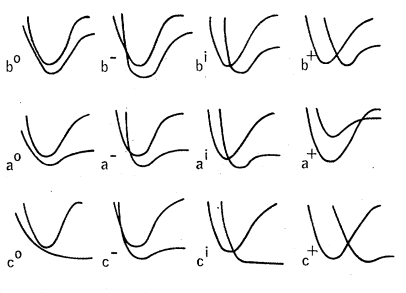

FIG. 1. Schematic illustration of different configurations of potential curves as function of the internuclear distance, leading to various subcases of predissociations from the stable to the less-stable state. The notations are the same as Mulliken's. The theory presented here is applicable to the laser-induced predissociation in all these subcases.

including the rotational contributions to the electronic potential curves. Second, selection rules for allowed nonresonant induced transition are given here. Third, in this paper both perturbative and nonperturbative results (each with their own usefulness depending on the laser intensity) are presented and compared to determine the validity of the former. In the following paragraphs, the significance of these points are discussed and the outline of the paper is given.

Herzberg[1] and Mulliken[2] have discussed various subcases of *field-free* molecular predissociation via crossing or close-lying electronic potentials. The division of various subcases is based on whether the dissociation asymptote of the unstable state lies (a) approximately at, (b) above, or (c) below the energy at which the potentials cross or approach each other closely. This distinction is significant because as seen in Fig. 1 the different subcases lead to different observable predissociation limits, etc.[1,2] The three subcases are further distinguished depending on whether the internuclear distance R_c of the crossing is smaller than (denoted by superscript "$-$"), about equal to (denoted by superscript i), or larger than (denoted by superscript "$+$") the equilibrium distance of the more stable state. A fourth variation in each subcase is that the unstable potential curve comes into close approach with the stable electronic potential without crossing it (denoted by superscript 0). The distinction of these variations is significant because the Franck-Condon factors in these variations are quite different.[1,2] The theory presented in Sec. I can be used to analyze all these subcases.

For a given laser intensity (which can be weak or strong), there is a time domain Δt ($\ll \gamma^{-1}$) such that the rate γ (per unit time) of laser-induced predissociation can be derived by *time-dependent* perturbation theory. Two such formulas are given in Sec. I, one valid up to moderate field intensity and the other being necessary for strong-field intensity. These formulas give a prescription of accurate (possibly numerical) evaluation of the laser-induced predissociation rate from *any* rotation-vibrational state of the molecule. In this section, we also give some selection rules for predicting nonresonant field-induced avoided crossing and the associated field-induced transitions.

For the solution of the interaction of the molecule with the laser radiation, we use theories developed from first principles.[11,12] For weak and moderate laser intensities, we can use well-known *stationary* perturbative solutions; and for strong intensity, highly accurate analytic solutions or exact numerical solutions are necessary.[6-11] The latter solutions of course include the perturbative solutions for the weaker field, but the calculation is less familiar than the perturbative calculations. Since a *small* radiative interaction can induce a significant predissociative probability after many vibrations during the lifetime of the bound molecular state, stationary perturbative results can be valid where this effect is physically significant.

In Sec. II, the perturbative results are compared with those of exact results and a criterion for the accuracy of the perturbative results is given. An approximate semiclassical result for the rate of nonresonant laser-induced predissociation is also given. The laser intensity necessary for experiments can be estimated by Eq. (2.19). A summary and discussion, and an appendix on the evaluation of the rotational factors occuring in the transition matrix elements are provided at the end of the paper.

I. GENERAL THEORY AND RESULTS

A. Weak to moderate field intensity-perturbative regime

Let the molecular eigenstate $\psi^{\pm}_{k\Lambda vJM}$ be written in the Born-Oppenheimer approximation as products of the electronic state $\varphi_{k\Lambda}$, the vibrational state $\chi_{vk\Lambda J}$, and the rotational state $\psi_{J\Lambda M}$:

$$\psi^{\pm}_{k\Lambda vJM} \equiv (1/\sqrt{2})[\varphi_{k\Lambda}(\vec{r}\,\phi R)\chi_{vk\Lambda J}(R)\psi_{J\Lambda M}(\theta\psi) \pm \varphi_{k-\Lambda}(\vec{r}\phi R)\chi_{vk\Lambda J}(R)\psi_{J-\Lambda M}(\theta\psi)], \quad \Lambda \neq 0; \tag{1.1}$$

$$\psi^{\pm}_{k0vJM} \equiv \varphi_{k0^{\pm}}(\vec{r}R)\chi_{vk0J}(R)\psi_{J0M}(\theta\psi), \quad \Lambda = 0$$

where θ, ψ, ϕ are the Euler angles shown in Fig. 2 relating the body-fixed coordinate system xyz to the space-fixed coordinate system $x'y'z'$; R is the internuclear distance and $\vec{r}$ denotes the collection of electronic coordinates in the body-fixed

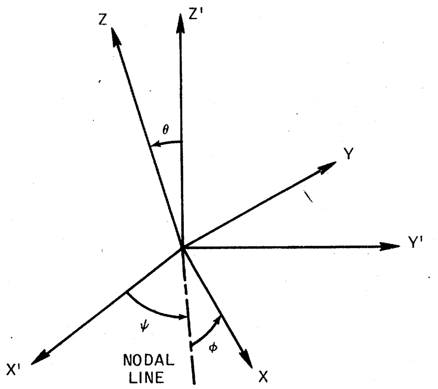

FIG. 2. Definition of the Euler angles relating the rotating body-fixed xyz axes to the space-fixed $x'y'z'$ axes. The internuclear axis of the diatom is usually chosen along the z axis. If the laser polarization $\hat{\epsilon}$ is linear, the z' axis may be chosen along it.

system. The coordinate of the first electron is chosen to be $(x_1, y_1 = 0, z_1)$. The electronic state $\varphi_{k\Lambda}$ can be given more explicitly[3]:

$$\begin{aligned} \varphi_{k\Lambda}(\vec{\mathrm{r}}\phi R) &= f_{k\Lambda}(\vec{\mathrm{r}}R)e^{i\Lambda\phi}/(2\pi)^{1/2}, \\ \varphi_{k-\Lambda}(\vec{\mathrm{r}}\phi R) &= f_{k\Lambda}(\{x_i - y_i z_i\}, R)e^{-i\Lambda\phi}/(2\pi)^{1/2}, \end{aligned} \tag{1.2}$$

where $\hbar\Lambda$ is the magnitude of the component of the electronic angular momentum along the internuclear axis $\hat{z}$; and k denotes the rest of the electronic state labels. For $\Lambda = 0$, the nondegenerate states φ_{k0^+} and φ_{k0^-} correspond to the Σ^+ and Σ^- states, respectively.[1] The normalization of the electronic state at each R is

$$\int dV \int_0^{2\pi} d\phi |\varphi_{k\Lambda}(\vec{\mathrm{r}}\phi R)|^2 = 1 . \tag{1.3}$$

The vibrational state $\chi_{vk\Lambda J}(R)$ for a given effective potential $U_{k\Lambda J}(R)$ is labeled by the vibrational quantum number v and is normalized according to

$$\int_0^\infty dR\, R^2 |\chi_{vk\Lambda J}(R)|^2 = 1 . \tag{1.4}$$

The rotational wave function $\psi_{J\Lambda M}(\theta\psi)$ of a symmetric top[1,3] is labeled by the square of total angular momentum $J(J+1)\hbar^2$ and its component $M\hbar$ along the space-fixed $\hat{z}'$ axis. It can be written

$$\psi_{J\Lambda M}(\theta\psi) = \Theta_{J\Lambda M}(\theta)e^{iM\psi} ,$$

with normalization

$$\int_0^{2\pi} d\psi \int_0^\pi d\theta \sin\theta |\psi_{J\Lambda M}(\theta\psi)|^2 = 1 . \tag{1.5}$$

Let the initial bound state of the molecule be $\psi^s_{k\Lambda vJM}$ and the final state be $\psi^{s'}_{k'\Lambda'EJ'M'}$, where s and s' stand for the "+" or "−" sign. The continuum wave function of the vibrational part of the final state is normalized such that[15]

$$\int dR\, R^2 \chi_{E'k'\Lambda'J'} \chi_{Ek'\Lambda'J'} = \delta(E' - E) . \tag{1.6}$$

We shall call the nonadiabatic Hamiltonian leading to field-free predissociation[3] $\hbar T$ and the radiative interaction Hamiltonian[9] h'. Since the transition does not require actual photon absorption or emission between the states $\psi^s_{k\Lambda vJM}$ and $\psi^{s'}_{k'\Lambda'EJ'M'}$, the first-order matrix element of h' between states of equal photon numbers is zero. The predissociative transition from the bound state to the continuum state is induced by an effective interaction between the two states via radiative coupling (or virtual transitions) to other states. We find the effective radiative interaction Hamiltonian $H'(R)$ at each internuclear separation R. This form of $H'(R)$ is valid if the initial molecular states are far off resonant from any intermediate molecular states connected by significant dipole moments. It is sufficient here that the radiative interaction is solved by standard stationary perturbative theory because we are considering weak to moderate laser intensity. To lowest nonvanishing order, the result for H' is[15]

$$H' = 6.8626 \times 10^{-15} \lambda^2 I \sum_{\alpha\beta\gamma} |\varphi_\alpha\rangle \mu_{\alpha\beta} \mu_{\beta\gamma} \Delta_{\beta\gamma} \langle\varphi_\gamma| , \tag{1.7}$$

where we have used greek subscripts to stand for the electronic state quantum labels $k\Lambda$, $k-\Lambda$, etc., and where the frequency factor[15]

$$\Delta_{\beta\gamma}(R) \equiv (w_\beta - w_\gamma)/[1 - (w_\beta - w_\gamma)^2/\omega^2] \tag{1.8}$$

is given in terms of the electronic potential energies $\hbar w_\beta(R)$ and the laser photon energy $\hbar\omega$, and the electric dipole moments μ (in a.u.) are defined

$$\mu_{\alpha\beta}(R) \equiv \langle\varphi_\alpha| - \sum q_i \vec{\mathrm{r}}_i' |\varphi_\beta\rangle \cdot \hat{\epsilon} , \tag{1.9}$$

where $\hat{\epsilon}$ is the laser polarization. In expression (1.7), λ in micrometers is the laser wavelength and I in W/cm^2 is the laser intensity.

The rate of predissociation (including both the laser-induced and field-free components) from the initial state $\psi^s_{k\Lambda vJM}$ to the final state $\psi^{s'}_{k'\Lambda'EJ'M'}$ is given by

$$\gamma_{vJM} = 2\pi\hbar \sum_{J'M'} |\langle\psi^{s'}_{k'\Lambda'EJ'M'}|H' + T|\psi^s_{k\Lambda vJM}\rangle|^2 , \tag{1.10}$$

provided that the time interval Δt, for which the above rate formula is valid, satisfies

$$\gamma_{vJM}\Delta t \ll 1 . \tag{1.11}$$

The continuum energy E is equal to the initial vibrational energy $E_{vk\Lambda J}$. If the initial-state population is given by the distribution g_{vJM} such that

$$\sum_{vJM} g_{vJM} = 1 , \tag{1.12}$$

then the total rate of predissociation is

$$\gamma = \sum_{vJM} g_{vJM} \gamma_{vJM} . \tag{1.13}$$

Kronig [see Eqs. (18) and (19) in Ref. 3] has evaluated the matrix element for field-free predissociation due to nonadiabatic terms. The quantity[15]

$$\langle\psi^{s'}_{k'\Lambda'EJ'M'}|T|\psi^s_{k\Lambda vJM}\rangle = (1/\hbar)\nu(kvJ\Lambda M, k'EJ\Lambda'M)\delta_{J'J}\delta_{M'M} \tag{1.14}$$

of his expressions. The matrix element is nonzero only if

$$\Lambda' = \Lambda \tag{1.15}$$

called the homogeneous predissociation, or if

$$\Lambda' = \Lambda \pm 1 \tag{1.16}$$

called the inhomogeneous predissociation. Furthermore transitions occur between states of the same parity ("+" or "−" under spatial inversion of $\psi^s_{k\Lambda vJM}$) only:

$$+\longleftrightarrow+,\quad -\longleftrightarrow-,\quad +\not\longleftrightarrow- . \tag{1.17}$$

For homonuclear diatoms, transitions are allowed between symmetric (under exchange of the two nuclei) states or between antisymmetric states only,

$$s\longleftrightarrow s,\quad a\longleftrightarrow a,\quad s\not\longleftrightarrow a. \tag{1.18}$$

With the space-fixed $\hat{z}'$ axis chosen along the linear polarization of the laser, we can evaluate the matrix elements μ's occuring in Eq. (1.7) as follows:

$$\begin{aligned}\mu_{\beta\gamma}(R\,\theta)&=\langle\varphi_{k''\Lambda''}|-\sum q_i z_i'|\varphi_{k\Lambda}\rangle\\ &=M_{\beta\gamma}(R)M_{\Lambda''\Lambda}(\theta),\end{aligned} \tag{1.19}$$

where the transition electric dipole moments

$$M_{\beta\gamma}(R)=\begin{cases}[-\frac{1}{2}iX_{k''\Lambda''K\Lambda}(R)+\frac{1}{2}Y_{k''\Lambda''k\Lambda}(R)]\,\delta_{\Lambda''\Lambda+1}\,,\\ [\frac{1}{2}iX_{k''\Lambda''k\Lambda}(R)+\frac{1}{2}Y_{k''\Lambda''k\Lambda}(R)]\delta_{\Lambda''\Lambda-1},\\ Z_{k''\Lambda''k\Lambda}(R)\delta_{\Lambda''\Lambda}\,,\end{cases} \tag{1.20}$$

with

$$\begin{aligned}X_{k''\Lambda''k\Lambda}(R)&\equiv\langle f_{k''\Lambda''}(\vec{r},R)|-\sum q_i x_i|f_{k\Lambda}(\vec{r},R)\rangle\,,\\ Y_{k''\Lambda''k\Lambda}(R)&\equiv\langle f_{k''\Lambda''}(\vec{r},R)|-\sum q_i y_i|f_{k\Lambda}(\vec{r},R)\rangle\,,\\ Z_{k''\Lambda''k\Lambda}(R)&\equiv\langle f_{k''\Lambda''}(\vec{r},R)|-\sum q_i z_i|f_{k\Lambda}(\vec{r},R)\rangle\,,\end{aligned} \tag{1.21}$$

and where the angular factors are

$$M_{\Lambda''\Lambda}(\theta)=\begin{cases}\sin\theta\delta_{\Lambda''\Lambda\pm1}\,,\\ \cos\theta\delta_{\Lambda''\Lambda}\,.\end{cases} \tag{1.22}$$

We note that if we use the following relation valid for $\Lambda\neq0^-$ (i.e., Σ^-):

$$f_{k-|\Lambda|}(\{x_iy_iz_i\},R)=f_{k|\Lambda|}(\{x_i-y_iz_i\},R)\,, \tag{1.23}$$

then the following relations enabling simplification in calculation hold:

$$\begin{aligned}X_{k''-\Lambda'',k-\Lambda}&=X_{k''\Lambda'',k\Lambda}\,,\\ Y_{k''-\Lambda'',k-\Lambda}&=-Y_{k''\Lambda'',k\Lambda}\,,\\ Z_{k''-\Lambda'',k-\Lambda}&=Z_{k''\Lambda'',k\Lambda}\,.\end{aligned} \tag{1.24}$$

But for $-\Lambda''=-1$ and $\Lambda=\Sigma^-$, the following relations hold instead:

$$\begin{aligned}X_{k''-1,k0^-}&=-X_{k''1,k0^-}\,,\\ Y_{k''-1,k0^-}&=Y_{k''1,k0^-}\,,\end{aligned} \tag{1.25}$$

since

$$f_{k0^-}(\{x_iy_iz_i\},R)=-f_{k0^-}(\{x_i-y_iz_i\},R)\,. \tag{1.26}$$

Now the matrix element $\langle\psi^{s'}_{k'\Lambda'EJ'M'}|H'|\psi^s_{k\Lambda vJM}\rangle$ responsible for nonresonant laser-induced transitions can be evaluated with the aid of Eq. (1.7) in the following simplified form:

Case (i): $\Lambda'\neq0$, $\Lambda\neq0$.

$$\begin{aligned}\langle\psi^{\pm}_{k'\Lambda'EJ'M'}|H'|\psi^{\pm}_{k\Lambda vJM}\rangle=6.8626\times10^{-15}\lambda^2I\,\tfrac{1}{2}[1+(-1)^{J'+J+\Lambda'+\Lambda}]\Big\{&\Big\langle\chi_{Ek'\Lambda'J'}\Big|\sum_{k''\Lambda''}M^{k''\Lambda''}_{k'\Lambda'k\Lambda}(R)M^{\Lambda''}_{J'\Lambda'J\Lambda M}\Big|\chi_{vk\Lambda J}\Big\rangle\\ &\pm\delta_{\Lambda'1}\delta_{\Lambda1}\Big\langle\chi_{Ek'1J'}\Big|\sum_{k''0^{\pm}}M^{k''0}_{k'1k-1}(R)M^{0}_{J'1J-1M}\Big|\chi_{vk1J}\Big\rangle\Big\}\,,\end{aligned} \tag{1.27}$$

where the factor

$$M^{k''\Lambda''}_{k'\Lambda'k\Lambda}(R)\equiv M_{k'\Lambda'k''\Lambda''}(R)M_{k''\Lambda''k\Lambda}(R)\Delta_{k''\Lambda''k\Lambda}(R)\,, \tag{1.28}$$

is R dependent whereas the factor

$$\begin{aligned}&M^{\Lambda''}_{J'\Lambda'J\Lambda M}\\ &\quad\equiv\langle\psi_{J'\Lambda'M'}(\theta\psi)|M_{\Lambda'\Lambda''}(\theta)M_{\Lambda''\Lambda}(\theta)|\psi_{J\Lambda M}(\theta\psi)\rangle\delta_{M'M}\,,\end{aligned} \tag{1.29}$$

is independent of any coordinates. We have used the properties under spatial inversion of various quantities (see Sec. IB) to obtain the above simplified result. Note further that it is much easier to perform the sum over $k''\Lambda''$ before the R integration. In the expression (1.27) and others given below, if the sum as a function of R is nearly constant over the region around $\bar{R}$ where the vibrational wave functions have significant overlap, then it is possible to simplify the calculation further by taking the sum outside the integral over R. For example, the first term in the curly brackets in Eq. (1.27) becomes, under this approximation,

$$\langle\chi_{Ek'\Lambda'J'}|\chi_{vk\Lambda J}\rangle\sum_{k''\Lambda''}M^{k''\Lambda''}_{k'\Lambda'k\Lambda}(\bar{R})M^{\Lambda''}_{J'\Lambda'J\Lambda M}\,,$$

where $|\langle\chi_{Ek'\Lambda'J'}|\chi_{vk\Lambda J}\rangle|^2$ is the Franck-Condon factor of the initial and final states.

The other expressions in case (i) are

$$\langle \psi^{\mp}_{k'\Lambda' E J' M'} | H' | \psi^{\pm}_{k\Lambda v JM} \rangle = 6.8626 \times 10^{-15} \times \lambda^2 I \tfrac{1}{2}[1-(-1)^{J'+J+\Lambda'+\Lambda}] \times \{\text{expression}\}, \qquad (1.30)$$

where the expression inside the curly brackets is identical to the one inside the curly brackets in Eq. (1.27).

Case (ii): $\Lambda' = 0$, $\Lambda \neq 0$. The results are

$$\langle \psi^{\pm}_{k'0v'J'M'} | H' | \psi^{\pm}_{k\Lambda v JM} \rangle = 6.8626 \times 10^{-15} \lambda^2 I (1/\sqrt{2})[1+(-1)^{J'+J+\Lambda}] \left\langle \chi_{Ek'0J'} \middle| \sum_{k''\Lambda''} M^{k''\Lambda''}_{k'0^{\pm}k\Lambda}(R) M^{\Lambda''}_{J'\Lambda' J \Lambda M} \middle| \chi_{vk\Lambda J} \right\rangle \qquad (1.31)$$

and

$$\langle \psi^{\mp}_{k'0v'J'M'} | H' | \psi^{\pm}_{k\Lambda v JM} \rangle = 6.8626 \times 10^{-15} \lambda^2 I \tfrac{1}{2}[1-(-1)^{J'+J+\Lambda}] \left\langle \chi_{Ek'0J'} \middle| \sum_{k''\Lambda''} M^{k''\Lambda''}_{k'0^{\pm}k\Lambda}(R) M^{\Lambda''}_{J'\Lambda' J \Lambda M} \middle| \chi_{vk\Lambda J} \right\rangle . \qquad (1.32)$$

Case (iii): $\Lambda' = 0$, $\Lambda = 0$. The results are

$$\langle \psi^{\pm}_{k'0v'J'M'} | H' | \psi^{\pm}_{k0vJM} \rangle = 6.8626 \times 10^{-15} \lambda^2 I [1+(-1)^{J'+J}] \left\{ M^{1}_{J'0J0M} \left\langle \chi_{v'k'0J'} \middle| \sum_{k''} M^{k''1}_{k'0^{\pm}k0^{\pm}}(R) \middle| \chi_{vk0J} \right\rangle + \frac{1}{2} M^{0}_{J'0J0M} \left\langle \chi_{v'k'0J'} \middle| \sum_{k''} M^{k''0^{\pm}}_{k'0^{\pm}k0^{\pm}}(R) \middle| \chi_{vk0J} \right\rangle \right\} ; \qquad (1.33)$$

and from consideration of symmetry of electronic wave functions under reflection of a plane through the internuclear axis, one has

$$\langle \psi^{\mp}_{k'0v'J'M'} | H' | \psi^{\pm}_{k0vJM} \rangle \approx 0 , \qquad (1.34)$$

for any J', J, etc.

The results of evaluating the factors $M^{\Lambda''}_{J'\Lambda' J\Lambda M}$ occuring in (1.27)–(1.33) are given in the Appendix. In Eq. (1.29), the selection rule $M' = M$ occurs because we have selected the space-fixed $\hat{z}'$ axis along the *linear* laser polarization. If there is linear polarization of another laser field or component of circular polarizations along the $\hat{x}'$ or the $\hat{y}'$ axis, the general selection rule is

$$M' = M, M \pm 1, M \pm 2 . \qquad (1.35)$$

In the Appendix, we show that the selection rule for J' is

$$J' = J, J \pm 1, J \pm 2 . \qquad (1.36)$$

Using this selection rule for the nonresonant laser-induced transition and that expressed in Eq. (1.14) for the field-free transition, the rate γ_{vJM} in Eq. (1.10) can be written

$$\gamma_{vJM} = 2\pi\hbar | \langle \psi^{s'}_{k'\Lambda' E JM} | H' | \psi^{s}_{k\Lambda v JM} \rangle + \langle \psi^{s'}_{k'\Lambda' E JM} | T | \psi^{s}_{k\Lambda v JM} \rangle |^2 + 2\pi\hbar \sum_{\substack{J'=J-2 \\ J' \neq J}}^{J+2} | \langle \psi^{s'}_{k'\Lambda' E J'M} | H' | \psi^{s}_{k\Lambda v JM} \rangle |^2 . \qquad (1.37)$$

Since $\langle \psi^{s'}_{k'\Lambda' E JM} | H' | \psi^{s}_{k\Lambda v JM} \rangle$ as seen from Eq. (1.20) and $\langle \psi^{s'}_{k'\Lambda' EJM} | T | \psi^{s}_{k\Lambda v JM} \rangle$ as seen from Eqs. (18) and (19) of Ref. 3 are complex numbers in general, therefore the $J' = J$ transition contains an interference term between the field-induced and the field-free predissociation, whereas other $J' \neq J$ transitions do not contain such interference effect. The $J' \neq J$ transitions represent new rotational states allowed by laser-induced transition that are not allowed for field-free transition.

B. Selection rules

In Sec. IA the selection rules (i) $M' - M = 0, \pm 1, \pm 2$ and (ii) $J' - J = 0, \pm 1, \pm 2$ have been given. Additional selection rules are given in this section.

(iii) Nonresonant laser-induced transitions are allowed between states $\psi^{s}_{k\Lambda v JM}$ of the same parity under spatial inversion; and not otherwise,

$$+ \longleftrightarrow +, \quad - \longleftrightarrow -, \quad + \not\longleftrightarrow - . \qquad (1.38)$$

To prove this statement, one shows H' in Eq. (1.7) is invariant under spatial inversion by noting first that each term in its sum contains a product of two matrix elements of $-\sum q_i \vec{r}_i \cdot \hat{\epsilon}$, and states $|\varphi_\alpha\rangle$, etc., occur as a product of bra and ket $|\varphi_\alpha\rangle\langle\varphi_\alpha|$; and secondly that for $\Lambda \neq 0$, each of the summations over α, β, and γ includes the $k-\Lambda$ term as well as the $k\Lambda$ term. The "±" parity of the molecular states $\psi^{\pm}_{k\Lambda v JM}$ in Eq. (1.1) is given by the factor $\pm(-1)^{J+\Lambda}$ because under spatial inversion[3]

$$\psi^{\pm}_{k\Lambda v JM} \rightarrow \pm(-1)^{J+\Lambda} \psi^{\pm}_{k\Lambda v JM} . \qquad (1.39)$$

One should not confuse the notations "±" denoting even-odd parity under spatial inversion with the superscript "±" in $\psi^{\pm}_{k\Lambda v JM}$.

(iv) For homonuclear diatom, nonresonant laser-induced transitions are allowed between molecular states $\psi^{\pm}_{k\Lambda v JM}$ that are both symmetric or both antisymmetric under the symmetry operation of interchanging the two nuclei, but not otherwise,

$$s \longleftrightarrow s, \quad a \longleftrightarrow a, \quad s \not\longleftrightarrow a . \qquad (1.40)$$

To prove this, one can show easily that H' is invariant under the interchange of the two identical nuclei by using the invariance of $-\sum q_i \vec{r}_i \cdot \hat{\epsilon}$ under the operation and the nature of the summations and the occurence of products of bra and ket of the same electronic state, as noted in connection with the proof of statement (1.38) above. The symmetry (antisymmetry) of the molecular states $\psi^{\pm}_{k\Lambda vJM}$ is given according the positive (negative) value of the factor $\pm(-1)^{g+J}$ because under exchange of the two nuclei[3]

$$\psi^{\pm}_{k\Lambda vJM} \rightarrow \pm(-1)^{g+J}\,\psi^{\pm}_{k\Lambda vJM}\,, \tag{1.41}$$

where g is 0 for a gerade electronic state and g is 1 for an ungerade electronic state.[1]

(v) For diatoms of equal nuclear charges (including homonuclear diatoms), nonresonant laser-induced transition between electronic states characterized by gerade (ungerade) symmetries is allowed if the quantity $M^{k''\Lambda''}_{k'\Lambda' k\Lambda}(R)$ defined in Eq. (1.28) does not vanish for some $k''\Lambda''$. It is easily seen that gerade-gerade and ungerade-ungerade transitions are allowed, whereas gerade-ungerade transitions are forbidden:

$$g \longleftrightarrow g, \quad u \longleftrightarrow u, \quad g \not\longleftrightarrow u\,. \tag{1.42}$$

(vi) Similarly the selection rules on the electronic quantum number Λ for allowed nonresonant laser-induced transition are given by nonvanishing value of $M^{k''\Lambda''}_{k'\Lambda' k\Lambda}(R)$ in Eq. (1.28) for some $k''\Lambda''$. Thus the allowed transitions are

$$\Lambda' - \Lambda = 0, \pm 1, \pm 2\,, \tag{1.43}$$

which we may call the *laser-induced homogeneous predissociation* ($\Lambda' - \Lambda = 0$), the *laser-induced inhomogeneous predissociation* ($\Lambda' - \Lambda = \pm 1$) and the *laser-induced new-channel predissociation* ($\Lambda' - \Lambda = \pm 2$), respectively. The last possibility is more intriguing because it is not allowed for field-free nonadiabatic transition [see Eqs. (1.15) and (1.16)]. Thus the laser-induced transition is easier to detect because it is free of any field-free competing transition to the same electronic channel.[7] This is different from the fact that *new* rotational states $J' \neq J$ are accessed by laser-induced transitions noted previously. This latter phenomenon holds for all cases in Eq. (1.43).

It is also seen that nonresonant laser-induced transitions are allowed for Σ^+-Σ^+ or Σ^--Σ^- transition and not Σ^+-Σ^-:

$$\Sigma^+ \longleftrightarrow \Sigma^+, \quad \Sigma^- \longleftrightarrow \Sigma^-, \quad \Sigma^+ \not\longleftrightarrow \Sigma^-\,. \tag{1.44}$$

The last forbidden transition $\Sigma^+ \not\longleftrightarrow \Sigma^-$ can be proved as stated in connection with result (1.34); but this result is peculiar to the approximation in $H'(R)$.

(vii) If electronic spin had been included in our molecular wave functions, then in Hund's cases (a) and (b), the resultant electron spin $\vec{S}$ of the initial and final molecular states obey

$$S' - S = 0\,, \tag{1.45}$$

since the effective Hamiltonian H' contains no operator on the spin wave functions. In addition,

$$\begin{aligned} &\Sigma' - \Sigma = 0 \quad \text{for Hund's case (a);} \\ &K' - K = 0,\ \pm 1,\ \pm 2 \quad \text{for Hund's case (b)}. \end{aligned} \tag{1.46}$$

(viii) Selection rules (1.43)–(1.46) presume that spin-orbit interaction in the molecule is negligible and are valid for molecular states described by Hund's cases (a) and (b). When spin-orbit interaction is large [Hund's case (c)], the states are characterized by the quantum number Ω instead of Λ. Therefore selection rules (1.43)–(1.46) are replaced by

$$\Omega' - \Omega = 0, \pm 1, \pm 2 \quad \text{for Hund's case (c).} \tag{1.47}$$

Selection rules (1.42)–(1.47) are useful in choosing a molecular candidate to observe the nonresonant laser-induced transitions. As seen from Eqs. (1.27)–(1.34), besides satisfying these selection rules so that there is nonvanishing induced transitions, it is desirable to have large electric dipole moments $M_{k'\Lambda' k''\Lambda''}(R)$ and $M_{k''\Lambda'' k\Lambda}(R)$ for some $k''\Lambda''$ at the region where the initial and final vibrational wave functions have significant overlap. *Selection rules (1.42)–(1.47) are also useful for deciding on the existence of avoided crossings in the electron-field adiabatic potentials induced by nonresonant laser radiation*[6,7] (see below). Significant avoided crossing is induced between electronic states with allowed virtual transitions to some common intermediate state(s).

C. Strong laser intensity–nonperturbative regime

When the laser intensity is sufficiently high such that stationary perturbative solution of the charge-radiation interaction becomes inaccurate, the nonperturbative solution given before[6-10] is necessary. In the theory of the radiative-dressed molecules,[11,12] the initial dressed molecular states are given by

$$\Psi_{\rho\sigma vJM} = \hat{\Psi}_{\rho\sigma}(\vec{r}\phi R\theta\xi)\hat{\chi}_{v\sigma JM}(R\theta\xi)\psi_M(\psi)\,, \tag{1.48}$$

for a laser field linearly polarized along z' axis. The nonperturbative solution of charge-field interaction gives the dressed adiabatic state $\hat{\Psi}_{\rho\sigma}$ labeled by the photon number ρ and electronic state quantum numbers $\sigma \equiv k\Lambda$. It is a function of the electronic coordinates $\vec{r}\phi$ at fixed internuclear distance R, at fixed angle θ between the nuclear axis from the polarization $\hat{\epsilon}$, and for given laser parameters ξ such as intensity, frequency, and polarization. Its energy eigenvalue $E_{\rho\sigma}(R\theta\xi)$ is the new

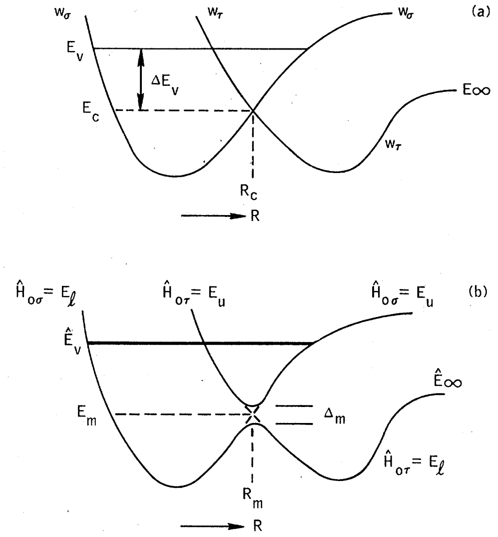

FIG. 3. Example of laser-induced predissociation of a molecular state with vibrational energy E_v in the stable w_σ to the less-stable potential w_τ. Upon laser irradiation the electron-field adiabatic potential surfaces are E_u and E_l connected by solid lines. An avoided-crossing energy gap Δ_m is induced by the radiation. The electron-field diabatic potential surfaces are $\hat{H}_{0\sigma}$ and $\hat{H}_{0\tau}$, connected by dashed lines. The molecular energy E_v is shifted to $\hat{E}_v$ and is also broadened due to the induced predissociation. (a) Molecular-potential curves with laser off. (b) Dressed-molecular potential curves with laser on.

electron-field adiabatic potential surface. The eigenstate of the nuclear motion on this potential surface $E_{\rho\sigma}(R\theta\xi)$ is $\hat{\chi}_{v\sigma JM}(R\theta\xi)$, which has been shown to be independent of ρ [see Eq. (2.15) in Ref. 11]. It is labeled by the quantum numbers $v\sigma JM$ of the field-free states that it approaches,[12]

$$\hat{\chi}_{v\sigma JM} \to \chi_{v\sigma J}(R)\Theta_{J\Lambda M}(\theta)\,, \tag{1.49}$$

as the laser intensity goes to zero adiabatically. Finally the rotational wave function $\psi_M(\psi)$ is given by

$$\psi_M(\psi) = (2\pi)^{-1/2}\, e^{iM\psi}\ . \tag{1.50}$$

M is a good quantum number for the above geometry. Similarly the final dressed molecular state is given by

$$\Psi_{\rho\tau E'J'M'} = \hat{\Psi}_{\rho\tau}\,\hat{\chi}_{E'\tau J'M'}\,\psi_{M'}\,, \tag{1.51}$$

where $\tau \equiv k'\Lambda'$. The rate of nonresonant laser-induced predissociation from the initial dressed adiabatic state to all accessible final states is given by

$$\gamma_{vJM} = 2\pi\hbar \sum |\langle \hat{\chi}_{E'\tau J'M'}\,\hat{\Psi}_{0\tau}|T|\hat{\Psi}_{0\sigma}\,\hat{\chi}_{v\sigma JM}\rangle|^2 \delta_{M'M}\,, \tag{1.52}$$

where we let $\rho=0$ because φ_σ becomes $\hat{\Psi}_{0\sigma}$ as the laser field is turned on adiabatically. The formula (1.52) is appropriate for any vibrational states in the molecular configurations a^0, b^0, and c^0 and for vibrational states whose energies are below the potential curve crossing in all the other subcases shown in Fig. 1.

When the vibrational energy is above the field-free true crossing between the potential curves w_σ and w_τ such as the example shown in Fig. 3(a), we need to describe the induced transition in terms of dressed diabatic states and diabatic electron-field potential surfaces. The reason is that as the strong laser field is turned on, an avoided crossing is induced at the field-free true crossing[6,7] so that new branches of adiabatic electron-field potential surfaces [such as E_u and E_l shown by solid lines in Fig. 3(b)] are formed and they obviously support very different rovibrational states.[11] The orignal vibrational and rotational state $\chi_{v\sigma J}\Theta_{J\Lambda M}$ becomes a dressed rovibrational state $X_{v\sigma JM}(R\theta\xi)$ with shifted energy $\hat{E}_v$, supported by the diabatic electron-field potential surface [such as $\hat{H}_{0\sigma}(R\theta\xi)$ connected by dashed line in Fig. 3(b)]. The dressed diabatic surface $\hat{H}_{\rho\sigma}(R\theta\xi)$ and its eigenfunction $\hat{\Phi}_{\rho\sigma}$ are related to the dressed adiabatic surfaces and eigenstates by a unitary transformation.[6,11] For the present problem, the initial and final dressed diabatic molecular states are

$$\hat{\Phi}_{0\sigma}(\vec{r}\phi R\theta\xi)X_{v\sigma JM}(R\theta\xi)\psi_M(\psi)$$

and (1.53)

$$\hat{\Phi}_{0\tau}(\vec{r}\phi R\theta\xi)X_{E'\tau J'M'}(R\theta\xi)\psi_{M'}(\psi)\,,$$

respectively. The rate of nonresonant laser-induced predissociation from the initial dressed diabatic state to all accessible final states is given by

$$\gamma_{vJM} = 2\pi\hbar \sum |\langle X_{E'\tau J'M'}\hat{\Phi}_{0\tau}|\hat{H} + T|\hat{\Phi}_{0\sigma}X_{v\sigma JM}\rangle|^2 \delta_{M'M}\,, \tag{1.54}$$

where the Hamiltonian $\hat{H}$ is given in terms of the adiabatic potential surfaces through a unitary transformation [see Eq. (2.20) of Ref. 6]. Both Eqs. (1.52) and (1.54) are valid over a time domain Δt such that $\gamma_{vJM}\Delta t \ll 1$.

II. COMPARISON OF STATIONARY PERTURBATIVE RESULTS WITH EXACT NUMERICAL RESULTS

The goal of this section is to compare the lowest-order nonvanishing results of stationary perturbative solutions with numerical exact results and to come up with a simple criterion of validity for the perturbative results. For this purpose, it is sufficient to use a simple semiclassical result called the modified Landau-Zener formula given in Eq.

(2.12) of Ref. 7. There are several additional advantages of using this result. Firstly, since it is expressed in terms of several physically interesting quantities, namely, the energy gap Δ_m of the laser-induced avoided crossing [see Fig. 3 (b)], and the ratio χ of the temporal slope of the dressed diabatic crossing to that of the field-free crossing, thus the comparison also gives the accuracy of the perturbative expressions for these quantities. Secondly, at high laser intensity, the transition probability per vibrational period of the crossing can be significant compared to unity so that the standard rate formulas like Eqs. (1.10), (1.52), and (1.54) are not valid. However the modified Landau-Zener formula can still provide a means of quantitative comparison at high transition probability, provided of course the assumptions of the formula are valid (see below).

For convenient reference in this work, we restate the formula here. The asymptotic transition probability T per half oscillation from the stable state to the less stable state is given as[7]

$$T = 1 - \exp(-2\pi q/|\alpha_0|)\,, \tag{2.1a}$$

where

$$q = (\tfrac{1}{4}\Delta_m^2 + |C_{12}''|^2)\chi^{-1}\,. \tag{2.1b}$$

In this formula, α_0 is the relative temporal slope of the field-free molecular crossing, namely,

$$|\alpha_0| = \left(\frac{2\Delta E_v}{m_r}\right)^{1/2} \frac{d}{dR}\,(w_\tau - w_\sigma)\,, \tag{2.2}$$

where ΔE_v is the energy difference of the vibrational energy E_v and the field-free crossing energy E_c, and m_r is the reduced mass of the vibrational motion. The quantity χ is the magnitude of the ratio of the temporal relative slope α of the dressed diabatic molecular crossing to α_0:

$$\chi = |\alpha/\alpha_0|\,, \tag{2.3a}$$

where

$$|\alpha| \equiv \left(\frac{2\Delta \hat{E}_v}{m_r}\right)^{1/2} \frac{d}{dR}\,(\Delta^2 - \Delta_m^2)^{1/2}\,, \tag{2.3b}$$

with $\Delta\hat{E}$ being the difference between the shifted vibrational energy $\hat{E}$ and the energy E_m at the dressed diabatic level crossing [see Fig. 3 (b)]. The quantity Δ_m is the minimum value of the energy difference $\Delta \equiv E_u - E_l$, as illustrated in Fig. 3 (b). Finally the quantity C_{12}'' is the residual coupling. The origin of Δ_m is purely radiative so that as the laser intensity I vanishes, Δ_m becomes zero. On the other hand, C_{12}'' contains the field-free interactions which are now modified by the field. As the laser field vanishes, it approaches the field-free value so that the formula (2.1) has the correct field-free limit.[7]

The formula (2.1) becomes a better approximation as the following approximations are more closely satisfied: (a) the momentum $(2m_r\Delta\hat{E})^{1/2}$ at the crossing $\gg \hbar/a_0$ so that the semiclassical description of the vibrational motion and the assumption of constant velocity are valid [see Fig. 3 (a)]; and (b) the variations of the quantities α, C_{12}'', and $\hat{H}_{12}$ [see Eqs. (2.9)–(2.11) of Ref. 7] as a function of the nuclear separation coordinate R are negligible in the narrow region of significant overlap between the bound and the free vibrational wave functions.

A. Stationary perturbative results

The field-induced energy gap[15] Δ_m at the minimum of the energy separation is equal to twice the effective coupling between the states φ_σ and φ_τ.[7] The perturbative result $\tilde{\Delta}_m$ expressed as a dimensionless ratio to the laser frequency ω is

$$\frac{\tilde{\Delta}_m}{\omega} = 1.3725 \times 10^{-14}\lambda^2 I \sum_{\beta\neq\sigma,\tau} \frac{\mu_{\tau\beta}\mu_{\beta\sigma}\Delta_{\beta\sigma}}{\omega}\,, \tag{2.4}$$

where Eq. (1.7) has been used.

In Eq. (2.4), we may use values of the transition moments μ's and the energy difference $(w_\beta - w_\sigma)$ at the crossing point R_c where $w_\sigma = w_\tau$. Strictly speaking, however, one should use their values at R_m where the minimum of the energy gap $E_u - E_l$ occurs.[7] The position for R_m can be determined at where the following equation is satisfied:

$$\frac{w_\tau(R) - w_\sigma(R)}{\omega} = -6.8626 \times 10^{-15}\lambda^2 I \times \sum_{\beta\neq\sigma,\tau} \frac{(\mu_{\tau\beta}^2 - \mu_{\sigma\beta}^2)\Delta_{\beta\sigma}}{\omega}\,. \tag{2.5}$$

Therefore at the laser intensity where these perturbation results are valid (see below), $[w_\tau(R) - w_\sigma(R)]/\omega$ is usually much less than and at most about equal to 0.001. The region $R_m - R_c$ can therefore be sufficiently narrow so that the variations of the transition moments and potential-energy differences are negligible. Also note that in these equations, $w_\beta - w_\sigma$ could very well be replaced by $w_\beta - w_\tau$ or $w_\beta - \frac{1}{2}(w_\tau + w_\sigma)$ at the same R_m even if $R_m \neq R_c$. The difference resulting from such choice belongs to higher-order corrections, as can be shown by use of Eq. (2.5).

The ratio χ of the field-dressed temporal slope α to the field-free temporal slope α_0 can be easily evaluated by Eqs. (2.3) and (2.2) if an analytic expression for α is given. By keeping the lowest-order nonvanishing terms, such an expression is

$$|\alpha| = \left(\frac{2\Delta E_v}{m_r}\right)^{1/2} \left|\frac{d(w_\tau - w_\sigma)}{dR} + s\right|\,, \tag{2.6}$$

where s is the change in the relative spatial slope due to optical Stark shifts of the two crossing levels:

$$s = 6.8626 \times 10^{-15} \lambda^2 I \times \frac{d}{dR} \left\{ -2\mu_{\tau\sigma}^2 \Delta_{\tau\sigma} + \sum_{\beta \neq \sigma, \tau} (\mu_{\tau\beta}^2 \Delta_{\beta\tau} - \mu_{\sigma\beta}^2 \Delta_{\beta\sigma}) \right\}. \tag{2.7}$$

We have assumed that over the range of laser intensity that Eq. (2.6) is valid (see below), the energy difference ΔE_v is sufficiently large that its change, $\Delta\hat{E}_v - \Delta E_v$, due to laser radiation is negligible.

Equation (2.6) is applicable to a quite general level crossing, subject only to the conditions of Landau-Zener model and of perturbation theory. An even simpler expression for χ is obtained if we assume additionally that, around the crossing, the dependence on R of the mean energy $\frac{1}{2}(w_c + w_\sigma)$, of the transition moments μ, and of the potential energies w_β $(\beta = \sigma, \tau)$ for those states φ_β *contributing significantly to the sums* in Eq. (2.7), are negligible compared to the R dependence of the energy difference $W \equiv w_\tau - w_\sigma$. Under these approximations, the resulting expression is

$$\tilde{\chi} = 1 - 3.4313 \times 10^{-15} \lambda^2 I \times \left\{ 4\mu_{\tau\sigma}^2 \Gamma_{\tau\sigma} + \sum_{\beta \neq \sigma, \tau} (\mu_{\tau\beta}^2 \Gamma_{\beta\tau} + \mu_{\sigma\beta}^2 \Gamma_{\beta\sigma}) \right\}, \tag{2.8}$$

where

$$\Gamma_{ij} \equiv [1 + (w_i - w_j)^2/\omega^2]/[1 - (w_i - w_j)^2/\omega^2]^2 .$$

B. Comparison with exact numerical results

In this section, we determine the accuracy of the perturbative results for $\tilde{\Delta}_m$ and $\tilde{\chi}$ by comparing them with the corresponding exact numerical results Δ and χ.[6,7] Although the results Eqs. (2.4) and (2.8) allow for the case $\mu_{\tau\sigma} \neq 0$, we note that only Eq. (2.8) contains the contribution due to $\mu_{\tau\sigma} \neq 0$. This latter contribution by itself has been compared with the corresponding exact numerical results in Sec. V of Ref. 6. The accuracy of this term has been given there.

In Ref. 7, we have calculated exact numerical results for the case $\mu_{\sigma\tau} = 0$, $\mu_{\sigma\beta} \neq 0$, and $\mu_{\tau\beta} \neq 0$ for one state φ_β (called $\varphi_{\sigma+}$ there). Thus we compare the corresponding results of Eqs. (2.4) and (2.8) with them and the relative errors are given in Tables I and II. Since all the other φ_β states in Eqs. (2.4) and (2.8) make additive contributions, the accuracy of one (typical) summand is indicative of that of the entire sum.

TABLE I. Relative error $\tilde{\Delta}_m/\Delta_m - 1$ of the perturbative result $\tilde{\Delta}_m$ [Eq. (2.4)] to the exact numerical results Δ_m, where Δ_m is the minimum energy gap of the field-induced avoided crossing. This is given as a function of the radiative interaction $G_\sigma = G_\tau$ [see Eq. (2.9)] and of the position of the nonresonant level w_β measured from the crossing. The laser frequency is ω. The notation $A\,(n)$ means $A \times 10^n$. The entries marked by "$\cdots$" indicate no comparison being made because no exact numerical values are available.

G_σ/ω \ ω_β/ω	1.5	2.0	5.5	10
0.01	0.001	3(−4)	2(−5)	6(−6)
0.05	0.024	0.007	5(−4)	2(−4)
0.1	0.092	0.028	0.002	6(−4)
0.3	0.598	0.229	0.019	0.005
0.5	1.394	0.757	0.050	0.015
1.0	$\cdots$	$\cdots$	0.175	0.057
1.5	$\cdots$	$\cdots$	0.336	0.120
2.0	$\cdots$	$\cdots$	$\cdots$	0.197

In the tables, the relative errors are given as a function of two dimensionless ratios: (i) w_β/ω, which measures the energy of the state φ_β from the level crossing point, in units of laser frequency ω; and (ii) G_α/ω, which measures the radiative interaction G_α in terms of the laser frequency ω. The latter quantity is related to laser intensity I in W/cm^2, wavelength λ in μm, and the transition moment $\mu_{\alpha\beta}$ in a.u. by

$$G_\alpha/\omega = 5.8577 \times 10^{-8} \lambda \mu_{\alpha\beta} I^{1/2}, \quad \alpha = \sigma, \tau. \tag{2.9}$$

TABLE II. Relative error $\tilde{\chi}/\chi - 1$ of the perturbative result $\tilde{\chi}$ [Eq. (2.8)] to the exact numerical result χ, where χ is the change in the relative slope of the crossing energy curves due to laser-induced optical Stark shifts. Since the variation of χ is not strongly dependent on the energy difference between the two crossing levels, namely, $w_\tau - w_\sigma$, the comparison is carried out for values of χ at $(w_\tau - w_\sigma)/\omega = 0.1$. The entries "0.0" mean that the relative error is less than 10^{-5}. The entry "c.b." stands for complete breakdown of the perturbative result $\tilde{\chi}$ because its value is negative. Other notations are explained in Table I.

G_σ/ω \ ω_β/ω	1.5	2.0	5.5	10
0.01	0.0	0.0	0.0	0.0
0.05	−7(−4)	−5(−5)	0.0	0.0
0.1	−0.009	−7(−4)	0.0	0.0
0.3	−0.290	−0.037	−1(−5)	5(−5)
0.5	c.b.	−0.092	−4(−5)	4(−5)
1.0	$\cdots$	$\cdots$	0.004	0.007
1.5	$\cdots$	$\cdots$	0.079	0.039
2.0	$\cdots$	$\cdots$	$\cdots$	0.227

For convenience of tabulation, we have chosen to present the special case $\mu_{\sigma\beta} = \mu_{\tau\beta}$. Of course, this is just as good as the general case $\mu_{\sigma\beta} \neq \mu_{\tau\beta}$ for the purpose of determining the accuracy of perturbative results.

Examination of the relative errors given in Table I lead to the conclusion that when the dominant terms in Eq. (2.4) satisfy the condition

$$\frac{1.3725 \times 10^{-14}\lambda^2 I \mu_{\tau\beta}\mu_{\beta\sigma}(w_\beta/\omega)}{1-(w_\beta/\omega)^2} < 0.01\,, \qquad (2.10)$$

the relative error in $\tilde{\Delta}_m$ is less than 1%. This region is marked by $G_\sigma/\omega < 0.05$ for $w_\beta/\omega = 1.5$, $G_\sigma/\omega < 0.1$ for $w_\beta/\omega = 2.0$, $G_\sigma/\omega < 0.3$ for $w_\beta/\omega = 5.5$, and $G_\sigma/\omega < 0.5$ for $w_\beta/\omega = 10$. However in the same region, $\tilde{\chi}$ is much more accurate according to Table II and the actual value of χ differs from unity by about 0.1% only, according to Table VI of Ref. 7. Therefore when Eq. (2.10) is satisfied, we may simply use

$$\tilde{\chi} = 1\,. \qquad (2.11)$$

We emphasize that it is the error in the transition probability, rather than in $\tilde{\Delta}_m$ and in $\tilde{\chi}$, that really matters. When the exponent in Eq. (2.1a) is small,

$$2\pi q/|\alpha_0| \ll 1\,, \qquad (2.12)$$

the transition probability T is proportional to q:

$$T = 2\pi q/|\alpha_0|\,. \qquad (2.13)$$

The relative error of the perturbative result for q, namely,

$$\tilde{q} \equiv \tilde{\Delta}_m^2/4\tilde{\chi} \qquad (2.14)$$

is given in Table III. For small q ($\ll 1$), this relative error is about twice that of $\tilde{\Delta}_m$.

TABLE III. Relative error $\tilde{q}/q - 1$ of the perturbative result $\tilde{q}$ [Eq.(2.14)] to the exact numerical result q, where q is the factor that characterizes the main effect of the laser field on the energy-curve crossing [see Eq. (2.1b) with $C''_{12} = 0$]. For $\tilde{q} \ll 1$, the relative error given here can also be that of the transition probability [see Eqs.(2.12) and (2.13)]. The notations used in this table are explained in Tables I and II.

G_σ/ω \ w_β/ω	1.5	2.0	5.5	10
0.01	0.002	6(−4)	4(−5)	1(−5)
0.05	0.050	0.014	0.001	3(−4)
0.1	0.202	0.058	0.004	0.001
0.3	2.594	0.570	0.038	0.011
0.5	c.b.	2.401	0.103	0.030
1.0	⋯	⋯	0.375	0.110
1.5	⋯	⋯	0.653	0.208
2.0	⋯	⋯	⋯	0.168

TABLE IV. Ratio $\exp(-2\pi\tilde{q}/|\alpha_0|)/\exp(-2\pi q/|\alpha_0|)$ of the perturbative elastic probability to the exact numerical value given as a function of the radiative interaction G_σ and the field-free parameter $|\alpha_0|$ [given in Eq. (2.15) in terms of the excess vibrational energy and the force difference of the field-free crossing]. It is seen that when $\tilde{\Delta}_m$ or $\tilde{q}$ is in error by (1–10)%, the error in the transition probability could be off by a factor of 2, to many orders of magnitude. Thus application of the stationary perturbative result should be limited to a parameter region with error less than 1%.

$\|\alpha_0\|/\omega^2$ \ G_σ/ω	0.01	0.05	0.1	0.3
10^{-6}	0.999	2(−5)	0.0	0.0
10^{-5}	1.000	0.338	3(−28)	0.0
10^{-4}	1.000	0.897	0.002	0.0
10^{-3}	1.000	0.989	0.530	0.0
10^{-2}	1.000	0.999	0.938	1(−15)
10^{-1}	1.000	1.000	0.994	0.032
1	1.000	1.000	0.999	0.709
10	1.000	1.000	1.000	0.966
10^2	1.000	1.000	1.000	0.997
10^3	1.000	1.000	1.000	1.000

On the other hand, when the transition probability is large so that Eq. (2.1a) in the exponential form must be used, a convenient quantity for comparison is the ratio of the perturbative value of the elastic probability $1-T$ to its exact value. This ratio is given by

$$\exp(-2\pi\tilde{q}/|\alpha_0|)/\exp(-2\pi q/|\alpha_0|)\,, \qquad (2.15)$$

and is listed in Table IV as a function of $|\alpha_0|/\omega^2$. The latter dimensionless ratio is related to the excess energy ΔE_v in eV above the curve crossing and the force difference F in eV/a_0 of the field-free crossing by

$$|\alpha_0|/\omega^2 = 0.111\,99\lambda^2 F(\Delta E_v/m_r)^{1/2}\,, \qquad (2.16)$$

where m_r in units of proton mass is the reduced mass of the vibrating particles. Here the laser wavelength λ in micrometers is present due to the introduction of ω in the left-hand side of the equation. The possible range of values of $|\alpha_0|/\omega^2$ of experimental interest is 10^{-6}–10^3. For a typical set of values of $\lambda = 1$ μm, $F = 0.1$ eV/a_0, and $\Delta E_v = 0.1$ eV, m_r = 10 proton masses, $|\alpha_0|/\omega^2$ has a value of ~10^{-3}. It is seen from Table IV that the approximate value for the elastic probability can be a factor of 2 to many orders of magnitude too small, whereas the corresponding error in $\tilde{\Delta}_m$ is only 1% to 10%. This is because of the magnification of any error in $\tilde{q}$ by the factor $2\pi/|\alpha_0|$ in the exponent. For this reason as well as the fact that once perturbative results begin to be inaccurate, it breaks down rapidly (see Tables I and II), we should not apply the perturbative results Eqs. (2.4) and (2.8) with error greater than 1% [i.e., when condition (2.10) is not satisfied].

C. Approximate formula for the rate

Finally, we want to address the remaining quantity $C_{12}^{\prime\prime}$ in Eq. (2.1b) that is modified by the laser field. We have shown in Eq. (2.6) of Ref. 7 that $C_{12}^{\prime\prime}$ reduces, in the limit of vanishing intensity, to the field-free nonadiabatic coupling $C_{\sigma\tau}^0$. It can be shown that under the same assumptions leading to the approximation $\hat{\chi} \cong 1$, it is also a good approximation to let

$$C_{12}^{\prime\prime} \cong C_{\sigma\tau}^0 . \tag{2.17}$$

Since a fast-oscillating field does not preferentially orient the molecules with respect to the laser polarization $\hat{\epsilon}$, therefore the molecules remain randomly oriented. The angle-averaged rate of nonresonant laser-induced predissociation from the vibrational level E_v is given by

$$\gamma_v = \frac{E_v}{8\pi\hbar} \int_0^{2\pi} d\psi \int_{-1}^{1} d\cos\theta \times \left[\left(\frac{\tilde{\Delta}_m}{\omega} \right)^2 + 4 \left| \frac{C_{\sigma\tau}^0}{\omega} \right|^2 \right] \Big/ \left(\frac{|\alpha_0|}{\omega^2} \right) , \tag{2.18}$$

where Eqs. (2.12)–(2.14), (2.11), and (2.17) have been used. For explicit states, the angular integrations are very simple to carry out analytically. The dimensionless ratios $\tilde{\Delta}_m/\omega$ and α_0/ω^2 are given by Eqs. (2.4) and (2.16), respectively. Aside from the expected difference arising from classical and quantum-mechanical "angle averaging," the result (2.18) can also be obtained from Eq. (1.10) by using semiclassical vibrational wave functions. Equation (2.18) is subject to the validity of conditions discussed in the paragraph preceding Sec. II A, and the condition (2.10). If valid, it can have semiquantitative accuracy.

To provide a rough estimate of the probability rate (per sec) induced by the laser only, the following relation is given,

$$\gamma_v \sim 10^{-26} \nu_v (\lambda I \mu_{\tau\beta} \mu_{\beta\sigma} \Delta_{\beta\sigma}/\omega)^2 F^{-1} (\Delta E_v / m_r)^{-1/2} , \tag{2.19}$$

where ν_v is the vibrational frequency per second of the vth vibrational level. For electric-dipole allowed virtual transitions, $\mu_{\tau\beta}$ and $\mu_{\beta\sigma}$ are about 0.5 a.u. For $\nu_v \sim 10^{14}$ sec^{-1}, $\Delta_{\beta\sigma}/\omega \sim 1$, $F \sim 0.5$ eV$/a_0$, $\Delta E_v \sim 0.1$ eV, $m_r \sim 10$ proton masses, $\gamma_v \sim 10^{-12} \lambda^2 I^2$. Therefore a CO_2 laser ($\lambda = 10\ \mu$m) of intensity $I \sim 10^8$ W/cm^2 would induce a predissociation rate of 10^6 sec^{-1} in such a molecule.

SUMMARY AND DISCUSSION

In conclusion, nonresonant laser-induced predissociation is analyzed with all molecular motions treated quantum mechanically. Formulas for calculating the rate of predissociations are given, one for weak to moderate field intensity [Eqs. (1.13) and (1.37)] and one for strong laser intensity [Eq. (1.52) or (1.54)]. Selection rules for allowed transitions without actual absorption or emission of the laser photons are given in Eqs. (1.35), (1.36), and (1.38)–(1.47) A simple criterion [Eq. (2.10)] for the error of the stationary perturbative result to be smaller than 1% is given. In addition, an approximate semiclassical formula for convenient estimate of the rate of nonresonant laser-induced predissociation is given in Eq. (2.18).

Note that the effective Hamiltonian H' in Eq. (1.7) is written perturbatively for the situations far off resonance from any significant intermediate molecular states. It differs from the standard result of a straightforward application of stationary perturbative theory in that it does not contain any intermediate rovibrational wave functions.[12] The advantage is the simplicity in calculations especially since intermediate electronic states are involved. The resulting selection rules as proved in the paper are consistent with results based on two-step transitions via virtual intermediate rovibronic states.

Field-free predissociation is a relatively rare process in molecules.[1] The facts that the laser-induced predissociation rate can be increased by increasing the laser intensity, etc., and that new rotational and new electronic states accessible in laser-induced transitions offer greater probability and richer phenomena for this process.

Although the physical situation dealt with in this paper is predissociation, the theory and the selection rules can similarly be applied to nonresonant laser-induced transitions in other physical contexts such as bound-bound transitions in diatoms, free-to-bound transitions such as inverse predissociation or two-body recombination, and free-free transitions during atomic collision.

Regardless of the specific physical context to which it is applied, the nonresonant laser-induced transitions addressed in this paper are different from Raman rovibronic transitions in (i) that only one laser field (frequency) is required here and no actual absorption of the laser photon is necessary and (ii) that transitions in the molecules occur between states of equal energies. For induced predissociation, an additional interesting aspect is that the final states are dissociative continuum states.

Finally, the nonresonant laser-induced transitions in general and predissociation in particular are also expected to occur in *polyatomic* molecules irradiated by lasers. The above theory can be applied with only appropriate notational changes in the description of the molecule.[16,12]

It has been stated in an earlier paper[7] that I_2 and Br_2 excited in the $B0^+u(^3\Pi)$ state can be induced to predissociate via the $1u(^1\Pi)$ state by the nonresonant effect described here. While this is true, observation to identify this effect may be very difficult in these molecular systems because of other more-dominant competing channels. The detailed reasons will be given in a forthcoming paper.

APPENDIX

The results of evaluating the factors $M^{\Lambda''}_{J'\Lambda' J\Lambda M}$ defined in Eq. (1.29) are given in this appendix. The explicit integration over the angular variable can be done but is quite tedious. Instead a group-theoretical method is used, and the results are expressed compactly in terms of known Clebsch-Gordan coefficients.[17,18]

(a) For $\Lambda'=\Lambda$, the case of laser-induced homogeneous transitions, only the following factors are needed:

$$M^{\Lambda}_{J'\Lambda J\Lambda M}=\langle\psi_{J'\Lambda M'}(\theta\psi)|\cos^2\theta|\psi_{J\Lambda M}(\theta\psi)\rangle\,,$$
$$=\frac{1}{6\pi}\left(\frac{2J+1}{2J'+1}\right)^{1/2}(2C^{2JJ'}_{0MM'}\,C^{2JJ'}_{0\Lambda\Lambda}+C^{0JJ'}_{0MM'}C^{0JJ'}_{0\Lambda\Lambda'})\,, \tag{A1}$$

$$M^{\Lambda\pm1}_{J'\Lambda J\Lambda M}=\langle\psi_{J'\Lambda M'}(\theta\psi)|\sin^2\theta|\psi_{J\Lambda M}(\theta\psi)\rangle$$
$$=\frac{1}{3\pi}\left(\frac{2J+1}{2J'+1}\right)^{1/2}(C^{0JJ'}_{0MM'}C^{0JJ'}_{0\Lambda\Lambda}-C^{2JJ'}_{0MM'}C^{2JJ'}_{0\Lambda\Lambda})\,. \tag{A2}$$

(b) For $\Lambda'=\Lambda\pm1$, the case of laser-induced inhomogeneous transition, the angular factors needed are

$$M^{\Lambda''}_{J'\Lambda\pm1 J\Lambda M}=\langle\psi_{J'\Lambda\pm1M'}(\theta\psi)|\sin\theta\cos\theta|\psi_{J\Lambda M}(\theta\psi)\rangle\,,$$
$$=\pm\frac{1}{2\pi}\left(\frac{2(2J+1)}{3(2J'+1)}\right)^{1/2}C^{2JJ'}_{0MM'}C^{2JJ'}_{\pm1\Lambda\Lambda\pm1}\,, \tag{A3}$$

where Λ'' may equal Λ or $\Lambda\pm1$. In the above statement, the upper (lower) signs must be used consistently throughout.

(c) For $\Lambda'=\Lambda\pm2$, the case of laser-induced new-channel transition,

$$M^{\Lambda''}_{J'\Lambda\pm2 J\Lambda M}=\langle\psi_{J'\Lambda\pm2M'}(\theta\psi)|\sin^2\theta|\psi_{J\Lambda M}(\theta\psi)\rangle\,,$$
$$=\frac{1}{\pi}\left(\frac{2(2J+1)}{3(2J'+1)}\right)^{1/2}C^{2JJ'}_{0MM'}C^{2JJ'}_{\pm2\Lambda\Lambda\pm2}\,, \tag{A4}$$

where $\Lambda''=\Lambda+1$ for the upper signs and $\Lambda''=\Lambda-1$ for the lower signs.

The notation $C^{J_1J_2J'}_{M_1M_2M'}$ for the Clebsch-Gordan coefficients is that $\vec{J}_1$ and $\vec{J}_2$ add to give $\vec{J}'$, and M_1, M_2, and M' are, respectively, their components. It is clear from the *triangle rule* associated with the Clebsch-Gordan coefficients appearing in Eqs. (A1)–(A4) that the selection rules

$$M'=M \tag{A5}$$

and

$$J'-J=0,\pm1,\pm2 \tag{A6}$$

follow. The selection rule (A5) is a consequence of our choice of the linear laser polarization $\hat{\epsilon}$ along the $\hat{z}'$ axis. If circular polarizations are used or if there is additional linear polarization components along x' or y' axes, then the matrix elements will be functions of ψ as well as θ. The Clebsch-Gordan coefficients would then be $C^{2JJ'}_{qMM'}$, where $q=0,\pm1,\pm2$. Therefore the general selection rule is

$$M'-M=0,\pm1,\pm2\,. \tag{A7}$$

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[12] A. M. F. Lau (unpublished).

[13] Lowering of potential barrier by optical Stark shift of the electronic potential surfaces is another example of nonresonant effect in molecules (see Ref. 9).

[14] The author is grateful to Dr. A. Kaldor for pointing this out.

[15] All eigenenergies and interaction energies in this paper have been divided by $\hbar$, except quantities denoted by E such as E, $E_{vK\Lambda J}$, E_v, and ΔE_v.

[16] See for example, G. Herzberg, *Molecular Spectra and Molecular Structure* (Van Nostrand Reinhold, New York, 1966), Vol. III.

[17] See, for example, W. G. Harter, C. W. Patterson, and F. J. Paixao, Rev. Mod. Phys. (to be published), and references cited. We thank Dr. Harter for a fruitful discussion.

[18] See, for example, A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University, Princeton, N.J., 1968).