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Radiative-dressed molecules: *Ab initio* theory and single/multiphoton dissociation with electronic transitions*†

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Molecules irradiated by intense laser fields become "dressed molecules" that possess significantly different properties due to changes in the electronic energy structures and wave functions. These new branches of distorted electron-field potential surfaces support different or new vibrational spectra. In this sense, a class of molecules is created with diagonal and off-diagonal properties that can be controlled by varying the laser intensity, frequency, and polarization. An *ab initio* theory that analyzes the dressed molecule with the field and their interaction treated as one dynamic system (rather than perturbatively) is formulated and summarized. The theory is applied to the study of single/multiphoton dissociation of molecules by intense lasers. Numerical results for the rate of $\mathrm{LiH}(X\,{}^1\Sigma^+,\ v=3)+4\hbar\omega(\lambda=1.0648\ \mu\mathrm{m},\mathrm{YAlG{:}Nd^{3+}})\rightarrow \mathrm{Li}(2p)+\mathrm{H}(1s)$ via the repulsive state $\mathrm{LiH}(\mathrm{B}\,{}^1\Pi)$ are given. Subsequent fluorescence from Li(2*p*) can be detected experimentally.

I. INTRODUCTION

Molecules basked in intense laser radiation are best analyzed as "radiative-dressed molecules." By this, it is meant that the molecular properties modified by interaction with the strong field (or fields) are significantly different, so that the molecule, the field, and their interaction are best analyzed theoretically or experimentally as one dynamical system. The value of such an approach can also be found in the study of the interaction of strong electromagnetic fields with atoms—the "dressed atom,"[1] from which the name is borrowed. However, it should be noted that the usual "dressed atom" picture[1] is restricted to resonant interaction so that the antiresonant terms are neglected. In the sense that the new electronic-field eigenenergies and wave functions are found including all higher-order effects and sidebands, our theory[2] of the dressed molecule is closer in spirit to the Autler-Townes[3] study of a two-level atom interacting with a strong electromagnetic field.

The essential part of the theory stated in Sec. II, namely the exact solution of electronic-field potential surfaces and wave functions, has been given before.[4–8,2] The solution involves a numerical iteration scheme simplified by recurrence relations. It is applicable to a general bound-charge system of n electronic (or if desired, electronic-vibrational) states and m laser fields (or modes of the electromagnetic field) as long as n and m are finite. These exact numerical results are also used to determine the validity domains of approximate analytic formulas. In the weak-field limit, they agree with and include the perturbative results. In the theory, *resonant* single-photon and multiphoton absorption and emission processes are treated on an equal basis from the start. *Nonresonant* (i.e., without *real* emission or absorption of photons) effects such as optical Stark shifts, field-induced splitting of degenerate levels, and radiative dressing of states (and hence modification of coupling between states) are included. Inputs into the theory are experimentally determined, theoretically calculated, or modeled *field-free* electronic energies and dipole or higher multipole matrix elements.

The development of the theory has been motivated by the use of laser radiation to *initiate* and to *control* intermolecular and intramolecular, nonreactive and reactive processes, and to direct energy-flow pathways, including those that involve electronic transitions. The theory can be applied to *real* atomic, diatomic, and polyatomic systems in a collision-free or collisional environment. The new physical processes that have been predicted include pulse-parameter and pulse-shape dependences of the excitation probability and nonadiabatic population inversion by single- and multiphoton absorption when atoms and molecules, relatively free from collisions, are irradiated by laser pulses. Hence, new laser actions to ground and intermediate states are possible.[2,5] When collisions become important, the variation of electronic energies with internuclear distances can induce *resonant* single- and multiphoton absorption (or emission) of photons that may be nonresonant in the separated-atom limit.[4,5] The intense field also induces energy structural changes like lowering of potential barrier, activation energies, etc. The formation of quasibound and bound molecules from the free colliding system due to absorption/emission or due to potential surface change is possible—a phenomenon useful in laser-induced chemical synthesis.[5,6] Recently we applied the theory to demonstrate laser control of atomic and molecular collisions, dissociations, and predissociations *without* absorption or emission of photons. Field-induced avoided crossing and new transition or reaction channels are induced by the incident field.[7,8]

However, in these published works,[4,5,7,8] no rigorous quantum treatment is given to the *bound* internuclear motion except the classical approximation. Since the class of situations treated in this paper involves the bound-free transitions of the *dressed* molecules, we give a precise quantum formulation in Sec. II of how the vibrational motions should be calculated. This theory has been applied to treat single- and multiphoton dissociation of molecules in an intense field as described in an unpublished report.[9] This is given here in Sec. III with numerical results for the four-photon dissociation of LiH($X\,^1\Sigma^+$).

II. *AB INITIO* FORMULATION

A. Dressed adiabatic states

The *total* Hamiltonian of the entire charge system (neutral or ionic diatom or polyatom) and the laser field is given in the center-of-mass (c.m.) frame of the charge system by

$$H_t = T + H\,, \tag{2.1}$$

where T is the kinetic energy of the relative nuclear motions and H is the sum[10] of the adiabatic (Born-Oppenheimer) Hamiltonian h of the charge system, the free-field Hamiltonian h_γ, and the charge-field interaction Hamiltonian h'. With the field interaction written in the Schrödinger representation, the time-independent eigenvalue solution[11] at each fixed internuclear frame $\underline{R}$,

$$H\hat{\Psi} = E\hat{\Psi}\,, \tag{2.2}$$

is known.[4-8,2] The eigensolutions $E_{\rho\sigma}$ and $\hat{\Psi}_{\rho\sigma}$ are denoted by their zero-field limit such that $\hat{\Psi}_{\rho\sigma}$ approaches the electronic state φ_σ and photon-number state $\Omega(N-\rho)$, N being the well-defined mean photon number in the coherent field. Merely for notational simplicity, the formulation is illustrated with one field or mode, characterized by the set ξ of parameters: intensity I, frequency ω, polarization $\hat{\epsilon}$, and wave vector $\hat{k}$ [if a higher multipole is used in (2.2)]. Reference 5 shows the similarity for the case of many fields. With the set of electronic coordinates denoted by $\underline{r}$, the total wave function Ψ is expanded as

$$\Psi = \sum_{\rho'\sigma'} \chi_{\rho'\sigma'}(\underline{R},\xi)\hat{\Psi}_{\rho'\sigma'}(\underline{r},\underline{R},\xi)\,, \tag{2.3}$$

and is substituted into the Schrödinger equation

$$H_t\Psi = E_t\Psi\,. \tag{2.4}$$

Multiplying from the left by $\hat{\Psi}_{\rho\sigma}$ and integrating over the electronic coordinates $\underline{r}$ and field "coordinates" (not ξ), we obtain

$$[T + U_{\rho\sigma}(\underline{R},\xi) - E_t]\chi_{\rho\sigma} = \sum_{\substack{\rho'\neq\rho\\ \sigma'\neq\sigma}} (\hat{\Psi}_{\rho\sigma}, T\chi_{\rho'\sigma'}\hat{\Psi}_{\rho'\sigma'})\,, \tag{2.5}$$

where the "best electronic-field potential surface" $U_{\rho\sigma}$ is given by

$$U_{\rho\sigma}(\underline{R},\xi) \equiv E_{\rho\sigma}(\underline{R},\xi) + (\hat{\Psi}_{\rho\sigma}, T\hat{\Psi}_{\rho\sigma})\,. \tag{2.6}$$

When $(\hat{\Psi}_{\rho\sigma}, T\hat{\Psi}_{\rho\sigma})$ is negligible, then the electronic-field potential surface is simply $E_{\rho\sigma}$, which was used in previous works.[4-9] In Eqs. (2.5) and (2.6), it is understood that T operates to the right on the wave function(s) *inside* the inner-product parentheses.

In the derivation, use is made of the fact that the terms

$$(\hat{\Psi}_{\rho\sigma}, \underline{\nabla}_R\hat{\Psi}_{\rho\sigma}) = 0\,, \tag{2.7}$$

because both the probability amplitudes $a_\nu(\beta)$'s and the electronic wave functions φ_β in

$$\hat{\Psi}_{\rho\sigma} = \sum_{\nu\beta} a_\nu^{\rho\sigma}(\beta)\varphi_\beta e^{i\nu\pi/2}\Omega(N-\nu) \tag{2.8}$$

are real [see Eq. (2.4) of Ref. 7].

If the nonadiabatic coupling terms on the right-hand side of Eq. (2.5) are negligibly small (e.g., because of slow internuclear motions), we obtain the Schrödinger equation

$$[T + U_{\rho\sigma}(\underline{R},\xi)]\chi_{\rho\sigma} = E_t\chi_{\rho\sigma} \tag{2.9}$$

for the internuclear motions. Thus there are *quantitative* criteria for the validity of Eq. (2.9). In the next paragraph, we make some qualitative physical remarks.

The above analysis is similar to Born's analysis of the field-free molecules, an improvement over the earlier Born-Oppenheimer analysis.[12] The physical reason for the separation of the slower motion of the nuclei from the fast electronic motion is well known. Considering the laser field as part of the fast-motion subsystem in the solution of Eq. (2.2) is physically useful whenever the field does not "couple" the internuclear motion effectively. This can be due to the high-frequency of the field ($\omega \sim$ electronic energy difference $\gg$ vibrational energy difference) *or* due to the symmetry of the charge system (e.g., zero permanent dipole moment of the diatom with like-charge nuclei). For collisional motion, the first condition corresponds to the condition that the collision time is long compared to the inverse of the photon frequency.[4,5] If the field couples the vibrational motion effectively (i.e., there is resonant-photon transition between vibrational states without electronic transition), one should treat the electronic-vibrational motions and the field as the fast-motion subsystem in Eq. (2.2).

There are several simplifications of the above equations. They are all based on the relations[11]

$$E_{\rho\sigma} = E_{0\sigma} - \rho\omega\,, \tag{2.10}$$

$$a_\nu^{\rho\sigma}(\beta) = a_{\nu-\rho}^{0\sigma}(\beta)\,, \tag{2.11}$$

given below Eq. (3.2) in Ref. 5 and on the fact that the cutoff value M is always measured from ρ (i.e., $\underline{a}^{\rho\sigma}$ consists of $\underline{a}_{\rho+M}^{\rho\sigma}, \ldots, \underline{a}_{\rho}^{\rho\sigma}, \ldots, \underline{a}_{\rho-M}^{\rho\sigma}$). It is then straightforward to show that

$$(\hat{\Psi}_{\rho\sigma}, T\hat{\Psi}_{\rho\sigma}) = (\hat{\Psi}_{0\sigma}, T\hat{\Psi}_{0\sigma})\,, \tag{2.12}$$

for any ρ. Then use of this and Eq. (2.10) in Eq. (2.6) shows that

$$U_{\rho\sigma} = U_{0\sigma} - \rho\omega\,. \tag{2.13}$$

This used in Eq. (2.9) implies that

$$\begin{aligned} [T + U_{0\sigma}(\underline{R}, \xi)]\chi_{\rho\sigma} &= (E_t + \rho\omega)\chi_{\rho\sigma}\,, \\ &= E_t\chi_{\rho\sigma}\,, \end{aligned} \tag{2.14}$$

where the second equality follows if we adopt the convention of measuring E_t from some value of the potential surface $U_{\rho\sigma}(\underline{R}, \xi)$, e.g., at $|\underline{R}| = \infty$. This is illustrated with E_a and E_b in Fig. 1 for $\rho = 1$. Then the comparison of Eqs. (2.9) and (2.14) shows that

$$\chi_{\rho\sigma} = \chi_{0\sigma}, \quad \text{for any } \rho\,. \tag{2.15}$$

Thus we need only to calculate one vibrational state $\chi_{0\sigma}$ for a given σ and a given E_t. All other $\chi_{\rho\sigma}$ for $\rho \neq 0$ are known due to the "periodic" nature of the electronic-field potential surfaces indicated by Eq. (2.13).

Use of Eqs. (2.10) and (2.11) also shows that the nonadiabatic coupling terms have simplifying relations,

$$\begin{aligned} (\hat{\Psi}_{\rho\sigma}, T\chi_{\rho'\sigma'}\hat{\Psi}_{\rho'\sigma'}) &= (\hat{\Psi}_{0\sigma}, T\chi_{\rho'-\rho,\sigma'}\hat{\Psi}_{\rho'-\rho,\sigma'}) \\ &= (\hat{\Psi}_{0\sigma}, T\chi_{0\sigma'}\hat{\Psi}_{\rho'-\rho,\sigma'})\,, \end{aligned} \tag{2.16}$$

with further use of Eq. (2.15). When these nonadiabatic terms are evaluated explicitly by substitution of Eq. (2.8) for $\hat{\Psi}_{0\sigma}$ and $\hat{\Psi}_{\mu\sigma'}$, one obtains two kinds of sums. One kind consists of terms with the field-free nonadiabatic coupling term multiplied by a factor of $a_\nu^{0\sigma}(\beta)a_\nu^{\mu\sigma'}(\beta')$ or by a product of $a_\nu^{0\sigma}(\beta)$ with a spatial derivative of $a_\nu^{\mu\sigma'}(\beta')$. Thus *the field-free nonadiabatic couplings are modified by the field.* There is another kind of sum which contains terms of the product of $a_\nu^{0\sigma}(\beta)$ and a spatial derivative of $a_\nu^{\mu\sigma'}(\beta)$ only—without the field-free nonadiabatic coupling terms. This latter kind is *nonadiabatic coupling through the field.* The $a_\nu(\beta)$'s are functions of the internuclear coordinates $\underline{R}$ (due to the $\underline{R}$ dependence of field-free potential surfaces and matrix elements) and of the field parameters ξ. Variation of these field parameters can induce nonadiabatic transitions between dressed states.[2] Thus in general the sources of nonadiabaticity in the dressed molecule (or dressed quasimolecule) can be both the slow motion in the charge system and the variation of the field parameters ξ. For Eq. (2.9) to be valid, nonadiabaticity in both of these has to be small. The adiabatic criterion for the former is well known.[12] The criteria for the latter source have also been given.[2]

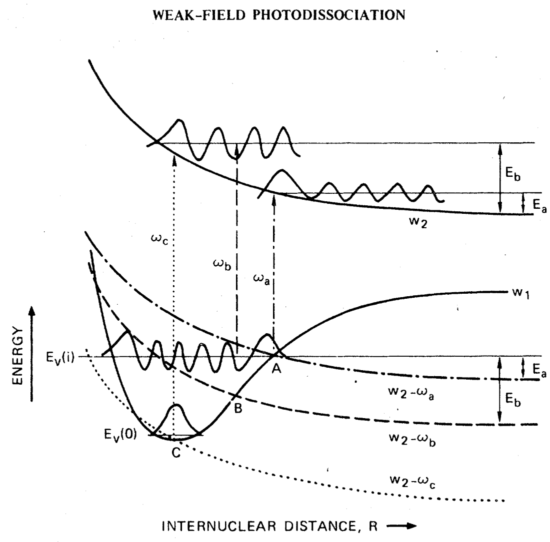


FIG. 1. Illustrations for three *separate* cases of weak-field dissociation with laser frequency ω_a, ω_b, or ω_c. Cases A and B are transitions from the vibrational level $E_v(i)$ to the upper dissociative levels drawn. In case A, the transition occurs predominantly at the classical turning points. In case B, it is away from the classical turning point. Case C is photodissociation from the ground vibrational state $E_v(0)$. In all three cases, a corresponding level $w_2 - \omega_i$ is drawn because energies are measured from the ground molecular state and $N\hbar\omega$, where N is the initial well-defined mean photon number in the coherent field, and because of the Franck-Condon principle.

One advantage of the analysis using the dressed molecule is that transitions of all sidebands induced by the laser field are considered simultaneously. For example, when there is one-photon absorption involving change in the electronic states (see Fig. 1), calculation of the transition probability amplitude by perturbative theory (valid for weak field) consists of taking the inner product of the dipole interaction between the states $\chi_2\varphi_2\Omega(N-1)$ and $\chi_1\varphi_1\Omega(N)$. The underlying perturbative assumption is that there is very little *state mixing:*

the probability amplitude $a_0(1)$ that the charge system remains in its initial state φ_1 after the field is turned on is close to unity. However, in intense fields, the probability amplitudes $a_\nu(\beta)$ with $(\nu, \beta) \neq (0,1)$ are significant.[7] *Thus the calculation of transition probability amplitude for the same process in the dressed-molecular picture involves matrix elements calculated by taking the inner product of $\chi_{12}\hat{\Psi}_{12}$ and $\chi_{01}\hat{\Psi}_{01}$ between nonadiabatic operators neglected in the adiabatic approximation of Eq. (2.9) or another Hamiltonian hitherto not yet considered.* The point is that both $\hat{\Psi}_{12} = \underline{a}^{12}$ and $\hat{\Psi}_{01} = \underline{a}^{01}$ consist of *all* sideband probability amplitudes $a_\nu^{12}(\beta)$ and $a_{\nu'}^{01}(\beta')$, so that simultaneous transitions between all *pairs* of sidebands is compactly described as transition between $\hat{\Psi}_{12}$ and $\hat{\Psi}_{01}$. This idea has been used in previous works.[2,4,5] The same can be said of the transition, say between $\hat{\Psi}_{01}$ and $\hat{\Psi}_{02}$, without photon absorption or emission.[7,8] For collisions in laser field, the dressed quasimolecular states are *the* properly defined initial and final states at large R, since they are coupled only by collisional motion.[4-8]

Another advantage of the dressed molecular picture is the systematic analysis of the vibrational motion. There are several situations of interest. The first is the shifts in the vibrational spectrum due to the fact that the electronic-field potential surfaces are distorted in shape from the field-free electronic potential energy. This effect is applicable to the vibrational states with energies *less than* $E_\nu(i)$ in Fig. 1 when a strong laser field of high frequency ω_a resonant at A between the two electronic states of a homonuclear diatom is turned on. These shifts among the vibrational energies of the same electronic potential may be called *intrasystem shifts*. There are *additional* larger relative shifts between vibrational energies of *different* electronic surfaces due to optical Stark shifts of the electronic potentials given by the solution of Eq. (2.2). These latter shifts may be called *intersystem shifts*.

The field polarizations also introduce new symmetries into the electronic-field potential surfaces through optical Stark shifts. For example, the electronic-field potential surfaces of a dressed diatom is not spherically symmetric.[5] The *vibrational modes* can also change due to the new angular dependence, corresponding to the change in collisional motion.[5]

Another situation is the new vibrational spectrum supported by new branches of *adiabatic* electronic-field potential surfaces. These new branches of potential surfaces can be due to the formation of resonant electronic-field avoided crossings,[4,5,13] as illustrated by the upper surfaces $E_{12}E_{01}$ in Fig. 2. Or it can be due to *nonresonant* field-induced avoided crossing[7,8] as illustrated in Fig. 1(b) of Ref. 8 for iodine molecule. The quantitative significance of the few effects on the vibrational motion mentioned above will be given in another paper.

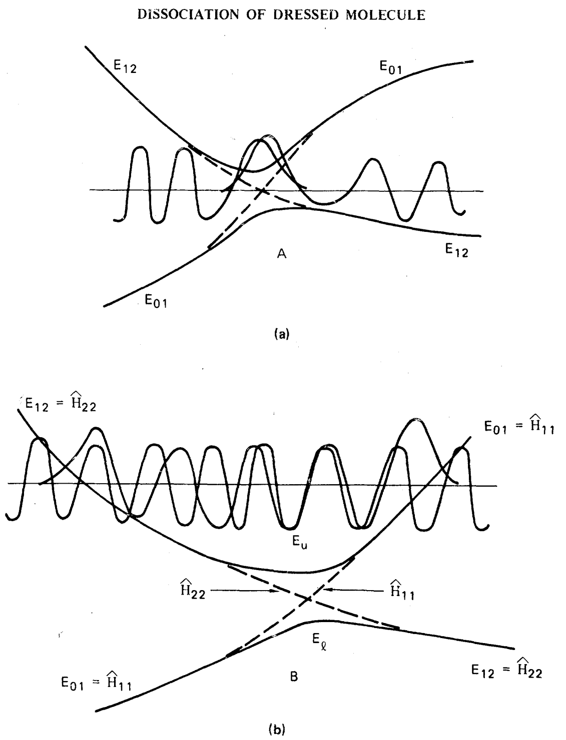


FIG. 2. When the laser field is strong, the adiabatic electronic-field potential surfaces of the field-dressed molecule show a significant avoided crossing around the resonance point. This is illustrated in diagrams (a) and (b), which correspond to regions A and B in Fig. 1. The new dressed *adiabatic* potential surface $E_{12}E_{01}$ (solid lines) can support previously nonexistent vibrational states (not shown). For the calculation of photodissociation probability, the dressed molecular vibrational states drawn in the diagrams are calculated using the dressed *diabatic* potential surfaces $\hat{H}_{ii}$ (dashed lines).

B. Dressed diabatic states

For the calculation of vibrational spectral shifts and new spectra described above, the *adiabatic* electronic-field surfaces are convenient. But in other situations where the transition probabilities between states involving an electronic-field *avoided* crossing are desired, it is often convenient to use the radiative-dressed *diabatic* states, $\hat{\Phi}_i$ with energy $\hat{H}_{ii}$. They are defined in Sec. II B of Ref. 7 in terms of the known adiabatic dressed states $\Psi_{\rho\sigma}$ and adiabatic energies $E_{\rho\sigma}$ (or $U_{\rho\sigma}$ here). They have the property that [see proof above Eq. (2.6) in Ref. 8] as the field is turned off, the energies

$\hat{H}_{ii}$ and states $\hat{\Phi}_i$ approach smoothly (i.e., without index-switching) the corresponding *unperturbed* electronic-field energies and states. In other words, they are more like these unperturbed quantities, as seen by comparing Fig. 2 with the corresponding regions A and B in Fig. 1.

Therefore, the vibrational wave function $X_i(\underline{R}, \xi)$ calculated with the dressed *diabatic* potential surface $\hat{H}_{ii}(\underline{R}, \xi)$ also approaches smoothly to the corresponding field-free vibrational wave function $x_i(\underline{R})$ calculated with the field-free electronic surface $w_i(\underline{R})$. These x_i and X_i are illustrated for the case of photodissociation in Figs. 1 and 2, respectively. The "diabatic" vibrational wave function $X_i(\underline{R}, \xi)$ differs from the field-free wave function $x_i(\underline{R})$ because $\hat{H}_{ii}(\underline{R}, \xi)$ differs from $w_i(\underline{R})$. Thus in the *diabatic* picture, the entire dressed wave function is $X_i(\underline{R}, \xi)\hat{\Phi}_i(\underline{r}, \underline{R}, \xi)$.

Then analysis using the $\hat{\Phi}_i$*'s as basis states is formally very similar to the corresponding field-free analysis.* For example, to study photo dissociation or predissociation in the dressed-molecular picture, the coupling matrix element between states $X_2\hat{\Phi}_2$ and $X_1\hat{\Phi}_1$ is given by

$$(X_1, \hat{H}_{12}X_2), \tag{2.17}$$

where $\hat{H}_{12}$ is calculated from the adiabatic dressed energies $E_{\rho\sigma}$ and $E_{\rho'\sigma'}$ through unitary transformation U [see Eq. (2.20) of Ref. 7]. For photodissociation, these $E_{\rho\sigma}$ and $E_{\rho'\sigma'}$ have $|\rho-\rho'| \geq 1$ depending on the number of photons absorbed (or emitted) in the transition. For predissociation, $\rho-\rho'=0$ since no photon is absorbed.[7,8]

Generally speaking, many of the classical, semiclassical, and quantum techniques[14] to calculate X_i and results in numerous theories[15] of *field-free* (or weak-field) inter- and intramolecular processes involving X_i can be adapted for use by replacing the corresponding field-free quantities with the *new* (field-dressed adiabatic or diabatic) quantities discussed above. One such result given by Landau[16] and summarized by Zener[17] is useful to us in the following section. The aspect of Landau's work useful to us is his use of JWKB wave functions for the vibrational motion to show that the transition probability with change of electronic states is simply given by the small-exponent limit of the Landau-Zener formula. The JWKB technique is an excellent approximation for the higher vibrational states. Landau's derivation is valid if the electronic crossing occurs away from the classical turning points. We can go through Landau's derivation with JWKB approximation for X_i in Eq. (2.17) based on the field-dressed diabatic quantities, and we obtain the corresponding formula in terms of the *dressed* quantities. That is, the transition probability per oscillation from the dressed vibrational state is given by[6] (for use in Sec. III, it is adequate to have the "small-exponent" limit of the Landau-Zener formula),

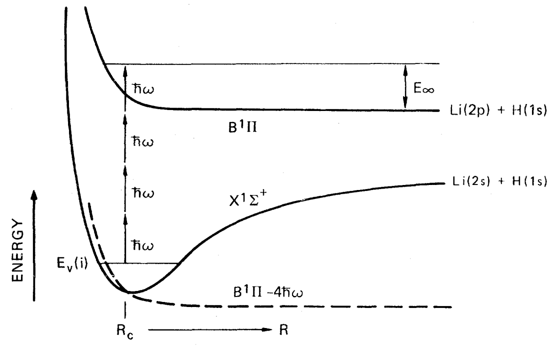
$$f = 4\pi p, \tag{2.18}$$

where

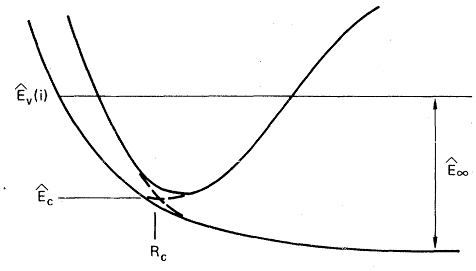
$$p = \hat{H}_{12}^2/\alpha, \tag{2.19}$$

$$\alpha = [2\Delta\hat{E}(i)/m_r]^{1/2} |\hat{s}\cdot\underline{\nabla}(\hat{H}_{22}-\hat{H}_{11})|, \tag{2.20}$$

where $\Delta\hat{E}(i) \equiv \hat{E}_v(i) - \hat{E}_c$ is the energy difference between the dressed-diabatic vibrational level $\hat{E}_v(i)$ and the energy $\hat{E}_c$ at the crossing point of $\hat{H}_{22}$ and $\hat{H}_{11}$ [Fig. 3(b)], m_r is the reduced mass, and $\hat{s}$ is the unit vector for the relative motion on the dressed potential surfaces at the diabatic crossing point. This formula is valid away from the classical turning points of X_i, such as the situations shown in case B of Fig. 2 and Fig. 3.



(a) WEAK-FIELD PICTURE



(b) DRESSED MOLECULE IN STRONG FIELD

FIG. 3. Schematic drawings for the four-photon dissociation of LiH by a YAlG:Nd^{3+} laser (a) in the weak-field picture and (b) in the dressed molecular picture for strong field. A third singlet state A $^1\Sigma^+$ (not drawn in this diagram) is also included in the calculation. In (b), the new branches of dressed adiabatic potential surfaces are drawn in solid lines, whereas the dressed diabatic surfaces are drawn in dashed lines where they differ from the adiabatic surfaces significantly. The vibrational energy $\hat{E}_v(i)$ calculated with the dressed diabatic potential surface is shifted from its zero-field value $E_v(i)$.

For the case A in Fig. 2 (or in general) one can resort to numerical techniques to find the wave functions X_i and their overlap factors.[14] Note that the effect of rotation is adequately treated in a first approximation by including contributions due to rotation in the dressed potential surfaces $U_{p\sigma}$ or $\hat{H}_{ii}$, similar to what is done in field-free analyses.[14,17]

III. SINGLE/MULTIPHOTON DISSOCIATION

We have applied the above dressed-molecular analysis to study the process, LiH($X\,{}^1\Sigma^+$, $i=3$) $+4\hbar\omega \rightarrow$ Li($2p$) + H($1s$) via the repulsive electronic state $B\,{}^1\Pi$. The photon wavelength is $\lambda = 1.0648\ \mu$m of a YAlG:Nd^{3+} laser. The situation is schematically shown in Fig. 3.

The input into our calculations are the three electronic potential energies of the lowest singlet states $X\,{}^1\Sigma$, $A\,{}^1\Sigma^+$, and $B\,{}^1\Pi$ and their electric dipole matrix elements. All these quantities except the electronic potential curve of $X\,{}^1\Sigma^+$ are taken from the *ab initio* results of Docken and Hinze.[18] Since their electronic energy of the $X\,{}^1\Sigma^+$ state differs from the experimental values by about 37 cm^{-1} around the four-photon resonance position ($\approx$ the equilibrium separation), we therefore use instead the best available empirical-fitted analytic expression of Crawford and Jorgensen.[19] Since the potential curve for the excited state $A\,{}^1\Sigma^+$ calculated by Docken and Hinze seems to agree well in this domain of R with the RKR curve, we adopted their results for this state as well as those for the $B\,{}^1\Pi$ state.

With ϕ defined as the angle between the molecular axis $\hat{k}$ and the linear polarization $\hat{\epsilon}$ of the laser field (Fig. 4), we have calculated $f(\phi)$ given by Eq. (2.18) for various intensities. The $f(\phi)$'s always have two main peaks for $\phi \cong \frac{1}{4}\pi$ and $\frac{3}{4}\pi$ showing that the molecular orientation favoring largest multiphoton dissociation is the one in which the couplings of all the transition moments to the polarization are equally optimized (i.e., not one gaining at the expense of the others). Figure 5 gives $f(\phi)$ at an intensity of 5×10^{11} W/cm^2. An external dc electric field $\vec{E}_0$ oriented at $\phi \simeq \frac{1}{4}\pi$ or $\frac{3}{4}\pi$ should enhance the photodissociative rate. The field strength required is given by $|\vec{d}\cdot\vec{E}_0| \sim kT$, where $\vec{d} = -2.3\hat{k}$ a.u. is the permanent dipole moment[18] in the ground electronic state of LiH.

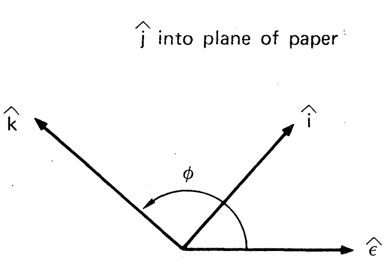


FIG. 4. Definition of the angle φ subtended between the internuclear axis $\hat{k}$ and the linear polarization $\hat{\epsilon}$ of the laser field.

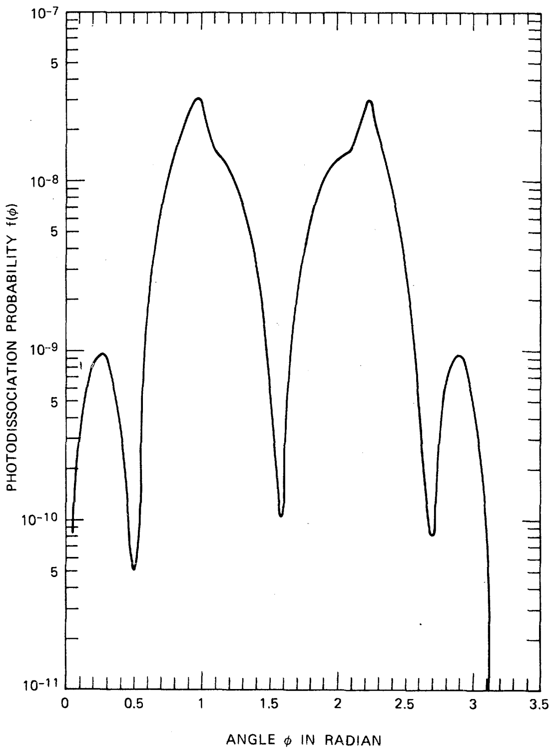


FIG. 5. Probability of dissociation *per vibration*, $f(\varphi)$ of the process LiH($X\ {}^1\Sigma^+, v=3$) $+4\hbar\omega$ ($\lambda = 1.0648\mu$m) $\rightarrow$ Li($2p$) + H($1s$) via LiH($B\ {}^1\Pi$) as a function of the angle φ defined in Fig. 4. The intensity of the YAlG laser for this curve is 5×10^{11} W/cm^2. The two strong peaks correspond to $\varphi \approx \frac{1}{4}\pi$ and $\frac{3}{4}\pi$. Therefore, the nonisotropic distribution of the dissociated products by multiphoton absorption is very different from that by single photon.

When a gas of diatoms is irradiated by a high-frequency (laser) field, the molecules are not preferentially oriented with respect to the field polarization $\hat{\epsilon}$. Therefore the averaged dissociative probability per vibration for random orientation of the molecular axis to $\hat{\epsilon}$ is given by

$$\bar{f}_r = \frac{1}{2}\int_{-1}^{1} d(\cos\phi) f(\phi) . \tag{3.1}$$

The photodissociation rate per second $\gamma(i)$ is given by

$$\gamma(i) = \nu_i \bar{f} , \tag{3.2}$$

where $\nu_i = E_v(i)/(2\pi\hbar)$ is the vibrational frequency per second.

The results for the fourth vibrational state $[i=3, E_v(i)=4642\ \text{cm}^{-1}]$ are presented in Fig. 6. It shows that the rate can be experimentally detected. The rate for the ground vibrational state is estimated to be smaller by a factor of 2 to 3. Note that for $i \leq 3$, molecules undergoing any transition to the $A\,^1\Sigma^+$ state by photoabsorption remain bound. Therefore the detection[20] of fluorescence from the decay of Li(2p) indicates dissociation via the $B\,^1\Pi$ state.

Since our theory treats single- and multiphoton transition *formally* the same, we could very well have done calculations for the same molecular dissociation by two- or single-photon absorption using the second-harmonic and fourth-harmonic YAlG photons, respectively. Then the dissociation rate would be significant at lower intensity than the case shown above. This can be readily done if there is sufficient experimental interest.

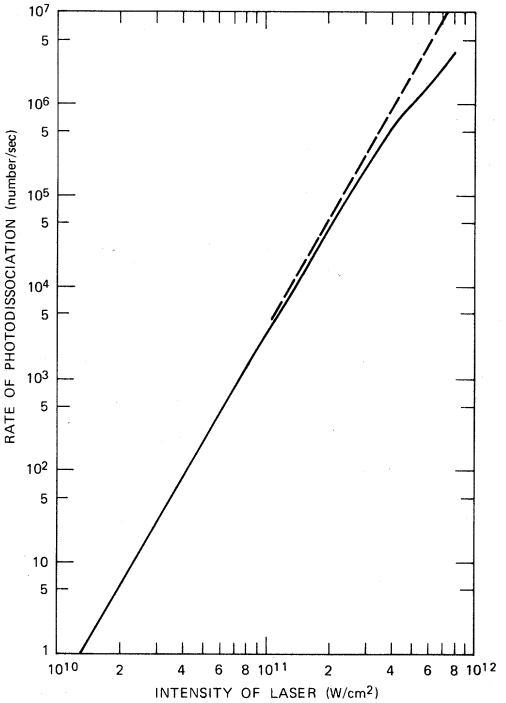


FIG. 6. Rate of production of Li(2p) by the process LiH($X\ ^1\Sigma^+, v=3$) $+ 4\hbar\omega$ ($\lambda = 1.0648\mu$m) $\rightarrow$ Li(2p) + H(1s) as a function of intensity of the YAlG laser. The atomic fluorescence from Li(2p) $\rightarrow$ Li(2s) $+\hbar\omega'$ can be experimentally detected. Solid line, rate for random orientation of the LiH molecule relative to the laser polarization. Dashed line, linear extrapolation (on the log-log plot) from the more moderate intensities.

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