A time-independent quantum mechanical theory for multiphoton dissociation of diatomic molecules

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A nonperturbative expression for the rate of dissociation from the ground vibrational state of a diatomic molecule in the presence of an infrared laser field is derived using R-matrix techniques. No rotating wave approximation and no metastable levels are introduced. The result is applied to a model system and to HF to obtain the dependence of multiphoton dissociation rate upon laser frequency and intensity. Dissociation is predicted at fields of order 10$^{17}$ W/cm$^2$.

I. INTRODUCTION

Since it was experimentally first shown feasible to dissociate small polyatomic molecules with infrared laser radiation in collision-free conditions,¹ considerable advance has been made in the theoretical understanding of this multiphoton process. The current theoretical models are able to account qualitatively for most of the distinctive features of such dissociation, and, for suitable choice of model and parameters, quantitatively.² However, a priori calculation has so far been hampered by the extreme complexity of the molecular level structure involved.

The limiting case of a small polyatomic molecule is a diatomic. With only one vibrational mode and no quasi-continuum, it offers a simple molecular level structure which may be dealt with explicitly. As the antithesis to a polyatomic molecule, in which absorption is believed to be dominated by the quasi-continuum, it is the ideal place to examine the effects of coherent absorption. Now, multiphoton dissociation of diatomic molecules is not observed at the field strengths currently available ($<10^{11}$ W/cm$^2$), a fact usually attributed to the lack of a quasi-continuum, i.e., to the relative sparseness of the molecular level structure.² It is thus also of interest to see whether dissociation of a sparse single mode vibrational (rotational) level system is expected to occur at all in a field of any strength less than that which would cause ionization. This may be as high as (10$^{18}$ W/cm²)³

Classical trajectory studies of Noid et al.³ on the interaction of an infrared radiation field with a diatomic molecule indicate that with a field strength of 10$^{14}$ W/cm$^2$, dissociation occurs on a time scale of picoseconds. However, despite their ready dynamical interpretation, classical studies are limited in that (i) accumulation of numerical errors and computer time limitations restrict trajectories to picosecond length in time, and (ii) classical mechanics may not provide an adequate description of coherent excitation.

With one exception,⁴ previous quantum studies have dealt primarily with multiphoton absorption within the bound level structure. Leasure et al.⁵ used Floquet analysis to investigate coherence of excitation and dependence of excitation probability on the initial internal state distribution and on the laser parameters. Schék et al.⁶ in a study of multiphoton absorption over the entire bound level manifold, introduced the possibility of subsequent dissociation by giving the uppermost bound level a rotational predissociative decay width. This causes an effective division into separate absorptive and dissociative processes, and introduces metastable states which are not well characterized. The predissociative decay width is assigned on the basis of the Wigner-Weisskopf approximation⁷; however, since the nonadiabatic couplings are in general not known, this decay width is somewhat arbitrarily parameterized by the molecular anharmonicity. We note that there is a similar equally unsatisfactory factor in the theories of MPD of polyatomics, where a discrete metastable level of unknown width is invoked in a similar phenomenological spirit to provide the transition from the coherent excitation observed in the lowest molecular energy region to the noncoherent excitation characteristic of the quasi-continuum.⁸

We develop here a nonperturbative expression for the rate of dissociation from the ground vibrational state of a diatomic molecule. The absorptive and dissociative parts are treated as a single process, in contradistinction to previous treatments of MPD, which consider a distinct two-step process, as mentioned above. In the theory presented here, we use basic R-matrix techniques to obtain a transition matrix element between the ground vibrational state and a scattering state matched asymptotically to the outgoing component of a dissociative state of the diatom. Although the R matrix employs a discrete set of molecular states, there is no need to postulate any metastable physical levels. Choice of this discrete set is indeed arbitrary, so long as it is square integrable over a finite region. The scattering state correctly includes all multiphoton couplings. The initial state is really a product state, namely ground molecular state x initial photon state of laser field. When one neglects depletion of the laser field by the dissociative interaction, which is valid at high field intensities, one obtains a truly time-independent transition rate referring to dissociation. This is directly related to the cross section. We also show that given that we are operating under "long-time excitation conditions," a time-depen-

³ Research supported by the Department of Energy Contract DE-AC02-78ER04908.
dent dissociation probability may be derived and we discuss the conditions under which this may be compared to the results of a predissociative type calculation such as that of Schek et al. 5

The main point of this work, therefore, is to show that multiphoton absorption by a single vibrational manifold can lead to dissociation at high field strengths as a result of molecule-field interactions alone, and to present a method of calculating the dissociation rate without introducing arbitrary metastable levels of the diatom. We also examine briefly the dependence of this rate on the form of the transition dipole function and on the intensity of the laser field.

II. THEORY

The molecule-field model has two degrees of freedom, the vibrational coordinate of the diatom and the photon occupancy of the field. (Rotations are neglected for simplicity but their inclusion does not cause serious additional problems, except to increase the size of basis.) Since the interaction is localized within a finite spatial region in the molecule fixed frame, we can treat the system as a scattering system, despite the non-localization of the photons. Then the vibrational coordinate becomes the translational (scattering) coordinate, and the field occupancy becomes the internal coordinate. We need the T-matrix elements between the initial state and the molecule-field states:

$$T_{if} = \langle \Phi_i | T | \Phi_f \rangle = \langle \Phi_i | H_f^* | \Psi^{(-)} \rangle,$$

where $\Phi_i$ = initial molecule state x field state; $| \alpha \rangle$ and $| \beta \rangle$ are "molecular" states, bound and free, respectively; $| n \rangle$ and $| n-m \rangle$ are field states with photon occupancy $n$ and $n-m$, respectively; $\Phi_i = | n \rangle | \alpha \rangle | n-m \rangle$ initial state; $H_f^* = \mu(r) E_0 \delta_{n,n-1}$ molecule-field interaction. The product states $\Phi_i$ and $\Phi_f$ are connected by energy conservation: the total energy is $E$ and molecular energies are $\epsilon_\alpha$, $\epsilon_\beta$ (Fig. 1). Then

$$E = E_\alpha + E_\beta = \epsilon_n + (n-m) \hbar \omega. \tag{2a}$$

$$\epsilon_\alpha + n \hbar \omega = \epsilon_\beta + (n-m) \hbar \omega. \tag{2b}$$

These T-matrix elements are then on the energy shell and may be considered as transition elements between states in a continuum over frequency $\omega$. Thus they satisfy the requirements that they represent the physical transitions. From these we directly obtain a rate of transitions per molecule with a standard result of scattering theory 4:

$$W_{if} = (2 \pi / \hbar)^2 | (E_i - E_f) \rho_{if} | T_{if} |^2,$$

where $W_{if}$ = rate of transitions from $\Phi_i$ to $\Phi_f$ per molecule per unit time. $\rho_{if}$ = density of final states, determined by the final state normalization. The problem then reduces to finding the scattering state $\psi^{(-)}$ which is asymptotically a pure outgoing wave and is a result of the multiphoton absorption from $| \alpha \rangle$. This state differs fundamentally from a photodissociative state as normally referred to 10; first, it will be arrived at non-perturbatively and so is the exact wave function, and second, it contains no incoming components. The system represents incident photon flux causing irreversible dissociation of the target molecule.

The full Hamiltonian is

$$H = H_\mu + H_F + H_I, \tag{4}$$

where

$$H_\mu = \frac{-\hbar^2}{2M} \frac{d^2}{dx^2} + V_\mu(r),$$

$$H_F = \hbar \omega (n+\frac{1}{2}),$$

$$H_I = \mu(r) E_0 \delta_{n,n-1}.$$  

$\psi^{(-)}$ is a solution to the Lippman-Schwinger equation 8

$$\psi^{(-)} = \Phi_\alpha + G_0 H_I \psi^{(-)} \tag{5},$$

where $\Phi_\alpha = | \beta \rangle | n-m \rangle$ and $G_0$ is the Green's function for the separable Hamiltonian $H_\mu + H_F$. We now use the R-matrix method 10 with a single interaction region ($\sigma, R$) on $r$, to obtain eigenfunctions and eigenvalues of $H$ in this region, subject to certain boundary conditions. From these the R matrix (the Green's function at the outer boundary) is constructed, and hence $\psi^{(-)}$. The box dimension $R$ must be large enough such that $\mu(R) = 0$. In practice we chose $R$ such that $V_\mu(R) \approx 0$ also, for a reason mentioned below. The $L_0^2$ basis in the interior region is a product of field states $\{| n \rangle \}$ and eigenfunctions of $H_\mu, \{ \phi_\mu(r) \}$, which satisfy the normal boundary conditions at the outer surface $r = R$

$$\left( \frac{\partial}{\partial r} - b \right) \phi_\mu(r, n) = \left( \frac{\partial}{\partial r} - b \right) \phi_{\mu'}(r) | n \rangle = 0 . \tag{6}$$

Note that the molecular eigenfunctions are written here as functions of the internuclear coordinate $r$, rather than in the conventional form as a function of $(r - r_0)$, where $r_0$ is the equilibrium bond length. This is done to emphasize that $r$ is also the translational coordinate.

Since the scattering wave function is independent of the constant $b$, 10 we take $b = 0$. If $V_\mu(R) \approx 0$, then the lowest bound states of $\phi_\mu(r)$ $(\epsilon_\mu < 0)$ are good approximations to the real physical bound states of $H_\mu$.

We define a one-sided Bloch operator as usual:
\[ \mathcal{L}_0 = \frac{\hbar^2}{2M} \delta(r-R) \frac{\partial^2}{\partial r^2} \]  

The full wave function \( \psi \) is then constructed in the internal region by formally solving the Schrödinger equation after \( \mathcal{L}_0 \psi \) has been added to both sides:

\[ (H - E + \mathcal{L}_0) \psi = \mathcal{L}_0 \psi \tag{8} \]

\[ \psi = (H - E + \mathcal{L}_g)^{-1} \mathcal{L}_g \psi \tag{9a} \]

\[ = \sum_{j=1}^{N} \frac{\langle \phi_j | \mathcal{L}_g | \psi \rangle}{E_k - E} \tag{9b} \]

where

\[ \langle \phi_j | \mathcal{L}_g | \psi \rangle = \sum_{i=1}^{N} a_i^* \phi_{ij} \approx \sum_{i=1}^{N} a_i^* \phi_{ij} (r) | n_i \rangle \tag{9c} \]

Matching \( \psi \) to its asymptotic outgoing form at \( r=R \) and truncating the product basis then gives:

\[ \psi(\infty) \approx \sum_{k=1}^{N} \left[ \frac{\langle \phi_k | \psi \rangle}{E_k - E} \right] \mathcal{L}_0 \psi(\infty) \tag{10} \]

\( \psi_k \) and \( E_k \), which we shall refer to as \( R \)-matrix eigenfunctions and eigenvalues, are the eigenfunctions and eigenvalues of \( H + \mathcal{L}_0 \), obtained by diagonalizing in the truncated basis \( \{ \langle \phi_k | \psi \rangle | n_i \rangle \} \). The asymptotic form of \( \psi(\infty) \) is the product of a depleted photon state \( | n - m \rangle \) and an outgoing wave normalized to unit energy density

\[ \left( \frac{M}{2 \pi \hbar^2 k} \right)^{1/2} e^{i \omega_0} \]

Energy normalization is the natural extension of box normalization from bound to continuum wave functions, and ensures conservation of atomic probability density. The interaction term \( H_I = \mu(r)E_0 \delta_{n_m} \) includes all dipole interactions between the molecule and the field. Since the final \( T \)-matrix elements must be energy conserving, then if the initial molecular state is the ground state, only field depletion interactions \( H_I = \mu(r)E_0 \delta_{n_m} \), can be included in the coupling of \( \phi_k \) to \( \psi(\infty) \).

The states \( \{ \phi_j \}_{j=1}^{N} \) and \( \psi(\infty) \) are thus true multiphoton states. Inserting Eq. (10) into (1) leads to an expression for \( T_{ij} \) in terms of the dipole matrix elements \( \mu_{kj} \), and of the expansion coefficients \( a_{kj} \)

\[ T_{ij} = \sum_{k=1}^{N} a_{kj} \frac{X_k^2 Y_k^2}{E_k - E} \tag{11} \]

with

\[ X_k = \sum_{\mu, n = m} a_{\mu}^* \phi_{\mu j} (R) \frac{\hbar^2}{2M} \left( \frac{M \hbar^2}{2 \pi \hbar^2 k} \right)^{1/2} e^{i \omega_0 R} \]

\[ Y_k = \sum_{\mu, n = m} a_{\mu}^* \phi_{\mu j} (| \mu |) \phi_{\mu j} \tag{11} \]

where, e.g., the sums indicated \( j; n \_n = n - m \) imply summation over those \( j \) states for which the \( n \_j \) equality holds.

Several points are pertinent here:

1. The zeroth order asymptotic state \( \Phi_0 = | \beta \rangle \langle | n - m \rangle \) is degenerate with a sequence of states with progressively higher translational energy and diminishing field occupancy. Formally these states correspond to different outgoing channels of the system. In forming \( W_{ij} \), the rate of dissociation, one should strictly sum over this entire sequence of isoenergetic states. However, excitation to states with progressively higher translational energy occurs with decreasing probability, since higher order photon processes are required. We make the assumption that the first energetically available dissociative "molecular" eigenstate compatible with absorption of an integral number of photons receives most amplitude, and neglect the contribution of higher energy translational states to both \( \psi(\infty) (r \rightarrow \infty) \) and \( W_{ij} \).

2. The outgoing wave component of \( \psi(\infty) (r \rightarrow \infty) \) could be more accurately represented by the WKB wave function

\[ \left( \frac{M}{2 \pi \hbar^2 k} \right)^{1/2} e^{i (2 \pi \omega_0 \delta_\omega)} \]

where \( \delta_\omega \) is the phase shift due to the molecular potential \( V_D (r) \).

3. The ground state of the oscillator \( | q \rangle \) has been represented in Eq. (11) by \( \phi_k (r) \), which, as we noted, is a good approximation to the real ground state if \( V_D (R) \approx 0 \), although the set \( \{ \phi_k (r) \} \) satisfies different formal boundary conditions from the real eigenfunctions. Alternatively, the ground state wave function, if known, could be used.

4. The entire dipole coupling matrix \( \mu(r) \) is used. No rotating wave approximation is made. The dissociation rate per molecule is then given by substituting Eq. (11) in Eq. (3). We can further obtain the cross section for dissociation, from the relation

\[ \sigma = W_{ij} / F, \tag{12} \]

where \( F = (eE_0^2)/(4\pi \mu_0 \omega) \), the photon flux. Like \( W_{ij} \), \( \sigma \) is frequency dependent.

The information we can get from this time-independent formalism corresponds to a "long time" excitation process, in which the temporal duration of the laser pulse is large relative to the time scale of the dissociative processes. Our time-independent transition rate \( W_{ij} \) can be simply related to a time-dependent probability of dissociation which then represents dissociation from an absorption induced steady state distribution over the molecular vibrational manifold. \( W_{ij} \) corresponds, rigorously, only to dissociation in the presence of \( n \) photons, but at high field intensities such that \( n \rightarrow \infty \), \( W_{ij} \) may be taken as the time-independent transition rate of molecules from the ground state \( | q \rangle \) in the presence of an electric field of constant intensity. This justifies using \( W_{ij} \) as a unimolecular rate constant. Hence the population of \( | q \rangle \) decays exponentially and the probability of dissociation is

\[ P_{Diss}(\omega, t) = 1 - e^{-W_{ij}t} C_q (0) \tag{13} \]

where \( C_q (t) \) is the population of \( | q \rangle \) at time \( t \).
TABLE I. Molecular parameters for a model system.

\[ V_0(r) = D \{ \exp[-2\alpha (r-r_p)] - 2 \exp[-\alpha (r-r_p)] \} \]
\[ D = 5.00 \text{ eV} \]
\[ \alpha = 0.2273 \text{ a}_0^2 \]
\[ M = 1.4919 \times 10^{-2} \text{ amu} \]
\[ r_p = 5.0 \text{ a}_0 \]
\[ R = 30.0 \text{ a}_0 \]
\[ \mu(r) = 0.4 \exp(-0.75r) \text{ eV}^{1/2} \text{ a}_0^{3/2} \]

III. CALCULATIONS AND RESULTS

We studied the dependence on laser frequency and intensity of the time-independent rate of dissociation from the ground state \( W_{ij} \) [Eq. (3)], for both a model potential with four bound states and for a more realistic potential simulating hydrogen fluoride.

A. Model system

Equations (3) and (11) were first tested on a Morse potential supporting only four bound states. The parameters used are given in Table I. The translational eigenfunctions \( \phi_n(r) \), which serve also as “molecular” eigenfunctions, were obtained by diagonalizing \( H_p \) in a primitive basis of sine functions satisfying zero derivative at \( r = R \):

\[ \phi_n^r = \sum_n C_{j}^n \frac{1}{R} \sin \left( \frac{n + \frac{1}{2}}{\pi R} r \right) . \]

We then form a product basis of molecule-field states \( \{ \phi_j \phi_n(r) \} \), diagonalize \( H + L \) in this to obtain the \( R \)-matrix states (9c) and then evaluate the \( T \)-matrix elements (11) and \( W_{ij} \) [Eq. (3)]. The product basis size \( N \) was increased by including product states with energy \( \epsilon_{ij} + \epsilon_{R} \), \( \hbar \omega \), within an increasing range of energy about \( \epsilon \) until \( |T_{ij}|^2 \) was regarded as satisfactorily converged. In this calculation, our criterion for convergence was that \( |T_{ij}|^2 \) be constant to within 0.1%. The field intensity is measured by the Rabi frequency \( \omega_R \), where \( \mu_0 E_0 = \hbar \omega \) and \( \mu_0 \) is the dipole transition moment between the ground and first excited “molecular” states. The ratio of field induced coupling to dissociation energy \( \hbar \omega_R / D \) provides an alternative useful estimate of the relative field strength. At a Rabi frequency of 174 cm\(^{-1} \) (\( \sim 10^{15} \text{ W/cm}^2 \)), convergence was obtained according to the above criterion with a primitive basis of 8 sin functions and \( N \sim 100 \). We note that at this field strength, the ratio \( \hbar \omega_R / D \) is a factor of 10–100 greater than that needed for dissociation of SF\(_6\).

Figure 2 shows the spectrum for dissociation from the ground vibrational state. The Rabi frequency here was 55 cm\(^{-1} \) (\( \sim 10^{14} \text{ W/cm}^2 \)). Sharp multiphoton resonances are seen at frequencies corresponding to integral divisors of the energy difference between the ground state and the unbond translational states, \( \epsilon_j - \epsilon_a \), where \( \epsilon_a > 0 \). At convergence, the position and magnitude of these resonances is independent of further increases in the size of the sine function basis. Varying the boundary position \( R \) does shift the positions of the peaks very slightly, reflecting the necessary small shifts in energy of the unbond translational states with \( R \). The overall structure of the spectrum remains unchanged however. The multiphoton process merges smoothly into the single photon dissociation as the frequency is increased: the sharp peak at 3.8 eV corresponds to the threshold for photodissociation.

In our model the intensity dependence and fluence dependence of the transition rate must be the same at high field intensities, since we have a constant transition rate over the pulse period. We find that \( W_{ij} \propto I^x \) with \( x = 1–3 \) for nonresonant frequencies at intensities such that \( \hbar \omega_R / D < 0.014 \). At higher intensities the resonance peaks shift slightly and \( x \) shows greater variations as a function of \( \omega \). In general, however, it decreases, presumably due to saturation effects. The frequency dependence of \( x \), the order of the multiphoton process, is shown in Fig. 3. On the same plot we also show \( m \), the
minimum integral number of photons required to reach the continuum from the ground state at each frequency. This would be the order predicted by perturbation theory. For the small order process in this model situation, $x$ is always very close to $m$.

### B. Hydrogen fluoride

The potential parameters were those used by Noid et al.\(^4\) and are summarized in Table II. Calculations were carried out for two functional forms simulating a realistic dipole moment \([\mu(r) = 0 \text{ as } r \to \infty]\), that of Noid et al.,\(^4\) $\mu_A$, and the other, $\mu_B$, having approximately the same maximum value and position but less curvature. These two functions are shown in Fig. 4.

A primitive basis of 60 sin functions spanning an internuclear $R$-matrix box of length $9a_0$ gave 20 of the (true) 22 bound states of the potential. The limiting computational factor in the use of a single $R$ matrix to span the interaction region is the size of the matrix $H + X_0$ which is to be diagonalized in the direct product space. Computation time and costs placed an upper limit of 550 on the size of the matrix we could diagonalize, and hence on the product space. Note that this matrix $H + X_0$ has to be re diagonalized at each frequency, since the field basis and hence also the product basis changes with laser frequency $\omega$. Thus, one does lose the usual advantage in the $R$-matrix method of requiring only a single diagonalization at one total energy. This upper limit on the direct product basis thus essentially determined the degree of convergence. For dipole function $\mu_A$, most calculations were done at a field strength of $I \approx 10^{13}$ W/cm$^2$. Using the previously adopted criterion of including molecule-field states within an increasing range of energy about $E = \varepsilon_0 + n\hbar\omega$, convergence of 1% in $|T_{1}\rangle |T_{1}\rangle$ was obtained. For $\mu_B$, most calculation was done at intensities $I \approx 10^{11}$ W/cm$^2$ and convergence of 2% in $|T_{1}\rangle |T_{1}\rangle$ was achieved. At this intensity, however, the corresponding results for the steepener function $\mu_B$ were only converged to a factor of 2.

Figures 5 and 6 show the spectrum of the transition rate $W_f$ calculated for a range of frequencies about the ground state—first vibrationally excited state resonant frequency $\omega_{01} = 0.494$ eV, with dipole functions $\mu_A$ and $\mu_B$, respectively. In Fig. 5 the laser intensity is $2.5 \times 10^{13}$ W/cm$^2$. Maximum dissociation occurs at a fre-
frequency $\omega_{\text{max}} = 0.470$ eV, redshifted from $\omega_0$. At this
field strength, dissociation is appreciable on a nanosecond time scale in this frequency region. (Here “appre-
ciable” means experimentally detectable, i.e., $P_{\text{diss}} \gg 10^{-4}$ ns.) This frequency of maximum dissociation is
significantly larger than the classical prediction of 0.428 eV. The spectrum near 0.420 eV is also shown in
Fig. 5. The same relative behavior is seen at higher laser intensity. Table III shows the dissociation rate for a few selected frequencies at intensities of $10^{14}$ and
$10^{15}$ W/cm$^2$, for $\mu_A$. With $I = 2.5 \times 10^{14}$ W/cm$^2$ there is 16% dissociation in a picosecond at $\omega = 0.470$ eV, and 2.9% dissociation per picosecond for $\omega = 0.420$ eV. The latter figure is in good agreement with the classical estimate, suggesting that at $\omega = 0.470$ eV there is a
strong component due to multiphoton resonances which cannot be reproduced by the classical description of excitation.

Figure 6 shows the same general features for dipole function $\mu_M$, but there are two points of contrast with the results for function $\mu_A$. Firstly, the dissociation rate at a given field strength is lower for the more slowly varying dipole function $\mu_M$. The laser intensity in Fig. 6 is $2.5 \times 10^{15}$ W/cm$^2$, comparison with Table III shows that the rate is less than that for $\mu_A$ at this intensity by factors of $3 \times 10^3$. This is expected from the larger higher order derivatives of $\mu_M$, which in a harmonic analysis would give rise to transitions between nonadjacent states, aiding absorption to high vibrational levels. Secondly, the maximum dissociation is seen for a frequency $\omega = 0.488$ eV, i.e., closer to the resonant frequency $\omega_0$.

Comparison of Fig. 6 with the experimental observations on small polyatomic systems$^{11,12}$ shows that although the prominent experimental feature of a maximum dissociation frequency red-shifted from $\omega_0$ is confirmed, we also see appreciable dissociation on the short wavelength side of $\omega_0$. Finally, it should be noted that these spectra do not show the prominent isolated resonances which are seen for the model potential in this region. There are two reasons for this. First, the computation limitations already discussed permitted only a low resolution scan, and second, the greater density of translational continuum states in the interior region for HF gives rise to many interfering resonances which are averaged over.

The intensity dependence of dissociation was examined at two frequencies and a marked difference between the behavior for the two dipole functions was observed. This is shown in Table IV, where $x$ and $m$ are defined as for the model problem (Fig. 3). For both dipole functions, the reduction of $x$ below $m$ shows the effect of high intensity in enhancing multiphoton absorption. This is considerably more significant for the 22 bound level system of HF than for the model potential, for which $x$ is actually very close to $m$ at all frequencies (Fig. 3). Most striking, however, is the magnitude of $x$ for $\mu_M$, which is less than one-half the value obtained for $\mu_A$. This clearly demonstrates the importance of the dipole function curvature and the contribution of higher order terms in the molecule-field coupling.

### IV. RELATION TO TIME DEPENDENT STUDIES

The spectral features of our time-independent transition rate $W_{\mu}$ are similar to those of the time-dependent dissociation probability obtained by Schek et al.$^5$ for the C–H bond. It is pertinent to ascertain the relation between this time-dependent dissociative rate for a pre-dissociative Morse oscillator and our time-dependent result derived for long time excitation [Eq. (13)]. Indeed the original motivation for this work was an attempt to obtain an estimate of the metastable level widths of the predissociative formulation.

We note first that the separation between excitation and decay processes implicit in use of a metastable state with associated decay width, is valid only under “short time” excitation conditions, i.e., when the pulse length is short relative to the lifetime of the metastable state. Under long time conditions, decay of the pulse masks the decay of excited “molecular” levels. In this case, the time-resolved dissociation probability cannot yield any information regarding the metastable “molecular” level widths. This is readily seen from the expression for the dissociation probability derived in Ref. 5:

$$P_{\text{diss}}(\omega, t) = 1 - \sum_j \left| b_j(\omega, t) \right|^2 e^{-\Gamma_M t} \left| b_M(\omega, t) \right|^2,$$

where $j = 0, 1, 2, \ldots, M - 1$, and $M$ is the highest bound level. The amplitudes $b_j$ are obtained from the time evolu-

### TABLE IV. Intensity dependence of dissociation rate for HF.

<table>
<thead>
<tr>
<th>$\mu$</th>
<th>eV</th>
<th>$x^a$</th>
<th>$m^b$</th>
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</thead>
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<td>$\mu_A$</td>
<td>0.488</td>
<td>3.1</td>
<td>12</td>
</tr>
<tr>
<td>$\mu_B$</td>
<td>0.488</td>
<td>8.1</td>
<td>12</td>
</tr>
<tr>
<td>$\mu_M$</td>
<td>0.492</td>
<td>8.9</td>
<td>12</td>
</tr>
</tbody>
</table>

$a$ is the order of the multiphoton process: $W_{\mu} \propto I^a$, where $W_{\mu}$ is the dissociation rate, $I$ is the laser intensity.

$b$ is the minimum integral number of photons needed for dissociation. Here $\rho_0 / D < 0.16$. 

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tion of the molecular system under the Hamiltonian $H = H_v + \mu E_v \cos(\omega t)$, where $H_v$ includes the predissociative decay width $\Gamma_v$. If the reciprocal decay width is very much less than the pulse duration $\tau$, then the third term in Eq. (15) rapidly goes to zero and $P_{\text{diss}}(\omega, t)$ is dominated by the second, absorptive term, which will be independent of $\Gamma_v$ in the limit when this is large. The spectral features then primarily reflect the absorption process. This is the situation pertaining with the C-H bond parameters used by Schek et al., where $\Gamma_v \tau = 1154$. Under short time conditions both terms contribute to the decay, and the dependency of all $b_l$ upon $\Gamma_v$ precludes inversion of $P_{\text{diss}}(\omega, t)$ to obtain $\Gamma_v$.

Thus the frequency and intensity dependence of our time-independent transition rate may be compared with those of the time-dependent dissociation probability for the predissociative Morse oscillator, but one cannot obtain an estimate of the “molecular” level widths from either spectrum. These remain a phenomenological parameter. We also note that since many diatomic predissociative lifetimes are of the order of $10^{12} - 10^{14}$ s, and the shortest available laser pulses are $10^{-12}$ s, a time-independent treatment of multiphoton dissociation is realistic and useful.

V. CONCLUSION

We have shown that it is possible to treat multiphoton absorption and dissociation consistently, in a conceptually simple manner, for a bound level system with only one (vibrational) degree of freedom. The result is an exact, time-independent rate of dissociation from the ground state of the diatomic, from which the cross section for multiphoton dissociation may be derived. At high field intensities this may be related to the time-dependent probability of dissociation obtained from the time-dependent studies of Schek et al. However, it is not possible to invert the time-resolved dissociation probability to obtain the molecular level widths. Consideration of the lifetimes involved shows that the time-independent framework is the more realistic and the more useful since it does not require input of phenomenological level widths.

For a trial calculation on HF we find dissociation at experimentally detectable levels ($P_{\text{diss}} \gg 10^{-6}$ in 1 ns) for field strengths of $10^{10} - 10^{12}$ W/cm$^2$, depending on the particular form used for the dipole function. The intensity dependence of the dissociation rate $W_v$ was found to vary considerably with different functional forms of $\mu(r)$, specifically, for relatively low field strength, where $W_v \propto I^4$, the more sharply varying dipole function has a lower exponent $x$. Comparison with the classical results for HF showed good quantitative agreement of the time dependent dissociation probability at the classically predicted frequency of maximum dissociation. The maximum for the quantum mechanical spectrum, however, is at a frequency closer to the $\omega_v$ resonant frequency. We attribute this difference to the inclusion of resonant multiphoton pathways in the quantum system.

Extension of the theory to include two lasers is straightforward in this time-independent formulation.

The addition of another term to the Hamiltonian is reflected in an increase in the size of the molecule-field basis and an additional set of coupling terms. With a single $R$-matrix diagonalization used to calculate the scattering wave function $\Psi(\epsilon)$, the limiting factor is computational, namely the size of the molecule-field basis needed to span the interaction region to get convergence. Investigating a two-laser system would require access to larger computation facilities than are currently available to us. An alternative would be to propagate the matrix elements $\langle \phi_l | (\mu(r) E_v) | \Psi(\epsilon) \rangle$ in a manner similar to the evaluation of Franck-Condon factors for photodissociation. Inclusion of the rotational manifold would involve similar considerations. The effect of neglect of rotational states cannot be predicted with certainty. Although partial rotational compensation for anharmonicity may be expected, transitions between nonadjacent vibrational levels high in the bound state manifold may still be necessary and it is not clear which will constitute the major bottleneck.


