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Citation: The Journal of Chemical Physics **101**, 3844 (1994); doi: 10.1063/1.467502
View online: http://dx.doi.org/10.1063/1.467502
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/101/5?ver=pdfcov
Published by the AIP Publishing

Theory of one- and two-photon dissociation with strong laser pulses

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(Received 4 April 1994; accepted 3 May 1994)

The theory of one- and two-photon dissociation processes with strong laser pulses for slowly varying multiple continua ("direct" dissociation) is developed. Closed form expressions for the state preparation and evolution during and after the excitation pulse are derived. We show how saturation of the photodissociation process as a function of the laser power sets in. We also show that for direct dissociation, the fragment state distribution is *independent* of the laser power. The dependence of spontaneous emission during dissociation (continuum Raman and resonance fluorescence) on the pulse intensity is studied. The formulation is extended to treating resonantly enhanced two-photon dissociation with strong laser pulses. Closed-form expressions for slowly varying pulses and slowly varying continua are derived. Using these expressions, the existence of adiabatic passage to the continuum (APC) by which a system executes a *complete* population transfer from an initial bound state to the continuum by following two guiding light pulses is established. A simple iterative scheme for going beyond the adiabatic approximation is introduced.

I. INTRODUCTION

One-photon molecular dissociation processes have been treated extensively in the weak-field regime.[1–8] The main objective of these studies has been the elucidation of the dynamical factors which determine the identity of the fragments and their final state (electronic, vibrational, and rotational) distributions. With the development of coherent and optimal control theories,[9,10] it has become clear that final state distributions can be controlled. In the weak-field regime, the reasons for control are well understood; they are a consequence of interference phenomena.[9] In contrast, in the strong-field regime, the situation is much more complicated.

The viability of the modern approaches[9,10] to laser induced selectivity, which emphasize the concepts of interferences, pulse shaping and coherence, has been verified experimentally.[11] In contrast, the sheer use of laser power, which was the central motif of past theories,[12] seems to be ineffective as far as controlling the final state distributions. One of the purposes of the present paper is to show why this is so.

A complete understanding of the effects of laser power is difficult to attain because with the increase in laser power, a "Pandora's box" full of new (e.g., multiphoton) processes opens up. The problem becomes more manageable if we consider the effect of strong laser fields on only one process, which is possible when the emergence of new processes with an increase in laser power can be avoided. For example, in many molecules, visible and UV photodissociation is accomplished by net absorption of just a single photon, even when the power is increased by a few orders of magnitude. This occurs when excited electronic states, in resonance with an additional photon absorption, do not exist.

Another example is that of two-photon dissociation enhanced by an intermediate bound state. As we show below, considerable simplifications occur in this case if one of the pulses is in near resonance with the ground-to-intermediate transition, but not with the intermediate-to-continuum transition and vice versa for the other pulse.

The interest in this case stems from our desire to dissociate/ionize molecules with visible or near UV light which is not energetic enough to induce a one-photon transition to the continuum. Although the presence of the intermediate state serves to greatly enhance the two-photon cross sections in the weak-field regime, the dissociation probability may become incomplete in the strong-field domain. The reason for this is that with the increase in laser power, back transitions from the intermediate to the ground state become more and more probable. Because the molecule is "protected" from dissociation while in its ground state, the dissociation probability may reach a saturation, or worse, flux may flow back from the continuum to the intermediate state.

In order to avoid this situation, one may consider employing a pulse configuration which induces an *adiabatic passage* to the continuum. Adiabatic passage processes, first discussed theoretically in the optical literature by Oreg *et al.*[13] and developed experimentally by Bergmann *et al.*,[14] enable, under certain conditions, the *complete* transfer of population from one bound level to another. Contrary to "π" pulses, which in principle achieve the same objective, the adiabatic passage effect is more robust. It is much less sensitive to the exact attributes of the pulse.

In the adiabatic passage experiments, as practiced by Bergmann *et al.*, one makes use of stimulated Raman scattering (hence the name STIRAP which stands for stimulated Raman adiabatic passage) to transfer the population from level 1 to level 3 via an intermediate level 2. The experiment is performed by first subjecting the molecule to laser frequency in near resonance with $\omega_{2,3}$—the transition frequency between levels 3 and 2—and then irradiating the system with a laser whose frequency is in near resonance with $\omega_{2,1}$—the transition frequency between levels 1 and 2. Bergmann *et al.*[14] showed that the above counterintuitive pulse sequence ("begin with the Stokes laser and end with the pump laser") is necessary for the complete population transfer to take place. What is also required are strong enough lasers, such that the adiabatic conditions $\Omega\Delta\tau \gg 1$, where Ω is the Rabi frequency, and $\Delta\tau$ is the duration, of either pulse apply.

 0021-9606/94/101(5)/3844/8/$6.00

If the effect could be extended to include final continuum states, i.e., when level 3 is part of a dissociative continuum, it would be possible to dissociate 100% of the molecules of interest. This would be attained by accessing the continuum (and hence dissociating the molecule) via a two-photon absorption (rather than a stimulated Raman) process. The demonstration that adiabatic passage to the continuum is indeed possible is the central result of the second part of this paper. (The case of the continuum as an intermediate state in the STIRAP arrangement has been considered by Carrol *et al.*[15] and Nakajima *et al.*[16] with different authors reaching different conclusions. This case is, however, quite unrelated to our present case; in executing STIRAP via an intermediate continuum one wishes to minimize, rather than maximize, the dissociation process.)

In general, the problem of dissociation in strong fields can be dealt with in a purely numerical fashion. Wave packet propagation methods[17–23] are available for treating excitation with pulses and time-independent close coupling and other techniques can be used for excitations with cw sources.[24–28]

In the two cases dealt with here, use of purely numerical methods is, however, not necessary. As we show below, these problems can be solved in essentially closed forms with no significant loss in accuracy. Needless to say, when such solutions are available, they are much more instructive than the purely numerical methods. For example, the formulas we develop explain clearly why a sheer increase in laser power cannot affect the final state distribution in the one- and two-photon cases. Another advantage of our method is that it relies exclusively on the computations of material matrix elements, as done in the weak-field domain. As a result, dissociation rates and probabilities for a variety of pulse configurations and field strengths may be obtained with no extra numerical effort.

The structure of this paper is as follows: In Sec. II, we develop the theory for the one-photon case. In Sec. III, we extend the theory to the two-photon case. We present computational results for the two cases in Sec. IV.

II. THEORY OF ONE-PHOTON DISSOCIATION

In this section, we present a solution of the pulsed one-photon dissociation problem for a slowly varying ("flat"[29]) continuum. The term "slowly varying" signifies that over the laser's bandwidth, there is little change in the bound–free cross sections. As shown below, for direct dissociation for which the absorption spectrum extends over thousands of wave numbers,[30] the continuum may be considered slowly varying even for the shortest (~10 fs) pulses currently available.[31]

We consider a molecule breaking apart into two fragments as a result of the action of a laser pulse of electric field $\varepsilon(t)=2\hat{\varepsilon}\varepsilon(t)\cos(\omega_L t)$. The total (matter plus radiation) Hamiltonian is

$$H_{\rm tot}=H-\boldsymbol{\mu}\cdot\boldsymbol{\varepsilon}(t), \tag{1}$$

where H is the radiation-free molecular Hamiltonian and $\boldsymbol{\mu}$ is the transition-dipole operator. We denote the bound eigenvalues and eigenfunctions of H as E_i and ψ_i and the analogous continuum quantities as E and $\psi(E,\mathbf{n}^-)$. The $\psi(E,\mathbf{n}^-)$ states go over in the long time limit to a product of a single internal state $\phi_{\mathbf{n}}$ (where $\mathbf{n}$ incorporates the identity of the fragments and their electronic, vibrational, rotational, etc. quantum numbers) and a plane wave

$$\langle\mathbf{R}|\mathbf{k}_{\mathbf{n}}\rangle\equiv\frac{1}{\sqrt{2\pi\mathbf{k}_{\mathbf{n}}}}\exp(i\mathbf{k}_{\mathbf{n}}\cdot\mathbf{R}) \tag{2}$$

describing the relative motion of the fragments

$$|\psi(E,\mathbf{n}^-)\rangle\xrightarrow{t\to\infty}|\phi_{\mathbf{n}}\rangle|\mathbf{k}_{\mathbf{n}}\rangle. \tag{3}$$

Assuming that the field is in near resonance with transitions from the initial bound state ψ_s to the continuum, we expand the full time-dependent wave function as

$$\Psi(t)=b_s(t)\psi_s\exp(-iE_st/\hbar)+\sum_{\mathbf{n}}\int dE\, b_{E,\mathbf{n}}(t)\psi(E,\mathbf{n}^-)\exp(-iEt/\hbar). \tag{4}$$

Insertion of Eq. (4) into the time-dependent Schrödinger equation

$$i\hbar\partial\Psi/\partial t=H_{\rm tot}\Psi(t) \tag{5}$$

and use of the orthogonality of the eigenfunctions of H results in a set of first-order differential equations for the b_s and $b_{E,\mathbf{n}}$ coefficients

$$i\hbar\frac{db_{E,\mathbf{n}}}{dt}=-\mu(E,\mathbf{n}|s)\varepsilon(t)b_s(t)\exp[i(\omega_{E,s}-\omega_L)t], \tag{6}$$

$$i\hbar\frac{db_s}{dt}=-\int dE\sum_{\mathbf{n}}\mu(s|E,\mathbf{n})\varepsilon(t)b_{E,\mathbf{n}}(t)\times\exp[-i(\omega_{E,s}-\omega_L)t], \tag{7}$$

where $\mu(E,\mathbf{n}|s)\equiv\langle\psi(E,\mathbf{n}^-)|\mu|\psi_s\rangle$, $\omega_{E,s}\equiv(E-E_s)/\hbar$, and we have invoked the rotating wave approximation.

Substituting the solution of Eq. (6)

$$b_{E,\mathbf{n}}(t)=\frac{-1}{i\hbar}\mu(E,\mathbf{n}|s)\int_{-\infty}^{t}dt'\varepsilon(t')b_s(t')\times\exp[i(\omega_{E,s}-\omega_L)t'] \tag{8}$$

into Eq. (7), we obtain that

$$b_s(t)=\frac{-1}{\hbar^2}\int dE\sum_{\mathbf{n}}|\mu(E,\mathbf{n}|s)|^2\times\int_{-\infty}^{t}dt'\int_{-\infty}^{t'}dt''\varepsilon(t')\varepsilon(t'')\times\exp[-i(\omega_{E,s}-\omega_L)(t'-t'')]b_s(t''). \tag{9}$$

In order to estimate the magnitude of the integral over E in Eq. (9), we parametrize the spectrum $\Sigma_{\mathbf{n}}|\mu(E,\mathbf{n}|s)|^2$ as

$$\sum_{\mathbf{n}}|\mu(E,\mathbf{n}|s)|^2=\overline{\mu^2(\omega_L)}A(E)/(\pi A(E_L)), \tag{10}$$

where

$$\overline{\mu^2(\omega_L)} \equiv \pi \sum_{\mathbf{n}} |\mu(E_L,\mathbf{n}|s)|^2, \tag{11}$$

$E_L = E_s + \hbar\omega_L$, ω_L being the laser's central frequency, and

$$A(E) = \Gamma_s/[(E-\mathscr{E}_s)^2 + \Gamma_s^2/4] \tag{12}$$

is a Lorentzian line shape centered about $\mathscr{E}_s$ whose FWHM is Γ_s.

With the above parametrization, the Fourier transform of the spectrum (the "ultrashort pulse autocorrelation function"[32,33])

$$F(t'-t'') \equiv \int dE \sum_{\mathbf{n}} |\mu(E,\mathbf{n}|s)|^2 \exp[-i\omega_{E,s}(t'-t'')] \tag{13}$$

is given as

$$F(t'-t'') = \frac{2\overline{\mu^2(\omega_L)}}{A(E_L)} \exp[-i(\mathscr{E}_s - E_s)(t'-t'')] \times \exp(-\Gamma_s|t'-t''|/2\hbar). \tag{14}$$

If Γ_s extends over 2000–5000 cm^{-1}, $\exp[-\Gamma_s(t'-t'')/2\hbar]$ decays in 1–2 fs. Since even for the shortest pulses available $\varepsilon(t')\varepsilon(t'')$ hardly changes over such small time differences, we are justified in approximating

$$\frac{\overline{\mu^2(\omega_L)}}{A(E_L)} \exp(-\Gamma_s|t'-t''|/2\hbar) \approx \hbar\overline{\mu^2(\omega_L)}\,\delta(t'-t'') \tag{15}$$

(which is strictly obtained in the $\Gamma_s \to \infty$ limit). Using Eqs. (14) and (15) in Eq. (9), we obtain that

$$b_s(t) = -\frac{\overline{\mu^2(\omega_L)}}{\hbar} \int_{-\infty}^{t} dt' \varepsilon^2(t') b_s(t'), \tag{16}$$

whose solution is

$$b_s(t) = b_s(-\infty)\exp\left[-\frac{\overline{\mu^2(\omega_L)}}{\hbar} \int_{-\infty}^{t} \varepsilon^2(t')dt'\right]. \tag{17}$$

The above is a statement of what may be termed the slowly varying continuum approximation (SVCA). We see that in this approximation $b_s(t)$ decreases monotonically with time, though not necessarily as an exponential function.

The SVCA need not be assumed for the continuum coefficients themselves because once we know $b_s(t)$, we can solve for $b_{E,\mathbf{n}}(t)$ with no further approximation. Assuming that

$$b_s(-\infty) = 1, \tag{18}$$

the $b_{E,\mathbf{n}}$ coefficients are given, using Eq. (8), as

$$b_{E,\mathbf{n}}(t) = \frac{-1}{i\hbar} \mu(E,\mathbf{n}|s) \int_{-\infty}^{t} dt' \varepsilon(t') \exp[i(\omega_{E,s} - \omega_L)t'] \times \exp\left[-\frac{\overline{\mu^2(\omega_L)}}{\hbar} \int_{-\infty}^{t'} \varepsilon^2(t'')dt''\right]. \tag{19}$$

The probability of populating a "free" state $\phi_{\mathbf{m}}|\mathbf{k}_{\mathbf{m}}\rangle$ at any given time is given as

$$P_{E,\mathbf{m}}(t) = |\langle\phi_{\mathbf{m}}|\langle\mathbf{k}_{\mathbf{m}}|\Psi(t)\rangle|^2. \tag{20}$$

Using Eq. (4), we have that

$$\langle\phi_{\mathbf{m}}|\langle\mathbf{k}_{\mathbf{m}}|\Psi(t)\rangle = b_s(t)\langle\phi_{\mathbf{m}}|\langle\mathbf{k}_{\mathbf{m}}|\psi_s\rangle\exp(-iE_st/\hbar) + \sum_{\mathbf{n}} \int dE\, b_{E,\mathbf{n}}(t)\langle\phi_{\mathbf{m}}|\langle\mathbf{k}_{\mathbf{m}}|\psi(E,\mathbf{n}^-)\rangle \times \exp(-iEt/\hbar). \tag{21}$$

Assuming that $\langle\phi_{\mathbf{m}}|\psi_s\rangle = 0$ (e.g., they belong to different electronic states), it follows from Eqs. (3) and (21) that in the long-time limit

$$P_{E,\mathbf{m}}(t\to\infty) = |\langle\phi_{\mathbf{m}}|\langle\mathbf{k}_{\mathbf{m}}|\Psi(t\to\infty)\rangle|^2 = |b_{E,\mathbf{m}}(t\to\infty)|^2. \tag{22}$$

It follows from Eqs. (8) and (22) that

$$P_{E,\mathbf{n}}(\infty)/P_{E,\mathbf{m}}(\infty) = |b_{E,\mathbf{n}}(\infty)/b_{E,\mathbf{m}}(\infty)|^2 = |\mu(E,\mathbf{n}|s)/\mu(E,\mathbf{m}|s)|^2. \tag{23}$$

We see that *irrespective of the SVCA*, the relative probabilities of populating different asymptotic states at a fixed energy E are *independent of the laser power*. This result complements a similar result obtained in the weak-field limit.[34]

In order to see explicitly how the continuum coefficients vary at finite times, we examine the above formulas for a Gaussian pulse envelope, centered about $t=0$,

$$\varepsilon(t) = \varepsilon_L \exp[-(t/2\alpha)^2]. \tag{24}$$

The Gaussian form allows for an analytic evaluation of the argument of the decaying exponential function of Eq. (17), since in that case, using Eq. (24),

$$\int_{-\infty}^{t} dt' \varepsilon^2(t') = \varepsilon_L^2 \alpha\sqrt{\pi/2}\left[1 + \mathrm{erf}\left(\frac{t}{\alpha\sqrt{2}}\right)\right]. \tag{25}$$

We obtain from Eqs. (17) and (25) that

$$b_s(t) = \exp\left\{-\frac{\overline{\mu^2(\omega_L)}}{\hbar} \varepsilon_L^2 \alpha\sqrt{\pi/2}\left[1 + \mathrm{erf}\left(\frac{t}{\alpha\sqrt{2}}\right)\right]\right\}, \tag{26}$$

which upon substitution in Eq. (8) yields for the continuum coefficients

$$b_{E,\mathbf{n}}(t) = \frac{-\varepsilon_L}{i\hbar} \mu(E,\mathbf{n}|s) \int_{-\infty}^{t} dt' \exp\left\{-(t'/2\alpha)^2 + i(\omega_{E,s} - \omega_L)t' - \frac{\overline{\mu^2(\omega_L)}}{\hbar} \varepsilon_L^2 \alpha\sqrt{\pi/2}\left[1 + \mathrm{erf}\left(\frac{t'}{\alpha\sqrt{2}}\right)\right]\right\}. \tag{27}$$

This is a simple closed-form expression involving an integral of an exponential function. In the weak-field domain, we can neglect the decay of b_s and the result reduces to

$$b_{E,\mathbf{n}}^{\mathrm{weak}}(t) = \frac{-\varepsilon_L}{i\hbar} \mu(E,\mathbf{n}|s) \int_{-\infty}^{t} dt' \exp[-(t'/2\alpha)^2 + i(\omega_{E,s} - \omega_L)t'], \tag{28}$$

which can be expressed analytically[33] as a complex error function.

III. THEORY OF RESONANTLY ENHANCED TWO-PHOTON DISSOCIATION

We now present the two-photon extension to the one-photon theory of the previous section. We consider a molecule, initially (chosen now as $t=0$) in state ψ_s, being excited to a continuum of states due to the combined action of *two* laser pulses of central frequencies ω_1 and ω_2. We assume that ω_1 is in near resonance with an intermediate bound state; ψ_0 and ω_2 is in resonance with the transition from ψ_0 to the continuum.

The total Hamiltonian of the system is written as

$$H_{\rm tot}=H-2\boldsymbol{\mu}_1\cdot\hat{\epsilon}_1\epsilon_1(t)\cos(\omega_1 t)-2\boldsymbol{\mu}_2\cdot\hat{\epsilon}_2\epsilon_2(t)\cos(\omega_2 t). \tag{29}$$

In the above, $\epsilon_1(t)$ and $\epsilon_2(t)$ are "slowly varying" electric field amplitudes, and $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ are the (electronic) transition dipoles. The expansion of the wave function now takes the form

$$\Psi(t)=b_s\psi_s\exp(-iE_s t/\hbar)+b_0\psi_0\exp(-iE_0 t/\hbar)+\sum_{\mathbf{n}}\int dE\, b_{E,\mathbf{n}}(t)\psi(E,\mathbf{n}^-)\exp(-iEt/\hbar). \tag{30}$$

Substitution of this expansion into the time-dependent Schrödinger equation and use of the orthogonality of the basis functions results in a set of first-order differential equations for the expansion coefficients. In the rotating wave approximation, this set of equations is of the form

$$i\hbar\frac{db_s}{dt}=-\mu_{s,0}\epsilon_1(t)\exp(-i\Delta_1 t)b_0(t), \tag{31}$$

$$i\hbar\frac{db_0}{dt}=-\mu_{0,s}\epsilon_1(t)\exp(i\Delta_1 t)b_s(t)-\epsilon_2(t)\sum_{\mathbf{n}}\int dE\,\mu(0|E,\mathbf{n})\exp(-i\Delta_E t)b_{E,\mathbf{n}}(t), \tag{32}$$

$$i\hbar\frac{db_{E,\mathbf{m}}}{dt}=-\mu(E,\mathbf{m}|0)\epsilon_2(t)\exp(i\Delta_E t)b_0(t),\qquad \mathbf{m}=1,\ldots,N, \tag{33}$$

where $\mu_{0,s}\equiv\langle\psi_0|\mu_1|\psi_s\rangle$, $\mu(E,\mathbf{n}|0)\doteq\langle\psi(E,\mathbf{n}^-)|\mu|\psi_0\rangle$, $\Delta_1\equiv(E_0-E_1)/\hbar-\omega_1$, $\Delta_E\equiv(E-E_0)/\hbar-\omega_2$, and we have assumed for simplicity that $\mu_{0,s}$ is real.

Following the procedure of solution of Eq. (6), we substitute the formal solution of Eq. (33)

$$b_{E,\mathbf{n}}(t)=\frac{-1}{i\hbar}\mu(E,\mathbf{n}|0)\int_0^t dt'\,\epsilon_2(t')\exp(i\Delta_E t')b_0(t') \tag{34}$$

into Eq. (32) to obtain

$$i\hbar\frac{db_0}{dt}=-\mu_{0,s}\epsilon_1(t)\exp(i\Delta_1 t)b_s(t)+\frac{\epsilon_2(t)}{i\hbar}\sum_{\mathbf{n}}\int dE|\mu(E,\mathbf{n}|0)|^2\times\exp(-i\Delta_E t)\int_0^t dt'\,\epsilon_2(t')\exp(i\Delta_E t')b_0(t'). \tag{35}$$

In the SVCA [see Eq. (16)], this expression turns into

$$i\hbar\frac{db_0}{dt}=-\mu_{0,s}\epsilon_1(t)\exp(i\Delta_1 t)b_s(t)-i|\epsilon_2(t)|^2\overline{\mu_2^2(\omega_2)}b_0(t), \tag{36}$$

where $\overline{\mu_2^2(\omega_2)}$ is defined in analogy to Eq. (11) as

$$\overline{\mu_2^2(\omega_2)}\equiv\pi\sum_{\mathbf{n}}|\mu(E_0+\hbar\omega_2,\mathbf{n}|0)|^2. \tag{37}$$

Equations (31) and (36) can be expressed in matrix notation

$$\frac{d}{dt}\mathsf{b}=\frac{i}{\hbar}\mathsf{g}\cdot\mathsf{b}(t), \tag{38}$$

where

$$\mathsf{b}\equiv[b_0,\exp(i\Delta_1 t)b_s] \tag{39}$$

and

$$\mathsf{g}=\begin{bmatrix} i\varepsilon_2^2\overline{\mu_2^2(\omega_2)} & \mu_{0,s}\epsilon_1 \\ \mu_{0,s}\epsilon_1 & \hbar\Delta_1\end{bmatrix}. \tag{40}$$

As a first step in solving Eq. (38), we diagonalize the g matrix

$$\mathsf{U}\cdot\mathsf{g}=\hat{\lambda}\cdot\mathsf{U}. \tag{41}$$

$\hat{\lambda}$ the eigenvalue matrix is given as

$$\lambda_{1,2}=\tfrac{1}{2}(\hbar\Delta_1+i\varepsilon_2^2\overline{\mu_2^2(\omega_2)}\mp\{[\hbar\Delta_1-i\varepsilon_2^2\overline{\mu_2^2(\omega_2)}]^2+4(\mu_{0,s}\epsilon_1)^2\}^{1/2}), \tag{42}$$

and U the diagonalizing transformation is given in terms of $\hat{\lambda}$ as

$$U_{1,1}=\mu_{0,s}\epsilon_1/\{[\lambda_1-i\varepsilon_2^2\overline{\mu_2^2(\omega_2)}]^2+(\mu_{0,s}\epsilon_1)^2\}^{1/2},\quad U_{2,2}=\mu_{0,s}\epsilon_1/[(\lambda_2-\hbar\Delta_1)^2+(\mu_{0,s}\epsilon_1)^2]^{1/2},$$

$$U_{1,2}=[\lambda_1=i\varepsilon_2^2\overline{\mu_2^2(\omega_2)}]/\{[\lambda_1-i\varepsilon_2^2\overline{\mu_2^2(\omega_2)}]^2+(\mu_{0,s}\epsilon_1)^2\}^{1/2},\quad U_{2,1}=(\lambda_2-\hbar\Delta_1)/\{(\lambda_2-\hbar\Delta_1)^2+(\mu_{0,s}\epsilon_1)^2\}^{1/2}. \tag{43}$$

U is nonunitary (otherwise no flux loss to the continuum manifold would occur). However, as can be easily seen from the symmetry of the complex g matrix [see Eq. (40)], U is *complex orthogonal*, i.e., it satisfies the complex relation

$$\mathsf{U}(t)\cdot\mathsf{U}^{\mathsf{T}}(t)=\mathsf{I}. \tag{44}$$

Operating with $\mathsf{U}(t)$ on Eq. (38) and defining

$$\mathsf{a}(t)=\mathsf{U}(t)\cdot\mathsf{b}(t), \tag{45}$$

we obtain that

$$\frac{d}{dt}\mathsf{a}=\left[\frac{i}{\hbar}\hat{\lambda}(t)+\mathsf{A}\right]\cdot\mathsf{a}, \tag{46}$$

where

$$\mathsf{A}\equiv\frac{d\mathsf{U}(t)}{dt}\cdot\mathsf{U}^{\mathsf{T}}. \tag{47}$$

We know from Eq. (44) that A is antisymmetric, hence

$$\mathsf{A}_{i,i}=0, \quad i=1,2. \tag{48}$$

If we assume that U varies slowly enough with time such that

$$\mathsf{A}_{i,j}\approx 0, \quad i\neq j \tag{49}$$

(i.e., we make an *adiabatic* assumption), Eq. (46) becomes

$$\frac{d}{dt}\mathsf{a}=\frac{i}{\hbar}\hat{\lambda}(t)\cdot\mathsf{a}(t), \tag{50}$$

and we obtain that

$$\mathsf{a}(t)=\exp\left[\frac{i}{\hbar}\int_0^t\hat{\lambda}(t')dt'\right]\mathsf{a}(0). \tag{51}$$

Using Eq. (39), and imposing the boundary condition

$$\mathsf{b}(0)=(0,1), \tag{52}$$

we obtain for the $b_s(t)$ and $b_0(t)$ coefficients

$$b_s(t)=U_{2,1}(t)\exp\left[\frac{i}{\hbar}\int_0^t\lambda_2(t')dt'\right]U_{2,2}(0)+U_{1,1}(t)\exp\left[\frac{i}{\hbar}\int_0^t\lambda_1(t')dt'\right]U_{1,2}(0) \tag{53}$$

and

$$b_0(t)=\exp(-i\Delta_1 t)\left\{U_{2,2}(t)\exp\left[\frac{i}{\hbar}\int_0^t\lambda_2(t')dt'\right]U_{2,2}(0)+U_{1,2}(t)\exp\left[\frac{i}{\hbar}\int_0^t\lambda_1(t')dt'\right]U_{1,2}(0)\right\}. \tag{54}$$

Given $b_0(t)$, the (channel specific) continuum coefficients $b_{E,\mathrm{n}}(t)$ are obtained directly via Eq. (34). It follows

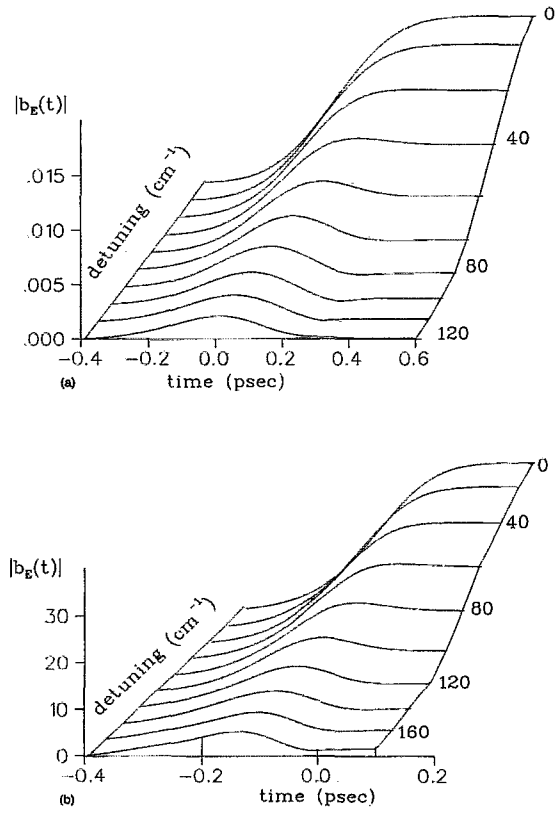


FIG. 1. Absolute value of the $b_{E,0}(t)$ coefficient as a function of field strength. Computations were performed for the $CH_3I\rightarrow CH_3+I(^2P_{1/2})$ process at $\hbar\omega_L=38\,000\ \mathrm{cm}^{-1}$. Zero signifies the free CH_3 $v=0$ umbrella vibration. (a) $\varepsilon_L=10^{-6}$; (b) 10^{-2}; and (c) 10^{-1} a.u. [ε_L is defined in Eq. (24)]. The pulse width is 120 cm^{-1} and the pulse peaks at $t=0$.

from Eqs. (34) and (54) that, as in the one-photon case, *the fragment state distribution in a two-photon dissociation via a single intermediate state is insensitive to the pulse strength and shape*. The only way of controlling the fragment state distribution in a two-photon dissociation process is by involving more than one intermediate state.[9] In fact, if the continuum is coupled by the field to just a single intermediate resonance, the above conclusion holds true for multiphoton dissociation as well.

We can go beyond the adiabatic approximation by solving Eq. (46) exactly in the following way: we start with the adiabatic solutions (51)

$$\mathsf{a}^{(0)}(t)=\mathsf{a}_{\text{adiab}}(t) \tag{55}$$

and improve each component of the $\mathsf{a}(t)$ vector as

$$\frac{d}{dt}a_i^{(1)}=\left(\frac{i}{\hbar}\lambda_i+A_{i,j}a_j^{(0)}/a_i^{(0)}\right)a_i^{(1)}, \quad i=1,2, \quad j\neq i, \tag{56}$$

which can be solved to give

$$a_i^{(1)}(t)=\exp\left\{\frac{i}{\hbar}\int_0^t dt'[\lambda_i(t')+A_{i,j}(t')a_j^{(0)}(t')/a_i^{(0)}(t')]\right\} \times a_i^{(1)}(0), \quad i=1,2, \quad j\neq i. \tag{57}$$

The solution is reintroduced into Eq. (56) and the iteration is continued until convergence. The procedure is expected to converge within few iterations for near adiabatic situations.

IV. COMPUTATIONS

We first present sample computations of one-photon dissociation. In Figs. 1(a)–1(c), we plot the transient continuum coefficients for the photodissociation of CH_3I,

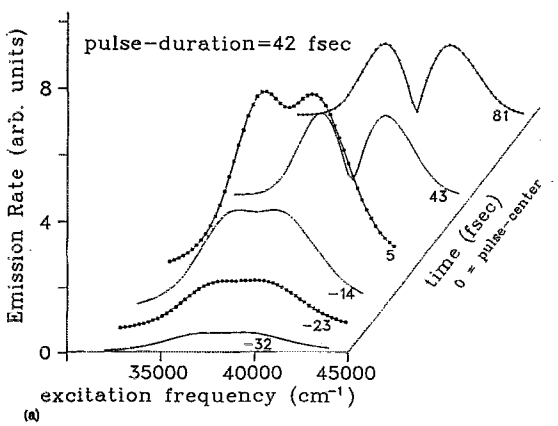
$$CH_3I \rightarrow CH_3+I$$

in the pseudotriatomic approximation[35] for laser pulses of increasing intensity.

As in the weak-field domain [see Fig. 1(a)], the energetic profile of the continuum coefficients at early times (as the pulse is switched on) is much wider than the frequency profile of the pulse. As time progresses, the energetic profile of the continuum coefficients narrows down (in a nonmonotonic fashion). In the weak-field domain, it narrows down to finally resemble the laser profile. As the field gets stronger, the final profile of the continuum coefficients becomes broader and broader.

The fact that the continuum profile starts out much broader than the laser profile is due[33] to the molecules actually seeing during the pulse's switch-on phase a much wider bandwidth than that of the full pulse. Contrary to the weak-field domain, for strong pulses, both power broadening of the final continuum population and temporal saturation are in evidence.

In the usual mechanism, power broadening is induced by the fact that continuum levels (for bound bound transitions these would be levels of the spontaneously emitted photon modes) closer to the pulse center (at ω_L) are saturated more



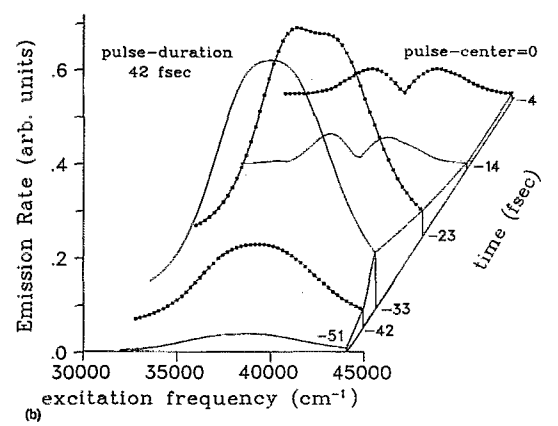


FIG. 2. Transient continuum emission as a function of the central frequency of an ultrashort excitation pulse peaking at $t=0$. Studied is CH_3I emitting from the dissociative $(^3Q_0+{}^1Q_1)$ excited states to the ground-state 3_1 vibration (the first excited C–I stretch). (a) Peak intensity$=10^{10}$ and (b) 10^{15} W/cm^2.

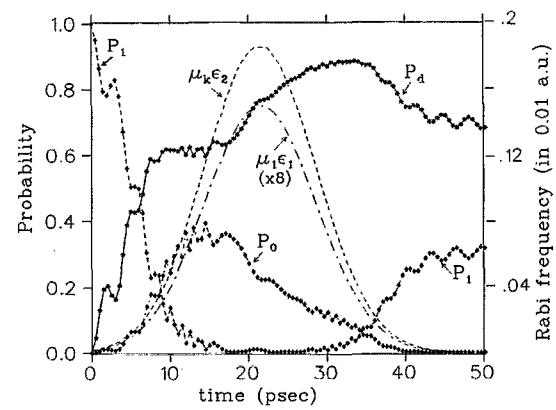


FIG. 3. Two-photon dissociation probabilities for coincident detuned ($\Delta_1=10$ cm^{-1}) pulses. Shown are the population of the ground state (P_1); the population of the intermediate state (P_0) and the sum of the populations of the continuum states (P_d). The $\overline{\mu^2(\omega_L)}\varepsilon_2$ pulse is marked by ---; the $\mu_1\varepsilon_1$ pulse is marked by ····· . The right-hand scale pertains to the pulses.

quickly than levels at the wings of the pulse. As a result, pumping of levels in the wings continues when levels closer to the pulse-center saturate. In contrast, in the present case, power broadening arises mainly as a result of the emptying of the ground state. This has the effect of shortening the interaction time between the continuum levels and the initial state. In frequency space, the shortening of the interaction time translates to the broadening of the the continuum profile relative to the laser's bandwidth.

Frequency broadening is also accompanied by temporal saturation. The signature of temporal saturation is the fact that the continuum level population ceases to change well before the end of the pulse. The stronger the pulse, the shorter the time needed to saturate the continuum, after which time, no net population transfer occurs, because even if new molecules are formed in the ψ_s state by radiative recombination, they are immediately redissociated by the strong pulse.

One of the consequences of the temporal saturation is that spontaneous emission from the continuum (i.e., "continuum Raman" and resonance fluorescence) settles into its postpulse values early on in the history of the pulse. The rate of spontaneous emission from the continuum to a final ψ_f bound state is obtained[33,36,37] according to the formula

$$\frac{dP_{f,s}(t)}{dt}=\frac{8}{\pi c^3\hbar^3\varepsilon_0}\left|\int dE\ \omega_{E,f}^{3/2}\sum_{\mathbf{n}}\mu(f|E,\mathbf{n})\mu(E,\mathbf{n}|s)\int_{-\infty}^{t}dt'\varepsilon(t')b_s(t')\exp\left[-i(\omega_{E,s}-\omega_L)(t-t')\right]\right|^2. \tag{58}$$

$b_s(t')$ is given by Eq. (17) for the one-photon case and by Eq. (53) for the two-photon case.

In Fig. 2, we present calculations of the rates by which CH_3I excited by a single photon from its ground vibrational state to the dissociative A continuum (composed of the $^3Q_0$ and $^1Q_1$ electronic states) spontaneously emits photons while undergoing a transition to the 3_1 vibrational state (i.e., the first excited C–I stretch vibration).

Shown are the emission rates as a function of the time and the central frequency of the excitation pulse. Quite clearly, as the excitation pulse gets stronger, the excitation-emission spectrum (the spontaneous emission as a a function of the excitation laser central frequency) assumes its post-pulse shape *even before the pulse reaches its peak.* This is due simply to the emptying of the population in the initial state by the strong excitation pulse. In the SVCA, any down transition from the continuum is followed by an up transition from the initial state to the continuum; the initial state, once emptied, never gets repopulated.

We now turn our attention to the two-photon case and show what happens when we apply the two pulses simultaneously (Fig. 3) and what happens when we delay the pulses (Fig. 4) in a model system for which $\omega_{0,s}=20\,000\ \mathrm{cm}^{-1}$ and $\omega_{E,0}=19\,000\ \mathrm{cm}^{-1}$. When the two pulses are applied simultaneously, the process starts with depletion of the initial state followed by a rise in the intermediate state which gets dissociated quite effectively. However, the transfer of population to the continuum is incomplete and, in fact, towards the end of the pulse, some flux starts flowing back from the continuum to the ground state via the intermediate state which is being emptied completely.

In contrast, when we first apply ε_2 and *then* ε_1, as in the STIRAP arrangement,[14] the dissociation is complete. As shown in Fig. 4, while the initial phase of the process is similar to that of the coincident pulses of Fig. 3, the second phase is different. During that phase, the intermediate state empties to the continuum rather than to the initial state. This behavior is due to the predominance of ε_2 throughout the process. Only when the initial state and the intermediate state are completely empty do we turn off ε_2.

We have shown that complete population transfer to the continuum is indeed possible. It should be noted, however, that the STIRAP type delay is not the only pulse arrangement that can cause a complete transfer to the continuum. In the future, we plan to analyze the dependence of $\lambda_{1,2}$ and U on the pulses' configurations and strengths to determine all the cases for which complete population transfer occurs. We shall also study the pulse parameters which guarantee the goodness of the adiabatic approximation.

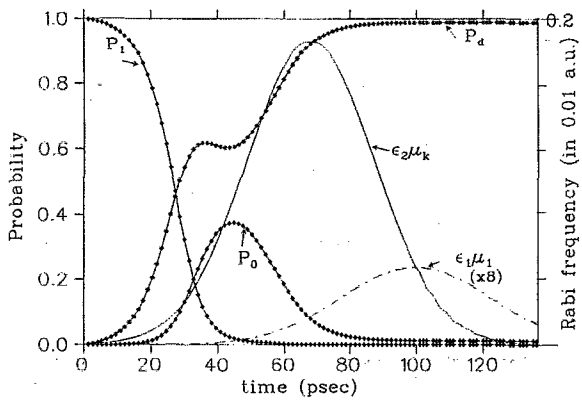


FIG. 4. The same as in Fig. 3 for a delayed-pulse configuration with minimal detuning ($\Delta_1=0.1\ \mathrm{cm}^{-1}$).

ACKNOWLEDGMENT

This paper was supported by Grant No. 89-397 of the U.S.–Israel Binational Foundation.

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