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Semiadiabatic treatment of photodissociation in strong laser fields

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A semiadiabatic treatment of the matter-field coupling is presented that accounts for the nonlinear variations affecting the widths and positions of laser-induced resonances in photodissociation as a function of the electromagnetic-field intensity. The procedure developed here goes beyond the widely used decoupled electronic-plus-field adiabatic treatment by retaining two "semiadiabatic" potentials that result from partial diagonalization of several blocks in the Floquet Hamiltonian. All closed channels lead to a unique multiphoton-dressed adiabatic closed channel that crosses a unique dressed adiabatic open channel. The remaining nondiagonal interaction is treated diabatically within a two-coupled-channel frame. The relative merits of diabatic approximations and of the semiadiabatic scheme are discussed within a large range of laser intensities and wavelengths on the example of $H_2{}^+(1s\sigma_g,\ v=0,\ J=1 \rightarrow 2p\sigma_u)$ photodissociation. Uniformally accurate results are reached for the semiadiabatic approach. This is very promising for studying field-induced nonlinearities for very intense lasers operating at rather short wavelengths where many electronic states including rotational structures may play a role.

I. INTRODUCTION

The theory of photodissociation has evolved along two parallel routes; one that is appropriate for the weak-field situation and the other one for the strong-field case. In each route the emphasis is put on different features of the process. The weak-field approach concentrates on complications that are inherent in the molecular dynamics: increasing number of internal degrees of freedom (i.e., electronic, vibrational, rotational, torsional, etc.), interferences between different arrangement channels resulting from the symmetry of the system, and three-body fragmentations involving continuum-continuum interactions. In the strong-field case interest is focused on the description of the additional field-induced degrees of freedom rather than the dynamics of the bare molecular system (which is generally assumed to be a simple diatomic molecule).

In weak-field theories the photon mediates the preparation of the initial state. The absorption is usually described by applying the Fermi golden rule to a bound-to-continuum transition. Similarly, in the time-dependent approach the decay process is described in the framework of the first-order perturbation theory.

The strong-field case requires nonperturbative approaches that describe simultaneously the absorption and dissociation processes. Time-dependent as well as time-independent treatments may be performed. The present work rests on a time-independent description of the process, derived from a fully quantal treatment of the molecule-plus-field system, or equivalently from a semiclassical approach in which the periodic time dependence of the electromagnetic field, treated as a classical oscillator, is eliminated via the Floquet theory. The nuclear dynamics takes places on "dressed" potential surfaces[1] which are eigenvalues of the electron-plus-field Hamiltonian and are very appropriate for discussing field-induced resonances. As in usual scattering calculations, one has to solve a (in principle infinite) set of second-order coupled equations in nuclear coordinates. We have recently[2] shown how such a system truncated to the minimal number of equations for reaching convergence (close-coupling method), accounts for the gradual changes in the resonance width and shift when the light intensity increases.

The selection of a suitable basis set to reduce the number of close-coupled equations is of primary importance. Two important types of basis-set expansions are commonly used. If the basis set is the same for all values of the dissociative coordinate it is referred to as *diabatic*.[3] The resulting Hamiltonian in this representation is nondiagonal and the ability of this basis to reach a given accuracy with a few channels relies on the smallness of the (field-intensity-dependent) couplings.

For strongly coupled systems, the situation is properly handled through the use of *adiabatic* basis functions that diagonalize the field-dependent Hamiltonian. The electronic-plus-field curves reflecting nuclear dynamics are just coupled by nonadiabatic terms that become less and less efficient as the field intensity increases and the curve crossings are more and more avoided.

From the numerical point of view, many algorithms are available as far as the diabatic representation is used (amplitude density,[4] de Vogelaere,[5] Numerov, Fox-Goodwin,[6] etc.). On the other hand, apart from Smith's diabatic transformation[7] and a reduced adiabatic-diabatic treatment,[8] only a limited number of algorithms have been developed for direct integration of the coupled equations in the adiabatic frame.[9]

Approximate treatments at several levels of sophistication have, however, been applied to photodissociation problems. In the context of strong radiative fields, a decoupling approximation has been used as a guide for the interpretation of optical nonlinearities.[2] More generally, the multistate curve crossings occurring in dressed-state representations have been handled using a uniform semiclassical theory.[10]

In this paper we extend our previous work on the adiabatic decoupling approximation[2] to a broader range of field intensities and wavelengths. Instead of one electronic-plus-field adiabatic state, two "semiadiabatic" states are retained which result from the partial diagonalization of several blocks in the Floquet Hamiltonian. The remaining nondiagonal interaction is treated diabatically within a two-coupled-channel frame. The theory is described in Sec. II. The results concerning the photodissociation of $H_2{}^+(1s\sigma_g, v=0, J=1\rightarrow 2p\sigma_u)$ are presented in Sec. III. The merits of diabatic and adiabatic basis sets and that of the decoupling scheme are discussed as a function of laser intensity and wavelength.

II. THEORY

A. Time-independent radiative close-coupling equations

Let us briefly recall the main steps of the time-independent description of the field-induced resonances which mediate the photodissociation process. The total Hamiltonian for the molecule-plus-radiation field is taken, within the Born-Oppenheimer approximation, as the sum of the three terms,

$$H(r,R)=H_{\mathrm{BO}}^{(0)}(r,R)+H_{\mathrm{rad}}+V_{\mathrm{int}}(r,R)\ , \tag{1}$$

namely, $H_{\mathrm{BO}}^{(0)}$ approximate molecular Hamiltonian, H_{rad} the free-radiation-field Hamiltonian, and V_{int} the matter-field interaction term. r and R stand for electronic and nuclear coordinates, respectively. By doing so we have omitted the intramolecular dynamical couplings between Born-Oppenheimer electronic states which are independent of the field strength and thus irrelevant for our discussion. We also assume that only two electronic states are involved in the process: a bound initial electronic state g and an electronically excited dissociative state d, and neglect any change in the rotation quantum number resulting from the interaction with the field.

In the dressed-molecule picture the total wave function is expanded on electronic-plus-field channel functions describing cascades of absorption-emission processes,

$$\Psi(r,R)=\sum_n [\psi_g(r,R)\chi_{g,n}(R)+\psi_d(r,R)\chi_{d,n}(R)]|n\rangle\ . \tag{2}$$

$|\psi_g\rangle|n\rangle$ and $|\psi_d\rangle|n\rangle$ are exact eigenstates of $H_{\mathrm{BO}}^{(0)}+H_{\mathrm{rad}}$ corresponding to the ground and excited electronic states with n quanta (photons) in the field. The R-dependent unknown mixing coefficients χ's (the vibrational wave functions in the diabatic potentials) can be obtained as solutions of a system of second-order differential equations. As it has been previously shown[2,11] the resulting set of close-coupled equations within the dipole approximation for the radiative interaction is

$$\begin{aligned}[T_R+V_{g,n+1}(R)-E]\chi_{g,n+1}(R)&\\ +V_{gd}(R)[\chi_{d,n}(R)+\chi_{d,n+2}(R)]&=0\ ,\end{aligned} \tag{3}$$

$$\begin{aligned}[T_R+V_{d,n}(R)-E]\chi_{d,n}(R)&\\ +V_{dg}(R)[\chi_{g,n-1}(R)+\chi_{g,n+1}(R)]&=0\ ,\end{aligned}$$

where T_R is the nuclear kinetic energy operator and $V_{\alpha n}(R)$ ($\alpha=g$ or d) the electron-plus-field potential energy, i.e., the BO potential surface shifted by the photon energy,

$$V_{\alpha n}(R)=V_\alpha(R)+n\hbar\omega\ .$$

The off-diagonal coupling terms V_{gd} represent the dipolar radiative interaction which connects electronic-field potential curves differing by one photon only ($V_{\alpha n,\beta m}=V_{gd}\delta_{n,m\pm1}$). This coupling can be expressed using either the electronic field (EF) or the radiation field (RF) gauge, leading to the *length* or *velocity* forms, respectively, for the dipolar interaction. The length form is

$$V_{gd}^L(R)=\boldsymbol{\mu}_{gd}(R)\cdot\mathcal{E} \tag{4}$$

where $\mathcal{E}$ is the electronic-field vector (assumed to be constant over the interaction region) and $\boldsymbol{\mu}_{gd}$ the electronic transition moment,

$$\boldsymbol{\mu}_{gd}(R)=\langle\psi_g(r,R)|e\mathbf{r}|\psi_d(r,R)\rangle_r\ , \tag{5}$$

resulting from integration over the electronic coordinates, with $\psi_{g(d)}$ the electronic wave functions of the two states involved. On the other hand, the RF gauge involves the dipolar interaction $\mathbf{A}\cdot\mathbf{p}$, with $\mathbf{A}$ the vector potential (also considered as constant in space) and $\mathbf{p}$ the electronic momentum operator. The resulting velocity form of the dipolar interaction is

$$V_{gd}^v(R)=\frac{e}{mc}\mathbf{A}\cdot\langle\psi_g(r,R)|\mathbf{p}|\psi_d(r,R)\rangle_r\ . \tag{6}$$

It can be related to the length from [Eqs. (4) and (5)] using the commutator relation for the Born-Oppenheimer electronic Hamiltonian H_{BO},

$$\mathbf{p}=-\frac{im}{\hbar}[\mathbf{r},H_{\mathrm{BO}}^{(0)}]\ ,$$

together with the relation $A=c/\omega\mathcal{E}$ between the amplitudes of the vector potential and field. One thus gets

$$V_{gd}^v(R)=\frac{V_g(R)-V_d(R)}{\hbar\omega}V_{gd}^L(R)\ . \tag{7}$$

Although both gauges lead obviously to the same results in an exact calculation, we show below (Sec. III) that one form or the other may be much more convenient for a specific type of calculation and for a given molecule.

Let us note here that when V_{gd} is restricted to couple the channels $|g,n+1\rangle$ and $|d,n\rangle$ only in Eq. (3) (i.e., neglecting the couplings between $|g,n\rangle$ and $|d,n+1\rangle$) the infinite set of equations (3) is partly decoupled into sets of 2×2 "Floquet blocks," each describing a single-photon absorption-emission process. The resulting "rotated-wave approximation" already goes beyond the usual lowest-order perturbative treatment (Fermi golden rule) and yields accurate results at intermediate field strengths.

The solution of Eqs. (3) subjected to Siegert-type boundary conditions[12] (regularity at the origin and outgoing wave behavior at infinite separation) leads to complex quasivibrational energies or field-induced Feshbach resonances whose imaginary parts are directly related to photodissociation rates. Accurate calculations may require a large number of coupled Floquet blocks depending on the field strength and the wavelength. Algorithms based upon the Fox-Goodwin propagator associated with the analytic continuation of the Hamiltonian by the complex rotation of the coordinate[13] are then prohibitively time consuming. We describe now alternatives to the exact solution of these coupled equations, based on the adiabatic representation.

B. Adiabatic representation and approximations

The adiabatic description incorporates the radiative couplings in the eigenvalues of the electronic-plus-field Hamiltonian. The vibrational motion adjusts itself continuously (adiabatically) to the perturbation induced by the field and for large radiative intensities, the number of such electronic-plus-field channels required to lead to convergence is expected to be smaller than in the diabatic representation.

The diagonalization of the potential matrix $\mathbf{V}(R)$ [Eqs. (4) and (6)] results into field-dependent eigenvalues and eigenvectors,

$$[\mathbf{V}(R)-W(R)\mathbf{I}]\mathbf{C}(R)=0\ , \tag{8}$$

$W_k(R)$ being the adiabatic potentials and $C_k(R)$ the weighting factors of the BO wave functions $\psi_\alpha(r,R)$ leading to adiabatic electronic-plus-field wave functions $\phi_k^{\rm ad}(r,R)$. The total wave function expanded on this field-dependent adiabatic basis involves R-dependent unknown coefficients $\chi_k^{\rm ad}(R)$ which are the adiabatic analogs of the nuclear wave functions $\chi(R)$ of Eqs. (3). They are now solutions of adiabatically coupled equations[8,9]

$$\left[\frac{\hbar^2}{2\mu}\left[\mathbf{I}\frac{d^2}{dR^2}+2\tau(R)\frac{d}{dR}+\rho(R)\right]+\mathbf{W}(R)-E\mathbf{I}\right]\chi^{\rm ad}(R)=0\ , \tag{9}$$

where $\mathbf{W}$ is the diagonal potential matrix, ρ is a symmetric potential correction given by

$$\rho_{kl}(R)=\left\langle\phi_k^{\rm ad}(r,R)\left|\frac{d^2}{dR^2}\right|\phi_l^{\rm ad}(r,R)\right\rangle_r \tag{10}$$

and τ an antisymmetric matrix with elements

$$\tau_{kl}(R)=\left\langle\phi_k^{\rm ad}(r,R)\left|\frac{d}{dR}\right|\phi_l^{\rm ad}(r,R)\right\rangle_r\ . \tag{11}$$

Finally, the Hellman-Feynman relation[14] gives an alternative expression for τ_{kl} in terms of the first derivative of $V(r,R)$ (molecular and molecule-plus-field couplings) with respect to R,

$$\tau_{kl}(R)=\frac{\left\langle\phi_k^{\rm ad}(r,R)\left|\dfrac{dV(r,R)}{dR}\right|\phi_l^{\rm ad}(r,R)\right\rangle_r}{W_k(R)-W_l(R)}\ . \tag{12}$$

When comparing Eqs. (3) and (9) one observes the following.

(i) Radiative potential couplings leading to a prohibitively large number of channels in the intense field regime do not appear in the adiabatic treatment.

(ii) Adiabatic interchannel interactions (nonadiabatic radial couplings) are large near the avoided crossing points where the adiabatic potentials are close to each other. Note that these couplings may be considered as negligible between different Floquet blocks as compared to their values within the block under consideration, resulting from the fact that the laser-frequency-dependent denominator may be very large from one block to the other.

(iii) The coupling terms contain an additional kinetic operator d/dR.

It is precisely this operator which is responsible for the computational complications arising when the integration of the coupled equations in the adiabatic representation is attempted. A generalized version of Numerov's method to handle photodissociation problems in the adiabatic frame has only recently been proposed[9] and its application to intense laser-field dissociation is now in progress. Smith's transformation[7] has often been referred to as a possible way to drip out the kinetic couplings and applied to electronic transitions taking place during a chemical reaction and to vibrational inelastic scattering.[15] More recently the formalism has been generalized to the study of the photodissociation of a polyatomic molecule (CH_3NO_2) showing complicated peak and dip patterns.[8] The procedure involves three steps: transformation from a diabatic to an adiabatic basis set, truncation of the adiabatic basis, and back transformation to a reduced-diabatic basis set.

A different "semiadiabatic" approach is adopted in this paper. The method is summarized in Fig. 1. Three Floquet blocks in the diabatic dressed-molecule picture are symbolized in Fig. 1(a) together with their corresponding field-amplitude-dependent potential couplings. They are separated by twice the photon frequency. The first step consists of diagonalizing all the "upper" Floquet blocks (involving more than $n+1$ photons) together with the ground state dressed with $(n+1)$ photons $V_{g,n+1}$. This is done using Eq. (8) and yields $(2N^++1)$ adiabatic molecule-plus-field potentials $W_i^+(R)$ [$i=1,2,\dots,(2N^++1)$ if N^+ is the total number of upper Floquet blocks which are retained to reach a given accuracy, the super-

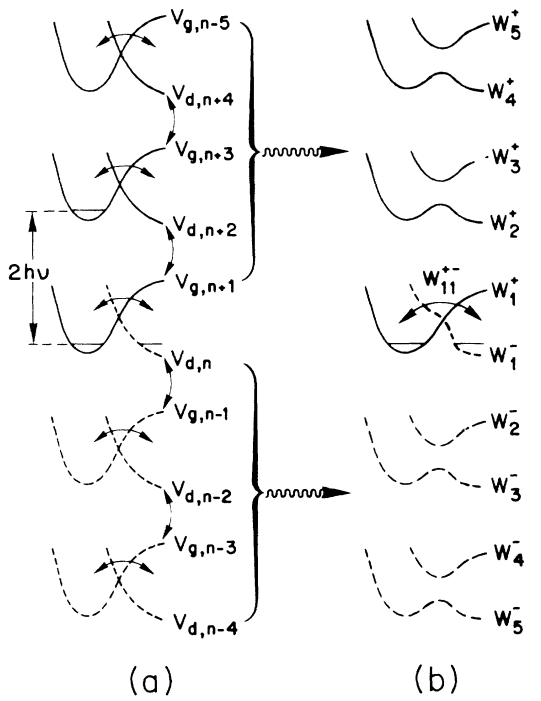

FIG. 1. (a) Diabatic and (b) semiadiabatic representation of dressed electronic potential curves. The solid lines correspond to the higher Floquet blocks, the dashed lines to the lower Floquet blocks. The arrows indicate the radiative couplings. The result of separate diagonalization within each group of curves is shown in (b).

script "plus" indicates that we are dealing with "upper" blocks]. The same operation is undertaken for the "lower" Floquet blocks (the ones which involve less than n photons) coupled to the dissociative state dressed with n photons $V_{d,n}$. The result is $(2N^-+1)$ adiabatic potentials $W_i^-(R)$ $[i=1,2,\ldots,(2N^-+1)$, the superscript "minus" being the analogous of "plus" for "lower" blocks]. It is to be noted that due to the selection rules [Eq. (4)] the matrices to be diagonalized are in tridiagonal form for which performant algorithms can be used. Within the "upper" (or "lower") blocks the adiabatic potentials with avoided curve crossing are represented on part (b) of Fig. 1. They are only coupled through the nonadiabatic kinetic terms of Eq. (9), which will be neglected in the following since the interblock energy gap is large. The only place where such a coupling would be important is the curve crossing occurring between $W_1^+(R)$ and $W_1^-(R)$ potentials. Instead of treating it adiabatically we calculate the residual field-dependent diabatic potential coupling between these two states. The two-step diagonalization (upper and lower blocks separately) leads to eigenvectors: $C_i^+(R)$ and $C_i^-(R)$ (i being the index of the corresponding eigenvalue). The "upper" (or "lower") block adiabatic wave functions as expanded on the diabatic basis (briefly noted as $|g$ or $d,n\rangle$) are given by

$$|\phi_i^\pm\rangle = \sum_{p=0} [C^\pm_{i,2p+1}(R)|g,i\pm 2p\pm 1\rangle + C^\pm_{i,2p}|d,n\pm 2p\rangle] \tag{13}$$

and the residual coupling is calculated through

$$\begin{aligned} W_{11}^{+-} &= \langle\phi_1^+|V|\phi_1^-\rangle \\ &= C_{11}^+(R)C_{10}^-(R)V_{g\,n+1,dn}(R)\ . \end{aligned} \tag{14}$$

The last step of the calculation is to reconsider the diabatically close-coupled equations within a two-channel frame,

$$\begin{aligned} [T_R+W_1^+(R)-E]\chi^+(R)+W_{11}^{+-}(R)\chi^-(R)&=0\ , \\ [T_R+W_1^-(R)-E]\chi^-(R)+W_{11}^{+-}(R)\chi^+(R)&=0\ , \end{aligned} \tag{15}$$

and to solve it with appropriate boundary conditions to obtain the resulting Feshbach resonances.

We conclude this section by recalling other types of adiabatic approximations used in Ref. 2, with respect to which the performances of the above "semiadiabatic" treatment will be checked in the next section. At intermediate laser intensities, a useful tool for the interpretation of optical nonlinearities is to restrict the adiabatic representation to a single Floquet block, thus excluding actual multiphoton absorptions. The corresponding adiabatic states accommodate laser-induced tunneling or *shape* resonances,[16] coupled to each other by nonadiabatic residual couplings. A further step in the approximation may be performed if the quasibound levels supported by the lower adiabatic potential, are far from the ones supported by the higher adiabatic potential. This is clearly the case for excitation wavelengths leading to avoided crossings at large interfragment separation. When the field parameters (i.e., intensity and wavelength) correspond to this particular regime, kinetic couplings may be neglected (decoupling approximation) and the shape resonances are obtained via direct integration of a single nuclear Schrödinger equation.

This approximation may already account for nonlinear effects within a single-photon picture, but it is severely restricted to moderate intensity and specific wavelengths.[2] We show now that the "semiadiabatic" approach described above has a much broader range of validity due to the inclusion of multiblock effects, and may handle a large number of coupled channels without prohibitive computational efforts.

III. RESULTS

To illustrate the main features of the semiadiabatic model we reconsider the photodissociation of $H_2{}^+(v=0,J=1)$ for which a thorough analysis of the nonlinear behavior of the laser-induced resonances has been previously conducted in the diabatic approach.[2] Only two electronic states were retained, namely, the ground $(1s\sigma_g)\,{}^1\Sigma_g^+$ and the dissociative $(2p\sigma_u)\,{}^1\Sigma_u^+$, given by uniform Morse-type representations:[17]

$$V_{\alpha 0}(R)=D_0\{\exp[-2\beta(R-R_e)]-2t_\alpha\exp[-\beta(R-R_e)]\}\quad(\alpha=g\text{ or }d)\ ,\qquad(16)$$

where the bound or repulsive character is related to the sign of t_α. The transition dipole moment is taken from Bunkin and Tugov,[17]

$$\mu_{gd}(R)=\mu+\frac{\mu'}{\beta y}\{1-\exp[-\beta y(R-R_e)]\}\ .\qquad(17)$$

All the parameters are listed in Ref. 2 and the resulting matter-field interaction is expressed there in the length form [Eq. (4)]. It is to be noticed that Eq. (17) with a negative value of β corresponds to an asymptotically *divergent* dipole. This did not bring numerical difficulties into the previous calculations, restricted to a range of laser wavelengths and intensities where bound-free transitions dominate the photodissociation process. For strong fields and especially when free-free transitions above the dissociation threshold become important,[18] it is more efficient to use the asymptotically *convergent* velocity from [Eqs. (6) and (7), with $V_d(R)-V_g(R)\rightarrow 0$ at large R] to avoid the otherwise increasing number of channels needed for convergency. All calculations presented in this paper are done with the matter-field interaction expressed (in cm^{-1}) as

$$V^{v}_{gd}(R)=\frac{1.17\times10^{-3}}{2\hbar\omega}[V_d(R)-V_g(R)]\sqrt{I}\,\mu_{gd}(R)\ ,\qquad(18)$$

with I in W cm^{-2} and μ_{gd} in atomic units.

Finally, we recall that a J-conserving approximation, neglecting the different rotational channels which are coupled by the laser field, is adopted.

As has been pointed out previously approximations in the diabatic and adiabatic frames may lead to quite different results (sometimes complementary) according to the characteristic parameters of the laser source (i.e., intensity and wavelength) and of the target molecule. Scaling values for these parameters are the characteristic internal frequency (vibrational or rotational) of the molecule and the wavelength $\lambda_{\max}$ which corresponds to the maximum of the dissociation line shape. In our specific example the vibrational mode frequency of H_2^+ in the energy region of interest is $\omega_v\simeq 2000\ \text{cm}^{-1}$ and $\lambda_{\max}\simeq 1250$ Å for absorption from the ground vibrational level.

For the forthcoming discussion we map the laser-field interaction parameters into a system with $(\omega/\omega_v,\ \lambda/\lambda_{\max})$ as coordinates and the point (1,1) as origin [see Fig. 2(a)]. $\lambda_{\max}$ is the laser wavelength and $\omega=\hbar^{-1}V_{gd}(R_c)$ the Rabi frequency, proportional to $\sqrt{I}$, at the crossing point R_c between the attractive and repulsive curves in a single-photon diabatic representation. Vertical dotted lines separate the plane into three intensity regimes which have already been defined in our previous work[2] and correspond to the weak $(\omega/\omega_v \ll 1)$, intermediate $(\omega/\omega_v\simeq 1)$, and strong $(\omega/\omega_v \gg 1)$ matter-field couplings, respectively. The upper half-plane corresponds to a c^+ type of dissociation (crossing point on the right, at $R_c>R_e$) and the lower half-plane to a c^- type of dissociation $(R_c<R_e)$.

All calculations are done by solving the coupled equations subject to Siegert-type boundary conditions. We refer to the well-documented technique of the analytic continuation of the Hamiltonian by complex rotation of the radial coordinate,[19] which leads to the resonance width Γ and energy shift ΔE from the zero-field position of the vibrational bound state. Three classes of approximations are studied and their performances are compared

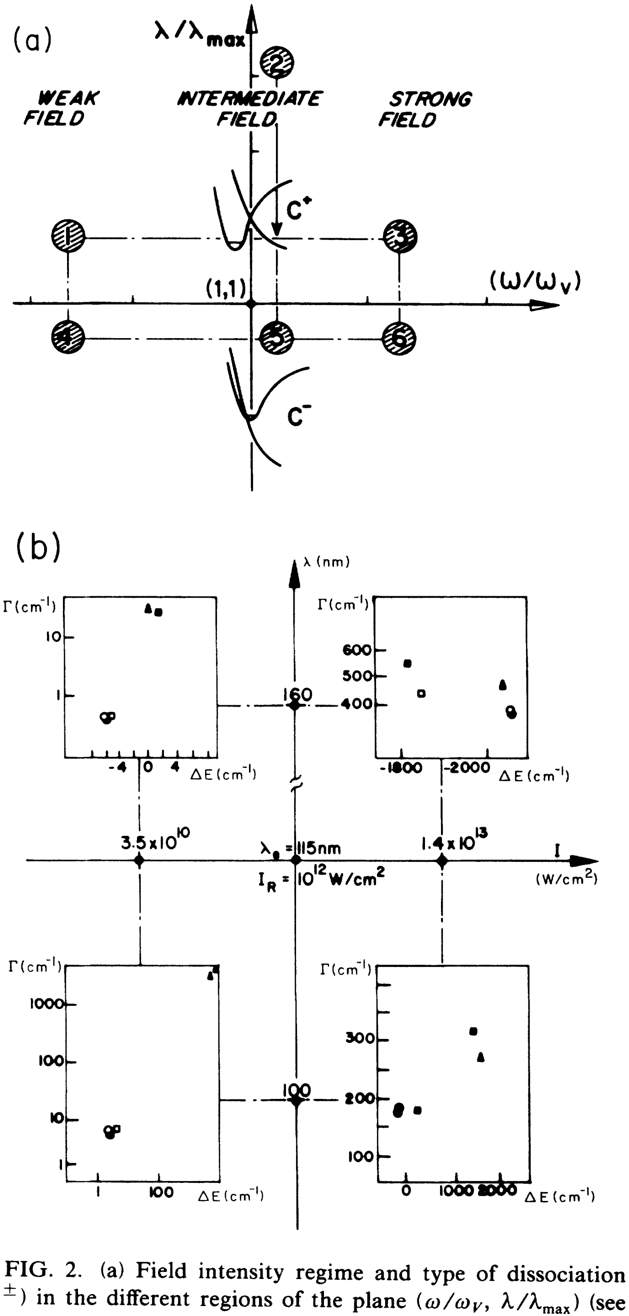

FIG. 2. (a) Field intensity regime and type of dissociation $(c^{\pm})$ in the different regions of the plane $(\omega/\omega_V,\ \lambda/\lambda_{\max})$ (see text). The circles place the six examples discussed in the text. (b) Comparison of the results obtained with different methods for the cases 1, 3, 4, and 6 of (a). ○, exact calculation; ●, semiadiabatic; □, single-photon diabatic; ■, single-photon adiabatic; △, multiblock adiabatic.

with converged diabatic calculations including five Floquet blocks.

(i) The single-photon two-channel diabatic approximation which neglects multiphoton (multiblocks) effects and leads to a Feshbach resonance. It is very appropriate in region I and still valid in region II where even important nonlinearities may be accurately reproduced.

(ii) Adiabatic approximations, which reduce the system to a single adiabatically dressed channel with a shape resonance. Multiblock effects may be partially included by diagonalizing the ten initial diabatic channels, instead of only two as in our previous work.[2] It is appropriate when the field intensity is large enough to well separate the channels resulting from the diagonalization, in order that the neglected nonadiabatic couplings are small. A situation which occurs in intermediate (diagonalization within a single Floquet block) or strong-field region (multiblock diagonalization) provided the laser frequency leads to a c^+ type of dissociation ($R_c > R_e$). In the opposite case the neglected upper adiabatic state is very much involved in the process and this approximation fails.

(iii) The present semiadiabatic approximation which again considers a Feshbach resonance between two multiphoton-dressed coupled channels resulting from a separate diagonalization of the upper and lower Floquet blocks. Nonadiabatic couplings within each group of states (upper and lower) are neglected. We show below that this approximation has a uniform validity over the intensity regime, at least for a c^+ type of crossing. For a c^- type of dissociation in a strong field the results are less accurate.

A numerical comparison between the different approximations and the fully converged close-coupled results is presented through six illustrative examples. They are labeled from 1 to 6 on Fig. 2(a) and are chosen according to the molecule-plus-laser characteristics in regions sampling the weak-, intermediate-, and strong-field regimes. Each situation corresponds to a field-induced curve crossing of the c^+ or c^- type. Numerical values for the resonance widths and shifts resulting from the different methods are collected in Table I and Fig. 2(b), for the weak and strong field regimes.

(1) Example 1 corresponds to a weak-field regime with c^+-type curve crossing. This is a typical situation where the single-photon diabatic approximation is valid and where single-channel adiabatic approaches fail. One obtains three figures of accuracy within the diabatic frame and a factor of 100 difference within the adiabatic frames when compared to the exact result. The semiadiabatic approximation reproduces within four figures of accuracy the width, as well as the position of the resonance.

(2) Example 2 is chosen in the intermediate-field regime with again a c^+-type curve crossing. The width and shift values obtained with the single-photon diabatic approximation differ from the exact results by 4% and 15%, respectively. These discrepancies can be interpreted in terms of field-induced nonlinearities. The field intensity is not large enough to bring adiabatic approximations within comparable accuracy. It is, however, to be noticed that a diagonalization taking into account multiphoton processes slightly improves the value of the width but achieves 1% of accuracy for the energy shift of the resonance. As in the previous example, the semiadiabatic approximation yields numerical values with four figures in common with the exact calculation.

(3) Example 3 illustrates a strong-field case with again

TABLE I. Results (in cm^{-1}) for the resonance width (Γ) and shift (ΔE) obtained with the different methods and for the six examples described in the text (see Fig. 2). I (in W/cm^2) is the laser intensity and λ (in *nm*) the wavelength.

		Type of calculation			
I (W/cm^2)	One-photon	Adiabatic			Converged
λ (nm)	diabatic	One photon	Multiphoton	Semiadiabatic	calculation
(1)					
$I = 3.5\times10^{10}$	0.6981	72.38	72.36	0.6977	0.6978
$\lambda = 160$	−5.221	0.091	−0.71	−6.01	−6.011
(2)					
$I = 3.5\times10^{12}$	88.353	183.18	177.01	84.831	84.830
$\lambda = 160$	−509.09	−505.47	−581.98	−584.14	−584.03
(3)					
$I = 1.4\times10^{13}$	442.77	538.14	482.01	393.06	393.51
$\lambda = 160$	−1877.79	−1860.58	−2141.94	−2152.87	−2152.06
(4)					
$I = 3.5\times10^{10}$	3.4294	1623.52	1623.48	3.4295	3.4295
$\lambda = 100$	1.377	2672.95	2672.59	1.128	1.128
(5)					
$I = 3.5\times10^{12}$	379.69	2173.95	2169.59	380.48	380.48
$\lambda = 100$	133.48	2322.67	2287.09	107.01	107.01
(6)					
$I = 1.4\times10^{13}$	1792.9	3240.1	2672.6	1781.2	1782.7
$\lambda = 100$	78.06	1467.1	1623.5	−46.95	−47.22

a c^+-type curve crossing. Field-induced nonlinearities mainly affect the resonance position and the single-photon diabatic approximation completely fails in reproducing it. Although adiabatic approximations are improved by diagonalizing over all Floquet blocks, their accuracy remains limited. This can be explained by referring to the $(v=0, J=1)$ right turning point which lies, for the wavelength under consideration, close to the avoided crossing, such that the neglected upper adiabatic channel is involved in the decay process. The semiadiabatic approach by including the nonadiabatic coupling at this point achieves three to four figures accuracy for the resonance width and position.

(4) Example 4 corresponds again to a weak-field case but here with a c^--type curve crossing; two parameters which advocate against the use of the adiabatic frame. As expected excellent agreement is obtained with the single-photon diabatic approximation, whereas adiabatic approximations are out of scale. With the semiadiabatic approximation one gets four to five figures accuracy even in this c^- type of configuration.

(5) Example 5 shows a reduction of the validity of the single-photon diabatic approximation for this intermediate-field strength responsible for the increasing nonlinearities in the resonance position. The two versions of the adiabatic approximation fail because of the c^--type curve crossing. But again five figures accuracy is achieved when using the semiadiabatic approach.

(6) Example 6 deals with the most unfavorable situation where the strength of the field invalidates single-photon descriptions (both diabatic and adiabatic) and the c^--type curve crossing, by mixing neighboring resonances limits the validity of the multiphoton adiabatic description. The semiadiabatic approximation partly takes into account this resonance mixing only at one crossing point between potentials resulting from the separate upper and lower Floquet blocks diagonalization, while the neglected nonadiabatic couplings are large in the vicinity. But even in this apparently unfavorable situation this approximation is surprisingly good, reproducing the width and the shift within two to three figures accuracy.

From these examples we conclude that the semiadiabatic approach is able to reproduce uniformally accurate results whereas the approximate diabatic or adiabatic descriptions have their respective domains of validity. Although in its present form this method yields *total* photodissociation cross sections only, without access to the energy distribution of the fragments, its simplicity and large range of validity make it very efficient to study nonlinear effects which would otherwise require prohibitively time-consuming calculations. Such cases would be encountered for very intense fields and rather short wavelengths, where many electronic states may play a role, or even in intermediate fields which actually couple (beyond the J-conserving approximation) a large number of channels with different J values. We have recently studied this rotational mixing in $H_2{}^+$ within the semiadiabatic approach of this paper,[20] including many Floquet blocks each with a whole rotational structure.

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