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Laser-induced resonances in molecular dissociation in intense fields

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Nonlinear variations affecting the widths and positions of laser-induced resonances in the molecular-dissociation process are discussed as a function of the electromagnetic field intensity. It is shown how the close-coupled equations of quantum scattering theory, taking into account multiphoton absorption and emission processes through the time-independent Floquet Hamiltonian, go beyond the widely used weak-field Fermi golden rule approximation. For the intermediate-field regime adiabatic electron-field channels can, in some cases, serve as a guide for the interpretation of nonlinearities, while for higher laser intensities very large field-induced mixings between molecular states predominate, requiring the introduction of an increasing number of Floquet blocks for converged calculations. The formalism is applied to the photodissociation of $H_2{}^+(1s\sigma_g,\ v=0,\ J=1\rightarrow 2p\sigma_u)$. Nonlinear effects appear for intensities larger than 10^{11} W/cm^2, for which experiments begin to be available.

I. INTRODUCTION

Nonlinear effects predominate in atomic and molecular systems subjected to strong radiation fields.[1] Essential alterations in configurational and dynamical properties affecting optical spectra are expected for field intensities above 10^{11} W/cm^2. These intensities are nowadays achievable with the advent of powerful lasers and lead to an increasing interest, both experimental and theoretical, in problems of photodissociation.

For low fields, perturbative treatments involve application of Fermi's golden rule to a bound-to-continuum transition for the photon absorption which is described by the traditional Franck-Condon principle.[2] At higher intensities a proper theoretical description should, however, be of nonperturbative nature with respect to the radiative interaction. A model which is widely used is that of the dressed molecule or electronic field surfaces[3] analogous to that of dressed atomic states.[4]

A direct consequence of such an approach is the prediction of laser-induced resonances which, of course, cannot be described by usual perturbation techniques.[5] The concept of resonance arises either when direct photodissociation is visualized as the analogue of predissociation as is emphasized by Bandrauk[6] or when the formalism of complex quasivibrational energy is used, based on the generalization of Floquet theory[7] to include the complete set of continuum as well as bound vibronic states as discussed by Chu.[8] These multiphoton situations involve discrete states embedded in continua. A convenient way to treat such problems is to solve the coupled equations of quantum scattering theory based on molecule-plus-field channels involving different photon numbers. They have recently been used within a time-dependent version of the artificial channel technique for calculating multiphoton dissociation cross sections including intense field situations.[5(b),9] In the present work, it is a time-independent framework which is retained and we study the gradual changes occurring in the field-induced widths and shifts of the vibronic levels when the light intensity increases.

In Sec. II, different theoretical approaches are reviewed, bridging the weak- to strong-intensity limits. A detailed description of the close-coupled-equation approach is given using the analytically continuated molecule-plus-field Hamiltonian. A simple case, namely, the photodissociation of $H_2{}^+$, serves as an illustration in Sec. III. Nonlinear field-induced effects are discussed over a range of wavelengths for which dissociation cross sections take important values. Finally, Sec. IV suggests an interpretation of some recent experiments on $H_2{}^+$ (Ref. 10) showing large nonlinear effects in the wings of the dissociation line shapes. Experimental studies of multiphoton processes in H_2, leading both to photoionization and photodissociation, are actively pursued in several groups[10,11] and have been our main motivation. With respect to the pioneer calculation of Chu,[8] the present work is a systematic study of nonlinear intensity dependence of the photodissociation lifetimes, within an efficient and flexible formalism which allows the use of numerical as well as analytical potential surfaces and coupling terms. Relation with similar studies of strong-field photoionization is outlined.

II. THEORY

Let us first recall the usual perturbative expression for the weak-field photodissociation cross sections. We consider a molecule (diatomic in this paper) undergoing direct photodissociation and assume that only two electronic states are involved in the process: a bound initial electronic state *g* and an electronically excited dissociative state *d*. In addition, we neglect any change in the rotation quantum number due to the interaction with the field (J-conserving approximation).

In the zeroth order Born-Oppenheimer approximation, the wave functions for the "bare" molecule (without external field) can be written

$$\Psi_\alpha^{(0)}(r,R)=\psi_\alpha(r,R)\chi_\alpha^{(0)}(R), \quad \alpha=g \text{ or } d \tag{1}$$

i.e., as products of an electronic part ψ_α and a nuclear part $\chi_\alpha^{(0)}$, r and R being the electronic and nuclear radial coordinates, respectively. The $\chi^{(0)}$'s are solutions of the field-free nuclear Schrödinger equations

$$[T_R+V_\alpha(R)-E_{\alpha,v}^{(0)}]\chi_{\alpha,v}^{(0)}(R)=0 , \tag{2}$$

where T_R and V_α ($\alpha=g$ or d) are the nuclear kinetic energy operator and the adiabatic potential energies. For the initial state ($\alpha=g$), $V_\alpha(R)$ has an attractive bound part [see Fig. 1(a)] and $\chi_{g,v}^{(0)}(R)$ is square integrable, whereas for the excited state ($\alpha=d$), $V_d(R)$ is repulsive and $\chi_{d,E}^{(0)}(R)$ is a continuum wave function which is taken to be energy normalized,

$$\langle \chi_{d,E}^{(0)}(R)|\chi_{d,E'}^{(0)}(R)\rangle_R=\delta(E-E') . \tag{3}$$

An external electromagnetic field couples the two states g and d via the interaction $V_{\text{int}}(R)$ which, in the dipolar approximation, is $\mu_{gd}(R)\cdot\mathcal{E}$ with $\mathcal{E}$ the electric field amplitude and $\mu_{gd}(R)$ the electronic transition dipole moment

$$\mu_{gd}(R)=\langle \psi_g(r,R)|\mu(r,R)|\psi_d(r,R)\rangle_r , \tag{4}$$

$\mu(r,R)$ being the dipole moment operator. The total Hamiltonian for the molecule-plus-radiation field is taken in the following as

$$H=H_{\text{BO}}^{(0)}+H_{\text{rad}}+V_{\text{int}} . \tag{5}$$

H_{rad} is the free-radiation field part and $H_{BO}^{(0)}$ is an approximate molecular Hamiltonian having as exact eigenfunctions the Born-Oppenheimer products listed in Eq. (1). The intramolecular coupling (nonadiabatic interactions) independent of the field strength thus irrelevant for our discussion, is omitted. To specify the basis set associated with $H_{\text{BO}}^{(0)}+H_{\text{rad}}$ we need to consider the relevant photon eigenstates. In the usual situation of weak photon fields only the zero-photon state $|\text{vac}\rangle$ and one-photon states $|\mathbf{k},\mathbf{e}\rangle$, where k is the wave number associated with a photon of energy $\hbar kc$ and $\mathbf{e}$ its polarization vector are considered. The eigenstates of $H_{\text{BO}}^{(0)}+H_{\text{rad}}$ involved in the description of photodissociation are then $\psi_g(r,R)\chi_{g,v}^{(0)}(R)|\mathbf{k},\mathbf{e}\rangle$ with energy $E_{g,v}^{(0)}+\hbar kc$ and $\psi_d(r,R)\chi_{d,E}^{(0)}(R)|\text{vac}\rangle$ with energy E.

The photodissociation cross section from the initial $\chi_{g,v}^{(0)}$ to the final $\chi_{d,E}^{(0)}$ state due to the absorption of one photon $(\mathbf{k},\mathbf{e})$ of frequency ω is proportional to[12]

$$\sigma_{gv}(E)\propto|\langle \chi_{g,v}^{(0)}(R);\mathbf{k},\mathbf{e}|T(E)|\chi_{d,E}^{(0)}(R)\rangle|^2 , \tag{6}$$

where $T(E)$ is the transition operator

$$\begin{aligned}T(E)=&V_{\text{int}}+V_{\text{int}}G_0^+(E)V_{\text{int}}\\&+V_{\text{int}}G_0^+(E)V_{\text{int}}G_0^+(E)V_{\text{int}}+\cdots\end{aligned} \tag{7}$$

and $G_0^+(E)$ the resolvent operator: $G_0^+(E)=\lim_{\epsilon\to0}(E-H_{\text{BO}}^{(0)}-H_{\text{rad}}+i\epsilon)^{-1}$. In Eqs. (6) and (7) E corresponds to the total energy which, by energy conservation, is $E=E_{g,v}^{(0)}+\hbar\omega$. The formal expression (6) is mainly used in the so-called first-order Born approximation where only the first term in Eq. (7) is retained leading to

$$\sigma_{gv}(E)=(4\pi^2\omega/c)|\langle \chi_{g,v}^{(0)}(R)|\mu_{gd}(R)|\chi_{d,E}^{(0)}(R)\rangle|^2_{E=E_{g,v}^{(0)}+\hbar\omega} , \tag{8}$$

which is known as the Fermi golden rule expression. A further approximation results from neglecting the (usually) slow dependence of μ_{gd} on R over the spatial extension of $\chi_{g,v}^{(0)}(R)$. This leads to the Condon approximation in which the dissociation cross section is proportional to the square of the overlap integral between the initial and final states and gives a convenient way for the practical calculation of cross sections. It is important to note that the first-order expression (8) is independent of the field intensity $I=(\epsilon_0 c/2)|\mathcal{E}|^2$, since both the first-order dissociation rate and the photon flux are proportional to I. We will see below that the cross section becomes intensity dependent at stronger field strengths due to the nonlinear behavior of the dissociation rate.

Questions which are now addressed are the following.

(i) At which field strengths are the previous first-order perturbation model in breakdown?

(ii) How can we go beyond the golden rule expression [Eq. (8)] for describing photodissociation probabilities in intense radiation fields?

We distinguish below two different ranges of field intensities: at intermediate values, only one photon processes have still to be considered, but beyond the first-order perturbation framework [Fig. 1(b)]. At higher intensities multiphoton processes become important [Fig. 1(c)].

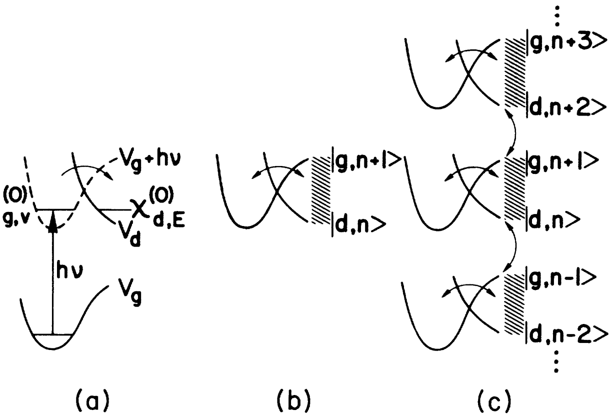

FIG. 1. Schematic representation of the photodissociation process involving a bound (g) and a dissociative (d) electronic state. The arrows represent the radiative couplings. (a) Usual weak-field representation (solid curves). The dashed curve represents the dressed potential curve of the g state. (b) Two-channel representation of the process, adequate for the intermediate-field case (region II of Fig. 2). (c) Multichannel representation for the strong-field case (region III of Fig. 2). Each pair of crossing curves represents one Floquet block, radiatively coupled to the two adjacent ones.

A rough estimation of field strengths inducing noticeable nonlinear effects prior to the introduction of multiphoton processes can be obtained by considering higher-order terms in the Born expansion of the transition operator [Eq. (7)]. The second term $V_{\text{int}} G_0^+(E) V_{\text{int}}$ does not contribute to the dissociation cross section (it rather represents the leading term for the resonant Raman photon scattering from the continuum). The ratio between the matrix elements of the third and the first terms can be given a simple approximate expression,[12]

$$\rho = \frac{\langle \chi_{g,v}^{(0)}; \mathbf{k}, \mathbf{e} | V_{\text{int}} G_0^+ V_{\text{int}} G_0^+ V_{\text{int}} | \chi_{d,E}^{(0)}; \text{vac} \rangle}{\langle \chi_{g,v}^{(0)}; \mathbf{k}, \mathbf{e} | V_{\text{int}} | \chi_{d,E}^{(0)}; \text{vac} \rangle}$$

$$\simeq \frac{\pi^2 k^2}{\hbar c} \sum_e \int d\hat{\mathbf{k}} | \langle \chi_{g,v}^{(0)}; \mathbf{k}, \mathbf{e} | V_{\text{int}} | \chi_{d,E}^{(0)}; \text{vac} \rangle |^2 , \quad (9)$$

where an average is carried out on all polarizations and **k** directions. For typical molecular parameters, taking λ of the order of 1500 Å and $\mu_{gd} \simeq 1$ Dy, we obtain $\rho \approx 10^{-4}$ for an electric field intensity of the order of 10^{10} W/cm^{-2}. The first-order perturbation approximation seems thus very good up to this intensity in this region of wavelength. It has already been shown[5(b),9] that above this limit, the photodissociation probability can not be discussed in terms of unperturbed (diabatic) Franck-Condon factors, based on the usual golden rule approximation.

An alternative and more efficient approach is to treat the total system (molecule and photons) as a whole, which leads to the representation

$$\psi_v(r,R) = \psi_g(r,R) \chi_{g,v}(R) | \mathbf{k}, \mathbf{e} \rangle + \psi_d(r,R) \chi_{d,E}(R) | \text{vac} \rangle , \quad (10)$$

where the R-dependent χ's are now unknown functions. We observe that this gives rise to a mixture of molecular dressed states[13] widely used in the description of molecular radiative collisions.[14,15] Introduction of ψ_v into the Schrödinger equation,

$$H \psi_v = E_v \psi_v , \quad (11)$$

premultiplication by all known functions and integration over the corresponding variables (electronic and field) lead to the well-known close-coupled equations of which the χ's are solutions,

$$[T_R + V_g(R) + \hbar\omega - E_v] \chi_{g,v}(R) + V_{\text{int}}(R) \chi_{d,e}(R) = 0 , \quad (12a)$$

$$[T_R + V_d(R) - E_v] \chi_{d,E}(R) + V_{\text{int}}(R) \chi_{g,v}(R) = 0 . \quad (12b)$$

Note that if the coupling between the molecule and the field is ignored, the equations are decoupled and the χ's are nothing but the vibrational functions $\chi^{(0)}$'s which are used in building the Born-Oppenheimer products [Eq. (1)].

One has therefore the situation of bound states $|g,v\rangle$ of $V_g(R)$ embedded in the continuum of $V_d(R)$; the analog of predissociation.[6] The dressed vibrational levels acquire a field-dependent width in addition to their shift and may be viewed as field-induced Feshbach resonances.

A definition of resonances which can unambiguously be extended to strong-field situations is the one which is associated to complex energy valued Siegert states.[16] These states are quantized solutions of Eqs. (12), regular at the origin ($R=0$), and behaving as purely outgoing waves for large R. This asymptotic behavior can only be achieved for complex values of energy,

$$E = E_r - i(\Gamma/2) , \quad (13)$$

where E_r and Γ ($\Gamma > 0$) are the resonance position and width. This definition is equivalent to the search for complex energy poles of the Green function of the system or those of the scattering matrix.[17] In the case of isolated resonances (a situation which holds for weak fields) they are obtained as solutions of the implicit equation

$$E - (E_{g,v}^{(0)} + \hbar\omega) - F(E) + i\pi | \langle \chi_{g,v}^{(0)} | V_{\text{int}} | \chi_{d,E}^{(0)} \rangle |^2 = 0 , \quad (14)$$

where

$$F(E) = \mathcal{P} \int dE' \frac{| \langle \chi_{g,v}^{(0)} | V_{\text{int}} | \chi_{d,E'}^{(0)} \rangle |^2}{E - E'} \quad (15)$$

is the energy shift, $\mathcal{P}$ indicating Cauchy's principal part integration.

Furthermore, when the implicit energy dependence of Eq. (14) is neglected, the width, given by twice the imaginary part of its solution

$$\Gamma_{g,v} = 2\pi | \langle \chi_{g,v}^{(0)} | V_{\text{int}} | \chi_{d,E}^{(0)} \rangle |^2_{E = E_{g,v}^{(0)} + \hbar\omega} , \quad (16)$$

is proportional to the photodissociation cross section [Eq. (8)] at the same order of matter-field interaction.

Let us finally mention a decoupling approximation[18] of the two coupled equations (12), in which the electronic-plus-field-Hamiltonian is diagonalized, leading to new laser-induced adiabatic electronic states.[3(a),19] They appear as tunneling or *shape* resonances (rather than as *Feshbach* resonances) and their width is calculated via direct integration of the one-dimensional Schrödinger equation with appropriate boundary conditions. This approximation is valid as far as the quasibound levels which are considered, supported by the lower adiabatic potential, are far from the ones supported by the higher adiabatic potential, a situation which occurs for intermediate-field strengths.

As far as the dressed-molecule picture taking into account only zero- and one-photon states is valid, the previous methods appear to be useful tools for investigating the dissociation probability beyond the golden rule limit at several levels of sophistication: large energy dependence of the discrete to continuum coupling, nonlinear effects, overlap between neighboring quasibound states. In strong photon fields, however, the situation is much more complicated due to the occurence of cascades of absorption-emission processes. A set of dressed channels corresponding to different photon numbers has to be defined which leads to the time-dependent Floquet Hamiltonian. Starting from a semiclassical time-dependent Hamiltonian in the dipole approximation for the matter-radiation coupling, a Fourier expansion of the Schrödinger equation leads to a matrix eigenvalue equation for the so-called quasienergy states[20]

$$H_F(R)\chi(R)=E\chi(R) , \tag{17}$$

where H_F is an infinite matrix with elements identified by two indices (α,n), the first one for the electronic states and the second one for the photon states. Its matrix elements have the form

$$(H_F)_{\alpha n,\beta m}=[T_R+V_\alpha(R)+n\hbar\omega]\delta_{\alpha\beta}\delta_{nm} \\ +V_{\rm int}(R)\delta_{n,m=n+1}(1-\delta_{\alpha\beta}) \quad (\alpha=g \text{ or } d) . \tag{18}$$

The resulting close-coupled equations, after integration over field variables, can be given a compact form which is a generalized version of Eqs. (12),

$$[T_R+V_g(R)+(n+1)\hbar\omega-E]\chi_{g,n+1}(R) \\ +V_{\rm int}(R)[\chi_{d,n}(R)+\chi_{d,n+2}(R)]=0 , \tag{19a}$$

$$[T_R+V_d(R)+n\hbar\omega-E]\chi_{d,n}(R) \\ +V_{\rm int}(R)[\chi_{g,n-1}(R)+\chi_{g,n+1}(R)]=0 , \tag{19b}$$

where each electron-field channel function is labeled by a pair of indices [g or d for the electronic part together with the specification of the photon number n; see Fig. 1(c)]. Note that the index v specifying the particular solution of Eqs. (12) has been dropped for the sake of simplicity. In contrast with the field-free situation there is no discrete spectrum on the real energy axis. The complex energy poles of the resolvent operator $(z-H_F)^{-1}$ are related to the positions and widths of the shifted and broadened quasienergy states. More precisely, Feshbach resonances arising in two-channel situations when the photodissociation by moderate fields is pictured as a predissociation are now replaced by the quasienergy states of the Floquet theorem.[21] The photodissociation probability is linked to the transition rates from rovibrational bound states (in the absence of the field) in one electronic state to the dissociation continuum of the other electronic state. As is pointed out by Chu[8] the quasienergy eigenvalues of H_F have an imaginary part which is directly related to photodissociation rates. They are obtained by solving the coupled equations (19) for the multiphoton process, subject to Siegert-type boundary conditions. A well documented technique in this context is the analytic continuation of the Hamiltonian by the complex rotation of the coordinate which will be briefly described in Sec. III. It has already been shown in various situations that this technique allows one to treat the wave function of the quasienergy resonance like that of a bound state with vanishing asymptotic behavior.[22] The number of Floquet blocks to be retained and the way to select them depend on the field strength, the wavelength, and on the accuracy which is looked for. Specific examples are given in Sec. III to illustrate these points.

It is noteworthy to observe that the dressed-channel approach, leading to a set of time-independent close-coupled equations, is also used to describe *ionization* processes in strong laser fields.[23–25] These collisional treatments of laser-induced atomic or molecular processes appear to be most fruitful to go beyond perturbation theory when continua (electronic or nuclear) are involved.

III. APPLICATION TO H_2^+ PHOTODISSOCIATION

The basic features of the theory developed so far are illustrated in the example case of the photodissociation of H_2^+ submitted to electromagnetic interactions with strengths bridging the weak- and strong-field limits. The two electronic states under consideration are the ground $(1s\sigma_g)^1\Sigma_g^+$ and the excited dissociative $(2p\sigma_u)^1\Sigma_u^+$ states. They will be represented by Morse-type potentials,[26]

$$V_\alpha(R)=D_0\{\exp[-2\beta(R-R_e)] \\ -2t_\alpha\exp[-\beta(R-R_e)]\} \quad (\alpha=g \text{ or } d) \tag{20}$$

where t_g and t_d are, respectively, positive and negative in Eq. (20) in order to represent bound or repulsive molecular force fields. As for the transition dipole moment, the Bunkin-Tugov form is taken[26]

$$\mu_{gd}(R)=\mu+\frac{\mu'}{\beta y}\{1-\exp[-\beta y(R-R_e)]\} . \tag{21}$$

Table I lists all the parameters needed in Eqs. (20) and (21) as extracted from Ref. 8. The resulting form for the interaction term is then

$$V_{\rm int}(R)=1.17\times10^{-3}\sqrt{I}\,\mu_{gd}(R)$$

with $V_{\rm int}$ in cm^{-1}, I in W/cm^2, and μ_{gd} in atomic units.

The calculations are performed using a multichannel quantization procedure based on the Siegert asymptotic conditions. When the interfragment coordinate R is rotated in the complex plane $(R\to Re^{i\theta})$ the wave function of a resonant state becomes vanishingly small at large R. Standard techniques used for the calculation of bound states can thus be used for resonances as they satisfy the same asymptotic conditions when analytically continued in the complex R plane. Two independent wave functions are propagated outwards and inwards starting from

TABLE I. Molecular parameters used for the H_2^+ calculations.

Potential	D_0 (cm^{-1})	$\beta(a_0^{-1})$	$R_e(a_0)$	t
$V_g(R)$	22 522.852	0.72	2.0	1.0
$V_d(R)$	22 522.852	0.72	2.0	−1.11
Transition dipole moment		$\mu(ea_0)$	$\mu'(e)$	y
$\mu_{gd}(R)$		1.07	0.396	−0.055

the origin and from large interfragment distance on a complex integration path. The starting amplitudes of these solutions are taken to be zero and a complex coordinate version of the Fox-Goodwin integrator[27] is used. The matching of the functions and of their first derivatives at some intermediate point can only be achieved for complex quantized energies corresponding to the positions and widths of resonances. The dependence of the energy versus the rotation angle θ is (for a wide amplitude of variation for θ) only due to possible inaccuracies in the integration algorithm. In particular there is no counterpart, in this direct calculation, to the so-called θ trajectories associated to variational methods which use square integrable basis set expansions to represent the analytic continuation of resonance wave functions.[8] An advantage of the present method is to allow use of numerical representation of molecular potentials and intramolecular couplings. Analytical forms are adopted here in order to compare our calculations with the variational ones,[8] but the so-called exterior-scaling technique, initially suggested by Simons,[28] allows to use numerical potentials in the internal region: the complex scaling is performed only beyond a certain critical radius, leading to an asymptotically convergent wave function in the external zone.

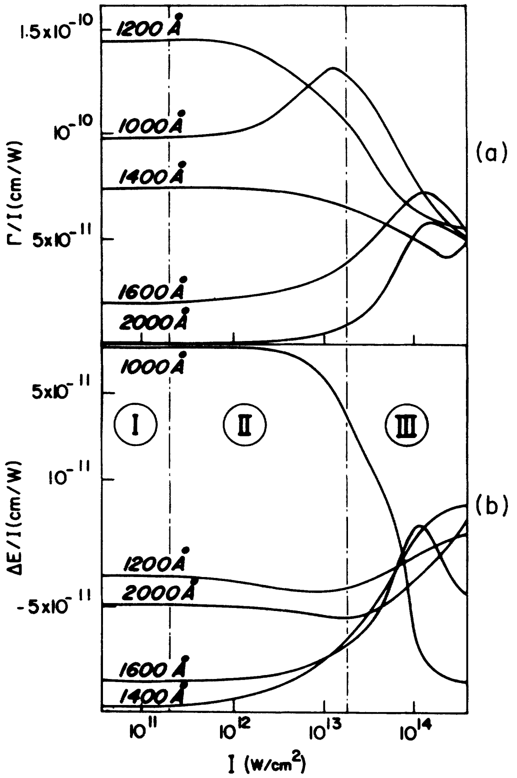

FIG. 2. Reduced ac Stark width (Γ/I) and shift ($\Delta E/I$) of the laser-induced resonance $H_2{}^+$ ($1s\sigma_g, v=0, J=1$) level, as a function of the laser intensity and frequency.

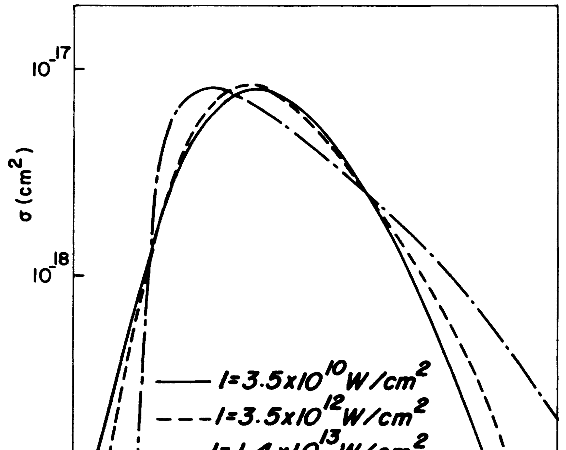

FIG. 3. Line shape for the photodissociation process of the ($v=0, J=1$) level of $H_2{}^+$ ground state, for different laser intensities.

The weak-field regime corresponds to a linear behavior of the linewidth Γ versus the intensity. Such a behavior is also to be expected for the field-induced energy shift ΔE. Figure 2 displays the values obtained for Γ/I and $\Delta E/I$ as a function of the intensity I over a range of wavelengths for which absorption is substantial. Linearity within three figures accuracy is obtained from a calculation including only one Floquet block (two dressed channels) as long as the intensity does not exceed $\approx 10^{11}$ W/cm^2 to $I \simeq 10^{13}$ W/cm^2 (region I in Fig. 2). This corresponds, precisely, to the region where Fermi's golden rule is valid and lowest-order perturbative techniques such as Franck-Condon–type calculations[29] can be successfully carried out. We have also performed a series of calculations to reproduce the photodissociation lineshapes of $H_2{}^+$ from the ($1s\sigma_g v=0, J=1$) and ($1s\sigma_g, v=1, J=1$) levels for a laser wavelength varying from 600 to 2400 Å. The results generated by using a propagation grid of 4000 points and an exterior scaling rotation angle $\theta=0.5$ rad are shown in Figs. 3 and 4. Their convergency against θ and other integration parameters is checked within five to six figures accuracy. For the field strength corresponding to Chu's calculations,[8] the agreement between the two sets of results is very satisfactory. The same type of agreement is observed when comparing to Dunn's[29] first-order perturbation results, the discrepancies in the long-wavelength part reflecting the difference of potentials and dipole moment used, as it has been checked numerically. Some characteristics of the energy shift considered as a function of the laser wavelength can be explained by referring to the photodissociation line shape. For wavelengths larger than the one corresponding to the maximum of the absorption ($\lambda_{\max} \simeq 1150$ Å), the negative contribution to the first-order energy-shift integral [Eq. (15)], calculated at $E=E_{g,v}^{(0)}+\hbar\omega$, prevails over the positive one and ΔE is negative. The reverse situation is valid for wavelengths shorter than $\lambda_{\max}$ (the dissociation continuum pushes down the discrete level). The absolute value decreases as the wavelength deviates from $\lambda_{\max}$. An exception to this behavior is observed for $\lambda=1200$ Å, which is very close to $\lambda_{\max}$. This corresponds to a Franck-Condon map [numerator of Eq. (15)] almost symmetrical with respect

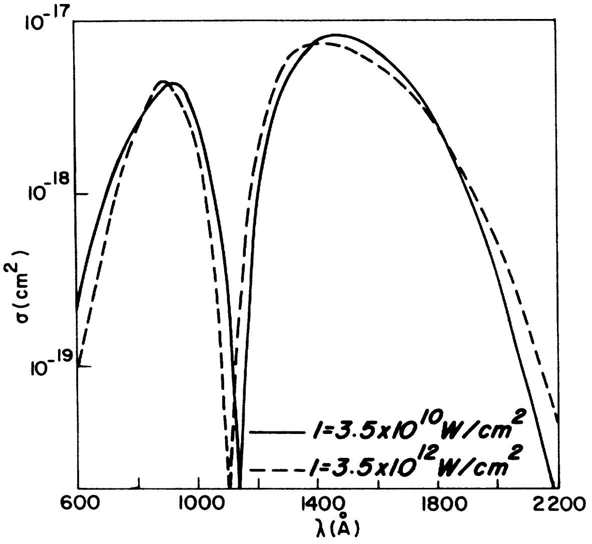

FIG. 4. Line shape for the photodissociation process of the ($v=1, J=1$) level of $H_2{}^+$ ground state, for different laser intensities.

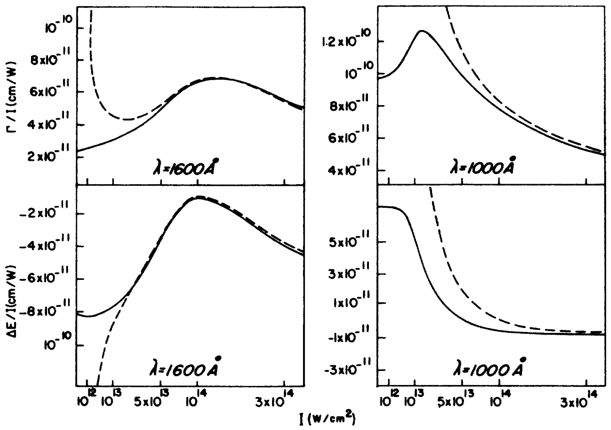

FIG. 5. Comparison between one-adiabatic-channel (dashed curves) and two-diabatic-channel (solid curves) calculations of the ac Stark shift and width of the $H_2{}^+$ ($1s\sigma_g$, $v=0, J=1$) resonance, for two laser wavelengths. For intensities above 10^{14} W/cm^2 converged calculations would require more than one Floquet block.

to $E_{g,v}^{(0)}$ leading to a near cancellation between the positive and negative contributions to the integral.

The nonlinear behavior of Γ and ΔE begins for intensities of about 10^{11} W/cm^2, as is clear from Fig. 2. There is an intermediate-field region, roughly extending from $I \approx 10^{11}$ W/cm^2 to $I \simeq 10^{13}$ W/cm^2 (region II in Fig. 2), where convergency is achieved within a single-photon description (one Floquet block), i.e., by two-channel nonperturbative calculations which already contain off-the-energy-shell contributions as well as neighboring resonance overlaps. Note that this intermediate field regime corresponds to electronic Rabi frequencies $\omega = \hbar^{-1} V_{\text{int}}$ of the same order of magnitude as the lowest vibrational frequencies of $H_2{}^+$($\omega_v \approx 2000$ cm^{-1}). Several points may be noticed.

(i) The range of validity of Fermi's golden rule is enlarged at longer wavelengths (i.e., smaller values of k), in agreement with Eq. (9).

(ii) The ratios Γ/I depart largely from constant values as the field strength increases. They are either increasing or decreasing depending on the wavelength. An interpretation of this behavior is presented in the Appendix. The nonlinearity is discussed both in terms of the energy dependence of the interstate Franck-Condon couplings including off-the-energy-shell effects on Γ's and the overlapping between neighboring resonances. Another approach is based on the decoupling approximation of the adiabatic electronic field channels which leads to the interpretation of enhanced values for Γ's as compared to the golden rule formula. For intermediate fields, one adiabatic-channel calculation gives nonlinear effects of the same order of magnitude as two diabatic-channel calculations, as it is shown on Fig. 5 for two wavelengths. Better agreement is reached at large wavelengths for which the adiabatic decoupling approximation is more valid (crossing beyond the right turning point, leading to a smooth upper adiabatic curve).

(ii) The ratios $\Delta E/I$ also show large changes as compared to their constant weak-field values. Their interpretation is closely related to the modification of the line shape which is slightly blue shifted in the intermediate field region II, such that the maximum of the absorption is now closer to $\lambda = 1000$ Å than to $\lambda = 1200$ Å corresponding to the maximum in the weak-field regime. This results in $|\Delta E|/I$ decreasing for $\lambda = 1000$ Å and increasing for $\lambda = 1200$ Å. For all other wavelengths $E_{g,v}^{(0)}$ is facing a flattening Franck-Condon map which, according to (Eq. (15), yields a decreasing behavior of $|\Delta E|/I$.

At higher-field intensities ($I > 10^{13}$ W/cm^2), several Floquet blocks must be taken into account in the multichannel quantization procedure, in order to reach convergency [see Fig. 1(c)]. They describe all the relevant processes involving different photon numbers, as long as one restricts the electronic states of $H_2{}^+$ to the two first ones (see the discussion below), and are simulataneously and self-consistently introduced in Eqs. (19). A careful optimization study is carried out for the determination of the most efficient blocks to fasten convergency. At some wavelengths, in particular $\lambda = 1000$ Å, we find that the inclusion of an upper Floquet block, which introduces two closed channels for the corresponding energy, has a larger effect than the lower Floquet block which adds two *open* channels. For field strengths up to 10^{14} W/cm^2 four Floquet blocks yield converged results within three to four figure accuracy for Γ and ΔE. The effect of these additional Floquet blocks is depicted on Fig. 6 for two wavelengths (1000 and 1600 Å) and calls for two comments.

(i) Multiblock effects induce larger changes in the shifts than in the widths [compare Figs. 6(a) and 6(b)], in accordance with the larger sensitivity of the shift to nonlinear effects already noted in the intermediate regime.

(ii) Shorter wavelengths, i.e., more energetic photons, increase the energy gaps between successive Floquet blocks involved in Eq. (21) and Fig. 1(c), with the consequence that only for larger field strengths the additional

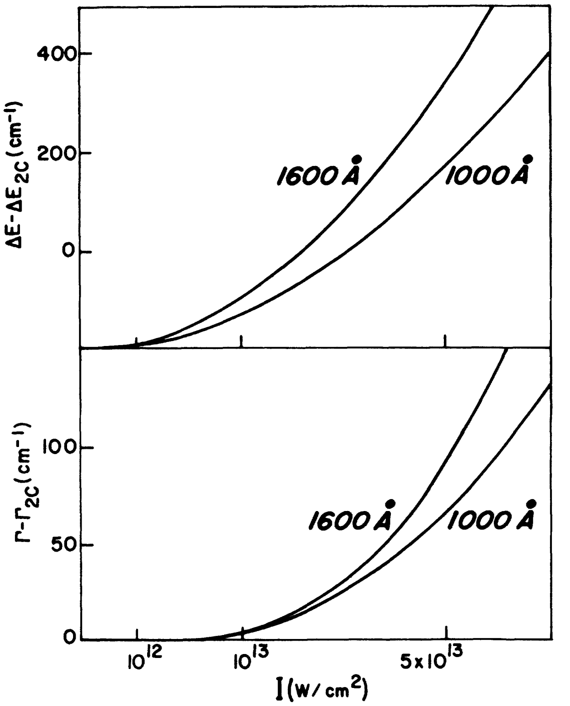

FIG. 6. Multiblock effects on the ac Stark width and shift at strong laser intensities. Γ_{2c} and ΔE_{2c} correspond to two-channel calculations, Γ and ΔE to fully converged calculations (including up to five Floquet blocks), for the case of the $H_2{}^+$ $(1s\sigma_g, v=0, J=1)$ level.

blocks induce non-negligible effects.

A further visualization of strong-field effects is obtained by comparing line shapes from a given $H_2{}^+$ level for increasing field strength. Figures 3 and 4 display a few of them, corresponding to the $(1s\sigma_g, v=0, J=1)$ and $(1s\sigma_g, v=1, J=1)$ levels. The bulk of the cross section is shifted towards shorter wavelengths at higher fields, as already noted by Chu.[8] At very large intensities ($I > 10^{14}$ W/cm^2), the line shape tends to flatten as it can be deduced from the almost common value of Γ/I obtained for different wavelengths in Fig. 2. Actually the accurate localization of the resonances within a multichannel quantization procedure involving more and more Floquet blocks becomes a challenging numerical problem. Another point to be noted is that higher excited electronic states of $H_2{}^+$, in particular the $(2s\sigma_g)$ and $(3d\sigma_g)^2\Sigma_g^+$ states which may be reached by one-photon absorption (with $\lambda < 1200$ Å) from the $(2p\sigma_u)^2\Sigma_u^+$ state, could play a role in the multiphoton processes at strong intensities. The corresponding dipole moments are smaller than for the $(2p\sigma_u)\leftarrow(1s\sigma_g)$ transition but not negligible.[30] Inclusion of these new channels in our closed-coupled system is straightforward but will of course increase the computational effort. Another possible extension of the present calculations is to take into account the change of molecular rotation quantum number due to the radiative interaction.[15] These effects will be discussed in a further publication in relation with a systematic experimental study.

As a conclusion at the present stage of the calculations, we note that the behavior of the dissociation probability with increasing field intensity is more diversified than in the case of atomic photoionization, where the ionization cross section generally saturates[25,31] (except for local enhancement due to the proximity of intermediate resonances). This results from the Franck-Condon map which leads to an additional complexity in photodissociation and molecular photoionization, as compared to the atomic case.

IV. DISCUSSION OF PRELIMINARY EXPERIMENTAL DATA

The photodissociation process of $H_2{}^+$ in a strong laser field has recently been observed in a multiphoton experiment on the hydrogen molecule:[10] $H_2{}^+$ ground-state ions are formed by absorption of five photons, enhanced by a four-photon intermediate resonance on a given level of the $E\,{}^1\Sigma_g^+$ Rydberg state of H_2 (see Fig. 7). Absorption of one more photon (at least) leads to dissociation along the $(2p\sigma_u)$ repulsive state.

Time-of-flight measurements yield the ratio of H^+ and $H_2{}^+$ ions produced, from which the photodissociation cross sections of $H_2{}^+$ in the first vibrational levels of the ground state are deduced (other sources of H^+ ions, e.g., two-photon ionization of H atoms resulting from the dissociation of the neutral molecule, are ruled out from the analysis of simultaneous measurements of the photoelectron spectrum). The values obtained for the laser intensity $I \approx 10^{11}$ W/cm^2 disagree with the theoretical ones calculated using the golden rule approximation.[29]

The preliminary measurements (a by-product of an ex-

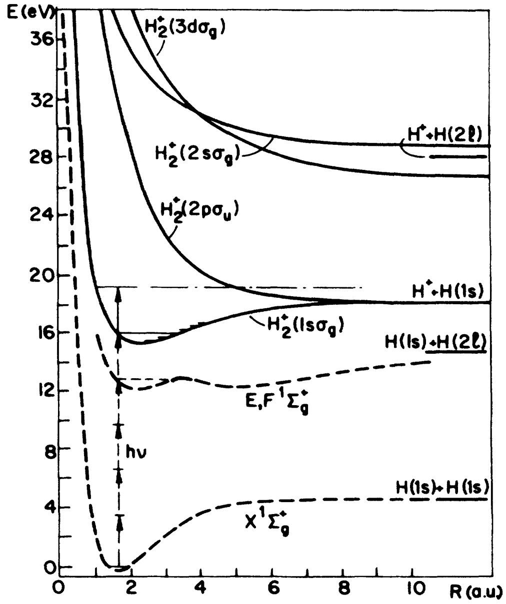

FIG. 7. Schematic energy diagram for H_2 (dashed lines) and $H_2{}^+$ (solid lines) potential curves involved in the multiphoton experiment of Ref. 10. Also are shown the two first ${}^2\Sigma_g{}^+$ excited states of $H_2{}^+$, not included in the present calculations.

periment essentially devoted to resonant multiphoton ionization studies) correspond to the far wings (λ > 3800 Å) of the absorption bands, way out of the wavelength scale of Figs. 3 or 4. In this energy range the photodissociation process is so weak that the absolute cross sections are extremely difficult to measure, and also to calculate precisely due to uncertainties in the molecular potentials and dipole moments at large distances. We have performed a test calculation of the intensity dependence of the dissociation width of the H_2^+ ($v=3$, $J=1$) level, for the experimental wavelength λ=3804 Å. For simplicity we have used the analytical molecular data presented in Table I, with up to three Floquet blocks in the coupled-equation system. Figure 8 shows that the nonlinear behavior of the dissociation width begins in the intensity range of the experiment, and could explain the discrepancy between the experimental values of the cross section and the values calculated within the golden rule approximation. This indication has to be confirmed in more favorable experimental conditions. A two-color experiment on H_2 is presently in progress using more energetic photons (shorter wavelength) for the H_2^+ dissociation step.[32] A systematic experimental study of the strong-field photodissociation of H_2^+ will then be possible and will allow a significant comparison with theoretical results.

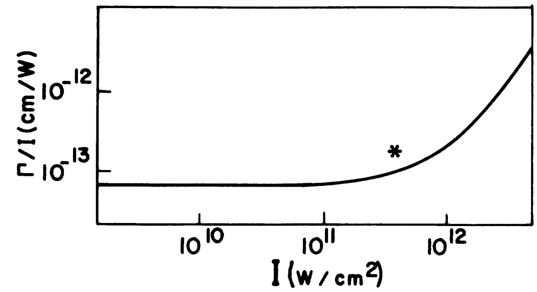

FIG. 8. Variation of the reduced width Γ/I of the H_2^+ ($1s\sigma_g$, $v=3, J=1$) level with the laser intensity for the wavelength λ=3804 Å used in Ref. 10. The star indicates the experimental value.

APPENDIX

This appendix is devoted to a detailed discussion of field-induced nonlinearities affecting resonance widths in the intermediate-intensity region II of Fig. 2. The argument is based on configuration interaction between neighboring resonances and the adiabatic-decoupling approximation valid for intermediate field strengths and for some wavelengths.

The starting point is the generalization of Fano's implicit equation [Eq. (14)] in a case where only two field-free vibrational levels $v_1=0$ and $v_2=1$ of the ($1s\sigma_g$) state are retained. Their interference leads to an implicit matrix equation to be solved with a complex energy as unknown,

$$\det\begin{vmatrix} E-E_{v_1}-F_{v_1v_1}(E)+i\pi\Gamma_{v_1v_1}(E) & -F_{v_1v_2}(E)+i\pi\Gamma_{v_1v_2}(E) \\ -F_{v_2v_1}(E)+i\pi\Gamma_{v_2v_1}(E) & E-E_{v_2}-F_{v_2v_2}(E)+i\pi\Gamma_{v_2v_2}(E) \end{vmatrix}=0 . \tag{A1}$$

The definitions for F and Γ's are the generalization of Eqs. 15 and 16, respectively,

$$F_{v_1v_2}(E)=\mathcal{P}\int dE'\frac{\bar{V}_{E'}^{v_1}V_{E'}^{v_2}}{E-E'} , \tag{A2}$$

$$\Gamma_{v_1v_2}(E)=\bar{V}_E^{v_1}V_E^{v_2} , \tag{A3}$$

with V_E^v a notation for $\langle\chi_{g,v}^{(0)}|V_{\text{int}}|\chi_{d,E}^{(0)}\rangle$ and the overbar designating the complex conjugate.

For λ=1200 and 1400 Å E_{v_1} lies in a region very close to the maximum of the $v_1=0$ absorption line shape which also corresponds to the minimum of the $v_2=1$ line shape. V_E^0 is large and V_E^1 is approximately zero for $E=E_{v_1}$ and their energy dependences are symmetrical with respect to E_{v_1}. The nondiagonal terms of Eq. (A1) can thus be neglected and the nonlinear behavior of Γ/I is to be discussed only in terms of the energy dependence of V_E^0 through the first element of the matrix displayed in Eq. (A1), which is nothing but the implicit equation (14). The lowest-order imaginary part of this equation has already been calculated in Eq. (16) and gives the linear contribution as a function of I. A second-order approximation proceeds by the evaluation of $|V_E^0|^2$ at an energy $E=E_0+\Delta E$; ΔE being the energy shift resulting from the lowest-order calculation. If E_0 lies on the left (right) side of the maximum of the $v=0$ absorption line shape ΔE is negative (positive) such that the lowest-order energy is now pushed down (up) and the absorption cross section decreases as is clear from Fig. 2. An additional second-order effect is obtained when the iterative calculation of $F_{00}(E)$ is performed using the first-order complex energy of the resonance. This gives rise to a negative imaginary part,

$$-\mathcal{P}\int dE'\frac{|V_{E'}^0|^2\Gamma_{00}(E_0)}{(E_0+\Delta E)^2\pi^2\Gamma_{00}^2(E_0)} ,$$

which also contributes to the width. The overall result is a decrease of Γ/I as the intensity I increases, at least in this intermediate regime II, for these wavelengths. Such a behavior is in conformity with the so-called resonance narrowing discussed by Mies and Krauss.[33]

For λ ≥ 1600 Å, E_{v_1} lies in the wing of the absorption line shape where $|V_E^0|$ is of the same order of magnitude as $|V_E^1|$. In addition there is no symmetrical behavior of V_E^0 and V_E^1 with respect to $E=E_{v_1}$. The nondiagonal terms of Eq. (A1) can not be neglected and the nonlinear behavior of Γ results both from the energy dependence of V_E^0 and V_E^1 and the neighboring resonance overlap and the preceding discussion in terms of Eq. (14) alone is no more valid. But, as the diabatic dressed curves cross each other at large energies (several thousands of wave numbers above $v_1=0$) and on the right of the classical turning point of $v_1=0$ (analogue to a c^+ predissociation case) the decoupling approximation in an adiabatic (avoided crossing) description of electronic field channels becomes reasonably valid as I increases. This results from the fact that the first tunneling resonances supported by the lower adiabatic channel are far from the Feshbach resonances of the higher adiabatic potential. As the intensity increases the shape of the tunnel is modified: its length and height are decreased leading to an increasing nonlinear behavior of Γ/I. It is clear that for field strengths above some critical value the tunneling resonance will be a real shape resonance located above the barrier, with a very large width which will not reflect the linear behavior resulting from the smallness of the Franck-Condon factor times a large coupling term $|V_{\text{int}}|^2$.

Finally, $\lambda=1000$ Å corresponds to a situation where V_E^0 and V_E^1 are not symmetrical with respect to E_0, they have both important amplitudes as the dressed channels cross on the left of the equilibrium distance resulting into $v_1=0$ and $v_2=1$ states well embedded in the continuum. We are, as previously, facing a situation of resonance overlapping, with a questionable validity of the adiabatic decoupling approximation in this analogue of a c^- case of predissociation. The preceding interpretation cannot be referred to, but we just observe an increasing nonlinear behavior of Γ/I as previously. The observed blue shift of the line shapes when going from weak- to strong-field regimes (Figs. 3 and 4) is just a consequence of the variation of the resonance widths discussed in this appendix.

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