Laser-induced resonant structures in a close-coupling calculation of two-frequency multiphoton dissociation of HD$^+$

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A time-independent close-coupling calculation of multiphoton dissociation of HD$^+$ from the ground vibrational level in two fields, each of intensity 10^{12} W/cm^2, and frequencies below the dissociation threshold, is presented. The lower frequency ω_1 is varied around the difference between the energies of the Stark shifted $v=6$ and $v=0$ levels, while the higher frequency ω_2 is varied by about 2000 cm^{-1} up to the dissociation threshold of the $v=0$ level. The dissociation linewidth of the initial $v=0$ level as a function of ω_1 is a Lorentzian (as expected for a simple resonant two photon dissociation process) whose height, position, and width all depend upon the value of ω_2. With respect to ω_2 this linewidth of the initial $v=0$ level exhibits a series of asymmetric peaks. The position of each of these peaks shifts considerably when ω_1 is changed. The energy of the intermediate resonance in the closed channel corresponding to the absorption of a single ω_1 photon strongly depends on the second frequency, ω_2. The peaks against ω_2 occur whenever this resonance, with a dominant $v=6$ character, coincides in energy with the Stark shifted $v=0$ level in the initial closed channel. [S1050-2947(99)01206-8]

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I. INTRODUCTION

Rapid theoretical and experimental progress in the study of the interaction of small molecules with intense laser fields [1] in the last few years has revealed many interesting, and sometimes surprising, effects which are directly related to the presence of the degrees of freedom of nuclear motion. The distortion of the electronic charge cloud by strong field-molecule interaction causes modifications of the potential surfaces on which the nuclei move and the nuclear motions, in turn, cause couplings between the modified electronic states. Thus, theoretical treatment of multiphoton dissociation (MPD) of these simple molecules requires consideration of nuclear motion on these coupled field-dressed potential surfaces.

From the beginning of such studies, the simplest one-electron diatomic molecule H$_2^+$ and, to a lesser extent, its isotopic analogue, HD$^+$, have played a key part in MPD studies due to their sparse distribution of excited electronic states and well known electronic structure. In fact, for these systems, in the intensity and frequency ranges for which theoretical and experimental work have been done, only the two lowest lying electronic states have been considered for understanding the dynamics. Much of the early advances in the theory of interactions of simple molecules like H$_2^+$ with intense laser fields has been summarized by Bandrauk *et al.* in their 1993 review [2]. Phenomena such as above-threshold multiphoton dissociation (ATMPD), and concepts like laser induced avoided crossings needed to understand such phenomena were also discussed there in a comprehensive way.

The study of HD$^+$ is of particular interest, because, as discussed later, this system, unlike its isoelectronic counterpart H$_2^+$, goes to distinguishable atomic states at large internuclear separation, with the electron either on the H or the D nucleus [3]. This also gives rise to radiative couplings at large internuclear separation very different from those for H$_2^+$. The displacement of the center of mass from the geometrical center gives rise to diagonal matrix elements of the dipole moment operator in both states, allowing radiative transitions within the same electronic state and thus raising the possibility of intermediate vibrational resonances in MPD of HD$^+$, which is not possible in its homonuclear isotopic counterpart. The enhancements in the two-photon dissociation (TPD) probability in two-frequency fields due to these intermediate resonances have been earlier investigated within the framework of a resolvent operator approach [4], which essentially depends on defining an effective Hamiltonian for the field-molecule system. The whole set of unperturbed eigenstates of this system was divided into two complementary spaces. The first space consisted of a few essential vibrotational levels, connected resonantly, and described by the projection operator P, and the second space containing all other eigenstates, was described by the projection operator $Q = 1 - P$. The Q space modifies the coupling matrix elements between the levels in the P space and their energies. These modified quantities were used to define the effective Hamiltonian in the P space only, whose equations of motion are solved explicitly. The modifications are generally calculated to the lowest nonvanishing order of perturbation in both the real and the imaginary parts of the matrix elements, though in principle their evaluation can be extended to higher orders [5].

This method of resonant MPD calculation is only applicable up to a certain value of the intensity, depending on the frequency and the coupling matrix elements. Above a certain range of intensity, isolation of a particular set of levels of an intrinsically multilevel system as the essential ones on the basis of a single criterion may become unacceptable. Complex multiphoton interactions involving many absorptions and stimulated emissions between any number of levels,

even those not included within the set of essential states, can take place. Also, backflow to the discrete levels from the continuum may occur. What is more, such transitions might sometimes occur also through highly off-resonant counter-rotating terms. For high enough intensities such interactions should be treated on the same footing as those between the resonant levels. Also, the so-called pole approximation, which is an important step in the essential states approach, may be questionable. In such situations the resolvent operator method for treating MPD is inappropriate. It was earlier estimated that the above-mentioned effects would start to be significant between 10^{11} and 10^{12} W/cm^2 for vibrationally resonant TPD of HD$^+$.

At such intensities, generally the radiative couplings are treated on the same footing as the field-free internuclear potentials and the solution of the Schrödinger equation for the nuclear motion for the field+molecule stationary Hamiltonian is sought on the strongly interacting potential curves. This is the close-coupling (CC) approach, and as many electronic Floquet basis states (with different number of photons) as required by the problem can be incorporated [6]. A complete description of the CC formalism and methodology is given in [2]. For this time-independent CC approach to be valid, the intensities should not vary significantly on the time scale of the fragmentation process, and there should be a sufficiently large number of field cycles within the rise time of the pulse which, in turn, should occupy a length of time substantially less than the time for which the intensity remains essentially constant. Based on these criteria, the method should not be used for any realistic estimate of the dynamical characteristic of the system for laser peak intensities exceeding 10^{14} W/cm^2 for HD$^+$. Indeed, within this intensity range the CC formulation has been applied to the ATMPD of H$_2^+$ [6,7] and very recently, of HD$^+$ [8].

In the present work we apply the CC formulation to two-frequency resonant MPD of the simplest heteronuclear molecular ion HD$^+$ from the ground vibrational level, when both frequencies are below the dissociation threshold. Our aim is to investigate the resonance structures in the dissociation rates of this system arising due to the presence of the dipole allowed vibrational transitions in the ground electronic state as a function of the frequencies. We shall interpret the structures as arising from changes in position and character of the laser induced resonances which are the eigenstates of the molecule dressed by two fields and described by the adiabatic Hamiltonian. This phenomenon is closely related to the ''laser induced continuum structure,'' or LICS for short, which was extensively investigated in the late seventies and throughout the eighties, mostly in the context of ionization of atoms in strong multifrequency fields [9]. More recently, however, extensive calculations have explored the possibility of gaining control over photodissociation branching ratios of Na$_2$ in two different electronic states by frequency tuning [10]. This was achieved through the change of relative contributions of two different interfering routes to photodissociation in two-frequency fields by such tuning. One of the lasers is used to excite laser induced vibrational rotational structures in the dissociative continuum created by the other laser. Basically this is photodissociation in the presence of stimulated resonance Raman process. The theory of such processes for a weak photodissociating and

strong stimulating Stokes field was formulated and the interpretation was given in terms of dressed states earlier by Bandrauk, Turcotte, and Giroux [11]. Up to now, however, for atoms as well as for molecules, theoretical treatment of such structures have mostly relied upon consideration of the excitation of a specific set of resonances which are mixed with the continuum by a second field, thus creating a new set of laser induced resonant levels. This approach is adequate for the system at the specified intensities as it is for non-Rydberg states of atom, but it is not very clear whether laser induced continuum structure due to vibrational rotational resonances in molecules could be realistically modeled in this way at higher intensities, particularly when a number of intermediate resonances may be involved. The CC method allows us to obtain the laser induced structures in the total dissociation rate due to the resonances for higher intensities and for any combination of frequencies without the need of any further approximations. In particular, all the bound and free vibrational levels of all electronic states are treated on equal footing and no particular set of levels is identified as the ''essential'' set. The counterrotating interaction terms are allowed to influence the dynamics, and the coupling between the continua and bound levels are not merely taken to be causing an irreversible decay, but are treated to all orders.

In the next section we give a brief formulation of the two-frequency CC problem and indicate how interesting information and physical understanding can be obtained from the solutions. Finally, we present the results that have been obtained with a small basis set at not too high intensities. Nevertheless, these results clarify some fundamental aspects of the very interesting behavior that may be exhibited by such systems.

II. CALCULATIONS

The total photodissociation linewidth from the ground level ($v=0$) of HD$^+$ in a two frequency field has been calculated as a function of the two frequencies ω_1 and ω_2. ω_1 is so chosen that the energy of this photon approximates the energy of a vibrationally excited (in this case the $v=6$ level) Stark shifted level with respect to the Stark shifted ground level, $v=0$. Of course we do not know these Stark shifts *a priori*. As we shall demonstrate, the assignment of the laser induced resonances to particular Stark shifted levels should be justified first and then these shifts would emerge in a natural way from the calculations along with the dissociation rates. In our case, the shifts being rather weak function of the frequencies, the resonances can be accurately located for any frequency, after a couple of iterative steps. ω_2 is varied over a wide range up to the dissociation threshold. We assume that all the molecules are aligned in the direction of field polarization by rapid rotational pumping and the emitted photofragments are all along this direction. This allows us to neglect the rotational part of the wave function and make a purely radial expansion of the nuclear wave functions. This approximation has been justified by more elaborate calculations for higher intensities [12], but this has been the usual approximation made in CC multiphoton absorptions of the simplest molecule H$_2^+$ over the whole range of intensities [7], though rotational effects were included in strong-field time-independent calculations of two step photodissociation

of Li_2 [13] and ATD of H_2^+ and HD^+ [8].

In HD^+, the transition moment between the two lowest electronic eigenstates (designated as GS and ES, which are linear combinations of the states designated as $1s\sigma_g$ and $2p\sigma_u$ in the absence of the symmetry breaking operator) vanishes in the asymptotic limit. This molecule has the same electronic structure as H_2^+, and in H_2^+ the transition moment diverges as $R/2$, at large internuclear separations R [14]. The two lowest electronic states are asymptotically degenerate in H_2^+. In HD^+, due to the mass difference between the nuclei, the symmetry is broken and the degeneracy of the electronic eigenstates is removed by nonadiabatic interactions arising from nuclear motion which, at large R, strongly couples the $1s\sigma_g$ and $2p\sigma_u$ Born-Oppenheimer states. The simple Born-Oppenheimer Hamiltonian appropriate for H_2^+ can be modified by making a unitary transformation which eliminates the symmetry breaking term in the kinetic energy [15] to first order in the inverse of the nuclear mass. To that order the new field-free molecular electronic Hamiltonian has no term involving derivatives with respect to R. But this transformation introduces new terms in potential energy and transforms the potentials. The symmetry of the potential is broken and new eigenstates GS and ES are defined which are linear combinations of the Born-Oppenheimer orbitals [3]. These are the field free solutions for the electronic wave function to first order in inverse nuclear mass at all R and their use entails only the neglect of higher order nonadiabatic effects [15]. Asymptotically, they go to the atomic states on D and H, respectively, giving the correct dissociation limit. The transition dipole moment between these two states vanish at large R and correct electronic density functions near dissociation are obtained. However, the diagonal matrix elements of the dipole moment operator in the new basis, the permanent dipole moments in the ES and GS field-free states, diverge as $R/3$ and $-2R/3$, respectively. Thus again in this new basis, after the elimination of the derivative with respect to R from the Hamiltonian, it is not possible to define appropriate field free states for a scattering calculation with proper boundary conditions.

In our earlier effective Hamiltonian approach, this divergence was avoided by using the velocity gauge form of the radiation matter interaction. This was also the approach of other authors interested in the CC studies of ATMPD of H_2^+ in its early stages. Unitary gauge transformations in such problems has been discussed in detail in [14]. Though it is well known that the fundamental quantum mechanical equations are gauge invariant [16], in practical problems the two gauges can give widely different results, particularly in two-state calculations. This is an old problem, addressed by Lamb in as early as 1952 [17]. Later, Lamb *et al.* pointed out that though in some cases the two gauges give identical results when the same set of eigenstates is used, there are situations where the completeness argument of intermediate states is not sufficient to ensure gauge invariance in a particular calculation [18]. In such a case, using the eigenstates of the unperturbed Hamiltonian with a velocity gauge does not give the correct answer, resulting in a discrepancy with experiment. This is because many highly off-resonant virtual transitions can become very important. More recently, a direct claim of the superiority of the length gauge form of the interaction has also been made in the context of the two-state

CC studies. Using a manifestly gauge invariant calculation, with a large enough electronic basis, the converged dressed potential curves [19] were found to give excellent agreement with the two-state dressed curves obtained from the length gauge form, but not with the two-state velocity gauge results [1]. It is now agreed that the length gauge representation is better for two-state calculations. This implies that earlier calculations of the MPD width of H_2^+ in velocity gauge (as in [6]) do not give correct results. In fact, it has been shown that the shifts and widths of the ground state are less by several orders of magnitude when the ATD calculations are done in the more appropriate length gauge [8].

The nonstandard diverging behavior in the length gauge can be changed by judicious truncation of the interaction. We have included an exponentially decaying cutoff function in the linearly diverging dipole matrix elements beyond $R = R_{cut}$. The value of R_{cut} was so adjusted as to have no effect on the total linewidth. As in our earlier work [8], the value of 20 a.u. for R_{cut} and 0.5 for the exponent in the decay function was found to be satisfactory when the integration of the CC equations was continued up to 30 or 40 a.u. A similar method was also used in [20]. Mies [21] also found that the truncation radius, after a certain value, does not have any effect on the total width or shift of any laser induced resonance, but the branching ratios to various photon number channels oscillate a bit. In our earlier work on above-threshold dissociation of HD^+ using full vibrational-rotational wave function, we also found that the above mentioned truncation radius led to the converged total rate values [8].

In this work, we do not consider the branching ratios to various Floquet channels corresponding to different numbers of absorbed photons and different photofragments. Reliable estimate of these ratios would require inclusion of a much larger number of Floquet (i.e., photon number) channels. Instead we have worked with a minimal Floquet basis, which, however, brings out the essential features of the nature of variation of the total (i.e., summed over channels) dissociation rate with the frequencies and helps us to understand how the intermediate resonances are determined by these frequencies. In this calculation we have included eight channels, which includes, apart from the initial one without absorption of a photon, both the GS and ES states with a single photon of any one kind absorbed, and with a single photon of each kind absorbed. These channels we felt to be the most important ones for capturing the main features of the frequency dependence of the dissociation process. A channel with absorption and emission of photons was included rather arbitrarily.

Henceforth during discussion, each channel will be labeled by the number of photons absorbed, i.e., by the notation (n_1, n_2) and either GS or ES depending on whether the electronic state involved is the ground bonding state or the upper antibonding one. The index for the electronic state may be omitted when there is no possibility of confusion. Such labels, of course, relate to the diabatic or the molecule+field state without the field-molecule interaction. The interaction terms cause a mixing of these diabatic states.

Thus the total wave function at a fixed total energy E can be expanded in a basis of these diabatic or bare molecule+field channel states $|d\rangle$

$$\Psi(E) = \sum_d |d\rangle F_d(R). \qquad (1)$$

Since we are neglecting molecular rotations, R is simply the scalar internuclear distance, and

$$|d\rangle = |\Lambda, n_1, n_2\rangle = \Phi_\Lambda(r,R)|N_1 - n_1, N_2 - n_2\rangle. \qquad (2)$$

Here Λ denotes the index of the electronic state whose wavefunction is $\Phi_\Lambda(r,R)$, r being the electronic coordinate, and n_1 and n_2 the number of photons of frequencies ω_1 and ω_2 absorbed whose initial numbers are N_1 and N_2, respectively. Thus here $|N_1 - n_1, N_2 - n_2\rangle$ is the photon number state with

$N_1 - n_1$ and $N_2 - n_2$ numbers of photons of frequency ω_1 and ω_2 respectively present. $F_d(R)$ are the components of the wave function $\mathbf{F}$ of radial nuclear motion in the channel states $\langle d|$.

The total Hamiltonian in the length gauge can be written as

$$H = T_R + H^0 + V_{\text{rad}}^L, \qquad (3)$$

where T_R is the nuclear kinetic energy operator and V_{rad}^L is the radiative interaction operator in the length gauge and

$$H^0|d\rangle = W_d^0(R)|d\rangle, \qquad (4)$$

$$W_d^0(R) = V_\Lambda(R) - n_1\hbar\omega_1 - n_2\hbar\omega_2 \xrightarrow[R\to\infty]{} E_\Lambda - n_1\hbar\omega_1 - n_2\hbar\omega_2. \qquad (5)$$

W_d^0 are the eigenvalues of the channel states with the origin shifted by the initial energy of the field, i.e., by $N_1\hbar\omega_1 + N_2\hbar\omega_2$. E_Λ is the asymptotic energy of the electronic state Λ and the observable asymptotic fragment kinetic energy is given by

$$\varepsilon_d = E - E_\Lambda + n_1\hbar\omega_1 + n_2\hbar\omega_2. \qquad (6)$$

For $\varepsilon_d \leq 0$ the channel d is closed and for $\varepsilon_d > 0$ it is open. Since the solution does not depend on the origin of the energy scale, all the energies have been measured with respect to $N_1\hbar\omega_1 + N_2\hbar\omega_2$, i.e., the initial field energy, and E is the total energy of the system measured from this origin.

The matrix form of the coupled equations for the wave function of the radial nuclear motion (of reduced mass μ) at a total energy E is given by

$$[\partial^2/\partial R^2 + 2\mu/\hbar^2(E - U)]F = 0, \qquad (7)$$

where

$$U_{dd'}(R) = W_d^0(R)\delta_{dd'} + V_{\Lambda\Lambda'}(R)\delta_{n_1',n_1\pm1}\delta_{n_2',n_2}$$
$$+ V_{\Lambda\Lambda'}(R)\delta_{n_1',n_1}\delta_{n_2',n_2\pm1}. \qquad (8)$$

Here $V_{\Lambda\Lambda'}(R)$ is the radial matrix element of the interaction operator between the electronic states Λ and Λ' in the dipole approximation. The form of $V_{\Lambda\Lambda'}(R)$ as a function of intensity is as given in our earlier work [7], but without the geometrical factor arising out of rotations.

The components of the matrix of the solution $F_d(E,R)$ of Eq. (7) can give us the required information when the solution is calculated over a large number of total energies. Let $F_{c,o}(E,R)$ be the component of the solution in the closed channel c, corresponding to the boundary condition of asymptotic outgoing wave components in all open channels and an incoming wave in the open channel labeled as o. Now, a wave packet representing any bound state in any diabatic closed channel becomes nonstationary in the presence of the radiation fields. Such a nonstationary wave packet can be expressed as a linear superposition of the time-

independent solutions of Eq. (7), i.e., different eigenstates of the total Hamiltonian H. Thus it acquires a finite width in energy. The extent of the spread of the initial wave packet over energy is directly related to the transition rate [14]. For a particular value of total energy the time independent differential probability $P_{o,ic}$ for any outgoing wave state o and any initial bound state i in the closed channel c can be defined by

$$P_{o,ic}(E) = |\langle F_{c,o}^*(E,R)|\chi_{i,c}(R)\rangle|, \qquad (9)$$

where $\chi_{i,c}(R)$ is the wave function of the field-free bound state i in the closed channel c. In the previous works [6,8,22] the position of the peak of the quantity P was used to identify the initial bound state in the presence of the laser field. The width of this integral over energy gave the transition rate from the initial state. For below threshold dissociation, c can also be taken to be any other closed channel with a number of photons absorbed, and in this work we shall see how an intermediate resonance in a closed channel with a single photon absorbed is indicated by values of P with a different c and i. It is well known that such intermediate resonances can cause enhancements of the total dissociation rate and it can be seen from the CC calculations that the position of such a resonance can be varied by a second laser. As mentioned earlier, these calculated characteristics of the dissociation linewidth include the effects of all closed and open channels to all orders and the excitation of all possible vibrational states, unlike other methods.

III. RESULTS AND DISCUSSIONS

In Fig. 1 we show the two lowest adiabatic potential energy curves corresponding to the electronic states GS and ES, respectively, for this system. The unperturbed bound level with the vibrational quantum number $v = 0$ on the GS potential has been shown. Also shown are the energy after the absorption of two photons of different frequencies and the energy of the field-free $v = 6$ level on GS. The arrows
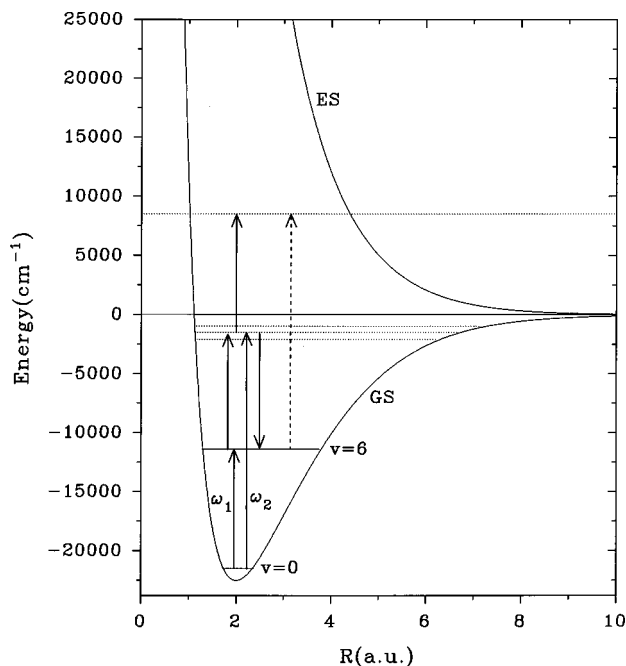
FIG. 1. The two lowest unperturbed *potential* energy curves GS and ES of HD$^+$, against internuclear separation R. The unperturbed bound vibrational levels with $v=0$ and $v=6$ are shown by solid lines. Positions of some other high-lying vibrational states near the dissociation threshold have been indicated by dashed lines. The arrows show some of the many possible radiative transitions.

indicate some of the possible transitions caused by absorption/stimulated emission of a single photon.

The variation of the linewidth of the initial level $v=0$ with the frequencies of the two photon fields was observed at fixed intensities of 10^{12} W/cm^2 for each of the fields. It was found that the overlaps $P_{d,v=0,(0,0)}(E)$ against the total en-

ergy E could be fitted by Lorentzians to an accuracy usually better than 0.5% even when they have decreased by three orders of magnitude from their peak values. The positions of the peaks of these Lorentzians at specific energies define the energy shift of the $v=0$ level in the two-frequency field ω_1 and ω_2. The integral over energy of the sum of these Lorentzian lines over all open channels d [which we shall designate as $P_0(E)$] gives unity exactly, confirming that the resonance obtained in the closed channel $n_1=n_2=0$ is indeed the field-free $v=0$ level, shifted and made unstable by the radiative interactions. This shift between the peak of $P_0(E)$ and the energy of the unperturbed $v=0$ level in the ground electronic state (-21515.93 cm^{-1}), found earlier by the solution of the Schrödinger equation, is very insensitive to the varying of ω_1 and ω_2. Specifically, the energy shift of the $v=0$ level under the action of the two fields is found to be 4.6 ± 0.3 cm^{-1} downwards, the exact value depending upon ω_1 and ω_2. However, the linewidths of these Lorentzians $P_0(E)$ vary over several orders of magnitude with changes in ω_1 and ω_2. They define the width of the $v=0$ level and hence the total transition rate to all open channels from this state in presence of the two fields.

In Fig. 2 we have plotted the sum of the overlaps over all open channels o, $P_0(E)$, against the total energy E for two different choices of ω_1 and ω_2. We see that in both cases the $P_0(E)$'s do indeed follow a Lorentzian shape to a very high degree of accuracy and the area under each of the curves is exactly equal to unity, in spite of their very different widths and peak values. This remains true for all other choices of ω_1 and ω_2. The transition rate and the halfwidth of the Lorentzian in cm^{-1} are related by a factor $2c$, where c is the velocity of light. This indicates that for our chosen values of the two intensities, the transition out of the $v=0$ level is purely exponential, characterized by a single decay constant and the initial laser induced dressed state from which the
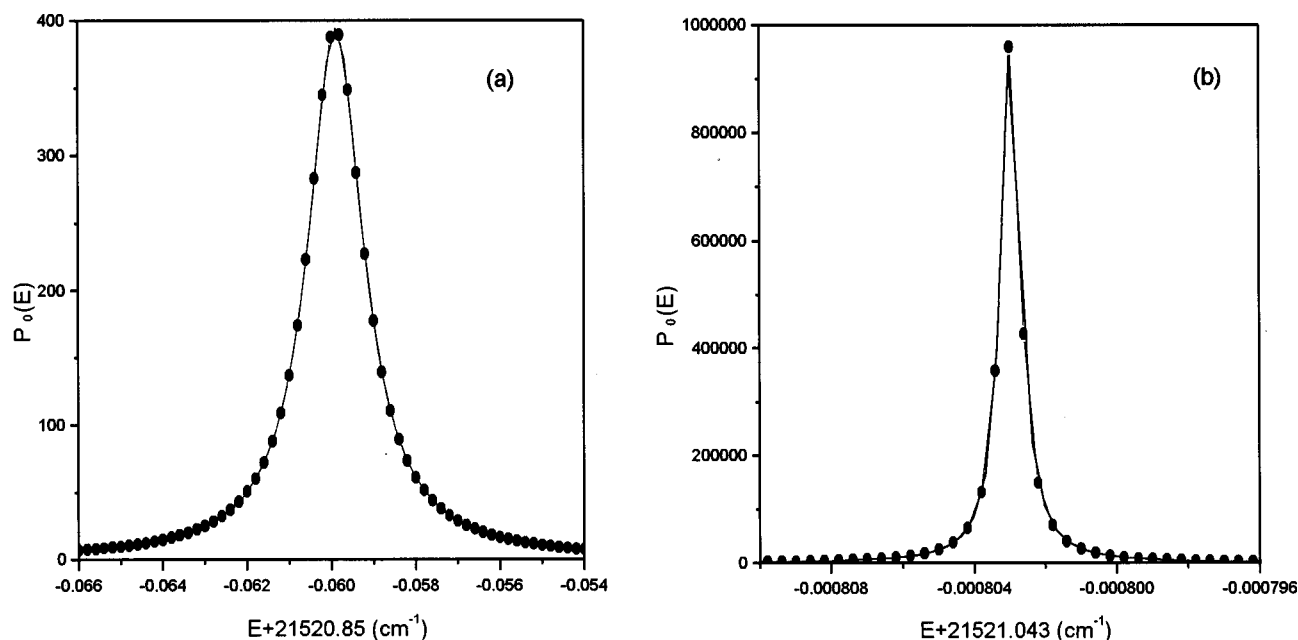

FIG. 2. P_0 against E for (a) $\omega_1=10\,024$ and $\omega_2=19\,840$ cm^{-1} and for (b) $\omega_1=10\,021$ and $\omega_2=20\,800$ cm^{-1}. The best Lorentzian fits through the calculated points are shown by the solid line.

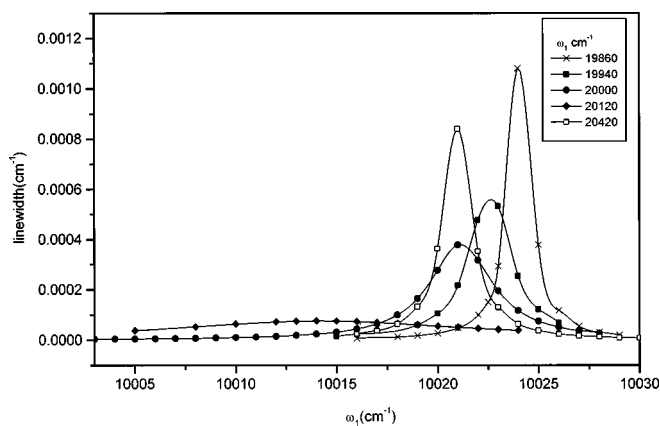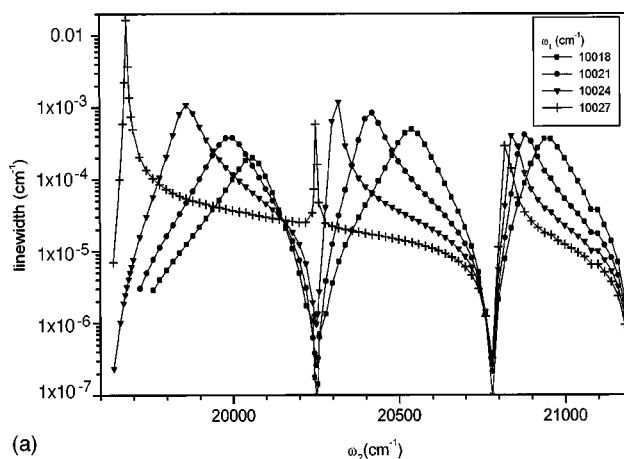FIG. 3. HWHM of the initial $v=0$ state as functions of ω_1 for different values of ω_2.

decay occurs is overwhelmingly the $v=0$ level, shifted by the radiative interactions.

The linewidths (HWHM) obtained are plotted against ω_1 for different values of ω_2 in Fig. 3. For some values of ω_2, the linewidth, and hence the transition rate, shows a sharp enhancement at specific values of ω_1, the exact value at which the peak occurs and its height depending on ω_2. For some other values of ω_2 there is practically no enhancement and the curve of linewidth against ω_1 is flat. These curves of the linewidth (and hence the transition rate) plotted against frequency have Lorentzian shape. This is to be expected for a one-photon resonance enhanced two-photon transition to the continuum. However, we note that the resonant frequency as well as the effectiveness of the single-photon resonance depends on the frequency of the second field ω_2.

In Figs. 4(a) and 4(b) we show the linewidths of the initial $v=0$ level as functions of ω_2 for four different values of ω_1. In the range of ω_2 shown, the linewidths show a number of asymmetric peaks separated by deep minima for each value of ω_1. The overall shape between the peaks suggests interference between different pathways and will be shown to be arising from two adjacent resonances. The successive values of ω_1 used are separated from each other by only 3 cm^{-1}. When ω_1 is changed by this amount, the positions of the peaks on the ω_2 axis undergo a large shift, for lower values of ω_2 [Fig. 4(a)]. As ω_2 approaches the dissociation threshold, the positions of the peaks become relatively insensitive to changes in ω_1 [Fig. 4(b)]. The relative heights of the peaks for different values of ω_1 gradually change in favor of lower ω_1 values as the peaks are observed for higher and higher values of ω_2. Also, the peaks at higher values of ω_2 are less sharp. Figure 5 shows the positions of the different peaks on the ω_2 scale as functions of ω_1. The most interesting feature is the large shift of the position in ω_2 of some of these peaks for small changes in ω_1.

We have calculated the sum of the overlaps of the component of the solution of the CC equations in the closed channel (1,0) GS with the field free vibrational wave function for $v=6$, i.e., $\Sigma_{d=0} P_{d,v=6,(1,0)}$ [which we shall henceforth call $P_6(E)$], as functions of energy. These overlaps generally exhibit a shape which is significantly non-Lorentzian in the wings (with a deviation of 10% or more

(a)
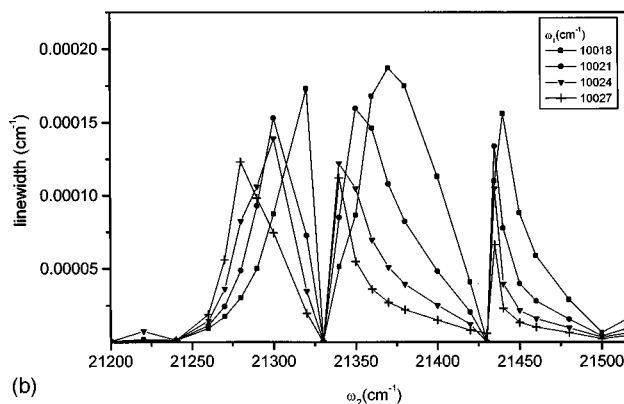
(b)

FIG. 4. (a) HWHM of the initial $v=0$ state as functions of ω_2 for different values of ω_1. (b) Same as (a) for a different range of ω_2.

from the best Lorentzian fit, when the overlaps decrease by more than one order of magnitude from the peak values. For a number of combinations of the two frequencies this quantity exhibits two peaks in energy, the sum of whose integrals
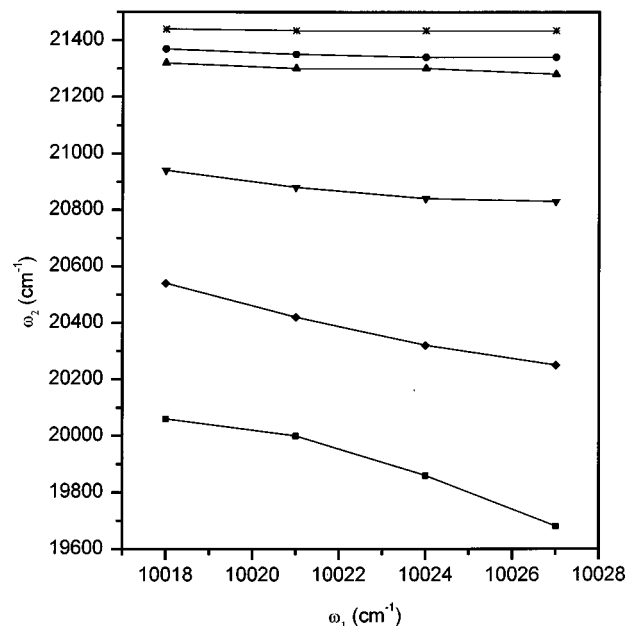

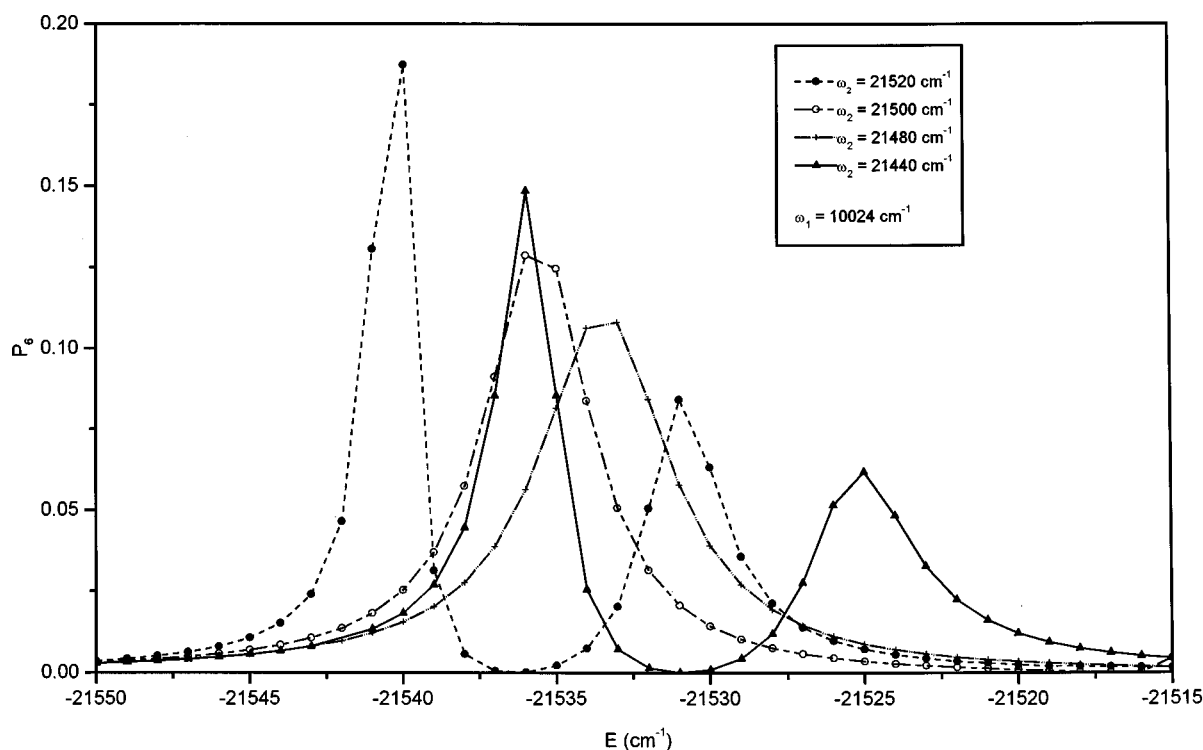FIG. 5. Location of the peaks of the width of the initial $v=0$ level in ω_1, ω_2 space.

FIG. 6. P_6 against E for $\omega_1 = 100\,24$ cm^{-1} and four different values of ω_2 near the dissociation threshold.

over energy, gives unity (Fig. 6).

However, for most combinations of frequencies there is only one value of the total energy for which $P_6(E)$ shows a significant peak. When for a particular choice of ω_1 and ω_2 the position in energy of this single peak of P_6 matches that of the peak of P_0, the linewidth of the initial $v=0$ level shows a maximum. This is shown in Fig. 7, where the positions in energy of the peaks of P_0 and P_6 have been plotted as functions of ω_2 for two different values of ω_1. The maxima of the transition rates are at the values of ω_2 where the two curves intersect. The integral of P_6 over energy around these coincidences gives a value of 0.93–0.98. This suggests that a localized $v=6$ vibrational level, made slightly diffused and broadened by radiative interactions, can be resonantly excited by absorption of a single ω_1 photon. The mixture of other levels in the closed (1,0) channel, at the specified energy, is negligible. However, the value of the energy at which the $v=6$ level is found is ω_2 dependent.

As we have seen earlier, the near horizontal line in Fig. 7 can be interpreted as the position of the eigenvalue of the shifted ground $v=0$ level. It follows that resonance excitation of the $v=6$ level in the (1,0) channel leading to enhancement of the transition rate from the $v=0$ level in the (0,0) channel occurs whenever the two energies match. By varying ω_2 the two levels can be tuned and detuned from each other a number of times.

When P_6 cannot be characterized by a single peak but instead has two different peaks, they are seen to be on either side of the peak of P_0, and both well detuned from it. In such cases only the sum of the area under the two peaks gives unity. This behavior characterizes the region of ω_2 between the two branches of the curve for peaks of P_6 against ω_2 in Fig. 7. This region is also characterized by deep minima of the transition rate from $v=0$. At these values

of ω_2, a single well defined vibrational state in the (1,0) channel, localized in energy cannot be resonantly excited from the $v=0$ level. Instead, the wave function in the (1,0) channel at the total energy equal to that of the initial state is diffuse with a large mixture from other vibrational levels.

It is to be stressed that this periodicity in the shift of the position of the resonances in the (1,0) channel corresponding to $v=6$ and their splitting with change in ω_2 occurs because of the presence of the closed (0,1) GS channel. In Fig. 7 the position of the $v=6$ level in the (1,0) GS channel, with the (0,1) GS channel excluded from the calculation, has been indicated by triangular symbols. Apart from a small irregularity in the vicinity of $\omega_2 = 20\,100$ cm^{-1}, the resonance position corresponding to $v=6$ shows only a small linear shift with ω_2. This type of variation is typically the one expected from the interaction of the (1,0) channel with the unstructured continuum of the (1,1) channel. Thus, in the familiar language of works on LICS the bound levels in the (0,1) channel get embedded in the continuum of the (1,1) ES channel by the action of the field ω_1, and this laser induced structure of the continuum strongly affects the level positions as well as the structure of the transition rates from $v=0$ as functions of ω_2. This is evident from Fig. 8 where, for a single value of ω_1, the linewidth of the $v=0$ level has been shown as a function of ω_2 with the (0,1) GS channel both included in and left out of the calculation. It is seen that the elaborate structure against ω_2 vanishes in the absence of the above channel because the (1,1) ES continuum becomes flat in the absence of embedding levels.

In the study of single frequency ATD of H_2^+ and other small molecules, it has been shown how the laser dressed adiabatic potential curves provide a framework within which the various features of the excitation and dissociation process can be qualitatively understood [6,8,23]. These adiabatic po-
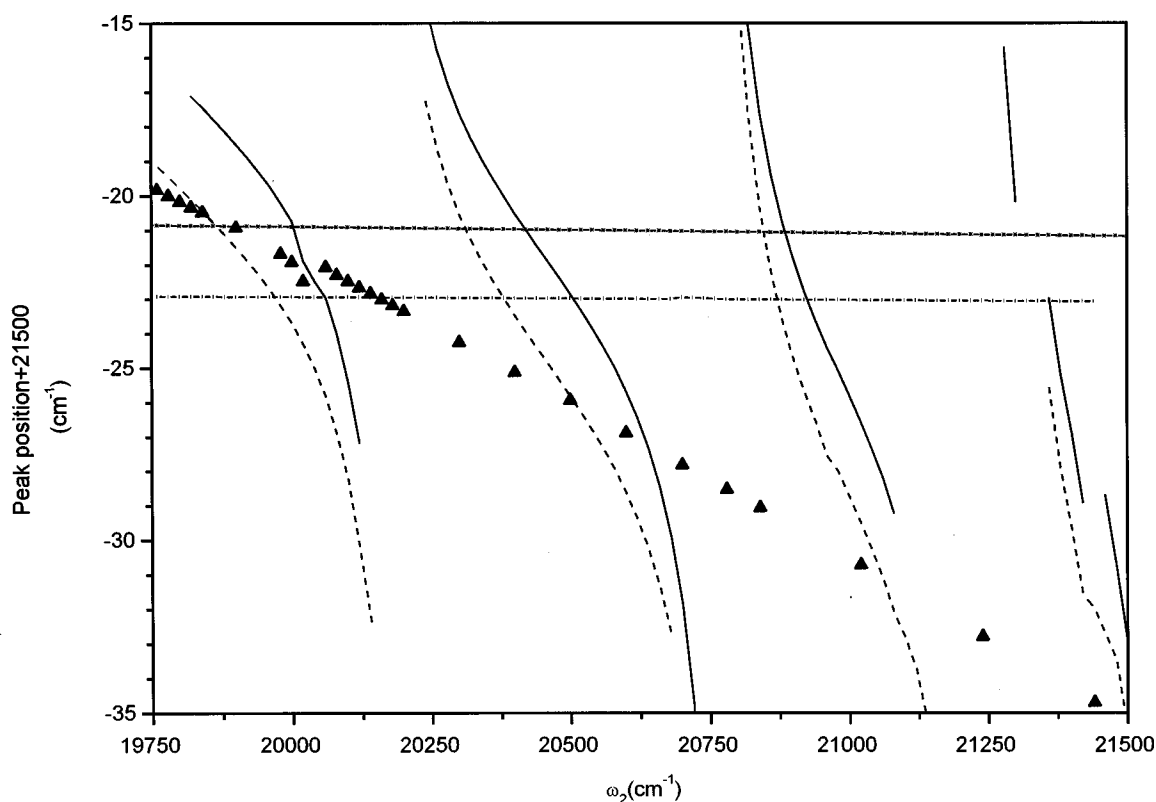
FIG. 7. The position in energy of the peaks of P_0 and P_6. The upper horizontal line gives the peak positions of P_0 for both ω_1 = 10 021 and 10 024 cm^{-1}. The solid and dashed curved lines denote the positions in energy of the peaks of P_6 for ω_1 = 10 021 and 10 024 cm^{-1}, respectively.

tential curves are obtained from the diagonalization of the total Hamiltonian for fixed nuclei, i.e., $H^0 + V_{rad}^L$ in Eq. (3). These adiabatic curves show a number of avoided crossings at the degeneracies of the diabatic potential curves (i.e., field+molecule energies for different channels as functions of internuclear separation) in case there is an effective coupling between these diabatic channels. The adiabatic eigenfunctions are themselves coupled by nonadibatic interaction arising from the kinetic energy operator for internuclear motion. These interactions may cause transitions between the eigenstates on different adiabatic potentials.

In our case, due to the interaction of the molecule with two different laser frequencies, the adiabatic potential curves have a much more complicated shape than in the single-frequency case. In Fig. 9(a) we have plotted the diabatic curves for three photon number channels each for the GS and ES levels. The horizontal line indicates the energy of the v = 0 level in the (0,0) channel. Figure 9(b) shows some of the (simplified) adiabatic potential curves for the same combination of frequencies. Two other channels, apart from the six shown in Fig. 9(a), have been included in the basis set during the diagonalization. These channels may cause additional avoided crossings in the adiabatic potential curves at larger values of R, the internuclear separation, due to higher order interactions. In general, such avoided crossings do not play a significant role in determining the total linewidth and discussion may proceed on the basis of the adiabatic potential curves depicted here. Inclusion of channels with an even larger number of photons absorbed would cause a number of higher order avoided crossings near the equilibrium region. These crossings may influence the dynamics at high intensi-

ties (as shown for high intensity ATD calculations where no intermediate resonance can be present [5–7]) but at our present level of intensities of below threshold frequency lasers, these crossings, corresponding to direct nonresonant high order multiphoton transitions, will not be very effective. It may be assumed that they will not drastically affect the overall pattern of variation of the characteristic resonance line shapes. Thus, for an easy understanding of the basic phenomenon of variation of resonant dissociation line shapes using two frequencies, it is probably adequate to confine ourselves to a small number of channels in the expansion of the CC wave function.
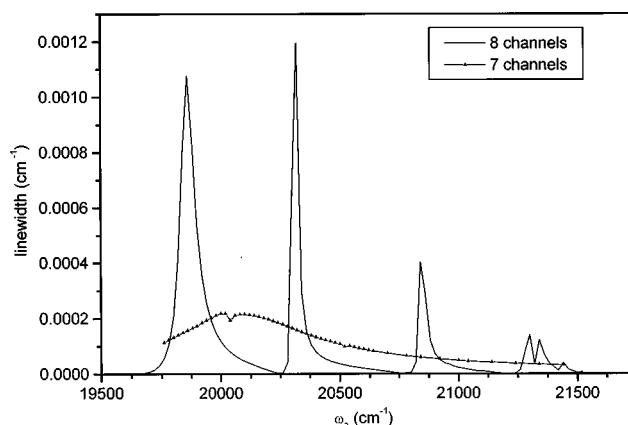

FIG. 8. Seven-channel and eight-channel dissociative linewidths of the initial v = 0 level in two-frequency fields compared for ω_1 = 10 024 cm^{-1}. The resonance structures against ω_2 vanish when the closed (0,1) GS channel is left out.
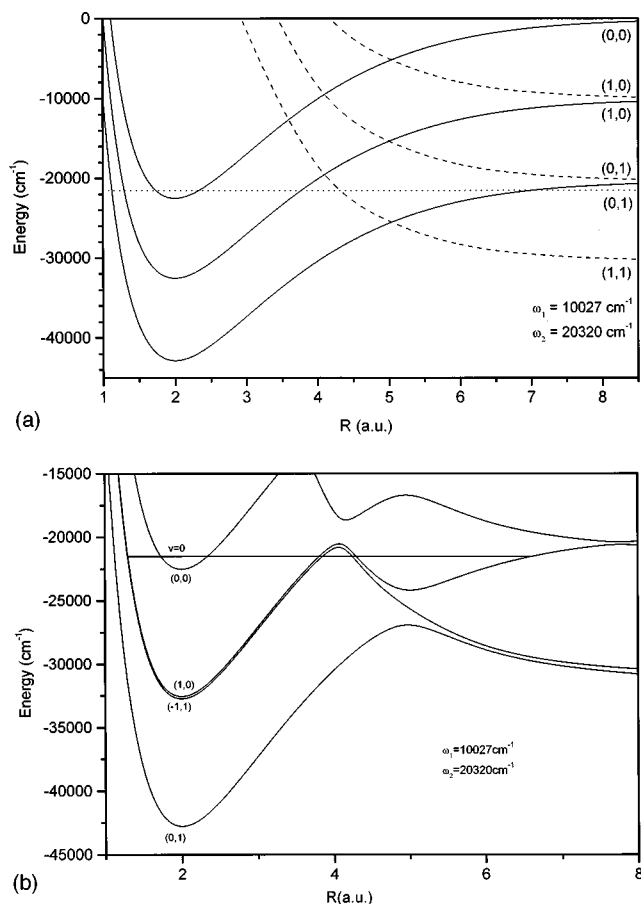
FIG. 9. (a) Some of the diabatic potential curves for the system HD$^+$ and the frequencies indicated. The diabatic photon number indices are indicated. (b) Some of the relevant adiabatic potential energy curves for the frequencies indicated and intensity of 10^{12} W/cm^2 for each field. The indices indicated for each curve is that of the diabatic potential with which it coincides near the minimum.

Near the minima of the potential curves, the mixing of the different photon number channels due to radiative interactions is very small and the adiabatic curves in this region have overwhelmingly (more than 99.9%) the photon number channel character indicated on Fig. 9(b). In other words, the adiabatic curves coincide with the diabatic ones near the minimum. Since the wave function of the initial $v=0$ level has an appreciable magnitude only in this region of internuclear separation R, the effect of mixing caused by the radiative interactions on the initial wave function is small and the shift negligible. The energy of the shifted $v=0$ level has been indicated by the horizontal line in the figure. Thus, in the absence of bound levels in other closed channels the dissociative decay rate would be extremely small.

However, the GS (1,0) potential curve has a strong one-photon interaction with the ES (1,1) curve near the initial energy. As a consequence, the adiabatic curve with GS (1,0) character near the minimum at 2.0 a.u. becomes dominantly the ES (1,1) curve beyond about 4 a.u., and again, at larger internuclear separations, the avoided crossing due to the radiative interaction with the ω_1 photon causes this adiabatic curve to have a predominantly GS (0,1) character at large separations. We neglect the higher order avoided crossings at

larger internuclear separations due to the presence of additional channels. They cause some further mixing of the diabatic states but do not affect the total linewidth at the present intensities.

By our choice of the frequency ω_1 the energy of the $v=6$ level in the diabatic (1,0) potential happen to fall near the first avoided crossing with the ES (1,1) state. From Fig. 9(b) it is evident that the radiative interactions are much more strongly felt by the $v=6$ level in the (1,0) channel compared to the $v=0$ level in the (0,0) channel, though it still remains reasonable to characterize the corresponding eigenstate in the adiabatic channel as the $v=6$ level in the GS (1,0) channel. This is so because over most of the region of internuclear separation R where the unperturbed wave function has an appreciable magnitude, the relevant adiabatic channel predominantly retains its GS (1,0) character (99.4% at $R=4.0$ a.u.). The mixing of the diabatic channels in the adiabatic potential, mainly between GS (1,0) and ES (1,1), leads to a shift of about 60–80 cm^{-1} between the vibrational eigenstate in the corresponding adiabatic potential and the unperturbed $v=6$ level in GS (1,0), depending on the value of ω_2.

Thus, energies of vibrational eigenstates in the adiabatic potential which corresponds to the (1,0) diabatic channel potential near equilibrium [which, for brevity, we henceforth denote as the (1,0) adiabatic potential] depends sensitively upon ω_2. This fact is apparent also from the figure. At large internuclear separation the same adiabatic potential has dominant GS (0,1) character and hence a shallow outer well caused by the single-photon avoided crossing near 5 a.u. The shape and depth of this well depend upon ω_2. The wave functions in the two regions can be properly matched only for energies which are different for different values of ω_2. Thus the eigenenergies in this adiabatic potential also depend upon ω_2.

When this eigenenergy closely matches the energy of the $v=0$ level in the adiabatic channel marked (0,0) [and which indeed can be identified with the diabatic (0,0) channel potential for our purpose] this $v=0$ level becomes more unstable. The two eigenfunctions in the two adiabatic channels can now become significantly coupled through nonadiabatic interactions, so that the initial state in the (0,0) channel can acquire some (1,0) character and dissociation is facilitated.

As ω_2 is increased, starting from such a resonant situation, the barrier height of the (1,0) adiabatic potential decreases, while the minimum of the shallow potential well on the right-hand side becomes more negative and its asymptotic value changes (neglecting the higher order avoided crossings). For a small increase in ω_2, a downward shift of the eigenenergy occurs while it still retains its $v=6$ character. The two adiabatic eigenenergies get detuned and the initial level cannot effectively mix with levels of the (1,0) channel. Hence the dissociation linewidth decreases. For larger changes of ω_2 the projection of the diabatic $v=6$, GS (1,0) channel wave function shows two peaks in energy on either side of the peak of P_0, showing that the $v=6$ character is shared by two neighboring eigenfunctions in the adiabatic channel. At some value of ω_2 we get a deep minimum in the dissociation linewidth. If we continue to modify the adiabatic potential by changing ω_2, the reso-

nance is restored with an eigenfunction which has a different structure in the outer well.

As ω_1 is increased the resonance occurs for lower values of ω_2. For smaller values of ω_2 the energy of the $v=0$ level remains well below the threshold of the relevant adiabatic potential which has a higher barrier. Thus the inner well wave function is less sensitive to ω_2, and if the resonance is destroyed by changing ω_1 (in steps of 3 cm^{-1} in our case), a relatively large change of ω_2 is required to restore it. This is clearly seen also from Fig. 7. However, as ω_2 increases further, the resonance region approaches the asymptotic energy of the adiabatic potential and the adiabatic eigenenergies become densely spaced. The low barrier of the adiabatic potential allows tunneling. Consequently, the sensitivity of the adiabatic eigenfunction in the inner well to ω_2 increases and change of ω_1 can be compensated and the resonance restored by much smaller changes of ω_2. However, this decrease in barrier height and the close spacing of the levels now make the resonance more diffused. In other words, though the dissociation linewidth from the $v=0$ level shows resonance peaks at certain values of the frequency ω_2, the resonances lose their $v=6$, GS (0,1) character to some extent.

IV. CONCLUSIONS

Our calculation demonstrates how the essential features of two-frequency below-threshold resonant two-photon dissociation processes are reproduced within the framework of a time-independent CC approach. Moreover, this approach, previously extensively applied to ATD of small diatomic molecules, is free from any limitation arising from the use of effective states expansion, perturbative treatment of a part of the Hamiltonian, and rotating wave approximations. It can also take into account all possibilities of above-threshold absorption and stimulated emission between continuum levels. Such processes may become significant at sufficiently high intensities.

At the intensities we have used, we have demonstrated the possibility of gaining control over an intermediate resonance in a particular diabatic photon absorption channel by the use of a second field of a different frequency. This field can be used to tune the intermediate resonances with the initial level. Such tuning is possible only because of the presence of bound levels that can be reached by the absorption of the second frequency photon. At higher intensities the higher order avoided crossings in the adiabatic potentials due to multiphoton absorptions and emissions (as opposed to single photon crossings in the present case) may be expected to affect the dynamics. Also, two or more diabatic levels may become involved in an intermediate resonance and such involvement may have important and interesting effect on their characteristic, changing the dissociation widths, and branching ratios in very interesting fashions.

ACKNOWLEDGMENTS

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