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Ionization, dissociation, and level shifts of H_2^+ in a strong dc or low-frequency ac field

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Using a complex basis-set expansion of the electronic wave function, we have calculated the induced shifts and widths of the first few electronic Σ levels of the H_2^+ molecular ion in the presence of a dc field, over a range of internuclear separations. We have also calculated, through order ω^2, the shifts and widths of the $1s$ and $2p$ levels (we use the field-free united-atom-limit quantum numbers) when an ac field of low frequency ω is present. In accord with Zuo and Bandrauk [Phys. Rev. A **52**, R2511 (1995)], we find that the $2p$ ionization width exhibits peaks as the internuclear separation is increased. We attribute these resonances to the mixing of the $2p$ state, which is localized in the higher well of the double-well electronic potential, with energetically nearby highly excited states that are localized in the lower well; over-the-barrier ionization from the lower well can proceed without the impediment of backscattering of the electron from the hump between the wells. Finally, we have calculated shifts and widths of various vibrational levels of the electronic ground state and the threshold intensities for dissociation of H_2^+ from some of these vibrational levels. We compare our results with the threshold intensity measured by Ilkov *et al.* [Phys. Rev. A **51**, R2695 (1995)] at the CO_2 laser wavelength. [S1050-2947(96)01411-4]

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I. INTRODUCTION

The breakup of an atomic or molecular system by strong low-frequency radiation is similar, in many circumstances, to breakup by a static electric field. The notion of tunneling in the presence of a slowly oscillating field was validated many years ago by Keldysh [1], who, in a seminal paper, calculated the modification to the formula for the tunneling rate arising from the oscillations of the field. However, tunneling is a quantum-mechanical phenomenon, and if the deBroglie wavelength of the active fragment of the system is extremely small compared to the width of the barrier through which this fragment must tunnel, the rate for breakup by tunneling is negligible. Therefore, while a molecule in the presence of a dc or low-frequency ac field can *ionize* by electron tunneling, it is unlikely to *dissociate* by ion tunneling since the deBroglie wavelength of a nucleus vibrating within a molecule is typically small, being proportional to $(m/M)^{1/4}$, where m and M are the electron and proton masses, respectively. On the other hand, a strong field distorts and suppresses the barrier through which a fragment must tunnel, and at sufficiently large field strengths the active fragment can simply pass over the top of the barrier, without tunneling [2–5]. Over-the-barrier breakup is a classically admissible process, which favors a smaller deBroglie wavelength since the active fragment is less likely to backscatter from the top of the barrier; a classical particle would not backscatter at all. Hence a molecule readily dissociates once the field strength exceeds the threshold at which it is classically possible for a nucleus to pass over the top of the barrier.

In this paper we present results of calculations of ionization and dissociation rates, and also level shifts, for the H_2^+ molecular ion in the presence of a dc field or a linearly polarized low-frequency ac laser field. The rate for ionization of H_2^+ is relatively small at the equilibrium internuclear separation of 2 a.u.; dissociation proceeds more easily than ionization [6]. However, Zuo and Bandrauk [7] have shown that ionization can become significant at moderately large values of the internuclear separation R. They found that when H_2^+ is irradiated by intense 1064-nm light, the ionization rate rises rapidly as R increases beyond 2 a.u. and exhibits maxima as R varies, the most prominent peak being at 10 a.u. Our results for the ionization rate are in qualitative agreement with theirs. However, our explanation for the existence of these resonances is slightly different from the one given by Zuo and Bandrauk: In Fig. 1 we show the electronic potential along the polarization axis when $R=9$ a.u. and a dc field of strength 0.0533 a.u. is present. At nonzero R the electronic potential consists of two Coulomb wells, one centered at each proton; [8] an external dc field distorts the wells, raising the outer edge of one well and depressing the outer edge of the other well [3,7,9,10]. We indicate the positions of various discrete autoionizing levels (we calculated both the positions and widths using the method described in

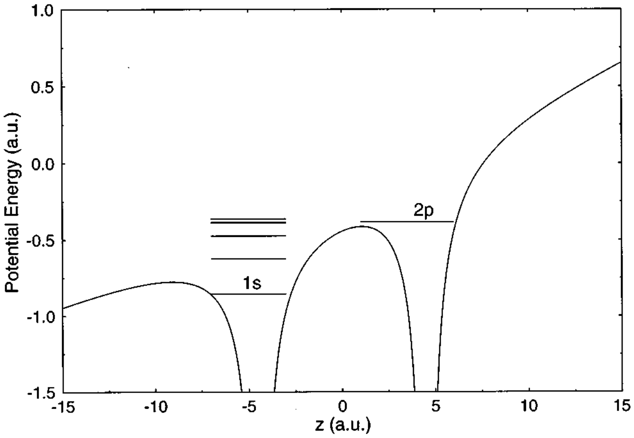

FIG. 1. Electronic potential for H_2^+ along the polarization (z) axis when $R=9$ a.u. and a dc field of strength 0.0533 a.u. is present. We show some of the discrete (autoionizing) levels in the wells.

Sec. II). The levels labeled $1s$ and $2p$ (these labels are the united-atom-limit quantum numbers of the field-free states) are the (autoionizing) ground-state levels in the lower and higher wells, respectively. We also show some of the excited autoionizing levels in the lower well and we have singled out one of these levels by a thick line since it is degenerate with the $2p$ level. Evidently, over-the-barrier ionization from the $2p$ state is possible and, following up on the earlier work of Codling *et al.* [9], Zuo and Bandrauk [7] argued that the most prominent peak in the ionization rate arises from over-the-barrier ionization out of the higher well. However, over-the-barrier ionization out of the higher well is impeded by backscattering of the electron from the hump between the wells; we argue that at certain values of R the electron can escape more easily by undergoing a resonant transition to an energetically nearby, but highly excited, state localized in the lower well; the hump between the wells does not impede over-the-barrier ionization out of the lower well.

We note that Seideman *et al.* [10] have studied a one-dimensional model of a molecular ion and have arrived at conclusions similar to those of Codling *et al.* and Zuo and Bandrauk. In addition, they discusssed the occurrence of resonant transitions from the higher to the lower well, followed by tunneling from the lower well; but they implied that this event was a feature of ionization from *highly charged* molecular ions, occurring when the outer hump of the lower well is above the energy of the ground state in the higher well.

We have also calculated the rates for dissociation of $H_2{}^+$ from the first few vibrational levels of the ground electronic state, over a range of field strengths, for both dc and ac fields. We find that the dissociation rate remains extremely small until the field strength reaches a value not too far below that at which a proton can pass over the top of the dc barrier. We compare our calculated threshold field strengths for dissociation with the threshold intensity measured by Ilkov *et al.* [11] using a CO_2 laser. We also comment on the validity of the quasistatic picture of over-the-barrier dissociation in the context of the experiment. As Ilkov *et al.* pointed out, the vibrational motion of the protons is not fast on the time scale of one oscillation of the CO_2 laser (wavelength 10 μm); we find that the corrections due to the oscillations of the field are small but non-negligible.

In our calculations we assumed that the $H_2{}^+$ molecular ion is aligned along the direction of the polarization axis of the field. This approximation is justified as long as the field is turned on rapidly (on the time scale of molecular rotation) and to sufficient strength that a large number of rotational levels are populated, with a wide distribution of angular momenta; see, e.g., [12]. For sufficiently strong fields, breakup occurs rapidly on the molecular rotation time scale, but can still occur slowly compared to the effective turn-on time of the field. Consequently, we make the Floquet ansatz for the wave function, whose validity rests on the periodicity of the Hamiltonian. In addition, we neglect the coupling between ionization and dissociation channels; in treating ionization we freeze the nuclei, i.e., we calculate the ionization rate at a fixed internuclear separation R, and in treating dissociation we describe the motion of the nuclei within the Born-Oppenheimer approximation, neglecting ionization.

In the next section we briefly describe the theory upon which our calculations are based. In Sec. III we present our results.

II. THEORY

We consider the $H_2{}^+$ molecular ion in a linearly polarized external electric field whose frequency is ω, whose peak field strength is F_0, and whose polarization axis coincides with the internuclear axis. In making the Floquet ansatz we approximate the wave function of the molecular system by a function that has the periodicity of the external electric field, multiplied by a dynamical phase factor $\exp[-iE_{\rm ac}(F_0,\omega)]t/\hbar]$, where $E_{\rm ac}(F_0,\omega)$ is the ac quasienergy. We express the ac quasienergy as

$$E_{\rm ac}(F_0,\omega)\equiv E_0+\Delta-i\Gamma/2, \tag{1}$$

where E_0 is the unperturbed energy of the level of interest and Δ and Γ are the field-induced shift and width. If the nuclei are frozen in place, $E_{\rm ac}(F_0,\omega)$ depends on the internuclear separation R, in addition to ω and F_0.

At low frequencies an exact solution of the Floquet eigenvalue problem for $H_2{}^+$ is difficult due to the large number of photons that participate in the breakup process. However, as shown elsewhere [13], we can expand $E_{\rm ac}(F_0,\omega)$ in an asymptotic series in powers of ω^2:

$$E_{\rm ac}(F_0,\omega)=\sum_{m=0}^{\infty} E^{(2m)}(F_0)\omega^{2m}. \tag{2}$$

This expansion describes only effects resulting from the *adiabatic* variation of the ac field; *nonadiabatic* effects arising from the discrete nature of the photon, i.e., effects arising from *multiphoton* thresholds and resonances, are not accounted for. The leading term $E^{(0)}(F_0)$ is just the average of the dc quasienergy $E_{\rm dc}(F)$ over all instantaneous values F of the ac field during one cycle; thus, with $F\equiv F_0\sin(\tau)$ at the instant t, where $\tau=\omega t$, we have

$$E^{(0)}(F_0)=\frac{1}{2\pi}\int_0^{2\pi} d\tau E_{\rm dc}(F). \tag{3}$$

The ω^2 expansion of the ac quasienergy is essentially an expansion in the "perturbation" $-i\hbar\omega\partial/\partial\tau$. Before writing down the coefficient $E^{(2)}(F_0)$ of the first correction, we need to establish some more notation. Let $H_{\rm dc}(F)$ denote the Hamiltonian of the molecule in the presence of a dc electric field of magnitude F and let $|\Phi_{\rm dc}(F)\rangle$ denote the eigenvector of $H_{\rm dc}(F)$ with eigenvalue $E_{\rm dc}(F)$. We require the generalized resolvent $G_{\rm dc}(F)$ for the dc Hamiltonian, defined as

$$G_{\rm dc}(F)=\frac{Q_{\rm dc}(F)}{E_{\rm dc}(F)-H_{\rm dc}(F)}, \tag{4}$$

where $Q_{\rm dc}(F)$ is the projection operator that annihilates $|\Phi_{\rm dc}(F)\rangle$. We also require the response vector

$$|\chi_{\rm dc}(F)\rangle=-i\hbar G_{\rm dc}(F)\dot{H}_{\rm dc}(F)|\Phi_{\rm dc}(F)\rangle, \tag{5}$$

where the overdot indicates the derivative with respect to τ, with $F=F_0\sin(\tau)$. The first correction in the ω^2 expansion is [13]

$$E^{(2)}(F_0)=\frac{1}{2\pi}\int_0^{2\pi}d\tau\langle\chi_{\mathrm{dc}}^{(*)}(F)|G_{\mathrm{dc}}(F)|\chi_{\mathrm{dc}}(F)\rangle, \tag{6}$$

where the asterisk on $\langle\chi_{\mathrm{dc}}^{(*)}(F)|$ in Eq. (6) indicates that in position space only the angular part, and not the radial part, of the bra is to be complex conjugated. We do not give explicitly further corrections here since we do not consider them, but an iterative scheme for calculating all corrections was given in Ref. [13].

Following, e.g., Bates and Reid [14], we resolve the electron position vector $\mathbf{r}$ into prolate spheroidal coordinates λ, μ, and ϕ where, with the polar axis along the internuclear axis, ϕ is the azimuthal angle, with r_a and r_b the distances of the electron from nuclei a and b,

$$\lambda=(r_a+r_b)/R, \tag{7}$$

$$\mu=(r_a-r_b)/R, \tag{8}$$

with $1\leqslant\lambda\leqslant\infty$ and $-1\leqslant\mu\leqslant 1$. The electronic Hamiltonian is cylindrically symmetrical about the internuclear axis and this remains true in the presence of the external electric field (which we assume points along the internuclear axis). We consider only Σ states, so that the electronic wave functions, at each fixed value of R, have no dependence on ϕ. The bare electronic Hamiltonian is separable in prolate spheroidal coordinates and is given as (hereafter we use atomic units, unless specified otherwise)

$$H^{\mathrm{el}}(R)=-\frac{1}{2}\nabla_{\mathbf{r}}^2-2\frac{(Z_a+Z_b)\lambda-(Z_a-Z_b)\mu}{R(\lambda^2-\mu^2)}, \tag{9}$$

where $Z_a=Z_b=1$ (in the case of $\mathrm{H}_2{}^+$) and

$$\nabla_{\mathbf{r}}^2=\frac{4}{R^2(\lambda^2-\mu^2)}\left[\frac{\partial}{\partial\lambda}\left((\lambda^2-1)\frac{\partial}{\partial\lambda}\right)+\frac{\partial}{\partial\mu}\left((1-\mu^2)\frac{\partial}{\partial\mu}\right)+\left(\frac{1}{(\lambda^2-1)}+\frac{1}{(1-\mu^2)}\right)\frac{\partial^2}{\partial\phi^2}\right]. \tag{10}$$

We have included the derivatives with respect to ϕ in $\nabla_{\mathbf{r}}^2$ for completeness only; as noted above, the electronic wave functions are ϕ independent for Σ states. In the presence of a dc electric field whose strength is F, the (dressed) electronic Hamiltonian is

$$H_{\mathrm{dc}}^{\mathrm{el}}(F,R)=H^{\mathrm{el}}(R)+F(R/2)\lambda\mu. \tag{11}$$

As in our earlier work [15] on multiphoton ionization of $\mathrm{H}_2{}^+$, we represent the electron wave functions on a discrete basis composed of functions $u_\nu(\lambda)$ and $v_\eta(\mu)$, where

$$u_\nu(\lambda)=\sqrt{-2i\kappa R}\,e^{i\kappa R(\lambda-1)}L_\nu(-2i\kappa R(\lambda-1)), \tag{12}$$

$$v_\eta(\mu)=P_\eta(\mu), \tag{13}$$

where $L_\nu(x)$ and $P_\eta(\mu)$ are Laguerre and Legendre polynomials, respectively, with ν and η non-negative integers, and κ lies in the upper right quadrant of the complex plane so that the functions $u_\nu(\lambda)$ can represent both closed (bound) and open (outgoing-wave) channels.

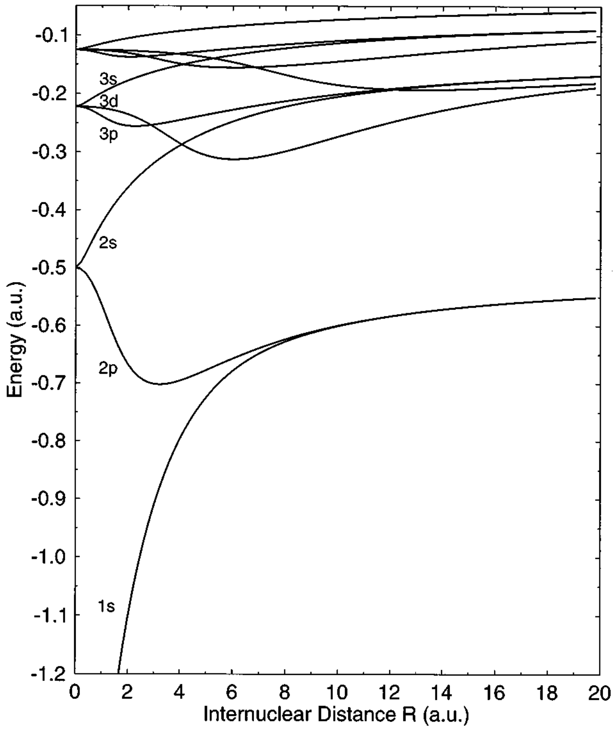

FIG. 2. Some energy levels of Σ electronic states of the bare $\mathrm{H}_2{}^+$ molecular ion vs internuclear separation R. The Coulomb repulsion between protons is not included. The levels are labeled by united-atom-limit quantum numbers.

As a preliminary test of our basis, we calculated the first few electronic Σ energy levels of the bare molecule, i.e., the eigenvalues of $H^{\mathrm{el}}(R)$, over a range of values of R; we obtained excellent agreement with Bates and Reid [14]. We show some of our results in Fig. 2, and we note here some of the salient features that are relevant to our discussion in the following section. We have labeled some of the levels by their united-atom-limit quantum numbers, i.e., by the principal and orbital angular momentum quantum numbers of the He^+ ion levels to which the molecular levels tend as $R\rightarrow 0$. There are many degeneracies at both the united-atom ($R=0$) and separated-atom ($R=\infty$) limits. As discussed above, the electronic potential consists of two Coulomb wells, with a barrier in between [8]. Since, in the absence of an external field, the two wells are similar and the electron can sit in either well with equal probability, there is a twofold degeneracy in the separated-atom limit, and this degeneracy is approached rapidly as R increases due to the exponentially small rate for the electron to tunnel from one well to the other. For example, the $1s$ and $2p$ levels are practically degenerate at $R=10$ a.u. and beyond, even though they approach the separated-atom-limit energy -0.5 a.u. rather slowly (as $1/R^4$, due to the polarization of the isolated H atom by the distant proton). As Zuo and Bandrauk [7] have already remarked, this near degeneracy of the $1s$ and $2p$ levels at only moderately large internuclear separations has important consequences for the field ionization of the molecular ion. Besides the degeneracies in the united- and separated-atom limits, there are also degeneracies at finite nonzero values of R. In fact, there are many true crossings of the levels, but no avoided crossings, implying the bare elec-

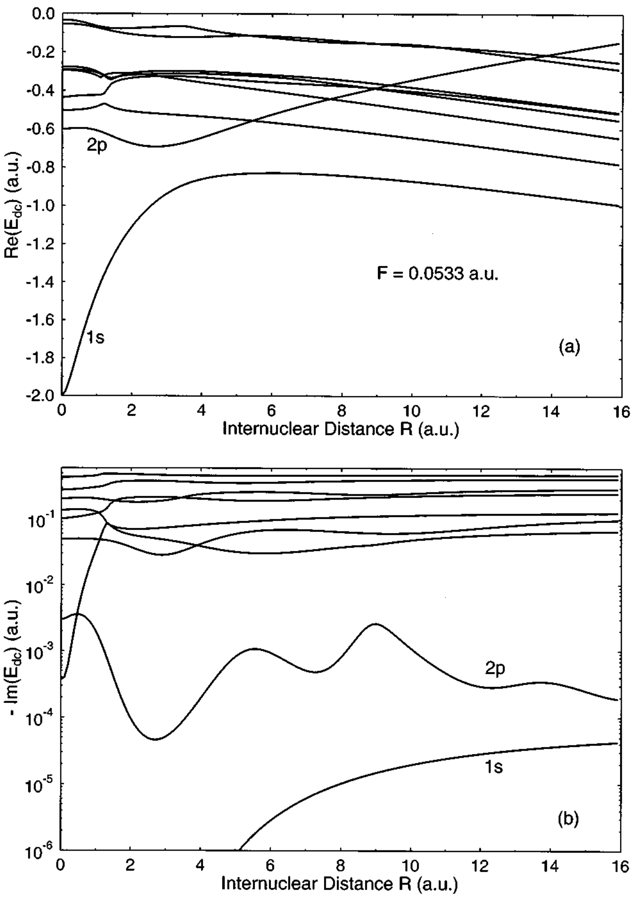

FIG. 3. (a) Real and (b) imaginary parts of the quasienergy vs R for various Σ electronic states of $H_2{}^+$ when a dc field of strength 0.0533 a.u. is present. The ordinate in (b) is the half-width due to ionization.

tronic Hamiltonian has a high degree of symmetry. As noted above, the Hamiltonian has cylindrical symmetry about the internuclear axis; it is also invariant with respect to the inversion of the electron coordinate through the midpoint of the internuclear axis, so that parity, gerade g or ungerade u, is a good quantum number. However, some Σ levels with the same parity (e.g., the $2s$ Σ_g and $3d$ Σ_g levels) cross, indicating a further ''hidden'' symmetry. This additional symmetry is already implied by the separability of the bare electronic Hamiltonian in prolate spheroidal coordinates at all values of R and is associated with an operator whose eigenvalue is the separation constant (also a good quantum number). A simple form for this operator was given by Coulson and Joseph [16]. In the united- and separated-atom limits, the electronic Hamiltonian is separable in parabolic coordinates, accounting for additional degeneracies in these limits. At asymptotically large R the prolate spheroidal coordinates are simply related to parabolic coordinates, e.g., $R(\lambda-1)$ and $R(\mu+1)$ become parabolic coordinates centered about proton a when $r_a \ll r_b$.

Finally, we consider the inclusion of the nuclear motion. Let M denote the mass of the proton and let $\mathbf{R}$ be the position vector of proton a relative to proton b. Working in the center-of-mass frame of the molecule and neglecting corrections of the order of the electron-proton mass ratio, the Hamiltonian of the molecule in the presence of a dc field of strength F is (with $Z_a = Z_b = 1$)

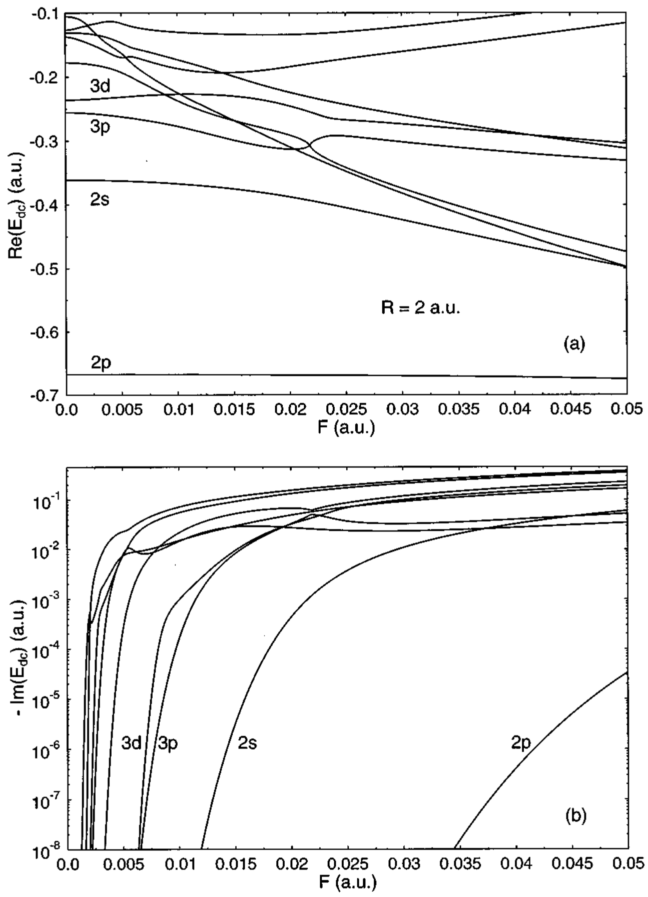

FIG. 4. (a) Real and (b) imaginary parts of the quasienergy vs the strength F of a dc field for various electronic states of $H_2{}^+$ at an internuclear separation $R = 2$ a.u.

$$-\frac{1}{M}\nabla^2_{\mathbf{R}} + \frac{1}{R} + H^{\mathrm{el}}_{\mathrm{dc}}(F,R).$$

Let $|\psi_n(R)\rangle$ be an eigenvector of the bare electronic Hamiltonian $H^{\mathrm{el}}(R)$, with discrete eigenvalue $E_n(R)$, $n = 0,1,\ldots$. We now replace $H^{\mathrm{el}}_{\mathrm{dc}}(F,R)$ by its matrix representation $\underline{H}^{\mathrm{el}}_{\mathrm{dc}}(F,R)$ on the basis $\{|\psi_n(R)\rangle\}$. This is consistent with the Born-Oppenheimer approximation. In addition, we restrict the nuclear motion to be along the polarization axis of the external field and hence replace $\nabla^2_{\mathbf{R}}$ by d^2/dR^2, with the boundary condition that the wave function vanishes at $R = 0$. (We therefore exclude the exchange of protons.) The Hamiltonian for the vibrational motion of the nuclei thereby becomes

$$H^{\mathrm{nu}}_{\mathrm{dc}}(F) = \underline{1}\left(-\frac{1}{M}\frac{d^2}{dR^2} + \frac{1}{R}\right) + \underline{H}^{\mathrm{el}}_{\mathrm{dc}}(F,R), \tag{14}$$

where $\underline{1}$ is the unit matrix. We solved the eigenvalue problem for this motion using the discrete variable representation method [17].

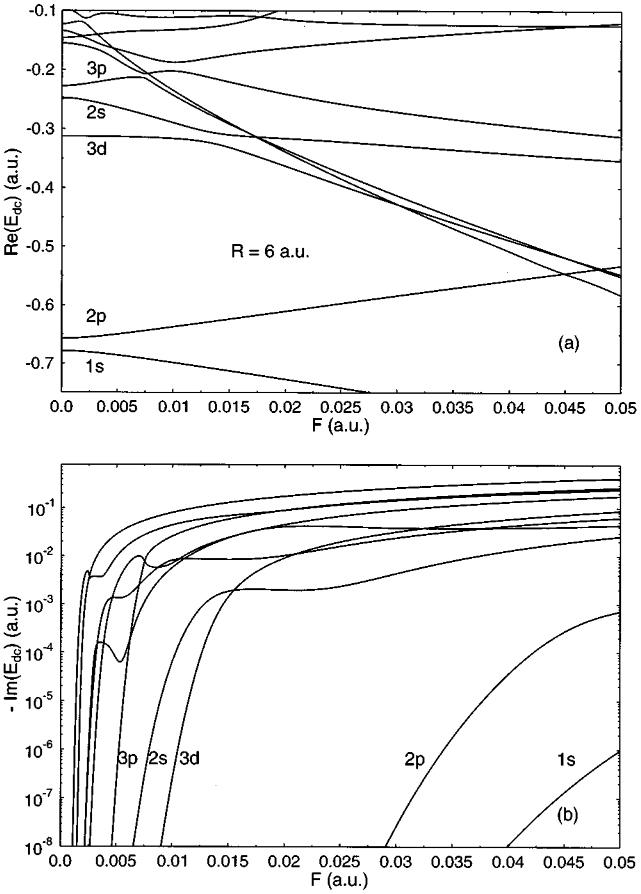

FIG. 5. Same as Fig. 3, but for $R=6$ a.u.

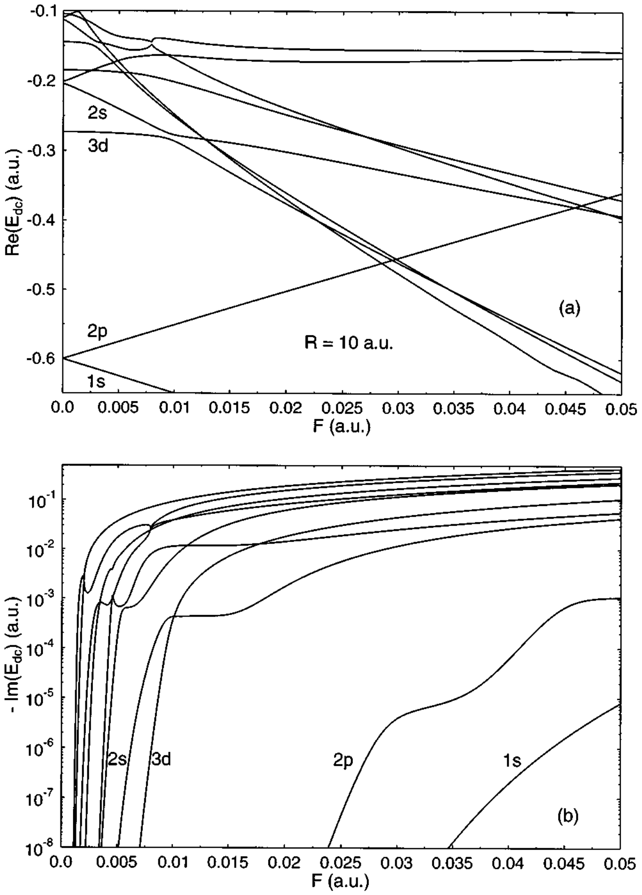

FIG. 6. Same as Fig. 3, but for $R=10$ a.u.

III. RESULTS

A. dc shifts and widths of electronic levels

In Fig. 3 we show, over a range of R, the real and imaginary parts of the quasienergies [the eigenvalues of $H_{\mathrm{dc}}^{\mathrm{el}}(F,R)$] of various electronic states of $\mathrm{H}_2{}^+$ in the presence of a dc field whose strength is $F=0.0533$ a.u. Recall that the half-width of a level, due to its decay, is, with a change in sign, the imaginary part of the quasienergy of that level. We continue to label the levels by the field-free united-atom-limit quantum numbers since as F vanishes the dressed electronic states reduce to the field-free eigenstates, except at $R=0$ and $R=\infty$.

We see in Fig. 3(a) that as R increases the real parts of the $1s$ and $2p$ quasienergies begin to diverge from each other at around $R=3$ a.u. Parity is no longer a good quantum number and the field-free degeneracy of the $1s$ and $2p$ levels in the separated-atom limit is removed. Rather, at large R, the real parts of the $1s$ and $2p$ quasienergies are split by FR since in the field-free limit the electron, in a state of definite parity, spends half the time about one proton and the other half about the other proton, so it has a root-mean-square average dipole moment of magnitude $R/2$ about the midpoint (center-of-mass) of the protons. Thus, when R is moderately large and increasing, the $1s$ level shifts downward by $FR/2$ and the $2p$ level shifts upward by $FR/2$. In general, for every pair of field-free levels of opposite parity that are degenerate in the separated-atom limit, one level shifts upward and the other downward when R increases in the presence of a field.

As R increases beyond 4 a.u. the real part of the $2p$ quasienergy undergoes several *true* crossings with the real parts of quasienergies of levels that, in the absence of the field, would be at much higher energy. A true crossing in the real (imaginary) parts of two quasienergies is normally accompanied by an avoided crossing in the imaginary (real) parts of these quasienergies [18], and evidently this is the case in Fig. 3. The avoided crossings experienced by the imaginary part of the $2p$ quasienergy result in peaks in the ionization width of the $2p$ level, seen in Fig. 3(b) at about $R=5$, 9, and 14 a.u. In the vicinity of a crossing the $2p$ state is mixed with energetically nearby ‘‘highly excited’’ states that have large ionization widths. As is evident from our discussion of Figs. 4–6 below, these highly excited states can decay through over-the-barrier ionization. Hence, once the molecular ion is transferred to one of these states it breaks up rapidly. Note that the peaks at $R=5$ and 14 a.u. are much weaker than the peak at 9 a.u. and peaks at still larger R (not shown) can be expected to be even weaker; we explain this feature in the next paragraph, where we elaborate further on the mechanism for enhancement of the $2p$ width.

As already illustrated in Fig. 1, an external dc field distorts the two-well electronic potential, raising the outer edge of one well and depressing the outer edge of the other well. In general, if the electron is in a state whose energy shifts upward as R increases, the electron spends more time in the higher well, and vice versa. Thus the breakdown of inversion

TABLE I. Comparison of our estimates (lower rows) with those of Zuo and Bandrauk [8] (upper rows) for the dc widths Γ_{1s} and Γ_{2p}, respectively, of the $1s$ and $2p$ energy levels of $H_2{}^+$. The dc field strength $F=0.0533$ a.u.

R (a.u.)	Γ_{1s} (a.u.)	Γ_{2p} (a.u.)
6	2.2×10^{-6}	9.8×10^{-4}
	5.69×10^{-6}	1.87×10^{-3}
10	1.3×10^{-5}	1.5×10^{-3}
	3.92×10^{-5}	2.20×10^{-3}
14	2.5×10^{-5}	2.8×10^{-4}
	7.30×10^{-5}	6.78×10^{-4}

symmetry leads to the localization of the electron in one of the wells [7,9,10]. Referring to Fig. 3 again, we see that, beyond 4 a.u., the $2p$ level shifts upward through levels that shift downward as R increases and hence at large R the $2p$ state is localized in the higher well, while the states corresponding to these downward shifting levels are localized in the lower well [19]. Therefore, the resonances in the $2p$ width result from the resonant transfer of the electron from a state in the higher well to a highly excited state in the lower well. Over-the-barrier ionization from the higher well, when it is possible, is impeded by backscattering as the electron attempts to pass over two humps: the one between the wells and the outer hump of the lower well; over-the-barrier ionization from the lower well can proceed more easily since the electron has to pass over only the outer hump of this well. As R increases, the outer hump of the lower well becomes narrower and less of an obstacle to over-the-barrier ionization, but this is offset by the fact that the probability of a transition from a state localized in the higher well to one localized in the lower well decreases as R increases since the overlap of the wave functions of the two states becomes small. Consequently, the resonance peak at 9 a.u. is the most prominent and resonances at very large R are barely noticeable.

Incidentally, not only is inversion symmetry lost in the presence of an external dc field, the hidden symmetry associated with the separability of the electronic Hamiltonian in spheroidal coordinates is also lost. However, at asymptotically large R this hidden symmetry is restored since the dressed electronic Hamiltonian is separable in parabolic coordinates. (In the separated-atom limit the external dc field exerts a spatially uniform force on the isolated hydrogen atom and in that respect it acts in a similar way to the isolated proton.)

Zuo and Bandrauk [7] have calculated the dc widths of the $1s$ and $2p$ levels at the field strength 0.0533 a.u., for $R=6$, 10, and 14 a.u. In Table I we compare our estimates of these widths with those of Zuo and Bandrauk. Our estimates are larger than those of Zuo and Bandrauk by a factor of about 2 or 3.

In Figs. 4–6 we show the quasienergies of various electronic levels over a range of dc field strengths and for $R=2$, 6, or 10 a.u. We see that the widths of the more excited levels, when plotted on a logarithmic scale, at first rise very rapidly as the field strength F increases (on a linear scale), but as F increases further these widths bend sharply and subsequently increase more gently, as is characteristic of the transition from electron tunneling to over-the-barrier ionization [20]. At $R=6$ and 10 a.u. the imaginary part of the $2p$ quasienergy undergoes avoided crossings corresponding to the true crossings of the real part of the $2p$ quasienergy with the real parts of quasienergies of highly exited states (the avoided crossing of the $2p$ quasienergy at $R=6$ a.u. is

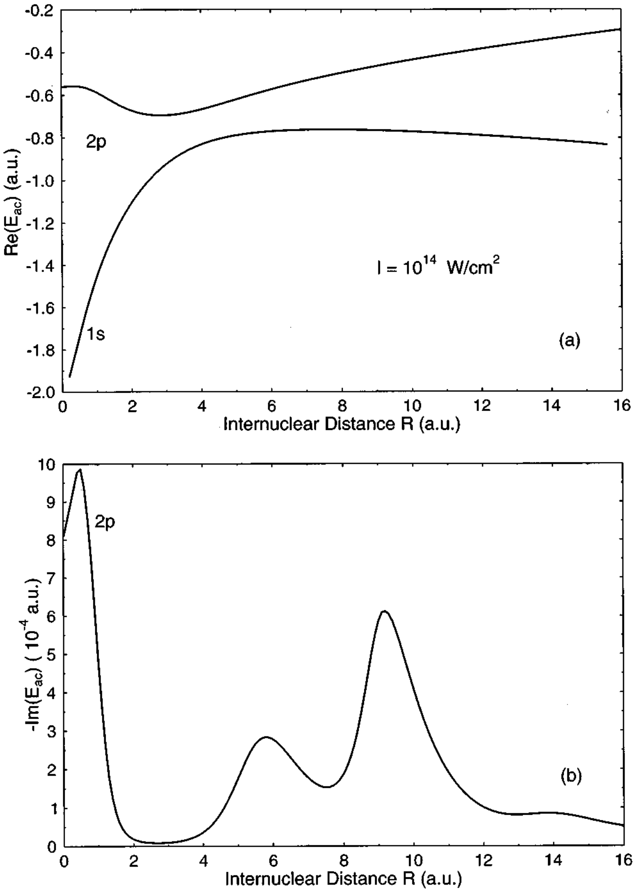

FIG. 7. (a) Real parts of the $1s$ and $2p$ quasienergies and (b) imaginary part of the $2p$ quasienergy, vs R, to zeroth order in the frequency when a linearly polarized ac field of intensity 1×10^{14} W/cm^2 is present.

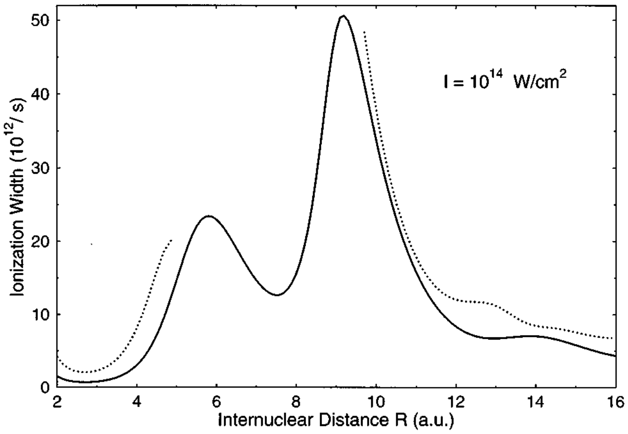

FIG. 8. $2p$ width, vs R, to zeroth order in the frequency (solid curve) and through second order in the frequency (dotted curve) when a linearly polarized ac field of wavelength 1064 nm and intensity 1×10^{14} W/cm^2 is present.

not so obvious; it would be obvious if we were to plot the width out to $F = 0.06$ a.u., which we have checked but not shown).

B. ac shifts and widths of electronic levels

In Fig. 3 we showed the quasienergies of various electronic states vs R when a dc field of strength $F = 0.0533$ a.u. is present. A dc field of this strength corresponds to the peak strength of a linearly polarized ac field whose intensity is 1×10^{14} W/cm^2. In Fig. 7 we show the cycle-averaged dc quasienergy, i.e., the (frequency-independent) zeroth-order term in the ω^2 expansion, vs R for the $1s$ and $2p$ electronic states when a linearly polarized ac field of intensity 1×10^{14} W/cm^2 is present. (We do not show the imaginary part of the $1s$ quasienergy since it is very small and would not be visible on a linear scale.) Cycle-averaging results in a significant decrease in the absolute heights of the peaks in the $2p$ width, which is reasonable since the magnitude of the ac electric field is small for part of the cycle. However, the ratios of the peak heights are not substantially altered.

We now consider the effect of including the first correction $E^{(2)}(F_0)\omega^2$ to our estimate of the $2p$ width. At values of R near a peak in the $2p$ width, this correction becomes meaningless since the $2p$ dc quasienergy is nearly degenerate with one or more other dc quasienergies and the ω^2 expansion should be reformulated to take into account these degeneracies (just as Rayleigh-Schrödinger perturbation theory must be reformulated when degeneracies are present in the absence of the perturbation). We have not carried out this reformulation. However, at values of R not too close to the peaks the first correction should be meaningful at sufficiently low frequencies. In Fig. 8 we show the result of including the first correction in the $2p$ width when the wavelength is 1064 nm (and the intensity is 1×10^{14} W/cm^2) and when R is not in the vicinity of a peak; evidently this correction is small.

Zuo and Bandrauk [7] have numerically solved the time-dependent Schrödinger equation for $H_2{}^+$, with nuclei frozen at various values of R, in the presence of a laser field, of wavelength 1064 nm, that is turned on linearly in five optical cycles (17.5 fs) and then held at the constant intensity 1×10^{14} W/cm^2. They find that significant population is transferred from the $1s$ state to the $2p$ state. In their calculation the continuum flux was removed at the boundaries of their numerical grid and they obtained a rate for ionization by fitting the loss of flux in a boundary region to a single exponential. In Fig. 1 of their paper, Zuo and Bandrauk [7] present results for the ionization rate of the molecule vs R; their results are qualitatively similar to our results for ionization from the $2p$ state, shown in Fig. 7, although our resonance peaks are at slightly different positions. Zuo and Bandrauk (see also [9] and [10]) attribute these peaks to over-the-barrier ionization directly from the $2p$ state [21]. As indicated above, we attribute these peaks to the resonant transfer of population out of the $2p$ state to one or more energetically nearby highly excited states localized in the lower well; over-the-barrier ionization from the lower well can proceed relatively unimpeded by electron backscattering.

Incidentally, the dressed $1s$ level does not have near degeneracies with other levels, over the range of R considered here, and therefore one might expect the ω^2 correction to the $1s$ quasienergy to be meaningful over this entire range of R. However, the calculation of $E^{(2)}(F_0)$ involves an integral over τ; see Eq. (6), recalling that $F = F_0 \sin(\tau)$. In Fig. 9 we show the real and imaginary parts of the integrand of $E^{(2)}(F_0)$ vs τ for the $1s$ quasienergy and for various values of R and an intensity of 1×10^{14} W/cm^2. The real and imaginary parts of the integrand of $E^{(2)}(F_0)$ vanish in the limit that τ tends to $\pi/2$ since the derivative of $F_0 \sin(\tau)$ vanishes. The imaginary part of the integrand of $E^{(2)}(F_0)$ also vanishes in the limit that τ tends to 0 since $F_0 \sin(\tau)$ vanishes and the ionization width is identically zero if there is no external field. However, the real part of the integrand of $E^{(2)}(F_0)$ at $\tau = 0$ becomes extremely large (and negative) as R increases since the field-free $1s$ and $2p$ levels become degenerate as R increases. Hence the ω^2 correction to the real part of the $1s$ quasienergy breaks down at large R.

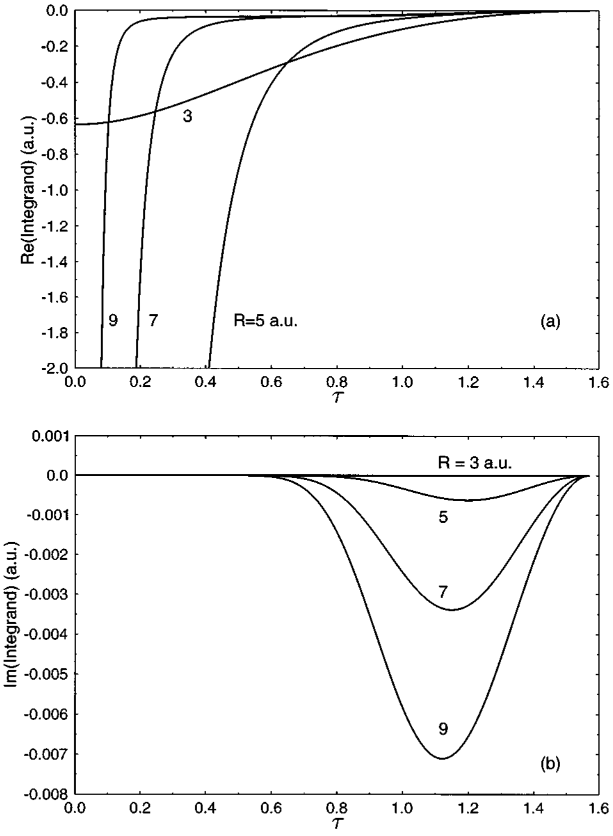

FIG. 9. (a) Real and (b) imaginary parts of the integrand of the coefficient of the ω^2 correction to the $1s$ quasienergy vs the integration variable τ for $0 \leqslant \tau \leqslant \pi/2$, for $R = 3$, 5, 7, and 9 a.u., and for an intensity of 1×10^{14} W/cm^2.

C. dc and ac shifts and widths of vibrational levels

Recently, Ilkov *et al.* [11] measured the rate for dissociation of $H_2{}^+$ in the presence of a CO_2 laser (wavelength 10 μm). The molecular ion was produced primarily in the $v = 2$ and 3 vibrational states after photoionization of the neutral H_2 molecule. The threshold intensity for dissociation of the molecular ion was measured (after assuming a model for fitting the data) to be $(1.65 \pm 0.2) \times 10^{13}$ W/cm^2. Using the chaotic dissociation model of Goggin and Milloni [22],

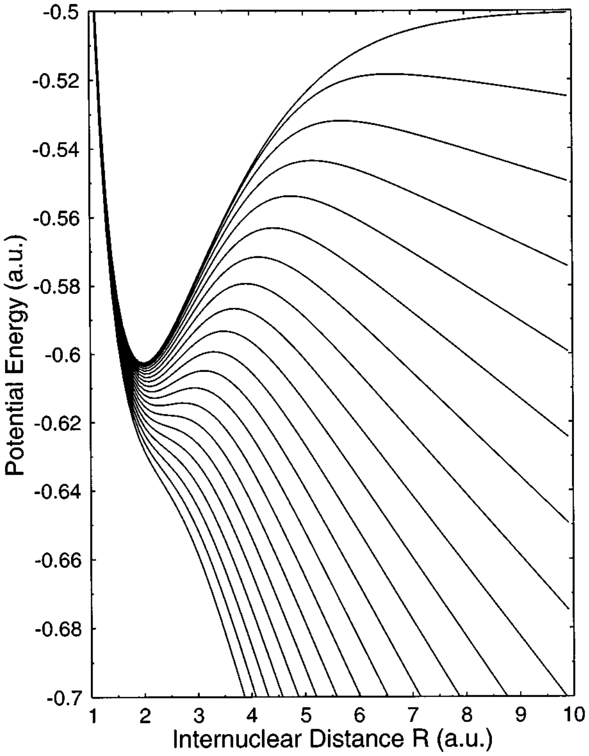

FIG. 10. Potential experienced by the protons when $H_2{}^+$ is in the ground electronic state and a dc field is present. The strength of the field varies from 0 (upper curve) to 0.1 a.u. (lowest curve) in steps of 0.005 a.u.

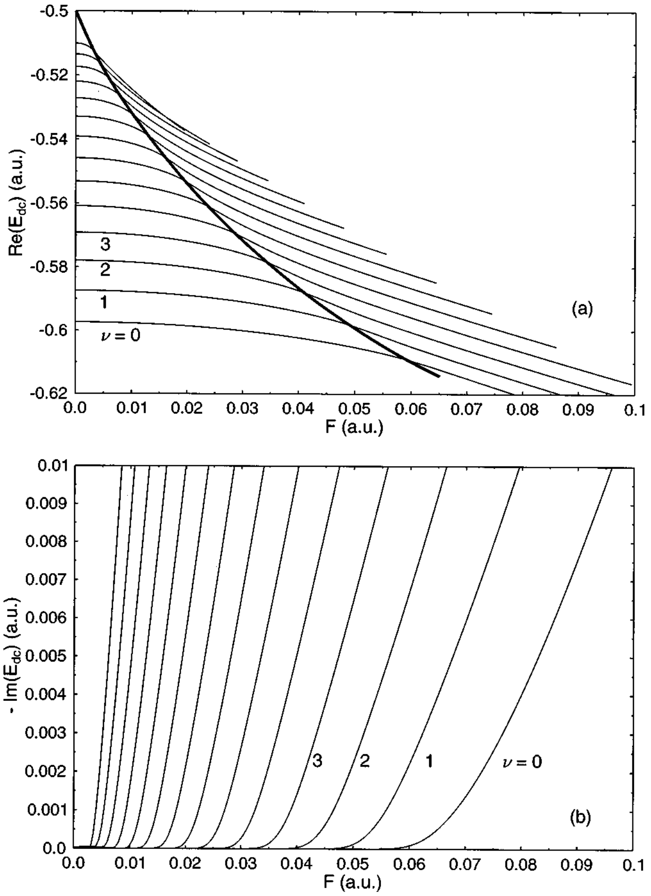

FIG. 11. (a) Real and (b) imaginary parts of the quasienergies of vibrational levels $v=0,1,\ldots,13$ when $H_2{}^+$ is in the ground electronic state and a dc field of strength F is present. The thick curve in (a) is the peak energy of the barrier experienced by the protons.

Ilkov *et al.* obtained the theoretical estimates 2.6×10^{13} W/cm^2 and 1.3×10^{13} W/cm^2 for the threshold intensities for dissociation from the $v=2$ and 3 vibrational states, respectively; these values are quite close to the measured threshold intensity.

In Fig. 10 we show the potential experienced by the protons when the electron is in the 1*s* state and a dc field of various strengths F is present [23]. At nonvanishing but moderately weak field strengths the potential has a wide barrier through which the protons can, in principle, tunnel to freedom, but, as noted in the Introduction, the tunneling rate is extremely small due to the relatively small de Broglie wavelength of a proton. As F increases, the barrier is suppressed and it becomes possible for the proton to pass over the top of the barrier. At very high field strengths the barrier disappears.

We have calculated the rates for dissociation by a dc field from the first 14 vibrational levels of the ground electronic state and we show our results in Fig. 11. As expected, the rate is extremely small for field strengths below the threshold at which over-the-barrier dissociation is possible. We have plotted the peak energy of the barrier vs F; this is the thick line in Fig. 11(a) and it is intersected by the real part of the quasienergy of each vibrational level at the over-the-barrier threshold for that level. Note we have used a linear scale to plot the dissociation rate in Fig. 11(b); on a linear scale the rate rises dramatically as F increases beyond the over-the-barrier threshold, making it easier to identify the threshold for dissociation by a dc field with the over-the-barrier threshold. The threshold field strengths for the $v=2$ and 3 vibrational states are 0.041 and 0.034 a.u., respectively, which correspond to peak values of ac fields that have intensities 5.9×10^{13} W/cm^2 and 4.2×10^{13} W/cm^2, respectively [24]. Cycle averaging the dc quasienergy results in threshold in-

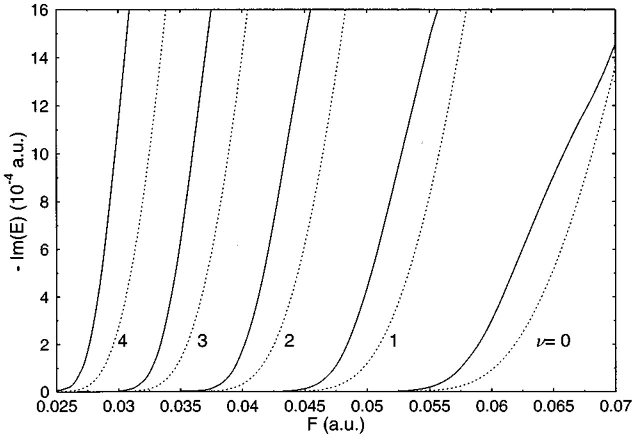

FIG. 12. Imaginary parts of the quasienergies of vibrational levels $v=0-4$ for a dc field (dotted curves) and an ac field of wavelength 10 μm (solid curves) vs the peak strength F of the field. The ac widths were estimated from the first two terms of the ω^2 expansion of the quasienergy.

tensities that are about 20% higher and therefore substantially higher than the values that were measured and calculated using the model of Goggin and Milloni.

Ilkov *et al.* have criticized the quasistatic picture of over-the-barrier dissociation in the context of their experiment since the vibrational motion of the nuclei is not fast on the time scale of one oscillation of CO_2 laser light. We note, however, that since the dissociation rate increases so dramatically as F increases beyond the threshold field strength, the probability for a proton to exit over the top of the barrier should be significant even though the allowed exit time is small on the time scale of vibrational motion. Furthermore, the top of the barrier is not only suppressed as F increases, it also moves to smaller values of R so that a proton does not have to travel so far to reach the exit. To investigate whether the oscillations of the CO_2 laser light invalidate the quasistatic picture, we have calculated the first correction $E^{(2)}(F_0)\omega^2$ to the cycle-averaged dc rate for dissociation from the $v=0-4$ vibrational states at the CO_2 laser wavelength (10 μm). There are no degeneracies to worry about in this calculation. In Fig. 12 we show our estimates of the half-widths based on including the first two terms of the ω^2 expansion and for comparison we show also the unaveraged dc half-widths (which are smaller than the cycle-averaged half-widths). We define the threshold intensity for dissociation by a low-frequency ac field as follows: We first observe that in the case of a dc field the half-width at the over-the-barrier threshold has about the same value, roughly 7×10^{-5} a.u., for all vibrational levels. Therefore a convenient definition of the ac threshold intensity is the intensity for which the ac half-width is equal to 7×10^{-5} a.u. Using this definition we find the ac threshold intensities for the $v=2$ and 3 vibrational states to be 5.3×10^{13} W/cm^2 and 3.6×10^{13} W/cm^2, respectively, which are 10–14 % lower than the dc threshold intensities and about 30% lower than the cycle-averaged dc threshold intensities, so that the ω^2 correction is non-negligible. Our values of the ac threshold intensities are still a factor of 2 or 3 larger than the values quoted by Ilkov *et al.*, but the discrepancies could be due to a number of factors. (i) There is no unique definition of the threshold intensity. (ii) Ilkov *et al.* fit their experimental data to a model that assumes the dissociation rate is zero below the threshold intensity and constant above, in conflict with our results shown in Figs. 11 and 12. Using this fit they obtain not only the threshold intensity but also the dissociation rate; they quote a rate of $(1.7\pm0.4)\times10^9$ s^{-1} compared to our much larger rate of 3×10^{12} s^{-1} (corresponding to a half-width of 7×10^{-5} a.u.). However, if we were to calculate the rate for dissociation from, say, the $v=2$ vibrational level at the threshold intensity 1.65×10^{13} W/cm^2 quoted by Ilkov *et al.*, we would obtain a much smaller rate of 2×10^7 s^{-1}. (iii) When Ilkov *et al.* used the model of Goggin and Milloni they made approximations for the dynamical quantities (e.g., potentials and dipole couplings) that differ from our approximations.

Finally, we concur with Dietrich and Corkum [5] that chaotic dissociation and over-the-barrier dissociation appear to be related. Inspection of Fig. 11 shows that Chirikov's condition for the onset of chaotic behavior, that the spacing between two neighboring resonances is smaller than the combined widths of the resonances, is satisfied not far above the threshold field strength.

Note added in proof. After completion of this work we learned that M. Plummer and J. F. McCann recently performed similar calculations of dc and ac widths of electronic levels of $H_2{}^+$. Their results [J. Phys. B (to be published)] are in excellent agreement with ours, where comparison is possible.

ACKNOWLEDGMENT

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peaked in the lower well. When a downshifting eigenstate is resonant with the $2p$ state its probability density is peaked in both wells.

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[24] These values are a little larger than the values quoted by Ilkov *et al.* The difference is due presumably to the difference in the approximations to the dynamical quantities (e.g., potentials and dipole couplings) used in the calculation; Ilkov *et al.* adopted the approximations described in Ref. [5].