Two-Color Coherent Control of H_2^+ Photodissociation in Intense Laser Fields

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We study the multiphoton dissociation of H_2^+ by a coherent superposition of an intense short pulsed laser radiation and one of its harmonics (second or third), in a phase-locked regime. We show that the total dissociation probability, the energy distribution, and the direction of ejection of the protons are very sensitive to the relative phase of the two radiations. A high degree of control may thus be achieved for the branching ratio between dissociation via bond-softening and above-threshold dissociation, in the realm of current experimental capabilities.

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Molecular dissociation in strong laser fields has been actively investigated in the past few years, both experimentally and theoretically. Several interesting processes have been found: (i) above-threshold dissociation (ATD) [1,2] with stimulated emission as well as multiphoton absorption occurring in the dissociation continuum; (ii) bond softening, [2,3] when a potential barrier in the dressed potential curves is sufficiently lowered by the radiative interaction that the initial vibrational level becomes unbound; (iii) suppression of dissociation, or stabilization [4] due to temporary vibrational trapping in upper potential wells in the dressed potential curves [5]. The relative importance of these three competing processes depends on the initial vibrational level, the laser intensity and wavelength, and the pulse duration. From the existing studies the ATD process appears to be the "loser," at least when starting from a mixture of vibrational levels, because dissociation by bond softening is very rapid as soon as the potential barrier can be overpassed.

We show in this Letter that ATD in H_2^+ can be strongly enhanced by combining the laser radiation with one of its harmonics and varying the relative phase between the two radiations, in a phase-locked regime. It has been already demonstrated that the coherent superposition of two different frequencies leads to interesting new phenomena in multiphonon atomic ionization [6-9], where the total ionization rate, the electron angular, and energy distribution [9] depend strongly on the relative intensity and phase of the two radiations. Although the mechanisms are distinctly different here, we find that the same type of behavior should be observable for multiphoton dissociation, including a pronounced asymmetry in the direction of proton ejection, for the case of even (second) harmonic where g and u symmetries can interfere with the same proton energy group. This work extends to strong-field and nonperturbative treatments of various proposals [10] that weak-field photodissociation and predissociation might be controlled by a coherent superposition of two phase-related radiations. Our theoretical study is designed to present realistic predictions concerning the coherent control of H_2^+ dissociation, within the realm of current experimental capabilities.

Using the splitting technique of the short-time propagator [11], we solve the time-dependent Schrödinger equation for H_2^+ in the classical electric field

$$\mathbf{E}(t)=f(t)[E_f\cos(\omega_f t)+E_h\cos(\omega_h t+\varphi)]\hat{\mathbf{e}}\,, \qquad (1)$$

with $\omega_h=2\omega_f$ for the second and $\omega_h=3\omega_f$ for the third harmonic (field amplitude E_h), combined with the fundamental radiation (amplitude E_f). Both frequencies are linearly polarized along $\hat{\mathbf{e}}$. The pulse shape is approximated by the Gaussian-like expression $f(t)=\sin^2(\pi t/2T_p)$, with total pulse duration $2T_p$.

The two-color dissociation process may be schematized as

$$H_2^+(1s\sigma_g,J,M,v)+n_f\hbar\omega_f+n_h\hbar\omega_h \rightarrow H^+ + H(1s)+\varepsilon(n_f,n_h), \qquad (2)$$

which already shows its complexity with respect to one-color dissociation: Each proton energy group may result from the absorption or stimulated emission of different combinations (n_f,n_h) of photons with the fundamental or harmonic frequencies. In addition, for the case of even (second here) harmonic both the u and g dissociation may lead to the same proton energy (e.g., $n_f=2$, g symmetry and $n_h=1$, u symmetry). This intrinsic many-channel aspect will favor interference effects which are shown below to dominate the whole process and are very sensitive to phase control. We chose the wavelength 780 nm, in the frequency domain of the Ti:sapphire laser which can deliver intense short pulses (in the range of 10^{15} W/cm^2, 150 fs) and is presently used by several groups of experimentators. For this wavelength, starting from the initial vibrational level $v=1$, the minimum number of photons required for dissociation by the fundamental radiation alone is $n_f=2$, while dissociation may occur with absorption of a single photon of the second (390 nm) or the third (260 nm) harmonic.

Our calculations only include the radiative coupling, in the dipole *length* representation, between the attractive

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TABLE I. $H_2{}^+$ total dissociation probability for a 150 fs laser pulse (total pulse duration $2T_p = 300$ fs). I_f, I_h, λ_f, and λ are the intensities and wavelengths of the fundamental and harmonic radiations. Initial vibrational level is $v = 1$. (a) Results for the second harmonic with different relative phase φ, compared to the one-color results. (b) Same for the third harmonic.

λ_f (nm)	I_f (W/cm^2)	λ_h (nm)	I_h (W/cm^2)	φ	Dissociation (%)
			(a)		
780	1×10^{14}				0.15
		390	3×10^{13}		0.03
780	1×10^{14}	390	3×10^{13}	0	27.30
				$\pi/2$	38.50
				π	27.30
			(b)		
780	1×10^{14}				0.15
		260	5×10^{12}		1.82
780	1×10^{14}	260	5×10^{12}	0	8.91
				$\pi/2$	7.36
				π	6.22
				$3\pi/2$	7.36

ground state $1s\sigma_g$ and the repulsive first excited state $2p\sigma_u$ of $H_2{}^+$. We also ignore the ionization of $H_2{}^+$, based on specific calculations of the ionization rate for the conditions of this paper, using codes developed by Krause, Schafer, and Kulander [12]. The laser parameters in our calculations avoid excessive competition with ionization as predicted by Chelkowski, Zuo, and Bandrauk [13] for stronger fields and shorter wavelengths.

It is now well established [2,14] that strong field dissociation with a linearly polarized laser yields fragments strongly oriented along the polarization vector $\hat{\mathbf{e}}$. The ions are detected in two groups ("forward" and "backward") if the detector is set on the polarization axis. This alignment results from optical pumping (probably already achieved during the ionization step from the neutral) to {high J, low M} rotational states in Eq. (2) which are dictated by the magnitude of the Rabi frequency [15]. This justifies our constraining the interatomic coordinate $\mathbf{R}$ along $\hat{\mathbf{e}}$: Defining $\cos\theta = \mathbf{R}\cdot\hat{\mathbf{e}}$, we can restrict the angular distribution analysis to the emission angles $\theta = 0$ and $\theta = \pi$, with respect to the polarization (and detection) axis.

In our framework of approximations the total wave function for $H_2{}^+$ is thus expressed as

$$\Phi(\mathbf{r},\mathbf{R},t) = \phi_g(\mathbf{r},\mathbf{R})F_g(R,\theta,t) + \phi_u(\mathbf{r},\mathbf{R})F_u(R,\theta,t), \quad (3)$$

where ϕ_g and ϕ_u are the $1s\sigma_g$ and $2p\sigma_u$ electronic wave functions and F_g, F_u summarize the symmetrized rovibrational nuclear wave functions. The radiative coupling $E(t)\mu_{gu}(R)\cos\theta$ depends on orientation and the present calculations are all performed with $\theta = 0$, and $H_2{}^+$ perfectly aligned in the field. We have also performed calculations with F_g and F_u expanded in a complete rotational basis set and have found quantitative confirmation of this alignment effect, for both one- and two-color interactions. These results validate the present model and will be presented in a longer paper.

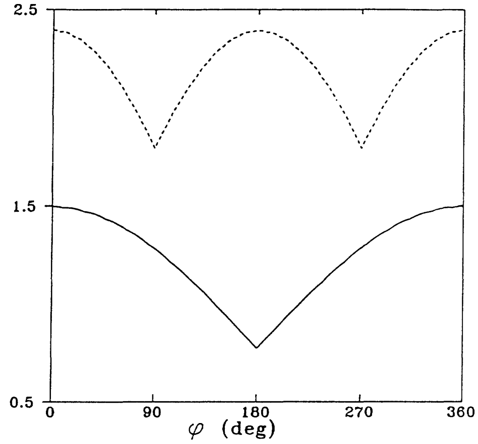

FIG. 1. Maximum laser intensity reached during the pulse as a function of the relative phase for the third (solid line, $I_h = 5\times10^{12}$ W/cm^2) and the second harmonic (dotted line, $I_h = 3\times10^{13}$ W/cm^2), with $\lambda_f = 780$ nm and $I_f = 10^{14}$ W/cm^2.

Table I shows that adding the second or third harmonic, even with a weak intensity, results in a dramatic enhancement of the total dissociation probability with respect to the one-color results. The magnitude and the phase dependence of these results demonstrate a very distinct difference between ionization and dissociation. At these wavelengths the global ionization process is well described by a tunneling model [8] and depends primarily on the maximum field strength displayed in Fig. 1, amplified by the nonlinearity of the process. Certainly here, the symmetry of the electric field with respect to the phase is reproduced in the dissociation probability (e.g., φ and $\varphi+\pi$ for the second harmonic). However, the phase dependence of the total probability is not simply related to the maximum value of the electric field [compare Table I(a) and Fig. 1], a first indication that dissociation occurs via interfering paths combining the two radiations and is closer to the less understood multiphoton limit in ionization, in the nonperturbative regime.

This appears more clearly from the proton energy distribution shown in Fig. 2 for the third harmonic with different phases. Each spectrum consists of three main peaks spaced by the energy $\hbar\omega_f/2 = 0.8$ eV. The second and third peaks are due to ATD with excess-photon energy equally shared between H and H^+. In terms of net numbers (n_f, n_h) of absorbed photons [see Eq. (2)], the three successive peaks could be labeled as I: (2,0); II: (3,0) degenerate with (0,1); III: (4,0) degenerate with (1,1). They correspond to the asymptotic dissociation limits I, II, III in Fig. 3, which shows the adiabatic field-dressed potential curves obtained by diagonalizing the time-independent two-color Floquet Hamiltonian with

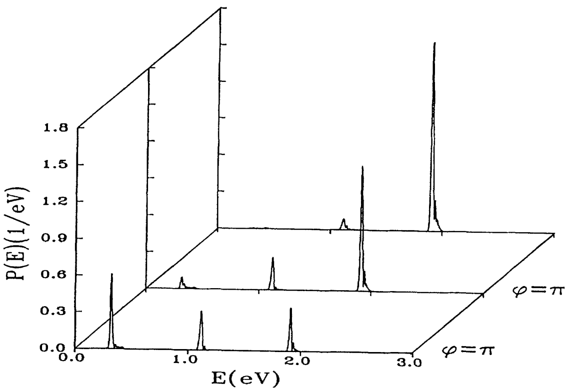

FIG. 2. Proton kinetic energy distribution for different phases of the third harmonic ($I_h = 5\times10^{12}$ W/cm^2) with respect to the fundamental 780 nm radiation ($I_f = 10^{14}$ W/cm^2). Total pulse duration 300 fs ($T_p = 150$ fs). Initial vibrational level is $v=1$.

commensurable frequencies [7], including the phase lag of the harmonic. However, it is clear from Fig. 3 that each of these limits may be reached by several dissociation paths involving stimulated emission as well as further absorption at the numerous avoided crossings in the adiabatic dressed curves. The most striking feature in Fig. 2 is the large enhancement of the ATD peak III for $\varphi=0$. This is consistent with the $\varphi=0$ curve in Fig. 3, which exhibits a high potential barrier preventing dissociation to the limit I, and favors diabatic passage to the limit III.

Another feature of two-color coherent photodissociation of homonuclear molecules is the phase-controllable asymmetry of ion ejection, in the case of even harmonics. At the end of the laser pulse ($t > 2T_p$) the system has reached the asymptotic region where ϕ_g and ϕ_u reduce to

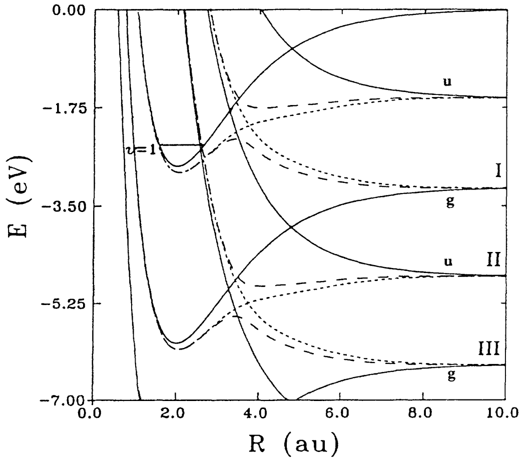

FIG. 3. $H_2{}^+$ $1s\sigma_g$ and $2p\sigma_u$ diabatic dressed potential curves for the 780 nm radiation with the third harmonic (solid line) and adiabatic with $\varphi=0$ (dotted line), and $\varphi=\pi$ (dashed line); $I_f = 10^{14}$ W/cm^2 and $I_h = 5\times10^{12}$ W/cm^2.

$$\begin{aligned}\phi_g &\to (1/\sqrt{2})[\phi_{1s}(\mathbf{r}-\mathbf{R}/2)+\phi_{1s}(\mathbf{r}+\mathbf{R}/2)]\,,\\ \phi_u &\to (1/\sqrt{2})[\phi_{1s}(\mathbf{r}-\mathbf{R}/2)-\phi_{1s}(\mathbf{r}+\mathbf{R}/2)]\,,\end{aligned} \tag{4}$$

in terms of atomic $1s$ orbits centered on one or the other proton. The wave function (3) becomes ($R\to\infty$)

$$\begin{aligned}\Phi \to (1/\sqrt{2})\{&\phi_{1s}(\mathbf{r}-\mathbf{R}/2)(F_g+F_u)\\ &+\phi_{1s}(\mathbf{r}+\mathbf{R}/2)(F_g-F_u)\}\,.\end{aligned} \tag{5}$$

This leads to the probabilities for forward ($\theta=0$) and backward ($\theta=\pi$) proton ejection:

$$\begin{aligned}P_+(\theta=0) &= P_{1s}(\theta=\pi)\\ &=\int |(1/\sqrt{2})(F_g-F_u)|^2 dR\\ &=\tfrac{1}{2}\int [|F_g|^2+|F_u|^2-\mathrm{Re}(F_g^*F_u)]dR\,,\\ P_+(\theta=\pi) &= P_{1s}(\theta=0)\\ &=\int |(1/\sqrt{2})(F_g+F_u)|^2 dR\\ &=\tfrac{1}{2}\int [|F_g|^2+|F_u|^2+\mathrm{Re}(F_g^*F_u)]dR\,,\end{aligned} \tag{6}$$

where the radial integrals are performed for R larger than the range of the molecular potentials. The two probabilities in (6) differ by an interference term between the g and u dissociation paths. In case of one color or two color with odd harmonic processes, u and g dissociations give negligible simultaneous contributions to the same energy peak, and the two probabilities in (6) are equal. But in the even harmonic case the interference term may be present, and leads to the asymmetry observed in Fig. 4. It is due to loss of inversion symmetry in the $\omega+2\omega$ field and reminds one of the angular distribution observed in two-color atomic ionization [9,10,16]. However, while the admixture of odd and even partial waves of photoelectrons explains the asymmetry in the atomic case, in $H_2{}^+$ it is associated with an admixture of the asymptotically degenerate σ_g and σ_u molecular states.

An experimental verification of this new feature seems feasible, with laser intensity carefully chosen [12] to avoid further ionization of the neutral fragments which would attenuate the initial asymmetry. Note the marked difference in the total dissociation probability for the two phases in Fig. 4, which introduces an additional element of control. Although our theoretical treatment does not yet include the permanent dipole moment associated with HD^+, we already anticipate that this forward-backward asymmetry obtained with the even harmonics will allow coherent control of the isotope ratio H^+/D^+ in both its angular and kinetic energy distributions. More generally, we think that the coherent superposition of an intense laser radiation and one of its harmonics should allow very interesting experimental manipulation of dissociation dynamics. A more systematic exploration of control as a

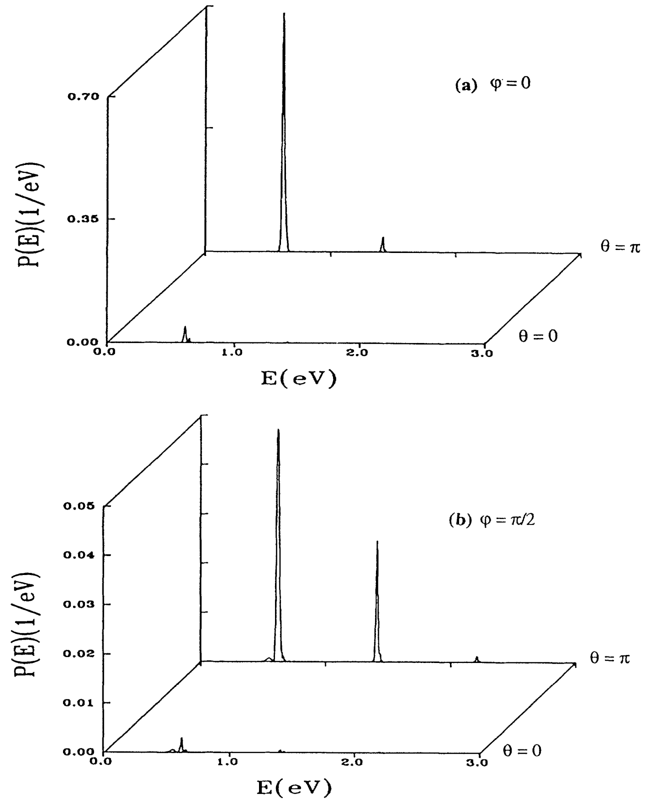

FIG. 4. (a) Forward ($\theta = 0$) and backward ($\theta = \pi$) proton kinetic energy distribution for the second harmonic with $\varphi = 0$. (b) Same for $\varphi = \pi/2$. The laser parameters are $\lambda_f = 780$ nm, $T_p = 150$ fs, $I_f = 2\times10^{13}$ W/cm^2, and $I_h = 2\times10^{12}$ W/cm^2. Here the initial vibrational level is $v = 3$. The total dissociation is 3.6% for $\varphi = 0$ and 0.4% for $\varphi = \pi/2$.

function of intensity, wavelength, and phase will be presented in a longer paper.

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