Enhancement of Vibrational Excitation and Dissociation of H_2^+ in Infrared Laser Pulses

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(Received 20 April 2012; published 18 October 2012)

We study vibrational excitations, dissociation, and ionization of H_2^+ in few-cycle laser pulses over a broad wavelength regime. Our results of numerical simulations supported by model calculations show a many orders-of-magnitude enhancement of vibrational excitation and dissociation (over ionization) of the molecular ion at infrared wavelengths. The enhancement occurs without any chirping of the pulse, which was previously applied to take account of the anharmonicity of the molecular vibrations. The effect is related to strong-field two- and higher-order photon transitions between different vibrational states.

The recent upsurge in the development of intense laser systems operating in the infrared (up to about 5 μm with current technology; for a review, see, e.g., Ref. [1]) was initiated by the interest in the scaling of strong-field parameters with the laser wavelength λ. For example, the cycle-averaged kinetic energy U_p (or ponderomotive energy) of an electron, oscillating in the laser field, increases quadratically with the wavelength. According to an established semiclassical picture [2–4], an electron, which is removed by the electric field of the laser from an atom or molecule, returns to the parent ion in the oscillating field with a maximum kinetic energy of 3.17 U_p. The return of the electron results in scattering of the electron or higher-order harmonic and attosecond pulse generation. An increase of the return energy at longer wavelengths, therefore, leads to radiation extending to high photon energies [5], up to the x-ray regime as demonstrated recently Ref. [6], as well as an increase in the sensitivity of ultrafast imaging techniques, such as laser-induced electron diffraction [7].

Beyond these applications there is now also a resurgent interest in exploring atomic and molecular strong-field phenomena in the infrared wavelength regime. Former experiments with CO_2 lasers operating at about 10 μm revealed the relevance of the (quasistatic) tunneling ionization picture for strong-field physics [8–10]. More recently, the surprising observation of an enhancement of the yield in the low-energy (near-threshold) part of the photoelectron spectrum [11] provided new insights into the ionization dynamics of atoms [12–14]. Since the corresponding photon energies are of the same order as the vibrational energy spacings in molecules, one may expect new insights into the coupling of electronic and nuclear dynamics from studies with infrared lasers as well.

Based on early experimental studies [10,15], it was concluded that strong laser pulses cannot induce a significant vibrational excitation and dissociation of a diatomic molecule without ionizing the molecule, unless the laser pulse is chirped to account for the anharmonicity of the molecular vibrations [16–18]. More recent observations of

a reversed ratio of the ionization-to-dissociation signal in the hydrogen molecular ion using unchirped pulses at near-infrared wavelengths [19,20], however, shed some doubts on this earlier general conclusion.

In view of the resurgence of strong laser systems at infrared wavelengths we reexamined molecular excitation, dissociation, and ionization of the molecular hydrogen ion with unchirped laser pulses over a broad wavelength regime. The results of our numerical calculations (see Fig. 1) show a strong many orders-of-magnitude enhancement of the dissociation probability (solid line: numerical simulations, dashed line: two-level model) in a wavelength regime of about 12 μm for a laser pulse of 10 field cycles and a peak intensity of 5×10^{13} W/cm^2. The dissociation probability at infrared wavelengths is about 10% and exceeds both the dissociation probability at near-infrared wavelengths as well as the ionization probability (dash-dotted line) at infrared wavelengths by a few orders-of-magnitude. We find that the enhancement is due to a strong coupling between different vibrational
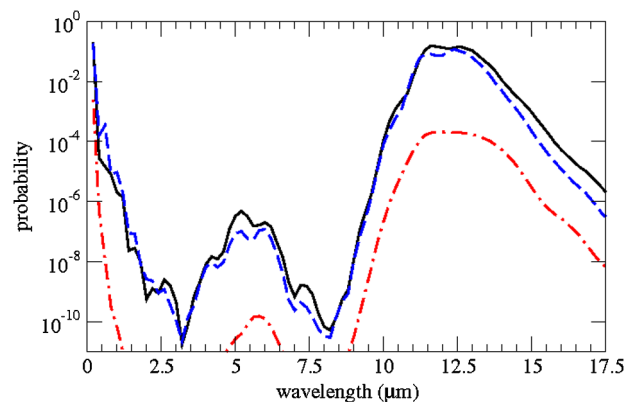

FIG. 1 (color online). Numerical results for the dissociation (black solid line: numerical simulations, blue dashed line: two-level model) and ionization probability (red dash-dotted line) of hydrogen molecular ion interacting with an intense laser pulse as a function of wavelength. Laser parameters: 5×10^{13} W/cm^2 and 10 field cycles.

states based on strong-field two- and higher-order photon transitions [21], which leads to a population of highly excited vibrational states and the efficient dissociation of the molecular ion without significant ionization.

We obtained our results via numerical solutions of the time-dependent Schrödinger equation within a standard two-dimensional (2D) model as well as a simple model including just two electronic states of the hydrogen molecular ion. In the 2D model the motion of the electron as well as the motion of the protons is restricted along the polarization direction of the linearly polarized laser field. The Hamiltonian of the system is given in length gauge as (Hartree atomic units, $e = m = \hbar = 1$, are used throughout):

$$H(x, R, t) = \frac{P^2}{2\mu_p} + \frac{p^2}{2} + x\mathcal{E}(t) + \frac{1}{\sqrt{R^2 + \alpha_p}}$$
$$- \frac{1}{\sqrt{(x - \frac{R}{2})^2 + \alpha_e}} - \frac{1}{\sqrt{(x + \frac{R}{2})^2 + \alpha_e}}, \quad (1)$$

where (P, R), and (p, x) are momentum operators and positions of the relative coordinate of the two protons and the electron, respectively. $\mu_p = M/2$ is the reduced mass with $M = 1836$ being the mass of the proton, and $\alpha_e = 1$ and $\alpha_p = 0.03$ are soft-core parameters. $\mathcal{E}(t) = \mathcal{E}_0 \cos(\omega t)\sin^2(\pi t/NT)$ is the electric field of the linearly polarized laser pulse. As mentioned before, we do not consider a chirping of the laser pulse. We used a spatial grid with resolution $\Delta x = 0.1$ a.u. and $\Delta R = 0.03$ a.u., a total number of 1200 and 3000 grid points in the x- and R-direction, respectively, and mask functions at the boundaries. In the two-level model we assume that the state of the molecular ion is described by a superposition of the two lowest electronic states and the corresponding nuclear dynamics at any time during the interaction with the external field. This leads to a set of coupled equations for the amplitudes of the electronic-vibronic states (for further details of the numerical calculations, see Ref. [21]). In our models we defined dissociation (and ionization in the 2D model) via the integration of the probability density with respect to the relative coordinate of the two protons (and the position of the electron) satisfying $R > 13$ a.u. (and $|x| > R/2 + 7$ a.u.). The population in the different vibrational states of the molecular ion were obtained by projecting the wave function at the end of the pulse onto the field-free vibrational eigenstates, which were obtained by imaginary time propagation.

The results in Fig. 1 show a good agreement between the dissociation probabilities obtained with the 2D numerical grid simulations and with the two-level model. As a function of wavelength we observe a strong decrease of the probability up to about 2.5 μm due to the nonlinearity of the process and the increase of the number of photons to be absorbed from the field. At longer wavelengths there are, however, two (broad) maxima at wavelengths, at which

the photon energy approximately equals ($\approx$ 5–6 μm) or halves ($\approx$ 11–13 μm) the spacings between vibrational energy levels in H_2^+. This indicates that the dissociation proceeds via an efficient vibrational excitation of the molecular ion. We note that the maximum dissociation probability at infrared wavelengths clearly exceeds the corresponding value at near-infrared wavelengths.

Before we further analyze the mechanism leading to this strong enhancement in the dissociation yield, we briefly turn our attention to the ionization of the molecule. The results in Fig. 1 show that the ionization yield is 3 or more orders-of-magnitude smaller than the dissociation probability at a given wavelength in the infrared. Thus, as observed in previous experiments at near-infrared wavelengths Refs. [19,20] and in contrast to a long-standing assumption [15,16], we find that significant dissociation of a diatomic molecule can be achieved in the infrared with negligible ionization of the molecule without chirping the pulse. Furthermore, we note that the dependences of the dissociation and ionization probabilities on the wavelength are very similar, indicating a strong relation between the two processes. To gain further insights we present in Fig. 2(a) the ionization probabilities as a function of the internuclear distance at 5×10^{13} W/cm^2 and $N = 5$ for three different wavelengths (black solid line: 12 μm, red dashed line: 10 μm, blue dash-dotted line: 5 μm). The results show that at the present laser parameters the ionization of the molecular ion likely proceeds via the mechanism of charge-resonance-enhanced ionization [22,23] at internuclear distances of about 10 a.u., which explains the close relation of the ionization signal to the efficient dissociation of the molecular ion. The dependence of the signal on the wavelength indicates the time scale needed to stretch the molecular ion. We also find that the probability to ionize the hydrogen molecular ion at equilibrium internuclear distance [open symbols in Fig. 2(b)] is about 10 orders-of-magnitude smaller than the dissociation probability and independent of the laser wavelength, in agreement with predictions of tunnel ionization [24] [dashed line in Fig. 2(b)].

The enhancement of the dissociation probability at infrared wavelengths is accompanied by a strong population of the excited vibrational levels in the hydrogen molecular ion [Fig. 3(a)], which indicates that the dissociation proceeds via vibrational excitation of the molecule and not via a transition from the ground state to the first excited electronic state at the equilibrium distance. We note that there is a strong total population ($> 10^{-2}$) in the vibrational excited states at about 5–6 μm and 10–12 μm. This excitation, however, results in a much stronger dissociation probability at the longer wavelengths as compared to the shorter ones (see Fig. 1). The reason becomes obvious from the results for the excitation probabilities of individual vibrational levels presented in the panels of Figs. 3(b) and 3(c) for the shorter and longer wavelength regime,
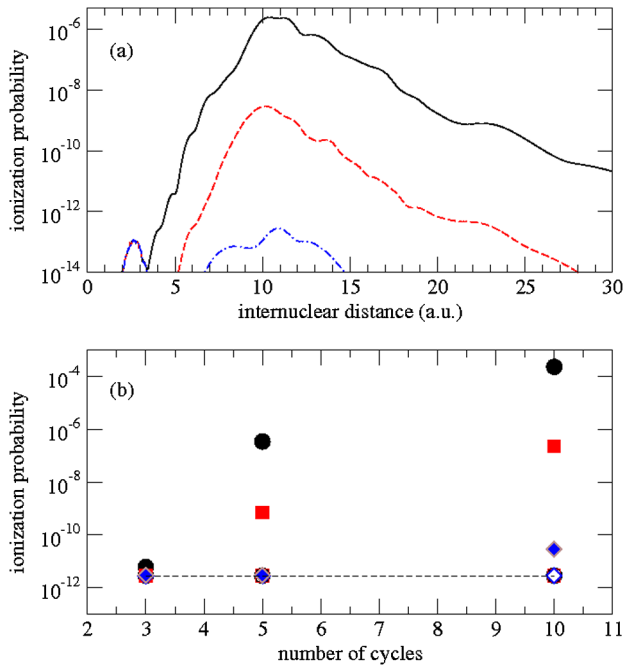
FIG. 2 (color online). (a) Probability of ionization of the hydrogen molecular ion as a function of internuclear separation R at 5×10^{13} W/cm^2 and $N = 5$ for three different wavelengths (black solid line: 12 μm, red dashed line: 10 μm, blue dash-dotted line: 5 μm). (b) Ionization probabilities integrated over $R = 0$–3.5 a.u. (open symbols) and over $R = 3.5$–30 a.u. (filled symbols) as a function of number of cycles for three different wavelengths (black circles: 12 μm, red squares: 10 μm, blue diamonds: 5 μm) at 5×10^{13} W/cm^2. The dashed line is the prediction for the tunnel ionization probability of an atom having the same ionization energy as the hydrogen molecular ion [24].

respectively. At the shorter wavelengths we observe that there is just one vibrational level strongly excited at a given wavelength. Thus, there appears to be a strong coupling between the ground state and one of the excited vibrational state levels, but no further efficient transfer of the excitation energy to higher vibrational levels and, therefore, small probability for dissociation only. In contrast, at the longer wavelengths, excitation of several vibrational levels is seen, in particular at about 12 μm at which we find the largest dissociation probabilities (Fig. 1). In view of the excitation within a few cycles of the electric field of the laser (see also Fig. 4) we expect that there is a transfer of energy directly from the ground state to several excited vibrational levels as well as an efficient energy transfer between the different vibrational excited levels, which results in a rapid excitation of high vibrational states and finally in dissociation of the molecule. At the longer wavelengths the photon energy approximately halves the energy spacing between adjacent vibrational levels in the hydrogen molecular ion and the ultrafast excitation is based on strong-field two- and higher-order photon transitions between the levels in this nonpolar molecule [21].
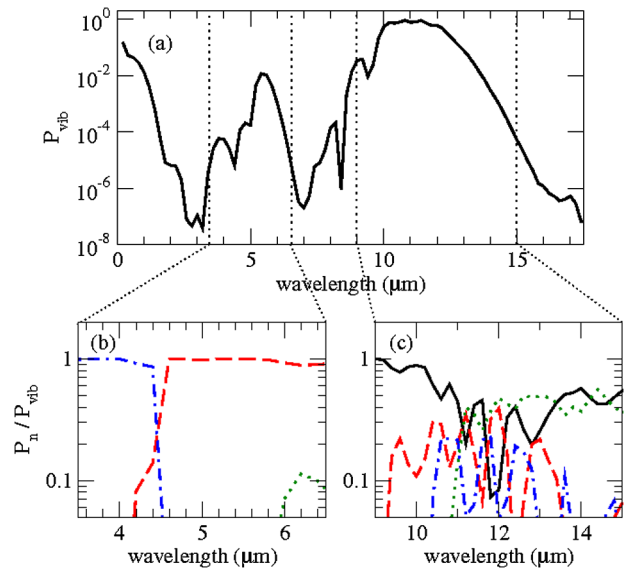

FIG. 3 (color online). (a) Total excitation probability in all vibrational states at the end of the pulse as a function of the laser wavelength. (b) and (c) Excitation probability in individual vibrational levels (black solid line $\nu = 1$, red dashed line $\nu = 2$, blue dash-dotted line $\nu = 3$, green dotted line $\nu = 4$), normalized to the total excitation probability. Pulse parameters are the same as in Fig. 1.

Our interpretation of a strong influence of direct transitions between the ground state and several excited vibrational levels at the present laser parameters is further supported by the results for the population in the ground state (left column, black solid line) and excited vibrational states (left column: total excited state population, dashed blue line and right column: population of lowest excited states) as a function of laser cycles at three different laser intensities, shown in Fig. 4. It is apparent that there is a rather strong excited state population induced by the shortest pulses of just 3 cycles at each of the three intensities considered. At the lowest intensity [panel (a), 3×10^{13} W/cm^2] the population in the excited states decreases while the ground state population increases with the increase of the pulse duration (without significant dissociation of the molecule). The decrease of the ground state population indicates the transition from a nonadiabatic to an adiabatic behavior for longer pulses at this intensity and can be well reproduced by calculations based on two-photon transitions between two vibrational levels [25]. In contrast, we observe significant dissociation in few-cycle pulses at slightly higher intensities [panels (b) and (c), 5×10^{13} W/cm^2 and 7×10^{13} W/cm^2 respectively]. The analysis of the population distribution in the lowest excited vibrational levels for a 3 cycle pulse shows that the excitation energy is more and more equally distributed over several levels as the intensity increases. In view of the duration of the pulse of just 3 cycles we assume that the population is achieved via direct transitions from the initial ground state rather than a ladder climbing
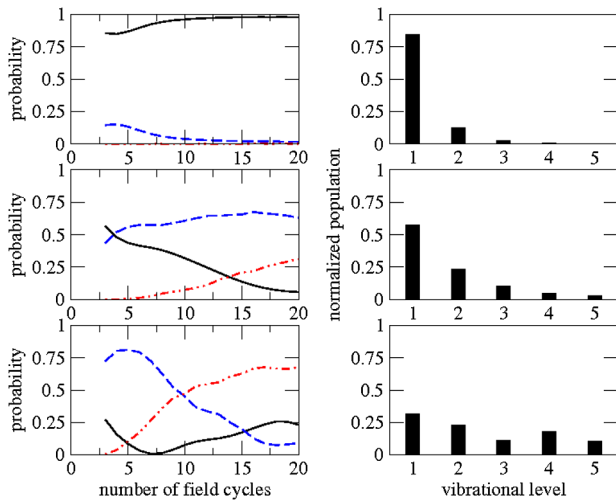
FIG. 4 (color online).   Left column: Population in the ground state (black solid line) and all excited (dashed blue line) vibrational states and dissociation probability (red dash-dotted line) as a function of the number of cycles at 12 μm and 3×10^{13} W/cm^2 (upper panel), 5×10^{13} W/cm^2 (middle), and 7×10^{13} W/cm^2 (lower panel). Right column: Population in the lowest excited vibrational states, normalized to the total excitation probability, in a 3 cycle pulse at 12 μm and 3×10^{13} W/cm^2 (upper panel), 5×10^{13} W/cm^2 (middle), and 7×10^{13} W/cm^2 (lower panel).

process. Towards dissociation this direct energy transfer is then likely accompanied by a coupling of different excited (but not necessarily adjacent) vibrational levels.

Before concluding, we note that recent studies have shown that predictions of the 2D numerical model, used in the present calculations, provide a qualitative understanding of molecular phenomena, which is sufficient in the present context. At near-infrared wavelengths a quantitative discrepancy with results of models based on a full dimensional description of the electron dynamics of up to a factor of 5 has been found [26,27]. It is challenging to apply such high-dimensional models to studies of ionization and dissociation in the infrared wavelength regime beyond 10 μm. In view of the orders-of-magnitude enhancement of dissociation over ionization at infrared wavelengths the results of the lower dimensional model and even the two-level model are, however, sufficient to demonstrate this new and topical phenomenon. To further support this argument, we note that the results for dissociation, obtained by the two methods in Fig. 1 (solid and dashed lines), vary by a factor of up to 5.5 in the wavelength regimes of present interest (5–6 μm and 11–13 μm). The result of a strong enhancement of dissociation at certain wavelengths, our interpretation and conclusions are supported by either one of these results and, therefore, do not depend on small (with respect to a logarithmic scale) quantitative variations.

In summary, we have predicted a strong enhancement of vibrational excitation and dissociation of H$_2^+$ with unchirped laser pulses at infrared wavelengths. The dissociation is accompanied with a low (negligible) ionization of the molecule via the process of charge-resonance-enhanced ionization at larger internuclear distances. The origin of the enhancement has been attributed to strong-field two- and higher-order photon transitions between different vibrational levels of the molecular ion. Our results show that, in contrast to earlier assumptions, a strong vibrational excitation of a diatomic molecule leading to its dissociation without ionization at infrared wavelengths appears to be possible without chirping the laser pulse and without taking account of the anharmonicity of the molecular vibrations.

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