Laser-induced molecular stabilization and trapping and chemical bond hardening in intense laser fields

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We study the intensity-dependent behavior of laser-induced vibrational quasi-energy (VQE) resonance structure and photodisociation rates of H$_2^+$ molecular ions in intense laser fields at 775 nm and report a novel new high-intensity phenomenon. At strong fields, the vibrational levels are shifted and broadened substantially and break into several separate VQE resonance groups. Distortion of the internuclear potential by the fields leads to the formation of various (field-dressed) adiabatic potential wells near multiphoton resonances which can support long-lived resonance states. The most striking finding is that high-lying VQE resonance states can in fact become more stabilized and longer lived at higher laser intensities, a phenomenon which may be termed as "bond hardening". Time-dependent calculations confirm the laser-induced stabilization phenomenon and reveals that molecular population may be trapped simultaneously in different potential wells, at different internuclear separations (multiple well trapping).

1. Introduction

Stimulated by the discoveries of a number of novel nonlinear phenomena in the response of atoms to strong laser fields, such as above-threshold ionization (1) (ATI) and multiple high-order harmonic generation (2), there is a growing new interest in the study of nonlinear multiphoton dissociation (MPD) dynamics of diatomic molecules (3-7). Notably experiments on molecular hydrogen revealed a new phenomenon, referred to as above-threshold dissociation (ATD) (3-5), analogous to ATI in atoms. Furthermore, the molecular bond can be "softened" (bond-softening) (5) by the fields, indicating molecules (in low-lying vibrational states) can be dissociated much more efficiently at higher laser intensities.

In this Letter, we explore the laser-induced vibrational quasi-energy resonance structure and time-dependent multiphoton dynamics of H$_2^+$ molecules and discuss an opposite and novel new high-intensity phenomenon: molecules can be stabilized and the chemical bond can be "hardened" (bond-hardening) in intense laser fields. We focus our study here on the case of 775 nm, as MPD/ATD experiments are being performed around this frequency (8). Theoretical prediction of laser-induced stabilization and bond hardening phenomena has been recently briefly reported elsewhere for a shorter (UV) wavelength case at 266 nm (9). In this Letter, we report for the first time that molecules can be trapped and stabilized at multiple (field-deformed) potential wells at different internuclear separations. Further, we explore the intensity-dependent vibrational quasi-energy resonance structure in strong fields at the longer wavelength, exhibiting delicate molecular structure deformation by the external fields.

2. Molecular structure deformation and stabilization in intense laser fields

We consider the response of the H$_2^+$ molecules to intense monochromatic laser fields. Only two electronic states (1σg and 2πu) will be of relevance here. In the presence of external electromagnetic fields, all the vibrational levels of the H$_2^+$ molecules
in the ground (1σg) electronic state are coupled to the dissociative continuum of the upper (repulsive) electronic state 2πσu, and thus become (shifted and broadened) vibrational quasi-energy (VQE) resonances. Each VQE resonance possesses an intensity- and frequency-dependent complex energy eigenvalue \( E_R = -\frac{i}{2} \Gamma \), the real part of which is related to the ac Stark shift and the imaginary part (width) provides the total MPD/ATD rate \([10]\). Our theoretical formulation of this problem follows the complex vibrational quasi-energy formalism \([10]\) developed previously based on the generalization of the Floquet theory \([11]\). The numerical computation of the complex quasi-energies can be expediently performed via the complex-scaling Fourier-grid Hamiltonian (CSFGH) technique \([7]\), recently developed for the eigensolution of the time-independent non-Hermitian Floquet Hamiltonian \([11]\). The procedure is simple to implement and allows accurate and efficient determination of complex VQEs of both low-lying and highly excited resonance states without the need of using basis set expansion. For example, using only (up to) 81 evenly distributed grid points to discretize the internuclear coordinate \( R \), we have obtained converged results (of at least four significant digits of accuracy) for all low- and high-lying resonance states being considered. The \( \text{H}_2^+ \) potential energy surfaces and the transition dipole moment used are the same as those given in ref. \([7]\). In performing the calculations, we adopt the velocity gauge to facilitate faster convergence in strong fields \([7]\). Up to 14 Floquet-state channels \( |g (\text{or } u), n \rangle \equiv |g (u) \rangle \otimes |n \rangle \), where \( g (u) \) stands for the 1σg (2πσu) electronic state and \( n \) is the Floquet Fourier index \( (n=0, \pm 1, \pm 2, \ldots) \), are used to achieve numerical convergency.

Figs. 1–3 show the real \( (E_R) \) and imaginary \( (\frac{1}{2} \Gamma) \) parts of the complex vibrational quasi-energies at 775 nm for laser intensity at \( I = 10^{11} \) (weaker field case), \( 5 \times 10^{12} \) (medium strong field case), and \( 5 \times 10^{13} \) W/cm² (strong field case), respectively. In figs. 1a–3a, the field-modified adiabatic potentials are displayed and labeled by the Floquet-state basis index \( |g (u), n \rangle \) in the asymptotic \( R \) region. The horizontal line segments at the left-side column represent the converged (real parts of the ) energies of VQE resonances. The line segments at the right-side column(s) denote the energy positions of bound vibrational levels of shape resonances supported by the corresponding adiabatic potential well(s). The imaginary (half-) widths \( (\frac{1}{2} \Gamma) \) of VQE resonances are shown in figs. 1b–3b in ascending order (labeled by \( \nu' \)) according to the magnitude of their corresponding \( E_R \) displayed in figs. 1a–3a.

Figs. 1a and 1b show the expected weak-field behavior. At this intensity \( (I = 10^{11} \text{ W/cm}^2) \), the (perturbed) VQE resonance positions shown in fig. 1a are very close to those of (field-free) vibrational states supported by the ground 1σg potential curve. The behavior of the photodissociation widths (fig. 1b) of these resonance states is also expected: low-lying states generally have smaller widths and longer (photodissociation) lifetimes than those of the highly lying levels. In fact, the photodissociation rates of higher-lying resonances \( (\nu' \geq 8) \) can be nine to ten orders of magnitude larger than the photodissocia-

\[^{11}\text{For reviews on generalized Floquet methods, see ref. [11].}\]
The situation becomes more delicate when the laser intensity increases. For example, at the medium-strong intensity $I = 5 \times 10^{12}$ W/cm$^2$, the gap of one-photon avoided crossing ($R \approx 5$ au) already becomes sufficiently large and the structure of VQE resonances significantly distorted. In fact, the VQE resonances now break into two groups (fig. 2a): a lower-lying resonance group ($\nu' = 0$–10) and a higher-lying resonance group ($\nu' \geq 11$), widely separated in energy. Another interesting feature here is that the energy positions of the upper group resonance states are in close resemblance with those of the bound states supported by the adiabatic potential well (labeled $|g, n=0\rangle$ asymptotically) near the one-photon avoided crossing. The photodissociation widths (fig. 2b) exhibits distinct behaviors for these two separated groups. The widths of the upper-group resonances ($\nu' \geq 11$) are consistently smaller than those of the higher members of the lower-lying group resonances (e.g. $\nu' = 7$–10). As compared with the weaker field case (fig. 1b), all the VQEs in the lower-lying group are now broadened substantially, i.e. molecules become more unstable in stronger fields, a phenomenon known as “bond softening”. These lower-lying group resonances (particularly those higher members) can tunnel through the adiabatic potential barrier labeled asymptotically by $|u, -1\rangle$ (fig. 2a). As the laser intensity increases, the height of the adiabatic potential barrier decreases, leading to more efficient photodissociation of the lower-lying group resonances. What is more striking here is the unexpected behavior of the upper group resonances. A comparison of figs. 1b and 2b reveals that the photodissociation rates of these VQE resonances ($\nu' \geq 11$) actually decrease with increasing laser intensity! That is, molecules become more stable at stronger fields, a novel phenomenon which may be termed as “bond hardening”. These bond hardened states arise from the trapping of molecular vibrational wavefunctions at longer ($R \approx 5$ au) internuclear separation by the (one-photon) adiabatic potential well. These trapped states are in fact not bound...
states but slowly leading quasi-bound resonance states due to the nonadiabatic couplings to other Floquet-state channels. As the laser intensity increases, the one-photon gap becomes larger, leading to weaker nonadiabatic couplings and therefore smaller photodissociation rates (widths). To our knowledge, this is the first report on the intensity-dependent lifetime behavior for highly excited vibrational states in intense laser fields.

As the laser intensity further increases to the strong-field regime, multiphoton avoided crossings now play a significant role and the resonance structure undergoes dramatic changes. Fig. 3 shows a strong field case at \( I = 5 \times 10^{13} \) W/cm\(^2\), in which the VQE resonances now break into several different groups. The topmost resonance-group states (\( v' = 16-19 \)) are well separated in energy from the lower-lying groups. These highest-lying resonances exhibit the following distinct features: (a) They are supported by the (now very shallow) adiabatic potential well near the one-photon avoided crossing region (\( R = 6.4 \) au). (b) Their photodissociation rates are extremely small, smaller than that of any lower-lying group resonance states. Molecules associated with these VQE states are therefore very stable against photodissociation even if their binding energies are very small, a full manifestation of the bond hardening phenomenon.

The analysis of lower-lying group resonances is less straightforward as their energy order can be intermixed. An approximate assignment of individual VQE state to each resonance group is given as follows: The three high-lying resonance states (\( v' = 12, 14, 15 \)) form a group. They are supported by the three-photon adiabatic potential well near \( R \approx 4.3 \) au (labeled asymptotically by \( |u, n = -1 \rangle \)). The second curve from the top in Fig. 3a). The VQE state \( v' = 13 \) does not belong to this group but is actually the continuation from a lower-lying group, namely, \( (v' = 7-11 \) and \( v' = 13 \)). The VQE states in this group are primarily supported by the five-photon adiabatic potential well (labeled asymptotically by \( |g, n = -2 \rangle \)) near \( R \approx 3.3 \) au. The assignment of the remaining lower-lying VQE states is less clear cut.

3. Time-dependent molecular photodissociation dynamics and laser-induced multiple well trapping

The time-independent CSFGH calculation described in section 2 provides intrinsic (time-averaged) properties (resonance energies and lifetimes, field-deformed internuclear potential) of \( \text{H}_2^+ \) molecules in intense laser fields. In this section, we discuss the time-dependent calculation through direct numerical solution of the Schrödinger equation, providing additional dynamical information regarding laser-induced stabilization and trapping phenomena.

The time-dependent coupled-channel Schrödinger equation for the MPD/ATD of \( \text{H}_2^+ \) molecules in laser fields is given by

\[
\frac{\partial}{\partial t} \psi(R, t) = [\hat{T} + \hat{\nu}(R, t)]\psi(R, t),
\]

where \( \hat{T} \) and \( \hat{\nu} \) are of 2 by 2 block form,

\[
\hat{T} = \begin{pmatrix} \hat{T}_R & 0 \\ 0 & \hat{T}_R \end{pmatrix}, \quad \hat{\nu}(R, t) = \begin{pmatrix} U_1(R) & D(R, t) \\ D^*(R, t) & U_2(R) \end{pmatrix}.
\]

Here \( \hat{T}_R \) is the radial kinetic energy operator of nuclear vibration, \( U_1(R) \) and \( U_2(R) \) are, respectively, the \( R \)-dependent electronic energy of \( 1\sigma_g \) and \( 2\sigma_g \) states, and \( F(R, t) \) is the electric-dipole coupling (in velocity gauge) [7] between the two electronic states. Eq. (1) is solved numerically by means of the split-operator technique [12],

\[
\psi(t + \Delta t) = \exp(-\frac{i}{2} \Delta t \hat{T}) \times \exp(-i\hat{\nu}(R, t + \frac{1}{2}\Delta t) \Delta t)
\times \exp(-\frac{i}{2} \Delta t \hat{T}) \psi(t).
\]

The propagation is implemented most expediently by fast Fourier transformation (FFT) [12,13]. For this coupled-channel problem, we first diagonalize \( \hat{\nu}(R, t) \) using the Fourier grid Hamiltonian method [7]. The momentum-space nuclear wavefunctions are used throughout the propagation. The nuclear wavefunction in coordinate space, if desired, can be obtained by a simple FFT at any given time. In the following calculations, the laser field is turned on with a 5 fs smooth ramp and then held constant in amplitude. The laser wavelength is fixed at 775 nm. The time mesh is one step per atomic unit and 1024 mesh.
points are used to span the momentum (k) space from k = -20 to 40 au. Since we aim at demonstrating the molecular dynamics in intense fields, we do not need to propagate very long time. Also as the computation is very rapid, we simply use this large number of mesh points in the R space to ascertain that the wavefunction in the R space will never hit the grid boundary. Note the k-space wavefunction is always localized so that a fixed k-space grid is sufficient.

We present below only the molecular photodissociation dynamics at a typical strong field I = 5 \times 10^{13} \text{ W/cm}^2, illustrating the salient features of laser-induced stabilization and multiple well trapping phenomena. Fig. 3a suggests that in order to have molecular wavefunction trapped in the one-photon adiabatic potential well region, the molecules must be initially prepared in some high-lying vibrational levels. Figs. 4a–4c show the time-development of the H_2^+ nuclear wavefunction initially prepared at the (unperturbed) \( v = 14 \) vibrational state. Under the influence of the fields, the time development of the wavefunction will be contributed from a group of high-lying VQE states, particularly the topmost resonance group shown in fig. 3a. We note that while the inner region of the initial wavepacket is rapidly dissociated, the wavepacket is evidently dominantly trapped at a larger internuclear separation (\( R \approx 6 \text{ au} \)) around the one-photon adiabatic potential well. This trapping of the wavefunction actually lasts much longer than 100 fs as shown in fig. 4c, consistent with the long lifetimes of the topmost group of resonances shown in fig. 3b.

Trapping in multiphoton adiabatic potential wells may be achieved if one prepares the molecules initially at some intermediate vibrational levels, following the guidance of fig. 3a. This is confirmed in fig. 5 where the time development of the H_2^+ wavefunction initially prepared at \( v = 8 \) is displayed. In fact, here we see that the wavefunction can be trapped at two different internuclear separations (indicated by vertical arrows in fig. 5) corresponding, respectively, to the trappings by the three- and five-photon adiabatic potentials wells.

In this connection, we note that population trapping at a three-photon adiabatic potential well at 770 nm has just been experimentally observed [8]. In this recent experiment, a mixture of initial (low-lying) vibrational levels of H_2^+ is created following the multiphoton ionization of H_2 molecules. Since the relative population of initial vibrational levels is not determined by the experiment, a quantitative comparison of the calculation (for example, ATD spectrum) with the experimental data is not straightforward. However, the phenomena of laser-induced stabilization and multiple well trapping in strong fields are well predicted by our theoretical study. Preparation of H_2^+ molecules in a specific excited vibrational level can in fact be achieved by different experimental techniques (see, for example, ref. [14]). Extension of these types of experiments to strong probing laser fields will allow the exploration...
of the laser-induced stabilization and chemical bond hardening phenomena predicted here and elsewhere [9].

Extension of the present work to the study of the effect of laser pulse shapes and the ATD spectra is in progress.

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