Light-Induced Vibrational Structure in H_2^+ and D_2^+ in Intense Laser Fields

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Molecular bond-softening and above-threshold dissociation of H_2^+ and D_2^+ in intense laser fields is reexamined using 160 fs pulses of 769 nm light. At intensities greater than $\sim 10^{13}$ W/cm^2 new features appear in the dissociation spectrum. These are consistent with the formation of trapped population in light-induced vibrational states, formed in the adiabatic potential near the three-photon resonance between the $1s\sigma_g$ and $2p\sigma_u$ states. Rovibrational structure of such light-induced states appears in the kinetic energy spectra of the ion fragments detected after multiphoton ionization.

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The behavior of molecules in strong laser fields is an area of active investigation. Multiphoton ionization (MPI) and above-threshold ionization (ATI) occur in molecules just as in atoms [1–6]. Additional degrees of freedom in molecules lead to some new phenomena as well. An example is above-threshold dissociation (ATD), in which the internuclear electronic potentials are mixed by the laser field at points of multiphoton resonance, causing the molecule to dissociate via several possible channels corresponding to the absorption of one, two, or more photons. A closely related phenomenon is bond softening, where the potential curves flatten, or "soften" in the vicinity of a multiphoton resonance [6–9].

These effects were observed first in dissociation spectra of H_2^+ and D_2^+ [6–8]. The initial experiments employed laser pulses that were much longer than the vibrational or rotational oscillation periods of the molecule. Recently, high intensity laser pulses with much shorter widths have become widely available [10,11]. Strickland *et al.* have used sub-100-fs pulses to essentially "freeze" the motion of molecular iodine during multiple ionization [4]. We report the results of 160 fs multiphoton ionization and dissociation of hydrogen and deuterium molecular ions. In addition to above-threshold dissociation, we find evidence for a new phenomenon: population trapping in light-induced vibrational states of the molecular ions.

Our experiments used 160 fs pulses of 769 nm light from a mode-locked and amplified Ti:sapphire laser. The focal spot diameter was estimated to be 15 μm, based on previous measurements in this apparatus, and corroborated by measurements of multiple ionization in xenon, where the relation between peak power and ionization threshold has been studied previously [12].

Typical ion kinetic energy spectra are shown in Fig. 1. The most prominent feature is a narrow peak that can be attributed to *two-photon* above-threshold dissociation [6]. The prominence of this peak is dramatically different than in the long-pulse regime, where most of the ions are in the lowest energy peak, corresponding to *one-photon* absorption from the bound vibrational level. The second ATD peak (actually one-half photon higher in energy since the two fragments share the excess photon energy) comes from three-photon absorption from the $1s\sigma_g$ lower state to the $2p\sigma_u$ upper state, followed by one-photon emission during dissociation.

The observed pulse-width dependence is consistent with the formation of a vibrational wave packet, i.e., a constructive superposition state of two or more vibrational levels produced during rapid ionization of the neutral parent molecule. Since this initial ionization of a neutral molecule is a high order process (at least ten photons are required at $\lambda = 765$ nm), its rate increases rapidly with intensity, and may approach or exceed the ion's vibrational period when ultrashort pulses are used. Thus, a vibrational wave packet may form in the vicinity of the ionic potential where there is overlap with the ground state of the parent molecule.

Figure 2 shows the results of a classical model designed to illustrate the wave-packet hypothesis. It plots the trajectory of a particle representing the deuterium molecular ion, executing bound motion in the "dressed" ground state internuclear potential. Dressed in this case means that the shape of the potential includes shifts due to the interaction of the ion with the intense laser pulse. The dominant shifts occur because the ground state ($1s\sigma_g$) and the repulsive first excited electronic state ($2p\sigma_u$) can be resonantly coupled by an odd number of photons. When an ion passes through such a resonance, it can adiabatically switch states via the emission or absorption of the requisite photons. A Floquet analysis was performed to calculate the shape of the gaps, or avoided crossings, which appear in the potential at internuclear separations R where there are odd-photon resonances. With an increase of the laser field, these gaps become wider, forcing the ion to take the adiabatic path. The *ab initio* calculation of this potential curve is described more fully in Refs. [5] and [8].

The model [13] assumed an initial ionization at an intensity of 1.4×10^{13} W/cm^2, on the rising edge of a 160 fs FWHM Gaussian pulse with peak intensity of 10^{15}

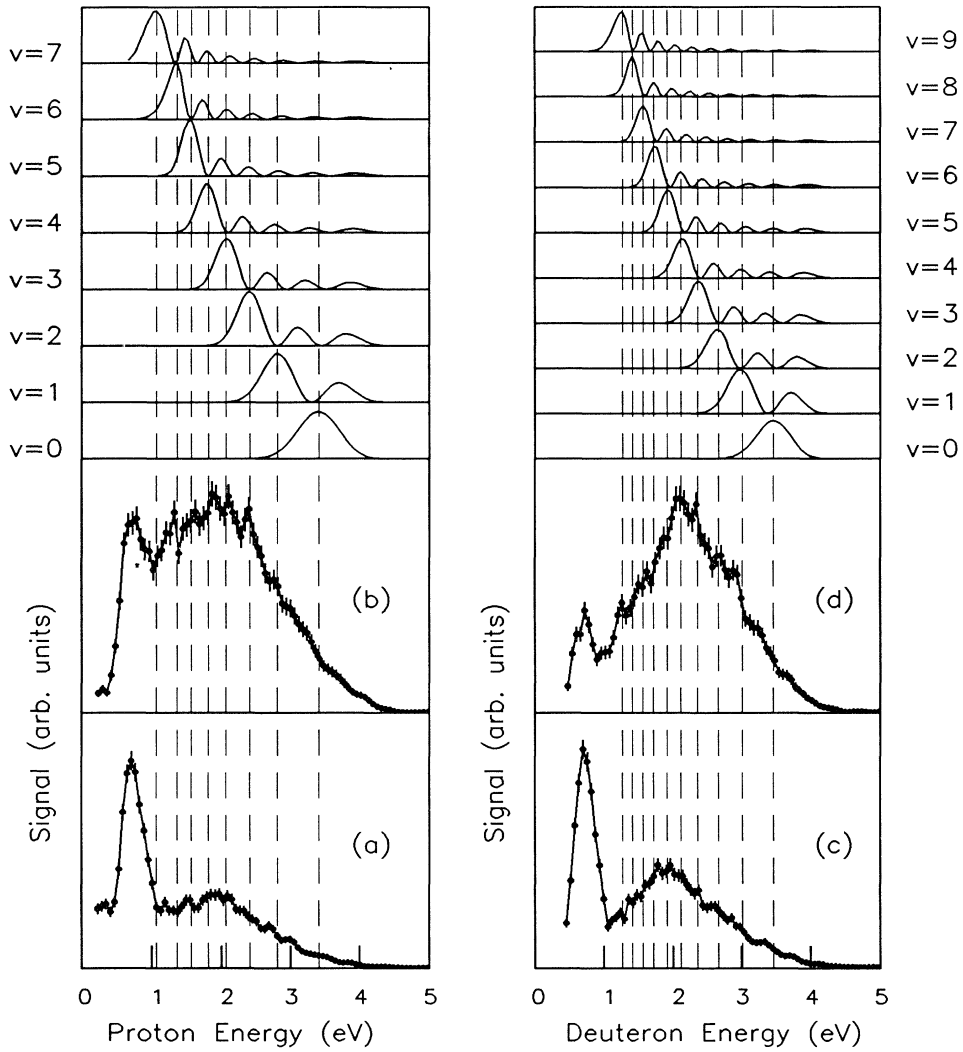

FIG. 1. Typical kinetic energy spectra of protons (a),(b) and deuterons (c),(d) detected along the laser polarization. The laser peak intensity was 10^{15} W/cm^2 for runs (a) and (c), and 2×10^{15} W/cm^2 for (b) and (d). Each run contained $\sim$10000 laser shots. The Franck-Condon overlaps between light-induced bound states of H_2^+ and D_2^+ molecular ions and the repulsive two proton (or two deuteron) Coulomb state form a series of maxima separated by the same intervals as the observed modulations in the spectra. The overlap integrals were calculated for the lowest eight (ten) vibrational states of the hydrogen (deuterium) molecular ion in the adiabatic potential well above the three-photon crossing. The calculations assume a laser intensity of 9×10^{13} W/cm^2 with the laser polarization along the internuclear axis.

W/cm^2. This ionization intensity agrees with our own previous observations, as well as those of others employing short laser pulses [1,3,5,14]. The classical vibrating ion in this model follows a trajectory that avoids single-photon dissociation, but dissociates via three-photon absorption followed by one-photon emission [15].

Figure 2 also shows that there is some probability for population to be trapped in a new potential well formed near the three-photon avoided crossing between the $1s\sigma_g$ and $2p\sigma_u$ states. Similar light-induced bound states near the one-photon avoided crossing have been predicted [16], and indirect evidence for them has been seen in previous work [1,17].

We associate these light-induced states with a totally new feature in our dissociation energy spectra in a 160 fs laser field: the broad distribution of faster ions with kinetic energies up to 5 eV. These faster ions form by ionization of the light-induced bound states in Fig. 2, followed by Coulomb repulsion of the bare nuclei, as shown schematically in Fig. 3. This trapping of population in light-induced states is quite natural within the context of the wave-packet model described above. About 15 fs after the ion is born, it reaches the outer turning point. The momentary laser peak intensity at this time is ≈ 2.9

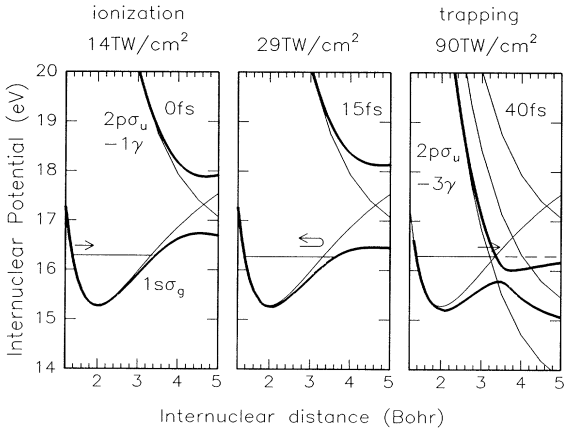

FIG. 2. A *possible* trapping scenario: During the second vibrational cycle the vibrational wave packet becomes trapped in the adiabatic well above the three-photon avoided crossing between $1s\sigma_g$ and $2p\sigma_u$ states of the molecular ion. The fine lines show the $1s\sigma_g$ ground state as well as the $2p\sigma_u$ state shifted down by integer numbers of photons.

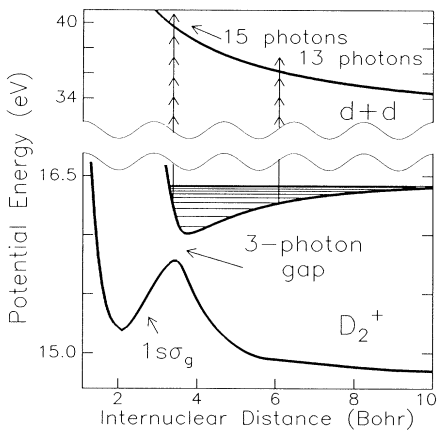

FIG. 3. At laser intensities sufficient to open the three-photon gap, vibrational population can be trapped in the new adiabatic potential well. The vibrational levels are calculated for a D_2^+ molecular ion exposed to intense (0.9×10^{14} W/cm^2) 769 nm radiation polarized along the internuclear axis. Unable to dissociate, these states can multiphoton ionize, producing two bare nuclei repelling each other. The number of photons needed to ionize depends on the internuclear distance at the moment of ionization.

$\times10^{13}$ W/cm^2 and the potential curves are moderately perturbed. However, the one-photon gap is still not wide enough for the ion to dissociate. Consequently, the ion just turns around, goes back to the inner turning point, and starts a new vibrational cycle. By the time the ion passes the three-photon gap (about 40 fs into the ion's life), the laser intensity is 9×10^{13} W/cm^2 and the gap is already open. Still, Landau-Zener theory [18] predicts a significant probability for a diabatic passage through the gap. As a result, the ion stays on the $1s\sigma_g$ curve and continues traveling to the right until it reaches the new outer turning point. By the time it returns to the three-photon gap again, the gap is wide open, forcing the ion to take the adiabatic pass. The ion now becomes trapped in the potential well above the three-photon gap, where it is exposed to the extremely high intensity at the peak of the laser pulse. The light intensity can become high enough for second ionization: $D_2^+ + 1\gamma = d + d + e$. In this case two deuterons forcibly repel each other, and produce the fast ions seen in the data.

There are several pieces of corroborating evidence for this trapping mechanism. These dissociation fragments were not present in previous experiments carried out with longer pulses. This is as expected, since the wave-packet formation mechanism requires that the three-photon gap increase appreciably during one vibration (i.e., $\sim$30 fs). The intensity dependence of these fast ions also differs markedly from the slow ions that are thought to be due to bond softening (see Fig. 1). The relative amount of signal in this broad distribution rapidly increases with laser intensity. This implies that these fast dissociation fragments result from a process particular to the high laser intensity.

Another mechanism that could lead to the production of fast dissociation fragments is simple sequential ionization. The second ionization step can take place at the 3γ crossing, or some time later when the nuclei have drifted apart and the laser intensity increased. However, this scenario cannot account for the general shape of the observed spectra. Immediate ionization of the molecular ion at the 3γ crossing produces a peak around 4.5 eV in the ion kinetic energy spectra, which is not observed. In the case of delayed ionization, we would expect a different high-energy cutoff in the spectra for protons versus deuterons, since they move apart at different rates. On the other hand, the similar general shape of the high-energy tail in hydrogen and deuterium spectra suggest that the mechanism for producing the fast ions is independent of vibration or rotation, but only depends on the shape of the internuclear potential.

The most interesting corroborating evidence for light-induced bound states is the structure in the spectra in Fig. 1. Each spectrum has slight periodic modulations superimposed on a broad ion distribution. The modulations are spaced farther apart for hydrogen than deuterium. These features suggest dissociative ionization of discrete states in the ion. The spacing is consistent with the vibrational state spacing in the light-induced potential well at the 3γ resonance. We have calculated the vibrational eigenvalues in this well as a function of laser intensity I, for polarization along the internuclear axis. At $I=9\times10^{13}$ W/cm^2, the Franck-Condon overlaps between these states and the repulsive two-proton (or two-deuteron) Coulomb state form a series of maxima separated by the same intervals as the observed modulations (see Fig. 1). Thus these light-induced vibrational states appear to exist for more than one vibrational period ($\approx$ 50 fs) in intensities of 10^{13} W/cm^2 or more.

The positions of these peaks depend on the shape of the

potential well, which in turn depends on the laser intensity at the moment of ionization. We therefore conclude that the ionization saturates for a 160 fs pulse when the intensity is approximately 9×10^{13} W/cm^2. The data also provide information about the change in the ionization probability as a function of the number of photons needed to ionize, since we observe that the ionization probability is relatively higher for lower-energy fragments than for higher-energy fragments: Faster fragments start at a steeper part of the Coulomb curve, requiring more photons to ionize.

This Franck-Condon overlap model provides only a qualitative explanation of our data. For example, it does not include homogeneous broadening of the peaks due to the finite lifetime of the light-induced vibrational levels in the intense laser field. Since the laser pulse is so short, we expect the lifetime is only a few vibrational periods at most. Also, the higher-energy dissociation fragments may be born at higher laser intensities, when the vibrational eigenvalues have shifted. In fact, the potentials change on the time scale of a single vibration. In addition, rotational effects might play an important role in our experiments. Even though the rotational period of the molecular ions is much longer then the characteristic time for the intensity change in the laser focus, the rotational motion will change drastically in a strong laser focus. In a simple classical electric dipole model, a moderate field strength of 3 V/Å (10^{14} W/cm^2) shortens the rotational period to 100 fs for the rotational ground state. Thus we expect complicated rovibrational motion of molecular ions. A complete quantum-mechanical time-dependent calculation is required before any quantitative interpretation is possible.

For higher frequency light, it should be possible to create light-induced bound states in the adiabatic potential well above the *one-photon* crossing. We do not see this, because for our wavelength the adiabatic potential near the one-photon gap is almost totally flat and cannot support vibrational states at the ionization intensity. This is the phenomenon of bond softening.

In conclusion, we report the first observation of above-threshold dissociation on subpicosecond time scales. We have observed fast dissociation fragments with spectral features that suggest the formation of light-induced bound vibrational states in the molecular ion. Such states are stable against dissociation, but can be detected by photoionization of the molecular ion.

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Note added.— While preparing this manuscript, we became aware of recent theoretical calculations of H_2^+ dissociation by intense laser fields [19,20]. Both groups found that depending on the initial distribution of vibrational population in $1s\sigma_g$ ground state and the laser pulse parameters, a significant portion of population can be trapped in light-induced vibrational bound states.

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