

Softening of the H_2^+ Molecular Bond in Intense Laser Fields

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We report a new kind of multiphoton dissociation in intense laser fields. H_2^+ molecular ions were formed in above-threshold ionization of H_2 gas by intense 532-nm, 100-ps laser pulses. Observations suggest that multiphoton couplings soften the molecular bond, resulting in dissociation at laser intensities over 50 TW/cm^2 . The ion-dissociation spectra have multiple peaks caused by multiphoton transitions during dissociation of H_2^+ .

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Interest in small diatomic molecules irradiated by intense laser light has been stimulated by high-intensity photoionization experiments on atoms. At intensities above 10 TW/cm^2 atoms exhibit "above-threshold" ionization (ATI), where they absorb more photons than the minimum needed to ionize.^{1,2} Molecules also exhibit ATI, but have additional degrees of freedom that lead to other new phenomena as well, such as multiphoton dissociation and dissociative ionization.³⁻⁶ Intense laser fields can alter the kinetic energies of molecular fragments, through Coulomb repulsion following rapid multiple ionization.⁷⁻⁹

In this Letter, we report a new phenomenon in intense fields: the softening of molecular bonds. For this study we have chosen nature's simplest molecule, the H_2^+ molecular ion. We find that in laser fields comparable to the internuclear binding fields ($\approx 3 \text{ V/\AA}$, or peak intensities of $\approx 100 \text{ TW/cm}^2$) molecules can become unstable. In effect, the internuclear potentials become repulsive. However, in contrast to the "Coulomb explosions" described above, where dissociation is caused by sudden removal of electrons, the strength of the repulsion due to bond softening is quite gentle, and does not involve removal of any electrons at all: Molecular fragments usually emerge with kinetic energy equivalent to less than one photon.

This new phenomenon is similar to ordinary photodissociation, where a molecule falls apart following excitation to a predissociating electronic state. The high-intensity version of the process differs, however, in that it involves both multiphoton absorption and stimulated emission. Many photons are absorbed, but most of their energy is returned to the photon field via stimulated emission during the dissociation, resulting in slow ion fragments. The suggestion that molecules might deform in this manner was proposed previously by others.¹⁰⁻¹² This is the first experimental verification of this phenomenon.

These experiments employed an amplified and frequency-doubled ($\lambda = 532 \text{ nm}$, $\hbar\omega = 2.33 \text{ eV}$), mode-locked Q -switched Nd-doped yttrium-aluminum-garnet laser, producing 25-mJ pulses between 70 and 100 ps in

duration at a repetition rate of 10 Hz. The light was focused to $15 \mu\text{m}$ inside an ultrahigh-vacuum chamber containing H_2 at a density between 10^7 and $10^{10}/\text{cm}^3$. The chamber contained separate field-free time-of-flight spectrometers for electrons and ions, as well as a static-field time-of-flight charge-mass spectrometer. Data include angle-resolved photoelectron spectra, angle-resolved proton kinetic-energy distributions, and measurements of the relative abundance of protons (H^+ ions), and H_2^+ molecular ions.

H_2^+ is readily formed from H_2 via multiphoton ionization with the same laser used to investigate bond softening in the molecular ion. In fact, we find that for 532-nm light, H_2^+ is a necessary intermediate on the dissociative pathway. Since there is some controversy about the mechanism for dissociation of diatomic molecules at other wavelengths and intensities, we briefly state the evidence for formation of H_2^+ in this experiment.

(1) At low intensities (below 50 TW/cm^2) formation of H_2^+ in several vibrational states is directly observed in photoelectron spectra (Fig. 1). At the same time atomic H spectra are conspicuously absent.

(2) H_2^+ is also the largest component of the residual ions measured after the laser pulse at low intensities (Fig. 1, inset).

Taken together, points 1 and 2 are irrefutable evidence for H_2^+ production at low intensities. Since the laser pulse turns on smoothly over a very long time compared to dissociation or ionization time scales, points 1 and 2 also suggest that H_2^+ is formed early in the laser pulse for higher pulse energies as well. Still stronger evidence, however, comes from direct measurements at the higher intensities.

(3) As the intensity increases the photoelectron spectral peaks merge into broad ATI features, but never approach the narrow peaks that characterize ATI in atoms¹³ (Fig. 1, trace B). This rules out dissociation of H_2 followed by ionization.

(4) Ionization while dissociation of H_2 is in progress would explain the nonatomic electron spectrum. (Note that ionization happens very rapidly compared to the

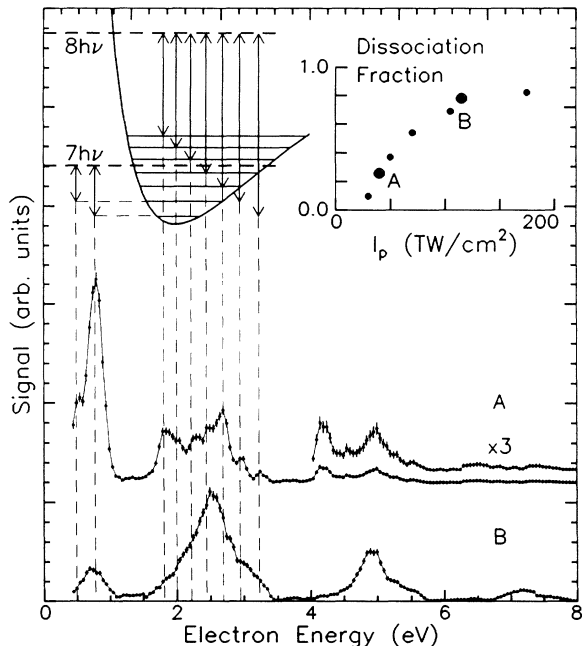


FIG. 1. ATI photoelectron spectrum for H_2 ionized by seven or more 532-nm laser photons. Detection was along the laser polarization direction. Different vibrational states in the H_2^+ $1s\sigma_g$ ground-state potential form discernible peaks in spectrum A, which had a peak laser intensity of $I_p \approx 50 \text{ TW/cm}^2$. In trace B, with $I_p \approx 100 \text{ TW/cm}^2$, these features have disappeared. Inset: The measured dissociation fraction vs I_p . For A, most of the ionized molecules did not dissociate, while for B, dissociation into protons was nearly complete.

slow motion of nuclei.) However, this possibility requires a mechanism to start the dissociation in H_2 . Since repulsive states in the neutral molecule cannot be reached easily by optical transitions (which are either spin-forbidden or are very-high-order double excitations), we are at a loss to provide such a mechanism. It is particularly unlikely, given that ionization of the neutral molecule occurs so readily at lower intensities, where dissociation is not observed. (See the dissociation fraction data displayed in Fig. 1.)

(5) Another possibility is double ionization, followed by so-called Coulomb explosion. This is ruled out in our experiments by direct measurements of the kinetic energy of ion fragments, to be discussed below.

(6) The only viable possibility is the one that we propose, namely, direct formation of H_2^+ followed by photodissociation. This is attractive from a theoretical point of view as well. Optical transitions strongly couple the ground state ($1s\sigma_g$) with a repulsive state ($2p\sigma_u$) in the molecular ion. Indeed this effect is closely related to the idea of bond softening, and will be discussed more fully below.

There are many other noteworthy features of these ATI spectra (peak widths, Franck-Condon behavior, Starks shifts); however, their description and analysis, as

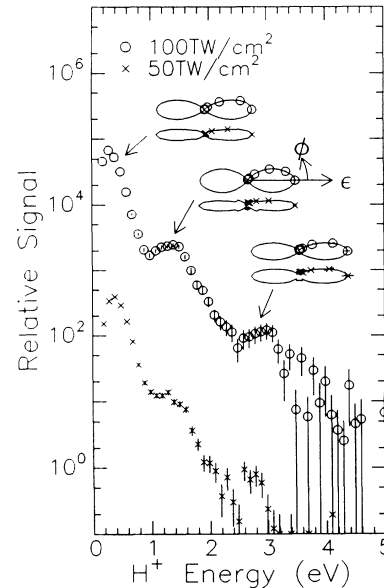


FIG. 2. Energy distribution and angular distribution of ions dissociated during photoionization of H_2 . Above about 50 TW/cm^2 , the ion spectra develop a series of peaks separated by $\approx \hbar\omega/2$. The ions are emitted along the laser polarization vector ϵ in narrow distributions that become somewhat broader for higher intensity, as shown.

well as comparisons with recent results from similar ATI experiments,^{3,6} are outside the scope of this paper, which deals with bond softening. The subject of ATI in atomic hydrogen will be taken up and discussed fully in a future longer paper.

When the H_2^+ dissociates, it produces a proton and a neutral atom which may subsequently ionize. The rapid onset of dissociation with intensity was investigated further by angle-resolved ion spectroscopy. Figure 2 shows the spectra and angular distributions at two intensities. The spectra consist of three broad peaks separated by approximately $\hbar\omega/2$. These regular resonances are similar to ATI, but they are due to absorption of several photons in excess of the minimum required for *dissociation*, rather than *ionization*.

The key to understanding this structure in the ion spectra lies in a closer comparison of Fig. 1 and the angular distributions in Fig. 2. At high intensities, the inset of Fig. 1 shows that nearly all molecules dissociate. These molecules are randomly oriented; however, the angular distributions of ion fragments in Fig. 2 are sharply peaked along the laser polarization. Therefore, *the molecular ions dissociate only when they are aligned with the polarization*. This is not too surprising, since the $1s\sigma_g$ ground state of H_2^+ interacts most strongly with the $2p\sigma_u$ repulsive state (see Fig. 3). These two states differ only in the relative phase of the electron wave function on the two protons. Therefore, there is a large dipole matrix element along the axis joining the nuclei. However, the low energy of the principal peak in

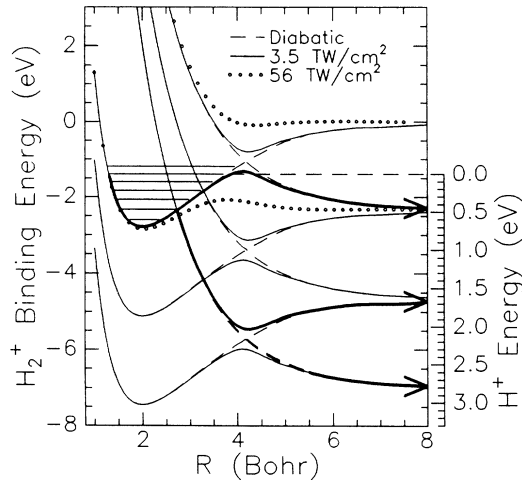


FIG. 3. The H_2^+ molecular potential deforms in the presence of intense light polarized along the internuclear axis. The figure shows the results of a Floquet calculation described in the text, for two intensities. At 3.5 TW/cm^2 the $v=6$ level is no longer bound. At still higher intensities, above about 50 TW/cm^2 , most vibrational levels in the $1s\sigma_g$ manifold are unbound. The bold lines trace the adiabatic and diabatic channels for dissociation of the molecule into the three peaks seen in Fig. 2.

the ion spectra cannot be explained by ordinary photoabsorption to this (or any other) repulsive electronic state: The wave functions of the populated vibrational states do not overlap at the one-photon resonance point, which occurs an internuclear separation of $\approx 4a_0$.

The one-photon resonance necessary to produce the low-energy ions may be induced by a deformation of the internuclear potential in the strong laser field. This softening of the molecular bond depends on the molecular *orientation*, since it is caused by the laser-induced coupling between the electronic states. Polarization along the internuclear axis couples the ground state to the $2p\sigma_u$ state, while perpendicular polarization couples much more weakly, through much higher-lying states such as $2p\pi$.

The deformation of the potential can be calculated by Floquet analysis.¹⁴ For example, Fig. 3 shows the results of an *ab initio* calculation involving twelve basis states, for polarization along the axis. The $1s\sigma_g$ - $2p\sigma_u$ coupling leads to deformations of the potential at points where the two states are separated by 1,3,5,... photons. The one-photon coupling dominates the shape of the potential. At the points of resonance, the molecular state may move adiabatically onto a new curve. This corresponds to the absorption or emission of photons. Diabatic transits of the resonances (nonavoidance of the crossings between curves) are also possible. Three paths to dissociation are shown by darkened lines in the figure. These are, in descending order, absorption of one photon, absorption of three photons, followed by emission of one

photon, and absorption of three photons. These result in ion fragments at the three kinetic energies shown in the data of Fig. 2.

From Fig. 3 it is evident that the energy eigenvalues of the vibrational states of H_2^+ must be functions of the laser electric-field strength, or more precisely the *component* of the field along the internuclear axis. As this quantity increases, the gap for the avoided one-photon crossing near $R=4a_0$ opens up, and the total number of vibrational levels in the ground state decreases.

An example illustrates the general dissociation process: Consider a molecule ionized into the $v=5$ state of the H_2^+ ground-state manifold (see Fig. 3). As the molecule rotates into alignment with the polarization, the $v=5$ state becomes unbound, due to the widening gap at the one-photon resonance ($R \approx 4a_0$). The molecule dissociates, producing a proton with kinetic energy equal to $(E_{v=5} + \hbar\omega - E_{\text{diss}})/2$. This photodissociation is essentially just one-photon absorption, with half of the energy going to each particle; however, the intense field is necessary in order to lower the energy of the crossing to permit the $v=5$ state to move far enough out in R to come into resonance with the predissociating state. In a photon picture, this lowering is due to the absorption and emission of many photons.

Alternatively, the molecule may predissociate by absorbing three photons at the resonance around $R=2.6a_0$. (The two-photon transition is forbidden by parity conservation.) In this case the state will evolve to a different final-state energy, two quanta higher than the energy given above, with one quantum going into the kinetic energy of each proton; or, if one photon is reemitted at the one-photon crossing, the protons may share only $1\hbar\omega$ more energy. The probability for making these adiabatic or diabatic transitions may be estimated using the Landau-Zener theory, which relates the crossing probability to the size of the adiabatic gap, the relative diabatic potential slopes at the crossing, and the speed of traversal through the crossing.¹⁵ We conclude the following. (1) The ratio of peaks in Fig. 2 is consistent with the crossing probabilities for the paths marked in Fig. 3, found by direct substitution into the Landau-Zener formulas in Ref. 13, averaged over the laser focus. (2) Higher intensities favor lower kinetic energies for the ion fragments, since all crossings become more adiabatic, and since lower vibrational levels may participate in the lowest-energy one-photon dissociation process as the adiabatic gap opens up.

In conclusion, we have observed a new form of molecular dissociation, peculiar to high-intensity multiphoton interactions. This new process is the softening of the molecular bond via multiphoton couplings in the molecule.

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¹⁴See, for example, F. H. M. Faisal, *Theory of Multiphoton Processes* (Plenum, New York, 1987), Chap. 10.

¹⁵See, for example, L. D. Landau and E. M. Lifshitz, *Quantum Mechanics*, Course of Theoretical Physics Vol. 3 (Pergamon, New York, 1965), p. 322ff.