

High-resolution multiphoton ionization and dissociation of H_2 and D_2 molecules in intense laser fields

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We report on the multiphoton ionization and dissociation of hydrogen and deuterium molecules in intense (8×10^{11} – 4×10^{13} W/cm²) laser fields. The investigations were performed with the second harmonics of two different laser systems, a 50-ps neodymium-doped yttrium lithium fluoride and a 10-ns neodymium doped yttrium aluminum garnet laser. Measurements included energy-resolved photoelectron and mass spectroscopy. In addition, we report on a measurement of the dynamics of different above-threshold dissociation branching ratios for H_2^+ and D_2^+ over a wide range of laser intensities. Our results support the dressed-molecule picture at least qualitatively, but differences do exist with the quantitative predictions.

Recently, the behavior of molecules in intense fields is attracting an increased amount of attention, especially in the studies of photodissociation dynamics. Studying molecules is more challenging because of their additional degrees of freedom compared to atoms. Molecular hydrogen represents the “model” molecular system for these studies because of its simple and well-known molecular structure and as a result should provide the foundation for future field-molecule studies. The effects of intense fields on H_2 have been studied lately by observing the above-threshold ionization and dissociation (ATI and ATD) phenomena through resonant [1, 2] and nonresonant [3–5] multiphoton ionization (MPI). Several models for the photodissociation of H_2 , dressed-molecular state model [5–7], for instance, have been proposed. Absence of rigorous treatments, difficulties in experiments, and insufficient resolution of the results leave the picture of the interaction between the potential surfaces of the H_2 molecule and the field still less than very well understood.

In this Rapid Communication, we report on “nonresonant” ionization and dissociation of H_2 and D_2 molecules in intense (8×10^{11} – 4×10^{13} W/cm²) laser fields. The molecules were irradiated by the second harmonic of both neodymium-doped yttrium aluminum garnet (Nd:YAG) and neodymium-doped yttrium lithium fluoride (Nd:YLF) lasers. The first ionization potential (I.P.) from the vibrationless H_2 ground state is 15.425 eV, requiring at least seven photons for ionization in the current experiment. The well-resolved intensity-dependent electron and proton spectra along with the comparison of data taken at two wavelengths (527 and 532 nm) and for two different isotopes is very useful in elucidating the interaction dynamics predicted by existing models.

The photon sources used are well-characterized Nd:YAG (1.06 μ m, 10 nsec, 10 Hz) and Nd:YLF (1.05 μ m, 50 psec, 1 kHz) lasers. Details of these laser sys-

tems have been described previously [8]. The intensity ranges for 532- and 527-nm radiations were 8×10^{11} – 9.7×10^{12} W/cm² and 5×10^{12} – 4×10^{13} W/cm², respectively. The apparatus consists of ultrahigh-vacuum chambers equipped with time-of-flight electron and mass spectrometers. The photoelectron spectrometer has an energy resolution of about 50 meV for 1-eV electrons. It is calibrated by the well-known ATI spectrum of xenon atoms. The mass spectrometer calibration was performed by weak-field photodissociation of chlorine [9] molecules. Its resolution was estimated to be about 100 meV for 1 eV protons. During an experiment, the number of ions produced in the ionization region was kept less than 50 per shot to minimize space charge effects.

Figure 1 shows a typical time-of-flight mass spectrum resulting from the 532-nm nonresonant MPI of H_2 and D_2 molecules at the same intensity, 9.7×10^{12} W/cm². Note the higher dissociation fraction of D_2 versus H_2 . Figure 2 shows the proton kinetic-energy spectra for H_2 taken at high and low intensity. Only the protons traveling towards the detector are shown for simplicity. Results obtained at 527 nm are very similar to those in Figs. 1 and 2. An increase in laser intensity from 2.7×10^{12} W/cm² to 9.7×10^{12} W/cm² results in an increase in the dissociation fraction [$H^+/(H^+ + H_2^+)$] of H_2 from 8% to 50% while dissociation fractions [$D^+/(D^+ + D_2^+)$] for D_2 molecules are relatively higher for the same intensity range, i.e., 12% and 65%, respectively.

In Fig. 1, the three peaks are labeled according to the number of photons being absorbed by H_2^+ ions leading to dissociation. According to our experimental results shown in Fig. 2, at the lower intensity most H_2^+ ions are dissociated from the $v_{av}^+ = 5$ vibrational level following the absorption of a single photon (major peak). The maximum of this peak is observed to shift from $v^+ = 5$ to 4 at higher intensities. With increasing intensity another

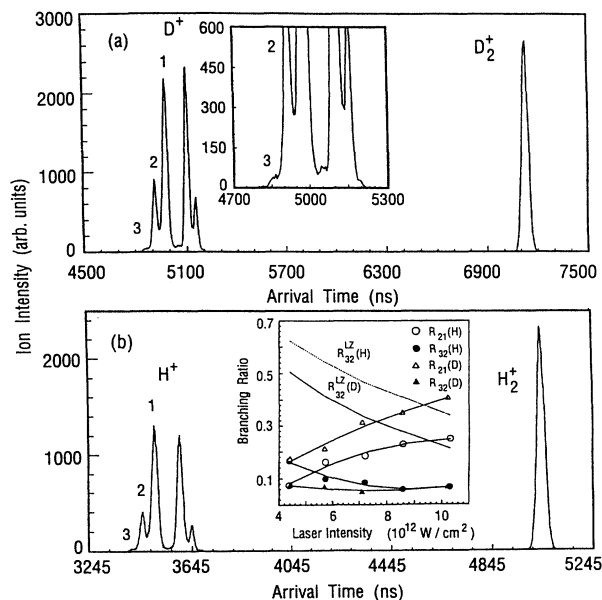


FIG. 1. Time-of-flight mass spectrum resulting from 532-nm MPI and dissociation of (a) D_2 and (b) H_2 at $9.7 \times 10^{12} \text{ W/cm}^2$. Peaks labeled 1, 2, and 3 indicate the number of photons absorbed in dissociation. The laser polarization is parallel to the flight tube's axis. An extraction electric field of 17 V/cm is used in the current experiment. The inset in (b) is a plot of the experimental and the LZ theory fragment ratios R as a function of intensity (see text).

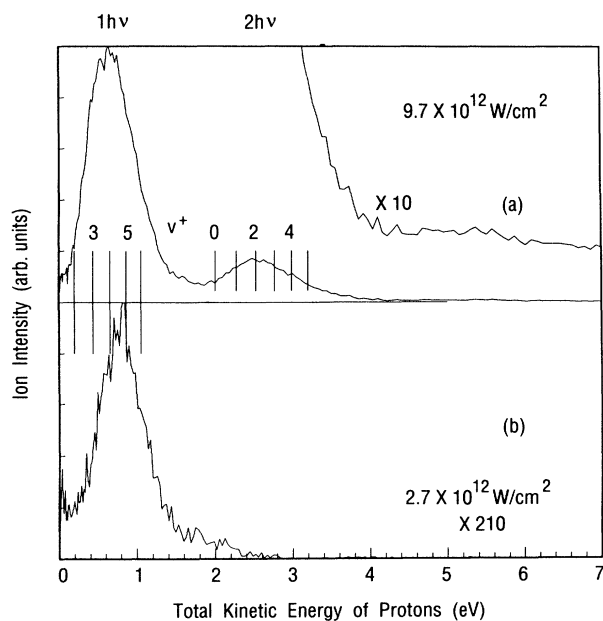


FIG. 2. Total kinetic-energy (twice the measured proton kinetic-energy) spectrum of H^+ fragments resulting from 532-nm dissociation of H_2^+ at (a) $9.7 \times 10^{12} \text{ W/cm}^2$ and (b) $2.7 \times 10^{12} \text{ W/cm}^2$. The tick marks show the position of the unperturbed ionic ground state's vibrational levels in one (left) and two (right) photon dissociation processes.

peak emerges corresponding to two-photon dissociation via $v_{av}^+ = 2$. Consequently, its separation is less than a photon total energy from the first peak and is intensity dependent. At still higher intensities a third peak appears about one photon total energy away from the second peak corresponding to a three-photon dissociation. The same general behavior is observed for deuterium. Similar kinetic-energy shifts were observed in the 527-nm (psec) spectra over an intensity range of $5 \times 10^{12} - 4 \times 10^{13} \text{ W/cm}^2$.

We have carefully examined the photodissociation of H_2^+ molecules by recording the proton kinetic-energy spectra and the H_2 photoelectron spectra simultaneously as a function of laser intensity. It appears that the amount of H^+ produced is proportional to that of photoelectrons due to seven- plus one-photon (7+1) ionization. In addition, energy conservation implies that seven second-harmonic photons of YAG (YLF) can populate only up to $v^+ = 3$ (4) vibrational levels in the ionic ground state, whereas the lowest intensity data have proton energies peaked at $v^+ = 5$. Thus we conclude that the H^+ peak around 0.7 eV (total energy) is due to the eight-photon ionization of H_2 followed by one-photon dissociation of H_2^+ .

Figure 3 shows the photoelectron spectra of H_2 at 532 and 527 nm at different laser intensities. For the entire dynamic range of laser intensities, the vibrational structure of seven- and eight-photon processes is resolvable as well as assignable to the unperturbed vibrational frequency of H_2^+ within experimental error. At either wavelength, no evidence is observed for photoionization of excited-state H atoms produced via neutral dissociation. Weak multiphoton ionization of ground-state H atoms is observed only in the photoelectron spectrum (PES) at the extreme intensities which is well beyond the saturation intensity for the molecular system. Some important features of the spectra should be pointed out here. (1) The low-intensity 527-nm photoelectron spectrum shown in Fig. 3(c) exhibits well-resolved $v^+ = 0-3$ vibrational bands whose intensity distributions are similar to the Frank-Condon factors expected from a direct seven-photon ionization between the $H_2 \ 1^1\Sigma_g^+$ and $H_2^+ \ 2^2\Sigma_g^+$ ground states. (2) As the 527-nm laser intensity is increased in Fig. 3 to $3 \times 10^{13} \text{ W/cm}^2$, only the low-energy electrons, specifically the $v^+ = 2$ and 3 bands, are suppressed proportional to the expected ponderomotive shifts in the ionization potential. No such suppression is observed with the 532-nm excitation due to the lower saturation intensity of H_2 in nanosecond pulses. (3) Over the entire intensity region for 532-nm excitation and those above 10^{13} W/cm^2 with 527 nm the photoelectron spectrum profiles are similar, i.e., for the seven-photon process most ions are formed in the $v^+ = 0$ level, suggesting a probable intermediate state resonance. (4) The maximum in the photoelectron distribution for the eight-photon process (ATI) shifts gradually from $v^+ = 5$ to 2 as the laser intensity is increased. (5) Finally, no dramatic shifts were observed in the positions of photoelectron kinetic energies as a function of laser intensities within our experimental resolution. However, the peaks are observed to become asymmetrically broadened

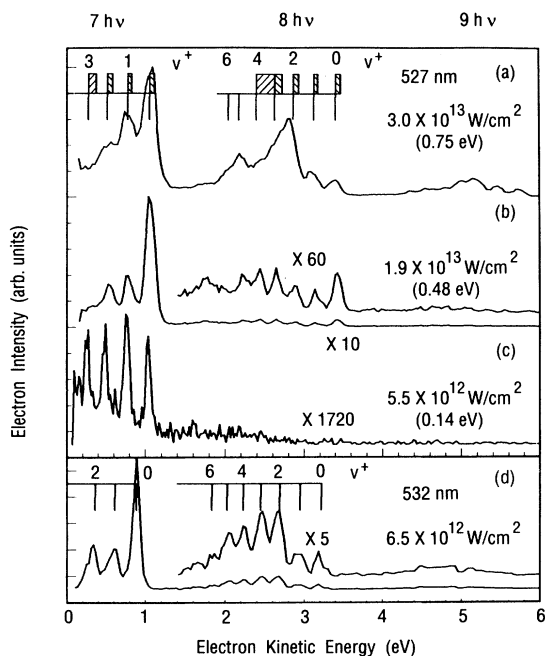


FIG. 3. Photoelectron spectrum of H_2 molecule taken at different laser intensities with 527- and 532-nm radiations. The data are normalized for gas density and number of laser shots. The tick marks indicate the unperturbed vibrational levels of the H_2^+ ground state via seven- and eight-photon ionization of the H_2 molecule. The hashed boxes are the shifts calculated using a Floquet method at the maximum 527-nm intensity of $3 \times 10^{13} \text{ W/cm}^2$. See Ref. [5] for the theoretical details. Note, the calculated $v^+=4$ shift could be overestimated due to its close proximity to the top of the potential and shifts for $v^+=5$ and 6 are not shown since they are unbound at this intensity. The numbers in parentheses are the corresponding ponderomotive energies at each intensity.

towards lower electron energies at the highest intensities.

The photodissociation of H_2^+ in an intense laser field has been explained by the mechanism of bond softening [5–7] in dressed-molecular states. In this model (see Fig. 13 in Ref. [5]), the laser field is considered as a strong perturber to the molecular potential. The potential curves couple and distort via the strong dipole interaction. According to the model, since the ground ionic state and the first repulsive state have symmetry $^2\Sigma_g^+$ ($1s \sigma_g$) and $^2\Sigma_u^+$ ($2p \sigma_u$), respectively, only 1, 3, 5, ... (odd number) photons can be used to dress the transition state because of parity conservation. However, a net even number of photon dissociation can also occur due to the absorption and stimulated emission of photons. Intense fields cause the laser-induced avoided crossing gap to open up. Any ions with vibrational energy within the gap should become unstable. As the laser intensity is increased and the molecular potentials distort, one should observe a negative shift in the proton kinetic energy corresponding to dissociation from the lower vibrational states of H_2^+ . Furthermore, the absorption of more photons ($N \geq 2$)

results in a series of peaks separated by about a photon (total) kinetic energy (ATD). Likewise, the distorted potentials result in a change in the vibrational energy eigenvalues resulting in a positive shift in the photoelectron spectrum.

Our results are generally in qualitative agreement with the bond-softening model but there remain some quantitative differences. In the current experiment, we observed apparent negative shifts in proton kinetic energies with increasing laser intensity with both 532-nm (nsec) and 527-nm (psec) pulses. The maximum population of the one-photon proton kinetic-energy peak shifts by ~ 200 meV over the entire intensity range. Likewise, the maximum of the ionic vibrational state distribution in the PES changes from high to low vibrational levels in a similar intensity range. However, we could not observe any commensurate positive energy shifts in the PES peak positions with increasing intensity although a broadening is clearly evident. An asymmetric broadening in our PES could result from spatial or temporal averaging in our experiment masking a “pure” energy shift. However, the sign of the observed broadening is opposite to that predicted by our model (see Fig. 3). This inconsistency could imply a shortcoming in our numerical method since only the vibrational motion in the distorted potential is included in our Floquet calculation. However, as the laser intensity increases, the ions can be populated in higher rotational states [7], causing the photoelectron peaks to broaden towards lower energies. Referring to the inset in Fig. 1(b), the ratio (R_{21}) of dissociation via two-photon versus the one-photon channels for H_2^+ changes from 7% to 25% as the intensity is increased to $9.7 \times 10^{12} \text{ W/cm}^2$. Furthermore, the ratio R_{32} for three- versus two-photon dissociation decreases from 16.5% to 6.5% in the same range. Interestingly, the behavior in D_2^+ is somewhat different, here the fraction R_{21} changes from 17% to 40% which is larger than H_2^+ . However, the D_2^+ ratio R_{32} is smaller ($\sim 6\%$) than H_2^+ and relatively constant over the entire intensity range. These branching-ratio effects can all be understood with the same model [7]. Physically, the increasing laser intensity corresponds to a larger avoided-crossing gap resulting in a decrease in the three-photon diabatic transition rate while favoring two-photon adiabatic passage (three-photon absorption, one-photon emission). Since H_2^+ and D_2^+ have a relatively large difference in vibrational frequencies due to their different masses, therefore at low intensities where the gap is not large enough to completely shut off the three-photon channel, D_2^+ molecules branch more efficiently through the two-photon adiabatic path as compared to H_2^+ due to the fact that a smaller vibrational frequency implies more adiabatic motion. Specifically, $R_{32}(H) > R_{32}(D)$ at low intensity. As the gap continues to widen, one should also observe the ratio R_{32} to decrease for both H_2^+ and D_2^+ molecules. Such behavior is clearly demonstrated in our experiments. We tried to model the fragment R_{32} ratios using simple Landau-Zener (LZ) theory [10], the results of which are shown in the Fig. 1(b) inset. The theory predicts well the general behavior of the ratios as the light intensity changes. However, the calculated ratios are approximately three times larger than the ex-

perimental values which could imply that the degree of deformation of the potential curves in our modeling is beyond the limits of applicability of simple LZ theory.

Speculations on the intermediate states involved in the 532-nm ionization of H_2 have been previously made by Verschuur, Noordam, and van Linden van den Heuvell [4] and Zavriyev *et al.* [5]. In Verschuur, Noordam, and van Linden van den Heuvell's [4] experiment, the ionization through the $B^1\Sigma_u^+$ ($v'=3$) with five-photon resonance and $GK^1\Sigma_g^+$ ($v'=2$) with six photons were considered to be the major processes. Zavriyev *et al.* [5] observed that at 532-nm both direct and resonantly enhanced ionization contribute to the ionization of the molecular ground state to different vibrational levels of ionic ground state. Unfortunately, the photoelectron spectra in either experiment could not be resolved. In our vibrationally resolved PES studies (Fig. 3) the 532-nm seven-photon process shows that the $v^+ = 0$ peak dominates the distribution. For 527-nm excitation (Fig. 3) at low intensity, the lowest four vibrations have comparable amplitude but the distribution becomes similar to 532-nm PES at high intensity. For 532-nm radiation, the energy difference ($E_{6h\nu} - E_{level}$) between six photons and unperturbed $G^1\Sigma_g^+$ ($v'=0$), $I^1\Pi_g$ ($v'=0$), and $J^1\Delta_g$ ($v'=0$) is only 121.9, 89.6, and 33.5 meV, respectively [11]. Ionizations from these intermediate Rydberg states to the ionic ground states are diagonal transitions, i.e.,

$\delta v = 0$. Consequently, there will be a wide range of laser intensities for which one can expect a resonant enhancement via dynamical shifts to occur for the $v'=0$ level, explaining its dominant population in our 532-nm PES. Moreover, for 527-nm excitation this difference is 271.9, 239.6, and 183.4 meV, respectively. This larger detuning implies that for low intensities the 527-nm process will be virtually nonresonant [see Fig. 3(c)]. However, for moderately high intensities a ponderomotive shift ≥ 0.18 eV (7×10^{12} W/cm²) will bring the various $v'=0$ states into resonance resulting in a PES spectrum similar to the 532-nm excitation.

In conclusion, the results presented in this paper support the qualitative predictions of a bond-softening model. Our well-resolved electron and mass spectra also provide quantitative data that will facilitate some important tests of numerical methods. However, certain questions remain unanswered, some of which we will try to address in a future, more complete article.

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