Strong-Field Dissociation and Ionization of $H_2{}^+$ Using Ultrashort Laser Pulses

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By using laser pulses (40 fsec) on the order of the vibrational period of $H_2{}^+$ and high-dynamic range detection electronics, we have removed, for the first time, the ambiguities in interpreting the proton kinetic energy spectrum resulting from the dissociation and ionization of $H_2{}^+$. We then use the kinetic energy spectrum to directly test recent calculations of the ionization rate of $H_2{}^+$ as a function of internuclear separation. [S0031-9007(97)04048-9]

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Although $H_2{}^+$ is the simplest of molecules, in strong laser fields, it exhibits surprising complex phenomena [1], not seen in atoms, such as above-threshold dissociation (ATD) [2], bond softening [2,3], and light-induced-bound states (LIBS) [3–5]. More recently, a new effect has been predicted theoretically: The ionization rate of $H_2{}^+$ varies as a function of internuclear separation, showing a maximum at a critical separation R_c [6–11]. Indirect [12,13] and more recent direct [14] evidence for this behavior in more complex molecules has been obtained. However, the interpretation of these experimental results is complicated by the multielectron nature of the molecules. Measurements of this ionization dependence in $H_2{}^+$, on the other hand, are complicated by the strong field phenomena mentioned above. We present new data on the dissociation and ionization of $H_2{}^+$ for which we have carefully eliminated the influence of ATD and LIBS. Furthermore, by understanding the intensity dependence of bond softening in detail, we can make a direct comparison with theory possible, for the first time. Our results on the ionization rate of $H_2{}^+$ as a function of internuclear separation agree quite well with theoretical calculations [8].

Two experimental advantages enable these measurements on $H_2{}^+$. First, our laser operates at a 1 kHz repetition rate which allows us to use ion counting to record the data, giving high dynamic range with no analog background [15]. This, in turn, allows us to accumulate spectra below the saturation intensity for the ionization of H_2 and $H_2{}^+$. These conditions create a well-defined experiment: Working below the saturation of H_2 means that essentially all of the $H_2{}^+$ ions are created at the temporal peak of the laser pulse, accurately defining the starting time for the subsequent dynamics. Little ionization occurs on the rising edge of the pulse. Furthermore, staying below saturation ensures that the signal comes from a small volume exposed to a relatively uniform peak intensity. Under these conditions, it is not possible to populate LIBS, as the laser intensity strictly decreases after the creation of the $H_2{}^+$ ion. Population of LIBS requires, first, a diabatic transition across the relevant multiphoton crossing, followed by adiabatic motion on the dressed potential curves [3,5]. This can only be achieved in a field increasing in time. Thus, our experiment excludes the influence of LIBS. However, we do see an H^+ spectrum identified as $H^+ + H^+$ similar to other groups who have interpreted this as evidence of the population of LIBS [1,3]. *Thus, the observation of this H^+ spectrum, in itself, cannot be used as evidence that LIBS have been populated.* In addition to avoiding the effects of LIBS, we will show that the one-photon coupling in our experiment is always saturated, which then eliminates the effects of ATD [2]. At the wavelength used in these experiments, vibrational levels 0–4 can only dissociate through the three-photon coupling, although they can eventually end up on either the two-photon or three-photon dressed state, depending on whether or not one photon was emitted during the dissociation. The three-photon channel corresponds to ATD. In our case, since the one-photon coupling is saturated, the molecule must follow the two-photon curve, avoiding ATD. Our second advantage results from the use of laser pulses with a half-width at half maximum (HWHM) in time of 20 fsec. (This is the relevant time scale because, as noted above, the $H_2{}^+$ ion is created at the peak of the laser pulse.) As this corresponds almost exactly to the vibrational period of $H_2{}^+$, the molecule has, at most, one chance to dissociate after being created. Upon ionization from the neutral $v = 0$ vibrational level, $H_2{}^+$ is left in a distribution of vibrational levels [16]. This creates a wave packet which moves out towards the attractive part of the ground state potential. When the wave packet reaches the outer turning point, 0.5 vibrational periods (T_{vib}) later, it can either dissociate through bond softening or reflect back. A subsequent attempt will be made at $1.5T_{\mathrm{vib}}$. However, at this point, the laser field has died away, and thus the dissociation can only happen once at one well-defined intensity. This places us in a regime quite different from recent experiments on $Ar_2{}^+$ [17].

The experiment is performed with 40-fsec (FWHM of a Gaussian profile), 0.5-mJ, 800-nm laser pulses focused with a parabolic mirror in a high-vacuum chamber (base pressure $<5 \times 10^{-10}$ torr). Ions are extracted and accelerated in a two-region 0.5 m time-of-flight (TOF) mass spectrometer. The ions are detected with a pair of microchannel plates (MCP). The MCP signal is amplified, sent through a fast discriminator, and recorded with a multihit 0.5-nsec resolution time-to-digital converter. The data can be recorded shot by shot at the 1 kHz laser repetition rate, allowing for high-dynamic range and correlation measurements.

Figure 1 shows the ${H_2}^+$ ion signal as a function of laser intensity. These data are needed to establish at what intensity the ionization saturates. Figure 2 shows a typical TOF spectrum for H^+ with the characteristic pairs of peaks, which are labeled in the following way:

$$\begin{array}{lllll} A: & {H_2}^+ & \rightarrow {H_2}^+ & (\text{Fig. 1}) & \\ B: & {H_2}^+(v = 5, 6) & \rightarrow H + H^+ + & (0\text{–}0.6\ \text{eV}) & \\ C: & {H_2}^+(v = 0\text{–}4) & \rightarrow H + H^+ + & (0.6\text{–}2.0\ \text{eV}) & . \quad (1) \\ D: & {H_2}^+ & \rightarrow H^+ + H^+ + & (2.0\text{–}10.0\ \text{eV}) & \end{array}$$

At 800 nm, the vibrational levels 5 and greater can dissociate through the one-photon curve, crossing with an energy release in the range indicated (channel B). This is known as bond softening [2]. Levels 0 through 4 require passing through the three-photon crossing (channel C). Some of the dissociating ${H_2}^+$ can ionize (channel D), while some ${H_2}^+$ never dissociate or ionize (channel A). The $H + H^+$ channels were unambiguously distinguished from $H^+ + H^+$ with correlation measurements [18]. Channels B and C were identified based on the expected kinetic energies for the various vibrational levels (Fig. 2). These channels represent all of the possible fates of an ${H_2}^+$ ion. What is most illuminating is to normalize out the overall increase in signal due to the intensity dependence of the H_2 ionization rate. We determine the total ionization probability of H_2 by summing all of the final state channels: $S_{\text{ION}} = S_A + S_B + S_C + S_D$, where S_X is the signal in the X channel. The individual signals in each channel were determined by fitting multiple Gaussian curves to the TOF data. S_{ION} is then used to normalize the signals from the individual channels, revealing just the intensity-dependent branching ratios, shown in Fig. 3. Several important features are evident. S_B, the one-photon dissociation channel, is constant at low intensity and then falls off. This means that the one-photon coupling is completely saturated. At higher intensity, this channel is depleted through ionization into channel D. The intensity where ionization becomes noticeable is consistent with the rise in channel D necessary to account for the depletion. S_C follows an I^3 power law, as would be expected for the three-photon dissociation process. The complete dissociation also involves a one-photon emission, but this step will also be saturated and not affect the power law dependence. We can see that ionization sets in before this channel saturates. The ratio of S_B to S_C should show the Frank-Condon distribution in ionizing from H_2 to ${H_2}^+$ [16]. Because of ionization and the lack of saturation of channel C, this cannot be directly verified from Fig. 3. However, if we remove the effects of ionization by assuming S_B is constant and letting $S_C = 1 - S_A - S_B$, we find that S_C/S_B approaches 3.7. This agrees well with the ratio expected from the Frank-Condon factors (3.6) if we only count $v = 5$ and 6 in channel B [19].

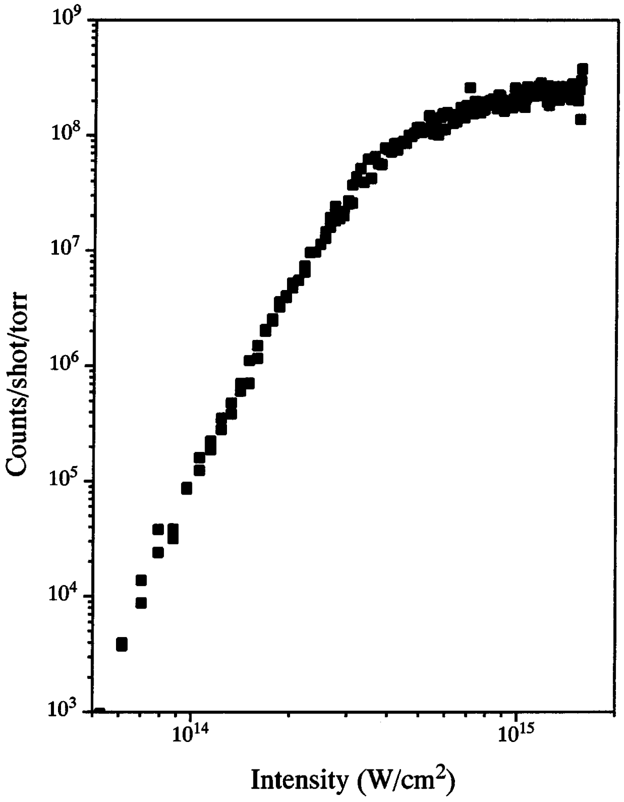

FIG. 1. ${H_2}^+$ signal as a function of laser intensity.

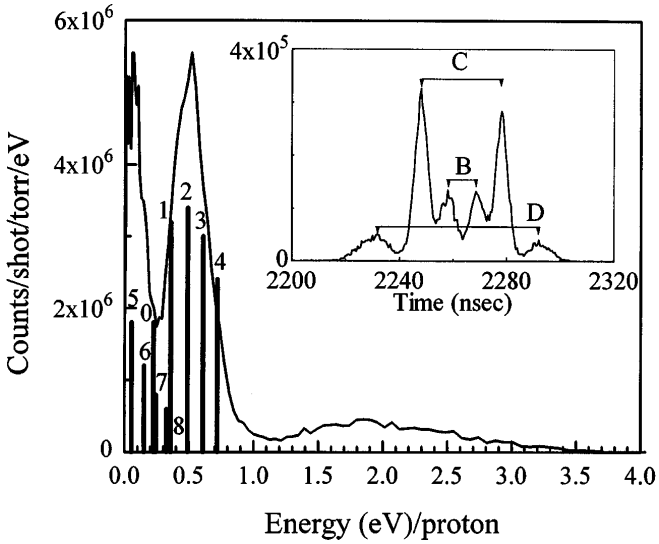

FIG. 2. Kinetic energy spectrum for H^+. The vertical bars represent the expected amplitude and energy of the different vibrational levels. The inset shows the raw TOF data with the different channels labeled.

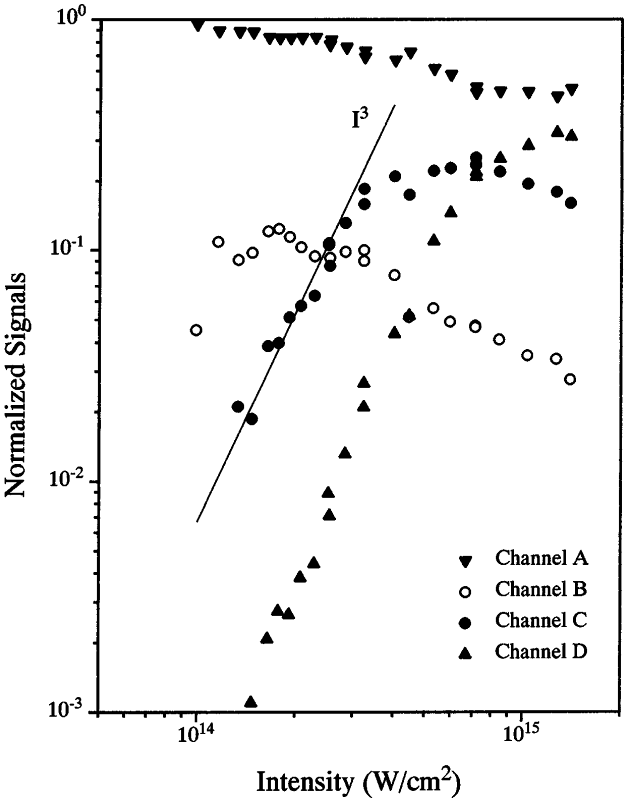

FIG. 3. Normalized signals for each channel (S_X/S_{ION}).

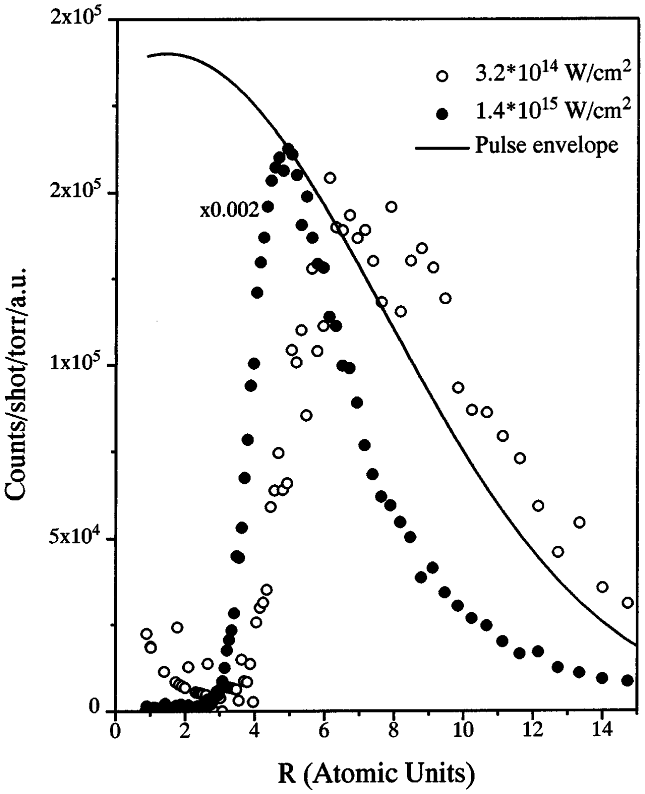

FIG. 4. Ionization signal as a function of internuclear separation and the laser intensity envelope.

Having understood the dissociation channels of $H_2{}^+$ in detail, we can now investigate the energy spectrum of channel *D*. Channels *B* and *C* produce outgoing nuclear wave packets which continuously probe the internuclear separation *R*. At some particular *R*, the wave packet might ionize. It would then be projected up to the $H^+ + H^+$ potential curve and gain an energy equal to e^2/R. By measuring the final kinetic energy of the ions in channel *D*, we can then directly measure the ionization rate as a function of *R*, shown in Fig. 4. One subtlety arises from the fact that the wave packet gains this Coulomb energy in addition to its initial energy. Thus, to use the Coulomb curve to map energy to internuclear separation, the initial energy must first be subtracted. We did this using the average kinetic energy of channel *C* (0.5 eV/proton). Figure 4 shows the results from two intensities, one above and one below saturation, to emphasize the distortion that can be caused by saturation effects. Clearly, at the higher intensity, the $H_2{}^+$ ionization has saturated before the wave packet has evolved to large internuclear separations, biasing the data to smaller separations. However, from Fig. 3 we can conclude that, at the lower intensity in Fig. 4, ionization into channel *D* has not saturated. These data can now be reliably interpreted as directly showing the ionization rate of $H_2{}^+$ as a function of internuclear separation.

Several groups have calculated the dependence of the ionization rate as a function of internuclear separation for a variety of molecules using many different techniques [6–11]. Interestingly, the general ionization dependence is rather insensitive to the number of electrons in the molecule, the charge state, or the wavelength, at least for low frequencies. Indeed, all of these calculations, except Ref. [9], considered relatively long wavelengths (790 to 1127 nm and dc fields) and show a maximum in the ionization rate from about 7 to 10 a.u. The calculations most comparable to our measurements are found in Ref. [8] on $H_2{}^+$. In fact, there appears to be two peaks in our data at 7 and 9 a.u. which correspond almost exactly to the structure present in the calculations in Ref. [8]. Because of the short laser pulse used in our experiment, the intensity drops as the molecule dissociates. We can plot the laser intensity as a function of *R*, if we use the same average kinetic energy, as above. Again, this is possible because, below saturation, we know the starting time of the wave packet and the initial internuclear separation (that of the neutral molecule). The field varies somewhat over the range of interest (Fig. 4). Despite this, these results agree exceptionally well with Fig. 1 of Ref. [8].

By using well-controlled experimental conditions, we have eliminated the effects of LIBS and ATD on the dissociation and ionization of $H_2{}^+$. This has allowed us to directly measure the dependence of the ionization rate on the internuclear separation of $H_2{}^+$. Our results agree quite well with theoretical calculations [8].

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Note added.—We have recently become aware of similar experiments by Walsh, Ilkov, and Chin [20]. However, their results are still potentially influenced by their pulse duration (150 fsec) and saturation of the data, effects that we have been careful to remove.

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