

Direct femtosecond laser excitation of the $2p$ state of H by a resonant seven-photon transition in H_2^+

G. N. Gibson, L. Fang, and B. Moser

Department of Physics, University of Connecticut, Storrs, Connecticut 06269, USA

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We observe Lyman- α radiation produced by the direct excitation of H_2^+ by 23-fs 800-nm laser pulses. The laser pulse first ionizes H_2 molecules and dissociates the ions through bond softening, leaving the molecules in the repulsive $2p\sigma_u$ state. The expanding H_2^+ ions enter a region of strong multiphoton coupling leading to a resonant seven-photon excitation of the $2s\sigma_g$ state. Finally, the $2s\sigma_g$ state dissociates into the $H(2s)$ and $H(2p)$ atomic limits. The latter state then decays through Lyman- α emission.

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The behavior of H_2^+ in high-intensity laser fields has been extensively studied [1] to understand various strong field effects, including charge-resonant enhanced ionization [2,3], rescattering [4,5], bond softening [6], sequential ionization [5], and correlated electronic and vibrational motion [4]. However, no studies have addressed the question of excitation of the molecule. Excitation of the repulsive molecular states leading to the $n=2$ dissociation limit would populate the $2s$ and $2p$ states of the hydrogen atom, and could be an interesting source of both metastable hydrogen and Lyman- α radiation. Novel sources of metastable hydrogen atoms are currently an active field of research [7] and the excitation scheme presented here represents an alternative.

Recent theoretical [8] and experimental [9–11] work suggests that multiphoton excitation may be a ubiquitous phenomenon in the strong-field interaction with molecules. However, studies in nitrogen and iodine suffer from a poor knowledge of the molecular potential energy curves. Thus, we chose to study H_2^+ as the potential energy curves are all known to high precision [12]. Furthermore, detection of excitation is straightforward through measuring the Lyman- α fluorescence.

Through various experiments on the Lyman- α fluorescence and supporting ion time-of-flight (TOF) measurements, we conclude that the following sequence of events leads to the generation of H atoms in the $2p$ state (see Fig. 1). First, an 800-nm laser pulse ionizes H_2 to H_2^+ . Second, the H_2^+ molecule experiences bond softening [6], leading to low-energy dissociation in the $2p\sigma_u$ state. Third, at an internuclear separation of 4.7 Å, there is a resonant seven-photon excitation from $2p\sigma_u$ to $2s\sigma_g$. The latter state is unbound and, finally, dissociates into the $H(2s)$ and $H(2p)$ states [13].

The laser consists of a standard amplified Ti:sapphire system producing 600- μ J pulses in 23 fs at a 1-kHz repetition rate [14]. Lyman- α fluorescence is detected with a vacuum-ultraviolet spectrometer and photomultiplier tube as described in Ref. [10]. Ion TOF measurements are made in a high-vacuum chamber as described in Ref. [15]. In addition, ions can be detected in coincidence, greatly improving the signal-to-noise ratio in certain experiments.

While we easily observe Lyman- α radiation, we first need to establish that it is produced by direct laser excitation, rather than through collisional excitation or recombination in the resulting plasma. Direct excitation will have a linear de-

pendence on gas pressure, while plasma processes will have a stronger than linear dependence [10]. Figure 2 shows the pressure dependence of the Lyman- α signal for two different pulse intensities. At low intensity, the signal is linear over the entire range of pressures used. At the higher intensity, the signal is linear up to about 200 mTorr, after which some plasma radiation is starting to occur. All of the following experiments were made at pressures well within the linear regime. While the pressure dependence has been used in the past to identify direct excitation [10,16], we made an independent measurement to confirm this, as follows. Our signal comes from the decay of the $H(2p)$ state, which is easily ionized. Thus, it should be possible to quench the fluorescence with a second weaker probe pulse. Figure 3 shows the

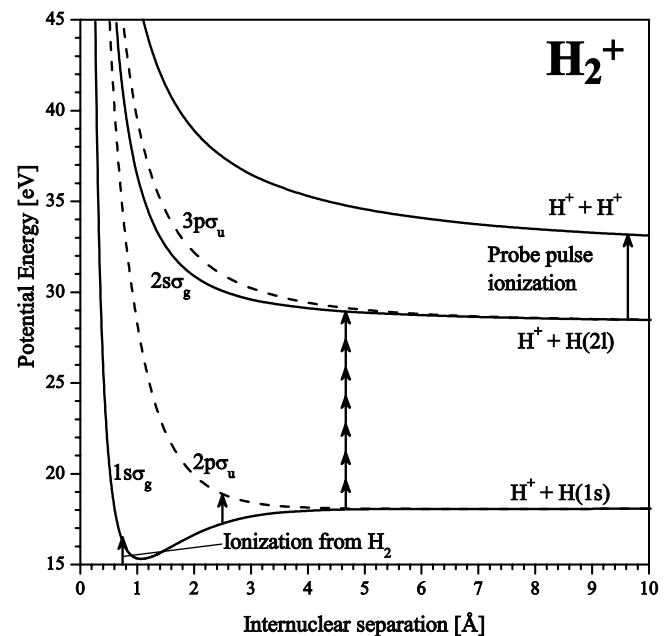


FIG. 1. Potential curves of H_2^+ and excitation pathway leading to the $H(2p)$ state. This pathway consists of ionization from the H_2 ground state to H_2^+ , followed by bond softening and resonant multiphoton excitation. Also shown is the probe pulse either for quenching of the Lyman- α radiation or for detection of a correlated $H^+ + H^+$ pair in the TOF experiment. The position of the probe pulse is shown for the internuclear separation corresponding to the delay used in the TOF experiment.

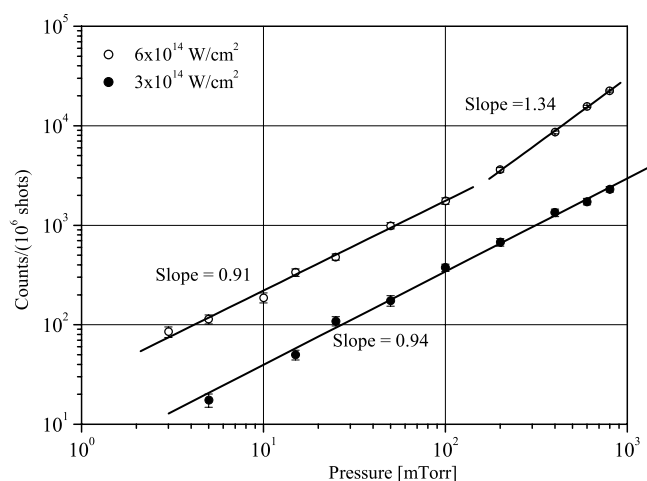


FIG. 2. Pressure dependence of the Lyman- α radiation for two different intensities.

Lyman- α signal as a function of the intensity of a probe pulse delayed by 500 fs. As can be seen, there is a substantial depletion of the fluorescence for weak probe intensities. Specifically, the probe pulse can only ionize H atoms excited before the probe pulse arrives. Since any resulting plasma will occur on a much longer time scale, at least the fraction of the signal being depleted by the probe must occur through direct excitation. While the data in Fig. 3 were taken with a fixed delay of 500 fs, the inset to Fig. 3 shows that depletion occurs within at most 100 fs of the pump pulse, providing essentially no time for plasma excitation. Thus, Figs. 2 and 3 unambiguously demonstrate that we have direct laser excitation of the H_2^+ molecule. Finally, the depletion experiment was also performed with circularly polarized light, as shown in Fig. 4. The signals are much weaker with circular polarization, but the depletion is still present.

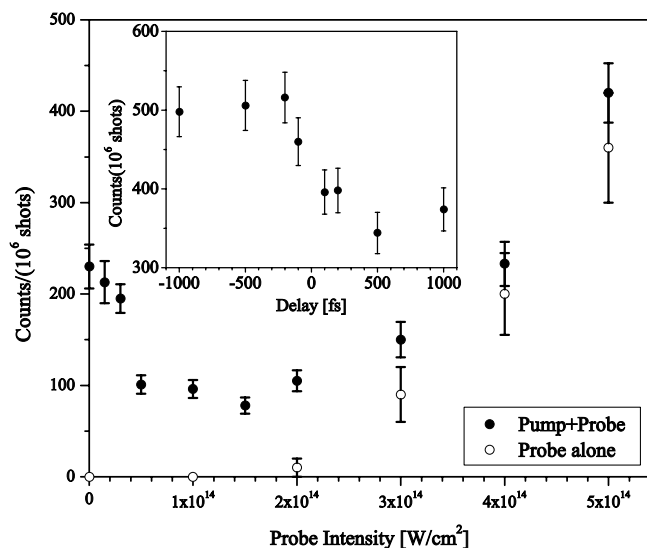


FIG. 3. Depletion of the Lyman- α radiation as a function of probe intensity at a fixed delay of 500 fs. Inset: depletion as a function of probe delay at a fixed intensity of 1.5×10^{14} W/cm 2 . Gas pressure is 50 mTorr and pump intensity 6×10^{14} W/cm 2 for both experiments.

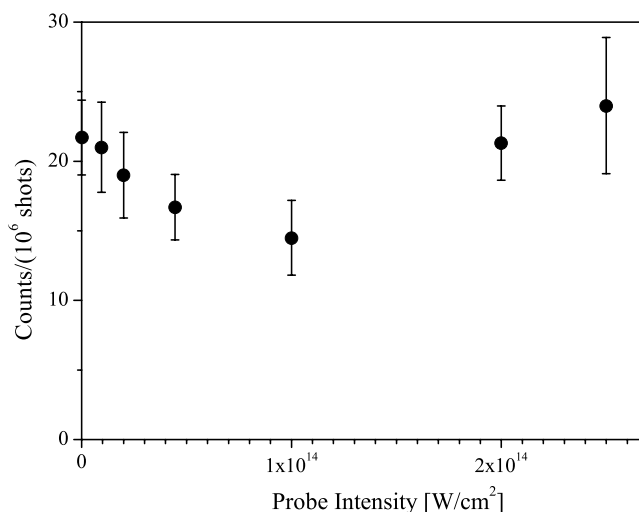


FIG. 4. Depletion of the Lyman- α radiation using circular polarization for both pump and probe pulses. Gas pressure is 50 mTorr and pump intensity is 3×10^{14} W/cm 2 .

Although we have established that the fluorescence is due to direct excitation, there are still two possible mechanisms for this excitation: resonant excitation and rescattering. If the laser pulse is interacting with just the H_2^+ molecule, we must have a resonant multiphoton transition between the initial and final states. However, the electron initially ionized from the original H_2 molecule could produce excitation through rescattering [4,17]. An important aspect of rescattering is that circular polarization prevents the ionized electron from returning to the original molecule, and, thus, any consequences of rescattering should disappear with circular polarization. Figure 4 demonstrates two things. First, since we see depletion, we know that we are producing Lyman- α radiation through direct rather than plasma excitation. Second, since we see direct excitation with circular polarization, it cannot result from rescattering. Thus, we are left with a resonant multiphoton transition to explain the Lyman- α radiation.

High-order multiphoton transitions can occur in any system which experiences a linear energy shift due to an external potential. Quantum systems with a linear Stark shift exhibit no ac Stark shift as it will average to zero over one cycle of the driving field. However, the strong coupling of the states gives rise to strong modulation of the levels, facilitating multiphoton transitions. This has been shown in molecular systems interacting with light where the degeneracy of dipole coupled charge-transfer states gives rise to a linear Stark shift [8]. This was also shown to be the case in flux qubits interacting with an external magnetic field [18], where 20-photon transitions with rf radiation were observed. Reference [8] considered a three-level system where one state is weakly coupled to the degenerate pair of charge transfer states. The energy levels of H_2^+ form a four-level system consisting of two pairs of degenerate strong coupled states where the coupling between the pairs is weak. Nevertheless, this energy level scheme will exhibit strong multiphoton transitions, just like the three-level scheme.

Figure 1 shows the structure of H_2^+ along with the relevant transitions. The multiphoton ionization of H_2 leaves

the molecular ion in the $1s\sigma_g$ state. Multiphoton excitation from this state at internuclear separations less than 3 \AA is unlikely as there are no coupled degenerate states in this range, as required by our theory of high-order multiphoton transitions [8]. For the molecule to reach larger separations, it must undergo bound softening [6], which can occur through the one-photon crossing at 2.45 \AA . This places the molecule on the $2p\sigma_u$ curve. While there are six excited states leading to the $n=2$ dissociation limits, we focus on the $2s\sigma_g$ and $3p\sigma_u$ states as these are the most strongly coupled and nearly degenerate pair among the excited states. With a wavelength of 800 nm and the need to conserve parity, the only allowed multiphoton transition is from the $2p\sigma_u$ to the $2s\sigma_g$ state via seven photons, at an internuclear separation of 4.7 \AA . At 4.7 \AA , the dipole coupling between the various states are the following [19]: $R(1s\sigma_g|2p\sigma_u)=4.4 \text{ a.u.}$ (atomic units), $R(2p\sigma_u|2s\sigma_g)=0.48 \text{ a.u.}$, $R(1s\sigma_g|3p\sigma_u)=0.47 \text{ a.u.}$, and $R(2s\sigma_g|3p\sigma_u)=6.4 \text{ a.u.}$, where $R(a|b)=\langle a|r|b\rangle$. These are favorable ratios of coupling strengths for our theory of strong-field resonant excitation to apply. Because the dissociating molecule reaches this resonance internuclear separation (4.7 \AA) during the laser pulse, we cannot time-resolve the excitation as we did in Ref. [11].

While we have identified the excitation pathway, there are two questions that cannot be answered from the fluorescence experiments. First, we cannot measure the dissociation energy of the $\text{H}^+\text{H}(2l)$ fragments, which is easily predicted from Fig. 1. Second, we cannot measure the excitation efficiency. Trying to measure the $\text{H}^+\text{H}(2l)$ channel directly in an ion TOF experiment is likely to be difficult as we do not expect the excitation efficiency to be very high, perhaps on the order of 1% [20]. This is due to the high ionization rate out of the $\text{H}(2l)$ state. Thus, the $\text{H}^+\text{H}(2l)$ signal would be swamped by the $\text{H}^+\text{H}(1s)$ signal. However, the depletion experiment discussed above suggests a way to measure the excited state dissociation channel directly. Since the ionization rate of the $\text{H}(2l)$ state will be much higher than the $\text{H}(1s)$ state, a weak probe pulse can selectively ionize the $\text{H}(2l)$ state and the resulting low-energy H^+H^+ channel can be detected through coincidence measurements.

Figure 5 shows the H^+ TOF coincidence spectrum with a probe pulse delayed by 50 fs . The peaks at 590 and 632 ns correspond to the normal ‘‘Coulomb explosion’’ channel [3] and is present without the probe pulse. The low-energy channel marked with the arrows only appears with the probe pulse and is the one we are interested in. The kinetic energy release of this peak depends on the pump-probe delay in a way consistent with Fig. 1, and certainly comes from the ionization of a low-energy H^+H channel. However, we need the intensity dependence of this peak to verify that it is not due to the ionization of the $\text{H}(1s)$ state. The signal between 597 and 623 ns comes from false coincidences.

Figure 6 shows the intensity dependence of the peaks marked in Fig. 5, as well as the ionization probability based on the Keldysh ionization rates. Note that the ionization of the $\text{H}(2p)$ state is not in the tunneling regime and so the full Keldysh theory [21] was used for both curves. At high probe intensity, the $\text{H}(1s)$ state can be ionized and makes up most of the signal. However, there is still a significant signal be-

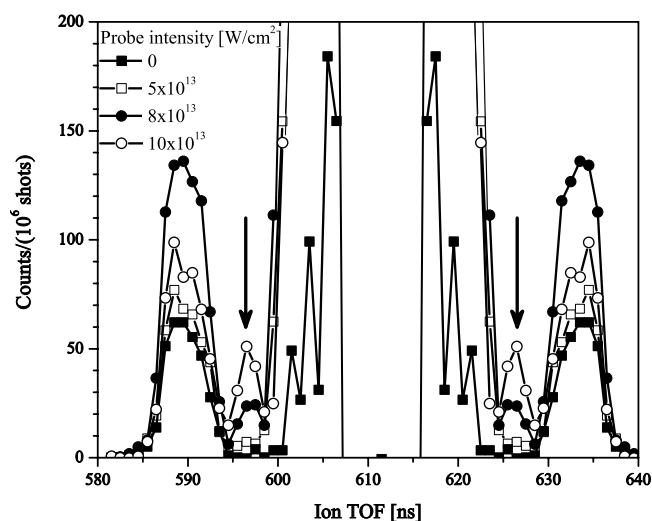


FIG. 5. TOF coincidence spectrum of H^+ for different probe energies. The arrows indicate the low-energy peaks that appear at low intensity corresponding to $\text{H}^+\text{H}(2p)\rightarrow\text{H}^+\text{H}^+$. Pressure is $5\times 10^{-8} \text{ Torr}$; pump intensity is $3\times 10^{14} \text{ W/cm}^2$.

low the threshold for $\text{H}(1s)$ ionization which must come from the $\text{H}(2p)$ state. The fits to the signal give a rough idea of the relative population in the two states. The result is that the $\text{H}(2p)$ has about 1% of the population of the $\text{H}(1s)$ state. The one discrepancy in the data concerns the threshold intensity for the ionization of the $\text{H}(2p)$ state. In the experiment we need more than $2\times 10^{13} \text{ W/cm}^2$, while the Keldysh model predicts $2\times 10^{12} \text{ W/cm}^2$. However, the TOF experiment is consistent with the fluorescence depletion experiment, i.e., the depletion does not fully set in until $4\times 10^{13} \text{ W/cm}^2$. Finally, the excitation pathway illustrated in Fig. 1 gives a kinetic energy release of 2.8 eV for the $\text{H}^+\text{H}(2p)$ dissociation channel. This compares well with

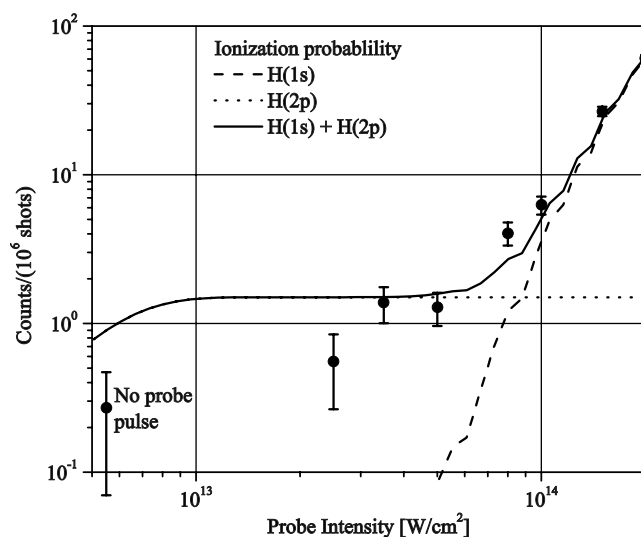


FIG. 6. Intensity dependence of the TOF coincidence signal along with Keldysh ionization probabilities for the $\text{H}(1s)$ and $\text{H}(2p)$ states.

the energy of 2.7 ± 0.2 eV for the peaks in Fig. 5 and supports both the identification of the excitation scheme in Fig. 1 and the peak in Fig. 5.

These experiments raise two questions concerning the ionization of excited states of molecules. First, as mentioned above, the Keldysh model does not fit the measured intensity required to ionize the $H(2p)$ state. This may be due a deficiency in the Keldysh model, or the fact that the ionization is actually occurring in a molecular system. Second, the depletion signal does not fully set in for 500 fs (Fig. 3). On the one hand, as the molecule comes apart, the $2p$ state gets closer in energy to the ionization limit, which would tend to increase the ionization rate and increase the depletion signal, as is observed. On the other hand, one might expect the ionization rate to reach a maximum at a critical internuclear separation for enhanced ionization [2,3] and then decrease. However, enhanced ionization was formulated for ground-state molecules in the tunneling regime, rather than excited

states in the multiphoton regime. Both these questions require further investigation.

In conclusion, we have observed Lyman- α radiation from a resonant seven-photon excitation of H_2^+ with a single femtosecond laser pulse. The proposed model for this excitation also predicts the generation of metastable hydrogen. This demonstrates a high-order multiphoton excitation mechanism that was predicted to occur in molecules. The excited state population is only about 1% partly due to the high ionization rate of the excited state. However, there may considerable room for improvement in the excitation rate. Most importantly, a tunable laser source will allow excitation of different electronic states at optimal internuclear separations. Moreover, in heavier molecules such as nitrogen, the excitation can occur in higher charge states with much higher ionization potentials, reducing the problem of ionization [22]. Such experiments are currently under way in our laboratory.

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