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Abstract

A tunable, high-intensity picosecond dye laser system has been employed with electron energy analysis to investigate the dynamics of (3+1) resonance-enhanced multiphoton ionization of H_2 via different vibrational levels of its $B\ {}^1\Sigma_u^+$ and $C\ {}^1\Pi_u$ electronic states. We observe production of molecular ions in various vibrational levels, with a shift to increased population of lower vibrational states of H_2^+ consistent with the a. c. Stark shift of the correspondingly lower vibrational levels of the C state into resonance with the three-photon energy of the laser. Clear evidence of direct dissociation of H_2 followed by single-photon ionization of the excited H atom is observed as well. Above threshold ionization of these two processes occurs readily. We also find that dissociative ionization is an increasingly important ionization pathway as the wavelength is increased. Finally, we see evidence of a new ionization pathway, which we assign to photoionization into a transient bound state created by the avoided crossing of the first repulsive electronic state of H_2^+, $|2p\sigma_u, n\rangle$, with the single-photon-dressed ground state of H_2^+, $|1s\sigma_g, n+1\rangle$.

Introduction

As theory and experiment converge on an understanding of intense-field photoionization of atoms,[1] the interest of the multiphoton community has turned to molecules. Specifically, the role of internal degrees of freedom in above-threshold ionization (ATI) has been examined, leading to discussions of above-threshold dissociation (ATD) of the H_2^+, molecular ion.[2,3] Most of the ATI experiments in H_2 have employed limited laser wavelengths, specifically Nd:YAG harmonics or excimer frequencies. For our study of the effects of resonances on the ATI of H_2, we employ a tunable dye laser system. This allows us to examine specific intermediate state resonances in the multiphoton ionization scheme, and trace their behavior in the presence of the intense laser field.

In this paper we discuss the results of our tunable ultraviolet H_2 photoionization dynamics study.[4] We excite rovibronic levels of the $B\ {}^1\Sigma_u^+$ and $C\ {}^1\Pi_u$ electronic states at the three-photon level, and ionize with a fourth photon. We use photoelectron energy analysis to probe the details of the photoionization process. Our experimental apparatus was described elsewhere;[4] briefly, we focus the frequency-doubled output of a pulse-amplified picosecond dye laser between the pole pieces of a "magnetic bottle" photoelectron spectrometer. We record the photoelectron time-of-flight distributions for a number of different excitation wavelengths ($288.5\ \text{nm} \leq \lambda \leq 304\ \text{nm}$) and peak laser intensities I_0, adjusting the H_2 pressure as I_0 is increased in order to keep the number of electrons produced each laser shot constant. The spectra presented here have all been converted to photoelectron energy and normalized to 1 x 10^{-8} torr pressure of H_2.

Molecular Photoionization

Typical photoelectron energy spectra recorded at 288.5 nm are presented in Fig. 1 for electron energies from 0.6 to 2.0 eV. Each spectrum was recorded at a different I_o (left vertical axis), and has been divided by the indicated scale factor (right vertical axis) then offset from the horizontal axis for display. At 288.5 nm the energy of three photons is just above the field-free energy of the $C\ ^1\Pi_u$ (v´=2) vibrational state. The peaks in Fig. 1 are assigned to molecular photoionization of H_2, producing H_2^+ in several vibrational levels (v^+). At the lowest I_o, most of the ions are produced with two quanta of vibrational energy, with some population of v+=1 and v+=3. This predominantly Δv=0 ionization is consistent with the Franck-Condon (FC) overlap of the vibrational manifolds of the neutral $C\ ^1\Pi_u$ and the ionic $X\ ^2\Sigma_g^+$ electronic states. As I_o increases, the relative production of v^+=1 increases until the v^+=1 peak equals the v^+=2 peak. This happens because the C v´=2 state is a.c. Stark shifted up and out of three-photon resonance by the electric field of the laser. Likewise, the C v´=1 state is shifted <u>into</u> three-photon resonance, then Δv=0 ionization produces H_2^+ ions in the v^+=1 vibrational level. The energy of the v^+=1 peak initially decreases as I_o increases, due to the increased Ponderomotive energy U_p in the portion of the laser focus where C v´=1 is in resonance. Further increases in I_o do not shift this peak further: it arises predominantly from Δv=0 resonant photoionization of the C v´=1 state, and at higher I_o this state is no longer in resonance. Similarly, the v^+=2 peak is initially shifted 20 meV (consistent with a small U_p at $I_o \approx 5 \times 10^{12}$ W/cm^2) but does not move further as I_o increases. This v+=2 peaks arises from the ever-expanding volume of the laser focus where the laser intensity is less than 10^{13} W/cm^2, and C v´=2 is in three-photon resonance. This behavior is the hallmark of resonances in ATI, as has been discussed in great detail by others.[1] Finally, we assign a broad photoelectron peak at 5.4 eV (not seen in Fig.1) to ATI of this molecular photoionization. We lack sufficient energy resolution to resolve the vibrational levels in this above-threshold electron peak.

Dissociation followed by atomic ionization

Electron energy spectra between 1.5 and 6.0 eV are presented in Fig.2 for λ= 297.5 nm. As the laser wavelength is tuned, the positions of the peaks shifts in a manner attributable to the change in total energy available. At 297.5 nm, the energy of three photons is just below the field-free energy of the $C\ ^1\Pi_u$ (v´=1) vibrational state. At the lower laser intensities this energy region of the photoelectron spectra is dominated by a peak at 2.63 eV which is very sharp at most laser intensities, occurs at the energy expected for single-photon ionization of H(3ℓ), and does not shift in position as I_o increases (the large shoulder toward lower photoelectron energy observed in Fig. 2 is assigned to a different ionization mechanism because of its wavelength dependence). We assign this peak to photoionization of H(3ℓ), resulting from direct dissociation of neutral H_2 followed by ionization. Photoionization occurs readily of H(3ℓ) since only one photon is required; however, we see no evidence for ionization of any other states of atomic H. At 297.5 nm, absorption of four photons is above the dissociation limit to produce H(3ℓ) but below the energy required to produce H(2ℓ). The absence of any H(2ℓ) suggest this dissociation occurs at internuclear distances R too large to curve-cross to potentials which correlate to H(2ℓ)+H($1s$) dissociation products. This is consistent with the population at the three-photon level of high vibrational levels in the $B\ ^1\Sigma_u^+$ state which have rather large (R > 5 bohr) outer turning points. Absorption of a fourth photon at this R will have a favorable FC overlap for transition into a neutral, doubly excited state similar to the $H_2^+\ |2p\sigma_u>$ repulsive state, converging to the dissociation limit of H($1s$) + H(3ℓ). The narrowness of the peak is understood in the context of the relative a.c. Stark shift of the excited (n=3) state and the ionization potential. Recent calculations[5] have shown that our use of >4 eV photons permits us to use the "high frequency approximation", because this excited state has an a.c. Stark shift nearly equal to that of the ionization potential. Therefore, no matter what intensity the ionization occurs at, the excess energy available for the photoelectron is always the same for our 1.5 ps laser pulses.

Dissociative Ionization

For 297.5 nm, the energy of the final peaks observed in these experiments are 2.4 eV and 3.75 eV. These high-energy peaks do not correspond to any low field processes. We traced the energy of these peaks as a function of laser wavelength to determine the responsible mechanisms. For the 2.4 eV peak, we observe a marked decrease in photoelectron energy as the photon energy decreases, but the decrease is not a simple function of the photon energy. We assign the 2.4 eV peak to dissociative ionization occurring after a two-photon absorption from the outer turning point of a vibrational level in the B state. This process can be resonantly enhanced by any of a number of doubly-excited states at the four-photon level (the same states which dissociate to produce excited H atoms). If we estimate R=5.5 bohr, the energy of the $H_2^+\ |2p\sigma_u>$ state at that R is 18.45 eV. Five photons at λ=297.5 nm add to 20.84 eV. The excess energy available for partitioning between the electron and the dissociating H($1s$) + H^+ is 20.84 - 18.08 = 2.76 eV; the excess energy above the $H_2^+\ |2p\sigma_u>$ state is 2.39 eV. The observed electron energy of 2.4 eV falls neatly between these two bounds. This behavior occurs at each wavelength studied, with the exception of the last wavelength (304 nm), where the observed electron energy is less than 5% larger than the upper bound calculated using our simple delta-function model for this absorption followed by dissociative ionization model. Dissociative ionization has been observed at other laser wavelengths by others, most notably by Rhodes and coworkers.[6]

Ionization into a transient laser-induced bound state

The evidence for a fourth photoionization mechanism in our study is as follows. With the possible exception $\lambda = 288.5$ nm, the electron spectra display a prominent electron peak near the photon energy. Although the peaks are broad, they are fairly symmetric and we find a decrease in peak energy that is nearly 1:1 with decreasing photon energy. This rules out a conventional, multiple-photon ATI explanation for these high-energy electrons. We assign these electrons to ionization into the adiabatic state formed by the avoided crossing of the n+1-photon dressed ionic bound state potential $|1s\sigma_g, n+1\rangle$ and the n-photon dressed ionic repulsive $|2p\sigma_u, n\rangle$ potential. This crossing creates two adiabatic states (upper and lower adiabatic potentials, UAP and LAP) from the diabatic states; it is the LAP that is responsible for the "bond softening" observed by others.[2,3] We are concerned with the UAP. Three-photon excitation of the *B* state prepares an H_2 molecule with large R. Two further photons are absorbed, and photoionization occurs into the UAP formed by the avoided crossing. We estimated the depth of the UAP by a simple two-state avoided crossing calculation involving only the $|1s\sigma_g, n+1\rangle$ and $|2p\sigma_u, n\rangle$ diabatic potentials. We diagonalized our adiabatic potentials to obtain their eigenvalues and eigenfunctions. For example, at $\lambda = 304$ nm and $I_0 = 1 \times 10^{13}$ W/cm^2, the UAP is bound by 1 eV, and supports 14 vibrational states. Finally, we calculated the FC overlap between vibrations in the *B* state and vibrations in the UAP. We found that the electron energies predicted by the best FC overlap with the *B* state agree qualitatively with the observed electron energies, but are approximately 0.4 eV lower than those observed. We are satisfied with this agreement, given the simple nature of our computation. Further computations await a better understanding of the effect of the strong laser field on the valence *B* state: our computation used the field-free potential which is almost certainly invalid at the laser intensities employed.

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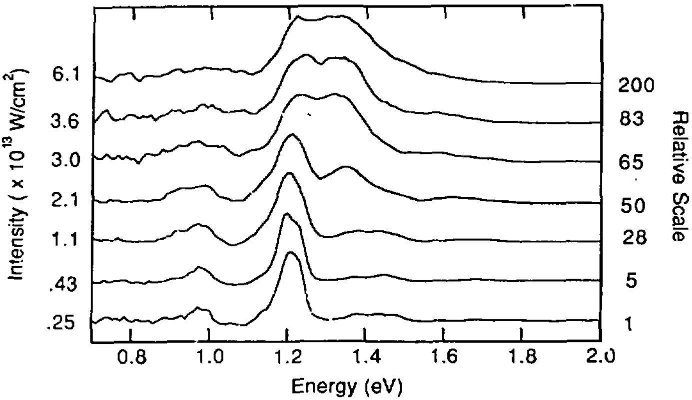

Figure 1. Photoelectron energy spectra recorded at 288.5 nm. Peak laser intensity for each spectrum is indicated on the left axis, and the amount by which each spectrum was divided for presentation purposes is indicated on the right axis.

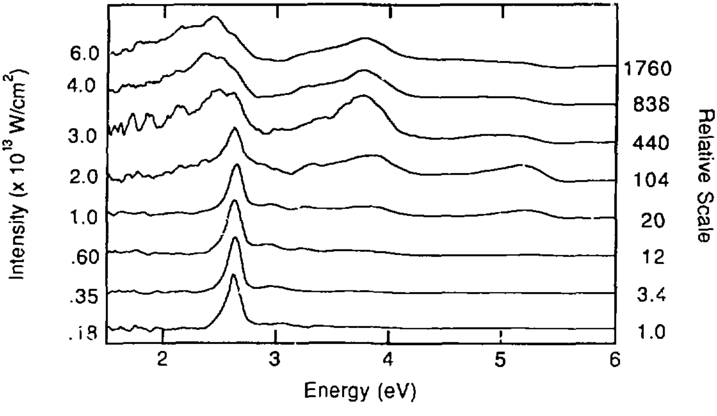

Figure 2. Photoelectron energy spectra recorded at 297.5 nm, all else the same as Fig.1.