Simplification of Photoelectron Spectra of H_2 in Intense Laser Fields

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The response of molecular hydrogen to multiphoton excitation with intense short laser pulses is probed using photoelectron spectroscopy. At wavelengths and laser intensities for which molecular Rydberg states are ac Stark shifted into resonance, the small quantum defects of molecular hydrogen and the loss of the ponderomotive energy to the electromagnetic field give rise to very simple photoelectron spectra that coincide with those of excited atomic hydrogen.

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Recent studies on multiphoton ionization of molecular hydrogen in intense laser fields have revealed a great diversity of photoelectron energy spectra that at times appear to defy assignment of specific excitation paths [1-3]. We show here that multiphoton ionization of molecular hydrogen in intense fields can give rise to very simple, atomiclike photoelectron features. These occur when molecular Rydberg states act as intermediates in the photoionization event. This finding is quite analogous to photoelectron spectra reported recently for atomic xenon [4,5], atomic hydrogen [6], and molecular nitrogen [7]. A key element for the appearance of these spectra is to bypass excitation of valence states by the proper choice of wavelength and intensity. We can account for the intensity dependence of the spectra using a simple model calculation.

The photoelectron spectra were recorded in a magnetic bottle, time-of-flight spectrometer [8] using an amplified, tunable, and frequency-doubled dye laser which delivers 1-mJ pulses of 1.5-ps duration. The peak intensities quoted are calculated for a 28-μm spot diameter (twice diffraction limit). Photoelectron spectra were recorded at nine wavelengths between 330 and 310 nm. In this case the three-photon energy lies below the $C\,^1\Pi_u$ state while the four-photon energy lies near the ionization limit of H_2 (see Fig. 1). Typical distributions taken at 326 and 318.5 nm are shown in Figs. 2 and 3, respectively. The electron energies expected from one-photon ionization of excited atomic hydrogen,

$$H(nl)+h\nu \rightarrow H^{+}+e\,, \tag{1}$$

are indicated in the figures. The spectra suggest that process (1) is a dominant ionization channel. This observation is made at high intensity for all wavelengths studied. At low intensities and bluer wavelengths, more complex spectra appear. The tick marks labeled by the vibrational quantum number v^{+} at the top of Fig. 3 give the energies expected for nonresonant five-photon ionization of H_2 leading to levels of $H_2{}^{+}(v^{+},J=0)$.

Figure 1 shows the relevant excited states of H_2 and the location of the vibrational wave function of the ground state $H_2(v=0)$. At molecular distances most of the excited states are well described by the Rydberg character derived from the core potential-energy curve of ground-state $H_2{}^{+}$. The most profound deviation from this pure Rydberg picture arises for the lowest $^1\Sigma$ states owing to their long-range ion pair character and at large internuclear separation for all states owing to the interaction with the Rydberg states belonging to the $2p\sigma$ core of the molecular ion [9].

We see from Fig. 1 that the Franck-Condon overlap into the $B\,^1\Sigma_u^+$ state is poor at 326 nm, and that the first "good" resonant states occur at the four-photon energy. This suggests that an important ionization channel may involve four-photon excited states of the molecule:

$$H_2+4h\nu \rightarrow H_2(nl\lambda,v)\,. \tag{2}$$

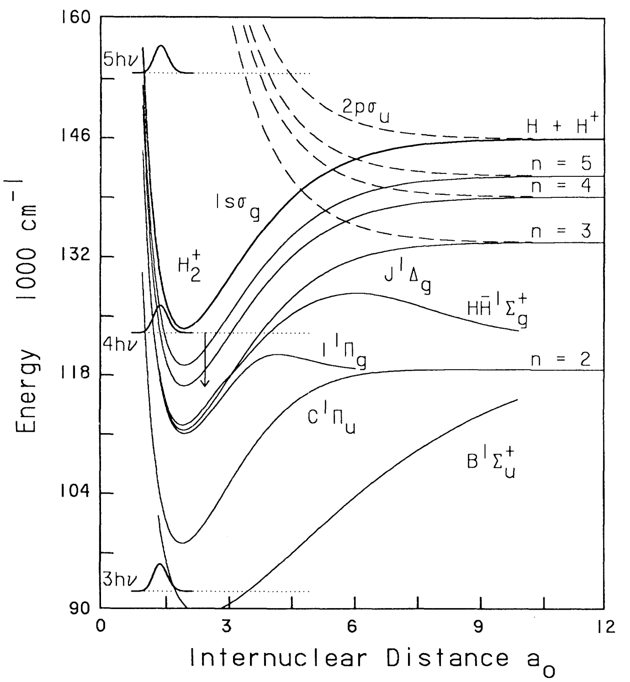

FIG. 1. Potential-energy diagram of relevant states of H_2. The energy scale is relative to the lowest level of H_2 $X\,^1\Sigma_g^+$. The multiphoton energies for 326 nm are marked. The magnitude of the arrow indicates the ponderomotive shift at 8×10^{13} W/cm^2.

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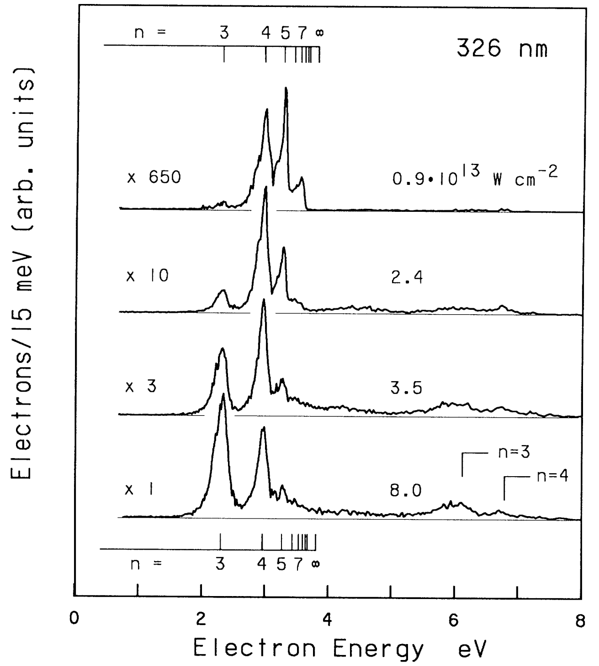

FIG. 2. Photoelectron spectra recorded at 326 nm at various intensities. The labels refer to electron energies expected from one-photon ionization of excited atomic hydrogen.

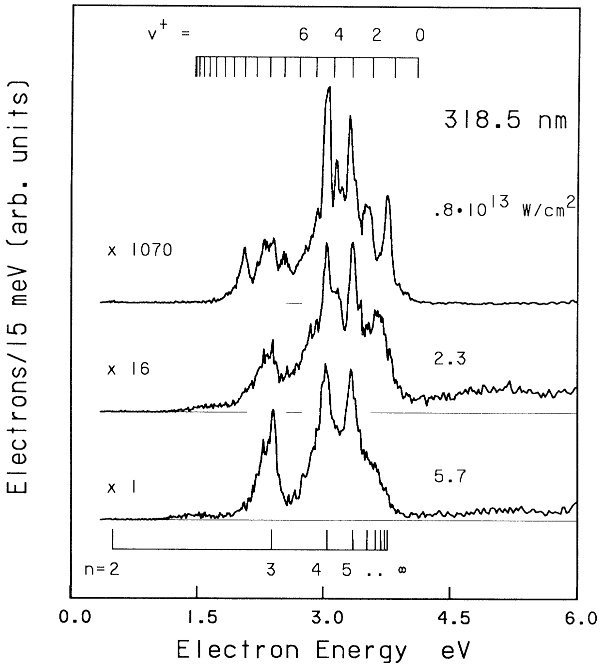

FIG. 3. Photoelectron spectra recorded at 318.5 nm at various intensities. Bottom labels are as in Fig. 2. The labels at the top give energies expected for nonresonant five-photon ionization into $H_2^+(v^+,J=0)$.

These are subsequently ionized by a fifth photon:

$$H_2(nl\lambda,v)+h\nu \rightarrow H_2^+(v^+)+e \,. \tag{3}$$

In the light of previous photoionization studies in strong fields [4-7] it appears natural to assume that at elevated intensity, specific intermediates are shifted into resonance due to the ac Stark effect. In a first approximation, we may assume that the Rydberg states experience [10] a shift equal to the ponderomotive energy of a free electron:

$$\varepsilon_p = 1153 I/(h\nu)^2 \,\mathrm{cm}^{-1} \,. \tag{4}$$

Here I is the laser intensity in units of 10^{12} W/cm^2, and $h\nu$ is the photon energy in eV. At the highest intensity shown in Fig. 2, Eq. (4) predicts a shift of 6400 cm^{-1}, about three vibrational spacings in H_2^+. The magnitude of this shift is indicated in Fig. 1 by the downward arrow. Specifically under these conditions, the vibrational levels $v=5,4,3$ of the states belonging to the $n=3$ manifold [11] become sequentially resonant with the four-photon dressed ground state. In addition, the vibrational levels $v=2,1,0$ for $n=4$, the levels $v=1,0$ for $n=5$, and the levels $v=0$ for $n=6$ and 7 are swept through resonance for such a pulse. The simplicity of the electron energy spectra observed can be reconciled with excitation to such a wide variety of vibrational states from five Rydberg manifolds if we consider the following.

The postulate that the ac Stark shift of the Rydberg electron is equal to the ponderomotive shift predicts that the photoelectron resulting from one-photon ionization of the Rydberg state [Eq. (3)] initially has the kinetic energy

$$E_e = h\nu - E_{H_2^+(v^+)} + E_{H_2(nl\lambda,v)} \,, \tag{5}$$

where the molecular energies quoted are at zero field. Here we have made the implicit assumption that the ac Stark shift of the ion core of the Rydberg state is equal to that of H_2^+.

Relation (5) describes the electron's energy when it is born in the field, irrespective of the intensity at which four-photon excitation of the molecular Rydberg state occurred. For a laser pulse of duration short compared to the time required by the electron to leave the focal region (a 3-eV electron moves 1 μm in 1 ps), this is also the final energy detected in the experiment [12]. The quantum defects of gerade Rydberg states of molecular hydrogen [11] are with few exceptions very small. Therefore, at the resolution of our electron spectrometer, 50 meV, the molecular photoelectron energies (5) are almost indistinguishable from those from excited atomic hydrogen ionized in process (1), provided that the final vibrational state of the molecular ion, v^+, is equal to that of the molecular Rydberg state, v. This last condition is fulfilled when the quantum defect of the Rydberg state is small at all internuclear distances sampled by the vibrational wave function. From the excitation sequence (2) and (3) we expect that H_2^+ will be produced in a variety of vibrational levels, depending on intensity and wavelength, but the electron's energy will merely reflect the quantum defect of the molecular Rydberg states being ionized, regardless of their vibrational quantum numbers.

Since specific vibrational levels of the molecular ion are rapidly photodissociated at the wavelengths used here, we should also consider the fate of the final ion state, and for that matter the fate of the molecular Rydberg core when subjected to intense fields. Photodissociation of the molecular ion proceeds through a transition from the $1s\sigma_g$ orbital to the repulsive $2p\sigma_u$ orbital [13]. The molecular Rydberg states share this very same core. To estimate the importance of molecular photodissociation,

$$H_2(nl\lambda,v)+h\nu \rightarrow H(1s)+H(nl)\,, \tag{6}$$

we approximate this cross section σ_{diss} by that calculated [12] for H_2^+. In Table I we compare these with the photoionization cross section for reaction (3), σ_{ion}, calculated using the generalized equation given by Lorents, Eckstrom, and Huestis [14] with zero quantum defect. The results in Table I show that dissociation dominates over ionization for the higher vibrational levels. However, owing to the small quantum defects, the electron signature from ionizing excited atoms formed in process (6) using a sixth photon is indistinguishable from that from molecular ionization.

To simulate the intensity dependence of the photoelectron spectra we use a simple model that neglects contributions from a three-photon intermediate. The model assumes as bound states the ground state $H_2(v=0)$ and the four-photon-excited Rydberg state $H_2(nl\lambda,v)$, and as continuum states the products from reactions (3) and (6). Following Holt, Raymer, and Reinhardt [15], the loss of ground-state hydrogen via a specific intermediate $|nl\lambda,v\rangle$ can, under our experimental conditions, be approximated by the time-independent rate

$$\Gamma_{nl\lambda v}=\frac{\Omega^2}{4}\,\frac{\gamma_2}{(4h\nu-E_{H_2(nl\lambda,v)}-\delta_2)^2+\gamma_2^2/4}\,. \tag{7}$$

Here γ_2 is the rate of loss due to ionization and dissociation:

$$\gamma_2=(\sigma_{\text{ion}}+\sigma_{\text{diss}})\Phi\,, \tag{8}$$

where Φ is the photon flux. The ac Stark shift of the Rydberg state, δ_2, is approximated by relation (4). We express the four-photon Rabi frequency Ω as

$$\Omega_{nl\lambda v}\propto\langle\chi_{v=0}|\chi_{v^+}\rangle I^2 n^{-3/2}\,, \tag{9}$$

where the χ's represent the vibrational wave functions of the ground state of H_2 and of the core state of the neutral molecule.

We have used expressions (7)-(9) to calculate rates for the four-photon intermediates with core states $v^+=0$-10 for the manifolds $n=3$-10, assuming zero quantum defect. The rates have been folded with a spatially and temporally Gaussian laser pulse profile. To simulate the electron energy spectra we evaluate the contributions from each Rydberg state (quantum number n) to the photoelectron signal at the energy $E_n=h\nu-R/n^2$, the value from Eq. (5) with zero quantum defect and $v=v^+$. Relative intensities of the calculated signal at energy E_n are shown in Fig. 4 for excitation at 326 nm.

The model predicts that at high intensity the photoelectron peak for $n=3$ dominates over the contribution from $n=4$ and 5 just as is observed in Fig. 2. As the peak intensity is lowered the contribution from $n=4$ first overtakes that from $n=3$, and at yet lower intensity the con-

TABLE I. One-photon ionization [14] and dissociation [13] cross sections for molecular Rydberg states of H_2 at 326 nm in units of 10^{-18} cm^2.

n	3	4	5	6	7
σ_{ion}	1.5	0.36	0.12	0.047	0.022
v	5	4	3	2	1
σ_{diss}	13	4.1	0.23	0.003	0.000006

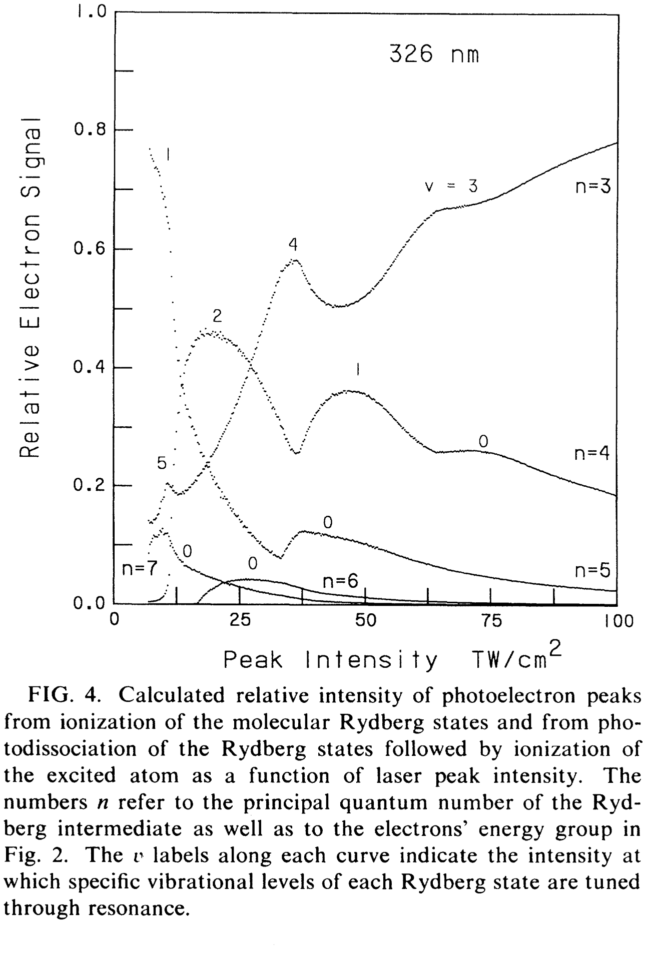

FIG. 4. Calculated relative intensity of photoelectron peaks from ionization of the molecular Rydberg states and from photodissociation of the Rydberg states followed by ionization of the excited atom as a function of laser peak intensity. The numbers n refer to the principal quantum number of the Rydberg intermediate as well as to the electrons' energy group in Fig. 2. The v labels along each curve indicate the intensity at which specific vibrational levels of each Rydberg state are tuned through resonance.

tribution from $n=5$ dominates, again consistent with what is found experimentally. The prediction of the basic features of the observed spectra is taken as an indication that the underlying model for explaining the photoelectron spectra is sound.

Why do more complex spectra appear at shorter wavelengths and at low intensities (see Fig. 3)? At shorter wavelength we access higher vibrational levels in the *B* state with better Franck-Condon factors. The non-Rydberg character of the *B* state well allows transitions that are *not* diagonal in vibration to four-photon states and to $H_2{}^+$. Photoelectron energies will then reflect the change in vibrational quantum number *and* the (unknown) ac Stark shift of the *B* state. The photoelectron spectra (as in Fig. 3) can simplify as the intensity is raised for two reasons. First, the ac Stark shift of the *B* state, if positive in energy, will shift vibrational levels with good Franck-Condon factors out of three-photon resonance—leaving open only the four-photon access to the Rydberg states. Second, the rate of four-photon excitation of the Rydberg states will eventually exceed the rate of three-photon excitation to the *B* state as the intensity rises.

The model calculation described above can also predict the rate of proton formation relative to $H_2{}^+$ and the influence of the ac Stark shift of the neutral Rydberg molecule on the proton energy distributions. A more detailed discussion of these predictions and how this model can be extended to include above-threshold dissociation [16] will be presented in a forthcoming paper.

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