Field Ionization of High-Lying States of H_2

E. Y. Xu, H. Helm, and R. Kachru

Chemical Physics Laboratory, SRI International, Menlo Park, California 94025

(Received 26 June 1987)

We report the first systematic study of the field ionization threshold of molecular Rydberg states. We find that the $v=0$ np series of both orthohydrogen and parahydrogen, converging to the lowest rotational state of H_2^+, with n ranging from 18 to 30, ionize at fields given by $1/16n_s^4$, with n_s, the effective quantum number at the field at which ionization takes place, given by $n_s = n - 0.5$. Our threshold-field measurements suggest that the ionization process is described classically.

The ionization by means of an external electric field of excited atoms has long attracted considerable experimental[1-7] and theoretical[8] interest. The field-induced ionization process in atoms is now a fairly well understood and a practically useful phenomenon. In some cases, such as in atomic hydrogen,[6-8] ionization occurs by tunneling of the electron through the potential barrier along the axis of the applied external field. In other cases, such as nonhydrogenic atomic states with finite quantum defects, the field ionization is described by a classical "saddle-point" model,[2] in which states are stable or unstable against ionization if they are below or above the saddle point in the combined Coulomb and external potential. Apart from its scientific interest, field ionization (FI) has important applications, such as selective detection with high sensitivity in experiments involving excited species.

It has long been known that the molecular Rydberg states are field ionizable,[9-11] and this phenomena has been employed in many experiments for the detection of the excited molecules. However, apart from the n^{-4} scaling of the ionization field,[9] where n is the principle quantum number, nothing else is known about the ionization mechanism. It is not known if these molecules ionize like a hydrogenic atom or like an alkali-metal atom. Also, it is not known to what extent the core rotation plays any role in the ionization process.

In this Letter we report for the first time the study of the onset of ionization of H_2 molecules in a single quantum state, when a quasistatic electric field is applied. We find that the $v=0$ np states of H_2, with n ranging from 18 to 30, and converging to the $N=0$ and 1 rotational states of the vibrationless H_2^+ core, ionize at fields close to the $1/16n^4$ classical limit. Furthermore, we find that for the Rydberg states studied thus far, the field ionization thresholds for states of different total angular momentum J (disregarding the spin), but same N, are the same, which suggests that the electron-core rotational interaction plays no part in the ionization process.

The experimental arrangement consists of a pulsed H_2 supersonic beam, which is turned on for 100 μs. The H_2 beam passes between two field plates, spaced 1 cm apart. One of the plates has a 7-mm-diam hole with a grid for ion extraction. The pulsed nozzle, the plates, and the detector are all housed in a vacuum chamber pumped to 3×10^{-8} Torr. When the H_2 beam is turned on, the pressure rises to 5×10^{-5} Torr and provides a high H_2-number density in the interaction region in a collision-free environment. The H_2 beam is intersected near the center of the plates by two counterpropagating tunable dye laser beams which are focused by a 10-cm-focal-length lens. The first dye laser beam, with $\lambda_1 = 200$-201 nm, is produced by our, first, frequency doubling the output of an yttrium-aluminum-garnet–pumped dye laser, and then Raman shifting the frequency-doubled output to the fourth anti-Stokes order in a high-pressure H_2 cell. The first dye laser with a typical energy of 100 μJ/pulse and a spectral width of 1 cm^{-1}, excites the H_2 molecules by a two-photon process from the initial $v''=0$, $J''=0$ (1) $X\,^1\Sigma_g^+$ ground state to the $v'=0$, $J'=0$ (1) $^1\Sigma_g^+$ E-F excited state. The second dye laser, with $\lambda_2 = 398$-403 nm, spectral linewidth of 0.5 cm^{-1}, and energy of 500 μJ/pulse, subsequently excites the molecules from the selected E-F state to a $v=0$, $J=0$ ($J=0,1$, and 2), np Rydberg state converging to the $N=0$ (1) rotational state of the H_2^+ ion core. The second dye laser is delayed in time with respect to the first one by 30 ns.

A high-voltage pulse of 0.3-μs rise time and up to 4-kV/cm field amplitude is applied on the extraction plates 0.5 μs after the laser pulses, field ionizing the Rydberg molecules and accelerating the H_2^+ ions formed into an electron multiplier. Since the FI pulse peaks and remains constant to about 5% of its value for about 0.2 μs before decaying rapidly, we are in fact measuring ionization rates that are in excess of 10^7 s^{-1}. The energy levels of the Rydberg series are first mapped out by our scanning the second laser wavelength while keeping the first dye laser fixed on a particular two-photon resonance from the ground state to the E-F state and setting the high-voltage pulse on the field plates to a value high enough to ensure complete ionization of states with $n > 18$.

The plot of the ion signal as a function of the second dye-laser wavelength is used to identify the np $J=0$, 1,

and 2 states. From the measured level positions and previous work by Herzberg and Jungen[12] and by Dieke,[13] we find that starting from the $J' = 1$, ortho ($J' = 0$, para) E-F state, we excite primarily the $J = 1$ and 2 ($J = 1$) np states, converging to the $N = 1$ ($N = 0$) limit of the H_2^+ ion. The excitation to the other allowed states is weak.

After the Rydberg states are identified, the two dye lasers are tuned to excite the H_2 molecule into an excited np state with a well-defined J and rotational quantum number of the ion core, N. The ionization probability as a function of the applied electric field is studied by our increasing the amplitude of the FI pulse from a small value until an observable threshold is detected. Figure 1 illustrates a typical dependence of the ionization signal as a function of the applied electric field. The abrupt onset of the field ionization is evident in Fig. 1, which shows that beyond the threshold the ionization signal increases rapidly. In Fig. 1, the bump in the ion signal near 500 V/cm is not reproducible, and is due to the signal being noisy. Furthermore, because of the noise in our signal we cannot rule out additional field ionization thresholds at higher fields.

Figure 2(a) shows the measured dependence of the ionization threshold field F_T as a function of the effective principal quantum number n_s, for the ortho-H_2 $J = 1$ and 2 Rydberg states converging to the $N = 1$ rotational state of H_2^+. $n_s = n - 0.5$ is the effective quantum defect of the np states, at the field at which ionization takes place. The error bars in Fig. 2 represent the uncertainty in our threshold measurement which is primarily due to the relatively low ion-collection efficiency of our setup. The threshold measurements for the np states that are missing in the plot shown in Fig. 2 were not measured because the excitation probability to these states from the E-F state is small as a result of perturbations from low-n
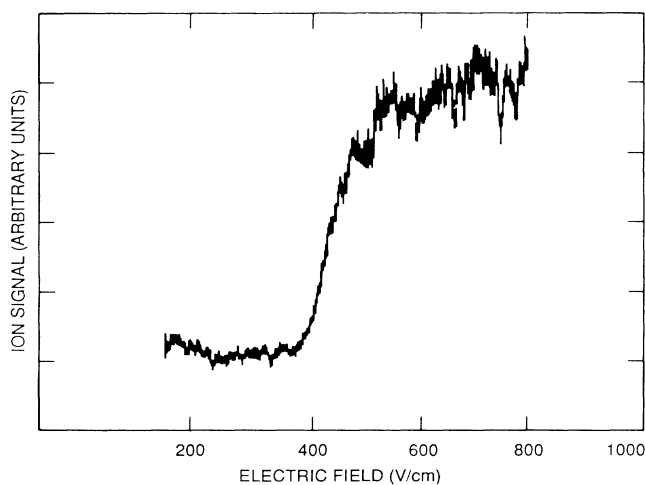
states converging to high vibrational states of H_2^+. The observed threshold agrees very well with the $1/16n_s^4$ field value, shown as a solid line in Fig. 2, implying that the ionization process is described classically (see discussion below).

The Coulombic potential experienced by the Rydberg electron in an external field is $V = -1/r - Fz$ (in atomic units), where F is the external electric field applied along the z axis. Since the saddle point in the combined potential occurs at a distance $z_s = F^{-1/2}$, the potential at the saddle point is given by $-2F^{1/2}$. Viewed classically, ionization occurs if the electron energy $W = -1/2n^{*2}$ is at or above the saddle-point potential. Note that $n^* = n - \delta$ is the effective quantum number, and δ is the quantum defect. Thus, classically, ionization occurs at $F_T = 1/16n^{*4}$, if the Stark shifts of the energy levels can be
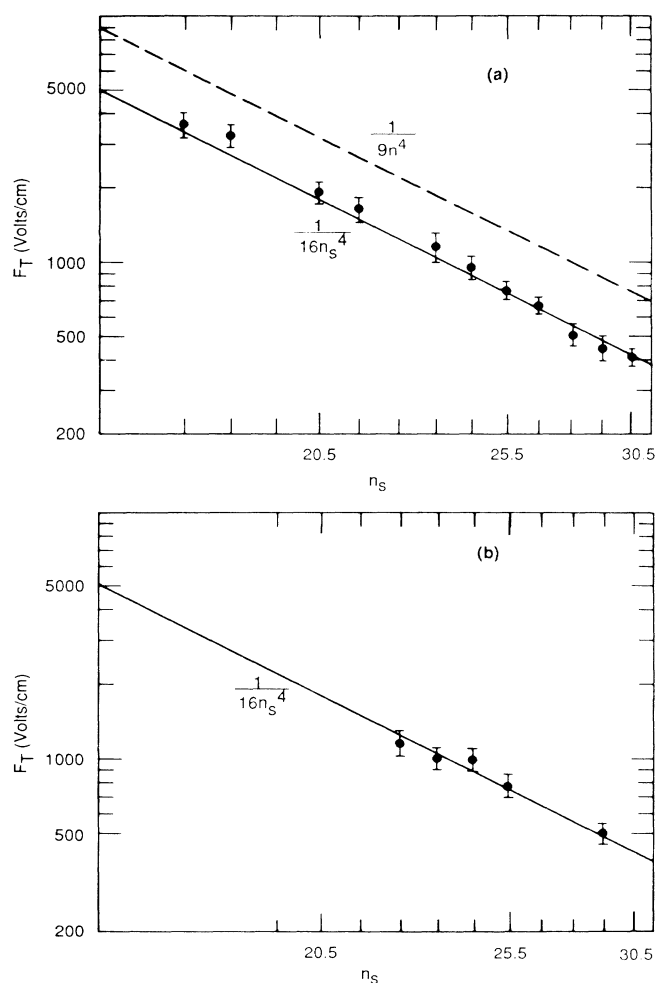

FIG. 2. Threshold field vs n_s ($= n - 0.5$) for (a) ortho-H_2 np states converging to the $N = 1$ rotational state of H_2^+, and (b) para-H_2 np states converging to the $N = 0$ state of H_2^+. The solid line is a plot of $F_T = 1/16n_s^4$ and the dashed line is a plot of $F_T = 1/9n^4$.

FIG. 1. Field-ionized ion signal as a function of the amplitude of the ionization pulse for $n = 30$, p state converging to the $N = 1$ rotation state of H_2^+.

neglected. In the H atom, because of the near perfect Coulomb symmetry, Stark levels from adjacent n manifolds cross each other as the electric field is increased. The red Stark states are on the same side as the saddle point, and the energy of the reddest Stark state of the n manifold is given to a good approximation by $W = -1/2n^2 - \frac{3}{2}n^2F + O(F^2)$. Thus the classical ionization field for the reddest member of the hydrogenic Stark manifold is given by $F_T = 1/9n^4$ and is plotted as a dashed line in Fig. 2(a). It is evident from Fig. 2(a) that the observed field-ionization data for the np states do not fit the $1/9n^4$ value.

For alkali-metal atoms and the H_2 np states, because of the non-Coulombic potential experienced by the electron in the region close to the core, the Coulomb symmetry is broken and, as a result, the states of a given n manifold are mixed with states of adjacent manifolds.[2] The state mixing due to the non-Coulombic potential is best illustrated with reference to a schematic Stark diagram, shown in Fig. 3. A schematic sketch of the Stark map is drawn because the quantum defects of most of the Rydberg series are unknown. We have assumed a quantum defect of 0.2 for the p state and a zero quantum defect for the higher l states, to illustrate the Stark map more clearly. This assumption does not affect the generality of
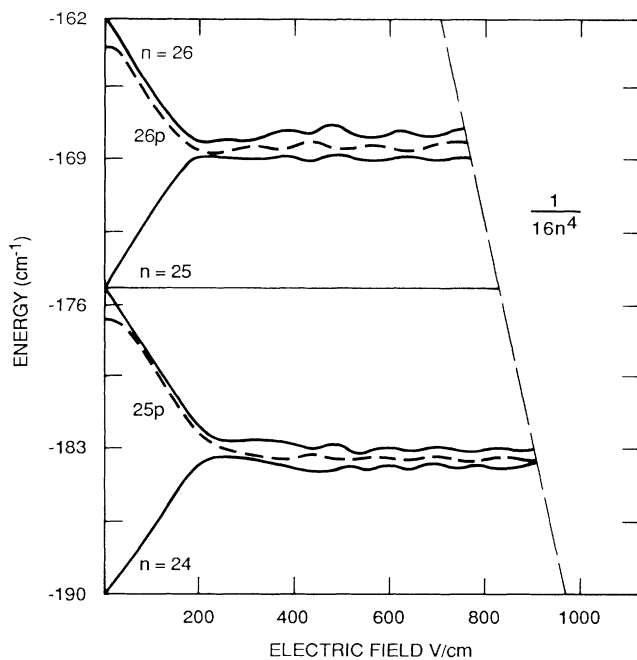
FIG. 3. Schematic of the $|m| = 1$ energy levels in the presence of electric field near $n = 25$. The solid and dashed lines show the approximate adiabatic paths for the ionization of states in the vicinity of $n = 25$. The classical ionization occurs at field values where Stark states intersect with the nearly vertical line representing the energy $W = 1/16n^4$.

the discussion below, because in the $|m| = 1$ Stark-state map, the p state has the largest quantum defect. Figure 3 shows the reddest, bluest, and the central, $|m| = 1$ Stark states of the $n = 24$, 25, and 26 manifold. In the discussion that follows we neglect, for simplicity, any interaction between states converging to different rotational states of H_2^+, and we also neglect the electron-core rotational interaction.

At moderate electric fields, the Stark effect becomes linear, until at fields of $1/3n^5$ the red members of the $n = 26$ manifold approach the blue members of the $n = 25$ manifold. The admixture of the $n = 25$ character in the red states of the $n = 26$ manifold, and vice versa, leads to avoided crossings between the states of the two manifolds. At fields greater than $1/3n^5$, there is no change in the energy of the reddest $n = 26$ Stark state and the bluest $n = 25$ state because of the repeated avoided crossings. The binding energy of the reddest $n = 26$ state and the bluest $n = 25$ state at the ionization field is thus approximately represented by an effective quantum number of 25.5. Since the np states are the reddest members of the $|m| = 1$ manifold, it is reasonable to expect that for these, and other nearby states, the field ionization threshold, if adiabatic, is given by $1/16n_s^4$, where $n_s = n - 0.5$. In Fig. 2, the $1/16n_s^4$ threshold field is shown as a solid line. It is evident from Fig. 2(a) that the agreement between the experimentally determined threshold field and that determined from $1/16n_s^4$ is good, except for $n = 19$, which has a somewhat larger field ionization threshold possibly due to perturbations from low-n members of high-v states.[12] The $1/16n_s^4$ threshold field observed for H_2 is similar to that observed for the low-l Na states.[5]

From the above discussion it is clear that for the slew rates that we have used in our experiment, the passage of the electron from the intermediate to the high fields is substantially adiabatic. For, if it were not so, we would have observed ionization thresholds near $1/9n^4$ which is far in excess of the observed values.

We have also studied the ionization threshold of the $J = 1$ np series converging to the $N = 0$ state of H_2^+, and these data are shown plotted as a function of n_s in Fig. 2(b). The ionization thresholds for the states of this series are the same as they are for the states converging to the $N = 1$ limit. However, there is more scatter in the data for the series converging to the $N = 0$ limit because of the overall lower signal. The n dependence of the ionization threshold as shown in Fig. 2(b) agrees quite well with the $1/16n_s^4$ scaling, with $n_s = 0.5$, and is shown as a solid line in the figure.

For the np Rydberg series converging to the $N = 1$ limit, we have made measurements of the ionization thresholds of states with the same N but different J values ($J = 1$ and 2) arising from the $J = N + l$ coupling of the electron orbital angular momentum and the core rotational angular momentum. We find no discernible difference in the ionization threshold of these states with different J. No measurements of the $J = 0$ np states were

made because the excitation to these states from the $J'=1$ E-F states is small. In addition, the 0.5-cm^{-1} linewidth of the second laser allows us to distinguish the $J=1$ and 2 states for $n<27$. However, for $n>27$, the observed ion signal represents field ionization from a mixture of $J=1$ and 2 states. Since we find no discernible difference in the ionization threshold for the np $J=1$ and 2 states below $n=27$, it is reasonable to expect the same for states with $n>27$. This result means that for the states we have studied, the core rotation does not play a significant part in the dynamics of the field ionization.

[1]Theodore W. Ducas, Michael G. Littman, Richard R. Freeman, and Daniel Kleppner, Phys. Rev. Lett. **35**, 366 (1975).

[2]Michael G. Littman, Michael M. Kash, and Daniel Kleppner, Phys. Rev. Lett. **41**, 103 (1978).

[3]R. F. Stebbings, C. J. Lattimer, W. P. West, F. P. Dunning, and T. B. Cooke, Phys. Rev. A **12**, 1453 (1975).

[4]Myron L. Zimmerman, Michael G. Littman, Michael M. Kash, and Daniel Kleppner, Phys. Rev. A **20**, 2251 (1979).

[5]T. F. Gallagher, L. M. Humphrey, W. E. Cooke, R. M. Hill, and S. A. Edelstein, Phys. Rev. A **16**, 1098 (1977).

[6]J. E. Bayfield and P. M. Koch, Phys. Rev. Lett. **33**, 258 (1974).

[7]P. M. Koch and D. R. Mariani, Phys. Rev. Lett. **46**, 1275 (1981).

[8]D. S. Bailey, J. R. Hiskes, and A. C. Riviere, Nucl. Fusion **5**, 41 (1965).

[9]C. F. Barnett, J. A. Ray, and A. Russek, Phys. Rev. A **5**, 2110 (1972).

[10]T. J. Morgan, C. F. Barnett, J. A. Ray, and A. Russek, Phys. Rev. A **20**, 1062 (1979).

[11]Ravinder Kachru and Hanspeter Helm, Phys. Rev. Lett. **55**, 1575 (1985).

[12]G. Herzberg and C. H. Jungen, J. Mol. Spectrosc. **41**, 425 (1972).

[13]*The Hydrogen Molecule Wavelength Tables of Gerhard Heinrich Dieke,* edited by H. M. Crosswhite (Wiley-Interscience, New York, 1972).