Field-Induced Ion-Pair Formation in Molecular Hydrogen

S. T. Pratt, E. F. McCormack, J. L. Dehmer, and P. M. Dehmer

Argonne National Laboratory, Argonne, Illinois 60439
(Received 3 October 1991)

We present the first experimental results on the electric-field dependence of the threshold for ion-pair formation in a molecular system. The results were obtained for the process $H_2 + h\nu \rightarrow H^+ + H^-$ by using a double-resonance excitation scheme via the $E,F\ ^1\Sigma_g^+$, $v=6$ level. The similarity of the long-range interaction in the ion-pair system with that of the electron-ion system leads to analogies between the field-induced process and the processes of field ionization and forced autoionization of Rydberg states of atoms.

Electric-field ionization of highly excited states of atoms [1-3] and molecules [4-7] has been the subject of numerous recent studies, and the process now appears to be well understood. Molecular hydrogen has served as the prototype molecular system, and studies of simple field ionization [4], forced autoionization [5], and field-induced dissociation [6,7] have all been performed. In this Letter, we present the first experimental results on the effect of external electric fields on the process of photon-induced ion-pair formation in hydrogen, that is, $H_2 + h\nu \rightarrow H^+ + H^-$. In particular, we focus on the electric-field dependence of the energetic threshold for ion-pair formation. Because the dominant contribution to the long-range interaction between the $H^+ + H^-$ products has the same $1/R$ (or $1/r$) dependence as that between the $H_2^+ + e^-$ products of field ionization, many of the same considerations should be applicable to the two processes. (Here R and r denote the internuclear separation and the electron-ion distance, respectively.) However, in addition to the obvious difference in the relative masses of the fragments in the two processes, the short- and medium-range interactions are substantially different. Although the $1/r$ potential is important for all r in the $H_2^+ + e^-$ system, no potential curves of H_2 display pure ion-pair character at all values of R [8,9]. At small to intermediate values of R, the relevant potential curves also contain significant contributions from neutral covalent configurations. The extent to which these configurations affect the interaction with the external electric field is of considerable interest. Although ion-pair formation from both the ungerade [9,10] and gerade [11] states of molecular hydrogen has been studied previously, external field effects were not examined.

The long-range potential relevant to field ionization of $M_J = 0$ levels corresponds [2,3] to

$$V(r) = -1/r - Fz \qquad (1)$$

in atomic units, where z is the component of r along the external field and F is the field strength. An analogous equation holds for ion-pair formation, with r and z replaced by R and Z. Although ionization or ion-pair formation can only occur for total energies greater than zero

when $F = 0$, in an electric field the barrier to ionization is reduced. The classical model for field ionization is based on the premise that when the barrier is reduced below the energy of the Rydberg state of interest, the atom or molecule will field ionize. From Eq. (1), it is readily found that the classical shift (Δ) in the ionization or ion-pair threshold [2,3] is $\Delta = 2\sqrt{F}$. In other units, $\Delta = a\sqrt{F}$, with $a = -6.11\ \text{cm}^{-1}/\sqrt{\text{V/cm}}$ and F in V/cm. Numerous experimental studies of field ionization of atoms and molecules have confirmed the $\sqrt{F}$ dependence [2,4,7,12], but small deviations from the pure Coulombic value of a have been observed. (Typical measured values [12] of a range from -3.9 to $-6.11\ \text{cm}^{-1}/\sqrt{\text{V/cm}}$.) These deviations are presumably due to small corrections to the purely Coulombic potential produced by the atomic or molecular cores. We now present the first results on the field dependence of the threshold for photon-induced ion-pair formation.

The hydrogen molecules were excited to the energy region of the ion-pair threshold by a pulsed double-resonance scheme via the $E,F\ ^1\Sigma_g^+$, $v'=6$ level; the ions produced were detected by using a time-of-flight mass spectrometer. Approximately 50–100 μJ of 193-nm light for the two-photon pump transition was generated in a β-BaB$_2$O$_4$ crystal by mixing the fourth harmonic of a Nd:YAlG laser (YAlG denotes yttrium aluminum garnet) with the fundamental of a dye laser operating at 706 nm. Approximately 400 μJ of 278- to 274-nm light for the probe transition was generated by frequency doubling the output of a second Nd:YAlG-pumped dye laser. The beams were combined on a dichroic mirror and focused into the ionization region of the time-of-flight mass spectrometer by a 250-mm focal-length lens. Except where noted, the polarizations of the pump and probe beams were parallel to each other and to the electric field defined by the mass spectrometer; the probe pulse was delayed ~50 nsec from the pump pulse. The two-photon pump transition frequencies are accurately known from previous measurements [13], and the probe laser frequency was calibrated to $\pm 0.5\ \text{cm}^{-1}$ by using the optogalvanic effect in Ar on the dye laser fundamental.

A pulsed valve was used to introduce pure H$_2$ into the

time-of-flight mass spectrometer through a 0.5-mm nozzle with a backing pressure of 3 atm. In measurements of the field dependence of the ion-pair threshold, a variable dc voltage was maintained across the two grids that defined the ionization region of the mass spectrometer. The field-free excitation spectrum was recorded by using a pulsed field of ~ 400 V/cm that was delayed by 50–100 nsec from the probe laser pulse. In all of the measurements discussed here, the gate of the mass spectrometer was set to detect H$^-$, which is unique to the ion-pair process in this energy region and provides a relatively background-free signal. This background-free signal is important because, as in the earlier single-photon ionization studies from the H$_2$ ground state [9,10], ion-pair formation is extremely weak compared to photoionization to H$_2^+ + e^-$ and because in the present experiments H$^+$ can be produced by a number of other processes.

Figure 1 shows a representative spectrum of the threshold for ion-pair formation in a dc field of 245.7 V/cm. The pump laser was tuned to the $Q(1)$ $E,F\,^1\Sigma_g^+(v'=6) \leftarrow X\,^1\Sigma_g^+(v''=0)$ transition, and the total energy with respect to $X\,^1\Sigma_g^+$, $v''=0$, $J''=0$ was calculated from the probe laser wavelength, the two-photon pump transition energy [13], and the rotational energy levels of the H$_2$ $X\,^1\Sigma_g^+$, $v''=0$ state [14]. By using the dissociation energy [13] of H$_2$ (36118.26 ± 0.2 cm^{-1}), the electron affinity of atomic hydrogen [15] (6083.06 ± 0.02 cm^{-1}), and the ionization potential of atomic hydrogen [16] (109678.758 cm^{-1}), the zero-field ion-pair threshold is calculated to be 139714.0 ± 0.2 cm^{-1}.

Figures 2(a) and 2(b) show the plots of the ion-pair thresholds as a function of the square root of the electric field that were obtained by pumping the $Q(0)$ and $Q(1)$ $E,F\,^1\Sigma_g^+(v'=6) \leftarrow X\,^1\Sigma_g^+(v''=0)$ transitions, respectively. An uncertainty in the data points of ~ 1 cm^{-1} results from the choice of the location of the onset of H$^-$ pro-
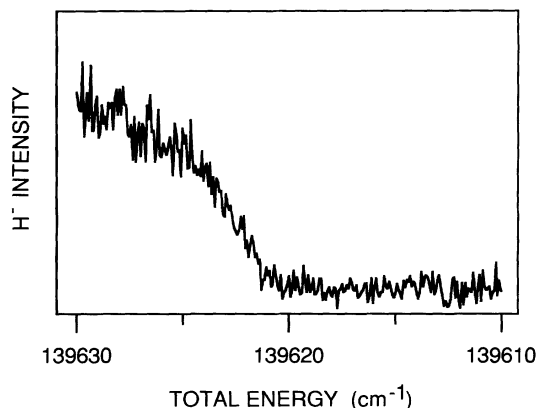
duction. Also shown are linear fits to the data that yield values of α of -5.9 ± 0.1 and -5.7 ± 0.2 cm$^{-1}/\sqrt{\text{V/cm}}$ in Figs. 2(a) and 2(b), respectively. The data clearly support the classical $\sqrt{F}$ dependence of the threshold for ion-pair formation, and the small deviations of α from the pure Coulomb value indicate that corrections to the $1/R$ potential do not significantly affect the process of field-induced ion-pair formation. The extrapolated zero-field thresholds correspond to 139714 ± 3 and 139711 ± 3 cm^{-1}, respectively, in good agreement with the previously determined value. With an improvement in the experimental precision of an order of magnitude, this extrapolation would allow an independent test of the H$_2$ dissociation energy of Ref. [13].

With the laser polarizations parallel to the electric field, all transitions will have $\Delta M_J = 0$, and only $M_J = 0$ levels will be populated in the $Q(0)$ spectrum. For field ionization, Cooke and Gallagher [3] have shown that for $M_J \geq 1$ a centrifugal term must be added to Eq. (1), leading to a threshold shift [2] of $\Delta = -2\sqrt{F} + |M_J|F^{3/4} + \frac{3}{16} M_J^2 F$. This equation should also apply to ion-pair formation, leading to an increase of approximately 8 cm^{-1} of the $M_J = 1$ threshold over the $M_J = 0$ threshold. Attempts to observe this shift in the $Q(0)$ spectrum by using perpendicular laser polarizations to excite $|M_J| = 1$ levels were unsuccessful because of the
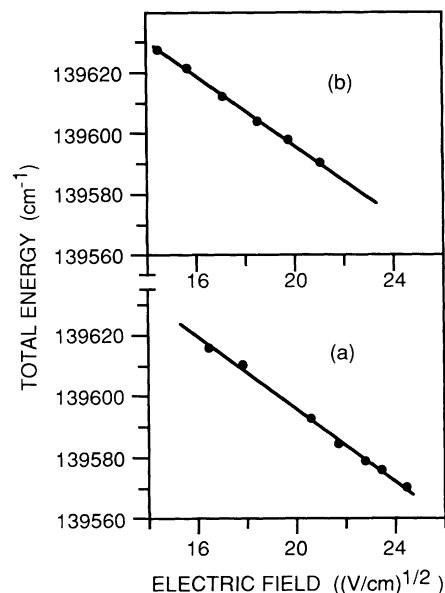

FIG. 2. (a) The threshold for ion-pair formation as a function of the square root of the electric field. The data were obtained by pumping the $Q(0)$ $E,F\,^1\Sigma_g^+(v'=6,J'=0) \leftarrow X\,^1\Sigma_g^+(v''=0,J''=0)$ two-photon transition, and the energy is with respect to the $X\,^1\Sigma_g^+$, $v=0$, $J=0$ ground state. The error bars are approximately the size of the data points. The solid line is a least-squares fit to the data. (b) Same as (a), but for the $Q(1)$ $E,F\,^1\Sigma_g^+(v'=6,J'=0) \leftarrow X\,^1\Sigma_g^+(v''=0,J''=0)$ two-photon transition.

FIG. 1. The H$^-$-ion signal produced from H$_2$ as a function of energy above the $X\,^1\Sigma_g^+$, $v=0$, $J=0$ ground state and with a dc field of 245.7 V/cm. The spectrum was obtained by pumping the $Q(1)$ $E,F\,^1\Sigma_g^+(v'=6,J'=1) \leftarrow X\,^1\Sigma_g^+(v''=0,J''=1)$ two-photon transition.

difficulty in purifying the 193-nm beam polarization without a prohibitive loss of signal. The polarization effects in the $Q(1)$ spectra are less dramatic because of the population of $M_J = 0, \pm 1$ levels in the $X\,^1\Sigma_g^+$, $v = 0$, $J = 1$ initial state.

From Eq. (1), the field-induced saddle point occurs at $R = 1\sqrt{F}$, corresponding to 4140 a.u. at a field strength of 300 V/cm. At this distance, covalent, "chemical" interactions are unimportant, and the $1/R$ term in the potential is expected to dominate; this accounts for the good agreement with the $\sqrt{F}$ form of the threshold's field dependence. We stress, however, that the mechanism for ion-pair formation following excitation from the $E,F\,^1\Sigma_g^+$, $v = 6$ intermediate level is not well understood. As in the single-photon ionization spectrum [9,10], direct excitation to the ion-pair continuum is expected to be weak. Although some penetration into the outer well displays ion-pair character, the dominant character of the $E,F\,^1\Sigma_g^+$, $v = 6$ intermediate level corresponds to the $v = 2$ level of the Rydberg-like inner well. As a result, in the region of the ion-pair threshold, the $v^+ = 2$ ionization continuum is expected to be very strong, although transitions to Rydberg series converging to the H_2^+ $X\,^2\Sigma_g^+$, $v^+ \geq 9$ thresholds may also be observed.
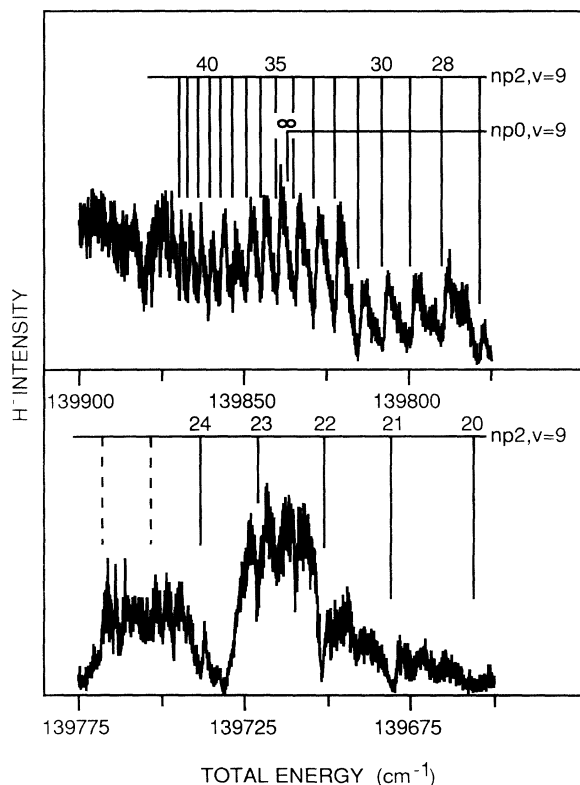
In confirmation of these expectations, Fig. 3 shows a

FIG. 3. A portion of the field-free excitation spectrum for ion-pair formation obtained by pumping the $Q(0)$ $E,F\,^1\Sigma_g^+$ ($v' = 6, J' = 0$) $\leftarrow$ $X\,^1\Sigma_g^+$ ($v'' = 0, J'' = 0$) transition. The total energy is with respect to the $X\,^1\Sigma_g^+$, $v'' = 0$, $J'' = 0$ ground state.

portion of the field-free excitation spectrum obtained by pumping the $Q(0)$ $E,F\,^1\Sigma_g^+$ ($v' = 6$) $\leftarrow$ $X\,^1\Sigma_g^+$ ($v'' = 0$) transition and by using a delayed pulsed drawout field. Spectra recorded with a dc field show the same broad features, but much of the sharp structure is unresolved. We believe this is due to the Stark splitting of the levels, which is not resolved with the present resolution. With the $Q(0)$ pump transition and overall three-photon process, two ungerade, np Rydberg series are expected for each vibrational threshold, with one converging to the $N^+ = 0$ limit and the other to the $N^+ = 2$ limit [17]. Although the $np2$, $v = 9$ series clearly stands out in Fig. 3, the high-lying members of the $np0$, $v = 9$ series are not readily identifiable. The important aspect of Fig. 3 is that, although the structure is congested, the background intensity approaches zero between some of the resonances, indicating that direct ion-pair formation is weak. Similarly, by continuity of the oscillator strength [18,19], it does not appear that highly bound ion-pair states are excited. Portions of Fig. 3 (e.g., from 139 700 to 139 725 cm^{-1}) have enhanced intensity with respect to the average intensity of the rest of the spectrum; similar behavior was observed in the gerade parity spectrum of Kung et al. [11]. These intensity modulations are probably due to interloping levels with low n and $v > 9$. Experiments are now being performed to make more definitive assignments for these interlopers.

Thus, as in the single-photon studies [9,10], the dominant mechanism for ion-pair formation must be predissociation of Rydberg states by states that correlate at large R with the ion-pair products. In a time-dependent picture, the Rydberg series converging to the $v^+ \geq 9$ thresholds are initially populated by laser excitation. These states are predissociated by states that dissociate to $H(1s) + H(nl)$, where $n = 2,3,4$ [9]. As the system propagates to larger R, the neutral predissociative curves cross the ion-pair curve, and some fraction of the trajectories cross over. These crossings occur at $R = 11$, 36, and 270 a.u. for neutral curves with $n = 2$, 3, and 4, respectively [20]. Once the system passes the $n = 4$ crossing on the ion-pair curve, it experiences the essentially pure $-1/R$-FZ potential, and because the saddle point occurs at much larger R, the threshold shift displays the expected behavior. The predissociative mechanism for ion-pair formation suggests that the field-induced shift of the threshold is actually a result of something closer to forced autoionization [21,22] than to true field ionization. That is, Rydberg states that are normally bound with respect to ion-pair formation are allowed to predissociate to ion pairs because of the field-induced reduction of the classical threshold. We are currently performing complementary experiments in this region of the spectrum by using photoelectron spectroscopy in an attempt to gain a fuller understanding of the ion-pair process and its competition with autoionization.

---

[1] See, for example, D. Kleppner, M. G. Littman, and M. L. Zimmerman, in *Rydberg States of Atoms and Molecules*, edited by R. F. Stebbings and F. B. Dunning (Cambridge Univ. Press, New York, 1983), p. 73.

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

[3] W. E. Cooke and T. F. Gallagher, Phys. Rev. A **17**, 1226 (1978).

[4] E. Y. Xu, H. Helm, and R. Kachru, Phys. Rev. Lett. **59**, 1096 (1987).

[5] E. Y. Xu, H. Helm, and R. Kachru, Phys. Rev. A **38**, 1666 (1988).

[6] W. L. Glab and J. P. Hessler, Phys. Rev. Lett. **62**, 1472 (1989).

[7] W. L. Glab and J. P. Hessler, Phys. Rev. A **42**, 5486 (1990).

[8] R. S. Mulliken, Am. Ceram. Soc. **88**, 1849 (1966).

[9] W. A. Chupka, P. M. Dehmer, and W. T. Jivery, J. Chem. Phys. **63**, 3929 (1975).

[10] K. E. McCulloh and J. A. Walker, Chem. Phys. Lett. **25**, 439 (1974).

[11] A. H. Kung, R. H. Page, R. J. Larkin, Y. R. Shen, and Y.

[12] See, for example, E. D. Poliakoff, J. L. Dehmer, A. C. Parr, and G. E. Leroi, Chem. Phys. Lett. **111**, 128 (1984), and references therein; Ch. Bordas, P. Brevet, M. Broyer, J. Chevaleyre, and P. Labastie, Europhys. Lett. **3**, 789 (1987); T. Ebata, Y. Anezaki, M. Fujii, N. Mikami, and M. Ito, J. Chem. Phys. **87**, 4773 (1983).

[13] E. F. McCormack and E. E. Eyler, Phys. Rev. Lett. **66**, 1042 (1991); E. F. McCormack, Ph.D. thesis, Yale University, 1989 (unpublished).

[14] I. Dabrowski, Can. J. Phys. **62**, 1639 (1984).

[15] H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data **14**, 731 (1985).

[16] C. E. Moore, in *Atomic Energy Levels*, U. S. National Bureau of Standards, National Standards Reference Data Series—34 (U.S. GPO, Washington, D.C., 1970).

[17] See, for example, M. A. O'Halloran, P. M. Dehmer, S. T. Pratt, J. L. Dehmer, and F. S. Tomkins, J. Chem. Phys. **90**, 930 (1989).

[18] A. C. Allison and A. Dalgarno, J. Chem. Phys. **55**, 4342 (1971).

[19] A. L. Smith, J. Chem. Phys. **55**, 4344 (1971).

[20] J. T. Lewis, Proc. Phys. Soc. London, Ser. A **68**, 632 (1955).

[21] W. R. S. Garton, W. H. Parkinson, and E. M. Reeves, Proc. Phys. Soc. London **80**, 860 (1962).

[22] W. Sandner, K. A. Safinya, and T. F. Gallagher, Phys. Rev. A **33**, 1008 (1986).

[12] T. Lee, Phys. Rev. Lett. **56**, 328 (1986).