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Forced rotational autoionization of high-lying states of H_2

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We report the observation of forced rotational autoionization of Rydberg states lying below the lowest ionization threshold of H_2^+, when a small external electric field is applied. Our observations are accounted for by an intuitive classical ionization model which relates the autoionization process to the lowering of the ionization threshold with the applied field.

Autoionization[1-7] involves the exchange of energy between a bound excited electron and the core to which the electron is attached. The study of autoionizing states elucidates the anisotropic interactions between the electron and the core at short distances.[6] In the absence of an external field, autoionization does not occur for states that lie below the lowest ionization threshold of the atom or the molecule. However, these states can be made to ionize in an external electric field. The application of the external electric field depresses the ionization threshold by producing a Stark continuum into which autoionization may occur, in the same manner as above threshold. This phenomenon, which was first discovered by Garton, Parkinson, and Reeves[8] in Ba, has been termed forced autoionization. In a molecule, the motion of the electron is coupled to electronic, vibrational, and rotational degrees of freedom of the ion core and it should, therefore, be possible to "force" the rotational and vibrational autoionization of the bound Rydberg electrons on excited core states. Such processes were first observed by Dehmer and Chupka[9] in H_2 and later by Janek, Mullins, Mahon, and Gallagher[10] and Knight, Sohl, Zhu, and Wang[11] in Li_2 and H_2, respectively.

In this Rapid Communication, we report a first systematic study of rotational autoionization of rotationally excited Rydberg states of H_2, lying below the lowest ionization threshold of H_2^+, when a small external electric field ($\sim$15 V/cm) is applied. Specifically, we have observed rotational autoionization of $n=22$, 23, 24, and 25 states of the para-H_2 series converging to the limit H_2^+ ($N=2$), called the *npz* series, shown in Fig. 1, and of the $19p$ ortho-H_2 state. These states lie below the lowest rotational state $N=0$ ($N=1$) of H_2^+ and converge to the first excited rotational state, $N=2$ ($N=3$) of the H_2^+ ion core. In order to elucidate a simple intuitive model for the process of forced rotational autoionization, we have determined the dependence of the rotational autoionization signal for the $23p2$ and $22p2$ states on the external electric field. We have also observed rotational autoionization of the members of the *np* Rydberg series converging to the $N=2$ rotational limit of H_2^+, which lie above the $N=0$ threshold when these states are excited from the $v'=0, J'=2$ level of the $E,F\,{}^1\Sigma_g^+$ state. In this case, the bound channel is primarily excited, and the rotationally autoionizing series appears in the form of bound resonances. In contrast, when the same *np* states are excited from the $J'=0$ level of the E,F state, the continuum character of the wave function is primarily excited and the series appears as window resonances or Beutler-Fano profiles[7] with the Fano q parameter of 0. This is the first time the same state has been observed both as window resonance and as a regular resonance, in a molecule.

The experimental arrangement consists of a pulsed supersonic H_2 beam, which is turned on for $\sim$100 μs. The pulsed H_2 beam passes between two field plates, spaced 0.5 cm apart. The H_2 beam is intersected near the center of the plates by two counterpropagating tunable dye laser beams which are focused by lenses of 15-cm focal length. The first dye laser beam, with $\lambda_1=200$–201 nm is produced by frequency-doubling the output of a tunable dye laser, and then Raman shifting to the fourth anti-Stokes order in a high-pressure H_2 cell. The second dye laser is pumped by an independent Nd-doped yttrium aluminum garnet laser so that the second dye laser can be delayed in time with respect to the first one. The first dye laser with

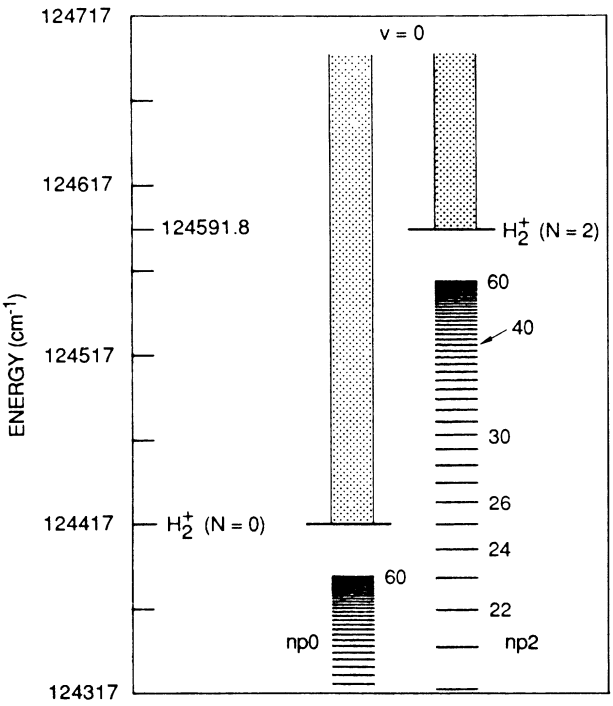

FIG. 1. Energy-level diagram of the H_2 $J=1$ $np0$ Rydberg states converging to the $H_2^+(N=0)$ ionization limit and the $np2$ states converging to the $H_2^+(N=2)$ limit. In this figure, the nearly degenerate $J=1$, 2, and 3 $np2$ states are shown degenerate.

a typical energy of 100 μJ/pulse and a spectral width of 1 cm^{-1}, excites the H_2 molecules in a two-photon process from the initial $v''=0$, $J''=0(2)$ $X\,^1\Sigma_g^+$ ground state to the $v'=0$, $J'=0(2)$ $^1\Sigma_g^+$ E,F excited state.[12] The second dye laser, with $\lambda=398$–403 nm, spectral linewidth of 0.5 cm^{-1}, and energy of 500 μJ/pulse, subsequently excites the molecule from the selected E,F state in the region around the lowest ionization threshold (see Fig. 1).

In the interaction region, a minimum dc electric field of 15 V/cm is always applied to remove the group of ions formed as a result of photoionization from the first laser and to separate them in time from the group of ions produced by the absorption of the second laser pulse. Figure 2 shows the excitation ion spectrum obtained when the second dye laser is scanned from 398–401 nm to excite from $J'=2$ levels of the $v'=0$ E,F state to the Rydberg states in the region around the ionization threshold. The progressively decreasing spacing between the resonances in the ion spectra in Fig. 2 shows the $np2$ Rydberg states converging to the $H_2^+(N=2)$ limit. The position of the resonances and their quantum defects relative to the $N=2$ limit[7] show that the ion resonances in Fig. 2 are the np Rydberg states converging to the $H_2^+(N=2)$ limit excited in the presence of a small (15 V/cm) electric field. The most striking observation in Fig. 2 is the appearance of the $n=24$ and 25 members of the np series even though they lie 2.2 and 16.3 cm^{-1} below the lowest $H_2^+(N=0)$ ionization limit. Furthermore, we have observed the onset of forced rotational autoionization of the $23p$ or $22p$ state as the electric field is increased.

At sufficiently high n, the electron-core rotational interaction becomes negligible and states of different J with the same N are nearly degenerate. There is a single $J=1$ np Rydberg series converging to the lowest $N=0$ rotational state of vibrationless H_2^+. Similarly, there are three nearly degenerate np Rydberg series, $J=1$, 2, and 3, converging to the first excited $N=2$ rotational state of H_2^+. Including the $J=3$ series converging to the $N=4$ state of H_2^+, there are five Rydberg series that can be excited by the second dye laser photon from the $J'=2$ E,F state. Owing to the required change in core rotational quantum number, the $J=1$ series converging to the $n=0$ limit and the $J=3$ series converging to the $N=4$ limit have small excitation probability. However, those np states ($J=1$, 2, and 3) which converge to $H_2^+(N=2)$ limit and lie above the $H_2^+(N=0)$ limit, can be excited with good transition probability and they can rotationally autoionize by the process $H_2(np,J)\rightarrow H_2^+(N=0)+e(\varepsilon l)$ where ε is the kinetic energy of the ejected electron. Rotational autoionization in H_2 was first observed by Herzberg and Jungen[7] and later by Dehmer and Chupka.[9]

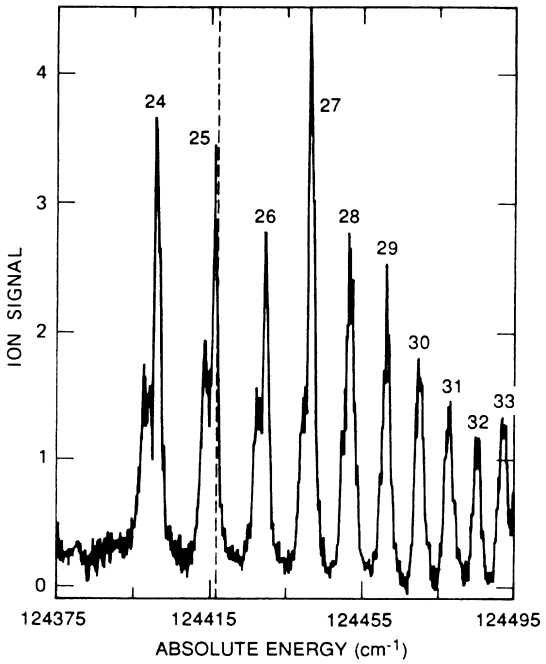

FIG. 2. A plot of the ion signal (arbitrary units) as the second dye laser wavelength is scanned to excite the $J=2$ E,F ($v=0$) state to the np Rydberg series in the vicinity of $H_2^+(N=0)$ threshold. The position of the threshold at zero field is indicated by the broken line.

Now consider a molecule in an electric field F, which is applied along the z axis. The Coulomb potential experienced by the Rydberg electron in an external field is $V=-1/r-zF$ (in atomic units).[13] Since the saddle point in the combined potential occurs at a distance of $z=F^{-1/2}$, the potential at the saddle point is $-2F^{1/2}$. Viewed classically, ionization occurs if the electron energy W is at or above the saddle-point potential. Thus, in the presense of the electric field the ionization potential is lowered by $-2F^{1/2}$.[14] Therefore, those np Rydberg states converging to the $H_2^+(N=2)$ limit which lie at energies between I and $I-2F^{1/2}$ [where I is the $H_2^+(N=0)$ ionization limit] are able to rotationally autoionize because the continuum channel is opened by the electric field for these states. This process is held responsible for the appearance of the $n=24$ and $n=25$ members in Fig. 2.

The most straightforward way to test the prediction of the classical model outlined above is to observe the spectra in the absence of dc field and confirm the disappearance of the $n=24p$ and $25p$ states. Our detection scheme, however, requires a minimum nominal field of about 15 V/cm as explained above. In order to check the prediction of the classical model, we note the following additional observations. First, note that as shown in Fig. 2, the $n=24p$ and $25p$ states appear when an electric field of only 15 V/cm is applied. This is consistent with our model, since these states require fields of 0.15 and 2.5 V/cm, respectively, for forced autoionization. It is worth noting that at fields of 15 V/cm, we do not observe the ion signal emanating from the excitation of the $n\leq 23p$ states. According to the classical model, the $n=23p$ state which lies 30 cm^{-1} below the $H_2^+(N=0)$ limit should ionize at a field of 30 V/cm. In Fig. 3 we show the appearance of the $23p$ ionization signal as the dc field is increased, while the second dye laser wavelength is kept fixed at the $E,F\rightarrow 23p$ transition wavelength. From Fig. 3, it is evident that the threshold field for rotational autoionization is $\sim$30 V/cm, in agreement with that obtained from the model outlined above. Similarly, we have observed the onset of rotational autoionization of the $22p$ state, and the observed threshold field (90 V/cm) agrees well with the classical model. We note that the forced rotational autoionization of the $25p$

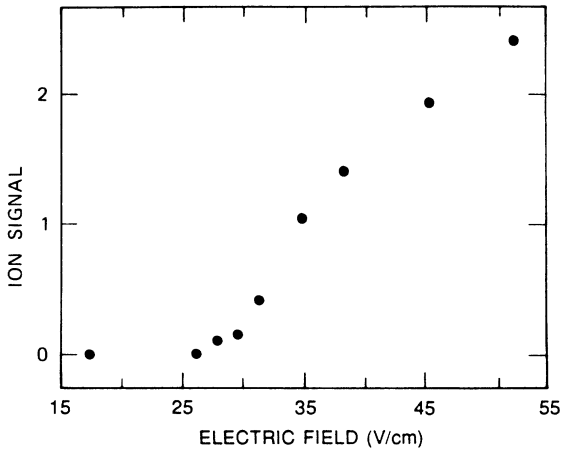

FIG. 3. A plot of the forced-rotational autoionization signal (arbitrary units) of the 23 p ($J=1$, 2, 3) state converging to the $H_2^+(N+2)$ limit as a function of the electric field.

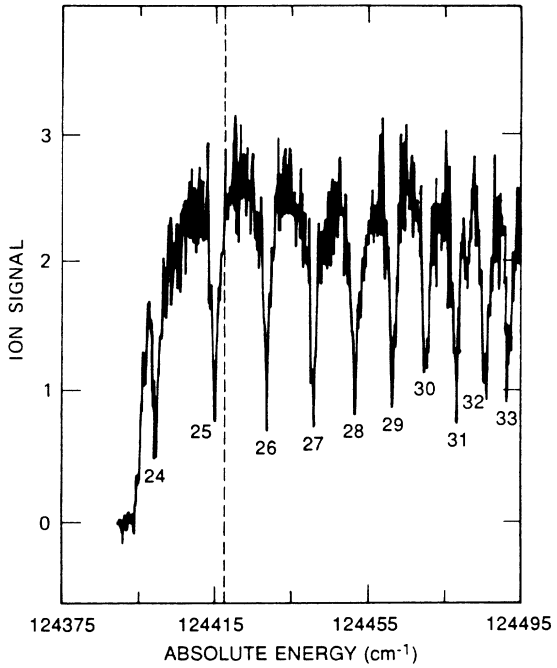

FIG. 4. A plot of the ion signal (arbitrary units) as the second dye laser wavelength is scanned to excite the $J=0$ E,F ($v=0$) state to the $J=1$ np Rydberg series in the vicinity of $H_2^+(N=0)$ threshold, which is shown as the broken line.

state converging to the $H_2^+(N=2)$ limit was the first observed by Dehmer and Chupka[9] in their experiment at a constant electric field of 10 V/cm. Recently, Knight, Zhu, and Wang[11] observed the forced rotational autoionization of the triplet 25d state.

We have also observed the $J=1$ np Rydberg states when excited from the $J'=0$ E,F state. In this case, the dipole section rules allow the excitation of a single $J=1$ np series converging to $H_2^+(N=2)$ limit, $np2$, and the $J=1$ np series converging to the $H_2^+(N=0)$ limit, $np0$. The ion spectrum from the $J=1$ np series excited in a 15 V/cm field is shown in Fig. 4.

In Fig. 4, the $J=1$ np resonances converging to $H_2^+(N=2)$ limit appear as windows[7,9] in the continuum of the $J=1$ series converging to the $H_2^+(N=0)$. These windows, which are quite symmetric, appear because laser excitation from the $J'=0$ state favors those electronic states that have primarily the $N=0$ H_2^+ ion core character. Thus, laser excitation, at energies greater than the $H_2^+(N=0)$ limit, favors primarily the $H_2^+(N=0)+e(\varepsilon l=1)$ open channel. In the vicinity of the $np2$ state converging to the $H_2^+(N=2)$ limit, the effective phase of the $N=0$ open channel undergoes a phase change of π,[15] and the effective transition moment goes to zero. The resonances in the ion signal shown in Fig. 4 do not reach zero value due to the finite bandwidth of the second laser and due to several continua that may be open due to the electric field. The symmetric window resonances indicate that the Fano-q-factor[15] (which is the ratio of the discrete excitation versus the continuum excitation) is nearly zero. The appearance of windows for the $n=24p$ and 25p states along with $n>26p$ states is evident from Fig. 4. The resonances shown in Fig. 4 are at the same position as those shown in Fig. 2, except that the resonances shown in Fig. 4 represent a single $J=1$ state, while those shown in Fig. 2 are due to the nearly degenerate $J=1$, 2, and 3 np states.

In examining the ion spectra of np Rydberg states shown in Fig. 2, in detail, it is clear that the peaks appear to be split into two or possible three states. From the laser excitation scheme, we expect that the $J=1$, 2, and 3 components converging to the $H_2^+(N=2)$ limit can be excited from $J'=2$ the E,F state. Based on parity considerations, it is possible for $J=1$ and $J=3$ states converging to the $H_2^+(N=2)$ limit to autoionize with the ejection of an electron with $l=1$ (p wave) and $l=3$ (f wave), respectively. However, in the absence of an external electric field no such open channel exists for the $J=2$ states. As a result, we expect that in the absence of an electric field, at most, two $np2$ resonances converging to the $H_2^+(N=2)$ limit will exist.

There is an additional possibility for producing the split structure in the Rydberg series excited from $J=2$ of the E,F state. The electric field mixes the εp and εd continua and J is no longer a good quantum number. A rough calculation indicates that if a quantum defect of 0.2 is assumed for the p state, then at a field of 15 V/cm at $n=26$ it has 5% d character mixed into it, thus allowing the autoionization of the $J=2$ state. A more detailed analysis of the split structure of the resonances in Fig. 2 is currently being carried out.

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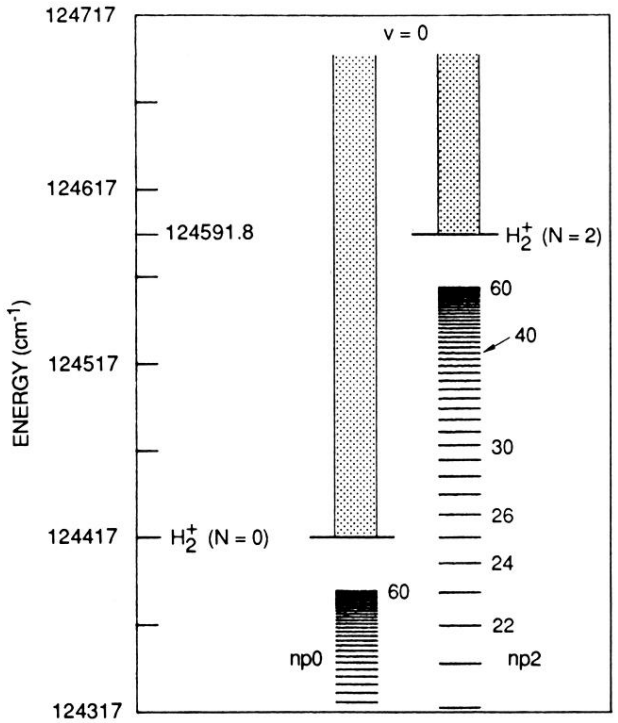

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