

## Observation of High- $n$ Rydberg Series ( $7 < n < 40$ ) of the $H_3$ Molecule

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Four series of Rydberg states converging to vibrationally excited  $H_3^+$  have been excited from long-lived levels of  $H_3$  in a fast (1.5 keV) molecular beam and have been observed to autoionize to  $H_3^+ + e$ . A fifth Rydberg series converging to  $H_3^+$  in its ground vibrational state has been detected through field ionization. A first analysis of the ionization potentials, quantum defects, and the nature of the long-lived species of  $H_3$  is presented.

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We report the first observation of discrete spectra of Rydberg states of the  $H_3$  molecule with high principal quantum numbers. The measurements were made with a coaxial laser-fast-neutral-beam photoionization spectrometer of very high sensitivity. The experiments were stimulated by evidence accumulating over the past years<sup>1-10</sup> that long-lived species of  $H_3$  could be formed in near-resonant charge transfer and that these species should have a photoionization threshold in the near ultraviolet.

Emission spectra from transitions among Rydberg states in the triatomic hydrogen molecule were first identified by Herzberg six years ago.<sup>1</sup> Four bands in the visible wavelength range and two in the infrared<sup>2-5</sup> have since been analyzed and assigned to transitions between electronic states of  $n=2$  and  $n=3$  Rydberg orbitals attached to the ground-state configuration of  $H_3^+$ ,  $(1sa_1')^2$ . These Rydberg states lie above the repulsive ground state of  $H_3$ ,  $(1sa_1')^2 2pe'$ . Lifetime broadening of the emission lines indicates that rapid predissociation occurs for the  $n=2$  levels with lifetimes  $\tau < 10^{-11}$  s. A possible exception from predissociation is the lowest rotational level of the  $2p^2 A_2''$  state<sup>2,3</sup> which we designate  $\bar{B}$ . The radiative lifetime of this species has been calculated<sup>9,11</sup> to be 87  $\mu$ s. This lowest configuration of the  $2p$  state may be considered to be a nonrotating  $H_3^+$  ion with a  $p$  orbital attached perpendicular to the molecular plane. It is characterized by the rotational quantum numbers  $N=0$ ,  $K=0$  and it does not experience rotational coupling to the  $H_3$  ground state.

Evidence for the existence of "metastable" species of  $H_3$  produced in the charge transfer of  $H_3^+$  was first reported in 1968 by Devienne.<sup>6</sup> Experiments performed since<sup>7-9</sup> have hardened this evidence. Recently Garvey and Kupperman<sup>10</sup> observed metastable  $H_3$  molecules with lifetimes exceeding 40  $\mu$ s emanating from a high-pressure arc source. The metastable species observed in the above experiments are believed<sup>9,10</sup> to be triatomic hydrogen molecules in the rotationless configuration of  $\bar{B} 2p^2 A_2''$  in its ground vibrational state.

The previously observed transitions  $n=3 \leftarrow n=2$ , when combined with the calculated energies<sup>11-13</sup> of the

$n=3$  states, suggest an ionization potential of the lowest level of the  $\bar{B}$  state of  $H_3$  of about 29 530  $cm^{-1}$ . We have scanned the region between 27 600 and 27 800 and between 28 700 and 29 600  $cm^{-1}$  and detected several Rydberg series of  $H_3$  in ionization.

The experiments were performed in the coaxial laser-fast-neutral-beam spectrometer shown schematically in Fig. 1.  $H_3^+$  ions are formed in a medium-pressure (1 Torr) discharge ion source and are extracted into a 1.5-keV ion beam. The beam is guided through a charge-transfer cell and through an aperture  $A7$  into the laser interaction region and enters a second energy analyzer,  $Q2$ . With no external electric fields applied between the charge-transfer cell and  $Q2$ , typically  $10^{-8}$  A of mass-analyzed  $H_3^+$  were transported past  $Q2$ . The cesium oven was then operated such that typically 10% to 40% of the ions suffered charge transfer, and the residual ion beam was deflected prior to entering  $A7$ . Following charge transfer a small secondary-electron emission current ( $\sim 0.1\%$  of the primary ion beam), from impact of neutral particles on the aperture  $A9$ , is observed and is used to monitor the stability of the ion beam and the cesium vapor pressure. The small magnitude of neutral beam current appearing in the parent ion-beam direction is due to the fact that the dominant charge-transfer channel is dissociative,<sup>9,14</sup> and most of the fragments are

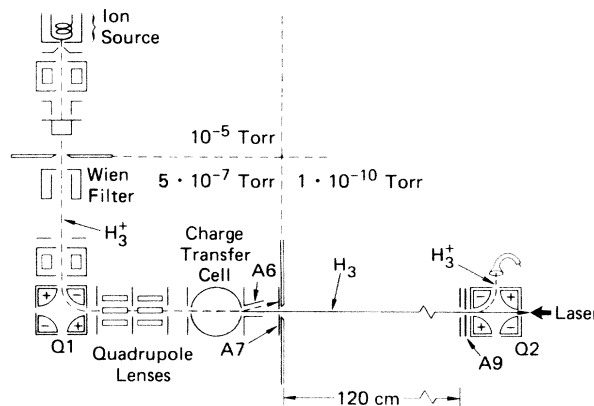


FIG. 1. Schematic of coaxial laser-fast-neutral-beam photoionization spectrometer.

ejected out of the beam.

Two classes of long-lived  $H_3$  species were observed to be formed in charge transfer. The first are molecules distributed over long-lived, high-lying electronic states that can be field ionized at moderate electric fields.<sup>15</sup> The second class, the subject of the current study, involves molecules in a lower-lying electronic state that can be selectively photoexcited in the near uv to states that lie in the autoionization or field-ionization continua.

Energetically lower-lying metastable species of  $H_3$  are detected when the neutral molecular beam is illuminated by the collinear dye-laser beam which is operated at 10 Hz and at pulse energies of typically 1  $\mu$ J. The 5-ns laser pulses have a spectral width of  $\sim 1$   $cm^{-1}$ . Photoexcitation events of beam molecules that lead to the formation of  $H_3^+$  are monitored by deflecting ions of the parent beam energy with  $Q2$  into a Channeltron. The Channeltron output signal is counted over a time window beginning typically 200 ns following the laser pulse and closing after 4  $\mu$ s (corresponding to the flight time of 1.5-keV  $H_3$  molecules over the field-free flight path between  $A7$  and  $A9$ ). In the absence of the laser, a background signal of  $10^{-4}$  counts/gate width is observed while the maximum counting rate for the strongest observed transitions is about 0.2 count per laser shot.

Figure 2 shows a portion of the excitation spectrum on an expanded scale, taken at wavelength increments of about 1  $cm^{-1}$ . For each point shown,  $H_3^+$  ion counts were accumulated over 640 laser shots. The data shown in Fig. 2 thus took 90 min to accumulate. A sample of an excitation spectrum covering higher  $n$  values is given in Fig. 3. The individual data points in this spectrum were accumulated over 160 laser shots, at a step size of 1  $cm^{-1}$ . This spectrum was recorded several times and reproducibly gave the peaks identified below. As in Fig. 2 the discrete peaks appear superimposed on a continuous, laser-induced back-

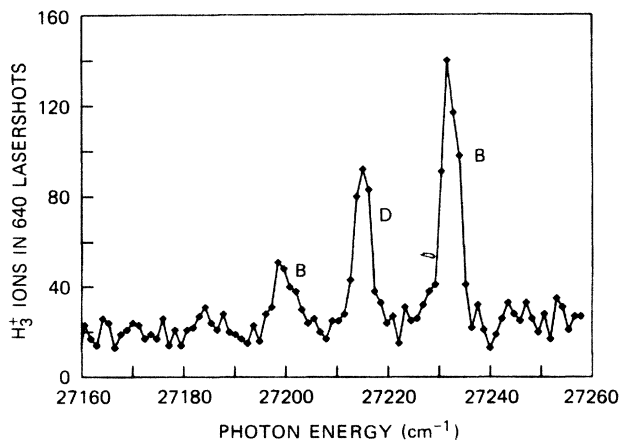


FIG. 2. Excitation spectrum of  $n = 7$  states of  $H_3$ .

ground.

To prove that the signal did not arise from the natural contamination of the mass-3 beam by  $HD^+$ , most of the experiments given below were repeated using as source gas an HD sample. It was found that the photoionization spectra observed for neutrals formed in charge transfer of  $HD^+$  bore no resemblance to those of neutrals formed from mass-3 ions of the natural hydrogen sample. Therefore we can exclude the possibility that HD is responsible for any of the features discussed below.

The discrete spectrum is readily assigned to transitions belonging to five Rydberg series which we label  $A, B', B, C,$  and  $D$ , as shown at the top of Fig. 3. The line positions in these series can be represented with a precision of better than 0.5  $cm^{-1}$  by use of the simple series expression

$$E_n = T_\infty - R / (n - \delta_{eff})^2. \tag{1}$$

With  $R = 109\,717.39$   $cm^{-1}$  a fit by Eq. (1) yielded the

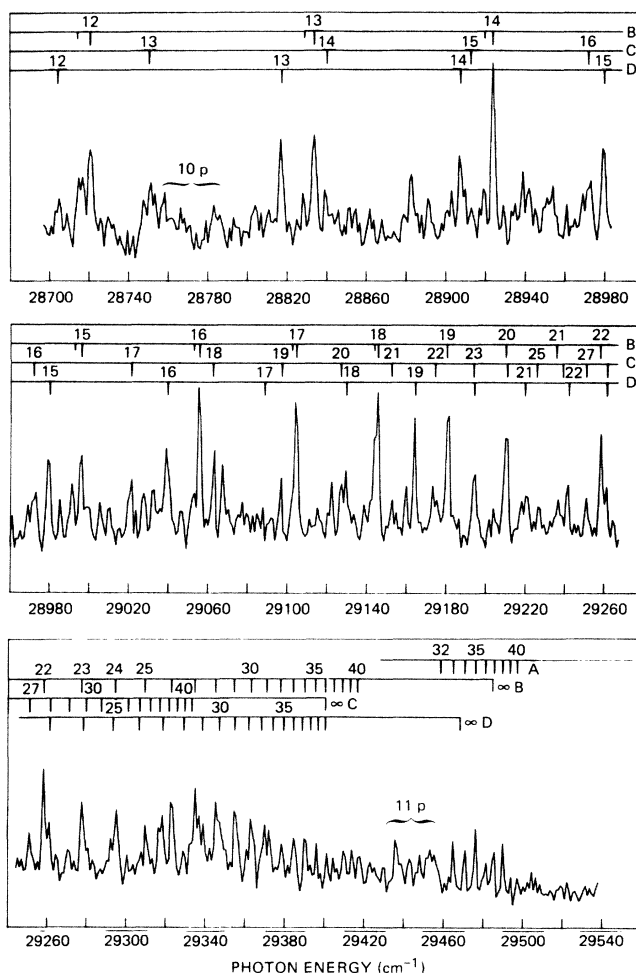


FIG. 3. Excitation spectrum of high- $n$  states of  $H_3$ . Four series are marked in the top of the figure. The series  $B'$  is indicated by the small tick marks along with series  $B$ .

TABLE I. Observed Rydberg series of  $H_3$  molecule. The state designation is  $(\nu_1, \nu_2, N, K)$  for the lower state and  $(\nu_1, \nu_2, N^+, G)$  for the  $H_3^+$  core.

Series	$\bar{B} 2p^2 A_2''$	Upper state $H_3^+$ core		$T_\infty$ ( $cm^{-1}$ )	$\delta_{eff}$	Observed $n$ range
A	(0,0,0,0)	(0,0,1,0)	...	29 566.0	<sup>a</sup>	33-40
B	(0,1,0,0)	(0,1,1,1)	<i>nd</i>	29 485.5	0.022	7,8,12-40
B	(0,1,0,0)	(0,1,1,1)	<i>ns</i>	29 485.5	0.073	7,12-32
C	(. . . .)	(. . . .)	<i>nd</i>	29 402.0	0.02	13-36
D	(1,0,0,0)	(1,0,1,0)	<i>nd</i>	29 469.5	0.02	7,12-32

<sup>a</sup>When series A is fitted together with the  $R0 (3s \leftarrow 2p)$  transition (Ref. 2) a value  $\delta_{eff} = 0.0803$  is obtained. When fitted together with the  $R0 (3d \leftarrow 2p)$  transition (Ref. 5)  $\delta_{eff} = 0.0095$  is obtained.

series limits  $T_\infty$  and effective quantum defects  $\delta_{eff}$  listed in Table I. The transition to  $n = 21$  in series B is observed to be anomalously weak. Several unassigned transitions appear in the spectrum. Between 28 750 and 28 790 and between 29 430 and 29 460  $cm^{-1}$  spectral observations were impeded by laser excitation of the stationary cesium target to the  $10p$  and  $11p$  fine-structure states of Cs. It was observed that following excitation of the cesium target, charge transfer of the excited cesium atoms with  $H_3^+$  occurs with high cross section specifically yielding  $H_3$  molecules in long-lived, highly excited states which undergo field ionization in Q2. The counting rate from these ions could only partially be suppressed by the electronic gating and contributes to the increased signal in the regions indicated in Fig. 3.

The energies of the Rydberg series limits given in Table I leave no doubt that the lower levels involved in the assigned transitions are part of the  $n = 2$  manifold of  $H_3$ . As discussed above, a single rotational level of  $n = 2$ , namely  $(N = 0, K = 0)$  of the  $\bar{B}$  state, is expected to live long enough to survive passage from the charge-transfer cell to the laser-interaction region. If this metastable level were to occur in only the ground vibrational state of  $\bar{B}$ , then transitions to Rydberg series which converge to the vibrational ground state of  $H_3^+$  should preferentially be excited.

Excitation of a Rydberg series in a  $\Delta\nu = 0$  transition from  $(\nu_1 = 0, \nu_2 = 0)$  ( $N = 0, K = 0$ ) will always lead to states that lie below the ionization threshold. Hence this lowest Rydberg series should, in the current experiment, only be detectable through field ionization which can occur at the entrance of Q2. To demonstrate the field-ionization properties of Q2, we show in Fig. 4 the Balmer series of atomic hydrogen, recorded under experimental conditions equivalent to those employed in the  $H_3$  experiments. Here 1.5-keV protons are charge-exchanged in the cesium vapor and then the resultant  $H(2s)$  atoms are photoexcited to  $np$  states. At the electric field strength used in the deflector Q2 ( $\sim 2.3$  keV/cm), levels above  $n = 25$  are effi-

ciently field ionized. The lowest Rydberg series of  $H_3$  is indeed observed in our spectra at high values of  $n$  through field ionization and it is marked as series A in Fig. 3. Extrapolation of this series with Eq. (1) gives a limiting energy of 29 566  $cm^{-1}$ , very close to the predicted ionization potential of  $(N = 0, K = 0)$  of the vibrationally unexcited  $\bar{B}$  state (29 530  $cm^{-1}$ ). For zero rotation the allowed transitions from the  $\bar{B}$  state are<sup>5</sup> to  $ns^2 A_1'$ ,  $nd^2 A_1'$ , and  $nd^2 E''$ . For  $n = 3$  and 4 their transition moments are predicted<sup>11</sup> to be of the order 1:8:12, and the quantum defects of the upper states are calculated<sup>11</sup> to be 0.07,  $-0.006$ , and  $-0.01$ , respectively. At the high  $n$  values where series A is observed, the splitting into the *ns* and *nd* components is not resolved.

The remaining four series appear in the current experiments at  $n$  values ranging from  $n = 7$  up to around 40. The appearance of low- $n$  members in these series requires that  $H_3^+$  ions are formed as a result of autoionization. Since off-diagonal vibrational transitions should only appear with small intensity and since the series limits observed are close to that of series A, we have to invoke the existence of more metastable levels

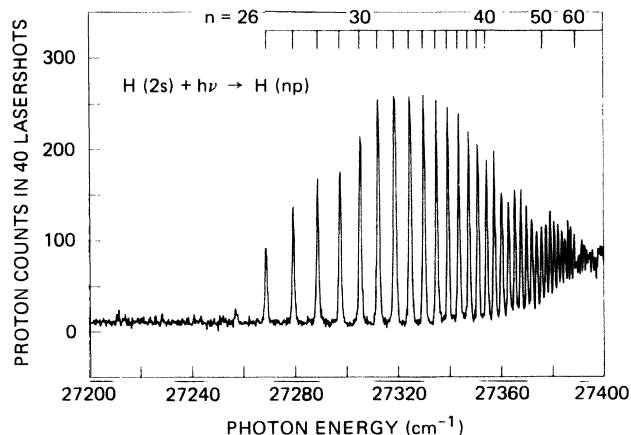


FIG. 4. Excitation spectrum of the Balmer series of  $H$  detected by field ionization in Q2 (see Fig. 1).

of the  $\bar{B}$  state. Predissociation of the  $\bar{B}$  state occurs through rotational coupling of the  $\bar{B}$  state with the repulsive ground state of  $H_3$ . Hence, the most likely candidates for additional long-lived levels of the  $\bar{B}$  state are rotationless molecules in excited vibrational levels. The presence of vibrationally excited  $H_3$  in the beam is not unexpected since we know from previous experiments that in near-resonant charge transfer, vibrational excitation of the parent is retained.<sup>16</sup> At this point, however, an assignment of the vibrational states involved here can only be a good guess and the vibrational identifications given below should be regarded as tentative.

Comparing the bond energy of  $H_3^+$  with that of the  $\bar{B}$  state, we expect the vibrational spacings in the neutral to be slightly higher than those of the ion. The observation that the limits of the series  $B$ ,  $B'$ ,  $C$ , and  $D$  are lower in energy than that of series  $A$  is consistent with their assignment to vibrationally excited cores. A second shred of information that may be used in the assignment is the observation that the intensity of  $n=21$  of series  $B$  is anomalously weak. If series  $B$  is assigned to the (0,1) vibration, an accidental resonance may occur with the  $n=11$  level of the series converging to the (1,0) vibrational level which is calculated<sup>17</sup> to lie at  $3191\text{ cm}^{-1}$ . Since access to the perturbing series in a  $\Delta\nu \neq 0$  transition is weak, it is plausible that the perturber at this point effectively drains<sup>18</sup> transition strength from the diagonal (0,1) series. The same vibrational assignment has to hold for series  $B'$  which converges to the same series limit as  $B$  (see Table I).

The assignment of series  $B$  and  $B'$  to an  $H_3^+$  core in the first excited bending mode and the assignment of series  $A$  to the vibrational ground state places the vibrational quantum of the lowest  $\nu_2$  mode in the  $\bar{B}$  state at  $2602\text{ cm}^{-1}$  as compared to  $2521\text{ cm}^{-1}$  in<sup>19</sup>  $H_3^+$ . The quantum defects and intensities observed for the series  $B$  and  $B'$  suggest that they belong to the  $nd$  and  $ns$  series, respectively. However, two inconsistencies appear. One is that the predicted intensity<sup>11</sup> for the  $ns$  series is lower by a factor of about 5 than that observed for  $B'$ . A possible explanation is that the expected higher autoionization rate for the  $ns$  series allows more efficient pumping of the  $ns$  members by the broad-band laser than the longer-lived (and therefore spectrally narrower)  $nd$  members. A second cause for concern may be that the effective quantum defects found for series  $B$  (and also  $C$  and  $D$ ) are positive (0.022), while the calculated (and unperturbed) quantum defects for the directly accessible  $3d$  and  $4d$  states<sup>11</sup> are small and negative. A shift in the sign of

the quantum defect could possibly be brought about by the interaction<sup>5</sup> of the  $nd$  states accessed here with the  $nd^2E'$  and  $np^2A_2'$  states.

It remains to assign the weaker series  $C$  and  $D$ . On the basis of intensity considerations alone, the series  $D$  could be attributed to the first excited symmetric stretch mode of  $H_3^+$ . An extension of the wavelength range to lower energies should pinpoint the lowest autoionizing member of each series and therefore help in the assignment. Such measurements are currently in preparation.

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