

## Autoionizing Rydberg States in Triplet Molecular Hydrogen

Ravinder Kachru and Hanspeter Helm  
*Molecular Physics Department, SRI International,  
 Menlo Park, California 94025*  
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We report the first observation of the autoionizing triplet  $nd$  series of  $H_2$  covering the region from  $n = 10$  to the series limit. The autoionizing states are produced by excitation of  $H_2$   $c^3\Pi_u^-$  molecules in a fast (1 keV) beam with a frequency-doubled pulsed dye laser, and the resulting  $H_2^+$  ions are detected. We have also resolved members of the high-lying  $nd$  series ( $25 < n < 35$ ) converging to the lowest vibrational state of the  $H_2^+$  ion by field ionization. A qualitative interpretation of the spectra in terms of a noninteracting single-channel Rydberg electron model is given.

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The vacuum ultraviolet (vuv) absorption spectroscopy of the  $H_2$  *ungerade* singlet states from the ground state has been extensively studied by Herzberg<sup>1</sup> and by Herzberg and Jungen.<sup>2</sup> More recently, two experimental approaches to study the autoionization of the  $H_2$  Rydberg states based on the detection of the resulting ions have been used. The first employs either the excitation of the *ungerade* singlet  $np$  states ( $n$  is the principal quantum number) from the ground state of  $H_2$  with a vuv photon<sup>3</sup> or stepwise resonant laser excitation schemes to the singlet series via the  $B$  state<sup>4</sup> or the  $E,F$  state.<sup>5</sup> A second approach, affording intrinsically higher resolution and allowing excitation in the near uv by a single photon, uses the metastable  $c^3\Pi_u$  state as the initial state to pump the Rydberg states of the triplet system.<sup>6</sup> This second approach is an extension of the detailed work on the  $n = 3$  and  $n = 4$  states of triplet hydrogen performed by Lichten, Wik, and Miller,<sup>7</sup> and by Eyler and Pipkin,<sup>8</sup> and of photodissociation studies of the  $c$  state<sup>9</sup> to Rydberg series which lie in the autoionization continuum.

Here we report for the first time the observation of the vibrationally autoionizing triplet  $nd$  Rydberg series of  $H_2$ , excited in a fast beam of  $H_2$   $c^3\Pi_u$ . We have detected the autoionizing  $nd$  series from  $n = 10$  up to the ionization limit converging to vibrational levels of the  $H_2^+$  ion between  $v = 1$  and 4. Autoionization of the Rydberg states was detected by separating the resulting  $H_2^+$  ions from the parent neutral beam and counting them. A similar study using excitation of the  $c$  state in a thermal beam and covering the spectral region around  $n = 12$ ,  $v = 1$  has been reported recently by Knight and Wang.<sup>10</sup> We have also detected by field ionization the excitation spectra of high  $nd$  states ( $n > 25$ ) converging to the  $v = 0$  limit of the ion.

The beam of metastable  $H_2$   $c^3\Pi_u$  molecules is produced by creating, first, a fast beam of  $H_2^+$  ions which subsequently undergo charge-transfer collisions in a Cs vapor cell. The  $H_2^+$  ions are formed in a low-pressure discharge ion source, and have a broad vibrational population distribution. The ions are accelerated to 1

keV energy with a concomitant compression in the Doppler velocity spread of the beam (80 MHz) which we observed to be practically unchanged after the neutralization of the ion beam by the near-resonant charge-transfer process in cesium.<sup>11</sup> The fast  $H_2$  beam formed by charge transfer in alkali-metal gases contains predominantly<sup>12</sup> molecules in the  $c^3\Pi_u$  state, along with the ground and other excited states. Molecules in the parity component  $^3\Pi_u^-$  are metastable, with a lifetime of 0.1–1.0 ms, while those in  $^3\Pi_u^+$  are rapidly predissociated via the  $b^3\Sigma_u^+$  state.<sup>13</sup> From observed line intensities we estimate that our fast  $H_2$  beam contains typically a flux of  $10^9$  metastable molecules/s.  $H_2^+$  ions that have not suffered charge transfer are removed from the beam and the neutral fast beam enters an ultrahigh vacuum chamber (pressure  $< 10^{-10}$  Torr) through a 1-mm-diam aperture. The molecules are then excited in a 100-cm-long field-free drift region, by a collinear dye-laser beam. The dye laser operates at 10 Hz and has an energy of typically 50  $\mu$ J/pulse after frequency doubling. The 5-ns pulses have a spectral width of 1  $\text{cm}^{-1}$  (0.1  $\text{cm}^{-1}$ ) in the low- (high-) resolution mode.

Ionizing states are detected by separation of the product  $H_2^+$  ions from the parent neutral beam into a Channeltron. The Channeltron output is shaped into 10-ns-long pulses and counted with a gated scaler. The gate is opened 200 ns after the dye-laser pulse and closed after 3  $\mu$ s (corresponding to the flight time of 1-keV  $H_2$  molecules over a distance of 100 cm, ensuring that only molecules excited in the field-free region of the apparatus are detected). In the absence of the laser, there are practically no  $H_2^+$  counts ( $< 10^{-4}$  count per gate width), while the maximum observed count rate for the strong transitions is 4–10 counts per laser pulse, corresponding to a count rate of up to 4 MHz.

A typical photoionization spectrum observed by scanning of the dye laser, with 1- $\text{cm}^{-1}$  linewidth, from 3360 to 3550 Å is shown in Fig. 1. The photoion signal shows contributions from direct photoionization,

vibrational autoionization, and field ionization. The threshold for direct photoionization (in  $\Delta v = 0$  transitions, where  $\Delta v = v' - v''$ ) from the  $N'' = 1, v'' = 0$  level of the  $c$  state lies at 3386 Å, decreasing to 3480 Å for the  $N'' = 1, v'' = 6$  level. The gradual increase in the continuous portion of the spectrum in Fig. 1 with decreasing wavelength reflects the consecutive opening of continuum channels for the individual vibrational levels of the  $c$  state. At wavelengths shorter than  $\sim 3400$  Å the continuum background appears constant, reflecting the wavelength independence of the direct-photoionization cross section near threshold. Superimposed on this background roughly 1000 discrete peaks occur, their linewidths apparently being limited by the laser bandwidth ( $1 \text{ cm}^{-1}$ ). At wavelengths longer than the  $v = 0$ , direct-ionization threshold, these peaks correspond to the  $\Delta v = 0$  excitation of the vibrationally autoionizing Rydberg series converging to vibrationally excited levels,  $v \geq 1$ , of the  $\text{H}_2^+$  core. A smaller number and less intense series of discrete transitions which populate vibrationally autoionizing levels in  $\Delta v \neq 0$  transitions are dispersed over the entire wavelength range covered. Finally, the group of intense discrete peaks near 3400 Å arise from the field ionization of the Rydberg series converging to the lowest vibrational level of the  $\text{H}_2^+$  core.

The Rydberg series converging to different vibrational states of  $\text{H}_2^+$  interact wherever there is a near degeneracy between the states of two or more series.<sup>2</sup> Thus the detailed assignment of the spectrum in Fig. 1 would entail a multichannel quantum-defect-theory (MQDT) analysis.<sup>14,15</sup> However, these vibrational interactions are for the most part localized and hence, spectral regions free of these interactions can be adequately described by a single-channel quantum-defect

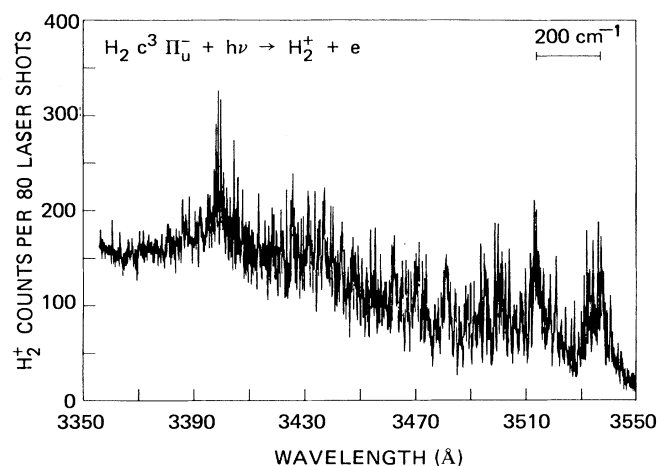


FIG. 1. Experimental spectrum obtained by scanning of the dye laser from 3360 to 3550 Å and detection of the resulting  $\text{H}_2^+$  ions.

analysis requiring no adjustable parameters. In a first attempt to analyze the observed spectra, we have chosen the simple single-channel approach which we describe below. In the angular momentum coupling scheme appropriate to high  $n$  (Hund's case- $d$  coupling),  $J' = N + l$ , where  $J'$  is the total angular momentum of the Rydberg state (excluding the electron spin), and  $N$  is the rotational quantum number of the  $\text{H}_2^+$  core, and  $l$  is the electron orbital angular momentum. We have calculated the Rydberg level positions of different  $J'$  taking into account the dipole and quadrupole polarizabilities of the ionic core.<sup>8</sup> Similarly, the excitation line strengths of the  $nd \leftarrow c$  transitions have been calculated by transformation of the Rydberg-state wave functions from the case- $d$  basis to the case- $b$  basis set,<sup>2</sup> the electron spin being neglected in this treatment. The transition probabilities were then computed by use of the familiar Hönl-London factors.<sup>16</sup> The calculation of the line intensities also included the familiar  $n^{-3}$  scaling due to the Coulomb wave function.

Our calculations show that from a given rotational state,  $N''$ , in the  $c$  state ( $N''$  is the total angular momentum excluding the electron spin) there are three transitions with nonzero dipole moment, which we label  $P(N'')ndN$ ,  $Q(N'')ndN$ , and  $R(N'')ndN$ , corresponding to excitation to  $nd$  states converging to the rotational quantum number of the ion core,  $N = N''$ , and with  $J'$  equal to  $N'' - 1$ ,  $N''$ , and  $N'' + 1$ , respectively. Note that the restriction  $N = N''$  applies only if vibrational or rotational interactions between different Rydberg series are neglected. Furthermore, if we assume that the Rydberg-electron radial wave function is hydrogenic, we find that the transition strength  $ns \leftarrow c$  is smaller than the corresponding  $nd \leftarrow c$  line strength by a factor of  $\frac{1}{30}$ . We have therefore ignored the excitation of the  $ns$  series in the calculation of the synthetic spectra.

The observed spectra (see Fig. 1) particularly on the long-wavelength end, appear as a progression of clusters of lines. As will be shown below these clusters arise from the overlap of different  $(n, v)$  bands of  $\Delta v = 0$  transitions. A portion of the experimental spectrum is compared with the calculated spectrum in Fig. 2. The top trace in Fig. 2 is the experimental spectrum, and the spectrum just below it is the composite synthetic spectrum including vibrational contributions from  $v = 1$  to 5, all for  $\Delta v = 0$ . The width of the lines in the synthetic spectrum was taken as  $1 \text{ cm}^{-1}$ , the laser linewidth. The lower spectra in Fig. 2 show the individual contributions from the vibrational levels  $v = 1-4$ . In the light of our previous photodissociation studies<sup>9,11</sup> in the fast  $\text{H}_2 c^3 \Pi_u$  beam we have assumed a rotational temperature of 500 K. For the simulations we have used the vibrational population distribution in the metastable  $c$  state determined by de Bruijn *et al.*

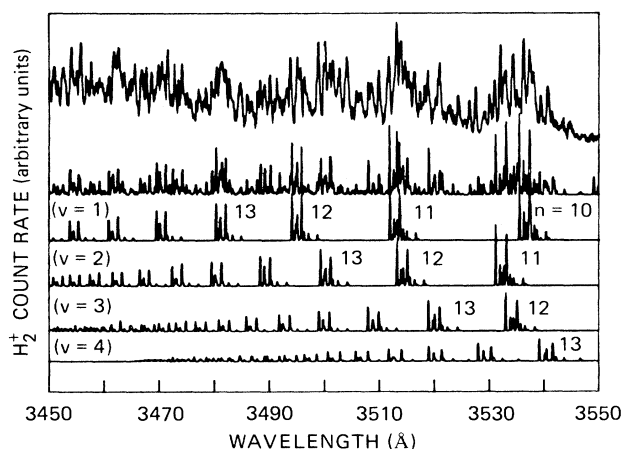


FIG. 2. A portion of the experimental spectrum is shown as the top trace. The second trace from the top is a synthetic spectrum of  $\Delta v = 0$  transitions including contributions from  $v'' = 1$  to 5. The remaining traces are the individual contributions from  $v'' = 1-4$ , respectively.

for charge transfer of  $H_2^+$  in  $Mg$ .<sup>12</sup> The energy levels of the  $c$  state were taken from Dieke's compilation,<sup>17</sup> corrected<sup>18</sup> by  $-149.6 \text{ cm}^{-1}$ , while the energy levels of the  $H_2^+$  ion were taken from the calculation of Wind.<sup>19</sup> Given the simple noninteracting model that we have employed in our calculations the agreement between the experiment and the synthetic spectrum is surprisingly good. Most of the lines shown in Fig. 2 are reproduced to within  $5 \text{ cm}^{-1}$ . Some of the lines in the experimental spectra are shifted, indicating localized interactions with states of different vibrational quantum number. Several intense lines appearing in the experimental spectrum are unaccounted for by the present simulations.

An initially unexpected result of our measurement was the observation of a number of very sharp and distinct peaks in the part of the spectrum near  $3400 \text{ \AA}$  (see Fig. 1). This part of the spectrum is shown on an expanded scale as the bottom trace in Fig. 3. An analysis of the level positions in this part of the spectrum showed that a Rydberg series with  $n$  ranging from 26 to 34, converging to the lowest vibrational state,  $v' = 0$ ,  $N = 1-3$ , of  $H_2^+$  is responsible for the observed lines. Since we detect  $H_2^+$  ions following the laser excitation of neutral metastable  $H_2$ , there are two possible mechanisms that account for the observation of these peaks. The first, which explains only part of the spectrum, is rotational autoionization of those  $v = 0$ ,  $nd$  states which converge to excited rotational states of  $H_2^+$  ion. The second mechanism, capable of explaining also the intense  $R(1)nd1$  series, the dominant contribution to the spectrum, is field ionization of the bound  $nd$ ,  $v' = 0$  states occurring in the 2-kV/cm field region of the quadrupole deflector employed to

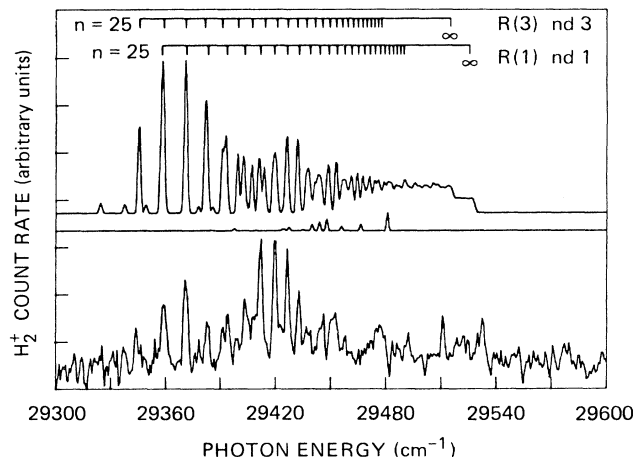


FIG. 3. The bottom trace shows the experimental spectrum near  $3400 \text{ \AA}$  on an expanded scale. The top trace shows the calculated transitions, originating from the  $v'' = 0$ , odd- $N''$  (ortho) states, to the  $v' = 0$ ,  $nd$  states. The  $R(1)nd1$  and  $R(3)nd3$  series limit along with Rydberg series converging to these limits are labeled above the top trace. The middle trace shows the calculated transitions from the  $v'' = 0$  levels to the  $v' = 1$ ,  $7d$  levels, taking into account the appropriate Franck-Condon factor.

separate the  $H_2^+$  ions from the  $H_2$  beam. Recently Sturuss, Sobol, and Lundeen reported observation of the  $n = 27$ ,  $v' = 0$  Rydberg levels of  $H_2$  by field ionization.<sup>20</sup> The field strength in our deflector ( $2 \text{ kV/cm}$ ) is consistent with the onset of the appearance of the peaks in Fig. 3 at  $n = 25$ . If a threshold field of  $1/4n^4$ , similar to that required to field ionize the H atom,<sup>21</sup> is assumed then a field of  $3.3 \text{ kV/cm}$  is required for  $n = 25$ . If, on the other hand, we assume that a  $1/16n^4$  threshold field is required for the adiabatic field ionization in alkali-metal atoms,<sup>22</sup> then a field of  $0.8 \text{ kV/cm}$  is required for  $n = 25$ . It appears reasonable to expect the field-ionization properties of the  $H_2 nd$  states to lie somewhere in between.

The top trace in Fig. 3 shows the calculated excitation spectrum of the transitions from the  $v'' = 0$ , odd- $N''$  (ortho) states to the allowed  $nd$  Rydberg states converging to the  $v' = 0$  limit of the  $H_2^+$  ion. Markers at the top of Fig. 3 indicate the location of the two most intense members of the  $v' = 0$  series,  $R(1)$  and  $R(3)$ . The general features of the observed spectrum are well reproduced by the top trace. Inclusion of para transitions in the synthetic spectrum results in a few extra peaks for  $n < 29$  which are not observed experimentally. We cannot offer an explanation for their absence (or shift) at this point but note that the  $v' = 0$ ,  $nd$  series with  $25 < n < 35$  lies in between the  $v' = 1$ ,  $n = 7$  and  $v' = 2$ ,  $n = 5$  Rydberg states. These two states are known to profoundly modify<sup>15</sup> the  $v' = 0$ ,  $np$  series in the singlet system.

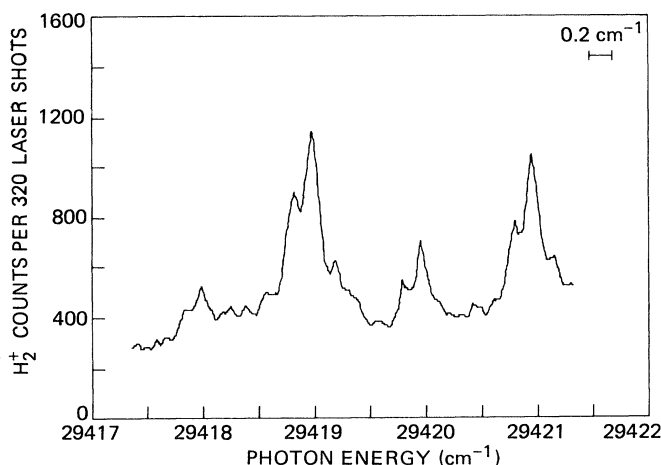


FIG. 4. A small segment of the spectrum shown in Fig. 3, recorded with the laser linewidth reduced to  $0.1 \text{ cm}^{-1}$ . The splitting of the peaks ( $\sim 0.2 \text{ cm}^{-1}$ ) arises from the fine-structure splitting of the  $c$ -state levels. The individual peaks fall within  $1 \text{ cm}^{-1}$  into the region of the calculated  $R(1)31d1$ ,  $R(2)32d2$ ,  $R(3)33d3$ , and  $Q(2)32d2$  lines of the  $v'=0$  series but no definite assignment can be made at this stage.

A portion of the field-ionization spectrum taken under high resolution is shown in Fig. 4 (laser linewidth of  $0.1 \text{ cm}^{-1}$ ). We have found that the general appearance of the experimental spectrum is reproduced in our calculations, but significant shifts from the calculated level positions appear at this level of resolution. In the light of the simplicity of our model calculation these differences are however not unexpected. It should be noted in the experimental spectrum of Fig. 4 that all peaks display a splitting at the level of  $\sim 0.2 \text{ cm}^{-1}$ . This splitting is due to the fine-structure splitting<sup>8</sup> of the  $c$ -state levels.

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