

# Energy difference between the ( $\nu=0$ , $R=1$ ) and the ( $\nu=0$ , $R=3$ ) states of $\text{H}_2^+$ , measured with interseries microwave spectroscopy of $\text{H}_2$ Rydberg states

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We measure several transitions between specific Rydberg levels in the nearly degenerate ( $\nu=0$ ,  $R=1$ )  $n=28$  and ( $\nu=0$ ,  $R=3$ )  $n=16$  Rydberg manifolds of  $\text{H}_2$  with microwave spectroscopy. These measurements can be combined with calculations of the Rydberg fine structure to deduce the energy difference between the two states of the free  $\text{H}_2^+$  core. The result,  $E(\nu=0, R=3) - E(\nu=0, R=1) = 288.85900(8) \text{ cm}^{-1}$ , represents the most precise determination to date of any spectral property of the hydrogen molecular ion, to our knowledge.

The hydrogen molecular ion  $\text{H}_2^+$  and its isotopic variants play a special role in molecular science because its properties can be calculated very precisely. Approximation schemes exist that, when relativistic and radiative corrections are included, give predictions of the binding energies of low-lying rovibrational states which are precise to  $5 \times 10^{-8}$ .<sup>1</sup> Despite the attractiveness of this fundamental system, only a handful of experimental measurements exist that have sufficient precision to test the details of these predictions and stimulate possible improvements in the theory.<sup>2</sup> The lack of such experimental data has been one of the motivations behind the development of methods of precision spectroscopy of high- $L$  Rydberg states of  $\text{H}_2$  (this work and Ref. 3), since the structure of these states can reveal substantially new, precise information about  $\text{H}_2^+$ .<sup>3</sup>

Perhaps the most basic form of spectroscopy of  $\text{H}_2^+$  is the study of the excitation energies of the rovibrational states of the ground electronic state. Since  $\text{H}_2^+$  has no permanent electric dipole moment, this structure cannot be studied easily by direct spectroscopy. It has, however, been deduced with moderate precision ( $\approx 10^{-3}$ ) from ultraviolet spectroscopy of the ionization limits of Rydberg series of  $\text{H}_2$  bound to different rovibrational states of  $\text{H}_2^+$ .<sup>4,5</sup> The analogous structure in  $\text{HD}^+$  has been studied much more precisely ( $\approx 10^{-6}$ ), using infrared laser spectroscopy.<sup>6,7</sup> In this Rapid Communication, we report a new form of indirect spectroscopy of  $\text{H}_2^+$  which, where applicable, gives even higher precision than the direct measurements of  $\text{HD}^+$ . In that we examine energy differences between two different  $\text{H}_2$  Rydberg series, this method may be considered similar to the above-mentioned studies that were based on Rydberg-series ionization limits. Higher precision, however, is achieved by using microwave spectroscopy to directly measure the energy difference between specific Rydberg levels bound to two different states  $\text{H}_2^+$ .

Figure 1 shows a few of the high- $L$  Rydberg states belonging to the ( $\nu=0$ ,  $R=1$ )  $n=28$  and ( $\nu=0$ ,  $R=3$ )  $n=16$  manifolds. By coincidence, the difference of rotational energies of the two  $\text{H}_2^+$  states ( $\approx 288 \text{ cm}^{-1}$ , and denoted  $\Delta E_R$ ) is almost exactly canceled by the difference in electronic binding energies of the  $n=28$  and 16 Rydberg levels. In the absence of Rydberg fine structure, the

zeroth-order energies of these two Rydberg manifolds (shown by dashed lines in Fig. 1) are separated by only  $0.25 \text{ cm}^{-1}$ , or 7.5 GHz. This makes it feasible to measure energy differences between specific Rydberg levels in the two manifolds using microwave spectroscopy, and thus indirectly determine the full rotational interval with high precision. In this experiment, we have measured six such energy differences, as indicated by the arrows in Fig. 1, each to a precision of about 1 MHz ( $3 \times 10^{-5} \text{ cm}^{-1}$ ). If the Rydberg fine structures were fully calculable to this precision, each measurement would independently determine the  $\approx 288 \text{ cm}^{-1}$  rotational interval to one part in  $10^7$ . In practice, the fine structure of the states in Fig. 1 can be calculated from first principles with varying degrees of precision ranging from  $\pm 50$  to  $\pm 2 \text{ MHz}$  using a polarization model,<sup>8,9</sup> where the calculations of the highest  $L$  states are the most precise. Reliance on this calculation leads to six redundant determinations of  $\Delta E_R$  that have a combined precision of about  $3 \times 10^{-7}$ . This is

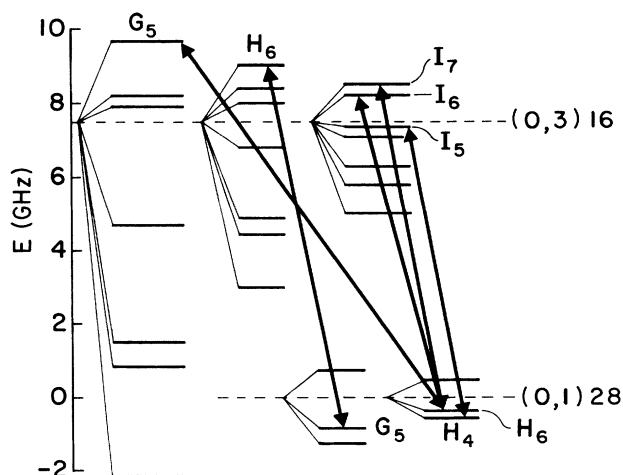


FIG. 1. An energy-level diagram showing the relevant electric-fine-structure states in the ( $0,1$ )  $n=28$  and ( $0,3$ )  $n=16$  Rydberg manifolds. The states involved in the measured transitions are denoted  $L_N$ , where  $\mathbf{N} = \mathbf{L} + \mathbf{R}$ . The arrows indicate the transitions reported in this experiment.

still precise enough to exceed the precision of any other measured spectral property of  $\text{H}_2^+$  or  $\text{HD}^+$ , and to pose a significant challenge to even the most precise calculations.

A schematic diagram of the experimental apparatus is shown in Fig. 2. 13-keV  $\text{H}_2^+$  ions are converted into  $\text{H}_2$  molecules in a charge exchange cell. Following the charge exchange, the remaining ions, and Rydberg states that have  $n \geq 22$ , are removed in a transverse, 6000-V/cm electric field. A particle current of about 1  $\mu\text{A}$ , consisting of ground-state and excited-state molecules, remains. The molecules then enter a laser interaction region, where a Doppler-tuned single-frequency  $\text{CO}_2$  laser excites those molecules that happen to be in a particular (0,1)  $n=10$   $L_N$  electric-fine-structure state to a (0,1)  $n=28$   $L'_N$  electric-fine-structure state. Generally, a few thousand molecules a second are put into the  $n=28$  manifold. These molecules are then driven, in the waveguide microwave region that follows, to an electric-fine structure state of the (0,3)  $n=16$  manifold. These normally forbidden transitions, between different Rydberg series, are allowed because of mixing between the nearly degenerate manifolds.

After the microwave interaction region the molecules pass through an  $\approx 2000\text{-V/cm}$  electric field. This field is sufficient to ionize all Rydberg states more weakly bound to their core than  $n=24$ , and will not ionize any Rydberg states that have  $n$  smaller than 20. The molecules in  $n=28$  are thus ionized, while the  $n=16$  states are not.<sup>10</sup> The resulting ions are deflected into a channeltron multiplier. The detected current is measured synchronously with modulation of the applied microwave field. Because of the differential ionization of the  $n=16$  and 28 states, a transition in the microwave region, which moves population from the  $n=28$  to the  $n=16$  manifold, will cause a reduction of the detected current.

Figure 3 is a representative spectra, the (0,1)  $n=28$   $H_6$  to (0,3)  $n=16$   $I_7$  electric-fine-structure (EFS) transition. Total accumulation time for this spectra is about 2 h. The structure evident in Fig. 3 is a consequence of the magnetic fine structure of the  $\text{H}_2$  molecule. We have successfully modeled this structure with an *ad hoc* Hamiltonian<sup>11</sup> as described elsewhere.<sup>9</sup> The stick diagram in Fig. 3 shows the predicted substructure of the transitions under study.

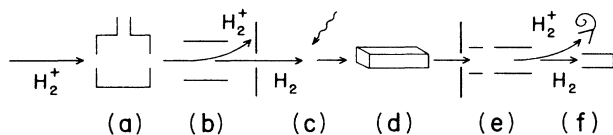


FIG. 2. A schematic diagram of the experimental apparatus.  $\text{H}_2$  is produced by charge capture by 13-keV  $\text{H}_2^+$  in the charge exchange cell (a), and the large electric field inside the initial stripper (b) removes large- $n$  ( $n \geq 22$ ) Rydberg states from the neutral beam. At the laser interaction region (c) a particular  $n=28$  electric-fine-structure state is populated from  $n=10$  with a Doppler-tuned, single-frequency,  $\text{CO}_2$  laser. These states are then excited in the microwave interaction region (d) to an  $n=16$  state. The remaining  $n=28$  states are ionized in (e), and detected in (f). The detection is synchronous with modulation of the microwave intensity.

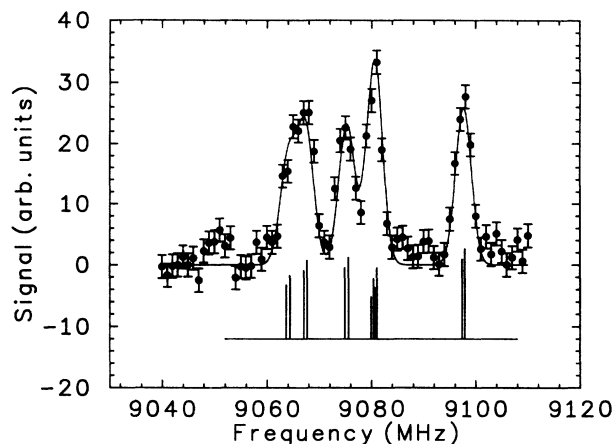


FIG. 3. The (0,1)  $n=28$   $H_6$  to (0,3)  $n=16$   $I_7$  microwave transition. The individual peaks are a consequence of the magnetic fine structure; the calculated energies and intensities are shown in the stick diagram. The solid line is the result of a least-squares fit using a sum of twelve Gaussian peaks and three adjustable parameters: the total intensity, the width, and the electric-fine-structure transition frequency.

Time-of-flight broadening in the approximately 28-cm-long spectroscopy region causes the peaks to have an intrinsic width of 3.6 MHz [full width at half maximum (FWHM)]. The solid line in Fig. 3 is a least-squares fit of the data using a sum of 12 Gaussian peaks.<sup>12</sup> Two weak transitions which comprise the small peak at 9050 MHz were not included in the fit. Only three parameters, a common intensity parameter, a common width, and the EFS transition frequency, were floated. The energies of the magnetic-fine-structure peaks, relative to the EFS interval, were fixed to calculated values, and the relative transition intensities were taken to be proportional to the statistical weights of the  $n=28$  levels. The fitted peak width was typically 3.5–3.8 MHz (FWHM), which compares well to the expected width. We have rechecked the accuracy of the magnetic-fine-structure Hamiltonian by comparing the relative separations of the partially resolved magnetic fine structure to the calculated values. The agreement was generally better than 0.4 MHz. Best values of the measured electric-fine-structure transition frequencies are shown in Table I, along with standard errors resulting from the fit.

The largest systematic uncertainty is caused by the possible presence of an electric field inside the interaction region, as these transitions are expected to shift by up to  $1000 \text{ MHz}/(\text{V/cm})^2$ . There are two sources of an electric field: accumulation of charges on surfaces and the Lorentz field caused by the incompletely shielded magnetic field of the Earth. We set limits on the magnitude of the electric field in three ways. First, the relatively narrow observed linewidth indicates the lack of substantial Stark broadening, limiting the possible stray field to less than 50 mV/cm. Second, while heating a surface appears to remove much of any accumulated surface charge,<sup>13</sup> we saw no shift of the observed transition frequencies larger than 0.5 MHz when our rf region was warmed to  $200^\circ\text{C}$ , thus indicating that fields caused by charge accumulation

TABLE I. Table of measured and calculated electric-fine-structure transition frequencies in MHz. In all cases the numbers in parenthesis are estimates of the one standard deviation uncertainty, and their derivation is discussed in the text. For each transition, the second column lists the results of a least-squares fit of the measured spectra. In the third column are these frequencies, corrected for the estimated electric field inside the spectroscopy region, 25(25) mV/cm. The final column contains the results of a polarization model calculation of the transition energies, assuming a rotational splitting of 288.859 00  $\text{cm}^{-1}$  between the (0,1) and (0,3) rotational levels of  $\text{H}_2^+$ .

Transition	$\nu_0^{\text{fit}}$	$\nu_0^{\text{xpt}}$	$\nu_0^{\text{calc}}$
$28H_4 \rightarrow 16I_5$	8028.95(6)	8028.5(9)	8028.9(20)
$28H_6 \rightarrow 16I_6$	8815.32(15)	8814.7(12)	8814.4(24)
$28H_6 \rightarrow 16I_7$	9052.89(6)	9052.3(12)	9052.3(24)
$28G_5 \rightarrow 16H_6$	10521.45(20)	10521.2(6)	10523.7(126)
$28H_6 \rightarrow 16G_5$	10637.60(20)	10637.0(12)	10602.3(490)

are probably less than 20 mV/cm. Finally, the measured magnetic field is less than 0.03 G, so that any Lorentz field at our beam velocity is less than 25 mV/cm. We thus estimate that the field inside the spectroscopy region is  $25 \pm 25$  mV/cm, and correct for the resulting Stark shifts using calculated Stark coefficients of each transition. The adjusted experimental frequencies, and their uncertainty, are shown in the third column of Table I.

The six measured intervals can be compared with polarization-model calculations of the Rydberg fine structure. The calculations use an effective potential,  $V_{\text{pol}}$ , which depends on calculated electric properties of  $\text{H}_2^+$ . The uncertainty of these fine-structure calculations can be estimated from the convergence of the contributions from terms in  $V_{\text{pol}}$  that are proportional to successively higher inverse powers of the Rydberg radial coordinate. This general method was first applied to calculate the fine structure of helium Rydberg states,<sup>14</sup> where it has now been confirmed both by experiment<sup>13</sup> and by precise variational calculations.<sup>15</sup> Similar calculations in  $\text{H}_2$  (Refs. 9 and 11) have been tested by precise measurements on  $n=10$  fine structure,<sup>11</sup> and also by measurements of series mixing between nearly degenerate Rydberg manifolds.<sup>9</sup>

In this model, the energy of the  $(\nu, R)nL_N$  Rydberg level is

$$E((\nu, R)nL_N) = E^{(0)}(\nu, R) + E^{(0)}(n, L) + E^{(1)} + E^{(p)}, \quad (1)$$

where  $E^{(0)}(\nu, R)$  is the free  $\text{H}_2^+$  energy, and  $E^{(0)}(n, L)$  is the zeroth-order Rydberg energy. The latter includes a small relativistic correction:

$$E^{(0)}(n, L) = \mathcal{R} \frac{2m_p + m_e}{2m_p + 2m_e} \left[ \frac{1}{n^2} + \frac{\alpha^2}{n^3} \left( \frac{1}{L+1/2} - \frac{3}{4n} \right) \right], \quad (2)$$

where  $\mathcal{R}$  is the infinite-mass Rydberg constant,  $m_e$  ( $m_p$ ) is the electron (proton) mass, and  $\alpha$  is the fine-structure constant.  $E^{(1)}$  is the first-order polarization energy and  $E^{(p)}$  is the energy shift due to perturbations with other Ryd-

berg series. As discussed in Ref. 9,

$$E^{(1)}((\nu, R)nL_N) = A_0 + A_2 \langle RL_N | P_2(\cos\theta) | RL_N \rangle + A_4 \langle RL_N | P_4(\cos\theta) | RL_N \rangle, \quad (3)$$

where  $\theta$  is the angular displacement of the Rydberg electron from the internuclear axis. Uncertainties in the values of the structure factors  $A_0$ ,  $A_2$ , and  $A_4$ , tabulated in Ref. 9, come from the convergence error, which is an estimate of the error that is caused by neglected higher-order terms, and from an estimated 0.1% uncertainty in the core parameters.<sup>16</sup> These dominate the theoretical error for predictions of the intervals measured here.  $E^{(p)}$ , which includes perturbations from both discrete and continuum levels, is computed using second-order perturbation theory in  $V_{\text{pol}}$ , except that, as discussed in Ref. 9, the contribution of a single, nearly degenerate level in the (0,1)  $n=28$  + (0,3)  $n=16$  system is calculated by diagonalizing a  $2 \times 2$  matrix. The contribution of  $E^{(p)}$  to the transition energies observed here is typically 3%, so that uncertainties in  $E^{(p)}$  are of minor importance in the total transition energy.

The fourth column of Table I lists the calculated frequencies and their associated errors. For this calculation we have assumed a particular value of  $\Delta E_R$  (288.859 00  $\text{cm}^{-1}$ ), which, as can be seen, gives good agreement with our measurement. Since the transition frequencies are almost exactly linear in  $\Delta E_R$ , it is clear that a change of only 0.0001  $\text{cm}^{-1}$  (3 MHz) will cause a significant discrepancy with experiment. Our best estimate of the rotational splitting is then 288.859 00(8)  $\text{cm}^{-1}$ . We note that the difference with the best published calculation [288.861(1)] is twice the quoted theoretical error, and that the measurement is an order of magnitude more precise. In response to a private communication of our measurement, we have obtained the results of an unpublished calculation which predicts 288.8589  $\text{cm}^{-1}$ , in good agreement with our measurements.<sup>17</sup> We may also compare this measurement with the results of studies of Rydberg-series ionization limits, 288.6(8)  $\text{cm}^{-1}$ .<sup>5</sup>

It is interesting to investigate what particular aspects of the calculations are being tested by this precision measurement. The most recent nonadiabatic calculations of the nonrelativistic eigenvalues for the (0,1) and (0,3) states indicate convergence to 0.0002  $\text{cm}^{-1}$ .<sup>17</sup> The uncertainties of the relativistic and radiative corrections in the energy difference between these two states are not known, but the total corrections are 0.0106 and  $-0.0020$   $\text{cm}^{-1}$ , respectively.<sup>17</sup> Thus the measurement we report here tests these most recent calculations to better than the convergence limit of the nonadiabatic calculation, and tests the relativistic and radiative corrections to 1% and 5%, respectively. This sensitivity to relativistic and radiative effects is comparable to the best existing measurements of  $\text{H}_2^+$ .<sup>18,19</sup>

The uncertainty of our measurement is dominated by theoretical uncertainties arising from the polarization model that was used to calculate the electric fine structure. We are optimistic that these theoretical errors can be considerably reduced by consistently including higher-order terms in the polarization potential. For example, an

analogous calculation by Drachman for the helium atom<sup>14</sup> predicts the  $10H$  fine-structure energy with a precision of 10 kHz, judging by the convergence error, and agrees to within 1 kHz with an independent variational calculation.<sup>15</sup> It should also be possible to improve the experimental precision of the interseries fine-structure intervals by up to 2 orders of magnitude, once a better measure of stray electric fields is developed. Thus, depending on pro-

gress in the theory, extremely precise measurements ( $\approx 10^{-9}$ ) of this particular rotational energy splitting could be feasible with this technique.

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<sup>7</sup>See, for example, Alan Carrington, Iain R. McNab, and Christine A. Montgomerie, *Mol. Phys.* **64**, 983 (1988), and included references.

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<sup>9</sup>P. W. Arcuni, E. A. Hessels, and S. R. Lundeen, *Phys. Rev. A* **41**, 3648 (1990).

<sup>10</sup>Since the  $(0,1) n=28$  and  $(0,3) n=16$  manifolds are nearly degenerate, an applied electric field that is sufficiently large to

Stark ionize the  $(0,1) n=28$  states should also cause electric-field induced autoionization of the  $(0,3) n=16$  states. Because of the weak coupling between the  $(0,1)$  and  $(0,3)$  channels, however, the time scale for autoionization is much larger than the time scale for direct Stark ionization. This allows the detector to discriminate in favor of the  $(0,1) n=28$  states.

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