

Observation of High-Angular-Momentum Rydberg States of H₂ in a Fast Beam

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(Received 12 November 1984)

Rydberg states of H₂ with $n = 10$, $L = 3-6$, formed in charge-capture collisions of (11 keV) H₂⁺ ions, are resolved spectroscopically by laser excitation of the $10 \rightarrow 27$ electronic transition, detected by Stark ionization of the upper state. Measured level positions are in good agreement with *a priori* predictions. The Rydberg spectrum identifies participating H₂⁺ core states as $\nu = 0$ (only) and $R = 0-3$, but relative line intensities appear anomalous.

PACS numbers: 33.20.Ea, 33.80.Eh, 35.20.My, 35.80.+s

The spectroscopy of highly excited Rydberg states of H₂ has been carefully studied in the case of $L = 1$ states,¹ revealing a rich structure that has been an important stimulus in the development of multichannel quantum-defect theory.² Other nonspectroscopic studies of H₂ Rydberg states have shown that stable ($\tau \geq 10^{-6}$ sec) highly excited states exist,^{3,4} and it has been suggested that these may be states of high orbital angular momentum.^{4,5} At lower n , states of this type ($L \geq 3$) have recently been studied⁶⁻⁸ and their structure found to be well described by a model including only long-range interactions between the excited electron and the H₂⁺ ion core. We report here the first spectroscopic identification of high- n , high- L states of H₂, confirming that such states are formed in charge exchange, and showing that their structure is well described by the same *a priori* model used at low n . Practical experimental access to such states could be an important new probe of the fundamental H₂⁺ ion. In addition, our observations indicate, by showing the complete absence of Rydberg states with vibrationally excited cores, that vibrational-electronic coupling is strong in this system, in contrast to some predictions, and raises other questions about the formation of these states.

The character of single-electron excited states of H₂ changes markedly when the coupling of the excited electron's angular momentum to the orientation of the H₂⁺ internuclear axis is much less than the free ion core's rotational energies. For Rydberg states of low L , this condition is satisfied only for sufficiently high n .^{1,2} States with $L > 2$, however, are always near the uncoupled limit (Hund's case *d*) because of the rapid decrease in coupling for nonpenetrating orbitals. In this case, both the Rydberg electron's orbital angular momentum (**L**) and the core ion's rotational angular momentum (**R**) are approximately good quantum numbers which couple to form $\mathbf{N} = \mathbf{L} + \mathbf{R}$, the total angular momentum exclusive of spin. The system is in many respects "atomlike" with the core playing the role of a deformed atomic nucleus of "spin" R . For example, radiative transitions between such states take place without change in core state ($\Delta\nu = \Delta R = 0$) and obey the usual atomic selection rules, $\Delta L = \pm 1$, $\Delta N = 0, \pm 1$.

In zeroth order, the energy of such a state is the sum of the energies of the free ion core with vibrational and rotational quantum numbers ν , R , and a hydrogen atom with principal quantum number n . For nonpenetrating orbits, further electron-core interactions are given approximately by^{8,9}

$$V = -\frac{1}{2} e^2 \frac{\alpha(\rho)}{r^4} - \left(\frac{e^2 \gamma(\rho)}{3r^4} + \frac{eQ(\rho)}{r^3} \right) \left(\frac{3}{2} \cos^2\theta - \frac{1}{2} \right), \quad (1)$$

where r is the electron's radial coordinate and θ is the angle between the ion axis and the electron position. The parameters Q , α , γ are all functions of the core internuclear separation ρ and represent the electric quadrupole moment and isotropic and anisotropic dipole polarizabilities of the free ion core. The expectation value of this perturbation in a basis set of case-*d* wave functions characterized by quantum numbers (ν, R, n, L, N) has been calculated explicitly in Ref. 8 in terms of the expectation values of core parameters Q , α , and γ for the free ion. The resulting structure depends sensitively on ν because of the dependence of α , γ , and Q on ρ .

Perturbations of this structure due to off-diagonal

matrix elements of Eq. (1), also given in Ref. 8, may be evaluated using calculated core energy levels.¹⁰ Since these matrix elements are on the order of 1 cm^{-1} for the states studied here, only very nearly degenerate levels can cause appreciable energy perturbations. Typically, only one or two perturbing levels (with $\Delta R = \pm 2$, $\Delta n = \mp 1$) dominate the total shift. For $n = 10$ states with vibrationally excited cores, the coupling represented by Eq. (1) can give rise to autoionization.¹¹ The lifetime of the $10G$ states against this process has been estimated as 10^{-9} sec,⁶ considerably longer than the lifetimes of lower- L states mediated by short-range interactions with the core,¹² but

much shorter than estimated lifetimes which ignore the long-range coupling.⁵

The apparatus used for these observations has been described elsewhere.¹³ A beam of 11.1-keV H_2^+ ions (~ 0.1 uA) is obtained from a duoplasmatron ion source, mass analyzed, and focused through a differentially pumped charge-exchange cell containing argon gas at about 0.010 Torr. Of the entering ions, about 10% undergo charge-exchange collisions and emerge as fast neutral H_2 , a fraction of which are in highly excited Rydberg states.³ Residual ions are removed from the beam by a deflection field and collimator. Then, after a drift time of about 0.5 μ sec, the H_2 beam is intersected by a cw CO_2 laser operating on the 001-100 $P(16)$ or $P(18)$ lines at 947.750 or 945.990 cm^{-1} , respectively.¹⁴ These lines are near enough to the $10 \rightarrow 27$ Rydberg transition that they may be tuned into exact resonance by changing the angle of intersection between the laser and the fast H_2 beam ($v/c = 0.00344$). Because the H_2 beam is nearly monochromatic, the laser resonance lineshape is Doppler free with a width of 0.01 cm^{-1} due principally to the angular width of the neutral beam. This leads to selective excitation to $n = 27$ of particular Rydberg levels in $n = 10$, e.g., the $\nu = 0, R = 1, L = 3, N = 4$, but not $N = 3$ level is excited. Finer structure due to electron and nuclear spins is unresolved. The transition is detected by Stark ionization of Rydberg states in the beam with $n > 24$, and deflection of the resulting ions into a Channeltron electron multiplier. The construction of the detector is such as to discriminate against H_2^+ and H^+ ions already in the beam as a result of collisional processes or of autoionization. A small background from naturally populated H_2 ($n > 24$) states is greatly reduced by increasing the ion deflection field sufficiently to remove these states by ionization. The magnetic field in the laser interaction region

was reduced to < 0.05 G by Helmholtz coils. The stray electric field in the same region was estimated as < 0.1 V/cm by study of the forbidden $10L \rightarrow 27L$ transition strength. The pressure throughout the neutral beam chamber was $< 10^{-7}$ Torr.

Figure 1 shows the observed laser-induced H_2^+ flux as a function of the intersection angle of the laser and H_2 beams (measured from antiparallel). These data were collected over 37 hours. The horizontal axes also show Δ , the difference of the Doppler-shifted laser frequency at each angle from the unperturbed $10 \rightarrow 27$ Rydberg transition frequency (946.584 cm^{-1}). A number of well resolved lines can be seen over a range of about 3 cm^{-1} which arise from high- L Rydberg states. Optical transitions corresponding to different core states appear superposed since the core state does not change in the transition. All the (strong) observed lines are accounted for by states with $\nu = 0, R = 0-3$ cores and $L = 3-6$. As expected, only one strong transition from each initial state is observed, corresponding to the transition $10, L, N$ to $27, (L+1), (N+1)$. Column 1 of Table I shows the line identification in terms of the initial state, in the notation $(R)L_N$, where L is given in spectroscopic notation and $\nu = 0, n = 10$ is understood. Column 2 shows the measured line position, Δ . The experimental error comes from reproducibility of the measured angle and 1% uncertainty in the beam velocity. Column 3 shows the predicted position if we take only the expectation value of Eq. (1) in the case- d basis, while column 4 gives the shift predicted by off-diagonal terms.¹⁵ The total in column 5 is in quite good agreement with observations. This result must be considered fortuitous in view of the stated "few percent" numerical uncertainty in the averaged core parameters used⁸ and the omission of higher-order terms from Eq. (1) which produce 3% corrections in the analogous states of atomic heli-

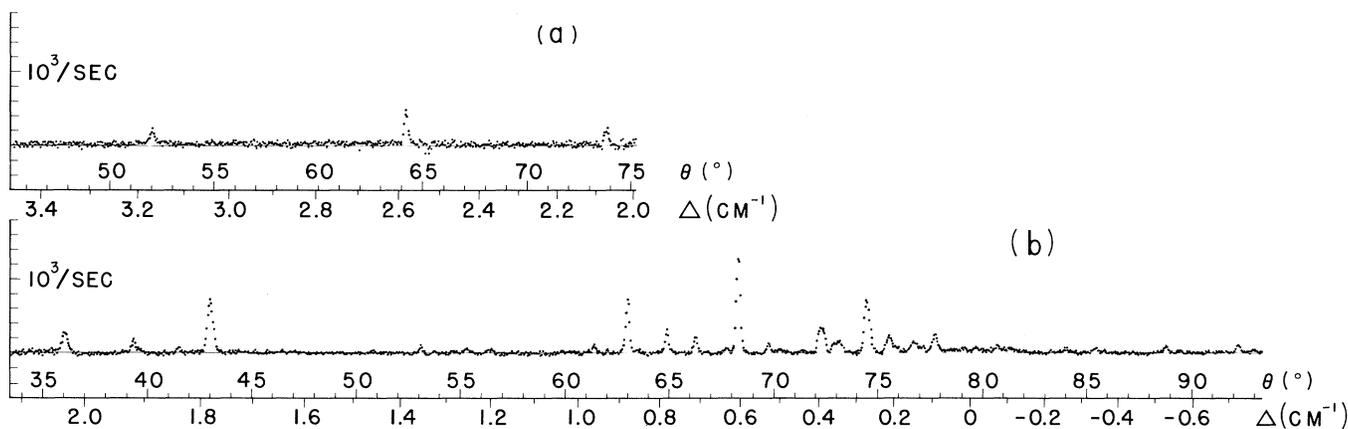


FIG. 1. Laser-induced flux of H_2^+ ions after Stark ionization as a function of the angle of intersection of the laser and H_2 beams. Case (a) is for the $P(16)$ and case (b) the $P(18)$ lines of the CO_2 laser. Also plotted on the horizontal axis is Δ , the difference between Doppler-shifted laser frequency and 946.584 cm^{-1} , the unperturbed $10 \rightarrow 27$ Rydberg transition frequency.

TABLE I. Identification of lines in the spectra of Fig. 1. The initial state is given in column 1 and in each case the final state has $\Delta\nu = \Delta R = 0$, $\Delta L = \Delta N = +1$. Observed position ($\Delta = \nu - 946.584$) is given in column 2 (asterisk denotes a blend with stronger line, and the double asterisk a line falling outside the range studied). Column 6 gives the observed strength. Predicted position is shown in column 5, with contributions from first- and second-order perturbation theory shown separately as E_1 and E_2 . Column 7 shows predicted line strengths obtained from Eq. (2), as described in the text.

Initial State (R)L _N	Line Position Obs.	Line Position Δ (cm-1) Calculated			Strength	
		E ₁	E ₂	Tot.	Obs.	Calc.
(0)F ₃	+0.96(2)	+1.02	-0.08	+0.94	0.6	1.9
(1)F ₄	+1.78(2)	+1.64	+0.13	+1.77	3.6	4.0
(1)F ₃	-0.73(1)	-0.83	+0.08	-0.75	0.6	3.1
(1)F ₂	+2.58(2)	+2.51	0.00	+2.51	2.4	2.3
(2)F ₅	+1.92(3)	+1.91	-0.01	+1.90	1.0	0.5
(2)F ₄	-----	-0.30	-0.01	-0.31	---	0.4
(2)F ₃	-----	-0.06	+0.16	-0.10	---	0.3
(2)F ₂	-----	+1.57	-0.02	+1.55	---	0.2
(2)F ₁	+3.17(2)	+3.16	-0.02	+3.14	1.2	0.2
(3)F ₆	+2.05(3)	+2.08	-0.07	+2.01	1.3	0.4
(3)F ₅	-----	-0.01	-0.08	-0.09	---	0.3
(3)F ₄	-----	-0.21	-0.09	-0.30	---	0.2
(3)F ₃	-----	+0.63	-0.07	+0.54	---	0.1
(3)F ₂	-----	+1.85	-0.04	+1.81	---	0.1
(3)F ₁	-----	+2.94	-0.01	+2.93	---	0.1
(3)F ₀	**	+3.56	-0.06	+3.50	---	0.1
(0)G ₄	*	+0.27	-0.02	+0.25	---	3.4
(1)G ₅	+0.61(1)	+0.57	+0.02	+0.59	6.4	7.0
(1)G ₄	-0.53(1)	-0.56	+0.02	-0.54	0.5	5.7
(1)G ₃	+0.88(2)	+0.86	-0.01	+0.85	3.7	4.6
(2)G ₆	+0.71(1)	+0.70	-0.01	+0.69	1.1	0.9
(2)G ₅	-----	-0.27	0.00	-0.27	---	0.7
(2)G ₄	-----	-0.23	+0.04	-0.19	---	0.6
(2)G ₃	*	+0.36	-0.01	+0.35	---	0.5
(2)G ₂	-----	+1.12	-0.01	+1.11	---	0.4
(3)G ₇	+0.78(2)	+0.78	-0.02	+0.76	1.7	0.6
(3)G ₆	-----	-0.11	-0.01	-0.12	---	0.5
(3)G ₅	-----	-0.30	-0.02	-0.32	---	0.4
(3)G ₄	-----	-0.07	-0.01	-0.08	---	0.3
(3)G ₃	*	+0.39	-0.01	+0.38	---	0.2
(3)G ₂	*	+0.88	-0.01	+0.87	---	0.2
(3)G ₁	-----	+1.28	-0.02	+1.26	---	0.1
(0)H ₅	+0.09(1)	+0.09	0.00	+0.09	1.3	2.0
(1)H ₆	+0.27(1)	+0.26	+0.01	+0.27	3.6	4.1
(1)H ₅	-0.34(1)	-0.35	+0.01	-0.34	0.4	3.4
(1)H ₄	+0.39(1)	+0.39	0.00	+0.39	1.8	2.9
(2)H ₇	+0.35(1)	+0.34	0.00	+0.34	0.7	0.5
(2)H ₆	-----	-0.18	0.00	-0.18	---	0.4
(2)H ₅	-----	-0.19	+0.01	-0.18	---	0.4
(2)H ₄	*	+0.10	0.00	+0.10	---	0.3
(2)H ₃	+0.53(1)	+0.52	0.00	+0.52	0.7	0.3
(1)I ₇	+0.14(1)	+0.14	0.00	+0.14	0.6	0.9
(1)I ₆	-----	-0.22	0.00	-0.22	---	0.8
(1)I ₅	+0.21(1)	+0.21	0.00	+0.21	1.6	0.7

um.¹⁶ Much more precise experimental determinations should be possible by direct microwave measurement of fine-structure intervals.¹³

The observed pattern of line intensities is more difficult to interpret. In order to contribute to the signal, both initial and final states of a transition must be stable for 10^{-6} sec against predissociation and autoionization. Predissociation is energetically allowed for all these states, but to influence relative intensities, it must involve angular momentum selection rules which to our knowledge have not been discussed theoretically. Vibrational autoionization is energetically allowed for $n=10$ states with $\nu > 0$. Since the H_2^+ beam is probably vibrationally excited,¹⁷ our observations suggest that this process proceeds rapidly, in agreement with lifetime estimates from Eq. (1). Rotational autoionization is energetically allowed for $n=27$ states with $R > 1$, but nevertheless, several lines are observed with $R=2,3$ cores. If the distributions of $n=10$ electrons and $\nu=0$ cores are isotropic in L and R respectively, and the core rotational populations obey a Boltzmann distribution, then the relative line intensities are expected to be⁷

$$I(R,L,N) = C_0 [2 - (-1)^R] \exp\left[-\frac{BR(R+1)}{KT_R}\right] \\ \times f(L)(2N+1)(2N+3) \\ \times \begin{Bmatrix} L+1 & N+1 & R \\ N & L & 1 \end{Bmatrix}^2, \quad (2)$$

where T_R is the rotational temperature, $B=29 \text{ cm}^{-1}$, and $f(L)$ accounts for the relative L -state populations and reduced matrix elements. The best match to Eq. (2), obtained with $T=156 \text{ K}$ and $f(L)$ adjusted to fit the strongest lines, is shown in column 7 of Table I. Comparison with observed intensities in column 6 indicates substantial discrepancies. A present, no explanation is known for the observed pattern of intensities. Previous studies of H_2 Rydberg formation by charge capture have already indicated other open questions, particularly an anomalously large excited-state fraction ($n > 11$) as compared with atomic hydrogen,³ and a spontaneous regeneration of once-ionized Rydberg levels.¹⁸ The present observations add to the suggestion that significant aspects of the population dynamics of these states remain to be explored.

We wish to acknowledge fruitful discussions with Edward E. Eyler, significant experimental help from Stephen L. Palfrey, and computational assistance from Muhammad Idrees. Financial support was provided by the National Science Foundation under Grant No. PHY83-12723 and in the experiment's earliest stages by the Research Corporation.

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