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Determination of the hyperfine structure of $H_2^+(\nu=0, R=1)$ by microwave spectroscopy of high-L n=27 Rydberg states of H_2

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The hyperfine-structure constants of the hydrogen molecular ion in its ground vibrational state are determined experimentally, by the study of the spin structure of high-L n = 27 Rydberg levels of the neutral hydrogen molecule. The results are $b_{1F} = 922.940(20)$, c = 128.259(26), d = 42.348(29), and f = -0.003(15) MHz.

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The hyperfine structure (HFS) of the molecular ion H_2^+ forms the finest level of structure of this simplest molecule. It is of interest both for fundamental reasons, and because transitions between hyperfine levels might be seen in astrophysical sources in analogy with the 21-cm line of atomic hydrogen [1]. A pioneering experimental study of this structure was reported in 1969 by Jefferts [2]. By observing microwave-induced changes in the photodissociation rates of H_2^+ ions confined to an rf trap, he measured the frequencies of 36 different hyperfine transitions, all in vibrationally excited states of $H_2^+(v=4-8)$, and determined the fivefold structure of the R = 1 levels for each of these vibrational levels. The structure could be described by an effective spin Hamiltonian

$$H_{\rm HFS} = b(\mathbf{I} \cdot \mathbf{S}) + c(\mathbf{I} \cdot \hat{\boldsymbol{\rho}})(\hat{\boldsymbol{\rho}} \cdot \mathbf{S}) + d(\mathbf{S} \cdot \mathbf{R}) + f(\mathbf{I} \cdot \mathbf{R}) , \qquad (1)$$

where I is the total proton spin, S is the H_2^+ electron spin, $\hat{\rho}$ the internuclear axis, and R the total H_2^+ angular momentum, excluding spin. The hyperfine constants *b*, *c*, *d*, and *f* are numbers, different for each rovibrational state of the ion, which depend on details of the H_2^+ wave function. The hyperfine constants determined from Jefferts's observations [3] have been virtually the only source of experimental information about H_2^+ hyperfine structure for 20 years. Since none of the lower vibrational states ($\nu \leq 3$) was observed, no experimental information was available about their hyperfine structure.

Considerable progress has been made in calculations of the H_2^+ hyperfine constants since 1969. Until recently, however, all such calculations were limited by making the "adiabatic approximation" for the H_2^+ wave function, namely, that it contains a single electronic state as a factor. This leads to errors on the order of m_e/m_p in the wave function and possibly in the calculated hyperfine constants [4]. Recently, a perturbative expression for the order m_e/m_p corrections to the adiabatic wave function has been developed [5]. Comparison with purely numerical calculations, where available [6], supports the expectation that residual errors in the resulting nonrelativistic wave function are on the order of $(m_e/m_p)^2$. Indeed, calculations of the dipole hyperfine constant, $b_{1F} = b + c/3$, with these nonadiabatic wave functions, agree with measurements in vibrationally excited states to about 10^{-5} ,

approximately the level where relativistic and radiative effects neglected in all calculations to date are expected to become significant.

Within the past few years, a new source of precise information about the properties of H_2^+ has emerged, based on the analysis of high-resolution microwave spectroscopy of nonpenetrating high-L Rydberg states of H₂. In effect the distant Rydberg electron acts as a sensitive probe of the various H_2^+ properties that are reflected in the H₂ Rydberg fine structure. Studies of this type have already been used to measure the quadrupole moment and dipole polarizabilities of $H_2^+(\nu=0, R=1)$ [7], and to determine very precisely the (0,1)-(0,3) rotational splitting [8]. Previous studies have also shown that the spin structure of high-L H₂ Rydberg states is related to the hyperfine structure of H_2^+ , and analyzed the structure in terms of an effective spin Hamiltonian that includes the hyperfine terms of Eq. (1), in addition to long-range magnetic spin interactions [9]. In the present study of high-L n = 27 states, the spin interactions involving the Rydberg electron spin are negligibly small, and the Rydberg structure can be described by the spin Hamiltonian

$$H_{\rm spin} = H_{\rm HFS} - 2 \frac{\alpha^2 \mathcal{R}}{r^3} \mathbf{L} \cdot \mathbf{S} , \qquad (2)$$

where H_{HFS} is given in Eq. (1), r is the Rydberg electron's radial coordinate, and \mathcal{R} is the Rydberg constant.

Figure 1 illustrates the structure of high-L H₂ Rydberg states, with particular attention given to the n = 27 states with L = 5 and 6 bound to the v=0, R = 1 state of H_2^+ . The zeroth-order energy is determined from the rovibrational state of the ion core and the principal quantum number of the Rydberg electron, and is therefore common to all of these states. The eigenstates are approximately the basis states characterized by (a) F = I + S, the total H_2^+ spin and (b) N=L+R, the total angular momentum exclusive of spin. The first quantum number is associated with the dipole hyperfine structure (HFS) of H_2^+ , $\Delta E = \frac{3}{2}(b + c/3)$, while the latter is associated with the electric fine structure (EFS) of the high-L Rydberg state [7]. As Fig. 1 illustrates, the Rydberg-state energy is, to a first approximation, the sum of these two independent effects. A finer level of structure, however, shown in expanded scale in Fig. 1 for the H_6 and I_6 states, results

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from coupling F and N to form $J_1 = F + N$. This structure is primarily due to the c and d terms in H_{HFS} . An even finer level of structure, not shown in Fig. 1 because it is unresolved in this experiment, results from coupling the Rydberg electron's spin S_R to J_1 to form the total angular momentum $J = J_1 + S_R$, producing a closely spaced doublet of levels whose center of gravity is equal to the energy at the J_1 level.

The fact that the EFS and HFS energies are comparable in size for the n = 27 states studied here allows the off-diagonal matrix elements of Eq. (2) to mix basis states of equal J_1 [10]. This allows electric dipole transitions to occur between n = 27 states, which violate the $\Delta F = 0$ selection rule, such as transition J in Fig. 1. Transitions of this type, which were unobservable in previous studies of n = 10 H₂ Rydberg states [9], reveal the relative positions of the F = 3/2 and F = 1/2 Rydberg manifolds, giving direct experimental information about the dipole hyperfine structure.

We have carried out extensive microwave spectroscopy in $(0,1)27L_N$ states of H₂, with $4 \le L \le 6$, measuring some 46 different transition energies. The experimental method is similar to previous studies [10]. A fast beam of H₂ Rydberg states is formed by neutralization of a 13keV H₂⁺ beam, a Doppler-tuned cw CO₂ laser excites particular n = 27 Rydberg states by promoting n = 10states present in the neutralized beam, and eventually the FIG. 1. Energy-level diagram for N = 27, L = 5 and 6 Rydberg states of H₂, bound to the (v=0, R=1) state of H₂⁺. The core hyperfine structure and Rydberg electric fine structure are illustrated for all states. In the case of H₆ and I₆ states, the finer level of spin structure associated with the quantum number $J_1=N+F$ is also shown in expanded scale, with energies due to diagonal ($E^{[1]}$) and offdiagonal ($E^{[2]}$) matrix elements of H_{spin} shown separately. The lettered transitions correspond to the microwave resonance signals of Fig. 2.

n = 27 population is measured by Stark ionization and collection of the resulting ions. The well-resolved EFS of the n = 10 states provides unambiguous selection of a particular n = 27 EFS level to be populated by the laser. Previous studies have shown that the Stark ionization behavior of n = 27 Rydberg levels depends on their EFS energy, with higher-energy states adiabatically ionizing at higher fields and vice versa. In this experiment, we utilize this contrasting Stark ionization behavior to detect microwave transitions between different n = 27 Rydberg levels. For example, suppose the $(0,1)27H_6$ state is excited by the CO₂ laser. Immediately afterwards, the beam passes through a microwave interaction region that may induce transitions to other n = 27 Rydberg states such as the $(0,1)27I_6$ state. If a transition occurs, it will lead to a change in the ion current detected after Stark ionization. In particular, since the H_6 and I_6 states undergo Stark ionization at slightly different fields, they will be deflected by different angles in the ionizing field. The subsequent deflection field that sweeps the product ions into the channeltron detector can be adjusted to maximize the difference in the detection efficiency of the two states, and thereby the microwave signal.

Figure 2 shows data from this set of $(0,1)27H_6$ - I_6 transitions. The microwave interaction region is a 1-m-long TEM transmission line [11], in which the microwaves propagate either parallel or antiparallel to the fast beam.



FIG. 2. Resonance spectra of $(0,1)27H_6$ - $(0,1)27I_6$ transitions in H₂. Microwaves are propagating parallel to the fast atomic beam. The spin structure components (A - J) are illustrated in Fig. 1.

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This gives a transit-time-limited resonance linewidth of about 1 MHz. Each peak was fit to a Gaussian resonance line shape to extract its center for both directions of microwave propagation, and these were averaged to eliminate first-order Doppler shifts. Small corrections were applied to correct for second-order Doppler shifts $(\leq 0.01 \text{ MHz})$ and ac Stark shifts $(\leq 0.6 \text{ MHz})$ [12]. The microwave interaction region was magnetically shielded (residual $B \leq 5$ mG) and was heated to 60 °C to retard surface charging, which could lead to stray electric fields [11]. The residual stray electric field was estimated to be 10(2) mV/cm rms by comparing measurements of the high-L EFS interval $(0,1)27K_6$ -K₇ with the value of this interval calculated in the higher-order polarization model [7], using the known Stark-shift rate of the interval. The data were corrected for the Stark shifts due to a field of this size (≤ 0.3 MHz), and corrected transition frequencies are listed in Table I. The errors shown there include only random errors. Uncertainties in the Stark shifts (dc and ac), which are highly correlated, were included separately in deducing the hyperfine constants.

With some redundancy, these 46 transition energies determine the relative positions of 37 Rydberg states, including the complete sixfold spin structure of four EFS states, the G_4 , H_5 , H_6 , and I_6 states and less complete spin structure of the G_5 , H_4 , and I_5 states. In order to extract the best values for the hyperfine constants b, c, d, and f, the transition frequencies were fit simultaneously to a model including the spin interactions of Eq. (2) and the EFS energies of each of the states listed above. The fitted transition energies, shown in Table I, are in good agreement with the measured frequencies, giving a χ^2 of 38 for 36 degrees of freedom. The best-fit values of the hyperfine constants are given in Table II, column 1. The quoted parameter errors include both random and systematic errors.

The fact that a single choice of constants accounts for the observed structure in all three L states suggests that there is no large perturbation of the hyperfine interactions due to the presence of the Rydberg electron, but clearly at some level the constants that characterize the Rydberg structure are expected to differ from those of the free ion. In the absence of any specific theoretical predictions, we speculate that the effective constants are proportional to the projection of the core electron onto its ground electronic state. This is less than 1 because of the polarization induced by the electric field of the Rydberg electron, and should be given by

$$P_{g} = 1 - K \langle r^{-4} \rangle_{nL} , \qquad (3)$$

where K is a constant depending on the polarizability and excitation energies of H_2^{+} . An analogous calculation for Rydberg states of helium [13] finds a value of K equal to $31/128 a_0^4$. Even if K were 100 times larger for H_2 , P_g would differ from 1 by only about 10^{-6} for the 27G state, and considerably less for higher L states. This suggests that perturbations of the hyperfine constants from their free ion values would be unobservably small in the present measurement. A purely empirical estimate of possible perturbations can be had by using the ansatz of Eq. (3) to write

$$b_{1F}(nL) = b_{1F}(\text{free})(1 - K \langle r^{-4} \rangle_{nL})$$
, (4)

and using this expression to fit the transition frequencies instead of a single number. Such a fit finds a value of Kconsistent with zero, and gives a value of $b(27H)/b(\text{free})=1-(7\pm7 \text{ ppm})$. Since other estimates suggest a small value of K, we still take the K=0 fitted constants as best estimates, but we assign an additional systematic error of ± 15 ppm to each of the measured hyperfine constants, to account for possible perturba-

TABLE I. Measured Rydberg transition energies and best-fit calculated values, both in MHz. Transitions are labeled by $L_N(F,J_1)$ for each state.

Transition	Observed	Fit
$G_4(1.5,4.5)-H_4(1.5,3.5)$	1417.830(32)	1417.860
$G_{4}(1.5,3.5)-H_{4}(1.5,3.5)$	1426.441(28)	1426.455
$G_{4}(1.5,3.5)-H_{4}(1.5,2.5)$	1428.476(50)	1428.485
$G_{4}(1.5, 4.5) - H_{4}(1.5, 4.5)$	1430.860(22)	1430.871
$G_{4}(1.5,3.5)-H_{4}(1.5,4.5)$	1439.486(29)	1439.466
$G_{4}(1.5,2.5)-H_{4}(1.5,2.5)$	1457.964(50)	1458.018
$G_{4}(1.5,5.5)-H_{4}(1.5,4.5)$	1466.131(25)	1466.113
$G_{4}(1.5, 5.5) - H_{4}(1.5, 5.5)$	1491.016(25)	1490.995
$G_4(0.5, 4.5) - H_4(1.5, 5.5)$	90.323(50)	90.298
$G_5(1.5, 5.5) - H_5(1.5, 5.5)$	1428.428(13)	1428.412
$G_{5}(1.5, 6.5) - H_{5}(1.5, 5.5)$	1432.829(24)	1432.800
$G_{5}(1.5, 5.5) - H_{5}(1.5, 4.5)$	1435.403(25)	1435.406
$G_{5}(1.5, 4.5) - H_{5}(1.5, 5.5)$	1447.669(21)	1447.680
$G_{5}(0.5, 5.5) - H_{5}(0.5, 5.5)$	1465.072(63)	1464.931
$G_{5}(1.5, 6.5) - H_{5}(1.5, 6.5)$	1466.947(19)	1466.962
$G_{s}(1,5,4,5)-H_{s}(1,5,3,5)$	1484.063(36)	1484.087
$G_{s}(1.5,3.5)-H_{s}(1.5,4.5)$	1493.735(35)	1493.802
$G_{s}(1.5, 3.5) - H_{s}(0.5, 4.5)$	118.478(27)	118.501
$H_{5}(1.5, 5.5) - I_{5}(1.5, 4.5)$	824.176(37)	824.176
$H_5(1.5, 4.5) - I_5(1.5, 4.5)$	831.178(25)	831.170
$H_5(1.5, 5.5) - I_5(1.5, 5.5)$	844.998(19)	844.961
$H_5(0.5, 5.5) - I_5(0.5, 5.5)$	847.219(31)	847.278
$H_5(1.5, 4.5) - I_5(1.5, 5.5)$	851.955(16)	851.956
$H_5(1.5,5.5) - I_5(1.5,6.5)$	870.403(17)	870.395
$H_5(1.5, 6.5) - I_5(1.5, 5.5)$	879.126(16)	879.124
$H_5(1.5, 6.5) - I_5(1.5, 6.5)$	904.537(14)	904.557
$H_5(0.5, 5.5) - I_5(1.5, 6.5)$	501.270(23)	501.279
$H_6(1.5, 6.5) - I_6(1.5, 6.5)$	742.241(13)	742.249
$H_6(1.5, 5.5) - I_6(1.5, 6.5)$	757.869(73)	757.803
$H_6(1.5, 5.5) - I_6(1.5, 5.5)$	763.680(14)	763.710
$H_6(0.5, 5.5) - I_6(0.5, 5.5)$	767.989(19)	767.987
$H_6(1.5, 6.5) - I_6(1.5, 7.5)$	775.067(35)	775.096
$H_6(1.5,7.5) - I_6(1.5,7.5)$	779.302(169)	779.205
$H_6(0.5, 6.5) - I_6(0.5, 6.5)$	780.141(187)	780.111
$H_6(1.5,5.5) - I_6(1.5,4.5)$	792.515(35)	792.481
$H_6(1.5, 4.5) - I_6(1.5, 4.5)$	825.050(11)	825.036
$H_6(1.5, 4.5) - I_6(0.5, 5.5)$	577.932(143)	578.030
$G_4(1.5, 4.5) - H_5(1.5, 5.5)$	301.642(42)	301.688
$G_4(0.5, 4.5) - H_5(0.5, 5.5)$	307.914(39)	307.907
$G_4(0.5,3.5)-H_5(0.5,4.5)$	309.466(42)	309.489
$G_4(1.5,5.5)-H_5(1.5,5.5)$	336.902(36)	336.931
$H_5(0.5, 5.5) - I_6(0.5, 6.5)$	179.029(31)	179.059
$H_5(1.5, 6.5) - I_6(1.5, 6.5)$	214.631 (27)	214.650
$G_4(1.5, 4.5) - H_6(1.5, 4.5)$	1272.561(36)	1272.535
$G_4(1.5,5.5)-H_6(1.5,5.5)$	1275.264(38)	1275.221
$G_5(1.5, 3.5) - H_6(1.5, 4.5)$	515.955(37)	515.962

TABLE II. $H_2^+(0,1)$ hyperfine constants, as obtained from H_2 Rydberg spin structure (column 1), and from adiabatic (column 2) and nonadiabatic (column 3) calculations. All results in MHz.

Constant	This work	Theory (Ref. [4])	Theory (Ref. [14])
b_{1F}	922.940(20)	923.361	922.990
c	128.259(26)	128.432	128.482
d	42.348(29)	42.399	42.421
f	-0.003(15)	-0.046	

tions. This increases the error in the fitted parameter b_{1F} from ± 0.015 to ± 0.020 MHz, but is insignificant for the other constants.

The hyperfine constants obtained from these studies represent direct experimental information about the ground-vibrational-state hyperfine structure of H_2^+ . It is of course possible to extrapolate the known constants at higher v back to v=0, but it is very difficult to estimate the possible uncertainty in such extrapolations since the functional dependence on v is unknown. Comparison of the measured constants with adiabatic calculations, column 2 in Table II [4], shows discrepancies of 0.046(2)%, 0.13(2)%, and 0.12(7)% for b_{1F} , c, and d, respectively. It would be plausible to attribute errors of this size to the inadequacy of the adiabatic approximation to the H₂⁺ wave function. However, comparison with recent calculations based on the more accurate nonadiabatic wave function of Babb and Dalgarno [14], column 3 of Table II, shows that only in the case of b_{1F} is the agreement with experiment improved. In that case, the nonadiabatic calculation leaves a discrepancy of 0.005(2)%, approximately the size expected from uncalculated radiative and relativistic contributions. In contrast, the nonadiabatic calculations of c and d leave discrepancies of about 0.17(2)% for c and 0.17(7)% for d. The origin of such large discrepancies is unclear in view of the apparent accuracy of the nonadiabatic H_2^+ wave functions and the fact that the relativistic and radiative

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effects not included in the calculation are not expected to be that large. One might question whether some complication in the H₂ Rydberg state spin structure intervenes to make the fitted c differ from the free H_2^+ value. While no theoretical work along these lines has yet been reported, it appears from the discussion above that, at least in the case of b_{1F} , no such complications occur that are large enough to account for the discrepancy in c. Also, comparison of the same nonadiabatic calculations with the measurements of c in vibrationally excited states [2,3] independently shows a pattern of discrepancies consistent with the v=0 result reported here. Thus there does not appear to be an obvious explanation for the discrepancy between theory and experiment for the constant c. Additional theoretical effort, evaluating relativistic and radiative corrections to H_2^+ hyperfine structure and exploring effects specific to H₂ Rydberg spin structure, will probably be required before an explanation is found. The latter studies would also facilitate even more precise determinations of H_2^+ hyperfine structure from future H₂ Rydberg spectroscopy of improved precision.

Using our values of the (0,1) hyperfine constants, the fivefold structure of the free $H_2^{+}(0,1)$ ion can be calculated, and the transition frequencies of possible astrophysical interest evaluated. We find 1412.244(37), 1404.433(37), 1392.668(36), 1315.722(51), 1296.146(44), 96.523(26), 19.576(33), and 7.811(36) MHz, which can be compared in one case (1404.3) with the extrapolation of Jefferts [2].

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