

at 450, 500, and 550°K, respectively, and in fair agreement with each other.

As to the mobility of Cs⁺ ions in helium, the polarization force is believed to be the dominating interacting force at such low energies. Langevin's theory¹⁶ (to this limit) gives a value of 15.8 cm²/V-sec in contrast with

¹⁶ P. Langevin, *Ann. chim. et phys.* **5**, 245 (1905).

18.5±0.5 cm²/V-sec determined by the present experiment. Tyndall *et al.*¹⁷ used shutter methods to determine the mobilities of alkali ions in helium and found a value of 18.4 cm²/V-sec for Cs⁺ ions in helium, in excellent agreement with the present experiment.

¹⁷ A. M. Tyndall, *The Mobility of Positive Ions in Gases* (Cambridge University Press, Cambridge, New York, 1938).

Hyperfine Structure of the Hydrogen Molecule in its Metastable ³Π_u State*

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The hfs of the hydrogen molecule in its metastable excited state ³Π_u is calculated theoretically using Amemiya's wave function. The theoretical separation of the *F*=3 and *F*=2 states is 618 Mc/sec, and that for the *F*=2 and *F*=1 states is 412 Mc/sec, for *K*=1, *J*=2; these separations are to be compared with the observed values of 707.55 Mc/sec and 462.44 Mc/sec, respectively. The theoretical second-order correction is found to explain the deviation of the observed values from the interval rule.

INTRODUCTION

THE hyperfine structure of the hydrogen atom in its ground state produces a resonance at 1420 Mc/sec. Observation of this radio-frequency line by means of radio telescopes gave us extensive data on the distribution of hydrogen atoms in space.¹ This line, however, is the only spectral line observed by radio telescopes so far. Since there exist so many hydrogen atoms in space, one expects that there must be some hydrogen molecules in space also. Bates² calculated the cross section of formation of molecules from atomic hydrogen by collision and recently McCrea and McNally³ estimated the rate of molecular formation at the surface of interstellar dust. The existence of molecular hydrogen, however, cannot be detected by using a radio telescope directly, since the ground state of the neutral hydrogen molecule does not have an appreciable hfs splitting. The difference between atomic and molecular hydrogen is due to the fact that in atomic hydrogen the spin of the electron produces a strong magnetic field at the center to produce a large interaction with the proton magnetic moment, while molecular hydrogen in its ground state cannot produce such a strong magnetic field since the resulting electronic spin and orbital angular momenta are both zero.

There are, however, possibilities of having an

appreciable hfs if one goes to the ionized hydrogen molecule H₂⁺. One of the present authors (M. Mizushima) did some calculations⁴ on this molecule ion, and Burk⁵ and Dalgarno *et al.*⁶ published calculations of the same nature independently. In this case the resulting electronic spin is 1/2 which produces a strong magnetic field for protons to couple. The other possibility is the neutral hydrogen molecule in its excited ³Π_u state. In this excited state the finite electronic angular momenta can produce a large magnetic hfs. This particular state, ³Π_u, happens to be a metastable state since the only other triplet state below this state is a ³Σ_u⁺ state which cannot be combined with our state by an electric dipole transition. The ³Σ_u⁺ state, to which our ³Π_u state goes by a forbidden transition, is a dissociative state. The molecule in the ³Π_u state, therefore, decays into atomic hydrogen through the ³Σ_u⁺ state.

Lichten⁷ first showed the metastability of this ³Π_u state in his molecular beam experiment. His later experiment⁸ showed that some states, including the states we are considering in this paper, have a lifetime of 0.1 to 0.5 msec, and the hfs of the *K*=1, *J*=2 state is such that

$$\begin{aligned}(F=3) &\leftrightarrow (F=2) = 707.55 \text{ Mc/sec,} \\ (F=2) &\leftrightarrow (F=1) = 462.44 \text{ Mc/sec.}\end{aligned}\quad (1)$$

Fontana⁹ recently calculated the fine structure of this state by using an approximate wave function.

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¹ For example, see J. L. Pawsey and R. N. Bracewell, *Radio Astronomy* (Oxford University Press, New York, 1955).

² D. R. Bates, *Monthly Notices Roy. Astron. Soc.* **111**, 303 (1951).

³ W. H. McCrea and D. McNally, *Monthly Notices Roy. Astron. Soc.* **121**, 238 (1960).

⁴ M. Mizushima, *Astrophys. J.* **132**, 493 (1960).

⁵ B. F. Burk, *Astrophys. J.* **132**, 514 (1960).

⁶ A. Dalgarno, T. N. L. Patterson, and W. B. Somerville, *Proc. Roy. Soc. (London)* **A259**, 100 (1961).

⁷ W. Lichten, *Phys. Rev.* **120**, 848 (1960).

⁸ W. Lichten, *Phys. Rev.* **126**, 1020 (1962).

⁹ P. R. Fontana, *Phys. Rev.* **125**, 220 (1962).

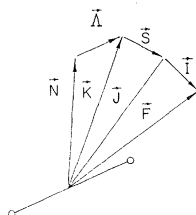
ROTATIONAL WAVE FUNCTION

Since $\Lambda = 1$ in our state of $^3\Pi_u$, the angular momentum quantum number K starts from 1, where

$$\mathbf{K} = \mathbf{N} + \mathbf{A}, \quad (2)$$

and N is the end-over-end rotational quantum number. The rotation constant is measured by Richardson¹⁰ to be about 910 kMc/sec, while the spin-orbit coupling constant is about 5 kMc/sec according to the theoretical estimation by Fontana.⁹ Hund's case b is, thus, a good approximation. (Fig. 1)

FIG. 1. Coupling of angular momenta.



There exists Λ doubling in this case. If we designate the wave function with \mathbf{A} parallel and antiparallel to the molecular z axis by $|K_\xi\rangle$ and $|K_\eta\rangle$, respectively, we obtain two possible wave functions:

$$|K_\pm\rangle = (1/\sqrt{2})\{|K_\xi\rangle \pm |K_\eta\rangle\}. \quad (3)$$

These two possible states, due to the Λ doublet, correspond to the possibility of ortho- and parahydrogen, or hydrogen with total nuclear spin 1 and 0. Since our electronic wave function is Π_u , or parity odd, the plus sign will make the electronic wave function antisymmetric and the minus sign will make it symmetric, with respect to the exchange of protons. The end-over-end rotational quantum number N produces an extra factor to this property under exchange of protons, given by $(-1)^N$, which can also be written as $(-1)^{K+1}$ if the quantum number K is used. We thus see that $|K_+\rangle$ is ortho if K is odd, and para if K is even, and the other way for $|K_-\rangle$. Since the para states do not have hfs, we are interested in ortho states only.

Spin angular momentum \mathbf{S} is coupled to \mathbf{K} to give \mathbf{J} . The coupled wave function $|K_\pm S J M\rangle$ is obtained in the well-known way. Since $S=1$ and $K \geq 1$, we have $J = K-1, K$, and $K+1$ states for every K . There is one ortho and one para state for each J, K set. Fontana⁹ calculated energy levels in the Hund's case b .

ELECTRONIC WAVE FUNCTION

The best electronic wave function available for our $^3\Pi_u$ state is the one calculated by Amemiya.¹¹ He tried the James-Coolidge type wave function which is made of a linear combination of terms like

$$2\pi[mnpq]_{\xi,\eta} = \exp(-\frac{1}{2}\lambda_1 - \lambda_2 \pm i\varphi_1)\lambda_1^m\lambda_2^n\mu_1^p\mu_2^q[(\lambda_1^2-1)(1-\mu_1^2)]^{1/2} \\ - \exp(-\lambda_1 - \frac{1}{2}\lambda_2 \pm i\varphi_2)\lambda_1^n\lambda_2^m\mu_1^q\mu_2^p \\ \times [(\lambda_2^2-1)(1-\mu_2^2)]^{1/2}, \quad (4)$$

with

$$\begin{aligned} \lambda_1 &= (r_{a1} + r_{b1})/R, \\ \lambda_2 &= (r_{a2} + r_{b2})/R, \\ \mu_1 &= (r_{a1} - r_{b1})/R, \\ \mu_2 &= (r_{a2} - r_{b2})/R, \end{aligned} \quad (4a)$$

where R is the internuclear distance, r_{ai} is the distance between the proton a and the electron i , while r_{bi} is the distance between the proton b and the electron i . φ_i is the azimuthal angle for the electron i measured around the molecular axis. ξ and η correspond to the sign $+$ and $-$ of $i\varphi$. Amemiya¹¹ took six terms [0000], [0020], [0011], [0002], [1000], and [0100] and published the best coefficients for these terms at the equilibrium distance of 1.90 a.u. The energy, equilibrium distance, and vibrational frequency obtained in his calculation agree very well with experiment.

SPIN HAMILTONIAN

The part of the Hamiltonian which is related to protons is

$$H_{\text{hfs}} = \sum_{i=1,2} \sum_{j=a,b} 2g_p\beta_n\beta \left[\frac{1}{r_{ij}^3} \mathbf{l}_i \cdot \mathbf{I}_j - (\mathbf{s}_i \cdot \mathbf{I}_j - 3s_{iR}I_{jR}) \frac{1}{r_{ij}^3} + \frac{8\pi}{3} \mathbf{s}_i \cdot \mathbf{I}_j \delta(\mathbf{r}_{ij}) \right], \quad (5)$$

where i refers to electrons, j refers to protons, g_p is the g factor of the proton ($g_p=5.6$), β_n is the nuclear magneton, β is the Bohr magneton, \mathbf{I}_j is the proton spin, \mathbf{l}_i the electron's orbital angular momentum, and s_{iR} means the component of \mathbf{s}_i along \mathbf{r}_{ij} .

The expectation value of $(r_{ij})^{-3}$ and $\delta(\mathbf{r}_{ij})$ can be calculated by using Amemiya's wave function.¹¹ The calculation is straightforward if we use the table of Kotani *et al.*¹² The result can be expressed as

$$\bar{H}_{\text{hfs}} = a\mathbf{A} \cdot \mathbf{I} + b\mathbf{S} \cdot \mathbf{I} + c(S_z I_z - \frac{1}{4}S_+ I_- - \frac{1}{4}S_- I_+) + d(S_+ I_+ + S_- I_-), \quad (6)$$

where the angular momenta \mathbf{A} , \mathbf{S} , and \mathbf{I} mean total electronic orbital, total electronic spin, and total nuclear spin angular momenta, respectively, and

$$\begin{aligned} S_\pm &= S_x \pm iS_y, \\ I_\pm &= I_x \pm iI_y. \end{aligned} \quad (7)$$

Numerical values for the coefficients a , b , c , and d are shown in Table I. Table I shows that the first term of Amemiya's wave function, namely, the [0000] term,

¹⁰ O. W. Richardson, *Molecular Hydrogen and Its Spectrum* (Yale University Press, New Haven, Connecticut, 1934).

¹¹ A. Amemiya, *Proc. Phys.-Math. Soc. Japan* **21**, 394 (1939).

¹² M. Kotani, A. Amemiya, E. Ishiguro, and T. Kimura, *Table of Molecular Integrals* (Maruzen, Ltd., Tokyo, 1955).

already gives a good approximation, which indicates that our final value is rather reliable.

TABLE I. Numerical values of hfs coupling constants.

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>
First term of Amemiya (a.u.)	0.189	1.852	-0.633	0.005
Final result (a.u.)	0.103	1.830	-0.738	0.003
Final result (Mc/sec)	23	417	-168	0.6

HYPERFINE STRUCTURE

Since the hfs coupling coefficients we obtained are about 400 Mc/sec, which is about 1/10 of the spin-orbit coupling constant, the first order theory should be good to calculate the hfs.

Take the wave function as

$$|K_{\pm}SJIF\rangle = (1/\sqrt{2})\{|K_{\xi}SJIF\rangle \pm |K_{\eta}SJIF\rangle\}, \quad (8)$$

where K_{ξ} and K_{η} refer to states in which the component of \mathbf{K} along the molecular axis is +1 and -1, respectively, as before.

The hfs energy levels are thus obtained from

$$\langle K_{\pm}SJIF | \bar{H}_{\text{hfs}} | K_{\pm}SJIF \rangle = \langle K_{\xi}SJIF | \bar{H}_{\text{hfs}} | K_{\xi}SJIF \rangle \pm \langle K_{\xi}SJIF | \bar{H}_{\text{hfs}} | K_{\eta}SJIF \rangle. \quad (9)$$

The calculation with the \bar{H}_{hfs} of (6) can be done following Frosch and Foley.¹³

We are particularly interested in the $K=1$ state. In that state, according to the discussion in a previous section, the K_+ state is an ortho state but the K_- state is a para state. Since only the ortho state can have hfs, we take the + sign in (9). Our result for the $K=1$, ortho state is

$$[F(F+1) - J(J+1) - 2][(a/8) + (b/4) - (c/8) + (3c/80)(J+2)(J-1) + (d/30)(2J^2 + 2J - 9)],$$

¹³ R. A. Frosch and H. M. Foley, Phys. Rev. **88**, 1337 (1952).

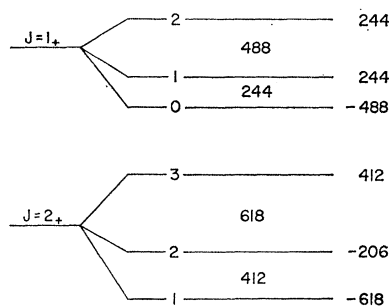


FIG. 2. Energy levels of $N=0$, $K=1$ ortho states, in Mc/sec.

where a , b , c , and d are coefficients shown in (6) and Table I. Note that the a , b , and c terms in (10) are obtained from the first term of (9), while the term with d came from the cross term of (9). Using Table I we obtain the hfs energy levels as shown in Fig. 2.

The theoretical frequencies for hfs transitions in the ($K=1$, $J=2$) state are

$$\begin{aligned} (F=3) \leftrightarrow (F=2) &= 618 \text{ Mc/sec,} \\ (F=2) \leftrightarrow (F=1) &= 412 \text{ Mc/sec,} \end{aligned} \quad (11)$$

which are not far from the experimental results (1), being about 10% too small.

The second-order term can be calculated in the same way and gives

$$[F(F+1)(F+4)(F-3)/6700] \times [(b^2/96) + (c^2/384)] \text{ Mc/sec,} \quad (12)$$

for the ($K=1$, $J=2$) states. The energy difference between the ($K=1$, $J=2$) and ($K=1$, $J=1$) states is calculated by Fontana⁹ to be 6.7 kMc/sec. The second-order correction is, thus, -9 Mc/sec for $F=2$, and -6 Mc/sec for $F=1$. They are just about enough to correct the experimental value (1) to satisfy the interval rule.

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