HYDROGEN MOLECULES AND ASTRONOMY: A REVIEW

by

W. B. Somerville[+], G. B. Field

and K. Dressler

Princeton University Observatory

January, 1965

"I write about molecules with great diffidence, having not yet rid myself of the tradition that atoms are physics, but molecules are chemistry, but the new conclusion that hydrogen is abundant seems to make it likely that the above-mentioned elements H, O, and N will frequently form molecules."

- Sir Arthur Eddington, 1937

[+] Present Address: University College, London

TABLE OF CONTENTS

PART A

THE THEORY OF THE HYDROGEN MOLECULE

by

W. B. Somerville

I. FORMULATION

The hydrogen molecule consists of two protons, labelled a and b, of charge + e and mass M, and two electrons, 1 and 2, of charge - e and mass m. The distances r_{a1}, r_{b2}, etc., are defined as indicated in Figure 1. The four particles of course are not necessarily in the same plane. The complete non-relativistic Schrödinger wave equation for the system is

$$\left\{-\frac{\hbar^2}{2M}\left(\nabla_a^2+\nabla_b^2\right)-\frac{\hbar^2}{2m}\left(\nabla_1^2+\nabla_2^2\right)+V-E\right\}\Psi\left(\underset{\sim}{r}_a,\underset{\sim}{r}_b,\underset{\sim}{r}_1,\underset{\sim}{r}_2\right)=0, \tag{1}$$

where $\underset{\sim}{r}_a$, etc., are referred to some arbitrary origin, and where the total potential energy

$$V=-e^2\left(\frac{1}{r_{a1}}+\frac{1}{r_{b1}}+\frac{1}{r_{a2}}+\frac{1}{r_{b2}}-\frac{1}{r_{12}}-\frac{1}{R}\right). \tag{2}$$

Although the total number of variables can be reduced from 12 to 8, the equation (1) is still much too complicated to permit accurate solution, and simplifying approximations must be introduced. The Born-Oppenheimer approximation is based on the fact that nuclear masses are of the order of thousands of electron masses; in consequence, the nuclei move much more slowly than do the

the electrons, and there is only a small change of nuclear positions in the time required for a complete electron orbit. It follows that to a good approximation the electronic part of the wave equation may be solved assuming the nuclei to be stationary, and the electronic and nuclear motions are taken to be completely separable,

$$\Psi\left(\underset{\sim}{r}_a, \underset{\sim}{r}_b, \underset{\sim}{r}_1, \underset{\sim}{r}_2\right) = \psi_e\left(\underset{\sim}{r}_1, \underset{\sim}{r}_2; R\right)\psi_N\left(\underset{\sim}{r}_a, \underset{\sim}{r}_b\right). \tag{3}$$

The electronic wave function ψ_e and eigenergy V_e are determined for fixed nuclei, of separation R, from

$$\left\{-\frac{\hbar^2}{2M}\left(\nabla_1^2 + \nabla_2^2\right) + V - V_e\right\}\psi_e = 0. \tag{4}$$

V_e is a function of R, and the motion of the nuclei is determined by placing them in a potential $V_e(R)$; for bound states of the molecule, V_e has a minimum at some equilibrium position R_e, and the nuclear vibration-rotation levels are located at energies within the potential well (cf. Figure 2). For large separations, the energy of the system must correspond to that of two separated atoms.

The nuclear wave equation is

$$\left\{-\frac{\hbar^2}{2M}\left(\nabla_a^2 + \nabla_b^2\right) + V_e(R) - E\right\}\psi_N = 0 \quad ; \tag{5}$$

equations (4) and (5) follow from equation (1) when the approximation (3) is introduced. Also, equation (4) follows from equation (1) if $M \longrightarrow \infty$, and indeed it may be shown that this method represents the zero-order approximation in an expansion of in powers of Ψ in powers of $(m/M)^{1/4}$. In practice, at least for Σ states, the accuracy is considerably greater than this expansion parameter

suggests (see Coulson, 1961, p. 55).

II. NUCLEAR VIBRATION AND ROTATION

Equation (5) for the nuclear motion is simplified considerably if the three coordinates of the center of mass are removed; it becomes

$$\left\{-\frac{\hbar^2}{2\mu}\nabla^2 + V_e(R) - E\right\}\psi(\underset{\sim}{R}) = 0, \tag{6}$$

where $\mu = \frac{M}{2}$ is the reduced mass and $\underset{\sim}{R}$ is the position vector from one nucleus to the other (e.g., Pauling and Wilson, 1935, p. 264).

Since V_e depends only on the single variable R, this equation is separable in spherical polar coordinates $\underset{\sim}{R} = (R, \Theta, \Phi)$, and we may write

$$\psi(\underset{\sim}{R}) = \mathcal{R}(R)\,\Theta(\theta)\,\Phi(\varphi). \tag{7}$$

The angular equations are immediately soluble and yield a surface harmonic,

$$\Theta(\theta)\,\Phi(\varphi) = Y_{J,M_J}(\theta,\varphi)$$

$$= \left\{\frac{(2J+1)(J-|M_J|)!}{4\pi(J+|M_J|)!}\right\}^{\frac{1}{2}} P_J^{|M_J|}(\cos\theta)\, e^{iM_J\varphi}, \tag{8}$$

where P is an associated Legendre function. The initial factor insures that the function is normalized to unity. Solutions exist only for certain values of the quantum numbers J and M_J,

$$J = 0, 1, 2, \cdots;$$
$$M_J = J, J-1, J-2, \cdots, -J. \tag{9}$$

The radial equation is:

$$\left\{-\frac{\hbar^2}{2\mu R^2}\frac{d}{dR}R^2\frac{d}{dR} + V_e(R) + \frac{J(J+1)\hbar^2}{2\mu R^2} - E\right\}\mathcal{R}(R) = 0. \qquad (10)$$

In principle, $V_e(R)$ is to be obtained by solution of the electronic equation (4), but in practice it is difficult to perform this with sufficient accuracy (cf. Section III), and it provides a set of numerical values so that equation (10) must be integrated numerically. It is usual to introduce a semi-empirical analytical form of the potential, containing variable parameters chosen to give agreement with observation, which enables equation (10) to be solved analytically; for example, a reasonable fit to the bottom of the potential well is obtained simply by using a parabola - the solutions for which correspond to a rotating harmonic oscillator - with improved accuracy if one introduces a cubic function or one of higher order. A particularly useful function is the Morse potential,

$$V(R) = D\left\{1 - e^{-\alpha(R-R_e)}\right\}^2, \qquad (11)$$

where D, α, and R_e are adjustable parameters. This reproduces the correct general behaviour of the actual function – for large R it has the constant value D, there is a minimum at $R=R_e$, and, at R=0, although finite it is very large and this is not a serious failing.

The solution of the equation using equation (11) is straightforward (Pauling and Wilson, 1935, Sec. 35d). An alternative procedure is to expand the potential in a Taylor series about the minimum and obtain the values of the higher derivatives empirically (Dennison and Hecht, 1962). The result is the same, to second order, and

$$\frac{E}{hc} = \omega_e\left(v+\tfrac{1}{2}\right) + B_e J(J+1) - \omega_e x \left(v+\tfrac{1}{2}\right)^2 - D_e J^2(J+1)^2 - \alpha_e\left(v+\tfrac{1}{2}\right) J(J+1), \quad (12)$$

referred to the electron potential minimum as zero. Higher terms may be included if required. Here v is the vibrational quantum number and solutions exist only when

$$v = 0, 1, 2, \cdots . \quad (13)$$

The first two terms in equation (12) are much larger than the other terms; the first term is the energy of a simple harmonic oscillator of frequency $\nu = \omega_e c$, and the second term is the energy of a rigid rotator. The remaining terms are the corrections due to anharmonicity, centrifugal distortion and the coupling of the two motions.

It should be noted that, when J=0 and v=0, there is an amount of "zero-point energy", so that the lowest vibration-rotation level is above the minimum of the potential curve by this amount. This fact is related to the Heisenberg uncertainty principle.

The rotational coefficients are given by

$$B_e = \frac{h}{4\pi c I_e}, \quad D_e = \frac{4B_e^3}{\omega_e^2}, \quad (14)$$

where $I = \mu R_e^2$ is the equilibrium moment of inertia. The remaining coefficients are to be determined empirically. The rotational levels are much more closely spaced than are the vibrational ones (for the ground state of H_2, ω_e =4395 cm^{-1} and B_e =60.80 cm^{-1}), so that we can speak of the rotational structure of the various vibrational levels.

The quantum number M_J does not influence the energy value, except in the

presence of a magnetic field. It serves to indicate that the level J has a statistical weight (2J + 1).

III. THE CALCULATION OF ELECTRONIC WAVE FUNCTIONS

The solution of equation (4) is a complex problem, and here only a summary will be given of the general techniques which have been applied. General surveys are contained in the books by Coulson (1961) and Slater (1963), and a bibliography up to 1959 has been given by McLean, Weiss and Yoshimine (1960).

The methods used may be regarded as extensions of techniques applied to the problem of the many-electron atom. Most of these make use of the Variational Principle: if ψ is any function of the variables involved, then

$$\frac{\int \psi^* H \psi \, d\tau}{\int \psi^* \psi \, d\tau} \geq E_o , \tag{15}$$

the integrations being over all variables (six for two electrons), where E_o is the lowest eigenvalue of the Hamiltonian H. The proof involves expanding ψ in terms of the complete orthonormal set of the eigenfunctions of H, $\varphi_0 , \varphi_1 , \cdots$, with associated eigenvalues $E_0 \leq E_1 \leq \cdots$, so that

$$\psi = \sum_i c_i \varphi_i \tag{16}$$

and

$$\text{LHS}(15) = \frac{\sum_i |c_i|^2 E_i}{\sum_i |c_i|^2} \geq \frac{\sum_i |c_i|^2 E_0}{\sum_i |c_i|^2} = E_0 = \text{RHS}(15), \tag{17}$$

with equality only if $\Psi = \varphi_0$ (for no degeneracy). An error δ in the wave function corresponds to an error δ^2 in the energy. If we impose the constraint $C_0 = 0$, i.e., choose Ψ such that

$$\int \Psi^* \varphi_0 \, d\tau = 0 \quad , \tag{18}$$

then we obtain an upper bound to E_1.

The technique is to introduce a trial function Ψ containing a number of algebraic parameters, which are then varied to minimize the left hand side of equation (15). If the parameters enter Ψ linearly, the minimization procedure reduces to the solution of a set of linear algebraic equations.

There have been two approaches to the selection of Ψ, the method of Configuration Interaction (C.I.) and the method of the Incomplete Separation of Variables (I.S.V.). In the C.I. method, we expand Ψ in terms of some known one-electron functions,

$$\Psi(\underset{\sim}{r}_1, \underset{\sim}{r}_2) = \sum_{i,j} a_{ij} \left\{ \varphi_i(\underset{\sim}{r}_1) \chi_j(\underset{\sim}{r}_2) \pm \chi_j(\underset{\sim}{r}_1) \varphi_i(\underset{\sim}{r}_2) \right\}, \tag{19}$$

the second terms being included for reasons of symmetry. For example, we may expand in terms of the hydrogen atom wave functions, and in fact the first quantum mechanical treatment of the hydrogen molecule (Heitler and London, 1927) used equation (19) in the form

$$\Psi(\underset{\sim}{r}_1, \underset{\sim}{r}_2) = N \left\{ \varphi_{1s}(r_{a1}) \varphi_{1s}(r_{b2}) \pm \varphi_{1s}(r_{a2}) \varphi_{1s}(r_{b1}) \right\}, \tag{20}$$

where N is a normalizing factor. This function does not contain any variable parameters, but if we include also terms such as $\varphi_{1s}(r_{a1})\varphi_{2s}(r_{b2})$ then a variation can be carried out. Very many calculations have been performed using expansions of this type. Of course, there is no need for φ_i or χ_j to have any physical significance.

The I.S.V. method is similar to the method for the helium atom introduced by Hylleraas (1928), which has been used to obtain results of extreme accuracy (Pekeris, 1958; Schwartz, 1962). In the atomic case, the only coordinates required are the radial distances r_1 and r_2 and the angle θ_{12} between their directions; the three other angles are superfluous. It is more convenient to use r_{12} than θ_{12}, and Hylleraas proposed a function

$$\psi = \sum_{ijk} C_{ijk} (r_1 + r_2)^i (r_1 - r_2)^j r_{12}^k \, e^{-\alpha(r_1+r_2)} \,. \tag{21}$$

For the molecule, the situation is more complicated, as only one coordinate may be dropped, and we have r_{a1}, r_{a2}, r_{b1}, r_{b2} and r_{12}. It is convenient to work with confocal elliptic coordinates (spheroidal cocrdinates),

$$\lambda_1 = \frac{r_{a1} + r_{b1}}{R} \,, \quad \mu_1 = \frac{r_{a1} - r_{b1}}{R} \,, \quad \varphi_1 \tag{22}$$

(sometimes written ξ_1, η_1, φ_1). These are independent and orthogonal, while r_{a1} and r_{b1} themselves are neither; the one-electron H_2^+ equation is separable and exactly solubable in these coordinates. Thus we take

$$\psi = \sum_{ijklm} C_{ijklm} \lambda_1^i \lambda_2^j \mu_1^k \mu_2^l r_{12}^m \, e^{-\alpha(\lambda_1+\lambda_2)} \,. \tag{23}$$

This method was applied to H_2 first by James and Coolidge (1933); recently Kolos and Roothaan (1960), using up to 50 terms, have obtained an energy value more accurate than the experimental one.

As in the atomic case, it is found that, for the same number of parameters, equation (23) gives much greater accuracy than equation (19), and also gives much faster convergence as the number of terms is increased. It seems that it requires a great many terms of equation (19) properly to represent the r_{12} - dependence of the wave function. Unfortunately, for more complicated systems the form (23) becomes prohibitive.

Calculations have been performed by both methods for several excited electronic states of H_2 although not to the same degree of accuracy as for the ground state.

IV. ELECTRONIC STATES

Each electron i in the molecule has a spin angular momentum $\underset{\sim}{s}_i$ and an orbital angular momentum $\underset{\sim}{l}_i$, of magnitude $s_i = \frac{1}{2}$ and $l_i = 0, 1, 2, - - -$. In Russell-Saunders coupling, which applies here with considerable accuracy, the individual $\underset{\sim}{s}_i$ combine to form the total electron spin angular momentum $\underset{\sim}{S}$, and the individual $\underset{\sim}{l}_i$ combine to form the total $\underset{\sim}{L}$. It follows from the discussion of Section V that $S = 0, 1$, and $L = 0, 1, 2, - - -$, for the two-electron case.

In H_2, $\underset{\sim}{L}$ is always very strongly coupled to the nuclear axis; it rotates about the axis so rapidly that $\underset{\sim}{L}$ itself loses any meaning, and what matters is the projection

$$\Lambda = | \underset{\sim}{L} \cdot \underset{\sim}{k} | , \qquad (24)$$

where $\underset{\sim}{k}$ is the unit vector along ab. Electron states are distinguished according to the value of Λ ; states with $\Lambda = 0$ are called Σ states; $\Lambda = 1$, Π ; $\Lambda = 2$, Δ ; and so on. This is a direct extension of the notation S, P, D, - - -, used for atomic states with L = 0, 1, 2, - - - .

In some cases, $\underset{\sim}{S}$ also is strongly coupled to the axis; its projection is

$$\Sigma = \underset{\sim}{S} \cdot \underset{\sim}{k} \tag{25}$$

and we introduce

$$\Omega = |\Lambda + \Sigma| . \tag{26}$$

(Note that the letter Σ is used for two entirely unrelated purposes; it is the symbol for a state with $\Lambda = 0$, and also it is the symbol for the $\underset{\sim}{k}$ component of $\underset{\sim}{S}$. This follows from the similar atomic usage of the letter S, and ultimately originates in the fact that the words "sharp" and "spin" start with the same letter.)

2 S + 1 is called the multiplicity of the level. When $\Lambda \neq 0$, the 2 S + 1 different values of Σ correspond to slightly different energy values ("fine structure"; cf. Section VIII), but even for $\Lambda = 0$, when there is no splitting, this name is used. The multiplicity is added to the term symbol as a left superscript; thus, $^3\Sigma$ is a state with S = 1 and $\Lambda = 0$, and $^1\Pi$ has S = 0 and $\Lambda = 1$.

V. THE COUPLING OF ANGULAR MOMENTUM VECTORS

In quantum mechanics, an angular momentum vector $\underset{\sim}{A}$ has magnitude $\sqrt{A\,(A+1)}$ in units $\hbar = h/2\pi$, where A is restricted to integral or half-integral values, and its projection on any axis in space may take only the 2A + 1 values A, A-1, - - -, -A. The rule for combining two such vectors is

$$\underset{\sim}{A} + \underset{\sim}{B} = \underset{\sim}{G},$$

$$G = A+B,\ A+B-1,\ - - -,\ |A-B|. \qquad (27)$$

In the hydrogen molecule, we have angular momenta of electron spin $\underset{\sim}{S}$ and electron orbital motion $\underset{\sim}{L}$, and we now write the part of the total angular momentum due to nuclear rotation as $\underset{\sim}{N}$. Neglecting the nuclear spin, these three may combine in different ways to form the total angular momentum $\underset{\sim}{J}$; these different coupling schemes give different sets of energy levels for the system. A classification of the different possibilities was made by Hund; here we consider only his cases a and b, which are those most commonly occurring.

In Hund's case a, both $\underset{\sim}{L}$ and $\underset{\sim}{S}$ are strongly coupled to the internuclear axis, and equations (24) to (26) apply, with

$$\underset{\sim}{J} = \underset{\sim}{N} + \Omega\underset{\sim}{k}. \qquad (28)$$

In case b, $\underset{\sim}{S}$ is not coupled to the axis, and we have

$$\underset{\sim}{K} = \underset{\sim}{N} + \Lambda\underset{\sim}{k},$$

$$\underset{\sim}{J} = \underset{\sim}{S} + \underset{\sim}{K}. \qquad (29)$$

(cf. Figure 3).

In case a, $\Omega\,k$ is the projection of $\underset{\sim}{J}$ on the axis; it follows that $J \geq \Omega$, so the rotational levels for a particular Ω or Λ) are given by

a: $\Omega, \Omega+1, - - -$

b: $\Lambda, \Lambda+1, - - -$

(30

and the lowest value is not 0 in the non - $^2\Sigma$ states. Further, $\underset{\sim}{N}$ is the part of $\underset{\sim}{J}$ (or $\underset{\sim}{K}$) which remains when the projection on the axis is subtracted; it follows that $\underset{\sim}{N}$ is not a quantum mechanical angular momentum in the sense defined above; its magnitude is not given in general by an integral or half-integral N. It is $\underset{\sim}{J}$ (in case a) and $\underset{\sim}{K}$ (in case b) which is to be taken as the rotational quantum number in the discussion of Section II. However, for an odd number of electrons J is half-integral and the treatment leading to equation (9) must be modified by including the coupling terms of Section VIII in the Hamiltonian.

In the presence of a nuclear spin $\underset{\sim}{I}$, the various coupling cases must be subdivided (cf. Townes and Schawlow, 1955, p. 196). The different schemes for cases a and b are illustrated in Figure 4, and will not be discussed in detail. Omitted is case b α, in which the nuclear spin is coupled to the axis although the electron spin is not, as this is expected never to occur. The total angular momentum is now called $\underset{\sim}{F}$.

For a fuller account, including energy level diagrams, reference is made to Herzberg's book (1950, pp. 218-226). For the hydrogen molecule, for $^2\Sigma$ states case b coupling applies, and for $\Lambda \neq 0$ the coupling is case b with a small admixture of case a.

VI. SYMMETRY

It follows from the indistinguishability of identical particles that the wave function must be either symmetrical or antisymmetrical with respect to the exchange of two such particles, i.e., that

$$\Psi(\underset{\sim}{r}_1, \underset{\sim}{r}_2) = \pm \Psi(\underset{\sim}{r}_2, \underset{\sim}{r}_1). \tag{31}$$

It is a consequence of the Pauli exclusion principle (which is an assumption additional to the Schrödinger equation) that the complete wave function, including spin, must be antisymmetrical with respect to the exchange of any two identical particles of spin $\frac{1}{2}$.

Let us write the hydrogen molecule function as

$$\Psi = \psi_e \chi_e \psi_{VIB} \psi_{ROT} \chi_N , \tag{32}$$

where χ_e and χ_N are respectively electronic and nuclear spin functions, and the other factors are electronic, vibrational and rotational spatial functions. The conclusions we reach do not depend on the possibility of separability; it simply makes the discussion clearer.

For the nuclei, ψ_e, χ_e and ψ_{VIB} depend only on R and so are always symmetrical, while ψ_{ROT} is symmetrical if K is even and antisymmetrical if K is odd. For spin $\frac{1}{2}$, there are two possible orientations; the component in any direction is $\pm \frac{1}{2}$ only. We write these two spin functions as α, corresponding to spin $\uparrow$, say, and β, with spin $\downarrow$. For the two nuclei, there are four possible combinations, three of which are symmetrical and

the other anti-symmetrical; the normalized nuclear spin functions are:

$$s: \quad \chi_N = \alpha(a)\alpha(b)$$
$$\beta(a)\beta(b)$$
$$\frac{1}{\sqrt{2}}\{\alpha(a)\beta(b) + \beta(a)\alpha(b)\} \tag{33}$$

and

$$a: \quad \chi_N = \frac{1}{\sqrt{2}}\{\alpha(a)\beta(b) - \beta(a)\alpha(b)\}. \tag{34}$$

Now, for the total function to be antisymmetrical, s space functions must combine with a spin functions, and vice versa; thus, K odd occurs with three times the frequency of K even:

K	Space symmetry	Nuclear spin	Modification
odd	a	s, ↑↑ , I = 1	ortho
even	s	a, ↑↓ , I = 0	para

Since there is a very small but non-zero rate for transitions between the two forms, for equilibrium at a particular temperature the Boltzmann factor must be included; also the population of a particular level is proportional to the statistical weight 2K + 1, in addition to this factor 2I + 1.

For the electrons also, there are three functions with S = 1 to one with S = 0, and this statistical weight factor must be included in calculating the populations of excited electronic states.

There are two important symmetry properties of the electronic spatial wave function ψ_e , which are connected with the selection rules for transitions:

i) Reflection in any plane containing the nuclei (e.g., ABCD of Figure 5): ψ_e is multiplied by ± 1, and + or - is added as a right superscript to the term symbol, $^1\Sigma^+$, etc. This ± symmetry is significant only for Σ states, since for non-zero Λ there is a degeneracy between + Λ and - Λ which means that $|\psi|^2$ need not be unchanged by this reflection (Herzberg, 1950, p. 217).

ii) Reflection in the plane bisecting the nuclear axis and perpendicular to it (EFGH). Again there is a ± symmetry (for nuclei of the same charge), which is called even-odd symmetry, and indicated by a subscript g or u on the term symbol (from the German gerade or ungerade). Thus we have symbols like $^1\Sigma_g^+$, $^3\Sigma_g^+$, $^1\Pi_u$, etc.

All these space and spin symmetries are independent of each other, apart from the a - s relation.

VII. TRANSITIONS

Radiative transitions may be allowed or forbidden to a certain order in the multipole expansion of the interaction; the first term in this expansion is the electric dipole moment, and the transition probability of dipole transitions from state a to state b is

$$\frac{64\pi^4 e^2}{3h\lambda^3 \omega_a} \left| \int \psi_a^* \sum_i \hat{r}_i \psi_b \, d\tau \right|^2 \quad \text{sec}^{-1}, \qquad (35)$$

summed over all relevant particles, where λ is the wavelength of the light emitted and ω_a is the statistical weight of state a. (This result is obtained using the methods of time-dependent perturbation theory; cf. Bates, 1961). Typically, magnetic dipole transition probabilities are 10^{-5} times equation (35),

and electric quadrupole ones are 10^{-8} times (35), so transitions for which (35) is non-zero are usually called "allowed", and those for which it is zero are "forbidden"; but such transitions may be allowed in higher order.

The electric dipole selection rule gives for the possible change in total angular momentum

$$\Delta J = 0, \pm 1 , \quad 0 \nleftrightarrow 0. \tag{36}$$

For quadrupole transitions, the selection rule is

$$\Delta J = 0, \pm 1, \pm 2 , \quad \begin{matrix} 0 \nleftrightarrow 0 \\ \frac{1}{2} \nleftrightarrow \frac{1}{2} \\ 1 \nleftrightarrow 0. \end{matrix} \tag{37}$$

In coupling schemes a and b, we have

$$\Delta \Lambda = 0, \pm 1 \quad , \tag{38}$$

$$\Delta S = 0 \quad , \tag{39}$$

in case a only

$$\Delta \Sigma_1 = 0, \tag{40}$$

$$\Delta \Omega = 0, \pm 1 : 0 \nleftrightarrow 0 \text{ for } \Delta J = 0, \tag{41}$$

and in case b only

$$\Delta K = 0, \pm 1 : 0 \nleftrightarrow 0 \text{ for } \Delta \Lambda = 0. \tag{42}$$

The various symmetries discussed in Section VI also introduce selection rules:

Nuclear symmetry $\quad s \nleftrightarrow s , \; a \nleftrightarrow a , \; s \nleftrightarrow a$ (43)

Even-odd $\quad g \nleftrightarrow u , \; g \nleftrightarrow g , \; u \nleftrightarrow u$ (44)

Plus-minus $\quad \Sigma_1^+ \nleftrightarrow \Sigma_1^+ , \; \Sigma_1^- \nleftrightarrow \Sigma_1^- , \; \Sigma_1^+ \nleftrightarrow \Sigma_1^-$ (45)

It must be emphasized that none of these rules is completely rigorously true; rules (38) to (42) hold only for dipole radiation, but fail even there for fairly strong spin-orbit coupling. Rules (43) to (45) also break down due to perturbations introduced by the small correction terms discussed in Section VIII. For a thorough discussion of selection rules and related topics, see Herzberg (1950, p. 653).

It follows from these rules that allowed electronic transitions in H_2 are as follows (cf. Figure 2): from the ground $^1\Sigma_g^+$ state, the first allowed transition is to the $^1\Sigma_u^+$ state at 11.2 eV; from the repulsive $^3\Sigma_u^+$ state to the $^3\Sigma_g^+$ state (or vice versa, in emission); etc. The lowest $^3\Pi_u$ state is metastable, but with a lifetime of about 10^{-3} seconds, as the selection rule (39) is not very rigorous (Lichten, 1960).

Vibrational transitions within the ground state of H_2 are forbidden as dipole transitions, since vibration is not an angular momentum and depends not on the transition dipole moment but on the permanent dipole moment of the system (Herzberg, 1950, p. 80). H_2 does not have a permanent dipole moment; it does have a quadrupole moment, and quadrupole transition bands have been observed (references in Herzberg; also Rank, Rao, Sitaram, Slomba and Wiggins, 1962).

Rotational transitions within a particular vibrational level are allowed by rule (42), $\Delta K = \pm 1$, but such transitions violate the symmetry condition (43) (which is essentially $\Delta I = 0$). Quadrupole transitions with $\Delta K = \pm 2$ are allowed. The perturbation caused by the nuclear spin-rotation interaction permits dipole transitions to occur, but with much reduced probability (see Part B, Section IV).

VII. CORRECTION TERMS TO THE ENERGY

There are interactions between the various angular momenta present in the molecule, and these must be added as small corrections to the Hamiltonian in equation (1); they cause shifts and splittings of the energy levels. These effects are zero if $c = \infty$, and must be derived from the relativistic wave equation for the system. Although the Dirac theory is a one-particle theory and there is no complete generalization, the two-particle interactions are known to second order in 1/c. (Bethe and Salpeter, 1957, discuss in detail the Dirac equation and the Breit and other two-particle equations. The molecular interactions for the simplest case, H_2^+, have been treated most fully by Dalgarno, Patterson and Somerville, 1960; see also Frosch and Foley, 1952, and Townes and Schawlow, 1955).

The interactions may be classified quantitatively in three ways:

electron-electron, order μ_0^2 : fine structure;

electron-nucleus, order $\mu_0 \mu_N$: hyperfine structure;

nucleus-nucleus, order μ_N^2 ;

where

$$\mu_0 = \frac{e\hbar}{2mc} \quad , \quad \mu_N = \frac{e\hbar}{2Mc} \tag{46}$$

are respectively the Bohr magneton and the nuclear magneton.

The best known hyperfine transition is that of the ground state of the hydrogen atom. The electron spin interacts with the nuclear spin to produce a

splitting of magnitude 1420 Mc/s.

For the spin-spin and spin-orbit interactions of two particles i and j, either protons or electrons, we have

$$H_{s\text{-}s} = \mu_i \mu_j g_i g_j \left\{ \frac{8\pi}{3} \underset{\sim}{S}_i \cdot \underset{\sim}{S}_j \delta(\underset{\sim}{r}) + \left[\frac{3}{r^5} (\underset{\sim}{S}_i \cdot \underset{\sim}{r})(\underset{\sim}{S}_j \cdot \underset{\sim}{r}) - \frac{\underset{\sim}{S}_i \cdot \underset{\sim}{S}_j}{r^3} \right] \right\} \quad (47)$$

and

$$H_{s\text{-}o} = \mu_i \mu_j g_i d \, \underset{\sim}{S}_i \cdot \underset{\sim}{L}_j \frac{1}{r^3} , \quad (48)$$

where $\underset{\sim}{r}$ is the radius between the two particles, d = 1 for "spin-own orbit" and d = 2 for "spin-other orbit" interactions, and

$$g_{electron} = 2.0023 , \; g_{proton} = 5.35 \quad (49)$$

Since S = 0 and $\Lambda = 0$ in the ground electronic state of H_2, there is neither fine nor hyperfine structure. The metastable $^3\Pi_u$ state has both; it has been studied experimentally by Lichten (1960, 1962) and theoretically by Fontana (1962) and by Frey and Mizushima (1962). For the para level K = 2, I = 0 and $\underset{\sim}{K}$ combines with $\underset{\sim}{S}$ to give J = 3, 2, 1, with energy separations

$$\begin{aligned} (J = 2 \leftrightarrow 1) &= 4928 \text{ Mc/s} \\ (J = 3 \leftrightarrow 2) &= 5898 \text{ Mc/s} \end{aligned} \quad (50)$$

for allowed fine-structure transitions. In the ortho level K = 1, I = 1 and coupling case $b_{\beta S}$ of Figure 4 applies; the J = 2 level has a hyperfine structure, such that

$$\begin{aligned} (F = 3 \leftrightarrow 2) &= 708 \text{ Mc/s} \\ (F = 2 \leftrightarrow 1) &= 462 \text{ Mc/s} . \end{aligned} \quad (51)$$

These are typical values for the fine and hyperfine splitting; the difference is not as large as the ratio μ_0/μ_N suggests.

In ortho levels of the ground electronic state, I = 1 and there is an interaction between the nuclear spin and the nuclear rotation. This type of interaction, for which a name such as "ultrafine structure" might be introduced, is exceedingly weak; this case has been examined experimentally by Kolsky, Phipps, Ramsey and Silsbee (1952) and theoretically by Auffray and Cooley (1961), and for K = 1 the allowed transitions are

$$\begin{aligned} (F = 0 \leftrightarrow 1) &= 546\ \text{kc/s} \\ (F = 1 \leftrightarrow 2) &= 54.8\ \text{kc/s}. \end{aligned} \tag{52}$$

IX. THE MOLECULAR ION H_2^-

The question of the stability of the ion H_2^- is an interesting one. The relevant potential curves are sketched in Figure 6; the solid-line curves are the usual potential curves for the hydrogen molecule. To H_2 in its ground state $^1\Sigma_g^+$ (curve AF) we may without altering the potential curve add a free electron which at infinity has zero energy; if the electron has at infinity energy greater than zero, the corresponding curve is parallel to AF and higher. The system "H_2 plus an electron which is not free" of course corresponds to bound states of the system H_2^-.

The ground state of H_2^- is a $^2\Sigma_u^+$ state. Early calculations on this system, using a variational trial function with a limited number of terms (Eyring, Hirschfelder and Taylor, 1936; Dalgarno and McDowell, 1956; Gupta, 1959), gave results

of the form of curve CDE of Figure 6, with a minimum at the point D. This minimum lies below the energy which a hydrogen molecule plus a free electron can have at this nuclear separation, and so by the Franck-Condon principle the transition $H_2^- \rightarrow H_2 + e$ is an absorption, and the ground state of H_2^- is stable. Next, Fischer-Hjalmars (1959) repeated the calculation with a rather more flexible trial wave function and obtained the curve BGDE. The minimum at D has disappeared, and instead there is a minimum at G which lies above the corresponding part of the curve for $(H_2 + e)$ and so is unstable, since dipole transitions are allowed between the two curves. Recently, a detailed numerical investigation has been made by Taylor and Harris (1963), and they obtain a curve of the form ADE which closely follows the $(H_2 + e)$ values for R less than about 1.6 Å.

One might think that with an even more complicated trial wave function the point G could be lowered still further, below the $(H_2 + e)$ curve, so that H_2^- would be stable. This is a false conclusion, however, for reasons discussed by Davidson (1962) and connected with the basic nature of the variational method. The points are, firstly, that the variational method gives an upper bound only to the lowest possible state of the particular space and spin symmetry chosen for the trial function, unless the lowest state is explicitly excluded by making the trial function orthogonal to it; and, secondly, that the system $(H_2 ({}^1\Sigma_g^+) + e)$ does have the same symmetry as $H_2^- ({}^2\Sigma_u^+)$ - it is necessarily in a spin doublet state, and has all spatial symmetries because of the infinity of states for the free electron - and it cannot be excluded from the trial function, again because of the infinity of wave functions for the free electron. It follows that, where the variational method gives an energy greater than $(H_2 + e)$, we cannot say more than this is an upper bound to the $(H_2 + e)$ value; it tells nothing at all about H_2^-. Thus the curves CD and BGD are

simply upper bounds to AD - gross upper bounds, because of the poor trial wave functions adopted. Of course, where the variational method gives a lower energy than (H_2 + e) can have at that R, it is certainly giving an upper bound to the H_2^- ($^2\Sigma_u^+$) energy.

What happens involves an effect called the potential energy curve non-crossing rule (see Coulson, 1961). This states that, if two curves of the same symmetry cross each other in a certain approximation, when more accurate calculations are carried out the curves repel each other at the crossing point and form two new curves which do not cross. So, in Figure 7, the curves WX and YZ become WZ and YX; the same repulsion effect occurs when two curves come very close together, without actually crossing.

In the present case, the two curves must cross somewhere, since at $R = \infty$, $E(H + H + e) > E(H + H^-)$, and at $R = 0$, $E(He^-) > E(He + e)$. It is probable that CDE is not far from the true curve in the first approximation, since a crossing at a smaller value of R would imply a fairly deep minimum at a fairly small nuclear separation - not the sort of behavior expected of a negative ion, and also Taylor and Harris conclude from the detailed structure of their wave function that any large departure from ADE is mathematically highly improbable. By the non-crossing rule, the original curves AF and CDE will be replaced by CF and ADE; a variational calculation gives an upper bound to ADE, and this agrees with the results of Taylor and Harris. It cannot be stated with complete certainty that there is not a second minimum in the curve, near the point D, but these results show nothing to suggest such a minimum. Thus, on the present evidence, the ground state of H_2^- is not stable.

Also shown in Figure 6 are the curve for H_2 ($^3\Sigma_u^+$) + e and Fischer-Hjalmers' results for H_2^- ($^4\Sigma_u^+$). The latter state has a different spin symmetry from all states below it, so that the variational calculation is valid, and by the spin selection rule $\Delta S = 0$ it is a metastable state. H_2^- has been

observed in a mass spectrometer (Khvostenko and Dukel'skii, 1958), and these observations may well have been of this metastable state; the fact that it has been very difficult to observe H_2^- suggests that the ground state does not have a deeply stable minimum.

General References

Herzberg, G. 1950, Spectra of Diatomic Molecules, 2nd edn. (Princeton: Van Nostrand).

Slater, J. C. 1963, Quantum Theory of Molecules and Solids, Vol. I (New York: McGraw-Hill).

Specific References

Auffray, J. P. and Cooley, J. W. 1961, Phys. Rev. 122, 1203.

Bates, D. R. 1961, in Quantum Theory, ed D. R. Bates, Vol. I (New York: Academic Press).

Bethe, H. A. and Salpeter, E. E. 1957, Quantum Mechanics of One- and Two-Electron Atoms (Berlin: Springer). Also in Handbuch der Physik 35.

Coulson, C. A. 1961, Valence, 2nd edn. (Oxford: University Press).

Dalgarno, A. and McDowell, M. R. C. 1956, Proc. Phys. Soc. A 69, 615.

Dalgarno, A., Patterson, T. N. L and Somerville, W. B. 1960, Proc. Roy. Soc. A. 259, 100.

Davidson, E R. 1962, J. Chem. Phys. 36, 1080.

Dennison, D. M. and Hecht, K. T. 1962, in Quantum Theory, ed. D. R. Bates, Vol. II (New York: Academic Press).

Eyring, H., Hirschfelder, J. O. and Taylor, H. S. 1936, J. Chem. Phys. 4, 479.

Fischer-Hjalmars, I. 1959, Ark. Fys. 16, 33.

Fontana, P. R. 1962, Phys. Rev. 125, 220.

Frey, D. A. and Mizushima, M. 1962, Phys. Rev. 128, 2083.

Frosch, R. A. and Foley, H. M. 1952, Phys. Rev. 88, 1337.

Gupta, B. K. 1959, Physica 25, 190.

Heitler, W. and London, F. 1927, Z. Phys., 44, 455.

Hylleraas, E. A. 1928, Z. Phys., 48, 469.

James, H. M. and Coolidge, A. S. 1933, J. Chem. Phys. 1, 825.

Khvostenko, V. I. and Dukel'skii, V. M. 1958, J. E. T. P. 7, 709.

Kolos, W. and Roothaan, C. C. J. 1960, Rev. Mod. Phys. 32, 219.

Kolsky, H. G., Phipps, T. E., Ramsey, N. F., and Silsbee, H. B. 1952, Phys. Rev. 87, 395.

Lichten, W. 1960, Phys. Rev. 120, 848.

_____. 1962, Phys. Rev. 126, 1020.

McLean, A. D., Weiss, A., and Yoshimine, M. 1960, Rev. Mod. Phys. 32, 211.

Pauling, L., and Wilson, E. B. 1935, Introduction to Quantum Mechanics (New York: McGraw-Hill).

Pekeris, C. L. 1958, Phys. Rev. 112, 1649.

Rank, D. H., Rao, B. S., Sitaram, P., Slomba, A. F., and Wiggins, T. A. 1962, J. O. S. A. 52, 1004.

Schwartz, C. 1962, Phys. Rev. 128, 1146.

Taylor, H. S., and Harris, F. E., 1963, J. Chem. Phys. 39, 1012.

Townes, C. H., and Schawlow, A. L. 1955, Microwave Spectroscopy, (New York: McGraw Hill).

PART B

HYDROGEN MOLECULES IN ASTROPHYSICS

by

G. B. Field

I. GENERAL CONSIDERATIONS

The interest in H_2 stems from the fact that it is the stable form of hydrogen at low temperatures. Its abundance relative to that of atomic hydrogen is given by the dissociation equation (Aller, 1963, p. 131),

$$\frac{p(H_2)}{p^2(H)} = \frac{g(H_2)}{g^2(H)} \left(\frac{h^2}{2\pi m k T}\right)^{\frac{3}{2}} \frac{8\pi^2 I}{h^2} \left(1 - e^{-\frac{h\nu}{kT}}\right)^{-1} e^{\frac{D}{kT}}, \tag{53}$$

provided that local thermodynamic equilibrium applies. For the densities appropriate in stellar atmospheres, equation (53) implies that $p(H_2) > p(H)$ for main-sequence stars later than M4 ($T < 3100^{\circ}K$) and for giant stars later than M7 ($T < 2400^{\circ}K$). H_2 is expected to be dominant in planetary atmospheres.

It is believed that the kinetic temperature throughout large regions of interstellar space is of the order of $100^{\circ}K$ and that the density is of the order of 1 cm^{-3}, so that one would expect H_2 to dominate there also on the basis of equation (53). However, the processes which form H_2 and destroy it are very different; H_2 is formed on the surface of grains whose temperature

is about 10°K, while it is destroyed by ultraviolet quanta whose color temperature is about 30,000 °K. Under such deviations from LTE, equation (53) is inapplicable. Rather, detailed calculations of rates of formation and destruction are necessary, as pointed out by Strömgren (1939), Spitzer (1948), and van de Hulst (1948). At the present time such calculations are rather inconclusive, but indicate that H_2 will dominate in at least limited regions of interstellar space.

It is particularly important to know the H_2 abundance in interstellar space because it may contribute substantially to the amount of gas present near the sun even though it is not readily observable. Gould, Gold, and Salpeter (1963) consider that amounts of H_2 up to five times the amount of atomic H observed by the 21-centimeter technique would not conflict with upper limits on the total mass density inferred from the galactic gravitational field. H_2 would also play an important part in the thermal properties of interstellar material. Not only is it a very effective cooling agent at the temperatures of interstellar gas, as suggested by Spitzer (1949), but its heat of formation (2.25 eV per atom) is considerably larger than the next most important form of energy of interstellar gas, turbulent energy (1.0 eV per atom).

In spite of the importance of H_2 as indicated above, the only positive detection of it at this writing has been in planetary atmospheres and in a few stars. The reason for this can be traced to the unfavorable location of its spectrum. The resonance lines of the electronic spectrum lie in the extreme ultraviolet (near the corresponding lines of atomic H), so that instruments above the atmosphere are required for their detection (Spitzer, 1956). Resonance lines due to interstellar H_2 should be readily detectable in B-star spectra, as they are permitted dipole transitions. The same lines in the

in the atmospheres of cool stars and of planets are of secondary interest, owing to the lack of a suitable ultraviolet continuum. Subordinate lines are unimportant both in interstellar space and in atmospheres because of the insufficient degree of excitation.

H_2 in its ground electronic state also possesses a rotation-vibration spectrum in the infrared (fundamental band around 2 μ), and a pure rotation spectrum in the far infrared (2-0 transition at 28 μ). Both of these are forbidden because H_2 has no permanent electric dipole moment, and therefore they occur only as quadrupole transitions, or, if the pressure exceeds 10 atmospheres, as collision-induced dipole transitions. As a result, the lines are discouragingly weak. Nevertheless, Herzberg (1938) calculated that the rotation-vibration spectrum, particularly the 3-0 band at 8000 Å, should be detectable in stellar and planetary atmospheres. Various authors such as Zwicky (1959) have suggested a search for the pure rotational transitions by interstellar H_2. A lively discussion has centered on whether or not transitions between states of different nuclear spin (ortho-para transitions) are to be expected in any strength. The current calculations indicate that such transitions are strongly forbidden both radiatively and collisionally under typical conditions in interstellar space. (They can occur collisionally above approximately 1000 ^{o}K, however.) In any case, even the transitions between states of the same nuclear spin are probably so weak that further technical developments will be needed for their detection, even if telescopes above the atmosphere are available.

As early as 1938 Herzberg suggested that the rotation-vibration spectrum of HD might be detectable even if D/H were very low, owing to the fact that HD has a small permanent dipole moment. Upper limits on line strengths in planets are now available. Detection of interstellar HD might be possible from

the isotope shift of electronic transitions. This would be particularly interesting since the ratio of atomic D to atomic H in interstellar space seems to be lower than the terrestrial value (Weinreb, 1962).

H_2 in its ground state of course possesses no fine structure and no hyperfine structure, and hence no radio spectrum like that of H. As pointed out in Section VIII, however, H_2 in the first excited rotational level (I = 1, K = 1) is split into three sublevels (F = 0, 1, and 2), by the magnetic interaction between the end-over-end motion of the nuclei and the nuclear spin, giving rise to radio-frequency lines at 54.8 and 546 kc/s. However, these transitions are far too weak to detect even if satellite techniques permit one to penetrate the ionosphere. H_2^+ has an unpaired electron and hence hyperfine structure for states of nonvanishing I and K. The precise location of the transitions in the I = 1, K = 1 level has been the subject of intensive theoretical study which is still inconclusive. The study of this species utilizing emission between the hyperfine states (Burke, 1954) would probably relate mostly to regions where strong stellar ultraviolet is acting on interstellar H_2 regions. HD has no fine or hyperfine structure, but its ultrafine structure is somewhat different, owing to the fact that I = $\frac{1}{2}$ or 3/2 rather than 0 or 1.

Various continua are associated with the H_2 molecule. Photoionization occurs for $\lambda < 804$ Å, while photodissociation through an excited state of atomic H occurs for $\lambda < 849$ Å. Both are permitted transitions and interstellar H_2 would cause observable absorptions in early-type stellar spectra if it were not for the fact that they are swamped by the photoionization continuum of atomic H ($\lambda < 912$ Å). Energetically, the repulsive $^3\Sigma_u^+$ state is accessible via a continuous absorption from the ground state, but this transition is a singlet-triplet one and is therefore rather strongly forbidden. A crude estimate for the

cross section at around 1500 Å is 10^{-26} cm^{-2} to judge from Gould and Salpeter (1963). This is barely possible to detect even in planetary atmospheres.

Calculations have been made of both the Rayleigh and Raman scattering cross sections. The Raleigh cross section is also of the order of 10^{-25} cm^2 in the ultraviolet, and of course even smaller in the visible and in the infrared. Nevertheless, it may contribute to the visual albedo of planets, and to the atmospheric opacity of planets and stars.

Wildt (1949) suggested that quasi-molecular hydrogen might provide a significant source of opacity in stellar atmospheres for $\lambda < 2000$ Å. The process involved is the analogue of photodissociation from the ground singlet state to an excited singlet state of the molecule, but involves a transition from the lowest triplet state to an excited triplet state instead. As the former is a repulsive state comprising simply two neighboring H-atoms, it is called a "quasi-molecule". This topic has been considered by later authors, and the most reliable conclusion is that the mechanism occurs, but is not quantitatively significant. Calculations of translational absorption (in which the photon energy goes into the motion of free molecules) have been made by Poll and Van Kranendonk (1961). According to Gaustad (1963), this process may be important in high-density conditions such as may be found deep in planetary atmospheres.

Processes involving H_2^+, such as photodissociation and quasi-molecular processes (analogous to those of H_2) have been considered by Bates (1952). Apparently these processes may be significant in stellar atmospheres where both H and H^+ are abundant. H_2^- has also been the subject of much discussion. As shown in Section IX of Part A, however, H_2^- has no stable bound state (although it has a metastable state whose energy is higher than $H + H^-$). It therefore exhibits no bound-free absorption. However, as we shall see below, free-free transitions by electrons in atmospheres abundant in H_2 contribute significantly to the continuous opacity.

II. PLANETARY ATMOSPHERES

Herzberg (1938) first pointed out the possibility of detecting the rotation-vibration spectrum of H_2 in planets. He had in mind the weak quadrupole transitions, and indeed the Q (1), S (0), S (1), and S (2) lines of the 3-0 band were first detected by Kiess, Corliss, and Kiess (1960) in the spectrum of Jupiter. In the meantime, however, Herzberg (1952) had already identified a 35-Å wide feature at 8270 Å discovered in spectra of Uranus and Neptune by Kuiper (1949) as the S (0) line of the pressure-induced 3-0 vibration-rotation band. Spinrad (1963) has recently found the S (0) line of the pressure-induced 4-0 band at 6420 Å in the spectrum of Saturn.

Most quantitative work, however, has been done on the quadrupole lines, which, unlike the dipole lines, have widths measured in milliangstroms and are not as subject to blending. Very high dispersion is required for their study. Table 1 shows the lines that have been observed in the atmospheres of Jupiter, Saturn, and Uranus.

Table 1 - following page.

Table 1

Quadrupole Lines in Planets

I. Jupiter

Band	Line	λ (Å)	Equivalent Width (mÅ)	References
3-0	S(0)	8272.7	40	1,2
			31	3
	S(1)	8150.7	80	1,2
			34	3
	S(2)	8046.4	7:	1,4
	Q(1)	8497.5	Trace	1
4-0	S(0)	6435.0	Blended	3
	S(1)	6367.8	8±2	3
	Q(1)	6567.7 (predicted)	≤ 3	3

II. Saturn

Band	Line	λ (Å)	Equivalent Width (mÅ)	References
4-0	S(0)	6435.0	Detected	5
	S(1)	6367.8	Detected	5

III. Uranus

Band	Line	λ (Å)	Equivalent Width (mÅ)	References
4-0	S(0)	6435.0	Detected	3

References:
1. Kiess, Corliss, and Kiess (1960)
2. Zabriskie (1962)
3. Spinrad and Trafton (1963)
4. Zabriskie (1960)
5. Münch and Spinrad (1963)

It would be desirable to interpret these results in terms of the amounts and temperature of H_2 above the reflecting layer, for comparison with data on CH_4 and other constituents, as this procedure would afford a reliable estimate of the H/C ratio in the solar system (of interest to cosmogony). This has been done with widely varying results. The first attempt by Zabriskie (1960, 1962) led to a value of N (the number of molecules in a square centimeter column above the clouds of Jupiter) equal to 4.6 km Am*, and a rotational temperature between

---

*An Amagat (Am) is the density of a gas at STP, so that 1 km Am is equivalent to 2.69×10^{24} molecules per cm^2. We use km Am rather than km atm because of the possibility of confusion with pressure units.

---

170 °K and 200 °K. Most recently Foltz and Rank (1963) have estimated that N on Jupiter maybe as much as 270 km Am. This 60-fold range of estimates arises out of a confusing array of observational and laboratory data, and theoretical interpretations. We shall show below that the most probable value lies in a three-fold range.

The first step is to establish the intrinsic strength of the strongest line of Table 1, the S (1) line of the 3-0 band. Let α_ν be the absorption coefficient per km Am, so that the optical depth along the path of a ray coming in at local zenith angle $Z_\odot$ and leaving at angle $Z_\oplus$ is

$$\tau_\nu = \alpha_\nu \int \rho \, ds = \alpha_\nu N \left(\sec Z_\odot + \sec Z_\oplus \right) \qquad (54)$$

if the temperature and hence α_ν is sensibly constant through the absorbing layer. The equivalent width of a weak line is then

$$S = \int \tau_\nu d\nu = S_o N \left(\sec Z_\odot + \sec Z_\oplus \right) \tag{55}$$

where

$$S_o = \int \alpha_\nu d\nu = 2.69 \times 10^{24} \frac{n_1}{n} \int \sigma_\nu d\nu$$

$$= 2.69 \times 10^{24} \frac{n_1}{n} \frac{h\nu}{c^2} B. \tag{56}$$

S_o has units km^{-1} Am^{-1} cm^{-1} if ν is in cm^{-1}. In these expressions n_1/n is the fraction of molecules in the lower level at the given temperature (0.67 in K = 1 at 300°K), σ_ν is the absorption cross section in cm^2, and B the usual Einstein coefficient for absorption (defined for unit spectral energy density).

The best experimental determinations of S_o are those of Rank, Fink, Foltz, and Wiggins (1964) for the 1-0, 2-0, and 3-0 S (1) lines. Their results for S_o are given in Table 2, along with values calculated from the B-values first given theoretically by James and Coolidge (1938). The disagreement between experiment and the early theory is quite pronounced, particularly for the 3-0 band.

Table 2
Strengths of S (1) Quadrupole Lines
10^3 S_o (km^{-1} Am^{-1} cm^{-1})

Band			Source	
1-0	2-0	3-0	Experimental or Theoretical	Author
73	12	1.1	E	Rank, Fink, Foltz & Wiggins (1963)
29	27	7.7	T	James and Coolidge (1938)
120	24	3.3	T	Rank, Rao, Sitaram, Slomba and Wiggins (1962)
91	13	1.5	T	Somerville (1964b)

The early theoretical results were based on values of $(3z^2 - r^2)$ averaged over the electronic wave functions of James and Coolidge. Newer results may be derived using the values of this parameter (related to the static quadrupole moment of the molecule at fixed internuclear separation) calculated from a 28-parameter wave function by Kolos and Roothan (1960). This has been done independently in the last two references of Table 2. The reason for the discrepancy between them is not clear, as details of the 1962 calculation are not available.

Both of the new theoretical values exceed the experimental ones for all three bands. According to James and Klemperer (1964) this is to be expected because the results obtained in this manner don't contain a correction factor less than unity which should be included for rotational effects. According to these authors the 1-0 results should be reduced by 32%, to 82 and 62 x 10^{-3} km^{-1} Am^{-1} cm^{-1} for the 1962 and 1964 calculations respectively. These values bracket the experimental one so that it appears that further effort may give substantial accord between theory and experiment for all three bands. All of the values are plotted in Figure 8.

In the meantime it seems prudent, as suggested by Spinrad and Trafton (1963), to utilize experimental results in converting equivalent widths to abundances. We therefore adopt S_o = 1.1 x 10^{-3} km^{-1} Am^{-1} cm^{-1} for the 3-0 S (1) line from Table 2.

The mean of the equivalent widths measured in the spectrum of Jupiter is 49 mÅ (weighting Spinrad and Trafton twice Kiess, Corliss, and Kiess on the basis of number of plates taken). This value (which is uncertain by about 50%) is 2.2 times the rms Doppler width at 170°K (estimated temperature of clouds according to Zabriskie, 1962), and corresponds to a frequency width of 7.4 x 10^{-2} cm^{-1}. One finds from equation (55) that N = 20 km Am, using $\langle \sec z_\odot + \sec z_\oplus \rangle = \pi$, appropriate when the spectrograph entrance slit is through the center of the disk. (The S_o used in the reduction must be corrected from that at 300°K

according to equation (3) by multiplying by 1.08, which is the ratio of the fraction of molecules in K = 1 at 170°K to that at 300°K).

This abundance of H_2 is a lower limit because it omits the effects of saturation, but even it is 4.4 times Zabriskie's estimate, largely because he relied on James and Coolidges' value of S_o which is quite incorrect according to newer data (Figure 8). From the curve of growth for Doppler broadening (Unsöld, 1938, p. 168) one estimates that the true value of N is 1.6 times that given by the unsaturated case, or 32 km Am. Even this may be somewhat too small because of an effect predicted by Dicke (1953) and experimentally verified for the 1-0 quadrupole band by Rank and Wiggins (1963). According to Dicke, molecular collisions can in certain cases actually cause a narrowing of a profile from the classical Doppler width by stopping a molecule before it can emit for enough wave periods to build up intensity at a Doppler-shifted frequency. This effect will dominate the usual collisional broadening if the collisions are such as not to perturb the states involved in the transition. Rank and Wiggins found that the measured width of the 1-0 S (1) line was only 75% of the pure Doppler width when the density was 1.5 Amagat. The density of the H_2 alone at the cloud level of Jupiter would be N/H, or about 1.5 Amagat for H = 20 km (μ = 3), so that a 25% reduction in intrinsic line width would obtain if the 3-0 band behaves like the 1-0. The curve of growth then suggests values of N as high as 50 km Am. This revision is very tentative, however, and is mentioned only to indicate the care that will be needed in the interpretation of future observations of this kind. It is unfortunate that "collisional narrowing" will result in a greater degree of saturation and even more uncertain abundance estimates if it is indeed present.

We now consider the 4-0 band, the detection of which led Foltz and Rank (1963) to suggest values of N up to 270 km Am. Their high estimates arise because the extrapolation of laboratory measurements of S_o from lower overtones up to the 4-0

band led to the expectation that it should be extremely weak. Revised estimates by Rank, et. al. (1964) give S_o (300°K) for the 4-0 line as 7.4×10^{-5} km^{-1} Am^{-1} cm^{-1}, equivalent to 8.0×10^{-5} at 170°K (see Figure 8). The observed equivalent width is 2.0×10^{-2} cm^{-1}, which with equation (55) yields N = 80 km Am, somewhat higher than the values indicated by the 3-0 band. The effects of saturation are small here. This estimate is uncertain not only because it is based only on an extrapolation to find S_o, but also because of an anomoly in the observed relative strengths of S (1) and Q (1) (Table 1). The observed ratio of S (1) to Q (1) is > 2.7. The "classical" ratio given by James and Coolidge (1938) is 1.7. However, the latter must be revised downward because the rotational correction factor less than unity applies to the S branch but not to the Q branch (James and Klemperer, 1964). Hence the discrepency is considerable, and although one possibility may be blending of the Q (1) line with solar H_2 (Spinrad, 1964a) part of the difficulty may be in an overestimate of the S (1) strength. Even reducing the equivalent width by one probable error would reduce N to 60 km Am. We conclude that the quadrupole data indicate a value of N between 30 and 80 km Am, with some preference for the smaller values.

Some evidence for the smaller values of N comes from upper limits on the Rayleigh scattering by H_2. From the polarizabilities given by Allen (1963) we find that the optical depth is

$$\tau(H_2) = \frac{2.4 \times 10^{-4}}{\lambda^4} N, \qquad (57)$$

where λ is in microns. Öpik (1962) calculates a total optical depth of 0.25 at 0.4 μ for the atmosphere above the clouds. The data of Gehrels and Teska (1962) suggest even lower values, as does a rocket measurement of the ultra-violet albedo (Stecher, 1964a). Since other components may contribute to the scattering, it is legitimate to consider 0.25 as an upper limit to $\tau(H_2)$ at 0.4 μ .

This implies $N < 27$ km Am.

We may also obtain crude information from the absence of the pressure-induced dipole lines in the spectrum of Jupiter. The blended feature at λ8166 in the laboratory spectra (Herzberg, 1952) is due mostly to double transitions (1-0 and 2-0) in which the colliding partners are both H_2 molecules. From Hare and Welsh (1958) we may write for the central optical depth in this feature

$$\tau = \frac{\rho^2(H_2) L \alpha}{\Delta\nu} , \qquad (58)$$

where $\Delta\nu$ is the effective line width (90 cm^{-1} at 170°K), α is the integrated absorption coefficient, and L is the effective path length ($L = \pi H/2$ for quadratic dependence on density and the slit centrally located). α is estimated to be roughly 0.05 km^{-1} Am^{-2} cm^{-1} from inspection of Herzberg's spectra. The absence of the feature in the Jovian spectra of Kiess, et. al. (1960) suggests that $\tau < 1$, which, using equation (58) with H = 20 km ($\mu = 3$), implies that $N = \rho H < 150$ km Am. If, as Öpik (1962) implies, helium is far more abundant in Jupiter than in the sun (42 times H_2 by number), one might expect to see the λ8270 feature, which is due to a normal 3-0 transition induced by a passing helium atom. In this case the appropriate value of α is roughly 0.004 km^{-1} Am^{-2} cm^{-1} for pure H_2, and half as large for an atmosphere dominated by helium (Hare and Welsh, 1958). The line width would be 66 cm^{-1} and H would be 14 km in this case. The observation that $\tau < 1$ then implies $N(H_2) < 80$ km Am. Both upper limits are consistent with what has been stated above, but the latter indicates that refined observations of both the quadrupole lines and the pressure induced dipole lines are capable of testing Öpik's hypothesis of helium enrichment.

We have shown that all data is consistent with N (H_2) between 30 and 80 km Am, but that the absence of strong Rayleigh scattering indicates that 30 km Am is the most likely value. Since N (CH_4) is 0.15 km Am (Kuiper, 1952), a nuclear abundance ratio of H/C = 400 is indicated. This agrees with the contention of Spinrad and Trafton (1963) that hydrogen is deficient in Jupiter, since the solar ratio is 1900 (Goldberg, Müller, and Aller, 1960). The latter ratio is supported by a precise spectroscopic determination of H/O = 1040 (Gaustad, 1964) and a determination of O/C = 1.7 in solar cosmic rays (Biswas, Fichtel, Guss, and Waddington, 1963). However, it should be borne in mind that saturation effects in the quadrupole lines and errors in the determination of the Rayleigh scattering could bring N (H_2) up to 80 km Am and hence H/C up to 1100 in Jupiter, not far from the solar value.

At this point we may mention the attempt of Owen (1963) to detect the 4-0 R (0) and P (1) lines of HD at 7377 Å and 7464 Å respectively in the spectrum of Jupiter. By comparing with plates taken through 1 km Am by Durie and Herzberg (1960), he deduced an upper limit of 0.5 km Am from the absence of these lines in Jupiter. The resulting lower limit on H/D is 120 if we adopt 30 km Am of H_2 - still far below the terrestrial value, 6400. Nevertheless one sees that the dipole moment in HD at least permits one to rule out considerable enrichment in deuterium.

The structure of the atmospheres of the major planets is certainly heavily influenced by the thermodynamic and optical properties of H_2, a major constituent. According to Peebles (1964), the models of Jupiter and Saturn which give the best fits to the observed external gravitational potentials are characterized by hot, deep atmospheres in which the density is 4-5 times lower than that of an isothermal atmosphere at the same pressure. He supposes that the atmosphere is in convective equilibrium, radiative processes being insufficient to transport the internal heat generated by radioactivity. (Öpik, 1962, argues that this heat from Juipter has

in fact been detected radiometrically, since the observed temperature of 128°K [Murray, Wildey, and Westphal, 1964] considerably exceeds that expected from the available solar energy. He places the heat flux at about 10^4 erg cm^{-2} sec^{-1}.)

In investigating the convective atmosphere of Jupiter, Peebles took relations of the form $p = \text{const} \times \rho^{\Gamma}$, where Γ was 1.4 at pressures below 10^3 atm and up to to 2.4 at higher pressures. The low-pressure value is correct for H_2 below 1000°K; the high-pressure value was assumed in order to keep the density from approaching the density of solid H_2 too quickly. While it may turn out that such $p - \rho$ relations are quite adequate for the problem at hand, questions arise concerning its validity for pressures above 10^3 atm. While it is true that finite molecular volume results in an increased Γ at high pressure, there are several effects which act in the opposite direction: excitation of vibrational degrees of freedom, dissociation to atomic hydrogen (because of high temperature and/or high pressure), and ionization of both molecules and atoms (because of high temperature and/or high pressure).

The temperatures along Peebles' curve 5 (the one with the highest value of Γ) can be estimated from a van der Waals equation of state, using the volume of the solid phase as the excluded volume. One obtains 1000°K at 10^3 atm, 2500°K at 10^4 atm, and 6600°K at 10^5 atm pressure. Vardya (1960), in a study of the thermodynamic properties of hydrogen-helium mixtures at low temperatures where H_2 is important, gives the effective value of Γ as 1.38, 1.29, and 1.26 at the corresponding temperatures and at low pressures, largely due to vibrational excitation. Presumably this effect would persist at high pressures. Again, assuming that the dissociation equilibrium constants given by Vardya are valid at high pressure, one finds 1% dissociation at 3×10^4 atm (3900°K), and 10% at 10^5 atm (6600°K). Since one might expect pressure dissociation to increase these amounts, dissociation may play a role in decreasing Γ even below the values given

above. Ionization will also tend in the same direction. We conclude that extension of Vardya's calculations on the properties of H_2 to the high pressures encountered in planetary atmospheres is needed in order to assess the correctness of Peebles' curves.

In addition, more study is needed before one can be certain that radiative processes are too ineffective to carry the heat flux with lower temperature gradients than the adiabatic. One way to check Peebles is to estimate the radiative flux which is appropriate for his assumed temperature gradients (2-3 degrees per km in the 10^4 - 10^5 atm pressure range). If this amount exceeds the "observed" 10^4 erg cm^{-2} sec^{-1} (which is certainly an upper limit in any case), one may conclude that convection is not necessary and that a lower temperature gradient would suffice.

To assess this question one needs accurate opacity tables for the conditions of interest. The only thing available at present is a study by Vardya (1964) made for stellar atmospheres. He included absorption by H^- and H_2^- and Rayleigh scattering by H and H_2, but did not include translational absorption. The free electrons are supplied by an admixture of easily ionized metals (0.2% by number). One can obtain opacities for the atmosphere of Jupiter by slight extrapolation of his tables. It appears that the radiative flux should considerably exceed 10^4 erg cm^{-2} sec^{-1} along Peebles' curve 5 for an extended range below 1750 km depth (where the pressure is 3×10^4 atm and the temperature is $3900^{\circ}K$). This suggests that the assumption of a convective atmosphere should be reevaluated using opacities which are more appropriate (including such things as translational absorption). A related investigation by Trafton (1964) treats the upper atmosphere of Jupiter ($p \simeq 1$ atm). He finds that pressure induced and translational absorption are strong enough so that 30 km Am gives $\tau = 3$. He finds that convection is likely below that level.

III. STELLAR ATMOSPHERES

As previously stated, the electronic spectrum of H_2 will be very hard to see in stellar atmospheres, because the cool atmospheres containing H_2 emit very little light in the extreme UV where the spectrum is found. The rotation-vibration spectrum, however, is found in the near infrared and can be studied in cool stars with high resolution spectrographs. At this writing, Spinrad (1964 a,b) has detected the 2-0 S (3) line in o Cet and R Aql and the 2-0 S(2) line in α Ori in the 1.2 micron region. H_2 abundances above the photosphere are estimated very roughly to be 10^{26} molecules/cm^2. As in the case of planets, such measures may ultimately give good information on H_2 abundance and on temperature.

Erkovich (1960) made further calculations on the quasimolecular (H + H) absorption which had been suggested by Wildt (1949). The problem was discussed by Zwaan (1962), who applied it to the solar atmosphere, finding that H + H absorption should dominate that of the metals in the spectral region between 2400 Å and 3000 Å. Stecher (1962) came to similar conclusions, finding that a discrepency in the limb darkening beyond 4800 Å could be rectified by the inclusion of Erkovich's H + H calculations in the opacity. Further work by Matsushima and Terashita (1964) demonstrated that one can attain excellent agreement with observations at the center of the disk if one includes Erkovich's H + H opacity and also metallic continua, while models omitting these opacities gave fluxes which were too high in the violet and too low at longer wavelengths.

It might appear that theory and observation are in good agreement concerning the role of H + H absorption in the Sun. However, a paper by Solomon (1964a) has thrown the whole question open again. According to this theoretical study, Erkovich used very unrealistic molecular potentials in deriving his opacities. Use of better

potentials results in a cross section which is only 1% of Erkovich's, making it of no importance in the Sun. The resolution of the observational discrepancy on the Sun is apparently to be found elsewhere. Solomon goes on to say that the ratio of H + H to H^- and to H opacities is small at all relevant pressures and temperatures, and will probably not be important in any stars.

Another phenomonon attributed to quasimolecular effects is the remarkable deviation of the flux of B stars from blackbody curves in the region 1500 Å to 3000 Å found by the early rocket experiments. Meinel (1963) postulated that the inverse process of quasimolecular absorption might be responsible, the $^3\Sigma_g^+$ molecules formed in a hot atmosphere by collision of excited (2^2S) H atoms and ground state (1^2S) H atoms emitting a continuum via a permitted transition to the lowest triplet state ($^3\Sigma_u^+$). This continuum, known from laboratory studies, resembles in shape the broad peak at about 2500 Å seen in the B-star spectra.

Two considerations now throw this suggestion into doubt. First, we have Solomon's calculations, which indicate that the H + H continuum is much weaker than previously supposed. Second, we have new observational data for B stars (Stecher, 1964b) which indicate that the discrepancies in the earlier results do not appear in all B stars. It should be noted that to obtain an emission peak (Meinel) rather than an absorption as in the Sun, one must postulate gross deviations from LTE or a very significant chromosphere which is hotter than the photosphere, or both. Whether it is reasonable to suppose that a good fraction of the light of B stars can be attributed to such phenomena is open to question in any case.

Even if the effects have not yet been detected, it is expected that H_2 will make significant contributions to the opacity in cooler stars. We have already mentioned the calculations by Vardya, which extend down to 2500°K, and include

the effects of H_2 Rayleigh scattering, H_2^- free-free absorption, and H_2^+ bound-free and free-free absorption.

Rayleigh scattering was found to contribute significantly at temperatures near 2500°K. H_2^- was included using the free-free cross-sections calculated by Somerville (1964a), which averaged about 1/3 of the corresponding values for H^-. The total opacity for p_e = 0.03 dynes cm^{-2} and T = 3000°K was increased 9% by H_2^-. H_2^+, calculated from Bates (1952), was found to make minor contributions (up to 5% at 6300°K). Similar results were found by Gingerich (1964), who found that H_2^+ contributed significantly in the Sun. Precise evaluation of the effects of H_2 are important because in late-type stars where H_2 is dominant, the H^- opacity exhibits a minimum at 1.6 μ, not far from the Planck maximum. This would lead to a sharp peak at 1.6 μ if the opacity dip were not filled in by other processes, such as those involving H_2 or H_2^-.

The calculations of Vardya (1960) giving adiabats covering the range of interest for late type stars, should permit accurate convective zones to be established. As he points out, however, there are anomolies in the calculated dissociation fractions owing to inadequate knowledge of the thermodynamic functions of H_2 at high temperatures.

IV. INTERSTELLAR SPACE

At this writing there is still no experimental proof that appreciable amounts of H_2 occur in interstellar space. Moreover, the theoretical results of Gould, Gold, and Salpeter (1963) predict the H_2/H ratio to be about unity only within an uncertainty of a factor of 10.

It might be thought that radiative association via the exothermic reaction, $H + H \rightarrow H_2$, would convert any atomic hydrogen present to the molecular form in a relatively short time. Collisions between H atoms occur about every 10^8 seconds under typical conditions in interstellar space, so that each atom has experienced some 3×10^9 collisions during the lifetime of the Galaxy. Each collision lasts about 10^{-13} seconds, giving a total duration of 3×10^{-4} seconds during which each atom is in collision. If the collision partners (H (1S) + H (1S)) form a $^1\Sigma_g^+$ state at large separations, an infrared transition down to a bound vibrational level of the same electronic state can occur; however, the transition probability is probably much less than that of the 1-0 transition (10^{-7} sec^{-1}) because of unfavorable overlap of the vibrational wave functions. The chance for an atom to form a molecule this way is therefore less than 3×10^{-11} over the entire lifetime of the Galaxy.

If the collision partners form a $^3\Sigma_u^+$ state, transitions to the ground $^1\Sigma_g^+$ electronic state are permitted by all selection rules except $\Delta S = 0$. As pointed out by Gould and Salpeter (1963), this rule can be violated only by singlet-triplet mixing. According to Section VIII, this can occur through the spin-spin interaction of the $^3\Sigma_u^+$ state, which admixes a percentage of singlet into that state, of order $H_{s\text{-}s}/H_o \simeq \alpha^2$, where α is the fine structure constant. The square of the dipole matrix element is therefore reduced from the value for a permitted transition by about $\alpha^4 \simeq 10^{-9}$. At 100°K, the separation between the two electronic states at closest approach on the repulsive curve corresponds to the emission of a photon near 100 μ, giving a transition probability of order 10^{-3} sec^{-1}. Although this is much larger than that of the quadrupole process, it still leads to an overall probability of only 3×10^{-7}. We conclude that arguments for H_2 abundance based on equation (53),

such as that of Zwicky (1959), cannot be trusted unless a much faster process can be found.

It might be thought that H and D could undergo radiative association more easily because HD possesses a small dipole moment. Since the 1-0 band of HD is about 200 times stronger than that of H_2, the overall probability of radiative association through the $^1\Sigma_g^+$ state of a D atom with a passing H atom might be raised to 6×10^{-9} -still negligible. The rate of association through the $^3\Sigma_u^+$ state is unchanged.

Van de Hulst (1948) was the first to point out that H_2 could form on the surfaces of interstellar grains . If H-atoms striking a grain readily stick to it for a considerable period, a layer of atoms is built up so that from time to time atoms come into close contact with each other. Formation of H_2 is then possible, the energy released going partly into heating the grain and partly into ejecting the newly formed molecule from the surface. McCrea and McNally (1960) calculated the expected rate of formation of H_2 molecules in interstellar space on the assumption that the recombination coefficient γ (defined as the probability that an atom striking a grain would leave as a molecule) is unity. This assumption has been carefully studied by Gould and Salpeter (1963), who find that it is correct provided that the grain temperature is greater than T_c (the temperature below which H_2 molecules would be absorbed on the surface, destroying catalytic properties), but less than T_m (the temperature at which H atoms are evaporated before undergoing reaction to form H_2). Fortunately, the range of temperatures calculated (7-15°K for T_c, 9-21°K for T_m) is often met in regions of interstellar space according to their calculations, so the value of averaged over considerable regions of space should exceed 0.1. This corresponds to an average input of 4×10^{-16} H_2 molecules per cm^3 per sec in clouds, if a

typical cloud density, $n_H = 10\ cm^{-3}$ is taken. Thus the cloud is on its way to complete conversion in 10^9 years. If γ is unity, 10^8 years are required. If the cloud undergoes an adiabatic collision with another cloud, the formation rate is increased as much as a factor of 100 because of the increased density and thermal speed behind the ensuing shock waves, as pointed out by McCrea and McNally. This would result in complete conversion into H_2 in several million years, approximately equal to the dynamical time scale.

If the heat of formation of the molecule is largely transferred to the grain at the moment of formation (as is sometimes supposed), one finds that a small temperature rise for the grains is sufficient to dissipate the energy as infrared radiation.

If the heat of formation is largely transferred into translational energy of the new molecule, the energy input to the gas is 2.2×10^{12} ergs per gram - several times greater than that owing to the cloud collision itself. One might think that this energy input during the compression phase of the collision would lead to explosive reexpansion of the cloud. Actually, the energy will probably be quickly transmitted to vibrational excitation of other molecules, with subsequent infrared emission, the temperature rise of the gas being thereby limited. Detailed treatment of the problem has not yet been made. It should be noted that once the conversion to H_2 has occurred, the heat of formation is not available again until the molecules have been dissociated again by some external agency.

Spitzer (1948) pointed out that an H_2 molecule is shielded in interstellar space from destruction by stellar radiation by the photoionization continuum of atomic H, since the latter starts at 13.6 eV while the photodissociation continuum of H_2 begins at 14.7 eV and the photoionization continuum of H_2 begins at 15.6 eV (see Figure 2). The photoionization of H leads to well-defined HII regions around hot stars, within which the ionization of H is substantially

complete and the opacity to photons with energies greater than 12.6 eV is relatively small. Hence an H_2 molecule can be dissociated or ionized only if it finds itself in an HII region. This process has been analyzed by Gould, Gold, and Salpeter (1963), who assumed that interstellar clouds could be visualized as particles moving at random in a volume partly occupied by ionizing radiation. Their result is that an H_2 molecule will be dissociated about 10^8 years after it is formed on the average, by virtue of an encounter of the cloud which it is in with an HII region. This number is not to be taken very seriously, however, as there are several complex phenomena involving the interaction of the high pressure HII regions with the neighboring HI clouds which have not been taken into account. Furthermore, there are a number of processes which could be competitive with encounters with HII regions as destruction mechanisms. Gould and Salpeter revised an earlier estimate of Kahn's (1955) for the dissociation by radiative excitation of the repulsive $^3\Sigma_u^+$ state, to a lifetime of 10^{10} years. Malville (1964) estimates that the forbidden transitions to the $^3\pi_u$ state may occur faster, leading to dissociation through the relatively rapid transition $^3\pi_u \longrightarrow {}^3\Sigma_u$. Dr. P. Solomon (1964b) has suggested the possibility that transitions to the $^1\Sigma_u$ state, followed by permitted transitions to the vibrational continuum of the ground state, may be effective in spite of small Franck-Condon factors. Calculations for the latter process have not been carried out, but it seems probable that the lifetime of H_2 against this process may be shorter still.

If the calculations of Gould, Gold, and Salpeter are correct, the time scales for association and disassociation are comparable, so that one expects that the H_2/ H ratio will vary dramatically from cloud to cloud, being greater than 1 for clouds which have not encountered an HII region recently ("old" molecules) and

less than 1 for those which contain "young" molecules. Hence the overall average of H_2/H is probably between 0.1 and 10, according to these authors. The necessary ultraviolet and infrared observations to establish this ratio observationally are eagerly awaited. Not only is one interested in the mean value of the ratio, but also in measurements on individual clouds. For example, evidence is accumulating that about 10% of all clouds have recently encountered an HII region. These clouds, distinguished by high velocity (often directed away from an HII region) and by abnormal optical properties which may be due to modification of the associated interstellar grains by intense radiation fields, should contain little H_2. High spectral resolution will be necessary to study this problem.

The degree of electronic, vibrational, and rotational excitation is, like the abundance of H_2, determined by statistical equilibrium considerations. It is usually assumed that electronic excitation is negligible in view of the short lifetime of the electronic levels and the comparative weakness of excitation processes. A possible exception is the $c^3\Pi_u$ state, which is metastable with respect to transitions to the repulsive $^3\Sigma_u$ state (selection rule [44]) and to the attractive $^1\Sigma_g$ state (selection rule [39]). Lichten (1960) has shown that the lifetime of the $c^3\Pi_u$ state is about 10^{-3} seconds in the laboratory. Herbig (1963) has suggested that absorptions from this state to higher states might be responsible for the diffuse interstellar line at 4430Å, the diffuse character of the line being due to perturbations of the molecular levels by the grains on which the molecules were assumed to be located. Since about 10^{-8} of the H_2 molecules would have to be in the $c^3\Pi_u$ state to account for the strength of λ4430 (even assuming $H_2/H \simeq 1$), the state would have to be excited about every 10^5 seconds. Herbig failed to find any excitation process more frequent than

every 10^{13} seconds. Malville (1964) has confirmed this result, pointing out that if the molecules were located on the surface of a grain, the lifetime of the $c^3\Pi_u$ state might not even be as great as 10^{-3} sec, leading to even smaller populations than Herbig found.

Vibrational excitation within the $^1\Sigma_g^+$ ground state is subject to the constraint that typical radiative lifetimes are of the order 10^6 - 10^7 seconds. ($A\,[1\text{-}0\ S\ (0)] = 2.9 \times 10^{-7}$ sec^{-1} from Table 2, for example.) Although molecules may be vibrationally excited at the time of formation, the fraction which remain so at any time is negligible since formation proceeds on a much longer time scale.

Collisional excitation is negligible inside cool clouds ($T \simeq 100^\circ$K) since $E\,(v = 1) / k = 6300^\circ$K. In the heated regions behind the shocks formed by collisions of clouds, where $T = 5000^\circ$K and $n_H = 40$ cm^{-3} might be typical values, the rate of excitation is higher. No doubt collisions with atoms and molecules would be effective, but no data on cross sections seem to be available. Even the small number of free electrons present in such a hot HI region would excite all rotational levels of the $v = 1$ level at a rate equal to 1.4×10^{12} sec^{-1}, according to Takayanagi and Nishimura (1960). Although the equilibrium population of the $v = 1$ level is still very small, the near infrared quanta which would be emitted as a result may be detectable, providing a tool by which to seek out hot clouds.

Radiative excitation via resonant fluorescence proceeds in the neighborhood of state which emit copious ultraviolet radiation. According to Osterbrock (1962), a line absorption in the Lyman ($b^1\Sigma_u^+ - X^1\Sigma_g^+$) or Werner ($c^1\Pi_u - X^1\Sigma_g^+$) band systems (much of which are longward of the Lyman limit) excites the molecule electronically, after which it decays into one of the vibrationally excited levels

of the ground state. The distribution over these states could be determined by the Franck-Condon factors for the transitions in question. Since the rate of excitation may attain 10^{-10} sec $^{-1}$, one might build up an excited population of the order of 10^{-3} in this way, but as Osterbrock points out, this activity will be confined to the immediate vicinity of hot stars, where the optical depths in the H_2 resonance lines are not too great.

Collisional rotational excitation within the vibrational ground state is rather rapid at the temperatures of ordinary cool clouds, E/k being 516°K for K = 2. Most authors have treated parahydrogen (K even) and orthohydrogen (K odd) as distinct species, with transitions between them completely forbidden. Newly formed molecules might be expected to be in the ground rotational level and therefore para - H_2, since the grain temperature is only about 10°K. Most authors have assumed that this is the case and therefore that only para - H_2 is present even when the molecule is excited to higher rotational levels.

This assumption may be incorrect. According to Gould and Salpeter (1963), hydrogen atoms trapped at various lattice sites on the surface of the grain diffuse quantum mechanically to neighboring sites where other H atoms may be located. From time to time two atoms approach close enough for the attractive $^1\Sigma_g^+$ potential to become effective (in the 1/4 of the cases which are electron spin singlet). This potential draws the atoms together, the energy thereby released being transmitted to the crystal lattice. This energy (4.5 eV) is far greater than that needed to excite the lower vibrational and rotational states, so that for a brief period, at least, the new molecules may be vibrationally and rotationally excited. It seems reasonable to assume that the various rotational levels in particular will be populated in proportion to their statistical weights alone, so that ortho -H_2 (nuclear spin triplet) will be 3/4 of the total, and

para -H_2 (singlet) only 1/4.

It is not clear how well the excitation energy will be transmitted to the crystal. If it is transmitted relatively well, the molecule will quickly drop into the lowest permitted rotational and vibrational level - v = 0, K = 0 for the para - H_2, and v = 0, K = 1 for the ortho - H_2. Even though K = 1 is over-populated relative to the Boltzmann population at 10°K, molecules in K = 1 cannot drop down to K = 0 radiatively (see below). The only way they can make such a transition is through mixing of the ortho and para states by perturbing forces such as might originate in the crystal lattice. For example, a nearby paramagnetic particle can have this effect. Therefore, if the heat of formation is easily transmitted to the grain, the fraction of ortho - H_2 which finally evaporates from the grains will be 3/4 if the perturbations by the lattice are too weak to effect ortho-para conversion, but will be negligible if the lattice perturbations are strong.

If the heat of formation is not easily transmitted to the grain, the vibrational energy of the new molecules may be enough to overcome the binding to the grain in a very short time, so that the molecules leave the grain with considerable excitation. In this case emission of vibrational and rotational quanta will quickly bring the molecules to v = 0, with 1/4 in K = 0 and 3/4 in K = 1. Further decay to K = 0 is strictly forbidden (see below). In summary, the assumption that new molecules are all para -H_2 is justified only if it can be shown that energy accommodation to the grain is complete and the grain lattice perturbations can cause ortho-para conversion in the time available.

The first calculation of the expected degree of rotational excitation of (assumed) para -H_2 in interstellar clouds was carried out by Spitzer (1949). He formulated the situation as a balance among collisional excitation and de-excitation processes, and radiative deexcitation. The radiative rates(Einstein A's)

depend on the quadrupole moment of the molecule averaged over the v = 0 vibrational wave function, and were given explicitly as

$$A(K, K-2) = 7.52 \times 10^{-13} \frac{K(K-1)(2K-1)^4}{2K+1} \text{ sec}^{-1} \tag{59}$$

amounting to 2.4×10^{-11} sec $^{-1}$ for the K = 2 $\rightarrow$ 0 transition. (These values would be slightly modified if the new quadrupole moments calculated by Kolos and Roothan, 1960, were to be used). The collisional rates were only estimated by Spitzer. This deficiency has now been remedied by Takayanagi and Nishimura (1960), who have calculated collisional excitation cross sections for H-H_2 collisions over a wide range of temperature. A typical excitation rate was 1.4×10^{-9} sec^{-1} (per unit H density) for K = 0 $\rightarrow$ 2 at 5000°K. They also explicitly solved the rather involved statistical equilibrium equations for all levels up to K = 8 (E/k = 6200°K) for n_H = 0.1 to 100 cm^{-3}, and for T from 200 to 5000°K. The results permit one to calculate the energy lost from the gas by emission of rotational quanta. The resulting curves are shown in Figure 9, and are fundamental to the study of the cooling of interstellar matter.

As mentioned previously, these calculations were carried out for para -H_2 alone, an assumption which may not be correct in view of the mode of formation. Further doubt is thrown on this assumption by Takayanagi and Nishimura, who point out that the atomic exchange reaction,

$$H + H_2(p) \longrightarrow H_2(o) + H \tag{60}$$

can go fairly rapidly in hot clouds where the atoms have enough energy to overcome a barrier involved in the reaction. According to Shavitt (1959), the process goes at a rate approximately equal to $1.9 \times 10^{-11} \exp(-3000/T)$ sec^{-1} per unit H density, so that the e - folding time for para-ortho conversion in a cloud with $n_H = 10\ cm^{-3}$ is 500 years at $3000^{\circ}K$, 3000 years at $1000^{\circ}K$, and 4 million years at $300^{\circ}K$. It appears that if the temperature in clouds following collisions even approaches $1000^{\circ}K$, considerable ortho -H_2 will be generated in the million years or so that the temperature endures. Detailed calculations would be needed to establish the para-ortho abundance ratio, and its effect on the cooling rate. Presumably the qualitative effect will be to diminish the cooling rate, since the lowest energy ortho -H_2 rotational transition, $K = 1 \longrightarrow K = 3$ has $E/k = 860^{\circ}K$.

We may briefly mention a modification of Takayanagi and Nishimura's calculations proposed by Gould and Salpeter (1963). They followed Osterbrock (1962) in assuming that the radiative transition $K = 2 \longrightarrow K = 1$, involving an ortho-para conversion, is much faster than the $K = 2 \longrightarrow K = 0$ quadrupole transition. This would have the effect that collisional excitations to K = 2 would always be effective in cooling the gas, whereas Takayanagi and Nishimura's calculations for $n_H = 10\ cm^{-3}$, say, showed that using the larger radiative lifetimes led to decreased cooling since many collisional excitations would be followed by collisional deexcitation. The effect is a factor of five decrease at $1000^{\circ}K$. As we shall discuss below, however, Osterbrock's assumption of a high $2 \longrightarrow 1$ rate is incorrect, so that Takayanagi and Nishimura's calculations are more nearly correct than Gould and Salpeter's in this respect.

Detection of interstellar H_2 can in principle be effected through the electronic, vibrational, or rotational transitions. All three have been

discussed in the literature. Following a preliminary communication by Spitzer and Zabriskie (1959), Spitzer, Dressler, and Upson (1965) have discussed in detail the expected interstellar absorption spectrum of H_2. Using Franck-Condon factors for the $X^1\Sigma_g^+ - b^1\Sigma_u^+$ Lyman band computed by R.W. Nicholls, they compute curves of growth for the 0-v R(0) lines, where v is between 0 and 13. It is found that the 0-1 (λ1092) and 0-4 (λ1049) lines, which should be relatively unobscured by stellar features, should be measurable in the star at 100 pc even if H_2/H is only 10^{-9}. Values of H_2/H in the expected range (0.1 to 10) would give highly saturated lines, making observations of a variety of lines of various degrees of saturation necessary to obtain reliable abundance estimates. On the other hand, values of H_2/H near unity would permit detection of much weaker features, such as those originating on excited rotational levels or in the isotopic molecule HD. Such measurements would give information about temperature and HD abundance. It is anticipated that an ultraviolet spectrograph of the required resolution will be flown in the third Orbiting Astronomical Observatory.

Vibrational transitions may be observable in the near infrared region. Gould and Harwit (1963) have calculated that the intensity of 1-0 vibrational emission at 2.22 μ (K = 2 $\rightarrow$ 0) and 2.12 μ (K = 3 $\rightarrow$ 1) should be detectable with present techniques even at the ground. Their intensity estimates are based on fluorescent excitation of v = 1 by ultraviolet light in the vicinity of hot stars in Orion. The mechanism has been discussed above. They point out that the number of infrared quanta received probably depends more on the intensity of stellar ultraviolet light in the Lyman and Weiner bands than on the number of molecules, since each UV quantum gives rise to a fixed number of infrared quanta, the density of molecules affecting only the geometrical location of the fluorescence.

An additional source of vibrational excitation is the collisions of clouds, which heat the gas to the point that collisional excitation is quite rapid. No calculations have been made of the expected intensity from hot clouds. It is possible that such clouds would be characterized by a vibrational excitation rate comparable to that by fluorescence, particularly if atom-molecule collisions are included.

Rotational quanta in the far infrared could also be observed in principle. Most of these would be obscured by the atmospheric absorption bands which prevail in the 10-100 μ region, although the K = 4 $\rightarrow$ 2 and K = 5 $\rightarrow$ 3 transitions at 12 and 9.5 μ respectively might be detectable from the ground. Zwicky (1959) proposed searching for the 84.4 μ line from the K = 1 $\rightarrow$ 0 transition. There is no doubt that this line would be strong if it were permitted by the selection rule (43), since the excitation energy is only E/k = 172°K. Zwicky gives a transition probability of 10^{-10} sec $^{-1}$ for the 1 $\rightarrow$ 0 transition - larger than the 2.4×10^{-11} sec $^{-1}$ for the 2 $\rightarrow$ 0 quadrupole transition. He apparently bases this estimate on a remark by Wigner quoted by Bonhoeffer and Harteck (1929). Reference to the original paper shows, however, that Wigner's estimate was meant to be an upper limit to A (1 $\rightarrow$ 0). In arriving at that upper limit, Wigner in effect assumed that the nuclear spin singlet and triplet states are mixed by perturbations of the order of μ_N/μ_o (equation [46]) appropriate for nuclear spin - electron orbit coupling. The actual perturbations in the $^1\Sigma_g^+$ ground state ($S = 0$, $\Lambda = 0$) are much smaller, of order μ_N^2 , and consequently the actual value of A (1 $\rightarrow$ 0) is very much smaller than 10^{-10} sec $^{-1}$. Raich and Good (1964) have carried through a detailed calculation and find that A (1 $\rightarrow$ 0) = 7.4×10^{-21} sec $^{-1}$, far too small to lead to a detectable 84.4 μ emission. For the same reason, Osterbrock's suggestion to search for the 2 $\rightarrow$ 1 line at 42.4 μ is invalid; A (2 $\rightarrow$ 1) = 8.5×10^{-19} sec $^{-1}$.

This leaves the 2 $\longrightarrow$ 0 quadrupole line at 28.2 μ, which proceeds with A = 2.4 x 10^{-11} sec^{-1}, and possibly higher lines with Δ K = 2. One might suppose on the basis of equation (59) that going to higher rotational lines would be advantageous, since A increases rapidly with K. However A (2 $\longrightarrow$ 0) is already comparable with the rate of collisional excitation under typical interstellar conditions, so the production of rotational quanta is in practice limited by the rate of collisional excitation. Takayanagi and Nishimura (1961) have calculated that the expected 28-μ flux at the top of the atmosphere is 8 x 10^{-5} n (H_2) erg cm^{-2} sec^{-1} $ster^{-1}$ in the galactic plane. It seems that this amount is too small to detect with present techniques. It appears that ultraviolet techniques offer the best opportunity of detecting interstellar H_2 at the present time.

We finally consider the role of H_2 in star formation. McCrea and McNally (1960) point out that the earliest stages of condensation of interstellar matter to form stars, H $\longrightarrow$ H_2 very rapidly for total densities above 10^3 cm^{-3} owing to the greatly increased rate of recombination on grains above 10^3 cm^{-3}, so that the later stages of condensation are concerned mainly with molecular hydrogen. Gaustad (1963) has studied the contraction to densities and temperatures such that H_2 is dissociated, and finds that for a protostar of one solar mass, the opacity of H_2 molecules (as well as all other opacities) is too small to prevent free-fall collapse beyond the H_2 - dissociation point through the confinement of compressional energy and build up of gas pressure. Less massive stars may be inhibited by pressure build up in the earlier phase where interstellar grains are the opacity source, but free-fall through the region where H_2 provide the opacity is indicated.

Cameron (1962) has considered the contraction beyond the point where H_2 begins to dissociate. He shows that enough energy can be absorbed by the rotational and vibrational degrees of freedom of the molecules, and by their

dissociation, to permit free-fall from a radius of about 100 AU (which is reached in free-fall according to Gaustad). Furthermore, the free-fall is not halted until the temperature has been raised enough to ionize first H and then He, which absorbs enough energy to permit contraction to 0.2 AU. Hence, taken together, the work of McCrea and McNally, Gaustad, and Cameron indicates that the entire collapse of a cloud from about 1 pc to 1 AU radius can take place in free-fall, H_2 exhibiting sufficient transparency in the early stages and sufficient heat capacity (including dissociation) in the later stages, to prevent the build-up of pressure that would be needed to slow down the collapse. Of course, rotational and magnetic forces can be important in the process of contraction to form stars. The studies so far indicate that they must dominate pressure forces if the contraction is to deviate from free fall.

REFERENCES

General

Herzberg, G. 1950, Spectra of Diatomic Molecules (Princeton: Van Nostrand), Second Edition.

Slater, J. C. 1963, Quantum Theory of Molecules and Solids, Vol. I, (New York: McGraw-Hill Book Co.).

Other References

Allen, C. W. 1963, Astrophysical Quantities (London: The Athlone Press).

Aller, L. H. 1963, Astrophysics: The Atmospheres of the Sun and Stars (New York: The Ronald Press Co.).

Bates, D. R. 1952, M.N., 112, 40.

Biswas, S., Fichtel, C. E., Guss, D. E. and Waddington, C. J. 1963, J. Geophys. Res., 68, 3109.

Bonhoeffer, K. F. and Harteck, P. 1929, Zs. Phys. Chem., B, 4, 113.

Burke, B. F. 1954, Jour. Geoph. Res., 59, 191.

Cameron, A. G. W. 1962, Icarus, 1, 13.

Dicke, R. H. 1953, Phys. Rev., 89, 472.

Durie, R. A. and Herzberg, G. 1960, Can. J. Phys., 38, 806.

Eddington, A. S. 1937, Observatory, 60, 99.

Erkovich, S. P. 1960, Optics and Spectroscopy, 8, 162.

Foltz, J. V. and Rank, D. H. 1963, Ap.J., 138, 1319.

Gaustad, J. E. 1963, Ap.J., 138, 1050.

_____. J. E. 1964, Ap.J., 139, 406.

Gehrels, T. and Teska, T. M. 1962, Comm. Lun Plan. Lab. (Arizona), 1, 167.

Gingerich, O. 1964, A. J. 69, 139.

Goldberg, L., Müller, E. A. and Aller, L. H. 1960, Ap.J. Suppl., 5, No. 45, 1.

Gould, R. J., Gold, T. and Salpeter, E. E. 1963, Ap.J. 138, 408.

Gould, R. J. and Harwit, M. 1963, Ap.J., 137, 694.

Gould, R. J. and Salpeter, E. E. 1963, Ap.J., 138, 393.

Hare, W. F. J. and Welsh, H. L. 1958, Can. J. Phys., 36, 88.

Herbig, G. H. 1963, Ap.J., 137, 200.

Herzberg, G. 1938, Ap.J. 87, 428.

_____, G. 1952, Ap.J. 115, 337.

James, H. M. and Coolidge, A. S. 1938, Ap.J., 87, 438.

James, T. C. and Klemperer, W. 1964, J. Chem. Phys., 40, 914.

Kahn, F. 1955, Mem. Soc. Roy. Sci. Liége, 15, 393.

Kiess, C. C., Corliss, C. H. and Kiess, H. K. 1960, Ap.J., 132, 221.

Kolos, W. and Roothan, C. C. J. 1960, Rev. Mod. Phys., 32, 219.

Kuiper, G. P. 1949, Ap.J., 109, 540.

Kuiper, G. P. 1952, The Atmospheres of the Earth and Planets (Chicago: University of Chicago Press).

Lichten, W. 1960, Phys. Rev., 120, 848.

Malville, J. M. 1964, Ap.J., 139, 198.

Matsushima, S. and Terashita, Y. 1964, A. J., 69, 143.

McCrea, W. H. and McNally, D. 1960, M. N. 121, 238.

Meinel, A. B. 1963, Ap. J. 137, 321.

Münch, G. and Spinrad, H. 1963, Mem. Soc. Roy. Sci. Liége, Ser. 5, 7, 541.

Murray, B. C., Wildey, R. L., and Westphal, J. A. 1964, Ap.J., 139, 986.

Öpik, E. J. 1962, Icarus, 1, 200.

Osterbrock, D. E. 1962, Ap.J., 136, 359.

Owen, T. C. 1963, Comm. Lun. Plan. Lab. (Arizona), 2, 65.

Peebles, P. J. E. 1964, Ap.J. 140, 328.

Poll, J. D. and Van Kranendonk, J. 1961, Can. J. Phys., 39, 189.

Raich, J. C. and Good, R. H. Jr. 1964, Ap.J., 139, 1004.

Rank, D. H., Fink, U., Foltz, J. V., and Wiggins, T. A. 1964, Ap.J., 140, 366.

Rank, D. H., Rao, B. S., Sitram, P., Slomba, A. F., and Wiggins, T. A. 1962 J. O. S. A., 52, 1004.

Rank, D. H. and Wiggins, T. A. 1963, J. Chem. Phys., 39, 1348.

Shavitt, I. 1959, J. Chem. Phys., 31, 1359.

Solomon, P. M. 1964a, Ap.J., 139, 999.

Solomon, P. M. 1964b, private communication.

Somerville, W. B. 1964a, Ap.J. 139, 192.

_____, 1964b, private communication.

Spinrad, H. 1963, Ap.J., 138, 1242.

_____, 1964a private communication.

_____, 1964b, Ap.J., 140, 1639.

Spinrad, H. and Trafton, L. M. 1963, Icarus, 2, 25.

Spitzer, L. Jr. 1948, Ap.J., 107, 6.

_____, 1949, Ap.J., 109, 337.

_____, 1956, Franklin Inst. of Philadelphia Monograph, 2, 69.

Spitzer, L. Jr., Dressler, K. and Upson, W. L., III 1965, Pub. Ast. Soc. Pacific, in press.

Spitzer, L. Jr. and Zabriskie, F. R. 1959, Pub. Ast. Soc. Pacific, 71, 412.

Stecher, T. P. 1962, A. J., 67, 587.

Stecher, T. P. 1964a, private communication.

_____, 1964b, Coll. Inst. d'Ap., Liége, 1964.

Strömgren, B. 1939, Ap.J., 89, 526.

Takayanagi, K. and Nishimura, S. 1960, Pub. Ast. Soc. Japan., 12, 77.

_____, Rep. Inst. Space Res. Japan, 15, 81.

Unsöld, A. 1938, Physik der Sternatmosphären (Berlin: Springer Verlag).

Van de Hulst, H. C. 1948, Harvard Obs. Monograph, 7, 73.

Vardya, M. S. 1960, Ap.J. Suppl., 4, 281.

_____, 1964, Ap.J. Suppl. 8, No. 80, 277.

Weinreb, S. 1962, Nature, 195, 367.

Wildt, R. 1949, Rev. d'Optique Theorique et Instrumentale.

Zabriskie, F. 1960, Ph. D. Dissertation, Princeton University.

Zabriskie, F. 1962, A. J., 67, 168.

Zwaan, C. 1962, Bull. Ast. Inst. Neth., 15, No. 519, 225.

Zwicky, F. 1959, Pub. Ast. Soc. Pacific, 71, 468.

PART C

SPECTROSCOPICALLY DETERMINED TERM VALUES AND TRANSITIONS IN H_2

by

K. Dressler

I. THE LANGUAGE OF MOLECULAR SPECTROSCOPISTS

A very large number of electronic, vibrational and rotational energy levels have been determined spectroscopically in the hydrogen molecule. A quick survey of electronic states and of the molecular "constants" describing the vibrational and rotational levels associated with these states can be obtained by inspection of Herzberg's book, p. 530 ff., Table 39 (1950). This table characterizes the electronic states in terms of the following constants, all expressed as term values in units of cm^{-1} ($T\ [cm^{-1}] = E\ [erg]\ /hc$)

T_e, ω_e, $\omega_e x_e$, $\omega_e y_e$, B_e, α_e.

Footnotes to the table give the additional constants γ_e, D_v, and H_v for some of the states. All these constants are defined by the relationships given below.

Molecular term values are expressed as sums of electronic, vibrational and rotational contributions to the total energy:

$$T\ (\text{molecule}) = T_e + G\ (v) + F\ (J). \tag{61}$$

The subscript "e" on the electronic term value T_e does not refer to "electronic" but to "equilibrium", i.e. T_e represents the energy of a physically non-existent state with the nuclei fixed at the equilibrium-internuclear distance (at the minimum of the potential curve). In order to calculate T_e, the observed vibrational levels of an electronic state are fitted to formula (61) with $J = 0$,

and with

$$G(v) = \omega_e (v + \tfrac{1}{2}) - \omega_e x_e (v + \tfrac{1}{2})^2 + \omega_e y_e (v + \tfrac{1}{2})^3 - \omega_e z_e (v + \tfrac{1}{2})^4 \ldots \quad (62)$$

T_e is then obtained by subtracting from the lowest observable energy level T_0 ($v = 0$, $J = 0$) the energy of zero-point vibration $G(0)$:

$$T_e = T_0 - G(0) = T_0 - \tfrac{1}{2} \omega_e + 1/4\, \omega_e x_e - \tfrac{1}{8} \omega_e y_e + \ldots \quad (63)$$

Similarly, the dissociation energies D_e and D_0 of an electronic state refer to dissociation from the minimum of the potential curve, and from the $v = 0$ state, respectively.

Rotational term values are described by rotational constants B, D, and H:

$$F_v(J) = B_v J(J + 1) - D_v J^2 (J + 1)^2 + H_v J^3 (J + 1)^3. \quad (64)$$

Sometimes the rotational constants of a set of vibrational levels within one electronic state are expressed in terms of equilibrium constants:

$$B_v = B_e - \alpha_e (v + \tfrac{1}{2}) + \gamma_e (v + \tfrac{1}{2})^2,$$
$$D_v = D_e - \beta_e (v + \tfrac{1}{2}),$$
$$H_v = H_e - \delta_e (v + \tfrac{1}{2}). \quad (65)$$

Formula (64) can be used to describe the rotational terms of the vibrational levels of the ground state and of unperturbed excited states. The deviations between observed and calculated term values are negligibly small provided that the constants B_v, D_v, and H_v are obtained directly from observations for each individual vibrational level, whereas the use of (65) should be avoided in reconstructing energy levels from published constants.

Similarly, formula (62) should be avoided whenever highest-precision term values including vibrational energy are desired. Instead formula (61) should be rewritten as

$$T_{total} = T_v + F(J), \quad (66)$$

and term values T_v including electronic and vibrational energy, should be taken from observations directly.

The electronic states of hydrogen are designated by a symbol $n_1 \ \ell_1 \ \lambda_1 \ n_2 \ \ell_2 \ \lambda_2$ giving the electron configurations $n_1 \ \ell_1 \ n_2 \ \ell_2$ of the state for vanishing internuclear distance (i.e. the corresponding state of the "united atom", viz. He), followed by the molecular quantum symbols λ_1, λ_2 describing the orientation of ℓ relative to the molecular axis (σ, π, δ, denote $\lambda = 0, 1, 2,$) and by symmetry subscripts g and u depending on whether ℓ is even or odd. The more important electronic states are further named with capital letters X, B, C... if they are spin-singlet states, and with l.c. letters a, b, c... if they are triplets. Finally, the states are characterized by a symbol giving the electronic symmetry. E.G. the full designations of the ground state and of the first excited singlet and triplet states would be:

$$1s\ \sigma_g \quad 2p\ \sigma_u \qquad B \quad {}^1\Sigma_u^+ \ ,$$

$$1s\ \sigma_g \quad 2p\ \sigma_u \qquad b \quad {}^3\Sigma_u^+ \ ,$$

$$(1s\ \sigma_g)^2 \qquad\qquad X \quad {}^1\Sigma_g^+ \ .$$

The finer details of angular momentum notations and of energy terms associated with electronic - and spin-angular momenta are discussed in Herzberg's book. The definitions of N and K given in Part A of this Review (p. 12) follow Herzberg's usage. However, it should be noted that a slightly different notation has been introduced in the mean time (Jenkins 1953), in which J retains its meaning (total angular momentum of the molecule excluding nuclear spins), whereas the former K (total angular momentum excluding nuclear and electron spins) is replaced by N, and the former N (rotation of the nuclei) is replaced by R. Much of this Review deals with $^1\Sigma$ states for which we need not distinguish between J, K, and N, or J, N, and R, since they all have identical values and meaning in this case.

II. THE ROTATIONAL STRUCTURE OF THE GROUND STATE

The most accurate determination of ground-state rotational energy levels is that carried out by Stoicheff (1957) in measurements of the Raman effect. Stoicheff's values of B_0, D_0 and H_0 are

$$\begin{aligned} B_0 &= 59.3392 \quad cm^{-1}, \\ D_0 &= 0.04599 \quad cm^{-1}, \\ H_0 &= 5.2 \times 10^{-5} \quad cm^{-1}. \end{aligned} \tag{67}$$

Rotational term values are presented in Table 3 as derived from (64) and (67). Also listed are the wave numbers, wavelengths and transition probabilities for pure rotational quadrupole transitions $J \rightarrow J-2$.

Table 3

Rotational Levels, Statistical Weights, and Transitions in the Ground State $X\ ^1\Sigma_g^+$, $v = 0$, of H_2.

J	F (J) cm^{-1}	g (J)	F (J)-F (J-2) cm^{-1}	μ(vac)	$A_{J \rightarrow J-2}$ sec^{-1}	τ year
0	0.000	1	–	–	–	
1	118.494	9	–	–	–	
2	354.390	5	354.390	28.2175	2.4×10^{-11}	1.3×10^{3}
3	705.536	21	587.042	17.0346	4.0×10^{-10}	0.8×10^{2}
4	1168.801	9	814.411	12.2788	2.4×10^{-9}	1.3×10^{1}
–						
8	4053.344	17	1638.407	6.1035		
0	4161.167	1	(v=1)			

The wave numbers obey the formula

$$F(J+2) - F(J) = (4B - 6D + \tfrac{27}{4} H)(J + \tfrac{3}{2}) - (8D - 34H)(J + \tfrac{3}{2})^3 + 12H(J + \tfrac{3}{2})^5. \tag{68}$$

The transition probabilities $A_{J \rightarrow J-2}$ have been given by Spitzer (1949):

$$A_{J \rightarrow J-2} = 7.52 \times 10^{-13} \frac{J(J-1)(2J-1)^4}{2J+1} \ sec^{-1}. \tag{69}$$

The statistical weights of the rotational levels of H_2, HD, and D_2 are:

$g(J) = 2J + 1$ for HD,

$g(J) = 3(2J + 1)$ for ortho - H_2 (odd J - values),

$g(J) = 1(2J + 1)$ for para - H_2 (even J - values),

$g(J) = 6(2J + 1)$ for ortho - D_2 (even J - values),

$g(J) = 3(2J + 1)$ for para - D_2 (odd J - values),

or, in general for a molecule with two identical nuclei of nuclear spin i :

$g(J) = (2i + 1)(i + 1)(2J + 1)$ for levels occurring with symmetric nuclear spin functions. (70)

$g(J) = (2i + 1)\, i\, (2J + 1)$ for levels occurring with anti-symmetric nuclear spin functions. (71)

III. THE VIBRATIONAL STRUCTURE OF THE GROUND STATE

There are 14 discrete vibrational levels associated with the electronic ground state of H_2. The most accurate information on the vibrational term values and rotational structure of these levels is due to Stoicheff (1957, v = 0), Rank et. al. (1962, 1963, v = 1 - 3), and Herzberg and Howe (1959, v = 4 - 14). Some values of the vibrational terms T_v and of the rotational constants are given in Table 4. Transitions between vibrational levels can occur in Raman scattering as well as in emission or absorption of quadrupole radiation and, at high pressure, of induced dipole radiation. In all of these cases the rotational selection rules are $\Delta J = 0, \pm 2$, with the additional restriction $J = 0 \not\rightarrow J = 0$ in the case of quadrupole radiation only. Table 5 presents the wavenumbers of the $v = 1 \leftarrow v = 0$ band of H_2 as observed by Rank et.al. (1962) at high pressure and as calculated from Rank's constants (cf. Table 4). The Q (0) line, which cannot occur as a quadrupole line, is given as observed by Stoicheff (1957) in the Raman spectrum. Measurements at lower pressures and extra-

polations of line frequencies to zero pressure were reported by Rank and Wiggins (1963).

Table 4

Vibrational Structure of Ground = State H_2

v	$_v(J = 0)$	B_v	D_v	H_v
0	0	59.3392	0.04599	5.20×10^{-5}
1	4161.167	56.3725	0.04392	4.15×10^{-5}
2	8087.135	53.4667	0.04218	3.84×10^{-5}
3	11782.366	50.6259	0.04088	3.64×10^{-5}
4	15250.36	47.8013	0.0397_1	3.50×10^{-5}
5	18491.92	44.958_4	0.0385_4	$3.4_2 \times 10^{-5}$
6	21505.65			
7	24287.83			
8	26830.97	Rotational constants not listed can be found in Herzberg and Howe (1959)		
9	29123.93			
10	31150.19			
11	32886.85			
12	34301.83			
13	35351.01			
14	35972.97	8.770_1	0.08467	-
D_0^o	36113			

Table 5

The 1 - 0 Vibration - Rotation Band of H_2

J	S (J)		Q (J)		O (J)	
0	4497.830	obs	4161.134	obs*	-	
1	4712.895	obs	4155.243	obs	-	
2	4916.990	obs	4143.440	calc	3806.777	calc
3	5108.399	obs	4125.853	calc	3568.201	calc

* Raman effect.

J denotes the lower state (J", v" = 0), J' denotes the upper state (J', v' = 1);

S (J), Q (J), O (J) denote transitions with $\Delta J = J' - J'' = +2, 0, -2$.

The most accurate experimental dissociation energies of H_2, HD, and D_2 are those derived by Herzberg and Monfils (1960) from the measurement of the long-wavelength limit of continuous absorption near 850 Å, corresponding to the process

$$H_2\ X\ ^1\Sigma_g^+,\ v = 0 \longrightarrow H\ (1s) + H\ (2p).$$

The threshold for transitions originating in the J = 0 level is found at

$$T_0\ (H_2) = 118372.1_5 \pm 0.2_0\ cm^{-1}. \tag{72}$$

The dissociation energy of the ground state D_0^o ($X\ ^1\Sigma_g^+$, v = 0, J = 0) into H (1s) + H (1s) is found by subtracting from T_0 the average excitation energy of the atomic 2p states (82259.0 ± 0.15 cm^{-1}):

$$D_0^o\ (H_2) = 36113.0_5 \pm 0.30\ cm^{-1}. \tag{73}$$

Herzberg and Monfils have computed a zero-point energy of $E_0(H_2) = 2179.2_7\ cm^{-1}$ for H_2, and hence $D_e^o\ (H_2)$ as measured from the minimum of the potential curve becomes

$$D_e^o\ (H_2) = 38292.3 \pm 0.5\ cm^{-1}. \tag{74}$$

Although the quantity D_e^o is not directly measurable, it is useful when different isotopes are compared since D_e^o is independent of nuclear mass. D^o_e also is the quantity which can be compared with theoretical calculations of the electronic energy of the hydrogen system with fixed nuclei. This comparison is discussed by Herzberg and Monfils.

The term values of the highest discrete levels of ground-state H_2 have been determined by Herzberg and Howe (1959) and are listed in Table 6. Comparison with the dissociation

Table 6

ROTATIONAL LEVELS OF H_2 NEAR DISSOCIATION LIMIT

J	T (v = 14)
0	35973.0
1	990.2
2	36022.8
3	067.6
4	117.8
5	153.4

energy $D_0 = 36113.0\ cm^{-1}$ (Herzberg and Monfils 1960, cf. Table 4) shows that the last observed level J = 5 of v = 14 lies 40 cm^{-1} above that limit and owes its existence to the presence of a potential barrier to dissociation at elevated J - values.

The ground state of HD has been investigated by Durie and Herzberg (1960). Their principal numerical results are given in Table 7.

Table 7

Ground - State Constants of HD.

$\omega_e = 3812.29_3$, $\omega_e x_e = 90.908$, $\omega_e y_e = 0.504$

v	T_v (J = 0)	B_v	D_v
0	0	44.668_7	0.0263_0
1	3632.14_9	42.742_7	0.0254_4
2	7086.88_3		
3	10367.56_3		
4	13476.87_6		

The v = 0 and v = 1 levels of D_2 have been investigated along with those of H_2 and HD by Stoicheff (1957).

IV. EXCITED STATES AND ELECTRONIC TRANSITIONS

The potential energy curves illustrated in Fig. 2 represent all molecular states resulting from the electron configurations 1 s n $\ell\lambda$ with n = 1 and 2. The observed term values of these and of known higher excited states of H_2 are given in Table 8 which is arranged in the form of an energy-level diagram. All triplet-state energies are taken from the very convenient table of H_2 energy levels by Dieke (1958), whereas Dieke's singlet-state energies were raised by 7 cm^{-1} as explained below. The values listed in Table 8 represent the lowest observable K-value of the v = 0 level, i.e. Σ , Π , and Δ -states are represented by their lowest K = 0, 1, and 2 - levels, resp., as given by Dieke. In cases of Π and Δ - states with Λ - doubling the component of lower energy is listed only.

The higher rotational and vibrational term values of the electronic states of H_2 are listed in Dieke's table as far as they were known and well established in 1958. The rotational and vibrational structures of many excited states are perturbed by mutual interactions between excited states, such that they can not be represented accurately by the rotational and vibrational constants of formulae (61) to (66). For this reason great caution must be exercised whenever B- or ω- are used to calculate excited state energy levels, whereas tables of energy levels such as, e. g., Dieke's (1958) or Namioka's (1964 a,b) present the actually observed levels no matter how much they may deviate from a regular, unperturbed structure.

Whereas all triplet-state energies in Table 8 were taken from Dicke's table, there has been more recent work in the vacuum ultraviolet which has resulted in more accurate and in more extended information on the $^1\Sigma_u^+$ and $^1\Pi_u$ - states of configurations 1s np. These states are, of course, the only ones appearing in the absorption spectrum, or in emission terminating in ground-state levels.

n	s	p		d		
	σ_g	σ_u	π_u	σ_g	π_g	δ_g
∞	124430 $(H_2^+, {}^2\Sigma_g^+)$					
6			u 121517 $^3\Pi_u$			
5			n 120132 $^3\Pi_u$			
4		B" 116886 $^1\Sigma_u^+$ f 111752 $^3\Sigma_u^+$	D'117893 $^1\Pi_u$ k 117556 $^3\Pi_u$	p117617 $^3\Sigma_g^+$ P117410 $^1\Sigma_g^+$	r 117714 $^3\Pi_g$ R 117588 $^1\Pi_g$	s 117980 $^3\Delta_g$ S 117834 $^1\Delta_g$
3	H 112957 $^1\Sigma_g^+$ h 112021 $^3\Sigma_g^+$	B' 110478 $^1\Sigma_u^+$ e 106832 $^3\Sigma_u^+$	D 112931 $^1\Pi_u$ d 111904 $^3\Pi_u$	g111948 $^3\Sigma_g^+$ G111812 $^1\Sigma_g^+$	i 112216 $^3\Pi_g$ I 112072 $^1\Pi_g$	j 112664 $^3\Delta_g$ J 112525 $^1\Delta_g$
			F $(2p\sigma)^2$ 103838 $^1\Sigma_g^+$			
2	E 99164 $^1\Sigma_g^+$ a 95226 $^3\Sigma_g^+$	B 90203 $^1\Sigma_u^+$ b 36113 $^3\Sigma_u^+$ continuum	C 99150 $^1\Pi_u$ c 95091 $^3\Pi_u$			
1	X 0 $^1\Sigma_g^+$					

TABLE 8

The most recent references regarding the energy levels of these states are listed in Table 9. The entries into Table 8 were taken from those references except for the C state. It was found that the more recent values for the B, B' and D states are 7 cm^{-1} higher than those adopted by Dieke in 1958; therefore Dieke's value for the C state was raised by 7 cm^{-1} also. All the other singlet states of Table 8 are of g - symmetry and their energies are connected to those of the u - states just discussed by well-known emission frequencies in the visible region. Therefore, the terms of all singlet - g - states were raised by 7 cm^{-1} from the values adopted in Dieke's table.

The position of the system of triplet states relative to the singlet ground state is based on connecting both the singlet and the triplet states to the same ionisation limit.

The ionisation potential of H_2 is defined as the energy difference between the v = 0, K = 0 levels of the ground states of H_2 and of H_2^+. The spectroscopic determination of this quantity is due to Beutler and Jüenger (1936):

$$I\,(H_2) = 124430\ cm^{-1}.$$

TABLE 9

Recent References Regarding the Singlet States of Series 1s np.

State			v	Authors
4p	D'	$^1\Pi_u$	0	Monfils 1961, Namioka 1964b
	B''	$^1\Sigma_u^+$	0	" "
3p	D	$^1\Pi_u$	0 - 2	Monfils 1961, Namioka 1964b
	B'	$^1\Sigma_u^+$	0 - 9	" "
2p	C	$^1\Pi_u$	0 - 4	Dieke 1958
			3 - 13	Monfils 1961, 1962
			5 - 14	Namioka 1964a
	B	$^1\Sigma_u^+$	0 - 13	Herzberg and Howe 1959
			14 - 35	Monfils 1961, 1962
			17 - 37	Namioka 1964a

The F $^1\Sigma_g^+$ state at 103838 cm^{-1} belongs to an electron configuration quite different from that of the other known excited states. It can be described by the "united-atom" symbol $(2p\,\sigma_u)^2$, or by the "separate-atom" symbol $(\sigma_u\ 1s)^2$; either way it corresponds to a configuration in which both electrons are excited. The rotational and vibrational structure of the state indicates a very shallow potential curve with a minimum at a very large internuclear distance ($\sim$ 2.3 Å compared to $\sim$ 1.0 Å in states of Rydberg series $1sn\,\ell\,\lambda$). The potential curve of the F state crosses, in a very low order of approximation, the right-hand branches of many of the other excited-state potential curves. For this reason strong interactions occur wherever these other excited states are of $^1\Sigma_g^+$ symmetry also, resulting in strongly perturbed rotational and vibrational structures of these states. Dieke's table lists 19 vibrational levels associated with a large internuclear equilibrium distance, and the five lowest ones of these are definitely assigned to the F state. It seems possible that the remaining 14 levels represent the higher vibrational levels of this state in interaction with vibrational levels of $^1\Sigma_g^+$ states of configuration 1sns and 1snd.

A number of the states listed in Table 8 have been mentioned in the astronomical literature in connection with electronic transitions of possible importance. The absorption of "quasi-molecular" hydrogen mentioned in Part B of this review involves transitions from the $2p\,\sigma\ ^3\Sigma_u^+$ repulsive state to the higher lying triplet -g- states, primarily the $2s\ ^3\Sigma_g^+$ state.

The coincidence between the broad interstellar absorption lines near 4430 and 5800 Å with lines of H_2 noted by Herbig (1963) involves transitions from the lowest levels of the slightly metastable $2p\ ^3\Pi_u$ state to the triplet states of configurations 4d and 3d.

The lines of the B $^1\Sigma_u^+ \leftarrow$ X $^1\Sigma_g^+$ transition (Lyman bands) provide the

most promising means of detecting molecular hydrogen in interstellar space (cf. Spitzer and Zabriskie 1959). Lists of wavelengths and of expected equivalent widths in the bands 0,0 to 13,0 of this transition (1110 - 955 Å) have been compiled by Spitzer et. al (1965).

The Werner bands, $C\ ^1\Pi_u \leftarrow X\ ^1\Sigma_g^+$, probably have greater intensities but fall into the less accessible region shortward of λ1010 Å .

ACKNOWLEDGEMENT

This work has been supported by the National Aeronautics and Space Administration under Grant NsG-414.

REFERENCES

Beutler, H. and Jünger, H. O. 1936, Z. Physik 100, 80; 101, 285.

Dieke, G. H. 1958, J. Mol. Spectr. 2, 494.

Durie, R. A. and Herzberg, G. 1960, Can. J. Phys. 38, 806.

Herbig, G. H. 1963, Ap.J. 137, 200.

Herzberg, G. 1950, Spectra of Diatomic Molecules, (Princeton: Van Nostrand).

Herzberg, G. and Howe, L. L. 1959, Can. J. Phys. 37, 636.

Herzberg, G. and Monfils, A. 1960, J. Mol. Spectr. 5, 482.

Jenkins, F. A. 1953, J. Opt. Soc. Am. 43, 425.

Monfils, A. 1961, Bull. Acad. Roy. Belg. (Sciences) 47, 585, 599, 816.

Monfils, A. 1962, Bull. Acad. Roy. Belg. (Sciences) 48, 460, 482.

Namioka, T. 1964a, J. Chem. Phys. 40, 3154.

Namioka, T. 1964b, J. Chem. Phys. 41, 2141.

Rank, D. H., Rao, B. S., Sitaram, P., Slomba, A. F. and Wiggins, T. A. 1962, J. Opt. Soc. Am. 52, 1004.

Rank, D. H. and Wiggins, T. A. 1963, J. Opt. Soc. Am. 53, 759.

Spitzer, L. 1949, Ap.J. 109, 337.

Spitzer, L., Dressler, K. and Upson, W. L. 1965, Pub. Astro. Soc. Pacific, in press.

Spitzer, L. and Zabriskie, F. R. 1959, Pub. Astro. Soc. Pacific, 71, 412.

Stoicheff, B. P. 1957, Can. J. Phys. 35, 730.

Tanaka, Y. 1944, Sci. Papers Inst. Phys. Chem. Res. (Tokyo) 42, 49.

LEGENDS FOR FIGURES

Fig. 1.- Distances between pairs of particles in the H_2 molecule. a and b are protons, 1 and 2 are electrons.

Fig. 2.- A sketch of the potential energy curves of the ground - and lower excited states. The v = 0 level of the ground state is taken as 0. Dissociation and ionization limits are shown.

Fig. 3.- Coupling of angular momenta in Hund's cases a and b. Case b (with a small admixture of case a for non - Σ states), applies for H_2.

Fig. 4.- Various coupling schemes for angular momenta including nuclear spin.

Fig. 5.- Symmetry planes for the molecule with nuclei a and b.

Fig. 6.- Energy curves for H_2^-. Dissociation into two atoms and into H and H^- is shown, as are the lowest singlet and triplet states of H_2.

Fig. 7.- Illustrating the energy curve non-crossing rule. Two curves like WX and YZ which cross in a certain approximation became WZ and YX in a higher approximation.

Fig. 8.- Strengths of the S(1) quadrupole rotation-vibration lines as a function of band designation. Curve represents measurements, points are theoretical.

Fig. 9.- Radiative loss per unit density of atoms and molecules for interstellar gas at various densities and temperatures. Note the large decrease in loss per atom as the atomic density is increased and the radiative deexcitations are quenched.

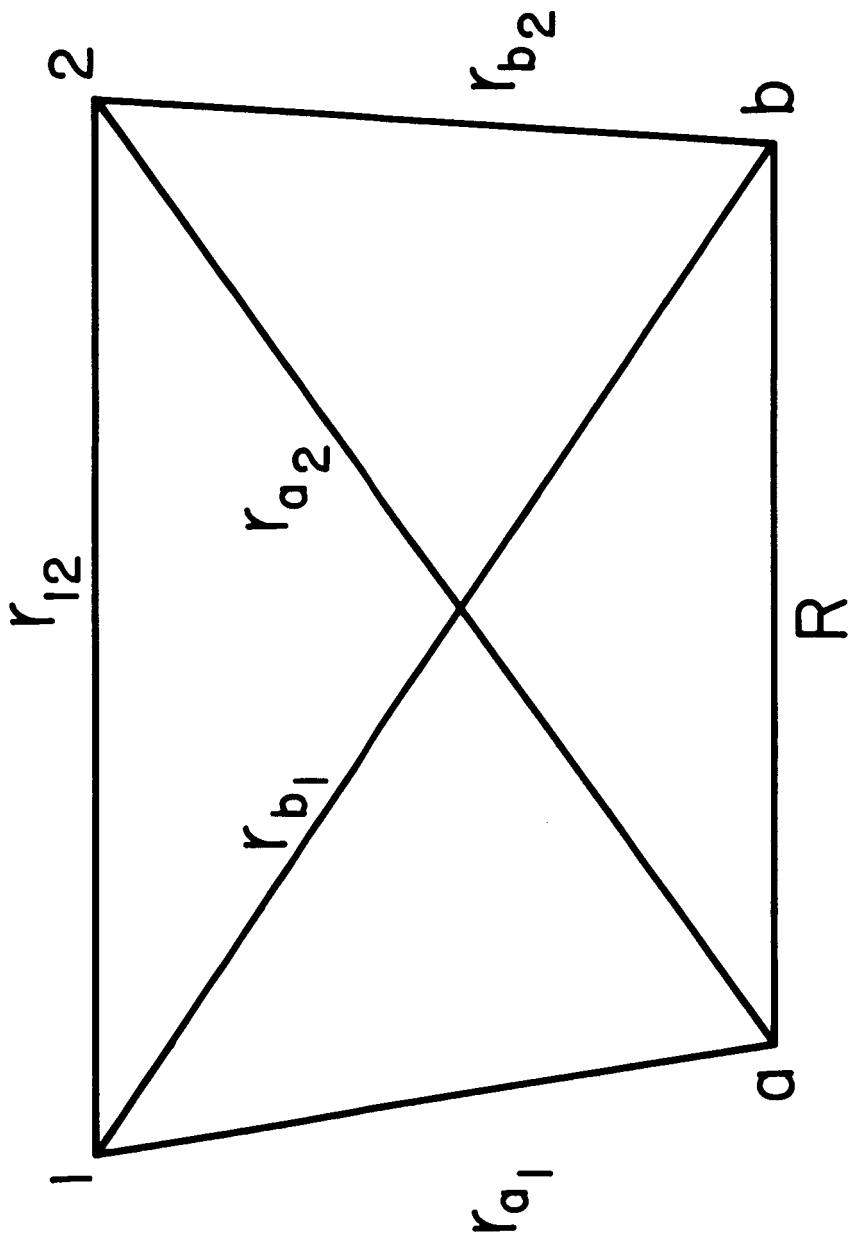


FIG.1

POTENTIAL ENERGY CURVES OF HYDROGEN

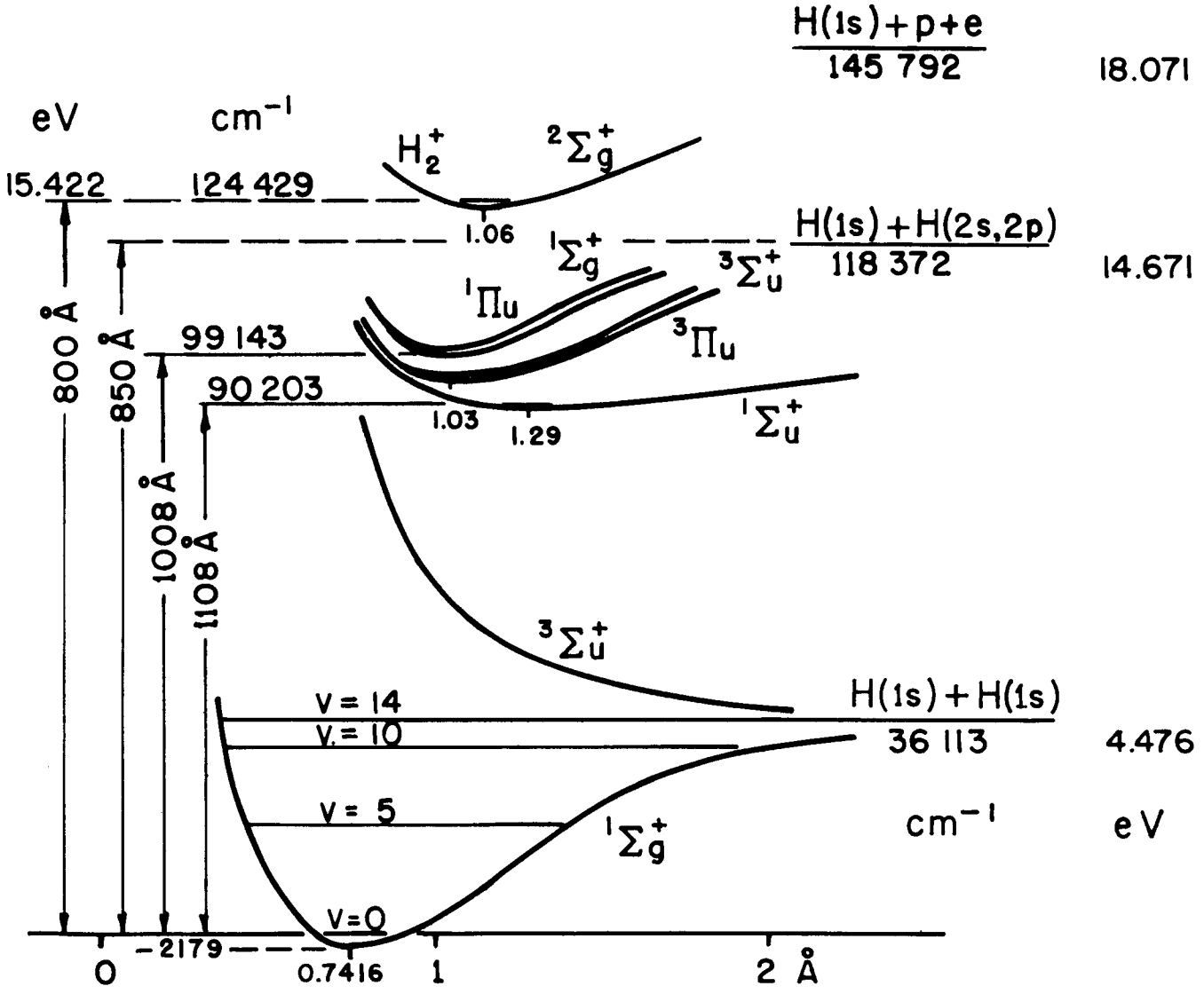


FIG. 2

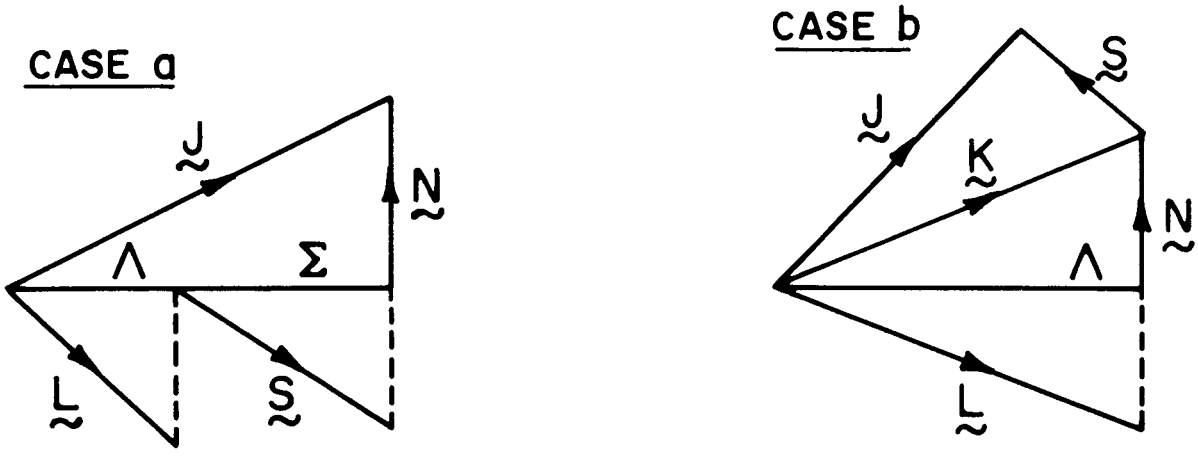


FIG.3

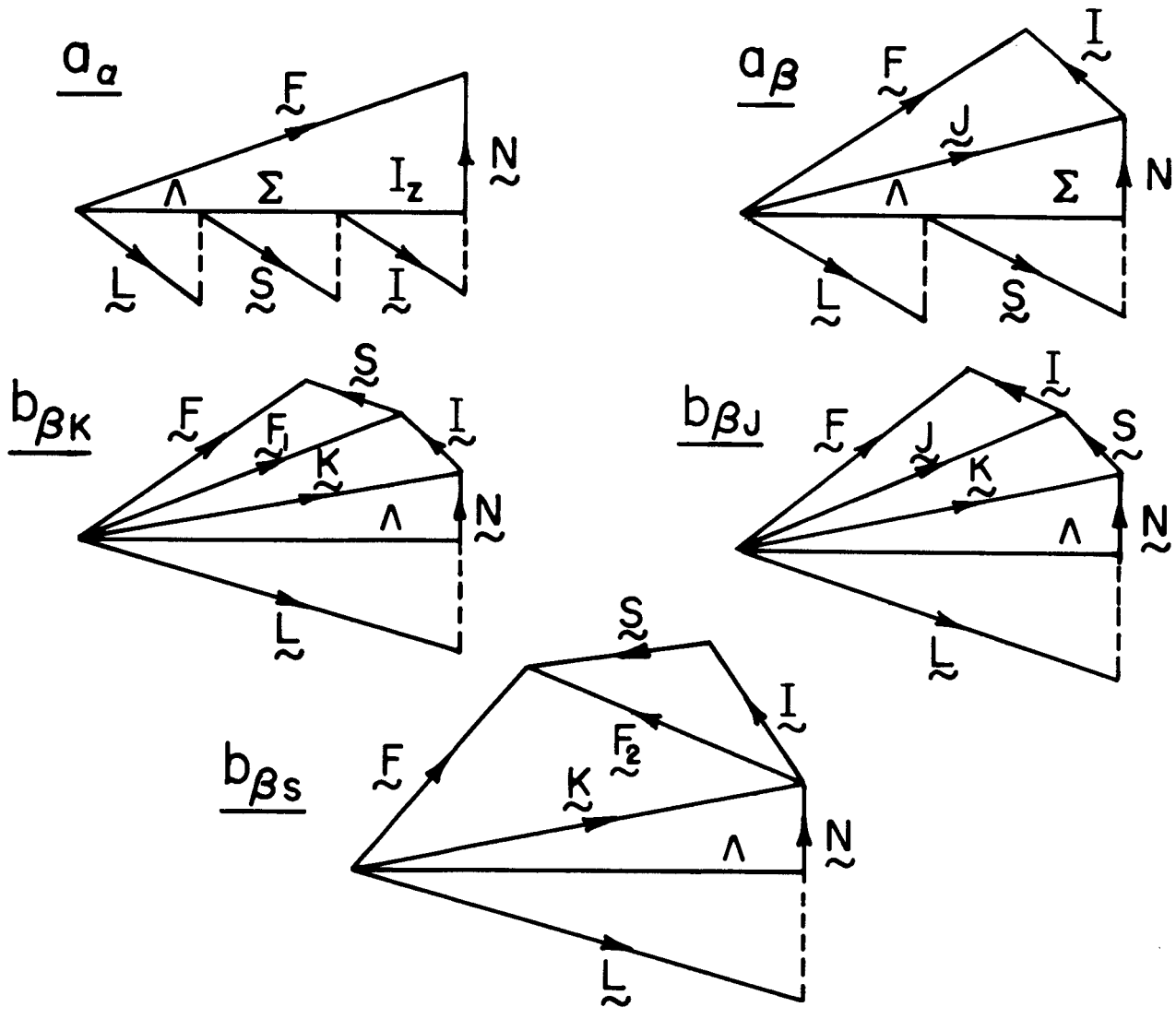

a_α
F
N
Λ
Σ
I_z
L
S
I
a_β
I
F
J
N
Λ
Σ
L
S
b_βK
S
F
F
I
K
N
Λ
L
b_βJ
I
F
J
S
K
N
Λ
L
S
b_βS
I
F
F_2
K
N
Λ
L

FIG. 4

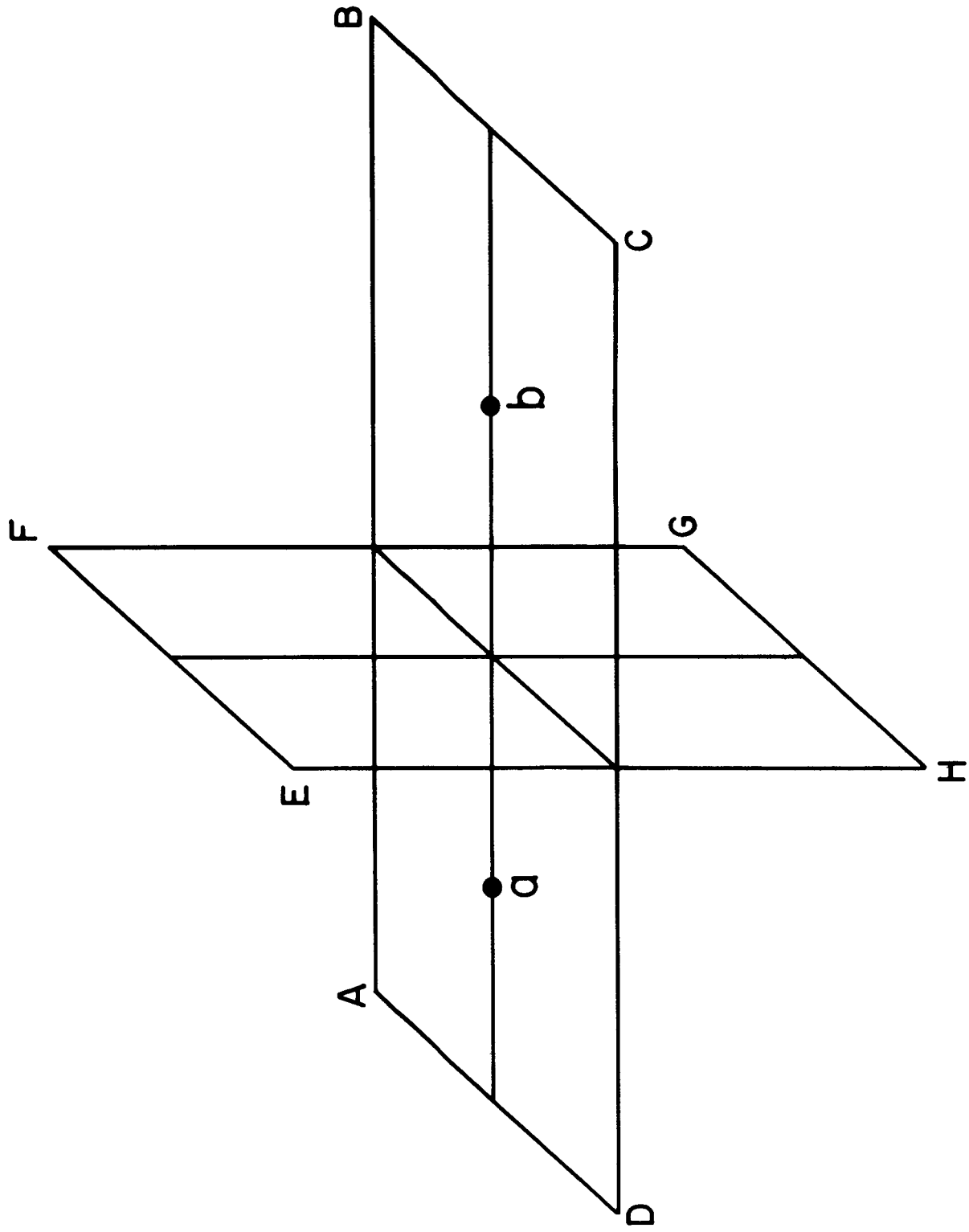


FIG.5

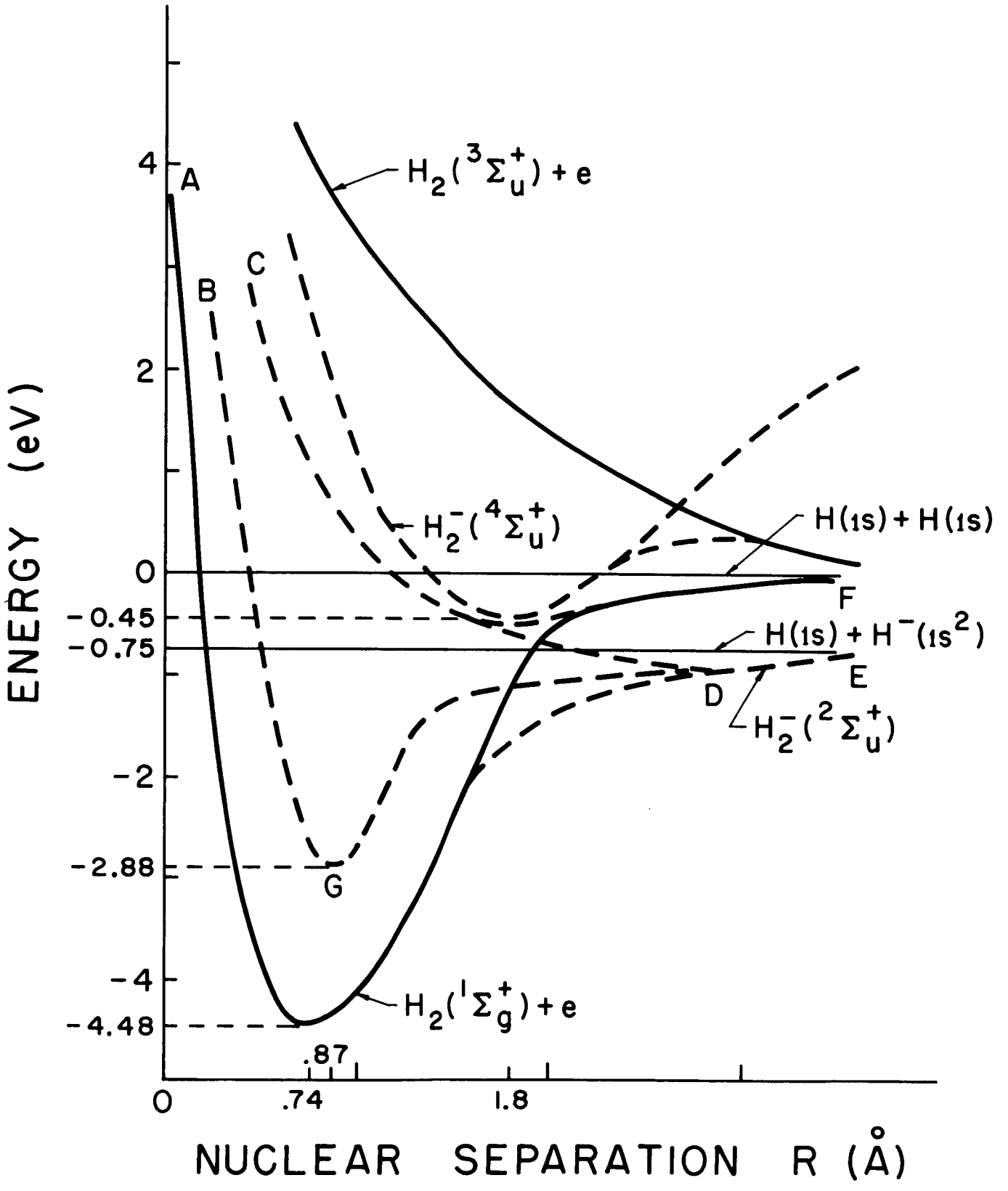

ENERGY (eV)
4
2
0
-2
-4
-0.45
-0.75
-2.88
-4.48
A
B
C
D
E
F
G
$H_2(^3\Sigma_u^+)+e$
$H_2^-(^4\Sigma_u^+)$
$H_2^-(^2\Sigma_u^+)$
$H_2(^1\Sigma_g^+)+e$
H(1s) + H(1s)
H(1s) + $H^-(1s^2)$
0
.74
.87
1.8
NUCLEAR SEPARATION R (Å)

FIG.6

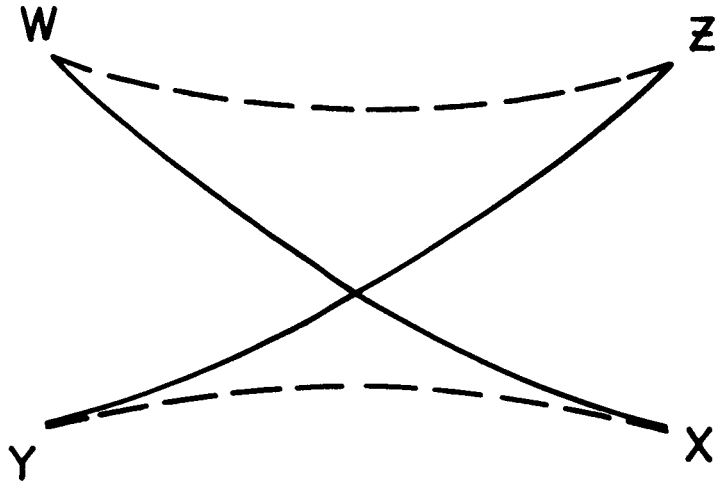
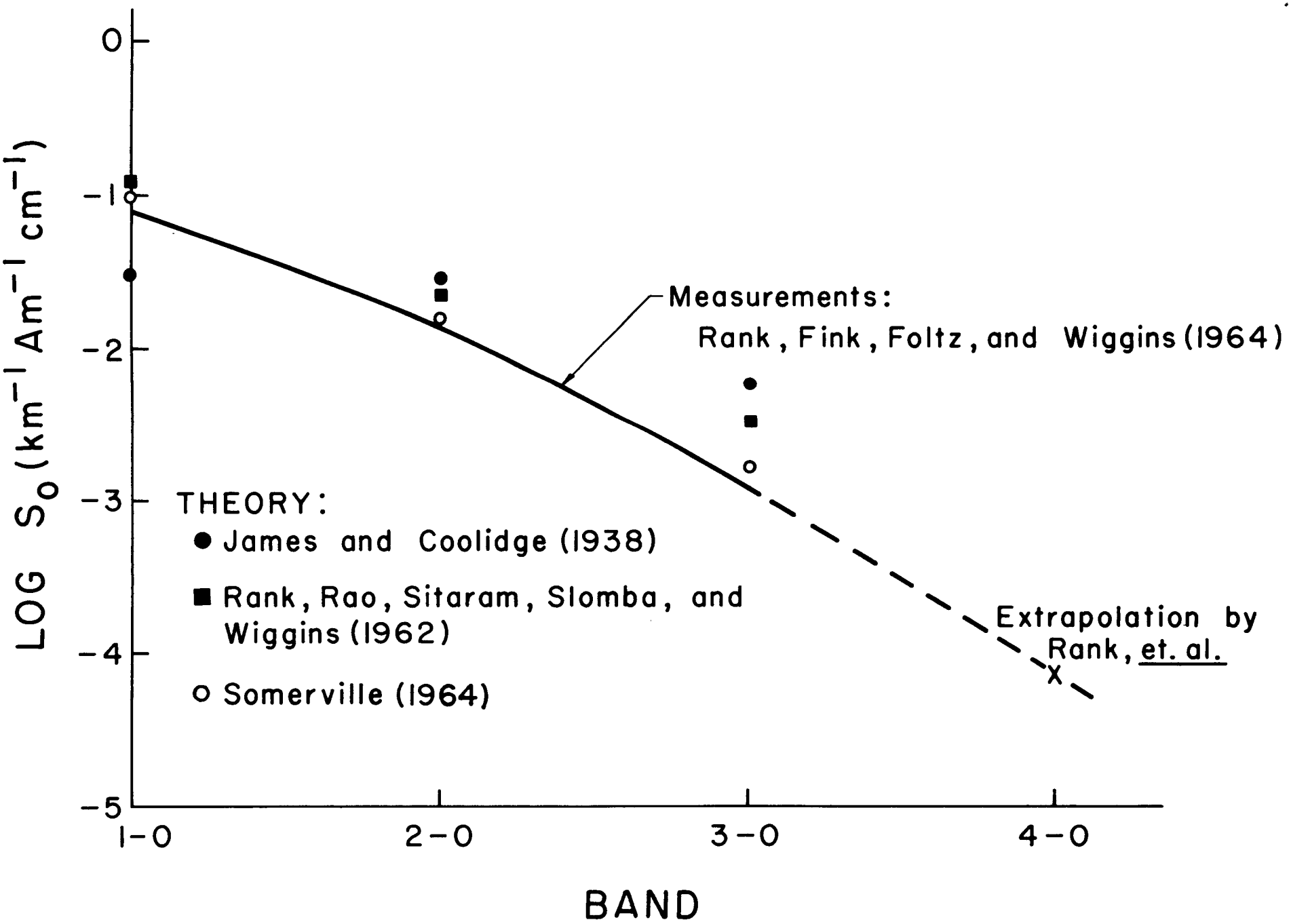


FIG. 7

FIG. 8


LOG S_0 (km^{-1} Am^{-1} cm^{-1})
0
-1
-2
-3
-4
-5
1-0
2-0
3-0
4-0
BAND
Measurements:
Rank, Fink, Foltz, and Wiggins (1964)
THEORY:
James and Coolidge (1938)
Rank, Rao, Sitaram, Slomba, and Wiggins (1962)
Somerville (1964)
Extrapolation by Rank, et. al.

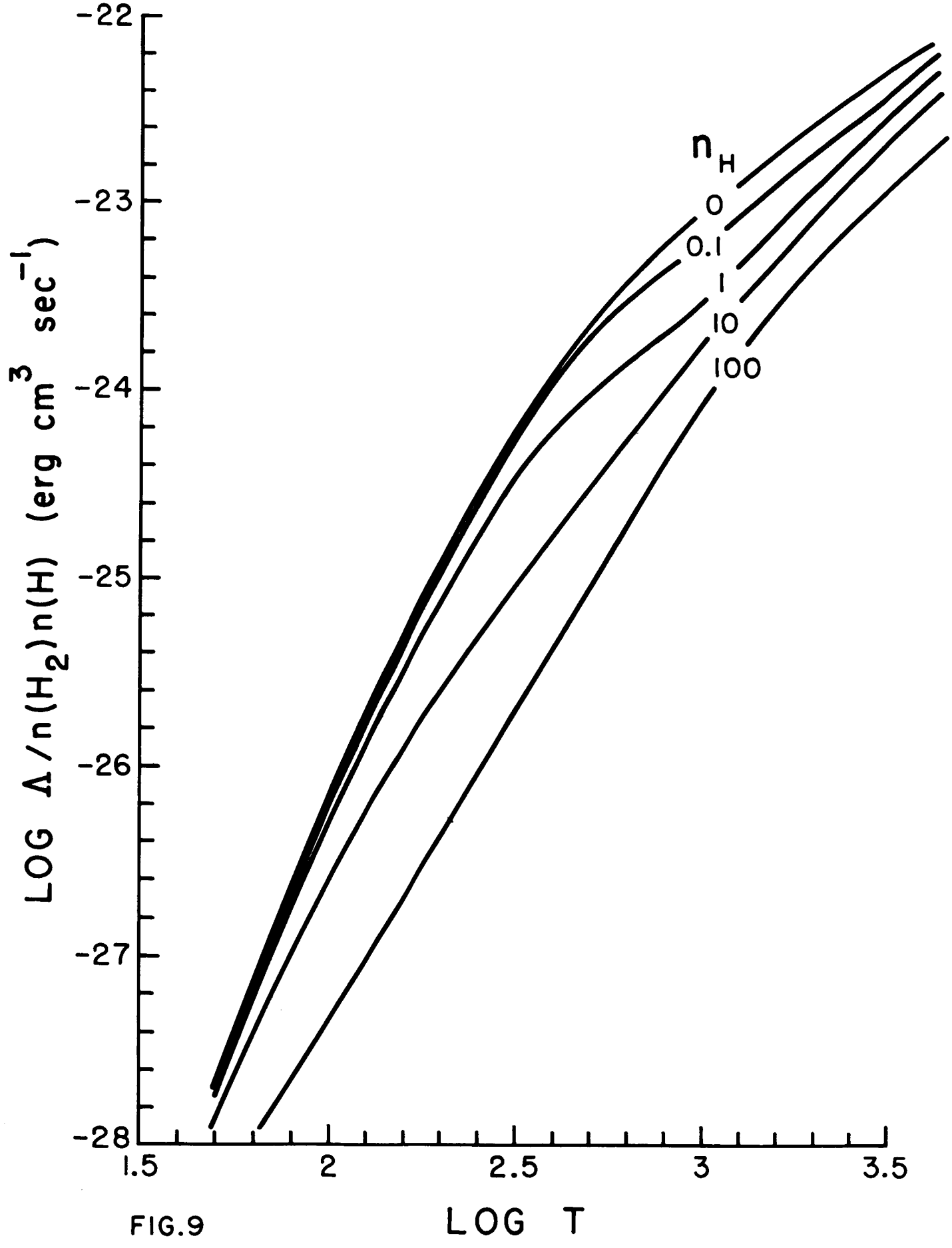

-22
-23
-24
-25
-26
-27
-28
LOG Λ/n(H2)n(H) (erg cm3 sec-1)
nH
0
0.1
1
10
100
1.5
2
2.5
3
3.5
LOG T

FIG.9