

HYDROGEN MOLECULES IN ASTRONOMY¹

BY G. B. FIELD,² W. B. SOMERVILLE,³ AND K. DRESSLER⁴

Princeton University Observatory, Princeton, New Jersey

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 (28)

1. INTRODUCTION

(by G. B. Field and W. B. Somerville)

The interest in the hydrogen molecule 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 (2)]

$$\frac{p(H_2)}{p^2(H)} = \frac{g(H_2)}{g^2(H)} \left(\frac{h^2}{2\pi mkT} \right)^{3/2} \frac{8\pi^2 I}{h^2} (1 - e^{-hv/kT})^{-1} e^{D/kT} \quad 1.1.$$

provided that local thermodynamic equilibrium applies. For the densities appropriate in stellar atmospheres, Equation 1.1 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 1.1. 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 $10^\circ K$, while it is destroyed by ultraviolet quanta whose color temperature is about $30,000^\circ K$. Under such deviations from thermodynamic equilibrium, Equation 1.1 is inapplicable. Rather, detailed calculations of rates of formation and destruction are necessary, as pointed out by Strömberg (130), Spitzer (120), and van de Hulst (139). At the present time such calculations are rather inconclusive, but indicate that H_2 will dominate in at least limited regions of interstellar space.

Gould, Gold & Salpeter (47) consider that the presence in interstellar

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² Present address: Berkeley Astronomy Department, University of California, Berkeley, California.

³ Present address: Astronomy Department, University College London, London, England.

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space of amounts of H_2 up to five times the amount of atomic H observed by the 21-cm technique would not conflict with upper limits on the total mass density inferred from the galactic gravitational field.

H_2 may also play an important part in the thermal properties of interstellar material. It is a very effective cooling agent at the temperatures of interstellar gas, as suggested by Spitzer (121), and its heat of formation (2.25 eV per atom) is large.

Owing to the unfavorable location of its spectrum, the only positive detection of H_2 at this writing has been in planetary atmospheres and in a few stars. 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 (122)]. 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 atmospheres of cool stars and of planets are of little interest, owing to the lack of a suitable ultraviolet continuum.) Subordinate lines are unimportant both in interstellar space and in atmospheres because of insufficient excitation.

Both the rotation-vibration bands (fundamental at 2.4μ) and pure rotational lines (2-0 at 28μ) occur only by quadrupole radiation, or, if the pressure exceeds 10 atm, as collision-induced dipole transitions. As a result, the lines are weak. Nevertheless, Herzberg (55) calculated that the rotation-vibration spectrum, particularly the 3-0 band at 8000 \AA , should be detectable in stellar and planetary atmospheres. Various authors, for example Zwicky (153), have suggested a search for the pure rotational transitions by interstellar H_2 .

H_2 in its ground state possesses no fine structure and no hyperfine structure, and hence no radio spectrum like that of H. However, as pointed out in Section 4.1.2, H_2 in the first excited rotational level ($I=1, J=1$) is split into three sublevels ($F=0, 1, \text{ and } 2$), 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 ("ultrafine" structure). 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 J . The precise location of the transitions in the $I=1, J=1$ level has been the subject of still inconclusive theoretical studies. Observation of H_2^+ , utilizing emission between the hyperfine states [Burke (14)], is most likely in regions where strong stellar ultraviolet is acting on interstellar H_2 regions.

Various continua are associated with the H_2 molecule. Photoionization occurs for $\lambda < 804 \text{ \AA}$, while photodissociation through an excited state of atomic H occurs for $\lambda < 849 \text{ \AA}$. Both are permitted transitions, and interstellar H_2 would cause observable absorptions in early-type stellar spectra were it not that they are swamped by the photoionization continuum of atomic H ($\lambda < 912 \text{ \AA}$). 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 strongly forbidden. A crude estimate for the cross section at around 1500 Å is 10^{-26} cm², according to Gould & Salpeter (49). This is barely possible to detect even in planetary atmospheres.

The Rayleigh cross section has been determined experimentally by Heddle (53) to be 2.1×10^{-24} cm² at 1216 Å and the Raman cross section has been calculated by Dalgarno & Williams (19) to be 1.1×10^{-25} cm² at the same wavelength. While both cross sections are much smaller at longer wavelengths, they may contribute to the visual albedo of the major planets, and to opacity of stellar atmospheres.

Wildt (147) suggested that quasi-molecular hydrogen might provide a significant source of opacity in stellar atmospheres for $\lambda < 2000$ Å. The process involves a transition from the lowest (repulsive) triplet state to an excited triplet state. 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 & Van Kranendonk (96). According to Gaustad (40), and Trafton (137), 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 (4). 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 (see Section 1.1.4). Free-free transitions by electrons in atmospheres abundant in H_2 contribute significantly to the continuous opacity.

1.1 THE HYDROGEN MOLECULES

1.1.1 *The structure of H_2 .*—The potential energy curves of the first few states of H_2 are illustrated in Figure 1. The total energy is plotted against internuclear distance r ; at $r = \infty$, the energy corresponds to that of two separate hydrogen atoms.

The notation used for electronic states is in direct analogy with that used for atoms [Herzberg (56)]. The notation for angular momenta is that introduced in 1953 by Jenkins (64); N replaces the former K (total angular momentum excluding all spins), and R replaces the former N (rotation of the nuclei). Note that, unless $\Lambda = 0$, R is not a proper quantum-mechanical angular momentum [Herzberg (56, p. 116)]. For light molecules, Russell-Saunders coupling applies and the total spin angular-momentum quantum number for two electrons takes values $S = 0$ or 1; the value of $2S + 1$ is a left superscript to the term symbol. The total electronic orbital angular momentum L is strongly coupled to the nuclear axis, and states are specified by the value of the projection

$$\Lambda = |L \cdot \mathbf{k}| \quad 1.2.$$

where \mathbf{k} is the unit vector along the nuclear axis. States with $\Lambda = 0$ are Σ

POTENTIAL ENERGY CURVES OF HYDROGEN

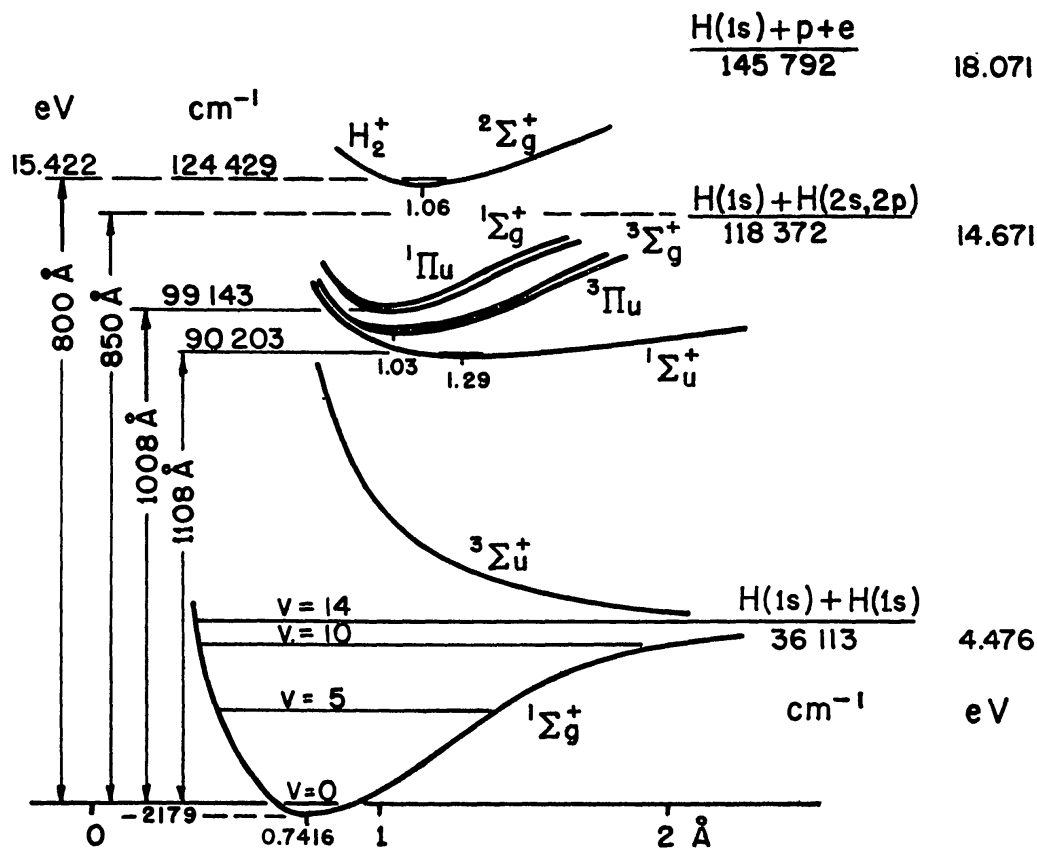


FIG. 1. Potential energy curves (schematic) of the ground state and lowest excited states of hydrogen. Excitation, dissociation, and ionization energies are shown relative to the $v=0$ level of the ground state.

states; $\Lambda=1$, Π states; $\Lambda=2$, Δ states; and so on. The subscript g or u and, for Σ states, the superscript $+$ or $-$ are concerned with symmetry properties of the electronic wave function. In H_2 , all known Σ states have Σ^+ symmetry.

The various electronic states are labeled alphabetically, with capital letters for singlet states and lower case letters for triplet states: thus, the ground state of H_2 is $X\ ^1\Sigma_g^+$ and the repulsive lowest triplet state is $b\ ^3\Sigma_u^+$.

Each electronic state possesses a set of vibration-rotation levels, corresponding to the motion of the nuclei. The various angular momenta in a molecule may combine in several ways; for the lowest states of H_2 , Hund's case b coupling applies, with a small admixture of case a for triplet states with $\Lambda \neq 0$. In case b coupling, the angular momenta of electron orbital motion L , nuclear rotation R , and electron spin S , combine as

$$\Lambda k + R = N, \quad N + S = J \quad 1.3.$$

TABLE I
THE GROUND STATE OF H₂

N	Space symmetry	Nuclear spin	Modification
Even	$+, s$	$a, I=0$	Para
Odd	$-, a$	$s, I=1$	Ortho

The quantum number N takes values $\Lambda, \Lambda+1, \Lambda+2, \dots$. The term value [$T(\text{cm}^{-1}) = E(\text{erg})/hc$] is given by

$$\begin{aligned}
 T(N, v) = & \omega_e(v + \frac{1}{2}) + B_e N(N + 1) \\
 & - \omega_e x(v + \frac{1}{2})^2 - D_e N^2(N + 1)^2 \\
 & - \alpha_e(v + \frac{1}{2})N(N + 1) + \dots
 \end{aligned} \tag{1.4}$$

referred to the electron potential minimum as zero. Here $v=0, 1, 2, \dots$ is the vibrational quantum number. Note the presence of zero-point energy, when $v=N=0$. The coefficients are determined empirically, as discussed in Section 3. If $S \neq 0$, there is a small energy difference between states of the same N but different J ; this is sometimes called ρ -type splitting. In Hund's case a , N is not defined and is to be replaced in Equation 1.4 by J , the total angular momentum excluding nuclear spin.

For a molecule such as H₂, whose nuclei are identical fermions, the total wave function must be antisymmetric with respect to interchange of the nuclei. A symmetric (s) space function goes with an antisymmetric (a) spin function, and vice versa. For H₂, the total nuclear spin is $I=0$ or 1. Table I shows the relations in the ground electronic state. The statistical weight is $(2N+1)(2I+1)$. The $+$ and $-$ in Table I refer to the behavior of the total wave function on *inversion*, simultaneously replacing \mathbf{r} by $-\mathbf{r}$ for every particle, and are not to be confused with the Σ^\pm symmetry. For states with $\Lambda \neq 0$, there is for each J a twofold degeneracy, with one positive and one negative component, which is removed with increasing rotation. This is Λ -type doubling.

There have been many calculations of the electronic wave function and energy for the ground state of H₂ [Slater (107)]. The object usually has been to test the validity of various approximate wave functions before applying them to more complicated systems; a similar use has been made of H₂⁺. The best results for H₂ itself are obtained by the method of James & Coolidge (61), in which the interelectron distance appears explicitly in the wave function; the most accurate function of this type is that obtained by Kolos & Roothaan (68).

1.1.2 *Transitions*.—The selection rules for electric dipole transitions between electronic states are

$$\Delta\Lambda = 0, \pm 1 \quad 1.5.$$

and

$$\Delta S = 0 \quad 1.6.$$

together with the symmetry rules

$$g \longleftrightarrow u, \quad g \longleftarrow \uparrow \rightarrow g, \quad u \longleftarrow \uparrow \rightarrow u \quad 1.7.$$

and

$$\Sigma^+ \longleftrightarrow \Sigma^+ \quad \Sigma^- \longleftrightarrow \Sigma^-, \quad \Sigma^+ \longleftarrow \uparrow \rightarrow \Sigma^- \quad 1.8.$$

Transitions forbidden by 1.5 and 1.7 may be allowed as magnetic dipole or electric quadrupole transitions, but with relatively much smaller probabilities [Garstang (39)].

It follows that the first allowed electronic transitions from the ground state $X \ ^1\Sigma_g^+$ are to the $B \ ^1\Sigma_u^+$ state at 11.2 eV (Lyman bands) and to the $C \ ^1\Pi_u$ state at 12.3 eV (Werner bands), and that the first allowed transition from the repulsive $b \ ^3\Sigma_u^+$ state is to the $a \ ^3\Sigma_g^+$ state. The $v=0$ level of the $^3\Pi_u$ state is metastable, decaying by magnetic dipole transitions to $b \ ^3\Sigma_u^+$ with an estimated lifetime of order 10^{-3} seconds [Lichten (71)]. The $v \geq 1$ levels of this state lie above the lowest vibration level of $a \ ^3\Sigma_g^+$ and so are not metastable.

Electronic transition integrals have been calculated by Shull (106), by Ehrenson & Phillipson (29), and by Peek & Lassette (95). The vibrational Franck-Condon factors have been considered by Patch (93) and Nicholls (87). These calculations are largely confined to the Lyman and Werner systems.

In an electronic transition, there are no selection rules for the vibrational quantum number; the probabilities of transition are determined by the overlap of the vibrational wave functions, in accordance with the Franck-Condon principle. The rotational selection rules depend on the particular angular-momentum coupling schemes which apply in the two states. In Hund's case b , the selection rules for electric dipole radiation are

$$\Delta J = 0, \pm 1; \quad 0 \longleftarrow \uparrow \rightarrow 0 \quad 1.9.$$

and

$$\Delta N = 0, \pm 1; \quad \Delta N \neq 0 \text{ for } \Sigma \longleftrightarrow \Sigma \quad 1.10.$$

and there is also the strict nuclear-symmetry rule

$$s \longleftrightarrow s, \quad a \longleftrightarrow a, \quad -s \longleftarrow \uparrow \rightarrow a \quad 1.11.$$

Within the ground state of H_2 , all rotation-vibration transitions are forbidden for electric dipole radiation, in three ways. Since this is a Σ state, Equation 1.10 becomes $\Delta J = \pm 1$, but these transitions violate Equation 1.11, as is seen from Table I, and so they are forbidden by the rotational selection rules. Secondly, dipole transitions are forbidden by the vibrational selection rules since H_2 does not have a permanent electric dipole moment, and thirdly, the electronic selection rule 1.7 is violated. The magnetic dipole moment $-(L+2S)e\hbar/2mc$ also is zero for this state, but electric quadrupole

transitions can occur— H_2 has a permanent quadrupole moment, $g \leftrightarrow g$ is allowed, and the rotational selection rule is

$$\Delta J = 0, \pm 1, \pm 2; \quad 0 \leftarrow \text{---} 0, \quad \frac{1}{2} \leftarrow \text{---} \frac{1}{2}, \quad 1 \leftarrow \text{---} 0 \quad 1.12.$$

Sets of transitions between two vibrational levels with $\Delta J = -2, -1, 0, +1$ and $+2$ are called respectively the *O*, *P*, *Q*, *R*, and *S* branches of the band, so in this case *O*, *Q*, and *S* branches can occur. One speaks of the $O(J)$ line, J referring to the lower state, and of the $v' \leftarrow v''$ band; the upper state always comes first and the sense of the arrow indicates emission or absorption.

The quadrupole transition probabilities for vibrational bands were calculated by James & Coolidge (62) and the results revised by Rank et al. (101) using the electronic wave function of Kolos & Roothaan (68). Results for the $S(1)$ line are in Table IV (cf. Section 2.1). The revised results are in only moderate agreement with experiment [Rank et al. (100)], but James & Klemperer (63) have pointed out that intensities for $S(1)$ are reduced by a factor 0.682 with allowance for the effect of rotation-vibration interaction; when this factor is applied to the results of Rank et al. (101), the agreement with experiment is improved.

For quadrupole rotational transitions within the lowest vibrational level, the transition probability has been calculated by Spitzer (121) to be

$$A(J \rightarrow J - 2) = 7.52 \times 10^{-13} \frac{J(J-1)(2J-1)^4}{2J+1} \text{sec}^{-1} \quad 1.13.$$

(This would be slightly modified if the new quadrupole moments calculated by Kolos & Roothaan were used.) The small perturbation caused by the nuclear spin-rotation interaction permits dipole transitions to occur but with much reduced probability. Wigner (146) estimated the order of magnitude to be 10^{-10}sec^{-1} , comparable to the value $2.44 \times 10^{-11} \text{sec}^{-1}$ for $J=2$ in Equation 1.13, but he was simply concerned with demonstrating that the process is slow in comparison with ordinary laboratory processes and he deliberately overestimated every factor. More realistic numbers in his formula give a much smaller result, and an accurate calculation by Raich & Good (98) has yielded

$$A(J \rightarrow J - 1) = 6 \times 10^{-20} \frac{J^6}{(2I+1)(2J+1)} \text{sec}^{-1} \quad 1.14.$$

I being the total nuclear spin of the upper level; this equals $8 \times 10^{-19} \text{sec}^{-1}$ when $J=2$.

Dipole transitions can occur because of the distortion caused by external perturbations of the molecule, such as the interaction with other molecules in a gas under a pressure of several atmospheres or the interaction with an applied electric field.

1.1.3 *Isotope effects.*—The properties of the molecule HD differ from those in H_2 in three ways: rotation and vibration energy levels are different; rotation and vibration transition probabilities are different—in particular,

TABLE II
PURE ROTATION TRANSITIONS IN THE GROUND STATE, $v=0$

J	H_2		HD	
	$\lambda(\mu)$	Transition	$\lambda(\mu)$	Transition
2-1	42.4	Induced Dipole	56.2	Dipole
1-0	84.4		112.1	
2-0	28.2	Quadrupole		

certain transitions are allowed as electric dipole transitions in HD which are forbidden in H_2 ; and interactions involving the nuclear spin are different (see Section 4). The electronic potential energy curves, symmetry properties, and selection rules depend only on the charge of the nuclei and not on the mass and so are completely unaltered.

The rotation-vibration structure is very different in the two cases, as is seen on comparing entries in Table V (cf. Section 3.1); some of the infrared wavelengths are compared in Table II. Within an electronic level, vibrational transitions are weakly allowed since HD has a small permanent electric dipole moment; this is the case for all heteronuclear molecules—the center of mass and the center of charge do not coincide. Further, for a heteronuclear system the nuclear a -s symmetry does not arise and the selection rule 1.11 is absent, so that dipole rotational transitions with $\Delta J = \pm 1$ can occur, both in vibrational bands and in the pure rotation spectrum. The electronic selection rule 1.7 still is violated for dipole transitions; by itself it is not a very rigorous rule and the dipole transitions are observed [Durie & Herzberg (27)].

1.1.4 *Molecular ions and polyatomic systems.*—The system H_2^+ is well known in the laboratory and is of theoretical interest because it is a one-electron system, so that the wave function can be obtained exactly in the fixed-nuclei approximation. The exact electronic wave functions for a number of states have been tabulated by Bates, Ledsham & Stewart (7) and the various electronic transition probabilities calculated; references are given by Nicholls & Stewart (88). Quadrupole rotation-vibration transitions and dipole transitions in isotopic species have been studied by Bates & Poots (9). Little is known about H_2^- . First reported with certainty by Khvostenko & Dukel'skii (66), its existence has been confirmed by other workers [Ionescu (60) and references there; Carter & Davis (16)] but the theoretical position is one of complete uncertainty. Davidson (22) pointed out a fundamental error in the earlier calculations which had predicted a stable ground state ($^2\Sigma_u^+$) and the calculation of Taylor & Harris (135) showed this state to be definitely unstable. It seemed that the observed ions must be in the $^4\Sigma_u^+$ state, predicted by Fischer-Hjalmar (31) to have a metastable minimum,

but later calculations by Taylor & Gerhausen (134) have failed to confirm this prediction. Thus, although H_2^- is known to exist, there is no certain theoretical knowledge of any bound state.

A number of polyatomic hydrogen molecules and ions are known to possess stable configurations: H_3 , H_3^+ , H_4^+ , and H_5^+ have all been observed. Little is known of the properties of these systems and we do not consider them further. However, they may be important under certain conditions—for example, the abundance of H_3^+ may considerably exceed that of H_2^+ in interstellar H_2 clouds [Martin, McDaniel & Meeks (75)].

2. HYDROGEN MOLECULES IN ASTROPHYSICS

(by G. B. Field)

2.1 PLANETARY ATMOSPHERES

Herzberg (55) 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 & Kiess (67) in the spectrum of Jupiter. In the meantime, however, Herzberg (57) had already identified a 35-Å wide feature at 8270 Å discovered in spectra of Uranus and Neptune by Kuiper (69) as the $S(0)$ line of the pressure-induced 3–0 vibration-rotation band. Spinrad (114, 115) has recently found the $S(0)$ line of the pressure-induced 4–0 band at 6420 Å in the spectrum of Uranus.

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

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 (150, 151) led to a value of N (the number of molecules in a square centimeter column above the clouds of Jupiter) equal⁵ to 4.6 km Am, and a rotational temperature between 170°K and 200°K. Most recently Foltz & Rank (33) have estimated that N on Jupiter may be 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 threefold range.

The first step is to establish the intrinsic strength of the strongest line of

⁵ 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.

TABLE III
QUADRUPOLE LINES IN PLANETS

I. Jupiter				
Band	Line	λ (Å)	Equivalent width (mÅ)	Authors
3-0	$S(0)$	8272.7	40	a, b
			31	c
	$S(1)$	8150.7	80	a, b
			34	c
	$S(2)$	8046.4	7:	a, d
4-0	$Q(1)$	8497.5	Trace	a
	$S(0)$	6435.0	Blended	c
	$S(1)$	6367.8	8 ± 2	c
	$Q(1)$	6567.7 (predicted)	≤ 3	c
II. Saturn				
Band	Line	λ (Å)	Equivalent width (mÅ)	Authors
4-0	$S(0)$	6435.0	10:	e, f
	$S(1)$	6367.8	10:	e, f
III. Uranus				
Band	Line	λ (Å)	Equivalent width (mÅ)	Authors
4-0	$S(0)$	6435.0	Detected	c
	$S(1)$	6367.8	Detected	c

a Kiess, Corliss & Kiess (67)

b Zabriskie (151)

c Spinrad & Trafton (119)

d Zabriskie (150)

e Münch & Spinrad (83)

f Spinrad (115)

Table III, 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

$$\tau_\nu = \alpha_\nu \int \rho ds = \alpha_\nu N (\sec Z_\odot + \sec Z_\oplus) \quad 2.1.$$

TABLE IV
STRENGTHS OF $S(1)$ QUADRUPOLE LINES
 $10^3 S_0$ ($\text{km}^{-1} \text{Am}^{-1} \text{cm}^{-1}$)

Band			Source	
1-0	2-0	3-0	Experimental or theoretical	Author
73	12	1.1	E	Rank, Fink, Foltz & Wiggins (100)
29	27	7.7	T	James & Coolidge (62)
120	24	3.3	T	Rank, Rao, Sitaram, Slomba & Wiggins (101)
82	16	2.3	T	James & Klemperer (63) + (101)

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

$$S = \int \tau_\nu d\nu = S_0 N (\sec Z_\odot + \sec Z_\oplus) \quad 2.2.$$

where

$$\begin{aligned} S_0 &= \int \alpha_\nu d\nu = 2.69 \times 10^{24} \frac{n_1}{n} \int \sigma_\nu d\nu \\ &= 2.69 \times 10^{24} \frac{n_1}{n} \frac{h\nu}{c^2} B \end{aligned} \quad 2.3.$$

The quantity S_0 has units $\text{km}^{-1} \text{Am}^{-1} \text{cm}^{-1}$ 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 $J=1$ 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). We shall adopt $S_0 = 1.1 \times 10^{-3} \text{km}^{-1} \text{Am}^{-1} \text{cm}^{-1}$ for the 3-0 $S(1)$ line from Table IV.

The mean of the equivalent widths measured in the spectrum of Jupiter is $49 \text{m}\text{\AA}$ (weighting Spinrad & Trafton two and Kiess, Corliss & Kiess one on the basis of number of plates taken). This value (which is uncertain by about 50 per cent) is 2.2 times the rms Doppler width at 170°K [estimated temperature of clouds according to Zabriskie (115)], and corresponds to a frequency width of $7.4 \times 10^{-2} \text{cm}^{-1}$. One finds from Equation 2.2 that $N = 20 \text{km Am}$, 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_0 used in the reduction must be corrected from that at 300°K according to Equation 2.3, by multiplying by 1.08, which is the ratio of the fraction of molecules in $J=1$ at 170°K to that at 300°K .)

This abundance of H_2 is a lower limit because it omits the effects of satura-

tion, but even it is 4.4 times Zabriskie's estimate, largely because he relied on James & Coolidge's value of S_0 , which is incorrect according to newer data (Figure 2). From the curve of growth for Doppler broadening [Unsöld (138, 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 (23) and experimentally verified for the 1-0 quadrupole band by Rank & Wiggins (102). 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 & Wiggins found that the measured width of the 1-0 $S(1)$ line was only 75 per cent of the pure Doppler width when the density was 1.5 Am. The density of H_2 alone at the cloud level of Jupiter would be N/H , or about 1.5 Am for a scale height $H=20$ km ($\mu=3$), so that a 25 per cent 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 tentative, however, and is mentioned only to indicate the care that will be needed in the interpretation of future observations of this kind. If "colli-

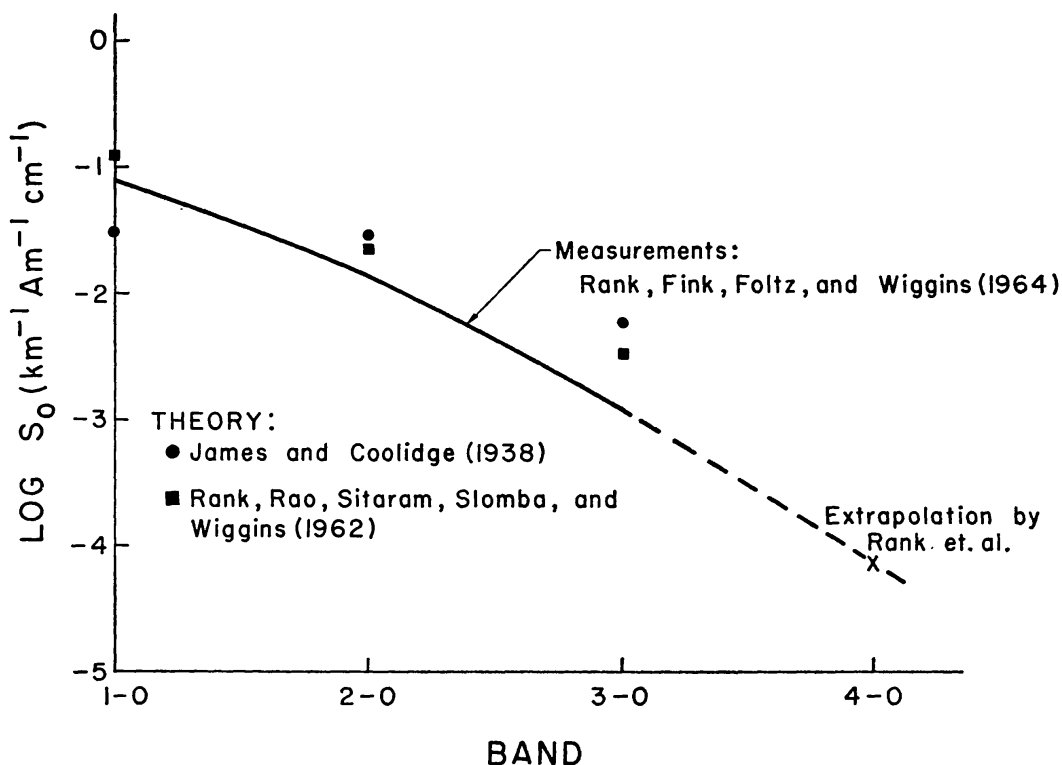


FIG. 2. Strengths of the $S(1)$ quadrupole rotation-vibration lines as a function of band designation. Curve represents measurements, points are theoretical.

sional narrowing" is indeed present it will result in a greater degree of saturation and even more uncertain abundance estimates.

We now consider the 4-0 band, the detection of which led Foltz & Rank (33) to suggest values of N up to 270 km Am. Their high estimates occur because the extrapolation of laboratory measurements of S_0 from lower overtones up to the 4-0 band suggested that it should be extremely weak. Revised estimates by Rank et al. (100) give S_0 (300°K) for the 4-0 line as $7.4 \times 10^{-5} \text{ km}^{-1} \text{ Am}^{-1} \text{ cm}^{-1}$, equivalent to 8.0×10^{-5} at 170°K (see Figure 2). The observed equivalent width is $2.0 \times 10^{-2} \text{ cm}^{-1}$, which with Equation 2.2 yields $N = 80 \text{ km Am}$, 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 on an extrapolation to find S_0 , but also because of an anomaly in the observed relative strengths of $S(1)$ and $Q(1)$ (Table III). The observed ratio of $S(1)$ to $Q(1)$ is >2.7 . The "classical" ratio given by James & Coolidge (62) 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 & Klemperer (63)]. Hence the discrepancy is considerable, and although one possibility may be blending of the $Q(1)$ line with solar $H\alpha$ [Spinrad (117)], part of the difficulty may be 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 (1) we find that the optical depth is

$$\tau(H_2) = \frac{2.4 \times 10^{-4}}{\lambda^4} N \quad 2.4.$$

where λ is in microns. Öpik (90) suggests that the contrast on photographs of the planet indicates a total optical depth of 0.25 at 0.4μ for the atmosphere above the clouds. The data of Gehrels & Teska (42) suggest even lower values. Stecher's rocket measurement of the ultraviolet albedo (126) fits a model which would have an optical depth of 0.1 at 0.4μ . Since other components may contribute to the scattering, it is legitimate to consider 0.25 as an upper limit to $\tau(H_2)$ at 0.4μ . This implies $N < 27 \text{ km Am}$.

We may also obtain crude information from the absence of the pressure-induced dipole lines in the spectrum of Jupiter. The blended feature at $\lambda 8166$ in the laboratory spectrum [Herzberg (57)] is due mostly to double transitions (1-0 and 2-0) in which the colliding partners are both H_2 molecules. From Hare & Welsh (52) we may write for the central optical depth in this feature

$$\tau = \frac{\rho^2(H_2) L \alpha}{\Delta \nu} \quad 2.5.$$

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). From inspection of Herzberg's spectra, α is estimated to be roughly $0.05\text{ km}^{-1}\text{ Am}^{-2}\text{ cm}^{-1}$. The absence of the feature in the Jovian spectra of Kiess et al. (67) suggests that $\tau < 1$, which, using Equation 2.5 with $H=20\text{ km}$ ($\mu=3$), implies that $N=\rho H < 150\text{ km Am}$. If, as Öpik (90) suggests, helium is far more abundant in Jupiter than in the sun (42 times H_2 by number), one might expect to see the $\lambda\ 8270$ 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 $0.004\text{ km}^{-1}\text{ Am}^{-2}\text{ cm}^{-1}$ for pure H_2 , and half as large for an atmosphere dominated by helium. The line width would be 66 cm^{-1} and H would be 14 km in this case. The observation that $\tau < 1$ then implies $N(\text{H}_2) < 80\text{ km Am}$. Both upper limits are consistent with what has been stated above, and the latter indicates that refined observations of both the quadrupole lines and the pressure-induced dipole lines may provide a test of Öpik's hypothesis of helium enrichment.

We have shown that all data are consistent with $N(\text{H}_2)$ between 30 and 80 km Am, but that the absence of strong Rayleigh scattering indicates that 30 km Am is the most likely value. [Stecher (128) points out that if particles mixed evenly with the H_2 contribute to the scattering, the optical path, and hence the apparent quadrupole absorption, can be increased over that appropriate for a distinct reflecting surface. If such is the case, as suggested by Münch, N might in fact be closer to 10 km Am.] Since $N(\text{CH}_4)$ is 0.15 km Am [Kuiper (70)], a nuclear abundance ratio of $\text{H}/\text{C}=400$ is indicated. This agrees with the contention of Spinrad & Trafton (119) that hydrogen is deficient in Jupiter, since the solar ratio is 1900 [Goldberg, Müller & Aller (45)]. The latter ratio is supported by a precise spectroscopic determination of $\text{H}/\text{O}=1040$ (41) and a determination of $\text{O}/\text{C}=1.7$ in solar cosmic rays (11). 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 $N(\text{H}_2)$ up to 80 km Am and hence H/C up to 1100 in Jupiter, not far from the solar value.

Owen (92) tried to detect the 4-0 $R(0)$ and $P(1)$ lines of HD at 7377 \AA and 7464 \AA respectively in the spectrum of Jupiter. By comparing with plates taken through 1 km Am by Durie & Herzberg (27), he deduced an upper limit of 0.5 km Am from the absence of these lines in Jupiter. The resulting lower limit of H/D is 120 if we adopt 30 km of H_2 —still far below the terrestrial value, 6400. The dipole moment of 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 (94), 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 (90) argues that this heat from Jupiter has in fact been detected radiometrically, since the observed temperature of 128°K due to Murray, Wildey & Westphal (84) 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 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 - ρ relations are adequate for the problem at hand, questions arise concerning its validity for pressures above 10^3 atm. Although 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, high pressure, or both), and ionization of both molecules and atoms (because of high temperature, high pressure, or both).

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 (140), 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 per cent dissociation at 3×10^4 atm (3900°K), and 10 per cent at 10^5 atm (6600°K). A recent study of the pressure dissociation of H_2 at high pressures by Vardya (143) shows that a significant increase in dissociation will occur at 10^5 atm. A rough calculation indicates 30 per cent dissociation at that point on Peebles' adiabat. Γ could be significantly reduced by this effect, and more calculations are needed.

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' assumption is to estimate the radiative flux that is appropriate for his assumed temperature gradients (2–3 degrees per km in the 10^4 – 10^5 atm pressure range). If this exceeds the "observed" 10^4 erg cm^{-2} sec^{-1} (certainly an upper limit in any case), one may conclude that convection is not necessary and that a lower temperature gradient would suffice.

To do this calculation one needs accurate opacity tables for the conditions of interest. The only opacity data available at present are those of

Vardya (142), calculated 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 per cent 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 $10^4 \text{ erg cm}^{-2} \text{ sec}^{-1}$ along Peebles' curve 5 for an extended range below 1750 km depth (where the pressure is $3 \times 10^4 \text{ atm}$ and the temperature is 3900°K). This suggests that the assumption of a convective atmosphere should be re-evaluated using accurate opacities (including contributions from translational absorption).

A related investigation by Trafton (137) treats the upper atmosphere of Jupiter ($p \simeq 1 \text{ atm}$). 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.

2.2 STELLAR ATMOSPHERES

As previously stated, the electronic transitions of H_2 will be difficult to detect in stellar atmospheres, because the cool atmospheres containing H_2 emit very little light in the extreme ultraviolet where the transitions are 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 (116, 117) has detected the 2-0 $S(3)$ line in $\alpha \text{ Ori}$, $\circ \text{ Cet}$, and R Aql , and the 2-0 $S(2)$ line in $\alpha \text{ Ori}$ in the 1.2 micron region. H_2 abundances above the photosphere are estimated very roughly to be 10^{26} molecules/cm². As in the case of planets, such measures may ultimately give good information on H_2 abundance and on temperature. In $\circ \text{ Cet}$, Spinrad finds total half-intensity widths up to 1 Å, which he attributes to turbulence.

Erkovich (30) made further calculations on the quasi-molecular ($H+H$) absorption which had been suggested by Wildt (147). The problem was discussed by Zwaan (152), 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 (125) came to similar conclusions, finding that a discrepancy 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 & Terashita (76) 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. However, Solomon (108) has made a more accurate calculation of the cross section, obtaining a value only 1 per cent of Erkovich's. This makes the process 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 prob-

ably not be important in any star. Soshnikov (113) has independently arrived at similar conclusions.

Another phenomenon attributed to quasi-molecular effects is the remarkable deviation of the flux of B stars from black-body curves in the region 1500 Å to 3000 Å found by the early rocket experiments. Meinel (78) postulated that the inverse process of quasi-molecular 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 (127)] 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 that 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 (110), which averaged about 1/3 of the corresponding values for H^- . The total opacity for $p_e=0.03$ dynes cm^{-2} and $T=3000^\circ K$ was increased 9 per cent by H_2^- . H_2^+ , calculated from Bates (4), was found to make minor contributions (up to 5 per cent at 6300°K). Similar results were found by Gingerich (44), 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 1.6μ , not far from the Planck maximum. This would lead to a sharp peak at 1.6μ if the opacity dip were not filled in by other processes, such as those involving H_2 , H_2^- , or other molecules such as H_2O . The peak at 1.6μ has recently been observed by Woolf, Schwarzschild & Rose (148). There is tentative evidence for additional continuous opacity at 0.9μ in M giants from the work on H_2O absorption lines by Spinrad & Newburn (118).

The calculations of Vardya (140), 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 anomalies in the calculated

dissociation fractions owing to inadequate knowledge of the thermodynamic functions of H_2 at high temperatures.

2.3 INTERSTELLAR SPACE

At this writing there is still no observational evidence that appreciable amounts of H_2 occur in interstellar space. The calculations of Gould, Gold & Salpeter (47), which predict a value of about unity for the H_2/H ratio, are uncertain by a factor of ten.

It might be thought that radiative association, $H+H\rightarrow H_2$, 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 & Salpeter (49), this rule can be violated only by singlet-triplet mixing. According to Section 4.1, 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 $H_{s-s}/H_0\sim\alpha^2$, 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 $\alpha^4\sim 10^{-9}$. 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^{-5} sec $^{-1}$. Although this is much larger than that of the quadrupole process, it still leads to an overall probability of only 10^{-9} . We conclude that arguments for H_2 abundance based on Equation 1.1, such as that of Zwicky (153), 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 (139) 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, in many cases, into ejecting the newly formed molecule from the surface. McCrea & McNally (77) 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 & Salpeter (49), 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 adsorbed 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). 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 γ 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 second in clouds, if a typical cloud density $n_H = 10 \text{ cm}^{-3}$ 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 & McNally. This would result in complete conversion into H_2 in several million years, approximately equal to the dynamical time-scale. Further discussions of H_2 formation and abundance have been given by Lambrecht & Schmidt (154) and by Knapp et al. (155).

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} erg 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 re-expansion 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. In fact, one can even visualize a dramatic cooling and squeezing of the cloud as the radiation from new molecules reduces the temperature and makes conditions favorable for further molecule formation. Detailed treatment of the problem should be undertaken.

Spitzer (120) 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 its photoionization continuum begins at 15.6 eV (see Figure 1). The photoionization of H leads to well-defined H II 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 H II region. This process has been analyzed by Gould, Gold & Salpeter (47), 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, because the cloud that it is in encounters an H II region. This number is not to be taken very seriously, however, as there are several complex phenomena involving the interaction of the high-pressure H II regions with the neighboring H I clouds which have not been taken into account. Furthermore, there are a number of processes which could be competitive with encounters with H II regions as destruction mechanisms. Gould & Salpeter revised an earlier estimate of Kahn's (65) for the dissociation by radiative excitation of the repulsive $^3\Sigma_u^+$ state, to a lifetime of 10^{10} years. Malville (74) points out that the forbidden transitions to the $^3\Pi_u$ state may occur faster, leading to dissociation through the relatively rapid transition $^3\Pi_u \rightarrow ^3\Sigma_u^+$. Solomon (109) 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 possible that the lifetime of H_2 against this process is smaller still.

If the calculations of Gould, Gold & Salpeter are correct, the time-scales for association and disassociation are comparable, so that one may expect the H_2/H ratio to vary substantially from cloud to cloud, being greater than 1 for clouds that have not encountered an H II region recently ("old" molecules) and less than 1 for those that contain "young" molecules. Hence the overall average of H_2/H is probably between 0.1 and 10, according to these authors. One is interested not only in the mean value of the ratio, but also in measurements on individual clouds. For example, evidence is accumulating that about 10 per cent of all clouds have recently encountered an H II region. These clouds, distinguished by high velocity (often directed away from an H II 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 rather than by thermodynamic equilibrium. 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. Herbig (54) has suggested that absorptions from this state to higher states might be responsible for the diffuse interstellar line at $4430\ \text{\AA}$, 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^{-2} of the H_2 molecules would have to be in the $c\ ^3\Pi_u$ state to account

for the strength of λ 4430 (even if $H_2/H \simeq 1$) and since the lifetime is about 10^{-3} seconds [Lichten (71)], the state would have to be excited about every 10^6 seconds. Herbig failed to find any excitation process more frequent than once every 10^{13} seconds. Malville (74) has confirmed this result, pointing out that if the molecules were located on the surface of a grain, the lifetime and hence the abundance of the $c^3\Pi_u$ state might be even smaller.

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; $A[1-0 S(0)] = 2.9 \times 10^{-7} \text{ sec}^{-1}$ from Table IV, for example. Although molecules may be vibrationally excited at the time of formation, the fraction which remains so at any time is negligible since formation proceeds on a much longer time-scale.

Collisional excitation is negligible inside cool clouds ($T \simeq 100^\circ\text{K}$) since $E(v=1)/k = 6300^\circ\text{K}$. In the heated regions behind the shocks formed by collisions of clouds, where $T = 5000^\circ\text{K}$ and $n_H = 40 \text{ cm}^{-3}$ 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 H I region would excite all rotational levels of the $v=1$ level at a rate equal to $1.4 \times 10^{12} \text{ sec}^{-1}$, according to Takayanagi & Nishimura (131). 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 stars which emit copious ultraviolet radiation. According to Osterbrock (91), 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 (many 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 $10^{-10} \text{ sec}^{-1}$, 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 $J=2$. Most authors have treated parahydrogen (J even) and orthohydrogen (J 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 & Salpeter (49),

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 $\frac{1}{4}$ 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 $\frac{3}{4}$ of the total, and para- H_2 (singlet) only $\frac{1}{4}$.

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— $v=0$, $J=0$ for the para- H_2 , and $v=0$, $J=1$ for the ortho- H_2 . Even though $J=1$ is overpopulated relative to the Boltzmann population at 10°K , molecules in $J=1$ cannot drop down to $J=0$ 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 near-by 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 $\frac{3}{4}$ 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 $\frac{1}{4}$ in $J=0$ and $\frac{3}{4}$ in $J=1$. Further decay to $J=0$ 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 (121). He formulated the situation as a balance among collisional excitation and de-excitation processes, and radiative de-excitation. The radiative rates (Einstein A 's) depend on the quadrupole moment of the molecule averaged over the $v=0$ vibrational wave function, and are given by Equation 1.13. The collisional rates were estimated only roughly by Spitzer. This deficiency has now been remedied by Takayanagi & Nishimura (131), who have calculated collisional excitation cross sections for H- H_2 collisions over a wide range of temperature. A typical excitation rate was $1.4 \times 10^{-9} \text{ sec}^{-1}$ (per unit H density) for $J=0 \rightarrow 2$ at 5000°K . They also explicitly solved the rather

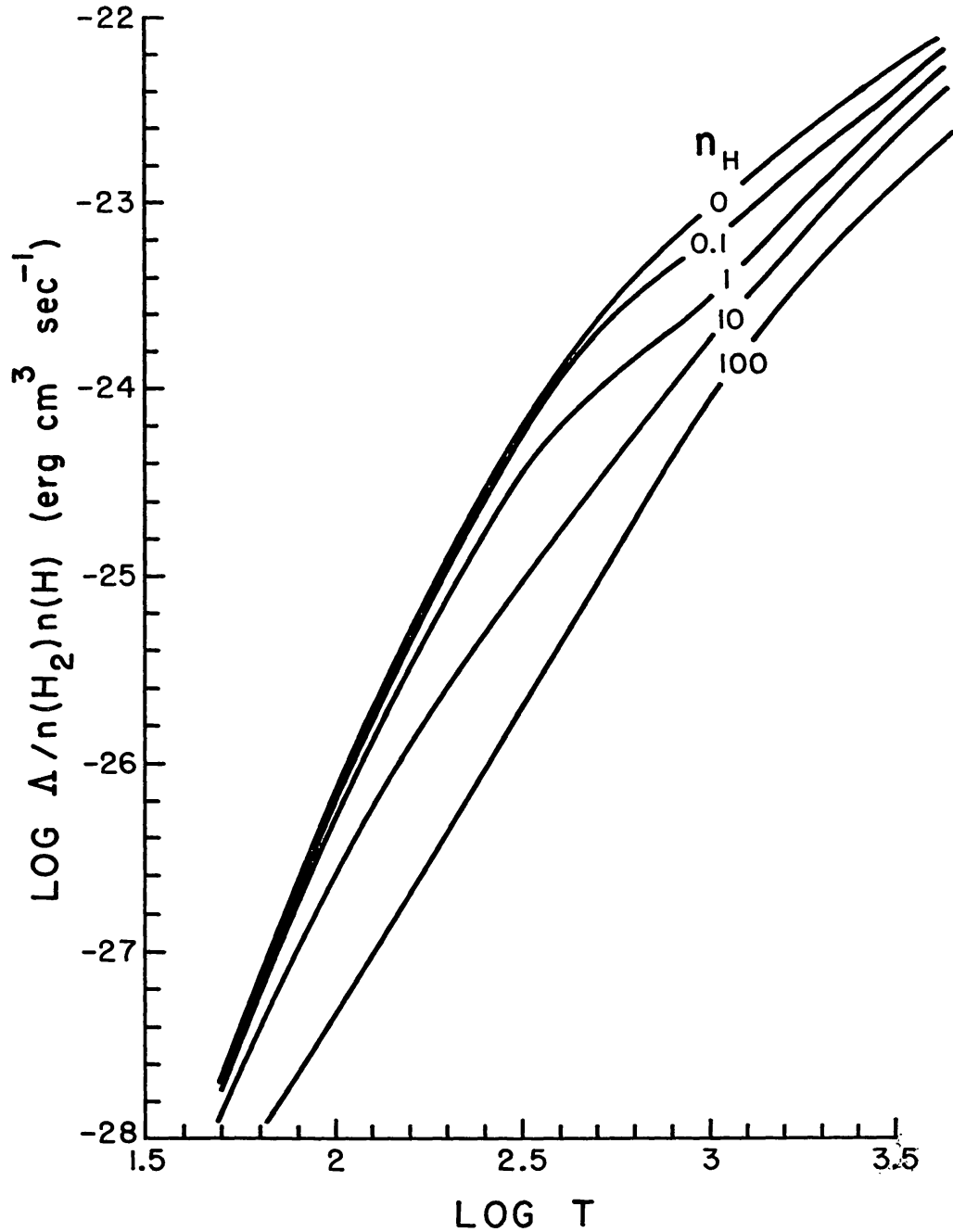


FIG. 3. Radiative loss per unit density of atoms and molecules for interstellar gas at various densities and temperatures. Note the large decrease in loss per atom as the atomic density is increased and the radiative de-excitations are quenched.

involved statistical equilibrium equations for all levels up to $J=8$ ($E/k = 6200^\circ\text{K}$) for $n_{\text{H}}=0.1$ 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 3, 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 & Nishimura, who point out that the atomic exchange reaction,



can go fairly rapidly in hot clouds where the atoms have enough energy to overcome the energy barrier involved in the reaction. According to Shavitt (104), the process goes at a rate approximately equal to $1.9 \times 10^{-11} \exp(-3000/T) \text{ sec}^{-1}$ per unit H density, so that the e -folding time for para-ortho conversion in a cloud with $n_{\text{H}} = 10 \text{ cm}^{-3}$ is 500 years at 3000°K , 3000 years at 1000°K , and 4 million years at 300°K . It appears that if the temperature in clouds following cloud collisions even approaches 1000°K , considerable ortho- H_2 will be generated in the million years or so that the temperature remains high. 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 $J=1 \rightarrow J=3$ has $E/k = 860^\circ\text{K}$.

We may mention a modification of Takayanagi & Nishimura's calculations proposed by Gould & Salpeter (49). They followed Osterbrock (91) in assuming that the radiative transition $J=2 \rightarrow J=1$, involving an ortho-para conversion, is much faster than the $J=2 \rightarrow J=0$ quadrupole transition. As we shall discuss below, however, Osterbrock's assumption of a high $2 \rightarrow 1$ rate is incorrect, so that Takayanagi & Nishimura's calculations are more nearly correct than Gould & 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 & Zabriskie (124), Spitzer, Dressler & Upson (123) have discussed the expected interstellar electronic absorption spectrum of H_2 in detail. Using Franck-Condon factors for the Lyman bands ($B \ ^1\Sigma_u^+ - X \ ^1\Sigma_g^+$) computed by Nicholls (87), they computed curves of growth for the $R(0)$ lines, in the bands 0-0 to 13-0. It was found that the 1-0 (λ 1092) and 4-0 (λ 1049) lines, which should be relatively unobscured by stellar features, should be measurable in a 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 an Orbiting Astronomical Observatory. These results have recently been revised somewhat by Solomon (109). His study of the Franck-Condon factors for the Lyman bands indicates that λ 1049 is

only 40 per cent as strong as found by using Nicholls' computations, and that the strongest lines are more likely to be the 7-0 (λ 1013) and 8-0 (λ 1002) lines. In addition, computations on lines in the Werner bands ($C^4\Pi_u \leftarrow X^2\Sigma_g^+$) show that the 1-0 (λ 986), 2-0 (λ 965), and 3-0 (λ 946) lines will exceed all other H_2 lines in strength. Of these, λ 946 seems to lie in the clearest region of the spectrum of stars earlier than B0, according to the calculations of Morton (82).

Vibrational transitions may be observable in the near infrared region. Gould & Harwit (48) have calculated that the intensity of 1-0 vibrational emission at 2.22μ ($J=2 \rightarrow 0$) and 2.12μ ($J=3 \rightarrow 1$) 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 as 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 Werner bands than on the number of molecules, since each ultraviolet 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 of the expected intensity from hot clouds have been made. 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 terrestrial absorption bands which prevail in the 10-100 μ region, although the $J=4 \rightarrow 2$ and $J=5 \rightarrow 3$ transitions, at 12 and 9.5 μ respectively, might be detectable from the ground. Zwicky (153) proposed searching for the 84.4 μ $J=1 \rightarrow 0$ transition. Zwicky gives a transition probability of $10^{-10} \text{ sec}^{-1}$ for the $1 \rightarrow 0$ transition—larger than the $2.4 \times 10^{-11} \text{ sec}^{-1}$ for the $2 \rightarrow 0$ quadrupole transition. He apparently bases this estimate on a remark by Wigner quoted by Bonhoeffer & Harteck (13). Revision of this estimate as explained in Section 1.1.2 shows that detection of the 1-0 line is impossible, as is that of the 2-1 line suggested by Osterbrock (91). This leaves the $2 \rightarrow 0$ quadrupole line at 28.2 μ , which proceeds with $A = 2.4 \times 10^{-11} \text{ sec}^{-1}$, and possibly higher lines with $\Delta J=2$. One might suppose on the basis of Equation 1.13 that going to higher rotational lines would be advantageous, since A increases rapidly with J . However, A ($2 \rightarrow 0$) 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 & Nishimura (132) have calculated that the expected 28- μ flux at the top of the atmosphere is $8 \times 10^{-5} n(H_2) \text{ erg cm}^{-2} \text{ sec}^{-1} \text{ ster}^{-1}$ in the galactic plane. This amount is marginally detectable with present techniques.

We finally consider the role of H_2 in star formation. McCrea & McNally (77) point out that in the earliest stages of condensation of interstellar matter

to form stars, H transforms into H₂ very rapidly for total densities above 10³ cm⁻³ owing to the greatly increased rate of recombination on grains above 10³ cm⁻³, so that the later stages of condensation are concerned mainly with molecular hydrogen. Gaustad (40) has studied the contraction to densities and temperatures such that H₂ is dissociated, and finds that for a protostar of one solar mass, the opacity of H₂ molecules (as well as all other opacities) is too small to prevent free-fall collapse beyond the H₂ dissociation point through the confinement of compressional energy and buildup of gas pressure. Less massive stars may be inhibited by pressure buildup in the earlier phase where interstellar grains are the opacity source, but free fall through the region where H₂ provides the opacity is indicated.

Cameron (15) has considered the contraction beyond the point where H₂ 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 a.u. (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 a.u. Hence, taken together, the work of McCrea & McNally, Gaustad, and Cameron indicates that the entire collapse of a cloud from about 1 pc to 1 a.u. radius can take place in free fall, H₂ exhibiting sufficient transparency in the early stages and sufficient heat capacity (including dissociation) in the later stages to prevent the buildup of pressure that would be needed to slow down the collapse. Of course, rotational and magnetic forces can be

TABLE V
VIBRATION-ROTATION STRUCTURE OF THE ELECTRONIC GROUND STATE
(all values in cm⁻¹)

	v	$T_v(J=0)$	B_v	D_v	H_v	References
H ₂	0	0	59.3392	0.04599	5.20×10^{-5}	129
	1	4161.167	56.3725	0.04392	4.15×10^{-5}	101, 103
	2	8087.135	53.4667	0.04218	3.84×10^{-5}	101, 103
	3	11782.366	50.6259	0.04088	3.64×10^{-5}	101, 103
	4	15250.36	47.8013	0.0397 ₁	3.50×10^{-5}	58
	5	18491.92	44.958 ₄	0.0385 ₄	$3.4_2 \times 10^{-5}$	58
Constants for the levels $v=6$ to $v=14$ are listed in (58)						
HD	0	0	44.668 ₇	0.0263 ₀	—	27
	1	3632.14 ₉	42.742 ₇	0.0254 ₄	—	27
	2	7086.88 ₈	40.838 ₈	0.0241 ₀	—	27
	3	10367.56 ₃	38.998 ₈	0.0244 ₃	—	27
	4	13476.87 ₆	37.140 ₁	0.0231 ₁	—	27

TABLE VI
THE 1-0 VIBRATION-ROTATION BAND OF H₂

<i>J</i>	<i>S</i> (<i>J</i>)	<i>Q</i> (<i>J</i>)	<i>O</i> (<i>J</i>)
0	4497.830 obs	4161.134 obs ^a	—
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

^a Raman effect.

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.

Gould (46) has also discussed the role of H₂ in star formation. He concludes that a protostar of 100 solar masses would radiate about 100 times the solar luminosity at 28 μ for about 10⁶ years. The flux from such an object at 500 pc might be detectable.

3. EXPERIMENTAL TERM VALUES

(by K. Dressler)

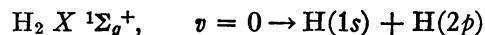
3.1 ROTATION—VIBRATION STRUCTURE OF THE GROUND STATE

There are 14 discrete vibrational levels associated with the electronic ground state of H₂. The lowest 5 to 10 rotational term values of all of these vibrational levels have been determined spectroscopically as indicated in Table V (58, 101, 103, 129), while information on HD is less complete (27, 129). The following relationship holds between the term values $T_v(J)$ and the constants given in Table V:

$$T_v(J) = T_v + B_v J(J + 1) - D_v J^2(J + 1)^2 + H_v J^3(J + 1)^3 \quad 3.1.$$

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 $J = 0 \rightarrow J = 0$ in the case of quadrupole radiation only. Table VI presents the wave numbers of the $v = 1 \leftarrow v = 0$ band of H₂ as observed by Rank et al. (101) at high pressure and as calculated from Rank's constants (cf. Table V). The $Q(0)$ line, which cannot occur as a quadrupole line, is given as observed by Stoicheff (129) in the Raman spectrum. Measurements at lower pressures and extrapolations of line frequencies to zero pressure were reported by Rank & Wiggins (103).

The most accurate experimental dissociation energies of H₂, HD, and D₂ are those derived by Herzberg & Monfils (59) from the measurement of the long-wavelength limit of continuous absorption near 850 Å, corresponding to the process



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

$$T_0(\text{H}_2) = 118372.1_{\pm 0.2_0} \text{ cm}^{-1}, \quad T_0(\text{HD}) = 118659.0 \pm 1.0 \text{ cm}^{-1}$$

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

$$D_0^0(\text{H}_2) = 36113.0_{\pm 0.30} \text{ cm}^{-1}, \quad D_0^0(\text{HD}) = 36399.9 \pm 1.0 \text{ cm}^{-1}$$

Herzberg & Monfils have computed a zero-point energy of $E_0(\text{H}_2) = 2179.27 \text{ cm}^{-1}$ for H_2 , and hence $D_e^0(\text{H}_2)$ as measured from the minimum of the potential curve becomes

$$D_e^0(\text{H}_2) = 38292.3 \pm 0.5 \text{ cm}^{-1}$$

Although the quantity D_e^0 is not directly measurable, it is useful when different isotopes are compared, since D_e^0 should be independent of nuclear mass. D_e^0 is also 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 & Monfils.

3.2 ELECTRONIC STRUCTURE

The potential energy curves of the seven lowest-lying electronic states of H_2 are illustrated schematically in Figure 1. Experimental term values for the $v=0$ levels of these and of all known higher excited states of H_2 are listed in Table VII which is arranged in the form of an energy-level diagram, ordering the states according to the configuration of the excited electron. Except for one state with a doubly excited configuration, all states are described by a configuration $1s\sigma_g n l \lambda$, where the n and l refer to the state at vanishing internuclear distance ("united atom"), and the molecular quantum number λ describes the orientation of l relative to the molecular axis (σ, π, δ denote $\lambda = 0, 1, 2$).

The term values listed in Table VII represent the lowest observable rotational and vibrational level of a given electronic state. Σ, Π , and Δ electronic states are therefore represented by their lowest $N=0, 1$, and 2 levels, respectively. In cases of Π and Δ states with Λ doubling, the component of lower energy is shown only. All triplet-state energies are taken from Dieke's convenient tables of H_2 energy levels (24). While Dieke's singlet-state energies were connected to the ground state on the basis of Tanaka's (133) and other early investigations in the vacuum ultraviolet, more recent work has resulted in more accurate and more extended information on the $^1\Sigma_u^+$ and $^1\Pi_u$ states of configurations $1s\sigma_g n p \lambda_u$, which are the states appearing in the absorption spectrum or in emission terminating in ground-state levels. Recent papers listing rotational and vibrational energy levels of these states are given in Table VIII.

The entries into Table VII for states listed in Table VIII are taken from the references listed in Table VIII except for the C state for which Dieke's

TABLE VII
EXPERIMENTAL TERM VALUES FOR $v=0$ LEVELS

n	$l=0$	$l=1$		$l=2$		
	$s\sigma_g$	$p\sigma_u$	$p\pi_u$	$d\sigma_g$	$d\pi_g$	$d\delta_g$
∞	124430 (H_2^+ , $^2\Sigma_g^+$)					
6			u 121517 $^3\Pi_u$			
5			D'' 120230 $^1\Pi_u$ n 120132 $^3\Pi_u$			
4		B'' 116886 $^1\Sigma_u^+$ f 111752 $^3\Sigma_u^+$	D' 117893 $^1\Pi_u$ k 117556 $^3\Pi_u$	p 117617 $^3\Sigma_g^+$ P 117410 $^1\Sigma_g^+$	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 $^3\Pi_u$	g 111948 $^3\Sigma_g^+$ G 111812 $^1\Sigma_g^+$	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 $^1\Sigma_g^+$ ($v=2$)			
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 $0^1\Sigma_g^+$					

value for the $v=0$ level was raised by 7 cm^{-1} following the observation that the more recently available values for the B , B' , and D states are 7 cm^{-1} higher than those adopted by Dieke in 1958. All remaining singlet states belong to g symmetry and their energies are connected to the “ u ” states of Table VIII by well-known emission frequencies in the visible region. Therefore the terms of all singlet states belonging to g symmetry were raised by 7 cm^{-1} relative to the values adopted in Dieke’s tables.

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 ionization limit. The spectroscopic ionization potential of H_2 , i.e. the energy difference between the $v=0$, $N=0$ levels of the ground states of H_2 and of H_2^+ , has been determined by Beutler & Jünger (10):

$$I(H_2) = 124429\text{ cm}^{-1}$$

The higher rotational and vibrational term values of the electronic states of Table VII are listed in Dieke’s tables (24) as far as they were known and well established in 1958, and in the papers listed in Table VIII for the states covered by that table.

The $F^1\Sigma_g^+$ state is described by the doubly excited electron configuration

TABLE VIII
RECENT WORK ON THE SINGLET STATES OF CONFIGURATION $1s, np$

State			v			Authors
			H ₂	HD	D ₂	
$5p\pi$	D''	${}^1\Pi_u$	0-2	0-2	0-2	a
$4p\pi$	D'	${}^1\Pi_u$	0-4 0	0-6	0-2	a b
$4p\sigma$	B''	${}^1\Sigma_u^+$	0-6 0	0-5	0-5	a b
$3p\pi$	D	${}^1\Pi_u$	0-14 0-2	0-8	0-15	a b
$3p\sigma$	B'	${}^1\Sigma_u^+$	0-6 0-9	0-5	0-8	a b
$2p\pi$	C	${}^1\Pi_u$	0-4 3-13 5-14	4-11	5-17	c d e f
$2p\sigma$	B	${}^1\Sigma_u^+$	0-13 14-35 17-37	18-34	21-44	g d e f

- a Monfils (81)
- b Namioka (86)
- c Dieke (24)
- d Monfils (79)
- e Namioka (85)
- f Monfils (80)
- g Herzberg & Howe (58)

$(2p\sigma_u)^2$. The rotational and vibrational structures of the lowest levels of that state indicate a very shallow potential curve with a minimum at a very large internuclear distance ($\sim 2.3 \text{ \AA}$ compared to $\sim 1.0 \text{ \AA}$ in states of Rydberg series $1s\sigma_g n l \lambda$). The potential energy curve of the F state can be thought of as crossing, in a very low order of approximation, the potential curves of many of the other excited states. 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 tables list 19 vibrational levels associated with a large internuclear 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 configurations $1s\sigma_g n s\sigma_g$.

4. THEORETICAL RESULTS

(by W. B. Somerville)

4.1 FINE AND HYPERFINE STRUCTURE

4.1.1 *Theory*.—The interactions between the various angular momenta and moments of the particles in a molecule produce small splittings of the energy levels. Fine structure is caused by the interaction between electronic angular momenta; the ‘ ρ -type’ splitting due to the interaction of \mathbf{S} and $\Delta\mathbf{k}$ is a fine structure. Interactions involving nuclei give rise to hyperfine structure. A nucleus with spin $i \geq 1$ has an electric quadrupole moment and this produces an electric quadrupole hyperfine structure.⁶ This is absent from H_2 , since $i = \frac{1}{2}$ for the proton, but present in HD and D_2 , since $i = 1$ for the deuteron. There are also magnetic-dipole hyperfine interactions between \mathbf{I} and \mathbf{S} and between \mathbf{R} (nuclear rotation) and \mathbf{S} . The Λ -type doubling produced by the interaction of \mathbf{L} and \mathbf{R} also is hyperfine in nature; however, the term hyperfine is often reserved for interactions involving the nuclear spin. There is also a much weaker interaction between \mathbf{I} and \mathbf{R} .

These energy corrections are of order α^2 , where $\alpha = e^2/\hbar c = 1/137.039$ is the dimensionless *fine structure constant*, and correspond to splittings of radio frequencies. For electrons, the Bohr magneton $\mu_0 = e\hbar/2 mc$ enters as a constant factor in the formula, while for nuclei it is the nuclear magneton $\mu_N = e\hbar/2 Mc$ which appears, where M is the proton mass. Fine structure is thus of order μ_0^2 and hyperfine structure of order $\mu_0 \mu_N$ or μ_N^2 ; however, the difference is usually much smaller than the ratio μ_0/μ_N would suggest, as is seen on comparing Equations 4.6 and 4.7 for the $c\ {}^3\Pi_u$ state of H_2 .

In the presence of nuclear spin \mathbf{I} , Hund’s coupling schemes must be subdivided [Townes & Schawlow (136)] and for case b there are three possibilities. The total angular momentum is called \mathbf{F} .

$$b_{\beta J}: \quad N + S = J, \quad J + I = F \quad 4.1.$$

$$b_{\beta S}: \quad I + S = F_2, \quad N + F_2 = F \quad 4.2.$$

$$b_{\beta N}: \quad N + I = F_1, \quad F_1 + S = F \quad 4.3.$$

The selection rules for magnetic dipole transitions are: $\Delta J = 0, \pm 1$; $\Delta F = 0, \pm 1$; etc.

4.1.2 *Application to H_2* .—In the ground state of H_2 , $S = \Lambda = 0$ and there is neither fine nor electron-nuclear hyperfine structure. However, there is present a very weak interaction between the nuclear spin \mathbf{I} and the nuclear

⁶ This intrinsic *nuclear* quadrupole moment must not be confused with the *molecular* quadrupole moment discussed in Section 1.1.2, which is due to the electron distribution and is present in H_2 .

rotation $R(\equiv J)$ and also a nuclear spin-spin interaction. This structure has been studied extensively by Ramsey and his colleagues (99), using molecular beam magnetic resonance techniques, and a theoretical discussion of the spin dipole term has been given by Auffray & Cooley (3). In ortho rotational levels, $I=1$ and $F=J, J\pm 1$; in this case there is no distinction between the b_β subdivisions. For $v=0, J=1$, the frequencies of allowed transitions are

$$\begin{aligned} f(F=0-1) &= 546 \text{ kc/s} \\ f(F=1-2) &= 54.8 \text{ kc/s} \end{aligned} \quad 4.4.$$

Investigations have also been made of D_2 [Ramsey (99)] and of HD [Quinn et al. (97)]. For D_2 , ortho states (even J) have $I=0$ or 2 and para states (odd J) have $I=1$. The structure for $J=1$ is similar to that for H_2 and the observed separations are

$$\begin{aligned} f(F=0-1) &= 198 \text{ kc/s} \\ f(F=2-1) &= 58.2 \text{ kc/s} \end{aligned} \quad 4.5.$$

The effect of the deuteron quadrupole moment is simply to increase the splitting. In the case of HD, nuclear-symmetry considerations are absent and the energy-level structure is more complicated.

The other state of H_2 which has been studied is the metastable $c^3\Pi_u(v=0)$. Since $\Lambda \neq 0$, there are both ortho and para states for each N ; all states have fine structure and the ortho states also have hyperfine structure. The coupling $b_{\beta J}$ of Equation 4.1 applies. An accurate measurement of the fine structure of the $N=2$ level of parahydrogen ($J=1, 2, 3; I=0$) was made by Lichten (72) with the result

$$\begin{aligned} f(J=2-1) &= 4928 \text{ Mc/s} \\ f(J=2-3) &= 5898 \text{ Mc/s} \end{aligned} \quad 4.6.$$

A calculation by Fontana (34) gave values consistent with these results and with the unresolved earlier measurements of Foster & Richardson (35, 36). Working with natural hydrogen, Lichten (73) measured the hyperfine structure of the $N=1, J=2$ ortho component ($I=1$) to be

$$\begin{aligned} f(F=3-2) &= 707.55 \text{ Mc/s} \\ f(F=2-1) &= 462.44 \text{ Mc/s} \end{aligned} \quad 4.7.$$

A calculation by Frey & Mizushima (38) gave reasonable agreement with this result.

4.1.3 *Application to H_2^+* .—The ground state of H_2^+ is a $^2\Sigma_g^+$ state, and so there is a hyperfine interaction between the electron spin and the nuclear rotation and, for odd values of N , also between the electron spin and the nuclear spin. There have been several calculations of the energy-level splitting and the results are not in complete agreement. The situation has recently been reviewed by Somerville (112) and the numerical values here are from his paper.

In the state $N=0$ there is no splitting. For $N=1$, the coupling scheme $b_{\beta S}$ of Equation 4.2 is appropriate; $I=1$ and $S=1/2$ so that the states are:

TABLE IX
HYPERFINE TRANSITIONS IN THE GROUND STATE OF H_2^+

(F, F_2)	Mc/s
$(5/2, 3/2) - (3/2, 1/2)$	1343
$(3/2, 3/2) - (3/2, 1/2)$	1427
$(1/2, 3/2) - (3/2, 1/2)$	1375
$(3/2, 3/2) - (1/2, 1/2)$	1452
$(1/2, 3/2) - (1/2, 1/2)$	1400

$F_2=1/2, F=3/2, 1/2; F_2=3/2, F=5/2, 3/2, 1/2$. The frequencies of the five most important transitions are given in Table IX; three other transitions are allowed, at much lower frequencies and with smaller probabilities. The uncertainty in these tabulated values is about ± 100 Mc/s. The strongest transition is probably the one at 1343 Mc/s.

4.2 CONTINUUM PROCESSES

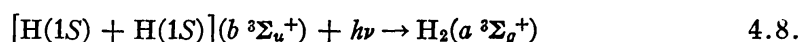
In this section, we consider the interaction with light in a continuous spectrum. Nonradiative collisional processes are not discussed, although they will influence abundances. Some of these processes are discussed in the books edited by Bates (5) and by Bates & Estermann (6).

4.2.1 *Absorption by H_2* .—A hydrogen molecule in its ground state may dissociate to form two separate neutral atoms by transitions either to the vibrational continuum of the ground state or to repulsive excited electronic states (or to bound states which subsequently decay to repulsive ones). There is also the possibility of photoionization, which may lead to a bound state of H_2^+ or by way of an unstable state to the system $H+H^+ + e$.

No detailed work has been done on the problem of vibrational dissociation but this process involves a strongly forbidden transition and so the transition probability must be very small. The first dissociative electronic process is that of absorption to the state $b\ ^3\Sigma_u^+$. This also is a forbidden transition; Gould & Salpeter (49) made a crude but reasonable estimate that the oscillator strength is of the order 10^{-9} . The significance of these small probabilities is discussed in Section 2.3.

The total ultraviolet absorption coefficient, including electronic transitions to excited states and photoionization, has been measured by a number of workers, most recently by Cook & Metzger (18) and Comes & Lessman (17); earlier references are given by Ditchburn & Öpik (25). Photoionization to the ground state of H_2^+ has been studied theoretically by Shimizu (105), Wacks (144), and Flannery & Öpik (32); Shimizu considered also the first repulsive state of the ion. There is fairly good agreement between theory and experiment.

Grandsire (50) has studied the $a\ ^3\Sigma_g^+ \rightarrow b\ ^3\Sigma_u^+$ continuous emission, both experimentally (cf. also 37) and theoretically. Some interest has been excited by the reverse process, 'quasi-molecular' free-bound absorption,



Calculations by Erkovich (30) led to an appreciable value for the absorption coefficient but Solomon (108) and Soshnikov (113) have repeated the work with greater accuracy and get a very much smaller answer. It seems that Erkovich used a simple form for the interatomic potential in the repulsive state outside the range of its validity.

4.2.2 *Absorption by other systems.*—There have been several calculations on the continuous absorption by H_2^+ . Photodissociation processes to $\text{H} + \text{H}^+$ are included in those listed by Nicholls & Stewart (88) and have been studied also by Bates (4) and Gibson (43); Boggess (12) has calculated the rate for the inverse free-bound emission, $^2\Sigma_u^+ \rightarrow ^2\Sigma_g^+$. Bates, Öpik & Poots (8) have considered photoionization processes, the final system being $\text{H}^+ + \text{H}^+ + e$. However, a measurement by Dunn (26) for $^2\Sigma_u^+ \leftarrow ^2\Sigma_g^+$ has given results in rather poor agreement with theory.

For H_2^- , little has been done. Gupta (51) made a calculation for one bound-free process but, since his wave function and potential curve turned out to be wrong (see Section 1.1.4), this work must be disregarded. Somerville (110) has considered the free-free electronic process



in a rather simple approximation (89) which neglects the molecular structure. The results are correct to within a factor of about two. It should be noted that the effect of stimulated emission was included in this work; the same is true of the author's similar calculation of He^- (111), although the fact is not explicitly stated in the paper.

The absorption process 4.9 is typical of a large number of possible free-free processes. Translational absorption by $\text{H}_2 + \text{H}_2$ has also been considered, where again the molecules are internally unaltered by the absorption. From the theory of Poll & van Kranendonk (96), Gaustad (40) has concluded that absorption by this process is negligible, except possibly at high densities; this is reasonable, since it is essentially a forbidden free-free vibrational transition. In such a collisional absorption, the internal energy of one of the molecules may change; this is the process which occurs in pressure-induced dipole radiation. In some cases, the internal states of both molecules may change simultaneously [Herzberg (57)].

4.3 THE SCATTERING OF LIGHT

Rayleigh scattering is a scattering without change of wavelength. Dalgarno & Williams (21) have calculated the Rayleigh cross section for H_2 to be

$$\begin{aligned} \sigma(\lambda) = & \frac{8.140 \times 10^{-26}}{\lambda^4} \left\{ 1 + \frac{1.572}{\lambda^2} + \frac{1.981}{\lambda^4} + \frac{2.307}{\lambda^6} \right. \\ & \left. + \frac{2.582}{\lambda^8} + \frac{2.822}{\lambda^{10}} + \mathcal{O}(\lambda^{-12}) \right\} \text{ cm}^2, \lambda \text{ in } 10^8 \text{ \AA} \end{aligned} \quad 4.10.$$

Vardya (141) and Dalgarno & Williams (20) have considered the Planck mean. Vardya used only the first term of Equation 4.10, with a less accurate numerical coefficient, and his results are seriously in error for $\lambda < 3000 \text{ \AA}$. Equation 4.10 holds down to $\lambda \simeq 1200 \text{ \AA}$, where the basic assumption of the Rayleigh theory that molecular dimensions are negligible in comparison with λ begins to break down, and the expansion diverges.

The Raman scattering of a photon results in an energy change equal to that of a molecular vibrational or rotational transition. This process has been considered by Dalgarno & Williams (19) for the scattering by H_2 of the Ly α line of atomic hydrogen.

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