

THE CONTINUOUS SPECTRUM OF THE HYDROGEN QUASI-MOLECULE

ROBERT O. DOYLE

Harvard College Observatory and Smithsonian Astrophysical Observatory,
Cambridge, Mass. 02138

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Abstract—A quantal calculation of the continuous absorption coefficient of the hydrogen quasi-molecule for the transition $1s\sigma 2s\sigma \ ^3\Sigma_g^+ \leftarrow 1s\sigma 2p\sigma \ ^3\Sigma_u^+$ is described. The calculation includes the explicit dependence of the matrix element of the electronic dipole transition moment on the rotational state of the molecule.

The detailed summation of the transition probability over all rotational states for temperatures at which several states are populated differs significantly from the probability given by the contribution of the rotationless ($J = 0$) state multiplied by the rotational partition function. The difference is larger than the errors resulting from the δ -function approximation to the continuum wave functions used in previously published calculations of this absorption coefficient.

I. INTRODUCTION

THEORETICAL calculations of the strength of continuous molecular spectra have generally proceeded from the approximation of GIBSON, RICE and BAYLISS⁽¹⁾ that the matrix element of the electronic dipole transition moment is independent of the rotational state J of the nuclei. The assumption of rotational independence is most likely to fail in the lightest molecules (with the widest spacing of the rotational levels), as has been noted by BUCKINGHAM, REID and SPENCE.⁽²⁾ They calculated matrix elements of the $2p\sigma \ ^2\Sigma_u^+ \leftarrow 1s\sigma \ ^2\Sigma_g^+$ transition for a few non-zero J -states in the hydrogen molecular ion H_2^+ and established the existence of a variation, but did not investigate it in detail. The present paper reports a calculation of the transition probability in the $1s\sigma 2s\sigma \ ^3\Sigma_g^+ \leftarrow 1s\sigma 2p\sigma \ ^3\Sigma_u^+$ continuum of H_2 in which we explicitly sum over rotation-dependent matrix elements, and gives a comparison of the summation to a rotationless calculation.

The electronic states $a \ ^3\Sigma_g^+$ and $b \ ^3\Sigma_u^+$, and transitions between them, were the subjects of an important series of papers by COOLIDGE and JAMES and their associates^(3–10) on the calculation of electronic wave functions, potential-energy curves, the dipole moment operator, and vibrational wave functions. In 1936⁽⁵⁾ they found that the Franck–Condon principle (constant dipole moment) was a poor approximation for continuous molecular spectra. In 1939⁽⁹⁾ they made the first calculation using a variable dipole moment. They published mean lifetimes for the first four vibrational states in $a \ ^3\Sigma_g^+$, and gave the relative (unnormalized) wavelength dependence of the emission intensity from these four states. However, they did not explicitly combine these and publish absolute emission or absorption coefficients.

In 1960 ERKOVICH⁽¹¹⁾ published quantitative calculations of the absorption into the first four vibrational states (intrinsically the same information as in the James and Coolidge calculations). However, he made an error in estimating the appropriate cross section for the number of collisions between ground-state hydrogen atoms in the $b^3\Sigma_u^+$ state (the number of "quasi-molecules"). The wavelength dependence of his result was correct, but the absolute strength of his calculation was too large by about two orders of magnitude, as was noted by SOLOMON⁽¹²⁾ and SOSHNIKOV.⁽¹³⁾

Solomon reported new calculations in which he extended the vibrational sum through $v' = 7$ for possible applications in high-temperature astrophysical problems. His results had a slightly different wavelength dependence from those of Erkovich, and were about one per cent of the absolute strength of the latter. Soshnikov published similar results, but he did not describe his calculation in detail.

Both Erkovich and Solomon used James and Coolidge's modification⁽⁹⁾ of the Condon "reflection" method⁽¹⁴⁾ (first used in a calculation by WINANS and STUECKELBERG⁽¹⁵⁾ and sometimes known by their names), in which the continuum wave function is replaced by a δ -function located at the classical turning point of the motion. James and Coolidge had found that, when modified to include the variable dipole moment, the δ -function approximation was superior to a Franck-Condon calculation (constant dipole moment) using full continuum wave functions.

We compare our rotationless calculation, which uses full continuum wave functions, with the δ -function calculation of Solomon and find that the difference is essentially the same as that reported in the original work of James and Coolidge. This independently confirms the size of the error that can be expected in δ -function calculations and the correctness of Solomon's calculation (to within his approximations).

However, we shall see that the difference between the rotationless calculation and the detailed summation over rotational states, for temperatures at which several rotational states are populated, is larger than the above difference between the δ -function calculation and that using full continuum wave functions. The detailed summation varies from twice the rotationless calculation at short wavelengths to two-thirds of it at long wavelengths. Thus, the neglect of rotational dependence of the matrix element is the major source of error at such wavelengths and temperatures.

An examination of the importance of this transition as a source of absorption in stellar atmospheres, reported elsewhere,⁽¹⁶⁾ indicates that it is a significant contributor to opacity near $\lambda = 1700 \text{ \AA}$ in the solar atmosphere.

2. THEORY

In the Born-Oppenheimer approximation, the eigensolutions of the Hamiltonian

$$H\chi_\alpha = [T_N + T_e + V(\mathbf{r}, \mathbf{R})]\chi_\alpha = E_\alpha\chi_\alpha, \quad (1)$$

where

$$T_N = \frac{\hbar^2}{2M} \nabla_{\mathbf{R}}^2, \quad T_e = - \sum_{i=1}^2 \frac{\hbar^2}{2m} \nabla_{\mathbf{r}_i}^2,$$

and $V(\mathbf{r}, \mathbf{R})$ is the total electrostatic interaction of the electrons and the nuclei, are products of an electronic wave function $\psi_a^{\mathbf{R}}$ and a nuclear wave function $\phi_a^{\mathbf{z}}$:

$$\chi_a(\mathbf{r}, \mathbf{R}) = \phi_a^{\mathbf{z}}(\mathbf{R})\psi_a^{\mathbf{R}}(\mathbf{r}). \quad (2)$$

The coordinate of the i th electron, with mass m , is \mathbf{r}_i ; \mathbf{r} stands for all electronic coordinates. The coordinate of the j th nucleus, with mass M , is \mathbf{R}_j ; \mathbf{R} is the internuclear distance.

The $\psi_a^{\mathbf{R}}$ are the solutions of the simplified Hamiltonian for \mathbf{R} fixed ($T_N = 0$):

$$[T_e + V(\mathbf{r}, \mathbf{R})]\psi_a^{\mathbf{R}} = \varepsilon_a^{\mathbf{R}}\psi_a^{\mathbf{R}}. \quad (3)$$

The $\phi_a^{\mathbf{z}}$ are the solutions of a Schrödinger equation for the nuclear motion in which the electronic coordinates have been averaged over and do not appear explicitly:

$$(T_N + \varepsilon_a^{\mathbf{R}})\phi_a^{\mathbf{z}}(\mathbf{R}) = E_a\phi_a^{\mathbf{z}}(\mathbf{R}). \quad (4)$$

The invariance of the Hamiltonian in equation (3) under rotation ensures that the eigenvalues $\varepsilon_a^{\mathbf{R}}$ are functions of only $R = |\mathbf{R}|$ (the nuclei move in a central potential). The nuclear equation (4) therefore separates into radial and angular parts,

$$\phi_a^{\mathbf{z}}(\mathbf{R}) = \mathcal{R}_{v,J}^a(R)R^{-1}\mathcal{Y}_J^M(\theta, \phi), \quad (5)$$

with \mathcal{Y}_J^M the spherical harmonics (eigenfunctions of \mathbf{J}^2 and J_Z) and $\mathcal{R}_{v,J}^a$ the solutions of the radial eigenvalue equation,

$$\frac{d^2}{dR^2}\mathcal{R}_{v,J}^a + \frac{2\mu}{\hbar^2}\left[E_a - \varepsilon_a(R) - \frac{J(J+1)\hbar^2}{2\mu R^2}\right]\mathcal{R}_{v,J}^a = 0. \quad (6)$$

Normalization of the angular functions is

$$\int \int \mathcal{Y}_J^{M*}(\theta, \phi)\mathcal{Y}_{J'}^{M'}(\theta, \phi) \sin \theta \, d\theta \, d\phi = \delta_{JJ'}\delta_{MM'}.$$

Normalization of the radial functions in the bound state is

$$\int \mathcal{R}_{v,J}^a\mathcal{R}_{v',J}^a \, dR = \delta_{vv'}.$$

In the repulsive state $b^3\Sigma_u^+$, we seek a solution to the nuclear equation that asymptotically corresponds to the stationary state of scattering

$$\phi_b^{\mathbf{K}}(\mathbf{R}) \sim e^{i\mathbf{K}\cdot\mathbf{R}} + f(\theta)e^{iKR}/R. \quad (7)$$

This is normalized to unit density of incident plane waves $e^{i\mathbf{K}\cdot\mathbf{R}}$, which are eigenfunctions of the linear momentum $\mathbf{K}\hbar$.

Expanding equation (7) in the spherical harmonics for axes along \mathbf{K} , we obtain

$$\phi_b^{\mathbf{K}}(\mathbf{R}) \sim \frac{\sqrt{(4\pi)}}{KR} \sum_{J''} (2J''+1)^{1/2} i^{J''} e^{i\delta_{J''}} \sin\left(KR - \frac{J''\pi}{2} + \delta_{J''}\right) \mathcal{Y}_{J''}^0(\theta, \phi). \quad (8)$$

It is convenient to identify a radial function associated with the J'' th angular state by the solution of the nuclear equation for the repulsive state which is regular at zero and asymptotically

$$\mathcal{R}_{k,J''}^b(R) \sim \sin\left(KR - \frac{J''\pi}{2} + \delta_{J''}\right). \quad (9)$$

The probability $B_v^{\beta \rightarrow \alpha}$ of an electric dipole transition from a state β to a state α , with $E_\beta < E_\alpha$, accompanied by absorption of a photon of energy $h\nu = E_\alpha - E_\beta$, averaged over all polarization directions is

$$B_v^{\beta \rightarrow \alpha} = \frac{8\pi^3\nu}{3hc} \left\langle \beta \left| \sum_i \mathbf{er}_i \right| \alpha \right\rangle^2 \quad (10)$$

for an incident beam of one photon crossing unit area per second per unit frequency interval.

In our particular case, we are interested in transitions between $b = 1s\sigma 2p\sigma^3\Sigma_u^+$, the lowest triplet electronic state of ungerade symmetry (odd in reflection of ψ_b^R about the origin), and $a = 1s\sigma 2s\sigma^3\Sigma_g^+$, the lowest triplet gerade state. In this case, the transition matrix element in (10) becomes

$$\begin{aligned} \left\langle \beta \left| \sum_i \mathbf{er}_i \right| \alpha \right\rangle &= \int \int \chi_\beta^*(\mathbf{r}, \mathbf{R}) \sum_i \mathbf{er}_i \chi_\alpha(\mathbf{r}, \mathbf{R}) \, d\mathbf{r} \, d\mathbf{R} \\ &= \int \phi_b^{\beta*}(\mathbf{R}) \left[\int \psi_b^{\mathbf{R}*}(\mathbf{r}) \sum_i \mathbf{er}_i \psi_a^{\mathbf{R}}(\mathbf{r}) \, d\mathbf{r} \right] \phi_a^{\alpha}(\mathbf{R}) \, d\mathbf{R} \\ &\equiv \int \phi_b^{\beta*}(\mathbf{R}) \mathbf{D}_{ba}(\mathbf{R}) \phi_a^{\alpha}(\mathbf{R}) \, d\mathbf{R}, \end{aligned} \quad (11)$$

where $\mathbf{D}_{ba}(\mathbf{R})$ is the electronic dipole moment operator.

Now, since a and b are both Σ states (zero orbital angular momentum of the electrons along the internuclear axis), the cylindrical symmetry ensures that the matrix element of the vector operator $\sum_i \mathbf{er}_i$ can only have a non-zero value along the internuclear axis,

$$\mathbf{D}_{ba}(\mathbf{R}) = D_{ba}(R)\hat{\mathbf{R}}, \quad (12)$$

which establishes its transformation properties under rotation in the space of the nuclei.

The total transition probability κ_ν per unit incident photon beam at a given frequency ν results from summing and integrating equation (10) over all initial and final states, weighted by the population $N(\beta)$ of the initial states and including the δ -function behavior of $B_v^{\beta \rightarrow \alpha}$ at frequencies that conserve the energy:

$$\kappa_\nu = \frac{8\pi^3\nu}{3hc} \sum_{\alpha} \int d\alpha \sum_{\beta} \int d\beta N(\beta) \left\langle \beta \left| \sum_i \mathbf{er}_i \right| \alpha \right\rangle^2 \delta[\nu - (E_\alpha - E_\beta)/h].$$

In our case, we are summing over the final bound states $\alpha = avJ'M'$ and integrating over the initial continuum states $\beta = b, \mathbf{K}$:

$$\begin{aligned} \kappa_\nu^{b \rightarrow a} &= \frac{8\pi^3\nu}{3hc} \sum_{\mathbf{K}} \sum_{J'} \sum_{M'} \int d\mathbf{K} N(b, \mathbf{K}) \\ &\times \left\langle b, \mathbf{K} \left| \sum_i \mathbf{er}_i \right| avJ'M' \right\rangle^2 \delta \left[\nu - \frac{1}{h} \left(E_{avJ'M'} - \frac{K^2\hbar^2}{2\mu} \right) \right]. \end{aligned} \quad (13)$$

Since K is a monotonic function of ν , we note that

$$\int d\mathbf{K} \delta(\nu - \nu_{\beta\alpha}) = \int \int K^2 \frac{dK}{d\nu} d\Omega \delta(\nu - \nu_{\beta\alpha}) \, d\nu = 4\pi K^2 \frac{dK}{d\nu} \Big|_{\nu_{\beta\alpha}},$$

and the rest of equation (13) is independent of Ω so that it becomes, from equations (5), (8), (9), (11) and (12),

$$\kappa_v^{b \rightarrow a} = \frac{8\pi^3 v}{3hc} \sum_v \sum_{J'} \sum_{M'} \sum_{J''} \frac{4\pi}{K^2} (2J'' + 1) N(b, \mathbf{K}) 4\pi K^2 \frac{dK}{dv} \times \left| \int \mathcal{R}_{K,J'}^b(R) D_{ba}(R) \mathcal{R}_{v,J'}^a(R) dR \int \int \mathcal{Y}_{J''}^{0*}(\theta, \phi) \hat{\mathbf{R}} \mathcal{Y}_{J'}^{M'}(\theta, \phi) \sin \theta d\theta d\phi \right|^2, \quad (14)$$

with $K^2 \hbar^2 / 2\mu = E_{avJ'M'} - hv$.

For temperatures at which the population of excited atomic states is negligible, three-quarters of all pairs of free atoms are in the $b^3\Sigma_u^+$ state; the remaining quarter are in the continuous part of the $X^1\Sigma_g^+$ ground state. The Maxwell-Boltzmann distribution of quasi-molecules among states K in the electronic state $b^3\Sigma_u^+$ is

$$N(b, \mathbf{K}) = \frac{3}{4} n_H^2 \frac{\hbar^3}{(2\pi\mu kT)^{3/2}} \exp\left(-\frac{K^2 \hbar^2}{2\mu kT}\right).$$

Finally, introducing the nuclear spin statistical weights of the rotational levels $\tilde{\omega}_{J'}^*$ and performing the sums over J'' and over the degenerate magnetic substates M' , we have our complete expression

$$\begin{aligned} \kappa_v^{b \rightarrow a} &= \frac{8\pi^3 v}{3hc} \frac{3}{4} n_H^2 \frac{\hbar^3}{(2\pi\mu kT)^{3/2}} \\ &\times \sum_v \sum_{J'} \exp\left[-\frac{(E_{avJ'} - hv)}{kT}\right] 2 \left(\frac{2\mu}{E_{avJ'} - hv}\right)^{1/2} \\ &\times \tilde{\omega}_{J'} \left\{ (J' + 1) \left[\int \mathcal{R}_{K,J'+1}^b(R) D_{ba}(R) \mathcal{R}_{v,J'}^a(R) dR \right]^2 \right. \\ &\quad \left. + J' \left[\int \mathcal{R}_{K,J'-1}^b(R) D_{ba}(R) \mathcal{R}_{v,J'}^a(R) dR \right]^2 \right\}, \quad (15) \end{aligned}$$

with

$$K = \left[\frac{2\mu}{\hbar} (E_{avJ'} - hv) \right]^{1/2},$$

and

$$\begin{aligned} \tilde{\omega}_{J'} &= \frac{1}{4}; \quad J' \text{ even} \\ &= \frac{3}{4}; \quad J' \text{ odd.} \end{aligned}$$

* In the $^3\Sigma_g^+$ state, symmetric under exchange of the electrons, the symmetric nuclear space wave functions (even J') require antisymmetric spin functions so that $\tilde{\omega}_{J'} = \frac{1}{4}$, the three symmetric functions being excluded by the required antisymmetric character of the total wave function under exchange of all the particles. Note that the average value of $\tilde{\omega}_{J'} (= \frac{1}{2})$ is just the symmetry factor or double counting factor in the number of different pairs in a collection of indistinguishable atoms.

3. COMPUTATIONS

In order to determine $\kappa_v^{b \rightarrow a}$, we need values for the two potential-energy curves $\varepsilon_a(R)$ and $\varepsilon_b(R)$ and values of the electronic dipole moment operator $D_{ba}(R)$.

(a) $\varepsilon_a(R)$ and the bound wave functions

Although the two other calculations of this absorption coefficient for high temperatures mentioned above^(11,12) used a simple Morse potential to represent the bound state, we do not, since there are several simple forms of potential curves that can be numerically integrated to give better agreement with the experimental energies than does the Morse curve. Moreover, numerical parameters for several other curves are known for $a^3\Sigma_g^+$ since it was used by COOLIDGE, JAMES and VERNON⁽⁷⁾ in a comparison of the relative accuracy of 14 different empirical potential curves. Their "best" curve was a power series expansion in terms of the square root of the Morse function which was first suggested by DUNHAM,⁽¹⁷⁾ and which we might call the Morse-Dunham function, since it combines the inherently appropriate shape of the Morse curve with the flexibility and ease of manipulation of Dunham's power series approach. It has the general form

$$\varepsilon_a(R) = D_0 \sum_{n=2}^N c_n (1 - e^{-\beta(r-r_e)/r_e})^n, \quad (16)$$

and is used in this computation with the following coefficients:⁽⁷⁾

$$\begin{aligned} D_0 &= 24459 \text{ cm}^{-1}; & c_2 &= 0.72550; & c_3 &= 0.02948; & c_4 &= 0.10522; \\ c_5 &= 0.05281; & c_6 &= 0.05525; & c_7 &= 0.02573; & c_8 &= 0.00601; \\ \beta &= 1.7104; & r_e &= 1.8677a_0. \end{aligned}$$

We numerically integrate equation (6) and locate eigenenergies by an iterative procedure,* finding eigenfunctions that are asymptotic to zero for both increasing and decreasing internuclear distance.

The computed vibrational term differences are compared with the observed⁽¹⁸⁾ in Table 1. The rotational term differences are compared in Table 2.^(18,19) Solutions are limited to states with energies less than about $17\,500 \text{ cm}^{-1}$ above the minimum of $a^3\Sigma_g^+$. This is approximately vibrational-rotational state $v = 8, J' = 0$ or $v = 0, J' = 25$. Above this energy, other molecular electronic states of the same symmetry exist ($1s\sigma n\lambda\sigma^3\Sigma_g^+$), which we neglect.

* For a given trial energy $E^{(n)}$ two logarithmic slopes $S_{\pm}^{(n)} = (1/\mathcal{R}_{v,J})(d\mathcal{R}_{v,J}/dR)$ of the wave function ($S^{(n)}$ corresponds to a solution of equation (6) that is asymptotic to zero for $R \rightarrow 0$, and $S_{\pm}^{(n)}$ to one asymptotic to zero for $R \rightarrow \infty$) are determined from the mean value of slopes asymptotically divergent upward and downward. The slopes $S_{\pm}^{(n)}$ are equal only for an eigenvalue of the energy $E^{(n)} = E_{v,J}$. A second iterative procedure linearly interpolates the differences $\Delta S^{(n)} = S_{\pm}^{(n)} - S_{\mp}^{(n)}$ at two successive trial energies for a new energy

$$E^{(n+1)} = E^{(n)} - \left(\frac{E^{(n)} - E^{(n-1)}}{\Delta S^{(n)} - \Delta S^{(n-1)}} \right) \Delta S^{(n)}$$

until $\Delta S^{(n+1)}$ is no improvement over $\Delta S^{(n)}$ (generally $\Delta S^{(n)} \approx 10^{-7} S^{(n)}$). The result is essentially the mean of two energies, whose wave functions are indistinguishable in the classical region and for the terminal loops but which eventually diverge and become infinite in opposite senses, as described by COOLIDGE, JAMES and PRESENT.⁽⁵⁾ Beyond the point of divergence, defined as a change of sign of $\mathcal{R}_{v,J}$ or $(d\mathcal{R}_{v,J}/dR)$, the wave functions are set equal to zero.

TABLE 1. COMPARISON OF THE OBSERVED⁽¹⁸⁾ VIBRATIONAL ENERGY DIFFERENCES (UPPER ENTRY) WITH COMPUTED (MIDDLE ENTRY); UNITS cm^{-1}

Δv	$K = 0$	$K = 1$	$K = 2$	$K = 3$	$K = 4$	$K = 5$
1-0	2524.32	2521.07	2514.55	2504.85	2492.00	2476.13
	2525.25	2521.99	2515.48	2505.77	2492.91	2476.98
	-93	-92	-93	-92	-91	-85
2-1	2388.26	2385.12	2378.80	2369.41	2357.06	2341.63
	2388.75	2385.57	2379.22	2369.81	2357.23	2341.70
	-49	-45	-42	-40	-17	-07
3-2	2256.10	2253.05	2246.91	2237.77	2225.60	2210.39
	2254.79	2251.6	2245.39	2236.04	2223.65	2208.29
	+1.31	+1.45	+1.52	+1.73	+1.95	+2.10
4-3	2126.86	2123.85	2117.78	2108.83	2096.57	
	2121	2118.0	2112	2103	2092	
	+6	+5.8	+6	+6	+5	
5-4		1996.57	1990.58	1981.75		
		1983.1				
		+13.5				
6-5		1869.80				
		1845.7				
		+24.1				
7-6		1742.15				
		1705.0				
		+37.2				
8-7		1612.5				
		1560.5				
		+52.0				

TABLE 2. COMPARISON OF THE OBSERVED^(18,19) ROTATIONAL ENERGY DIFFERENCES (UPPER ENTRY) WITH COMPUTED (MIDDLE ENTRY); UNITS cm^{-1}

ΔK	$V = 0$	$V = 1$	$V = 2$	$V = 3$	$V = 4$
2-0	199.51	189.75	180.26	171.05	162
	199.64	189.86	180.34	170.94	162
	-13	-11	-08	+11	0
3-1	330.76	314.54	298.83	283.57	268.5
	330.98	314.71	298.95	283.37	269
	-22	-17	-12	+20	-5
4-2	459.44	436.91	415.05	393.73	372.5
	459.75	437.18	415.18	393.45	373
	-31	-27	-13	+28	-5
5-3	584.64	555.85	528.02	500.9	
	585.02	556.23	528.17	500.4	
	-38	-38	-15	+5	
6-4	705.57	670.91	636.93	604.09	
	705.94	671.10	637.13	603.49	
	-37	-19	-20	+60	
7-5	821.24	780.62	741.29		
	821.75	781.08	741.36		
	-51	-46	-07		

TABLE 2 (continued)

ΔK	$V = 0$	$V = 1$	$V = 2$	$V = 3$	$V = 4$
8-6	931.17				
	931.84				
	-67				
9-7	1035.07				
	1035.69				
	-62				

(b) $\varepsilon_b(R)$ and the continuum wave functions

The repulsive interaction potential of two ground-state hydrogen atoms in parallel spin states was recently calculated by KOLOS and WOLNIEWICZ,⁽²⁰⁾ who gave a table of numerical values. We find it more convenient to use an analytic approximation to an earlier second-order perturbation theory calculation by DALGARNO and LYNN,⁽²¹⁾ which differs only slightly from the more recent values:

$$\begin{aligned} \varepsilon_b(R) &= 109\,737.3 \left[\frac{e^{-2.3R}}{R} (2 + 2.334R + 0.78R^2 + 1.036R^3 \right. \\ &\quad \left. + 1.728R^4) - 0.0062 \right]; \quad 0 \leq R \leq 2; \\ &= 109\,737.3(5.7722R^2 e^{-2.35R} + 181 \cdot R^3 e^{-6.034R}); \quad 2 < R \leq 4; \\ &= 109\,737.3(20.533e^{-1.77R} - 13 \cdot R^{-6} - 428 \cdot R^{-8}); \quad 4 < R. \end{aligned} \quad (17)$$

The dimensions are cm^{-1} ; R is in a_0 (atomic units).

With this potential curve, the nuclear equation is integrated numerically, this time to give wave functions asymptotic to zero for decreasing internuclear distance only. At large internuclear distance these continuum wave functions are made asymptotic to amplitude unity, in accordance with equation (9).

For each bound state v, J' , a unique set of 20 continuum wave functions is determined, 10 with $J'' = J' + 1$ and 10 with $J'' = J' - 1$. Each continuum function is located below the upper state by 1 of 10 standard transition energies, which enables us to sum equation (15) without interpolation. Figure 1 shows $\varepsilon_a(R)$ and $\varepsilon_b(R)$ and some typical wave functions. Figure 2 illustrates the effect of the addition of rotational potential energy.

(c) The electronic dipole moment $D_{ba}(R)$

Values of the electronic dipole moment were calculated by JAMES and COOLIDGE⁽⁹⁾ for 10 internuclear separations between $1.3a_0$ and $2.9a_0$. They estimate the probable error as "a very few percent". To interpolate values analytically, we use the following polynomial, which fits the 10 points with an accuracy of better than 2 per cent,

$$D_{ba}(R) = 2.358 + 0.4857R - 0.9268R^2 + 0.3605R^3 - 0.04451R^4; \quad R \leq 2.9a_0. \quad (18)$$

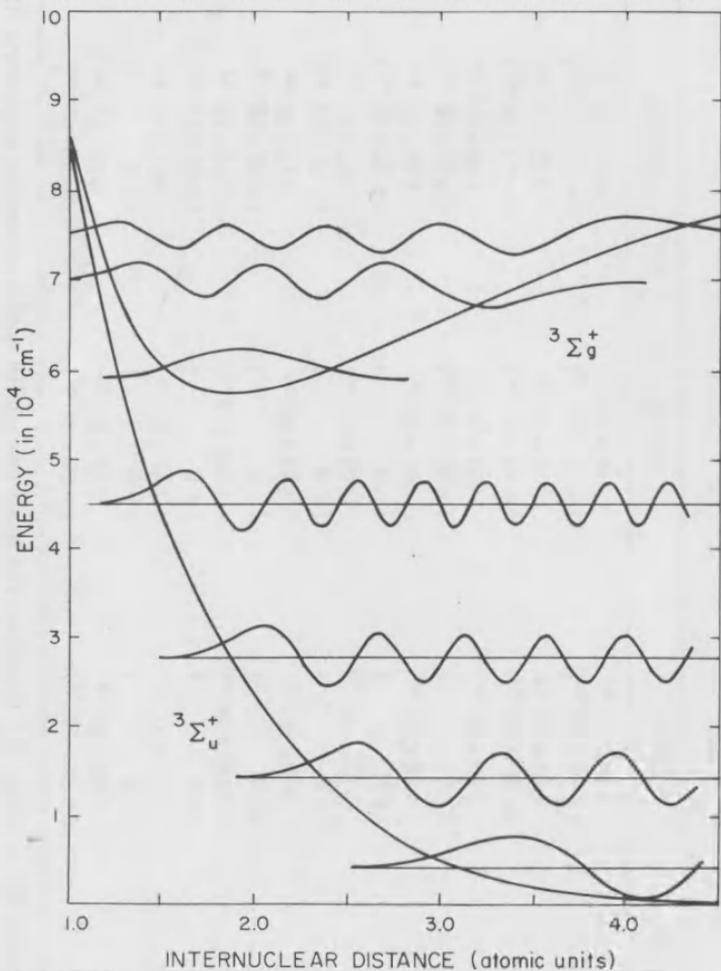


FIG. 1. The potential energy curves of $1s2s2\sigma \ ^3\Sigma_g^+$ and $1s2p\sigma \ ^3\Sigma_u^+$ of H_2 . Some typical continuum wave functions and the $v = 0$, $v = 5$, and $v = 8$ vibrational wave functions in the bound state are shown.

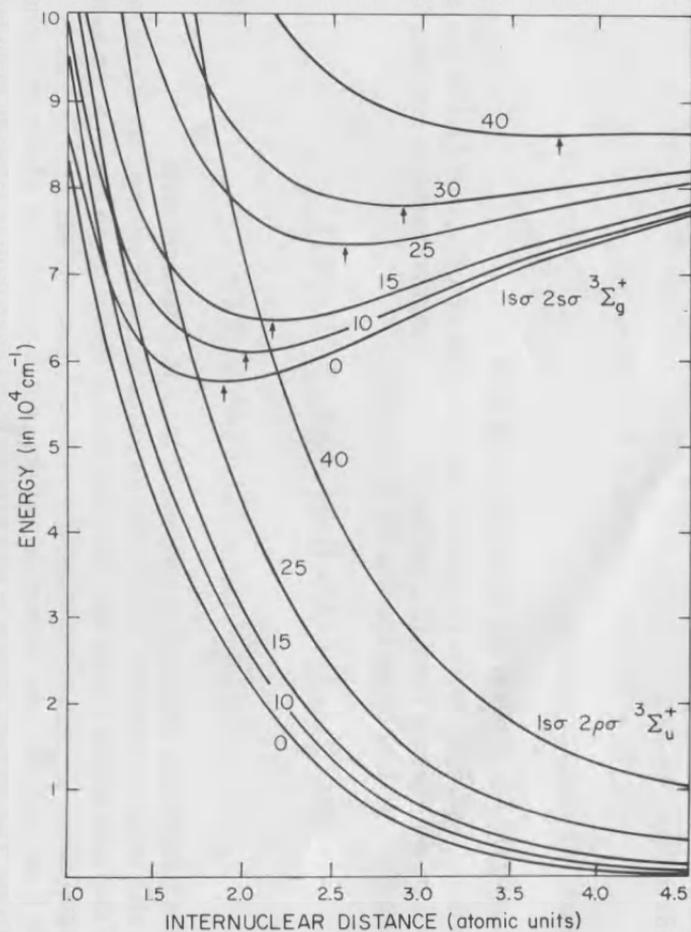


FIG. 2. Potential-energy curves of $1s\sigma 2s\sigma \ ^3\Sigma_g^+$ and $1s\sigma 2p\sigma \ ^3\Sigma_u^+$ of H_2 showing the effect of the addition of rotational potential energy through rotational quantum state $J = 40$. Arrows indicate minima of bound-state curves.

From perturbation theory, a series expansion of $D_{ba}(R)$ for large internuclear separation in inverse powers of the separation is found to have R^{-7} as the leading term. Fitting to equation (18) at $2.9a_0$, we have

$$D_{ba}(R) = 7031R^{-7} - 17\,334R^{-8}; \quad R > 2.9a_0.$$

The dimensions are ea_0 (atomic units).

(d) *Truncation of the infinite sums and other sources of error*

The rotational remainder terms in equation (15) from the cutoff values $J_c(v)$ to $J = \infty$ are estimated by multiplying the J_c th contribution by a rotational partition function for the remaining states and replacing the sum by an integral:

$$\begin{aligned} Z(J_c, T) &\equiv \sum_{J_c}^{\infty} \tilde{\omega}_J(2J+1) \exp -[J(J+1)\hbar^2/2\mu r_c^2 kT] \\ &= \frac{\mu r_c^2 kT}{\hbar^2} \exp -[J_c(J_c+1)\hbar^2/2\mu r_c^2 kT], \end{aligned} \quad (19)$$

where r_c is the equilibrium internuclear distance of the J_c th rotational state.

We can also make an estimate of the effect of v -truncation by noting that the strong exponential decrease usually means that the contribution from a given v -level is the same order of magnitude as the sum of contributions from all higher v -levels.

In Table 3 we give the final numerical results, which include the above rotational remainder terms. The amount shown in parentheses is the contribution (already included)

TABLE 3. CONTINUOUS ABSORPTION COEFFICIENT OF THE HYDROGEN QUASI-MOLECULE*

Wavelength (Å)	3000°K	5000°K	8000°K
1540	3.40×10^{-42} ($+0.4 \times 10^{-42}$)	5.48×10^{-42} ($+1.5 \times 10^{-42}$)	6.18×10^{-42} ($+3.2 \times 10^{-42}$)
1750	6.21×10^{-43} ($+0.3 \times 10^{-43}$)	2.18×10^{-42} ($+0.3 \times 10^{-42}$)	3.92×10^{-42} ($+1.3 \times 10^{-42}$)
2000	5.93×10^{-44} (+0)	4.86×10^{-43} ($+0.4 \times 10^{-43}$)	1.49×10^{-42} ($+0.2 \times 10^{-42}$)
2222	9.10×10^{-45} (+0)	1.49×10^{-43} (+0)	6.75×10^{-43} ($+0.2 \times 10^{-43}$)
2500	1.128×10^{-45} (+0)	4.02×10^{-44} (+0)	2.82×10^{-43} ($+0.1 \times 10^{-43}$)
3000	5.50×10^{-47} (+0)	6.30×10^{-45} (+0)	8.53×10^{-44} ($+0.7 \times 10^{-44}$)
3640	2.893×10^{-48} (+0)	1.041×10^{-45} (+0)	2.65×10^{-44} ($+0.1 \times 10^{-44}$)
4500	1.33×10^{-49} (+0)	1.47×10^{-46} (+0)	7.24×10^{-45} (+0)
6667	9.79×10^{-52} ($+0.2 \times 10^{-52}$)	5.32×10^{-48} ($+0.8 \times 10^{-48}$)	6.72×10^{-46} ($+2.8 \times 10^{-46}$)

* For the $1s\sigma 2s\sigma \rightarrow 1s\sigma 2p\sigma$ transition. The upper entry is the double summation of equation (15) corrected for rotational truncation. The lower entry is the correction for vibrational truncation. The units are cm^5 per H atom squared. To get the absorption cross section per H atom, multiply by the density n_H . To get $k_{\nu}^{b \rightarrow a}$ in cm^{-1} , multiply by n_H^2 .

of the last vibrational level. At 3000°K and 1540 Å the absorption coefficient is $3.40 \times 10^{-42} \text{ cm}^5$ and the last v -term contributes 0.04×10^{-42} to the sum, so that 3.44×10^{-42} is a slight overestimate of the total contribution from all v . The results in Table 3 and those for other temperatures are shown in Fig. 3.

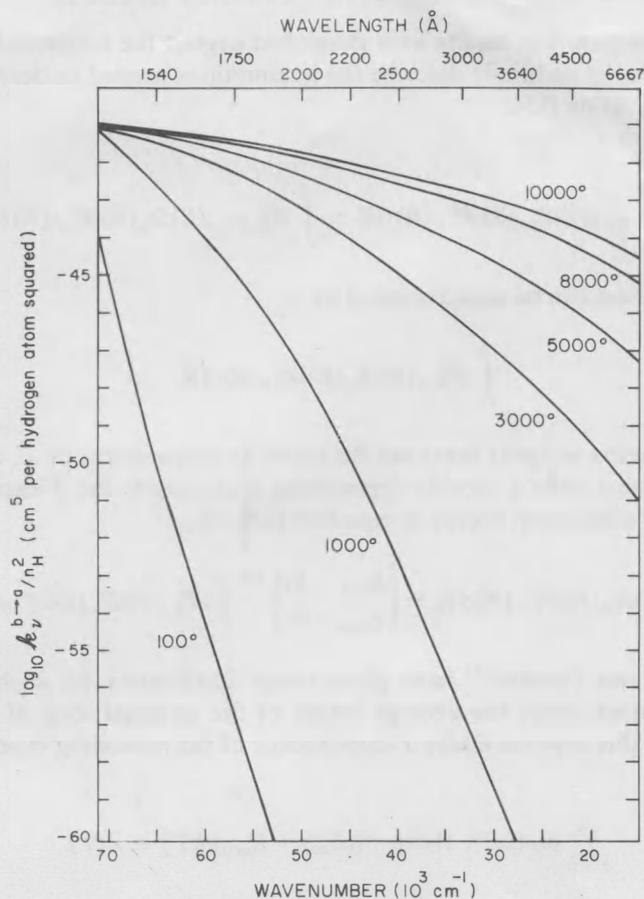


FIG. 3. The total absorption coefficient of the transition from the $1s\sigma 2p\sigma \ ^3\Sigma_u^+$ state of the hydrogen quasi-molecule to the bound $1s\sigma 2s\sigma \ ^3\Sigma_g^+$ state of H_2 . To get the absorption cross section per hydrogen atom, multiply by the density n_H . To get $K_v^{b \rightarrow a}$ in cm^{-1} multiply by n_H^2 .

Values of the individual rotational remainder terms for each level v and the fractional contribution each vibrational level makes to the total transition probability can be found in DOYLE.⁽²²⁾ This reference also includes a discussion of the sources of error in the calculation. The major uncertainty is the electronic dipole moment operator $D_{ba}(R)$, which contributes the bulk of a fixed probable error of ± 10 per cent below densities of $n_H = 10^{21} \text{ cm}^{-3}$ and temperatures of 8000°K. Above this temperature the errors involved in neglecting higher electronic states become of the same order of magnitude (± 10 per cent) and increase with increasing temperature. Above this density an estimate of the neglect of

three-body collisions indicates that about 10 per cent of the photon absorptions occur when a third hydrogen atom is within molecular dimensions ($< 5a_0$) of the quasi-molecule, and this too increases with increasing density.

4. COMPARISON WITH PREVIOUS RESULTS

In order to compare our results with those that neglect the rotational dependence of the matrix element, let us briefly describe the assumptions needed to derive the rotationless result from equation (15).

First, we note that

$$\int \mathcal{R}_{K,J'+1}^b(R) D_{ba}(R) \mathcal{R}_{v,J'}^a(R) dR \simeq \int \mathcal{R}_{K,J'-1}^b(R) D_{ba}(R) \mathcal{R}_{v,J'}^a(R) dR,$$

and that both of these can be approximated by

$$\int \mathcal{R}_{K,J'}^b(R) D_{ba}(R) \mathcal{R}_{v,J'}^a(R) dR.$$

Second, the matrix element must not be taken as independent of J' , as is frequently assumed; but it must have a specific dependence that cancels the J' -dependence of the square root of the continuum energy in equation (15), viz.,

$$\int \mathcal{R}_{K,J'}^b(R) D_{ba}(R) \mathcal{R}_{v,J'}^a(R) dR \simeq \left(\frac{E_{avJ'} - h\nu}{E_{av0} - h\nu} \right)^{1/4} \int \mathcal{R}_{K,0}^b(R) D_{ba}(R) \mathcal{R}_{v,0}^a(R) dR. \quad (20)$$

COOLIDGE, JAMES and PRESENT⁽⁵⁾ have given rough justification for such a dependence by a WKB argument about the average height of the terminal loop of the continuum wave function. In this case the entire J' -dependence of the remaining expression is in the terms

$$\sum_{J'=0}^{\infty} \tilde{\omega}_{J'} (2J'+1) \exp -[(E_{avJ'} - E_{av0})/kT] \equiv Z(T). \quad (21)$$

If we make the third assumption that the spacing of the rotational levels in the bound state is that of a rigid rotator at the equilibrium internuclear separation of the bound state,

$$E_{avJ'} - E_{av0} = J'(J'+1)\hbar^2/2\mu r_0^2, \quad (22)$$

then the rotational partition function $Z(T)$ becomes,

$$Z(T) = \frac{2\mu r_0^2 kT}{\sigma \hbar^2} = \frac{\mu r_0^2 kT}{\hbar^2}. \quad (23)$$

Note that the symmetry factor $\sigma = 2$ (Pauli exclusion of half of the nuclear spin states) appears explicitly.

If we make these three approximations, equation (15) becomes

$$\begin{aligned} \kappa_v^{b \rightarrow a} = & \frac{8\pi^3 \nu}{3hc} \frac{3}{4} \frac{n_H^2}{(2\pi\mu kT)^{3/2}} \frac{h^3}{\sigma \hbar^2} \frac{2\mu r_0^2 kT}{\sigma \hbar^2} \\ & \times \sum_v \exp -[(E_{av0} - h\nu)/kT] 2 \left(\frac{2\mu}{E_{av0} - h\nu} \right)^{1/2} \\ & \times \left[\int \mathcal{R}_{K,0}^b(R) D_{ba}(R) \mathcal{R}_{v,0}^a(R) dR \right]^2, \end{aligned} \quad (24)$$

an expression that is approximately equivalent to multiplying the $J' = 0$ contribution of equation (15) by the rotational partition function (23), and which we shall therefore refer to as the $J' = 0$ calculation in Figs. 4, 5, and 6.

Finally, if we use the Condon "reflection method"^(14,15) and replace the continuum wave function by a δ -function different from zero only at the classical turning point of the motion $R_T(E_{av0} - h\nu)$, the matrix element in equation (24) becomes

$$\int \mathcal{R}_{K,0}^b(R) D_{ba}(R) \mathcal{R}_{v,0}^a(R) dR \sim D_{ba}(R_T) \mathcal{R}_{v,0}^a(R_T). \quad (25)$$

The calculations by SOLOMON⁽¹²⁾ using this approximation are also shown in Figs. 4, 5, and 6.

The differences between the δ -function calculation and the $J' = 0$ calculation, which uses complete continuum wave functions, are generally the same as those found by JAMES and COOLIDGE⁽⁹⁾ (see their Fig. 4), with the δ -function calculation overestimating

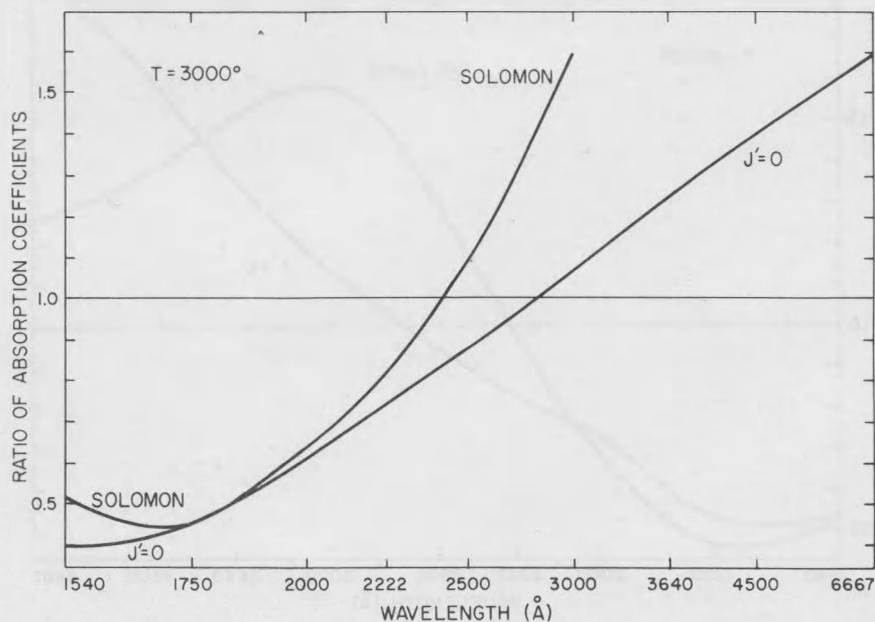


FIG. 4. The ratio of the $J' = 0$ approximation, equation (24), to the detailed summation over rotational states, equation (15); and the ratio of Solomon's (1964) calculation using the δ -function approximation, equation (25), to the detailed summation.

the long-wavelength contributions and underestimating those at short wavelengths. The strong variations in the difference at long wavelengths are probably caused by the different potential-energy curves used by Solomon.

5. CONCLUSIONS

The errors introduced into calculations of continuous molecular spectra with the assumption that all rotational states contribute the same as the $J' = 0$ rotational state are of the same order of magnitude as or larger than those introduced by the use of δ -functions as continuum wave functions, for temperatures at which several rotational states are populated.

For the purposes of a rough calculation, we suggest that a minimum account may be taken of the rotational dependence if we use as typical matrix element in equation (24) not that for the $J' = 0$ rotational state but that for the state with the known maximum population at the given equilibrium temperature. For the temperatures of Figs. 4 to 6, which are typical of stellar surface temperatures, the rotational states with the maximum thermal population in the bound state $1s\sigma 2s\sigma^3\Sigma_g^+$ are $J_{\max}(3000^\circ\text{K}) = 5.0$, $J_{\max}(5000^\circ\text{K}) = 6.6$, and $J_{\max}(8000^\circ\text{K}) = 8.4$. The accuracy of this approximation is being investigated.

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