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Dipole moments and transition probabilities of the $a\,^3\Sigma_g^+$—$b\,^3\Sigma_u^+$ system of molecular hydrogen

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Multiconfiguration variational calculations are carried out of the electronic wave functions of the $a\,^3\Sigma_g^+$ and $b\,^3\Sigma_u^+$ states of molecular hydrogen, and the electric dipole transition moment between them is obtained. The dipole moment is used in a calculation of the probabilities of radiative transitions from the discrete vibrational levels of the $a\,^3\Sigma_g^+$ state to the vibrational continuum of the repulsive $b\,^3\Sigma_u^+$ state as functions of the wavelength of the emitted photons, and a comparison is made with measurements of the emission spectra of the $v'=0$ levels of H_2 and of D_2. The total transition probabilities and radiative lifetimes of levels $v'=0$—20 are presented.

INTRODUCTION

The $a\,^3\Sigma_g^+$—$b\,^3\Sigma_u^+$ transition of molecular hydrogen is a major contributor to the opacity in stellar atmospheres[1,2] and an important source of emission in laboratory experiments and possibly in the ultraviolet spectrum of the Jovian planets. James and Coolidge[3] calculated the electronic eigenfunctions and transition dipole moment for internuclear distances R between $1.3a_0$ and $2.9a_0$ and presented values of the emission spectra and radiative lifetimes of the lowest four vibrational levels of the $a\,^3\Sigma_g^+$ state. An arbitrary extrapolation of the dipole moment function to other values of R was employed by Doyle[1,2] to compute the continuum absorption coefficient as a function of wavelength.

We present the results of multiconfiguration variational calculations for nuclear separations R between $0.1a_0$ and $20a_0$ which we use to determine the emission spectra and radiative lifetimes of the vibrational levels $v'=0$ through 20 of the $a\,^3\Sigma_g^+$ state.

ELECTRONIC WAVE FUNCTIONS

The wave functions (Ψ_a,Ψ_b) for the $a\,^3\Sigma_g^+$ and $b\,^3\Sigma_u^+$ states of H_2 were constructed from orthonormal one-electron orbitals (ϕ) according to the expansion

$$\Psi_{(a,b)}=\sum_{\substack{i,j\\(i\geq j)}}^{N} C_{ij}\{\phi_i(1)\phi_j(2)\}\ . \tag{1}$$

For $i=j$, $\{\phi_i(1)\phi_j(2)\}$ is a simple product of orbitals and, for $i\neq j$,

$$\{\phi_i(1)\phi_j(2)\}=\frac{1}{\sqrt{2}}\{\phi_i(1)\phi_j(2)\pm\phi_j(1)\phi_i(2)\}\ , \tag{2}$$

where the upper sign is taken for singlet states and the lower sign for triplet states. The C_{ij} are optimized variationally by diagonalizing the Hamiltonian matrix obtained from the configurations included in the representation of $\Psi_{(a,b)}$.

The orbitals are expanded in terms of nuclear-centered Gaussian basis functions with exponents scaled from those of Huzinaga[4] with the addition of a $1s$ exponent of 0.006 37 and a $2p$ exponent of 0.006 872 9, each selected to minimize linear dependence by taking the product of the previous exponent and the ratio of the previous two. The contraction coefficients of the basis functions are adopted from Huzinaga[4] and Guberman.[5] The exponents and contraction coefficients are listed in Table I. The first six exponents are appropriate to H($1s$) (Ref. 5) and the next four to H($2s$) (Ref. 4). The basis set in Table I leads to a total of $12\sigma_g$, $12\sigma_u$, $5\pi_{ux}$, $5\pi_{gx}$, $5\pi_{uy}$, and $5\pi_{gy}$ orbitals. By generating all possible configurations we obtained a 194-configuration wave function for the $b\,^3\Sigma_u^+$ state and a 172-configuration wave function for the $a\,^3\Sigma_g^+$ state.

DIPOLE MOMENT

The dipole transition moment is the matrix element of z_1+z_2 between the two multiconfiguration wave functions

$$D(R)=|\langle\Psi_a|z_1+z_2|\Psi_b\rangle|\ , \tag{3}$$

where z_1 and z_2 are the coordinates of electrons 1 and 2 along the internuclear axis. Table II is a list of the calculated values of $D(R)$ together with those obtained by James and Coolidge.[3] There is close agreement between the two calculations. The multiconfiguration wave functions yield a dipole moment which exhibits a considerable variation with R. The dipole moment continues to be large beyond the range considered by James and Coolidge[3] and we expect their computed lifetimes to be too large. Our calculated dipole moment joins smoothly to the limiting value of 2.5314 at $R=0$ obtained from the oscillator

TABLE I. Gaussian basis functions. Contiguous basis functions with contraction coefficients other than unity are contracted into a single basis function.

Type	Exponents	Contraction coefficients
s	82.474	0.005 535 2
	12.398	0.044 669 7
	2.8391	0.193 758 4
	0.814 72	0.824 468 5
	0.271 84	1.0
	0.099 483	1.0
	4.6935	0.136 629 4
	0.582 74	0.925 125
	0.042 726	1.0
	0.0165	1.0
	0.006 37	1.0
$p_{x,y,z}$	1.458 369	0.008 33
	0.346 270	0.065 50
	0.111 912	1.0
	0.042 163	1.0
	0.017 023	1.0
	0.006 872 9	1.0

strength of the $1s2s\ {}^3S-1s\,2p\ {}^3P$ transition of helium. It is consistent also with the long-range form calculated by Stephens,[6]

$$D(R)\sim 1.053\,498+9.058\,87/R^3\ . \tag{4}$$

Equation (4) was used in the calculations for $R>13a_0$. A cubic spline fit to the calculated values of $D(R)$ was used at other internuclear distances.

TABLE II. Dipole moment of the transition $a\,{}^3\Sigma_g^+-b\,{}^3\Sigma_u^+$.

R (a_0)	$D(R)$ (a.u.)[a]	$D(R)$ (a.u.)[b]	R (a_0)	$D(R)$ (a.u.)[a]
0.5	2.515		3.2	0.6058
0.75	2.394		3.5	0.5681
1.0	2.155		4.0	0.5378
1.1	2.031		4.5	0.5401
1.25	1.831		5.0	0.5673
1.3	1.764	1.719	6.0	0.6535
1.4	1.632		7.0	0.7305
1.5	1.507	1.503	8.0	0.7940
1.7	1.287	1.289	9.0	0.8582
1.87		1.128	10.0	0.9282
1.9	1.110		15.0	1.056
2.0	1.036	1.012	20.0	1.055
2.1	0.9711	0.975	100.0	1.054
2.3	0.8634	0.845		
2.5	0.7795	0.742		
2.7	0.7139	0.673		
2.9	0.6625	0.611		

[a] This work.
[b] James and Coolidge, Ref. 3.

TRANSITION PROBABILITIES

The spontaneous transition probabilities from a discrete level v' to a continuum level k'' is given in $\mathrm{s}^{-1}/\mathrm{cm}^{-1}$ by[7]

$$A_{v'k''}=9.23\times 10^{-12} g \nu^3_{v'k''}\,|\langle \chi_{v'}(R)\,|\,D(R)\,|\,\chi_{k''}(R)\rangle|^2\ , \tag{5}$$

where $\nu_{v'k''}$ is the photon frequency in cm^{-1}, $\chi_{v'}$ and $\chi_{k''}$ are, respectively, the normalized rotationless discrete and continuum vibrational eigenfunctions obtained by solving the nuclear equation of motion in the appropriate interaction potential $V(R)$ with the boundary condition

$$\chi_{k''}\sim\left[\frac{2\mu}{\pi k''}\right]^{1/2}\sin(k''R+\eta)\ , \tag{6}$$

k'' being the final-state wave number. Because the $b\,{}^3\Sigma_u^+$ state is repulsive, only continuum vibrational eigenfunctions exist and the lifetime for the vibrational level v' of the $a\,{}^3\Sigma_g^+$ state is given by

$$\tau_{v'}^{-1}=\int A_{v'k''}d\nu_{v'k''}\ . \tag{7}$$

We used the potential energies $V_a(R)$ and $V_b(R)$ for the $a\,{}^3\Sigma_g^+$ and $b\,{}^3\Sigma_u^+$ states derived by Kolos and Wolniewicz.[8,9] The potentials were extended to small distances $R\le 1a_0$ by the short-range forms

$$V_a(R)=-1.550\,23+\frac{1}{R}+0.640\,450\,3R-0.069\,133\,5R^2 \tag{8}$$

and

$$V_b(R)=-1.133+\frac{1}{R}+0.635R-0.123R^2\ . \tag{9}$$

TABLE III. Total transition probabilities and lifetimes of the vibrational levels of the $a\,{}^3\Sigma_g^+$ state of H_2. Powers of ten are shown in square brackets.

v'	$\int A_{v'k''}d\nu_{v'k''}$ (s^{-1})	$\tau_{v'}$ (s)[a]	$\tau_{v'}$ (s)[b]
0	8.60[7]	1.16[−8]	1.19[−8]
1	9.82[7]	1.02[−8]	1.10[−8]
2	1.09[8]	9.17[−9]	1.01[−8]
3	1.19[8]	8.40[−9]	9.7[−9]
4	1.28[8]	7.81[−9]	
5	1.37[8]	7.30[−9]	
6	1.45[8]	6.90[−9]	
7	1.56[8]	6.41[−9]	
8	1.68[8]	5.95[−9]	
9	1.82[8]	5.49[−9]	
10	2.01[8]	4.98[−9]	
11	2.28[8]	4.39[−9]	
12	2.69[8]	3.72[−9]	
13	3.35[8]	2.99[−9]	
14	4.49[8]	2.23[−9]	
15	6.59[8]	1.52[−9]	
16	9.59[8]	1.04[−9]	
17	1.09[9]	9.17[−10]	
18	1.09[9]	9.15[−10]	
19	1.00[9]	9.96[−10]	
20	7.87[8]	1.27[−9]	

[a] This work.
[b] James and Coolidge, Ref. 3.

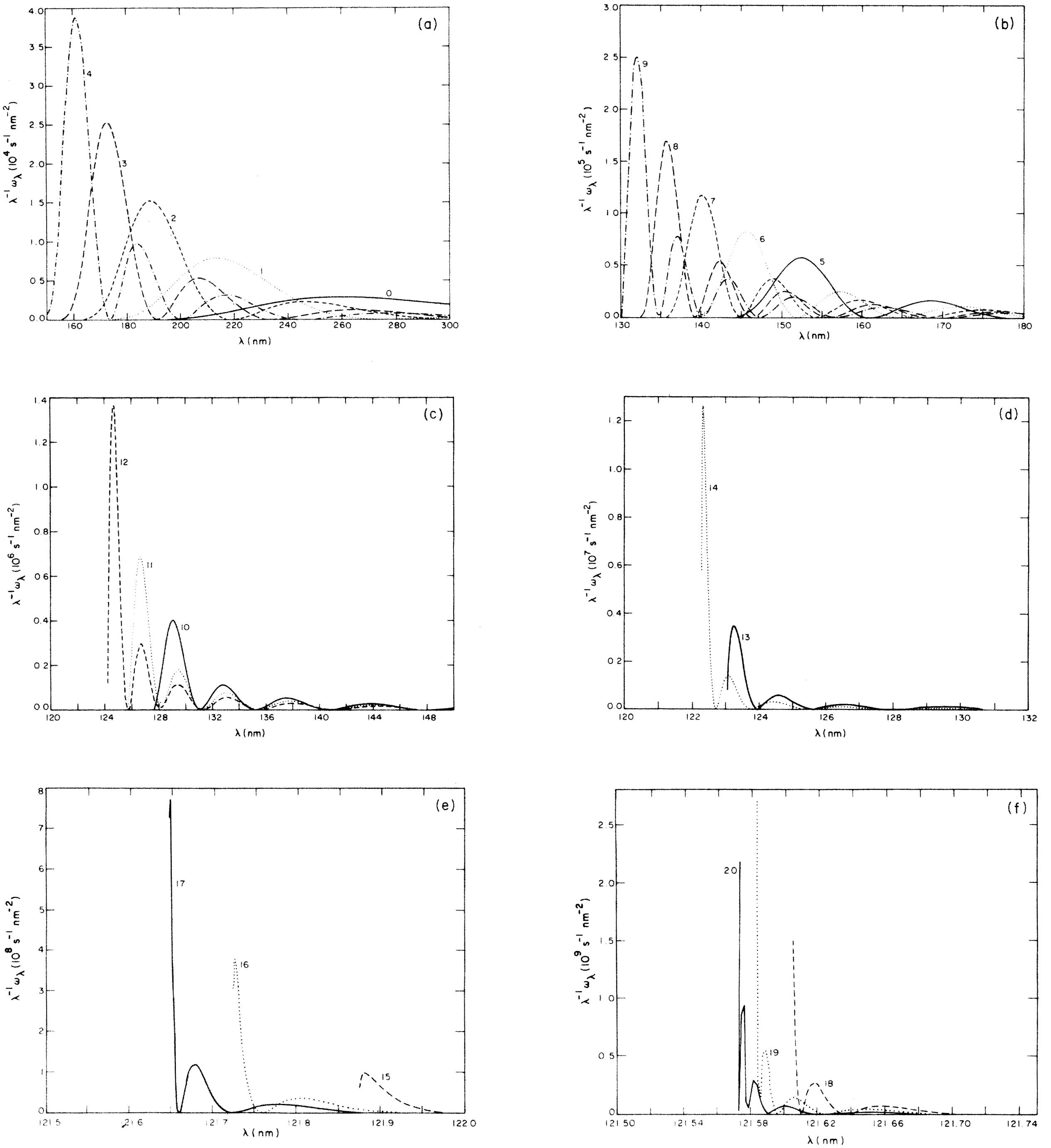

FIG. 1. The spontaneous emission spectra $\lambda^{-1}\omega_\lambda$ arising from vibrational levels v' of the $a\,{}^3\Sigma_g^+$ state of H_2, where λ is the wavelength in nm. The spectra are labeled by v'. Note the changes in scale.

For $R > 10a_0$, the potentials were extrapolated to join smoothly to the asymptotic expressions[10,11]

$$V_a(R) = -\frac{1.109\,858}{R^3} - \frac{174.1659}{R^6} - \frac{26\,378.31}{R^8} \tag{10}$$

and

$$V_b(R) = -\frac{6.4990}{R^6} - \frac{124.4}{R^8} - \frac{3285.0}{R^{10}} . \tag{11}$$

The equations of nuclear motion were integrated by the standard Numerov procedure. The total transition probabilities and lifetimes for vibrational levels up to $v'=20$ are presented in Table III together with the lifetimes calculated by James and Coolidge.[3] An energy stepsize of 10^{-3} a.u. was used in integrating the transition probability $A_{v'k''}$, except for $v' \geq 12$, where 10^{-6} a.u. was necessary to ensure convergence near threshold. The computation was checked by the sum rule[7]

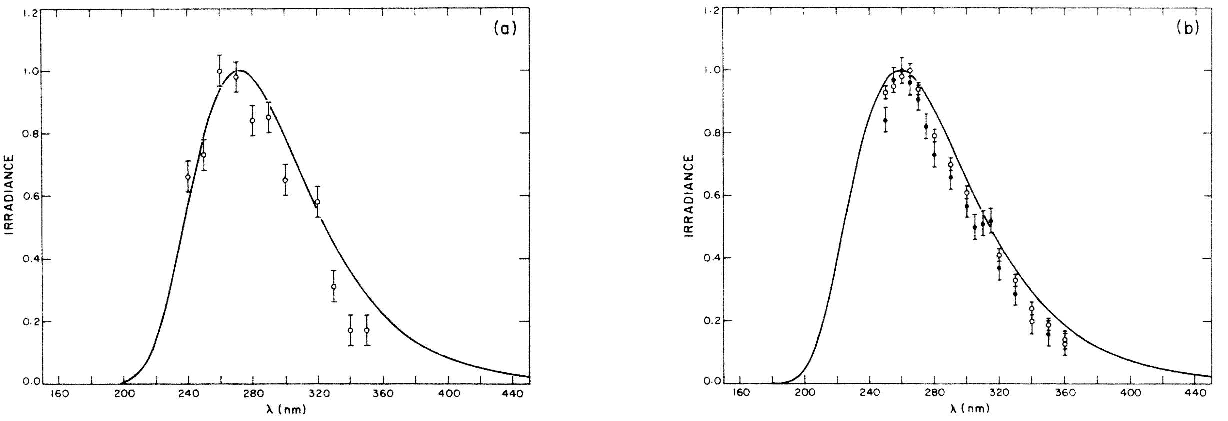

FIG. 2. (a) The spectral irradiance $\lambda^{-1}\omega_\lambda$ of H_2 in arbitrary units measured by Lishawa *et al.* (Ref. 16) and predicted for emission from the $v'=0$ level of the $a\,^3\Sigma_g^+$ state. ● and ○ are the measured values for electron impact energies of 11.60 eV (●) and 11.75 eV (○), respectively. (b) Same as 2(a) for D_2, for an electron impact energy of 11.45 eV.

$$\langle \chi_{v'} | D^2 | \chi_{v'} \rangle = \frac{1}{\mu} \int | \langle \chi_{k''} | D | \chi_{v'} \rangle |^2 k'' dk'' , \qquad (12)$$

in a.u. The rule was satisfied to within 1% for $v' \le 5$ and 3% for $v' \le 19$. For $v'=20$, the error was 30%. The value of the lifetime is correspondingly uncertain.

Both sets of theoretical lifetimes agree within experimental error with the measured values of Imhof and Read[12] and Smith and Chevalier[13] which refer to levels $v'=0$—3. As anticipated our lifetimes are slightly smaller than those of James and Coolidge.[3] In Fig. 1 we give the emission spectra arising from each vibrational level v' in the form of $\lambda^{-1}\omega_\lambda$ as functions of λ, where λ is the emission wavelength in nm and

$$\omega_\lambda = \frac{10^7}{\lambda^2} A_{v'k''} . \qquad (13)$$

The spectra resulting from electron-impact excitation of the $a\,^3\Sigma_g^+$ states of H_2 and D_2 have been measured by Coolidge,[14] Smith,[15] and Lishawa *et al.*[16] The experiments of Smith[15] appear to be in error.[14] Those of Coolidge[14] and Lishawa *et al.*[16] agree well.

Lishawa *et al.*[16] measured the irradiance as a function of wavelength resulting from impact excitation of H_2 by electrons with mean energies of 11.60 eV and 11.75 eV. The threshold for excitation of the $v'=0$ level is 11.787 eV and of the $v'=1$ level 12.101 eV. Lishawa *et al.*[16] estimate that at 11.8 eV half the electrons had sufficient energy to excite the $v'=0$ level, but less than 5% were energetic enough to excite the $v'=1$ level. The Franck-Condon factors for the $a\,^3\Sigma_g^+ - X\,^1\Sigma_g^+$ transition are 0.208 for the 0-0 band and 0.255 for the 1-0 band. The excitation to $v'=1$ contributes, at most, 12% of the total irradiance. Emission from $v'=1$ peaks at 210 nm and its contribution to the irradiance which was measured between 250 nm and 360 nm may be neglected.

Figures 2(a) and 2(b) are comparisons of the measured[16] relative irradiance $\lambda^{-1}\omega_\lambda$ for H_2 and D_2, respectively, with the theoretical values for emission from $v'=0$. The agreement is excellent.

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