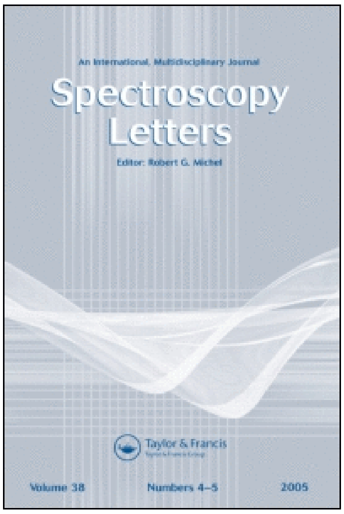

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MORSE FRANCK-CONDON FACTORS AND R-CENTROIDS FOR SOME LYMAN BANDS OF H_2, HD AND D_2.

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ABSTRACT

Using new rotational and vibrational constants, Morse Franck-Condon factors and r-centroids are computed for 108 Lyman bands of astrophysical importance H_2, HD and D_2 molecules. Experimental oscillator strengths conjoint with Morse Franck-Condon Factors for six Lyman bands of molecular hydrogen yield radiative lifetimes for v = 0-5 levels of the B $^1\Sigma_u^+$ state that are inconsistent with the experimental lifetime measurements. The limitation of analytic Morse function in the region of small internuclear separation for the B $^1\Sigma_u^+$ state of H_2 is discussed. The r-centroids ($r_{v'v''}$) are found to increase with frequencies of the Lyman bands of H_2, HD and D_2. For a sequence, $\Delta r \equiv r_{v'+1,v''+1} - r_{v'v''}$ is constant. A comparison of $r_{v'v''}$ values of the Lyman bands shows that $r_{v'v''}$ of the band (v'v'') increases in going from H_2 to D_2 .

INTRODUCTION

The absorption of radiation by H_2, HD and D_2 is of considerable astrophysical importance (Field et al. 1966; Stecher & Williams 1967; Trauger 1972; Trauger et al. 1973; Barrett 1973) in the studies of planetary and interplanetary spectra. The Lyman bands of diatomic molecules H_2,HD and D_2 lie in the vacuum ultraviolet region. The growing interest of astronomy in this region and the abundances of H_2 and D_2 in the interstellar medium encourage the discussion of fundamental wavelength, intensity and mean internuclear distance associated with a band of the Lyman system of these molecules. Franck-Condon factors for the H_2 Lyman band system have been the subject of study by many workers (Allison & Dalgarno 1969,1970; Halmann & Laülicht 1966,1967; Spindler 1966,1969; Nicholls 1965; Geiger & Topschowsky 1966).Because, new rotational and vibrational constants are available for the electronic states of H_2, HD and D_2 (Bredohl & Herzberg 1973; Dabrowski & Herzberg 1974; Herzberg & Howe 1959; Wilkinson 1968) the study of Morse Franck-Condon factors and related quantities is needed. In this communication we report the Morse Franck-Condon factors and r-centroids for 108 Lyman bands of H_2, HD and D_2 molecules. Using our Morse Franck-Condon factors conjoint with experimental oscillator strengths (Fabian & Lewis 1974) for six Lyman bands of molecular hydrogen we estimate radiative lifetimes for v = 0-5 levels of the B $^1\Sigma_u^+$ state and, where possible, compare with experimental lifetime measurements (Hesser 1968). Further, we discuss the properties of r-centroids and the limitation of analytic Morse function for the B $^1\Sigma_u^+$ state of H_2.

METHOD OF COMPUTATION

The intensity of a $v' \rightarrow v''$ transition (Herzberg 1950) in emission is

$$I_{v'v''} = N_{v'} \, hc \, A_{v'v''} \, \nu_{v'v''} \tag{1}$$

where $\nu_{v'v''}$ is the frequency of the transition, $N_{v'}$ is the population in the excited state and $A_{v'v''}$ is the Einstein coefficient which is given by the expression

$$A_{v'v''} = \frac{64\pi^4 \nu^3_{v'v''}}{3h} R_e^2(r_{v'v''}) | <\Psi_{v'}\Psi_{v''}> |^2 \quad (2)$$

Here R_e is the electronic transition moment which is assumed to be independent of internuclear distance. $\Psi_{v'}$ and $\Psi_{v''}$ are the vibrational wave functions of the upper and lower states $r_{v'v''}$ is the r-centroid, defined by equation (5), associated with the $v' \rightarrow v''$ transition. It follows from equ. (1) & (2) that

$$I_{v'v''} = K' N_{v'} \nu^4_{v'v''} R_e^2 (r_{v'v''}) q_{v'v''} \quad (3)$$

where K' is an appropriate constant and $q_{v'v''} (= |<\Psi_{v'}\Psi_{v''}>|^2)$ is the Franck-Condon factor. Equation (3) can be written as:

$$I_{v'v''} = K N_{v'} P_{v'v''} \quad (4)$$

where $P_{v'v''}$ is the band strength for the $v' \rightarrow v''$ transition. For the evaluation of Franck-Condon factors, the vibrational wave functions are required for the upper and lower states. We have used the method of Fraser & Jarmain (1953) with r_e-shift correction for the evaluation of Franck-Condon factors of the Lyman bands of H_2, HD and D_2.

The r-centroid $(r_{v'v''})$ of a $v' \rightarrow v''$ transition in a diatomic molecular band system has been defined by Nicholls & Jarmain (1956):

$$r_{v'v''} = \frac{<\Psi_{v'} r \Psi_{v''}>}{<\Psi_{v'}\Psi_{v''}>} \quad (5)$$

where r is the internuclear separation. We have used the quadratic equation and graphical methods of Nicholls &

Jarmain (1956) to find r-centroids of the Lyman bands of H_2, HD and D_2.

The band oscillator strengths ($f_{v'v''}$), combined with the Franck-Condon factors for branching to lower states, allows the computation of vibrational-lifetimes (Schadee 1967; Tatum 1967) from

$$\tau_{v'} = \frac{1.5\, q_{v'v''}\, \nu_{v'v''}\, g_1}{(\Sigma_{v''}\, q_{v'v''}\, \nu^3_{v'v''})\, f_{v'v''}\, g_2} \tag{6}$$

where g_1 and g_2 are the upper and lower state degeneracies.

RESULTS AND DISCUSSIONS

We have used the experimental molecular parameters: w_e, $w_e x_e$, B_e, α_e and r_e (obtained from B_e values) for the $B\ ^1\Sigma_u^+$ and $X\ ^1\Sigma_g$ states of H_2,HD and D_2 reported by Dabrowski & Herzberg (1974), Bredohl & Herzberg (1973), Wilkinson (1968) and Herzberg & Howe (1959) for the computations of Morse Franck-Condon factors and r-centroids of the Lyman bands of these molecules. The results are tabulated in Table 1 along with the available frequencies of the Lyman bands. To obtain radiative lifetimes for v = 0-5 levels of the $B\ ^1\Sigma_u^+$ state of molecular hydrogen (equ. 6) we have used the weighted mean Lyman band oscillator strengths obtained from photoelectric absorption measurements by Fabian & Lewis (1974). These lifetimes are tabulated in table 2 and, where possible, are compared with the experimental lifetimes obtained by phase-shift technique (Hesser 1968). A comparison of these radiative lifetimes (table 2) shows that the theoretical lifetimes are inconsistent with the experimental lifetime measurements for the $B\ ^1\Sigma_u^+$ state of H_2 (Hesser 1968). Further, the approximation that R_e is independent of internuclear separation (equ. 2) is true for v' = 0-13 levels (Dalgarno & Allison 1968) of the

TABLE 1 : (a) Morse Franck-Condon factors (b) r-Centroids by graphical method (c) r-Centroids by quadratic equation (d) Frequencies of the Lyman bands of H_2, HD and D_2

Bands		H_2	HD	D_2
1		2	3	4
(0,0)	(a)	0.01741	0.00208	0.00001
	(b)	0.815	0.934	1.137
	(c)	0.814	0.933	1.142
	(d)	90203.55**	90399.86**	90633.79**
(0,1)	(a)	0.06603	0.01194	0.00011
	(b)	0.785	0.910	1.123
	(c)	0.777	0.904	1.123
	(d)	86042.21+++	86767.71+++	85976.00+
(0,2)	(a)	0.12328	0.03388	0.00057
	(b)	0.750	0.884	1.103
	(c)	0.742	0.877	1.103
	(d)	82116.23+++	83312.98++	84764.88+
(0,3)	(a)	0.14980	0.06477	0.00137
	(b)	0.720	0.861	1.088
	(c)	0.703	0.847	1.083
	(d)	78420.99§	80032.30++	82007.87*
(0,4)	(a)	0.13157	0.09108	0.00489
	(b)	0.682	0.838	1.073
	(c)	0.638	0.813	1.063
	(d)	74952.98§	76922.98++	
(0,5)	(a)	0.08733	0.10079	0.00997
	(b)	0.637	0.814	1.055
	(c)	-	0.774	1.042
	(d)	71711.42§		76887.77*
(1,0)	(a)	0.06309	0.01290	0.00016
	(b)	0.910	1.010	1.190
	(c)	0.900	1.000	1.188
	(d)	91521.78**	91547.09**	91575.95**
(1,1)	(a)	0.06259	0.28569	0.00065
	(b)	0.880	0.985	1.172
	(c)	0.870	0.975	1.170
	(d)	87360.62+++	87914.94++	86918.16+
(1,2)	(a)	0.09308	0.08558	0.00495
	(b)	0.852	0.960	1.158
	(c)	0.841	0.950	1.151
	(d)	83434.64+++	84460.21++	85707.04*
(1,3)	(a)	0.02026	0.08651	0.01329
	(b)	0.822	0.930	1.142
	(c)	0.809	0.924	1.131
	(d)	79739.40§	81179.53++	82950.18*

(continued)

TABLE 1 (continued)

1	2	3	4
(1,4)	(a) 0.00273 (b) 0.795 (c) 0.775 (d) 76271.39§	0.05009 0.917 0.897 78070.22++	0.02582 1.125 1.112 80308.18*
(1,5)	(a) 0.04169 (b) 0.767 (c) 0.737 (d) 73029.83§	0.01129 0.895 0.868	0.06241 1.110 1.093 77780.12*
(2,0)	(a) 0.12486 (b) 1.002 (c) 0.980 (d) 92803.35**	0.04074 1.082 1.064 92666.22**	0.00111 1.245 1.234 92498.80**
(2,1)	(a) 0.11078 (b) 0.967 (c) 0.953 (d) 88642.05+++	0.09504 1.056 1.041 89034.07++	0.00687 1.227 1.215 87841.01+
(2,2)	(a) 0.01337 (b) 0.940 (c) 0.926 (d) 84716.07+++	0.08666 1.035 1.018 85579.34++	0.02063 1.201 1.198 86630.65*
(2,3)	(a) 0.01219 (b) 0.912 (c) 0.899 (d) 81020.83§	0.02924 1.012 0.995 82298.66++	0.03956 1.192 1.179 83873.16*
(2,4)	(a) 0.04377 (b) 0.885 (c) 0.872 (d) 77552.82§	0.00003 0.980 0.971 79189.35++	0.05341 1.177 1.161 81230.76*
(2,5)	(a) 0.10672 (b) 0.860 (c) 0.847 (d) 74311.26§	0.01653 0.967 0.947	0.05278 1.160 1.142
(3,0)	(a) 0.17111 (b) 1.070 (c) 1.054 (d) 94049.98**	0.08445 1.156 1.126 93758.60**	0.00479 1.300 1.279 93403.39**
(3,1)	(a) 0.03972 (b) 1.057 (c) 1.029 (d) 89888.82+++	0.10765 1.130 1.104 90126.45++	0.02243 1.280 1.261 88745.60+
(3,2)	(a) 0.01297 (b) 1.025 (c) 1.004 (d) 85962.84+++	0.03152 1.105 1.082 86671.72++	0.04874 1.260 1.243 87535.22*

(continued)

TABLE 1 (continued)

1	2	3	4
(3,3)	(a) 0.06230 (b) 1.000 (c) 0.982 (d) 82267.60§	0.00121 1.080 1.060 83391.04++	0.06336 1.245 1.226 34777.71*
(3,4)	(a) 0.03315 (b) 0.967 (c) 0.954 (d) 78799.59§	0.03506 1.056 1.038 80281.73++	0.05250 1.227 1.208
(3,5)	(a) 0.00930 (b) 0.942 (c) 0.929 (d) 75558.03§	0.01945 1.032 1.016	0.02244 1.208 1.190 79607.63*
(4,0)	(a) 0.17877 (b) 1.175 (c) 1.125 (d) 95263.18**	0.13080 1.231 1.184 94825.60**	0.01502 1.342 1.322 94290.44**
(4,1)	(a) 0.00021 (b) 1.150 (c) 1.100 (d) 91101.80+++	0.06912 1.205 1.164 91193.45++	0.05038 1.322 1.305 89632.65+
(4,2)	(a) 0.06788 (b) 1.115 (c) 1.076 (d) 87175.82+++	0.00000 1.176 1.143 87738.72++	0.07246 1.304 1.288 88422.36*
(4,3)	(a) 0.03869 (b) 1.082 (c) 1.052 (d) 83480.58§	0.04718 1.151 1.122 84458.04++	0.05349 1.298 1.270 85664.68*
(4,4)	(a) 0.05303 (b) 1.052 (c) 1.038 (d) 80012.57§	0.03953 1.126 1.102 81348.73++	0.01730 1.279 1.254
(4,5)	(a) 0.07279 (b) 1.020 (c) 1.006 (d) 76771.01§	0.31345 1.105 1.098	0.00371 1.260 1.237 80494.80*
(5,0)	(a) 0.14966 (b) 1.270 (c) 1.198 (d) 96443.4***	0.15894 1.300 1.243	0.36460 1.385 1.367 95160.3***
(5,1)	(a) 0.03265 (b) 1.230 (c) 1.174 (d) 89904.99+++	0.01572 1.275 1.222	0.08609 1.368 1.350 90502.55+

(continued)

TABLE 1 (continued)

1	2	3	4
(5,2)	(a) 0.09020	0.02288	0.06975
	(b) 1.205	1.246	1.352
	(c) 1.149	1.201	1.332
	(d) 85979.01+++		89292.28*
(5,3)	(a) 0.12432	0.03656	0.03333
	(b) 1.165	1.220	1.335
	(c) 1.131	1.182	1.316
	(d) 84660.60§		86534.17*
(5,4)	(a) 0.12922	0.47736	0.02406
	(b) 1.135	1.196	1.322
	(c) 1.118	1.161	1.299
	(d) 81192.59§	-	83892.71*
(5,5)	(a) 0.10953	-	0.08272
	(b) 1.105	1.171	1.304
	(c) 1.094	1.141	1.282
	(d) 77951.03§	-	81364.39*

* Bredohl & Herzberg (1973).
** Wilkinson (1968).
*** Dabrowski & Herzberg (1974).
\+ Calculated values.
++ Calculated from vibrational quanta of the ground state given by Durie & Herzberg (1960).
+++ Calculated from vibrational quanta of the ground state given by Stoicheff (1957).
§ Herzberg & Howe (1959).

B $^1\Sigma_u^+$ state. Even RKR Franck-Condon factors of the Lyman bands (Spindler 1966,1969) do not give complete agreement with the experimentally determined relative band strengths (Geiger et al. 1966,1969). This shows that the potential curve of the B $^1\Sigma_u^+$ state of H_2 deviates strongly from the analytic Morse function in the region of small internuclear separation. Thus, inspite of improved molecular parameters available for H_2, the Morse Franck-Condon factors cannot be used for further studies of the Lyman bands of H_2 (Namioka 1965; Nicholls 1965; Geiger & Topschowsky 1966).

Jarmain et al. (1956) on the basis of the study of a number of band systems have established that $\Delta r \equiv r_{v'+1,v''+1} - r_{v',v''}$

TABLE 2. Comparison of theoretical and experimental lifetimes of $B\ ^1\Sigma_u^+$ state of H_2.

Vibrational level	Lifetime (in nsec)	
	Theoretical	Experimental[$]
0	4.8	-
1	9.7	-
2	5.9	-
3	5.9	0.8
4	3.7	0.8
5	2.1	0.8

$ Hesser (1968).

in a sequence remains constant. The same property can be visualized for $\Delta v = 0$ sequence of Lyman bands of H_2, HD & D_2 (Table 1). Further, Nicholls & Jarmain (1956) have pointed out that for most of the band systems $\Delta r \approx 0.01$ A. This difference basically depends on the width of the potential curves involved in the transition. In our case, $\Delta r > 0.01$ A which shows that the potentials involved in the Lyman band system for H_2, HD and D_2 are wide. Table 1 shows that r-centroids increase with frequencies of the Lyman bands of H_2, HD & D_2. A comparison of $r_{v'v''}$ values of the Lyman bands shows that $r_{v'v''}$ of the band (v'v'') increases in going from H_2 to D_2 (Table 1).

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