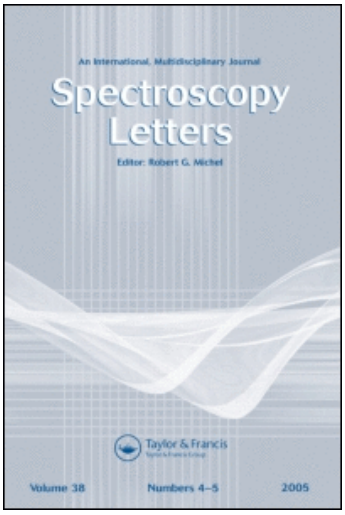

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Franck–Condon Factors and r-Centroids for the B–, C–, F–, and G–X Band Systems of YF Molecule

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Abstract: The Franck–Condon factors and r-centroids, which are very closely related to relative transition probabilities, have been evaluated by a more reliable numerical integration procedure for the $B^1\pi$–$X^1\Sigma^+$, $C^1\Sigma^+$–$X^1\Sigma^+$, $F^1\Sigma^+$–$X^1\Sigma^+$, and $G^1\pi$–$X^1\Sigma^+$ band systems of the YF molecule, using suitable potentials.

Keywords: B–, C–, F–, and G–X band systems, Franck–Condon factors, r-centroids, YF molecule

INTRODUCTION

The knowledge of transition probabilities is required to explain the intensity distribution in a molecular band system. To a good approximation, Franck–Condon (FC) factors are proportional to these transition probabilities. Accurate values of FC factors and related quantities are essential to obtain the radiative lifetime and vibrational temperature of the source.

Dealing with 300 diatomic molecules of known or of possible astrophysical interest, Sauval and Tatum[1] report polynomial expressions for the partition functions and equilibrium constants for the molecule YF also.

To the best of our knowledge, there has been no report on the FC factors and r-centroids for the $B^1\pi$–$X^1\Sigma^+$, $C^1\Sigma^+$–$X^1\Sigma^+$, $F^1\Sigma^+$–$X^1\Sigma^+$, and $G^1\pi$–$X^1\Sigma^+$ band systems of the YF molecule in the literature. However, Hamilton et al.[2] calculated the Franck–Condon intensities for the $B^1\pi$–$X^1\Sigma^+$ and

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$C^1\Sigma^+ - X^1\Sigma^+$ band systems without an explicit presentation of the numerical values of Franck–Condon factors for a complete set of transition levels, which leads to lack of data. Therefore, the reliable values of FC factors and r-centroids for these band systems of the YF molecule have been determined by the numerical integration procedure, using suitable potentials.

FRANCK–CONDON FACTORS AND r-CENTROIDS

Mathematically, one can write the intensity $I_{\nu'\nu''}$ of a molecular band for $\nu'-\nu''$ electronic transition in emission as[3]

$$I_{\nu'\nu''} = DN_{\nu'}E^4_{\nu'\nu''}\left[\int \psi_{\nu'}R_e(r)\psi_{\nu''}dr\right]^2, \tag{1}$$

where D is a constant, partially depending on the geometry of the apparatus, $N_{\nu'}$ is the population of the level ν', and $E_{\nu'\nu''}$ is the energy quantum, where $\psi_{\nu'}$ and $\psi_{\nu''}$ are the vibrational wave functions for the upper and lower states, respectively. Here, $R_e(r)$ is the electronic transition moment, and the variation of R_e with r is slow and hence $R_e(r)$ can be replaced by the averaged value $\bar{R}_e$ over a band system

$$I_{\nu'\nu''} = DN_{\nu'}E^4_{\nu'\nu''}\bar{R}_e^{\,2}\left[\int \psi_{\nu'}\psi_{\nu''}dr\right]^2, \tag{2}$$

A more realistic procedure would be to rewrite Eq. (2) as given by Nicholls[4]

$$I_{\nu'\nu''} = DN_{\nu'}E^4_{\nu'\nu''}R_e^{\,2}(\bar{r}_{\nu'\nu''})\left[\int \psi_{\nu'}\psi_{\nu''}dr\right]^2, \tag{3}$$

where the square of the overlap integrals is termed the Franck–Condon factor

$$q_{\nu'\nu''} = \left|\int \psi_{\nu'}\psi_{\nu''}dr\right|^2. \tag{3}$$

The r-centroid is a unique value of internuclear separation that may be associated with a given $\nu'-\nu''$ band and is defined as

$$\bar{r}_{\nu'\nu''} = \frac{\int \psi_{\nu'}r\psi_{\nu''}dr}{\int \psi_{\nu'}\psi_{\nu''}dr}. \tag{4}$$

For a proper understanding of the intensity distribution in the band systems of the molecules, it is necessary to choose suitable potentials. The potential energy curves for the electronic states B, C, F, G, X of YF have been constructed using Morse[5] function and also by Rydberg–Klien–Rees (RKR) procedure as modified by Vanderslice et al.[6,7] It is found that the Morse function represents the potential for all the electronic states of YF quite adequately because RKR curves are coincident with Morse ones. The

computation of the FC factor is made by Bates' method of numerical integration[8] according to the detailed procedure provided by Nagarajan et al.,[9] Partal et al.,[10] and Rajamanickam et al.[11] Morse wave functions are calculated at intervals of 0.01 Å for the range of r respectively from 1.84 Å to 2.22 Å, from 1.69 Å to 2.28 Å, from 1.79 Å to 2.19 Å and from 1.71 Å to 2.25 Å for all the experimentally observed vibrational levels of each state of the B–X, C–X, F–X, and G–X band systems of the YF molecule. Integrals in Equations (3) and (4) for the FC factors ($q_{v'v''}$) and r-centroids ($\bar{r}_{v'v''}$) are computed numerically, and the results are presented respectively in Tables 1, 2, 3, and 4 for the systems B–X, C–X, F–X, and G–X of the YF molecule, respectively. The wavelength ($\lambda_{v'v''}$) data[2,12] are also entered in the respective tables for all the systems. The molecular constants used in the current study are collected from the compilation of Huber and Herzberg.[13]

RESULTS AND DISCUSSION

For the B–X system of YF molecule, the FC factors indicate that (0, 0) band is most intense, and all the four observed bands have considerable intensity (FCF $>$ 0.1). In the C–X system, the FC factors indicate that the (0,0), (0,1), (0,2), (1,0), (1,2), (1,3), (1,4), (2,0), (2,1), (2,4), (2,5), (3,1), (3,3), (3,5), (3,6), (3,7), (4,1), (4,2), (4,4), (4,7), (4,8), (5,2), (5,8), and (5,9) bands are intense (FCF $>$ 0.1) and all other bands are comparatively weak.

Table 1. $q_{v'v''}$ and $\bar{r}_{v'v''}$ for B–X system of YF

	v''	
v'	0	1
0	(a) 0.399	0.382
	(b) 1.969	2.017
	(c) 6293.6	6554.1
1	(a) 0.349	0.002
	(b) 1.928	2.001
	(c) 6088.8	—
2	(a) 0.166	0.178
	(b) 1.888	1.939
	(c) 5897.8	—
3	(a) 0.056	0.206
	(b) 1.849	1.899
	(c) —	5934.0

(a) $q_{v'v''}$; (b) $\bar{r}_{v'v''}$ (Å); (c) $\lambda_{v'v''}$ (Å).

Table 2. $q_{v'v''}$ and $\bar{r}_{v'v''}$ for C–X system of YF

	v''									
v'	0	1	2	3	4	5	6	7	8	9
0	(a) 0.386	0.380	0.174	0.049	0.010	0.001	*	*	*	*
	(b) 1.970	2.018	2.067	2.116	2.167	2.219				
	(c) 5295.5	5475.0	5666.0	5868.9	—	—				
1	(a) 0.352	*	0.220	0.262	0.125	0.035	0.007	*	*	*
	(b) 1.929		2.026	2.075	2.124	2.174	2.226			
	(c) 5154.6		5505.7	5697.0	5901.1	6117.3	6346.4			
2	(a) 0.175	0.175	0.082	0.051	0.234	0.189	0.074	0.018	0.003	*
	b) 1.890	1.938	1.984	2.036	2.083	2.132	2.182	2.234	2.288	
	c) 5022.9	5184.8	5355.6	5537.1	5728.4	5932.3	6149.3	6381.6	—	
3	(a) 0.063	0.225	0.027	0.159	*	0.146	0.217	0.119	0.036	0.007
	(b) 1.851	1.898	1.947	1.993		2.092	2.140	2.190	2.241	2.295
	(c) 4899.3	5052.6	5214.6	5386.2	5567.6	5760.4	5964.5	6182.0	6414.8	—
4	(a) 0.019	0.137	0.161	0.004	0.143	0.035	0.05Ù	0.204	0.159	0.061
	(b) 1.812	1.859	1.907	1.951	2.002	2.046	2.101	2.148	2.197	2.249
	(c) 4782.2	4928.5	5082.9	5245.5	5418.0	5599.7	5792.7	5997.7	6215.8	6447.9
5	(a) 0.005	0.057	0.171	0.069	0.053	0.078	0.091	0.008	0.158	0.183
	(b) 1.773	1.821	1.868	1.916	1.962	2.011	2.056	2.116	2.156	2.204
	(c) —	—	4872.8	—	—	—	—	—	—	—

(a) $q_{v'v''}$; (b) $\bar{r}_{v'v''}$ (Å); (c) $\lambda_{v'v''}$ (Å); $^{*}q_{v'v''} = 0$.

Table 3. $q_{v'v''}$ and $\bar{r}_{v'v''}$ for F–X system of YF

	v''		
v'	0	1	2
0	(a) 0.686	0.262	0.047
	(b) 1.955	2.029	2.100
	(c) 3573.2	3655.6	—
1	(a) 0.254	0.260	0.353
	(b) 1.890	1.963	2.037
	(c) 3504.6	3583.9	—
2	(a) 0.052	0.328	0.059
	(b) 1.824	1.899	1.970
	(c) —	3515.5	—
3	(a) 0.008	0.118	0.295
	(b) 1.756	1.835	1.909
	(c) —	3526.5	—

(a) $q_{v'v''}$; (b) $\bar{r}_{v'v''}$ (Å); (c) $\lambda_{v'v''}$ (Å).

Table 4. $q_{v'v''}$ and $\bar{r}_{v'v''}$ for G–X system of YF

	v''							
v'	0	1	2	3	4	5	6	7
0	(a) 0.737	0.223	0.037	0.004	*	*	*	*
	(b) 1.952	2.036	2.104	2.173				
	(c) 3204.0	3270.0	3338.3	—				
1	(a) 0.228	0.352	0.316	0.091	0.014	0.001	*	*
	(b) 1.880	1.958	2.047	2.113	2.183	2.250		
	(c) 3149.9	3213.8	3279.7	3347.9	—	—		
2	(a) 0.034	0.330	0.133	0.325	0.145	0.030	0.004	*
	(b) 1.797	1.890	1.960	2.057	2.123	2.192	2.259	
	(c) —	3159.8	3223.5	3289.4	3357.4	—	—	
3	(a) 0.003	0.085	0.348	0.030	0.284	0.191	0.051	0.008
	(b) 1.683	1.810	1.899	1.945	2.067	2.139	2.201	2.269
	(c) —	3108.1	3169.8	—	3299.0	3366.9	—	—
4	(a) *	0.011	0.140	0.313	*	0.221	0.223	0.076
	(b)	1.703	1.822	1.907		2.078	2.141	2.210
	(c)	—	—	—		3308.7	3376.4	—
5	(a) *	0.001	0.025	0.190	0.251	0.013	0.153	0.238
	(b)	1.511	1.722	1.834	1.914	2.086	2.089	2.150
	(c)	—	—	—	—	—	3318.3	3385.8

(a) $q_{v'v''}$; (b) $\bar{r}_{v'v''}$ (Å); (c) $\lambda_{v'v''}$ (Å); (d) $^{*}q_{v'v''} = 0$.

For the F–X system, the FC factors imply that (0,0), (0,1), (1,0), (1,1), (1,2), (2,1), (3,1), and (3,2) bands are the bright ones. In the case of the G–X system, the FC factors suggest that (0,0) band is the most intense and the following bands (0,1), (1,0), (1,1), (1,2), (1,3), (2,1), (2,2), (2,3), (2,4), (3,2), (3,4), (3,5), (4,2), (4,3), (4,5), (4,6), (5,3), (5,4), (5,6), and (5,7) are slightly less.

For all the band systems of YF molecule, it is found that $r_e' > r_e''$ and hence the r-centroid values increase with an increase in wavelength [except (5,2) band in C–X band system], which is expected in the red degraded band system. The r-centroid value for (0,0) transition is slightly greater than $(r_e' + r_e'')/2$, and hence the potentials are not very anharmonic. If $\bar{r}$ and $\bar{r}_1$ are the r-centroid values corresponding with the bands (ν', ν'') and ($\nu' + 1$, $\nu'' + 1$), then the difference of r-centroid values $\bar{r}_1 - \bar{r}$ would exceed 0.01 Å only if the potentials are very wide. Here the sequence differences are found to vary from 0.01 Å to 0.03 Å, 0.004 Å to 0.02 Å, 0.007 Å to 0.011 Å, and 0.002 Å to 0.02 Å for the B–X, C–X, F–X, and G–X band systems, respectively.

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REFERENCES

1. Sauval, A. J.; Tatum, J. B. *Astrophys. J. Suppl. Ser.* **1984**, *56*, 193.
2. Hamilton, C. E.; Lesiecki, M. L.; Allamandola, L. J.; Nibler, J. W. *J. Chem. Phys.* **1982**, *76*, 189.
3. Rajamanickam, N. Intensity distribution in band spectra and the dissociation energies of the diatomic molecules. Ph.D. thesis. Mysore University: Mysore, India, 1987.
4. Nicholls, R. W. J. *Quant. Radiat. Trans.* **1974**, *14*, 233.
5. Morse, P. M. *Phys. Rev.* **1929**, *34*, 57.
6. Vanderslice, J. T.; Mason, E. A.; Maisch, W. G.; Lippincott, E. R. *J. Mol. Spectr.* **1959**, *3*, 17.
7. Vanderslice, J. T.; Mason, E. A.; Maisch, W. G.; Lippincott, E. R. *J. Mol. Spectr.* **1960**, *5*, 83.
8. Bates, D. R. *Proc. Roy. Soc. London* **1949**, *A196*, 217.
9. Nagarajan, K.; Fernandez Gomez, M.; Lopez Gonzalez, J. J.; Rajamanickam, N. *Astron. Astrophys. Suppl. Ser.* **1998**, *129*, 157.
10. Partal, F.; Fernandez Gomez, M.; Lopez Gonzalez, J. J.; Rajamanickam, N. *Astrophys. Space Sci.* **2000**, *272*, 345.
11. Rajamanickam, N.; Nagarajan, K.; Raja, V. *Spectrosc. Lett.* **2001**, *34*, 43.
12. Shenyavskaya, E. A.; Maltsev, A. A.; Gurvich, L. V. *Optics Spectrosc.* **1966**, *21*, 374.
13. Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure, Vol. IV., Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.