Journal of the Serbian Chemical Society
JSCS@tmf.bg.ac.yu • www.shd.org.yu/JSCS
www.shd.org.yu
J. Serb. Chem. Soc. *73* (5) 555–560 (2008) UDC 546.289'161+546.28'161:531.64:517.956.2
JSCS–3737 *Original scientific paper*

Franck–Condon factors and r-centroids for the diatomic fluorides of germanium and silicon

S. KANAGAPRABHA, R. RAJESWARA PALANICHAMY* and V. SATHIYABAMA

Department of Physics, N. M. S. S. V. N College, Madurai – 625 019, Tamilnadu, India

(Received 7 November 2006, revised 9 February 2007)

Abstract: A suitable potential energy function was found by analysing the potential functions proposed by Morse, Mohammad and Rafi *et al.* for the $A^2\Sigma^+$–$X^2\Pi_{3/2}$ and $B^2\Sigma^+$–$X^2\Pi_{3/2}$ band systems of GeF and the $^1\Sigma$–$^1\Pi$ band system of SiF. It was found that the potential proposed by Rafi *et al.* is in close agreement with the Rydberg–Klein–Rees (R–K–R) potential. Using this potential, the wave functions were evaluated by the Wentzel–Kramer–Brillouin (W–K–B) method. The Franck–Condon factors and r-centroids were computed by a numerical integration technique. The results are compared with available theoretical values. The intensities of the various bands were investigated.

Keywords: Franck–Condon factor; r-centroid; potential function; GeF and SiF.

INTRODUCTION

Spectroscopic research on the intensities in molecular spectra has two main components: (a) experimental intensity measurements in emission or absorption and (b) theoretical studies (including *ab initio* quantum mechanical calculation) of molecular potentials, eigenfunctions and the quantities derived there from, such as Franck–Condon (F–C) factors and r-centroids.[1] Detailed knowledge of F–C factors and r-centroids is essential for the calculation of many important data, such as radiative life times, vibrational temperatures of the sources and relative band strengths. The intensity distribution of various bands in any band system is mainly governed by the F–C factors. Singh[2] analysed the vibrational translation probabilities and r-centroids for diatomic fluorides of Si and Ge. Previously, the F–C factors and r-centroids were evaluated with the wave function computed using the Wentzel–Kramer–Brillouin (W–K–B) method for the SiH molecule.[3] Nagarajan *et al.*[4] computed the F–C factors and r-centroids for the SiF molecule. In the previous works,[2,4] the Morse potential[5] was used to find the wave function but not all of them obey the Morse potential.[5] In this work, a suitable potential energy function was found by analysing the potential functions proposed by

---

* Corresponding author. E-mail: rrpcaspd2003@yahoo.com

doi: 10.2298/JSC0805555K

Morse,[5] Mohammad[6] and Rafi *et al.*[7] for the $A^2\Sigma^+–X^2\Pi_{3/2}$ and $B^2\Sigma^+–X^2\Pi_{3/2}$ band systems of GeF and the $^1\Sigma–^1\Pi$ band system of SiF. It was found that the potential proposed by Rafi *et al.*[7] is in close agreement with the Rydberg–Klein–Rees potential.[8–10] Hence, this problem was revisited with the Rafi *et al.*[7] potential and the wave functions were evaluated using the W–K–B method. The F–C factors and r-centroids were computed by numerical integration techniques.

F–C factors and r-centroids

The intensity of each individual transition between vibrational levels for an allowed electronic transition is governed by F–C factors. The intensity of a v′,v′′ transition in emission is given by:

$$I_{v',v''} = (164/3h^4c^3)E^4_{v',v''}[\int_0^\infty \Psi_1(v')R_e(r)\Psi_2(v'')\mathrm{d}r]^2 \tag{1}$$

where c is the velocity of light, $E_{v',v''}$ is the energy difference and R_e is the electronic transition moment. When R_e varies only slowly with r, R_e may be replaced by an average value, $R_{e,av}$. The quantity in the square brackets of Eq. (1) can then be written as:

$$R_{v',v''} = R_e \int_0^\infty \Psi_1(v')\Psi_2(v'')\mathrm{d}r \tag{2}$$

Eqation (2) defines the so-called vibrational transition moment. The integral in the bracket in Eq. (2) is called the overlap integral and its square is known as the F–C factor. Thus, the F–C factor can be written as:

$$q_{v',v''} = [\int_0^\infty \Psi_1(v')\Psi_2(v'')\mathrm{d}r]^2 \tag{3}$$

where $\Psi_1(v')$ and $\Psi_2(v'')$ are the wave functions corresponding to the vibrational states v' and v'', respectively.

The r-centroid is a unique value of internuclear separation, which may be associated with a v→v'' band and is defined as:

$$r_{v',v''} = \frac{\int r\Psi(v')\Psi(v'')\mathrm{d}r}{\int \Psi(v')\Psi(v'')\mathrm{d}r} \tag{4}$$

RESULTS AND DISCUSSION

The molecular constants for the $A^2\Sigma^+–X^2\Pi_{3/2}$ and $B^2\Sigma^+–X^2\Pi_{3/2}$ band systems of GeF and the $^1\Sigma–^1\Pi$ band system of SiF are given in Table I. The wave functions were obtained by the W–K–B method following the procedure of Wu.[11] Then, the F–C factors for the $A^2\Sigma^+–X^2\Pi_{3/2}$ and $B^2\Sigma^+–X^2\Pi_{3/2}$ band systems of GeF were determined by the numerical integration technique and the values are given in Table II and Table III. For comparison, the F–C factors calculated by Singh[2] are also given in parentheses. From Table II, it can be seen that the (0–2) band is the most intense one of the $A^2\Sigma^+$–$X^2\Pi_{3/2}$ band system, although the intensities of the other bands (2–2), (1–0) and (0–1) are also comparable with that of the (0–2) band. The results are in close agreement with the values computed by Singh[2] for the (0,1) and (0,3) bands. For all the other bands, there is a small deviation. This is because in this work the Rafi *et al.*[7] potential function was employed, whereas Singh[2] used the Morse potential function for computation of the wave function. From Table III, it can be seen that the (0–0) band is the most intense of the $A^2\Sigma^+$–$X^2\Pi_{3/2}$ band system. The intensities of the other bands (3–2), (1–0), (1–3) and (4–2) are comparatively intense. The F–C factors computed for $^1\Sigma$–$^1\Pi$ band system of SiF molecule are given in Table IV, together with the values calculated by Nagarajan *et al.*[4] It can be seen from Table IV that the (0–0) band is the most intense one, followed by the bands (1–0), (1–1), (2 − 1) and (3–2) bands, which are also intense.

TABLE I. Molecular constants of GeF and SiF molecules

Molecules	States	Molecular constants						
		ω_e / cm^{-1}	D_e / cm^{-1}	R_e / Å	B_e / cm^{-1}	α_e / cm^{-1}	μ / 10^{-23} g	$\omega_e x_e$/ cm^{-1}
GeF	$X^2\Pi_{3/2}$	667.33	35343.6	1.7443	0.36659	0.00266	2.519938	3.15
	$A^2\Sigma^+$	413.03	37943.46	1.8659	0.32035	0.00299	2.519938	1.124
	$B^2\Sigma^+$	796.99	43951.91	1.6817	0.39440	0.00255	2.519938	3.613
SiF	$^1\Sigma$	1011.20	53256.53	1.5500	0.62200	0.00041	1.837054	4.8
	$^1\Pi$	856.70	39039.09	1.6030	0.57950	0.00043	1.837054	4.7

TABLE II. Franck–Condon factors for the $A^2\Sigma^+$–$X^2\Pi_{3/2}$ band system of GeF

v'/v"	0	1	2	3	4	5
0	0.1214	0.2407	0.2978	0.1413	0.0394	0.0052
	(0.182)	(0.258)	(0.2275)	(0.1444)		
1	0.2643	0.0484	0.0049	0.0566	0.1120	0.1606
	(0.334)	(0.108)	(0.0155)	(0.069)		
2	0.1804	0.0839	0.2681	0.0458	0.0002	0.0449
	(0.252)	(0.0175)	(0.162)	(0.098)		
3	0.0153	0.1579	0.0660	0.0349	0.0736	0.1960
	(0.180)	(0.128)	(0.0385)	(0.034)		
4	0.0504	0.0970	0.0142	0.0375	0.0156	0.0089
5	0.0729	0.0434	0.3411	0.0001	0.0242	0.0307

For $A^2\Sigma^+$–$X^2\Pi_{3/2}$ and $B^2\Sigma^+$–$X^2\Pi_{3/2}$ band systems of GeF, the r-centroids were computed using the wave function computed by the W–K–B method. The evaluated values of the r-centroids are given in Tables V and VI. The r-centroid values calculated by Singh[2] are also given in parentheses for comparison. From Table V, it can be seen that the r-centroid value is high for the (4–4) band. The values for the other bands (0–4), (0–5), (1–4) and (1–5) are comparable with that of the (4–4) band. From Table VI, it can be seen that the r-centroid value is high for the (3–1) and (5–3) bands. For the $^1\Sigma$–$^1\Pi$ band system of SiF, the computed r-centroid values are given in Table VII. For comparison, the r-centroids calculated by Nagarajan *et al.*[4] are also given in parentheses. From Table VII, it can be seen that the r-centroid value for the (4–0) band has a higher value compared to the other bands. It is found that the values calculated in this study are in close agreement with those computed by Singh[2] and Nagarajan *et al.*,[4] for some bands, while there are small deviations for some other bands.

TABLE III. Franck–Condon factors for the $B^2\Sigma^+$–$X^2\Pi_{3/2}$ band system of the GeF molecule

v'/v"	0	1	2	3	4	5
0	0.4872	0.0493	0.1915	0.0468	0.0141	0.0046
	(0.512)	(0.333)	(0.1175)	(0.030)	(0.005)	(0.020)
1	0.3639	0.0041	0.2523	0.2245	0.01378	0.0551
	(0.3485)	(0.0535)	(0.2805)	(0.2065)	(0.0168)	(0.002)
2	0.0955	0.0498	0.0035	0.0793	0.1768	0.1560
	(0.1135)	(0.3142)	(0.0095)	(0.1375)	(0.1605)	(0.4495)
3	0.0206	0.1112	0.0432	0.0015	0.1095	0.1118
	(0.0235)	(0.215)	(0.1735)	(0.0858)	(0.046)	(0.0355)
4	0.0085	0.1416	0.2162	0.0396	0.0819	0.0004
	(0.0017)	(0.1155)	(0.211)	(0.0675)	(0.523)	(0.0015)
5	0.0002	0.0725	0.1562	0.1805	0.0063	0.0102
	(0.0024)	(0.0015)	(0.1365)	(0.105)	(0.002)	

TABLE IV. Franck–Condon factors for the $^1\Sigma$–$^1\Pi$ band system of SiF molecule

v'/v"	0	1	2	3	4	5
0	0.6625	0.1619	0.0809	0.0265	0.0030	0.6625
	(0.602)	(0.297)	(0.082)	(0.017)		(0.602)
1	0.3211	0.3084	0.2002	0.1663	0.0932	0.3211
	(0.314)	(0.145)	(0.316)	(0.163)		(0.314)
2	0.1005	0.3659	0.0676	0.1435	0.1776	0.1005
	(0.074)	(0.363)	(0.007)	(0.228)		(0.074)
3	0.0185	0.1351	0.3228	0.0027	0.0912	0.0185
	(0.010)	(0.160)	(0.293)	(0.016)		(0.010)
4	0.0006	0.0780	0.2077	0.1806	0.0038	0.0006
	(0.000)	(0.032)	(0.228)	(0.188)		(0.000)
5	0.6625	0.1619	0.0809	0.0265	0.0030	0.6625
	(0.602)	(0.297)	(0.082)	(0.017)		(0.602)

TABLE V. r-Centroids for the $A^2\Sigma^+$–$X^2\Pi_{3/2}$ band system of the GeF molecule

v'/v"	0	1	2	3	4	5
0	1.8130	1.8460	1.8710	1.9173	1.9733	1.9914
	(1.802)	(1.8415)	(1.877)	(1.910)		
1	1.7808	1.8347	1.7660	1.9031	1.9503	1.9591
	(1.7745)	(1.8175)	(1.855)	(1.890)		
2	1.7401	1.8341	1.8299	1.9396	1.6953	1.9227
	(1.743)	(1.793)	(1.833)	(1.869)		

TABLE V. Continued

v'/v"	0	1	2	3	4	5
3	1.5826 (1.702)	1.8153 (1.764)	1.8500 (1.8085)	1.7977 (1.847)	1.9844	1.9393
4	1.8512	1.8086	1.6501	1.8889	2.0015	1.6268
5	1.7561	1.8705	1.7822	0.9156	1.9008	2.0520

TABLE VI. r-Centroids for B$^2\Sigma^+$–X$^2\Pi_{3/2}$ band system of the GeF molecule

v'/v"	0	1	2	3	4	5
0	1.718 (1.716)	1.680 (1.672)	1.645 (1.627)	1.593 (1.5795)	1.541 (1.5265)	1.537 (1.4585)
1	1.767 (1.7675)	1.747 (1.7245)	1.681 (1.681)	1.655 (1.637)	1.621 (1.591)	1.590 (1.5405)
2	1.832 (1.8185)	1.8011 (1.7755)	1.769 (1.733)	1.676 (1.690)	1.637 (1.647)	1.614 (1.602)
3	1.787 (1.870)	1.872 (1.826)	1.791 (1.7835)	1.459 (1.7415)	1.697 (1.6995)	1.612 (1.657)
4	1.832 (1.922)	1.845 (1.8775)	1.853 (1.834)	1.811 (1.792)	1.766 (1.750)	1.641 (1.7085)
5	1.455 (1.9755)	1.865 (1.929)	1.856 (1.8845)	1.873 (1.8415)	1.802 (1.7995)	1.773 (1.7585)

TABLE VII. r-Centroids for the $^1\Sigma$–$^1\Pi$ band system of the SiF molecule

v'/v"	0	1	2	3	4
0	1.57812 (1.576)	1.66833 (1.523)	1.68932 (1.472)	1.70321 (1.420)	1.77614
1	1.52432 (1.637)	1.57137 (1.585)	1.68216 (1.532)	1.69184 (1.481)	1.68393
2	1.47979 (1.679)	1.51988 (1.646)	1.54269 (1.597)	1.70369 (1.541)	1.71522
3	1.42256 (1.762)	1.45379 (1.706)	1.52266 (1.650)	1.27250 (1.599)	1.71479
4	2.06379 (1.833)	1.45631 (1.771)	1.46030 (1.715)	1.51068 (1.665)	1.92671

CONCLUSIONS

A suitable potential energy function was fitted for the A$^2\Sigma^+$–X$^2\Pi_{3/2}$ and B$^2\Sigma^+$–X$^2\Pi_{3/2}$ band systems of GeF and the $^1\Sigma$–$^1\Pi$ band system of SiF and the Franck–Condon factors and r-centroids values were evaluated. It was found that, for the $^1\Sigma$–$^1\Pi$ band system of GeF and for the $^1\Sigma$–$^1\Pi$ band system of SiF, the (0,0) band is the most intense. However, for the A$^2\Sigma^+$–X$^2\Pi_{3/2}$ band system of GeF, the (0,2) band is the most intensive. The obtained results are compared with the values computed by Singh[2] and Nagarajan *et al.*[4] It is found that the calculated values are in close agreement with them only for a few bands. For all the other bands, there is a deviation. This may be because different potential functions were employed for the computation and to the different methods adopted for the computation.

*Acknowledgement***.** The authors are indebted to the college management for their constant encouragement.

ИЗВОД

ФРАНК–КОНДОНОВИ ФАКТОРИ И r-ЦЕНТРОИДИ ЗА ДВОАТОМСКЕ ФЛУОРИДЕ ГЕРМАНИЈУМА И СИЛИЦИЈУМА

S. KANAGAPRABHA, R. RAJESWARA PALANICHAMY и V. SATHIYABAMA

Department of Physics, N. M. S. S. V. N College, Madurai – 625 019, Tamilnadu, India

Анализом функција потенцијалне енергије које су предложили Morse, Mohammad и Rafi са сарадницима, нађене су погодне функције за $A^2\Sigma^+–X^2\Pi_{3/2}$ и $B^2\Sigma^+–X^2\Pi_{3/2}$ системе трака GeF и $^1\Sigma–^1\Pi$ систем SiF. Установљено је да је потенцијал који је предложио Rafi са сарадницима у доброј сагласности са Rydberg–Klein–Rees потенцијалом. Користећи овај потенцијал израчунате су таласне функције помоћу Wentzel–Kramer–Brillouin методе. Франк–Кондонови факори и r-центроиди су израчунати нумеричком интеграцијом. Резултати су упоређени са доступним теоријским вредностима. Испитивани су интензитети различитих трака.

(Примљено 7. новембра 2006, ревидирано 9. фебруара 2007)

REFERENCES

1. M. Singh, J. Chaturvedi, *Astrophys. Space Sci.* **1** (1987) 135
2. J. Singh, *Ind. J. Pure App. Phys.* **13** (1974) 204
3. R. Rajeswarapalanichamy, R.Veluchamy, *Ind. J. Pure App. Phys.* **29** (1991) 274
4. K. Nagarajan, M. Fernandez Gomez, J. J. Lopez Gonzalez, N. Rajamanickam, *J. Astron Astrophys. Suppl. Sep.* **129** (1998) 157
5. P. M. Morse, *Phys. Rev.* **34** (1929) 57
6. S. N. Mohammad, *Ind. J. Pure Appl. Phys.* **23** (1985) 188
7. M. Rafi, A. Bakry, N. Al-Senanj, Fayyazuddin, *Ind. J. Phys.* **74B** (2000) 485
8. R. Rydberg, *Z. Phys.* **73** (1931) 376
9. O. Klein, *Z. Phys.* **76** (1932) 221
10. A. L. G. Rees, *Proc. Roy. Soc. London* **59** (1947) 998
11. W. T. You, *Proc. Phys. Soc.* **65A** (1952) 63.