

# Franck-Condon factors and r-centroids for certain band systems of gallium and indium mono-fluorides

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For the first time, the Franck-Condon factors and r-centroids, which are very closely related to vibrational transition probabilities, have been evaluated for the bands of  $A^3\Pi_0^+ - X^1\Sigma^+$ ,  $B^3\Pi_1^- X^1\Sigma^+$ , and  $C^1\Pi - X^1\Sigma^+$  systems of GaF and InF molecules. A numerical integration procedure is followed to evaluate these transition probability parameters, using a suitable potential.

*Keywords:* FC factors; r-centroids; GaF and InF molecules

Por primera vez se evalúa el factor de Franck-Condon y los centroides r, los cuales están íntimamente relacionados con las probabilidades de transición vibracional. Estos son evaluados para las bandas de  $A^3\Pi_0^+ - X^1\Sigma^+$ ,  $B^3\Pi_1^- X^1\Sigma^+$  y para los sistemas  $C^1\Pi - X^1\Sigma^+$  de las moléculas de GaF y InF. La evaluación de los parámetros de transición se realiza mediante un procedimiento de integración numérica usando un potencial adecuado.

*Descriptores:* Factores FC; centroides r; moléculas de GaF y InF

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## 1. Introduction

The theoretical prediction of intensity distribution in the spectra of many diatomic molecules, which are of interest in astrophysics, is necessary for an understanding of the physico-chemical conditions of the emitting sources. The intensity distribution of various bands in any band system is mainly governed by the Franck-Condon (FC) factors. The transition probability parameters such as FC factors and r-centroids are required for diagnostic applications in astrophysics, astrochemistry and allied subjects. A precise knowledge of FC factors and related quantities are essential for an understanding and the calculation of many important data for the molecules *e.g.*, radiative life times, vibrational temperatures and kinetics of the energy transfer.

Sauval and Tatum [1] have noted the presence of GaF and InF molecules in the stellar and cometary spectra. Welti and Barrow [2,3], Barrow *et al.* [4-6] and Nampoori *et al.* [7] have analysed the band systems of mono-fluorides of gallium and indium, which belong to group 13. From these vibrational and rotational analyses, Huber and Herzberg [8] compiled reliable molecular constants. However there has been no earlier report on FC factors and r-centroids of GaF and InF. Therefore FC factors and r-centroids for the band systems  $A^3\Pi_0^+ - X^1\Sigma^+$ ,  $B^3\Pi_1^- X^1\Sigma^+$ , and  $C^1\Pi - X^1\Sigma^+$  of GaF and InF molecules have been calculated in this work.

Fraser and Jarman [9] have suggested an analytical method for the evaluation of FC factors and r-centroids. However, the results of this method are only indicative of trends [10]. Therefore a numerical integration procedure is followed to evaluate these parameters, using a suitable potential.

## 2. Franck-Condon factors and r-centroids

The intensity of each individual transition between vibrational levels for an allowed electronic transition is governed by the overlap of vibrational probability factors in the upper and lower states termed Franck-Condon factors (FC) which depend upon geometry changes in the upper and lower electronic states and can be given as the square of the overlap integral

$$q_{\nu'\nu''} = \left| \int \psi_{\nu'} \psi_{\nu''} dr \right|^2 = |\langle \psi_{\nu'} | \psi_{\nu''} \rangle|^2, \quad (1)$$

where  $\psi_{\nu'}$  and  $\psi_{\nu''}$  are the vibrational wave functions for the upper and lower states, respectively. The r-centroid is a unique value of internuclear separation, which may be associated with a  $\nu' - \nu''$  band and defined as

$$\bar{r}_{\nu'\nu''} = \frac{\langle \psi_{\nu'} | r | \psi_{\nu''} \rangle}{\langle \psi_{\nu'} | \psi_{\nu''} \rangle}. \quad (2)$$

From Eq. (2) it can be seen that r-centroid is a weighted average with respect to  $\psi_{\nu'} \psi_{\nu''}$  of the range of  $r$  values experienced by the molecule in both states of the  $\nu' - \nu''$  transition.

For a proper understanding of the intensity distribution in the band systems of the molecules, it is necessary to choose a suitable potential. The Morse [11] potential yields accurate FC factors for a vibrational transition involving low quantum numbers [12,13]. Morse wave functions are calculated at intervals of 0.01 Å for every observed vibrational level of each state of  $A^3\Pi_0^+ - X^1\Sigma^+$ ,  $B^3\Pi_1^- X^1\Sigma^+$ , and  $C^1\Pi - X^1\Sigma^+$  band systems of GaF and InF molecules. The necessary molecular constants are collected from the compilation of Huber and Herzberg [8] and they are given in Table I. The range of r-values for  $A - X$ ,  $B - X$  and  $C - X$  systems of GaF and InF molecules are presented in Table II.

TABLE I. Molecular constants

Molecule	Molecular Constants	Molecular States			
		A	B	C	X
GaF	$\omega_e$ ( $cm^{-1}$ )	663.02	662.10	542.35	62.2
	$\omega_e x_e$ ( $cm^{-1}$ )	2.18	1.45	9.55	3.2
	$\mu_A$	14.8932747	14.8932747	14.8932747	14.8932747
	$r_e$ ( $\text{\AA}$ )	1.7467	1.7444	1.7780	1.774369
	$\omega_e$ ( $cm^{-1}$ )	575.20	572.25	463.90	535.35
InF	$\omega_e x_e$ ( $cm^{-1}$ )	3.676	2.63	7.35	2.64
	$\mu_A$	16.3028614	16.3028614	16.3028614	16.3028614
	$r_e$ ( $\text{\AA}$ )	1.9455	1.9440	1.966	1.985396

TABLE II. Range of r-values

Molecule	System	Range of r values
GaF	$A^3\Pi_0^+ - X^1\Sigma^+$	1.57 $\text{\AA}$ to 2.01 $\text{\AA}$
	$B^3\Pi_1^- X^1\Sigma^+$ ,	1.54 $\text{\AA}$ to 2.04 $\text{\AA}$
	$C^1\Pi - X^1\Sigma^+$	1.55 $\text{\AA}$ to 2.16 $\text{\AA}$
InF	$A^3\Pi_0^+ - X^1\Sigma^+$	1.69 $\text{\AA}$ to 2.40 $\text{\AA}$
	$B^3\Pi_1^- X^1\Sigma^+$ ,	1.73 $\text{\AA}$ to 2.38 $\text{\AA}$
	$C^1\Pi - X^1\Sigma^+$	1.76 $\text{\AA}$ to 2.32 $\text{\AA}$

TABLE III.  $q_{\nu'\nu''}$  and  $\bar{r}_{\nu'\nu''}$  for A – X system of GaF

$\nu', \nu''$	$\lambda_{\nu'\nu''}(\text{\AA})$	$q_{\nu'\nu''}$	$\bar{r}_{\nu'\nu''}(\text{\AA})$
0,0	3018.9	0.891	1.764
1,0	2960.5	0.105	1.891
1,1	3015.1	0.683	1.773
2,1	2957.6	0.197	1.896
2,2	3011.4	0.494	1.781
3,2	2954.8	0.273	1.900
3,3	3008.1	0.328	1.789
4,3	2951.6	0.328	1.905
4,4	3004.8	0.192	1.797

Once the appropriate wave functions are obtained, Franck-Condon factors ( $q_{\nu'\nu''}$ ) and r-centroids ( $\bar{r}_{\nu'\nu''}$ ) can be evaluated by integrating numerically the above said Eqs. (1) and (2). The computation of FC factor is made by Bates's [14] method of numerical integration according to the detailed procedure provided by Partel *et al.* [15]. The obtained results appear in Tables III, IV and V for A – X, B – X and C – X systems of GaF and in Tables VI, VII and VIII for A – X, B – X and C – X systems of InF respectively. The

wavelengths ( $\lambda_{\nu'\nu''}$ ) data [4, 7] are also entered in the respective tables for all systems.

TABLE IV.  $q_{\nu'\nu''}$  and  $\bar{r}_{\nu'\nu''}$  for B – X system of GaF

$\nu', \nu''$	$\lambda_{\nu'\nu''}(\text{\AA})$	$q_{\nu'\nu''}$	$\bar{r}_{\nu'\nu''}(\text{\AA})$
0,0	2988.8	0.868	1.763
0,1	3044.8	0.121	1.656
1,0	2931.2	0.124	1.878
1,1	2985.1	0.619	1.770
1,2	3040.2	0.221	1.669
2,1	2928.2	0.232	1.880
2,2	2981.5	0.393	1.778
2,3	3036.0	0.291	1.682
3,2	2925.5	0.313	1.882
3,3	2977.9	0.209	1.785
3,4	3031.9	0.322	1.696
4,3	2923.2	0.356	1.884
4,4	2975.1	0.080	1.791
5,4	2921.9	0.357	1.887
5,5	2972.8	0.012	1.790
6,5	2921.0	0.317	1.888

TABLE V.  $q_{\nu'\nu''}$  and  $\bar{r}_{\nu'\nu''}$  for C – X system of GaF

$\nu', \nu''$	$\lambda_{\nu'\nu''}(\text{\AA})$	$q_{\nu'\nu''}$	$\bar{r}_{\nu'\nu''}(\text{\AA})$
0,0	2112.4	0.991	1.783
0,1	2140.3	0.008	2.295
0,2	2168.6	0.003	1.879
1,1	2116.6	0.943	1.796
1,2	2144.3	0.037	2.142
1,3	2172.2	0.011	1.938
2,1	2094.6	0.050	1.552
2,2	2121.7	0.825	1.807
2,3	2149.2	0.092	2.080
2,4	2177.2	0.029	1.979
3,2	2100.8	0.135	1.647
3,3	2127.8	0.627	1.814
3,4	2155.2	0.158	2.052
3,5	2182.9	0.063	2.007
4,3	2108.1	0.260	1.707
4,4	2135.0	0.376	1.812
4,5	2162.3	0.205	2.039
4,6	2190.0	0.111	2.028
5,5	2143.7	0.143	1.781
5,6	2170.7	0.196	2.035
5,7	2198.6	0.158	2.045

TABLE VI.  $q_{\nu',\nu''}$  and  $\bar{r}_{\nu',\nu''}$  for  $A - X$  system of InF

$\nu', \nu''$	$\lambda_{\nu',\nu''}(\text{\AA})$	$q_{\nu',\nu''}$	$\bar{r}_{\nu',\nu''}(\text{\AA})$
0,0	3282.5	0.814	1.970
0,1	3340.3	0.163	1.878
0,2	3400.1	0.022	1.799
1,0	3222.6	0.174	2.069
1,1	3278.4	0.521	1.981
1,2	3335.7	0.246	1.884
1,3	3394.5	0.052	1.805
2,1	3219.4	0.284	2.080
2,2	3274.6	0.326	1.993
2,3	3331.1	0.279	1.890
2,4	3389.3	0.082	1.810
3,2	3216.5	0.351	2.090
3,3	3271.1	0.198	2.008
3,4	3327.0	0.282	1.895
3,5	3384.3	0.109	1.815
4,3	3213.7	0.390	2.102
4,4	3267.8	0.115	2.026
4,5	3322.8	0.268	1.901
4,6	3379.5	0.130	1.820
5,4	3211.2	0.409	2.113
5,6	3319.0	0.244	1.906
5,7	3374.9	0.146	1.825
6,5	3219.9	0.418	2.126
6,7	3315.4	0.218	1.911
7,6	3206.8	0.419	2.138
7,8	3311.9	0.191	1.915
7,9	3366.5	0.162	1.833
8,7	3204.9	0.418	2.151
9,8	3203.3	0.415	2.165
10,9	3202.0	0.413	2.179
11,10	3200.9	0.411	2.193
12,11	3200.0	0.409	2.206

### 3. Results and discussions

The FC factors of  $A - X$ ,  $B - X$  and  $C - X$  systems of both GaF and InF molecules indicate that the (0,0) band is the most intense one. The other prominent bands are (1,1) and (2,2) of  $A - X$ , (1,1) of  $B - X$  and (1,1), (2,2) and (3,3) of  $C - X$  systems of GaF molecule. In the case of InF molecule the (1,1) band of  $A - X$  and  $B - X$  systems and (1,1), (2,2), (3,3) and (4,4) bands of  $C - X$  are prominent. For both GaF and InF molecules, all other bands are comparatively less intense.

It is of interest to note that the r-centroid value of (0,0) band is slightly greater than  $(r'_e + r''_e) / 2$  for all the band sys-

TABLE VII.  $q_{\nu',\nu''}$  and  $\bar{r}_{\nu',\nu''}$  for  $B - X$  system of InF

$\nu', \nu''$	$\lambda_{\nu',\nu''}(\text{\AA})$	$q_{\nu',\nu''}$	$\bar{r}_{\nu',\nu''}(\text{\AA})$
0,0	3196.9	0.794	1.969
0,1	3251.8	0.177	1.882
0,2	3308.4	0.026	1.806
1,0	3140.0	0.189	2.062
1,1	3193.2	0.468	1.979
1,2	3247.4	0.267	1.890
1,3	3303.2	0.063	1.813
2,1	3137.0	0.308	2.070
2,2	3189.5	0.249	1.990
2,3	3243.1	0.296	1.898
2,4	3298.2	0.103	1.820
2,5	3354.9	0.023	1.753
3,4	3239.2	0.285	1.906
3,5	3293.6	0.137	1.828
3,6	3349.2	0.039	1.760
4,3	3131.7	0.394	2.086
4,5	3235.3	0.250	1.915
4,6	3289.0	0.163	1.836
4,7	3343.8	0.057	1.767
5,4	3129.3	0.385	2.095
5,6	3231.8	0.203	1.925
5,7	3284.9	0.178	1.844
5,8	3338.8	0.075	1.775
6,5	3127.2	0.355	2.104
6,7	3228.5	0.152	1.936
6,9	3334.4	0.092	1.783
7,8	3225.8	0.105	1.948
7,10	3330.4	0.106	1.791

TABLE VIII.  $q_{\nu',\nu''}$  and  $\bar{r}_{\nu',\nu''}$  for  $C - X$  system of InF

$\nu', \nu''$	$\lambda_{\nu',\nu''}(\text{\AA})$	$q_{\nu',\nu''}$	$\bar{r}_{\nu',\nu''}(\text{\AA})$
0,0	2337.9	0.971	1.983
1,1	2342.5	0.939	1.998
2,2	2347.8	0.935	2.013
2,4	2406.3	0.034	1.957
3,3	2354.1	0.921	2.026
3,5	2412.2	0.056	2.017
4,4	2361.5	0.860	2.036
4,6	2418.8	0.087	2.076
5,7	2426.7	0.128	2.127

tems of both GaF and InF molecules that proves that the potentials are not very anharmonic.

Experimental findings show that  $A - X$  and  $B - X$  band systems of both GaF and InF molecules are violet degraded band systems [8]. In the present study, since  $r'_e < r''_e$  for these four band systems, the r-centroid value decreases with an increase in wavelength [Tables III, IV, VI & VII], which confirms that these four systems are violet degraded band systems. The sequence differences for  $A - X$  and  $B - X$  band systems of GaF and InF molecules are found to be a constant and is about  $0.01 \text{ \AA}$  which suggests that the potentials of these systems are not so wide.

In the  $C - X$  band system of both GaF and InF molecules, since there are red degraded bands and violet degraded bands as experimentally shown [8], there is no smooth relationship between r-centroid values and wavelengths [Tables V & VIII] as expected. The sequence difference is also found to be varying between  $0.002 \text{ \AA}$  and  $0.15 \text{ \AA}$  and  $0.01 \text{ \AA}$  and  $0.06 \text{ \AA}$  for the  $C - X$  band system of GaF and InF molecules, respectively.

One can expect such a similarity for the band systems of mono-fluorides of group 13 elements Ga and In.

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