FRANCK–CONDON FACTORS AND *R*-CENTROIDS FOR THE BAND SYSTEM $a^1\Pi$–$X^1\Sigma^+$ OF THE InH MOLECULE

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The Franck–Condon factors (vibrational transition probabilities) and *r*-centroids have been evaluated by a numerical integration procedure for the bands of the $a^3\Pi_1$–$X^1\Sigma^+$ system of the InH molecule using a suitable potential.

The theoretical prediction of intensity distribution in the molecular band requires knowledge of vibrational transition probabilities which are to a good approximation proportional to the Franck–Condon factors, $q_{v'v''}$. A precise knowledge of Franck–Condon factors and related quantities is essential for understanding and calculation of many important data for the molecules, e.g. radiative lifetimes, vibrational temperatures and kinetics of energy transfer. In the present study we deal with the InH molecule and its band system $a^1\Pi$–$X^1\Sigma^+$ for which, to our best knowledge, no Franck–Condon factors and *r*-centroids have been reported. We calculated reliable values for Franck–Condon factors and *r*-centroids for this band system by an accurate numerical integration procedure using a suitable potential.

CALCULATIONS

One of the parameters which controls the intensity distribution in the emission of molecular bands is the Franck–Condon factor which is the square of the overlap integral[2]

$$q_{v'v''} = \langle v' | v'' \rangle^2 , \qquad (1)$$

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where $|v'\rangle$ and $|v''\rangle$ are the vibrational wave functions for the upper and lower states, respectively. The *r*-centroid is a value of internuclear separation which may be associated with a v'–v'' band and it is defined as

$$\bar{r}_{v'v''} = \frac{\langle v'|r|v''\rangle}{\langle v'|v''\rangle} . \tag{2}$$

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[3] potential yields accurate Franck–Condon factors, especially for vibrational transition involving low quantum numbers[4].

The potential energy curves for the *a* and *X* electronic states of InH have been constructed using the Morse function[3] and by Rydberg–Klein–Rees (RKR) procedure as modified by Vanderslice et al.[5]. In Table I, the computed values of the turning points are given for the molecular vibration in the electronic states *a* and *X* of InH. It is found that the Morse function represents the potential energy curves of the two states quite adequately since the RKR curve is very similar to the Morse curve. For the computation of Franck–Condon factors we used Bates's method[6] of numerical integration according to the procedure developed by Rajamanickam[7 - 12]. Morse wave function were calculated with a grid of $0.01 \cdot 10^{-10}$ m in the range of *r* from $1.42 \cdot 10^{-10}$ m to $2.44 \cdot 10^{-10}$ m for every observed vibrational level in the two states. Once the appropriate wave functions are obtained, the Franck–Condon factors can be evaluated by integrating the expression in Eq. (*1*). In the case of Morse wave function, Fraser and Jarmain[13] suggested a procedure for the analytical integration of the overlap integral.

TABLE I
Turning points (in 10^{-10} m) and $G(v)$ values (in cm^{-1}) in the *a* and *X* states of InH

State	v	$G(v)$	Morse		RKR	
			$r_{\max}$	$r_{\min}$	$r_{\max}$	$r_{\min}$
a	0	695.03	1.943	1.631	1.943	1.631
	1	1 980.43	2.102	1.552	2.126	1.541
	2	3 060.56	2.219	1.509	2.293	1.476
	3	3 856.60	2.307	1.483	2.434	1.426
X	0	731.63	2.004	1.700	2.006	1.701
	1	2 157.39	2.149	1.614	2.152	1.617
	2	3 534.63	2.263	1.560	2.267	1.565
	3	4 865.14	2.366	1.521	2.370	1.528

However, the results generally only indicate the trends[14]. The integration is therefore carried out numerically in the present study. Also the $\langle v'|r|v''\rangle$ integrals needed for $\bar{r}_{v'v''}$ were computed numerically. The calculated Franck–Condon factors and r-centroids $\bar{r}_{v'v''}$ are entered in Table II along with the wavelengths data[15], $\lambda_{v'v''}$. The molecular constants[1] used in the present study are listed in Table III.

RESULTS AND DISCUSSION

The Franck–Condon factors indicate that the $\Delta v = 0$ sequence bands are most intense followed by $\Delta v = \pm 1$ sequence. Since there are red degraded bands and blue degraded bands, there is no clear relationship between the r-centroids and the wavelengths, as in the case of the $a^3\Pi$–$X^1\Sigma^+$ system of GaH (ref.[16]). Since both GaH and InH are the hydrides of group III elements, one can expect such a similarity. In the present study, the $q_{v'v''}$ and $\bar{r}_{v'v''}$ values have been evaluated by the accurate numerical integration

TABLE II
Franck–Condon factors, $q_{v'v''}$, and r-centroids, $\bar{r}_{v'v''}$ for the band system a–X of InH

v', v''	$\lambda_{v'v''}$, 10^{-10} m	$q_{v'v''}$	$\bar{r}_{v'v''}$, 10^{-10} m
0,0	5 915.41	0.925	1.830
0,1	6 460.29	0.063	1.417
1,0	5 497.43	0.078	2.221
1,1	5 964.97	0.824	1.889
1,2	6 498.95	0.069	1.302
2,1	5 603.93	0.109	2.322
2,2	6 072.72	0.796	1.954
3,3	6 276.59	0.790	2.016

TABLE III
Molecular constants[1] for the a and X states of InH

Constant[a]	$a^3\Pi_1$	$X^1\Sigma^+$
ω_e	1 415.1	1 476.0
$\omega_e x_e$	43.50	25.61
$\omega_e y_e$	−13.14	0.3
B_e	5.399	4.994
α_e	0.235	0.142
r_e	1.7678	1.8380

[a] r_e in 10^{-10} m, the other constants in cm^{-1}.

method and therefore can be considered reliable. As a result one can conclude that the sequence differences are not found to be uniform. For example, in the $\Delta v = 0$ sequence the differences for $\bar{r}_{v'v''}$ are 0.059 . 10^{-10} m (between 0,0 and 1,1), 0.065 . 10^{-10} m (between 1,1 and 2,2) and 0.062 . 10^{-10} m (between 2,2 and 3,3), in the $\Delta v = +1$ sequence the difference is 0.101 . 10^{-10} (between 1,0 and 2,1) and in the case of the $\Delta v = -1$ sequence the difference is 0.115 . 10^{-10} m (between 0,1 and 1,2). This will happen for a band system which have both blue and red degraded bands[16].

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