

LETTERS TO THE EDITOR

FRANCK-CONDON FACTORS AND *r*-CENTROIDS OF <sup>3</sup>Π-X<sup>1</sup>Σ SYSTEM OF InCl MOLECULE

THE band spectrum of InCl was studied by Patrikahn and Hochberg<sup>1</sup>, Wehrli and Miescher<sup>2</sup>, Youngner and Winans<sup>3</sup>, Ashrafunnisa *et al.*<sup>4,5</sup> and Rao *et al.*<sup>6</sup>. As *r*-centroids and Franck-Condon factors play an important role in finding out the variation of electronic transition moment with internuclear distance, it is worthwhile to compute the *r*-centroids and Franck-Condon factors of the bands of <sup>3</sup>Π<sub>0,1</sub> - X<sup>1</sup>Σ sub-systems of InCl molecule. In the present calculations, the necessary constants are taken from the work of the authors<sup>4-6</sup>.

The *r*-centroids (*r*<sub>*v'*,*v''*</sub>), representing the characteristic internuclear separation of a *v'* → *v''* transition in a diatomic molecular band system, has been defined by Nicholls and Jarman<sup>7</sup> as

$$r_{v',v''} = \int \psi_{v'} r \psi_{v''} dr / \int \psi_{v'} \psi_{v''} dr$$

where  $\psi_{v'}$  and  $\psi_{v''}$  are the vibrational wave functions

of the upper and lower states and *r* is the internuclear distance. In the present work, the quadratic method has been used for the evaluation of *r*-centroids for the bands of A-X and B-X systems of InCl molecule and the results are presented in Tables I and II respectively. A smooth curve has been obtained when a graph is drawn between *r*<sub>*v'*,*v''*</sub> and  $\lambda_{v',v''}$  as reported earlier by Nicholls and Jarman in several cases.

As  $|da/a|$  is greater than 5%, the Franck-Condon factors of A-X and B-X sub-systems of InCl molecule are calculated by employing the analytical method of Fraser and Jarman<sup>8</sup> with *r*<sub>*e*</sub>-shift correction and are presented in Tables I and II along with the wavelengths of the band heads and *r*-centroids. It is from Tables I and II that the bands *v'* = 4 (*v''* = 0) and *v''* = 5 (*v'* = 0) could not be experimentally observed due to the negligibly small values of the Franck-Condon factors.

TABLE I

Franck-Condon factors and *r*-centroids of A<sup>3</sup>Π<sub>0</sub> - X<sup>1</sup>Σ system of InCl molecule

<i>v'</i>	<i>v''</i>	0	1	2	3	4	5
0	<i>a</i>	0.565	0.301	0.099	0.027	0.006	0.001
	<i>b</i>	2.368	2.315	2.269	2.228	2.191	2.158
	<i>c</i>	3599.2	3640.5	3682.5	3726.2	3758.5	3812.5
1	<i>a</i>	0.343	0.104	0.279	0.174	0.069	0.022
	<i>b</i>	2.433	2.372	2.319	2.273	2.232	2.195
	<i>c</i>	3556.2	3596.4	3637.4	3678.98	3621.3	3764.4
2	<i>a</i>	0.082	0.382	0.000	0.166	0.194	0.110
	<i>b</i>	2.509	2.437	2.376	2.323	2.277	2.236
	<i>c</i>	3514.6	3553.9		3634.5	3575.9	3717.8
3	<i>a</i>	0.011	0.178	0.295	0.036	0.066	0.167
	<i>b</i>	2.602	2.513	2.441	2.378	2.327	2.281
	<i>c</i>	3474.5	3513.0	3552.0		3632.0	3673.0
4	<i>a</i>	0.001	0.032	0.254	0.179	0.101	0.011
	<i>b</i>	2.718	2.606	2.518	2.445	2.384	2.331
	<i>c</i>	3435.7	3473.4	3511.5	3550.2		

*a*—Franck-Condon factors; *b*—*r*-centroids; *c*—Wavelengths in Å.U.

TABLE II  
 Franck-Condon factors and *r*-centroids of  $B^3\Pi_1 - X^1\Sigma$  system of InCl molecule

$v'$	$v''$	0	1	2	3	4	5
0	<i>a</i>	0.586	0.291	0.092	0.024	0.006	0.001
	<i>b</i>	2.368	2.314	2.267	2.226	2.190	2.157
	<i>c</i>	3498.9	3538.0	3577.5	36.187		
1	<i>a</i>	0.333	0.128	0.284	0.165	0.063	0.019
	<i>b</i>	2.435	2.372	2.318	2.271	2.230	2.193
	<i>c</i>	3459.2		3535.3	3574.6	3614.5	3654.9
2	<i>a</i>	0.072	0.391	0.004	0.183	0.190	0.101
	<i>b</i>	2.516	2.349	2.375	2.321	2.275	2.234
	<i>c</i>	3419.6	3453.8		3532.8	3571.8	3611.4
3	<i>a</i>	0.008	0.162	0.323	0.023	0.088	0.172
	<i>b</i>	2.617	2.580	2.443	2.379	2.325	2.279
	<i>c</i>	3381.9	3418.3				3569.3
4	<i>a</i>	0.000	0.025	0.240	0.216	0.082	0.022
	<i>b</i>	2.752	2.621	2.524	2.447	2.383	2.329
	<i>c</i>		3381.1	3417.1			

*a*—Franck-Condon factors; *b*—*r*-centroids; *c*—Wavelengths in Å.U.

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#### RELAXATION TIMES AND ACTIVATION ENERGIES OF SUBSTITUTED TOLUENES AND THEIR DIPOLAR MIXTURE

THE present communication reports the relaxation times and activation energies of 3-fluoro-6-amino toluene, 3-fluoro-6-nitro toluene and their dipolar mixtures in dilute solutions of benzene at 3 cm microwave

region. The measurements have been made at 20°, 30° and 40°C, in order to calculate free energies of activation for the process of dipole orientation and viscous flow. It has been concluded that the molecules are relaxed predominantly by a process of overall molecular rotation, and relaxation time of dipolar mixture is the average of the relaxation times of the two molecules.

Relaxation times  $\tau$  were determined from the fixed frequency method of Gopala Krishna<sup>1</sup> for dilute solutions as discussed in an earlier paper<sup>2</sup>. Standing wave technique of Roberts and Von Hippel<sup>3</sup> was used for measurement of dielectric constant  $\epsilon'$  and the loss factor  $\epsilon''$ . Activation energies have been calculated using Eyring's<sup>4</sup> equation.

All the substances used are of L.R. grade (B.D.H.). Analar benzene (B.D.H.) has been distilled before use. The values of relaxation time and thermodynamic parameters are reported in Table I.

It is observed from the table that the relaxation time of 3-fluoro-6-amino toluene is smaller than that of 3-fluoro-6-nitro toluene. This is not only due to the smaller size of the former molecule but also due to the intramolecular rotation of the amino group round its bond with the ring.

It is evident from the table that the relaxation time obtained for dipolar mixture in benzene is the average of the two individual relaxation times of the polar components. The experimental results suggest that there is no association or complex formation, as