

RKR FRANCK-CONDON FACTORS AND r -CENTROIDS FOR $B^2\Sigma-A^2\pi$ TRANSITION OF CN

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ABSTRACT

A new band system of CN ($B^2\Sigma - A^2\pi$) has been observed by LeBlanc. The intensities of some of the bands in the system have been recently measured microphotometrically by Gorbal. In the present work we have computed Franck-Condon factors and r -centroids by the RKR procedure and using these results in conjunction with the intensity measures of Gorbal, we have evaluated the electronic transition moment variation with internuclear distance for the system, which is

$$R_e(r) = \text{Const.} \times (1 - 0.143r)$$

INTRODUCTION

CN is a widely studied diatomic molecule. The study of this molecule has become more important in recent times, owing to its relation with problems concerning atmospheric re-entry etc.

One of the less known transitions— $B^2\Sigma-A^2\pi$ of CN molecule has been observed by LeBlanc¹. The same system has been reproduced in our laboratories by Gorbal². While LeBlanc made eye-estimates of intensities of the vibrational bands of the system, Gorbal measured intensities using a microphotometer. Schoonveld³ calculated Franck-Condon factors (FCF) and r -centroids ($\bar{r}_{v',v''}$) for bands up to vibrational quantum numbers $v' = v'' = 19$ using Morse potential function.

If one intends studying the electronic transition moment variation with internuclear distance [$R_e(r)$] one should be in the possession of accurate intensity values of vibrational bands and the corresponding FCFs and $\bar{r}_{v',v''}$ s. Since Morse potential function

is not generally valid for high quantum numbers and further, eye-estimates of intensities proposed by LeBlanc being not very accurate, we have been prompted to use the more realistic RKR procedure for evaluating FCFs and $\bar{r}_{v',v''}$ s. These FCFs have been used in conjunction with the measured intensity values of Gorbal to study the electronic transition moment variation with internuclear distance.

COMPUTATION OF FCFs AND $\bar{r}_{v',v''}$ s

Using the empirical data³ turning points of the true potential energy curves for both the states involved in the transition under study have been evaluated and listed in Table I. These turning points are used to construct the potential energy curves.

Vibrational wave functions for the following vibrational states have been computed using WKB approximation-method at intervals of 0.01\AA .

$B^2\Sigma$ State $v = 0, 1, 2, \dots, 9$

$A^2\pi$ State $v = 0, 1, 2, \dots, 6$

TABLE I

Turning Points

$B^2\Sigma$ State of CN			$A^2\pi$ State of CN		
v	r_{\min} (\AA)	r_{\max} (\AA)	v	r_{\min} (\AA)	r_{\max} (\AA)
0	1.104, 673	1.203, 262	0	1.182, 362	1.289, 932
1	1.074, 416	1.246, 537	1	1.149, 026	1.336, 462
2	1.055, 088	1.279, 093	2	1.127, 691	1.371, 141
3	1.040, 200	1.307, 429	3	1.111, 271	1.401, 101
4	1.027, 876	1.333, 424	4	1.097, 702	1.428, 392
5	1.017, 265	1.357, 942	5	1.086, 040	1.453, 944
6	1.007, 892	1.381, 464	6	1.075, 778	1.478, 298
7	0.999, 463	1.404, 295	7	1.066, 585	1.501, 773
8	0.991, 780	1.426, 644	8	1.058, 247	1.524, 593
9	0.984, 702	1.448, 661	9	1.050, 610	1.546, 924
10	0.978, 123	1.470, 465	10	1.043, 558	1.568, 878

Using these vibrational wave functions, FCFs and $\bar{r}_{v'v''}$ s for some of the vibrational transitions have been evaluated and listed in Tables II A and II B. In the same tables are given Schoonveld's FCFs and $\bar{r}_{v'v''}$ s for comparison.

one gets the $R_e(r)$ expression by fitting the points to a straight line or some curve by the least squares technique, one has to rescale the points by the usual technique proposed by Turner *et al.*⁵; but for this procedure to be applied one should be able to group the observed

TABLE II A
Franck-Condon Factors

$v' \backslash v''$		0	1	2	3	4	5	6
0	x	0.294	0.323, 8	0.219	0.104	0.045	0.018	..
	*	0.301	0.324	0.206	0.101	0.042	0.016	..
1	x	0.410	0.014	0.060	0.161	0.159	0.106	..
	*	0.407	0.010	0.082	0.172	0.154	0.094	..
2	x	0.233	0.174	0.138	7.652-4	0.054	0.110	..
	*	0.221	0.180	0.127	6.303-6	0.070	0.130	..
3	x	0.071	0.305	0.012	0.158	0.053	0.004	..
	*	0.061	0.307	0.026	0.157	0.036	0.008	..
4	x	..	0.156	0.240	..	0.086	0.092	..
	*	..	0.146	0.271	..	0.106	0.085	..
5	x	..	0.035	0.258	0.138	0.700	0.029	..
	*	..	0.029	0.222	0.187	0.042	0.045	..
6	x	0.068	0.276	0.052	0.106	..
	*	0.060	0.271	0.104	0.087	..
7	x	9.899-5	2.727-4	0.011	..	0.274	..	0.119
	*	6.928-10	5.638-5	5.881-3	..	0.293	..	0.112
8	x	0.273	..
	*	0.294	..
9	x	3.610-5	1.582-5	0.207
	*	2.816-12	4.877-8	0.282

x : RKR FCFs (present authors)

* : Schoonveld's FCFs with Morse potential.

EVALUATION OF $R_e(r)$

Vibrational intensity values along with FCFs can yield the important parameter, the electronic transition moment variation with inter-nuclear distance. Here one uses the method of r -centroids described by Nicholls *et al.*⁴ One plots $(I/\nu^4 q_{v'v''})^{1/2}$ vs $\bar{r}_{v'v''}$.

In this expression, I is the intensity value of the band, ν the frequency of the band and q the FCF. Before bands into clear v'' progressions. In our present case, however, this is not possible as the number of bands observed in the system is very small. Hence rescaling for this system is impossible. The intensities of bands required for evaluating $R_e(r)$ are tabulated in Table III

TABLE II B
 r -Centroids (in Å)

v' \ v''		0	1	2	3	4	5	6
0	x	1.195	1.152	1.138	1.110	1.082	1.065	..
	*	1.193	1.162	1.134	1.109	1.085	1.062	..
1	x	1.231	1.181	1.175	1.146	1.121	1.117	..
	*	1.229	1.174	1.172	1.142	1.115	1.091	..
2	x	1.272	1.240	1.202	1.073	1.155	1.121	..
	*	1.270	1.241	1.198	1.991	1.151	1.122	..
3	x	1.315	1.278	1.275	1.201	1.173	1.179	..
	*	1.318	1.279	1.267	1.208	1.168	1.169	..
4	x	..	1.325	1.289	..	1.222	1.191	..
	*	..	1.327	1.290	..	1.218	1.179	..
5	x	..	1.385	1.328	1.301	1.242	1.230	..
	*	..	1.387	1.337	1.303	1.229	1.232	..
6	x	1.495	1.341	1.176	1.248	..
	*	1.398	1.347	1.319	1.245	..
7	x	1.257	1.517	1.463	..	1.348	..	1.264
	*	7.534	1.662	1.490	..	1.357	..	1.255
8	x	1.361	..
	*	1.369	..
9	x	1.320	1.123	1.380
	*	4.686	1.510	1.381

x : RKR r -centroids (present authors).

* : Schoonveld's r -centroids with Morse potential.

TABLE III

Band	ν (cm ⁻¹)	$I_{est.}$ (LeBlanc)	$I_{measured}$ (M. R. Gorbai)
7-6	20239.7	9	..
4-2	21341.9	10	..
5-3	21554.0	10	..
4-1	23103.7	7	40
5-2	23290.4	27	88
6-3	23451.1	17	37
7-4	23583.8	88	64
8-5	23683.8	11	20
9-6	23809.1	55	..

DISCUSSION

As one can see from Table II A, there is generally good agreement between Morse FCFs and FCFs evaluated by RKR procedure; however, for transitions involving high quantum numbers ($v > 3$), there is disparity between the two sets of FCFs. This is expected, because, as stated already, Morse potential function does not generally hold at high vibrational quantum numbers.

Since the bands in question involve high quantum numbers, we felt RKR FCFs were more reliable for the study of $R_e(r)$.

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The $R_e(r)$ expressions turn out to be
 (1) $R_e(r) = \text{Const} \times (-1 + 0.118r)$ LeBlanc's eye estimated intensity values with RKR FCFs.
 (2) $R_e(r) = \text{Const.} \times (1 - 0.143r)$ Gorbai's measured intensity values with RKR FCFs.

1. LeBlanc, F. J., *J. Chem. Phys.*, 1968, 48, 1841.
2. Gorbai, M. R., *Ph.D. Thesis*, Karnatak University, Dharwar, India, 1977.
3. Schoonveld, L., *J.Q.S.R.T.*, 1972, 12, 1139.
4. Nicholls, R. W. and Jarman, W. R., *Proc. Phys Soc.*, 1956, 69 A, 253.
5. Turner, R. G. and Nicholls, R. W., *Canad. J. Phys.*, 1954, 32, 475.