

Astrophysical molecule CN : vibronic transition probability parameters

B. Karthikeyan¹, K. Balachandra Kumar¹, N. Rajamanickam^{1*} and S. P. Bagare^{2†}

¹Physics Research Centre, VHNSN College, Virudhunagar 626 001, India

²Indian Institute of Astrophysics, Bangalore 560 034, India

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Abstract. Astrophysical applications are broadened by the emerging consensus on the vibration-electronic (vibronic) transition probability parameters such as Franck - Condon (FC) factors & r - centroids of some molecular species like CN , which could be useful in the identification of molecular lines and in the estimation of relative abundance of the species in various celestial bodies especially in the interstellar medium. Such important parameters, that is FC factors and r - centroids, have been computed by a reliable numerical integration procedure for the bands of $E^2 \Sigma^+ - X^2 \Sigma^+$, $D^2 \Pi_i - A^2 \Pi_i$, $E^2 \Sigma^+ - A^2 \Pi_i$, $F^2 \Delta_r - A^2 \Pi_i$ and $J^2 \Delta_i - A^2 \Pi_i$ systems of astrophysical molecule CN , using a suitable potential. For $E - X$ system, the improved values of FC factors from the revised molecular constants are given along with the already reported values.

Keywords : CN molecule - astrophysical sources - Franck-Condon factors & r-centroids.

1. Introduction

The CN molecule is of considerable astrophysical importance, since many of its transition lines/bands are observed in interstellar medium (Gredel et al., 1991), in various stars like Orion A (Saleck et al., 1993), in solar spectrum (Porfir'eva, 1986), in comets like Comet

*e-mail: nrmanickam@rediffmail.com

†e-mail: bagare@iiap.res.in

Halley (Prieto et al., 1986), in late F and G-dwarfs (Barry, 1978), in 11 late-type giants (Tompkin et al., 1975), etc., and can be used to determine the nitrogen abundance in these sources (Combi, 1980). It is also of importance in combustion and other terrestrial processes. Much effort has therefore been devoted to establishing reliable transition probabilities for the band systems of *CN* molecule.

Signatures of many diatomic molecules have been identified in spectra of a variety of such above astrophysical sources. The intensity distribution of the vibrational bands within an electronic transition is largely controlled by the square modulus of the vibrational overlap integral, the so-called Franck-Condon (FC) factor. A precise knowledge of the FC factors and other related quantities such as r-centroids provide direct information about the electronic transition moment, band strength, radiative lifetime, population of particular molecular quantum state, vibrational temperature of the source and the kinetics of energy transfer. Evaluation of reliable FC factors is therefore necessary especially for the astrophysically significant diatomic molecules.

To the best of our knowledge, no report on the FC factors and r-centroids for the band systems $D - A$, $E - A$, $F - A$ and $J - A$ of *CN* has yet appeared in the literature. In the case of system $E - X$, the FC factors were reported by Ramakrishna Rao and Lakshman (1972). However, the molecular constants used by them were those reported by Lutz (1970), which were slightly revised in a later analysis reported in Huber and Herzberg (1979). We have adopted the revised constants for our study. The reliable values of FC factors and r-centroids for all these band systems of the astrophysically important molecule *CN* have been calculated in this present study using a numerical integration procedure considering a suitable potential, as described in the following section.

2. Franck-Condon factors and r-centroids

By the quantum mechanical treatment, one can arrive at the intensity ($I_{v'v''}$) of a molecular band (v', v'') for an electronic transition in emission (Bagare, 1980 and Rajamanickam, 1987) as

$$I_{v'v''} = DN_{v'}E_{v'v''}^4 R_e^2(\bar{r}_{v'v''})q_{v'v''} \quad (1)$$

where D is a constant partly depending on the geometry of the apparatus, $N_{v'}$ is the population of the level v' , $E_{v'v''}$ is the quantum energy which is the difference between the energies of upper vibrational level v' and lower vibrational level v'' , $q_{v'v''}$ is the Franck-Condon factor, $\bar{r}_{v'v''}$ is the r-centroid and R_e is the electronic transition moment.

We know that the square modulus of the vibrational overlap integral is termed as the FC factor

$$q_{v'v''} = |\langle \psi_{v'} | \psi_{v''} \rangle|^2 \quad (2)$$

where $\psi_{v'}$ and $\psi_{v''}$ are the vibrational wave functions for the upper and lower states respectively. The r-centroid is seen to be a weighted average with respect to $\psi_{v'}\psi_{v''}$ of the

range of r values experienced by the molecule in both states of the $v' - v''$ transition. That is,

$$\bar{r}_{v'v''} = \frac{\langle \psi_{v'} | r | \psi_{v''} \rangle}{\langle \psi_{v'} | \psi_{v''} \rangle} \quad (3)$$

For vibrational transition involving low quantum numbers, the Morse (1929) potential yields accurate FC factors and r-centroid values. The method of computation of the FC factors is done by Bates (1949) using numerical integration and the detailed procedure is in Partal Urena et al. (2000). Here, we have calculated the Morse potential functions for all the states at intervals of 0.01 Å, whereas r varies from 1.01 Å to 1.56 Å, from 1.05 Å to 1.75 Å, from 1.08 Å to 1.45 Å, from 1.03 Å to 1.60 Å and from 1.13 Å to 1.70 Å for the systems $E^2 \Sigma^+ - X^2 \Sigma^+$, $D^2 \Pi_i - A^2 \Pi_i$, $E^2 \Sigma^+ - A^2 \Pi_i$, $F^2 \Delta_r - A^2 \Pi_i$ and $J^2 \Delta_i - A^2 \Pi_i$ respectively. The FC factors $q_{v'v''}$ and r-centroids $\bar{r}_{v'v''}$ are computed numerically for the band systems $E - X$, $D - A$, $E - A$, $F - A$ and $J - A$ and the results are presented in Tables 1 - 5. In Table 1, we have also presented the Ramakrishna Rao and Lakshman (1972) values of FC factors and r-centroids for $E - X$ system. The available wavelengths of band origin (Lutz 1970 for $E - X$, Douglas et al 1954 for $D - A$, Lutz 1971 for $E - A$, Jha et al. 1965 for $F - A$, Carroll 1956 for $J - A$) are also included in the tables. The molecular constants used in present study are collected from the compilation of Huber and Herzberg (1979). In the case of $E - X$ system, the molecular constants used by Ramakrishna Rao and Lakshman (1972) and the compiled values of Huber and Herzberg (1979) are entered in Table 6 for a comparison.

3. Results and discussion

The FC factors of the $E - X$ system indicate that the bands (0, 2), (0, 3), (0, 4), (1, 1), (1, 2), (1, 5), (2, 1), (3, 0), (4, 0) and (5, 0) should be relatively intense in the CN spectrum and all other bands should be comparatively weak. In the case of $D - A$ system, only the two bands (0, 6) and (0, 7) would be more intense. For the $E - A$ system, the bands (0, 0), (0, 1), (0, 2), (1, 0), (1, 2), (1, 3) and (1, 4) must be more intense compared to others. The FC factors of $F - A$ system reveal that the bands (0, 1), (0, 2), (0, 3), (0, 4), (1, 1), (1, 5), (1, 6), (2, 0), (2, 7), (2, 8), (3, 0) and (3, 9) should be more intense. In the case of $J - A$ system, the FC factors indicate that the most intense band is (2, 1) and the other prominent bands are (4, 0) and (1, 1).

Ramakrishna Rao and Lakshman (1972) reported FC factors for the $E - X$ system by the approximate analytical integration method (Fraser and Jarman 1953) which are only indicative of trends and not reliable (Jarman and Fraser 1953). They also evaluated the r-centroids by quadratic equation method as well as by graphical method. However, those r-centroid values may not often lie in the range common to vibrational levels v' and v'' and hence these methods are questionable to use safely (James, 1966). Therefore,

Table 1. Franck-Condon factors and r - centroids of $E - X$ band system.

	$v'' = 0$	$v'' = 1$	$v'' = 2$	$v'' = 3$	$v'' = 4$	$v'' = 5$
$v' = 0$	a) i) 0.018	0.089	0.197	0.260	0.226	0.135
	ii) 0.020	0.090	0.188	0.239	0.206	0.125
	b) i) 1.249	1.271	1.293	1.317	1.343	1.371
	ii) 1.245	1.266	1.288	1.311	1.334	1.359
c) 1695.9	1756.7	1821.2	1889.7	1962.5	2040.0	
$v' = 1$	a) i) 0.065	0.173	0.145	0.020	0.031	0.160
	ii) 0.066	0.167	0.140	0.025	0.014	0.082
	b) i) 1.231	1.252	1.272	1.287	1.330	1.350
	ii) 1.228	1.248	1.270	1.291	1.314	1.338
c) 1649.1	1706.6	*	*	*	*	
$v' = 2$	a) i) 0.125	0.148	0.012	0.055	0.118	0.021
	ii) 0.120	0.142	0.015	0.030	0.004	—
	b) i) 1.214	1.233	1.247	1.280	1.299	1.312
	ii) 1.212	1.232	1.252	1.273	1.295	1.317
c) 1605.3	1659.8	*	*	*	*	
$v' = 3$	a) i) 0.167	0.058	0.026	0.100	0.006	0.063
	ii) 0.155	0.061	0.024	0.071	—	—
	b) i) 1.198	1.216	1.241	1.258	1.263	1.307
	ii) 1.197	1.216	1.236	1.256	1.277	1.298
c) 1564.4	*	*	*	*	*	
$v' = 4$	a) i) 0.175	0.003	0.088	0.023	0.044	0.065
	ii) 0.134	0.005	0.145	—	—	—
	b) i) 1.182	1.194	1.222	1.236	1.265	1.280
	ii) 1.183	1.201	1.220	1.240	1.260	1.280
c) 1526.1	*	*	*	*	*	
$v' = 5$	a) i) 0.154	0.014	0.079	0.007	0.074	†
	ii) 0.130	0.083	—	—	—	—
	b) i) 1.167	1.188	1.204	1.232	1.244	—
	ii) 1.169	1.187	1.205	1.224	1.243	—
c) 1490.5	*	*	*	*	*	

a) FC factors $q_{v'v''}$: i) present study ; ii) Rao and Lakshman (1972)

b) r - centroids $\bar{r}_{v'v''}(\text{\AA})$: i) present study ; ii) Rao and Lakshman (1972)

c) Wavelength of band origins $\lambda_{v'v''}(\text{\AA})$

† $q_{v'v''} \approx 0$

* The bands which are not observed experimentally

we may consider our $q_{v'v''}$ and $\bar{r}_{v'v''}$ values, calculated by numerical integration method using revised molecular constants, as reliable and more accurate.

On comparing the present and already reported $q_{v'v''}$ values, we may observe that the percentage of deviation between two sets lies within 9 percent for experimentally

Table 2. Franck-Condon factors and r - centroids of $D - A$ band system.

	$v'' = 0$	$v'' = 1$	$v'' = 2$	$v'' = 3$	$v'' = 4$	$v'' = 5$	$v'' = 6$	$v'' = 7$
$v' = 0$	a) †	†	0.007	0.024	0.058	0.106	0.153	0.178
	b)		1.389	1.409	1.430	1.451	1.472	1.494
	c)		*	*	*	*	2899.0	3043.1
$v' = 1$	a) †	0.007	0.030	0.072	0.113	0.114	0.067	0.012
	b)	1.358	1.378	1.397	1.417	1.437	1.457	1.475
	c)	*	*	2466.8	2575.5	2692.4	*	*
$v' = 2$	a) 0.003	0.021	0.063	0.101	0.086	0.027	†	0.044
	b) 1.329	1.348	1.367	1.386	1.405	1.423		1.469
	c) *	*	*	2409.1	2512.7	*		*
$v' = 3$	a) 0.008	0.041	0.087	0.082	0.023	0.004	0.052	0.063
	b) 1.319	1.337	1.356	1.374	1.392	1.422	1.435	1.454
	c) *	*	2262.6	2355.1	*	*	*	*

Table 3. Franck-Condon factors and r - centroids of $E - A$ band system.

	$v'' = 0$	$v'' = 1$	$v'' = 2$	$v'' = 3$	$v'' = 4$
$v' = 0$	a) 0.270	0.407	0.243	0.071	0.009
	b) 1.283	1.319	1.360	1.409	1.479
	c) 2006.34	2080.96	*	*	*
$v' = 1$	a) 0.324	0.021	0.155	0.310	0.149
	b) 1.249	1.265	1.330	1.367	1.416
	c) 1941.27	*	*	*	*

Table 4. Franck-Condon factors and r - centroids of $F - A$ band system.

	$v'' = 0$	$v'' = 1$	$v'' = 2$	$v'' = 3$	$v'' = 4$	$v'' = 5$	$v'' = 6$	$v'' = 7$	$v'' = 8$	$v'' = 9$
$v' = 0$	a) 0.057	0.180	0.265	0.241	0.153	0.071	0.025	0.007	0.002	†
	b) 1.301	1.331	1.361	1.391	1.423	1.456	1.490	1.525	1.562	
	c) *	*	2123.5	2204.9	2291.5	2383.4	*	*	*	
$v' = 1$	a) 0.141	0.192	0.054	0.008	0.120	0.196	0.161	0.085	0.032	0.009
	b) 1.281	1.309	1.337	1.377	1.402	1.433	1.466	1.499	1.534	1.571
	c) *	*	*	*	2229.3	2316.4	2409.2	2507.8	2613.1	*
$v' = 2$	a) 0.190	0.072	0.016	0.123	0.062	0.002	0.095	0.176	0.149	0.078
	b) 1.262	1.289	1.324	1.349	1.377	1.431	1.445	1.476	1.509	1.544
	c) *	*	*	*	*	*	2342.0	2435.5	2534.6	2640.5
$v' = 3$	a) 0.188	0.002	0.097	0.047	0.017	0.107	0.044	0.007	0.105	0.166
	b) 1.244	1.261	1.301	1.326	1.364	1.389	1.416	1.464	1.487	1.519
	c) *	*	*	*	*	*	*	*	2462.5	*

observed bands. For the bands which are not observed experimentally, the percentage of deviation may vary from 8 to 97 percent.

We know that if \bar{r} and \bar{r}_1 are the r -centroid values corresponding to the bands (v', v'') and $(v' + 1, v'' + 1)$, then $\bar{r}_1 - \bar{r} \approx 0.01 \text{ \AA}$ for most systems and $\bar{r}_1 - \bar{r}$ would exceed 0.01 \AA only if the potentials are very wide (Nicholls et al., 1955). Since the sequence difference

Table 5. Franck-Condon factors and r - centroids of $J - A$ band system.

	$v'' = 0$	$v'' = 1$
$v' = 0$	a) 0.011	0.055
	b) 1.317	1.342
	c) 1796.3	1855.9
$v' = 1$	a) 0.038	0.124
	b) 1.302	1.326
	c) 1761.7	*
$v' = 2$	a) 0.076	0.140
	b) 1.288	1.311
	c) 1729.2	*
$v' = 3$	a) 0.108	0.099
	b) 1.274	1.296
	c) 1698.6	*
$v' = 4$	a) 0.127	0.043
	b) 1.261	1.282
	c) 1669.8	*

a) FC factors $q_{v'v''}$ b) r - centroids $\bar{r}_{v'v''}(\text{\AA})$ c) Wavelength of band origins $\lambda_{v'v''}(\text{\AA})$ † $q_{v'v''} \approx 0$

* The bands which are not observed experimentally

Table 6. Molecular constants.

Molecular State	E		X	
	Present Study	Rao et al(1972)	Present Study	Rao et al(1972)
ω_e	1681.43	1681.43	2068.59	2068.705
$\omega_e x_e$	3.60	3.60	13.087	13.144
B_e	1.4871	1.4871	1.89974	1.8996
α_e	0.00643	0.00643	0.017369	0.01735
r_e	1.3245	1.3195	1.17182	1.1718

of r-centroid in our systems is found to be nearly a constant and is about 0.01 \AA , we can say that the width of the potentials are not so wide.

In all the above discussed systems of CN molecule, we have to note that since the r-centroid value $\bar{r}_{v'v''}$ increases as the wavelength ($\lambda_{v'v''}$) increases following $r'_e > r''_e$, the bands are degraded towards the red region.

Even though the CN molecule has been astrophysically well established, our present study would be helpful in the identification of CN lines in new astrophysical sources and

in the confirmation of our discussed band systems of CN in already identified sources. Some of the transitions of CN are of renewed interest in the study of the interstellar medium and the star forming regions.

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