

Carbon phosphide ($B^2\Sigma^+ - A^2\Pi_i$) band system: RKR Franck-Condon factors and r -centroids

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Abstract. Franck-Condon factors and r -centroids based on Rydberg-Klein-Rees potential have been computed for the CP ($B^2\Sigma^+ - A^2\Pi_i$) band system. These results are compared with the Morse values and discussed.

Keywords. Carbon phosphide; Rydberg-Klein-Rees; r -centroids; Franck-Condon factors.

1. Introduction

Band spectroscopic methods used for the determination of temperature of sources and for the study of physical processes occurring in various radiative sources require an accurate knowledge of transition probabilities. Because of this the calculation of Franck-Condon (FC) factors ($q_{v', v''}$) and r -centroids ($\bar{r}_{v', v''}$) of diatomic molecules, particularly those of astrophysical interest, has drawn the attention of many workers. Bands belonging to (B–A) system of carbon phosphide (CP) have been observed in the stellar spectra (Swings 1958). Also the spectra of CP are of potential interest in applied problems like ablation of special heat shields and in some oxygen-deficient phosphorus containing rocket exhausts (Wentink and Spindler 1970).

The band system of CP designated as $B^2\Sigma^+ - A^2\Pi_i$ (λ 4390–4660 Å) was first excited in the laboratory and analysed by Barwald *et al* (1934). The Morse $q_{v', v''}$ have been reported for this band system (Singh and Pathak 1969) by an approximate method due to Fraser and Jarman (1953). The results of $\bar{r}_{v', v''}$ reported by Wentink and Spindler (1970) are not in agreement with those of Singh and Pathak. Further it has been reported that the true potential-energy curve (RKR) of $A^2\Pi_i$ state differs from the Morse model (Murthy and Murthy 1970). It is therefore intended to present in this paper the $q_{v', v''}$ and $\bar{r}_{v', v''}$ of CP appropriate to the RKR potential model.

2. Theory

In an electronic transition involving the vibrational levels v' and v'' of a diatomic molecule, the emitted radiation has the intensity

$$I_{v', v''} = \left(\frac{64 \Pi^4}{3} \right) N_{v'} c v^4 R_e^2 (\bar{r}_{v', v''}) q_{v', v''} \quad (1)$$

where N_v is the population of the initial state, ν is the frequency in wave-numbers of the band origin and $R_e(\bar{r}_{v', v''})$ is called the electronic transition moment.

The quantities $q_{v', v''}$ and $\bar{r}_{v', v''}$ can be expressed in terms of the vibrational state functions $|v\rangle$ of the levels v' and v'' as

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

and

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

3. Franck-Condon factors and r -centroids

For $A^2 \Pi_i$ state the reported (Murthy and Murthy 1970) true potential energy curve is adopted for the computation of the vibrational wave functions. Following the procedure explained therein the r_{max} and r_{min} values have been obtained for the $B^2 \Sigma^+$ state also and the results are presented in table 1. Molecular data required for the calculation are taken from Herzberg (1950).

WKB method offers a suitable procedure to obtain the wave functions appropriate to true potential energy curves. Wu (1952) has given expressions for generating the wave-functions in different regions of the potential energy curve.

In the present study, the true potential energy curve was divided into segments running through four successive turning points for each limb. The potential energies $U(r)$, at intervals of 0.01 Å were interpolated by Lagrange's method. Inserting the $U(r)$ values in Wu's expressions, the eigen-functions were determined in the range 1.46–2.05 Å for each v .

The accuracy of the wave function is checked by evaluating B_v using the Jarman's (1963) expression

$$B_v = \frac{h}{8\pi^2\mu} \langle v | 1/r^2 | v \rangle \quad (4)$$

where μ is the reduced mass of the molecule in atomic weight units. Matrix elements in equation (4) have been evaluated numerically. B_v values calculated for $A^2 \Pi_i$ state are shown in table 2 along with the observed values obtained from

Table 1. True potential energy curve of $B^2 \Sigma^+$ state of CP

v	Turning points in Å	
	r_{max}	r_{min}
0	1.762	1.625
1	1.821	1.581
2	1.865	1.555
3	1.902	1.533
4	1.937	1.516
5	1.969	1.500

Table 2. Calculated and observed values of B_v (cm^{-2}) for $A^2\Pi_1$ state of CP

v	B_v (obs.)	B_v (calc.)
0	0.6942	0.6946
1	0.6865	0.6858
2	0.6788	0.6771
3	0.6711	0.6713
4	0.6634	0.6629
5	0.6557	0.6587

Table 3. Franck-Condon factors and r -centroids for CP (B-A) system

v'' v'	0	1	2	3	4	5
	0.989	0.003	0.009	0.000	0.000	
	0.951	0.040	0.009	0.000	0.000	
	1.689	2.567	1.714	1.970	1.672	
	1.685	1.922	1.816	2.167	1.838	
	0.009	0.961	0.010	0.020	0.000	
	0.048	0.845	0.080	0.026	0.001	
	1.246	1.702	2.428	1.732	0.413	
	1.498	1.694	1.937	1.831	2.155	
	0.005	0.015	0.919	0.012	0.033	
	0.000	0.111	0.719	0.114	0.052	
	1.817	1.258	1.713	2.526	1.729	
	2.572	1.537	1.700	1.955	1.845	
	0.001	0.015	0.022	0.857	0.018	
	0.001	0.000	0.185	0.582	0.139	
	1.532	1.804	1.303	1.723	2.521	
	1.697	3.914	1.569	1.703	1.974	
		0.005	0.023	0.052	0.825	
		0.003	0.000	0.263	0.442	
		1.594	1.825	1.449	1.739	
		1.732	..	1.597	1.701	
5		0.000	0.020	0.023	0.094	0.423
		0.000	0.006	0.002	0.336	0.311
		1.192	1.647	1.871	1.571	1.742
		1.493	1.771	0.674	1.621	1.692

First row: RKR $q_{v'v''}$; second row: Morse $q_{v'v''}$; third row: RKR $\bar{F}_{v'v''}$ and fourth row: Morse $\bar{F}_{v'v''}$.

B_0 and a_0 . The close agreement between the two values indicates the reliability of the wave-functions generated.

Matrix elements in equations (2) and (3) were evaluated numerically for F-C factors and r -centroids. All the computations were carried out on a National Elliott 803 Computer at Hindustan Aeronautics Ltd., Bangalore. Table 3 contains

RKR $q_{v', v''}$ and $\bar{r}_{v', v''}$ for all the observed bands of CP (B-A) system along with Morse results by the numerical procedure of Murthy and Murthy (1967).

4. Discussion

Morse $q_{v', v''}$ and $\bar{r}_{v', v''}$ obtained by the numerical procedure of Murthy and Murthy are in agreement with those of Wentink and Spindler (1970). It may be noted that even for low quantum numbers, $q_{v', v''}$ and $\bar{r}_{v', v''}$ of RKR and Morse differ appreciably. According to the vibrational sum rule $\sum_{v'} q_{v', v''} = \sum_{v''} q_{v', v''} = 1$. It is seen from the table 3 that vibrational sum rule is not fulfilled by the observed bands. It is therefore possible to expect additional bands of (B-A) system in the spectrum of CP molecule.

The $\bar{r}_{v', v''}$ falls outside the range of classical turning points for some transitions with small $q_{v', v''}$. In general the r -centroids do not show smooth variation with the wavelength. This is particularly noticeable with bands of small $q_{v', v''}$. These inferences are in conformity with the non-smooth variation of r -centroids calculated by direct evaluation of expression (3) as contrasted to the results by graphical procedure (Murthy 1972). RKR $q_{v', v''}$ and $\bar{r}_{v', v''}$ reported here have to be preferred as these calculations depend on the experimentally determined potential.

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