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Astrophysical molecule S_2 : Vibrational transition probability data

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Abstract. The Franck-Condon factors (vibrational transition probabilities) and *r*-centroids have been computed by the more reliable numerical integration procedure for the bands of $C^3\Sigma_u^- \rightarrow X^3\Sigma_g^-$ and $D^3\,\Pi_{u,r} \rightarrow X^3\Sigma_g^-$ systems of the astrophysically significant S_2 molecule using the suitable potential.

Key words : Franck-Condon factors and *r*-centroids—*C, D* → *X* band systems—S_2 molecule

1. Introduction

Elemental sulphur has assumed great importance because of its occurrence in the interstellar medium (relative abundance 0.0001) resulting in the formation of a variety of molecules which have been detected in the dense clouds (Oppenheimer & Dolgarno 1974). Recently, Hearn *et al.* (1983), using the International Ultraviolet Explorer Space Craft, observed strong emission bands of S_2 from comet IARS-Araki-Alcock 1983 d. On the basis of spatial profiles, they concluded that the lifetime of this molecule is nearly 450S and the production rate is 2×10^{25} S^{-1}. The laboratory experiments have revealed several triplet and singlet transitions in S_2. Further a Rydberg series, consisting of electronic transitions C–X, E, F–X, suggesting the first ionization potential of 9.39 eV for disulphur, has also been identified (Huber & Herzberg 1979). Tanaka & Ogawa (1962) also observed the C → X and D → X bands in the emission spectra.

The transition probability parameters are required for diagnostic application in astronomy, astrophysics and allied subjects (Nicholls 1977). The theoretical prediction of intensity distribution in the spectra of many diatomic molecules which are of interest in astrophysics is necessary for an understanding of the physico-chemical conditions of the emitting sources. The Franck-Condon factors and *r*-centroids are important for determining the variation of electronic transition moment with internuclear separation (Rajamanickam 1985, 1987a, 1987b, 1988a, 1988b, 1991a, Dhuvaragai Kannan & Rajamanickam 1992).

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Keeping in view the above facts we have carried out the calculation of Franck-Condon factors and *r*-centroids for the triplet band systems $C^3\Sigma^-_u$, $D^3\Pi_{u,r} \rightarrow X^3\Sigma^-_g$ of S_2 by the more reliable numerical integration procedure.

2. Franck-Condon factors and r-centroids

One of the parameters which controls the intensity distribution in the emission of molecular bands is the Franck-Condon (FC) factor. The square of the overlap integral is termed as FC factor (Bates 1952)

$$q_{v'\,v''} = (\int \psi_{v'}\, \psi_{v''}\, dr)^2 \qquad \ldots (1)$$

where $\psi_{v'}$ and $\psi_{v''}$ are the vibrational wavefunctions for the upper and lower states, respectively. The *r*-centroid is a unique value of internuclear separation which may be associated with a $v' \rightarrow v''$ band and defined as

$$\bar{r}_{v'\,v''} = \frac{\int \psi_{v'}\, r\, \psi_{v''}\, dr}{\int \psi_{v'}\, \psi_{v''}\, dr} \qquad \ldots (2)$$

For a proper understanding of the intensity distributions in the band systems of the molecules, it is necessary to choose a suitable potential. The Morse potential (Morse 1929)yields accurate Franck-Condon factors, especially for vibrational transitions involving low quantum numbers (Patil 1978).

The computation of the Franck-Condon factors is made by Bates's method (1949) of numerical integration according to the detailed procedure provided by Tawde & Sreedhara Murthy (1959) and Rajamanickam (1988c). Morse (1929) wave functions were calculated at intervals of 0.01Å for range of *r* from 1.67Å to 2.14Å and 1.73Å to 2.07Å for every observed vibrational level of C → X and D → X states respectively. Once the appropriate wave functions are obtained, the Franck-Condon factors can be evaluated by integrating the expression (1). In the case of Morse function, Fraser & Jarmain (1953) gave a procedure for the analytical integration of the overlap integral. The results are generally, however, only indicative of trends (Jarmain & Fraser 1953) . The integration is therefore carried out numerically in the present study. The definition of *r*-centroid offers a method of computing *r*-centroids directly. Integrals in equations (1) and (2) for the Franck-Condon factors ($q_{v'v''}$) and *r*-centroids ($\bar{r}_{v'v''}$) were computed numerically and the resultes are entered in table 1 and table 2 for the states C → X and D → X respectively. The wavelength ($\lambda_{v'v''}$) and intensity ($I_{v'v''}$) data (Tanaka & Ogawa 1962) are also entered. The molecular constants used in the present sutdy are collected from Huber & Herzberg (1979).

Table 1. Franck-Condon factors and r-centroids for the (C → X) system

v', v''	$\lambda_{v'v''}$ (Å)		$I_{v'v''}$	$q_{v'v''}$		$\bar{r}_{v'v''}$ (Å)	
	Present study	Verma *et al.* (1988)		Present study	Verma *et al.* (1988)	Present study	Verma *et al.* (1988)
0,0	1797.66	1797.6	3	0.317	–	1.852	1.8520
0,2	1845.31	1845.31	3	0.204	–	1.789	1.7948
0,3	1869.67	1869.66	3	0.091	–	1.761	1.7705
0,4	1894.50	1894.49	1	0.034	–	1.733	1.7484
0,5	1919.81	1919.8	1	0.011	–	1.707	1.7282
0,6	1945.48	–	0	0.003	–	1.682	–
1,0	1771.33	1771.33	0	0.390	–	1.889	1.8915
1,3	1841.80	1841.8	1	0.199	–	1.795	1.7989
1,4	1865.49	1865.49	1	0.159	–	1.766	1.7745
1,5	1889.93	1889.93	1	0.086	–	1.739	1.7522
3,6	1857.36	–	1	0.102	–	1.778	–

Table 2. Franck-Condon factors and r-centroids for the (D → X) system

v', v''	$\lambda_{v'v''}$ (Å)		$I_{v'v''}$	$q_{v'v''}$		$\bar{r}_{v'v''}$ (Å)	
	Present study	Verma *et al.* (1988)		Present study	Verma *et al.* (1988)	Present study	Verma *et al.* (1988)
0,0	1702.66	1702.26	1	0.811	0.5423	1.875	1.8761
0,1	1723.40	1723.40	2	0.168	0.3154	1.797	1.8180
0,2	1750.93	1750.93	0	0.020	0.1121	1.721	1.7790
1,2	–	1726.99	–	0.258	0.2713	1.803	1.8226
1,3	1748.25	1748.25	0	0.049	0.1879	1.727	1.7827
2,3	1719.10	1719.10	0	0.297	0.1432	1.809	1.8273

3. Results and discussion

Verma & Mahajan (1988) have reported Morse Franck-Condon factor by the approximate r_e-shift method for the band system D → X of S_2 and r-centroids by the quadratic equation method for both band systems (C → X and D → X) which are not safest (James 1966). The reported $q_{v'v''}$ and $\bar{r}_{v'v''}$ values by Verma & Mahajan (1988) are also given in tables 1 and 2 for comparison. There are, however, large differences in Verma & Mahajan (1988) values of $q_{v'v''}$ values from the present results. In the GaH band system also such large differences in $q_{v'v''}$ values have been reported by approximate r_e-shift and accurate numerical integration methods (Rajamanickam *et al.* 1991b). Reasonably high values of Franck-Condon factors for these transitions suggest that a serious experimental attempt must be made to improve, in order to get intense spectra.

Since $r'_e < r''_e$, $\bar{r}_{v'v''}$ decreases with the increase in wavelength which is expected in the blue degraded band systems. The sequence difference for these systems is found to be constant and is less than 0.01Å.

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