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# Vibrational transition probabilities of the bands of the BaO (A $^1\Sigma-X^1\Sigma$ ) system

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**Abstract.** The band spectrum of BaO has been obtained by spraying barium chloride solution into a flame. The integrated intensities of the bands have been determined by photographic photometry. The experimental results along with the theoretically computed Franck-Condon factors have been used to evaluate a relation between  $R_e$ , the electronic transition moment, and  $r$ , the internuclear separation, in the form

$$R_e(\bar{r}_{v',v''}) = \text{constant} (1 - 0.536r).$$

This relation has been used to obtain improved Franck-Condon factors. The theoretically computed Franck-Condon factors, with and without the inclusion of  $R_e$  variation, have been compared with the experimental band strengths.

## 1. Introduction

The study of molecular spectra has been a powerful tool in the investigation of astrophysical problems. The recent improvements in technique and methods, both on the theoretical and experimental sides, have enhanced such importance.

The BaO molecule is an astral molecule, found, for instance, in  $\beta$ -pegasi (Davis 1947). If this molecule is therefore studied in the laboratory through its spectrum, on the one hand, and if Franck-Condon factors,  $r$  centroids and the  $R_e$  variation are computed theoretically, on the other, one could infer some of the physical conditions obtaining in the distant stars, like  $\beta$ -pegasi.

## 2. Experimental investigation

The BaO (A  $^1\Sigma-X^1\Sigma$ ) band system has been obtained by spraying barium chloride solution into a flame. The usual low temperature of flames enables one to get the spectrum free from unwanted line spectra. The flame was obtained with a burner of the Lundegardh design (Twyman 1951). This design had to be modified to suit the present requirements of a steady flame over a considerable length of time. A Hilger glass-prism spectrograph with the range 4000–15 000 Å was used to photograph the band spectrum, on Ilford rapid process panchromatic plates (R40).

The intensities of the bands have been determined by photographic photometry (Tawde and Patankar 1943). The areas under the contours obtained on a Moll's self-recording microphotometer were measured. These areas were taken to be proportional to the intensities of the bands. Necessary corrections were applied for overlap of neighbouring bands by suitable extrapolation methods. The resulting measures of integrated intensities were expressed in terms of the most intense band of the system, which happened to be the (2, 1) band. These results have already been published elsewhere by one of the authors (Walvekar 1961). However, they are reproduced in table 1 as they form an important part of this work.

## 3. Theoretical computations

### 3.1. Under constancy of $R_e$

Firstly, treating the diatomic molecule BaO as a simple harmonic oscillator, harmonic wave functions have been computed and the corresponding Franck-Condon factors

**Table 1. Integrated intensities, Franck–Condon factors and  $r$  centroids for the BaO ( $A^1\Sigma-X^1\Sigma$ ) system**

Band ( $v', v''$ )	Integrated intensity (relative)	Franck–Condon factor with harmonic wave functions	Franck–Condon factor with anharmonic wave functions	$r$ centroids
1	2	3	4	5
(0, 0)	9.48	0.010	0.009	a 2.032 <sub>3</sub> b 2.032
(0, 1)	11.9	0.04	0.048	a 2.037 <sub>5</sub> b 2.037 <sub>5</sub>
(0, 2)	77.3	0.085	0.120	a 2.08 b 2.08
(1, 0)	22.5	0.054	0.039	a 2.014 <sub>3</sub> b 2.014
(1, 1)	94.4	0.128	0.125	a 2.038 b 2.037 <sub>5</sub>
(1, 2)	94.2	0.360	0.163	a 2.043 <sub>5</sub> b 2.043 <sub>5</sub>
(2, 0)	54.3	0.134	0.107	a 1.996 <sub>7</sub> b 1.996 <sub>5</sub>
(2, 1)	100	0.156	0.184	a 2.018 <sub>9</sub> b 2.020 <sub>5</sub>
(2, 2)	17.4	0.055	0.076	a 2.043 <sub>4</sub> b 2.043 <sub>5</sub>
(3, 0)	54.4	0.206	0.132	a 1.979 <sub>1</sub> b 1.979 <sub>5</sub>
(3, 1)	30.7	0.073	0.097	a 2.002 <sub>4</sub> b 2.002 <sub>5</sub>
(3, 3)	31.8	—	0.066	a 2.052 b 2.05
(3, 4)	12.9	—	—	a — b 2.06

$r$  centroids are in Å. a,  $r$  centroids by direct method; b,  $r$  centroids by graphical method.

evaluated. For this purpose the method due to Manneback has been used. Next, to see the effect of mechanical anharmonicity on the Franck–Condon factors, use has been made of the numerical integration method of Bates (1949) to evaluate the so-called anharmonic wave functions, and these, in turn, are used to compute Franck–Condon factors. Both the sets of Franck–Condon factors have then been compared with the experimental  $I/\nu^4$  values. (Here  $I$  = integrated intensity of the band,  $\nu$  = the band frequency.) The Franck–Condon factors with harmonic wave functions and anharmonic wave functions have been given in table 1.

Table 2 shows the comparison of Franck–Condon factors with the experimental  $I/\nu^4$  values. Both these quantities (Franck–Condon factor and  $I/\nu^4$ ) have been expressed in terms of the values for the first band in each progression.

It is seen from table 2 that there is generally better agreement between experimental and theoretical results after inclusion of the mechanical anharmonicity, as one would expect. However, the ratios of the experimental values to the theoretical ones do not come close to unity. Hence there is further scope for refinement in theory. This is obviously possible by consideration of the variation of the electronic transition moment with inter-nuclear separation. This has been done in the following section.

**Table 2.** Comparison of Franck–Condon factors, with  $I/\nu^4$  values, ‘smoothed’ Franck–Condon factors and ratios of ‘smoothed’ Franck–Condon factors to  $I/\nu^4$  values for BaO ( $A^1\Sigma-X^1\Sigma$ ) system

Band ( $v', v''$ )	Franck– Condon factor (simple harmonic)	Franck– Condon factor (anharmonic)	Ratio $\delta_{SH}$ $= \frac{I/\nu^4}{(FC)_{SH}}$	Ratio $\delta_{AH}$ $= \frac{I/\nu^4}{(FC)_{AH}}$	‘Smoothed’ (FC) <sub>AH</sub> relative	Ratio $\delta_{SMAH}$ $= \frac{I/\nu^4}{(FC)_{SMAH}}$
1	2	3	4	5	6	7
(0, 0)	1	1	1	1	1	1
(0, 1)	3.89	5.11	0.38	0.29	5.43	0.54
(0, 2)	8.30	12.64	1.38	0.91	20.96	0.66
(1, 0)	1	1	1	1	3.37	1
(1, 1)	2.37	3.16	2.03	1.52	14.20	1.12
(1, 2)	6.63	4.12	0.87	1.40	19.84	0.98
(2, 0)	1	1	1	1	7.06	1
(2, 1)	1.168	1.72	1.84	1.25	17.00	0.94
(2, 2)	0.41	0.71	1.07	0.62	9.22	0.34
(3, 0)	1	1	1	1	6.60	1
(3, 1)	0.35	0.74	1.87	0.89	7.02	0.62
(3, 3)	0.33	0.50	2.78	0.54	8.72	0.72

### 3.2. Under variation of $R_e$

There is so far no theoretical method of obtaining a relation between  $R_e$  and  $r$ . The semi-empirical methods of  $r$  centroids due to Nicholls and Jarman (1956) have been employed in the present investigation to get the desired relation between  $R_e$  and  $r$ . The  $r$  centroids computed from the relation

$$\bar{r}_{v'v''} = \frac{\int \psi_{v'}(r)r\psi_{v''}(r) dr}{\int \psi_{v'}(r)\psi_{v''}(r) dr} \quad (1)$$

and also by the graphical method have been given in table 1. The  $r$  centroids so obtained have been used, along with the experimental intensity measures, to obtain the following relation between  $R_e$  and  $r$ :

$$R_e(\bar{r}_{v'v''}) = \text{constant}(1 - 0.536r). \quad (2)$$

Equation (2) has been used to obtain ‘smoothed’  $(FC)_{SMAH}$  ( $(FC)_{AH}$  smoothed) factors. These are listed in table 2.

As before these ‘smoothed’ Franck–Condon factors have been compared with experimental data (see table 2). Column 6 gives Franck–Condon factors relative to the Franck–Condon factor of the (0, 0) band, but while evaluating the  $\delta$  of column 7 Franck–Condon factors have been expressed in terms of Franck–Condon factors for the first band in each progression.

If one compares columns 5 and 7 of table 2, it is seen that agreement between experimental and theoretical results is much better with the inclusion of  $R_e$  variation than without it. This is as it should be, as the electronic transition moment is bound to vary with the internuclear separation. However, the following remark about the  $R_e$  variation will not be out of place: as mentioned earlier, the present method of obtaining  $R_e$  variation is not a pure analytic method—it is semi-empirical depending as it does on the experimental values of intensities. Thus the derived  $R_e(r)$  expression is only an inference—an estimate of the true variation of  $R_e$  with  $r$ . Also, in the method of  $r$  centroids or in the graphical method are inherent approximations which do not generally hold. This has been pointed out recently by James (1966). Thus, unless we have an expression for  $R_e(r)$  derived on purely theoretical considerations, we cannot possibly think of making a true comparison between theoretically predicted transition probabilities and experimental  $I/\nu^4$  values.

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