

Potential energy curves for the $B^2\Sigma$ and $X^2\Sigma$ states of scandium monoxide*

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Abstract. For the $B^2\Sigma$ and $X^2\Sigma$ states of scandium monoxide, the potential energy curves are constructed by the Rydberg-Klein-Rees and the Morse methods. Morse model is shown to be adequate for the ($B \rightarrow X$) band system of ScO. The r_e values are found to be 1.717 Å and 1.665 Å for the B and X states respectively.

Keywords. Scandium monoxide; potential energy curves.

1. Introduction

Spectroscopic methods are being applied to understand the physical nature of laboratory flames and discharges, and the conditions prevailing in astrophysical sources. With this objective, there has been a number of studies of the intensity distribution of the band systems of diatomic molecules. For a quantitative interpretation of the measured intensities it is necessary to employ a potential function which adequately describes the molecular electronic state. The interatomic potential is expressed in various empirical forms. Of these, the Morse function (Morse 1929) is widely employed as it provides a convenient analytical expression for the potential. However, it has been found that the Morse model cannot represent adequately many an electronic state. Morse function, therefore, requires to be examined before adopting for any molecular state. One can construct the true potential energy curve using the experimental energy levels and compare with the Morse model.

This paper describes the choice of the potential functions for the states $B^2\Sigma$ and $X^2\Sigma$ of scandium monoxide (ScO). Transition between these states gives rise to a well developed band system in the blue-green region of the electromagnetic spectrum. Bands belonging to this system have been observed in the spectra of late type stars (Bobrovnikoff 1933), of cool stars (Swings 1933), of the stars of M-type (Davis 1940, 1947), and of χ -Cygni (Tcheng Mao Lin 1949). ScO ($B \rightarrow X$) band system is of astrophysical significance.

2. ScO ($B \rightarrow X$) System

In order to construct the true potential energy curves reliable molecular constants are needed. The ScO ($B \rightarrow X$) band system has been analysed for the vibrational constants ω_e , $\omega_e x_e$ and the rotational constants B_e , a_e (Meggers and Wheeler 1931, Åkerlind 1962, Adams *et al* 1968). These constants are given in table 1. The

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Table 1. Molecular constants and α_e -deviation

State	ω_e cm ⁻¹	$\omega_e x_e$ cm ⁻¹	r_e (Å)	B_e cm ⁻¹	α_e (obs) cm ⁻¹	α_e (calc)	α_e -deviation
$B^2\Sigma$	825.0	4.50	1.717	0.4848	0.0032	0.0035	9%
$X^2\Sigma$	971.6	3.95	1.665	0.5152	0.0033	0.0029	12%

values of r_e , the equilibrium internuclear separation have been recalculated by the authors, for reasons explained in section 6.

3. Criterion for the choice of the potential model

Based on the Morse model Pekeris (1934) has given an expression for α_e the vibration-rotation constant in terms of ω_e , $\omega_e x_e$ and B_e . Difference between the calculated α_e and the observed value of α_e serves as an index for the deviation of the Morse function from the true potential function (Herzberg 1950).

For the B and X states of ScO vibration-rotation constants have been calculated from the Pekeris' relation

$$\alpha_e = \frac{6 \sqrt{\omega_e x_e B_e^3}}{\omega_e} - \frac{6 B_e^2}{\omega_e} \quad (1)$$

The resulting α_e values are given in table 1. Deviation in the calculated α_e value is expressed as per cent of the observed value. It is apparent that the deviation is significant for both the states and it is necessary to compute the true potential energy curves.

4. Rydberg-Klein-Rees (RKR) method for the true potential energy curve

Potential energy curves are constructed by calculating the turning points r_{\pm} of nuclear vibration. Using spectroscopic data Rydberg (1931, 1933) gave a graphical procedure which was further developed by Klein (1932). Rees (1947) provided analytical expressions for f_v and g_v of Klein. These expressions are convenient when the vibrational terms are well represented by a quadratic in $(v + \frac{1}{2})$, v being the vibrational quantum number. However, the quadratic representation is inadequate over the whole experimental range, and the inclusion of cubic and higher terms makes the calculations for f_v and g_v involved.

But the vibrational terms can be expressed in quadratic form over different ranges so that the entire range can be covered by a series of quadratics. Characterising each range by a set of ω_i , $(\omega x)_i$, B_i and α_i which are derived from the molecular constants, Vanderslice *et al* (1959, 1960) extended the Rees' method as applicable to the entire range. Still the calculational labour remained enormous and a further simplification was effected by Singh and Jain (1962). The simplified expressions are

$$f_v = \left(\frac{8\pi^2 \mu c}{h} \right)^{-1/2} Z_v \quad (2)$$

$$g_v = \left(\frac{2\pi^2 \mu c}{h}\right)^{1/2} \sum_1^v [2\alpha_1 (\omega x)_1^{-1} (U_v^{1/2} - U_{v-1}^{1/2}) + \{2B_1 - \alpha_1 \omega_1 (\omega x)_1^{-1}\} (Z_v - Z_{v-1})] \quad (3)$$

with

$$Z_v = (\omega x)_1^{-1/2} \ln \left\{ \frac{\omega_1 - 2 (\omega x)_1 (v + \frac{1}{2})}{\omega_1 - 2 (\omega x)_1^{1/2} U_v^{1/2}} \right\} \quad (4)$$

where μ is the reduced mass, c the velocity of light, h the Planck's constant and U_v the vibrational term value. The turning points for each vibrational level are given in terms of f_v and g_v :

$$r_{\pm} = \left(f_v^2 + \frac{f_v}{g_v}\right)^{1/2} \pm f_v \quad (5)$$

5. Computational procedure

Vibrational term values U_v are calculated using the expression

$$U_v = \omega_e (v + \frac{1}{2}) - \omega_e x_e (v + \frac{1}{2})^2 \quad (6)$$

For ranges each of four vibrational levels ω_1 , $(\omega x)_1$ and B_1 , α_1 are derived by least squaring $U_v/(v + \frac{1}{2})$ and B_v respectively as functions of $(v + \frac{1}{2})$. The values so obtained are used for the middle two levels only to calculate r_{\pm} .

For the purposes of comparison the turning points are also obtained by the Morse model, by solving the equation†

$$U_v = D \{1 - \exp[-\beta (r - r_e)]\}^2 \quad (7)$$

where

$$D = \omega_e^2/4\omega_e x_e \quad \text{and} \quad \beta = \left(\frac{8\pi^2 \mu c}{h} \omega_e x_e\right)^{1/2}$$

Table 2 contains the turning points for the observed vibrational levels of the *B* and *X* states of ScO.

6. Conclusions

For a majority of diatomic molecules, the ground state is usually represented adequately by the Morse model. The α_e -deviation, if there is any, will be very small and comparatively much less than the deviation of excited states. In the case of ScO (*B* → *X*) band system the ground state *X*²Σ has a larger α_e -deviation than that of the excited *B*²Σ state.

The RKR and the Morse curves for each state almost coincide, the difference being only 0.003 Å at the highest observed levels. Since the observed (*B* → *X*) band spectrum of ScO involves only low quantum numbers ($v \sim 6$) the Morse curve can be as well adopted for this band system.

Åkerlind (1962) gives r_e values for *B* and *X* states as 1.720 Å and 1.668 Å respectively. Using these values in the present work both RKR and Morse curves

† The computations were made on a National Elliott (803) digital computer at the Hindustan Aeronautics Limited, Bangalore.

Table 2. Potential energy curves

State	v	$U_v(\text{cm}^{-1})$	Turning points (Å)			
			RKR		Morse	
			r_+	r_-	r_+	r_-
$B^3\Sigma$	0	411.3	1.779	1.661	1.779	1.661
	1	1227	1.828	1.623	1.829	1.624
	2	2034	1.865	1.598	1.866	1.599
	3	2832	1.896	1.579	1.897	1.581
	4	3621	1.924	1.563	1.926	1.565
	5	4401	1.950	1.549	1.952	1.552
	6	5172	1.974	1.537	1.977	1.540
$X^2\Sigma$	0	484.8	1.722	1.614	1.722	1.613
	1	1448	1.768	1.579	1.767	1.578
	2	2404	1.801	1.556	1.800	1.555
	3	3352	1.830	1.539	1.828	1.537
	4	4292	1.855	1.524	1.853	1.522
	5	5224	1.879	1.512	1.876	1.509

were constructed. The two sets of r_{\pm} showed a large difference which is not expected as the curves coincide at low v -values even where the α_0 deviation is as large as 30% (Murthy and Murthy 1970). It was therefore necessary to recalculate the r_0 values given in table 1 using the B_0 values.

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