Vol. A58 (1980) ACTA PHYSICA POLONICA No 2

THE RELATIVE BAND STRENGTHS OF a_2—X_2, b_2—X_2 SYSTEMS AND THE DISSOCIATION ENERGY OF THE CeO MOLECULE

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(Received December 6, 1979)

The true potential energy curve of the X_2 state of the astrophysically important gaseous CeO molecule was constructed using the R–K–R–V method. The dissociation energy of the molecule was evaluated by curve fitting techniques. The relative band strengths of the a_2–X_2, b_2–X_2 systems of CeO were evaluated.

1. Introduction

An accurate knowledge of the dissociation energies of molecules is very important in astrophysics and chemical physics. It has been pointed out [1] that an uncertainty of 0.3 eV in the dissociation energy leads to an uncertainty of a factor of 2 in the molecular solar abundance and even a larger factor for cooler stars. A knowledge of the band strengths is required in order to relate intensity data to relative vibrational level populations. Information on population distributions is important to evaluate the temperature of the sources.

Increasing attention is now given to the electronic spectrum of CeO as more information regarding its occurrences in low-temperature S type stars is accumulating [2–4]. In view of its occurrence in S type stars, we studied the relative band strengths of a_2–X_2, b_2–X_2 systems and evaluated the dissociation energy of CeO molecule, using the vibrational data of Watson [5] and Ames and Barrow's [6] rotational data of a (0, 1) band of an a_2–X_2 system and a (1, 1) band of a b_2–X_2 system of CeO.

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2. Computational procedure

The rotational constant, B_e, is calculated using relation [7]

$$B_v = B_e - \mathscr{L}_e(v+\tfrac{1}{2}). \tag{1}$$

The constant, $\mathscr{L}_e$, is calculated by using the Pekeris relation [8]

$$\mathscr{L}_e = \frac{6(w_e x_e B_e^3)^{1/2}}{w_e} - \frac{6B_e^2}{w_e} . \tag{2}$$

At the outset the B_v value is substituted for B_e in Eq. (2) and $\mathscr{L}_e$ is estimated. Then the values of B_e and $\mathscr{L}_e$ were determined from equations (1) and (2) using an iterative technique [9].

The true potential energy curves were calculated from experimentally determined vibrational energy levels, using the method of Rydberg, Klein and Rees, as modified by Vanderslice et al. [10]. The true potential energy curves have been used to estimate the dissociation energies of diatomic molecules [11–15] in a number of cases by fitting an empirical potential energy curve. The potential energy curves are constructed using the empirical potential function of Szöke and Baitz [16] by calculating the U values for each of the $R_{\min}$ and $R_{\max}$ values obtained by the R–K–R–V method:

$$U(r) = D_e\left[1-\exp\left(-\frac{n\Delta r^2}{2r}\right)\right]\left[1-a\left(\frac{b^2 n}{2r}\right)^{1/2}\Delta r \exp\left\{-\left(\frac{b^2 n}{2r_e}\right)^{1/2}\Delta r\right\}\right], \tag{3}$$

where $n = de/D_e^{1/2}$, $a = 0.35\ e^{1/2}$ when $e = (e_1 e_2)^{1/2}$, e_1 and e_2 are the electro-negativities of the atoms, d is obtained from the force constant formula $K_e = d(e_1 e_2 D_e)^{1/2}/r_e$ and $b = 1.065$.

In order to calculate the D_e, the depth of the potential well, potential energy curves are constructed with different D_e values in steps of 0.01 eV ranging from 1 eV to 20 eV and the curves thus obtained are correlated with the true curve. The D_e value which gives the maximum correlation coefficient is the true depth of the potential well. The dissociation energy, D_0^0, is calculated using the relation:

$$D_e = D_0^0 + 1/2 w_e - 1/4 x_e w_e. \tag{4}$$

Assuming that the electronic transition moment $(R_e(\bar{r}_{v',v''}))$ is a constant for the entire system, the relative band strengths can be calculated as follows:

$$p_{v'v''}^{\text{rel}} = p_{v'v''}/p_{v'v''}^{\max}, \tag{5}$$

$$p_{v'v''} = R_e^2(\bar{r}_{v'v''})q_{v'v''}, \tag{6}$$

where $p_{v'v''}^{\max}$ is the maximum band strength, $q_{v'v''}$ is the Franck-Condon factor.

3. Results and discussion

The depth of the potential well ($D_e = 7.35$ eV) of the X_2 state of CeO was estimated by fitting the electro-negativity potential curve to the true curve. The Szöke and Baitz curve for the correct D_e^0 value and the true potential energy curve are given in Table I.

It can be seen, from the Table I, that the Szöke and Baitz potential function reproduces the true curve very accurately. The ground state dissociation energy (D_0^0) value of 7.30 eV obtained is in agreement with the approximate value of 7.7 eV reported by Herzberg [7] and is only slightly lower than the value of 8.03±0.2 eV given by Gaydon [17] based on mass-spectrometric determinations.

TABLE I

R-K-R-V and Szöke-Baitz potential energy curves of the CeO X_2 state

v	R-K-R-V			Szöke-Baitz $D_e = 7.35$ eV	
	U (cm^{-1})	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$U_{\min}$ (cm^{-1})	$U_{\max}$ (cm^{-1})
0	420.00	1.757	1.863	419.31	420.25
1	1257.52	1.722	1.906	1255.56	1257.17
2	2090.52	1.699	1.937	2088.76	2091.13
3	2918.65	1.681	1.963	2918.15	2920.86
4	3741.53	1.665	1.986	3744.68	3747.38

The Franck-Condon factors were evaluated using the analytical method of Jarmain and Fraser [18] with an r_e-shift correction. The r-centroids which are useful for studying the electronic transition moment function (R_e-function) were evaluated using the quadratic

TABLE II

Franck-Condon factors, relative band strengths and r-centroids of the a_2-X_2 and b_2-X_2 systems of CeO molecules

a_2-X_2 System				b_2-X_2 System			
v', v''	Franck-Condon factors	r-centroids Å	Relative band strengths	v', v''	Franck-Condon factors	r-centroids Å	Relative band strengths
0,0	0.9147	1.829	1.00	0,0	0.9807	1.819	1.00
0,1	0.0802	1.929	0.09	0,1*	0.0189	2.034	0.02
1,0	0.0826	1.696	0.09	1,0	0.0192	—	0.02
1,1	0.7551	1.839	0.83	1,1	0.9421	1.830	0.96
1,2*	0.1471	1.937	0.16	1,2*	0.0377	2.040	0.04
2,1	0.1561	1.717	0.17	2,1	0.0386	—	0.04
2,2	0.6106	1.849	0.67	2,2	0.9030	1.840	0.92
2,3*	0.2009	1.945	0.22	2,3*	0.0562	2.047	0.06
3,2	0.2195	1.734	0.24	3,2	0.0583	—	0.06
3,3	0.4818	1.859	0.53	3,3	0.8635	1.850	0.88
3,4*	0.2420	1.953	0.27	3,4*	0.0745	2.054	0.08
4,3*	0.2721	1.750	0.30	4,3	0.0780	—	0.08
4,4*	0.3691	1.868	0.40	4,4	0.8238	1.860	0.84
4,5*	0.2708	1.960	0.30	4,5*	0.0924	2.060	0.09

* Bands expected.

method of Nicholls and Jarmain [19]. The values of relative band strengths of the a_2-X_2 and b_2-X_2 systems are given in Table II along with the Franck-Condon factors and r-centroids. From the magnitude of the relative band strengths, it can be concluded that the bands marked with asterisk are also expected to be found in the spectra of gaseous CeO.

The authors thank the University Grants Commission and Council of Scientific and Industrial Research, New Delhi, for financial assistance. We also wish to thank the staff and authorities of the Computer Centre, A. U., Waltair, for their cooperation and free computer time.

Editorial note. This article was proofread by the editors only, not by the authors.

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