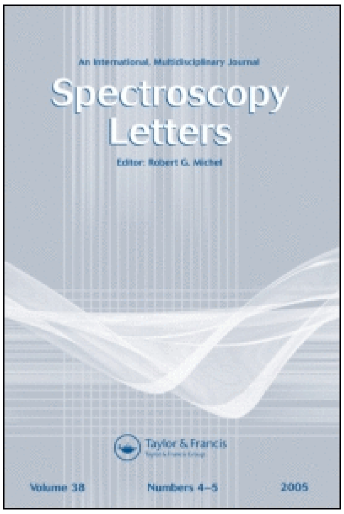

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Transition Probabilities and Dissociation Energy of Bid Molecule

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TRANSITION PROBABILITIES AND DISSOCIATION ENERGY OF BiD MOLECULE.

Key words Franck-Condon factors and r-centroids, dissociation energy, BiD Molecule

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Abstract The Franck-Condon (FC) factors (transition probabilities) and r-centroids have been evaluated by the reliable numerical integration procedure for the bands of the $BO^+ \rightarrow XO^+$ system of BiD molecule, using a suitable potential. The dissociation energy for the electronic ground state of BiD has been estimated by fitting the empirical potential function to the experimental potential energy curve , using correlation coefficient.

1. Introduction

A detailed knowledge of transition probability parameters (Franck-Condon factors and r-centroids) is essential for understanding and calculation of many important data for the molecules, e.g., radiative lifetime, vibrational temperatures and kinetics of energy transfer.

The bond dissociation energy of a diatomic molecule is the most direct measure of the strength of the bond and therefore of the stability of the chemical combination between the constituent atoms, that is, the very existence of the molecule. Astrophysicists, chemists and spectroscopists are therefore concerned with the determination of reliable values of dissociation energies for diatomic molecules.

To the best of our knowledge, there has been no report on the Franck-Condon (FC) factors, r-centroids and dissociation energy of BiD molecule. Therefore reliable values of FC factors and r-centroids for the bands of $BO^+ \rightarrow XO^+$ system of BiD have been computed by a more accurate

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numerical integration procedure, using a suitable potential. The precise value of the dissociation energy for BiD has also been estimated by fitting the empirical potential function by Steele and Lippincott[1] to the experimental potential energy curve, using the correlation coefficient. The function used in the present study is another version of Lippincott et al [2] function.

2. Franck-Condon factors and r-centroids

The square of the overlap integral is termed as FC factor

$$q_{v'v''} = < \psi_{v'} \mid \psi_{v''} >^{2} \quad \text{———————} \quad (1)$$

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

$$\bar{r}_{v'v''} = \frac{< \psi_{v'} \mid r \mid \psi_{v''} >}{< \psi_{v'} \mid \psi_{v''} >} \quad \text{———————} \quad (2)$$

The Morse [3] potential yields accurate FC factors especially for vibrational transition involving low quantum numbers[4,5]. The computation of the FC factor is made by Bates's [6] method of numerical integration according to the detailed procedure provided by Rajamanickam et al[7]. Morse [3] wave functions are calculated at intervals of 0.01 A° for the range of r from 1.54 A° to 2.15 A° for every observed vibrational level of each state. Integrals in Eqn. (1) and (2) for FC factors ($q_{v'v''}$) and r-centroids ($\bar{r}_{v'v''}$) are computed numerically for the bands of the B - X system of BiD. The results are presented in Table 1. The molecular constants used in the present study are collected from compilation of Huber and Herzberg [8].

3. Dissociation Energy

It is possible to evaluate the dissociation energy of diatomic molecule by fitting the empirical potential function to the experimental potential curve, using a correlation coefficient [5,9,10]. The procedure consists of determining the D_e - parameterised empirical potential function which best fits the experimental potential energy curve for the electronic ground state of the molecule.

The ground state experimental potential energy curve for BiD is constructed by Rydberg-Klein-Rees (RKR) method as modified by Vanderslice et al.[11,12]. The adequacy of the Steele and Lippincott [1] function to represent the ground state of BiD is tested by the correlation coefficients. D_e is varied over a range of 1 eV to 3 eV in steps of 0.1 eV. The correlation coefficient is maximum when D_e = 2.1 eV. Only relevant results of D_e and correlation coefficients are given in Table 2. The estimated dissociation energy (D_0^0) for the BiD molecule is 2.03 + 0.06 eV. The error indicated in the result takes into account the 3% error inherent to the Steele and Lippincott function [13].

4. Conculsions

The FC factors of B - X system of BiD molecule indicate that the $\Delta v = 0$ sequence bands are most intense followed by $\Delta v = \pm 1$ sequences.

Using the relation $D_e = \omega_e^2 / 4\omega_e x_e$, the dissociation energy D_0^0 for the BiD is found to be 2.58 eV. The dissociation energies obtained with this method are often too high [4]. Gaydon's [14]

Table 1 : **Franck - Condon factors and r-centroids**

v' v"	$q_{v'v''}$	$r_{v'v''}$ A°
0,0	0.987	1.809
1,0	0.015	2.517
1,1	0.961	1.844
2,1	0.017	2.728
2,2	0.899	1.876

Table 2 : **Dissociation energy and Correlation Coefficient**

D_e ($_e$V)	Correlation Coefficient
2,0	0.9998463
2,1	0.9998555
2,2	0.9995625

relation $D_e = \omega_e^2 / (5.33\ \omega_e x_e - 2\ B_e)$ yields the D_0^0 value as 2.05 eV. The estimated dissociation *energy D = 2.03 ± 0.06 $_e$v is in good agreement with this value.*

The results of the present study are significant since the Steele and Lippincott function is suited for BiD molecule. The difference in electronegativities of Bi and D indicates that the bonding between Bi and D is of covalent type. The Steele and Lipponcott function being based on δ -type model of binding is dispensably covalent in nature [15]. The force constant for the electronic ground state of BiD also indicates that the dissociation energy obtained in the present study is of correct order as compared with those for other molecules whose force constant values are nearly equal to that of BiD value. The molecular constants evaluated from the electronic spectra are capable of giving the most accurate dissociation energies for diatomic molecules [16]. The molecular constants from the electronic spectra studies have been used in the present study and therefore the results can be considered reliable.

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