

PD molecule: transition probabilities and dissociation energy

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The Franck-Condon (FC) factors (transition probabilities) and r-centroids have been evaluated by the more reliable numerical integration procedure for the bands of $A^3\Pi_i - X^3\Sigma^-$ system of molecule PD, using a suitable potential. The dissociation energy for the electronic ground state of PD molecule has been estimated by fitting the empirical potential function to the experimental potential energy curve, using correlation coefficient.

Keywords: Franck-Condon factors and r-centroids; dissociation energy; PD molecule.

Los factores de Franck-Condon (probabilidades de transición) y los centroides r han sido evaluados por el método de integración numérica más confiable para las bandas del sistema de molécula PD $A^3\Pi_i - X^3\Sigma^-$ usando un potencial adecuado. La energía de disociación para el estado base de la molécula PD ha sido estimada ajustando la función empírica del potencial a la curva de energía experimental, usando el coeficiente de correlación.

Descriptores: Factores de Franck-Condon y centroides r ; energía de disociación; molécula PD.

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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 such as radiative lifetimes, vibrational temperatures of the source and relative band strengths. The FC factors are useful in studies of radiative transfer in the atmospheres of stellar and other astronomical objects which contain molecular species [1].

For a molecular species to form and remain stable against dissociating influences in any environment, astronomical, chemical and so on, the temperature must be sufficiently low and other energetic interactions must be sufficiently mild so that the probability of breaking a chemical bond, once formed, is low. Since the dissociation energy is a prime factor in such phenomena, astrophysicists, chemists and spectroscopists are concerned with the determination of reliable values of dissociation energies for the diatomic molecules.

Johnson and Sauval [2] reported the presence of PH molecule in cool M-giant stars, Sauval and Tatum [3] identified the PH molecule in the stellar and cometary spectra, Fegley,Jr and Prinn [4] noted PH in the deep atmosphere of the Uranus and therefore PD molecule has also considerable interest.

The present study deals with the PD molecule and its $A^3\Pi_i - X^3\Sigma^-$ band system for which, to the best of our knowledge, no FC factors and r-centroids have been reported [5]. The compilation of Huber and Herzberg [5] presents a doubtful value for the dissociation energy D_0^0 of PD molecule. Therefore, reliable values of FC factors and r-centroids for the bands of A-X system of PD molecule have been computed by a more accurate numerical integration procedure, using a suitable potential. The precise value of the

dissociation energy for PD molecule has also been estimated by fitting the empirical potential function provided by Szoke and Baitz[6] to the experimental potential energy curve, using the correlation coefficient.

2. Franck-Condon factors and r-centroids

Mathematically, one can write the intensity $I_{v'v''}$ of a molecular band for a $v' - v''$ electronic transition in emission as

$$I_{v'v''} = DN_{v'} E_{v'v''}^4 R_e^2 (\bar{r}_{v'v''}) q_{v'v''}, \quad (1)$$

where D is a constant, partially depending on the geometry of the apparatus, $N_{v'}$ the population of the level v' , $E_{v'v''}$ the energy quantum, $q_{v'v''}$ the Franck-Condon factor, $\bar{r}_{v'v''}$ the r-centroid and R_e the electronic transition moment. The square of the overlap integral is termed as Franck-Condon (FC) factor

$$q_{v'v''} = |\langle \Psi_{v'} | \Psi_{v''} \rangle|^2, \quad (2)$$

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

$$\bar{r}_{v'v''} = \frac{\langle \Psi_{v'} | \bar{r} | \Psi_{v''} \rangle}{\langle \Psi_{v'} | \Psi_{v''} \rangle}. \quad (3)$$

The Morse [7] potential yields accurate FC factors especially for vibrational transition involving low quantum numbers[1,8]. The computation of the FC factor is made by Bates's [9] method of numerical integration according to the

procedure detailed in Prithivikumaran *et al.* [10]. Morse wave functions are calculated at intervals of 0.01 Å for the range of r from 1.22 Å to 1.74 Å for every observed vibrational level of each state of PD molecule. Integrals in equations (2) and (3) for FC factors ($q_{v'v''}$) and r-centroids ($\bar{r}_{v'v''}$) are computed numerically for the bands of A-X system of PD molecule and the results are entered in Table I. The molecular constants used in the present study are collected from the compilation of Huber and Herzberg [5].

TABLE I. Franck-Condon factors and r-centroids for PD molecule.

$v'v''$	$q_{v'v''}$	$\bar{r}_{v'v''}$ (Å)
0,0	0.846	1.450
0,1	0.123	1.656
1,0	0.146	1.303
1,1	0.393	1.462

3. Dissociation energy

In the recent years many investigators have adopted the spectroscopic method of curve fitting to estimate the reliable values of dissociation energies for diatomic molecules [11, 12]. A brief account of the method employed is given here to evaluate the dissociation energies of diatomic molecules.

A curve fitting procedure involves the comparison of experimental potential energy curve with the potential energy curves involving empirical potential functions. The accuracy of the estimation of D_e by the curve fitting method depends on how best the empirical potential function agrees with the experimental potential energy curve.

The experimental potential energy curves for the electronic ground states of the molecules under investigation are represented by r_{min} and r_{max} values for the observed vibrational levels. For these $r_{max,min}$ values, the energies $U(r)$ are calculated with the Szoke and Baitz[6] electronegativity function by varying the D_e value. A correlation coefficient is determined between the calculated $U(r)$ and the experimental $G(v)$ values. The dissociation energy referred to $v = 0$ level is given by $D_0^0 = D_e - G(0)$.

The ground state experimental potential energy curve for PD molecule is constructed by Rydberg-Klein-Rees(RKR) method as modified by Vanderslice et al[13]. The adequacy of Szoke and Baitz electronegativity function to represent the ground state of PD molecule is tested by the correlation coefficients. D_e is varied over a range of 2 eV to 4 eV in steps of 0.1 eV. The correlation coefficient is maximum when $D_e=3.1$ eV. Only relevant results of D_e and correlation coefficients are given in Table II. The estimated dissociation energy (D_0^0) for the PD molecule is 3.0 eV .

TABLE II. Dissociation energies and Correlation coefficients related to PD molecule.

Molecule	D_e (eV)	Correlation coefficient
	3.0	0.9999898
PD	3.1	0.9999956
	3.2	0.9999644

4. Conclusions

The FC factors of A-X system of PD molecule indicate that the $\Delta v = 0$ sequence bands are most intense followed by $\Delta v = \pm 1$ sequences. The sequence difference for the band system of PD molecule is found to be 0.012 Å ,which suggests that the potentials are not so wide. The r-centroid value for (0,0) transition is slightly greater than $(r'_e + r''_e)/2$ which proves that the potentials are not very anharmonic

Using the relation $D_e = \omega_e^2/4\omega_e X_e$, the dissociation energy D_0^0 for PD molecule is found to be 3.79 eV. The dissociation energies obtained with this method are often too high[14]. The compilation of Huber and Herzberg[2] presents a doubtful value of D_0^0 for PD molecule as 3.06 eV. Gaydon's [15] relation $D_e = \omega_e^2/(5.33\omega_e X_e - 2B_e)$ yields the D_0^0 value for PD molecule as 3.04 eV. The estimated dissociation energy $D_0^0= 3.0$ eV for PD molecule is in good agreement with the value obtained from Gaydon's relation. It is of interest to note that the Szoke and Baitz electronegativity function suits the PD molecule whose constituent atoms have the same electronegativity values.

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