Calculating Franck Condon Factor and Potential Curves for X²Σ⁺-A²Π System of BeBr Molecule

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Keyword: (X²Σ⁺ - A²Π) system of BeBr molecule; Potential Curve; Franck Condon Factors

ABSTRACT

The present work concerns by study of spectroscopic properties for Beryllium monobromide BeBr. Franck Condon Factor of BeBr molecule had been calculated theoretically for ground state X²Σ⁺ and excited state A²Π by special integrals by depending on spectroscopic constants for this molecule. The Dissociation energy and potential curves of this molecule is studied in this work by using Hua potential function, the results of potential curves and Franck Condon Factors converge with other researchers results.

1. INTRODUCTION

Spectroscopic studies of diatomic molecules are useful in more of fields such as astrophysics and combustion physics. Beryllium monobromide molecule is the one least known experimentally, In several prior works, In a brief note by Reddy and Rao[1], the first report on BeBr investigation dates back to 1967,with the observation of a bluish color emission when a mixture of bromine and argon was passed over warm beryllium metal powder and attributed to transitions in BeBr. Later expanded in an article[2]. A rotational analysis study on the 0-0 band of the (X²Σ⁺ - A²Π) system, performed by Caleer et al.[3].

Theoretically, early attempts at estimating theoretically the intensities of (X²Σ⁺ - A²Π) transitions by Kuz menko and Chumak [4] through the calculation of Franck Codon factors using Morse potential function.

2. Theoretical Aspects

2.1 Dissociation Energy and Hua Potential function

The Dissociation energy is the energy that would be necessary to dissociate the molecule if it could be at the minimum of the potential energy curve. Because of the zero point energy, this is impossible, and therefore [5]:

$$D_e = D_0 + 1/2 \tag{1}$$

D_0 is the measured dissociation energy and $1/2 \ v_0$ is the zero point energy measured in cm^{-1} unit and the values of D_e and D_0 have the same units.

One of relations for dissociation energy is called Herzberg relation [5]:

$$D_e = \frac{\omega_e{}^2}{4\,\omega_e \chi_e} \tag{2}$$

On the other hand, one of functions of potential called Hua potential function has the form[6]:

$$U_{Hua}(r) = D_e \left[\frac{1 - e^{-b(r-r_e)}}{1 - ce^{-b(r-r_e)}}\right]^2 \tag{3}$$

where b = a (1- c)   where a, re and D_e have the same physical significant as in the Morse potential function and   c is an additional constant[6]. This potential function indicate an alternative way to evaluate anharmonic overlap integrals starting from the wave functions of Hua potential function.

2.2 Franck Condon Factor

For many problems in molecular spectroscopy, such as study of electronic absorption and emission of a molecular system, preliminary it is necessary to have Franck-Condon factors for transition between vibrational states of upper and lower electronic states of the molecule. In fact, the Franck-Condon factors represent one of the most useful and comprehensive concepts for the study of radiative and non-radiative processes in molecular systems. Intensity of a vibronic transition is controlled by Franck-Condon factor that is defined as the square of the vibrational overlap (or Franck-Condon) integral [6,7]:

$$q_{v'v''} = \left| \int \Psi_{v'} \Psi_{v''} dr \right|^2 \tag{4}$$

where, $\Psi_{v'}$ and $\Psi_{v''}$ are the vibrational wave functions corresponding to the vibrational levels of the upper and lower electronic states v', v'', respectively. Since the molecules vibrate in an anharmonic way, it is necessary to use a potential function, which describes the real movement of the molecules in the best way. We have employed the Hua potential to obtain the vibrational wave functions and have calculated the Franck-Condon factors.

Calculating Franck-Condon factors is related with time-independent Schrödinger equation:

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + U(r) \right] \Psi_v = E_v \Psi_v \tag{5}$$

The most accurate values of Franck-Condon factors are obtained using the true Rydberg-Klein-Rees (RKR) potential curves. To construct the RKR potential curves we need a set of sufficient spectroscopic data. However, all of the spectroscopic data for all molecules in all their electronic states is not available. In the absence of exact expressions for the vibrational wave function ψ_v one may use the Eigen functions derived from some approximate potential functions. Consequently, the methods for the calculation of Franck-Condon factors depend on the choice of approximate Eigen function Ψ_v obtained by the solving Schrödinger equation with approximate potential functions. The various potential functions have been proposed to calculate these factors, such as Morse, which is the most popular empirical potential function because of its simple form. We use the Eigen functions of Schrödinger equation for Hua potential function. Consider the wave functions of Hua potential [6]:

$$\Psi_v = N_v \left[\frac{b}{v!} \times \frac{\Gamma[2\rho_o(v)+v+1]}{\Gamma[2\rho_o(v)+v]} \times \frac{\Gamma[2\rho_c+v+1+2\rho_o(v)]}{\Gamma[2\rho_c+v+1]\Gamma[2\rho_o(v)]} \times \frac{2\rho_c+2v+1+2\rho_o(v)}{2\rho_c+2v+1} \right]^2 x^{\rho_o(v)} (1-x)^{\rho_c+\frac{1}{2}}$$
$$\times \; F[-v,1+v+2\rho_o(v)+2\rho_c,1+2\rho_c,1+2\rho_o(v);x] \tag{6}$$

where, F[…] is the Jacobi Polynomial, Γ[…] is the Gamma function,
$N_v = 1$ for c > 0, and for c < 0 N_v equal:

$$N_v = \left[\frac{\sin\sin(2\rho_o(v)-2\rho)\pi}{\sin\sin(-2\rho\pi)} \right]^{1/2} \tag{7}$$

$$\rho_\circ(\overline{v}) = \frac{\left[t^2(Q-1) - \rho_c\overline{v} - \frac{\overline{v}^{-2}}{2} - \frac{1}{8} \right]}{(\rho_c + \overline{v})} \tag{8}$$

$$t = \frac{2D_e}{\hbar\overline{\omega}_e(1-c)} \tag{9}$$

$$x = ce^{-b(r-r_e)} \tag{10}$$

$$\overline{\omega}_e = a\left(\frac{2D_e}{\mu}\right)^{1/2} \tag{11}$$

$$\overline{v} = v + \frac{1}{2} \tag{12}$$

$$\rho_c = \pm\left[\frac{1}{4} + t^2(Q-1)^2\right]^{1/2} \tag{13}$$

$$Q = \frac{1}{c} \tag{14}$$

Here $\overline{\omega}_e$ is the vibrational frequency in cm^{-1} and $\pm$ in Eq. (13) refers to the sign of c. We denote various quantities in Eq. (6) for two states v', v'' by a single and a double prime, respectively, and choose x' as the variable in the integral Eq. (4), and in continue omit the prime from for simplicity, then we have :

$$dr = -\frac{dx'}{b'x'} = -\frac{dx''}{b''x''}, x'' = hx'^\gamma \tag{15}$$

$$h = \frac{c''e^{b''(r_e'-r_e'')}}{c'^\gamma}, \gamma = \frac{b''}{b'} \tag{16}$$

Using this variable, the integral in Eq. (4) can be written as [8]:

$$I(v',v'') = -\frac{N_{v'}N_{v''}}{b'}\int_0^1 \frac{(hx^\gamma)^{\rho_\circ(v')}}{x}$$
$$\times\left[1-(hx^\gamma)\right]^{\rho'+1/2} x^{\rho_\circ(v'')}(1-x)^{\rho''+1/2}$$
$$\times F\left[-v',1+v'+2\rho_\circ(v')+2\rho',1+2\rho_\circ(v');hx^\gamma\right] \times F\left[-v'',1+v''+2\rho_\circ(v'')+2\rho'',1+2\rho_\circ(v'');x\right]dx \tag{17}$$

for (c> 0).

And:

$$I(v',v'') = -\frac{N_{v'}N_{v''}}{b'}\int_0^\infty \frac{(hx^\gamma)^{\rho_\circ(v')}}{x}$$
$$\times\left[1-(hx^\gamma)\right]^{-\rho'+1/2} x^{\rho_\circ(v'')}(1-x)^{-\rho''+1/2}$$
$$\times F\left[-v',1+v'+2\rho_\circ(v')-2\rho',1+2\rho_\circ(v');hx^\gamma\right] \times F\left[-v'',1+v''+2\rho_\circ(v'')-2\rho'',1+2\rho_\circ(v'');x\right]dx \tag{18}$$

3. RESULTS AND DISCUSSION

Spectroscopic properties of BeBr molecule are studied such as dissociation energy, potential curves for "Hua function" for ground $X^2\Sigma^+$ state phnd exited state $A^2\Pi$ and Franck Condon Factor. The relation used to calculate dissociation energy is (eq. 2), and here are the results in table (1). The D_e values are found to be (35670.4 cm^{-1}) and (35080.1 cm^{-1}) for $X^2\Sigma^+$ and $A^2\Pi$ respectively, that dissociation due to approaching the bond length (r) from infinity values, where this is one of three conditions of potential curve.

Table (1): Dissociation energy obtained (cm⁻¹)

State	D_e (cm⁻¹)
$X^2\Sigma^+$	35670.4 cm⁻¹
$A^2\Pi$	35080.1 cm⁻¹

To calculate Hua potential for BeBr molecule Eq. (3) is used for the ground state $X^2\Sigma^+$ and the excited state $A^2\Pi$ by depending on dissociation energy, bond length, spectroscopic constants (table 2) and c parameter [6], and here are the results of Hua potential for BeBr molecule for the ground state $X^2\Sigma^+$ and the excited state $A^2\Pi$ in table 3 and Fig. 1.

The calculations appear the maximum value of Hua potential is (26372 cm⁻¹) in ground state of BeBr molecule at (r = 8 a_o) which is the maximum value of bond length. At bond length (r = 3.6 a_o), which is the equilibrium bond length of the molecule for ground state $X^2\Sigma^+$, the potential equal 515 cm⁻¹ , then the potential increase by increasing bond length until reach at the point which happen in it the dissociation because that the diatomic molecules dissociate when the value of (r) increase to determinate limit.

The $X^2\Sigma^+$ and $A^2\Pi$ potential-curve from Hua calculations Fig. 1 are in quantitative agreement with another researcher's curves [4].

Table 2   The spectroscopic constants for BeBr molecule measured (cm⁻¹) [1,3].

Spectroscopic constant	$X^2\Sigma^+$	$A^2\Pi$
T_e	0	26661
ω_e	715.9	700.0
$\omega_e x_e$	3.592	3.492
B_e	0.5455	0.5349
r_e (Å)	1.955	1.975

Where T_e: electronic energy above ground state (cm⁻¹), ω_e: the fundamental vibration frequency (cm⁻¹), $\omega_e x_e$: the anharmonicity constant (cm⁻¹), B_e: the rotational constant at equilibrium bond length (cm⁻¹), r_e: equilibrium bond length of the molecule (A°).

Table 3   Hua potential function for ground state $X^2\Sigma^+$ and exited state $A^2\Pi$.

	$X^2\Sigma^+$	$A^2\Pi$
r (a_o)	$U_{Hua}(r)$ cm⁻¹	$U_{Hua}(r)$ cm⁻¹
2.6	24885	54100
2.8	21376	50312
3	14122	39895
3.2	6121	34721
3.4	2253	29941
3.6	515	26455
3.8	923	27375
4	1637	28293
4.2	2520	30256
4.4	4611	31731
4.6	7922	32110
4.8	9571	31325

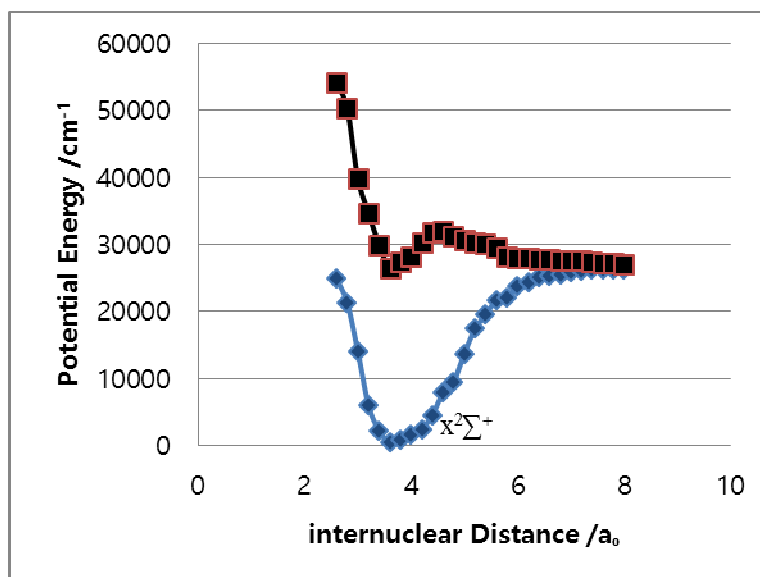| 5 | 13711 | 30725 |
5.2	17441	30351
5.4	19533	30102
5.6	21729	29627
5.8	22111	28253
6	23785	28001
6.2	24351	27954
6.4	25121	27812
6.6	25371	27733
6.8	25522	27682
7	25851	27610
7.2	26177	27593
7.4	26282	27428
7.6	26296	27317
7.8	26301	27253
8	26372	27122

Fig. 1   Calculated Hua potential curves for $X^2\Sigma^+$ and $A^2\Pi$ states .

On the other hand Results of Franck Condon Factor (FCF), to calculate Franck-Condon factor, Eqs. (17) and (18) are used, and here are the results in table 4. The obtained Franck-Condon factors are agreed with another researcher [9].

Table 4   Franck-Condon factors of BeBr molecule $X^2\Sigma^+$-$A^2\Pi$ transition.

V``/ V`	0	1	2	3
0	0.975	0.044	0.002	0.003
1	0.095	0.835	0.073	0.004
2	0.001	0.077	0.862	0.081
3	0.000	0.000	0.110	0.103
4	0.000	0.000	0.001	0.002

The Franck Condon principle states that after a molecule are excited from its ground electronic state the nuclear conformation must readjust. This lead in general, an increase in the "allowed" vibronic transition and hence greatly influences the observed spectrum. Also it is seen from the

Table 4 that the (0, 0), (1, 1), (2, 2) bands are strongest (higher intensity) and that the FC system of the successive bands in the $\Delta v = 0$ sequence fall off rapidly in the A-X system of BeBr as v' and v'' increase. The magnitude of the FC factors from Table 4 indicates that the sum rule is satisfied for v' and v'' progressions. The FC factors are found to be small (less intensity) in $\Delta = \pm 1$ in the case of $X^2\Sigma^+$- $A^2\Pi$ system of BeBr molecule.

4. CONCLUSIONS

The values of FCF for A-X system for BeBr molecule shows that for the vibrational bands $\Delta v = 0$ has higher intensity of BeBr molecule followed by less intensity of $\Delta v = \pm 1$, this is in in consisten with the expected quantum theoretical values for Franc Condon principle. The Franck-Condon factors have good values by using integral method depending on Hue potential function and vibration quantum number for ground $X^2\Sigma^+$ state and exited state $A^2\Pi$, Our results are agreed with Franck-Condon principle. Dissociation energies of BeBr molecule have calculated for ground $X^2\Sigma^+$ state and exited state $A^2\Pi$ and showed that bond length (r) has an effect upon the values of the dissociation energies, where the dissociation happen when (r) approach from infinity values. The potentials of BeBr molecule by using Hua function for ground $X^2\Sigma^+$ state and exited state $A^2\Pi$ are in good agreement with another researcher's results and the important notice that bond length (r) with spectroscopic constants have an effect upon values of the potential.

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