Lambda doubling calculation for Li₂ molecule

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Abstract

The theoretical emission spectrum of B 1Π_u-X 1Σ_g^+ transition, calculation of Lambda doubling, the relation between wave number ν_p, ν_Q, ν_R and rotational state energies F(J), F(J+1) with rotational quantum number J respectively of Li₂ molecule have been carried out for BΠ_u state using rotational , vibrational constant for both ground and excited states for vibrational transitions ν''=0 to ν'=0-9 using rotational levels J=0 up to J=20.

Introduction

The spectra of diatomic molecule contain a large numbers of spectral lines, where these are due to the fine structure of vibrational and rotational transitions [1]. So, for electronic state Π of diatomic molecule each rotational level is split into a closely spaced levels called ( Lambda doubling ) which correspond to the linear combinations of the +Λ and -Λ projections of orbital angular momentum [2,3].

Hund’s coupling case is used to describe the molecular states and analysis of angular distributions from two-photon ionization of Na₂ had been carried out [4].

Many researches had been carried out calculation of Λ-doubling constant. An experimental spectroscopic study had been carried out by using supersonic nozzle beam for determine the spectroscopic constant and Λ-doubling of Rb₂ in B-X system [5]. Theoretical study of Λ-doubling for the asymmetry of the orbital part of the electronic wave functions in 1Π, 3Π and 3Π is carefully examined [6].

A study for BΠ_u state of Na₂ molecule had been carried out by measuring the rotation-vibration energy levels [7]. Kaldor [8] studies Li₂ ground and excited states by the open-shell coupled – cluster method. Energy curves of Cs₂ had been carried out using compact effective potentials (CEP) and core polarization potentials (CPP) [9]. LiLi et al [10] studied the change in hyperfine qantum number, e/f parity transitions and Λ-doubling component in the Na₂ bΠ_u state. Zaitsevskii and Skolyarov [11] studied experimentally and theoretically Π state of the NaK dimer. An experimental studies of the NaK 13Σ_g→a3Σ_u+ continua. A calculation of Λ-doubling constants for rovibrionic levels of the B1Π_u and D1Π_u states of NaRb molecule had been carried out [18]. Λ-doubling for the B1Π_u state of Li₂ had been carried out [19]. Also, Λ-doubling investigation of 51Π_g Rydberg state
of Na₂ using optical – optical double resonance spectroscopy had been done by Tsai et al [20].

**Theory part**

The emission of the molecule appears as lines which composed from combination of rotation, vibration and electronic of spectral transitions between the electronic states, when the change in rotational quantum number is \( \Delta J = 1 \), the R-branch will appear. Whereas when \( \Delta J = -1 \), P-branch will appear and when \( \Delta J = 0 \), Q-branch will appear. The parent lines \( R(J) \) and \( P(J) \) represent the emission spectrum.

The values of energy for these bands can be determined using the following equation [4]:-

\[
\nu = \nu_o + \left( B_v - B_v \right) m + \left( D_v - D_v \right) m_2 + \left( D_v - D_v \right) m_4
\]

\[
-2 \left( D_v + D_v \right) m_3 - \left( D_v - D_v \right) m_4
\]

For \( R \) (m=J+1) and for \( P \) (m = J) lines.

\[
\nu = \nu_o + \left( B_v - B_v \right) J(J+1)
\]

\[
-\left( D_v - D_v \right) J^2 (J+1)^2
\]

For the Q-lines, where \( \nu_o \) is the band origin and can be determined from the equation [21]:-

\[
\nu_o = \Delta T_e + \Delta G_v
\]

and

\[
\Delta T_e = T_e - T_e
\]

\[
\Delta G_v = G_v - G_v
\]

\[
\Delta T_e = T_e - T_e
\]

\[
\Delta G_v = G_v - G_v
\]

Where \( T_e \) is the energy of the electronic state, \( G_v \) is the energy of the vibrational state \( B_v, B_v \) are the rotational constants for excited and ground levels respectively.

\( B_e \) is determined from the following equation [2]:-

\[
B_e = B_e - \alpha_e (v+1/2)
\]

Where \( \alpha_e \) is the rotation-vibration interaction constant and it is determined by [1, 2]:-

\[
\alpha_e = \left( 6(\omega_e \alpha_e B_e^{3/2}/\omega_e^2) - (6B_e^2/\omega_e) \right)
\]

\( B_e \) is the rotational constant at equilibrium bond length and is determined by the following equation [1]:-

\[
B_e = h/(8\pi^2 \mu r_e^2 c)
\]

where \( \mu \) is the reduced mass.

\( D_e \) is the first centrifugal correction for the vibrational level \( v \) and it is determined by the following equation [2]:-

\[
D_e = D_e + \beta_e (v+1/2)
\]

and

\[
D_e = 4B_e^3/\omega_e^2
\]

\( \beta_e \) is the rotation –vibration interaction constant and is determined by the equation [21]:-

\[
\beta_e = D_e \left[ \left( 8\omega_e \chi_e/\omega_e \right) - \left( 5 \alpha_e/B_e \right) - \left( \alpha_e^2/24 \omega_e \right) \right]
\]

\[
\beta_e = D_e \left[ \left( 8\omega_e \chi_e/\omega_e \right) - \left( 5 \alpha_e/B_e \right) - \left( \alpha_e^2/24 \omega_e \right) \right]
\]

The study of \( \Lambda \)-doubling is important for understanding the molecular structure. This doubling results from the split in one level which is produced from the interaction between the electronic and rotational motions [2, 21]. It increases with increasing of \( J \). Therefore, for all rotational levels between \( \Lambda \neq 0 \) degenerate doubly and the energy difference is very small for the two \( \Lambda \) component having the same value of \( J \). So, the rotational levels are composed from coupling of the very close distance because of inversely polarity which is denoted by \( e \) and \( f \) which is positive or negative depending on the value of \( J \).

This small distance between \( \Lambda \)-components is represented by the following equation [18, 22]:-

\[
\Delta F_{ef} = q_\Lambda J(J+1)
\]

Where \( q_\Lambda \) is the \( \Lambda \)- doubling constant which is determined by the following equation [2, 21 and 22]:-

\[
q_\Lambda = 2\left[ (B_v^2(l+1)) / \Delta E(\Pi, \Sigma) \right]
\]

where \( l \) is the rotational angular momentum and equals 1.

\( \Delta E(\Pi, \Sigma) \) the energy difference between \( \Pi \) and \( \Sigma \) states.

\( B_e \) is same for two states.

The four following equation can be used for the calculation of \( \Lambda \)- doubling values for the emission of \( P, Q \) and \( R \) transition [3]:-

\[
\Delta F_{ef} = \left[ R(J+1) - Q(J) \right] - \left[ F(J+1) - F(J) \right]
\]

... (13)
\[ \Delta F_{e\sigma} = [R(J) - Q(J-1)] - [F(J) - F(J-1)] \]  \hspace{1cm} (14) \\
\[ \Delta F_{e\sigma} = [F(J) - F(J-1)] - [Q(J) - P(J-1)] \]  \hspace{1cm} (15) \\
\[ \Delta F_{e\sigma} = [F(J+1) - F(J)] - [Q(J+1) - P(J)] \]  \hspace{1cm} (16)

where J represents the rotational quantum number for upper level in the excited electronic state. F(J) can be calculated by the following equation [1, 2, 21]:

\[ F(J) = B_v \left[ J(J+1) - \Lambda \right] \]  \hspace{1cm} (17)

Results and Conclusions
Spectroscopic data of Li₂ molecule is listed in Table 1:

<table>
<thead>
<tr>
<th>State/ Constant</th>
<th>( X^1\Sigma^+_g )</th>
<th>( B^1\Pi_u )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_e )</td>
<td>0 cm⁻¹</td>
<td>20439.4 cm⁻¹</td>
</tr>
<tr>
<td>( \omega_e )</td>
<td>351.43 cm⁻¹</td>
<td>269.69 cm⁻¹</td>
</tr>
<tr>
<td>( r_e )</td>
<td>2.672Å</td>
<td>2.936Å</td>
</tr>
<tr>
<td>( \omega_e\chi_e )</td>
<td>2.592 cm⁻¹</td>
<td>2.744 cm⁻¹</td>
</tr>
</tbody>
</table>

1- Relation between \( \Lambda \)-doubling constant \( q_\Lambda \) with \( \nu \)
\( \Lambda \)-doubling calculation had been carried out by applying Eq.12 for all vibrational transitions. It is observed that \( q_\Lambda \) is inversely proportional to \( \nu \) as show in Fig. 1a and 1b. The reason for that is the difference of values of the rotational constant \( B_v \) for the electronic state for different bands. \( B_v \), which depends on bond length, depends on vibrational quantum number according to Eq.5. The value of \( B_v \) reduced when \( \nu \) increasing.

\[ \Delta F_{e\sigma} = \left[ F(J) - P(J) \right] - \left[ R(J) - Q(J) \right] \]

Fig. 1: a) The relation between \( \nu \) and \( q_\Lambda \)-lambda 

b) The relation between \( B_v \) and \( q_\Lambda \)-lambda

2- Relation of wave number \( \nu_P \), \( \nu_Q \) and \( \nu_R \) with \( J \)
It was shown from Fig. 2 that the wave number \( \nu_P \) for the spectral line P has almost a constant value with the increasing of J for the band (0-0), (0-1) ... (0-9); therefore the wave number of the spectral line P is inversely proportional with increasing of J for the band (0-0), ... (0-9). The wave number \( \nu_R \) of the spectral line R is proportional to J for all band (0-0), ... (0-9).

The reason is due to the effect of \( (B_v^- - B_v^+) \) \( \Delta \) and \( \left( D_v^- - D_v^+ \right) \) \( \Delta \) in the calculation of the wave numbers \( \nu_P \), \( \nu_Q \) and \( \nu_R \) according to the Eqs 1 and 2. Also, it was observed that the rotational constant of the excited electronic state \( B_v^- \) is smaller than that of the ground electronic state \( B_v^+ \) for \( K_2 \) molecule, i.e. \( B_v^- > B_v^+ \) with an increase in J values. This causes an increase in the values of the wave numbers of the R lines with J and decreases the wave number values of the P lines with increasing J values. For Q lines, the wave number values are almost constant with increasing in J values according to the equations mentioned above. Q lines are considered as the center of the spectral band when \( \Delta J = 0 \). It is clear from Fig. 2 that the maximum transition in the (0-0) band, corresponds to Franck Condon principle for most linear molecule. The transition (0-0) is considered to be of greatest probability and most spectral density.

For the bands (0-1), ... (0-9), the wave numbers of \( \nu_P \) and \( \nu_Q \) from \( J \geq 10 \), increase with increasing of J and it occurs when the difference between \( B_v^- \) and \( B_v^+ \) is large, i.e. \( B_v^- << B_v^+ \) in this case an overlap will appear between Q-band and P-band.
Fig. 2: Change of wave number values $\nu_p$, $\nu_Q$ and $\nu_R$ with $J$.

3-Relation between the rotational energy levels $F(J)$, $F(J+1)$ with $J$

It is observed from Fig. 3 for (0-0) band, the distance between the rotational levels increases with increasing the values of $J$ for all bands and this is in agreement with Herzberg [2], King [21] and Graybeal [1]. The distance between rotational levels of $B^1\Pi_u$ state of Li$_2$ molecule increases with increasing the value of $J$.

![Graph showing $F(J)$ vs. $J$](image)

Fig. 3: The relation the rotational level energy $F(J)$, $F(J+1)$ determined in cm$^{-1}$ and $J$ for Li$_2$.

4-Relation between $\Lambda$-doubling value (\(\Delta F_{\epsilon f}\)) with $J$

It is observed from Fig. 4 by applying Eq. 11 that $\Lambda$-doubling value increases with increasing of $J$ value and according to $q_{\Lambda}$ values. It is in agreement with Herzberg [2], King [21] and Graybeal [1], i.e. the distance between $\Lambda$-component increases with increasing of $J$ value.

![Graph showing $\Delta F_{\epsilon f}$ vs. $J$](image)

Fig. 4: The relation between $\Lambda$-doubling value in cm$^{-1}$ and $J$ for (0-9) band of Li$_2$ by applying Eq. 11

Conclusion

From the Figs 1a) and 1b) the dependence of $q_{\Lambda}$ on the vibrational quantum number $\nu$ is clear. So, the rotational constant, which dependence on $\nu$, can be into account to show the values of $q_{\Lambda}$ according to Eq. 12 within certain electronic transition i.e. $B\Pi_u$ \textsuperscript{-} $X\Sigma^+_g$ transition. The values of $\nu_p$, $\nu_Q$, $\nu_R$ are different because of values of B, $B'$ which one is greater. Fig. 2 shows that, in the vibronic transitions, $B$ is greater than $B'$. It shows also the effect of terms $J+1$, - $J$ and $J$ mentioned in Eqs 1 and 2 for R, P and Q bands. In Fig. 4 the behavior of $\Lambda$-doubling value was parabolic manner, whereas its behavior was linear.

References

1. J.D.Graybeal, 1988, Molecular