Relative intensity distribution in the rotational structure for $B^1\Sigma^+$- $A^1\Pi$ and $B^1\Sigma^+$- $X^1\Sigma^+$ electronic systems of BeO molecule

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Abstract

Theoretical spectroscopic study of Beryllium Oxide has been carried out, Boltzmann distribution of P, Q and R branches in the range of ($0\leq J\leq 13$) at temperature 4200K for (0-0) band for electronic transitions $B^1\Sigma^+$-$A^1\Pi$ and $B^1\Sigma$-$X^1\Sigma$. The Boltzmann distribution of these branches has a maximum values at equal J approximately while the values of relative population are different. For the $B^1\Sigma^+$- $X^1\Sigma^+$ transition the branch's lines extend towards lower wavenumber. This is because ($B_{v'}$-$B_{v''}$) value is negative, i.e $B_{v'} < B_{v''}$ For $B^1\Sigma^+$-$A^1\Pi$ transition branch's lines extend towards higher wave number .This is because ($B_{v'}$-$B_{v''}$) value is positive, i.e. $B_{v'} > B_{v''}$.

Key words
Boltzman distribution, electronic transitions, Beryllium Oxide molecule.

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توزيع الشدة النسبية في التركيب الدوراني للأنتقالات الالكترونية $B^1\Sigma^+$- $X^1\Sigma^+$ و $B^1\Sigma$-$A^1\Pi$ لجزيئة اوكسيد البريليوم

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الخلاصة

اجريت دراسة نظرية لجزيئة اوكسيد البريليوم تضمنت توزيع بولتزمان للفروع P,Q,R ضمن مدى الاعداد الكمية الدورانية ($0\leq J\leq 13$) في درجة حرارة 4200K للحزمة (0-0) للأنتقالات الألكترونية $B^1\Sigma^+$- $X^1\Sigma^+$ و $B^1\Sigma^+$-$A^1\Pi$. توزيع بولتزمان له قيمة عظمى عند قيمة مساوية الى J بينما قيم التوزيع النسبي للفروع تختلف .اذ تتجه خطوط الفروع نحو الاعداد الموجية القصيرة للأنتقال الألكتروني $B^1\Sigma^+$- $X^1\Sigma^+$ ذلك بسبب ان الحد ($B_{v'}$-$B_{v''}$) سالب أي ان $B_{v'} < B_{v''}$ اما عند الأنتقال الألكتروني $B^1\Sigma^+$-$A^1\Pi$ فإن خطوط الفروع تتجه نحو الأطوال الموجية الطويلة ذلك بسبب ان الحد ($B_{v'}$-$B_{v''}$) أي ان $B_{v'} > B_{v''}$.

Introduction

Beryllium oxide (BeO), also known as beryllia, is an inorganic compound with the formula BeO. This colourless solid is a notable electrical insulator with a higher thermal conductivity of some metals; beryllium oxide is a white crystalline oxide. Beryllium oxide can be prepared by calcining (sintering) beryllium carbonate, dehydrating beryllium hydroxide or igniting the metal. It has Melting point 2507 °C, 2780 K and boiling point 3900 °C, 4173 K [1]. Much interest is being focused on the theoretical aspeets of the Beryllium Oxide molecule which had astrophysical importance like other oxide of alkaline earths [2]. Lagerqvist (1948) measured the potential energy curve and the dissocation energy for ground state, first excited state and second excited state for Beryllium oxide [3]. Tawde et al (1960) calculated Franck - Condon factors for system and transition probabilities for Beryllium oxide[4]. Yoshimine (1964) calculated spectroscopic constant of ground state of BeO molecule [5]. Lto et al (1992) calculated the wave numbers for P,Q and R branches of $B^2\Sigma$-$X^2\Sigma$ system of CN molecule [6]. Hirao et al (2000) calculated the intensity for P,Q and R branches of $A^2\Pi$ -$X^2\Sigma$ of MgBr molecule (0-0) band [7]. Gang (2003) calculated P,Q and R branches for A-X system of WO molecule for (0-0) band [8]. Szajnal et al (2010) calculated the wave numbers for P and R branches of (0-0) (1-1) (1-2) bands of the system $C^1\Sigma$ -$X^1\Sigma$ of AIH molecule [9].

Theory

The absorption or emission of electromagnetic radiation in visible and UV regions results from the transition between the electronic energy levels of the molecules. The spectra of diatomic molecules contain a large numbers of lines. This complexity in the spectrum is due to fine structures of vibrational rotational transitions. The nature of the rotational fine structure of electronic transition is largely dependent upon the levels or states involved in the transition. The transition between the levels had been governed by selection rules according to quantum mechanics. In diatomic molecules with net angular momentum Λ, the selection rule is $\Delta\Lambda = 0, \pm 1$,where in this paper for electronic transition $B^1\Sigma^+$- $X^1\Sigma^+$,$\Delta\Lambda=0$ and for electronic transition $B^1\Sigma$-$A^1\Pi$, $\Delta\Lambda=-1$ [10]

the spectral transition for the molecule will be given by the relationship

$$\Delta E = \Delta Te + \Delta G\,v + \Delta F\,J, \qquad (1)$$

$$E' - E'' = Te' - Te'' + Gv' - G\,v'' + F\,J' - F\,J, \qquad (2)$$

where ΔTe represent the energy difference between electronic state, $\Delta G\,(v)$ represent the difference between the vibrational energy level and $\Delta F\,J$ represent the difference between the rotational energy levels. The vibration energy is given by the relationship [11].

$$Gv = \omega_e \left[v + \tfrac{1}{2}\right] - \omega_e x_e \left[v + \tfrac{1}{2}\right]^2, \qquad (3)$$

where v is vibrational quantum number,
ωe is the harmonic vibration constant, and $\omega_e x_e$ is the anharmonicity constant the rotational energy given by the relationship

$$F(J) = Bv\,J(J + 1) \qquad (4)$$

where J is rotational quantum number

$$B_v = Be - \alpha e\left[v + \tfrac{1}{2}\right], \qquad (5)$$

eq(5) represent is relation of rotational constant and vibrational quantum number
Where Be is the rotational rotational coustant corresponding to the equilibrium bond distance α_e is the vibration - rotation interaction constant.
The spectra lines calculated of $R(J)$,$P(J)$,$Q(J)$ using the following equations [11]

$$P(J) = v_0 - (B_v + B_v)\,J + (B_v - B_v)\,J^2 \qquad (6)$$

$$R(J) = v_0 + 2B_v + (3B_v - B_v)\,J + (B_v - B_v)J^2 \qquad (7)$$

$$Q(J) = v_0 + (B_v' - B_v'')J + (B_v' - B_v'')J^2 \qquad (8)$$

v_0 is the frequency of the band origin could be given by this equation

$$v_0 = \Delta T_e + \Delta G_V, \qquad (9)$$

The intensities of the observed lines in the spectrum are proportional to the number of molecules in the initial state. The thermal rotational (T_{rot}) and vibrational populations (T_{vib}) are calculated following the Boltzmann distributions [12, 13] :

$$\frac{N\,g_e}{N0} = \frac{\exp(-Ee/kB\ \ T_{ele})}{Q_e}\ \frac{g_v\exp(-Ev/KB\ \ T_{vib})}{Q_v}\ \frac{g_J\exp(-Er/kB\ T_{rot})}{Q_r} \qquad (10)$$

The distribution of the molecules among the electronic states will correspond to the equilibrium at temperature (T_{elec}), among the vibrational states to a temperature (T_{vib}) and among the rotational states to a temperature (T_{rot}), then:

$$T = T_{elec} = T_{vib} = T_{rot} \qquad (11)$$

The partition function can be computed from the translational, rotational vibrational and electronic partition functions, can be written

$$Q_{elec} = \Sigma\, g_e \exp(-E_e/k_B T_{elec}) \qquad (12)$$

g_e is the electronic degeneracy the electronic degeneracy (statistical weighting factor) is $g_e = (2s+1)$, for Σ- Σ transition and $g_e = 2(2s+1)$ for others.

$$Q_{vib} = \Sigma\, g_v \exp(-E_v/k_B T_{vib}) \qquad (13)$$

g_v is unity for the vibration of a diatomic molecules.

$$Q_{rot} = \Sigma\, g_J \exp(-E_r/k_B T_{rot}) \qquad (14)$$

g_J is the rotational degeneracy equal (2J+1).

$S_{J'J''}$ is the Hönl-London factor lines calculated using the following equations [11]

$B^1\Sigma$-$A^1\Pi$ transition, ΔΛ=-1

$$S_J^R = (J+2-\Lambda)(J+1-\Lambda)/4(J+1) \qquad (15)$$

$$S_J^Q = (J+1-\Lambda)(J+\Lambda)(2J+1)/4J(J+1) \qquad (16)$$

$$S_J^P = (J-1+\Lambda)(J+\Lambda)/4J \qquad (17)$$

For the $B^1\Sigma^+$-$X^1\Sigma^+$ transition, ΔΛ=0

$$S_J^R = (J+1+\Lambda)(J+1-\Lambda)/(J+1) \qquad (18)$$

$S_J^Q = (2J+1)\Lambda^2/J(J+1)$ =0 (because Λ for Σ state=0) (19)

$$S_J^P = (J+\Lambda)(J-\Lambda)/J \qquad (20)$$

Results and Discussion

The spectroscopic constants of Beryllium oxide molecule were given in Table1.

***Table 1: The diatomic constants for the ground states and the excited state of BeO used in calculation* [14].**

State	$X^1\Sigma^+$	$A^1\Pi$	$B^1\Sigma^+$
T_e cm^{-1}	0	9405.61	2153.941
ω_e cm^{-1}	1487.32	1144.24	1370.82
$\omega_e x_e$cm^{-1}	11.830	8.415	7.746
Be	1.6510	1.3661	1.5758
αe	0.0190	0.01628	0.0154
re(cm)	1.3309×10^{-8}	1.4631×10^{-8}	1.3623×10^{-8}

Relative intensity calculated by using eq(10), then product Boltzmann factor with Hönl-London factor. Fig.1 shows the distribution of P and R branches as a function of rotational quantum number J. It can be observed that the distribution shapes are different in the values and R branch is higher than P .The relative population of rotational levels of $B^1\Sigma^+$-$X^1\Sigma^+$ transition with (0-0) band at 4200 K. Since $B_{v'} < B_{v''}$, the curves be at maximum values at J_{max} =8 for R branch and P branches approximately.

Fig.2 shows distribution of these branches as a function of wavenumber. For the $B^1\Sigma^+$-$X^1\Sigma^+$ transition branch's lines extend towards lower wave number. This is because ($B_{v'}$-$B_{v''}$) value is negative, i.e. $B_{v'} < B_{v''}$. In this transition the spectra line Q was missing because ΔΛ=0.

Table 2: The values of relative intensity for P,R branches for $B^1\Sigma^+$ -$X^1\Sigma^+$ transition.

J	N/N0-R BeO	N/N0-P BeO
0	3.76E-05	
1	2.26E-04	1.13E-04
2	5.65E-04	3.77E-04
3	1.06E-03	7.92E-04
4	1.70E-03	1.36E-03
5	2.47E-03	2.06E-03
6	3.35E-03	2.87E-03
7	4.21E-03	3.68E-03
8	4.80E-03	4.27E-03
9	4.74E-03	4.26E-03
10	3.68E-03	3.34E-03
11	1.93E-03	1.77E-03
12	5.36E-04	4.94E-04
13	5.52E-05	5.13E-05

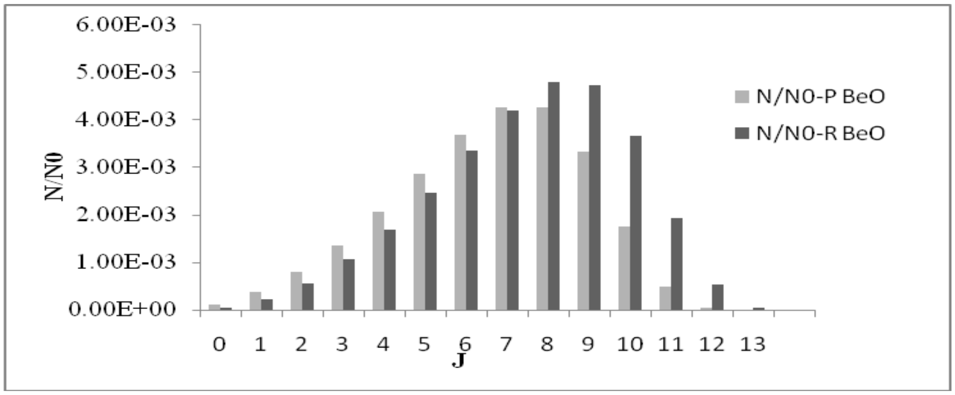

Fig. 1: Relative population of $B^1\Sigma^+$ -$X^1\Sigma^+$ as a function of J for BeO molecule.

Fig.3 shows the distribution of P,Q and R branches as a function of rotational quantum number J. It can be observed that the distribution shapes are different in the values and Q branch is higher than P and R branches. The relative population of $B^1\Sigma$-$A^1\Pi$ transition with (0-0) band at 4200 ^{o}K. Since $B_{v'} > B_{v''}$, the curves be at maximum values at J_{max} =8 for Q,P branch and R branches approximately. Fig.4 shows distribution of these branches as a function of wavenumber. For this transition, branch's lines extend towards higher wavenumber. This is because ($B_{v'}$-$B_{v''}$) value is positive, i.e. $B_{v'} > B_{v''}$. In this transition appear Q branch because $\Delta\Lambda$=-1.

Table 3: The values wavenumbers and relative intensity for P,R branches for $B^1\Sigma^+$ -$X^1\Sigma^+$ transition.

Wavenumber-R (cm^{-1})	N/N0-R	Wavenumber-P (cm^{-1})	N/N0-P
21199.88	3.76E-05		
21202.93	2.26E-04	21193.43	1.13E-04
21205.86	5.65E-04	21190.03	3.77E-04
21208.68	1.06E-03	21186.51	7.92E-04
21211.39	1.70E-03	21182.88	1.36E-03
21213.97	2.47E-03	21179.14	2.06E-03
21216.44	3.35E-03	21175.27	2.87E-03
21218.80	4.21E-03	21171.29	3.68E-03
21221.04	4.80E-03	21167.20	4.27E-03
21223.16	4.74E-03	21162.99	4.26E-03
21225.17	3.68E-03	21158.66	3.34E-03
21227.06	1.93E-03	21154.22	1.77E-03
21228.83	5.36E-04	21149.66	4.94E-04
21230.49	5.52E-05	21144.98	5.13E-05

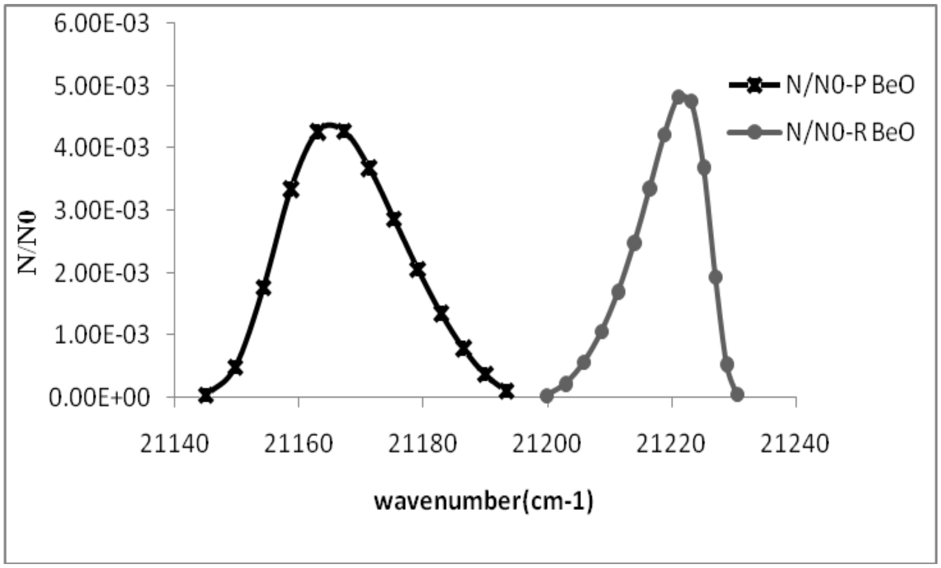

Fig.2: Relative population of $B^1\Sigma^+$ - $X^1\Sigma^+$ as a function of wavenumber for BeO molecule.

Table 4: The values of relative intensity for Q, P and R branches for $B^1\Sigma^+$ - $A^1\Pi$ transition.

J	N/N0-R	N/N0-Q	N/N0-P
0	0.00E+00	9.36E-06	
1	2.81E-05	8.43E-05	6.46E-05
2	9.38E-05	2.34E-04	1.62E-04
3	1.97E-04	4.60E-04	3.02E-04
4	3.38E-04	7.60E-04	4.85E-04
5	5.14E-04	1.13E-03	7.08E-04
6	7.16E-04	1.55E-03	9.60E-04
7	9.20E-04	1.97E-03	1.21E-03
8	1.07E-03	2.27E-03	1.38E-03
9	1.07E-03	2.26E-03	1.37E-03
10	8.40E-04	1.76E-03	1.06E-03
11	4.45E-04	9.30E-04	5.57E-04
12	1.25E-04	2.60E-04	1.55E-04
13	1.30E-05	2.69E-05	1.61E-05

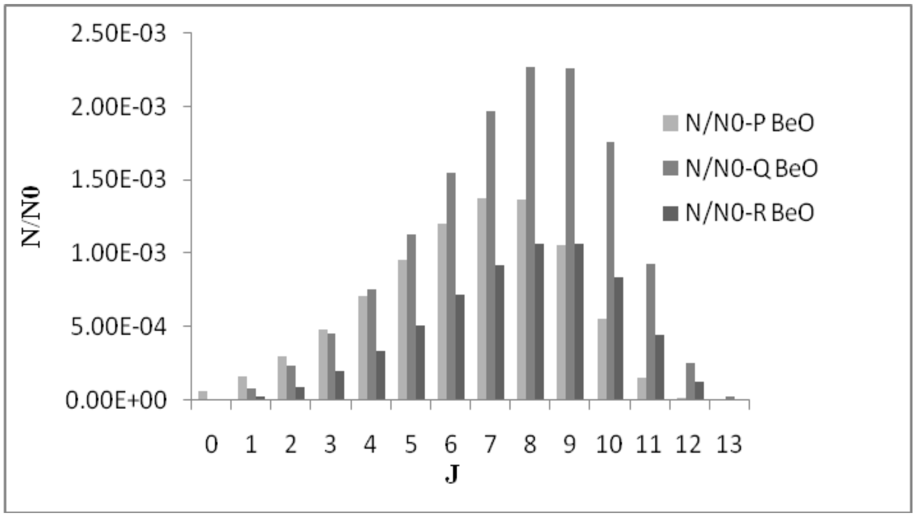

Fig.3: Relative population of $B^1\Sigma^+$ - $A^1\Pi$ as a function of J for BeO molecule.

Table5: The values of relative and wavenumber for Q,P and R branches for $B^1\Sigma^+$ - $A^1\Pi$ transition.

Wavenumber-R (cm^{-1})	N/N0-R	Wavenumber-Q (cm^{-1})	N/N0-Q	Wavenumber-P (cm^{-1})	N/N0-P
11964.95	0.00E+00	11961.79	9.36E-06		
11968.57	2.81E-05	11962.24	8.43E-05	11959.07	6.46E-05
11972.64	9.38E-05	11963.14	2.34E-04	11956.81	1.62E-04
11977.16	1.97E-04	11964.49	4.60E-04	11954.99	3.02E-04
11982.13	3.38E-04	11966.30	7.60E-04	11953.63	4.85E-04
11987.56	5.14E-04	11968.55	1.13E-03	11952.72	7.08E-04
11993.43	7.16E-04	11971.26	1.55E-03	11952.26	9.60E-04
11999.75	9.20E-04	11974.42	1.97E-03	11952.25	1.21E-03
12006.53	1.07E-03	11978.03	2.27E-03	11952.69	1.38E-03
12013.76	1.07E-03	11982.09	2.26E-03	11953.58	1.37E-03
12021.43	8.40E-04	11986.60	1.76E-03	11954.93	1.06E-03
12029.56	4.45E-04	11991.56	9.30E-04	11956.72	5.57E-04
12038.14	1.25E-04	11996.97	2.60E-04	11958.97	1.55E-04
12047.17	1.30E-05	12002.84	2.69E-05	11961.66	1.61E-05

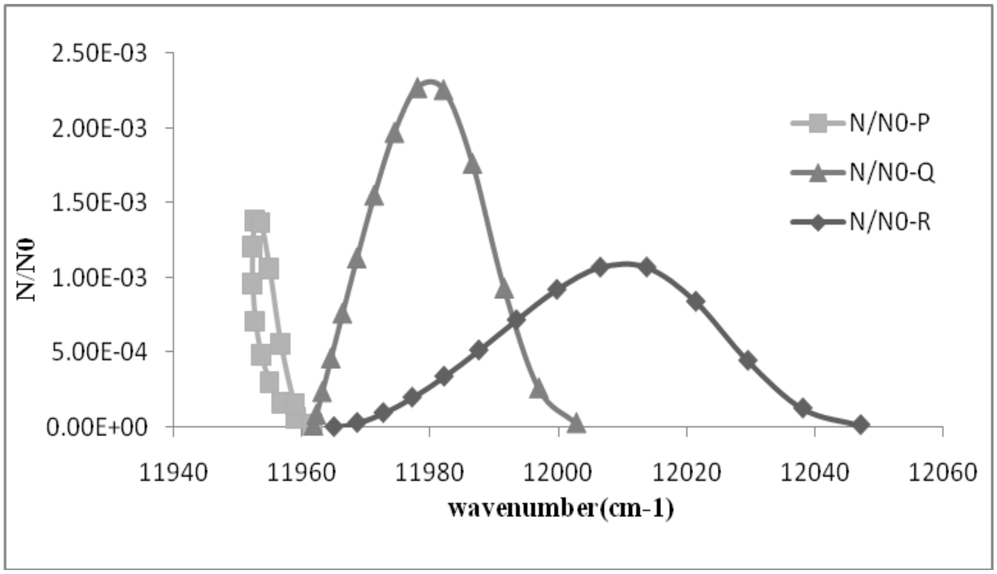

Fig.4: Relative population of $B^1\Sigma^+$ - $A^1\Pi$ as a function of wavenumber for BeO molecule.

Conclusions

1-The Boltzmann distribution of P,Q,R branches has a maximum values at equal J. The intensity of Q branch are more than of P and R branches for $B^1\Sigma^+$ - $A^1\Pi$ electronic transition, while for $B^1\Sigma^+$ -$X^1\Sigma^+$electronic transition the intensity of R branch be more than for P branch.

2-The branch's lines extend towards higher wavenumber for $B^1\Sigma^+$-$A^1\Pi$ electronic transition, while for $B^1\Sigma^+$-$X^1\Sigma^+$electronic transition transition the branch's lines extend towards lower wave number depending on B'_v and B''_vvalues.

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