Determination and study the energy characteristics of vibrational-rotational levels and spectral lines of GaF, GaCl, GaBr and GaI for ground state

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ABSTRACT

A theoretical study of four gallium monohalides molecules (GaF, GaCl, GaBr and GaI) of ground state $^1\Sigma^+$ by using computer model is presented to study the energy characteristics of vibrational-rotational levels as a function of the vibrational and rotational quantum number, respectively. The calculations has been performed to examine the vibrational- rotational characteristics of some gallium halides molecules. These calculations appeared that all energies (G_v , $E_{v,J}$, and $F_{v,J}$) increase with increasing vibrational and rotational quantum number and by increasing the vibrational quantum number, and by increasing the vibrational quantum number, the vibrational constant will decrease. Also theoretical study of spectra of these molecules for ground state $^1\Sigma^+$ has been carried out. The values of spectral lines R(J) and P(J) were calculated and the relationship between the spectral lines and the rotational quantum number was established. The results appeared the spectra line values R(J) increases when the values of rotational quantum number decrease but the spectra line values P(J) decrease when the values of rotational quantum number increase, also the spectra line values P(J) decrease when the values of (m) increase, while the values of R(J) increase at first, then decrease showing Fortrar parabola.

1. INTRODUCTION

The gallium monohalides play an important role as intermediates in the production of new high frequency and opto-electronic semiconductor devises[1]. Spectroscopic investigations on the diatomic halides of gallium have been the subject of much interest for a long time[2,3]. The general behavior of the spectrum of gallium monohalides is very similar to the one described for indium monohalides[4]. The ground state of all gallium monohalides is of the $^1\Sigma^+$ similar to other diatomic molecules formed by IIIA group elements (e.g., B, Al, Ga, and In) with halogens (e.g., F, Cl, Br, and I).

In 1933, Partrikaln and Hochberg[2]first observed the electronic spectrum of the GaCl radical. Miescher and Wehrli [5] recorded the electronic band spectrum of GaCl, GaBr, and GaI in both emission and absorption. Grabandt et al.[6]investigated the photoelectron spectra of gallium monohalide molecules. First measurements of pure rotational transitions of gallium monohalides GaCl, GaBr, and GaI were done by Barrett and Mendel[7].

Recently ab initio based MRDCI calculations on GaI molecule reported by Dutta et al.[8]. Further microwave spectral studies on the gallium monohalides have been carried out by a number of researchers and most recently, Lenthe et al.[9]performed DFT calculations to evaluate nuclear quadrupole coupling constants of a number of metal halide molecules, including the GaX molecules and most recently ab initio study of the ground state of GaCl reported by Yanget al.[10] also reveal that the ground states of GaI and GaCl are $^1\Sigma^+$ type.

2. THEORY

Theory of any vibrational –rotational state expressed in its wave number equivalent and measured in cm⁻¹ units, can be written to a good approximation as[11]:

$$E_{v,J} = G_v + B_v J(J+1) - D_v J^2(J+1) + \dots \dots \dots (1)$$

Where v: the vibrational quantum number equal 0,1,2,3...etc., J: the rotational quantum number equal 0,1,2,3,...etc., B_v: rotational constant for vibrational state v,

D_v: the centrifugal distortion constant for vibrational state v, G_v: the vibration energy

$$B_v = B_e - \alpha_e \left(v + \frac{1}{2}\right) + (\text{smaller correction terms, in a power series in } \left(v + \frac{1}{2}\right) \dots (2)$$

$$G_v = \omega_e \left(v + \frac{1}{2}\right) - \omega_e x_e \left(v + \frac{1}{2}\right)^2 + (\text{smaller terms}) \dots \dots \dots (3)$$

The rotational energy is given by the following expression:

$$F_{v,J} = J(J+1)[B_e - \alpha_e \left(v + \frac{1}{2}\right)] \dots \dots \dots (4)$$

Where: B_e : the equilibrium rotational constant, α_e the vibrational-rotational coupling constant, ω_e the fundamental vibrational constant, ω_ex_e the first anharmonic correction constant.

By satisfying the selection rules of vibrational quantum number (ΔV = 1) and rotational quantum number (ΔJ = ±1), we have an allowed vibration- rotation absorption transition in diatomic will all electrons spin-paired. Those transition with (ΔJ = -1) are said to be members of the "P branch" and those with (ΔJ = +1) come the "R branch".

The spectra lines were calculated using of the following equations[12]:

$$R(J) = G_v + 2B_{v'} + (3B_{v'} - B_{v''})J + (B_{v'} - B_{v''})J^2 \quad (5)$$

$$P(J) = G_v - (B_{v'} + B_{v''})J + (B_{v'} - B_{v''})J^2 \quad (6)$$

The Fortrat parabola curve could be found from the relation among R(J), P(J) and m using the following equation[13,14]:

$$R(J), P(J) = G_v + (B_{v'} + B_{v''})m + (B_{v'} - B_{v''})m^2 \quad (7)$$

Where m=J+1 for R(J) and m=-J for P(J).

3. RESULTS AND DISCUSSION

In the present work, the calculations of the vibrational and rotational energy as a function of vibrational and rotational quantum number, respectively for gallium monohalides molecules (GaF, GaCl, GaBr and GaI) are presented by using computer model and by depended on spectroscopic constants for ground state χ¹Σ⁺ for these molecules as shown in table (1).

Table 1. Spectroscopic constants of gallium halides of ground state measured in cm⁻¹ and r_e in a.u.[15,6,9,16]

molecule	Spectroscopic constants of ground state χ ¹ Σ ⁺					
	T _e	ω _e	ω _e x _e	r _e	B _e	α _e
GaF	0	622.10	3.286	1.774	0.359535	0.2864235
GaCl	0	365.70	1.249	2.202	0.149913	7.9359
GaBr	0	266.70	0.83	2.349	0.082797	3.26677
GaI	0	216.60	0.50	2.576	0.056895	1.8890

By using equation (2), B_v rotational constant for vibrational state for all gallium halides is calculated and figure (1) and table (2) show its variation with the vibrational quantum number v.

Table 2. Rotational constant in cm^{-1} for vibrational state ($v=1,2,\dots,10$)

V	Rotational constant of molecule in cm^{-1}			
	GaF	GaCl	GaBr	GaI
0	0.3581	0.1495	0.0828	0.0568
1	0.3552	0.1487	0.0825	0.0566
2	0.3523	0.1479	0.0822	0.0564
3	0.3495	0.1471	0.0819	0.0562
4	0.3466	0.1463	0.0816	0.056
5	0.3437	0.1455	0.0813	0.0558
6	0.3409	0.1447	0.081	0.0556
7	0.338	0.1443	0.0807	0.0554
8	0.3351	0.1443	0.0804	0.0553
9	0.3323	0.1442	0.0801	0.0552
10	0.3294	0.1441	0.0798	0.055

It is seen that B_v decreases with increasing v for all molecules and particularly at high values of v for GaF. The values for GaCl, GaBr and GaI appear closet values that due to the small difference between the equilibrium rotational constant of these molecules.

The calculations of the vibrational energy of all molecules are made by using equation (3) and the results of calculation are shown in table (3) and figure (2). It can be seen that this factor varies linearly with the vibrational quantum number and the highest value is determined for GaF molecule, that is due to the fact the constants of the GaF molecule are several orders of magnitude larger than that for the other molecules (GaCl, GaBr and GaI).

Table 3. Vibration energy in cm^{-1} for vibrational state ($v=1,2,\dots,10$)

V	Vibrational constant of molecules in cm^{-1}			
	GaF	GaCl	GaBr	GaI
0	310.39	182.58	133.17	108.19
1	925.92	545.75	398.43	323.79
2	1534.88	906.43	662.23	538.39
3	2137.27	1264.61	924.57	751.99
4	2733.08	1620.29	1185.45	964.59
5	3327.33	1973.47	1444.88	1176.19
6	3904.99	2324.16	1702.86	1386.79
7	4481.09	2672.35	1959.38	1596.39
8	5050.63	3018.04	2214.44	1804.99
9	5613.58	3361.24	2468.04	2012.59
10	6169.97	3701.94	2720.19	2210.33

It is quite important to know the rotational energy levels $F_{v,J}$ in order to predict the population of each vibrational-rotational level. Since the distribution of these level depends on the fraction of energy transferred to the vibrational degree of freedom of a molecule, which is a reaction product. By using the values of B_v to calculate the rotational energy (equation 4) as a function of the rotational quantum number at various values of vibrational quantum number (v). the results of the rotational energy at vibrational states are presented in figures (3,4,5,6 and 7) and tables (4,5,6,7 and 8).

Table 4. Rotational energy in cm^{-1} at vibrational state ($v=0$) and $J=(0,\dots,10)$

J	Rotational energy of molecules in cm^{-1}			
	GaF	GaCl	GaBr	GaI
0	0	0	0	0
1	0.716	0.299	0.1656	0.1136
2	2.1486	0.897	0.4968	0.3408
3	4.2972	1.794	0.9936	0.6816
4	7.162	2.99	1.656	1.136
5	10.743	4.485	2.484	1.704
6	15.0402	6.279	3.4776	2.3856
7	20.0536	8.372	4.6368	3.1808
8	25.7832	10.764	5.9616	4.0896
9	32.229	13.455	7.452	5.112
10	39.391	16.445	9.108	6.248

Table 5. Rotational energy in cm^{-1} at vibrational state ($v=1$) and $J=(0,\dots,10)$

J	Rotational energy of molecules in cm^{-1}			
	GaF	GaCl	GaBr	GaI
0	0	0	0	0
1	0.7104	0.2974	0.165	0.11332
2	2.1312	0.8922	0.495	0.3396
3	4.2624	1.7844	0.99	0.6792
4	7.104	2.974	1.65	1.132
5	10.656	4.461	2.475	1.698
6	14.9184	6.2454	3.465	2.3772
7	19.8912	8.3272	4.62	3.1696
8	25.5744	10.7064	5.94	4.0752
9	31.968	13.383	7.425	5.094
10	39.072	16.357	9.075	6.226

Fig. (4) Rotational energy at vibrational stat $v=1$ as a function rotational quntum number

Table 6. Rotational energy in cm^{-1} at vibrational state ($v=2$) and $J=(0,...10)$

J	Rotational energy of molecules in cm^{-1}			
	GaF	GaCl	GaBr	GaI
0	0	0	0	0
1	0.7046	0.2994	0.1644	0.1128
2	2.1138	0.8982	0.4932	0.3384
3	4.2276	1.7964	0.9864	0.6768
4	7.046	2.994	0.644	1.128
5	10.569	4.491	2.466	1.692
6	14.7966	6.2874	3.4524	2.3688
7	19.7288	8.3832	4.6032	3.1584
8	25.3656	10.7784	5.9184	4.0608
9	31.707	13.473	7.398	5.076
10	38.753	16.467	9.042	6.204

Fig. (5) Rotational energy at vibrational stat $v=2$ as a function rotational quntum number

Table 7. Rotational energy in cm^{-1} at vibrational state ($v=3$) and $J=(0,\dots,10)$

J	Rotational energy of molecules in cm^{-1}			
	GaF	GaCl	GaBr	Gal
0	0	0	0	0
1	0.699	0.2834	0.1638	0.1124
2	2.097	0.8502	0.4914	0.3372
3	4.194	1.7004	0.9828	0.6744
4	6.99	2.834	1.638	1.124
5	11.385	4.251	2.457	1.686
6	15.939	5.9514	3.4398	2.3604
7	21.252	7.9352	4.5864	3.1422
8	27.324	10.2024	5.8968	4.0464
9	34.155	12.753	7.371	5.058
10	41.745	15.587	9.009	6.182

Fig. (6) Rotational energy at vibrational stat $v=3$ as a function rotational quntum number

Table 8. Rotational energy in cm^{-1} at vibrational state ($v=4$) and $J=(0,...10)$

J	Rotational energy of molecules in cm^{-1}			
	GaF	GaCl	GaBr	GaI
0	0	0	0	0
1	0.6932	0.2926	0.1632	0.112
2	2.0796	0.8778	0.4896	0.336
3	4.1592	1.7556	0.9792	0.672
4	6.932	2.926	1.632	1.12
5	10.398	4.389	2.448	1.68
6	14.5572	6.1446	3.4272	2.352
7	19.4096	8.1928	4.5696	3.136
8	24.9552	10.5336	5.8752	4.032
9	31.194	13.167	7.344	5.04
10	38.126	16.093	8.976	6.16

Fig. (7) Rotational energy at vibrational stat $v=4$ as a function rotational quntum number

From results above it is seen that the rotational energy increases with the rotational quantum number at vibrational states for all gallium halides molecules and the highest value is determined for GaF at vibrational state $v=3$ as would be expected, and the lowest value is determined for GaI at vibrational state $v=4$. Also the values for GaCl, GaBr and GaI appear closet values that due to the small difference between the equilibrium rotational constant of these molecules, but values of GaF are far from values of other molecules by a small magnitudes that due to the difference in B_e for GaF with other molecules is larger than the difference in B_e between (GaCl, GaBr and GaI) molecules.

Also table (9) and figure (8) show the variation of the total energy which is called the vibrational-rotational energy at vibrational state $v=0$ as a function of rotational quantum number. It can be shown that the variation is as in figure (2) which means that the vibrational energy has predominate values in comparison with the rotational energy, all previous results are converge from other researchers values [17,18,19].

Table 9. Vibrational-rotational energy in cm^{-1} for vibrational state ($v=0$)

J	Vibrational-rotational energy of molecules in cm^{-1}			
	GaF	GaCl	GaBr	GaI
0	310.3863	182.5828	133.173	108.1873
1	311.1025	182.8817	133.3385	108.3036
2	312.5349	183.4797	133.6697	108.528
3	314.6835	184.3767	134.1665	108.8688
4	317.5483	185.5727	134.8289	109.3232
5	321.1292	187.0677	135.6569	109.8912
6	325.4264	188.8617	136.6505	110.2433
7	330.4397	190.9547	137.8097	111.3132
8	336.1692	193.3467	139.1345	112.1125
9	342.6149	196.0377	140.6249	113.4412
10	349.7768	199.0276	142.2809	114.4352

After that the spectra lines $R(J)$ and $P(J)$ values have been calculated for gallium halides molecules (GaF, GaCl, GaBr, and GaI) and (1-0) band by using equations (5 and 6), and by depended on spectroscopic constants in table (1). It appears from tables (10,11,12 and 13) and figures (9,10,11 and 12), that the spectral lines values $R(J)$ and $P(J)$ are influenced by difference between B_v and $B_{v'}$. the spectral lines values $R(J)$ increase with the increasing of J , whereas the spectra lines values $P(J)$ decrease with the increasing of J . In addition note that the spectra line $Q(J)$ was missing because in the Σ transition of the electronic angular moment $\Lambda=0$.

Table 10. Spectra lines P(J) and R(J) in cm^{-1} for (1-0) band of GaF molecule
For GaF molecule

J	P(J)	R(J)
0	615.532	616.2425
1	614.8158	616.9472
2	614.0939	617.6463
3	613.3662	618.3396
4	612.6329	619.0272
5	611.8938	619.7091
6	611.1512	620.3852
7	610.3985	621.0557
8	609.6422	621.7204
9	608.8803	622.6654
10	608.1126	623.0327

Fig. (9) Relation between spectra lines R(J) and P(J) measure in cm^{-1} and rotational quantum number J in (1-0) band of GaF

Table 11. Spectra lines P(J) and R(J) in cm^{-1} for (1-0) band of GaCl molecule

For GaCl molecule		
J	P(J)	R(J)
0	363.1723	363.4697
1	362.8733	363.7655
2	362.5727	364.0597
3	362.2705	364.3523
4	361.9667	364.6433
5	361.6613	364.9327
6	361.3543	365.2205
7	361.0457	365.5067
8	360.7355	365.7913
9	360.4237	366.0743
10	360.1103	366.3557

Table 12. Spectra lines P(J) and R(J) in cm^{-1} for (1-0) band of GaBr molecule

For GaBr molecule		
J	P(J)	R(J)
0	265.254	265.419
1	265.0884	265.5834
2	264.9222	265.7472
3	264.7554	265.9104
4	264.588	266.073
5	264.42	266.235
6	264.2514	266.3964
7	264.0822	266.5572
8	263.9124	266.7174
9	263.742	266.876
10	263.571	267.036

Table 13. Spectra lines P(J) and R(J) in cm^{-1} for (1-0) band of GaI molecule
For GaI molecule

J	P(J)	R(J)
0	215.5992	215.7127
1	215.4853	215.8258
2	215.371	215.9385
3	215.2563	216.0508
4	215.1412	216.1627
5	215.0257	216.2742
6	214.9098	216.3853
7	214.7935	216.496
8	214.6768	216.6063
9	214.5597	216.7162
10	214.4422	216.8257

Equation (7) has been used to calculating Fortrat parabola and the results appear in tables (14,15,16 and 17) and figures (13,14,15 and 16). It appears that the spectra lines values $R(J)$ at $m=J+1$ increase at first, then decrease because the third term in right side of equation (7) becomes larger than the second one, therefore, we find that $R(J)$ values deviate, forming Fortrat parabola and extreme curving representing the band head towards red region. As regards the spectra lines values $P(J)$ at $m= -J$, they decrease when increasing m values.

Table 14. Spectra lines $P(J)$ and $R(J)$ in cm^{-1} for (1-0) band of GaF molecule at ($J=0, 10, 20, 30, \dots, 200$)

J	For GaF molecule			
	m	P(J)	m	R(J)
0	0	615.532	1	616.2425
10	-10	608.1126	11	623.0327
20	-20	600.1212	21	629.2509
30	-30	591.5578	31	635.8752
40	-40	582.4224	41	639.9713
50	-50	572.715	51	644.4735
60			61	648.4037
70			71	651.7619
80			81	654.5481
90			91	656.7623
100			101	658.4045
110			111	659.4747
120			121	659.9729
130			131	659.8991
140			141	659.2533
150			151	658.0355
160			161	656.2457
170			171	653.8839
180			181	650.9501
190			191	647.4443
200			201	643.3665

Fig. (13) Fortrat Parabola by (1-0) band of GaF

Table 15. Spectra lines P(J) and R(J) in cm^{-1} for (1-0) band of GaCl molecule at (J=0, 10, 20, 30,, 200)

J	For GaCl molecule			
	m	P(J)	m	R(J)
0	0	363.1723	1	363.7697
10	-10	360.1103	11	366.3557
20	-20	356.8883	21	369.0817
30	-30	353.5063	31	371.6477
40	-40	349.9643	41	374.0537
50	-50	346.2623	51	376.2997
60			61	378.3857
70			71	380.3117
80			81	382.0777
90			91	383.6837
100			101	385.1297
110			111	386.4157
120			121	387.5417
130			131	388.5077
140			141	389.3137
150			151	389.9597
160			161	390.4457
170			171	390.7717
180			181	390.9377
190			191	390.9437
200			201	390.7897

Fig. (14) Fortrat Parabola by (1-0) band of GaCl

Table 16. Spectra lines P(J) and R(J) in cm^{-1} for (1-0) band of GaBr molecule at (J=0, 10, 20, 30,, 200)

J	For GaBr molecule			
	m	P(J)	m	R(J)
0	0	265.254	1	265.419
10	-10	263.571	11	267.036
20	-20	261.828	21	268.593
30	-30	260.025	31	270.087
40	-40	258.162	41	271.527
50	-50	256.239	51	272.904
60			61	274.221
70			71	275.478
80			81	276.675
90			91	277.812
100			101	278.889
110			111	279.906
120			121	280.863
130			131	281.76
140			141	282.597
150			151	283.374
160			161	284.091
170			171	284.748
180			181	285.345
190			191	285.882
200			201	286.359

Fig. (15) Fortrat Parabola by (1-0) band of GaBr

Table 17. Spectra lines P(J) and R(J) in cm^{-1} for (1-0) band of GaI molecule at ($J=0, 10, 20, 30, \dots, 200$)

J	For GaI molecule			
	m	P(J)	m	R(J)
0	0	215.5992	1	215.7127
10	-10	214.4422	11	216.8257
20	-20	213.2452	21	217.8987
30	-30	212.0082	31	218.9317
40	-40	210.7312	41	219.9247
50	-50	209.4142	51	220.8777
60			61	221.7907
70			71	222.6637
80			81	223.4967
90			91	224.2897
100			101	225.0427
110			111	225.7557
120			121	226.4287
130			131	227.0617
140			141	227.6547
150			151	228.2077
160			161	228.7207
170			171	229.1937
180			181	229.6267
190			191	230.0197
200			201	230.3727

Fig. (16) Fortrat Parabola by (1-0) band of GaI

4. CONCLUSIONS

The main conclusion from this work that there is a small variation in the G_v , $E_{v,J}$, and $F_{v,J}$ for gallium monohalides molecules for different values of v as it can be shown in all figures and the variation approximately in the same manners for all molecules except GaF molecule which has values far rather than other molecules, that due to rotational constant B_v for this molecule. All

energies increase with increasing vibrational and rotational quantum number and by increasing the vibrational quantum number, the vibrational constant will decrease. The spectra line values $R(J)$ increases when the values of rotational quantum number decrease but the spectra line values $P(J)$ decrease when the values of rotational quantum number increase. Also the spectra line values $P(J)$ were decrease when the values of (m) increase, while the values of $R(J)$ increase at first, then decrease showing Fortrar parabola.

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