



DETERMINATION OF ROTATIONAL TEMPERATURE OF GaCl FROM B³Π₁ - X¹Σ⁺ SYSTEM

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Abstract:

The high resolution spectra of GaCl molecule were recorded in the 28000 - 30000 cm⁻¹ region, in emission, on BOMEM DA8 Fourier transform spectrometer using a microwave discharge. Rotational structure of (0,0) and (0,1) bands of the B³Π₁ - X¹Σ⁺ system of GaCl molecule were recorded. Intensity distribution among the well-resolved rotational lines of P, branch for each band were recorded and average rotational temperature calculated from these lines has been determined as 1660± 4 K.

Keywords: Intensity distribution, Rotational temperature, GaCl molecule.

Introduction

The vibrational and rotational temperature derived from the band spectra are of importance in spectroscopy, chemical physics, thermodynamics etc. Group IIIA halides are of great interest to the molecular spectroscopists as few of them show the potential laser transitions [1,2]. Under optimal experimental conditions GaCl, GaBr, InBr etc molecules show strong emission bands in visible region. There are some bound free transitions in these molecules and therefore the situation is favorable for lasing action. Besides these few band systems like A³Π₀ - X¹Σ⁺ and B³Π₁ - X¹Σ⁺ show intense bands. Many workers [3,4] and the references therein have studied the band spectra of GaCl in emission as well as in absorption. The emission band spectra of GaCl, especially in UV region consists of two overlapping violet degraded band systems namely A³Π₀ - X¹Σ⁺ and B³Π₁ - X¹Σ⁺. The mono-halides of group IIIA elements usually give their main band systems in the range 2500 to 4500 Å.

Theory:

Herzberg [5] has given expression for the Hönl London factors which are as follows, The Hönl London factor for P branch is given by,

$$S_{JJ^{\prime}P} = (J''-1-\Lambda'')(J''-\Lambda'') / (4(J'')) \text{ in terms of } J'' \text{ ----- (1)}$$

$$S_{JJ^{\prime}P} = (J'+1-\Lambda')(J'+2-\Lambda') / 4(J'+1) \text{ in terms of } J' \text{ ----- (2)}$$

For P branch lines J' = J-1 and J'' = J.

Thus substituting these J' = J-1 in eqn. (1 & 2) we get,

$$S_J^P = (J-1-0)(J-0) / 4(J) = (J-1)(J) / 4J = (J-1) / 4 \text{ ----- (3)}$$

Same results is obtained if we substitute J'' = J in eq. (1 & 2). Thus in the equations for P

branch lines, S_{JJ''} are to be replaced by [(J-1)/4].

$$B_v' = B_e' - \alpha_e'(v+1/2) \text{ ----- (4)}$$

The B_e' and α_e' are known so B_v' can be calculated.

Experimental Setup:

The molecule GaCl is excited in a microwave discharge through a flowing mixture of gallium chloride vapor and helium gas. The Microwave power (2450 MHz, 180 Watts) and gas pressure (1 to 2 Torr) were optimized by observing the emission signal. A spherical lens was used to focus the signal into the interferometer. The spectra in the region 28000 - 30000 cm⁻¹ were recorded with BOMEM DA8 Fourier transform spectrometer with an apodized resolution of 0.035 cm⁻¹ using a quartz UV beam splitter, photomultiplier detector, and appropriate filter. Sixty scans were co added to obtain an improved signal to noise ratio [6]. The prints of the traces of (0,0) and (0,1) bands are shown in figures 1 to 2 respectively. The areas of the profiles of the rotational lines were measured with the help of a digital planimeter with an accuracy of 10⁻² cm² and more. From the slope of each graph the rotational temperature is calculated. Average intensity of each line was employed to calculate the rotational temperature. Results are summarized in Table 1.

Calculations of Rotational Temperature:

The line profiles of the (0,0) and (0,1) bands of B-X bands are properly shaped using the Origin software. The profiles thus obtained are subjected to the intensity measurements. The J assignments once known can be used with intensity data to calculate the rotational temperature. The intensity of spectral line in an emission is given by the expression [5]

$$I_{J^{\prime}J''} = A S_{J^{\prime}J''} \exp [-F_v(J') hc / kT] \text{ ----- (5)}$$

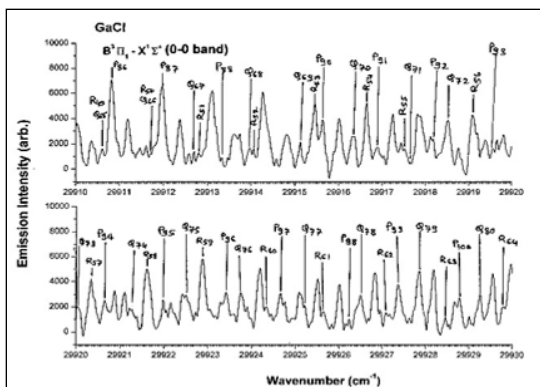


Fig. 1: Rotational fine structure of (0,0) band of B³Π₁ - X¹Σ⁺ system of GaCl molecule

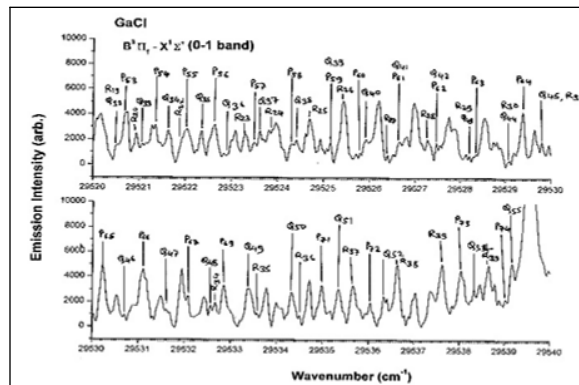


Fig. 2: Rotational fine structure of (0,1) band of B³Π₁ - X¹Σ⁺ system of GaCl molecule

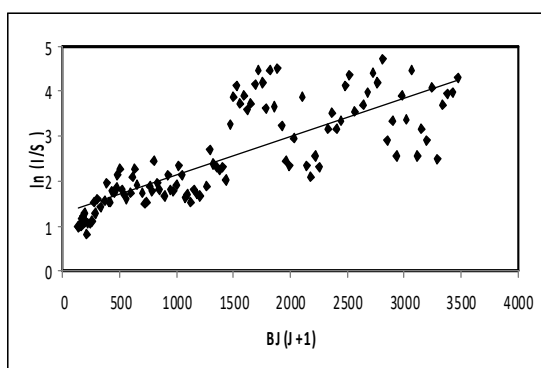


Fig. 3: Determination of rotational temperature from P branch of (0,0) band of the B³Π₁ - X¹Σ⁺ system of GaCl

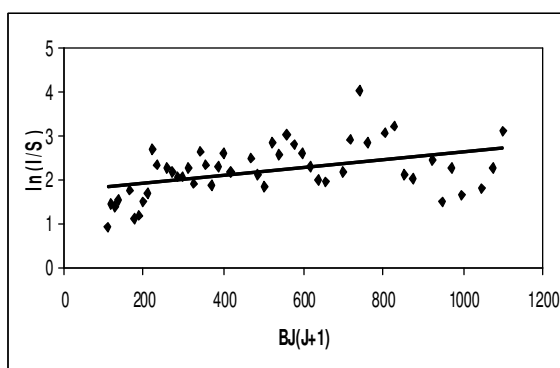


Fig. 3: Determination of rotational temperature from P branch of (0,1) band of the B³Π₁ - X¹Σ⁺ system of GaCl

Table 1: Rotational Temperatures

Band	B v	Branch	Slope x10 ⁻³	Rot. Temp.
(0,0) Band	0.157959	P	8.62	1664
(0,1) Band	0.156909	P	8.66	1657
Mean				1660 K

Where the intensity I is the intensity of a rotational line resulting from a transition J' to J'', A is a constant, S_{J,J'} is Hönl London factor. F_v(J') is a term value in cm⁻¹. h, c, k, and T are Planck's constant, velocity of light, Boltzmann constant and temperature respectively. Taking natural logarithm,

$$\ln(I_{J''} / S_{J''}) = \text{Constant} - F_v(J') hc / kT$$

Where F_v(J) = B_v J'(J'+1) - D_v J²(J+1)² ----- (6)

But D_v being small the second term in above eqⁿ (RHS) can be neglected.

Thus F_v(J) = B_v J'(J'+1)

The eqⁿ (6) becomes,

$$\ln(I_{J''} / S_{J''}) = \text{Constant} - B_v J'(J'+1)(hc/kT)$$

----- (7)

Thus if a graph between LHS on y-axis and J'(J'+1) on x axis is plotted a straight line with slope (dy/dx) equal to (B_v' hc/kT) is expected.

The rotational temperature can be estimated from the equation,

$$T = (B_v hc/k) (1/\text{slope}) \text{ ---- (8)}$$

Results and discussion:

The high resolution Fourier transform profiles of the rotational lines of the (0,0) and (0,1) bands of B-X system are shown in figures 1 and 2 respectively. The wave numbers and J numbering is taken from reference [6]. Because of high resolution, the spectrum is recorded in fragments. Each time the intensity scale is constant so that a uniform measurement could be recorded. Unlike photographic process, there is no need to calibrate the response of emulsion to the radiation. Moreover, for rotational bands, the region is fairly small. The response of the photomultiplier detector is supposed to be quite linear compared to emulsions. The plots

of P, branch lines for each band viz (0-0) and (0-1), bands of B-X system are plotted as shown in the Fig. 3 and Fig. 4, and by measuring the slopes, the temperatures are calculated [7].

The average temperature estimated is 1660 ± 4 K which shown in Table 1. This indicates that the source used for excitation is fairly cool and hence the separation of P, Q and R branch line profiles can be clearly seen. This temperature is a gas kinetic temperature and should not be confused with the actual temperature of the source. The Doppler width in such cool sources is considerably reduced and thus the lines show sharp contours. Since there is no report of either vibrational temperature or rotational temperature earlier to this work, we conclude that the results are consistent with the dissociation energy 39865cm^{-1} of a molecule which is quite low.

References

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