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Fourier transform spectral study of $B^2\Sigma^+$–$X^2\Sigma^+$ system of AlO

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Abstract

The spectrum of $B^2\Sigma^+$–$X^2\Sigma^+$ system of AlO has been recorded on BOMEM DA8 Fourier transform spectrometer at an apodized resolution of 0.05 cm^{-1}. Nineteen bands of the $\Delta v = 1, 0, -1$, and -2 sequences of this band system have been analyzed for the rotational structure. Out of which seven bands, viz. 3–2, 4–3, 2–3, 3–4, 4–5, 5–6 and 6–7 have been analyzed for the first time. The rotational lines of these 19 bands along with 20 earlier analyzed bands, a total of 7200 lines, have been fitted in a simultaneous least squares fit. The study has resulted in determining more precise vibrational and rotational constants of the two states. Because of the high resolution employed it became necessary to invoke H_0 and H_1 coefficients, and a fifth order term to explain the anomalous spin-doubling observed in the $v'' = 5$, 6 and 7 levels of the $X^2\Sigma^+$ state.

Keywords: High resolution; Fourier transform; AlO; Emission spectra

1. Introduction

The blue–green system, $B^2\Sigma^+$–$X^2\Sigma^+$ transition, of AlO has been known for over 100 years and extensively studied both experimentally and theoretically [1–11,17–19,23,24]. The astrophysical importance of AlO and its aeronomical significance is well known [12–16,21,23]. The existence of AlO molecule in cool stellar atmospheres has been shown through the identification of B–X system in spectrum of some normal Mira giants and Mira variables [12,16]. In stars of lower temperature the absorption of the head of 0–0 band (λ 4842 Å) of the B–X system strengthens. In normal Mira giants because of higher temperature the band is seen in emission. In Mira variables the AlO absorption is greater than in normal giants and the maximum intensities far exceed those obtained in the normal M giants. The strengthening of AlO (λ 4842 Å) intensity, in these stars is quite variable from cycle to cycle. The possibility of some sort of interference could not be ruled out. It was suggested to look for some other system of AlO, such as $A^2\Pi_i$–$X^2\Sigma^+$ system. Temperatures and densities in the upper atmosphere, as well as differential excitation of solar radiation have been inferred from observations on B–X system of AlO, following release of organoaluminium compounds [13–15].

Over the years several workers have tried to give a vibrational expression involving the observed bands of the B–X system [1–11]. Roy [5] tried to give an improved vibrational expression compared to Mecke [1]. But as it has been recently confirmed that, since some of the band heads of the system are shifted due to interaction of $A^2\Pi_i$ state with the ground $X^2\Sigma^+$ state [28], it would never have been possible to find a perfect expression with minimum obs.–cal. differences. A sudden drop of intensity in the bands 4–7, 6–7, 5–7, 10–7 and those involving $v'' \geqslant 5$ and 8 was noticed by Rosen [7]. Making use of the extrapolated B_v values he concluded that in the vibrational levels $v'' \geqslant 6$, 7 and 8 predissociation sets in at $N = 60$, 44 and 18, respectively. He also concluded that all the bands of $v'' \geqslant 9$ progressions were predissociated. On the basis of this

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observation Rosen proposed a low dissociation energy for the ground state. Lagerqvist et al. [9] observed some more bands of the same transition involving $v'' = 5$. He stated that the predissociations observed by Rosen might have been illusory; which later turned out to be really true. In the bands with $v'' \geqslant 6$ the rotational lines go off because of perturbations and not because of predissociations. Shimauchi [10] photographed the spectra in air, nitrogen, oxygen and argon using high-grade aluminium rods as electrodes. She was able to record the bands with $v' = 16$ and $v'' = 12$ and for the first time indicated that $v'' = 9$ level of $X^2\Sigma^+$ state is raised by 10 cm^{-1} on account of perturbation by certain state. Shimauchi's vibrational analysis was most extensive. Goodlett and Innes [11], Mahieu et al. [20], Singh et al. [25], Coxon and Naxakis [27] and Saksena et al. [28] tried to determine the sign and magnitude of γ''_0 on some consideration or other but it was Yamada et al. [29] who gave most accurate value of γ''_0 using microwave data. An attempt was made by Bernard and Gravina [23] to calculate the rotational line positions of six bands of $A^2\Pi_i$–$X^2\Sigma^+$ transition. These authors have taken the spin-doubling constants of $v = 0$, 1 and 2 levels of the $X^2\Sigma^+$ states as $+0.00073$ cm^{-1}, -0.00022 cm^{-1} and -0.00134 cm^{-1}, respectively (see Table 1, Ref. [23]). How these values were arrived at is not very clear since it has already been known that the spin-doubling constant γ''_v increases with v and has a positive sign [25,26,28].

In the light of the above we decided to record the high resolution spectra of AlO molecule using F.T. spectrometer to understand the behaviour of spin-doubling constant, γ''_v of the ground $X^2\Sigma^+$ state. In turn, the study also helped in understanding the reasons due to which, so far, it was not possible to find an unique vibrational expression for the $B^2\Sigma^+$–$X^2\Sigma^+$ system of AlO by all the previous workers.

2. Experimental

The spectrum of AlO was excited in a microwave discharge (2450 MHz, 180 W) through a flowing mixture of $AlCl_3$ vapours, buffer gas argon and a small amount of oxygen. The $AlCl_3$ kept in a small quartz boat of side arm of a discharge tube was heated by an electrical furnace and vapours, along with argon and oxygen, were let-in the discharge zone. The gas pressures were so optimized as to give very intense characteristic glow of AlO [22]. A spherical lens was used to focus the emission signal into the interferometer. The spectra in the region 18 000–22 000 cm^{-1} were recorded with BOMEM DA8 Fourier transform spectrometer with an apodized resolution of 0.05 cm^{-1} using quartz UV beam splitter and silicon detector. The emission signal being strong no filter was required. Fifty scans (integration time ~75 min.) were coadded to obtain an improved signal-to-noise ratio. The estimated rotational temperature from the rotational structure was ~1700 K. The accuracy of the measurements is expected to be better than 0.005 cm^{-1}.

Table 1
Head measurements of the bands of $B^2\Sigma^+$–$X^2\Sigma^+$ transition (in cm^{-1})

Sr. no.	Δv	v'–v''	R_2 head	N[b]	R_1 head	N[b]	Δv
1	4	5–1	23919.005[a]	10	23918.846[a]	10	0.159
2	4	6–2	23794.177[a]	11	23793.977[a]	11	0.200
3	4	7–3	23676.038[a]	11	23675.806[a]	11	0.232
4	4	8–4	23564.653[a]	11	23564.369[a]	11	0.284
5	4	9–5	23460.083[a]	12	23459.717[a]	11	0.366
6	4	10–6	23362.057[a]	12	23361.600[a]	12	0.457
7	4	11–7	23270.735[a]	12	23270.145[a]	12	0.590
8	3	3–0	23210.161[a]	11	23210.004[a]	11	0.157
9	3	4–1	23085.894[a]	12	23085.717[a]	12	0.177
10	3	5–2	22968.421[a]	12	22968.207[a]	12	0.214
11	3	6–3	22857.673[a]	12	22857.420[a]	12	0.253
12	3	7–4	22753.627[a]	13	22753.321[a]	12	0.306
13	3	8–5	22656.430[a]	12	22656.045[a]	12	0.385
14	3	9–6	22565.902[a]	13	22565.402[a]	13	0.500
15	3	10–7	22482.120[a]	14	22481.439[a]	14	0.681
16	2	2–0	22362.536[a]	13	22362.365[a]	12	0.171
17	2	3–1	22245.623	13	22245.421	13	0.202
18	2	4–2	22135.484	13	22135.253	13	0.231
19	2	5–3	22032.095	14	22031.819	13	0.276
20	2	6–4	21935.480	14	21935.127	14	0.353
21	1	1–0	21507.742	14	21507.546	14	0.196
22	1	2–1	21398.166	14	21397.975	14	0.191
23	1	3–2	21295.440	15	21295.176	15	0.264
24	1	4–3	21199.368	15	21199.006	15	0.362
25	0	0–0	20645.852	16	20645.585	16	0.267
26	0	1–1	20543.706	16	20543.500	16	0.206
27	−1	0–1	19682.250	19	19682.021	19	0.229
28	−1	1–2	19594.361	20	19594.018	19	0.343
29	−1	2–3	19513.194	21	19512.785	20	0.409
30	−1	3–4	19438.842	22	19438.318	21	0.524
31	−1	4–5	19371.420	23	19370.738	22	0.682
32	−1	5–6	19310.854	25	19309.900	24	0.954
33	−1	6–7	19257.550	33	19256.224	31	1.326
34	−2	0–2	18733.664	24	18733.287	23	0.377
35	−2	1–3	18660.020	25	18659.530	24	0.490
36	−2	2–4	18593.223	26	18592.635	26	0.588
37	−2	3–5	18533.528	28	18532.655	27	0.873
38	−2	4–6	18480.752	31	18479.588	30	1.164
39	−2	5–7	18435.915	37	18434.105	34	1.810

Note: The accuracy of the R_2/R_1 heads is ~±0.03 cm^{-1}.
[a] These are calculated positions.
[b] Rotational number N, where head is formed.

3. Discussion

In the case of B–X band system of AlO, the efforts to obtain unique expression using head measurements could not succeed earlier because of two reasons. One, as the origin to vertex separation [32] differs vastly from bands of positive to negative sequences, resulting in large obs.–cal. differences and secondly, due to rapid increase in the spin-doubling constant γ''_v, in the $v'' \geqslant 4$–7 the separation of the two heads R_2 and R_1, involving these levels also increases very rapidly (see Table 1). The band head positions shown in Table 1 are either the observed band heads in the F.T. spectrum recorded in the present study or the interpolated values from the least squares fit of rotational lines of all the bands.

Being a $^2\Sigma$–$^2\Sigma$ transition the γ'_v and γ''_v are highly co-related and cannot be estimated independently using the