On the Infrared $A^2\Pi_i - X^2\Sigma^+$ System of Aluminium Monoxide in Relation with the Spectra of M Giant- and Mira-Type Stars

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From combinations between known ultraviolet transitions of the AlO molecule line positions in the $A^2\Pi_i - X^2\Sigma^+$ system are tentatively proposed. Indeed, the available data on the $C^2\Pi_r \rightarrow X^2\Sigma^+$ and $C^2\Pi_r \rightarrow A^2\Pi_i$ transitions permit us to derive about 2400 energy level differences in the A–X system corresponding to the six v-connected bands 0–0, 0–1, 0–2, 1–0, 1–1 and 1–2. A unique and consistent set of rovibrational constants is derived from a global fitting, allowing to reproduce the observed differences with a total standard deviation of 0.053 cm^{-1}. A catalogue of vacuum line wavenumbers in the six bands is generated and can be made available on request. The synthetic spectra are expected to represent properly the true spectra at least up to $J \sim 35.5$ and can therefore be of usefulness for the detection of the system in the spectra of M giant- and Mira-type stars.

Franck-Condon factors and r-centroïds appropriate to RKR potentials and estimates of intensities in emission are given for bands up to $v' = 5$, $v'' = 8$.

More reliable values for the internal partition functions and dissociation constants of AlO are computed for temperatures between 1000 and 8000 K. All the known and predicted electronic states are taken into account, and present or recent values for the molecular parameters and dissociation energy are used.

1. Introduction

The existence of the AlO molecule in cool stellar atmospheres has first been shown through the identification of the blue-green bands of the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ system in the spectrum of the variable star Mira Ceti [1] and then in the spectra of normal M giant stars of type later than M3 [2]. The behaviour of the strongest band of the system, the 0–0 band with head at 4842 Å, was thoroughly analyzed [3] from a survey of numerous spectrograms. The conclusions were that in the spectra of normal M giant stars the intensities of the absorption bands of AlO are well correlated with the spectral type as defined from the TiO criterion; on the other hand, in Mira-type variable stars the AlO bands can greatly vary from cycle to cycle, being abnormally strong or weak for the spectral type or even at times going over into emission.

Luck and Lambert [4] and Murty [5] have emphasized the need for another electronic transition to be observed in the stellar spectra in order to better determine the depth of formation of the AlO molecules and the temperature changes occurring within the atmosphere during the times when AlO is observed. Founding upon ab initio calculations of band oscillator strengths [6] and estimated molecular column densities for M-type stars [7], Luck and Lambert suggested that the $A^2\Pi_i \rightarrow X^2\Sigma^+$ system could be detectable; they finally concluded that the simultaneous observations of the blue-green and the infrared $A \rightarrow X$ transitions should provide important information as to the nature of the mechanisms controlling the Mira phenomenon.

Unfortunately, the $A \rightarrow X$ system has not yet been observed in rotation. Knight and Weltner [8] first observed the absorption from the ground state to low vibrational levels of the A state; then the chemiluminescence from the $A \rightarrow X$ transition [9], [10] was investigated but no direct information is available until now as to the expected most intense bands of the system which do appear in the 2 μm region. A first attempt to detect the 1–0 band [4] in high-resolution spectra of Mira-type stars (o Cet, R Leo, W Hya) and M supergiants (W Ori, α Her, α Sco), based on extrapolated constants for the $A^2\Pi_i$ ($v = 1$) level, appeared negative, but the possible uncertainty in the predictions of the line posi-

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tions was evaluated to 1 cm^{-1}. Molecular constants now exist for the A state ($v = 0, 1$) from the works of McDonald and Innes [11] on the $D^2\Sigma^+ \rightarrow A^2\Pi_i$ ($v = 0$) system and Singh and Saksena [12, 13] on the $E^2\Delta_i \rightarrow A^2\Pi_i$ ($v = 0, 1$) and $C^2\Pi_r \rightarrow A^2\Pi_i$ ($v = 0, 1$) systems respectively, while the constants of the $X^2\Sigma^+$ state are already known very accurately from earlier studies up to $v = 5$.

The aim of this paper is to present a homogeneous set of molecular constants for the X ($v = 0, 1, 2$) and A ($v = 0, 1$) states and propose a catalogue of line wavenumbers. The calculations of the synthetic spectra for the six bands 0–0, 0–1, 0–2, 1–0, 1–1 and 1–2 are based upon combinations of recent accurate measurements of the ultraviolet transitions $C \rightarrow X$ [14] and $C \rightarrow A$ [13]. Using the present constants, Franck-Condon factors and r-centroïds are then given together with estimates of the relative intensities in emission for bands up to $v' = 5$, $v'' = 8$. Finally, new estimations of the internal partition functions (since X and A states are the major contributors) and equilibrium dissociations constants are made based on present or recent spectroscopic data (particularly for the dissociation energy of AlO.

2. The $A^2\Pi_i \rightarrow X^2\Sigma^+$ System of AlO from Combinations of Ultraviolet Transitions

a) Method and data processing

Seven electronic states of the AlO molecule are known through the observation of nine band systems involving either the $X^2\Sigma^+$ ground state or the low-lying $A^2\Pi_i$ state ($T_e \sim 5405.5$ cm^{-1}). Therefore it appears possible to predict the infrared A–X transition by application of the combination principle in two ways, from the following combinations, $[D^2\Sigma^+ - X^2\Sigma^+] - [D^2\Sigma^+ - A^2\Pi_i]$ or $[C^2\Pi_r - X^2\Sigma^+] - [C^2\Pi_r - A^2\Pi_i]$, hereafter DX – DA or CX – CA. The available analyses of the $D \rightarrow X$ [15] and $D \rightarrow A$ [11] systems restrict the possible predictions to the $A \rightarrow X$ 0–0, 0–1, and 0–2 bands, up to $J \sim 45.5$. We preferred to make use of the $C \rightarrow X$ and $C \rightarrow A$ systems for which more recent analyses [14, 13] permit to predict 6 bands, the 0–0, 0–1 and 0–2 bands up to $J = 64.5$ and the 1–0, 1–1 and 1–2 bands up to $J = 38.5$, without any extrapolation in the branches involving the $A^2\Pi_{1/2}$ substate.

Furthermore, it is to be noted that no perturbations have been observed in either the X or the A state with the exception of a weak shift (~ 0.1 cm^{-1}) of the $A^2\Pi_{3/2}$ ($v = 1, J = 56.5$) level [12].

From the combination CX – CA, 14 different "branches" can be obtained which do not correspond to any of the 12 expected branches of a $^2\Pi \rightarrow {}^2\Sigma$ transitions, for example:

$$R_2(J)\,(CX) - R_{21}(J)\,(CA) = \text{“}Q_{ff}(J)\text{”}\,(AX)\,,$$
$$^{S}R_{21}(J) \quad - P_{21}(J+2) = \text{“}S_{ee}(J)\text{”}\,,$$
$$Q_1(J) \quad - P_{12}(J+1) = \text{“}R_{fe}(J)\text{”}\,,$$
$$^{O}P_{12}(J) \quad - R_{12}(J-2) = \text{“}O_{ff}(J)\text{”} \quad \text{etc.}\ldots.$$

These pseudobranches are not observed (the selection rule $+ \leftrightarrow +$, $- \leftrightarrow -$ is violated); they are only representative of energy differences between $A^2\Pi_i$ and $X^2\Sigma^+$ levels (in an analogous way the combination DX – DA yields 9 different "branches"). Over 2400 differences could be obtained relative to the six v-connected bands involving the levels $X^2\Sigma^+$ ($v = 0, 1, 2$) and $A^2\Pi_i$ ($v = 0, 1$); they were fitted simultaneously to corresponding calculated term value (X state) or energy matrix eigenvalue (A state) differences using an iterative non-linear least squares procedure. For the X state the usual rotational term-values for $^2\Sigma^+$ states have been used. The energy-matrices used for the description of $^2\Pi$ states have been given elsewhere [16]. The final adjustments are operated after checking the significance of the small parameters within ± 2 standard deviation limits ($2\sigma_p$), removing observed differences deviating by more than 3 times the total standard deviation (3σ) from their calculated values. Thus, a unique and consistent set of rotational constants is derived, generating the remaining 2400 differences with typical rms errors of about 0.06 cm^{-1}.

b) Results: Rovibrational constants for the X and A states

In Table 1 are gathered the rotational constants for the X and A states which resulted from the final adjustment and corresponding to a total standard deviation $\sigma = 0.053$ cm^{-1}. In view of obtaining a set of parameters as homogeneous and realistic as possible it appeared preferable to keep a number of them fixed to theoretical or already known values, the adjustment remaining quite equivalent

Table 1. Rotational constants (in cm^{-1}) in the $X^2\Sigma^+$ and $A^2\Pi_i$ states of AlO[a].

$X^2\Sigma^+$	$v=0$	$v=1$	$v=2$
T_v	0	965.453(11)	1916.825(13)
B_v	0.638289(57)	0.632465(59)	0.626663(60)
$D_v \times 10^5$	0.1059(14)	0.1068(15)	0.1090(15)
$H_v \times 10^{12}$	−0.574	−0.581	−0.589
$\gamma_v \times 10^3$	0.73(30)	−0.22(35)	−1.34(37)

$A^2\Pi_i$	$v=0$	$v=1$
T_v	5281.747(8)	6002.477(12)
B_v	0.534378(56)	0.529399(75)
$D_v \times 10^5$	0.1123(13)	0.1048(39)
$H_v \times 10^{12}$	−0.239	−0.243
A_v	−127.6428(97)	−127.926(13)
$A_J \times 10^4$	−0.323(39)	−0.32
$p \times 10^2$	−0.735(48)	−1.011(52)
$p_J \times 10^5$	−0.271(21)	−0.593
$q \times 10^4$	0.37(13)	0.37

[a] Numbers in parentheses represent the uncertainty $2\sigma_p$ (twice the standard deviation on the estimated value of the parameter) in unit of the last quoted digit. In the final adjustment some parameters were kept fixed to the values given without indication of $2\sigma_p$ (see text, § 2b).

as regard to the synthetic spectra. Thus, owing to the strong correlations between H''_v and H'_v constants and the fact that their differences only were revealed at the limit of significance, theoretical values were imposed. To this end, we computed the centrifugal distortion constants for both states, using the method elaborated by Hutson [17] for diatomic molecules and based upon a numerically specified potential curve (RKR potentials were determined for this purpose). The values obtained for H'_v and H''_v are in Table 1; as to the observed D'_v and D''_v values, they show good agreement with the theoretical ones ($D''_0 = 0.110 \times 10^{-5}$; $D'_0 = 0.116 \times 10^{-5}\ cm^{-1}$), indicating that the vibration-rotation approximation is appropriate. In the $A^2\Pi_i$ ($v=0$) level the parameters A_J, p_J and q appeared significant but in the level $v=1$ they could not be determined (owing to the lack of available data for high J-values). Consequently, the same values in $v=1$ as in $v=0$ were admitted and kept fixed, except for p_J for which the value derived from the analysis of the $E \rightarrow A$ transition [12] was adopted. A difficulty appeared in the determination of the spin-doubling constant γ in the X state. From our adjustments neither the earlier experimental value $\gamma_0 = 0.010\ cm^{-1}$ [18] nor the more recent ones could be confirmed. Theoretical calculations by Mahieu et al. [19] show that the spin-doubling in the ground state must be small (arising essentially from second-order interactions with the regular $C^2\Pi$ state) and positive ($\gamma = +0.0035\ cm^{-1}$) with a very weak vibrational dependence; this result supports the experimental value they found ($\gamma_0 = +0.0050\ cm^{-1}$) from the analysis of new high-resolution spectra obtained in a low-temperature discharge. Let us also quote the former value $\gamma = +0.0014\ cm^{-1}$ derived from ESR spectroscopy [8].

When keeping the $\gamma_{0,1,2}$ parameters fixed to the values by Mahieu et al., the quality of our adjustment decreases significantly ($\sigma = 0.071\ cm^{-1}$). Therefore we finally retained the values reported in Table 1 since they permit to reproduce the observed energy-level differences with the highest accuracy and certainly generate more realistic synthetic spectra.

The molecular constants relative to the equilibrium position in the X and A states are given in Table 2. The values of ω_e and $\omega_e x_e$ in A state which could not be deduced directly from our results were calculated iteratively from Pekeris' formula, assuming that the true potential curve is well represented by a Morse function. They differ significantly from the admitted values $\omega'_e = 728.5\ cm^{-1}$, $\omega'_e x'_e = 4.15\ cm^{-1}$ [11]. The same procedure if applied to the ground state yields $\omega''_e = 979.40\ cm^{-1}$, $\omega''_e x''_e = 6.98\ cm^{-1}$ in excellent agreement with the observed values.

c) *The catalogue*

Vacuum line wavenumbers relative to the synthetic spectra of the bands 0–0, 0–1, 0–2, 1–0,

Table 2. Equilibrium constants in cm^{-1} adopted for the $X^2\Sigma^+$ and $A^2\Pi_i$ states of AlO[a].

Parameter	$X^2\Sigma^+$	$A^2\Pi_i$
T_e	0	5405.5
ω_e	979.51	731.03
$\omega_e x_e$	7.04	5.15
B_e	0.641589	0.537261
α_e	0.005793	0.004963
$D_e \times 10^5$	(0.1098)	(0.1160)
$\beta_e \times 10^8$	(0.91)	(0.74)
$H_e \times 10^{12}$	(−0.57)	(−0.24)
r_e (Å)	1.6176	1.7677

[a] ω_e and $\omega_e x_e$ in A state have been calculated iteratively from Pekeris' formula. Centrifugal distortion constants obtained from Hutson's method are given in parentheses.

1–1 and 1–2 have been arranged in a catalogue which is available upon request to the authors [20]. They are generated from the set of constants given in Table 1 and listed according to the J-numbering for the eight observable branches, up to $J = 65.5$. Let us dwell on the fact that the line wavenumbers calculated beyond $J = 21.5$ and $J = 38.5$ for the subbands involving the $A^2\Pi_{3/2}$ ($v = 1$) and $A^2\Pi_{1/2}$ ($v = 1$) levels respectively are extrapolated and should be used cautiously. For comparison, we also give the calculations for (i) the 0–0 band generated from the combination DX – DA, (ii) the 0–0 and 1–0 bands generated from the set of constants obtained when keeping the spin-splitting parameters fixed as discussed above. So, we could verify that the deviations between the corresponding line positions in these different cases were generally small, in any case less than 0.18 cm^{-1} for $J \leqq 36.5$.

To sum up, the proposed line positions are expected to represent properly the true spectra at least up to the intensity maxima in the branches which occur for $30.5 \leqq J \leqq 36.5$ in the range of effective temperatures in the atmospheres of the concerned stars.

3. Aspect of the $A^2\Pi_i \rightarrow X^2\Sigma^+$ Band System

a) Franck-Condon (FC) factors, r-centroïds and band intensities

The potential of the A state is shifted to a considerably longer internuclear distance than that of the ground state ($\Delta r_e = 0.150$ Å). This leads to a widely opened Condon parabola with overlapping sequences. Using the constants given in Table 2 we have determined the RKR potentials for both states and calculated the FC factors ($q_{v'v''}$) and r-centroïds ($r_{v'v''}$) for bands up to $v' = 5$ and $v'' = 8$ (Table 3). These quantities can be useful for evaluating the variation of the electronic transition moment with internuclear separation. The rotational dependence of the FC factors which was found to be negligibly small in all bands, the effect never exceeding 6% of the rotationless factors at $J = 60.5$, is not given here. Estimates of relative emission intensities were made following the well-known relation

$$I_{v'v''} = K N_{v'} R^2_{v'v''} \nu^4_{v'v''} q_{v'v''}$$

where K is a constant, $N_{v'}$ the population of the level v', $R_{v'v''}$ the electronic transition moment at the value $r_{v'v''}$, and $\nu_{v'v''}$ the transition frequency. Basing on previous studies [6], the dependence of R_e with $r_{v'v''}$ was taken into account. We have imposed the constraint of a Boltzmann distribution for the upper state population corresponding to a temperature $T = 2500$ K, appropriate to the stars under consideration. A multiplicative factor has been introduced for convenient display, so as the intensity of the strongest 2–0 band is fixed to 100.

b) Aspect of the bands

Twelve rotational branches characterize a $^2\Pi \rightarrow {}^2\Sigma$ band. The separation between the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ subbands which is large in the A → X system ($\sim 128\ cm^{-1}$) shows that the A state closely follows Hund's case (a) coupling. In that case and for an

Table 3. Franck-Condon factors, relative intensities in emission and r-centroïds for bands of the A → X system of AlO [a].

v'	v''					
	0	1	2	3	4	5
0	0.059 42.1 1.6924	0.191 56.6 1.7233	0.281 28.2 1.7554	0.246 6.1 1.7893	0.143 0.4 1.8252	0.058 0.0 1.8638
1	0.145 78.4 1.6694	0.195 49.4 1.6983	0.045 4.6 1.7252	0.020 0.7 1.7729	0.157 1.2 1.8002	0.214 0.2 1.8351
2	0.196 100.0 1.6476	0.067 17.5 1.6738	0.026 3.1 1.7128	0.133 6.1 1.7381	0.040 0.5 1.7640	0.020 0.1 1.8194
3	0.193 88.9 1.6269	0.001 0.3 1.6255	0.107 13.3 1.6851	0.031 1.8 1.7080	0.040 0.8 1.7519	0.111 0.7 1.7777
4	0.154 61.4 1.6070	0.027 6.1 1.6384	0.082 10.2 1.6616	0.011 0.6 1.7025	0.092 2.4 1.7214	0.002 0.0 1.7116
5	0.107 35.6 1.5879	0.080 16.0 1.6165	0.017 1.9 1.6376	0.071 4.2 1.6725	0.018 0.6 1.6914	0.055 0.7 1.7338
6	0.067 18.3 1.5696	0.109 18.6 1.5969	0.002 0.2 1.6387	0.072 0.1 1.6498	0.009 0.3 1.6898	0.065 1.0 1.7058
7	0.038 8.5 1.5517	0.105 15.1 1.5783	0.032 2.8 1.6071	0.026 1.3 1.6278	0.056 1.6 1.6605	0.008 0.1 1.6741
8	0.021 3.8 1.5344	0.084 10.1 1.5604	0.068 5.2 1.5875	0.000 0.0 1.5739	0.062 1.7 1.6387	0.010 0.2 1.6761

[a] First entry: rotationless FC factor; second entry: relative intensities proportional to $R^2_{v'v''} \times \nu^4_{v'v''} \times q_{v'v''} \times \exp(-G_0(v')/kT)$, for $T = 2500$ K; third entry: rotationless r-centroïd (Å).

inverted $^2\Pi$ state, the intensity factors of the different branches are as follows

$$P_2 \text{ and } {}^{Q}P_{21}: \frac{(2J'+1)(2J'+3)}{J'+1},$$

$$Q_2 \text{ and } {}^{R}Q_{21}: \frac{(2J'+1)^3}{J'(J'+1)},$$

$$R_2 \text{ and } {}^{S}R_{21}: \frac{4J'^2-1}{J'+1},$$

$$P_1 \text{ and } {}^{O}P_{12}: \frac{4J'^2-1}{J'+1},$$

$$Q_1 \text{ and } {}^{P}Q_{12}: \frac{(4J'^2-1)(2J'+3)}{J'(J'+1)},$$

$$R_1 \text{ and } {}^{Q}R_{12}: \frac{(2J'+1)(2J'+3)}{J'}.$$

Taking account of the coincidence of the satellite branches with main branches due to the very small value of the spin-splitting in the ground state ($R_2(J-1)$ with ${}^{R}Q_{21}$ (J), etc.) one can expect to observe only four branches in each subband: ${}^{S}R_{21}$, $R_2+{}^{R}Q_{21}$, $Q_2+{}^{Q}P_{21}$, P_2 for the $^2\Pi_{1/2} \rightarrow {}^2\Sigma^+$ subband with respective intensities in the ratios 1:3:3:1 for the same J'' value (except for the lowest rotational lines) and R_1, $Q_1+{}^{Q}R_{12}$, $P_1+{}^{P}Q_{12}$, ${}^{O}P_{1/2}$ for the $^2\Pi_{3/2} \rightarrow {}^2\Sigma^+$ subband with similar intensity ratios.

The bands of the system are degraded to longer wavelengths and four branches show a head reached for very low J-values. For example in the 0–0 band, the heads in the ${}^{S}R_{21}$-, R_2-, R_1-, and Q_1-branches are formed at $J=7.5$, 1.5, 7.5 and 2.5 respectively, far from the intensity maxima in the branches which occur at $J \sim 36.5$ for $T=2500$ K. The situation is

Table 4. Predicted vacuum line wavenumbers (cm^{-1}) in the 1–0 band of the A → X system of AlO.

J	1 SR21	2 R2	3 Q2	4 P2	5 R1	6 Q1	7 P1	8 OP12	J
0.5	6068.569	6067.273	6065.694		5939.566				0.5
1.5	6069.955	6067.374	6064.741	6063.131	5940.926	5938.289			1.5
2.5	6071.128	6067.260	6063.575	6060.891	5942.063	5938.372	5935.736	5931.909	2.5
3.5	6072.087	6066.933	6062.195	6058.439	5942.977	5938.233	5934.542	5929.439	3.5
4.5	6072.833	6066.393	6060.602	6055.772	5943.670	5937.871	5933.126	5926.747	4.5
5.5	6073.365	6065.639	6058.796	6052.893	5944.140	5937.287	5931.488	5923.834	5.5
6.5	6073.684	6064.671	6056.777	6049.800	5944.388	5936.481	5929.628	5920.699	6.5
7.5	6073.789	6063.490	6054.544	6046.495	5944.414	5935.453	5927.546	5917.342	7.5
8.5	6073.680	6062.095	6052.098	6042.975	5944.217	5934.203	5925.242	5913.763	8.5
9.5	6073.358	6060.486	6049.440	6039.243	5943.798	5932.730	5922.717	5909.962	9.5
10.5	6072.822	6058.664	6046.568	6035.297	5943.157	5931.036	5919.969	5905.940	10.5
11.5	6072.073	6056.627	6043.482	6031.139	5942.293	5929.119	5916.999	5901.696	11.5
12.5	6071.109	6054.377	6040.184	6026.767	5941.207	5926.980	5913.808	5897.230	12.5
13.5	6069.932	6051.913	6036.673	6022.181	5939.898	5924.619	5910.395	5892.543	13.5
14.5	6068.541	6049.235	6032.948	6017.383	5938.367	5922.036	5906.760	5887.635	14.5
15.5	6066.937	6046.343	6029.010	6012.372	5936.614	5919.231	5902.903	5882.505	15.5
16.5	6065.118	6043.237	6024.860	6007.147	5934.638	5916.203	5898.824	5877.154	16.5
17.5	6063.085	6039.917	6020.496	6001.709	5932.440	5912.954	5894.524	5871.581	17.5
18.5	6060.838	6036.382	6015.919	5996.058	5930.019	5909.482	5890.003	5865.788	18.5
19.5	6058.378	6032.634	6011.129	5990.194	5927.376	5905.789	5885.259	5859.773	19.5
20.5	6055.703	6028.671	6006.126	5984.116	5924.510	5901.873	5880.295	5853.537	20.5
21.5	6052.814	6024.494	6000.910	5977.826	5921.422	5897.736	5875.109	5847.080	21.5
22.5	6049.711	6020.102	5995.481	5971.322	5918.112	5893.376	5869.701	5840.403	22.5
23.5	6046.393	6015.496	5989.839	5964.605	5914.579	5888.794	5864.072	5833.504	23.5
24.5	6042.862	6010.676	5983.984	5957.675	5910.823	5883.991	5858.222	5826.385	24.5
25.5	6039.116	6005.641	5977.915	5950.532	5906.845	5878.965	5852.150	5819.045	25.5
26.5	6035.155	6000.391	5971.634	5943.176	5902.645	5873.718	5845.858	5811.484	26.5
27.5	6030.980	5994.927	5965.140	5935.606	5898.222	5868.249	5839.344	5803.703	27.5
28.5	6026.591	5989.248	5958.432	5927.823	5893.577	5862.558	5832.609	5795.701	28.5
29.5	6021.987	5983.354	5951.512	5919.827	5888.710	5856.645	5825.653	5787.479	29.5
30.5	6017.168	5977.245	5944.378	5911.618	5883.620	5850.511	5818.476	5779.037	30.5
31.5	6012.135	5970.922	5937.032	5903.196	5878.308	5844.154	5811.079	5770.374	31.5
32.5	6006.887	5964.384	5929.472	5894.560	5872.773	5837.576	5803.460	5761.492	32.5
33.5	6001.424	5957.630	5921.699	5885.711	5867.017	5830.777	5795.621	5752.389	33.5
34.5	5995.746	5950.662	5913.714	5876.649	5861.037	5823.755	5787.561	5743.066	34.5
35.5	5989.854	5943.478	5905.515	5867.373	5854.836	5816.513	5779.280	5733.524	35.5
36.5	5983.746	5936.079	5897.103	5857.885	5848.412	5809.048	5770.779	5723.762	36.5

not favourable to the observation of characteristic features and the detection of the system in stellar spectra should only be based upon the identification of the rotation lines. The most intense bands of the system appear to be the 2–0, 3–0, 1–0 and 0–1 bands. Among the six calculated bands the 1–0 band is the strongest one and the most favourably situated relatively to the telluric absorption and thus it appears of usefulness to present here the synthetic spectrum of the band (Table 4).

4. Partition Functions and Dissociation Constants

In this section we recompute the internal partitions functions for AlO (in the temperature range from 1000 to 8000 K) by taking account of all the observed [21] as well as the unobserved electronic states predicted by Schamps [22] with energies up to 40 000 cm^{-1}; we derive the dissociation constants using for the dissociation energy of AlO the value $D_0^0 = 5.27 \pm 0.04$ eV recommended in [21]. A precise knowledge of these quantities is indeed necessary for atmosphere calculations in red giant stars. The most recent works make use of spectroscopic data anterior to the compilation of Huber and Herzberg. Tsuji [23] who gives a polynomial expression for $\log_{10} K_p(T)$ and Scalo and Ross [24] adopt $D_0^0 =$ 4.60 eV while Johnson and Sauval [25] take $D_0^0 =$ 5.00 eV. Owing to the very important role played by the dissociation energy in the determination of the equilibrium constants, the calculated molecular density strongly depends on the adopted value (at 2500 K, an uncertainty of 0.5 eV in D_0^0 corresponds to a factor of 10 in the molecular density). The value of Huber and Herzberg which is significantly different (in a favourable sense for the production of AlO molecules) is certainly more realistic since it was derived from a critical review of the most recent laser fluorescence studies and a re-interpretation of the long wavelength limit of an absorption continuum. Furthermore, it shows good agreement with the latest mass spectroscopic results ($D_0^0 =$ 5.24 eV in [26]).

The internal partition functions $Q_{AlO}(T)$ were obtained by summing the weighted Boltzman factors over the electronic states. For the X and A states (the major contributors in the temperature range considered here) the present data have been used; the large spin-splitting in the A state has been taken into account by separate summation for the two substates with appropriate electronic statistical weights. For the other observed states, data from [21] were used while for the predicted states the vibrating rotator approximations were assumed.

The values obtained for $Q_{AlO}(T)$ were then used to determine the equilibrium dissociation constant $K_p(T)$ from the well-known expression [27]

$$K_p(T) = \frac{p_{Al}\, p_O}{p_{AlO}} = \left(\frac{2\pi\mu kT}{h^2}\right)^{3/2} kT \cdot \frac{Q_{Al}(T)\, Q_O(T)}{Q_{AlO}(T)} \exp\left(-D_0^0/kT\right)$$

corresponding to the dynamical equilibrium

$$AlO \overset{T}{\rightleftarrows} Al + O$$

Table 5. Internal partition functions and dissociation equilibrium constants for AlO.

T(K)	$Q_{AlO} \times 10^{-4}$	$\log_{10} K_p$ (dyn · cm^{-2})
1000	0.2921	−14.9722
1200	0.3861	−10.4512
1400	0.4961	−7.2203
1600	0.6244	−4.7962
1800	0.7738	−2.9109
2000	0.9474	−1.4037
2200	1.1482	−0.1719
2400	1.3793	0.8529
2600	1.6435	1.7184
2800	1.9438	2.4586
3000	2.2828	3.0985
3200	2.6632	3.6572
3400	3.0874	4.1489
3600	3.5580	4.5850
3800	4.0774	4.9742
4000	4.6483	5.3238
4200	5.2730	5.6394
4400	5.9543	5.9257
4600	6.6948	6.1867
4800	7.4974	6.4255
5000	8.3652	6.6448
5200	9.3011	6.8470
5400	10.3085	7.0340
5600	11.3907	7.2075
5800	12.5514	7.3688
6000	13.7941	7.5193
6200	15.1228	7.6600
6400	16.5414	7.7920
6600	18.0540	7.9159
6800	19.6648	8.0326
7000	21.3780	8.1427
7200	23.1981	8.2468
7400	25.1294	8.3454
7600	27.1764	8.4390
7800	29.3437	8.5281
8000	31.6359	8.6129

where the p's are partial pressures and the Q's are the internal atomic or molecular partition functions; μ is the reduced mass and D_0^0 the dissociation energy of the molecule. The atomic partition functions for the atoms Al and O were computed using the polynomial coefficients given by Irwin [28].

In Table 5, the internal partition functions and logarithmic dissociation equilibrium constants are listed for the temperature range 1000−8000 K in steps of 200 K. For practical applications, the tabulated $\log_{10} K_p$ in dyn. cm^{-2} can be approximated as a function of $\theta = 5040.39/T$ by the following polynomial obtained using the least-squares method

$$\log_{10} K_p(\theta) = 11.7987 - 4.9688\,\theta - 0.16975\,\theta^2 + 0.029733\,\theta^3 - 0.0018908\,\theta^4,$$

which reproduces the data with a standard-deviation $\sigma = 0.0018$.

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