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AIR FORCE CAMBRIDGE RESEARCH LABORATORIES
L. G. HANCOM FIELD, BEDFORD, MASSACHUSETTS

AIO Resonant Spectrum for Upper Atmosphere Temperature Determination

OVE HARANG

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UPPER ATMOSPHERE PHYSICS LABORATORY PROJECT 7635

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AIO Resonant Spectrum for Upper Atmosphere Temperature Determination

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Abstract

The release of diatomic species, in particular AlO, into the upper atmosphere at twilight results in luminous clouds that display the resonance electronic-vibrational-rotational spectrum of the released species. The intensity distribution of the vibrational-rotational bands is temperature dependent. Assuming thermal equilibrium of the released species with ambient, the ambient temperature can be determined. Using the AlO molecular parameters, Franck-Condon factors, and the solar intensity in the upper atmosphere, the population of AlO in the vibrational and rotational levels and the relative band intensities are calculated, tabulated, and charted. These charts will be useful for upper atmosphere temperature measurements from AlO luminous clouds.

Foreword

This report was prepared for the Air Force Cambridge Research Laboratories by Ove Harang. The work was initiated under Contract No. AF 19(628)-5731 with Northeastern University, Boston, Massachusetts, and completed under Contract No. AF 61 (052)-906 with the Auroral Observatory, Tromso, Norway.

Because of its importance as a guideline for upper atmosphere temperature measurements from fluorescent chemical releases, it is being published in an AFCRL series to give it wider distribution.

Symbols

e	electronic charge
m	electronic mass
c	velocity of light
h	Planck's constant
$v' (v'')$	vibrational state of upper (lower) electronic state
$K' (K'')$	rotational state of upper (lower) electronic state
N_A, N_V, N_K	population of an electronic, vibrational, rotational level
$\theta, \theta_V, \theta_{XA}$	solar intensity measured in photons $\text{sec}^{-1} \text{cm}^{-2} \text{Hz}^{-1}$
$T, T(A, v', K')$	term value for a level
$A(A, X)$	Einstein factor for spontaneous emission between states A and X
f_{XA}	f-value for a transition X-A
g_X	degree of degeneracy of level X
$S(A, X)$ $S(A, v', K', v'', K'')$	line strength between two states A and X or between two rotational levels K' and K''
$S(v', v'')$	band strength
$q(v', v'')$	Franck-Condon factor for transition v', v''
$p(v', v'')$	transition probability between two levels v', v''
$\bar{r}(v', v'')$	r-centroid for transition v', v''

Symbols

R_e	}	electronic transition moment
R		
(ν', ν'')	}	frequency for a transition
(ν', K', ν'', K'')		
$I(\nu', \nu'')$	}	emission of an electronic-vibrational transition in photons $\text{cm}^{-3} \text{sec}^{-1}$
$I_{\nu' \nu''}$		

Contents

1. INTRODUCTION	1
2. THE AIO MOLECULE	1
3. THE POPULATION OF v'' LEVELS IN THE GROUND STATE	4
4. SOLAR INTENSITY	5
5. THE ABSORPTION-EMISSION PROCESS	7
6. THE VIBRATIONAL SPECTRUM	9
7. INTENSITIES OF TOTAL SEQUENCES	12
8. ERRORS INVOLVED IN THE COMPUTATION	13
9. THE ROTATIONAL INTENSITY DISTRIBUTION	15
10. BAND PROFILES	16
11. RADIATIVE DYNAMICAL EQUILIBRIUM	17
ACKNOWLEDGMENTS	21
REFERENCES	23

Illustrations

1. Term Diagram of the AlO Molecule	2
2. The $A^2\Sigma^+$ and $X^2\Sigma^+$ Levels	3
3. Population of Vibrational Levels of AlO	5
4. Rotational Population of the Ground Vibrational Level $v'' = 0$ of AlO	6
5. Photon Intensity on the Top of the Atmosphere	7
6. Population of the Upper States for Various Temperatures	10
7. Intensity Ratio of Bands Within Different Sequences of AlO as a Function of Temperature	11
8. Intensity Ratio of Sequences as a Function of Temperature	12
9. Intensity Ratio of Bands Within the $\Delta v = +1$ and -1 Sequence as a Function of Temperature	14
10. Synthetic Spectrum of the $\Delta v = 0$ Sequence for Various Temperatures, 2.5 Å Slit Function	16
11. Synthetic Spectrum of the $\Delta v = +1$ Sequence for Various Temperatures, 4.5 Å Slit Function	17
12. Effect of Fraunhofer Correction on Synthetic Spectrum	18
13. Relative Population for the Case Where Lower Levels are not Thermalized	20

AIO Resonant Spectrum for Upper Atmosphere Temperature Determination

1. INTRODUCTION

In recent years, rocket releases of TMA (trimethyl aluminum) trails were performed for upper atmosphere wind studies. When the TMA is released into the atmosphere, it reacts with atomic oxygen in a chemiluminescent reaction forming AIO (aluminum-monoxide). If the trail is exposed to sunlight, a brilliant spectrum is obtained of the blue-green system of AIO ($A^2\Sigma^+ - X^2\Sigma^+$) (Blanton et al, 1961; Armstrong, 1963; and Rosenberg et al, 1964).

Another way of creating AIO is to release an exploding charge seeded with metallic aluminum into the upper atmosphere (Authier et al, 1962, 1963; Armstrong, 1963; and Harang, 1964).

The vibrational-rotational band intensity distribution of the AIO spectrum is temperature dependent. The temperature of the upper atmosphere can be determined through analysis of the AIO spectrum (Authier et al, 1962, 1963, 1964; Harang, 1964; and Authier, 1964).

2. THE AIO MOLECULE

Figure 1 shows the term diagram of the AIO molecule, with transitions indicated.

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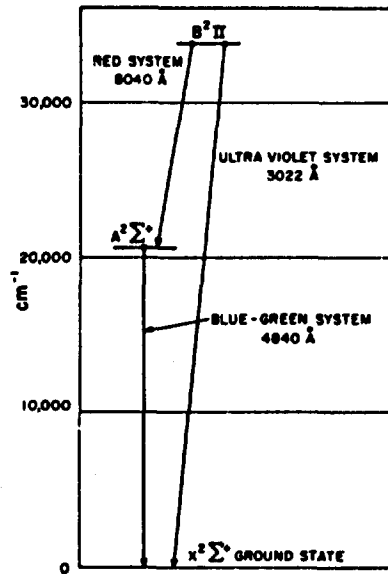


Figure 1. Term Diagram of the AlO Molecule

The only electronic transition recorded in rocket releases is the "blue-green" system $A^2\Sigma^+ - X^2\Sigma^+$. The ultraviolet system $B^2\Pi - A^2\Sigma$ is in a spectral region where photoelectric sensitivity drops appreciably. The intensity of the ultraviolet system is expected to be weak, because the solar radiation intensity at 3000 \AA is one fifth that at 5000 \AA : if the f -values of the two transitions are the same, the absorption intensity of the blue-green system should be five times stronger than the ultraviolet system.

The red system, which shows up only together with the ultraviolet, is expected to be far weaker than the ultraviolet because of the ν^3 factor in the Einstein coefficient. In the present model, only the blue-green system is considered in resonance radiation, neglecting possible filling up of the $A^2\Sigma^+$ level from the $B^2\Pi$ level.

Figure 2 shows the two electronic-vibrational levels and the vibrational-potential curves plotted as a function of internuclear distance. Each vibrational level is built up of rotational levels. The position of a certain electronic-vibrational-rotational level, T , is expressed by the quantum numbers of the electronic, vibrational, and rotational state.

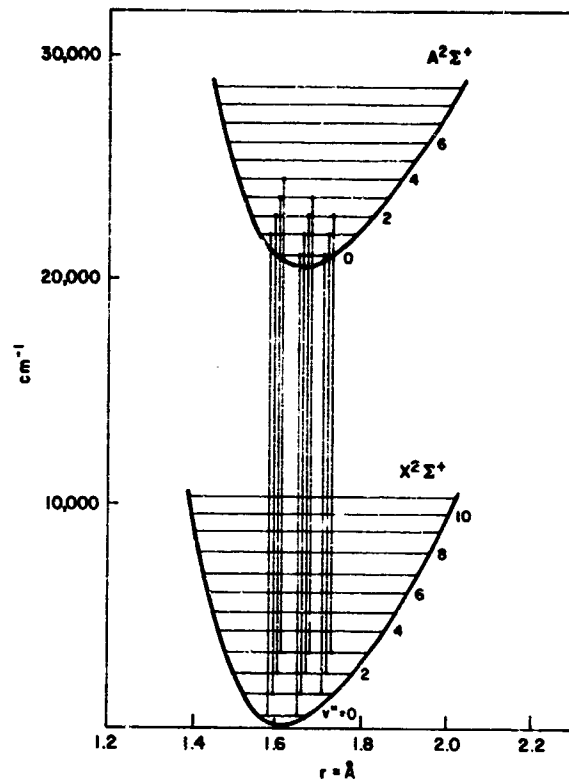


Figure 2. The $A^2\Sigma^+$ and $X^2\Sigma^+$ Levels

$$T(n, v, K) = T_e(n) + T_v(n, v) + T_K(n, v, K)$$

where

$$T_v(n, v) = \omega_n(v + 1/2) + \omega_{x_n}(v + 1/2)^2 + \omega_{y_n}(v + 1/2)^2$$

$$T_K(n, v, K) = B_v K(K+1) + D_n K^2(K^2 + 1)$$

$$B_v = B_n - \alpha(v + 1/2)$$

$$D_n = 4B_n^3/\omega_n^2.$$

The molecular parameters T_e , ω , ω_x , ω_y , B_e , and α are taken from a survey of the AIO molecule by Tyte and Nicholls (1964).

In this report, the following set of parameters was used:

State	T_e	ω	ω_x	ω_y	B_e	α
$A^2\Sigma^+$	20.68895	870.05	3.52	0.0	0.6040	0.0044 cm^{-1}
$X^2\Sigma^+$	0.0	979.23	6.97	0.0	0.6413	0.0058 cm^{-1}

3. THE POPULATION OF v'' LEVELS IN THE GROUND STATE

Following the formation of AlO molecules, they will collide with air molecules, and the populations of the different rotational and vibrational levels will be given by the Boltzmann distribution law.

For vibration levels

$$N_{v''} = Q_v^{-1} \exp - (G_0(v'')/0.6958T),$$

where

$$Q_v = \sum_{v''} \exp - (G_0(v'')/0.6958T),$$

and

$$G_0(v'') = (\omega - \omega_x) v'' - \omega_x (v'')^2.$$

For rotational levels

$$N_{K''} = (2K'' + 1) Q_K^{-1} \exp - (F(K'')/0.6958T),$$

where

$$Q_K = \sum_{K''} (2K'' + 1) \exp - (F(K'')/0.6958T),$$

and

$$F_K = B K'' (K'' + 1) - D (K'')^2 (K'' + 1)^2.$$

Figures 3 and 4 show plots of the populations $N_{v''}$ and $N_{K''}$ as a function of the levels and for different temperatures. Here $N_{v''}$ and $N_{K''}$ are normalized, $\sum_{v''} N_{v''} = \sum_{K''} N_{K''} = 1$.

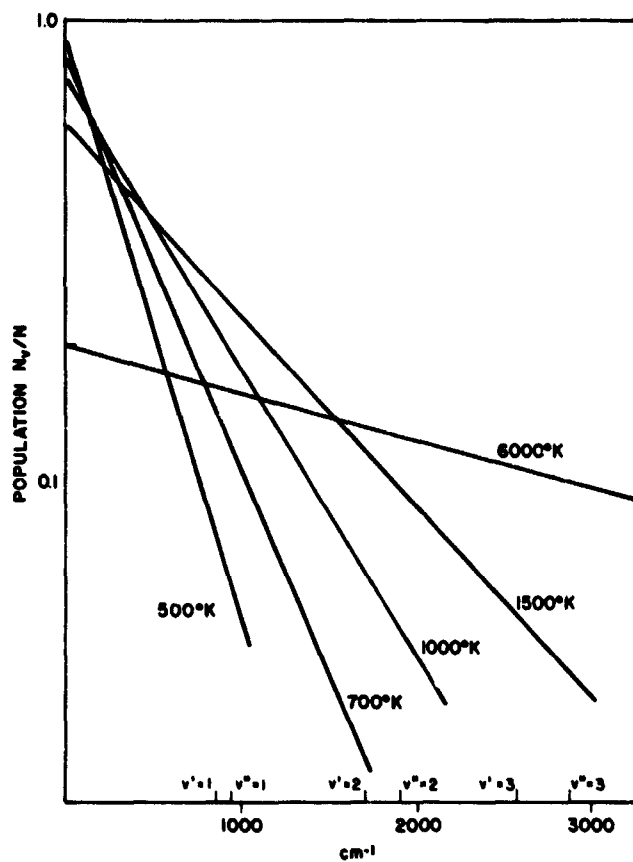


Figure 3. Population of Vibrational Levels of AlO

4. SOLAR INTENSITY

To compute the absorption rates, we need to know the photon intensity of the solar radiation on the top of the atmosphere. Figure 5 shows the intensity measured in photons $\text{cm}^{-2} \text{sec}^{-1}/(\text{cm}^{-1})$ and in photons $\text{cm}^{-2} \text{sec}^{-1} \text{Hz}^{-1}$ as a function of wave numbers. The values are deduced from the Handbook of Geophysics (1960) integrated over intervals of 50 Å and 100 Å, including the Fraunhofer lines that are about 0.1 to 0.5 Å wide.

The rotational lines of AlO are about 0.5 Å apart, except at the bandhead.

For vibrational analysis, the entire band intensity is measured, covering about 20 to 30 Å. Solar intensities averaged over 20 to 30 Å do not deviate much from values averaged over 50 Å.

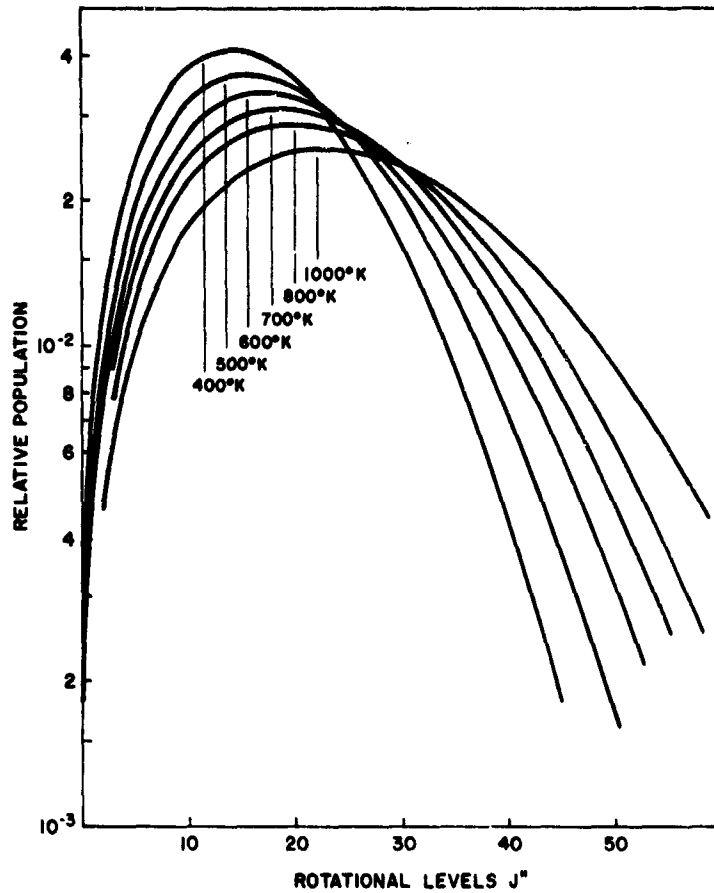


Figure 4. Rotational Population of the Ground Vibrational Level $v'' = 0$ of AlO

The emission from a certain v' -level is caused by absorption from several v'' -levels, so this will tend to smooth out the deviation from the averaged solar intensity at the wavelength of an individual transition.

There exists one strong and broad Fraunhofer line, H_{β} , which happens to lay just on the P-branch of the 0-0 transition. For 600°K this correction amounts to less than 10 percent of the branch, which is less than 5 percent for the entire 0-0 transition.

For rotational analysis, it is of importance to consider the Fraunhofer correction of solar intensity for those rotational lines which are strong in absorption.

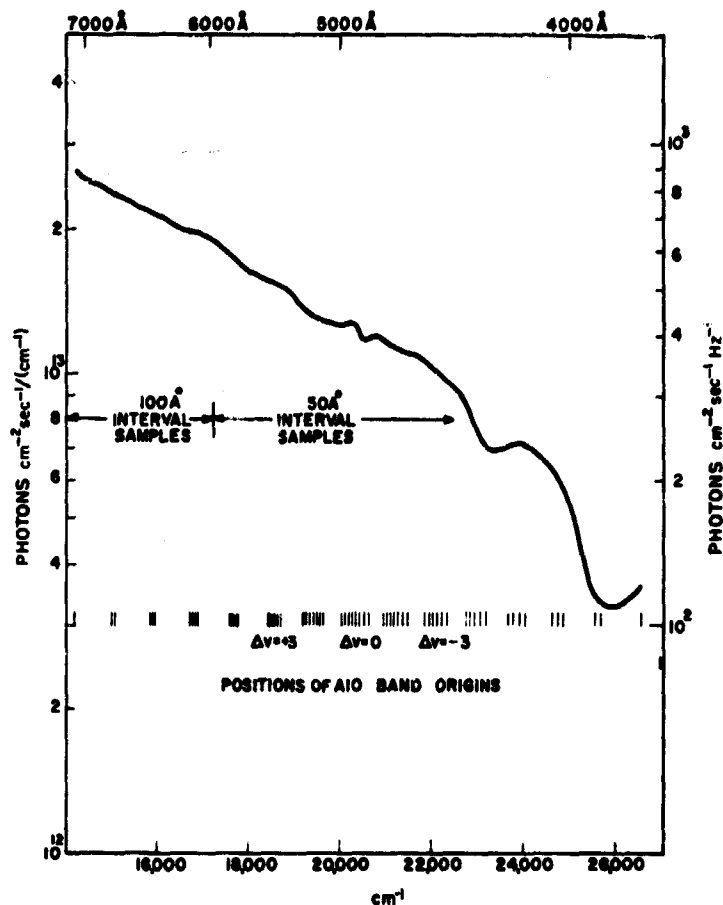


Figure 5. Photon Intensity on the Top of the Atmosphere

5. THE ABSORPTION-EMISSION PROCESS

In order to compute the theoretical intensities of bands and lines of an assembly of AIO molecules in the upper atmosphere exposed to solar radiation, the following model is considered.

A short time after formation of AIO, the molecules will attain thermodynamic equilibrium with the atmosphere, and the vibrational and rotational levels will have a population according to the Boltzmann distribution law.

The molecules undergo a resonant absorption followed by emission. The transition probability is in the order of $10^7 - 10^8 \text{ sec}^{-1}$.

The emission-absorption processes will tend to perturb the thermal distribution of the lower levels. It is assumed that the rate of the absorption-emission process is relatively slow, so that there is a sufficient time lapse between each

absorption-emission process per molecule to allow the molecules to readjust to the Boltzmann distribution through collisions with atmospheric molecules.

This depends on the f -value of the electronic transition of the AlO molecule, the collision frequency in the upper atmosphere, and the cross section for collisional deactivation of vibrational levels.

The rate of excitation from level X to level A is expressed by:

$$\frac{dN_A}{dt} = N_X \frac{\pi e^2}{m c} f_{XA} \theta_\nu = N_X \frac{8 \pi^3}{3 h c} \frac{S(A,X)}{g_X} \theta_\nu \nu$$

where θ is the solar photon intensity, which is about $400 \text{ photons cm}^{-2} \text{ sec}^{-1} \text{ Hz}^{-1}$ in the region where AlO absorbs. The f -value is unknown, but it must be reasonably large because the trail is almost as brilliant as a sodium trail. The density of sodium atoms in such trails is probably of the same order of magnitude as that of AlO, and the f -value of sodium is 0.98.

If f_{XA} is in the order of 0.1 to 1, there will be about 1 to 0.1 absorptions per second per molecule, which leaves the molecule about 1 to 10 sec to attain thermal distribution between each excitation.

The number of collisions required for thermal redistribution varies within large limits. The collision frequency in the upper atmosphere is 2 to $3 \times 10^3 \text{ sec}^{-1}$ at 100 km, $20 \text{ collisions sec}^{-1}$ at 150 km, and $10 \text{ collisions sec}^{-1}$ at 170 km, according to the U.S. Standard Atmosphere 1962. This problem is further discussed under Section 11.

The line strength $S(A,X)$ for an allowed transition is defined as:

$$S(A,X) = |R_{AX}|^2 = |\langle A | \bar{p} | X \rangle|^2$$

where \bar{p} here is the dipole moment. The degeneracy g_X of the lower state of AlO equals two (doublet).

The electronic levels are composed of vibrational levels, and the expression for absorption from a lower level v' to an upper level v'' is

$$\frac{dN_{v'}}{dt} = N_X N_{v''} \frac{8 \pi^3}{3 h c} \nu(v', v'') S(v', v'') \theta(v', v'')$$

Here the band strength is (Tyte and Nicholls, 1964):

$$S(v', v'') = R_e^2 (1 - 0.46 \bar{F}(v', v''))^2 q(v', v'')$$

The vibrational levels are in turn composed of rotational levels. The rate of population of an upper rotational level K' from the lower level K'' is

$$\frac{dN_{K'}}{dt} = N_X N_{v''} N_{K''} \frac{8\pi^3}{3hc} \nu(v', K', v'', K'') S(v', v'') \frac{S(K', K'')}{2K'' + 1}.$$

The transition considered for AlO is $A^2\Sigma^+ - X^2\Sigma^+$, thus $K' - K''$ can only have values of $+1$ or -1 .

$$K' - K'' = -1 \text{ (P-branch), } S(K', K'') = K' + 1 = K''$$

$$K' - K'' = +1 \text{ (R-branch), } S(K', K'') = K' = K'' + 1$$

In emission, the rate of electronic transitions from A to X is:

$$\frac{dN_A}{dt} = N_A A_{AX} = N_A \frac{64\pi^4 \nu_{AX}^3}{3hc^3} \frac{S(A, X)}{g_A}.$$

Here the degeneracy g_A also equals two.

The rate of vibrational transition is:

$$\frac{dN_{v'}}{dt} = N_A N_{v'} \frac{64\pi^4 \nu(v', v'')^3}{3hc^3} S(v', v''),$$

and a similar expression for a rotation transition is:

$$\frac{dN_{K'}}{dt} = N_A N_{v'} N_{K'} \frac{64\pi^4 \nu(v', K', v'', K'')^3}{3hc^3} S(v', v'') \frac{S(K', K'')}{2K'' + 1}.$$

6. THE VIBRATIONAL SPECTRUM

The population rate for level v' caused by absorption is:

$$\frac{dN_{v'}}{dt} \propto \sum_{v''} N_{v''} S(v', v'') \nu(v', v'') \theta(v', v'').$$

The depopulation rate caused by emission from an upper level v' is:

$$\frac{dN_{v'}}{dt} \propto N_{v'} \sum_{v''} \nu(v', v'')^3 S(v', v'').$$

These two rates are equal in dynamic equilibrium and we can deduce the relative population as

$$N_{v'} \propto \frac{\sum_{v''} N_{v''} S(v', v'') \nu(v', v'') \theta(v', v'')}{\sum_{v''} \nu(v', v'')^3 S(v', v'')}$$

Figure 6 shows the plots of the relative population $N_{v'}/N_{v'=0}$ as a function of temperature.

Having computed the values of $N_{v'}/N_{v'=0}$, the intensities of the bands can be computed:

$$I(v', v'') \propto \left[\frac{\sum_{v''} N_{v''} S(v', v'') \nu(v', v'') \theta(v', v'')}{\sum_{v''} S(v', v'') \nu(v', v'')^3} \right] S(v', v'') \nu(v', v'')^3.$$

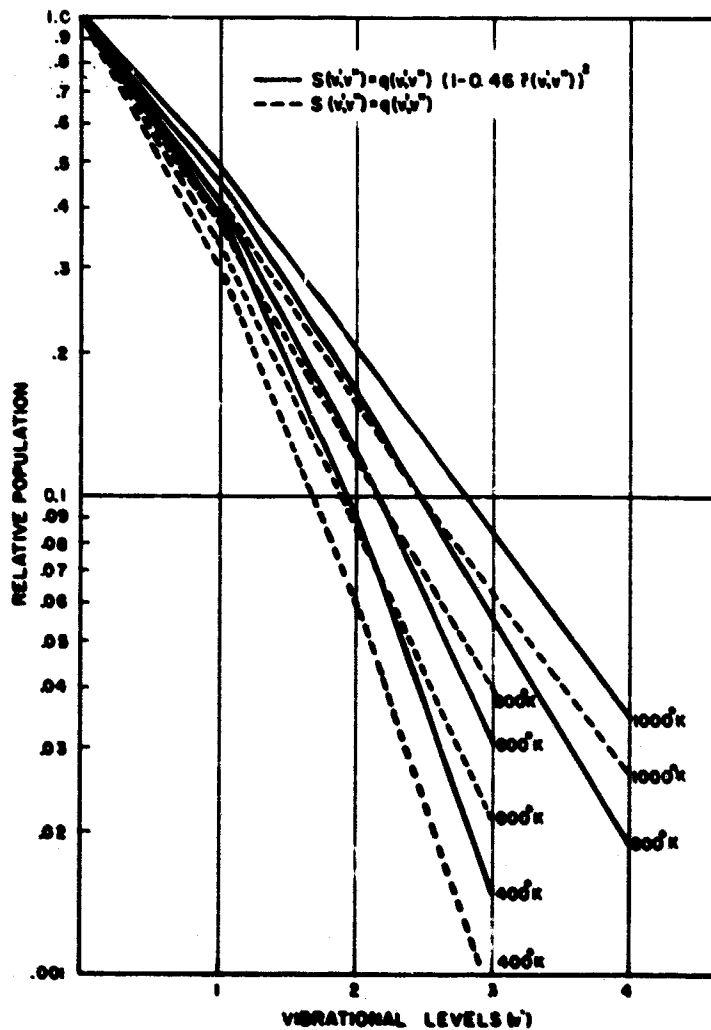


Figure 6. Population of the Upper States for Various Temperatures

Figure 7 gives the relative intensities of bands within the $\Delta v = -1, 0,$ and $+1$ sequence as a function of temperature. The sequence which is the most sensitive to temperature variation is the $+1$ sequence. Unfortunately, the intensity of this sequence is the weakest of the three sequences (see Figure 8). The strongest one, the $\Delta v = 0$ sequence, shows almost no temperature dependence.

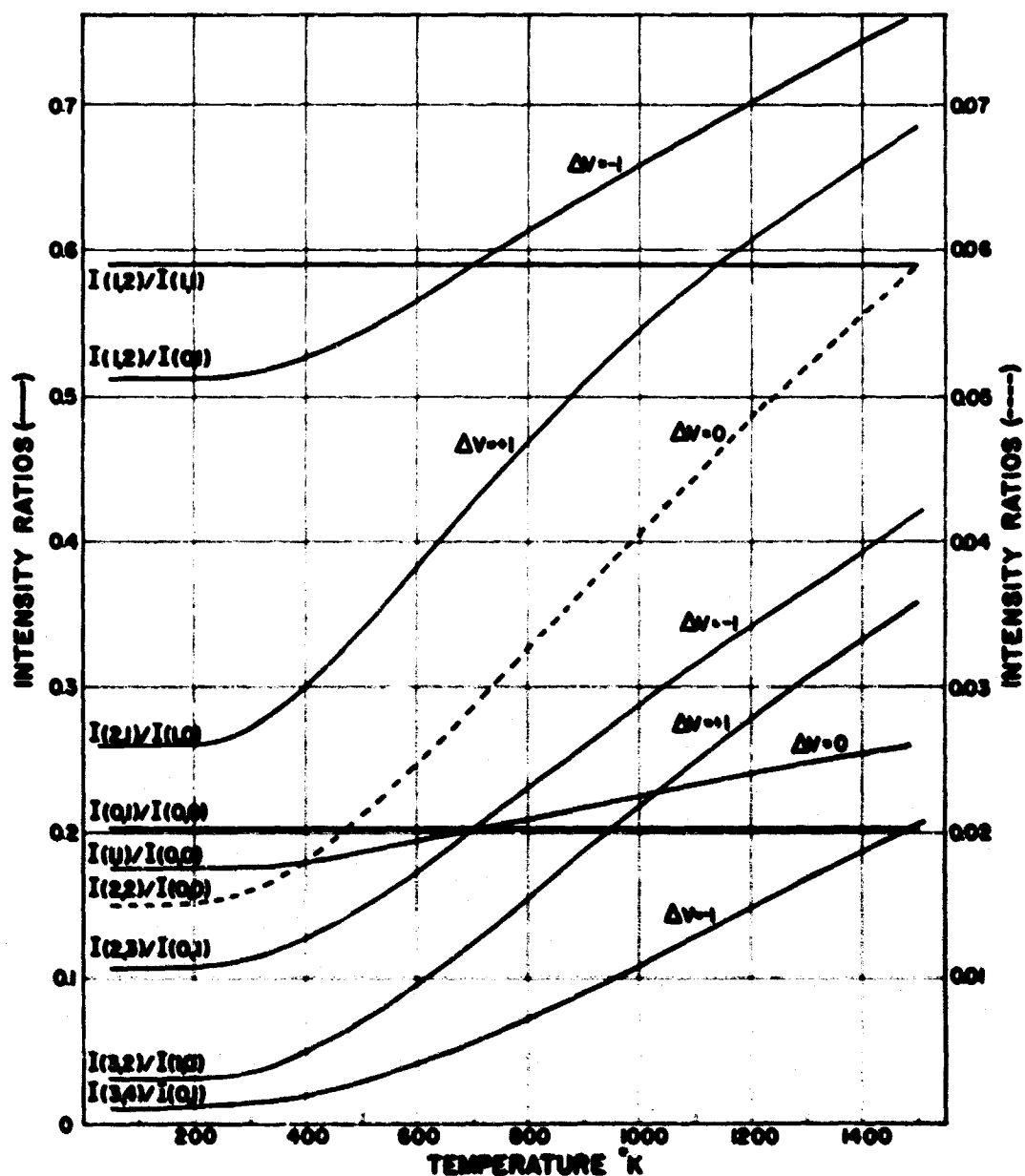


Figure 7. Intensity Ratio of Bands Within Different Sequences of AlO as a Function of Temperature

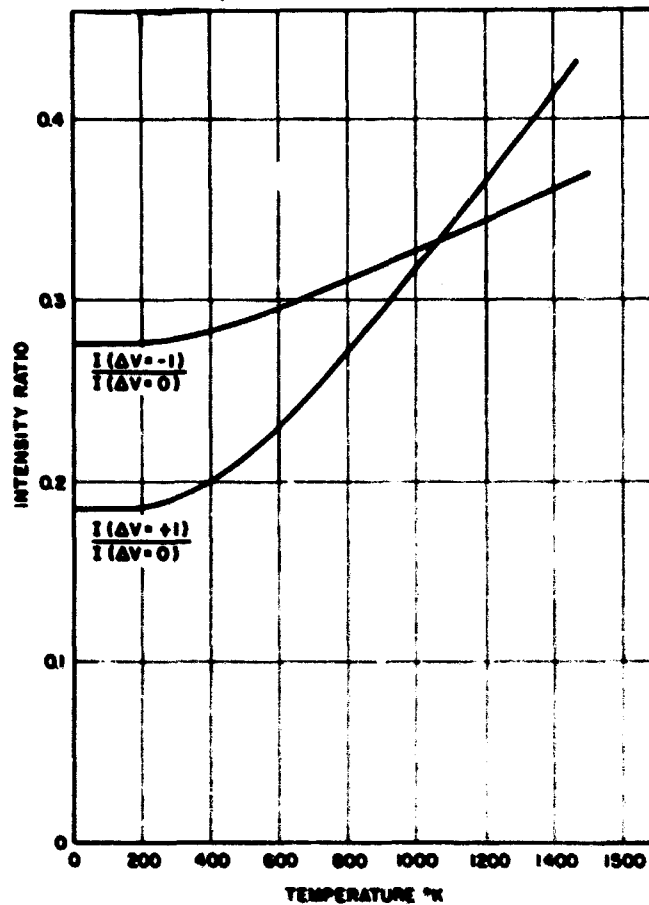


Figure 8. Intensity Ratio of Sequences as a Function of Temperature

7. INTENSITIES OF TOTAL SEQUENCES

So far, the band intensities within each sequence and their temperature variation were deduced. There is also a temperature dependence of the total intensity ratio of different sequences.

Using the intensities computed in Section 5, all the intensities within each sequence can be added. The intensity ratios $\Delta\nu = -1/\Delta\nu = 0$ and $\Delta\nu = +1/\Delta\nu = 0$ are plotted in Figure 8 as a function of temperature.

The advantage of measuring the sequence intensities is that it is not necessary to use a high-resolution spectrometer. A photometer with interference filters of 50 Å half-width will suffice.

The optical throughput of a photometer can be made very big compared to a spectrometer, and the intensities can be measured with high precision.

In order to deduce temperatures, the filter profile must be known as well as the transmission of the optical system and the sensitivity of the detector. But even without precise knowledge of these constants, we can record variations along trails and obtain a temperature profile, although an absolute value of the temperature might be difficult to obtain.

It is noticed that there is very little temperature dependence for temperatures below 500°K.

8. ERRORS INVOLVED IN THE COMPUTATION

The accuracy of the computed intensities depends mainly on the following items:

1. The validity of the model adopted, that is, complete thermalization of the lower v^n -levels between each excitation-emission event, and
2. The accuracy of the parameters used in the computation.

The parameters used are as follows. The transition strength $S(v', v^n)$ expressed by the product of the Franck-Condon factor $q(v', v^n)$ and the electronic transition factor $(1 - 0.46 (v', v^n))^2$, and the intensity of the solar radiation corrected for the Fraunhofer absorption lines $\theta(v', v^n)$.

Until recently, all temperature deductions were based on the approximation that the transition strength $S(v', v^n)$ is expressed by the Franck-Condon factor $q(v', v^n)$ without the r -centroid correction.

The five curves in Figure 9 illustrate how the relative intensities of bands are affected by some adjustment of the transition strengths and solar intensities.

Curve 1. The transition strengths $S(v', v^n)$ were calculated using the $q(v', v^n)$ values with r -centroid correction. The solar intensities were obtained from the Handbook of Geophysics (1960).

Curve 2. Transition strengths as in Curve 1, but with solar intensities equivalent to those of a blackbody at 6000°K.

Curve 3. Without any r -centroid correction, $F = 0$, but with the same solar intensities as in Curve 1.

Curves 4 and 5. With the intensity ratios computed by Authier (1964) and Armstrong (1963) respectively, where the transition strengths $S(v', v^n)$ were calculated using only the Franck-Condon factors.

From the five curves in Figure 9, the following conclusions can be reached:

1. The intensity ratios are not very sensitive to errors in the solar intensities.
2. The r -centroid correction is important. Without this correction, the deduced temperatures will be far too high (about 300°K for the -1 sequence and about 100°K for the 0 sequence).

3. There are some discrepancies between our computed ratios and those taken from Authier (1964) and Armstrong (1963). The latter are shown as dashed curves.

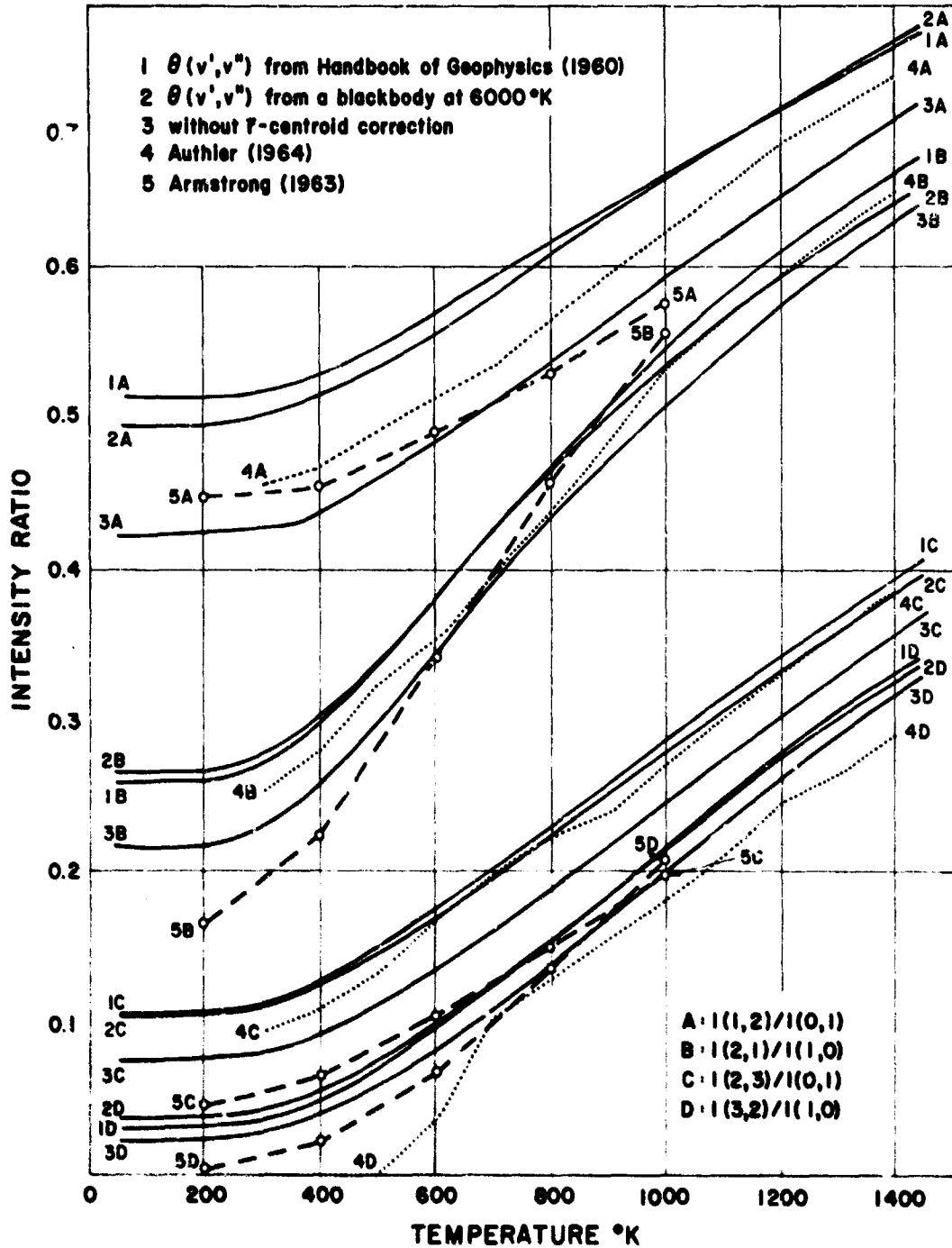


Figure 9. Intensity Ratio of Bands Within the $\Delta v = +1$ and -1 Sequence as a Function of Temperature

9. THE ROTATIONAL INTENSITY DISTRIBUTION

The rate of absorption into an upper level K' is

$$\begin{aligned}
 \frac{dN_{K'}}{dt} &= \sum_{K''} \sum_{v''} N_X N_{v''} N_{K''} \frac{8\pi^3}{3hc} \nu(v', K', v'', K'') \frac{S(K', K'')}{2K'+1} \theta(v', K', v'', K'') \\
 &= N_X \frac{8\pi^3}{3hc} \sum_{v''} N_{v''} S(v', v'') \left[N_{K'+1} \frac{K'+1}{2K'+3} \nu(v', K', v'', K'+1) \theta_P + \right. \\
 &\quad \left. + N_{K'-1} \frac{K'}{2K'-1} \nu(v', K', v'', K'-1) \theta_R \right] \\
 &\equiv N_X \frac{8\pi^3}{3hc} A(v', K'), \quad \text{where } N_{K''} = \frac{2K''+1}{Q_K} \exp\left(-\frac{F(K'')}{0.6952T}\right). \quad (1)
 \end{aligned}$$

The rate of emission from an upper level K' is

$$\begin{aligned}
 \frac{dN_{K'}}{dt} &= \sum_{K''} \sum_{v''} N_A N_{v'} N_{K'} \frac{64\pi^4}{3hc^3} \nu(v', K', v'', K'')^3 S(v', v'') \frac{S(K', K'')}{2K'+1} \\
 &= N_A \frac{64\pi^4}{3hc^3} \frac{N_{v'} N_{K'}}{2K'+1} \sum_{v''} S(v', v'') \left[(K'+1) \nu(v', K', v'', K'+1)^3 + \right. \\
 &\quad \left. + K' \nu(v', K', v'', K'-1)^3 \right] \equiv N_A \frac{64\pi^4}{3hc^3} N_{v'} N_{K'} \frac{1}{2K'+1} E(v', K'). \quad (2)
 \end{aligned}$$

These two rates are equal, and the population in the upper states is, therefore, given by

$$N_A N_{v'} N_{K'} \frac{64\pi^4}{3hc^3} = N_X \frac{8\pi^3}{3hc} (2K'+1) \frac{A(v', K')}{E(v', K')}. \quad (3)$$

The theoretical intensities are

$$I(v', K', v'', K'') = N_X \frac{8\pi^3}{3hc} \frac{A(v', K')}{E(v', K')} S(v', v'') S(K', K'') \nu(v', K', v'', K'')^3 \quad (4)$$

with

$$I_P = N_X \frac{8\pi^3}{3hc} \frac{A(v', K')}{E(v', K')} \cdot S(v', v'') \cdot (K'+1) \cdot \nu(v', K', v'', K'+1)^3 \quad (5)$$

and

$$I_R = N_X \frac{8\pi^3}{3hc} \frac{A(v', K')}{E(v', K')} \cdot S(v', v'') \cdot K' \cdot \nu(v', K', v'', K'+1)^3 \quad (6)$$

In order to compute I_P and I_R , we must know the solar intensities corrected for Fraunhofer lines for transitions which are strong in absorption.

We select only the following vibrational transitions which have to be corrected for Fraunhofer absorption: $v' - v'' = 0-0, 0-1, 1-0,$ and $1-1$. Thus, about 500 lines of importance are obtained.

10. BAND PROFILES

Using Eq. (4) for the theoretical intensities of the lines, the band profiles for different temperatures can be computed.

To be able to compare these band profiles with the recorded ones, a convolution with a known slit function is performed. The empirical slit function is obtained by letting the spectrometer scan a single line.

Figure 10 shows a group of theoretical spectra for temperatures ranging from 300°K to 900°K, all smeared with a slit function of 2.5 Å width. The spectral range is in the domain of $\Delta v = 0$, with three vibrational transitions.

Figure 11 shows band profiles from the $\Delta v = +1$ sequence, smeared with a slit function of 4.5 Å width. The band profiles were corrected for Fraunhofer absorption.

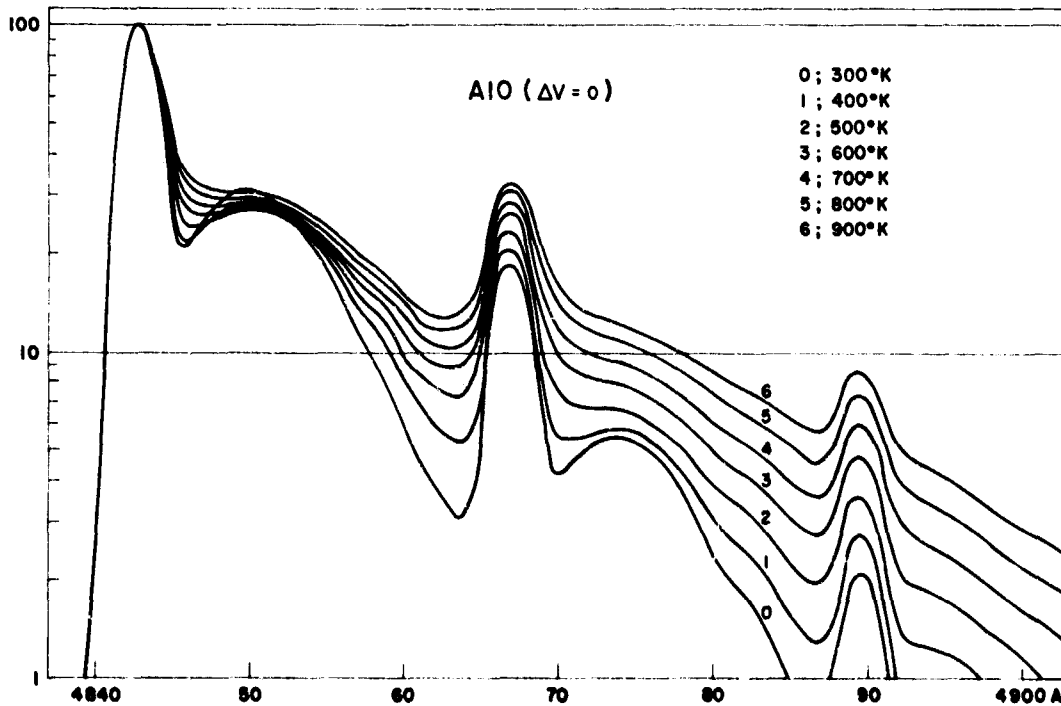


Figure 10. Synthetic Spectrum of the $\Delta v = 0$ Sequence for Various Temperatures, 2.5 Å Slit Function

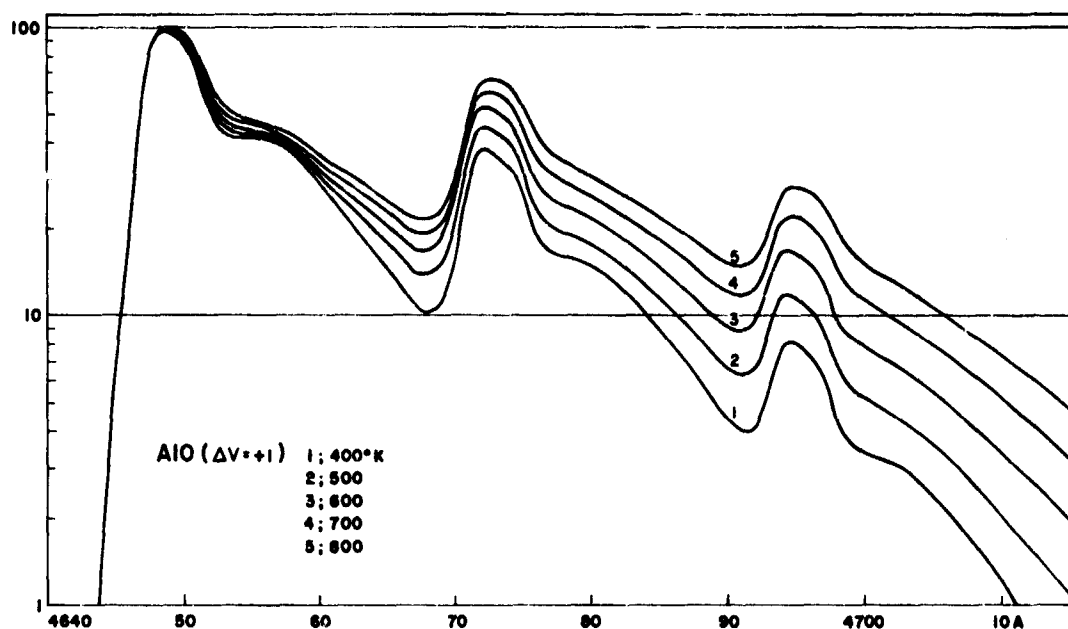


Figure 11. Synthetic Spectrum of the $\Delta v = +1$ Sequence for Various Temperatures, 4.5 Å Slit Function

The effect of Fraunhofer absorption on the emission bands is demonstrated in Figure 12 for a temperature of 700°K. These profiles were obtained by using the same slit function as for Figure 10. It is seen that the two profiles differ appreciably.

11. RADIATIVE DYNAMICAL EQUILIBRIUM

The deduction of temperatures from spectra is based upon the assumption that the molecules undergo a sufficient number of collisions to thermalize their distribution of vibrational levels between each excitation-emission process.

To see what the vibrational spectrum would look like were this not the case, we assume now that the rate of collisional redistribution is very slow compared to the rate of excitation followed by emission.

The rates of the electronic transition into and from an upper level are, respectively:

$$\left[\frac{dN'_A}{dt} \right]_{in} = N_A \frac{8 \pi^3 \bar{\nu}}{3hc} R_e^2 \bar{\theta}_v \quad \text{and} \quad \left[\frac{dN'_A}{dt} \right]_{out} = N'_A \frac{64 \pi^4 \bar{\nu}^3}{3hc^3} R_e^2 .$$

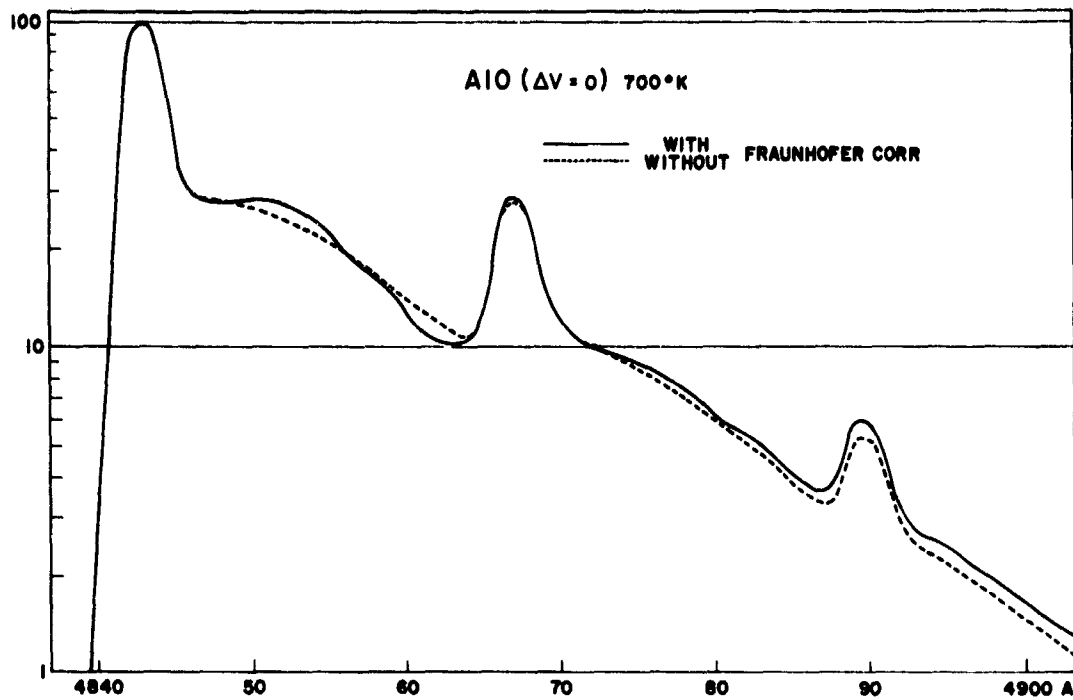


Figure 12. Effect of Fraunhofer Correction on Synthetic Spectrum

These two rates must be equal for stationary-state conditions:

$$N'_A = N_A \frac{c^2}{8\pi\nu^2} \bar{\theta}_\nu.$$

Taking into account the vibrational levels, the rate of transitions into an upper level ν' is equal to the rate of transitions from that level:

$$\sum_j N_j'' \nu_{ij} S_{ij} \theta_{ij} = N_i' \frac{\bar{\theta}_\nu}{\nu^2} \sum_k S_{ik} \nu_{ik}^3.$$

Here

$$\nu_{ij} = \nu(\nu_i', \nu_j''), \quad \theta_{ij} = \theta(\nu_i', \nu_j''),$$

and

$$S_{ij} = S(\nu_i', \nu_j'') \approx |R_c|^2 (1 - 0.46 \bar{r}(\nu_i', \nu_j''))^2 q(\nu_i', \nu_j'').$$

For the lower level, we obtain the equation

$$N_1'' \sum_m v_{ml} S_{ml} \theta_{ml} = \frac{\bar{\theta}}{v^2} \sum_n N_n' S_{nl} v_{nl}^3.$$

By eliminating N' and N'' between the two systems, two sets of homogeneous equations are obtained, the solution of which gives the relative vibrational populations N_i' and N_j'' in the upper and lower electronic state.

$$N_i' \sum_k W_{ik} = \sum_j U_{ij} \frac{\sum_n N_n' W_{nj}}{\sum_m U_{mj}}$$

$$N_1'' \sum_m U_{ml} = \sum_n W_{nl} \frac{\sum_j N_j'' U_{nj}}{\sum_k W_{nk}}$$

where $W_{ik} \equiv S_{ik} v_{ik}^3$ and $U_{ml} \equiv S_{ml} v_{ml} \theta_{ml}$.

Let us consider values of v' and v'' from 0 to 7. The two systems are homogeneous sets of eight equations each, and it enables us to deduce the relative values of $N_{v'}'/N_{v'=0}'$ and $N_{v''}''/N_{v''=0}''$. Figure 13 shows the values of $N_{v'}'/N_{v'=0}'$ plotted as a function of v' (the trace marked "8 levels").

Our system is limited to eight equations, and it is an open question if it is sufficient. In order to see the trend, we reduce the system to six and then to four equations, which we solve.

Figure 13 shows that the curves marked "6 levels" and "4 levels" do not deviate much from the "8 level" curve, which indicates that the system is sufficiently large.

Comparing Figure 13 with Figure 6, it is seen that the assumption of solar radiation equilibrium leads to relative populations in the upper vibrational levels which are far greater than those obtained by assuming thermal equilibrium with the ambient. Since the number of collisions required for vibrational thermalization is usually large ($10^2 - 10^4$), it would appear that the vibrational temperature will be equal to ambient temperature at altitudes up to 120 km, where the collision frequency is about 150 sec^{-1} . However, experiments performed by Blamont et al (1961) and by AFCRL (to be published) indicate that plausible temperatures can be deduced from clouds deposited as high as 170 km (approximately one collision sec^{-1}). This means that most of the upper state molecules are excited from thermalized ground state molecules. This could be due to continuous formation of AIO from the released TMA. Clearly, the rate processes have to be examined in more detail for accurate temperature measurements.

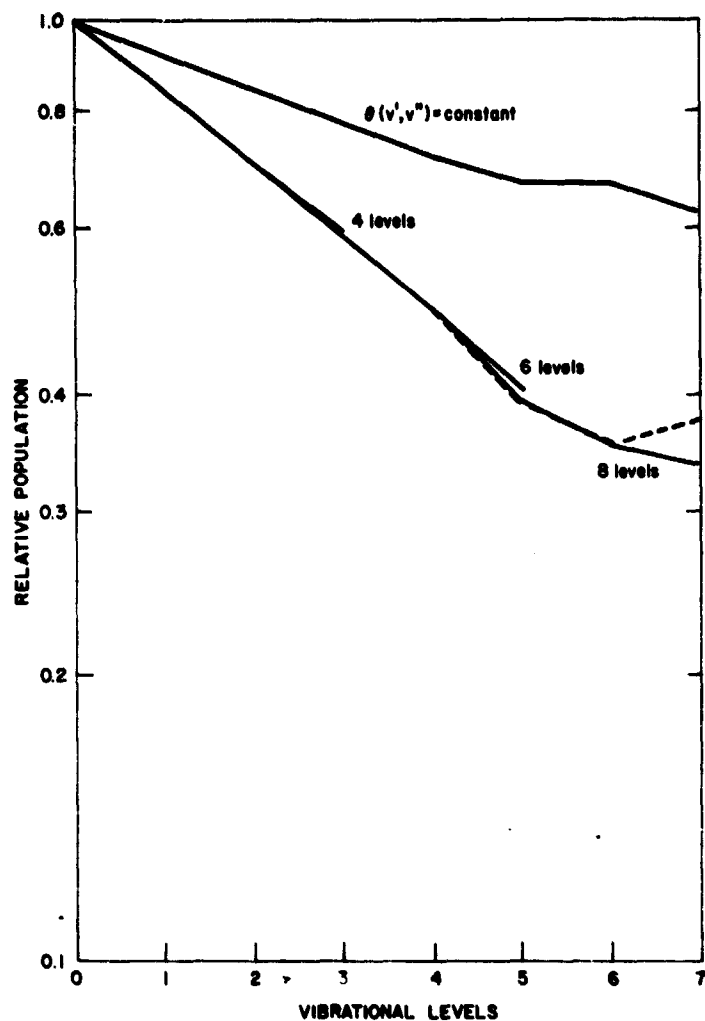


Figure 13. Relative Population for the Case Where Lower Levels are not Thermalized

It is also questionable if the population is sensitive to errors in the value of the transition strength $S(v', v'')$. By leaving out the r -centroid correction, the values of $S(v', v'')$ become equal to the Franck-Condon factors. The solution of the set of equations based on this simplification is indicated by a dashed line in Figure 13. It does not deviate much from the other one.

The solar intensity changes within the range of the spectrum of AlO by a factor of ten. To determine how the population is influenced by the shape of the solar intensity curve, we let the intensity be constant and obtained the curve marked " $\theta(v', v'') = \text{constant}$." A small inaccuracy in the solar intensity curve would not greatly change the $N_{v',0}/N_{v',0}$ values.

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