INTERNAL PARTITION FUNCTION FOR THE NO MOLECULE; INTEGRATED LINE ABSORPTION CROSS-SECTIONS FOR THE $A^2\Sigma\text{-}X^2\Pi$ $\gamma(1\text{-}0)$ AND $\gamma(2\text{-}0)$ BANDS

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Abstract—Internal partition functions for the NO molecule have been calculated for the range 100–1000 K at 10 K intervals using a direct summation over all the individual levels involved. Relative populations of the $v = 0$ level of the fundamental $X^2\Pi$ state have been deduced.

The integrated line absorption cross sections of the $\gamma(1\text{-}0)$ and $\gamma(2\text{-}0)$ bands have been determined for the same range of temperature.

I. INTRODUCTION

IN RECENT years, nitric oxide NO, one of the minor atmospheric constituents, has appeared to play an important role in stratospheric processes, especially with regard to ozone photochemistry (see Nicolet[1]). Thus the determination of NO distribution above the tropopause has become an important problem of stratospheric aeronomy. A method of investigation is to observe the NO absorption lines in the solar spectrum. But a correct quantitative interpretation requires knowledge of the absolute line intensities of NO in the spectral range considered, in order to determine the integrated line absorption cross sections as a function of temperature. It is the purpose of this work to provide these needed data.

II. PARTITION FUNCTION AND RELATIVE POPULATION

The internal partition function for the NO molecule is given by the expression

$$Q_T = 2 \sum_v \sum_{\Sigma=-1/2}^{+1/2} \sum_{J=1/2}^{\infty} (2J+1)\{\exp - [hcE(v,\Sigma,J)/kT]\} \tag{1}$$

where v and J are the vibrational and rotational quantum numbers respectively, Σ is the spin projection on the internuclear axis ($\pm \frac{1}{2}$), E is the energy of the ground state expressed in cm^{-1}, h and k are Planck's and Boltzmann's constants, respectively, and T is the absolute temperature.

The energy $E(v, \Sigma, J)$ can be calculated by means of the expression derived by Bennett[2] for the energies of a doublet in the intermediate case, using experimental values of the $X^2\Pi$ ground state molecular constants. The adopted values taken from James and Thibault[3] are listed in Table 1, where A_v is the spin–orbit coupling constant, B_v is the rotational constant, D_v is the centrifugal distorsion constant, and γ_v is the spin–rotation interaction constant.

The internal partition function has been computed for the temperature range 100–1000 K, at

Table 1. $X^2\Pi$ ground state molecular constants (cm^{-1})

v	A_v	B_v	D_v	γ_v
0	123·160	1·69618	5·510^{-6}	10^{-4}
1	122·911	1·67862	5·510^{-6}	10^{-4}

10 K intervals, by direct summation of equation (1) to yield Q_T. The summation was performed only for the $v = 0$ and $v = 1$ levels since the contribution of the upper vibrational levels to the summation is negligibly small. For comparison, we have also calculated the partition function according to the approximate expression (see MAYER and MAYER[4])

$$Q_A = 2\frac{[1 + \exp - (hc\,\Delta W/kT)]}{[1 - \exp - (hc\omega/kT)]} \left(\frac{kT}{hcB_e} + \frac{1}{3} + \frac{1}{15}\frac{hcB_e}{kT} \cdots\right);\qquad(2)$$

here ΔW is the separation between the spin components, $\omega = 1903·855\,\text{cm}^{-1[5]}$ is the vibrational frequency, and $B_e = 1·70487$ is the ground state rotational constant.[6] Table 2 gives the results obtained in 50 K steps. The first column refers to Q_A and the second column to Q_T.

Assuming that NO is in thermodynamic equilibrium, we are able to deduce the relative population N_J/N_{total} of the two spin components in the $v = 0$ state, namely,

$$\frac{N_J}{N_t} = \frac{2(2J + 1)\exp - [hcE(\Sigma, J)/kT]}{Q_T}.\qquad(3)$$

Figure 1 shows the relative populations in the $X^2\Pi$ state for $v = 0$ at a temperature of 220 K;

Table 2. Internal partition function for the temperature range 100–1000 K: (a) according to the approximate expression: Q_A; (b) by direct summation over all levels: Q_T

| $T(°K)$	Q_A	Q_T
100	96·7934	98·7475
150	161·8117	163·9535
200	232·7122	235·1090
250	306·8969	309·6195
300	383·0912	386·2031
350	460·6682	464·2317
400	539·3599	543·4429
450	619·1129	623·7909
500	700·0003	705·3550
550	782·1636	788·2757
600	865·7734	872·7138
650	951·0064	958·8241
700	1038·0314	1046·7421
750	1127·0027	1136·5765
800	1218·0575	1228·4083
850	1311·3157	1322·2915
900	1406·8809	1418·2563
950	1504·8421	1516·3111
1000	1605·2755	1616·4470
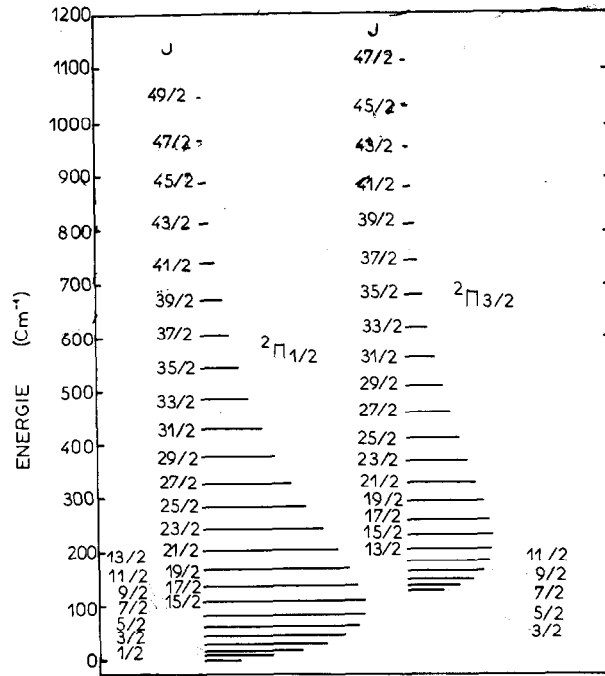
Fig. 1. Relative populations of the $X^2\Pi$, $v = 0$, levels for 220 K.
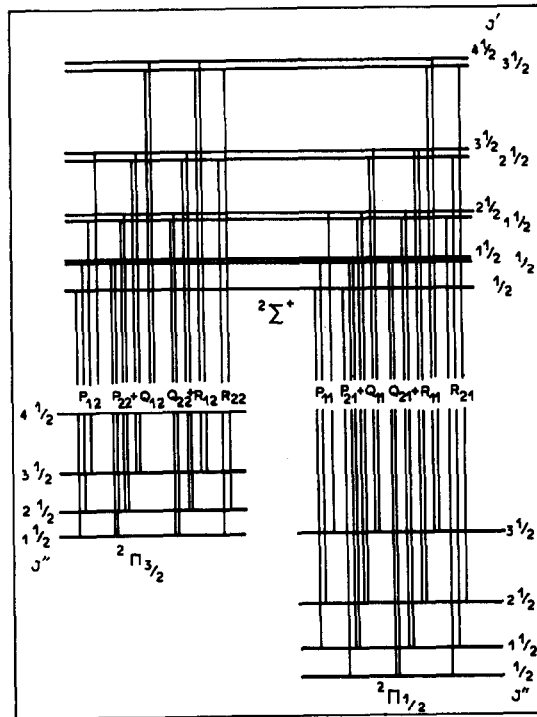

Fig. 2. Energy-level diagram for NO.

the levels are represented as horizontal bars with lengths proportional to their population. We chose 220 K as an example of a typical temperature for the lower stratosphere.

Detailed tabulations of population ratios may be obtained on request from the authors.

III. INTEGRATED LINE ABSORPTION CROSS-SECTIONS
OF THE $\gamma(1-0)$ AND $\gamma(2-0)$ BANDS

The existence of a transmission window in the atmosphere between the Schumann–Runge bands of molecular oxygen and the Hartley bands of ozone enables us to observe NO bands appearing in this spectral range. Among these bands, two γ-bands have large transition probabilities: the $\gamma(1-0)$ and $\gamma(2-0)$ bands. Figure 2 shows a schematic diagram of all possible transitions within a γ-band. Figure 3 gives the solar spectrum available at different altitudes from 15 km up to 35 km at a zenithal angle of $0°$. The calculation was performed allowing for the ozone and molecular oxygen absorption and the Rayleigh attenuation. The O_2 and O_3 cross sections were taken from ACKERMAN;[7] the computation was made for various zenith angles.

The method used for the determination of the integrated line absorption cross-sections $\int \sigma_\nu \, d\nu$ of the $\gamma(1-0)$ and $\gamma(2-0)$ bands is essentially the same as that already described (CIESLIK and NICOLET[8]), viz.,

$$\int \sigma_\nu \, d\nu = [\pi e^2 S_J / mc^2 (2J + 1)] f_{v'v''}(N_J / N_t),$$ (4)

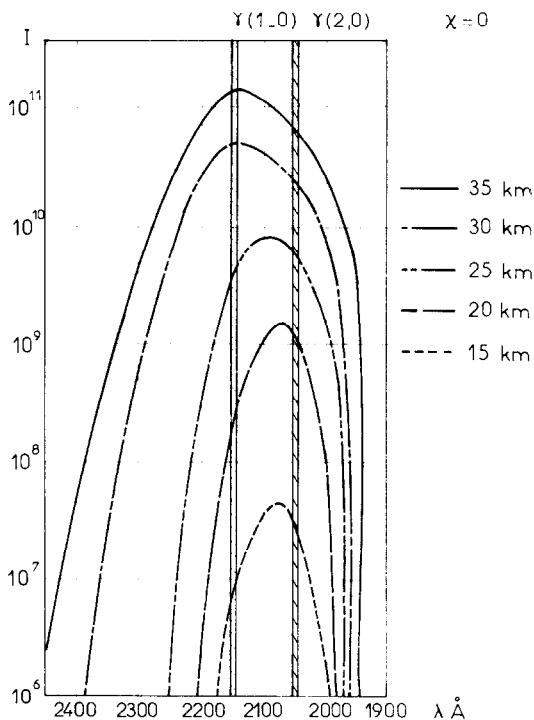where σ_ν is the absorption cross section (cm^2), ν is the line wave number (cm^{-1}), N_J is the

Fig. 3. Solar spectrum intensity $(ph\ cm^{-2}\ sec^{-1}\ Å^{-1})$ available at different altitudes, from 15 kms up to 35 kms, at a zenithangle of $0°$.
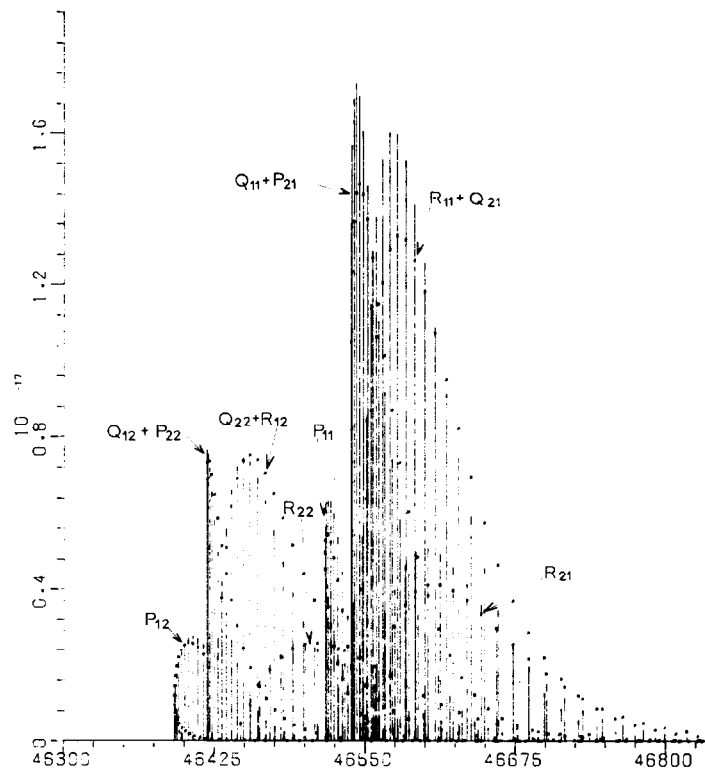
Fig. 4. The $\gamma(1\text{–}0)$ band: integrated line absorption cross-sections for 220 K and 280 K.

number of molecules in the lower state of the transition, N_t is the total number of molecules, S_J is the Hönl–London factor, and $f_{v'v''}$ is the band oscillator strength.

The oscillator strengths of the NO γ-bands were measured by several investigators. We used here the most recent values, obtained by FARMER et al.[9] using the 'Hook' technique; their results are in agreement with absorption measurements of WEBER and PENNER[10] and BETHKE.[11] For the Hönl–London factors, we use the expressions derived by BENNETT[2] for the general doublet transition. As a check of our calculation, we also computed the S_J factors as given by EARLS[12] for a $^2\Sigma\text{–}^2\Pi$ transition, when the $^2\Pi$ state is intermediate between cases (a) and (b). We obtained the same numerical results for the first three significant figures.

The computation of $\int \sigma_v \, d\nu$ was carried out for the 100–1000 K temperature range. In Figs. 4 and 5, the integrated line cross-sections for the $\gamma(1\text{–}0)$ and $\gamma(2\text{–}0)$ bands are plotted, respectively, as functions of wavelength for 220 K and 280 K, these temperatures being representative of the two extremes encountered in the stratosphere. The wavenumbers of the lines are from GERO and SCHMID[13] The numerical values at any temperature can be obtained on request from the authors.

CONCLUSION

These results permit a quantitative interpretation of the absorption spectra of the $\gamma(1\text{–}0)$ and $\gamma(2\text{–}0)$ bands taken in the stratosphere. The method used in the present work can also be applied to the calculation of line intensities within any other NO absorption band which is not subject to perturbations in the free molecule. This condition is fulfilled for all γ- and ϵ-bands and for most
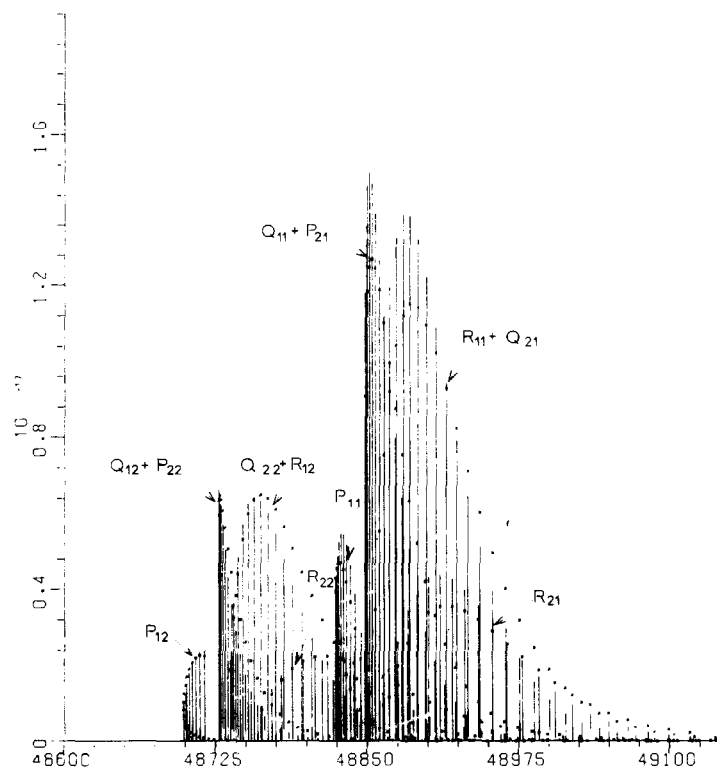
Fig. 5. The $\gamma(2-0)$ band: integrated line absorption cross sections for 220 K and 280 K.

of the β-bands. The $\delta(0-0)$ and $(1-0)$ bands, however, undergo homogeneous perturbations caused by the presence of the $\beta(7-0)$ and $(10-0)$ bands in their spectral range (Lagerqvist and Miescher[14]). In these cases, the line integrated cross-sections can only be calculated if the elements of the perturbation-matrix are known; the Hönl–London factors of Bennett[2] must be modified in order to take these matrix elements into account. NO band systems other than those mentioned above all lie at wavelengths lower than 180 nm where solar radiation does not reach the stratosphere, being strongly absorbed by the oxygen molecules.

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