

I N S T I T U T D ' A E R O N O M I E S P A T I A L E D E B E L G I Q U E

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The aeronomic dissociation of nitric oxide

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## FOREWORD

"The Aeronomic Dissociation of Nitric Oxide" is also given as Scientific Report of the Ionospheric Research Laboratory of the Pennsylvania State University and will be published in Planetary and Space Science.

## AVANT-PROPOS

"The Aeronomic Dissociation of Nitric Oxide" sera reproduit comme Scientific Report de l'Ionospheric Research Laboratory of the Pennsylvania State University et sera publié dans Planetary and Space Science.

## VOORWOORD

"The Aeronomic Dissociation of Nitric Oxide" zal worden weergegeven als Scientific Report van het Ionospheric Research Laboratory of the Pennsylvania State University en zal verschijnen in Planetary and Space Science.

## VORWORT

"The Aeronomic Dissociation of Nitric Oxide" wird auch als Scientific Report des Ionospheric Research Laboratory of the Pennsylvania State University ausgegeben werden und wird in Planetary and Space Science hergestellt werden.

# THE AERONOMIC DISSOCIATION OF NITRIC OXIDE

by

S. CIESLIK and M. NICOLET

## *Abstract*

A detailed study is made of the atmospheric attenuation of the dissociation of nitric oxide in the mesosphere and stratosphere. The nitric oxide dissociation profile depends on the absorption of the discrete Schumann-Runge bands of  $O_2$ . The major contribution to the dissociation rate of NO is the predissociation of the  $\delta(0-0)$  and  $\delta(1-0)$  bands which can reach the stratosphere.

## *Résumé*

Une étude détaillée de l'atténuation atmosphérique de la dissociation de l'oxyde nitrique dans la mésosphère et dans la stratosphère est faite. Le profil de dissociation de l'oxyde nitrique dépend de l'absorption dans les bandes discrètes de Schumann-Runge de  $O_2$ . La contribution la plus importante à la vitesse de dissociation de NO est la prédissociation des bandes  $\delta(0-0)$  et  $\delta(1-0)$ , qui peut atteindre la stratosphère.

### *Samenvatting*

Een gedetailleerde studie werd gemaakt van de atmosferische verzwakking van de dissociatie van stikstofoxyde in de mesosfeer en de stratosfeer. Het dissociatieprofiel van stikstofoxyde hangt af van de discrete Schumann-Runge banden van  $O_2$ . De voornaamste bijdrage tot de dissociatieverhouding van NO is de predissociatie van de  $\delta(0-0)$  en  $\delta(1-0)$  banden die de stratosfeer kunnen bereiken.

### *Zusammenfassung*

Eine umständliche Analyse der atmosphärischen Verminderung der Stickoxyddissoziation in der Mesosphäre und in der Stratosphäre wird vorgestellt. Die Dissoziationsverteilung des Stickoxyds hängt von der Absorption in der Schumann-Runge Banden von  $O_2$  ab. Der wichtigste Beitrag zur NO - Dissoziation ist die Prädissoziation der  $\delta(0-0)$ - und  $\delta(1-0)$ - Banden, die die Stratosphäre erreichen kann.

## 1. INTRODUCTION

The predissociation of nitric oxide was introduced in aeronomic studies by Bates (1952) as a dissociation process of NO produced in the upper atmosphere (Nicolet, 1945). Recent observations (Barth, 1964, 1966 ; Pearce, 1969 ; Meira, 1971) of nitric oxide in the lower thermosphere indicate that nitric oxide is produced there (Norton, 1967 ; Norton and Barth, 1970 ; Strobel *et al*, 1970 ; Nicolet, 1970a) by the reaction of molecular oxygen with atomic nitrogen in its first excited level  $N(^2D)$ . The predissociation of  $N_2$  in the system  $a^1\Pi_g - A^1\Sigma_g$  of the Lyman-Birge-Hopfield bands, 7-0 at 1250 Å, 8-0 at 1226 Å and 9-0 at 1205 Å (Bates, 1954 ; Nicolet, 1954, 1965, 1970 ; Strobel, 1971) leads to a small production of nitrogen atoms which cannot be more than  $10 \text{ atoms cm}^{-3} \text{ sec}^{-1}$  at 100 km and, consequently, to a very small production of nitric oxide molecules in the mesosphere.

With an assumed lifetime of the upper states of NO of about  $10^{-6} \text{ sec}$ , a photodissociation coefficient  $J_{NO} = 10^{-7} \text{ sec}^{-1}$  was deduced at zero optical depth (Bates, 1954 ; Nicolet, 1965) or with a transition probability of about  $2 \times 10^7 \text{ sec}^{-1}$  (Callear and Smith, 1964) to a photodissociation coefficient  $J_{NO} = 5 \times 10^{-6} \text{ sec}^{-1}$  (Nicolet, 1970a). In that case, the  $\delta(1-0)$  band of the system  $C^2\Pi - X^2\Pi$  of NO was considered as the principal band (Flory and Johnston, 1935, 1946) leading to a direct predissociation process in the whole thermosphere. A first investigation by Strobel *et al* (1970) led to  $J_{NO} = 4 \times 10^{-6} \text{ sec}^{-1}$  at zero optical depth with the predissociation in the  $\gamma$  bands ( $v' > 3$ ) and the  $\beta$  bands ( $v' > 6$ ). More recently, Strobel (1971) has introduced all  $\delta$  and  $\epsilon$  bands for the study of the predissociation effect. With the introduction of such bands he found that the total photodissociation coefficient of nitric oxide at zero optical depth reaches more than  $10^{-5} \text{ sec}^{-1}$  which is a very large value. However, since the whole  $\delta(0-0)$  band does not predissociate, particular attention must be paid to the detailed structure of the absorption in this spectral region.

In this paper the effects of the dissociation of nitric oxide will be considered in the mesosphere and stratosphere since there is an important source of NO in the stratosphere (Nicolet, 1970b) which is due to the reaction of nitrous oxide with atomic oxygen in its first excited level, namely  $N_2O + O(^1D) \rightarrow 2 NO$ . Particular attention must be devoted to the penetration of solar radiation in the upper stratosphere with its effects on the predissociation of NO.

## 2. PREDISSOCIATION OF NO

The electronic absorption spectrum of nitric oxide which starts in the region of the ozone absorption (Hartley band) extends into the region of the absorption of the Schumann-Runge bands of molecular oxygen (see Herzberg, 1958 ; Heicklen and Cohen, 1968). The spectrum has been studied by a number of investigators (see Watanabe, 1958). Recent important results have been obtained by Callear and coworkers (1963 - 1970) and by Miescher and coworkers (1958 - 1969).

Our knowledge of the various electronic states of this molecule [ see potential energy curves, Gilmore (1965) ] permits the application of the Franck-Condon principle to determine the probabilities of the various predissociation processes. We are interested here in the transition between the ground electronic state  $X^2\Pi$  and the  $A^2\Sigma^+$ ,  $B^2\Pi$ ,  $C^2\Pi$  and  $D^2\Sigma^+$  states (Fig. 1) which correspond to the  $\gamma$ ,  $\beta$ ,  $\delta$  and  $\epsilon$  bands, respectively.

The dissociation energy of NO is  $52400 \pm 10 \text{ cm}^{-1}$  (Callear and Pilling, 1970), and predissociation occurs in the  $\gamma$  system ( $A^2\Sigma^+ - X^2\Pi$ ) for vibrational levels  $v' > 4$  ( $\lambda < 1880 \text{ \AA}$ ) and in the  $\beta$  system ( $B^2\Pi - X^2\Pi$ ) for vibrational levels  $v' > 7$  ( $\lambda < 1910 \text{ \AA}$ ) for which emission has never been observed. In the  $\delta$  system ( $C^2\Pi - X^2\Pi$ ) no emission has been seen for  $v' > 0$  but is observed for  $v' = 0$ . The  $\delta(0-0)$  band at  $1910.2 \text{ \AA}$  and  $\delta(0-1)$  band at  $1981.4 \text{ \AA}$  have been observed with great detail in emission by Ackerman and Miescher (1969) who show that there is an indication for the presence of a predissociation near  $52400 \text{ cm}^{-1}$  ( $\lambda = 1908.4 \text{ \AA}$ ). According to Callear and Pilling (1970),  $\text{NO}(C^2\Pi)_{v=0}$  undergoes spontaneous predissociation for levels above  $F_1(5/2)$ , which are above the dissociation limit  $52400 \text{ cm}^{-1}$ . The values of the coefficient of spontaneous predissociation,  $D_{ji} = 1.65 \times 10^9 \text{ sec}^{-1}$ , and of the coefficient of spontaneous transition to the normal state  $X^2\Pi$ ,  $A_{ji} = 5.1 \times 10^7 \text{ sec}^{-1}$  (Callear and Pilling, 1970), indicate that predissociation occurs more rapidly than emission at levels above  $F_1(5/2)$ . Furthermore, molecular nitrogen may lead to the deactivation of NO ( $C^2\Pi_{v=0}$ ) according to the following reaction (Callear and Smith, 1964):  $\text{NO}(C^2\Pi)_{v=0} + \text{N}_2(X^1\Sigma_g^+)_{v=0} \rightarrow \text{NO}(X^2\Pi)_{v=0,1} + \text{N}_2(A^3\Sigma_u^+)_{v=0,1}$  with a quenching rate coefficient at room temperature  $k_q(\text{N}_2) = 1.5 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1}$ . Such a rate coefficient induces the transition  $\text{NO} + \text{N}_2 \rightarrow \text{NO} + \text{N}_2$  in the lower stratosphere where the concentration of molecular nitrogen reaches  $10^{18} \text{ cm}^{-3}$ , i.e. a deactivation coefficient,  $a_{ji} = 1.5 \times 10^9 \text{ sec}^{-1}$ , of the same order of magnitude as  $D_{ji}$  the coefficient of spontaneous predissociation.

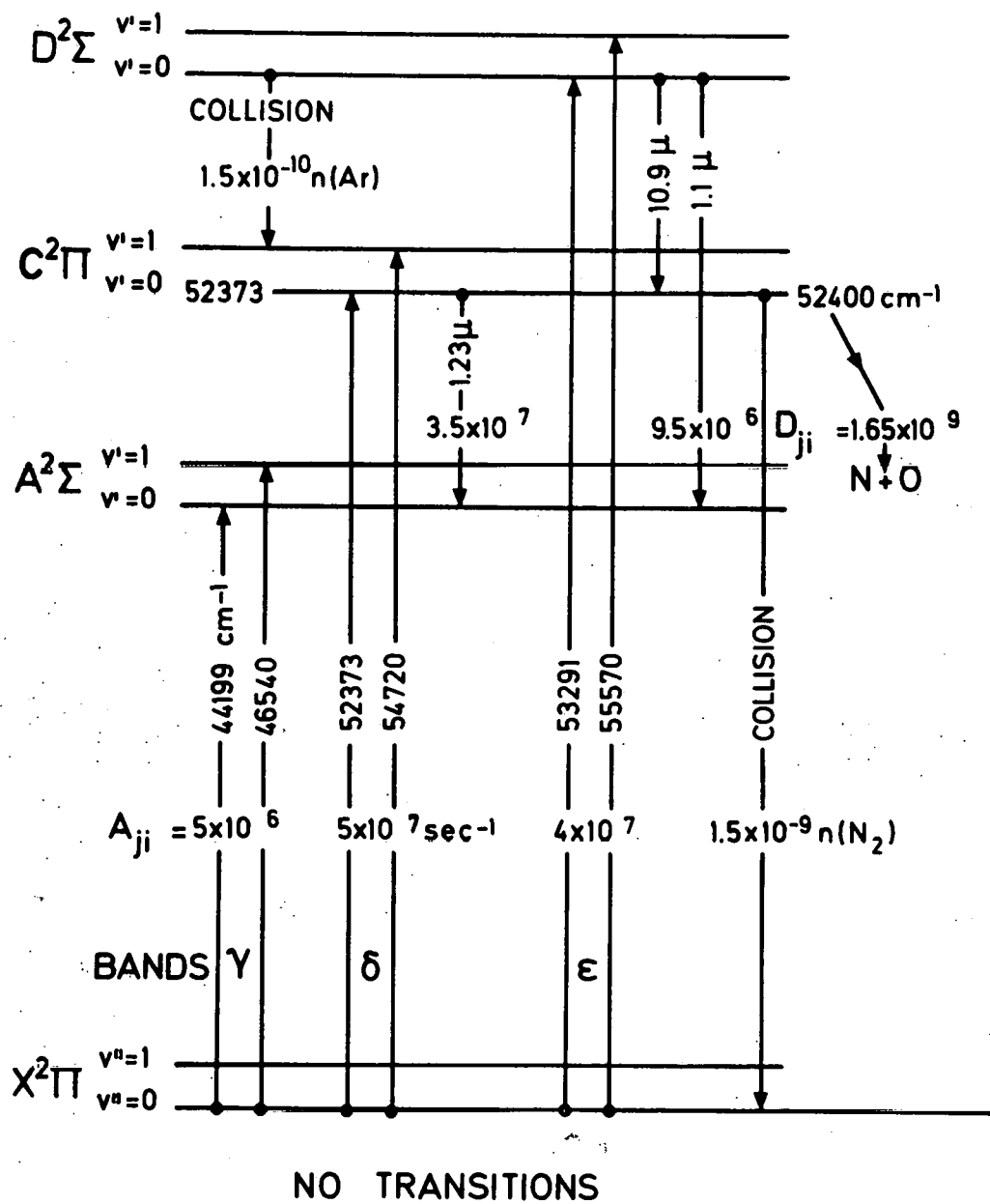


Fig. 1.- Nitric oxide transitions.

As far as the  $\epsilon$  system ( $D^2\Sigma^+ - X^2\Pi$ ) is concerned, it has been shown by Callear and Pilling (1970 a, b) that the rate of spontaneous predissociation of  $NO(D^2\Sigma^+)_{v=0} \rightarrow N + O$  is small compared with the rate of spontaneous emission  $D^2\Sigma^+ \rightarrow X^2\Pi$ . The coefficient of the spontaneous emission  $A_{ji} = 4.1 \times 10^7 \text{ sec}^{-1}$  and the coefficient of the spontaneous predissociation is  $D_{ji} < 8 \times 10^6 \text{ sec}^{-1}$ . The route for spontaneous predissociation which was found for  $NO(C^2\Pi)$  is closed for  $NO(D^2\Sigma^+)$  and the effect of argon inducing the transition  $NO(D^2\Sigma^+)_{v=0} \rightarrow NO(C^2\Pi)_{v=0}$ , according to Callear and Pilling (1970a), does not play any role as an aeronomic reaction. Furthermore, the quenching rate coefficient by  $N_2$  which is five times less than for  $C^2\Pi$ , can also be neglected.

Consequently, the aeronomic dissociation of nitric oxide corresponds to predissociation processes in the  $\delta$  bands,  $\beta(v' > 7)$  bands and  $\gamma(v' > 4)$  bands and not the  $\epsilon$  bands.

### 3. DISSOCIATION COEFFICIENTS AT ZERO OPTICAL DEPTH

In order to determine the relative importance of the various dissociation processes, a first step is to consider that the predissociation mechanism leads to complete dissociation of the molecule after an absorption process of the solar radiation.

If the solar radiation temperature is constant over the relevant range of the NO absorption band, the dissociation coefficient at zero optical depth is given by

$$J_{\infty}(\text{band}) = \beta_S \rho(\nu) B_{v',v''} \quad (1)$$

where  $B_{v',v''}$  is the transition probability of the transition between  $v'$  and  $v''$  the upper and lower vibrational states, respectively;  $\rho(\nu)$  is the energy density of solar radiation, reduced at the top of the earth's atmosphere by  $\beta_S = 5.4 \times 10^{-6}$ , the dilution factor.

The transition probability  $B_{v',v''}$  is related to the probability for spontaneous emission  $A_{v',v''}$  by

$$g_{v'} B_{v',v''} = g_{v''} A_{v',v''} / 8\pi h\nu^3 \quad (2)$$



where  $g_{v'}$  and  $g_{v''}$  are the degeneracies of the lower and upper states, respectively. If it is assumed that the distribution function of the solar radiation density is given by Planck's formula for a black-body emission, the dissociation rate coefficient becomes, (1) and (2),

$$J_{\infty}(\text{band}) = \beta_S \frac{g_{v'}}{g_{v''}} \frac{A_{v',v''}}{e^{h\nu/kT_{S-1}}} \quad (3)$$

where  $\nu$  is the average frequency and  $h$  and  $k$  are Planck and Boltzmann constants, respectively. The solar radiation temperature in the spectral region of the  $\beta$ ,  $\gamma$  and  $\delta$  predissociated bands of NO is not yet known with sufficiently great accuracy. Considering the number of photons available at the top of the earth's atmosphere (Ackerman, 1971), it may be said that the radiation temperature cannot be more than 4800 °K and may reach 4600 °K. In order to determine the precise photodissociation coefficient due to solar radiation of  $\lambda\lambda$  1908-1750 a very careful analysis of the solar spectrum is still required in the spectral range of the Schumann-Runge bands.

Since there is generally no emission of the predissociated bands, no  $A_{v',v''}$  value and transition probability parameters are available from absorption measurements. An exception is, however, given by the  $\delta(0-0)$  band of NO which radiates about thirty times slower than it dissociates. Callear and Pilling (1970) have determined the radiative lifetime of the  $C^2\Pi_{v=0} \rightarrow X^2\Pi$  transition to be equal to  $5.1 \times 10^7 \text{ sec}^{-1}$ .

Bethke (1959) has measured the band oscillator strengths of the  $\beta$ ,  $\gamma$ ,  $\delta$  and  $\epsilon$  bands of NO with great accuracy and the reliability of these measurements for the  $\beta$ ,  $\gamma$  and  $\epsilon$  bands have been established by recent measurements (Farmer *et al.*, 1972; Callear and Pilling, 1970).

The adopted parameters are given in Table I. The electronic oscillator strengths  $f(v',v'')_{el}$  given by

$$f(v',v'')_{el} = \frac{f(v',v'') \bar{\nu}}{q(v',v'') \nu(v',v'')} \quad (4)$$

are taken from Ory (1964) and Ory *et al* (1964). In this formula  $f(v'v'')$  is the band oscillator strength,  $\bar{\nu}$  is the weighted average frequency of the whole band system,  $q(v'v'')$  is the Franck-Condon factor. Since  $f(v'v')$  is related to the emission probability  $A_{v',v''}$ , by

$$A_{v',v''} = \frac{g_{v''}}{g_{v'}} \cdot \frac{8 \pi^2 e^2 \nu^2}{mc} \cdot f(v'v'') = \frac{g_{v''}}{g_{v'}} \times 0.667 \nu^2 f(v'v'') \quad (5)$$

where  $e$  and  $m$  are the charge and mass of the electron, respectively, it is possible to determine the various values of the probability of spontaneous emission as indicated in Table I. Except for  $\beta(12-0)$ , all transition probabilities of spontaneous emission  $A_{v',v''}$ , which do not reach  $10^6 \text{ sec}^{-1}$ , correspond to transitions which are less important than those of the  $\delta$  bands. Since the transition probability of the  $\delta(0-v'')$  bands is  $5.1 \times 10^7 \text{ sec}^{-1}$  (Callear and Pilling, 1970), i.e.  $1.0 \times 10^7 \text{ sec}^{-1}$  for the transition  $\delta(0-0)$ , it is clear that the principal photodissociation process of nitric oxide occurs in the  $\delta$  bands. With a radiation temperature of  $4700^\circ \text{K}$ , the photodissociation coefficient at zero optical depth is

$$J_{\text{NO}}(\delta, 0-0) = (6 \pm 1) \times 10^{-6} \text{ sec}^{-1} \quad (6a)$$

for  $T = 4700^\circ \text{K} \pm 50^\circ$ , or

$$J_{\text{NO}}(\delta, 0-0) = (6 \pm 2) \times 10^{-6} \text{ sec}^{-1} \quad (6b)$$

for  $T = 4700^\circ \pm 100^\circ \text{K}$ .

The difference of  $\pm 50^\circ \text{K}$  or  $\pm 100^\circ \text{K}$  indicate that the exact value should be in the range of  $4$  to  $8 \times 10^{-6} \text{ sec}^{-1}$  with perhaps a tendency towards the lower values. Since Callear and Pilling (1970) have revised Bethke's values of the oscillator strength for the  $\delta(0-0)$  band, it would be possible that a correction should also be applied to the  $\delta(1-0)$  band. Without considering any change, the transition probability of  $\delta(1-0)$  is  $1.1 \times 10^7 \text{ sec}^{-1}$  which leads to a photodissociation coefficient at zero optical depth

$$J_{\text{NO}}(\delta, 1-0) = (3 \pm 0.5) \times 10^{-6} \text{ sec}^{-1} \quad (7)$$

if the radiation temperature is  $4650^{\circ} \pm 50^{\circ} \text{K}$  (cf Ackerman *et al.*, 1971).

Thus it can be concluded that the photodissociation coefficient of NO at zero optical depth is not far from  $10^{-5} \text{ sec}^{-1}$ .

The relatively less intense  $\beta$  and  $\gamma$  band system lead to the following photodissociation coefficients at zero optical depth

$$J_{\text{NO}} (\beta, 7-0) = (1.1 \pm 0.2) \times 10^{-7} \text{ sec}^{-1} \quad (8)$$

for  $T = 4700 \pm 50^{\circ} \text{K}$  ;

$$J_{\text{NO}} (\beta, 8-0) = (1.5 \pm 0.2) \times 10^{-7} \text{ sec}^{-1} \quad (9)$$

for  $T = 4650 \pm 50^{\circ} \text{K}$ , and

$$J_{\text{NO}} (\beta, 9-0) = 1.6 \times 10^{-7} \text{ sec}^{-1} \quad (10)$$

$$J_{\text{NO}} (\beta, 10-0) = 1.3 \times 10^{-7} \text{ sec}^{-1} \quad (11)$$

$$J_{\text{NO}} (\beta, 11-0) = 1.0 \times 10^{-7} \text{ sec}^{-1} \quad (12)$$

$$J_{\text{NO}} (\beta, 12-0) = 5.2 \times 10^{-7} \text{ sec}^{-1} \quad (13)$$

for  $T = 4600^{\circ} \text{K}$  which seem to be the temperature adapted to the spectral range of  $54000 - 57000 \text{ cm}^{-1}$ .

$$J_{\text{NO}} (\gamma, 4-0) = (9 \pm 2) \times 10^{-8} \text{ sec}^{-1} \quad (14)$$

for  $T = 4650^{\circ} \pm 50^{\circ} \text{K}$  and

$$J_{\text{NO}} (\gamma, 5-0) = 1.1 \times 10^{-8} \text{ sec}^{-1} \quad (15)$$

for  $T = 4600^{\circ} \text{K}$ .

Thus, this method of obtaining the photodissociation coefficient of NO at zero optical depth shows that the principal effect comes from the absorptions in the  $\delta$  bands which are about 10 times more efficient than the  $\beta$  and  $\gamma$  bands.

#### 4. THE PHOTODISSOCIATION OF NO IN THE MESOSPHERE AND STRATOSPHERE

The photodissociation of nitric oxide in the mesosphere and stratosphere depends on the absorption by the Schumann-Runge bands of molecular oxygen. Recent absorption cross section measurements with the determination of the structure of the (0-0) to the (18-0) Schumann-Runge bands (Ackerman and Biaumé, 1970 ; Ackerman *et al*, 1970) made it possible to compute the O<sub>2</sub> absorption cross sections at very close intervals and to determine (Kockarts, 1971) the penetration of solar radiation in the chemosphere.

The  $\beta$ (12-0) band of NO is in the spectral range of the (16-0) band of the Schumann-Runge system of molecular oxygen where the O<sub>2</sub> absorption cross section is greater than  $10^{-20}$  cm<sup>2</sup>. The unit optical depth is reached in the lower thermosphere near the mesopause and the photodissociation of the most important  $\beta$  band can be neglected even in a detailed calculation of the NO dissociation in the mesosphere and stratosphere.

The  $\delta$ (1-0) band between 54500 and 54900 cm<sup>-1</sup> in the spectral region of the (9-0) and (10-0) Schumann-Runge bands of O<sub>2</sub>, which has an absorption cross section not less than  $5 \times 10^{-22}$  cm<sup>-2</sup>, leads to a mesospheric dissociation of NO. The band  $\delta$ (0-0) between 52200 and 52550 cm<sup>-1</sup> is in the spectral range of the (5-0) Schumann-Runge band of O<sub>2</sub>, which has an absorption cross section no larger than  $5 \times 10^{-23}$  cm<sup>2</sup>, can be easily pre-dissociated below the stratopause ; the unit optical depth is reached in the region of 35-40 km.

In order to determine the penetration of the solar radiation in the chemosphere, the atmospheric model used by Nicolet (1970) has been adopted. Table II gives the oxygen and ozone concentrations used for this computation.

The integrated absorption cross section of a rotational line is related to its oscillator strength  $f(J'J'')$  by the expression (see for example Nicholls, 1969)

$$\int_L \sigma_{\text{NO}}(\nu) d\nu = \frac{\pi e^2}{mc^2} f(J'J'') N_{J''}/N_{\text{tot}} \quad (16)$$

If  $S_{J'J''}$  is the Hönl-London factor of the  $J' - J''$  transition, the oscillator strength  $f(J'J'')$  is related to the band absorption oscillator strength by (see, for example, Farmer, Hasson and Nicholls, 1972)

$$f(J,J'') = f(v'v'') \frac{S_{J'J''}}{2J'' + 1} \quad (17)$$

Finally,  $N_{J''}/N_{\text{tot}}$  is the relative population of the rotational level  $J''$  of the lower state. It follows the Boltzman distribution and is given by (see Herzberg, 1950)

$$\frac{N_{1J''}}{N_{\text{tot}}} = \frac{(2J'' + 1) e^{-hc F_1(J'')/kT}}{Q} \quad (18)$$

for the  ${}^2\Pi_{1/2}$  component, and

$$\frac{N_{2J''}}{N_{\text{tot}}} = \frac{(2J'' + 1) e^{-hc F_2(J'')/kT}}{Q} \quad (19)$$

for the  ${}^2\Pi_{3/2}$  component of the ground state X  ${}^2\Pi$  of NO.

$F_1(J'')$  and  $F_2(J'')$  are the term values and are given by

$$F_1(J'') = B_0 \left[ \left( J'' + \frac{1}{2} \right)^2 - 1 - \frac{1}{2} \left\{ 4 \left( J'' + \frac{1}{2} \right)^2 + Y(Y - 4) \right\}^{1/2} \right] - D_0 J''^4 \quad (20)$$

$$F_2(J'') = B_0 \left[ \left( J'' + \frac{1}{2} \right)^2 - 1 + \frac{1}{2} \left\{ 4 \left( J'' + \frac{1}{2} \right)^2 + Y(Y - 4) \right\}^{1/2} \right] - D_0 (J'' + 1)^4 \quad (21)$$

The numerical values (Herzberg, 1950) of the rotational constants  $B_0$  and  $D_0$  are  $1.696 \text{ cm}^{-1}$  and  $5 \times 10^{-6} \text{ cm}^{-1}$ , respectively, while  $Y$ , the spin-orbit coupling constant, is equal to  $124.2/B_0$ . Finally, the internal partition function is written as follows

$$Q = 2 \sum_{J''} (2J'' + 1) \left[ e^{-hcF_1(J'')/kT} + e^{-hcF_2(J'')/kT} \right] \quad (22)$$

The term values and relative populations which have been calculated by means of equations (18) and (19) are given in Table III and have been used for the calculation of the rotational line intensities. With calculation of the  $S_{J,J''}$  factors based in the formulas derived by Kovacs (1969), it is possible to determine the integrated absorption cross-section of the individual lines in a band. The result of this computation is illustrated in Fig. 2 and Fig. 3 where the absorptions of  $\delta(0-0)$  and  $\delta(1-0)$  bands are compared with that of the  $\beta$  bands, respectively. The experimental data are from Lagerqvist and Miescher (1958) and Ackermann and Miescher (1969). It is clear that the effect of the  $\beta$  bands is not important in the mesosphere and stratosphere compared with the absorption of the  $\delta$  bands. An example of absorption cross sections of the principal lines of the  $\delta(0-0)$  band is given in Table IV for a temperature of  $220 \text{ }^\circ\text{K}$ .

Using the molecular oxygen cross sections which are available every  $0.5 \text{ cm}^{-1}$  in the Schumann-Runge bands for various temperatures from  $180 \text{ }^\circ\text{K}$  to  $300 \text{ }^\circ\text{K}$  (Kockarts, 1972) it is possible to find the optical depth at the wavelength of each rotational line of NO and to determine the true absorption in the atmosphere. The ozone absorption cross section can be taken as a constant over each band interval and the numerical values are those adopted by Ackerman (1971). In fact the optical depth is written as follows :

$$\tau_\lambda = \int_z^\infty \sigma_\lambda(O_2) n(O_2) dz' + \sigma(O_3) \int_z^\infty n(O_3) dz' \quad (23)$$

Since the absorption cross sections for molecular oxygen are temperature dependent, it is considered under the integral sign. Figures 4a and 4b show how the  $O_2$  and NO lines are related in the  $\delta(0-0)$  and  $\delta(1-0)$  bands. Results of calculation at various temperatures are illustrated in Fig. 5 where the total contents  $10^{20} \text{ O}_2 \text{ molecules cm}^{-2}$  to  $10^{23} \text{ cm}^{-2}$  correspond to altitudes of about 75 km and 25 km, respectively. If the temperature effect is not important in the mesosphere where the optical depth is small it cannot be neglected at

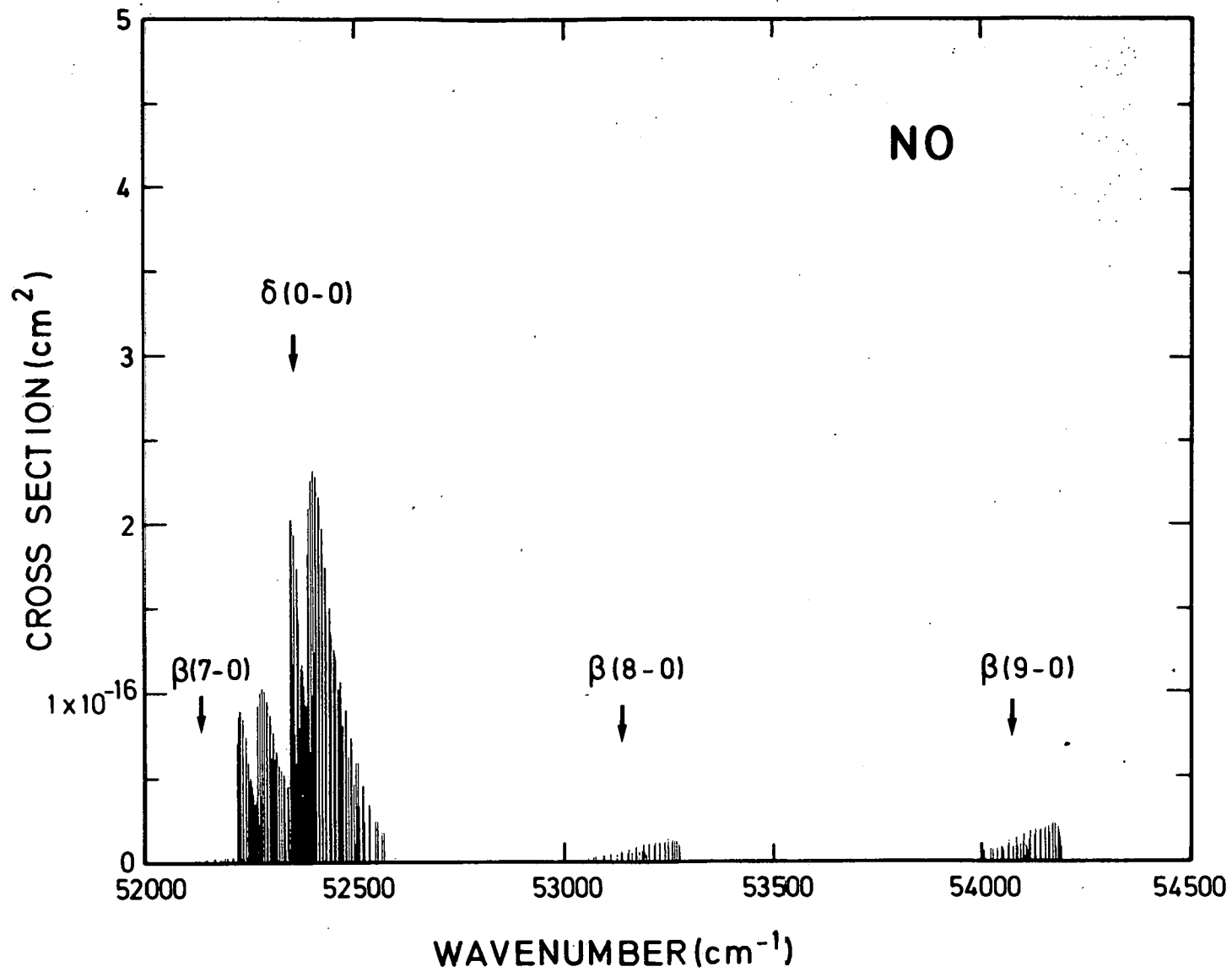


Fig. 2.- Structure of the absorption of nitric oxide in the spectral range of the  $\delta(0-0)$  band.

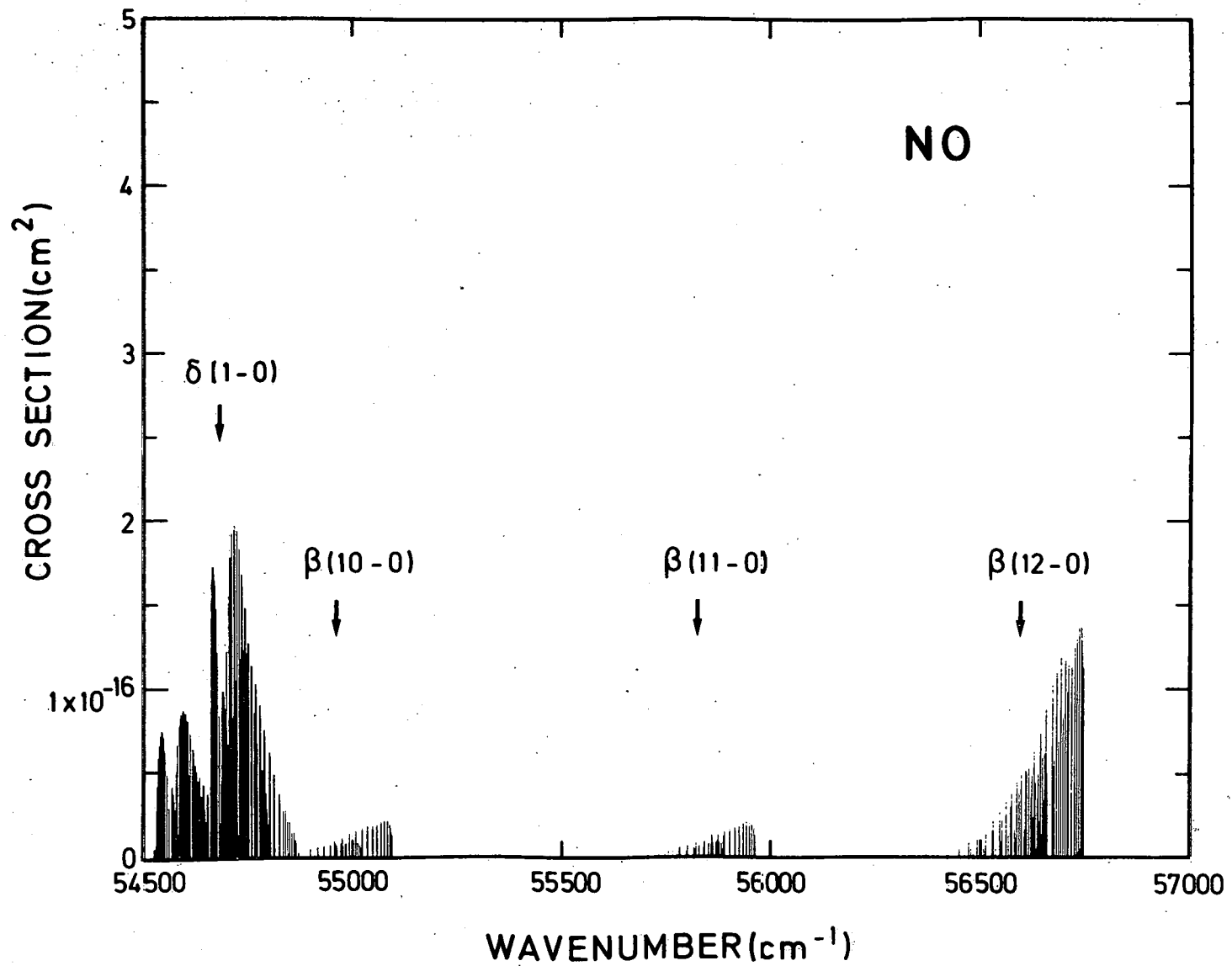


Fig. 3.- Structure of the absorption of nitric oxide in the spectral range of the  $\delta(1-0)$  band.



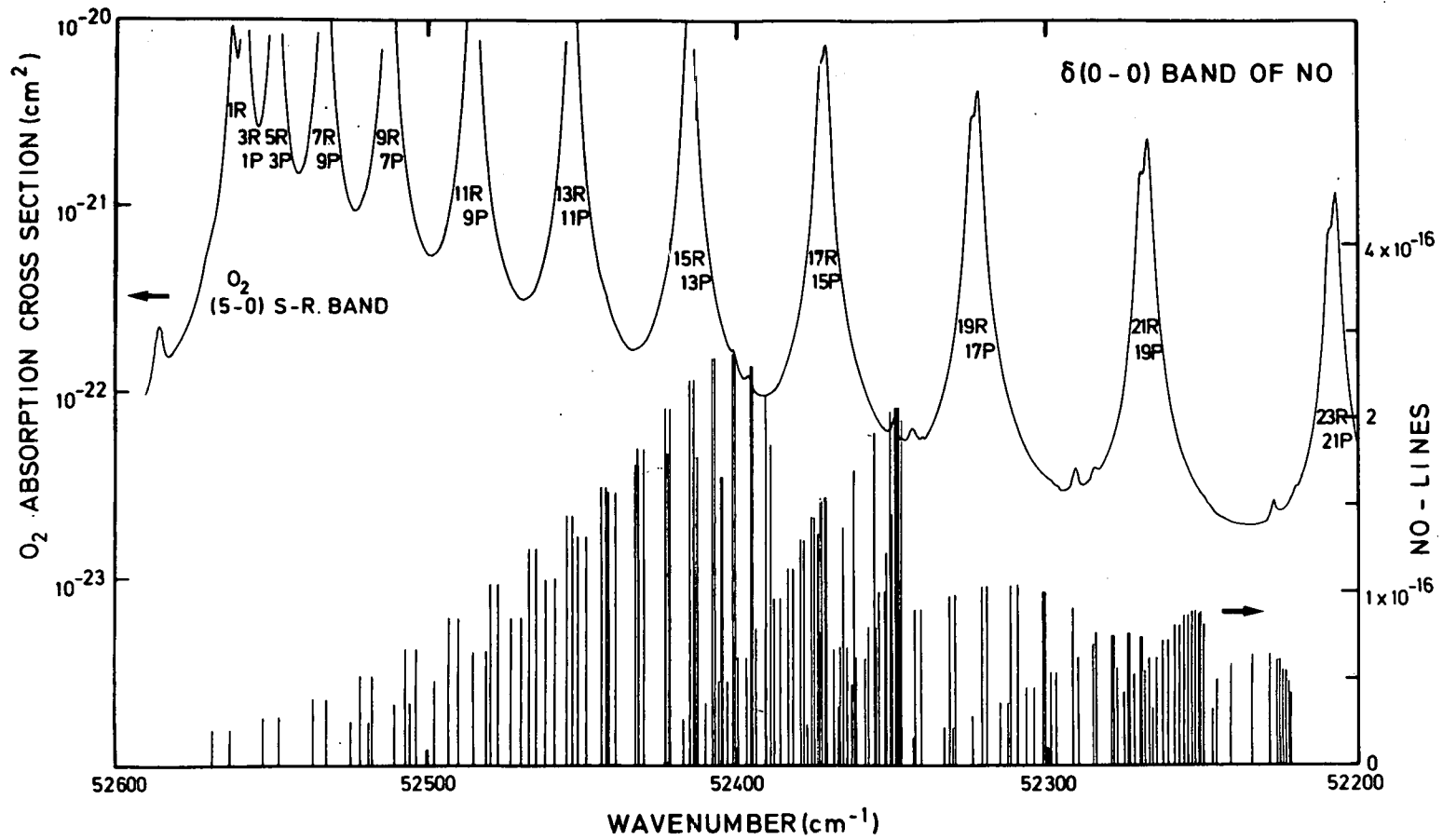


Fig. 4a.- Detailed structure of the (5-0) band of the Schumann-Runge system of O<sub>2</sub> and of the δ(0-0) band of nitric oxide.

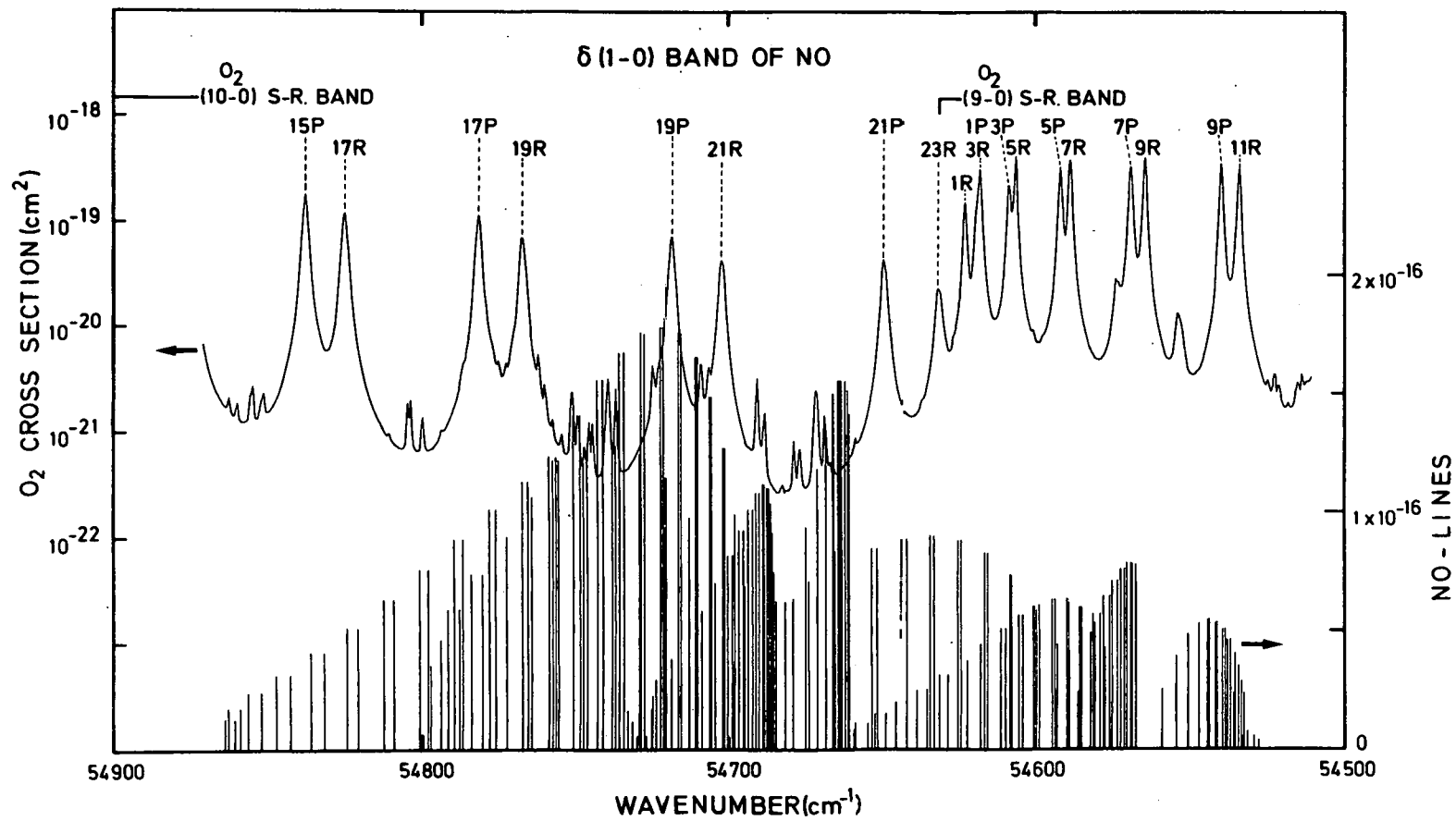


Fig. 4b.- Detailed structure of the (9-0) and (10-0) bands of the Schumann-Runge system of O<sub>2</sub> and of the δ(1-0) band of nitric oxide.

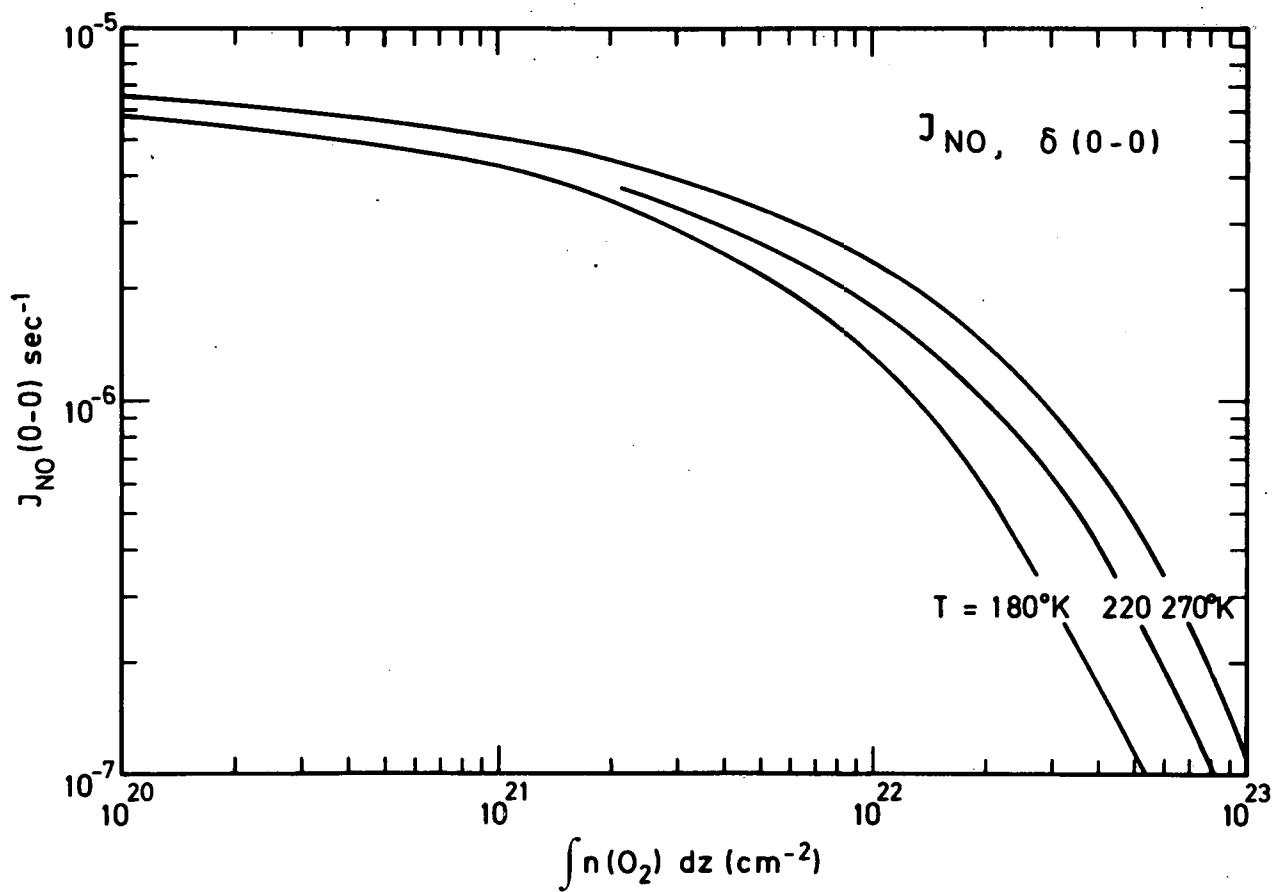


Fig. 5.- Photodissociation coefficient of NO due to the predissociation in the  $\delta(0-0)$  band. Differences associated with the temperature affecting the  $O_2$  band structure.

the stratopause ( $4 \times 10^{21}$  molecules  $\text{cm}^{-2}$  for an overhead sun) and in the whole stratosphere. For such a reason the calculation of the vertical distribution of  $J_{\text{NO}}$  has been made with the average temperatures indicated in Table II.

There is no possibility to use an *average* absorption cross section in order to determine the reduction factor of the photodissociation coefficient of NO in the mesosphere and stratosphere. Two figures 6a and 6b show that the equivalent cross section varies with the temperature and with the altitude (total number of  $\text{O}_2$  molecules) in a vertical column. It is, therefore, impossible to use an average absorption cross section of molecular oxygen in the determination of the NO dissociation coefficient. The effect of the ozone absorption, which has been introduced with the correction factors as given in Table V, becomes important only in the lower stratosphere and is negligible in the mesosphere. Finally, the effect of the deactivation of the  $\text{C } ^2\Pi$  state by  $\text{N}_2$  is not negligible in the stratosphere; it is given in Table VI which shows that the quenching effect increases from the stratopause to the tropopause by a factor of about 4.

In order to calculate the photodissociation coefficient of nitric oxide in the mesosphere and stratosphere we assume that the predissociation in the  $\delta(0-0)$  and  $\delta(1-0)$  bands is responsible for the whole dissociation of NO, that the absorption by  $\text{O}_2$  follows the distribution of temperature given in Table II and that the absorption by  $\text{O}_2$  and  $\text{O}_3$  depends on the concentrations which are indicated in Table II. From the information tabulated above it is possible to deduce the photodissociation coefficients which can be used with a certain approximation in the mesosphere and stratosphere.

In part 2 we arrived at values for  $J_{\text{NO}}(\delta,0-0)$  at zero optical depth (formula 6a) between  $4$  and  $8 \times 10^{-6} \text{ sec}^{-1}$  for radiation temperatures between  $4600^\circ\text{K}$  and  $4800^\circ\text{K}$ , respectively. With the information tabulated by Ackerman (1971) on the solar flux, the photodissociation coefficient  $J_{\text{NO}}(\delta,0-0)$  at zero optical depth is

$$J_{\text{NO}}(\delta, 0-0)_\infty = 6.9 \times 10^{-6} \text{ sec}^{-1} \quad (24)$$

which could correspond to a radiation temperature of  $4750^\circ\text{K}$ . It seems therefore, that the photodissociation coefficient cannot be significantly higher than indicated by expression

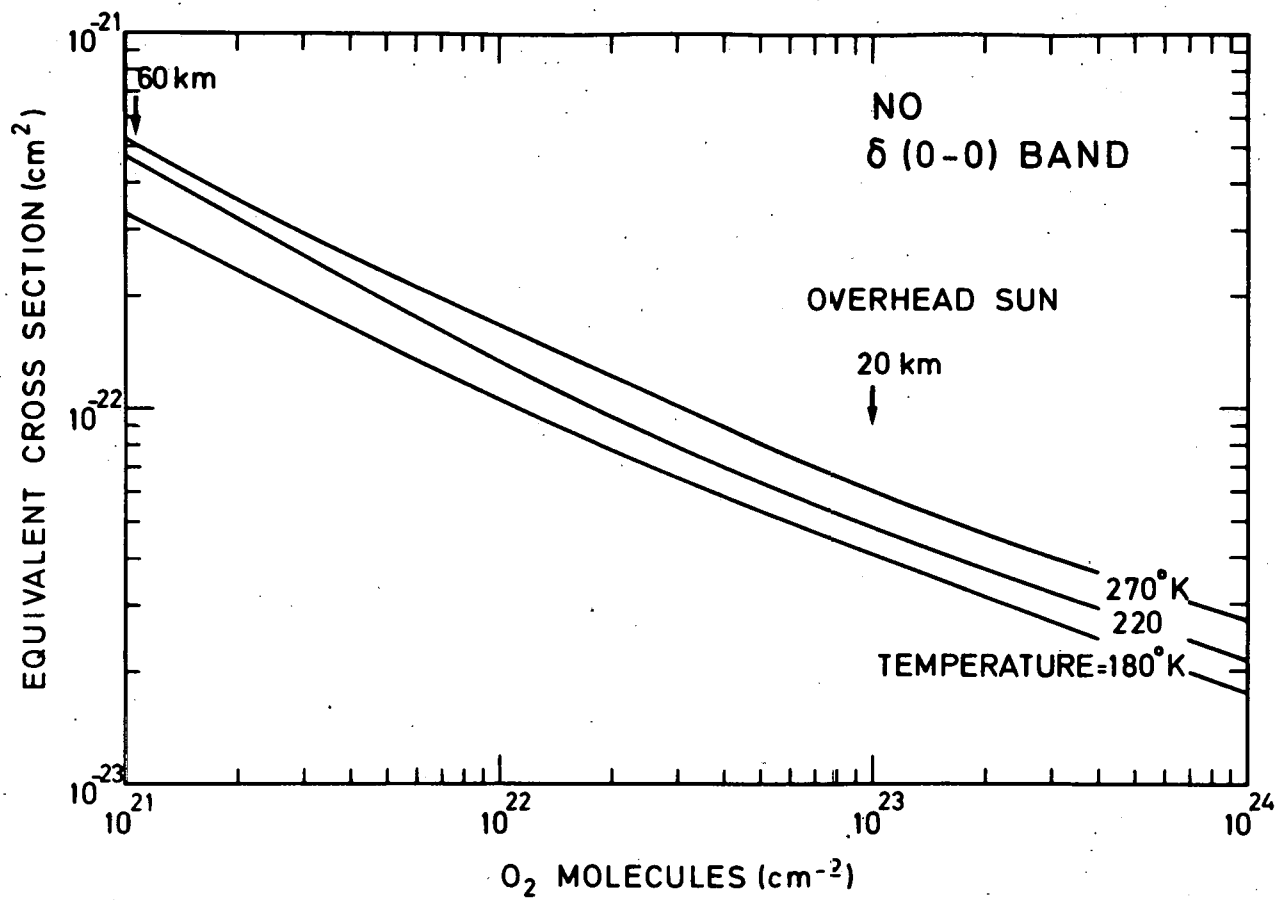


Fig. 6a.- Equivalent absorption cross section of molecular oxygen in the spectral range of the  $\delta(0-0)$  band of NO.

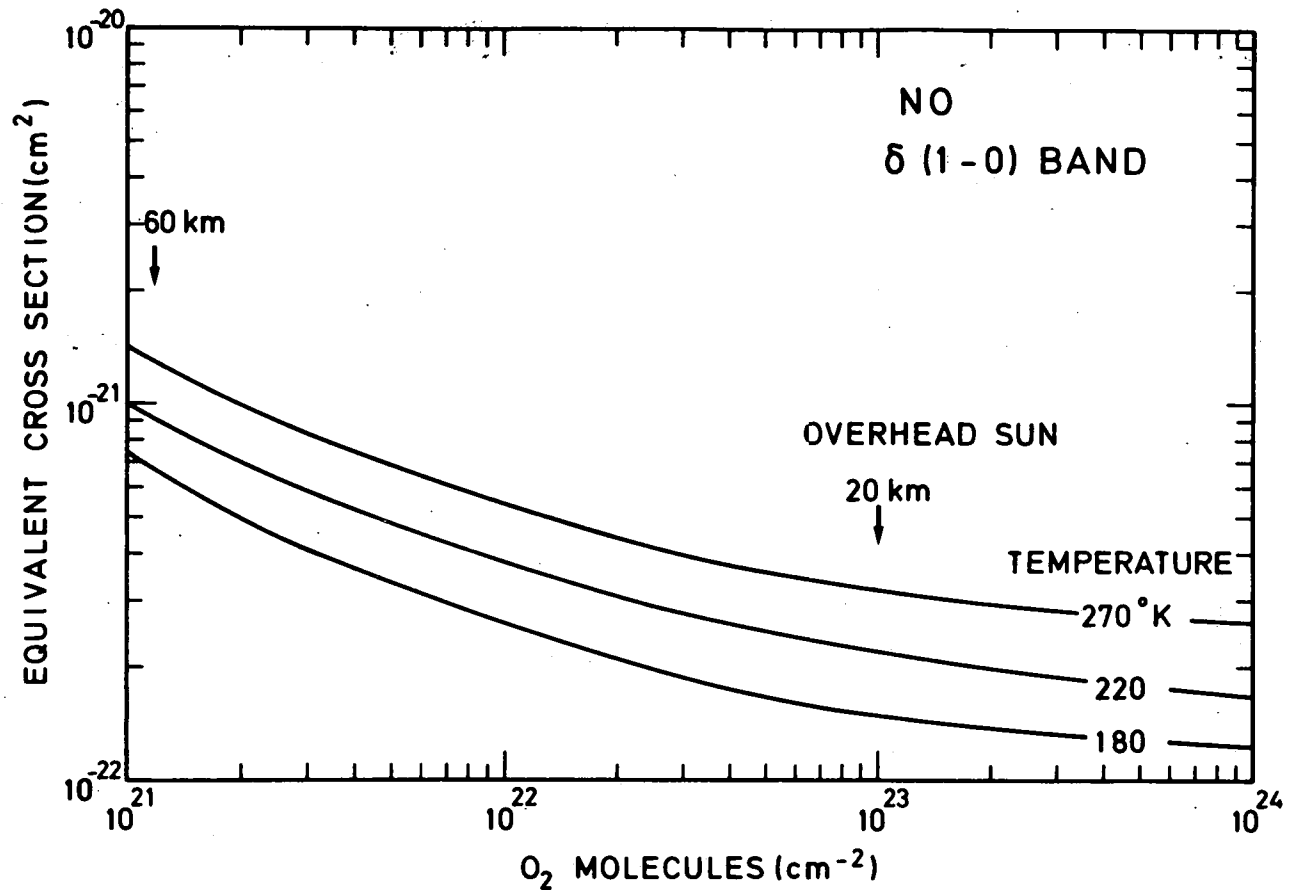


Fig. 6b.- Equivalent absorption cross section of molecular oxygen in the spectral range of the  $\delta(1-0)$  band of NO.

(24) but could be less depending on the solar radiation temperatures which have been recently obtained.

As far as the photodissociation coefficient  $J_{\text{NO}}(\delta, 1-0)$  is concerned, it is really difficult to adopt a precise value. Since it is assumed that the oscillator strength of  $\delta(1-0)$  as given by Bethke can be used it does set a lower limit on the value of the dissociation coefficient :

$$J_{\text{NO}}(\delta, 1-0)_{\infty} \geq 3 \times 10^{-6} \text{ sec}^{-1} \quad (25)$$

The final photodissociation coefficients are given in Table VII for two solar zenith angles ( $0^\circ$  = overhead sun and  $60^\circ$ ). This set of values of  $J_{\text{NO}}$  between 85 and 25 km has been obtained by considering  $J_{\text{NO}}(\delta, 0-0)$  as a maximum value and  $J_{\text{NO}}(\delta, 1-0)$  as a minimum value. At the present it is not possible to obtain more accurate values. A new interpretation of the absorption data of the  $\delta(1-0)$  band is required and a very precise determination of the solar flux in the spectral ranges of  $\delta(0-0)$  and  $\delta(1-0)$  is also needed.

### *CONCLUSION*

The major contribution to the dissociation of NO in the mesosphere and stratosphere is the predissociation of the  $\delta(1-0)$  and  $\delta(0-0)$  bands. A sufficiently precise value will be obtained when the solar flux in the spectral regions  $\lambda\lambda$  1910 and 1830 A is known with great accuracy. Another determination is required in order to check the experimental value of the oscillator strength of  $\delta(1-0)$  band. In any case the vertical distribution of the photodissociation coefficient of nitric oxide requires the detailed analysis of the rotational absorption of the Schumann-Runge bands.

### *ACKNOWLEDGMENT*

We are indebted to Prof. Miescher for his unpublished data on NO bands.

**TABLE I : Electronic oscillator strengths, Franck-Condon factors and emission probabilities  
for nitric oxide bands**

Band	$f(v'v'')$	$q(v'v'')$	$A v'v''$ ( $\text{sec}^{-1}$ )	Spectral range ( $\text{cm}^{-1}$ )
$\beta(7-0)$	$4.3 \times 10^{-3}$	$2.8 \times 10^{-2}$	$1.9 \times 10^5$	52100 - 52500
$\beta(8-0)$	$6.1 \times 10^{-3}$	$2.9 \times 10^{-2}$	$4.1 \times 10^5$	53000 - 52300
$\beta(9-0)$	$7.9 \times 10^{-3}$	$4.9 \times 10^{-2}$	$7.0 \times 10^5$	54000 - 54200
$\beta(10-0)$	$6.5 \times 10^{-3}$	$5.9 \times 10^{-2}$	$7.2 \times 10^5$	54900 - 55100
$\beta(11-0)$	$5.7 \times 10^{-3}$	$6.7 \times 10^{-2}$	$7.5 \times 10^5$	55700 - 56000
$\beta(12-0)$	$3.3 \times 10^{-2}$	$7.2 \times 10^{-2}$	$4.4 \times 10^6$	56300 - 56800
$\gamma(4-0)$	$2.3 \times 10^{-3}$	$5.1 \times 10^{-2}$	$5.1 \times 10^5$	53200 - 53400
$\gamma(5-0)$	$2.3 \times 10^{-3}$	$1.2 \times 10^{-2}$	$1.4 \times 10^5$	55500 - 55700



TABLE II : Temperature, oxygen and ozone total contents for an overhead sun

$z$ (km)	$T$ (°K)	$\int_z^{\infty} n(\text{O}_2) dz'$ ( $\text{cm}^{-2}$ )	$\int_z^{\infty} n(\text{O}_3) dz'$ ( $\text{cm}^{-2}$ )
15	211	$5.1 \times 10^{23}$	$6.6 \times 10^{18}$
20	217	$2.3 \times 10^{23}$	$5.5 \times 10^{18}$
30	235	$5.2 \times 10^{22}$	$2.4 \times 10^{18}$
40	268	$1.4 \times 10^{22}$	$4.4 \times 10^{17}$
50	274	$4.0 \times 10^{21}$	$4.4 \times 10^{16}$
60	253	$1.1 \times 10^{21}$	$4.5 \times 10^{15}$
70	211	$2.7 \times 10^{20}$	$5.4 \times 10^{14}$
80	177	$4.8 \times 10^{19}$	$1.4 \times 10^{14}$

TABLE III : Energies of the rotational levels of  $X^2\Pi(v=0)$  state and relative populations for  $T = 220^{\circ}\text{K}$ .

$J''$	$F_1(J'')$ ( $\text{cm}^{-1}$ )	$N_1(J'')/N_{\text{Tot}}$	$F_2(J'')$ ( $\text{cm}^{-1}$ )	$N_2(J'')/N_{\text{Tot}}$
0.5	0.00	0.01499		
1.5	5.01	0.02902	124.81	0.01325
2.5	13.37	0.04121	133.41	0.01880
3.5	25.07	0.05090	145.44	0.02317
4.5	40.12	0.05767	160.92	0.02617
5.5	58.52	0.06126	179.83	0.02775
6.5	80.26	0.06210	202.18	0.02798
7.5	105.34	0.06023	227.96	0.02701
8.5	133.77	0.05627	257.17	0.02510
9.5	165.54	0.05079	289.81	0.02253
10.5	200.65	0.04440	325.88	0.01957
11.5	239.11	0.03767	365.38	0.01649
12.5	280.91	0.03105	408.30	0.01349
13.5	326.05	0.02489	454.64	0.01073
14.5	374.54	0.01942	504.39	0.00830
15.5	426.36	0.01476	557.56	0.00625
16.5	481.53	0.01093	614.15	0.00459
17.5	540.03	0.00789	674.14	0.00328
18.5	601.87	0.00556	737.53	0.00229
19.5	667.05	0.00382	804.33	0.00155
20.5	735.57	0.00256	874.52	0.00103
21.5	807.42	0.00167	948.11	0.00066
22.5	882.60	0.00107	1025.09	0.00042
23.5	961.11	0.00067	1105.45	0.00026
24.5	1042.95	0.00040	1189.19	0.00015
25.5	1128.11	0.00024	1276.31	0.00009
26.5	1216.60	0.00014	1366.81	0.00005
27.5	1308.42	0.00008	1460.67	0.00002
28.5	1403.55	0.00004	1557.89	0.00001

TABLE III : Energies of the rotational levels of X <sup>2</sup>Π(v=0) state and relative populations for T = 220 °K (continued).

J''	F <sub>1</sub> (J'') (cm <sup>-1</sup> )	N <sub>1</sub> (J'')/N <sub>Tot</sub>	F <sub>2</sub> (J'') (cm <sup>-1</sup> )	N <sub>2</sub> (J'')/N <sub>Tot</sub>
29.5	1502.00	0.00002	1658.48	0.00000
30.5	1603.76	0.00001	1762.42	0.00000
31.5	1708.83	0.00000	1869.70	0.00000
32.5	1817.21	0.00000	1980.34	0.00000
33.5	1928.89	0.00000	2094.31	0.00000
34.5	2043.87	0.00000	2211.61	0.00000
35.5	2162.15	0.00000	2332.25	0.00000
36.5	2283.73	0.00000	2456.20	0.00000
37.5	2408.59	0.00000	2583.48	0.00000
38.5	2536.73	0.00000	2714.07	0.00000
39.5	2668.16	0.00000	2847.96	0.00000

TABLE IV : Wavenumbers and absorption cross-sections at the center of the strongest lines of the various branches of the  $\delta(0-0)$  band of NO at 220 °K.

Branch	$J''$	$\nu(\text{cm}^{-1})$	$\sigma(\text{cm}^2)$	Branch	$J''$	$\nu(\text{cm}^{-1})$	$\sigma(\text{cm}^2)$
$P_{11}$	$6\frac{1}{2}$	$\left\{ \begin{array}{c} 52350.7 \\ 52348.3 \end{array} \right\}$	$2.0 \times 10^{-16}$	$P_{12}$	$6\frac{1}{2}$	$\left\{ \begin{array}{c} 52228.7 \\ 52228.5 \end{array} \right\}$	$5.0 \times 10^{-17}$
$R_{11}$	$6\frac{1}{2}$	$\left\{ \begin{array}{c} 52401.4 \\ 52400.7 \end{array} \right\}$	$2.3 \times 10^{-16}$	$R_{12}$	$6\frac{1}{2}$	$\left\{ \begin{array}{c} 52279.4 \\ 52278.6 \end{array} \right\}$	$5.2 \times 10^{-17}$
$P_{21}$	$6\frac{1}{2}$	$\left\{ \begin{array}{c} 52373.4 \\ 52372.7 \end{array} \right\}$	$1.2 \times 10^{-16}$	$P_{22}$	$6\frac{1}{2}$	$\left\{ \begin{array}{c} 52251.3 \\ 52250.8 \end{array} \right\}$	$8.9 \times 10^{-17}$
$R_{21}$	$5\frac{1}{2}$	$\left\{ \begin{array}{c} 52422.9 \\ 52422.1 \end{array} \right\}$	$1.5 \times 10^{-16}$	$R_{22}$	$5\frac{1}{2}$	$\left\{ \begin{array}{c} 52301.6 \\ 52300.7 \end{array} \right\}$	$1.0 \times 10^{-16}$

TABLE V : Reduction factors of the photodissociation coefficient by ozone in the  $\delta(0-0)$  and  $(1-0)$  bands of NO. Overhead conditions.

Altitude (km)	$\delta(0-0)$	$\delta(1-0)$
50	0.98	0.97
45	0.94	0.90
40	0.81	0.73
35	0.57	0.42
30	0.32	0.17
25	0.15	$5.56 \times 10^{-2}$
20	$6.99 \times 10^{-2}$	$1.76 \times 10^{-2}$
15	$4.23 \times 10^{-2}$	$8.18 \times 10^{-3}$

TABLE VI : Reduction factor of the photodissociation coefficient  $J_{NO}$  of the  $\delta(0-0)$  band due to  $N_2$  quenching.

Altitude (km)	$\delta(0-0)$	Altitude (km)	$\delta(0-0)$
50	0.98	30	0.80
45	0.97	25	0.64
40	0.95	20	0.45
35	0.90	15	0.27

TABLE VII : Photodissociation coefficients of NO versus height in the mesosphere and stratosphere ( $\text{sec}^{-1}$ )

Altitude (km)	$\delta(0-0)$ band		$\delta(1-0)$ band	
	$\text{sec}\chi = 1$	$\text{sec}\chi = 2$	$\text{sec}\chi = 1$	$\text{sec}\chi = 2$
85	$6.80 \times 10^{-6}$	$6.72 \times 10^{-6}$	$2.84 \times 10^{-6}$	$2.70 \times 10^{-6}$
80	$6.64 \times 10^{-6}$	$6.41 \times 10^{-6}$	$2.61 \times 10^{-6}$	$2.42 \times 10^{-6}$
75	$6.33 \times 10^{-6}$	$5.95 \times 10^{-6}$	$2.36 \times 10^{-6}$	$2.12 \times 10^{-6}$
70	$5.80 \times 10^{-6}$	$5.31 \times 10^{-6}$	$1.94 \times 10^{-6}$	$1.62 \times 10^{-6}$
65	$5.22 \times 10^{-6}$	$4.65 \times 10^{-6}$	$1.54 \times 10^{-6}$	$1.16 \times 10^{-6}$
60	$4.44 \times 10^{-6}$	$3.61 \times 10^{-6}$	$9.08 \times 10^{-7}$	$5.03 \times 10^{-7}$
55	$3.54 \times 10^{-6}$	$2.53 \times 10^{-6}$	$4.65 \times 10^{-6}$	$1.68 \times 10^{-7}$
50	$2.53 \times 10^{-6}$	$1.51 \times 10^{-6}$	$1.75 \times 10^{-7}$	$3.19 \times 10^{-8}$
45	$1.52 \times 10^{-6}$	$6.83 \times 10^{-7}$	$3.61 \times 10^{-8}$	$2.07 \times 10^{-9}$
40	$6.64 \times 10^{-7}$	$1.94 \times 10^{-7}$	$2.44 \times 10^{-9}$	$1.73 \times 10^{-11}$
35	$1.70 \times 10^{-7}$	$2.53 \times 10^{-8}$	$1.80 \times 10^{-11}$	$1.71 \times 10^{-15}$
30	$3.36 \times 10^{-8}$	$1.78 \times 10^{-9}$	$2.97 \times 10^{-14}$	$6.22 \times 10^{-22}$
25	$6.92 \times 10^{-13}$	$1.49 \times 10^{-16}$	$2.93 \times 10^{-22}$	

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