

Predissociation of Nitric Oxide in the Mesosphere and Stratosphere

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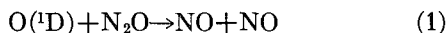
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ABSTRACT

Absorption of solar photons by nitric oxide in the wavelength ranges 181.3–183.5 and 189.4–191.6 nm leads to predissociation of the molecule in the mesosphere and upper stratosphere. Molecular oxygen controls the penetration of the required solar irradiance via absorption in the Schumann-Runge bands, while attenuation due to ozone becomes significant in the upper stratosphere. The calculation of the nitric oxide dissociation rate is complicated by the need to include all rotational fine structure in both the NO and O₂ cross sections. The dissociation rate computed here for the upper mesosphere is a factor of 3.6 less than that reported in past work when currently accepted values of the oscillator strengths and solar irradiance are used. In addition, improved molecular parameters describing the O₂ cross section predict less attenuation of the dissociation rate with decreasing altitude than results previously available.

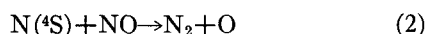
1. Introduction

The role played by nitric oxide as a major participant in the stratospheric photochemical balance has been appreciated since the work of Crutzen (1971). Its importance in the formation of the D-region was realized much earlier (Nicolet and Aiken, 1960) while the study of nitric oxide in the thermosphere was stimulated by *in situ* measurements of the gas (Barth, 1964). A firm understanding of the origin and distribution of odd nitrogen in the earth's atmosphere is difficult to achieve due in part to the high stability of N₂ against dissociation when exposed to ultraviolet radiation. The sources of odd nitrogen in the stratosphere and mesosphere must be attributed to vertical transport of N₂O upward from the troposphere followed by the reaction



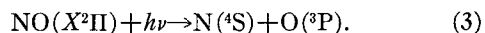
and to downward transport of NO from the thermosphere where it is produced by ion chemistry. Norton and Barth (1970), Strobel (1971), Nicolet and Peetermans (1972), Brasseur and Nicolet (1973), Strobel *et al.* (1976) and Frederick and Rusch (1977) have discussed details of odd nitrogen chemistry in the various altitude regimes.

A quantitative evaluation of the sinks of odd nitrogen presents a problem as difficult as that of the sources. The reaction



proceeds rapidly and is the only efficient chemical loss of NO_x. In the thermosphere ion chemistry provides a source of atomic nitrogen for reaction (2);

however, below the mesopause the only means of producing nitrogen atoms is the predissociation of nitric oxide



Nitric oxide molecules are excited from the $v'=0$ level of the X²Π ground term to the $v'=0$ and 1 levels of the excited C²Π term giving rise to the δ(0-0) and δ(1-0) absorption bands, respectively. Predissociation occurs for all levels with energy greater than that of $v'=0, J'=\frac{5}{2}$ due to the presence of a repulsive state, tentatively identified as a⁴Π by Callear and Pilling (1970a). Predissociation occurs in systems other than the δ bands, although Cieslik and Nicolet (1973) have shown that only the δ bands are of primary importance in the mesosphere and upper stratosphere. Under atmospheric conditions, the predissociation competes with emission (Ackerman and Miescher, 1969) and quenching by N₂ (Callear and Smith, 1964). Strobel (1971) pointed out the aeronomic importance of NO predissociation and Cieslik and Nicolet (1973) conducted the first detailed study of the process. However, since the time of these calculations there have been significant revisions in several of the input parameters to which the dissociation rate is sensitive. This paper is a re-examination of process 3 in the stratosphere and mesosphere using recent molecular data. Special attention is given to the uncertainties in the NO dissociation rate profile due to the error bars associated with the input quantities.

2. Absorption by nitric oxide in the delta bands

Callear and Pilling (1970a,b) have discussed the experimental evidence for predissociation of the C²Π

TABLE 1. Constants used in computing term values and line positions in the nitric oxide delta bands.

a. Band constants		
State	B (cm ⁻¹)	D (cm ⁻¹)
X ² Π _{1/2} (v''=0)	1.695857	5.569×10 ⁻⁶
X ² Π _{3/2} (v''=0)	1.696302	5.569×10 ⁻⁶
C ² Π _{1/2} (v'=0)	1.981	4.0 ×10 ⁻⁶
C ² Π _{3/2} (v'=0)	1.982	4.0 ×10 ⁻⁶
C ² Π _{1/2} (v'=1)	1.948	4.0 ×10 ⁻⁶
C ² Π _{3/2} (v'=1)	1.966	4.0 ×10 ⁻⁶
b. Band head wavenumbers		
Transition	Band head (cm ⁻¹)	
C ² Π _{1/2} (v'=0) - X ² Π _{1/2} (v''=0)	52 372	
C ² Π _{3/2} (v'=0) - X ² Π _{3/2} (v''=0)	52 380	
C ² Π _{1/2} (v'=1) - X ² Π _{1/2} (v''=0)	54 697	
C ² Π _{3/2} (v'=1) - X ² Π _{3/2} (v''=0)	54 742	

term of NO and concluded that predissociation of the v'=0 level is 35±5 times faster than radiation. However, the predissociation line widths are sufficiently small that they have not been experimentally separated from the Doppler widths (Herzberg *et al.*, 1956). No emission has been observed from levels of C²Π with v' ≥ 1 which implies efficient predissociation here (Ackerman and Miescher, 1969). The integrated cross section of a line in the transition C²Π(v', J') ← X²Π(v'', J'') is

$$\int \sigma_i(v) dv = \frac{\pi e^2}{mc^2} f(v', v'') \frac{S_i(J'')}{2J''+1} N(v'', J'', \rho'', \Sigma''), \quad (1)$$

where $f(v', v'')$ is the band oscillator strength, $S_i(J'')$ the rotational line strength whose algebraic form depends on the particular line i considered (P_{11} , R_{11} , etc.), and $N(v'', J'', \rho'', \Sigma'')$ the fractional population of the lower state. The quantities e , m and c are the electron charge, electron mass and speed of light, respectively, and the index $\rho=1, 2$ indicates that the lines are Λ doubled. The parameter $\Sigma''=1, 2$ denotes the ²Π_{1/2} and ²Π_{3/2} substates, respectively. We compute N from a Boltzmann distribution

$$N(v'', J'', \rho'', \Sigma'') = \frac{(2J''+1) \exp[-hc\nu(v'', J'', \rho'', \Sigma'')/kT]}{Q(T)}, \quad (2)$$

where $Q(T)$ is the partition function given by

$$Q(T) = \sum_{\Sigma} \sum_{\rho} \sum_{J} \sum_{v} (2J+1) \exp[-hc\nu(v, J, \rho, \Sigma)/kT] \quad (3)$$

and $\nu(v, J, \rho, \Sigma)$ is the term value of the level. The remaining quantities in Eq. (3) are temperature T , Planck's constant h and Boltzmann's constant k . The rotational line strengths used in (1) refer to the

individual components of the Λ doublets and therefore are consistent with the definition of the lower state fractional population [Eq. (2)].

Herzberg (1950) has discussed the lines which appear in transitions of the type ²Π-²Π when both the upper and lower states are described by the same Hund's coupling case. However, the C²Π term of NO is described by Hund's "case b," while "case a" applies to the X²Π ground state. Erkovich *et al.* (1964) have derived rotational line strengths for such transitions and have shown their results to be in good agreement with the observed emission spectra of the NO $\delta(0-0)$ band. We use their results in (1).

A discrepancy has existed in the literature concerning values of the oscillator strengths for the NO δ bands. Bethke (1959) deduced the values

$$f(0-0) \approx 2.49 \times 10^{-3},$$

$$f(1-0) \approx 5.78 \times 10^{-3},$$

from pressure-broadened absorption spectra. The $f(0-0)$ and $f(1-0)$ values stated above are actually the sums of the f values of the $\delta(0-0)$ and $\beta(7-0)$ and of the $\delta(1-0)$ and $\beta(10-0)$ bands, respectively, since there is considerable overlap of the pressure-broadened lines. However, the δ bands provide the dominant contribution. The work of Callear and Pilling (1970b) produced a result, $f(0-0) = 5.6 \times 10^{-3}$, a factor of 2.2-2.3 above the Bethke value. The aeronomic calculations of Cieslik and Nicolet (1973) adopted the large $f(0-0)$ of Callear and Pilling and also multiplied Bethke's value for $f(1-0)$ by a scaling factor near 2.2. However, the work of Mandelman and Carrington (1974) has produced a value $f(0-0) = 2.2 \times 10^{-3}$ in good agreement with the original result of Bethke (1959). The smaller value of $f(0-0)$ now appears to be well established and we therefore see no reason to doubt Bethke's result for $f(1-0)$. For the present work we adopt the values

$$f(0-0) = 2.2 \times 10^{-3},$$

$$f(1-0) = 5.4 \times 10^{-3},$$

where the oscillator strength for the $\beta(10-0)$ band as tabulated by Cieslik and Nicolet has been subtracted from Bethke's value to obtain $f(1-0)$. The agreement between the original Bethke (1959) value and the more recent result for the $\delta(0-0)$ band leads us to adopt an error bar of only ±10% on the band oscillator strengths.

Standard formulas exist from which one can compute the positions of all lines in the $\delta(0-0)$ and $\delta(1-0)$ bands (Herzberg, 1950; Cieslik and Nicolet, 1973). However, a simple analytic formula often fails to account for energy-level perturbations in the molecule (Brix and Herzberg, 1954; Ben-Aryeh, 1973), and we therefore prefer to use the line position measurements of Lagerqvist and Miescher (1958) which were usually able to resolve individual components of the Λ -doublets.

Where measurements were not available, we computed line positions from the formula used by Cieslik and Nicolet (1973). This was necessary for all Q branches and lines with $J \gtrsim 20$. The molecular constants used for the $C^2\Pi$ term are those of Lagerqvist and Miescher (1958) and for $X^2\Pi$ were the recent values of Kristiansen (1977). Table 1 lists these constants together with the band head values of Lagerqvist and Miescher (1958).

The final input to the cross-section calculation is the line shape. Cieslik and Nicolet (1973) effectively assumed a delta-function profile with the entire integrated cross section concentrated at the line center. We have associated a Voigt profile with each rotational line which allows for the combined effects of predissociation and Doppler broadening (Frederick and Hudson, 1979). Since the predissociation line width has not actually been measured we wish to examine the effect of varying this parameter on the NO dissociation rate. Although the core of a line is adequately described by a Doppler profile, a small predissociation width can significantly influence the line wings. Herzberg *et al.* (1956) examined the δ -bands in absorption with a spectrograph capable of distinguishing lines separated by 0.35 cm^{-1} (see also

Brix and Herzberg, 1954). The spectra did not appear diffuse which requires the combined full-widths due to predissociation and Doppler broadening to be less than this value. This implies a predissociation half-width (at half maximum), ΔL , less than 10^{-1} cm^{-1} . The Heisenberg uncertainty principle allows an order of magnitude estimate of ΔL as follows: The line width is associated with an energy spread of $\Delta E = hc\Delta L$. The lifetime of the state prior to predissociation is $\Delta t = 1/D$, where D is the predissociation frequency measured by Callear and Pilling (1970a) to be $1.65 \times 10^9 \text{ s}^{-1}$ for the $\delta(0-0)$ band. Since $\Delta E\Delta t \approx h/2\pi$, we obtain $\Delta L \approx D/(2\pi c) = 9 \times 10^{-3} \text{ cm}^{-1}$. Thus, the line half-width of the $\delta(0-0)$ band is likely of order $1 \times 10^{-2} \text{ cm}^{-1}$. We adopt this value for both the $\delta(0-0)$ and $\delta(1-0)$ bands as the best estimate but also perform calculations for half-widths of $5 \times 10^{-2} \text{ cm}^{-1}$. These line width values represent crude estimates. However, as demonstrated later the adopted factor of 5 spread leads to only small changes in the computed NO predissociation rate. The absorption cross section for the $\delta(0-0)$ bands was computed between 52 200 and 52 800 cm^{-1} in wavenumber steps of $2 \times 10^{-2} \text{ cm}^{-1}$ so as to resolve the shape of each line. For the $\delta(1-0)$ bands we considered the wavenumber range 54 500

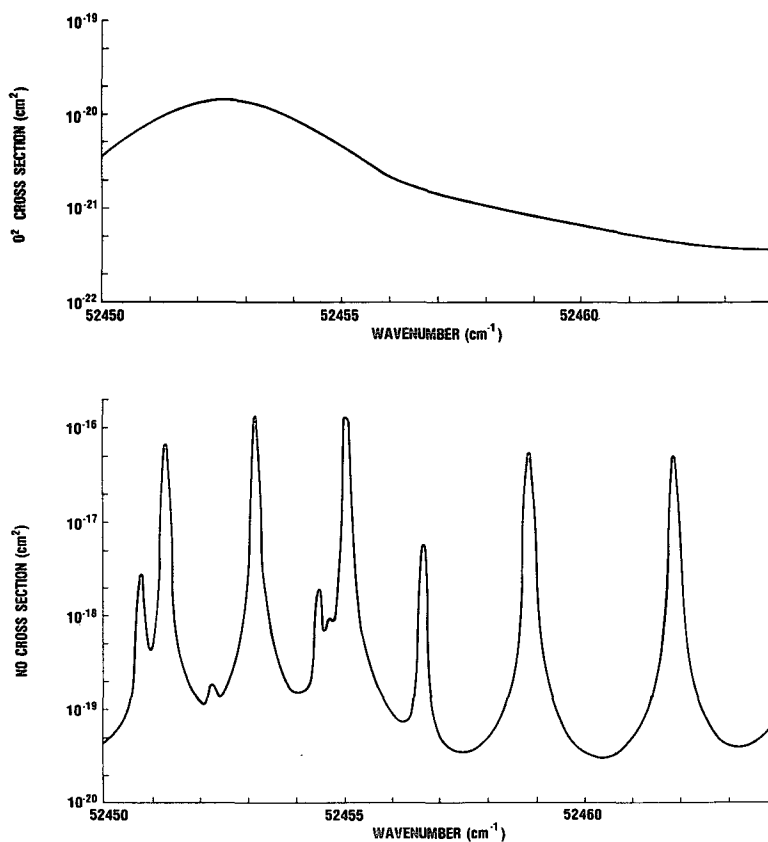


FIG. 1. Cross sections of NO and O_2 in the spectral region of the $\delta(0-0)$ and (5-0) Schumann-Runge bands. The wavenumber interval shown covers approximately 0.052 nm centered on 190.63 nm . The temperature is 250 K .

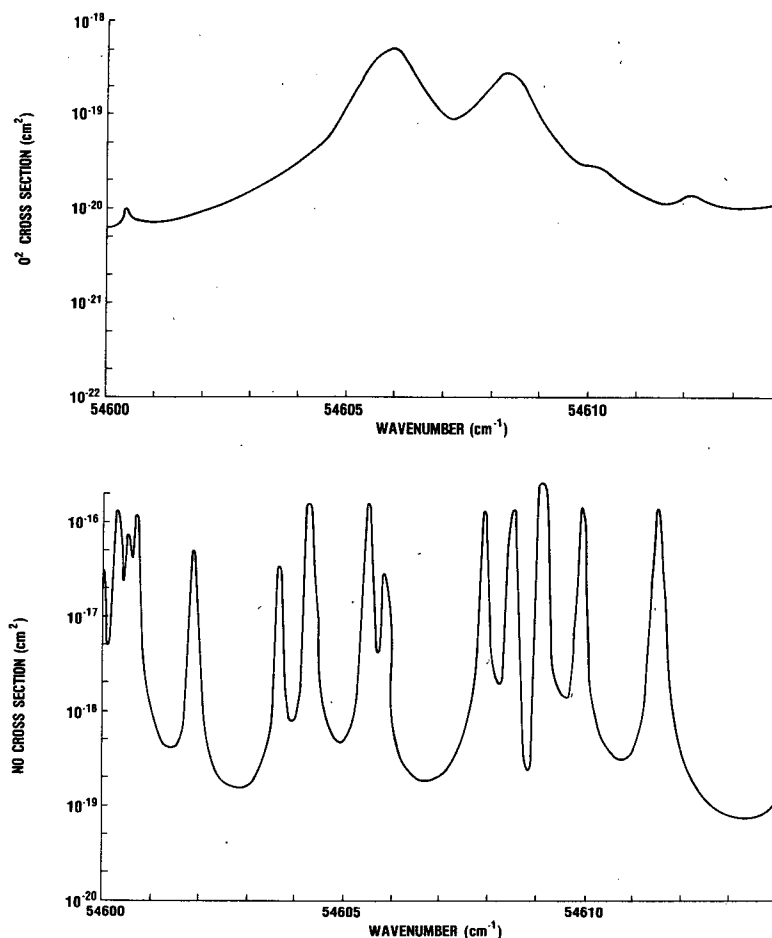


FIG. 2. Cross sections of NO and O₂ in the spectral region of the $\delta(1-0)$ and $(9-0)$ Schumann-Runge bands. The wavenumber interval shown covers approximately 0.048 nm centered on 183.13 nm. The temperature is 250 K.

to 55 150 cm⁻¹. Figs. 1 and 2 present cross sections for portions of the $\delta(0-0)$ and $\delta(1-0)$ bands at a temperature of 250 K. The inclusion of the detail shown in Figs. 1 and 2 is necessary for aeronomic calculations as discussed in the next section.

3. Aeronomic application

The NO dissociation rate J (s⁻¹) as a function of altitude z and solar zenith angle θ is

$$J(z, \theta) = \int d\lambda \sigma_d(\lambda, z) F(\lambda, z, \theta), \quad (4)$$

where λ is wavelength and $\sigma_d(\lambda, z)$ (cm²) is the NO dissociation cross section which is altitude-dependent as discussed below. The solar irradiance which reaches altitude z is

$$F(\lambda, z, \theta) = F(\lambda, \infty) \exp[-\tau(\lambda, z) \sec \theta], \quad (5)$$

where $F(\lambda, \infty)$ is the unattenuated irradiance and τ the vertical optical depth. Eqs. (1)–(3) show that

the NO total absorption cross section is temperature and therefore altitude dependent; however, absorption does not lead to dissociation in all cases. The dissociation cross section σ_d is related to the total cross section by

$$\sigma_d(\lambda, z) = \frac{D}{A + D + k[\text{N}_2]} \sigma(\lambda, z), \quad (6)$$

where D is the rate of spontaneous predissociation for the band considered, A the rate for spontaneous radiation, k the rate coefficient for quenching by N₂. For the $\delta(0-0)$ band we adopt the values $k(0-0) = 1.5 \times 10^{-15}$ m³ s⁻¹ of Callear and Smith (1964), $D(0-0) = 1.65 \times 10^9$ s⁻¹ and $A = 5.1 \times 10^7$ s⁻¹ as given by Callear and Pilling (1970a). The $v' = 0$ level of NO ($C^2\Pi$) also radiates to $A^2\Sigma(v' = 1)$ which in turn predissociates so that this is implicitly contained in the adopted value of $D(0-0)$. There are apparently no measurements of the quenching or spontaneous predissociation rates of the $C^2\Pi$ ($v' = 1$) level; however, based on the absence of observed emission we can

neglect $A(1-0)$ in Eq. (6). If we adopt the D and k values of the 0-0 band as a rough guide to those for 1-0, then the ratio $k[N_2]/D$ is unity when $[N_2] = 1.1 \times 10^{24} \text{ m}^{-3}$ which corresponds to an altitude of 21–22 km. Since the wavelengths involved are near 182.5 nm, such altitudes are lower than need be considered and we can assume $\sigma_d(\lambda, z) = \sigma(\lambda, z)$ for the $\delta(1-0)$ band.

The major problem encountered in applying (4) to the aeronomic dissociation of NO comes in evaluating the solar flux that penetrates to a given altitude as a function of wavelength. The optical depth in the spectral region of interest is controlled primarily by molecular oxygen absorption in the Schumann-Runge (SR) bands ($B^3\Sigma-X^3\Sigma$). A predissociation is involved in O_2 which leads to a cross section with rotational line structure similar to that in NO, except that the predissociation line widths are comparable to or larger than the Doppler widths. The $\delta(0-0)$ band of NO overlaps the (5-0) SR band and $\delta(1-0)$ coincides with the (9-0) and (10-0) SR bands. We have computed the O_2 cross section as a function of temperature using the oscillator strengths and line widths determined by Frederick and Hudson (1979). Table 2 lists values for the three most important bands together with the uncertainty limits given by the authors and compares them to the results of Ackerman *et al.* (1970) which were used in the work of Cieslik and Nicolet (1973). The newer line widths agree with the older results within the limits of the error bars for the 5-0 and 9-0 bands; however, the 10-0 line width deduced by Frederick and Hudson (1979) is a factor of 4 smaller than that of Ackerman *et al.* (1970). Since the cross section in the wings of a line is proportional to the line width, the $\delta(1-0)$ dissociation rate computed here will experience less attenuation than predicted in the work of Cieslik and Nicolet (1973). Figs. 1 and 2 illustrate small portions of the O_2 cross section in the spectral region of the NO $\delta(0-0)$ and $\delta(1-0)$ bands, respectively. The O_2 cross section appears to vary slowly with wavenumber only because of the extremely fine scale used for the abscissas. It is apparent in Figs. 1 and 2 that the line widths in the O_2 Schumann-Runge bands are much greater than those of the NO δ bands. To a first approximation one could assume that the O_2 cross section is constant over the

TABLE 2. Predissociation line widths of O_2 in the Schumann-Runge bands which overlap the NO δ -bands.

Band	ΔL (cm ⁻¹)*	Error limits on ΔL (cm ⁻¹)*	ΔL (cm ⁻¹ **
5-0	1.17	1.00–1.46	1.15
9-0	0.38	0.21–0.60	0.55
10-0	0.21	0.17–0.23	0.85

* Predissociation half-widths of Frederick and Hudson (1979).

** Predissociation half-widths of Ackerman *et al.* (1970).

TABLE 3. Model atmosphere used in the NO dissociation rate calculation.

Z (km)	Column O_2 (m ⁻²)	Column O_3 (m ⁻²)	T (K)	$\tau(O_3)^*$ $\delta(1-0)$	$\tau(O_3)^*$ $\delta(0-0)$
90	8.323+22**	1.123+16	186.9	8.28-7	5.68-7
85	2.025+23	4.139+16	188.9	3.05-6	2.09-6
80	4.781+23	1.526+17	198.6	1.12-5	7.72-6
75	1.084+24	5.628+17	208.4	4.15-5	2.85-5
70	2.364+24	2.073+18	219.6	1.53-4	1.05-4
65	4.945+24	8.388+18	233.3	6.18-4	4.24-4
60	9.926+24	3.065+19	247.0	2.26-3	1.55-3
55	1.920+25	9.523+19	260.8	7.02-3	4.82-3
50	3.608+25	2.917+20	270.7	2.15-2	1.48-2
45	6.758+25	9.362+20	264.2	6.90-2	4.74-2
40	1.299+26	2.580+21	250.4	1.90-1	1.31-1
35	2.595+26	7.595+21	236.5	5.60-1	3.84-1
30	5.382+26	1.712+22	226.5	1.26+0	8.66-1
25	1.145+27	3.376+22	221.6	2.49+0	1.71+0
20	2.480+27	5.639+22	216.7	4.16+0	2.85+0

* $\tau(O_3)$ is the vertical optical depth due to ozone. Reported values are based on mean cross sections for the NO $\delta(1-0)$ and $\delta(0-0)$ bands of 7.37×10^{-19} and $5.06 \times 10^{-19} \text{ cm}^2$, respectively.

** Read 8.323+22 as 8.323×10^{22} .

entire width of a nitric oxide absorption line as was done by Cieslik and Nicolet (1973). However, the inclusion of line broadening in NO leads to a cross section of order 10^{-19} cm^2 between the lines which should be included in detailed calculations.

The final quantity required in the dissociation rate calculation is the incident solar irradiance $F(\lambda, \infty)$ in Eq. (5). The currently accepted values in the spectral region of the Schumann-Runge bands are smaller than those used in aeronomy several years ago. This study adopts the absolute irradiance measurements of Heroux and Swirbalus (1976) which are a factor of 1.5–1.6 smaller than those in the tabulation of Ackerman (1971). An additional complication arises from the fine-structure in the incident solar spectrum. High-resolution spectra reported by Moe *et al.* (1976) reveal irradiance variations of a factor of 2 or more over wavelength intervals of order 10^{-2} nm in width. In many cases of aeronomic interest such structure does not have significant impact on a numerical result since a large degree of cancellation occurs on integration. It is not obvious that this will be the case for the NO dissociation rate and we include the solar finestructure in the calculation. Therefore, we have normalized the high-resolution spectra of Moe *et al.* (1976) to the 1 nm band-averaged results of Heroux and Swirbalus (1976). Since the wavelength scale of spectra of Moe *et al.* (1976) has an uncertainty of $\pm 2.5 \times 10^{-3} \text{ nm}$, we examine the response of the NO dissociation rate to shifts of this magnitude.

4. Results

We have computed altitude profiles of the NO dissociation rate for the $\delta(0-0)$ and $\delta(1-0)$ bands using Eq. (4) and the temperature, O_2 and O_3 profiles

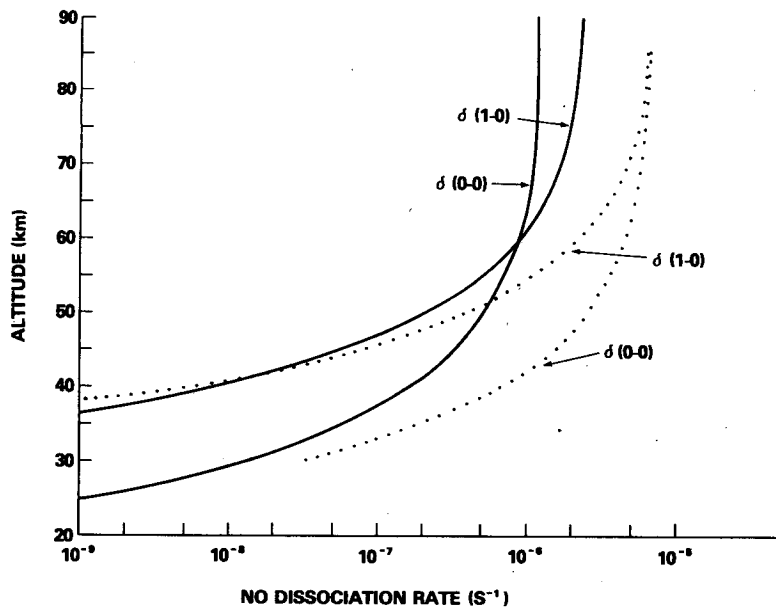


FIG. 3. Altitude profiles of the NO dissociation rate in the $\delta(0-0)$ and $\delta(1-0)$ bands for an overhead sun. The dotted curves are the results of Cieslik and Nicolet (1973).

presented in the *U.S. Standard Atmosphere 1976*. Table 3 summarizes the model atmosphere. Figs. 3 and 4 present the dissociation rate results for solar zenith angles of 0° and 60° , respectively, and the new calculations are compared with those of Cieslik and Nicolet (1973). The new values reported here were computed with a NO line width (half-width and half-maximum) of $1 \times 10^{-2} \text{ cm}^{-1}$. For an overhead sun the $\delta(0-0)$ band dissociation rate is reduced to $1/e$ of its

unattenuated value between 45 and 50 km, while the $\delta(1-0)$ band result experiences a $1/e$ attenuation by 60 km. For a solar zenith angle of 60° the e -folding heights are 50–55 and 65 km for the $\delta(0-0)$ and $\delta(1-0)$ bands, respectively. Below 30 km the total dissociation rate falls off rapidly due primarily to the absorption by O_2 , although as shown in Table 3 the effect of ozone must be included. In the upper mesosphere the new result for the sum of the $\delta(0-0)$ and

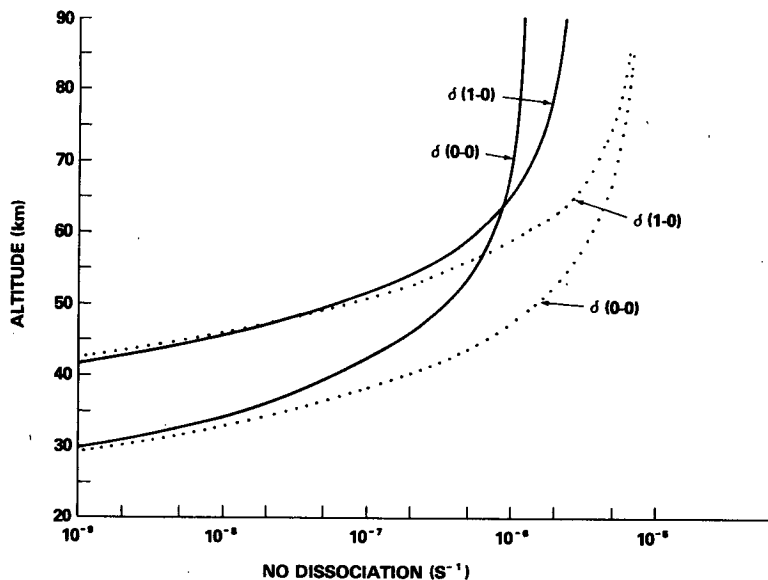


FIG. 4. Altitude profiles of the NO dissociation rate in the $\delta(0-0)$ and $\delta(1-0)$ bands for a solar zenith angle of 60° . The dotted curves are the results of Cieslik and Nicolet (1973).

$\delta(1-0)$ rates lies a factor of 3.6 below that of Cieslik and Nicolet (1973). However, the O_2 line widths deduced by Frederick and Hudson (1979) lead to a weaker attenuation of the $\delta(1-0)$ band dissociation than previously predicted and the old results intersect the new profile between 40 and 45 km for an overhead sun despite the large difference in the unattenuated rates.

The unattenuated results of Cieslik and Nicolet (1973) for $\delta(0-0)$ and $\delta(1-0)$ were 6.9×10^{-6} and $7.2 \times 10^{-6} \text{ s}^{-1}$, respectively, for the solar irradiance data of Ackerman (1971). The values deduced in the present work lie in the range $1.15\text{--}1.38 \times 10^{-6} \text{ s}^{-1}$ for $\delta(0-0)$ and $2.76\text{--}2.57 \times 10^{-6} \text{ s}^{-1}$ for $\delta(1-0)$ where the spread refers to a temperature interval from 150 to 300 K. We note that the results of Cieslik and Nicolet (1973) predict unattenuated rates for $\delta(0-0)$ and $\delta(1-0)$ which are nearly equal to each other while the values computed here differ among themselves by a factor of 2. The ratio of the newer results is consistent with expectation as is seen from the following argument. The oscillator strength of the $\delta(1-0)$ band is a factor of 2.45 larger than that for $\delta(0-0)$, and rotational levels of the $C^2\Pi(v'=0)$ state do not predissociate until J' reaches 7/2. This gives an "effective oscillator strength" for dissociation in the $\delta(0-0)$ band which is roughly 80% of the reported value. Finally, the incident solar flux in the $\delta(0-0)$ band is a factor of 1.5–1.6 greater than that for $\delta(1-0)$. Thus, the expected ratio of the $\delta(1-0)$ dissociation rate to that for $\delta(0-0)$ is $2.45/(0.80 \times 1.55) \approx 2.0$, in agreement with the exact calculation.

Table 4 contains a compilation of the final results in sufficient detail for use in aeronomic models. In the application of these values to model atmospheres other than that employed here, the dissociation rate should be expressed as a function of the O_2 column content listed in Table 3 with ozone attenuation appropriate to the particular case being studied. Errors introduced by using the results with realistic temperature profiles other than that given in Table 3 are small compared to the uncertainties discussed below.

Error bars to be placed on the values in Table 4 are due to 1) uncertainties in the NO predissociation line width, 2) errors in the O_2 and NO line positions, 3) errors in the wavelength scale of the high resolution solar spectrum, 4) the range of possible values for the molecular parameters given in Table 2, and 5) uncertainties in the absolute magnitudes of the NO oscillator strengths and solar irradiance of Heroux and Swirbalus (1976). We have evaluated the effect of these error sources on the dissociation rate for a solar zenith angle of 60° . Calculations performed for a NO line half-width at half-maximum, ΔL , of $5 \times 10^{-2} \text{ cm}^{-1}$ differed slightly from those reported in Table 4 for $\Delta L = 1 \times 10^{-2} \text{ cm}^{-1}$. The $\delta(0-0)$ band result shows no sensitivity to ΔL in the mesosphere. At 50 km the two sets of results differ by only 0.17%, while at 30

TABLE 4. Dissociation rate of nitric oxide (J) for various solar zenith angles (θ)*.

Z (km)	J ($\theta=0^\circ$) (s^{-1})	J ($\theta=30^\circ$) (s^{-1})	J ($\theta=60^\circ$) (s^{-1})	J ($\theta=85^\circ$) (s^{-1})
a. $\delta(0-0)$ band				
90	1.23–6**	1.22–6	1.21–6	1.13–6
85	1.22–6	1.21–6	1.19–6	1.05–6
80	1.20–6	1.18–6	1.15–6	9.62–7
75	1.16–6	1.14–6	1.09–6	8.41–7
70	1.09–6	1.07–6	9.95–7	6.81–7
65	9.94–7	9.72–7	8.82–7	4.90–7
60	8.77–7	8.50–7	7.34–7	2.98–7
55	7.26–7	6.92–7	5.52–7	1.37–7
50	5.39–7	4.99–7	3.54–7	4.03–8
45	3.40–7	3.03–7	1.77–7	5.87–9
40	1.75–7	1.47–7	6.66–8	2.22–10
35	6.44–8	5.00–8	1.49–8	5.32–13
30	1.38–8	9.18–9	1.25–9	7.69–18
25	1.13–9	5.74–10	1.70–11	9.10–27
20	1.86–11	5.69–12	1.08–14	6.04–45
b. $\delta(1-0)$ band				
90	2.48–6	2.46–6	2.38–6	2.05–6
85	2.34–6	2.32–6	2.22–6	1.82–6
80	2.16–6	2.13–6	2.02–6	1.49–6
75	1.95–6	1.92–6	1.76–6	1.05–6
70	1.72–6	1.63–6	1.42–6	5.57–7
65	1.32–6	1.26–6	9.94–7	1.90–7
60	9.10–7	8.38–7	5.66–7	3.08–8
55	5.10–7	4.46–7	2.35–7	1.24–9
50	2.13–7	1.71–7	5.77–8	5.37–12
45	5.94–8	4.13–8	6.64–9	3.44–16
40	8.33–9	4.56–9	2.10–10	6.36–24
35	2.88–10	1.00–10	3.76–13	3.56–39
30	4.40–13	5.89–14	1.11–18	0
25	7.30–19	1.28–20	3.72–30	0
20	6.54–31	1.64–34	3.70–54	0

* The reported values are based on a predissociation half-width at half-maximum of $1 \times 10^{-2} \text{ cm}^{-1}$.

** Read 1.23–6 as 1.23×10^{-6} .

and 20 km the differences are 7.3 and 14%, respectively. At 60 km the $\delta(1-0)$ band result for $\Delta L = 5 \times 10^{-2} \text{ cm}^{-1}$ is 1.5% larger than that for $\Delta L = 1 \times 10^{-2}$, increasing to 4.5 and 11% at 30 and 20 km, respectively. Uncertainties in the O_2 and NO line positions have negligible effects on the dissociation rate until large optical depths are reached. The same spectrograph produced both the O_2 and NO line positions used here and these measurements have an estimated uncertainty of $\pm 0.1 \text{ cm}^{-1}$ (Brix and Herzberg, 1954). Therefore, we have performed calculations which shifted the O_2 and NO lines relative to each other by this amount. For the $\delta(0-0)$ band this leads to changes in the dissociation rate of less than 1% above 60 km with a maximum change from the values in Table 4 of only 5–7% between 30 and 20 km. The maximum change at low altitudes for the $\delta(1-0)$ band was 9.7%. Uncertainties in the wavelength scale of the solar irradiance measurements of Moe *et al.* (1976) can influence with NO dissociation rate by shifting

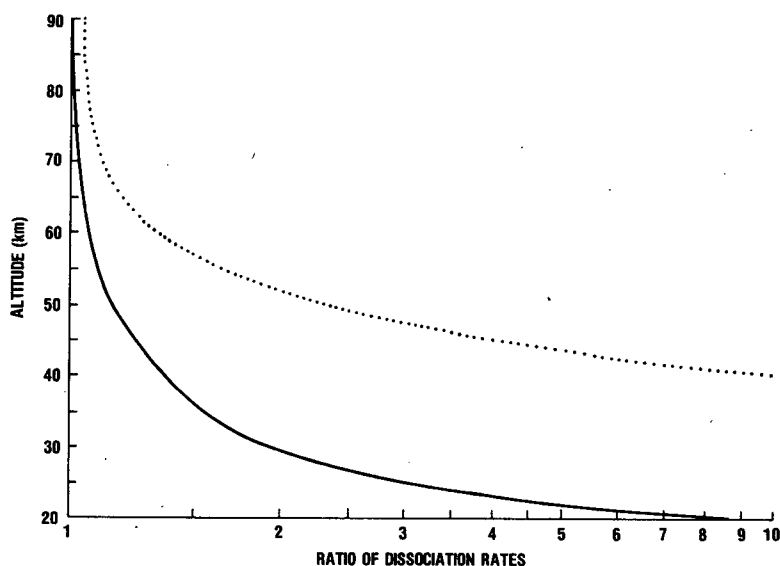


FIG. 5. Ratio of the NO dissociation rate computed using the O_2 band parameters at the lower limit of the error bars in Table 2 to that using the best estimates for the oscillator strengths and line widths. Solid line gives result for the $\delta(0-0)$ band. The dotted line refers to the $\delta(1-0)$ band. Results are for a solar zenith angle of 60° .

the spectral finestructure with respect to the atmospheric absorption bands. We have found this effect to be 3% or less over the entire altitude range of interest when the wavelength offset is $\pm 2.5 \times 10^{-3}$ nm.

Uncertainties in the O_2 Schumann-Runge band parameters are more significant than those discussed above. Fig. 5 presents the ratio of the $\delta(0-0)$ band dissociation rate based on the best oscillator strengths and line widths in Table 2 to that computed with the O_2 parameters at the lower limit of the error bars. The analogous result for the $\delta(1-0)$ band is also shown for a solar zenith angle of 60° . As one approaches large column abundances the solar irradiance near the O_2 line centers is absorbed leaving only that in the wings, where the cross section is proportional to the line width. The irradiance reaching a given level is therefore greatest when the line widths are minimal. At 50 km the uncertainty in the $\delta(0-0)$ band dissociation rate due to the O_2 parameter error bars is $\sim 14\%$, increasing to almost a factor of 2 by 30 km and to a factor of ~ 8.5 by 20 km. Below 30 km the dissociation rate is sufficiently small that it has little aeronomic importance so the large uncertainties are of no consequence. The uncertainties for the $\delta(1-0)$ band are factors of 1.35, 2.30 and approximately 10 at 60, 50 and 40 km, respectively. Finally, for the last error source mentioned above, Heroux and Swirbalus (1976) assign an absolute accuracy of $\pm 20\%$ to their solar irradiance measurements, and we have adopted an error bar of $\pm 10\%$ on the NO band oscillator strengths.

From the above estimates we place an error bar

of $\pm 30\%$ on the unattenuated dissociation rates in both the $\delta(0-0)$ and $\delta(1-0)$ bands. For an altitude of 50 km the true $\delta(0-0)$ band dissociation rate lies between 0.6 and 1.6 times the value in Table 4 while the true $\delta(1-0)$ band value should be between 0.3 and 3.2 times the reported result. At 30 km the $\delta(1-0)$ band is of negligible importance while the actual $\delta(0-0)$ band result should lie between 0.3 and 2.8 times the best estimate in Table 4.

5. Discussion

Values of the unattenuated dissociation rate of nitric oxide in the $\delta(0-0)$ and $\delta(1-0)$ bands computed with currently accepted molecular parameters are smaller than results reported in the past by factors of 5.3 and 2.7, respectively. In addition, the latest band constants for the O_2 absorption spectrum lead to less attenuation of the $\delta(1-0)$ band rate that previously believed. The computed dissociation rate is insensitive to spectral structure in the solar irradiance and to small uncertainties in the O_2 and NO line positions. However, in the upper and middle stratosphere the effect of uncertainties in the O_2 opacity becomes significant and by 30 km can lead to dissociation rate errors of a factor of 2-3 for typical solar zenith angles.

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