A New Calculation of Nitric Oxide Photolysis in the Stratosphere, Mesosphere, and Lower Thermosphere

K. MINSCHWANER

National Center for Atmospheric Research, Boulder, Colorado

D. E. SISKIND

E. O. Hulburt Center for Space Research, Naval Research Laboratory, Washington, D. C.

Photodissociation of nitric oxide in the middle and upper atmosphere is examined using a line-by-line approach to describe absorption in the NO δ bands and O₂ Schumann-Runge bands. The new analysis of O₂ absorption results in greater transmission of ultraviolet radiation in the Schumann-Runge (5-0) band in comparison with previous studies, leading to increased rates for photolysis of nitric oxide in the $\delta(0-0)$ band. Reduced transmission in the O₂ (9-0) and (10-0) Schumann-Runge bands produces smaller photolysis rates for the NO $\delta(1-0)$ band. Absorption in strong lines of the NO δ bands is shown to make a nonnegligible contribution to atmospheric opacity at wavelengths which are important for NO photodissociation. Representative distributions of nitric oxide are used to quantify possible changes in the NO photolysis rate over the course of a solar cycle. As a result of changes in the NO abundance in the thermosphere, modulation of the photolysis frequency at lower altitudes may be opposite in phase to variations in the solar irradiance. For solar zenith angles greater than 60°, photolysis rates at altitudes below 100 km may be smaller during solar maximum compared to solar minimum. A method is described which enables rapid calculation of NO photolysis frequencies, allowing also for effects of varying opacity by nitric oxide.

1. INTRODUCTION

Absorption of ultraviolet radiation by nitric oxide initiates the primary pathway for destruction of odd nitrogen $(NO_x = NO + NO_2)$ in the middle atmosphere. A predissociation of NO occurs for wavelengths less than about 191 nm

$$NO + h\nu \rightarrow N + O$$
 (1)

Atomic nitrogen may then react with NO to form molecular nitrogen

$$N + NO \rightarrow N_2 + O$$
 (2)

Reactions (1) and (2) represent a net loss of two NO molecules. This sink is the dominant loss process for NO_x in the upper stratosphere, mesosphere, and lower thermosphere.

Early estimates of the photolysis frequency of nitric oxide, $J_{\rm NO}$, were made by *Bates* [1954], *Strobel et al.* [1970], and *Strobel* [1971], although the first quantitative calculation to explicitly account for the NO rotational line structure was that of *Cieslik and Nicolet* [1973]. They demonstrated that the dominant contribution was due to predissociation in the (0-0) and (1-0) delta bands (*C-X*). Weaker absorption, occurring primarily in the beta bands (*B-X*, v' > 6) and gamma bands (*A-X*, v' > 3), was expected to play a minor role in determining the overall photolysis frequency in the stratosphere and mesosphere. The magnitude of $J_{\rm NO}$ at zero optical depth was estimated to be greater than 1×10^{-5} s⁻¹. It was then shown by *Frederick and Hudson* [1979a] (hereinafter referred to as FH79) that values for the oscilla-

Copyright 1993 by the American Geophysical Union.

Paper number 93JD02007. 0148-0227/93/93JD-02007\$05.00 tor strengths used by Cieslik and Nicolet [1973] were likely to have been over a factor of 2 too large. FH79 calculated revised values of $J_{\rm NO}$ which were later parameterized by Allen and Frederick [1982] in a form suitable for photochemical models. Nicolet and Cieslik [1980] (hereinafter referred to as NC80) also obtained reduced estimates of $J_{\rm NO}$ using smaller values for the oscillator strengths. An analytic approximation of their results was presented by Nicolet [1979]. Finally, Frederick et al. [1983] showed that NO absorption in the thermosphere could provide sufficient opacity in the cores of strong lines to reduce the photolysis frequency in the stratosphere and mesosphere. They suggested that self absorption by NO could introduce a coupling mechanism between the thermosphere and middle atmosphere.

We have evaluated the photodissociation of nitric oxide using the latest spectroscopic information for both NO and O_2 . The photolysis frequency of nitric oxide is given by

$$J_{\rm NO}(z,\chi) = \sum_{i=1}^{n} \int \sigma_i({\rm NO},\lambda,z) F(\lambda,z,\chi) d\lambda \qquad (3)$$

where σ is the NO cross section and F is the solar flux that reaches altitude z at angle χ and wavelength λ . Attenuation of the flux depends primarily on absorption by O₂ and O₃. As pointed out by *Frederick et al.* [1983], absorption by NO has little effect on the spectrally averaged opacity of the atmosphere because it is concentrated in the peaks of narrow lines, but the depletion of available photons at wavelengths where the cross section is large may significantly reduce $J_{\rm NO}$ at lower altitudes. The integral in equation (3) is evaluated separately for each dissociating NO band, denoted by the subscript i, and the total photolysis frequency is determined from the sum over all bands. As in FH79 and NC80, the focus here will concern photolysis in the $\delta(0-0)$ and $\delta(1-0)$ bands since they provide the dominant contribution to NO photodissociation. For completeness, however, we will also examine the role of the minor bands in determining the total photolysis rate.

One of the motivations for the present study relates to improvements in the treatment of atmospheric transmission in the O₂ Schumann Runge (S-R) bands. Photodissociation of nitric oxide in the $\delta(0-0)$ band is governed largely by absorption in the S-R (5-0) band of O₂, while $\delta(1-0)$ band photolysis is affected by attenuation of radiation in the S-R (9-0) and (10-0) bands. The complicated structure of both δ and S-R band cross sections necessitates a high resolution treatment of S-R band absorption. Laboratory studies by Yoshino et al. [1983] and Lewis et al. [1986] produced revised values for O₂ spectroscopic constants, S-R band oscillator strengths, and line predissociation widths which were not available to FH79 and NC80. The calculations described here involve a line-by-line treatment of transmission in the O₂ S-R bands [Minschwaner et al., 1992] which incorporates the new spectroscopic data.

Improved understanding of the variability of $J_{\rm NO}$ is now possible as a result of progress in characterizing the solar cycle behavior of NO in the upper atmosphere. Frederick et al. [1983] showed that absorption by nitric oxide in the thermosphere was likely to be important in determining the magnitude of $J_{\rm NO}$ at lower altitudes, but little was known at that time about the variation in thermospheric NO over time scales corresponding to a complete solar cycle. Measurements from the Solar Mesosphere Explorer (SME) during the declining phase of solar cycle 21 indicate a large solar cycle effect; thermospheric abundances of NO decreased by almost an order of magnitude from 1982 to 1986 [Barth et al., 1988]. More recently, Clancy et al. [1992] and Eparvier and Barth [1992] have observed nitric oxide near the peak of Solar Cycle 22 and have reported comparatively large values, up to 6 times larger than those observed in 1982 by SME. It is of interest to see what effect this variability could have on the photodissociation of nitric oxide in the stratosphere and mesosphere. Furthermore, there has been a heightened interest in developing coupled models of the upper and middle atmosphere [e.g., Roble and Dickinson, 1989]. In order to adequately study the possible link between thermospheric and middle atmospheric odd nitrogen, it is necessary to be able to perform rapid photolysis calculations which allow for varying amounts of NO opacity.

We begin by outlining the procedures used to calculate cross sections for nitric oxide in section 2. Results for the photolysis frequency are presented in section 3, followed by a discussion of the solar cycle variation of $J_{\rm NO}$ in section 4. A parameterization suitable for use in photochemical models is developed in section 5 which allows for use of an arbitrary NO column to account for effects of self absorption, facilitating the study of possible coupling between the upper and middle atmosphere. The impact of continuing uncertainties in NO spectroscopic parameters is addressed in section 6, and concluding remarks are contained in section 7.

2. NITRIC OXIDE CROSS SECTIONS

The nitric oxide cross section is determined by performing a detailed calculation of the rotational structure of each band. The cross section is a function of altitude through the temperature dependence of the population of energy states and the thermal broadening of line profiles. We evaluate the cross section at discrete wavenumbers, ν , using a lineby-line approach. The first step involves calculation of the integrated absorption cross section for a spectral line, given by

$$\int \sigma_{\rm NO}(\nu) d\nu = \left[\frac{\pi e^2}{mc^2}\right] f(v',v'') \frac{S(J',J'')}{[2J''+1]} \frac{N_{J''}}{N_{tot}} \qquad (4)$$

Standard notation is used here to define the rotational and vibrational quantum numbers, J and v, where primed quantities refer to the upper electronic state and double primes denote the lower state. The collection of constants within brackets on the right-hand side of equation (4) equals 8.829×10^{-13} cm. The band oscillator strength, f(v', v''), has been the subject of several investigations and some disagreement over the last few decades. Originally, Bethke [1959] reported 2.49×10^{-3} for the overlapping $\delta(0.0) + \beta(7.0)$ 0) bands, and 5.78×10^{-3} for the $\delta(1-0) + \beta(10-0)$ bands, with the δ bands providing the dominant contribution in both cases. However, the oscillator strength for the $\delta(0-0)$ band measured by Callear and Pilling [1970b] was over twice as large as Bethke's. This larger value was used in photolysis calculations by Cieslik and Nicolet [1973]; additionally, they scaled Bethke's value for the $\delta(1-0)$ band by a factor of about 2. Since then, Mandelman and Carrington [1974] and Cieslik [1977] reconsidered this question and they both obtained oscillator strengths near the original Bethke values. Aeronomic studies by FH79 and NC80 employed the smaller values for the δ band oscillator strengths, resulting in lower values for $J_{\rm NO}$ compared with earlier work by *Cies*lik and Nicolet [1973]. While we agree with FH79 that the weight of the evidence supports the Bethke values, it should also be noted that measurements by Guest and Lee [1981] imply values for δ band oscillator strengths that are 50% larger than Bethke's, although their results are still significantly lower than in Callear and Pilling [1970b]. No reason was advanced by Guest and Lee for this discrepancy, and we have adopted the same oscillator strengths as FH79 (2.2 $\times 10^{-3}$ for the (0-0), 5.4 $\times 10^{-3}$ for the (1-0)). In section 6 we discuss the consequences of this assumption.

The quantity S(J', J'') is the Hönl-London factor for a transition between rotational levels J'' and J'. Following FH79, we use the formulae of *Erkovich et al.* [1964] to calculate S(J', J''). These expressions are based on the assumption that the upper electronic state (C) can be described by Hund's case b, while the lower electronic state (X) follows Hund's case a. A total of 12 branches are considered: six (P, Q, R, and three satellite branches) from each of the two substates of the X ground state.

There are two limitations associated with the use of the Erkovich formulae. First, the C state coupling is not pure Hund's case b, and second, perturbations between the B and C states can affect the rotational intensities. We calculated revised cross sections using Hönl-London factors given by Kovacs [1969], which account more explicitly for intermediate coupling cases. Effects on calculated photolysis rates for the $\delta(0-0)$ band were small: the difference was less than 8% at all altitudes. Regarding the C state perturbation, the B and C state coupling has been shown to be localized over a relatively small range of rotational levels [Lagerquist and Miescher, 1958; Mandelman and Carrington, 1974] and we found our calculated value of J_{NO} to be largely insensitive to the relative intensities of a small number of rotational lines. Indeed, the success of the parameterization described

in section 6 is directly related to the validity of assuming a nearly random distribution of intensities.

The last term in equation (4) represents the fractional population of the J'' level of the ground state. We assume that the population follows a Boltzmann distribution of energy levels according to

$$N_{J''} = 0.5 \times (2J'' + 1)(e^{-hcF_1(J'')/kT} + e^{-hcF_2(J'')/kT})$$
(5)

The symbols F_1 and F_2 refer to the rotational term values for the $\Omega = 3/2$ and 1/2 substates of the X ground state. Standard expressions are employed to evaluate individual term values (e.g., equations (20) - (22) of *Cieslik and Nicolet* [1973], see *Eparvier and Barth*, [1992] for an update on the spectroscopic constants). The normalization factor, N_{tot} , is obtained by summing over all values of $N_{J''}$. The factor of 0.5 accounts for the fact that each level is counted twice in N_{tot} due to lambda doubling.

The frequencies of individual lines are additional quantities which are required as input to line-by-line calculations of the cross section. Line locations were taken from the table of lines given by Lagerquist and Miescher [1958]. They observed only the strong lines (J'' < 12.5 - 18.5), however, and did not list any of the dim Q branches at all. In order to account for the minor lines, we extended the calculation to include higher rotational levels (up to J'' = 39.5), and the Q and satellite branches, using the difference in upper and lower state term values to determine line positions. Lines in the $\delta(0-0)$ band which lie below the NO dissociation limit at J' = 5/2 [Rottke and Zacharias, 1985] were excluded in all of our calculations since they do not contribute to the photodissociation of nitric oxide.

The line shape is described by a Voigt profile [Drayson, 1976] which allows for line broadening due to predissociation and thermal (Doppler) effects. Over a typical range of atmospheric temperatures. Doppler widths for the NO δ bands range from 0.09 to 0.14 cm^{-1} , full width at half maximum (FWHM). Values for the predissociation half widths are less easily characterized. For the $\delta(0-0)$ bands, FH79 applied the uncertainty principle to the predissociation rate determined by Callear and Pilling [1970a] and arrived at an estimated width of 0.02 cm^{-1} (FWHM). In the absence of similar information regarding the predissociation rate of the v' = 1 state, FH79 adopted the same value for predissociation widths in the $\delta(1-0)$ band. This assumption may not be correct. Recent work [Tsukiyama et al., 1988] suggests that the predissociation rate increases with energy above the dissociation limit and that the v' = 1 level has a shorter lifetime than the v' = 0 level. In fact, Hart and Bourne [1989] state that the line widths for the (1-0) transition are in the range 0.2 to 0.3 cm^{-1} , a factor of 10 greater than adopted by FH79. Unfortunately, they do not support this statement with a figure and some uncertainty still exists in accepting this result. If we use the same analysis employed by FH79 to relate the line width to the predissociation rate, D, then a width of 0.25 cm⁻¹ implies $D = 4.7 \times 10^{10} \text{ s}^{-1}$. This is 20 times faster than the rate quoted by Hart and Bourne later in the same paper, and 10 times faster than reported by Benoist D'Azy et al. [1975] who claim to have observed weak fluorescence from the v' = 1 level. We therefore believe that until more convincing evidence is presented, it is premature to conclude that line widths for the (1-0) band are as broad as suggested by Hart and Bourne [1989]. The predissociation width for both bands will be taken here to

be 0.02 cm^{-1} (FWHM). As indicated later, the line width can play an important role in determining the effect of NO opacity on the photodissociation rate.

The magnitude of the cross section at each wavenumber is determined from the sum of contributions from nearby lines. We found that including all lines within a 25 cm⁻¹ spectral window was sufficient to adequately characterize the magnitude of the cross section between individual lines. All calculations were carried out using a 0.05 cm⁻¹ spectral grid, which provides approximately three points per line half width. Cross sections computed at higher resolution showed no significant differences, indicating that a grid spacing of 0.05 cm⁻¹ is sufficient to capture essentially all of the rotational structure of the δ bands.

Computed cross sections of nitric oxide are shown in Figure 1 for the $\delta(0.0)$ band, and Figure 2 for the $\delta(1.0)$ band. Corresponding cross sections for the O₂ S-R bands [Minschwaner et al., 1992] are also displayed in Figures 1 and 2. Line widths for the NO δ bands are more than an order of magnitude smaller than for the O₂ S-R bands, resulting in a much finer structure in the nitric oxide cross section.

Comparison of our NO δ band cross sections with FH79 revealed significant $(>10 \text{ cm}^{-1})$ differences in the locations of weak lines not included in the tabulation by Lagerquist and Miescher [1958]. The reason for the discrepancy is not obvious given that FH79 employed the same procedures adopted here to estimate line positions for the Q branch and the higher rotational levels of the R and P branches. We checked our results using the same technique to calculate line positions for J'' < 19.5, R and P branches (for the $\delta(0-0)$ band), and compared them with values from the Lagerquist and Miescher [1958] tabulation. Large differences were found for values of J'' less than about 6.5 due to perturbations in the upper electronic state, which is why we employ the observed positions for these lines. On the other hand, differences between calculated and observed positions for the higher values of J'' were less than 1 cm⁻¹, and no trend in the error was detected for increasing values of J''. It



Fig. 1. Cross sections for nitric oxide in the $\delta(0.0)$ band (solid) and for oxygen in the S-R (5-0) band (dashed), calculated at temperatures of 250 K and 265 K, respectively. Temperatures were chosen to be consistent with the formulation discussed in section 5. The O₂ cross sections have been multiplied by a factor of 10^{-3} for clarity of presentation.



Fig. 2. Cross sections for nitric oxide in the $\delta(1-0)$ band (solid) and for oxygen in the S-R (9-0) and (10-0) bands (dashed), calculated at temperatures of 250 K and 235 K, respectively. The O₂ cross sections have been multiplied by a factor of 10^{-5} .

seems unlikely therefore that calculated positions of higher rotational lines are in error by more than 1 or 2 wavenumbers. Contributions to $J_{\rm NO}$ from absorption in the untabulated lines are at most 20% and 10%, respectively, for the $\delta(0-0)$ and $\delta(1-0)$ bands. Consequently, uncertainties in the spectral locations of these lines are expected to have a negligible impact on computed photolysis rates.

3. PHOTODISSOCIATION OF NITRIC OXIDE

Predissociation of nitric oxide does not necessarily occur following absorption of a photon: a finite number of transitions result in emission or are quenched by collision with N_2 . The probability of predissociation from the excited electronic state is determined by

$$P = \frac{D}{A + D + k_q[N_2]} \tag{6}$$

where D is the rate of spontaneous predissociation, A the rate of spontaneous emission, and k_q the rate constant for quenching by N₂. We adopt the values $D = 1.65 \times 10^9 \text{ s}^{-1}$ and $A = 5.1 \times 10^7 \text{ s}^{-1}$ for the rates of spontaneous predissociation and emission from the $C^2 \Pi_{v'=0}$ state [Callear and Pilling, 1970a]. The quenching rate constant of the $C^2 \Pi_{v'=0}$ state is taken from the work of Callear and Smith [1964], who obtained $k_q = 1.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. The magnitude of P for the $\delta(0-0)$ band thus varies from approximately unity in the mesosphere to about 0.6 at 25 km.

For the $C^2 \Pi_{v'=1}$ state, the observations of *Benoist D'Azy* et al. [1975] and *Hikida et al.* [1987] both imply a very small emission yield compared to predissociation (about 0.01). We may therefore assume that A is negligible compared to D, as did FH79. There are unfortunately no measurements of the rate of collisional deactivation from the $C^2 \Pi_{v'=1}$ state, but if the rate is comparable to that of the v' = 0 state, then $P \simeq 1$ for the $\delta(1-0)$ band above 40 km. Owing to strong attenuation of solar radiation by the S-R (9-0) and (10-0) bands, the contribution to the total photolysis of nitric oxide by the $\delta(1-0)$ bands is negligible below about 40 km, and we will assume that all absorption in the $\delta(1-0)$ band leads to predissociation.

In all of the results that follow, we employ temperature dependent cross sections of nitric oxide and oxygen; attenuation by ozone is determined using cross sections given by DeMore et al. [1992]; vertical profiles of temperature, pressure, and ozone are taken from the U.S. Standard Atmosphere (1976); values for the solar irradiance are adopted from SUSIM (Solar Ultraviolet Spectral Irradiance Monitor) measurements [VanHoosier et al., 1988]. The SUSIM irradiances are quoted at 0.05-nm intervals, about 300 times larger than the spectral grid used to calculate cross sections and photolysis frequencies. Linear interpolation was used to estimate irradiances on the higher resolution grid. We examined the possible consequences of neglecting fine structure in the solar spectrum by employing the high-resolution (0.007 nm) solar radiances of Moe et al. [1976] to compute NO photolysis frequencies. Additional calculations were performed using a spectrally degraded (0.15 nm) version of the same solar radiance data. Differences between the two sets of Jvalues were less than 4%, indicating an apparent lack of correlation between the solar spectrum and the NO cross section, at least on spectral scales smaller than 0.15 nm.

Photodissociation frequencies for the NO $\delta(0-0)$ and $\delta(1-$ 0) bands are shown in Figure 3a and compared with FH79. At this point we have not yet included the contribution to atmospheric opacity from NO absorption in order to compare our calculation with previous results. The photolysis frequencies taken from FH79 are based on the same model atmosphere used here; thus discrepancies indicated in Figure 3a arise primarily from differences in solar irradiances and attenuation by the O_2 S-R bands. We calculate J values at zero optical depth of 2.57×10^{-6} s⁻¹ for the $\delta(0-0)$ band and 3.23×10^{-6} s⁻¹ for the $\delta(1-0)$ band, which are about a factor of 1.9 and 1.2 larger, respectively, than values reported by FH79. The differences are qualitatively in agreement with the larger SUSIM irradiances used in our calculation, about a factor of 1.6 higher in both bands compared to the values of Heroux and Swirbalus [1976] used by FH79.

Differences in the vertical profiles of photolysis are a result of dissimilar cross sections for the O₂ S-R bands. Values used here for the O_2 (5-0) band allow for deeper penetration of solar radiation than calculated by FH79. Our J value for the $\delta(0-0)$ band is more than a factor of 3 larger in the stratosphere. The difference in transmission is a consequence of narrower O₂ line widths assumed in our calculation compared with FH79, who based their analysis on the O₂ cross sections of Frederick and Hudson [1979b]; more recent measurements [Cheung et al., 1990] indicate that line widths for the O_2 (5-0) band are between 10 and 15% smaller than the value determined by Frederick and Hudson [1979b]. The situation is more complicated for the S-R (9-0) and (10-0) bands, the dominant source of atmospheric opacity in the NO $\delta(1-0)$ spectral region. We employ line widths for the (10-0) band [Cheung et al., 1990] which are more than a factor of 2 larger than the value given by Frederick and Hudson [1979b]. The band oscillator strength, however, is about 40% smaller [Yoshino et al., 1983]. Line widths for the O₂ (9-0) band [Cheung et al., 1990] are about 25% larger than the value determined by Frederick and Hudson [1979b]. The net effect, as indicated in Figure 3a, is that the new S-R cross sections exhibit greater attenuation, resulting in a re-



Fig. 3. (a) Photolysis frequencies of NO in the $\delta(0-0)$ and $\delta(1-0)$ bands (solid curves) for a solar zenith angle of 60°. Atmospheric opacity by NO has been neglected. Corresponding values from *Frederick and Hudson* [1979a] are shown by the dashed curves. (b) Ratio of combined ($\delta(0-0)+\delta(1-0)$) photolysis frequencies, neglecting NO opacity. The dashed curve represents the ratio of J values calculated here to those presented by *Frederick and Hudson* [1979a]. The dotted curve gives the ratio of our results to values determined using the method described by *Nicolet* [1979]. All J values were calculated for a solar zenith angle of 60°.

duction of the $\delta(1-0)$ photolysis frequency at lower altitudes compared with FH79.

The ratio of our combined $(\delta(0-0) + \delta(1-0))$ J values to the results of FH79 and NC80 are displayed in Figure 3b. We have used the analytic expression given by *Nicolet* [1979] to adopt NC80's results to the U.S. Standard Atmosphere (1976) and a solar zenith angle of 60°. Most of the disagreement with FH79 and NC80 above 80 km is likely the result of larger values for the solar irradiance adopted here. There is a cancellation of effects from greater transmission in the O₂ (5-0) band and less transmission in the (9-0) and (10-0) bands compared with previous results, except in the stratosphere where the contribution from the $\delta(0-0)$ band dominates the combined photolysis frequency.

We also examined the photodissociation of NO due to absorption in the $\beta(9-0)$ and $\beta(12-0)$ bands, as indicated in Figure 4. Consideration of the relative magnitudes of β band oscillator strengths suggests that these two bands furnish the major contribution to photodissociation in the β bands. High-resolution cross sections for the $\beta(9-0)$ and $\beta(12-0)$ bands were computed using values for the oscillator strengths determined by *Bethke* [1959]. Predissociation widths were assumed to be the same as for the δ bands, 0.02 cm^{-1} , and probabilities for predissociation (equation

(6)) were taken to be unity. The latter assumption may not be strictly correct; however, it is appropriate for estimating the maximum possible contribution to nitric oxide predissociation. Figure 4 shows the β band photolysis frequencies along with results for the sum of the $\delta(0-0)$ and $\delta(1-0)$ bands. At zero optical depth the $\beta(12-0)$ band photodissociation amounts to about 7% of the J value for the combined δ bands. By scaling the relative magnitudes of oscillator strengths and appropriate solar irradiances to the $\beta(9-0)$ J value, we estimate the contribution to NO photodissociation due to absorption in the $\beta(7-0)$ through $\beta(12-0)$ bands to be 12% at most. The most dominant β band, the $\beta(12-0)$, ocurrs in a spectral region which is strongly attenuated by the O₂ S-R (15-0) and (16-0) bands, as indicated in Figure 4. As a result, the sum contribution from the β bands is reduced to less than 1% below about 80 km. In fact, the contribution to $J_{\rm NO}$ from bands other than the $\delta(0-0)$ and $\delta(1-0)$ is likely to be even smaller than we have indicated here and also given by NC80. Recent measurements of the β and γ bands show that predissociation is very slow even for vibrational levels above the dissociation limit [Tsukiyama et al., 1988; Gadd et al., 1991). We will thus neglect the small contributions from the β and γ bands in all of the results that follow.

The consequences of including absorption by nitric oxide in computing atmospheric transmission are illustrated in Figure 5, which shows the ratio, R, of the photodissociation frequency calculated including opacity by NO to that which neglects NO opacity:

$$R(z) = \frac{\int \sigma_{\rm NO}(\lambda, z) F(\lambda, z, \chi) e^{-\tau_{\rm NO}(\lambda, z, \chi)} d\lambda}{\int \sigma_{\rm NO}(\lambda, z) F(\lambda, z, \chi) d\lambda}$$
(7)

where $\tau_{\rm NO}$ is the optical path for nitric oxide determined by integrating the product of the cross section and local concentration of NO over a slant path above altitude z. We used the "medium" NO distribution, shown in Figure 6a and discussed further in the next section, to determine the column abundance of nitric oxide.



Fig. 4. Nitric oxide J values for the sum of the $\delta(0-0)$ and $\delta(1-0)$ bands (solid), the $\beta(9-0)$ band (dotted), and the $\beta(12-0)$ band (dashed) at a solar zenith angle of 60°. Opacity by NO has been neglected.



Fig. 5. Ratio of the nitric oxide J value calculated including attenuation by NO to that which neglects NO opacity, as defined by equation (7) in the text. Ratios for the $\delta(0-0)$ band are shown at solar zenith angles of 60° (dashed) and 80° (solid). The $\delta(1-0)$ ratios are also presented for solar zenith angles of 60° (triangles) and 80° (circles). The optical path for NO was determined using the "medium" nitric oxide profile shown in Figure 6a.

The results shown in Figure 5 confirm the suggestion of Frederick et al. [1983] that absorption by nitric oxide in the upper atmosphere can influence the magnitude of $J_{\rm NO}$ at lower altitudes. There remain, however, some puzzling differences in the details of how this effect is manifested between our calculations and those of Frederick et al. [1983]. First, we find a significantly smaller effect which can be interpreted as follows: Calculated values for the cross section near the centers of prominent lines are in the range 0.5- 1×10^{-16} cm² and $1-2 \times 10^{-16}$ cm² for the $\delta(0-0)$ and $\delta(1-1)$ 0) bands, respectively (see Figures 1 and 2). For a solar zenith angle of 60°, the slant column of nitric oxide is about 1.5×10^{15} cm⁻² at 40 km altitude, and corresponding optical paths range from 0.08 to 0.15, and 0.15 to 0.30. The ratios for this case are consistent with optical paths of this magnitude, as J values are reduced by transmission factors of about $\exp(-0.1) \simeq 0.9$ and $\exp(-0.2) \simeq 0.8$ for the $\delta(0-0.2)$ 0) and $\delta(1-0)$ bands, respectively. However, Frederick et al. [1983] found a value of about 0.55 for both bands at 40 km using a similar distribution of nitric oxide (compare our Figures 6a and 6b with Figures 1a and 1b from Frederick et al. [1983]). This result would appear to require a nitric oxide cross section of the order of 4×10^{-16} cm², a value which is larger than our estimate for the mean cross section near the strong lines of both bands.

Second, the shape of R(z) indicated in Figure 5 differs from that given by *Frederick et al.* [1983]. They found that the ratio defined by equation (7) attained a minimum value in the upper stratosphere and approached unity in the lower stratosphere. While we are aware of two possible processes that could be responsible for this behavior, neither seems sufficient. First, the variation of temperature with altitude can affect the rotational population of energy levels, causing a mismatch between strong lines in the stratosphere and those at higher altitudes. The rate of NO photodissociation in the stratosphere therefore would not be influenced by NO absorption in the mesosphere and thermosphere. We investigated this effect and found changes in the rotational structure of the cross section to be negligible in affecting NO self absorption. Second, the penetration of radiation in the O_2 S-R bands may be correlated with the cross section of nitfic oxide such that enhanced attenuation of radiation by O_2 occurs in spectral regions corresponding to strong lines in the NO cross section. As a result, the primary contribution to NO photolysis in the stratosphere might shift to absorption in weak lines where effects of self absorption are not important. However, as discussed in section 5, we find no significant correlations between O_2 and NO cross sections which could allow equation (7) to approach a value of unity in the stratosphere.

4. SOLAR CYCLE BEHAVIOR

Changes in the magnitude of the ultraviolet irradiance and in the overburden of NO, both related to solar activity, may have a significant effect on the photodissociation of NO. The variation in solar flux in the spectral region 180-191 nm has been estimated by *Lean et al.* [1992] to be approximately 8%, whereas NO amounts show much larger variability. We employ three NO profiles, shown in Figure



Fig. 6. (a) Vertical profiles for the concentration of nitric oxide. The "low NO" curve (solid) is based on the measurements presented by Barth [1989]; the "med NO" curve (dashed) follows the analysis by Siskind et al. [1990]; the "high NO" curve (dotdashed) represents the observations by Mickley et al. [1992] and Eparvier and Barth [1992]. Both the "low" and "med" profiles employ a mixing ratio of 10 ppbv in the mesosphere. (b) Profiles for the vertical column of nitric oxide above the indicated altitude, determined using the distributions shown in Figure 6a. The measurement by Clancy et al. [1992] is indicated by the circle, and the range of SBUV measurements reported by McPeters [1989] is shown by the horizontal line.

6a, in order to represent the large variations in NO abundances observed over the last decade. The curve labeled "medium NO" assumes a constant mixing ratio of 10 ppby for mesospheric NO; it merges with the thermospheric profile analyzed by Siskind et al. [1990]. This profile is similar to the baseline case employed by Frederick et al. [1983]. Until recently, it was believed that this thermospheric profile (taken in November 1981 at an F10.7 index of 233) was representative of NO during high solar activity. Measurements during Solar Cycle 22 suggest much larger amounts, however, which are indicated by the curve labeled "high NO" in Figure 6a. The mixing ratio in this profile increases up to about 100 ppbv at 75 km, which is consistent data from the Halogen Occultation Experiment on board the Upper Atmospheric Research Satellite [Mickley et al., 1992]. Above 75 km the "high NO" profile agrees with the thermospheric measurement of Eparvier and Barth [1992]. The curve labeled "low NO" has a peak thermospheric density of 8×10^6 $\rm cm^{-3}$, and is representative of the SME profiles seen in 1984-1986 and reported by Barth [1989]. It should be noted that the indicated variation in NO abundances leads to greater opacity during periods of maximum solar irradiances.

Figure 6b presents the integrated column densities which correspond to the three curves in Figure 6a. Also indicated is the column NO measurement by *Clancy et al.* [1992], taken during a period of high solar activity, and the range of NO column densities determined from analysis of 7 years of solar backscattered ultraviolet (SBUV) observations [*McPeters*, 1989]. As noted earlier, the "medium NO" profile was used in the calculations for Figure 5.

To simulate the extremes of the solar cycle variation we will use the "low" and "high" NO distributions, defining the solar cycle influence on J_{NO} as follows:

$$\Upsilon = 1.08 \times J(\text{High NO})/J(\text{Low NO})$$
(8)

The factor of 1.08 represents the scaling applied to the SUSIM solar flux to approximate the range of values expected between solar maximum and minimum [Lean et al., 1992].

Figure 7 shows the value of Υ for a range of solar zenith angles ($\chi = 0^{\circ}, 60^{\circ}$ and 80°). Because it is defined here as a function of the slant column of NO, the solar cycle variation of $J_{\rm NO}$ depends on the solar zenith angle. However, at all solar elevations there exists a region near 75 km where the photolysis frequency is actually smaller during solar maximum as compared to solar minimum, i.e., $\Upsilon < 1$. In this region the additional shielding from larger thermospheric densities of NO at solar maximum is more than sufficient to compensate for the 8% increase in solar irradiances. The effect may be quite pronounced during winter at high latitudes. For solar zenith angles greater than 60°, the value of Υ is less than one everywhere below 100 km. We should note that two-dimensional models predict net downward motion in the high-latitude mesosphere during winter, and it has been postulated that the thermosphere can be a source of odd nitrogen for the stratosphere under these conditions [Solomon et al., 1982]. The results shown in Figure 7 support this idea, as the shielding effects of NO opacity (and thus the enhanced lifetime of NO against photolysis) maximize precisely during those conditions when the thermospheric source is greatest (solar maximum) and downward transport is most effective.

Fig. 7. The solar cycle variation of NO photodissociation in the δ bands as defined by equation (8) in the text. The cases shown correspond to solar zenith angles of 0° (solid), 60° (dashed), and 80° (dot-dashed).

5. OPACITY DISTRIBUTION FUNCTIONS

Opacity distribution functions (ODFs) provide an accurate and economical means of evaluating photodissociation rates and mean transmission of solar radiation [Fang et al., 1974; Minschwaner et al., 1993]. We begin with mean values for the solar irradiance, $\overline{I_o}$, in spectral intervals defined by individual O₂ S-R bands. In each band we assign six values for the O_2 cross section, σ_{O2}^i . These values are obtained by sorting O_2 cross sections within a given band in order of increasing values. Figures 8 and 9 show the result of performing this operation on the O_2 cross sections displayed in Figures 1 and 2, respectively. The abscissa is transformed in both cases from wavelength to the ODF, which can be viewed as the probability of the cross section being less than the assigned value, $\sigma(ODF)$, within the spectral interval. Integrations over wavelength can instead be carried out over the ODF with substantial computational savings. The histograms shown in Figures 8 and 9 indicate the six values that are used to represent the magnitude of the cross section over the entire band. The O_2 cross sections are appropriate for a temperature which corresponds approximately to an altitude where the mean optical depth is one. Use of this temperature minimizes the error in using ODFs to calculate O_2 photolysis rates. Evaluation of O_2 photodissociation and transmission is easily accomplished using equations (A6) and (A7) given by Minschwaner et al. [1993]. The mean transmission in each S-R band can be used to compute photolysis frequencies for species with cross sections that are approximately constant over individual bands (such as N_2O and the chlorofluorocarbons).

The complex structure of NO δ band cross sections, however, requires special treatment in applying ODFs to calculate the photodissociation rate. For each O₂ cross section we further assign two values for the NO cross section, $\sigma_{\rm NO}^{i,j}$, and two weighting factors, $W_{\rm NO}^{i,j}$. The cross sections are obtained by applying, for each O₂ S-R band, the same transformation from spectral space to ODF space that is used for the O₂





Fig. 8. Opacity distribution functions for the O₂ S-R (5-0) band (dot-dashed curve) obtained by sorting the O₂ cross sections shown in Figure 1. The histogram (dot-dashed lines) indicates the six values that are used for integration over the opacity distribution function. Cross sections for nitric oxide in the $\delta(0-0)$ band (solid curves) have been spectrally mapped to the O₂ opacity distribution function, and then rearranged in order of increasing values within each subinterval defined by the O₂ histogram.

cross section. Values of the NO cross section within each band are thus piggybacked from spectral to ODF space, a procedure which is related to the spectral mapping method described by West et al. [1990]. Then, within each ODF subinterval defined by the O_2 histograms in Figures 8 and 9, the NO cross sections are resorted in order of increasing values. This shuffling no longer preserves the spectral correspondence between O₂ and NO cross sections within each subinterval, but the consequences of this procedure are minimal because correlations between the cross sections at this spectral scale are not significant. The two values for the NO cross section and corresponding weights are obtained from mean values across 90% and 10% of the ODF subinterval. The weighting factors represent the fraction of the total spectral interval which is occupied by the corresponding mean value of the cross section. This choice of quadrature was found to provide the highest accuracy for assessing NO opacity effects.

The photolysis frequency for NO within a given S-R band is determined by

$$J_{\rm NO}(z) = \Delta \lambda \ \overline{I_o} \ T_{\rm O3}(z) \ P(z) \sum_{i=1}^{0} \exp[-\sigma_{\rm O2}^{i} N_{\rm O2}(z)]$$
$$\sum_{j=1}^{2} W_{\rm NO}^{i,j} \sigma_{\rm NO}^{i,j} \exp[-\sigma_{\rm NO}^{i,j} N_{\rm NO}(z)]$$
(9)

where $\Delta\lambda$ is the spectral width of the S-R band; N_{O2} and N_{NO} are the slant columns of O₂ and NO, respectively, above altitude z; absorption by ozone in the Hartley band is determined using a transmission factor, $T_{O3} = \exp[-\sigma_{O3}N_{O3}]$, where σ_{O3} is the mean ozone cross section in the spectral interval and N_{O3} is the slant column of ozone. It is important also to include the predissociation probability, P(z), given by equation (6).

Values of σ for the O₂ S-R (5-0), (9-0), and (10-0) bands,

and σ and W for the NO $\delta(0-0)$ and $\delta(1-0)$ bands are listed in Table 1. We employ a temperature of 250 K to calculate NO cross sections for both bands. This choice of temperature represents the best compromise for minimizing the accumulated error in NO photolysis rates over the altitude range from 30 to 120 km. The sum of the weights for the S-R (10-0) band equals 1 because the NO $\delta(1-0)$ cross section completely spans the spectral interval, as shown in Figure 9. Within the S-R (5-0) and (9-0) bands, however, there exists regions where NO cross section is zero; the range of values for the ODF does not always span the entire subinterval as shown in Figure 8. Zero values in the first column for the $\delta(0-0)$ band in Table 1 indicate that the NO cross section is zero over portions of the S-R (5-0) spectral interval where the smallest 5% of the O_2 cross sections occur. A similar situation exists for the overlap between the $\delta(1-0)$ and S-R (9-0) bands, except that the zero values for the NO cross section extend to spectral regions occupied by the smallest 25% of the cross sections in the S-R (9-0) band.

Photolysis frequencies calculated using quantities from Table 1 are compared to line-by-line results in Figure 10a. Opacity by nitric oxide was determined using the "medium" NO profile from Figure 6a. Excessive attenuation in the O_2 (5-0) band below 30 km produces $\delta(0-0) J$ values which are significantly smaller than line-by-line results. A similar behavior is observed for the $\delta(1-0)$ band, except in this case the ODF technique overestimates the J value within a region between about 30 and 50 km. Nearly all of the discrepancies arising between the ODF and line-by-line results can be attributed to the use of a single temperature to characterize the O_2 cross section within a given band. The transmission at large O_2 paths is confined to narrow windows where the magnitude of the O₂ cross section is particularly sensitive to temperature. The ratio of the combined $(\delta(0-0) + \delta(1-0)) J$ values are displayed in Figure 10b. Maximum errors in the photolysis rate occur at large solar zenith angles; however, for $\chi = 80^{\circ}$ the error is less than 15% above 35 km and even for $\chi = 90^{\circ}$ (not shown) the error remains less than 30%



Fig. 9. Same as Figure 8, except that the dot-dashed curve and histogram refer to the O₂ S-R (10-0) band, and the solid curves correspond to mapped cross sections for the NO δ (1-0) band.

TABLE 1. Opacity Distribution Functions for O2 and NO

	i = 1	$\imath = 2$	i = 3	i = 4	i = 5	i = 6
O ₂ (5-0) Band, NO δ(0-0) Band, 190.2-192.5 nm						
$\sigma_{\rm O2}^i$	1.12e-23	2.45e-23	7.19e23	3.04e-22	1.75e-21	1.11e-20
$W_{ m NO}^{i,1}$	0.00e+00	5.12e02	1.36e-01	1.65e-01	1.41e-01	4.50e-02
$\sigma_{\rm NO}^{i,1}$	0.00e+00	1.32e-18	6.35e-19	7.09e–19	2.18e-19	4.67e-19
$W_{ m NO}^{i,2}$	0.00e+00	5.68e-03	1.52e-02	1.83e-02	1.57e-02	5.00e-03
$\sigma_{ m NO}^{i,2}$	0.00e+00	4.41e-17	4.45e-17	4.50e-17	2.94e-17	4.35e-17
O ₂ (9-0) Band, NO δ(1-0) Band, 183.1-184.6 nm						
$\sigma_{\rm O2}^i$	1.35e-22	2.99e-22	7.33e-22	3.07e-21	1.69e-20	1.66e-19
$W_{ m NO}^{i,1}$	0.00e+00	0.00e+00	1.93e-03	9.73e-02	9.75e-02	3.48e02
$\sigma_{\rm NO}^{i,1}$	0.00e+00	0.00e+00	3.05e-21	5.76 e –19	2.29 e- 18	2.21e-18
$W_{ m NO}^{i,2}$	0.00e+00	0.00e+00	2.14e-04	1.08e-02	1.08e-02	3.86e-03
$\sigma_{ m NO}^{i,2}$	0.00e+00	0.00e+00	3.20e-21	5.71e-17	9.09e-17	6.00e-17
O_2 (10-0) Band, NO $\delta(1-0)$ Band, 181.6-183.1 nm						
σ_{O2}^i	2.97e-22	5.83e-22	2.05e-21	8.19 e- 21	4.80e-20	2.66e-19
$W_{ m NO}^{i,1}$	4.50e-02	1.80e-01	2.25e-01	2.25e-01	1.80e-01	4.50e-02
$\sigma_{ m NO}^{i,1}$	1.80e-18	1.50e-18	5.01e-19	7.20e-20	6.72e-20	1.49e-21
$W_{ m NO}^{i,2}$	5.00e-03	2.00e-02	2.50e-02	2.50e-02	2.00 e -02	5.00e-03
$\sigma_{ m NO}^{i,2}$	1.40e-16	1.52e-16	7.00e-17	2.83e-17	2.73e-17	6.57e–18

The values of $\overline{I_o}$ used in equation (9) are $3.98 \times 10^{11} \text{ s}^{-1} \text{ cm}^{-2} \text{ nm}^{-1}$ for the O₂ (5-0) band, $2.21 \times 10^{11} \text{ s}^{-1} \text{ cm}^{-2} \text{ nm}^{-1}$ for the (9-0) band, and $2.30 \times 10^{11} \text{ s}^{-1} \text{ cm}^{-2} \text{ nm}^{-1}$ for the (10-0) band. (Read 1.117×10^{-23} .)

above 50 km. Due to difficulties associated with evaluating transmission at very large O_2 optical paths, the combined NO J value determined by our parameterization should not be considered reliable when it falls below a factor of 10^{-5} of the value at zero optical depth.

6. DISCUSSION OF UNCERTAINTIES

The largest potential for error in our results originates from uncertainties in spectroscopic quantities for nitric oxide, particularly the oscillator strengths for the $\delta(0-0)$ and $\delta(1-0)$ bands and predissociation widths for the $\delta(1-0)$ band. As indicated earlier, the range of measured values for the oscillator strengths suggests that the associated uncertainty may be of the order of $\pm 25\%$. We point out that values used here are on the low side of this range, which allows for the possibility that actual cross sections for the NO δ bands may be 50% larger than we calculate. In the absence of NO opacity effects, such an increase in the cross section would produce a similar change in the NO photolysis rate at all altitudes. The effect of self absorption by NO should tend to mitigate variations in the photolysis rate due to changes in the magnitude of the oscillator strength. We performed sensitivity studies which included absorption by nitric oxide using the "medium" NO profile from section 4, and found that an increase of 50% in the oscillator strength led to enhancements of only 30 to 40% in the stratospheric photolysis rate.

Cross sections used in the ODF parameterization can easily be adapted to accommodate different values for the oscillator strengths. For example, the $\delta(0-0)$ band cross sections are scaled according to

$$\sigma'_{\rm NO} = \sigma_{\rm NO} \frac{f'(0-0)}{(2.2 \times 10^{-3})} \tag{10}$$

where $\sigma'_{\rm NO}$ is the revised value for the cross section and f'(0-0) is the new oscillator strength for the $\delta(0-0)$ band. The correction for the $\delta(1-0)$ band is similar, except that the denominator contains the oscillator strength used for the $\delta(1-0)$ band, $f(1-0) = 5.4 \times 10^{-3}$.

Uncertainties regarding predissociation widths of spectral lines in the $\delta(1-0)$ band become particularly important in assessing the effects of self absorption by NO. Since the spectrally integrated cross section is proportional only to the band oscillator strength, the photolysis rate neglecting NO opacity could be regarded as the product of the oscillator strength and the mean solar intensity. The J value would thus be independent of the line width. However, the primary influence of NO self absorption occurs at line peaks where the magnitude of the NO optical depth will be strongly affected by the line width. We note that for predissociation widths less than the Doppler width ($\simeq 0.1 \text{ cm}^{-1}$), changes in the predissociation width will have the largest effect in line wings, with little influence near line centers. On the other hand, the large value measured by Hart and Bourne [1989] ($\simeq 0.25 \text{ cm}^{-1}$) will significantly reduce the magnitude of the cross section in line centers. To gauge the impact on NO photolysis rates, we computed the $\delta(1-0)$ cross section using the line width suggested by Hart and Bourne [1989]. The ratio of the photolysis frequency calculated using the larger line width (0.25 cm^{-1}) to the value determined using a narrower line profile (0.02 cm^{-1}) is presented in Figure 11. Opacity by NO was included in both cases according to the "medium" NO profile from section 4. The J value is larger



Fig. 10. (a) Ratios of NO J values calculated using the ODF method to the line-by-line results. The NO $\delta(0-0)$ band is shown for solar zenith angles of 0° (dashed) and 60° (solid); the $\delta(1-0)$ band is also shown for 0° (triangles) and 60° (circles). Opacity by NO was accounted for using the "medium" NO profile shown in Figure 6a. (b) Ratios of ODF to line-by-line J values for the sum of the $\delta(0-0)$ and $\delta(1-0)$ bands at solar zenith angles of 0° (solid), 60° (dashed), and 80° (dot-dashed).



Fig. 11. Ratio of NO J values in the $\delta(1-0)$ band assuming a predissociation line width of 0.25 cm⁻¹ to J values computed using a width of 0.02 cm⁻¹ for zenith angles of 60° (triangles) and 80° (circles). The "medium" NO profile from Figure 6a was used to determine nitric oxide opacity.

for the case where lines are broader because the peak values for the cross section are smaller; attenuation of radiation by NO is consequently diminished. Comparison with the results shown in Figure 5 indicates that assumption of a 0.25 cm⁻¹ predissociation width for the $\delta(1-0)$ band may significantly reduce the effect of NO self absorption on the $\delta(1-0)$ photolysis rate. Our results concerning the solar cycle variation of J_{NO} (Figure 7), which are based on the narrower line width, may therefore overstate the NO opacity effect above 80 km if the predissociation width is indeed as large as suggested by *Hart and Bourne* [1989].

The correction to our ODF parameterization to account for a different line width is more complicated than the scaling for alternative values of the oscillator strength. Since a change in the line width creates an opposite effect in the magnitude of the cross section in line centers compared to line wings, we treat the two cases separately. The values denoted by $\sigma_{\rm NO}^2$ in Table 1 represent the NO cross section near line centers, whereas the $\sigma_{\rm NO}^1$ are more appropriate for line wings. First, we note that the magnitude of the cross section in line centers is inversely proportional to the line width, regardless of whether the line is described by a Gaussian (Doppler broadening), or by a Lorentzian (predissociation broadening) profile. The following correction can thus be applied to the values of $\sigma_{\rm NO}^2$ to allow for a predissociation width other than 0.02 cm⁻¹:

$$\sigma_{\rm NO}^{2'} = \sigma_{\rm NO}^2 \left(\frac{0.074}{\Gamma} - \frac{0.0011}{\Gamma^2} \right)$$
(11)

where Γ is the new predissociation width (FWHM) in units of per centimeter. This expression was derived to provide the correct behavior for both large and small values of Γ compared to the typical Doppler width. The quantity in parentheses in equation (11) is approximately 1 for $\Gamma =$ 0.02 cm^{-1} , while for $\Gamma > 0.1 \text{ cm}^{-1}$ it varies approximately as $0.074/\Gamma$. It can be shown that the factor of 0.074 is related to the normalization factors for Gaussian and Lorentzian line profiles.

For the cross section in line wings, σ_{NO}^1 , we note that correction reduces essentially to the ratio of Lorentzian profiles. If we take the mean distance between lines to be 0.20 cm⁻¹, then the correction takes the form

$$\sigma_{\rm NO}^{1'} = \sigma_{\rm NO}^1 \left(\frac{8.02 \ \Gamma}{0.16 + \Gamma^2} \right) \tag{12}$$

where we use the same notation as in equation (11). The errors in photolysis rates calculated using the above corrections to the cross sections given in Table 1 are no larger than those already indicated in Figure 10a.

7. CONCLUDING REMARKS

The combination of higher values for the solar flux and greater atmospheric transmission in the $\delta(0.0)$ band of NO leads to larger rates for photodissociation of nitric oxide in this work compared with previous studies; corresponding rates for loss of NO_x should be enhanced as well. This increase in $J_{\rm NO}$ is somewhat diminished by explicit consideration of the opacity due to NO absorption. A more substantial consequence of self absorption by NO concerns the solar cycle variability of $J_{\rm NO}$ and the potential impact on concentrations of NO_x and O₃ in the stratosphere and mesosphere.

Our results emphasize the importance of a precise treat-

ment of attenuation by the O₂ S-R bands in calculating the NO photolysis rate. This work offers an improvement in this respect over previous studies of NO photodissociation due to the availability of more accurate spectroscopic data on the O_2 S-R bands. Unfortunately, the same cannot be said regarding the current status of NO spectroscopy in the δ bands. Further laboratory study of the δ bands is clearly warranted in light of the large uncertainties in values for the band oscillator strengths, predissociation widths, and emission and quenching rates. All of these quantities are important in determining the magnitude of the NO photolysis rate, but we have found that values for the predissociation widths, in particular, can have a significant impact on the effect of opacity by NO, with potentially important consequences for the solar cycle variation of the photolysis frequency.

Acknowledgments. We thank T. G. Slanger for useful discussions of recent laboratory studies of nitric oxide. K. M. wishes also to acknowledge the support and advice of J. W. Firor and G. Brasseur. This paper benefitted from the the constructive comments of an anonymous reviewer.

References

- Allen, M., and J. E. Frederick, Effective photodissociation cross sections for molecular oxygen and nitric oxide in the Schumann-Runge bands, J. Atmos. Sci., 39, 2066-2075, 1982.
- Barth, C. A., Reference models for thermospheric NO, in MAP Handbook 31, pp. 126-138, University of Illinois, Urbana, 1989.
- Barth, C. A., Tobiska, W. E., D. E. Siskind, and D. D. Cleary, Solar-terrestrial coupling: Low-latitude thermospheric nitric oxide, *Geophys. Res. Lett.*, 15, 92-94, 1988.
- Bates, D. R., The physics of the upper atmosphere, in *The Earth* as a *Planet*, Chapter 12, edited by G. Kuiper, pp. 576-643, University of Chicago Press, Chicago, Ill., 1954.
- Benoist D'Azy, O., R. Lopez-Delgado, and A. Tramer, NO fluorescence decay from low-lying electronic states excited into single vibronic levels with synchrotron radiation, *Chem. Phys.*, 9, 327-338, 1975.
- Bethke, G. W., Oscillator strengths in the far ultraviolet, I, Nitric oxide, J. Chem. Phys., 31, 662-668, 1959.
- Callear, A. B., and M. J. Pilling, Fluorescence of nitric oxide, VII, Quenching rates of NO $C^2 \Pi(v=0)$, and its rate of radiation to NO $A^2 \Sigma^+$, energy transfer efficiencies, and mechanisms of predissociation, *Trans. Faraday Soc.*, 66, 1618-1634, 1970a.
- Callear, A. B., and M. J. Pilling, Fluorescence of nitric oxide, VI, Predissociation and cascade quenching of NO $D^2\Sigma^+(v=0)$ and NO $C^2\Pi(v=0)$, and oscillator strengths of the $\delta(0,0)$ and $\delta(1,0)$ bands, Trans. Faraday Soc., 66, 1886-1906, 1970b.
- Callear, A. B., and I. W. M. Smith, Fluorescence of nitric oxide, III, Determination of the rate constants for predissociation, collisional quenching, and spontaneous radiation NO $C^2 \Pi(v = 0)$, Discuss. Faraday Soc., 37, 96-111, 1964.
- Cheung, A. S.-C., K. Yoshino, J. R. Esmond, S. S.-L. Chiu, D. E. Freeman, and W. H. Parkinson, Predissociation line widths of the (1,0) - (12,0) Schumann-Runge absorption bands of O₂ in the wavelength region 179-202 nm, J. Chem. Phys., 92, 842-849, 1990.
- Cieslik, S., Determination experimentale des forces d'oscillateur des bandes β , γ , δ et ϵ de la molecule NO, Bull. Cl. Sci. Acad. R. Belg., 63, 884-901, 1977.
- Cieslik, S., and M. Nicolet, The aeronomic dissociation of nitric oxide, Planet. Space Sci., 21, 925-937, 1973.
- Clancy, R. T., D. W. Rusch, and D. O. Muhleman, A microwave measurement of high levels of thermospheric nitric oxide, *Geo*phys. Res. Lett., 19, 261-265, 1992.
- DeMore, W. B., S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. E. Kolb, and M. J. Molina, Chemical kinetics and photochemical data for use in stratospheric modeling, Evaluation No. 10, JPL Publ. 92-20, Jet Propuls. Lab., Pasadena, Calif., 1992.

Drayson, S. R., Rapid computation of the Voigt profile, J. Quant.

Spectrosc. Radiat. Transfer, 16, 611-614, 1976.

- Eparvier, F. G. and C. A. Barth, Self-absorption theory applied to rocket measurements of the nitric oxide $(1,0) \gamma$ band in the daytime thermosphere, J. Geophys. Res., 97, 13723-13731, 1992.
- Erkovich, S. P., Y. V. Pisarevskii, and F. S. Ageshin, A method of determining oscillator strengths for electron transitions in molecules, *Opt. Spectrosc.*, 17, 15-17, 1964.
- Fang, T. M., S. C. Wofsy, and A. Dalgarno, Opacity distribution functions and absorption in the Schumann-Runge bands of molecular oxygen, *Planet. Space Sci.*, 22, 413-425, 1974.
- Frederick, J. E. and R. D. Hudson, Predissociation of nitric oxide in the mesosphere and stratosphere, J. Atmos. Sci., 36, 737-745, 1979a.
- Frederick, J. E., and R. D. Hudson, Predissociation line widths and oscillator strengths for the 2-0 to 13-0 Schumann-Runge bands of O₂, J. Mol. Spectrosc., 74, 247-256, 1979b.
- Frederick, J. E., R. B. Abrams, and P. J. Crutzen, The delta band dissociation of nitric oxide: A potential mechanism for coupling thermospheric variations to the mesosphere and stratosphere, J. Geophys. Res., 88, 3829-3835, 1983.
- Gadd, G. E., D. L. Huestis, and T. G. Slanger, Rotationallevel-dependent radiative lifetimes and branching ratios in $NO(B^2\Pi)(v = 7, \Omega = 1/2, 3/2)$, J. Chem. Phys., 95, 3944-3954, 1991.
- Guest, J. A., and L. C. Lee, Quantitative absorption and fluorescence studies of NO between 1060 and 2000 Å, J. Phys. B At. Mol. Phys., 14, 3401-3413, 1981.
- Hart, D. J., and O. L. Bourne, High-resolution coherent VUV spectroscopy of $NO[C^2\Pi(1) B^2\Pi(10), B^2\Pi(11)]$ and $CO[B^1\Sigma^+(0)]$, Chem. Phys., 133, 103-112, 1989.
- Heroux, L., and R. A. Swirbalus, Full-disc solar fluxes between 1230 and 1940 A, J. Geophys. Res., 81, 436-440, 1976.
- Hikida, T., T. Suzuki, and Y. Mori, Fluorescence lifetime studies of NO $A^2\Sigma^+(v = 5, N = 9)$, $B^2\Pi_{3/2}(v = 8, j = 8.5)$, $C^2\Pi_{3/2}(v = 1, j = 8.5)$, $D^2\Sigma^+(v = 0, N = 5)$ and $D^2\Sigma^+(v = 1, N = 9)$, Chem. Phys., 118, 437-444, 1987.
- Kovacs, I., Rotational Structure in the Spectra of Diatomic Molecules, pp. 126-128, Elsevier, New York, 1969.
- Lagerquist, A., and E. Miescher, Absorptionsspektrum des NO-Molekuls Feinstruktur-Analyse der δ und β banden und homogene storung $C^2\Pi$ - $B^2\Pi$, Helv. Phys. Acta, 31, 221-262, 1958.
- Lean, J., M. VanHoosier, G. Brueckner, D. Prinz, L. Floyd, and K. Edlow, SUSIM/UARS observations of the 120 to 300 nm flux variations during the maximum of the solar cycle: Inferences for the 11-year cycle, *Geophys. Res. Lett.*, 19, 2203-2206, 1992.
- Lewis, B. R., L. Berzins, and J. H. Carver, Oscillator strengths for the Schumann-Runge bands of O₂, J. Quant. Spectrosc. Radiat. Transfer, 36, 209-232, 1986.
- Mandelman, M., and T. Carrington, The f-value of the NO $\delta(0,0)$ band by the line absorption method, J. Quant. Spectrosc. Radiat. Transfer, 14, 509-521, 1974.
- McPeters, R. D., Climatology of nitric oxide in the upper stratosphere, mesosphere, and thermosphere: 1979 through 1986, J. Geophys. Res., 94, 3461-3472, 1989.
- Mickley, L. J., J. E. Frederick, and J. M. Russell III, Measurements of nitric oxide from the Halogen Occultation Experiment, Eos Trans. AGU, 73, Fall Meeting Suppl., 1992.
- Minschwaner, K., G. P. Anderson, L. A. Hall, and K. Yoshino, Polynomial coefficients for calculating O₂ Schumann-Runge cross sections at 0.5 cm⁻¹ resolution, J. Geophys. Res., 97, 10103-10108, 1992.
- Minschwaner, K., R. J. Salawitch, and M. B. McElroy, Absorption of solar radiation by O₂: implications for O₃ and lifetimes of N₂O, CFCl₃, and CF₂Cl₂, J. Geophys. Res., 98, 10543-10561, 1993.
- Moe, O. K., M. E. VanHoosier, J.-D. F. Bartol, and G. E. Brueckner, A spectral atlas of the Sun between 1175 and 2100 Angstroms, Nav. Res. Lab. Rep. 8056, Washington, D. C., 1976.
- Nicolet, M., Photodissociation of nitric oxide in the stratosphere and mesosphere: Simplified numerical relations for atmospheric model calculations, *Geophys. Res. Lett.*, 6, 866-868, 1979.

- Nicolet, M., and S. Cieslik, The photodissociation of nitric oxide in the mesosphere and stratosphere, *Planet. Space Sci.*, 28, 105-115, 1980.
- Roble, R. G. and R. E. Dickinson, How will changes in carbon dioxide and methane modify the mean structure of the mesosphere and thermosphere, *Geophys. Res. Lett.*, 16, 1441-1444, 1989.
- Rottke, H., and H. Zacharias, Photoionization of single rotational levels in excited $B^2\Pi$, $C^2\Pi$, and $D^2\Sigma^+$ states of ¹⁴N¹⁶O, J. Chem. Phys., 83, 4831-4844, 1985.
- Siskind, D. E., C. A. Barth, and D. D. Cleary, The possible effect of solar soft X rays on thermospheric nitric oxide, J. Geophys. Res., 95, 4311-4317, 1990.
- Solomon, S., P. J. Crutzen, R. G. Roble, Photochemical coupling between the thermosphere and the lower atmosphere, 1, Odd nitrogen from 50 to 120 km, J. Geophys. Res., 87, 7206-7220, 1982.
- Strobel, D. F., Odd nitrogen in the mesosphere, J. Geophys. Res., 76, 8384-8393, 1971.
- Strobel, D. F., D. M. Hunten, and M. B. McElroy, Production and diffusion of nitric oxide, J. Geophys. Res., 75, 4307-4321, 1970.
- Tsukiyama, K. T. Munakata, M. Tsukakoshi, and T. Kasuya, Fluorescence lifetimes of NO $A^2\Sigma^+(v'=3 \text{ and } 4)$, $C^2\Pi(v'=$

0), and $D^2\Sigma(v'=0)$ studied by tunable VUV laser excitation, Chem. Phys., 121, 55-62, 1988.

- VanHoosier, M. E., J.-D. F. Bartoe, G. E. Brueckner, and D. K. Prinz, Absolute solar spectral irradiance 120 nm-400 nm (results from the Solar Ultraviolet Spectral Irradiance Monitor-SUSIM-experiment on board Spacelab 2), Astrophys. Lett. Commun., 27, 163-168, 1988.
- West, R., D. Crisp, and L. Chen, Mapping transformations for broadband atmospheric radiation calculations, J. Quant. Spectrosc. Radiat. Transfer, 43, 191-199, 1990.
- Yoshino, K., D. E. Freeman, J. R. Esmond, and W. H. Parkinson, High resolution absorption cross section measurements and band oscillator strengths of the (1,0)-(12,0) Schumann-Runge bands of O₂, *Planet. Space Sci.*, *31*, 339-353, 1983.

K. Minschwaner, Advanced Study Program, National Center for Atmospheric Research, P. O. Box 3000, Boulder, CO 80307.

D. E. Siskind, E. O. Hulburt Center for Space Research, Naval Research Laboratory, Code 7641, Washington, D. C. 20375.

> (Received April 30, 1993; revised July 16, 1993; accepted July 19, 1993.)