

Calculations of the Temperature Dependence of the NO₂ Photodissociation Coefficient in the Atmosphere

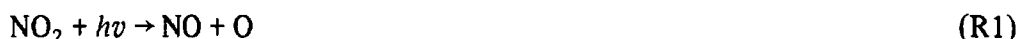
S. MADRONICH*, D. R. HASTIE, B. A. RIDLEY**, and H. I. SCHIFF
Department of Chemistry, York University, Downsview, Ontario, Canada, M3J 1P3

Abstract. The photodissociation coefficient, J_{NO_2} , of NO₂ in the atmosphere was calculated at 235 and 298 K using the measured temperature dependences of the absorption cross-sections and quantum yields. These calculations gave a ratio $J_{\text{NO}_2}(298 \text{ K})/J_{\text{NO}_2}(235 \text{ K}) = 1.155 \pm 0.010$ which is only weakly dependent on altitude, surface albedo and solar zenith angle.

Key words: Atmosphere, photolysis, nitrogen dioxide, photodissociation coefficient, temperature effect.

1. Introduction

The photodissociation of NO₂ by solar radiation:



is an important process in atmospheric chemistry. In the stratosphere it is intimately involved in the ozone catalytic cycles and in the partitioning of the 'odd nitrogen' species. In the troposphere it is the major process that produces 'odd oxygen' which leads to the formation of photochemical oxidants.

The photodissociation coefficient, J_{NO_2} , at a given altitude and solar zenith angle is generally calculated in atmospheric models from the expression:

$$J_{\text{NO}_2} = \int \sigma(\lambda) \phi(\lambda) F(\lambda) d\lambda \quad (1)$$

where $\sigma(\lambda)$ and $\phi(\lambda)$ are the NO₂ absorption cross-sections and photodissociation quantum yields, respectively, and $F(\lambda)$ is the solar actinic flux which has both direct and diffuse components. Most calculations tacitly assume that J_{NO_2} is temperature invariant, although both $\sigma(\lambda)$ and $\phi(\lambda)$ are reported to be temperature dependent (e.g., JPL, 1982). Since large temperature gradients exist in the atmosphere, the neglect of this temperature

* Present address: Aerochem Research Laboratories, PO Box 12, Princeton NJ 08540, U.S.A.

** Present address: National Center for Atmospheric Research, PO Box 3000, Boulder, CO 80307, U.S.A.

dependence of J_{NO_2} in models will affect conclusions based on comparisons of atmospheric measurements with model calculations. For example, the measured ratio of $[\text{NO}]/[\text{NO}_2]$ which is largely dominated by J_{NO_2} (Ridley and Schiff, 1981; Ridley and Hastie, 1981) is often used as a test for models.

The objective of this paper is to examine the effect of including reported temperature dependences of $\sigma(\lambda)$ and $\phi(\lambda)$ on calculations of J_{NO_2} . A computer algorithm is first used to solve Equation (1) for 235 and 298 K on the assumption that the earth has no atmosphere or surface albedo. This provides values which we will call 'extraterrestrial' J_{NO_2} . Atmospheric and surface effects are then considered to determine the ratio of J_{NO_2} at these two temperatures as a function of altitude, albedo and solar zenith angle.

2. Method and Results

Extraterrestrial, differential J_{NO_2} values are calculated from the integrand of Equation (1). The extraterrestrial solar flux was taken from the detailed tabulations of Thekaekara (1974) for the wavelength range 300–420 nm and from Ackerman (1971) for shorter wavelengths. The NO_2 absorption cross-sections and quantum yields used in the calculations were the literature values shown in Table I. In the wavelength region where no low temperature quantum yield data are available, the high temperature values were used. Calculations were performed at 1 nm intervals using extraterrestrial solar flux data from 200 to 400 nm. Spectral data were interpolated or averaged according to whether they were or were not available with resolution better than 1 nm. Use of wavelength intervals greater than about 5 nm in the calculations was found to introduce significant over-estimates of J_{NO_2} . For example, a 10 nm rather than a 1 nm interval resulted in a 5% larger value of J_{NO_2} (Madronich, 1982).

Table 1. NO_2 absorption cross-sections and quantum yields

	Reference	Wavelength range (nm)
σ (298 K)	Bass <i>et al.</i> (1976) ^a	185–410.25
	Davenport (1978)	411–420
σ (235 K) ^b	Bass <i>et al.</i> (1976) ^a	290–410.25
	Davenport (1978) ^c	411–420
ϕ (298 K)	= 1	200–297
	Jones and Bayes (1973) ^a	297–375.5
	Harker <i>et al.</i> (1977) ^a	375–420
	Davenport (1978)	390.1–420.8
ϕ (235 K) ^b	Davenport (1978) ^d	389.8–419.7

^a Source of JPL (1982) recommendations.

^b For wavelengths outside ranges shown, high temperature data were used.

^c Interpolated to 235 K from measurements at 226 K and 247 K.

^d Interpolated to 235 K from measurements at 223 K and 300 K.

The wavelength dependence of the extraterrestrial, differential J_{NO_2} values, at 298 and 235 K and the differences between them are shown in Figure 1. The extraterrestrial values of J_{NO_2} , computed from the areas under the curves in Figure 1 are 7.46×10^{-3} and $8.55 \times 10^{-3} \text{ s}^{-1}$ at 235 and 298 K respectively, corresponding to a 14.6% increase with temperature over this 63 K range.

An increase of about 4% can be attributed to the temperature dependence of the quantum yield while the remaining 11% is due to the temperature dependence of the

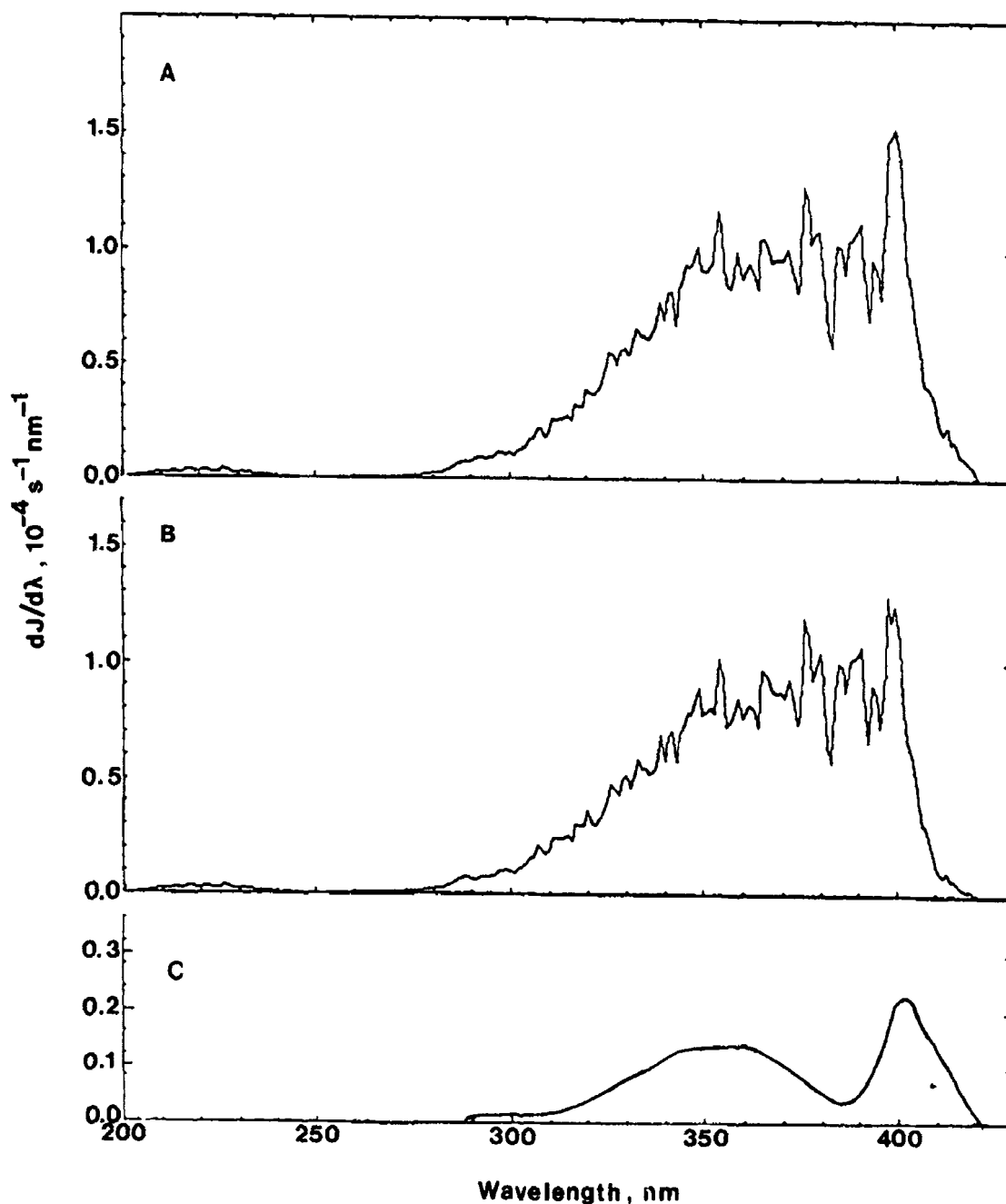


Fig. 1. Wavelength dependence of the differential photodissociation coefficient of NO_2 . Curve A at 298 K; curve B at 235 K; curve C is the smoothed difference between curves A and B.

absorption cross-section over this temperature range. About one third of the increase (5%) occurs at wavelengths longer than 398 nm, the thermodynamic dissociation threshold. Below 398 nm, only the absorption cross-section shows significant temperature dependence and accounts of the greater part (10%) of the calculated temperature dependence of J_{NO_2} .

These results are in contrast with the laboratory measurements of Dickerson *et al.* (1982) who report NO_2 photodissociation rate coefficients from 227 to 401 K based on experiments with a flow tube actinometer illuminated with a Xe lamp. These authors report a $5.5 \pm 0.6\%$ increase in the NO_2 photodissociation coefficient between 235 and 298 K and claim good agreement with their calculations of the temperature dependence of J_{NO_2} . However, they based their calculations on the measurements by Davenport (1978) of the temperature dependence of the absorption coefficients and quantum yields over the wavelength region 390–420 nm. Figure 1 shows that only about one third of the temperature dependence of J_{NO_2} is accounted for in this wavelength region, while two-thirds occurs at shorter wavelengths. The discrepancy between the two calculations is, therefore, largely attributable to our inclusion of the data of Bass *et al.* (1976) which was neglected by Dickerson *et al.* (1982). Our calculations agree with the J_{NO_2} measurements only if the low temperature cross-sections of Bass *et al.* (1976) are rejected.

The 298 and 235 K data of Bass *et al.* (1976) are the current recommendations of NASA (1979) and JPL (1982) for NO_2 absorption coefficients for use in photochemical calculations and are in good agreement, both in absolute values and in temperature dependence, with the measurements of Davenport (1978) over the 389.9 to 410 nm wavelength range in which the measurements overlap. At shorter wavelengths, only the temperature dependence measurements reported by Bass *et al.* (1976) are available. The 10% scatter in their data does not affect the precision of our J_{NO_2} calculations since our integration smooths over a large number of data points. Interference from the NO_2 dimer, N_2O_4 , was considered in detail by Bass *et al.* (1976) who argue that the temperature dependence of the NO_2 absorption cross-section is observed both at wavelengths where the absorption of N_2O_4 is large and where it is small. There therefore appears to be no clear reason for rejecting the low temperature absorption cross-section measurements.

The quantum yield values of Harker *et al.* (1977) are included in the recent recommendations by NASA (1979) and JPL (1982) despite a suggestion by Demerjian *et al.* (1980) that they may include systematic errors ranging from 10 to 15%. These values are also in excellent agreement with the measurements of Davenport (1978). Quantum yields less than unity for wavelengths less than the thermodynamic threshold of 398 nm currently lack theoretical justification (CODATA 1982), but have been observed in all recent studies on NO_2 (Jones and Bayes, 1973; Harker *et al.* 1977; Davenport, 1978). However, uncertainties in the quantum yield at these short wavelengths will not have a large effect on the temperature dependence of J_{NO_2} .

To evaluate the temperature dependence of J_{NO_2} in the real atmosphere absorption and scattering effects were considered. The attenuation of the solar actinic flux by NO_2 , O_2 and O_3 above the altitude of interest was evaluated using absorption coefficients at 298 K recommended in CIAP (1974) and JPL (1982). Since this attenuation is relatively

weak, the temperature dependences of these absorption coefficients were neglected. Rayleigh scattering cross-sections were calculated according to the method of Elterman (1968). Scattering by clouds or aerosols was not included.

Multiple scattering was calculated using the method of successive orders of scattering described by Isaksen *et al.* (1977) with 50 atmospheric layers, each 1 km thick. Our calculations differ with respect to the direction of propagation of scattered light which Isaksen *et al.* (1977) take to be always parallel to the incoming solar beam. Luther (1980) has described a method of using more realistic, isotropic scattering in models without sacrificing computational simplicity. In our algorithm either model, as well as intermediate cases can be selected by using an adjustable parameter which simulates the degree of anisotropy introduced by the Rayleigh phase function, by oblique crossing of atmospheric layers and by surface albedo. A detailed comparison of the two models will be presented elsewhere. For the calculations reported here, only the purely isotropic model (Luther, 1980) and a Lambertian albedo are used.

Since it is our intention to make comparisons of these calculations with summertime, J_{NO_2} measurements (Madronich *et al.*) made at Gimli, Manitoba (50.62° N), altitude profiles of the concentration of atmospheric constituents used in the scattering calculation were taken for mid summer, 50° N conditions. The air density profile was obtained by interpolation of the 45° N and 60° N July standard atmosphere (U.S. Standard Atmos. Suppl. 1966) and the O₂ profiles by multiplying these numbers by 0.2095. The O₃ profiles were obtained from summertime ozone sonde data at Gimli up to 40 km. Above this altitude the O₃ mixing ratio was assumed to be constant at 6 ppmv. The NO₂ profile between 10 and 40 km was taken from Evans *et al.* (1978) for Yorkton, Saskatchewan (51.3° N). Below 10 km and above 40 km, the theoretical values of Chang (1979) were used.

Since Rayleigh optical depths vary smoothly with wavelength and molecular absorption is relatively unimportant, a coarser 20 nm integration interval was used. These calculations were made with the incoming solar flux taken as unity and gave, for each wavelength interval, a scale factor by which the differential extraterrestrial J_{NO_2} value (Figure 1) had to be multiplied to account for the terrestrial effects and the solar zenith angle. The terrestrial J_{NO_2} values were then obtained by integrating over the wavelength range. The percentage increases of J_{NO_2} at 298 K relative to 235 K are shown in Figure 2 as a function of altitude for different values of solar zenith angle and albedo. The 298 K values remain between 14.6 and 16.5% greater than the 235 K values and only marginally greater, on average, than the 14.6% change in the extraterrestrial value of J_{NO_2} . The small shift in the wavelength distribution of actinic flux as a result of molecular scattering appears to have only a minor effect. Although inclusion of clouds and aerosols will affect the absolute values of J_{NO_2} they should not seriously alter the ratios shown in Figure 2 in the light of the weak temperature dependence found for multiple Rayleigh scattering.

Most modellers assume that J_{NO_2} is independent of temperature. Our calculations show that a 63 K change in temperature can result in a 15% change in J_{NO_2} which, in turn, can have an appreciable affect on model calculations of atmospheric concentrations and processes. For example, measurements of the [NO]/[NO₂] ratio in the stratosphere

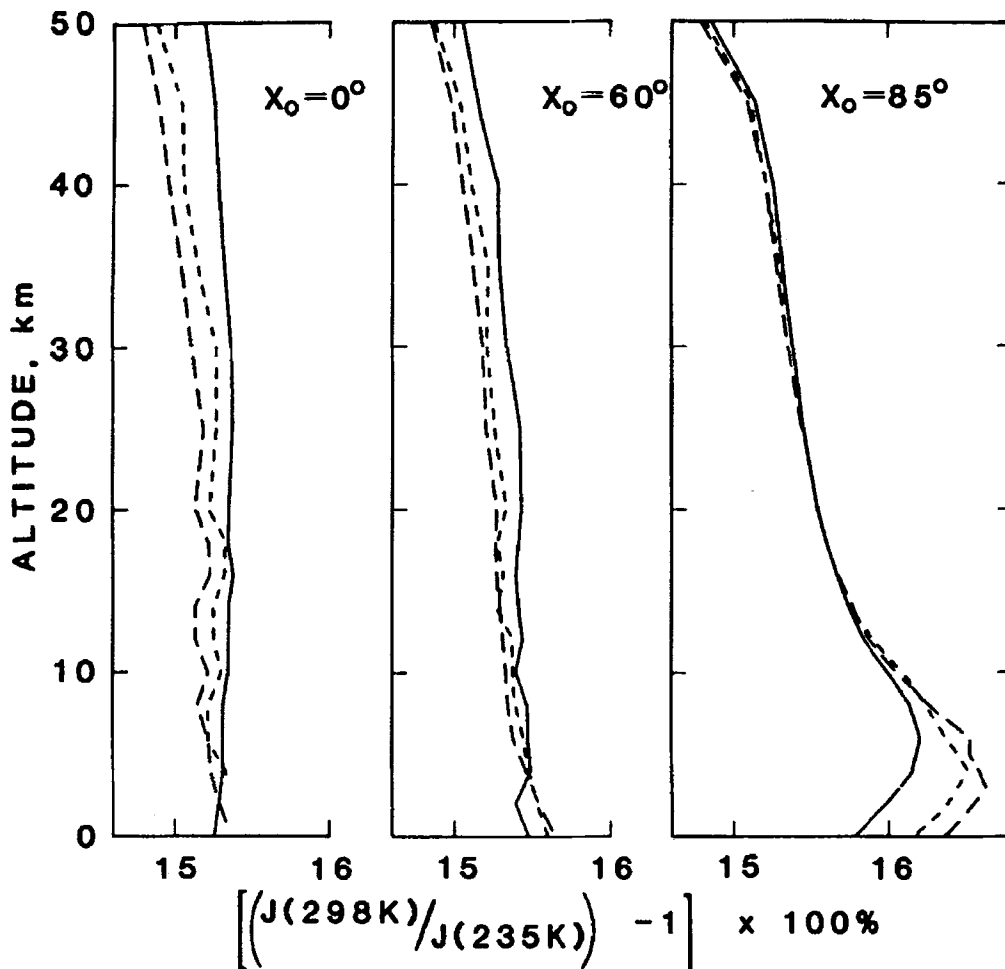


Fig. 2. The ratio of the photodissociation coefficients of NO_2 at 298 and 235 K as a function of altitude for several solar zenith angles, χ_0 , and surface albedos: — — .00; - - - - 0.25; — 1.00.

are currently being made to this accuracy as a test of current models. Since the ratio is largely dominated by J_{NO_2} , its temperature dependence should be considered when comparing models with measurements. The values calculated here are based on a rather limited data base for reported temperature dependences of $\sigma(\lambda)$ and $\phi(\lambda)$. Additional measurements of these quantities would be valuable.

References

- Ackerman, M., 1971, Mesospheric models and related experiments, G. Fiocco, Ed. D. Reidel, Dordrecht, pp. 149-159.
- Bass, A. M., Ledford, A. E., and Laufer, A. H., 1976, Extinction coefficients of NO_2 and N_2O_4 , *J. Res. Nat. Bureau Standards*, 80A, 143-162.
- Chang, J., private communication.

- CIAP Monograph 1, 1974, *The Natural Stratosphere of 1974*, U.S. Department of Transportation, Washington, D.C.
- Davenport, J. E., 1978, Determination of NO₂ photolysis parameters for stratospheric modelling, *FAA Report No. FAA-EQ-7-14*.
- Demerjian, K. L., Schere, K. L., and Peterson, J. T., 1980, Theoretical estimates of actinic (spherically integrated) flux and photolytic rate constants of atmospheric species in the lower troposphere, *Adv. Environ. Sci. Technol.* 10, 369-460.
- Dickerson, R. R., Stedman, D. H., and Delany, A. C., 1982, Direct measurements of ozone and nitrogen dioxide photolysis rates in the troposphere, *J. Geophys. Res.* 87, 4933-4945.
- Elterman, L., 1968, UV, visible and IR attenuation for altitudes to 50 km, *Environ. Res. Papers No. 285*, AFCRL-68-0153.
- Evans, W. F. J., Fast, H., Kerr, J. B., McElroy, C. T., O'Brien, R. S., Wardle, D. I., McConnell, J. C., and Ridley, B. A., 1978, *WMO Symposium, Toronto, Ontario*.
- Harker, A. B., Ho, W., and Ratto, J. J., 1977, Photodissociation quantum yields of NO₂ in the region 375 to 420 nm, *Chem. Phys. Lett.* 50, 394-397.
- Isaksen, I. A., Midtbo, K. H., Sunde, J., and Crutzen, P. J., 1977, A simplified method to include molecular scattering and reflection in calculations of photon fluxes and photodissociation rates, *Geophys. Norveg.* 31, 11-26.
- JPL, 1982, Chemical kinetic and photochemical data for use in stratospheric modelling: Evaluation Number 5, *JPL Publication 82-57*, Pasadena, California.
- Jones, I. T. N. and Bayes, K. D., 1973, Photolysis of nitrogen dioxide, *J. Chem. Phys.* 59, 4836-4844.
- Luther, F. M., 1980, *Annual Report to the FAA*, UCRL-50042-80, Lawrence Livermore Laboratory, Livermore, California.
- Madronich, S., 1982, Measurements of the photodissociation coefficient of NO₂ in the stratosphere, PhD Thesis, York University.
- Madronich, S., Hastie, D. R., Ridley, B. A. and Schiff, H. I., to be published.
- NASA, 1979, The stratosphere present and future, *NASA Publication 1049*.
- Ridley, B. A., and Schiff, H. I., 1981, Stratospheric odd nitrogen: nitric oxide measurements at 32° in autumn, *J. Geophys. Res.* 86, 3167-3172.
- Ridley, B. A. and Hastie, D. R., 1982, Stratospheric odd nitrogen: NO measurements at 51° N in summer, *J. Geophys. Res.* 86, 3162-3166.
- Thekaekara, M. P., 1974, Extraterrestrial solar spectrum, 3000-6000 Å at 1 Å intervals, *Appl. Optics* 13, 518-522.
- U.S. Standard Atmosphere, 1976, NOAA, NASA, U.S. Air Force, NOAA-S/T 76-1562, Washington, D.C.