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JNO₂ at high solar zenith angles in the lower stratosphere

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Abstract. In situ measurements of NO, NO₂, O₃, HO₂, ClO, pressure, and temperature have been made at high solar zenith angles (SZA, 70° - 93°) in the lower stratosphere. These measurements are used to derive the photolysis rate of NO₂, JNO₂, using a time-dependent method. The resultant JNO₂ values and the results of a multiple-scattering actinic flux model show a linear relationship throughout the SZA range. The difference of the two sets of JNO₂ values of about 11% suggests that the model scattering calculation is very accurate at high SZA conditions near sunrise and sunset.

Introduction

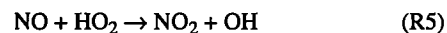
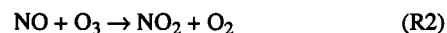
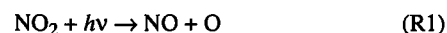
Calculated photolysis rates are an essential part of stratospheric photochemical modeling. Their accuracy depends on both calculated solar actinic flux modeling and laboratory-measured photolysis cross sections. Validation is often partially achieved through in situ solar flux measurements as a function of SZA. The photolysis rate of NO₂, JNO₂, is of particular interest because it can be derived photochemically from a small set of in situ measurements: NO, NO₂, O₃, ClO, BrO, and HO₂. In previous studies, the agreement between photochemically derived and radiative model JNO₂ values for SZAs < 85° was within 8% [Gao *et al.*, 1997] and less than 15% [Del Negro *et al.*, 1999] in the lower stratosphere. The agreement is well within the combined uncertainties associated with the measurements, model calculations, reaction rate coefficients, absorption cross sections, and photolysis quantum yields. These intercomparisons provided an important evaluation of the accuracy of J-value calculations and covered a wide range of parameters (solar zenith angles (SZAs), surface albedo, terrain/cloud height, pressure, and temperature) that affect actinic flux [Swartz *et al.*, 1999]. However, because of this wide coverage, it is difficult to test individual factors. Fur-

thermore, the intercomparisons were limited to SZAs of less than 85° due to the use of a steady state approximation for the derived JNO₂ [Del Negro *et al.*, 1999 and references therein].

In this paper we present a time-dependent method for deriving photochemical JNO₂ values at SZAs beyond 85° in the lower stratosphere (19 - 20 km). The method makes use of in situ measurements of both NO₂ and NO during four stratospheric flights of the NASA ER-2 high-altitude aircraft [Del Negro *et al.*, 1999]. These flights include high SZAs (89° - 93°) in the period before sunset or after sunrise. The analysis is simplified by nearly constant values of latitude, pressure (p), temperature (T), and O₃ for these periods. We show that under these conditions the precision of the derived JNO₂ values depends only on the precision of the NO/NO₂ ratio which is about 7 to 20% for the results presented here. A comparison of photochemically derived and model JNO₂ values indicates that the calculation of direct and scattered light at high SZAs is accurate in the 310 to 410 nm wavelength range in the lower stratosphere.

Calculations of JNO₂

Photochemical method. The basic photochemical relationship between NO and NO₂ is governed by the chemical reactions:



Typical relaxation time between NO and NO₂ is about 100 s. Other reactions involving NO_x (= NO + NO₂) are ignored since their photochemical lifetimes are a few hours or longer [Kawa *et al.*, 1992]. Reactions (R1) - (R5) contribute to changes in NO₂ through:

$$\begin{aligned} d[\text{NO}_2]/dt = & (k_2[\text{O}_3] + k_3[\text{ClO}] + k_4[\text{BrO}] + k_5[\text{HO}_2])[\text{NO}] \\ & - J\text{NO}_2 [\text{NO}_2] \end{aligned} \quad (1)$$

where the square brackets denote concentrations, and k_n is the rate coefficient for reaction (Rn) [DeMore *et al.*, 1997]. Equation (1) can be solved for JNO₂ as:

$$\begin{aligned} J\text{NO}_2 = & ((k_2[\text{O}_3] + k_3[\text{ClO}] + k_4[\text{BrO}] + k_5[\text{HO}_2])[\text{NO}] \\ & - d[\text{NO}_2]/dt)/[\text{NO}_2]. \end{aligned} \quad (2)$$

In the steady state approximation, $d[\text{NO}_2]/dt$ is set to zero. This approximation is valid in general only at SZAs less than 85° [Webster, 1987; Kawa *et al.*, 1990]. Between 85° and sunrise or sunset (~94° at 20 km), solar flux changes too rapidly for this approximation to be valid.

The flights used here occurred in April and September 1997 near Fairbanks, Alaska (65°N). In situ flight measurements include NO, NO₂, O₃, HO₂, ClO, p, and T. The treatment and sources of the flight data are the described in Del Negro *et al.*

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Table 1. Mean and Standard Deviation of Measured O₃, Latitude, p, and T Values from Four Flights of the ER-2 Aircraft.^a

Measurement	April 30, 1997	September 11, 1997	September 14, 1997	September 15, 1997
O ₃ (ppmv) ^b	2.5 (0.14)	1.8 (0.04)	1.8 (0.14)	1.8 (0.08)
NO _x (ppbv) ^c	0.59 (0.05)	0.93 (0.03)	0.64 (0.07)	0.62 (0.05)
Latitude (°)	64.0 (0.15)	64.4 (0.07)	64.4 (0.08)	64.6 (0.10)
p (hPa)	65.3 (1.12)	62.2 (0.58)	61.8 (1.25)	60.8 (0.77)
T (K)	227 (0.8)	222 (0.4)	219 (0.7)	219 (0.5)

^aData set corresponds to points shown in Figure 3. The first number is the mean and the second is the standard deviation.

^bppmv = parts per million by volume

^cppbv = parts per billion by volume

[1999]. Table 1 gives the mean and standard deviation of O₃, NO_x, latitude, p, and T values from each flight. Data are not available for HO₂ on September 14 and 15, or for BrO during any of the flights. Although the contributions of the BrO and HO₂ terms in (2) are less than 3% and 1%, respectively, HO₂ and BrO values from a photochemical steady state model [Salawitch *et al.*, 1994; Wennberg *et al.*, 1999] are used for completeness.

In the time-dependent analysis presented here, d[NO₂]/dt is derived from the NO and NO₂ time series made in the SZA range of 88° to 93° near both sunrise and sunset. In the time series, however, every 10-s data point effectively represents a different air parcel due to the aircraft's high speed (~200 m/s) and atmospheric variability. To use NO₂ measured from such a time series to calculate representative d[NO₂]/dt values, all air parcels must be photochemically equivalent. This requires that (i) air parcels are sampled at the same latitude in order that the time dependence of solar irradiation is the same and (ii) the partitioning between NO and NO₂ depends only on solar flux. The first criterion is met within a few tenths of a degree latitude (Table 1). Note also that the local time for individual air parcels must be used to calculate d[NO₂]/dt, since the variation of NO₂ is a function of sun position. The second criterion requires that the values of O₃, p, and T be nearly constant. All are reasonably constant as indicated in Table 1. In this data set the net contribution of the ClO, BrO, and HO₂ terms in (2) is 8% at 70° SZA decreasing to about 2% at 90° [Del Negro *et al.*, 1999] and, thus generally represents a negligible contribution to the high-SZA analysis here.

NO_x is not sufficiently constant to calculate d[NO₂]/dt directly from the time series data. As an alternative, a normalized derivative is used to calculate d[NO₂]/dt. In this case, NO₂ is first normalized to NO_x and the quantity d([NO₂]/[NO_x])/dt is calculated. The d[NO₂]/dt term is then calculated by multiplying d([NO₂]/[NO_x])/dt by NO_x. This approach is valid for two reasons. First, NO_x in any given air parcel along the flight track is essentially constant for 85° < SZA < 93° because NO_x photochemical production and loss is small over the associated time interval. Second, since NO₂ equals NO_x in the dark, NO₂/NO_x values just after sunrise or before sunset are equivalent to the fractional change of NO₂ from the dark values found just before sunrise or after sunset, respectively. Therefore, NO₂/NO_x values in different air parcels are independent of absolute NO₂ values and inter-comparable. A useful calculation of d[NO₂]/dt using this method requires that a second-order polynomial function be first fitted to the NO₂/NO_x data at high SZA before calculating values of d[NO₂]/dt. The fit prevents random noise in the NO and NO₂ measurements from affecting the calculated d[NO₂]/dt ratio. The total error in d[NO₂]/dt is estimated to be about ±13%.

The ratio of calculated d[NO₂]/dt and k₂[O₃][NO] terms is shown in Figure 1. Values of the ratio that exceed 0.1, which typically occur for SZAs greater than about ~90°, indicate the importance of the time-dependent term for photochemically derived JNO₂. Below 90°, the ratio is less than 0.1 and approaches zero as SZA decreases. At the high latitudes of these flights, SZAs change relatively slowly even at high SZAs. At lower latitudes, d[NO₂]/dt generally is more significant compared to k₂[O₃][NO] for 85° < SZA < 90°. The different SZA dependence between sunrise and sunset in Figure 1 is specific to these flights, depending in large part on the differences in p, T, and O₃.

Model calculations. Model JNO₂ values were calculated with two independent, spherical, isotropic, multiple-scattering models of the atmospheric radiation field, utilizing total column ozone and surface reflectivity as measured by the Total Ozone Mapping Spectrometer (TOMS). The model results, provided by the Johns Hopkins University Applied Physics Laboratory [Swartz *et al.*, 1999 and references therein] and the Jet Propulsion Laboratory [Salawitch *et al.*, 1994 and references therein], were used in Del Negro *et al.* [1999] and were referred to as APL_{TOMS} and JPL_{TOMS}, respectively. The uncertainty associated with calculated JNO₂ values is estimated to be ±15% based on uncertainties for the radiative flux and NO₂ photolysis cross sections. The average difference between the two sets of JNO₂ values is about 3% for SZAs less than 85°, and reduces to negligible at 93° SZA. Only APL_{TOMS} results are shown below since JPL_{TOMS} results lead to essentially the same conclusions.

Results and Discussion

Figure 2 illustrates radiative model JNO₂ versus photochemically derived JNO₂ values, for 89° < SZA < 93°. The photochemical values are shown with the calculated values of d[NO₂]/dt (Figure 2A) and with the steady state approximation (Figure 2B). The inclusion of the d[NO₂]/dt term significantly tightens the correlation between the two sets of JNO₂ values. Although this is not a proof of correctness, the tighter correlation in Figure 2A provides a consistency check of the time-dependent method. As shown, the correlation is linear throughout the JNO₂ value range. The slope of a linear fit through the origin is about 1.13 (R = 0.99), slightly larger than those reported by Del Negro *et al.* [1999, plate 4b], but within range of reported data. The average difference between the two sets of JNO₂ values (~13%) is significantly smaller than the uncertainties in either photochemically derived values (~60%, cf. Del Negro *et al.* [1999]) or radiatively modeled values. The results are also consistent with Bösch *et al.* [2000], who report good agreement between measured and calculated radiation flux for JNO₂ at high SZAs at altitudes between 2.5 and 30 km.

Figure 2A is extended to higher JNO₂ values by including the lower SZA data from the four flights (Figure 3). Photochemical JNO₂ values derived using the steady state approximation fall in the range of 4 × 10⁻³ s⁻¹ to 0.01 s⁻¹. The correlation with model values is linear over this range of approximately two orders of magnitude. The slope of the fitted line in this case is about 1.11 (R = 0.98), very close to that found with only the higher SZA data. The results presented in Figures 2 and 3 extend the high SZA limit used in Del Negro *et al.* [1999] from 85° to 93° SZA.

For the photochemically derived JNO₂ values, the precision generally depends on the quality of the measurements used in Equation (2) as well as p and T variations (used in determining reaction rates). Due to the low concentrations of HO₂, ClO, and BrO and slowly varying SZAs in these flights, JNO₂ in a majority of air parcels can be approximated as

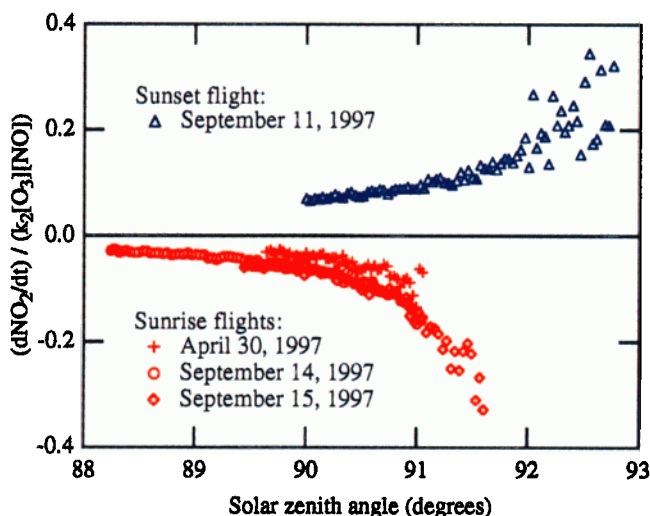


Figure 1. Ratio of $d[NO_2]/dt$ to $(k_2[O_3][NO])$ as a function of SZA for sunrise (red) and sunset (blue) flights. The analysis is limited at high SZA by the declining signal-to-noise of the NO data.

$$JNO_2 \approx k_2[O_3][NO] / [NO_2]. \quad (3)$$

Because p , T and O_3 for each flight were virtually constant and their measurement uncertainties are small, the precision of a photochemically derived JNO_2 value therefore depends primarily on the precision of NO/NO_2 . Furthermore, since the flight-to-flight variations in P and T were small (Table 1), uncertainty in k_2 does not affect the overall precision of photochemically derived JNO_2 . For SZAs $< 87^\circ$, the 1- σ precision of NO/NO_2 is estimated to be 10% and is dominated by the error in NO_2 . For $87^\circ < SZAs < 89^\circ$ the precision is about 7%, and increases linearly to 20% (NO dominant) at 93° SZA. The estimated 1- σ precision of NO/NO_2 is shown in Figure 3 as dashed lines. As can be seen,

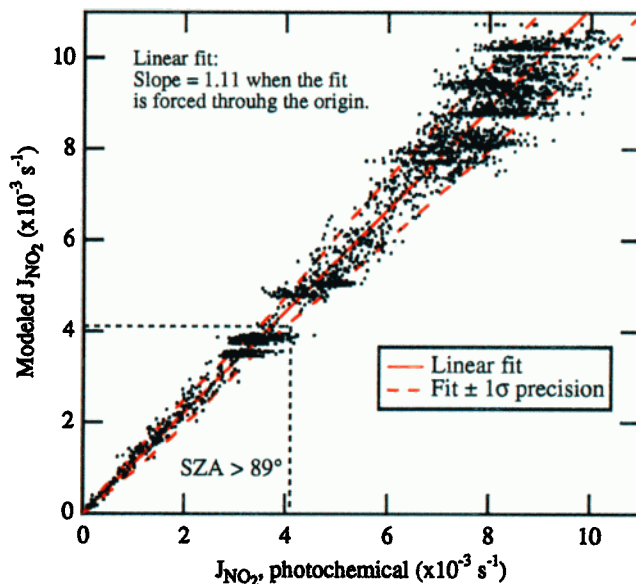


Figure 3. The extension of Figure 2A to higher JNO_2 values ($70^\circ < SZA < 89^\circ$). Data from all four flights are included. The steady-state approximation is used for deriving the points with $SZA < 89^\circ$. A linear fit gives a slope of 1.11 ($R = 0.98$) with a forced zero intercept.

they indeed envelop a majority of the photochemically derived JNO_2 values.

The model JNO_2 values are generally insensitive to albedo and cloud top height for $70^\circ < SZAs < 93^\circ$ [Swartz *et al.*, 1999]. For the conditions considered here, the changes in modeled JNO_2 values are less than 10% and 8% when albedo varies between 0 and 0.6 and terrain/cloud top height from ground to 6 km, respectively. More importantly, the standard deviations of the ratios of JNO_2 values calculated with albedo and/or terrain/cloud top height kept at zero to values reported here are less 5% over this

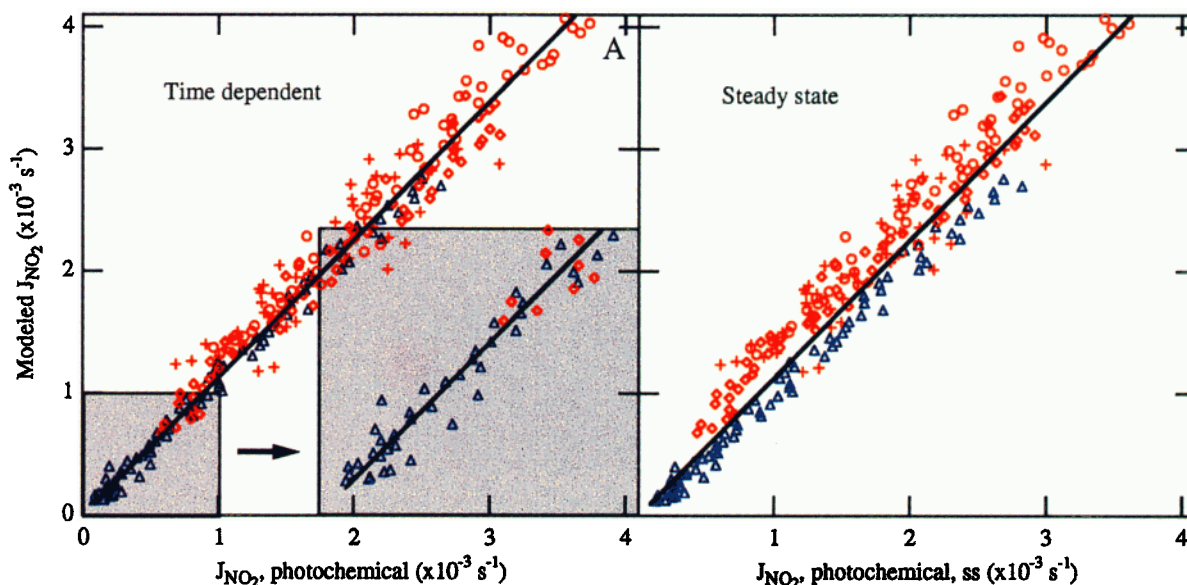


Figure 2. Radiative model JNO_2 values plotted versus photochemically derived JNO_2 values where (A) the latter are derived using the time-dependent method (Equation (2)) or (B) using the steady state assumption ($d[NO_2]/dt = 0$). The photochemical data set is the same as that shown in Figure 1. Data for the lowest range of JNO_2 are expanded in an inset for (A). Symbols and colors are used the same way as in Figure 1. A linear fit to the data in (A) has a slope of 1.13 with a forced zero intercept. The fit is also shown in (B) as a visual aid.

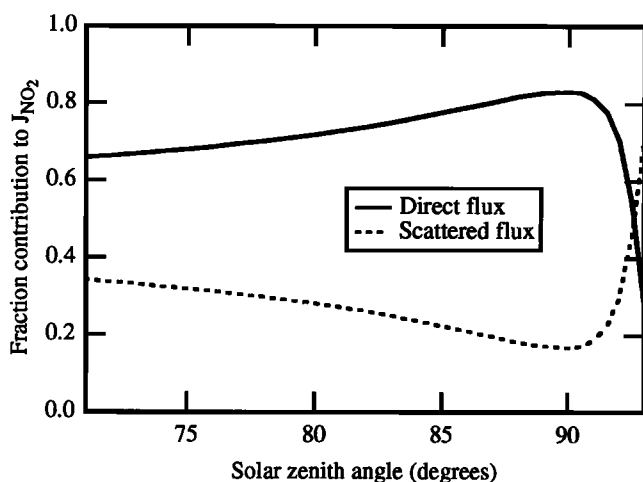


Figure 4. Modeled fractional contributions of direct and scattered flux to JNO₂ as a function of SZA at 20 km.

SZA range. Atmospheric refraction has a negligible effect on JNO₂ at SZAs < 90°. Because the wavelength (310 - 410 nm) dependence of JNO₂ is also fairly insensitive to SZA for the range considered here and because of constant P and T, the uncertainty in the NO₂ photodissociation cross section does not affect the precision of the model results.

The most significant factor affecting the accuracy of model JNO₂ in this SZA region is the amount of scattering of the solar irradiance as a function of SZA. Results of the scattering model shown in Figure 4 show that the contribution to JNO₂ of direct solar flux varies from about 65% at 70° to over 80% at 90° and then to less than 30% at 93°. The scattering contribution varies inversely with the direct component. Therefore, the linearity of the correlations in Figures 2 and 3 indicates that the model treatment of the direct and scattered contributions to the radiation field are accurate to approximately 7 - 20% on average over the SZA range of 70° to 93° SZA.

Conclusions

In situ measurements of chemical species and atmospheric parameters were used to derive values of JNO₂ in the lower stratosphere using a time-dependent, photochemical method. The method accounts for the departure of NO and NO₂ abundances from steady state values. JNO₂ values were calculated for the SZA range of 88° to 93° near sunrise and sunset and extended to 70° using the steady state approximation, thereby extending the range of previous studies. The precision of the photochemically derived JNO₂ values, shown to be 7 - 20%, is dependent only on the precision of the measured NO/NO₂ ratio.

Model JNO₂ values derived from calculations of direct and scattered solar flux show a linear relationship with photochemically derived values over the full SZA range. The slope of a linear fit is 1.11 (1.13 if only data at SZA > 89° are used). The

agreement of modeled and photochemically derived JNO₂ values is consistent with several previous studies. The good linear relationship at high SZA demonstrates that the modeling of scattered light in the 310 - 410 nm wavelength range near sunrise and sunset is accurate to within the precision of measurements used in the photochemical derivation.

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