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STRATOSPHERIC O₃ AND NO₂ OBSERVATIONS AT THE SOUTHERN POLAR CIRCLE
IN SUMMER AND FALL 1988

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Abstract. A visible spectrometer dedicated to ozone and NO₂ monitoring for the next few years has been installed at the French Antarctica base of Dumont d'Urville at 66°S, 140°E. The first three months of data in Austral summer and fall allow the observation of the NO₂ seasonal decay together with its diurnal variation. The data are found incompatible with the currently accepted NO_x photochemistry. A conversion of nitrogen compounds into another storage species is required. The reaction which probably involves N₂O₅ should be active at temperature as high as -45°C.

Introduction

Because of the large and fast variation of the lengths of day and night, NO₂ seasonal cycles at high latitude are extremely sensitive to nitrogen oxides partitioning. Observations are therefore of primary interest for testing photochemical models [Solomon and Garcia, 1983]. Although the spring ozone depletion problem has put pressure onto experimental groups to perform observations in polar regions, the data available for summer and fall is still incomplete. Satellite observations [Mount et al., 1984, Chu and McCormick, 1986] and ground-based measurements by Noxon et al [1983] and Shibasaki et al [1986] respectively at 71°N and 69°S have provided average seasonal cycles with a total NO₂ summer maximum of about $7 \cdot 10^{15}$ mol cm⁻² and a winter minimum at 1 to $2 \cdot 10^{15}$ mol cm⁻². This cycle is currently interpreted by conversion of NO₂ into N₂O₅ during the polar night. The only daily data available at higher latitude are those of Keys and Johnston [1986] at 78°S. They show a fast NO₂ column decay at the end of summer over a period of about 40 days. Except during the very first few days, the rate of diurnal variation was found to be constant and, therefore, the authors concluded a reasonable consistency with a simple NO₂ to N₂O₅ conversion scheme. In order to contribute to the understanding of the photochemistry of the polar regions, a new visible spectrometer has been installed at the French base of Dumont d'Urville (66°S, 140°E). The instrument is identical to the one installed in Northern Sweden and described in a companion paper [Pommereau and Goutail, 1988]. It allows zenith sky observations during sunrise and sunset, between 290 and 590 nm. Ozone is measured in the Chappuis bands between 450 and 560 nm, while NO₂ is determined in the 400-500 nm spectral region. The achieved precision is estimated to be ± 2 DU for the first species and $2 \cdot 10^{14}$ mol cm⁻² for the second, while an absolute uncertainty of the order of 15% exists at the moment for both, coming from the estimation of the optical path of the scattered light. Measurements began on January 16, 1988 and will be continued over the next years. Data are processed in real time at the station, and the results which will be discussed below were transmitted every week since the beginning.

Data

Ozone and NO₂ columns recorded between 16 January and 1 May 1988 are displayed on Figure 1 together with stratospheric weather information measured daily by radio-sondes at the station. Turn-around, that is stratospheric wind rotation from the East to the West, occurs at the beginning of the period, followed by the gradual build up of the polar vortex. Temperature decreases slowly at first and more rapidly after the equinox. Wind speed increases from 5 to 10 knots up to 70 knots in April.

Ozone, around 350 DU in average, varies little during the first month. Day to day fluctuations appear later, related to oscillations of wind direction and speed. The NO₂ content is observed to be steady during the first week, at a value of $7 \cdot 10^{15}$ mol cm⁻² in agreement with previous ground-based observations at the same latitude in summer [Shibasaki et al., 1986, Noxon et al., 1983]. After 22 January, the evening column appears to decrease at a constant rate of $4.5 \cdot 10^{13}$ mol cm⁻² day⁻¹ for two months. After early April, the decay rate decreases and NO₂ varies in phase with the stratospheric temperature. Figure 2 shows the correlation between the NO₂ column and the 50 hPa temperature. During the first two months, the column reduces by a factor of 2 when the temperature varies by only 5°C and therefore they are rather independent. After day 82, the correlation between the two quantities is similar to the one already observed in the Northern hemisphere in winter (Pommereau and Goutail, 1988). The relative difference between evening and morning which reveals the diurnal variation, is negligible at the beginning, maximum by the end of February, and reduces progressively afterwards (Figure 3). Its maximum amplitude of 30% is identical to the one observed in March at the Northern Polar Circle.

Discussion

These findings are in good agreement with the observations at 78°S by Keys and Johnston [1986], that is a linear evening decay at the same rate of $5 \cdot 10^{13}$ mol. cm⁻²/day and an identical maximum amplitude of the diurnal variation. This evolution was found by the authors in agreement with a slow conversion of NO₂ into N₂O₅ in polar regions in autumn. However, due to the different locations in latitude of the two sites, there are important discrepancies: summer and winter NO₂ columns are larger by a factor of two at the polar circle than at 78°S; the decay process duration lasts 80 days against 40 days at 78°S; the diurnal variation amplitude develops progressively during one month in our case instead of 2 to 3 days. This can be explained by the fast transition between polar day and night at extreme latitudes.

In order to interpret the data, simplified photochemical calculations have been conducted following the method described in Solomon and Garcia (1983). Chemical and photolysis rates are identical to the ones used in the companion paper. NO₂ is assumed to be distributed in a 8 km thick layer centered at 30 km. Figure 4(A) shows the N₂O₅ fraction which is photolysed each day during the period. Before day 100, the N₂O₅ formed at night will be totally removed the following day. Figure 4(B) shows the

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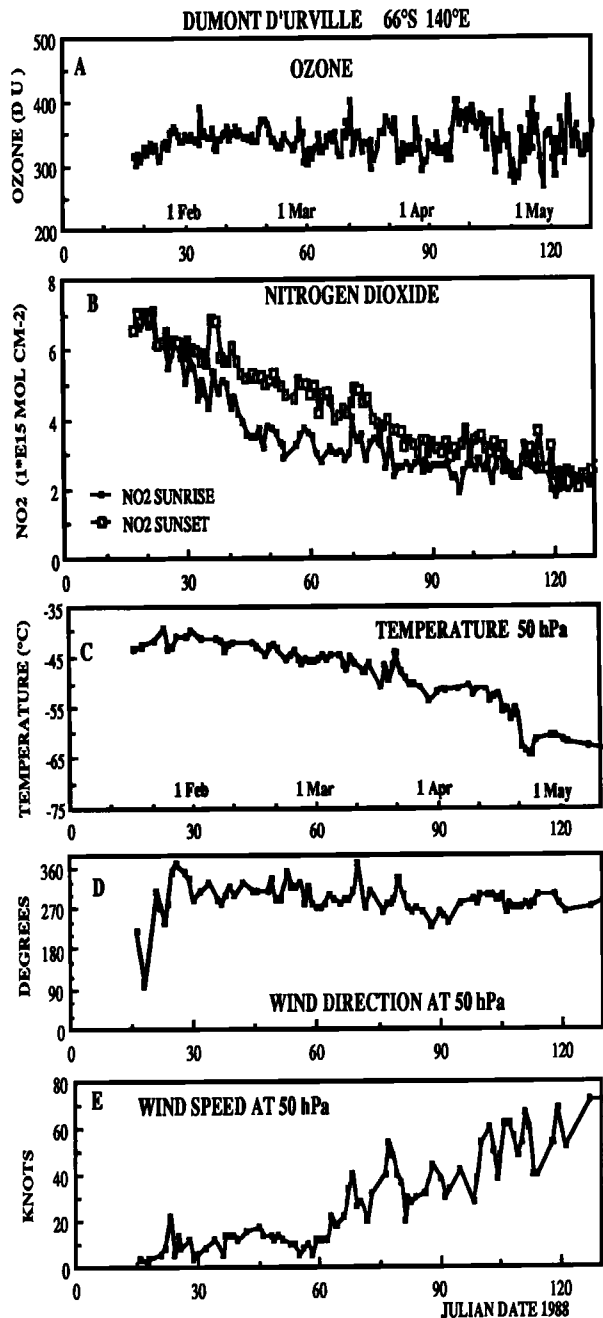
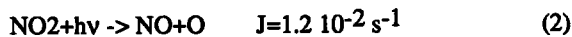
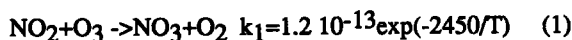


Fig. 1. Morning and evening ozone and Nitrogen Dioxide columns observed at Dumont d'Urville from 16 January until 9 May, 1988 and temperature, wind direction and speed at 50 hPa measured by daily radio-sondes at the same station.

observed NO₂ and calculated NO₂ decays at night controlled by reactions:



When using the current photochemical rates (Standard) the computed diurnal variation is by far larger than the observed one. When using an increased temperature dependence for reaction (1) (2600 instead of 2450), and a

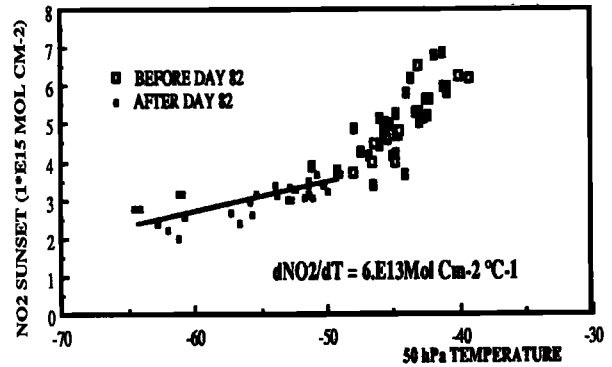


Fig. 2. Correlation between evening NO₂ column and 50 hPa temperature. During the first month of observations, NO₂ is reduced by a factor of 2 while the temperature varies by 5°C only. After mid-February the two quantities are related by a factor similar to the one observed in winter and spring in the northern hemisphere [Pommereau and Goutail, 1988].

reduced NO₂ photolysis rate at 90° SZA of $5 \cdot 10^{-3} \text{ s}^{-1}$, exactly as we did in the Northern Hemisphere, the data and the calculations are in better agreement (Adjusted). Some over-estimation appears at the end of the period which would be reduced if the 10 hPa temperatures colder than at 50 hPa in fall, have been taken. The maximum amplitude of the NO₂ diurnal variation at the end of February is the result of a balance between the increasing night duration and the decreasing temperature which reduces the NO₂ recombination rate. The diurnal variation amplitude is not limited by the N₂O₅ photolysis as shown on Figure 4(A). Therefore the currently accepted scheme of a slow conversion of NO_x species into N₂O₅, cannot be responsible for the NO₂ seasonal decay.

The fact that the decay appears both at 78°S and 66°S, when the sun zenith angle reaches 93° on the evening, shows that NO₂ reduction only happens by night. NO₃ and N₂O₅ are the only NO_x species present at night besides NO₂. Noxon et al [1980] proposed that an NO₃ "scavenger" present in the stratosphere converts active NO_x into some storage species. In that case the NO₂ decay should develop progressively from zero after January 22 in parallel to the night duration. This is not what is observed. The seasonal decay rate is constant from 22 January. In agreement with the analysis of direct NO₃ measurements in Antarctica by Sanders et al [1987], our data do not support the NO₃ "scavenger" hypothesis. The discontinuity of the NO₂ destruction rate is more consistent with a scheme involving N₂O₅. N₂O₅ needs NO₃ to be formed, which

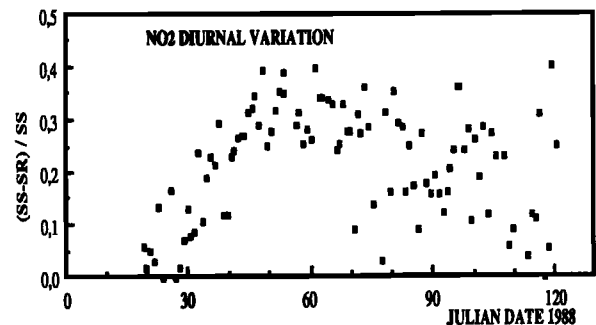


Fig. 3. NO₂ diurnal variation calculated as (sunset-sunrise) vs sunset.

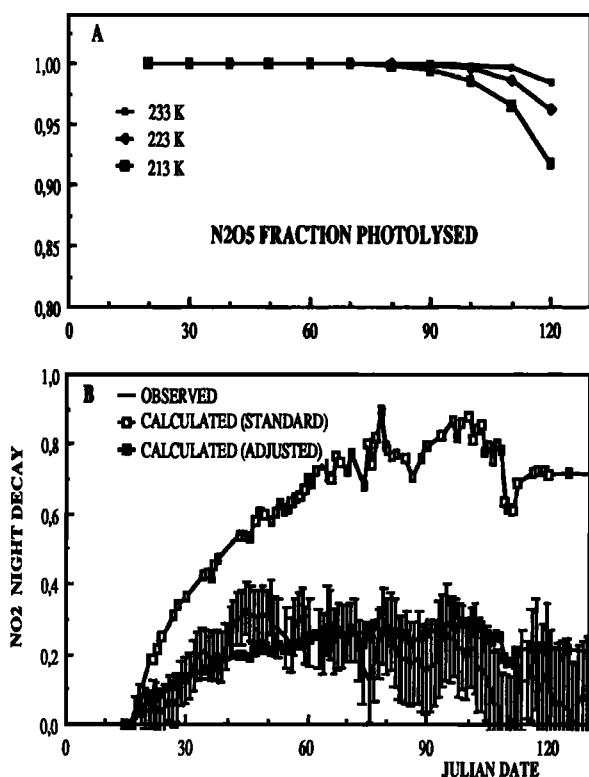


Fig. 4. (A) Fraction of N₂O₅ which is photolysed each day at 30km for three temperatures : 213, 223 and 233 K; (B) NO₂ nighttime recombination into N₂O₅: a) observed (error bars); b) calculated from standard photochemistry; c) calculated with adjusted coefficient (see text).

means a sun zenith larger than 93°, but after it is formed, it will be present until it photodissociates the following day. On Figure 5, the "N₂O₅ night" duration is defined as sun zenith angle larger than 93° on the evening and 80° on the morning. On January 22 its duration is already 5 hours. A NO_x conversion into a storage species by night involving N₂O₅ would be compatible with our observations. The

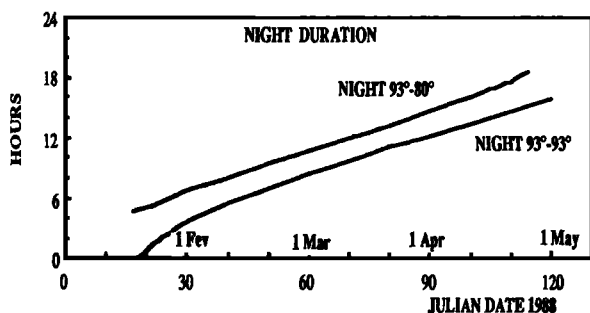


Fig. 5. Night durations at Dumont d'Urville in summer and fall. Night defined as sun zenith angle larger than 93° corresponds to period of possible transformation of NO₂ into NO₃. The 93°-80° night defines the period where N₂O₅ may be present : formation after 93° on the evening, photolysis after 80° on the morning.

possibility of converting N₂O₅ into HNO₃ has been already discussed, for example by Solomon and Garcia [1983] and Wofsy [1978]. Austin et al [1986] have shown that an HNO₃ source is required to interpret observations of this last species at high latitude but were unable to identify conclusively the responsible reaction. We can add that N₂O₅ appears to be involved, that the reaction should be active at temperature as high as -45°C, and that the storage species should have no diurnal variation.

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