

Nitrogen Dioxide—Optical Absorption in the Visible

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Nitrogen dioxide (NO₂) has absorption features in the ultraviolet, blue, and green regions of the optical spectrum. Values of total columnar NO₂ range from 0.4×10^{-3} to about 5×10^{-3} cm NO₂ (STP) and yield optical depths from 0.008 to 0.087 at 390 nm, the wavelength of maximum absorption. The presence of NO₂ absorption must be considered in precision multiwavelength atmospheric turbidity studies. Previous reported values of the Angstrom power law coefficient are probably too large because NO₂ absorption was not accounted for.

INTRODUCTION

Nitrogen dioxide (NO₂) absorbs light in the ultraviolet, blue, and green regions of the optical spectrum [Hall and Blacet, 1952]. Because NO₂ is always present in the atmosphere, its effect should be considered in studies of atmospheric extinction, especially when measurements are made in the wavelength region $300 < \lambda < 550$ nm. The inclusion of NO₂ extinction is particularly important in attempting to derive the wavelength dependence of extinction caused by the presence of atmospheric aerosols [Shaw *et al.*, 1973]. In past studies involving atmospheric turbidity the inclusion of NO₂ absorption effects has generally been neglected, and this likely has introduced errors into previously reported values of aerosol extinction.

In this paper, values of optical depth arising from NO₂ for typical conditions are reported. These values should be useful to investigators who are making precision measurements of aerosol extinction. In addition to pointing out the existence of NO₂ absorption, an important effect associated with the diurnal variation of NO₂ concentration on the Langley plot method of determining atmospheric optical depths is discussed. It is shown that the presence of varying NO₂ can yield incorrect values of extrapolated extraterrestrial solar spectral irradiance and incorrect values of total atmospheric extinction.

CHARACTERISTICS OF ATMOSPHERIC NO₂

Physical Characteristics

A review of atmospheric NO₂ has been provided by Ackerman [1975]. What follows is more or less a simplified phenomenological description of atmospheric NO₂.

Brewer *et al.* [1973] and Noxon [1975] report that NO₂ occurs in two layers, in the troposphere, probably mostly within the planetary boundary layer, and in the stratosphere.

The NO₂ columnar amount in the tropospheric layer is caused mainly by a combination of biological activity in soils and man-related surface emissions. The columnar amount is highly variable, variations of a factor of about 100 being reported. In urban areas, especially in urban areas with photochemical smog, it is to be expected that the average amount and variability of NO₂ will be relatively larger than in nonurban areas. The temporal variability of NO₂ in the tropospheric layer usually maximizes near noon [Brewer *et al.*, 1973], but there are also times when the opposite occurs. The constantly fluctuating nature of the planetary boundary layer results in a situation which makes the prediction of lower-layer NO₂ overburden difficult. However, Brewer *et al.* [1973] report that the

tropospheric overburden of NO₂ in unpolluted Canadian air is generally of the order of 1×10^{-3} atm cm (STP) at night (1×10^{-3} atm cm (STP) = 8.5×10^{15} molecules cm⁻²). It tends to be larger at dawn than at sunset and is greatly reduced near noon. Tropospheric NO₂ amounts in a polluted atmosphere approach several milliatmospheric centimeters (STP) (S. Kotate, personal communication, 1975).

The stratospheric NO₂ layer is the result of complex reactions involving NO, odd oxygen, sunlight, and other minor constituents. There are probably also significant dynamic terms that affect the amount of NO₂ overburden. Preliminary data indicate a strong increase in NO₂ mixing ratio with height in the stratosphere up to about 40 km, implying that there may be heavy diffusion of NO₂ from the upper stratosphere into the troposphere.

Because of the complexity of the NO₂ chemistry and its dependence on photochemical reactions it is no surprise to learn that there is experimental evidence indicating that the NO₂ columnar amount undergoes a diurnal variation. Unfortunately, the 'shape' of the NO₂ diurnal variation in the stratosphere is still somewhat open to question. Brewer *et al.* [1973] report a maximum amount of stratospheric NO₂ near solar noon. If this is true, it may be caused by photolysis of NO₃ (which can be produced by NO₂ + O₃ → NO₃ + O₂ at night) to yield NO₂ + O. Noxon [1975], on the other hand, reports that stratospheric NO₂ undergoes a minimum in daytime, probably caused by photolysis of NO₂ to yield NO + O. Brewer *et al.* [1973] report that there is about 0.5×10^{-3} atm cm (STP) of NO₂ overhead in the stratosphere at sunrise. Noxon [1975] lists values of NO₂ ranging from 0.4 to 2×10^{-3} atm cm (STP).

When the reported values of NO₂ measurements are all taken together, it seems that in general one can expect to find a total overburden of NO₂ ranging from about 0.4 to 5×10^{-3} atm cm (STP), the largest values being found in or near urban locations and the smaller values over the polar regions and oceans.

Optical Characteristics of NO₂ Absorption

The absorption coefficient for NO₂ [Hall and Blacet, 1952] consists of a semicontinuum with superimposed structure modulating about the continuum. The smoothed absorption curve peaks at $\lambda = 390$ nm with maximum absorption coefficient there of roughly $a = 17.5$ cm⁻¹ (base *e*, referred to $p = 760$ mm Hg). The wavelengths where $a = a_{\max}/2$ occur at about 325 and 480 nm. The structure in the NO₂ absorption curve can be characterized roughly as sinusoidal with average spacing between peaks and valleys of 5 nm and average modulation amplitude of $\delta a = \pm 3$ cm⁻¹.

It has been reported [Hall and Blacet, 1952; Brewer *et al.*,

1973] that NO₂ obeys Beer's law of absorption and that pressure dependence on the absorption coefficient can for all practical purposes be ignored. It is thus permissible to describe the extinction effect of NO₂ in terms of an optical depth, $\tau = al$ (where a is the absolute extinction coefficient in units per centimeter and l is the overburden expressed in atmospheric centimeters (STP)). Using the overburdens and the extinction coefficients listed above, one deduces that at $\lambda = 390$ nm the optical depth arising from NO₂ absorption would be expected to lie in the range $0.008 < \tau \text{ NO}_2 < 0.087$.

EFFECTS OF NO₂ ON ATMOSPHERIC TURBIDITY STUDIES

If NO₂ absorption is neglected in multiwavelength atmospheric turbidity studies, the value of the aerosol extinction in the blue and green may be overestimated, in some cases severely overestimated. This in turn will lead to an erroneous estimation of the Angstrom wavelength coefficient α (where it is assumed that $\tau_{\lambda}(\lambda) = C\lambda^{-\alpha}$). Since NO₂ absorption has not been considered in previous work, it is quite probable that the reported values of α may be too large. Neglect of NO₂ also has the effect of changing the form of the size distribution of atmospheric aerosols if the size distribution is determined by inverting the wavelength dependence of the measured aerosol extinction coefficient. If atmospheric turbidity measurements are to be corrected for NO₂ absorption, one must derive an independent measure of total NO₂; this can be done by using the methods developed by Noxon [1975] or Brewer *et al.*, [1973], which involve measuring differential absorption by NO₂ at two or more wavelengths located in adjacent peaks and valleys of the NO₂ absorption curve structure.

To give an indication of the effect of neglecting NO₂ absorption, I have analyzed multiple wavelength aerosol extinction data (made with a filter wheel sun photometer) for a clear day in Fairbanks with and without corrections for NO₂ absorption. The columnar amount of NO₂ was estimated to be 0.5×10^{-3} atm cm (STP) from analysis of a spectrum of the sun acquired with a 0.5-m Ebert spectrometer. A least squares fit to a power law form of aerosol extinction spectrum $\tau_A = C\lambda^{-\alpha}$ gave values of α equal to $\alpha_1 = 1.6$ for the case where NO₂ absorption was neglected and $\alpha_2 = 0.4$ for the case where NO₂ absorption was accounted for. This clearly shows that neglecting NO₂ absorption can introduce serious errors in the determination of the aerosol extinction spectrum.

ERRORS IN LANGLEY PLOT CAUSED BY NO₂

The Langley method involves taking a series of monochromatic measurements of solar intensity I_j , made at varying air masses m_j , $j = 1, 2, \dots, m_{\text{obs}}$, and fitting them to Beer's law [$\ln(I_j/I_0) = m_j\tau$] to derive I_0 and τ [Shaw *et al.*, 1973]. Obviously, it is improper to apply the method if τ is temporarily varying, that is, if $\tau = \tau(m)$. As has been mentioned, one expects to find a diurnal variation in NO₂ amount, so $\tau \text{ NO}_2 = \tau \text{ NO}_2(t)$. Nevertheless, the method has been commonly used in the past, assuming $\tau = \text{const}$, especially to derive τ but sometimes also to derive the extraterrestrial solar irradiance I_0 [e.g.,

Thekaekara, 1974]. An obvious test for temporally varying τ would at first sight be to test the quality of regression fit of the data to Beer's law, a large variance indicating a nonconstant τ . However, as has been pointed out [Russell and Shaw, 1975], low variance in the Langley fit does not at all insure that τ is not temporally varying, since there are analytical forms of $\tau(t)$ which yield linearity between $\ln I$ and m . For example, if the time variation of τ can be approximated as a parabolic variation centered on solar noon, then an almost linear Langley plot (a plot of $\ln v$ versus m) will result (for details, see Russell and Shaw [1975]). In the case of NO₂ absorption, since there is a dependence on photochemistry, one might expect to find something approximating a parabolic variation in $\tau(t)$ about solar noon, and this could indeed yield an almost linear Langley plot from which one would derive an incorrect value of τ_{total} and an incorrect value of zero air mass intercept I_0 . The neglect of NO₂ absorption may be part of the reason for the large variations in reported values of solar spectral irradiance in the near-ultraviolet to green region of the optical spectrum.

CONCLUSION

NO₂ absorption, if it is not independently measured and accounted for, can sometimes introduce significant errors into the determination of optical aerosol extinction and into the values of solar spectral irradiance obtained from Langley plot intercepts. If accurate work is to be done in assessing aerosol extinction or in deriving the solar spectral irradiance from ground level stations, one must correct for NO₂ absorption.

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