A Parameterization of Solar Absorption by Nitrogen Dioxide[1]

Frederick M. Luther

Lawrence Livermore Laboratory, University of California, Livermore 94550

(Manuscript received 12 June 1975, in revised form 11 February 1976)

ABSTRACT

An analytic expression for the specific heating rate due to solar absorption by nitrogen dioxide is derived by approximating the solar insolation and absorption cross section by simple functions of wavelength. The analytic expression agrees with a detailed calculation to within $\pm 2\times 10^{-22}$ W throughout the range of NO_2 column densities investigated (up to 10^{20} cm^{-2}). The error is within $\pm 0.3\%$ for NO_2 column densities less than 2×10^{17} cm^{-2}. The error is generally within $\pm 5\%$ for the larger column densities which rarely, if ever, occur in the atmosphere.

1. Introduction

The importance of solar absorption by nitrogen dioxide has been discussed by Hesstvedt and Isaksen (1974) for the lower atmosphere and by Luther (1976) for the stratosphere. As indicated in the latter study, the increase in solar absorption by NO_2 may be comparable in magnitude to the decrease in solar absorption due to reduced ozone for stratospheric perturbations involving the injection of NO_x. In addition to affecting stratospheric heating, changes in stratospheric NO_2 concentrations also affect surface temperature through the solar and longwave radiation balance (Callis *et al.*, 1975). In order to include solar absorption by NO_2 in atmospheric models used for climatic assessment, a method of parameterization is required which consumes little computation time.

Most of the absorption by NO_2 occurs in the wavelength interval 300–710 nm. In this spectral interval, solar absorption by other gaseous species in the atmosphere is weak; thus solar absorption by NO_2 can be treated independently without introducing significant errors [For a zenith angle of 60° NO_2 absorbs approximately 0.2% (Luther, 1976) and O_3 approximately 3% of the incoming solar flux in this wavelength interval.] Rayleigh scattering can be neglected since virtually all of the absorption by NO_2 occurs above 20 km altitude where there is little molecular scattering.

2. The model

The solution of the one-dimensional, purely absorbing, source-free radiative transfer equation at a particular altitude z, solar zenith angle θ, and atmospheric distribution of NO_2 $\{N_{NO_2}(z)\}$, is given by

$$F_\lambda(z,\theta,\{N_{NO_2}\}) = F_\lambda(\infty)\exp[-\tau_\lambda(z,\{N_{NO_2}\})\sec\theta], \quad (1)$$

where $F_\lambda d\lambda$ is the flux in the direction θ in the wavelength interval $d\lambda$ about λ, $F_\lambda(\infty)d\lambda$ represents the incident solar flux outside the atmosphere, and the optical depth τ_λ is defined by

$$\tau_\lambda(z,\{N_{NO_2}\}) \equiv \int_z^\infty N_{NO_2}(z')\sigma(\lambda)dz', \quad (2)$$

where $\sigma(\lambda)$ is the absorption cross section (cm^2) of an NO_2 molecule and N_{NO_2} is the number density (cm^{-3}) of NO_2 molecules. The rate of absorption $Q(z,\theta)$ of solar radiation by NO_2 per unit volume, i.e., per unit area in a layer 1 cm deep, is obtained by integrating over wavelength and is given by

$$Q(z,\theta) = \int_\lambda \sigma(\lambda)F_\lambda(z,\theta)N_{NO_2}(z)d\lambda. \quad (3)$$

For convenience and for simplification of the discussion, we introduce two additional quantities: the specific heating rate q and the integrated column density of NO_2, U_{NO_2}, which are defined by

$$q \equiv Q/N_{NO_2} \quad (4)$$

$$U_{NO_2}(z) \equiv \int_z^\infty N_{NO_2}(z')dz'. \quad (5)$$

By introducing these quantities, solar heating by NO_2 can be expressed in terms of a single independent quantity (the product $U_{NO_2}\cdot\sec\theta$). The optical depth is related to integrated column density by

$$\tau_\lambda = \sigma(\lambda)U_{NO_2}(z). \quad (6)$$

[1] This work was performed under the auspices of the U. S. Energy Research and Development Administration under Contract W-7405-Eng-48 and supported in part by the Climatic Impact Assessment Program, Office of the Secretary, U. S. Department of Transportation.

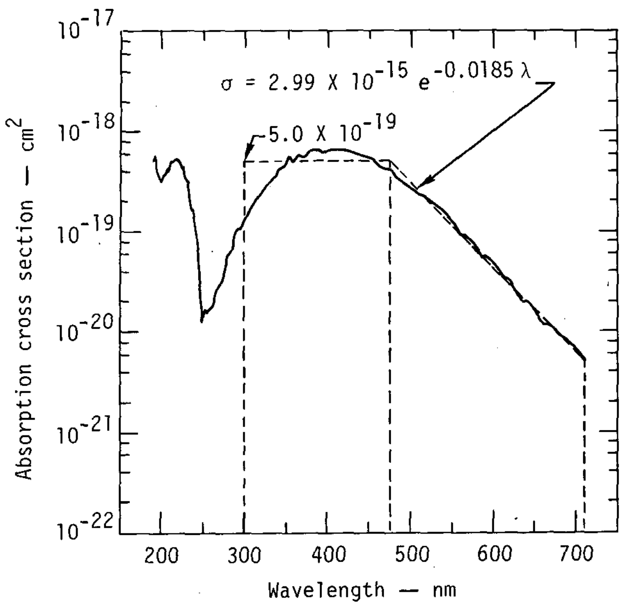

FIG. 1. The absorption cross section of NO_2 as a function of wavelength and approximations (dashed curves) to the absorption cross section used in the modeling procedure.

3. Results

The spectral variation of the absorption cross section for NO_2 is shown in Fig. 1. Data are taken from Hall and Blacet (1952) for 190–400 nm and from Leighton (1961), who cites Dixon (1940), for 400–710 nm. Values of $F_\lambda(\infty)$ from Ackerman (1971) are shown in Fig. 2.

The absorbed flux was computed as a function of $U_{NO_2}\cdot\sec\theta$ using a detailed calculation in which the wavelength interval 190–710 nm was divided into 116 subintervals. The results, which neglect molecular scattering effects, are shown in Fig. 3. For comparison,

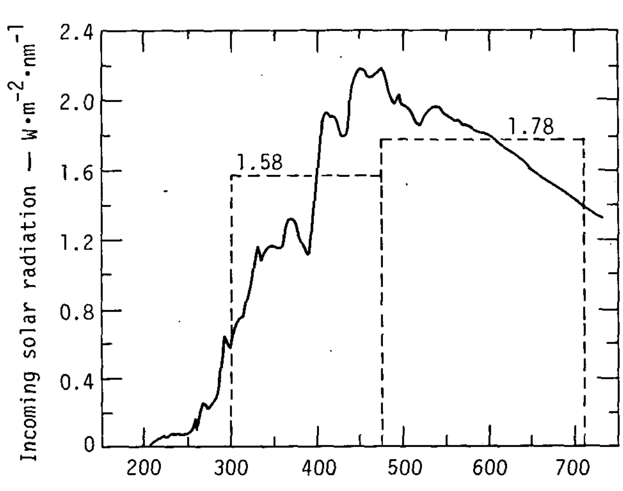

FIG. 2. The spectral distribution of incoming solar radiation (from Ackerman, 1971) and the average values (dashed curves) used in the modeling procedure.

the incident solar flux in this wavelength interval is 699 W m^{-2}. Although the range of values used for $U_{NO_2}\cdot\sec\theta$ is much greater than the vertical column density of NO_2 in the atmosphere ($\sim 10^{16}$ cm^{-2}), this range is useful for large values of θ and for determining the values of the constants used in the parameterization. The column density can be converted to atm-cm by multiplying by 3.719×10^{-20}.

The specific heating rate q is shown as a function of $U_{NO_2}\cdot\sec\theta$ in Fig. 4. The specific heating rate represents the slope of the absorbed flux plotted against $U_{NO_2}\cdot\sec\theta$ as would be apparent if a linear scale had been used for the abscissa in Fig. 3. Since q is nearly constant for values of $U_{NO_2}\cdot\sec\theta<10^{17}$ cm^{-2}, the absorbed flux may be approximated in this region by a linear function of $U_{NO_2}\cdot\sec\theta$. For many applications, this simple method of parameterization is quite accurate, but for perturbation studies in which the value of $U_{NO_2}\cdot\sec\theta$ exceeds 10^{17} cm^{-2}, another method is needed. Following a methodology similar to that of Lindzen and Will (1973), an analytic expression for q is developed which describes the heating rate for a broad range of values of $U_{NO_2}\cdot\sec\theta$.

The expression for q is obtained by approximating σ and $F_\lambda(\infty)$ by expressions which are easily integrated when substituted into Eq. (3). The absorption cross section for NO_2 is approximated as follows:

$$\sigma=\begin{cases}\sigma_1=5.0\times10^{-19}\,[\mathrm{cm}^2] & \text{for } 300\text{–}475\text{ nm}\\ \sigma_2 e^{-a\lambda}=2.99\times10^{-15}e^{-0.0185\lambda}\,[\mathrm{cm}^2] & \text{for } 475\text{–}710\text{ nm}\end{cases}\tag{7}$$

in which λ is expressed in nm (see Fig. 1). For each of these spectral intervals, average values of $F_\lambda(\infty)$ are assumed as follows (see Fig. 2):

$$\bar{F}_\lambda(\infty)=\begin{cases}F_1(\infty)=1.58[\mathrm{W\ m^{-2}\ nm^{-1}}] & \text{for } 300\text{–}475 \text{ nm}\\ F_2(\infty)=1.78[\mathrm{W\ m^{-2}\ nm^{-1}}] & \text{for } 475\text{–}710 \text{ nm}\end{cases}\tag{8}$$

Values for $F_1(\infty)$ and $F_2(\infty)$ were determined by a weighted least-squares fit of the data shown in Fig. 4. Substituting (7) and (8) into (3) and integrating, we obtain the following expression for q:

$$q(U_{NO_2}\cdot\sec\theta)=175F_1(\infty)\sigma_1\exp(-\sigma_1 U_{NO_2}\cdot\sec\theta)+\frac{F_2(\infty)}{aU_{NO_2}\cdot\sec\theta}\{\exp[-\sigma_2 U_{NO_2}\cdot\sec\theta\exp(-710a)]-\exp[-\sigma_2 U_{NO_2}\cdot\sec\theta\exp(-475a)]\}.\tag{9}$$

Values of q determined by Eq. (9) (dashed curve) and by the detailed calculation (solid curve) are shown in Fig. 4 and in Table 1. The analytic expression agrees with the data to within $\pm2\times10^{-22}$ W throughout the range of the table. The error is within $\pm0.3\%$ for values of $U_{NO_2}\cdot\sec\theta<2\times10^{17}$ cm^{-2}. The error is generally within $\pm5\%$ for the larger values which rarely, if ever, occur.

This parameterization applies to absorption of the

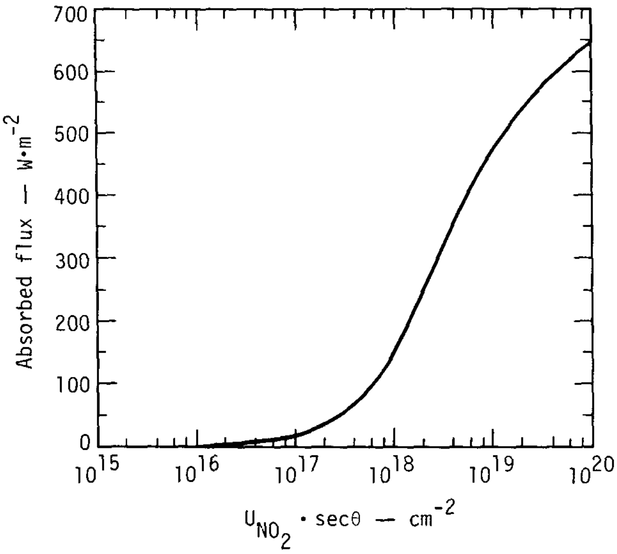

FIG. 3. Absorbed flux as a function of $U_{NO_2}\cdot\sec\theta$.

direct solar beam. Absorption of the upward scattered flux may be approximated by multiplying Eq. (9) by the albedo of the underlying atmosphere (including the earth's surface and clouds) and by substituting an appropriate expression for $U_{NO_2}\cdot\sec\theta$. Letting $U_{NO_2}(0)$ represent the column of NO_2 down to the level at which scattering occurs, then the optical path length of the upward scattered flux may be expressed as $U_{NO_2}(0)\cdot\sec\theta+[U_{NO_2}(0)-U_{NO_2}(z)]\,\overline{\sec\theta}$, where $\overline{\sec\theta}$ is the average value of $\sec\theta$ for the upward scattered flux (often assumed to be 1.66).

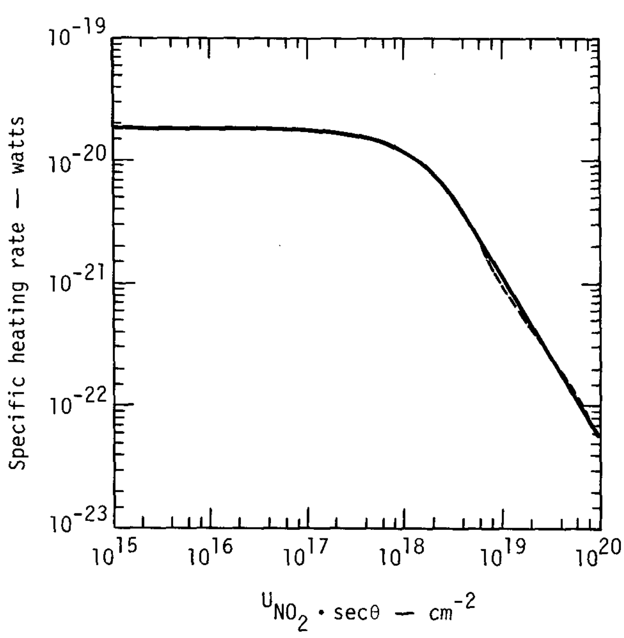

FIG. 4. Specific heating rate as a function of $U_{NO_2}\cdot\sec\theta$ as determined by the detailed calculation (solid curve) and Eq. (9) (dashed curve).

TABLE 1. Absorbed flux and specific heating rates as determined by the detailed calculation and the analytic expression.

$U_{NO_2}\cdot\sec\theta$ (cm^{-2})	Absorbed flux (W m^{-2})	q Detailed calculation (W)	q From Eq. (9) (W)
5.00E+13	9.081E−03	1.816E−20	1.812E−20
1.00E+14	1.816E−02	1.816E−20	1.812E−20
5.00E+14	9.080E−02	1.816E−20	1.811E−20
1.00E+15	1.816E−01	1.815E−20	1.811E−20
2.00E+15	3.631E−01	1.815E−20	1.810E−20
4.00E+15	7.258E−01	1.813E−20	1.808E−20
6.00E+15	1.088E+00	1.811E−20	1.807E−20
8.00E+15	1.450E+00	1.809E−20	1.805E−20
1.00E+16	1.812E+00	1.808E−20	1.804E−20
2.00E+16	3.616E+00	1.799E−20	1.796E−20
4.00E+16	7.198E+00	1.783E−20	1.780E−20
6.00E+16	1.075E+01	1.767E−20	1.765E−20
8.00E+16	1.427E+01	1.750E−20	1.750E−20
1.00E+17	1.775E+01	1.734E−20	1.735E−20
2.00E+17	3.470E+01	1.657E−20	1.661E−20
4.00E+17	6.638E+01	1.513E−20	1.524E−20
6.00E+17	9.533E+01	1.384E−20	1.399E−20
8.00E+17	1.218E+02	1.268E−20	1.286E−20
1.00E+18	1.461E+02	1.163E−20	1.183E−20
2.00E+18	2.413E+02	7.733E−21	7.890E−21
4.00E+18	3.513E+02	3.857E−21	3.824E−21
6.00E+18	4.102E+02	2.250E−21	2.128E−21
8.00E+18	4.468E+02	1.495E−21	1.367E−21
1.00E+19	4.723E+02	1.091E−21	9.893E−22
2.00E+19	5.396E+02	4.362E−22	4.284E−22
4.00E+19	5.948E+02	1.811E−22	1.906E−22
6.00E+19	6.224E+02	1.061E−22	1.132E−22
8.00E+19	6.398E+02	7.120E−23	7.562E−23
1.00E+20	6.519E+02	5.135E−23	5.389E−23

These results demonstrate that solar absorption by NO_2 can be parameterized with reasonable accuracy in spite of rather crude approximations of the solar insolation and absorption cross section.

REFERENCES

Ackerman, M., 1971: Ultraviolet solar radiation related to mesospheric processes. *Mesospheric Models and Related Experiments*, G. Fiocco, Ed., Reidel, 149–159.

Callis, L. B., V. Ramanathan, R. E. Boughner and B. R. Barkstrom, 1975: The stratosphere: Scattering effects, a coupled 1-D model, and thermal-balance effects. Presented at the Fourth International Conference on the Climatic Impact Assessment Program, Cambridge, Mass., 4–7 February (Proceedings in preparation).

Dixon, J. K., 1940: The absorption coefficient of nitrogen dioxide in the visible spectrum. *J. Chem. Phys.*, **8**, 157–160.

Hall, T. C., Jr., and F. E. Blacet, 1952: Separation of the absorption spectra of NO_2 and N_2O_4 in the range of 2400–5000 Å. *J. Chem. Phys.*, **20**, 1745–1749.

Hesstvedt, E., and I. S. A. Isaksen, 1974: On NO_2 absorption of solar radiation and its rôle in the heat budget of the lower atmosphere. Institute Report Series No. 6, Institutt for Geofysikk, Universitet i Oslo.

Leighton, P. A., 1961: *Photochemistry of Air Pollution*. Academic Press, 300 pp.

Lindzen, R. S., and D. I. Will, 1973: An analytic formula for heating due to ozone absorption. *J. Atmos. Sci.*, **30**, 513–515.

Luther, F. M., 1976: Solar absorption in a stratosphere perturbed by NO_x injection. *Science* (in press).