

## The Equivalent Mean Absorption Cross Sections for the O<sub>2</sub> Schumann-Runge Bands: Application to the H<sub>2</sub>O and NO Photodissociation Rates<sup>1</sup>

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(Manuscript received 21 March 1974, in revised form 1 June 1974)

### ABSTRACT

Absorption of solar radiation by O<sub>2</sub> in the Schumann-Runge band region is important not only for the production of O(<sup>3</sup>P) in the atmosphere, but also for H<sub>2</sub>O and NO photodissociations which depend upon the rotational structure of the O<sub>2</sub> absorption lines. The equivalent mean absorption cross sections for the O<sub>2</sub> Schumann-Runge bands and NO band intensities are computed and presented in a form to be applicable in calculations of the O<sub>2</sub>, H<sub>2</sub>O and NO photodissociation rates under varied atmospheric conditions.

### 1. Introduction

Photodissociation of O<sub>2</sub> is the main source of odd oxygen particles in the earth's atmosphere, and the O<sub>2</sub> Schumann-Runge bands (1750–2000 Å) give the largest contribution to the O<sub>2</sub> photodissociation in the region between about 60 and 100 km. H<sub>2</sub>O and NO photodissociation in the mesosphere and stratosphere depend largely upon the rotational line structure of the absorption cross section for the O<sub>2</sub> Schumann-Runge bands ( $\sigma_{S-R}$ ) (see Brinkmann, 1969; Nicolet, 1970; Park, 1972; Cieslik and Nicolet, 1973).

However,  $\sigma_{S-R}$  for the entire bands is not known well from experiments (e.g., Watanabe, 1958; Farmer *et al.*, 1968; Ackerman *et al.*, 1970). Ackerman *et al.* computed a theoretical profile of  $\sigma_{S-R}$  assuming a Lorentzian line shape, the line-integrated intensities, the half-width, and the rotational line positions.

Adopting this profile of  $\sigma_{S-R}$ , Kockarts (1970) studied the photodissociation rates of O<sub>2</sub> and H<sub>2</sub>O in the atmosphere, and suggested that these rates have to be computed by using  $\sigma_{S-R}$  for each atmospheric condition (e.g., zenith angle, temperature, O<sub>2</sub> density, etc.) because no set of mean cross sections can be derived for a general use.

Later, Cieslik and Nicolet (1973) computed a theoretical profile of the NO absorption cross sections ( $\sigma_{NO}$ ) assuming a Doppler line shape in the Schumann-Runge band region. By adopting these profiles of  $\sigma_{NO}$  and  $\sigma_{S-R}$  (see also Kockarts, 1972), Cieslik and Nicolet studied the NO photodissociation rate, and indicated that this rate should also be computed for a given dis-

tribution of atmospheric temperature and O<sub>2</sub> density and zenith angle.

Therefore, the results of Kockarts (1970) and Cieslik and Nicolet (1973) are restricted to a particular atmospheric condition. This study will extend these results to a variety of atmospheric models, and make it possible to obtain the O<sub>2</sub>, H<sub>2</sub>O and NO photodissociation rates in the O<sub>2</sub> Schumann-Runge band region for a number of distributions of atmospheric temperature, O<sub>2</sub> density, and zenith angle.

### 2. Results and discussion

#### a. O<sub>2</sub> and H<sub>2</sub>O photodissociation rates

The photodissociation rates for O<sub>2</sub> and H<sub>2</sub>O for a band interval are defined as

$$J_{S-R}(O_2) = \bar{I}_{B\infty} \exp[-\bar{\sigma}_{O_3} N(O_3)] \times \int_{\text{band}} \sigma_{S-R}(\nu) \exp[-\sigma_{S-R}(\nu) N(O_2)] d\nu, \quad (1)$$

$$J_{S-R}(H_2O) = \bar{I}_{B\infty} \exp[-\bar{\sigma}_{O_3} N(O_3)] \bar{\sigma}_{H_2O} \times \int_{\text{band}} \exp[-\sigma_{S-R}(\nu) N(O_2)] d\nu, \quad (2)$$

where  $\bar{I}_{B\infty}$  is the solar intensity per unit wavenumber at the top of the atmosphere assumed constant over a band interval (Table 1),  $N(O_2)$  and  $N(O_3)$  the O<sub>2</sub> and O<sub>3</sub> column densities respectively,  $\bar{\sigma}_{O_3}$  and  $\bar{\sigma}_{H_2O}$  the O<sub>3</sub> and H<sub>2</sub>O mean absorption cross sections, respectively, and  $\nu$  the wavenumber. The Schumann-Runge cross section  $\sigma_{S-R}$  is computed according to Ackerman *et al.* (1970) for a temperature of 250K. Values of the absorption cross sections for the Herzberg continuum

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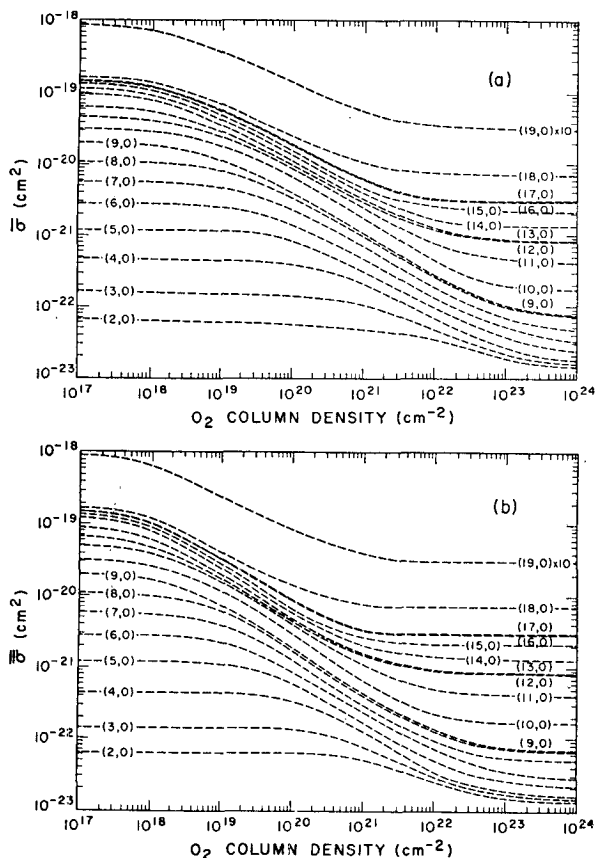


FIG. 1. The equivalent (a) exponential mean  $\bar{\sigma}$  ( $\text{cm}^2$ ) and (b) pre-exponential mean  $\bar{\sigma}$  ( $\text{cm}^2$ ) absorption cross sections for the  $\text{O}_2$  Schumann-Runge bands as a function of  $\text{O}_2$  column density. Numbers on each curve are the  $\text{O}_2$  band (see Table 1). The values of  $\bar{\sigma}$  and  $\bar{\sigma}$  for the (19,0) band are multiplied by 10.

(Ditchburn and Young, 1962) have been included in the computation.

The integrals in Eqs. (1) and (2), i.e.,

$$S(\text{O}_2) = \int_{\text{band}} \sigma_{\text{S-R}}(\nu) \exp[-\sigma_{\text{S-R}}(\nu)N(\text{O}_2)] d\nu, \quad (3)$$

$$S(\text{H}_2\text{O}) = \int_{\text{band}} \exp[-\sigma_{\text{S-R}}(\nu)N(\text{O}_2)] d\nu, \quad (4)$$

are computed over a band interval (from a band head to the next band head).

For convenience in applying the computed  $\sigma_{\text{S-R}}$  to atmospheric photochemistry, the equivalent mean absorption cross sections over each band are defined as functions of the  $\text{O}_2$  column density in the following manner. The integrals  $S(\text{O}_2)$  and  $S(\text{H}_2\text{O})$  defined in Eqs. (3) and (4) are rewritten as

$$S(\text{O}_2) \equiv \bar{\sigma}(N) \exp[-\bar{\sigma}(N)N(\text{O}_2)] \int_{\text{band}} d\nu, \quad (5)$$

$$S(\text{H}_2\text{O}) \equiv \exp[-\bar{\sigma}(N)N(\text{O}_2)] \int_{\text{band}} d\nu, \quad (6)$$

where the exponential mean  $\bar{\sigma}(N)$  and the pre-exponential mean  $\bar{\sigma}(N)$  are defined to be constant over each band interval, and are functions of the  $\text{O}_2$  column density.

By knowing the values of  $S(\text{O}_2)$  and  $S(\text{H}_2\text{O})$  calculated from (3) and (4), and by using (5) and (6), the equivalent mean cross sections,  $\bar{\sigma}(N)$  and  $\bar{\sigma}(N)$ , can be computed for each band interval as functions of the  $\text{O}_2$  column density. The values of  $\bar{\sigma}(N)$  and  $\bar{\sigma}(N)$  are plotted as a function of  $\text{O}_2$  column density in Fig. 1. These results show that both  $\bar{\sigma}(N)$  and  $\bar{\sigma}(N)$  strongly depend upon the  $\text{O}_2$  column density.

The  $\text{O}_2$  and  $\text{H}_2\text{O}$  photodissociation rates [Eqs. (1) and (2)] may now be rewritten by using  $\bar{\sigma}(N)$  and  $\bar{\sigma}(N)$  as

$$J_{\text{S-R}}(\text{O}_2) = \bar{I}_{B\infty} Q_{\text{O}_2} \bar{\sigma}(N) \times \exp[-\bar{\sigma}(N)N(\text{O}_2)] \int_{\text{band}} d\nu, \quad (7)$$

$$J_{\text{S-R}}(\text{H}_2\text{O}) = \bar{I}_{B\infty} Q_{\text{O}_2} \bar{\sigma}(N) \times \exp[-\bar{\sigma}(N)N(\text{O}_2)] \int_{\text{band}} d\nu, \quad (8)$$

where

$$Q_{\text{O}_2} = \exp[-\bar{\sigma}_{\text{O}_2}N(\text{O}_2)]. \quad (9)$$

The vertical distributions of  $J_{\text{S-R}}(\text{O}_2)$  and  $J_{\text{S-R}}(\text{H}_2\text{O})$  for a model atmosphere given in Table 2, and for the wavelength region (1750–2000 Å), are shown in Fig. 2, derived by using the values of  $\bar{\sigma}$  and  $\bar{\sigma}$  from Fig. 1. The results of Kockarts (1970) are also shown in Fig. 2. Kockarts evaluated  $J_{\text{S-R}}(\text{O}_2)$  and  $J_{\text{S-R}}(\text{H}_2\text{O})$  [Eqs. (1) and (2)] for the same atmospheric condition by using the exact profile of  $\sigma_{\text{S-R}}$  for a given temperature at each height, and concluded in his study that it is not possible to derive mean absorption cross sections which can be used simultaneously for the  $\text{O}_2$  and  $\text{H}_2\text{O}$  photodissocia-

TABLE 1. The band head for the  $\text{O}_2$  Schumann-Runge bands from (19,0) to (2,0), and solar flux for each band [ $\bar{I}_{B\infty} \int_{\text{band}} d\nu$ ] (after Ackerman, 1971).

Band $\nu'$ ( $\nu''=0$ )	Band head (Å)	Solar flux ( $\text{cm}^{-2}\text{sec}^{-1}$ )
19	1753.46	$3.26 \times 10^{10}$
18	1755.79	$4.51 \times 10^{10}$
17	1758.94	$6.02 \times 10^{10}$
16	1763.06	$7.91 \times 10^{10}$
15	1768.33	$1.04 \times 10^{11}$
14	1774.92	$1.32 \times 10^{11}$
13	1783.00	$1.68 \times 10^{11}$
12	1792.61	$2.07 \times 10^{11}$
11	1803.79	$2.49 \times 10^{11}$
10	1816.50	$3.14 \times 10^{11}$
9	1830.76	$4.00 \times 10^{11}$
8	1846.51	$4.91 \times 10^{11}$
7	1863.72	$6.00 \times 10^{11}$
6	1882.43	$7.24 \times 10^{11}$
5	1902.54	$9.10 \times 10^{11}$
4	1924.20	$1.30 \times 10^{12}$
3	1947.33	$1.65 \times 10^{12}$
2	1971.20	$2.21 \times 10^{12}$

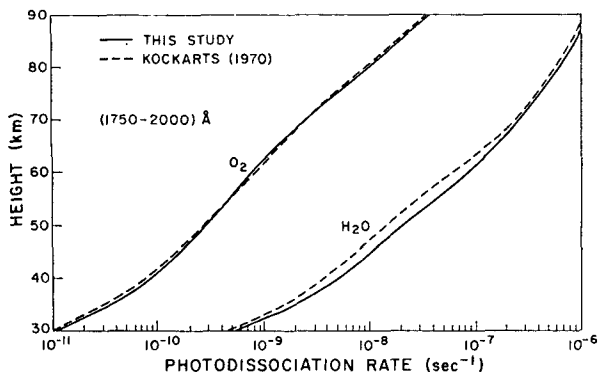


FIG. 2. Vertical distributions of photodissociation rates of  $O_2$  and  $H_2O$  for an overhead sun in the  $O_2$  Schumann-Runge band region.

tion rates. This was because Kockarts considered only one set of mean cross sections (e.g.,  $\bar{\sigma}$ ) to be used for both  $J_{S-R}(O_2)$  and  $J_{S-R}(H_2O)$ .

As shown in Fig. 2, agreement of the results between this study (using  $\bar{\sigma}$  and  $\bar{\sigma}$  for 250K) and Kockarts (using  $\sigma_{S-R}$  for different temperature at each height) is very good. This would imply that both  $\bar{\sigma}$  and  $\bar{\sigma}$  are actually applicable to the calculations of  $J_{S-R}(O_2)$  and  $J_{S-R}(H_2O)$  of the  $O_2$  Schumann-Runge band region for any atmospheric condition, and that they are not sensitive to a change in temperature below about 100 km.

Small differences in the values of  $J_{S-R}(O_2)$  and  $J_{S-R}(H_2O)$  shown in Fig. 2 can be neglected, for instance, in the case of ozone photochemistry (see Park, 1972).

It should be noted that the formula used for the  $H_2O$  photodissociation rate [Eq. (8)] can be used for other gases such as  $O_3$ ,  $CO_2$ ,  $HNO_3$  and  $N_2O$  in this spectral region.

*b. NO photodissociation rate*

The values of equivalent mean absorption cross sections ( $\bar{\sigma}$ ) for the  $O_2$  Schumann-Runge bands presented above cannot be used for calculations of NO photodissociation rates in the atmosphere. The NO bands at wavelengths  $< 2000 \text{ \AA}$  have Doppler half-widths of about  $0.1 \text{ cm}^{-1}$  in the middle atmosphere

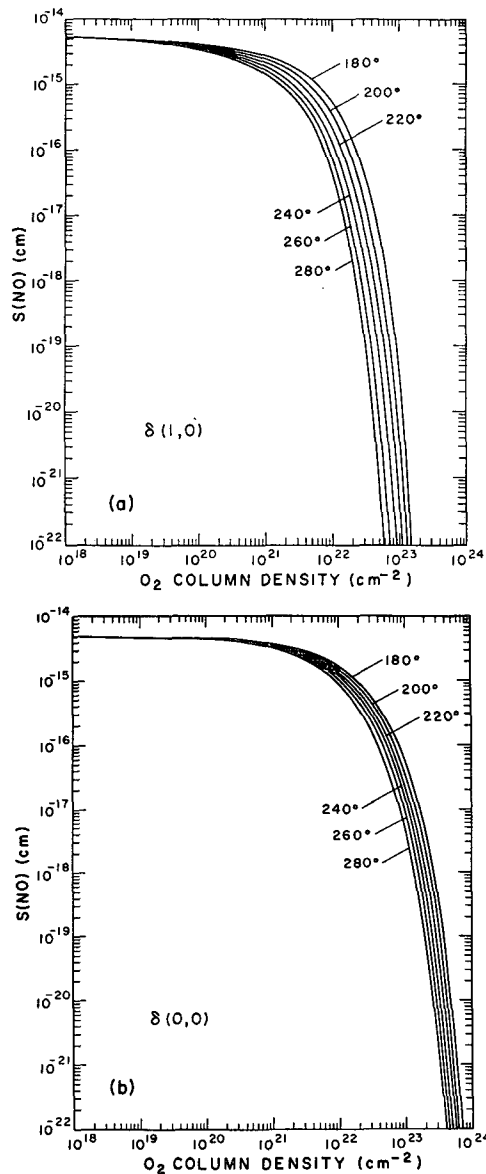


FIG. 3. Distribution of the integral  $S(NO)$  [cm, Eq. (11)] as a function of the  $O_2$  column density for various temperatures. Numbers on each curve are temperature ( $^{\circ}K$ ):

- (a)  $NO \delta(1,0)$  band (1822–1835  $\text{\AA}$ )
- (b)  $NO \delta(0,0)$  band (1902–1915  $\text{\AA}$ ).

TABLE 2. Model atmosphere and correction factors,  $Q_{O_3}$  and  $Q_{N_2}$ , used for the computations of  $J_{S-R}(O_2)$ ,  $J_{S-R}(H_2O)$  and  $J_{S-R}(NO)$  (after Kockarts, 1970, and Cieslik and Nicolet, 1973).

Height (km)	T ( $^{\circ}K$ )	$\int_z^{\infty} O_2 dz$ ( $cm^{-2}$ )	$\int_z^{\infty} O_3 dz$ ( $cm^{-2}$ )	$Q_{O_3}$		$Q_{N_2}$	
				$\delta(1,0)$	$\delta(0,0)$	$\delta(1,0)$	$\delta(0,0)$
90	177	6.5 (18)	2.6 (13)	1.0	1.0	1.0	1.0
80	177	4.8 (19)	1.4 (14)	1.0	1.0	1.0	1.0
70	211	2.7 (20)	5.4 (14)	1.0	1.0	1.0	1.0
60	253	1.1 (21)	4.5 (15)	1.0	1.0	1.0	1.0
50	274	4.0 (21)	4.4 (16)	0.97	0.98	1.0	0.98
40	268	1.4 (22)	4.4 (17)	0.73	0.81	1.0	0.95
30	235	5.2 (22)	2.4 (18)	0.17	0.32	1.0	0.80

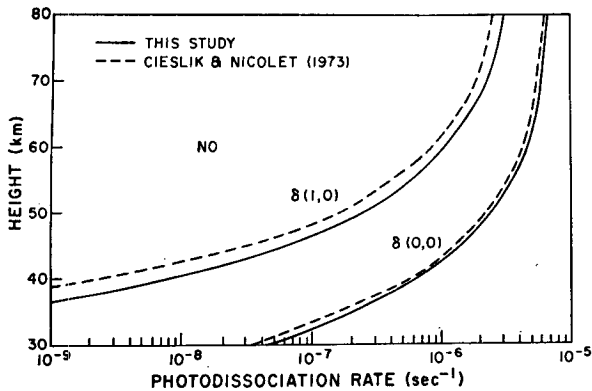


FIG. 4. Vertical distributions of photodissociation rates of NO for an overhead sun for the  $\delta(1,0)$  and the  $\delta(0,0)$  bands.

which is much smaller than that of the  $O_2$  bands discussed here (see Cieslik and Nicolet, 1973).

The NO photodissociation rate,  $J_{S-R}(\text{NO})$ , therefore, should be computed by knowing the absorption cross sections in a smaller wavenumber interval ( $0.1 \text{ cm}^{-1}$ ) by

$$J_{S-R}(\text{NO}) = \bar{I}_{B\infty} Q_{O_2} Q_{N_2} \int_{\text{band}} \sigma_{\text{NO}}(\nu) \times \exp[-\sigma_{S-R}(\nu)N(O_2)] d\nu, \quad (10)$$

where  $Q_{N_2}$  is the quenching factor due to the collisional de-excitation of an upper state of NO (Table 2) and other symbols have the same meaning as before. The computation methods and data used for  $\sigma_{\text{NO}}$  are the same as Cieslik and Nicolet (1973). However, this study adopted the band-integrated intensity for  $\delta(1,0)$  from Bethke (1959) which includes the value of  $\beta(10,0)$ .

Cieslik and Nicolet (1973) found in their study that most photodissociation of NO occurs in the  $\delta(C^2\Pi - X^2\Pi)$ ,  $\beta(B^2\Pi - X^2\Pi)$ , and  $\gamma(A^2\Sigma^+ - X^2\Pi)$  bands, and that the  $\delta(1,0)$  band (1822–1835 Å) and  $\delta(0,0)$  band (1902–1915 Å) have the largest contributions below the mesopause. Since both the NO  $\delta$  bands and the  $v''=1$  sequence of the  $O_2$  Schumann-Runge bands are located in the  $v''=0$  window regions of the  $O_2$  bands, and since the absorption profile of the  $v''=1$  is highly dependent upon the temperature, the NO photodissociation rate becomes a strong function of both temperature and  $O_2$  column density.

The integral in Eq. (10), i.e.,

$$S(\text{NO}) = \int_{\text{band}} \sigma_{\text{NO}}(\nu) \exp[-\sigma_{S-R}(\nu)N(O_2)] d\nu, \quad (11)$$

is evaluated using the values of  $\sigma_{\text{NO}}$  and  $\sigma_{S-R}$  computed in this study for a wavenumber interval of  $0.1 \text{ cm}^{-1}$  for temperatures from 180 to 280K, and for  $N(O_2)$

from 0 to  $10^{24} \text{ cm}^{-2}$ . These are shown in Fig. 3 as functions of temperature and  $O_2$  column density.

The NO dissociation rate [Eq. (10)], can be rewritten by using Eq. (11) as

$$J_{S-R}(\text{NO}) = \bar{I}_{B\infty} Q_{O_2} Q_{N_2} S(\text{NO}). \quad (12)$$

To compute this quantity for a particular model atmosphere (see Table 2)  $\bar{I}_{B\infty}$  is assumed to be  $7.6 \times 10^8$  photons per ( $\text{cm}^2 \text{ sec}$ ) per ( $\text{cm}^{-1}$ ) for the  $\delta(1,0)$  band and  $1.4 \times 10^9$  photons per ( $\text{cm}^2 \text{ sec}$ ) per ( $\text{cm}^{-1}$ ) for the  $\delta(0,0)$  band (see Ackerman, 1971). The values of  $S(\text{NO})$  are taken from Fig. 3 by interpolation for the corresponding  $O_2$  column density and temperature of each height. The derived values of  $J_{S-R}(\text{NO})$  for the  $\delta(1,0)$  and  $\delta(0,0)$  bands for this atmosphere are shown in Fig. 4 as a function of height, and are compared with those of Cieslik and Nicolet (1973). Cieslik and Nicolet calculated  $J_{S-R}(\text{NO})$  for the same atmospheric condition but used exact profiles of  $\sigma_{\text{NO}}$  (every  $0.1 \text{ cm}^{-1}$ ) and  $\sigma_{S-R}$  [every  $0.5 \text{ cm}^{-1}$  from Kockarts (1972)] for the temperature at each height. Two sets of values for  $\delta(1,0)$  shown in Fig. 4 are systematically different by a factor of about 1.2, perhaps due to different values of  $\sigma_{S-R}$ , and band-integrated intensity and solar flux per unit wavenumber indicated earlier.

In their study of the NO photodissociation, Cieslik and Nicolet indicate that  $J_{S-R}(\text{NO})$  should be computed using  $\sigma_{S-R}$  and  $\sigma_{\text{NO}}$  for a given distribution of atmospheric temperature and  $O_2$  density in succession from the top to the bottom of the atmospheric region. In that case, it becomes very difficult to apply their results to the atmosphere in general because their results are good for only one distribution of temperature and  $O_2$  density for a given zenith angle. Fig. 4 shows, however, that agreement is very good between the approximation used in this study and the exact study of Cieslik and Nicolet. This is because the solar flux reaching a particular level is determined approximately within a scale height of that level. Therefore, the NO photodissociation rate can be approximated by using  $S(\text{NO})$  from Fig. 3 for each height of the atmosphere by knowing the  $O_2$  column density and temperature at that level.

### 3. Conclusion

Contrary to the conclusions of Kockarts (1970) and Cieslik and Nicolet (1973), it is possible to approximate the photodissociation rates of  $O_2$ ,  $H_2O$  and NO in the  $O_2$  Schumann-Runge band region for any atmospheric condition from Eqs. (7), (8) and (12) using the values of  $\bar{\sigma}$ ,  $\bar{\sigma}$  and  $S(\text{NO})$  shown in Figs. 1 and 3.

*Acknowledgments.* The author is grateful to Drs. Julius London and Gary E. Thomas for their helpful comments and suggestions. Support for the research came from the Atmospheric Sciences Section, National Science Foundation, under Grants GA-28688X and

GA-10838 and the Department of Transportation through NSF Grant GA-28688X1. Acknowledgment is also made to the National Center for Atmospheric Research, which is sponsored by the National Science Foundation, for the computing time used in this research.

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