

# Reports

## Atmospheric Carbon Dioxide and Aerosols: Effects of Large Increases on Global Climate

**Abstract.** *Effects on the global temperature of large increases in carbon dioxide and aerosol densities in the atmosphere of Earth have been computed. It is found that, although the addition of carbon dioxide in the atmosphere does increase the surface temperature, the rate of temperature increase diminishes with increasing carbon dioxide in the atmosphere. For aerosols, however, the net effect of increase in density is to reduce the surface temperature of Earth. Because of the exponential dependence of the backscattering, the rate of temperature decrease is augmented with increasing aerosol content. An increase by only a factor of 4 in global aerosol background concentration may be sufficient to reduce the surface temperature by as much as 3.5°K. If sustained over a period of several years, such a temperature decrease over the whole globe is believed to be sufficient to trigger an ice age.*

The rate at which human activities may be inadvertently modifying the climate of Earth has become a problem of serious concern (1). In the last few decades the concentration of CO<sub>2</sub> in the atmosphere appears to have increased by 7 percent (2). During the same period, the aerosol content of the lower atmosphere may have been augmented by as much as 100 percent (3). How have these changes in the composition of the atmosphere affected the climate of the globe? More importantly, is it possible that a continued increase in the CO<sub>2</sub> and dust content of the atmosphere at the present rate will pro-

duce such large-scale effects on the global temperature that the process may run away, with the planet Earth eventually becoming as hot as Venus (700°K) or as cold as Mars (230°K)?

We will report here on the first results of a calculation in which separate estimates were made of the effects on global temperature of large increases in the amount of CO<sub>2</sub> and dust in the atmosphere. It is found that even an increase by a factor of 8 in the amount of CO<sub>2</sub>, which is highly unlikely in the next several thousand years, will produce an increase in the surface temperature of less than 2°K. However, the effect on surface temperature of an increase in the aerosol content of the atmosphere is found to be quite significant. An increase by a factor of 4 in the equilibrium dust concentration in the global atmosphere, which cannot be ruled out as a possibility within the next century, could decrease the mean surface temperature by as much as 3.5°K. If sustained over a period of several years, such a temperature decrease could be sufficient to trigger an ice age!

To perform these calculations we adopt a model atmosphere that reflects present-day globally averaged conditions. The values of the various parameters used in the atmospheric model are given in Table 1.

The model atmosphere is divided into

60 layers, each with a thickness of ½ km, from the surface to an altitude of 30 km. The temperature decreases with altitude with a lapse rate of 6.5°K per kilometer until it attains a value of 218°K. Above this level the atmosphere is assumed to be isothermal. The concentrations of H<sub>2</sub>O and CO<sub>2</sub> listed in Table 1 were adopted for the layers of the model.

The outgoing flux is computed for every 10-cm<sup>-1</sup> interval in the infrared between 4 and 100 μm from the equation

$$B_{\nu} = B_{\alpha_{\nu}} e^{-\tau_{\nu_0}} + \int_0^{\tau_{\nu_0}} B_{\nu}(T_z) e^{-\tau_{\nu z}} d\tau_{\nu z} \quad (1)$$

where  $B_{\nu}$  is the total blackbody radiation in a 10-cm<sup>-1</sup> frequency interval reaching the top of the atmosphere;  $B_{\alpha_{\nu}}$  is the surface radiation;  $\tau_{\nu z}$  is the total optical thickness of the atmosphere above height  $z$ , given by

$$\tau_{\nu z} = \beta \int_z^{\infty} (K_1 \rho_1 + K_2 \rho_2) dz$$

where  $K_1$  and  $K_2$  are the absorption coefficients of CO<sub>2</sub> and H<sub>2</sub>O, and  $\rho_1$ ,  $\rho_2$ , are their respective densities;  $\beta$ , the average increase in optical path length from diffuse radiation, is taken to be 1.66.

Equation 1 was integrated over frequencies between 4 and 100 μm to obtain the total radiation emitted by Earth to space. As indicated in Table 1, one-half of Earth is considered to be cloud-covered at an effective radiating altitude of 5.5 km. The clouds are assumed to be "black" to infrared radiation, and, therefore, the outgoing

Table 1. Parameters used in the atmospheric model.

Parameter	Value
Surface temperature, $T_s$ (global average)	288°K
Surface pressure, $P_0$	1013 mb
Tropospheric lapse rate ( $dT/dz$ )	-6.5°K/km
Relative humidity (surface)	75 percent
Vertical distribution of water vapor mixing ratio ( $w$ )	$w_z/w_0 = (p_z/p_0)^4$
Cloud cover (global average)	50 percent
Effective cloud top height	5.5 km
CO <sub>2</sub> amount	0.3 part per thousand

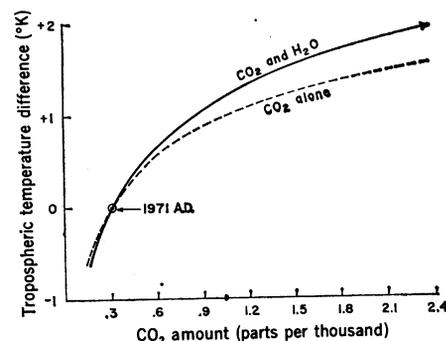


Fig. 1. Change in tropospheric temperature as a function of the amount of CO<sub>2</sub> in the atmosphere. The dashed curve is computed for constant surface absolute humidity, and the solid curve is for the case in which surface relative humidity is maintained constant. Note that the rate of temperature increase diminishes with increasing CO<sub>2</sub> in the atmosphere.

flux for Earth over the cloudy region is computed only from the cloud top and the atmosphere above the cloud level.

The total radiation leaving the Earth-atmosphere system from the model described above was found to be 0.3450 cal/cm<sup>2</sup> per minute. For this calculation the absorption coefficients for CO<sub>2</sub> and water vapor of Elsasser and Culbertson (4) were used, except for the region from 7 to 14 μm for which the values of Prabhakara and Rasool (5) were used. The total *outgoing* radiation flux calculated here will be in balance with the *incoming* solar radiation for a planetary albedo of 31 percent; this value is close to the observed value of 30 percent (6) and the computed estimate of 33 percent (7). A planetary albedo of 31 percent in this model can be reconciled by assuming an albedo of 52 percent for the clouds and 10 percent for the cloudless regions of Earth (8).

The values given by the model atmosphere described above for both outgoing and incoming radiation seem to be in close agreement with the values measured by meteorological satellites (6). We conclude, therefore, that the model reflects the present-day conditions of the atmosphere of Earth.

To calculate the effect of an increase in CO<sub>2</sub> on the surface temperature, we recompute the total outgoing flux,  $\int B_v dv$ , from the model atmosphere for assumed increases in the CO<sub>2</sub> amount by factors of 2, 4, 6, and 8. The effect of increase in CO<sub>2</sub> is to reduce the outgoing infrared flux to space. This reduction takes place because  $\rho_1$  has increased, which augments the opacity  $\tau_{v_2}$ ; therefore, for a given surface temperature  $T_s$ ,  $\int B_v dv$  must decrease. Hence, in order to balance the incoming solar flux (which does not change in the model with the increase in CO<sub>2</sub>), the temperature in the troposphere and at the surface must increase (9). The computed values of the increase in tropospheric temperature required to balance the incoming solar flux, for several values of CO<sub>2</sub> concentration in the atmosphere, are presented in Fig. 1. The dashed curve represents the case in which the *absolute* humidity near the surface is assumed to be constant; the solid curve is computed for the case in which the surface layer is maintained at a constant *relative* humidity. In the latter case a higher temperature is produced because there is more water vapor in the warmer atmosphere. The assumption of maintaining relative

humidity as constant is believed to be meteorologically more sound (10, 11).

From our calculation, a doubling of CO<sub>2</sub> produces a *tropospheric* temperature change of 0.8°K (12). However, as more CO<sub>2</sub> is added to the atmosphere, the *rate* of temperature increase is proportionally less and less, and the increase eventually levels off. Even for an increase in CO<sub>2</sub> by a factor of 10, the temperature increase does not exceed 2.5°K. Therefore, the runaway greenhouse effect does not occur because the 15-μm CO<sub>2</sub> band, which is the main source of absorption, "saturates," and the addition of more CO<sub>2</sub> does not substantially increase the infrared opacity of the atmosphere. But, if the CO<sub>2</sub> concentration in the atmosphere becomes so high that the total atmospheric pressure is affected (which will require a CO<sub>2</sub> increase by a factor of 1000 or more), then the absorption bands will broaden, the opacity will increase, and the temperature may start to rise so rapidly that the process could run away (13). However, this appears to be only a remote possibility for Earth, even on a geological time scale, as a large buildup of CO<sub>2</sub> in the atmosphere will be severely restrained by its interaction with the oceans, the biosphere, and the crust (14).

The main conclusion of this part of the study is that even an order of magnitude increase of CO<sub>2</sub> in the atmosphere by human activities, which at the present rate of input is not expected within the next several thousand years, may not be sufficient to produce a runaway greenhouse effect on Earth. On the short time scale, if CO<sub>2</sub> is augmented by another 10 percent in the next 30 years, the increase in the global temperature may be as small as 0.1°K.

A calculation of the effect of aerosols on the global temperature is much more complicated than is the calculation for CO<sub>2</sub>. Aerosols, depending on the composition, number, size, and shape of their particles, will scatter and absorb not only the solar radiation but also the planetary radiation, and in varying proportions. If the backscattering of the incoming visible radiation by the aerosols is more significant than the reduction of the far infrared radiation flux to space, the planetary albedo will then increase more rapidly than the greenhouse effect and the net result will be a cooling of Earth. If the reverse is true, then the aerosols will tend to warm Earth. Absorption of radiation by aerosols is also important and must be considered. We

will now estimate the magnitude of scattering and absorption of both visible and infrared radiation by typical atmospheric aerosols by using the theory of multiple scattering.

Consider an aerosol layer just above Earth's surface (with surface albedo  $\alpha_s$ ). Let  $r$  be the fraction of sunlight backscattered to space from the aerosol layer, and let  $\alpha$  be the fraction absorbed in the aerosol layer. Then the transmission through the aerosol layer is  $t = 1 - r - \alpha$ . If the average reflectivity of the surface of Earth is  $\alpha_s$ , and the transmission of the aerosol layer from below is again  $t$ , then the total or "effective" albedo of the combined surface-aerosol system,  $\alpha_E$ , is

$$\alpha_E = r + t\alpha_s t + t\alpha_s r\alpha_s t + \dots$$

where, by summing the infinite series,

$$\alpha_E = r + [t^2\alpha_s/(1 - \alpha_s r)] \quad (2)$$

A two-stream approximation to the multiple scattering problem (15, 16) is used to compute the backscatter fraction  $r$  and the transmission fraction  $t$  of an aerosol layer of optical thickness  $\tau_\lambda$ :

$$r = \frac{(u+1)(u-1)[e^{\tau'} - e^{-\tau'}]}{(u+1)^2 e^{\tau'} - (u-1)^2 e^{-\tau'}}$$

and

$$t = \frac{4u}{(u+1)^2 e^{\tau'} - (u-1)^2 e^{-\tau'}}$$

where

$$u = \left\{ \frac{1 - \omega_0 \langle \cos \theta \rangle}{1 - \omega_0} \right\}^{1/2}$$

and

$$\tau' = \sqrt{3} u (1 - \omega_0) \tau_\lambda$$

The optical thickness of an aerosol layer is

$$\tau_\lambda = \sigma_\lambda \Delta z$$

where  $\sigma_\lambda$  is the average extinction coefficient (per kilometer) of the layer and  $\Delta z$  (in kilometers) is the average depth. Since the extinction coefficient is proportional to the number of aerosol particles,  $\tau_\lambda$  will increase if the rate of the particulate loading of the atmosphere increases, either by more frequent volcanic activity or by a rapid industrialization of the world.

To determine numerical values of  $t$  and  $r$  for a given aerosol layer of optical thickness  $\tau_\lambda$ , we need to know  $\omega_0$ , the single scattering albedo, and  $\langle \cos \theta \rangle$ , the asymmetry factor. The single scattering albedo,  $\omega_0$ , depends upon the imaginary part of the refractive index

of the dust particles,  $n_1$ , and determines the amount of absorption of radiation of a given wavelength by the particles. The asymmetry factor  $\langle \cos \theta \rangle$  describes the degree of forward scattering and depends upon the real part of the refractive index of the aerosols,  $n_r$ . For 100 percent forward scattering,  $\langle \cos \theta \rangle = 1$ ; for isotropic scattering (50 percent backscatter),  $\langle \cos \theta \rangle = 0$ ; and for 100 percent backscatter,  $\langle \cos \theta \rangle = -1$ . These parameters are described further by Hansen and Pollack (17).

Values of  $\langle \cos \theta \rangle$ ,  $\omega_0$ , and  $\sigma_\lambda$  have been computed (16) for both visible and infrared wavelengths from Mie theory, on the assumption of a particle size distribution  $n(r) = r^{-4}$  [where  $n(r)$  is the number of particles with radius  $r$ , and the particle size range is  $0.1 \mu\text{m} < r < 10 \mu\text{m}$ ] and for  $n_r = 1.5$ . For visible radiation the median wavelength chosen is  $\lambda_{\text{VIS}} = 0.55 \mu\text{m}$ , and for infrared,  $\lambda_{\text{IR}} = 10 \mu\text{m}$ .

The value of  $\langle \cos \theta \rangle$  was computed to be 0.64 for these parameters. As for  $\omega_0$ , because of the uncertainty in  $n_1$ , we consider two extreme values,  $\omega_0$  equal to 0.99 and 0.90, in the visible. The former value corresponds to negligible aerosol absorption, and the latter number is for the case in which aerosol

absorption and backscatter fractions are equal at about  $\tau_{\text{VIS}} = 0.5$ . The value of  $n_1$  is known to increase rapidly in the infrared, which implies a large absorption fraction and, therefore, a small value of  $\omega_0$ . Again, two values for  $\omega_0$ , 0.83 and 0.28, were considered, corresponding to  $n_1 = 0.01$  and  $n_1 = 0.1$ , respectively.

Lastly,  $\sigma_\lambda$  was computed for the visible and the infrared for Mie scattering. For  $\omega_0 = 0.99$  in the visible and  $\omega_0 = 0.28$  in the infrared,  $\sigma_{\text{IR}}/\sigma_{\text{VIS}} = 0.108$ . The result is in agreement with the earlier calculation of Barnhardt and Steele (18, figure 4).

In Fig. 2a, we plot the variation in the solar flux absorbed by the Earth-atmosphere system computed for various values of  $\tau_{\text{VIS}}$  of the aerosol layer. When there are no aerosols ( $\tau_{\text{VIS}} = 0$ ), the absorbed solar flux is computed to be  $0.35125 \text{ cal/cm}^2$  per minute. This corresponds to a planetary albedo of 29.75 percent due to clouds and the surface. However, as the aerosols increase, the albedo of the *cloudless* fraction of Earth increases (19) and the absorbed solar flux decreases, as is shown in Fig. 2a. In the same figure, we also plot the values of infrared flux to space for various surface tempera-

tures, computed as a function of infrared optical thickness  $\tau_{\text{IR}}$  and for the case  $\omega_0 = 0.28$ . The other case,  $\omega_0 = 0.83$ , produces infrared flux curves, in the range of  $\tau_{\text{IR}}$  considered here, that are nearly identical with the plotted case; it is, therefore, omitted from the figures. The most significant result is that the effect of aerosols on the visible radiation is much more pronounced than is their effect on the infrared. The reasons for this difference are: (i) for this aerosol layer,  $\tau_{\text{IR}} = 0.108 \tau_{\text{VIS}}$ , and (ii) the top of the aerosol layer has been assumed fixed at 1 km. The consequence of this assumption is that, even if the aerosol layer were infinitely opaque to the infrared radiation from below, the total outgoing flux would be decreased by only  $0.0084 \text{ cal/cm}^2$  per minute (computed from the model atmosphere of Table 1), because the top of the aerosol layer now behaves as a black cloud top and radiates at a temperature that is (at most)  $6.5^\circ\text{K}$  colder than the surface.

In Fig. 2a, the point of intersection of the solar and infrared flux curves determines the equilibrium surface temperature,  $T_s$ ,  $^\circ\text{K}$ , as a function of optical thickness of the aerosols. This result is cross-plotted in Fig. 2b for the two values of  $\omega_0$  used in Fig. 2a.

It is noteworthy that the *rate* of decrease in surface temperature at smaller optical thicknesses is small, whereas, for larger values of  $\tau_{\text{VIS}}$  ( $> 0.1$ ), the surface temperature falls precipitously with increasing opacity because of the exponential dependence of the backscattering on  $\tau_{\text{VIS}}$ .

The next important problem is to determine the optical thickness of the aerosols at the present time and the rate at which this thickness is expected to increase in the next several decades.

In seeking to determine the present optical thickness of the aerosols, it is important to note that the value needed here is a global average of the equilibrium dust content of the atmosphere. Although several measurements of the atmospheric opacity in the visible have been made at various locations, particularly over the cities (20), only very few studies of the global background turbidity due to aerosols are available (21, 22). Porch *et al.* (21) actually measured the total scattering coefficient of the atmosphere over remote, least polluted regions of the United States; after subtracting the Rayleigh part, they found a value of  $\tau_{\text{VIS}}$  due to

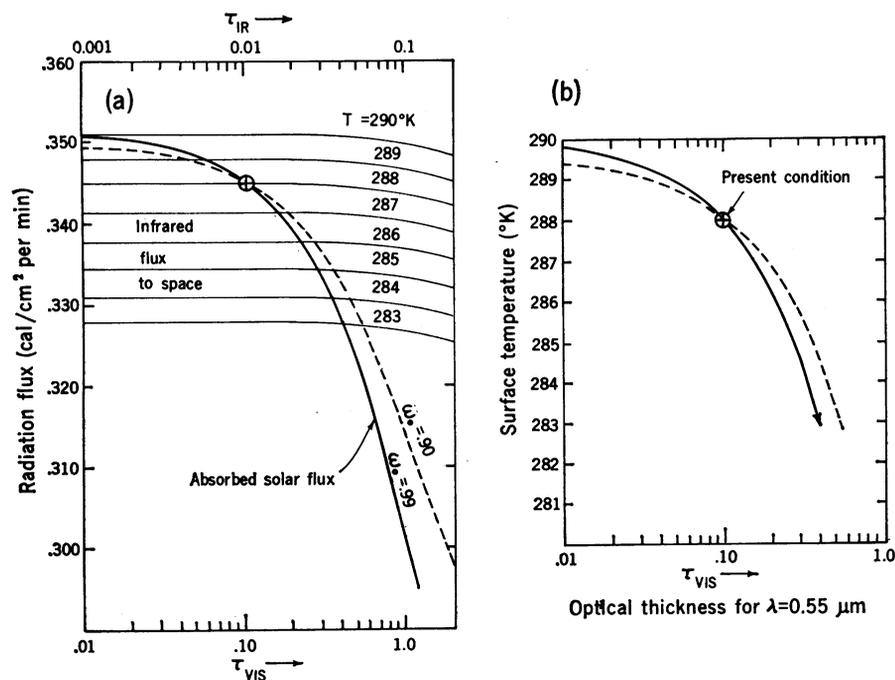


Fig. 2. (a) Both the absorbed solar radiation and infrared flux to space are plotted as a function of increasing accumulation of aerosols in the atmosphere. The absorbed solar flux decreases rapidly with increasing optical depth for both values of the single scattering albedo parameter,  $\omega_0$ . The infrared flux to space, calculated for several values of surface temperature, is practically unaffected by increasing aerosols. (b) The intersection of infrared and visible flux values, which determine the surface temperature for a given optical thickness,  $\tau_{\text{VIS}}$ , are cross-plotted. Note that the rate of decrease in the global temperature grows with increasing aerosols.

aerosols in the range between 0.032 and 0.18, with the majority of the values lying around 0.10. These numbers also agree with recent observations of Herman *et al.* (22). We therefore adopt here a value of  $\tau_{\text{VIS}} = 0.1$ .

In regard to the rate of secular increase in the global background opacity of the aerosols, several recent studies suggest that the global dust content of the atmosphere has been increasing during the last few decades, perhaps by as much as a factor of 2 in the last 60 years (23, 24).

Even if we assume that the rate of scavenging and of other removal processes for atmospheric dust particles remains constant, it is still difficult to predict the rate at which global background opacity of the atmosphere will increase with increasing particulate injection by human activities. However, it is projected that man's potential to pollute will increase six- to eightfold in the next 50 years (24). If this increased rate of injection of particulate matter in the atmosphere should raise the present global background opacity by a factor of 4, our calculations suggest a decrease in global temperature by as much as 3.5°K. Such a large decrease in the average surface temperature of Earth, sustained over a period of few years, is believed to be sufficient (25) to trigger an ice age. However, by that time, nuclear power may have largely replaced fossil fuels as a means of energy production.

S. I. RASOOL  
S. H. SCHNEIDER

*Institute for Space Studies, Goddard Space Flight Center, National Aeronautics and Space Administration, New York 10025*

#### References and Notes

1. Report of the Study of Critical Environmental Problems (SCEP), *Man's Impact on the Global Environment* (M.I.T. Press, Cambridge, Mass., 1970); *Global Effects of Environmental Pollution*, S. F. Singer, Ed. (Reidel, Dordrecht, Netherlands, 1970); H. E. Landsberg, *Science* **170**, 1265 (1970).
2. J. M. Mitchell, in *Global Effects of Environmental Pollution*, S. F. Singer, Ed. (Reidel, Dordrecht, Netherlands, 1970), p. 139.
3. W. E. Cobb and H. J. Wells, *J. Atmos. Sci.* **27**, 814 (1970).
4. W. M. Elsasser and M. F. Culbertson, *Meteorol. Monogr.* **4**, No. 23 (1960).
5. C. Prabhakara and S. I. Rasool, in *Rocket and Satellite Meteorology*, H. Wexler, Ed. (North-Holland, Amsterdam, 1963), p. 234.
6. T. H. Vonder Haar and V. E. Suomi, *J. Atmos. Sci.* **28**, 305 (1971).
7. J. London and T. Sassamori, *Space Res.* **11**, 639 (1971).
8. The global average surface albedo of 10 percent is the value given by Manabe and Wetherald (11, p. 244).
9. In the model the lapse rate is held fixed at 6.5°K per kilometer, which is the average critical value for convective stability. Any

increase in the surface temperature alone would result in a superadiabatic lapse rate, which is convectively unstable.

10. F. Möller, *J. Geophys. Res.* **68**, 3877 (1963).
11. S. Y. Manabe and R. T. Wetherald, *J. Atmos. Sci.* **24**, 241 (1967).
12. Our computed surface temperature increase for an increase in the amount of CO<sub>2</sub> by a factor of 2 is less than one-third that of Manabe and Wetherald (11). There are three reasons for this difference: (i) The absorption coefficients for CO<sub>2</sub> used by Manabe and Wetherald [from G. Yamamoto and T. Sasamori, *Sci. Rep. Tohoku Univ. Ser.* **510** (No. 2), 37 (1958)] are higher than ours [from (4)]. (ii) In our calculations the temperature throughout the troposphere varies at the fixed critical lapse rate, whereas in Manabe and Wetherald's calculations the increase in temperature is confined to the lower troposphere, and the upper troposphere and stratosphere show an actual decreasing temperature. (iii) Our method of calculation for the overlap of H<sub>2</sub>O and CO<sub>2</sub> absorption bands and our evaluation of the radiative flux integrals are not identical with theirs. However, since we are interested in studying the very long-term effects of increasing CO<sub>2</sub>, up to a factor of 10 or more, the shape of the curves shown in Fig. 1, which indicates a leveling off of the temperature increase, is the major point of emphasis, rather than the absolute value of temperature change for a doubling of CO<sub>2</sub> in the atmosphere.
13. S. I. Rasool and C. DeBergh, *Nature* **226**, 1037 (1970).
14. At this point, it is important to remind ourselves that the kind of model used here deals only with global-averaged changes in a single component of the complex Earth-atmosphere heat balance and does not couple perturbations in this component to simultaneous changes in the other variables. However, given the complexity of the total system, it is reasonable to use these methods to investigate the effect of small changes in a single variable—for instance, the amount of CO<sub>2</sub>.
15. C. Sagan and J. B. Pollack, *J. Geophys. Res.* **72**, 469 (1967).
16. J. E. Hansen, personal communication. We are indebted to Dr. Hansen for making these Mie scattering calculations for us, for sug-

gesting the use of the two-stream approximation, and for checking the fluxes obtained by the two-stream approximation against some exact solutions (which agree to within about 5 percent) to the multiple scattering problem [see, for example, J. E. Hansen, *Astrophys. J.* **155**, 565 (1969)].

17. J. E. Hansen and J. B. Pollack, *J. Atmos. Sci.* **27**, 265 (1970).
18. E. A. Barnhardt and J. L. Steele, *Appl. Opt.* **9**, 1337 (1970).
19. It must be noted that the cooling effect of the aerosols depends upon the condition that the aerosol will increase  $a_p$ . If the surface albedo is very large to start with and the aerosol absorption fraction is as large as the backscatter, then the aerosol could conceivably warm the atmosphere [see Eq. 2 and the comment by S. H. Schneider (*J. Appl. Meteorol.*, in press)]. However, this would occur only in the local cases where  $a_s$  is large ( $\approx 25$  percent), and, at the same time,  $\alpha$  is comparable to or larger than  $r$ . Possibly, certain industrial aerosols over a snow-covered surface might have a local warming effect, but for the average over Earth's surface, where  $a_s \sim 10$  percent, the effect of aerosols is to raise  $a_p$ .
20. R. A. Bryson and W. M. Wendland, in *Global Effects of Environmental Pollution*, S. F. Singer, Ed. (Reidel, Dordrecht, Netherlands, 1970), p. 130.
21. W. M. Porch, R. J. Charlson, L. F. Radke, *Science* **170**, 315 (1970).
22. B. M. Herman, S. R. Browning, R. J. Curran, *J. Atmos. Sci.* **28**, 419 (1971).
23. P. W. Hodge, *Nature* **229**, 549 (1971). He finds a 9 percent decrease in atmospheric transmission in the visible above Mount Wilson during the past 50 years. This corresponds to an increase by a factor of 2 in the background opacity of the atmosphere.
24. J. H. Ludwig, G. B. Morgan, T. B. McMullen, *Eos Trans. Amer. Geophys. Union* **51**, 468 (1970).
25. M. I. Budyko, *Tellus* **21**, 611 (1969); W. D. Sellers, *J. Appl. Meteorol.* **8**, 392 (1969).
26. We again thank Dr. J. E. Hansen for his many contributions. The work was done while S.H.S. held a NAS-NRS resident research associateship at the Institute for Space Studies, Goddard Space Flight Center, NASA.

7 April 1971; revised 18 May 1971

## Normal Atmosphere: Large Radical and Formaldehyde Concentrations Predicted

**Abstract.** *A steady-state model of the normal (unpolluted) surface atmosphere predicts a daytime concentration of hydroxyl, hydroperoxyl, and methylperoxyl radicals approaching  $5 \times 10^8$  molecules per cubic centimeter and a formaldehyde concentration of  $5 \times 10^{10}$  molecules per cubic centimeter or 2 parts per billion. A radical chain reaction is proposed for the rapid removal of carbon monoxide, leading to a carbon monoxide lifetime as low as 0.2 year in the surface atmosphere.*

Although numerous workers (1) have studied the photochemistry of minor constituents in the upper atmosphere, less attention has been paid to the photochemistry of the atmosphere near the ground where significant concentrations of water vapor, methane, carbon monoxide, ozone, and oxides of nitrogen are naturally present (2).

The dissociation of ozone at the ground level by sunlight in the wavelength range from 2900 to 3400 Å produces metastable atomic oxygen, O(<sup>1</sup>D). The metastable species is rapidly quenched by collisions with air

molecules, but a small fraction,  $1 \times 10^{-2}$ , reacts with water to produce hydroxyl radicals at a rate exceeding  $10^5$  molecule  $\text{cm}^{-3} \text{sec}^{-1}$ . The hydroxyl radicals then react with carbon monoxide, ozone, and methane to produce hydroperoxyl radicals, which, in turn, oxidize nitric oxide to nitrogen dioxide and reform hydroxyl radicals. These chain reactions, which rapidly interconvert hydroxyl and hydroperoxyl radicals, may provide the dominant mechanism for removing atmospheric carbon monoxide and methane and for producing formaldehyde in the normal