sible to investigate biological specimens with resolutions near 100 Å. Improvements in x-ray resists should eventually make exposure times much shorter than 1 second possible.

E. SPILLER, R. FEDER
J. TOPALIAN, D. EASTMAN
W. GUDAT, D. SAYRE
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

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Microwave Measurement of Mesospheric Carbon Monoxide

Abstract. *Ground-based observation of atmospheric absorption of solar radiation at a wavelength of 2.6 millimeters has provided the first measurement of mesospheric carbon monoxide. The measurement agrees with photochemical predictions of a carbon monoxide source in the lower thermosphere due to dissociation of carbon dioxide by solar radiation, and has implications for the magnitude of vertical transport in the mesosphere.*

Photochemical calculations predict that CO is produced in the earth's upper atmosphere by the solar ultraviolet dissociation of CO_2 (*1, 2*). We here report detection of the $J = 0 \rightarrow 1$ CO rotational transition at a frequency of 115,271.2 Mhz (wavelength, 2.6 mm) in the solar absorption spectrum. This absorption feature is due to CO in the earth's mesosphere and lower thermosphere and is the first experimental confirmation of the photochemical predictions. It provides a value for the CO column density at altitudes above ~ 65 km and information on the CO distribution in the altitude region ~ 40 to 80 km.

Ground-based microwave radiometric techniques like that used here for studying the earth's upper atmosphere were first suggested by Barrett and Chung (*3*), and are discussed in detail elsewhere (*4*). These techniques have previously been used to measure absorption or emission from ozone and molecular oxygen in the stratosphere (*5*). Voronov *et al.* (*6*) have also reported detection of the 115-Ghz CO line in the solar absorption spectrum. We are, however, suspicious of the measurement of Voronov *et al.*, since our analysis indicates that it implies a CO mixing ratio in the middle stratosphere which is $\sim 10^4$ times larger than that given by other measurements (*7*).

Our measurements were made on several days in April and May 1975 with the 4.6-m-diameter millimeter wavelength antenna and receiver of the Aerospace Corporation in El Segundo, California (latitude 34°N, sea level elevation). Measurements for 1 day are shown in Fig. 1. Although our data have not been closely examined for variations in the CO signal during the several days of measurement, no noticeable variation was apparent from a cursory examination. The beam width of the antenna was ~ 0.1 solar diameter; the spectral resolution of the multichannel filter bank used with the receiver was 0.25 Mhz and covered a total bandwidth of 8 Mhz. The frequency of the observed absorption line agrees exactly with laboratory measurements (*8*) of the $0 \rightarrow 1$ transition frequency of CO, proving that the line is due to CO, and the observed elevation dependence shows that it originated in the terrestrial atmosphere. The pressure-broadened half-width of the CO line in the atmosphere is ~ 3 Mhz/mbar, as discussed below, and the observed half-width of ~ 0.3 Mhz shows that the absorption occurred at pressures lower than ~ 0.1 mbar, corresponding to altitudes above ~ 65 km.

The absolute scale for the CO opacity $\Delta\tau_{CO}$ shown in Fig. 1 was determined from the expression

$$\Delta\tau_{CO} = \frac{\Delta T_A e^{m\tau}}{\eta_B T_\odot m} \quad (1)$$

where ΔT_A is the measured antenna temperature, calibrated by observation of sources whose temperatures are known; $T_\odot$ (~ 7000°K) is the 2.6-mm brightness temperature of the sun, based on the data compiled by Linsky (*9*); η_B is beam efficiency (~ 0.78) calculated for the Aerospace antenna when observing the sun at 2.6 mm; m is air mass; and τ is opacity at zenith of the lower atmosphere. (Thermal emission by the atmospheric CO adds another term in the denominator of Eq. 1, but this term is negligible.) The value of τ at the time of the measurement of Fig. 1 was determined to be 0.6 by observing the dependence of solar intensity with air mass. The difference in the values of τ corresponding to the two sidebands of our double-sideband receiver was approximately a factor of 2, based on our calculations and the data of Ulich and Haas (*10*), and was accounted for in determining τ. We estimate the uncertainty in the absolute scale in Fig. 1 to be 10 percent.

The column density of CO above ~ 65 km can be deduced from the measured absorption feature. The absorption coefficient k_ν of this CO transition, within the range of atmospheric temperatures and frequencies ν sensed in our measurement, is

$$k_\nu = 7.4 \times 10^{-9} \frac{N_{CO}}{T^2} f(\nu)\ \text{cm}^{-1} \quad (2)$$

which can be obtained from standard absorption coefficient expressions and the known CO molecular parameters [for example, see (*11*)]. In Eq. 2 N_{CO} is the CO number density in molecules per cubic centimeter, T is temperature in °K, and $f(\nu)$ is the line shape function in seconds, normalized such that $\int f(\nu)d\nu = 1$. Integration of Eq. 2 over frequency and the observation path yields for the CO column density

$$\int N_{CO} dl = 1.4 \times 10^8 \langle T^2 \rangle \int \tau_\nu d\nu \quad (3)$$

where $\int N_{CO} dl$ is in molecules per square centimeter, $\langle T^2 \rangle$ is the average squared temperature of the absorbing CO molecules, $\tau_\nu = \int k_\nu dl$ is the opacity at frequency ν, and $\int \tau_\nu d\nu$ is in reciprocal seconds. The measured value of $\int \tau_\nu d\nu$ corresponding to a zenith observation is $(1.8 \pm 0.2) \times 10^3$ sec^{-1}, which yields for the CO vertical column density above ~ 65 km

$$\int_{h > 65\ \text{km}} N_{CO} dh = (1.0 \pm 0.3) \times 10^{16}\ \text{cm}^{-2}$$

where h is altitude. The uncertainty in the CO column density is due to the ~ 10 percent uncertainty in measurement accuracy and to the uncertainty in the temperature of the absorbing CO, which was assumed to be 200° ± 25°K, based on rocketsonde temperature data up to 70 km in altitude (obtained from the Point Mugu rocketsonde station 50 km northwest of the measurement location) and on model atmospheres above 70 km.

The shape of the absorption line provides information on the vertical distribution of CO. Below ~ 75 km collisional line

broadening dominates and the line width varies by 10^4 from the surface to this altitude. Above ~ 75 km, Doppler (thermal) broadening of the line dominates and the line width is a weak function of altitude. The observed spectral interval of 8 Mhz, and the fact that the CO line is optically thin, implies that our measurement is insignificantly affected by CO below ~ 40 km.

To investigate the implications of the measurement on the vertical distribution of CO, numerical integrations of the radiative transfer equation were performed using various CO profiles and model atmospheres. The Voigt shape was used for the line shape function (*12*). For the collisional half-width we used

$$\Delta\nu_c = 2.4p(300/T)^{0.8}\,\text{Mhz} \qquad (4)$$

where p is the total pressure (millibars) and T is temperature (°K). The numerical coefficient in Eq. 4 is from laboratory measurements of CO broadened by N_2 at 300°K (*13*). The temperature dependence in Eq. 4 is assumed and is typical for collisional line broadening of this type. Standard expressions were used for the Doppler half-width (*11*).

Three CO profiles used in the calculations are shown in Fig. 2; absorption lines calculated for these profiles are shown in Fig. 1. Smoothing by the receiver filters, which decreases the opacity at a line center, was included in the calculations. Up to altitudes of 70 km the temperature and pressure used in the calculations were obtained from Point Mugu rocketsonde measurements made on the same day as our observations. Above 70 km the 30°N July model atmosphere (*14*) was used for temperature and pressure (below 70 km this model agrees well with the rocket measurements). We also performed calculations using the 30°N January model atmosphere (*14*). The difference in the calculated absorption using these two models amounted to ~ 20 percent, which indicates the uncertainty due to temperature.

Above 50 km curve A of Fig. 2 corresponds to Wofsy *et al.*'s calculated CO profile A (*2*), and curve C corresponds to Hays and Olivero's calculated CO profile F (*1*). Below 50 km curves A and C were constrained to smoothly fit the stratospheric CO mixing ratio as measured by other techniques (*7*). Profile A yields too small a CO absorption while profile C yields too large an absorption, compared to the measurement. Furthermore, profile C yields an unproportionally wide absorption line, indicating that C has relatively too much CO at lower altitudes. Profile B was selected to smoothly fit profile A at 60 km and profile C at 100 km and to yield an absorption line consistent with our measurements. Crutzen (*15*) recently calculated a CO profile very similar to B, but having slightly higher values in the altitude range 60 to 80 km.

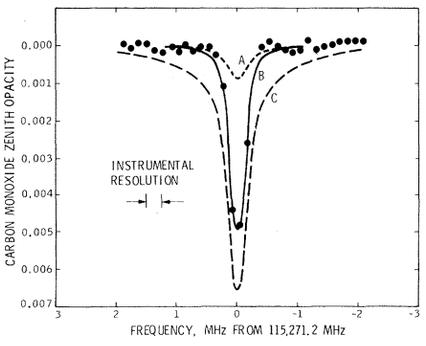

Fig. 1. Measured and calculated CO zenith opacity. The measurements, indicated by points, were obtained on 5 May 1975 between 1 p.m. and 6 p.m. Pacific Standard Time and have been scaled to zenith values. Data points obtained 2 Mhz to either side of the frequency interval shown here were not included since they fell on a straight line within the noise level of the measurement. Curves A, B, and C give calculated absorption for the correspondingly labeled profiles of Fig. 2.

Although profile B in Fig. 2 yields a calculated absorption consistent with our measurements, it should be noted that there is no unique CO profile, particularly above ~ 80 km, corresponding to the measured absorption. However, the requirement that the CO profile be consistent both with our measurement and, at higher altitudes, with results from photochemical calculations that are in good agreement with each other at these altitudes, leads to the conclusion that B should fairly accurately represent the true atmospheric CO profile. This being the case, perhaps the most significant result of our measurement is its implication for vertical transport in the mesosphere. The measurement suggests that at ~ 75 km the eddy diffusion coefficient is $\sim 3 \times 10^5$ cm^2 sec^{-1}, as used by Hays and Olivero and by Crutzen. Below ~ 60 km, where the CO profile is affected by recombination of CO with OH as well as oxidation of CH_4 to form CO, our measurement is consistent with the calculations of Crutzen and of Wofsy *et al.*, which include these effects.

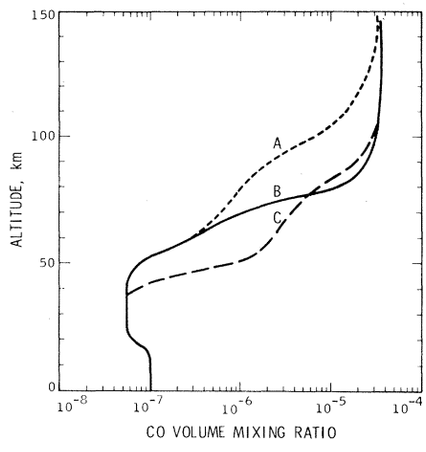

Fig. 2. Carbon monoxide mixing ratio profiles used in calculating the correspondingly labeled spectra in Fig. 1. As discussed in the text, the measurements reported here are principally sensitive to CO at altitudes between ~ 40 and ~ 80 km. Profile B is consistent with our measurements, with measurements by other techniques at lower altitudes, and with reported photochemical calculations for higher altitudes.

Note added in proof. In November 1975, we measured the 115-Ghz CO line in the atmospheric thermal emission spectrum using the Kitt Peak radio telescope of the National Radio Astronomy Observatory. The strength and shape of the measured emission line are consistent with those of the absorption line reported here. This CO line has also been recently measured in the spectrum of Venus and Mars (*16*).

J. W. WATERS
Space Sciences Division, Jet Propulsion Laboratory, Pasadena, California 91103
W. J. WILSON
F. I. SHIMABUKURO
Electronic Research Laboratory, Aerospace Corporation, El Segundo, California 90250

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