

REPLY TO THE PAPER OF MURCRAY ET AL.

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The preceding article by Murcay et al. (1974), entitled "Observations of the Solar Spectrum in the 1800-2100 cm^{-1} Region and the Search for NO Lines", concludes that solar spectra available at this time permit derivation of only an upper limit for the stratospheric NO mixing ratio. However, spectra taken in May, June, and July 1973 by means of balloon- and aircraft-borne spectrometers (Ackerman et al., 1973, 1974; Fontanella et al., 1974) have allowed us to determine the stratospheric abundance of nitric oxide. The sample spectrum shown in Ackerman et al. (1973, 1974) which corresponds to the tracing shown for 22.3 km in Figure 1 does not, of course, present sufficient information to permit the derivation of the published vertical distribution of NO; the whole set of spectra observed by means of the balloon-borne spectrometer flown in May 1973 was used. The spectra available to us will not be published until all the features observed have been satisfactorily interpreted. However, those pertinent to NO have been analyzed, and enable us to briefly report on the abundance of nitric oxide.

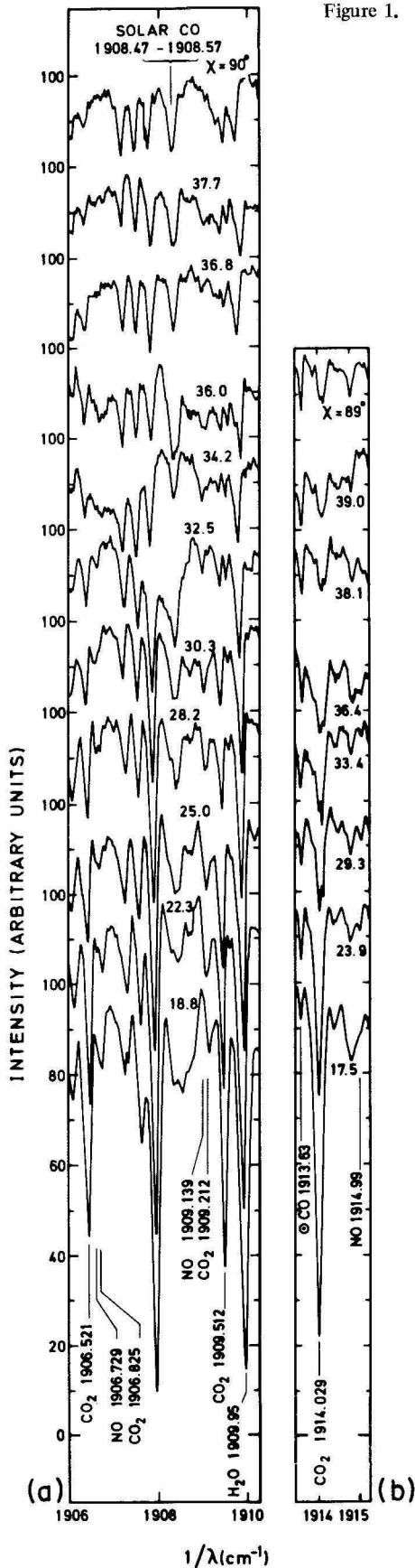
In the spectral range considered (1901.5 to 1915.2 cm^{-1}), many solar and telluric absorption lines occur; interference between several constituents is clearly a problem, particularly when relatively small absorptions have to be quantitatively interpreted. Murcay et al. (1974), considering the effect of CO_2 , state that the inferred NO absorption could be largely traced to CO_2 lines of the $(12^202) - (01^101)$ transitions, whose intensity is 10% of that of the strong CO_2 lines of the $(11^102) - (00^001)$ transitions. The importance of these lines is overstated by Murcay et al., as shown below, and the comparison between the measured and the calculated IR spectra presented by Fontanella et al. (1974) for the conditions of the aircraft measurements at 15 km are not relevant to a criticism of the results published by Ackerman et al. (1973, 1974), which were obtained at 40 km. The integrated absorption cross-sections and positions of the CO_2 lines listed by MacClatchey et al. (1973) are in agreement (within experimental uncertainties) with our measurements, and have been used in our interpretation. Three NO lines, belonging to the R_{11} branch, have been used for the quantitative evaluation of NO in the optical path reported for the balloon experiment by Ackerman et al. (1973, 1974). They occur at 1903.112 cm^{-1} , 1909.139 cm^{-1} and 1914.993 cm^{-1} . They were chosen because

they are the strongest components of the NO doublets considered, and are subject to the least contamination by other absorbers in the spectral range covered by the balloon-borne spectrometer. The NO line at 1903.112 cm^{-1} shows, in addition, a spectral separation from a nearby CO_2 line larger than the instrumental half-width; this can be seen in Figure 4 of the paper by Murcay et al. (1974), where, as stated by those authors, the 30-km, 93° path, temperature, and pressure have been used to approximate the 40-km, 94° path in Ackerman et al. (1973, 1974). The NO line at 1909.139 cm^{-1} is separated by only 0.10 cm^{-1} from the CO_2 line. The NO line is not, however, 10 times less intense than the main CO_2 line at 1909.512 cm^{-1} , as stated by Murcay et al. (1974), but about 70 times less intense. Its integrated absorption cross-section is more than 500,000 times smaller than the integrated absorption of the nearby NO line. For a CO_2 mixing ratio of 3×10^{-4} by volume, the CO_2 line has an absorption equal to the absorption of NO at a NO mixing ratio of the order of 6×10^{-10} . This is a value close to the published number for the altitude of 22.5 km. In addition, as shown in Figure 1a of this reply, the observation of spectra taken at successively larger solar zenith angles is very instructive. While the minimum altitude reached by the solar rays decreases, the absorption at 1909.1 cm^{-1} occurs at the same place and is progressively shifted below 25 km towards the position of the CO_2 line at 1909.2 cm^{-1} , showing the smaller and smaller contribution of NO, whose mixing ratio decreases with decreasing altitude. Above 30 km the NO absorption can be considered as uncontaminated by CO_2 and the quantitative evaluation is quite straightforward. For lower altitudes the CO_2 contribution can be evaluated specifically because the small CO_2 lines beside the main CO_2 lines occur twice as frequently in the spectrum as the NO doublets do.

Finally, no CO_2 line occurs close to the NO line at 1914.993 cm^{-1} . The evolution of this absorption feature from one spectrum to the next is shown in Figure 1b of this reply. The non-uniformly-mixed vertical distribution of NO in the stratosphere observed under the conditions of the balloon experiment is also quite obvious here, as was also concluded by Fontanella et al. (1974) (see their section on NO and Figures 4, 5 and 6).

From the experimental evidence presented here, it should be apparent that the interpretation of the data need not be restricted to setting an upper limit on the

Figure 1. Intensity of solar radiation versus wavenumber recorded by means of the balloon-borne spectrometer (Ackerman et al., 1973).



- a. The spectral region from 1906.0 cm^{-1} to 1910.2 cm^{-1} recorded during sunset is shown. The upper spectrum corresponds to a solar zenith angle, x , of 90° . For each of the other spectra x was larger. The minimum altitude reached by the solar radiation in the atmosphere is also indicated. Two main CO_2 lines are indicated at 1906.521 cm^{-1} and at 1909.512 cm^{-1} . Two small CO_2 lines are also marked at 1906.825 cm^{-1} and at 1909.212 cm^{-1} . According to MacClatchey et al. the integrated absorption is about 20% larger for the first one than for the second one. The first one is obviously resolved from the NO line at 1906.729 cm^{-1} that predominates at 30.3 km. The NO line at 1909.139 cm^{-1} was chosen for the evaluation already published because its integrated absorption is twice as large as that of the line at 1906.729 cm^{-1} . It can be considered as uncontaminated above 30 km, and its presence cannot be ruled out at $x = 90^\circ$ or in the spectrum marked 18.8 km when the CO_2 contribution has been subtracted. Features remaining unchanged throughout the series of spectra are due to solar absorption. Some of them have not yet been identified; identification is in progress, using the spectra taken at higher solar elevations.
- b. The spectral region from 1913.5 cm^{-1} to 1915 cm^{-1} recorded during sunset is shown. The upper spectrum corresponds to a solar zenith angle, x , equal to 89° . For each of the other spectra x was larger than 90° and the minimum altitude reached by the solar radiation in the atmosphere is indicated. The NO line observed at 1914.99 cm^{-1} is not contaminated by CO_2 . It is separated by 0.45 cm^{-1} and by 0.34 cm^{-1} respectively from the two closest CO_2 lines, due to the $(12^202) - (01^101)$ transitions that occur at 1914.541 cm^{-1} and at 1915.328 cm^{-1} . This NO line has not been considered by Murcay et al. in Figure 4 of their paper, where the upper limit of the synthetic spectra is the solar CO line at 1914.73 cm^{-1} . The NO line appears clearly on the spectra at 38.1 km, 36.4 km, 33.4 km, 29.3 km, and 23.9 km, and is detectable at 39.0 km and 17.5 km. The solar CO line observed at 1913.63 cm^{-1} in this figure, and others shown in Figure 1, indicate that the solar absorptions computed by Murcay et al. (1974) under the same conditions as described by Goldman et al. (1973) are overestimated in intensity, and moreover do not represent the observed relative intensity distribution of the solar lines.

NO mixing ratio. It is evident, however, that no firm conclusion could have been derived from the observed spectral range if the resolution had been three times lower, as is the case for the experimental spectra published by Murcay et al. Their spectra yield about 10 times less information because the absorptions are three times less intense and three times less resolved. The situation would have also been less propitious if the observations had been performed from 30 km (as was the case for the experiments reported by Murcay et al.) instead of 40 km, since the geometric factors related to the shape of the earth make the method of limb observation more effective for depression angles of 3 to 5 degrees, corresponding to minimum altitudes of the solar grazing rays that are 10 to 25 km lower than the altitude at which the instrument is flown. For this reason, the availability of 11×10^6 ft³ balloons was important.

In conclusion, we want to emphasize that it is evident from the arguments presented here that Ackerman et al. (1973) had spectra available to them that allowed the determination of stratospheric NO.

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