Stratospheric measurements of continuous absorption near 2400 cm^{-1}

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Solar occultation spectra obtained with a balloon-borne interferometer have been used to study continuous absorption by N_2 and CO_2 near 2400 cm^{-1} in the lower stratosphere. Synthetic continuum transmittances, calculated from published coefficients for far-wing absorption by CO_2 lines and for pressure-induced absorption by the fundamental band of N_2, are in fair agreement with the observed stratospheric values. The continuum close to the ν_3 R-branch band head of CO_2 is sensitive to the CO_2 far-wing line shape. Therefore, given highly accurate knowledge of the N_2 continuum from laboratory data, high-resolution stratospheric spectra provide a sensitive means for *in situ* testing of various air-broadened CO_2 line shapes at low temperatures.

I. Introduction

It is well known that tropospheric absorption spectra obtained over long paths in the atmospheric window near 2400 cm^{-1} are affected by continuous absorption by N_2 and CO_2.[1] Since the optical depth of continuous absorption by both molecules is proportional to the square of atmospheric pressure, the absorption per unit path length will be greatly reduced in the upper atmosphere. However, as pointed out by Farmer and Houghton,[2] appreciable continuous absorption can arise over the long atmospheric paths in a limb-viewing experiment. In this paper we report the measurement of the $N_2 + CO_2$ continuum in a stratospheric solar spectrum obtained during sunset with a balloon-borne Michelson interferometer.

The N_2 and CO_2 continua have different origins. Absorption by CO_2 arises from the superposition of the extreme wings of many distant lines, primarily those of the intense ν_3 fundamental band. Absorption coefficients measured at higher frequencies beyond the ν_3 R-branch band head are much less than those predicted by a Lorentz profile,[3–5] and no theory is available at present that can account for the laboratory data. The (1,0) fundamental band of N_2 has its band origin at 2329.9 cm^{-1}. Absorption from this band is very weak for an isolated N_2 molecule, since the transition dipole moment is zero for homonuclear molecules. However, the pressure in the terrestrial atmosphere is sufficient for appreciable pressure-induced absorption to be detectable in IR experiments over long atmospheric paths.

Accurate knowledge of the absorption properties of both processes is required for several reasons. Continuum absorption will be present in the CO_2 band proposed for remote sensing of atmospheric temperature from satellites and balloon-borne platforms.[6–8] For accurate simulation of atmospheric transmittances measured in the 4.3-μm region, it is necessary to use the proper line shape for CO_2 and to account for absorption by the N_2 continuum.[1,9–11] The atmospheric window in this region is astrophysically interesting because it contains the first-overtone vibration–rotation bands of SiO, which have been observed in late-type stars,[12] and the hydrogen lines Brackett α and Humphreys 14. Spectrophotometry of celestial objects from ground-based observatories is affected by continuous absorption in this spectral region, but the extinction can be accurately accounted for by standard photometric reduction procedures.[13,14]

In this paper transmittances derived from measured stratospheric spectra are compared with synthetic values based on a model atmosphere and laboratory absorption coefficients for the N_2 and CO_2 continuum. It is important to examine the quality of the fit as a necessary check on the accuracy of the extrapolation of the laboratory data for both gases to the low temperatures and pressures of the stratosphere. This comparison is particularly important for establishing the

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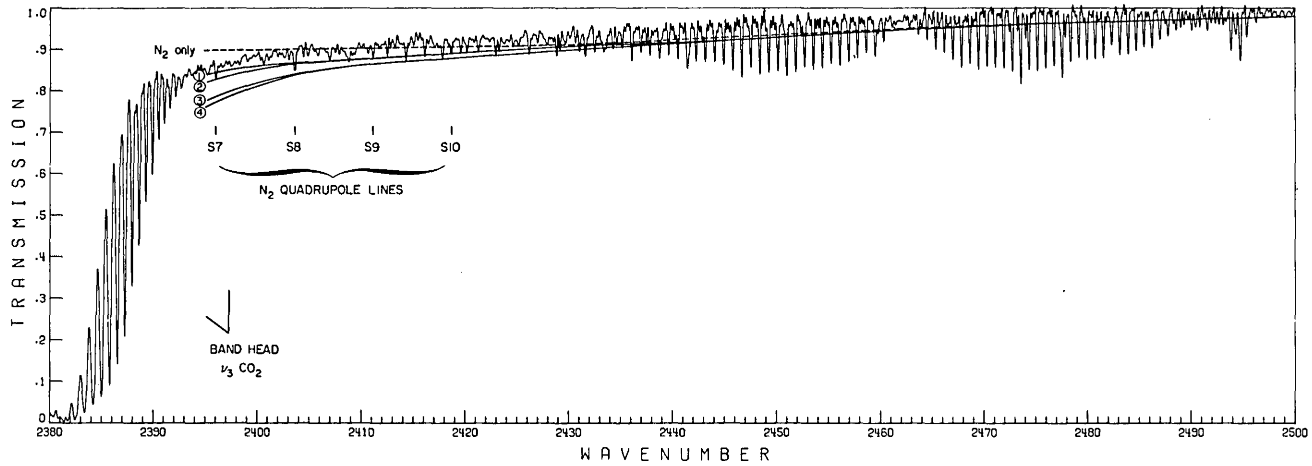

Fig. 1. Comparison of a stratospheric transmittance spectrum obtained from balloon observations (float altitude 37 km) with synthetic monochromatic continuum transmittances. Observed spectrum (resolution 0.13 cm^{-1}) was derived from the point-by-point ratio of a solar-occultation spectrum (mean geometric tangent altitude 21.8 km) to a high-sun spectrum. Dashed curve shows transmittances calculated for N_2 absorption alone, while the smooth solid curves correspond to transmittances calculated for N_2 continuum absorption and sub-Lorentzian far-wing absorption by CO_2 (see text). Location of the ν_3 $^{12}C^{16}O_2$ R-branch band head and several of the stronger lines of the S-branch of the N_2 (1,0) quadrupole spectrum are marked.

temperature-dependence of the air-broadened far-wing CO_2 line shape in the 4.3-μm region, since linewidths in this spectral region have not been measured in the laboratory below room temperature.

II. Observations

The observational data were obtained with a Michelson interferometer during a balloon flight near Palestine, Tex., 18 May 1976. Several low air-mass solar absorption spectra were recorded prior to sunset, and ten were obtained during sunset from a float altitude of 37 km and at an unapodized resolution of 0.13 cm^{-1}. Experimental details of the flight and trace gas mixing ratio profiles deduced from the spectra have been published.[15]

Figure 1 is an atmospheric transmittance spectrum in the 2380–2500-cm^{-1} region. The transmittances were calculated from the point-by-point ratio of the amplitudes in a spectrum recorded at a mean solar zenith angle of 94.0° (corresponding to a geometric tangent altitude of 21.8 km) to the values recorded in a high-sun spectrum. This procedure eliminates the variation with wavelength of the solar flux and of the interferometer–filter–detector system. Removal of these effects is essential for measurement of the relatively weak continuous absorption present in this spectral region. The background level of the transmittance spectrum has been normalized to unity near 2610 cm^{-1}, where continuous absorption is negligible and line absorption is sufficiently small that the background level can be established. We estimate that the transmittances are accurate to $\sim$1%. The curves also plotted in Fig. 1 will be discussed in a later section.

From the observational data it can be seen that telluric line absorption is relatively weak between 2400 and 2500 cm^{-1}. The strongest lines in Fig. 1 arise from the $\nu_1 + 2\nu_2^0$ band of N_2O (center at 2462 cm^{-1}), the $\nu_1 + \nu_3 - 2\nu_2^0$ band of CO_2 (center at 2429 cm^{-1}), and the $2\nu_4$ band of CH_4 (center at 2612 cm^{-1}). In the figure we have marked the positions of the strongest lines of the S branch of the N_2 (1,0) quadrupole vibration–rotation band, which have also been identified by Goldman *et al.*[16] in aircraft and ground-based spectra.

III. Calculations

For comparison with the stratospheric observations, we have calculated the continuous opacity of N_2 and CO_2 at 5-cm^{-1} intervals between 2395 and 2500 cm^{-1} using a multilayered atmospheric model. The pressure and temperature profiles of Farmer *et al.*[15] were assumed along with constant volume mixing ratios for CO_2 and N_2 of 0.000325 and 0.781, respectively. Slant paths were computed including the effects of refraction. The continuum calculations were not extended to wave numbers of <2395 cm^{-1} because of the onset of strong absorption by high-J lines of the ν_3 fundamental band of CO_2. The strength of the continuum is difficult to determine within the band head because of the strong temperature dependence of the absorption coefficients of these lines. The effects of continuous absorption within the CO_2 band head on retrievals of stratospheric temperature and pressure are discussed by Park *et al.*[17]

In our calculations we have assumed that continuous absorption by H_2O and aerosol extinction are negligible. Although water vapor polymers may form at stratospheric temperatures and absorb in this spectral region,[18] the concentration of H_2O in the stratosphere is too low for monomer or polymer continuum absorption to be detectable even over long atmospheric paths. Similarly, in the absence of major volcanic eruptions, stratospheric aerosol extinction in the 4.3-μm region is quite small.[19]

A. N_2 Absorption

Laboratory measurements[2,20-23] indicate that the optical depth of pressure-induced absorption by N_2 is proportional to the square of the density at constant temperature. For a homogeneous atmospheric path of length l the optical depth of N_2 absorption at wave number ν can be written

$$\tau_\nu(N_2) = k_{\nu,\mathrm{eff}}(N_2)\rho^2 l, \tag{1}$$

where $k_{\nu,\mathrm{eff}}(N_2)$ is the effective absorption coefficient of air (km^{-1} amagat^{-2}) for N_2 absorption at wave number ν, and ρ is the atmospheric density in amagats.

In our calculations we have adopted the absorption coefficients presented by Burch *et al.*[22] in their Fig. 3-3. These results are based on an extrapolation to 230 K of their measurements at four temperatures between 280 and 457 K. The absorption coefficients have been calculated for an atmospheric path and account for the mixing ratio of N_2 in air (0.781 by volume) and assume that the ratio of the foreign to self-broadened absorption coefficients is 0.95, a value derived for this spectral interval at room temperature. The temperature of the extrapolated coefficients (230 K) is close to the temperature of the lower stratosphere where most of the absorption occurs in the spectrum considered here. Since the extrapolated coefficients do not extend below 2400 cm^{-1}, we assume that the absorption coefficient at 230 K is the same at 2395 cm^{-1} as at 2400 cm^{-1}. Both the Burch *et al.*[22] and Shapiro and Gush[21] room temperature data indicate that the N_2 absorption coefficients are nearly the same at these two wave numbers.

B. CO_2 Absorption

In the literature the sub-Lorentzian absorption coefficient in the distant wing of a CO_2 line has been expressed by an empirical modified Lorentz line shape function

$$\kappa_\nu = \frac{S}{\pi} \frac{\alpha\chi(|\nu - \nu_0|)}{(\nu - \nu_0)^2 + \alpha^2}, \tag{2}$$

where S is the line strength, α is the Lorentz halfwidth, ν_0 is the wave number at line center (cm^{-1}), and χ is an empirical form factor, which is assumed to be the same for all lines and a function of $|\nu - \nu_0|$ only. Near the line center both theoretical and laboratory studies indicate that χ is close to unity.[24,25]

Laboratory data[3-5] and ground-based and airborne atmospheric transmittance spectra[10,26] have been used to deduce the functional form of $\chi(|\nu - \nu_0|)$ in the 2400-cm^{-1} region. Since all the laboratory data for this region were obtained at room temperature, it is not known whether $\chi(|\nu - \nu_0|)$ is truly independent of temperature. In the 7000-cm^{-1} region the measurements of Burch *et al.*[4] indicate that the form factor for N_2-broadened CO_2 is less at elevated temperatures than at room temperature.

We have calculated CO_2 absorption coefficients with four different N_2-broadened sub-Lorentzian line shape forms,[3-5,26] a $T^{-0.75}$ dependence of the collisional halfwidths for all lines,[27] and CO_2 line parameters from the most recent update of the AFGL compilation.[28] The values of $\chi(|\nu - \nu_0|)$ were determined from analytical expressions[3,26] or were read from graphs presented by the authors.[4,5]

In our computations we have included a total of 10,248 carbon dioxide lines between 2200 and 2450 cm^{-1} with $S \geq 10^{-26}$ cm^{-1}/molecule cm^{-2} at 296 K. The temperature dependence of the line strengths has been calculated from the standard relation[29]; the total internal partition function values of Gray and Young[30] were adopted. Normalization of the line shape function requires $S = \int k_\nu d\nu$; for lower stratospheric conditions this relation is satisfied to better than 0.1% with all four far-wing line shape functions. As noted by Bernstein *et al.*,[31] most of the absorption beyond the band head at room temperature and reduced temperatures is contributed by the tails of distant lines near the intensity maximum of the R branch of the intense ν_3 band. At 230 K the contribution of all lines from weaker CO_2 bands is only ~2% of the total absorption near 2400 cm^{-1}. If the absorption coefficients of all lines are calculated with a $T^{-0.5}$ dependence of the Lorentz halfwidth rather than $T^{-0.75}$, the absorption coefficients at 230 K are 10% lower.

In Fig. 2 are plotted CO_2 absorption coefficients (cm^{-1} atm^{-1}) for pure CO_2 at 230 K. For all four sub-Lorentzian line shapes, the absorption decreases rapidly to higher wave numbers beyond the CO_2 band head. The absorption coefficients are larger at 230 K than at 296 K because the Lorentz halfwidth is larger at the lower temperature and because of the temperature dependence of the line strengths. Absorption coefficients calculated with the Winters *et al.*[3] and with the Cann *et al.*[5] line shapes (curves 1 and 2, respectively, of Fig. 2) are almost equal in magnitude and are ~2.5 times larger at 2400 cm^{-1} than absorption coefficients computed with the Susskind and Mo[26] (curve 3 of Fig. 2) and Burch *et al.*[4] (curve 4 of Fig. 2) line shapes.

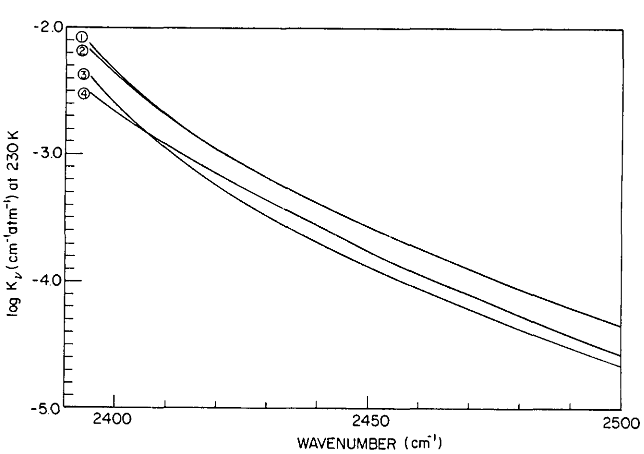

Fig. 2. Absorption coefficients for continuous absorption by pure CO_2 at 230 K. Curves correspond to different far-wing line shapes (see text).

IV. Comparison Between Observed and Calculated Transmittance

The results of our calculations are presented in Fig. 1 along with the observed transmittance spectrum. The solid curves are synthetic monochromatic $CO_2 + N_2$ continuum transmittances calculated with the four different CO_2 line shape functions. Values are also shown for N_2 absorption only (dashed line). For convenience, the results of the calculations and the observed continuum transmittances are listed in Table I. The observed continuum transmittance values have been derived by drawing a smooth curve across the upper envelope of the transmittance spectrum including in the fit only regions where discrete line absorption is small.

The calculations provide further evidence that the primary component of the continuous absorption throughout most of the window region is N_2. The CO_2 contribution is small at frequencies greater than $\sim$2440 cm^{-1} but rises rapidly with decreasing wave number and is approximately equal to the N_2 contribution at the CO_2 band head. At frequencies $>$2415 cm^{-1}, transmittances calculated with different line shape functions differ by $<$0.01, but at 2395 cm^{-1} there is a range of 0.075 in the transmittance values.

Although the observed and calculated transmittances are in fair agreement, the calculated absorption values are on the average $\sim$0.02 higher than the observed values in the spectral region dominated by N_2 absorption (2430–2500 cm^{-1}). Although the true wavelength dependence of the measured continuum is difficult to determine beyond 2450 cm^{-1} because of the small magnitude of this absorption, there is some suggestion that the observed N_2 continuum absorption decreases more rapidly with wave number than is predicted from the absorption coefficients extrapolated to 230 K by Burch *et al.*[22] The low temperature (77 K) measurements of Sheng and Ewing[23] indicate that continuous absorption by N_2 falls off more sharply with increasing wave number as the temperature is lowered. We are currently calculating the N_2 absorption coefficient at stratospheric temperatures making use of both the Sheng and Ewing[23] low temperature measurements and the Burch *et al.*[22] measurements near room temperature and at elevated temperatures.

In the region near the CO_2 band head, the shape of the continuum is dominated by the overlapping far wings of the strong ν_3 absorption lines and is very sensitive to the sub-Lorentzian line shape assumed in the calculations. Transmittances calculated with the Burch *et al.*[4] and Susskind and Mo[26] form factors (curves 1 and 2, respectively, in Fig. 1) are quite close to the observed values, while the line shapes of Cann *et al.*[5] and Winters *et al.*[3] (curves 3 and 4) lead to transmittances that considerably overestimate the absorption in the band head region. It is impossible, however, to determine unambiguously the appropriate CO_2 form factor from our data at this time without first making the most accurate possible determination of the N_2 absorption coefficients in this region. Laboratory measurements of the N_2 continuum at stratospheric temperatures will make it possible to use high-resolution stratospheric solar-occultation spectra to determine accurately the CO_2 far-wing line shape in the 4-μm region at low temperature.

V. Comparison with Upper Tropospheric Measurements

Recently Bernstein *et al.*[31] have presented measurements of atmospheric transmittance in the 4.0–5.3-μm region obtained with a Michelson interferometer (resolution = 3.8 cm^{-1}) from altitudes of 5.48, 8.53, and

Table I. Observed and Calculated Continuum Transmittances

Wave number (cm^{-1})	Observed	$N_2 + CO_2$ with different form factors				N_2 only
		Burch	Winters	Susskind	Cann	
2395.0	0.853	0.838	0.763	0.820	0.774	0.897
2400.0	0.885	0.856	0.813	0.850	0.817	0.897
2405.0	0.900	0.867	0.841	0.867	0.843	0.899
2410.0	0.909	0.876	0.860	0.878	0.860	0.900
2415.0	0.916	0.883	0.873	0.886	0.873	0.902
2420.0	0.926	0.890	0.882	0.892	0.882	0.904
2425.0	0.931	0.896	0.890	0.898	0.890	0.907
2430.0	0.937	0.902	0.898	0.904	0.898	0.910
2435.0	0.944	0.909	0.906	0.910	0.905	0.916
2440.0	0.951	0.916	0.914	0.917	0.913	0.922
2445.0	0.956	0.924	0.922	0.925	0.922	0.929
2450.0	0.961	0.932	0.930	0.932	0.930	0.935
2455.0	0.965	0.938	0.937	0.939	0.937	0.941
2460.0	0.970	0.945	0.944	0.946	0.944	0.948
2465.0	0.973	0.952	0.951	0.952	0.951	0.954
2470.0	0.980	0.957	0.957	0.958	0.956	0.959
2475.0	0.985	0.963	0.962	0.963	0.962	0.964
2480.0	0.985	0.967	0.966	0.967	0.966	0.968
2485.0	0.985	0.970	0.970	0.971	0.970	0.971
2490.0	0.985	0.973	0.973	0.973	0.973	0.974
2495.0	0.985	0.976	0.975	0.976	0.975	0.977
2500.0	0.985	0.979	0.978	0.979	0.978	0.979

12.2 km. Transmittances were determined from solar spectra by assuming that atmospheric absorption is negligible at 2031 and 2710 cm^{-1} and correcting for the wavelength dependence of the solar flux and instrument response function.

Their data in the 2390–2500-cm^{-1} region are particularly interesting. As expected, the absorption across the interval decreases with increasing wave number in the 5.48-km altitude spectrum but appears to increase with increasing wave number for the spectra obtained from higher altitudes. The change of the slope across this interval at higher altitudes is not confirmed by our measurements and may have resulted from errors in the removal of the instrumental and solar response functions. We note that the sharp absorption feature observed by Bernstein *et al.*[31] near 4.05 μm is a solar line and identify it as Brackett α of atomic hydrogen at 2467.8 cm^{-1}. Ground-based spectra[32,33] have led to the same assignment for this line. Several weaker Fraunhofer lines are also present in this spectral region.

VI. Summary

We have presented the first stratospheric measurements of continuous absorption by N_2 and CO_2 in the atmospheric window near 2400 cm^{-1}. The detection and accurate measurement of the wavelength dependence of this continuum between 2400 and 2500 cm^{-1} were made possible by the long-path advantage of a solar occultation experiment and by the capability to remove the wavelength dependence of the instrument response and solar flux by ratioing the amplitudes to those of a high-sun spectrum.

The comparison of these measured transmittances to calculated values, based on laboratory measurements, has shown that while there is fair agreement between observed and calculated values, the wavelength dependence of N_2 absorption coefficients at stratospheric temperatures needs to be measured in the laboratory. If the shape of the N_2 continuum at low temperatures can be determined accurately through laboratory measurements, high-resolution stratospheric solar occultation spectra such as the one we have presented here may then be used to infer air-broadened far-wing CO_2 line shape in the ν_3 band head region at low temperatures.

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