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ANNUAL TECHNICAL SUMMARY REPORT

EXPERIMENTAL INVESTIGATION OF THE INFRARED ABSORPTION BY ATMOSPHERIC GASES

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SECTION 1

INTRODUCTION AND SUMMARY

This report summarizes work done under Contract NOnr 3560(00) during the period 1 May 1966 through 31 July 1967. Section 2 contains a brief description of four experiments which are complete, or nearly complete, but have not yet been reported. Abstracts of reports and papers published during the report period are presented in Section 3.

SECTION 2

WORK NOT REPORTED

SHAPES OF THE EXTREME WINGS OF CO_2 ABSORPTION LINES

Data obtained previously on the absorption by CO_2 in the regions above the heads of the 1.4 μ, 2.7 μ, and 4.3 μ bands have been analyzed. We have found from these data that the extreme wings of collision-broadened CO_2 lines absorb much less than would be expected from Lorentz shaped lines. The absorption in the wings is also quite different for the different broadening gases studied, CO_2, N_2, O_2, A, He, and H_2. The shapes are different in different spectral regions and vary with temperature in a manner which cannot be explained by existing theories. All the figures have been drawn and a rough draft of the text of a paper has been completed.

ABSORPTION BY H_2O BETWEEN 0.8 AND 1 MICRON

Measurements have been made on the absorption in the 0.8 - 1 micron region by H_2O samples with paths up to more than one kilometer. These data are intended to supplement those in a previous report (U-3704). The previous

data were particularly useful in determining band and line strengths, while the recent results are valuable in determining line widths and in calculating the absorption over long atmospheric paths. The relative broadening of H_2O lines by H_2O, N_2, O_2 and CO_2 was also investigated. Nearly all the data have been analyzed and a report has been started.

ABSORPTION BY N_2O AND CH_4

Measurements on N_2O samples covering wide ranges of pressures and absorber thicknesses have been made between 1.3 and 2.5 microns and from 6 to 9 microns. The strengths of the major bands and the half-widths of several lines have been determined. Several spectral curves have also been obtained for CH_4 absorption over extremely long atmospheric paths. The reduction and analysis of these data are approximately 80% complete.

ABSORPTION BY H_2O IN THE 8-12 MICRON WINDOW

The 30 meter multiple-pass absorption cell has been employed to measure the attenuation by H_2O in the 8-12 micron atmospheric window. There is considerable attenuation by the "continuum" which arises from the extreme wings of lines whose centers occur on either side of this region. The attenuation of 10.6 μ laser radiation by H_2O is as great as, or greater than, the attenuation by CO_2. Our preliminary results indicate that most of the continuum absorption is due to self-broadened H_2O lines, even though the N_2 pressure may be one hundred times as great as the H_2O pressure. Therefore, the H_2O attenuation coefficient is approximately proportional to the H_2O pressure, making the attenuation proportional to the square of the H_2O pressure. It is apparent that the usual band models employed in other spectral regions would not be applicable. Most of the measurements will be repeated since they are difficult to make and are subject to considerable error.

SECTION 3

ABSTRACTS OF REPORTS AND PAPERS

"Absorption by H_2O Between 5045-14,485 cm^{-1} (0.69-1.98 Microns)," by Darrell E. Burch and David A. Gryvnak.

The absorption by water vapor in six spectral regions within 5045-14485 cm^{-1} (1.98-0.69 μ) has been investigated. Samples at high pressures are pre-

sented to provide data from which line strengths and band strengths can be determined, while samples at lower pressures provide information from which line widths can be found. Transmission spectra are shown along with extensive tables of transmittance, integrated absorptance, and integrated absorption coefficient. The integrated absorption coefficients in cm^{-1} gm^{-1} cm^2 were found to be as follows: 5045-5670 cm^{-1}, 3.16 ± 0.16 x 10^4; 6640-7700 cm^{-1}, 2.54 ± 0.13 x 10^4; 8560-9030 cm^{-1}, 1.66 ± 0.08 x 10^3; 9940-11,420 cm^{-1}, 895 ± 50; 11,795-12,765 cm^{-1}, 57.2 ± 2.7; and 11,905-14,485 cm^{-1}, 56.1 ± 2.8. (key words - H_2O, infrared, absorption, and band strength)

"Absorption by CO_2 Between 1800 and 2850 cm^{-1} (3.5-5.6 Microns)," by David A. Gryvnak, Richard R. Patty, Darrell E. Burch, and Earl E. Miller.

Transmission spectra in the 1800-2850 cm^{-1} region have been obtained for more than 100 samples of CO_2 and CO_2 mixed with N_2 and A. The spectral resolution was 2.5 cm^{-1}. Sample pressures varied from 0.0055 to 742 torr with absorber thicknesses covering the range from 0.081 to 84,400 atm cm_{STP}. Spectra of several samples at the lower pressures show the effect of Doppler broadening. Measurements in the 2400-2560 cm^{-1} region provide information about the absorption by the extreme wings of collision-broadened lines. Replotted transmission spectra and extensive tables of integrated absorptance for 116 samples are included. (key words - CO_2, infrared, absorption, Doppler broadening, and collision broadening)

"Absorption by CO_2 Between 7125 and 8000 cm^{-1} (1.25-1.40 Microns)," by Darrell E. Burch, David A. Gryvnak, and Richard R. Patty.

Transmission spectra in the 7125-8000 cm^{-1} region have been obtained for CO_2 samples with absorber thicknesses as great as 2.18 x 10^5 atm cm_{STP}. Three absorption bands not observed previously have been identified, and the strengths of several bands have been determined. Transmission spectra and a table of integrated absorptance versus wavenumber are included for five representative samples. (key words - CO_2, infrared absorption, and band strengths)

"Strengths, Widths, and Shapes of the Lines of the 3 µ CO Band," by Darrell E. Burch and David A. Gryvnak.

Spectral curves of several CO samples have been used to investigate the 3 µ band whose center is near 6350 cm^{-1}. The strength of the band for the common $C^{12}O^{16}$ isotope has been found to be 0.0130 ± 0.0005 atm^{-1} cm^{-1}_{STP} cm^{-1}. An empirical equation, $F_m = 1 - 0.011$ m has been derived to account for the influence of vibration-rotation on line strengths. The half-widths of the self-broadened lines at 1 atm pressure vary from

approximately 0.090 cm^{-1} at $|m|=1$ to 0.062 cm^{-1} at $|m|=20$. The widths of self-broadened lines are 1.08 ± 0.005 times as great as N_2-broadened lines at the same pressure. The Lorentz line shape appears to be appropriate for the collision-broadened lines within a few cm^{-1} of their centers; but the extreme wings of the lines are sub-Lorentzian. (key words - CO, band strength, line strengths, line width, and line shapes)

"Absorption by CO_2 Between 3100 and 4050 cm^{-1} (2.5-3.2 Microns)," by Darrell E. Burch, David A. Gryvnak, and Richard R. Patty.

Transmission spectra between 3100 and 4050 cm^{-1} have been obtained for 26 samples of CO_2 and CO_2 + N_2. Absorber thicknesses have varied from approximately 1 to 200,000 atm cm with pressures from about 0.01 to 15 atm. The strengths of the more important bands, including some not previously observed, have been determined. Spectral features due to several other less-important bands have also been identified. Replotted transmission spectra and extensive tables of integrated absorptance for several samples are included. (key words - CO_2, infrared, absorption, and band strengths)

"Absorption of Infrared Radiation by CO_2 and H_2O. I. Experimental Techniques," by Darrell E. Burch, David A. Gryvnak, and Richard R. Patty.

The experimental techniques used in an extensive laboratory investigation of the infrared absorption and emission by CO_2 and H_2O are described. Apparatus discussed include two multiple-pass absorption cells with base lengths of approximately one and 29 meters, gas-handling systems, a prism spectrometer and a grating spectrometer with their accessories, and a system used to digitize absorption spectra. Also discussed are methods used in gas sampling, checking for possible sources of error, and recording and analyzing the data. Detailed results and discussions of data are planned for subsequent papers in this series. (key words - H_2O, CO_2, absorption cells, and spectrometer)