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IITRI Report V6048-25
(Quarterly Report No. 25)

RADIATIVE ENERGY TRANSFER ON ENTRY INTO MARS AND VENUS

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Submitted by

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for

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Office of Advanced Research and Technology
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FOREWORD

This report was prepared by the IIT Research Institute, Chicago, Illinois, for NASA Contract NASr-65(01). The contract is monitored by Dr. John Howe of the Office of Advanced Research and Technology, NASA Headquarters, Washington, D. C. In this report, integrated absorption values for some infrared bands of C_2H_4, C_2H_6, CF_4, and SO_2 are presented. The principal investigator at IIT Research Institute is Mr. William O. Davies. Mr. J. W. Helbron has assisted in the research.

Respectfully submitted,

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ABSTRACT

The integrated absorption has been measured for several strong bands of ethylene, ethane, tetrafluoromethane (carbon tetrafluoride), and sulfur dioxide in the 6 to 8 μ spectral region. The bands were pressure-broadened with helium; the absorption was determined from the slopes of Beer's Law plots of observed absorption vs optical density. The values obtained in this study are compared where possible with previous measurements.

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I. INTRODUCTION

The measurements of integrated absorption values for four infrared bands of several gases are presented in this report. These include (1) the C_2H_4 ν_{12} band, (2) the $C_2H_6(\nu_6 + \nu_8)$ combination band, (3) the $CF_4(\nu_1 + \nu_4)$ combination band, and (4) the SO_2 ν_3 band. The values of the integrated absorption were determined from measurements of the infrared spectral transmission by integrating over the region of measureable absorption. The absorber partial pressure and total gas pressure were chosen to avoid saturation effects and to provide sufficient rotational line broadening that the entire band strength can be measured. Both of these factors were determined experimentally. The apparent integrated absorption was then determined for several optical densities, and the data fit to a Beer's Law plot. The best values of integrated absorption were obtained from the slopes of these plots using a least squares method.

The spectrophotometer system used for these measurements was previously described.(1) An ac infrared source is provided by chopping the radiation from either a globar or blackbody cavity. The radiation is passed through an absorption cell and to a monochromator. The output from the detector is converted to a dc signal with a phase lock amplifier coupled to the chopping frequency, and this signal is displayed on a chart recorder.

The best values for integrated absorption these four bands are:

$C_2H_4\ \nu_{12}$	47 atm^{-1} cm^{-2}
$C_2H_6(\nu_6 + \nu_8)$	76 atm^{-1} cm^{-2}
$CF_4(\nu_1 + \nu_4)$	27 atm^{-1} cm^{-2}
$SO_2\ \nu_3$	578 atm^{-1} cm^{-2}

These results are compared to previous measurements where possible.

II. OBSERVATIONS

The experimental arrangement for the absorption measurements consists of an infrared source, absorption cell, monochromator, detector, and recording system (Fig. 1). The measurements presented here were made with an absorption cell of two cm path length. A Perkin-Elmer Model 83 infrared monochromator with a NaCl prism was used. The detector was a liquid nitrogen cooled photoconductive Ge:Au cell, biased for optimum detectivity. The output signal from this cell is amplified and fed into a lock-in amplifier. This amplifier is essentially a narrow band-pass filter whose center frequency is adjustable to that of the chopper. A reference signal is furnished to the amplifier by a lamp and photodiode arrangement which monitors the chopping frequency. The amplifier locks-in on this frequency and provides a dc signal that can be reproduced on a chart recorder.

Absorption measurements were made on infrared bands of four molecules in the spectral region from six to eight microns. These include (1) $C_2H_4\ \nu_{12}$ band at 1444 cm^{-1} (6.93 μ), (2) the $C_2H_6(\nu_6 + \nu_8)$combination band at 1450 cm^{-1} (6.73 μ), (3) the $CF_4\ (\nu_1 + \nu_4)$ combination band at 1535 cm^{-1} (6.51 u), and (4) the $SO_2\ \nu_3$ band at 1361 cm^{-1} (7.35 μ). Absorption measurements were made over a range of optical paths up to 10 atm-cm at the wavelengths of strongest absorption to determine the optical paths required to avoid saturation.

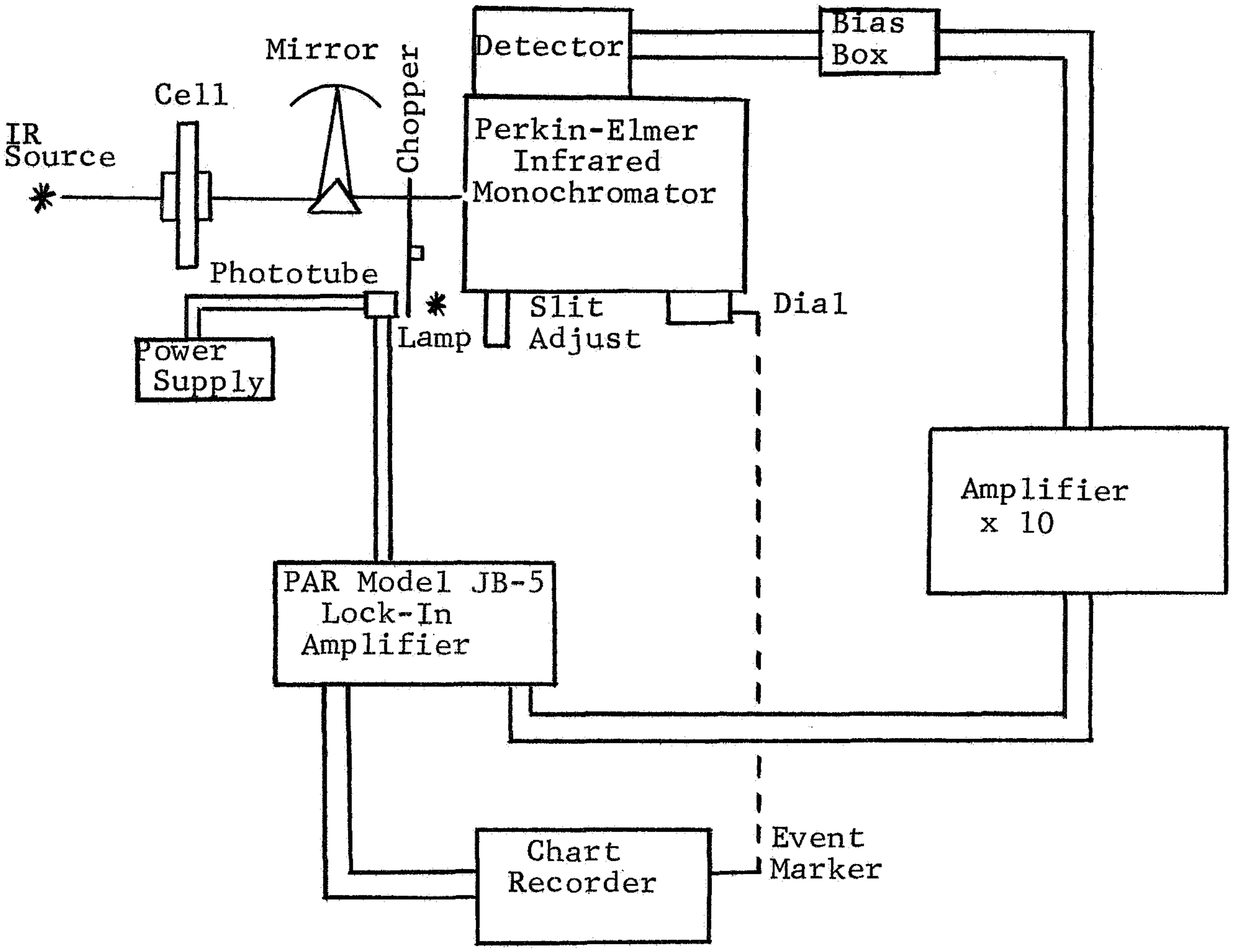

Fig. 1 Schematic/Flow Diagram for Absorption Cell Measurements

The band absorption was measured over a range of total gas pressures from 0.5 atm to 14.6 atm (200 psig) to select total pressures that provided adequate pressure broadening. Helium was used as the broadening gas. The pressure used for the integrated absorption measurements was 14.6 atm for all bands, even though preliminary investigations indicated that broadening was complete for some bands at pressures lower than 200 psig.

III. RESULTS AND DISCUSSION

The determination of the integrated absorption requires that the rotational lines be sufficiently broadened that the entire strength of the absorption band can be measured, and the absorber path length be chosen to avoid saturation effects. Measurements were made to insure that both of these criteria were satisfied. The selection of the proper absorber concentration can be based on observations of the strongest part of the band. The fractional absorption is determined as a function of absorber path length, and a region identified for which this absorption is linear with the absorber concentration. It can then be assumed that no saturation occurs in weaker parts of the band.

If the measured absorption is to reflect the entire strength of the band, a sufficiently high total gas pressure must be used to ensure broadening of the rotational lines. The required pressure depends on the relative values of line width and spacing, and will therefore be somewhat different for each gas. It is, to a lesser degree, dependent on the foreign gas used to provide the rotational line broadening, because the collision diameter is different for the various broadeners. The pressure required to broaden the absorber gas with a particular foreign gas can be determined by observing the absorption as a function of pressure with a constant absorber partial pressure. The variation of the quantity $\int I/I_o \, d\omega$ as a function of total gas pressure was measured for these bands and it was determined that all were completely broadened at the pressure used.

These two sets of preliminary measurements were used to select the experimental conditions for measuring the integrated absorption of the bands. These measurements were made at a total pressure of 14.6 atm. The integrated absorptions were determined from a plot of $\ell n\ I_o/I$ vs ω . The area under this curve was measured with a compensating polar planimeter. A Beer's Law plot was then made of $\alpha p\ell$ vs $p\ell$, where $\alpha = 1/p\ell \int \ell n\ I_o/I\, d\omega$ and $p\ell$ is the optical density in atmosphere-centimeters. A least squares calculation was made from the data in the Beer's Law plot to determine the best value of integrated absorption. The integrated absorption values obtained from these measurements are summarized in Table I, and compared to previous measurements.

On the basis of the observations presented here, it is concluded that:

(1) The integrated absorption of the $C_2H_4\ \nu_{12}$ band obtained in this study is in agreement with that given by Golike (2) et al and Hammer(3) within experimental error, but considerably less than that given by Thorndike.(4) As previously noted(1) in the discussion of the $C_2H_4\ \nu_3$ band, Golike et al, suggested that improvements in the knowledge of the vibrational spectrum of ethylene and infrared techniques accomplished since the time of Thorndike's measurements (1947), were expected to yield a more reliable value for the integrated absorption.

Their value does differ from both Thorndike et al, and dispersion measurements. If the experimental techniques and instruments are sufficiently improved to affect the C_2H_4 band, then the C_2H_6 bands might be expected to be similarly affected; such is not the case.

(2) The integrated absorption of the $C_2H_6(\nu_6 + \nu_8)$ combination band is in excellent agreement with the values of Thorndike(5) and Nyquist et al.(6)

(3) An examination of the literature provided no values for comparison with the CF_4 and SO_2 integrated absorption. Some work has been done on the fundamental bands of CF_4 by Schatz and Hornig,(7) but apparently none on the combination band.

The sources of error in experimental determinations of integrated absorption may generally be divided into three categories:(8) (a) sampling errors, (b) recording errors, and (c) measurements errors.

(a) Sampling Errors --- these errors can be caused by adsorption of gas on the cell walls, accuracy of measuring pressures, and improper mixing of the test gas with the broadening gas. The effects of adsorption of gas on the cell walls are not known precisely for these experiments. Based on the discussions of Burch et al ,(8) it is believed that these effects were less then those due to other causes. Burch et al, found that the mixing in short path length cells was complete within a few seconds, but that several minutes mixing time was required for cells having valves that were joined to the cells by several inches of tubing, and was probably due to slow diffusion through small-bore tubing. During the course of the present measurements, at least five minutes mixing time was allowed before any scans were made. Another scan was made several minutes later and a comparison of the two scans revealed no significant differences in the traces. Gauge errors were less than five percent for all gases tested except SO_2. Since the measurements of SO_2 required low values of partial pressure for values of optimum optical density, the gauge errors were probably between ten and fifteen percent.

(b) Recording Errors --- the primary sources of error in the recording system are source drifts and noise fluctuations in the equipment. Both globars and black body cavities have been used as the IR source. The black body cavity was more stable over long periods and was used for the measurements on C_2H_4 and C_2H_6. Because of a breakdown in the black body control unit a globar was used for the other measurements. Since a background scan must first be obtained and then followed by a test scan, the background scan must be transposed onto the test gas scan in order to obtain the ratio I_o/I. Any drifts of the source which occur during this period would contribute significantly to the recording errors. Care was taken to insure that measurements were made only after the source has been on for four or more hours. Measurements of drift made over relatively long periods of time indicate that stability is improved if the source is allowed to remain operational for several hours. A drift of the chart recorder zero level constitute a possible source of error, although this feature was checked often. Since total absorption is independent of slit width,(8) a sufficiently large slit was used to increase the signal-to-noise ratio.

(c) Measurement Errors --- determination of the values of I_o/I from the chart recorder traces and the actual area measurement with the planimeter are not considered major sources of error in this present study. The contribution of these error sources to the integrated absorption were evaluated at no greater than one percent. If a drift were encountered during the course of a scan, a significant error could be introduced when determining the I_o/I ratio. To serve as a check on this problem, frequent background scans were made and compared.

Based upon the above discussions, the total error for measurements of C_2H_4, C_2H_6, and CF_4 is estimated at ± 10 percent. For measurements of SO_2, the error is estimated at ± 15 percent.

TABLE I

INTEGRATED ABSORPTION

(atm^{-1} cm^{-2})

C_2H_4 ν_{12} Band				$C_2H_6(\nu_6 + \nu_8)$ Band		
Golike, *et al*[2] 1956	Hammer[3] 1951	Thorndike, *et al*[4] 1947	Present Study 1968	Thorndike[5] 1947	Nyquist, *et al*[6] 1957	Present Study 1968
44	51	70	47	76	78	76

$CF_4(\nu_1 + \nu_4)$ Band	SO_2 ν_3 Band
Present Study 1968	Present Study 1968
27	578

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