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INFRARED RADIATION MEASUREMENTS OF COMBUSTION GASES

by

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SUMMARY

Spectral absorption measurements of CO at 1200° K were carried out at pressures of 0.5, 1, 2 and 3 atmospheres and optical path lengths of 5, 10 and 20 centimeters. The sapphire windows used at the ends of the absorption test path are transparent in the 0.2 to 7 μ wave length region. The data obtained therefore cover the fundamental (4.67 μ) and the first overtone absorption bands. Spectral and integrated absorptivites for the CO fundamental band were evaluated from these measurements and are presented herein. Results for the first overtone absorption band are presented only for the 20 centimeter path length at pressures of 1, 2 and 3 atmospheres. At shorter path lengths the amount of absorption was insufficient to permit accurate computation of spectral absorptivity.

A literature search of previous experimental investigations pertaining to infrared absorption characteristics of CO and CO_2 has been completed. A summary of existing data is presented in tabular form.

INTRODUCTION

Knowledge of the infrared radiative properties of rocket exhaust gases is required in many applications. Examples include the prediction of radiative heating to the base regions of multi-engine vehicles and the long-range detection of ballistic missiles. The magnitude and characteristics of this infrared radiation depends on the flame composition and temperature.

Analytical studies of the radiative heating from rocket exhaust plumes indicated the need for complete and accurate spectral absorption data. Although numerous investigations of CO_2 and H_2O have been reported recently, the results are for a maximum temperature of 2000 $^{\circ}$F or are restricted to a narrow wavelength region. Furthermore, existing theories for predicting infrared radiation from high temperature gases are based on highly idealized physical models. The validity and applicability of the results predicted from these theories require experimental confirmation.

The objective of the present study is to obtain the spectral characteristics of a number of common combustion products under a variety of accurately known thermodynamics and optical conditions. Considerations leading to the design and fabrication of an experimental apparatus for this purpose are given in reference 1. This equipment consists of a graphite resistance furnace with an inert ceramic tube liner for the containment of high-temperature gases, and an optical system for detection of the infrared absorption. The test optical path is limited to the central zone of the furnace by the use of window holders at each end. Hot-pressed zinc selenide windows were originally employed because this material is transparent in the 1-20 μ

wavelength region and inert to H_2O, CO_2 and CO up to a temperature of 540 ^{O}F.
In order to keep these windows below this limit it was necessary to water
cool the holders in which they were mounted.

Data for the fundamental band of CO at temperatures of 300° K and 1800° K
and at pressures from 0.25 to 3.0 atmospheres obtained with this system were
reported in reference 1. Although agreement with existing results was with-
in 15 percent, the substantial temperature variation along the test optical
path caused by the water-cooling of the windows made the comparison open to
some question. Because of this the water-cooled window holders were replaced
with alumina tubes and sapphire used for the windows in place of zinc
selenide.

Spectral absorption measurements of CO were made with these modifications.
The pressure was varied from 0.5 to 3 atmospheres and the optical path length
from 5 to 20 centimeters. Spectral and total band absorptivities determined
from these measurements are presented in this report.

SPECTRAL ABSORPTION CURVES FOR CO AT 1200° K

A detailed description of the infrared spectral absorption system constructed for this investigation is given in reference 1. The temperature variation through the optical test path has been substantially reduced by replacing the water-cooled window holders with alumina tubes and using sapphire for the windows in place of zinc selenide. The deviation from the maximum center temperature is reduced to within 80° K when the center temperature is 1200° K (see Fig. 2 of reference 2).

Since there is some overlapping of the CO and the 4.3 CO_2 fundamental bands, it is essential that no CO_2 is present when making CO spectral measurements. Special care was therefore taken to remove any CO_2 that might be in the CO supply used. In spite of this, initial results indicated the presence of CO_2. This source of this CO_2 was traced to the oxygen absorbed by the alumina tube window holders. At the high temperatures involved in this experiment the absorbed O_2 can combine with the CO to produce significant amounts of CO_2. It was found that this could be eliminated by providing for a very small continuous flow of CO through the test cell. A check of the spectral data in regions where there is no overlapping of CO and CO_2 bands showed that the temperature distribution was not affected.

To investigate the functional dependance of the spectral and total band absorption on pressure and optical depth, three path lengths of 5, 10, and 20 cm were selected. The detection of an appreciable amount of

absorption at the lowest pressure dictated the minimum path length, the maximum was determined by the furnace length. Data was obtained by setting the path length and then recording the absorption spectra at pressures of 0.5, 1, 2 and 3 atmospheres.

The recorded spectra were analyzed as described in reference 1, page 19. Spectral absorptivities were calculated for a series of wave numbers. They were plotted as a function of wave number. The resulting spectral absorption profiles for the CO fundamental band are shown in Figs. 1, 2 and 3.

Analytical studies predict that the most effective absorption band for CO is at 4.67 μ, which corresponds to a vibrational quantitive number change from 0 to 1. Although there are many other possible changes, the only other important one is from 0 to 2 which corresponds to a wave length of 2.35 μ. This band is much weaker than the 4.67 μ band. Consequently its presence can be detected only at comparatively long path lengths and high pressures.

During the present tests the signal from the monochrometer was amplified as much as possible (i.e., such that fluctuations due to noise were less than 3% of the full scale reading). As a result there was a noticable absorption effect in the 2.35 μ region for both the 10 and 20 centimeter path length runs for pressures of 1, 2 and 3 atmospheres. Spectral band absorptivities for the 20 centimeter path length are shown in Fig. 4. As can be noted the maximum value is of the order of 0.1. In

the case of the 10 centimeter path length the absorption is reduced by about one half. Because of this it was not possible to obtain accurate values for spectral absorptivities from the experimental data.

The integrated band absorptivity is defined by

$$A_i = \int_{band} A_w \, dw$$

It is thus equal to the area under the spectral absorptivity curve. The integrated band absorptivities of CO fundamental and first overtone as functions of pressure and path length are summarized in Tables I-a and I-b respectively.

SUMMARY OF EXISTING EXPERIMENTAL DATA FOR
THE INFRARED RADIATIVE PROPERTIES OF CO AND CO_2

During the past few years, numerous experimental investigations have been reported in the literature for the gaseous radiative properties in the infrared range. It is intended here to summarize in a systematic way the range of thermodynamic and optical conditions, the spectral range, and the technique employed in obtaining and interpreting existing experimental data for CO and CO_2. Similar summaries for other common radiating gases are being constructed and will be reported later. These summaries will help not only to check the consistency of data from various sources under the same experimental conditions but also to indicate where additional measurements are needed.

The experimental data are summarized in Tables 2 to 5. The general type of apparatus employed by each investigator is listed first along with the technique employed for obtaining the desired optical conditions and interpreting the experimental results. Thermodynamic conditions include temperature, total pressure, and normalized optical depth which is equal to optical depth (partial pressure x path length) divided by total pressure in units of cm atm/atm = cm. The classifications given under the heading, Optical Region, are based on theoretical considerations.

Infrared Radiation Data of CO

Infrared radiation data for CO at room temperature are available for almost all conditions of importance. Remarkable consistency is indicated between Penner and Weber's data and Burch and Williams' data for integrated

intensity. Those data by Burch and Williams have been correlated success-
fully by Oppenheim and Ben-Aryeh (JQSRT $\underline{4}$, 559, 1964) using the Elsasser
model. In the strong-line-approximation region the effect of foreign gas
broadening has been investigated by Burch, Singleton and Williams (Appl.
Opt. $\underline{1}$, 359, 1962). Hence emissivities for any thermodynamic conditions
encountered in engineering systems can be obtained from these two sources.

For CO at high temperature, however, experimental data are very limited.
Also important is the fact that none of the measurements available are in the
weak region or definitely in the strong region. The effect of foreign gas
broadening at high temperature has never been investigated either. Therefore
measurements in both the weak and the strong regions at various temperatures
should be made.

Infrared Radiation Data of CO_2

Extensive data also exist for CO_2 at room temperature. For the three
most important band regions, the integrated intensities for $2.7\,\mu$ and
$4.3\,\mu$ given by Eggers and Crawford and the integrated intensity for 15μ
given by Kaplan and Eggers are believed to be accurate. In the strong region
Howard's data in 0.3 to 7μ region have been correlated by Larmore and
Passman (see p. 58, Infrared Radiation by H. L. Hackforth, McGraw-Hill, 1960)
using the Elsasser band model.

At high temperatures experimental values of the integrated intensities
for the 2.7μ region are in good agreement with theoretical results. More
measurements in the strong region, however, are needed.

For the 4.3μ region experimental values for the integrated intensities are believed to be accurate only for those data taken above 2000° K. Further experimental work in the strong region and comparison of result with existing theory are desirable.

Edwards' data are the only existing data for 15μ region at high temperature.

PROJECT SCHEDULE

Efforts to correlate and compare the data obtained on CO to present theory have been initiated, and will be continued during the coming quarter. Concurrent with this analytical study modification of the alumina window holders and further testing is planned. The glass frit braze used to hold the sapphire windows in the alumina tubes has not proved satisfactory. Leaks have developed during operation at 1200 to 1500 K. A design incorporating a platinum wire gasket has been conceived and will be developed.

REFERENCES

1. W. H. Giedt, C. L. Tien and others, "The Study of Base Heating by Radiation from Exhaust Gases", Final Report, Contract No. NAS 8-850, NASA, Institute of Engineering Research, University of California, Berkeley, California (1964).

2. M. M. Abu-Romia, L. S. Wang and W. H. Giedt, "Infrared Radiation Measurements of Combustion Gases", Second Quarterly Progress Report, Contract No. NAS 8-850, NASA, Institute of Engineering Research, University of California, Berkeley, California, 1964.
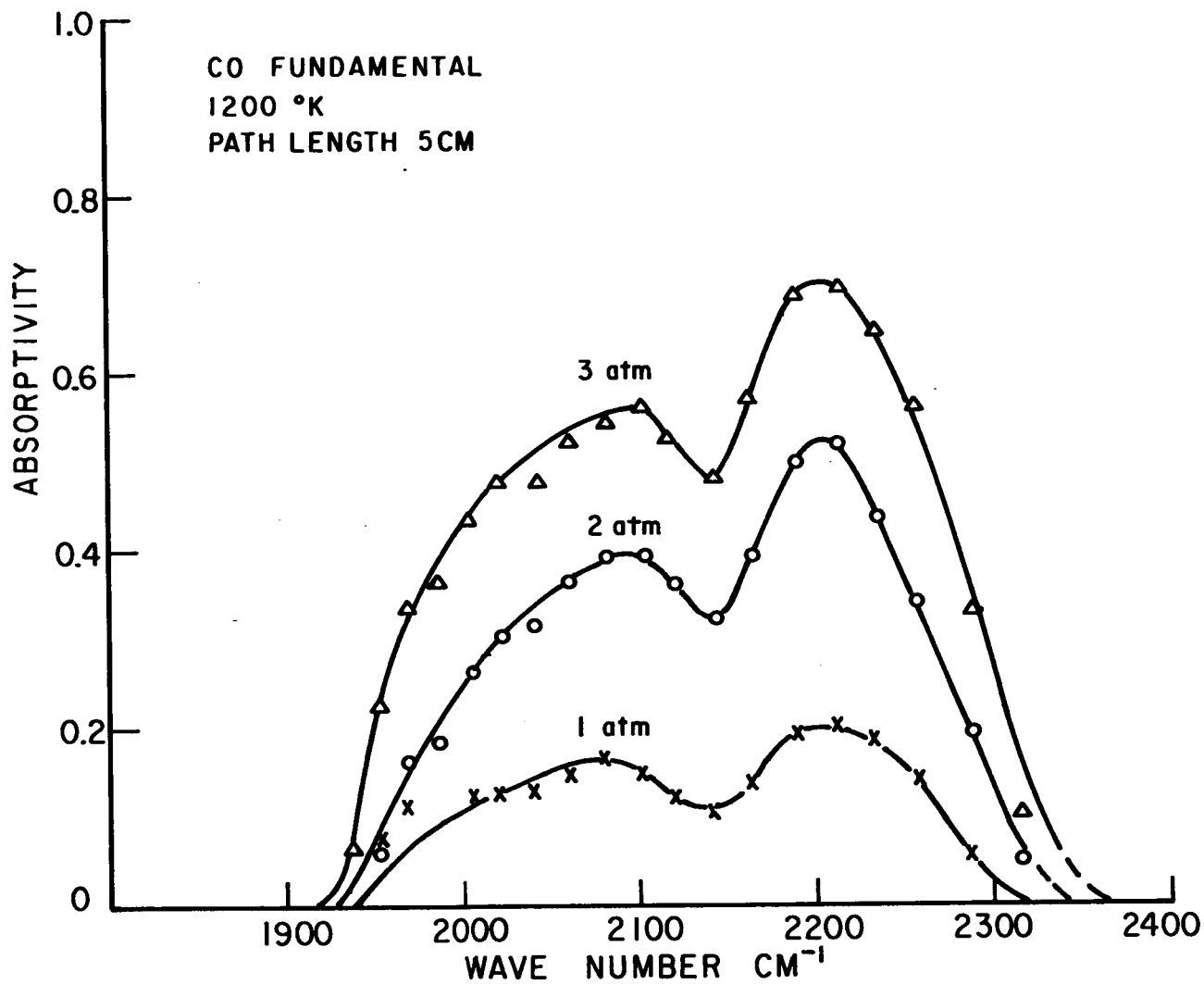
FIG. I SPECTRAL ABSORPTIVITY OF FUNDAMENTAL
BAND OF CO GAS AT TEMPERATURE 1200 °K
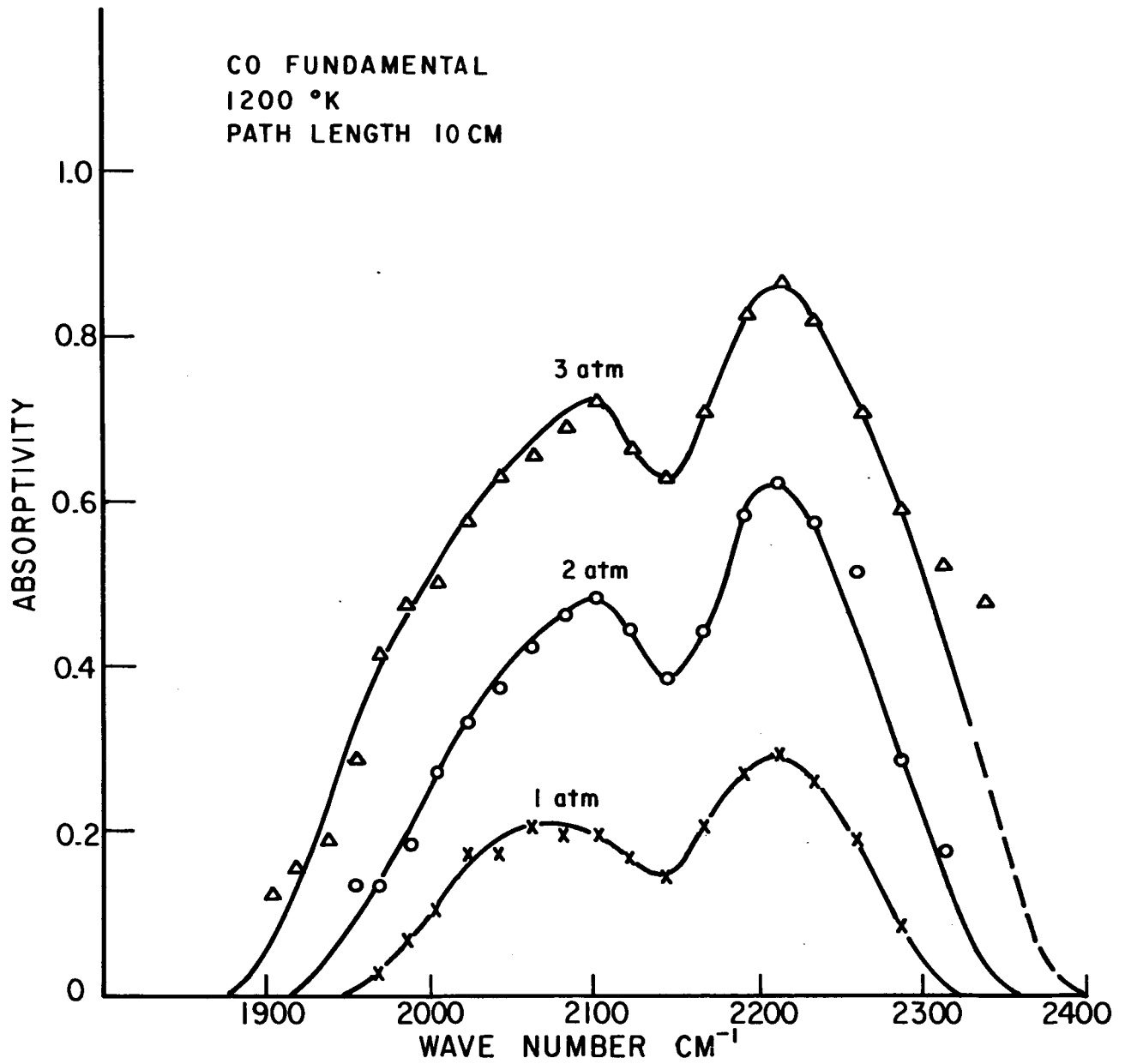AND AT PATH LENGTH 5 CM

FIG. 2   SPECTRAL ABSORPTIVITY OF FUNDAMENTAL
BAND OF CO GAS AT TEMPERATURE 1200 °K
AND AT PATH LENGTH 10 CM

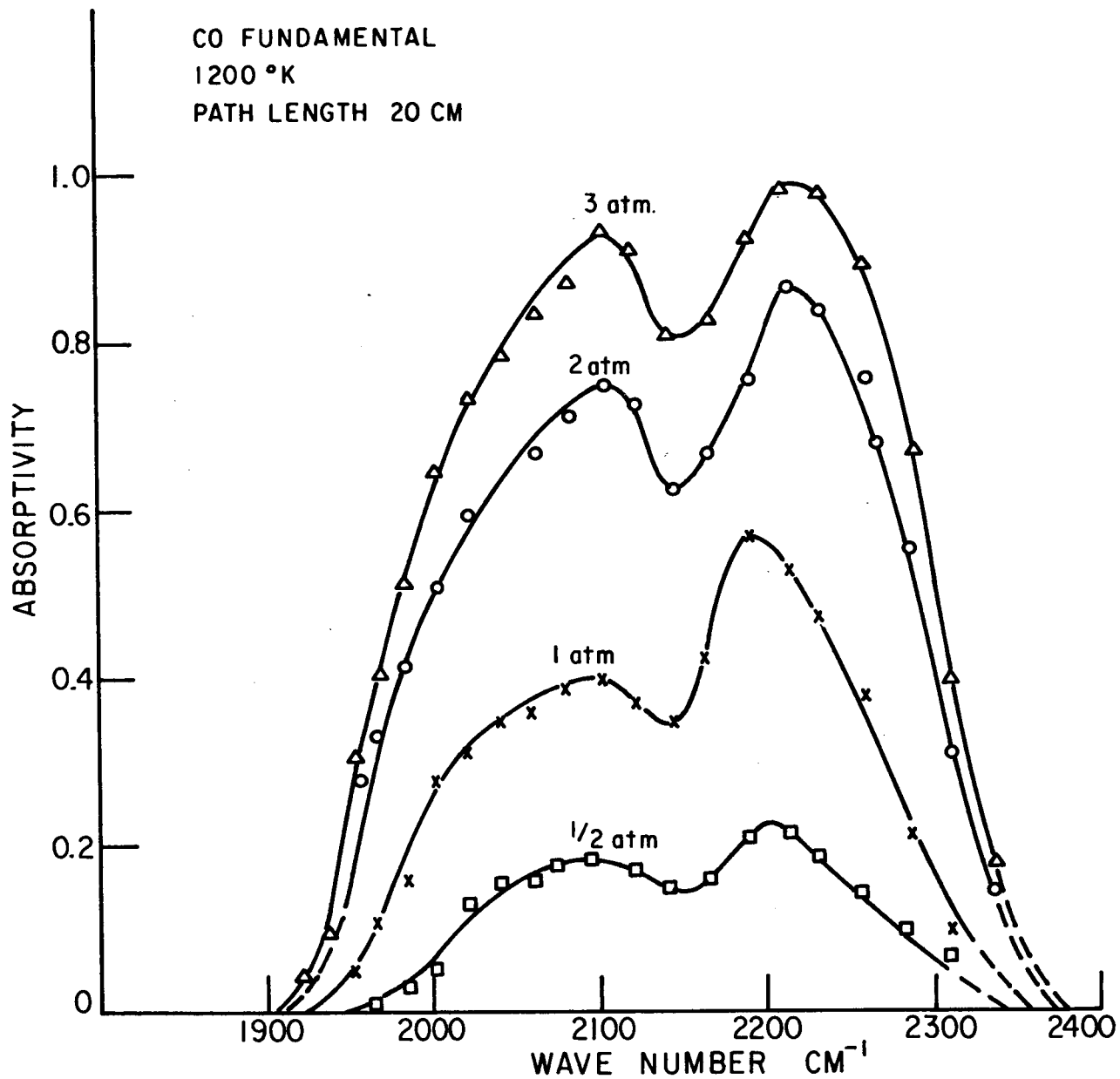FIG. 3   SPECTRAL ABSORPTIVITY OF FUNDAMENTAL
BAND OF CO GAS AT TEMPERATURE 1200 °K
AND AT PATH LENGTH 20 CM

CO FIRST OVERTONE
1200 °K
PATH LENGTH 20 CM

3 atm

2 atm

1 atm

ABSORPTIVITY

0.12 0.1 0.08 0.06 0.04 0.02 0

WAVE NUMBER CM^{-1}

3900 4000 4100 4200 4300 4400 4500 4600
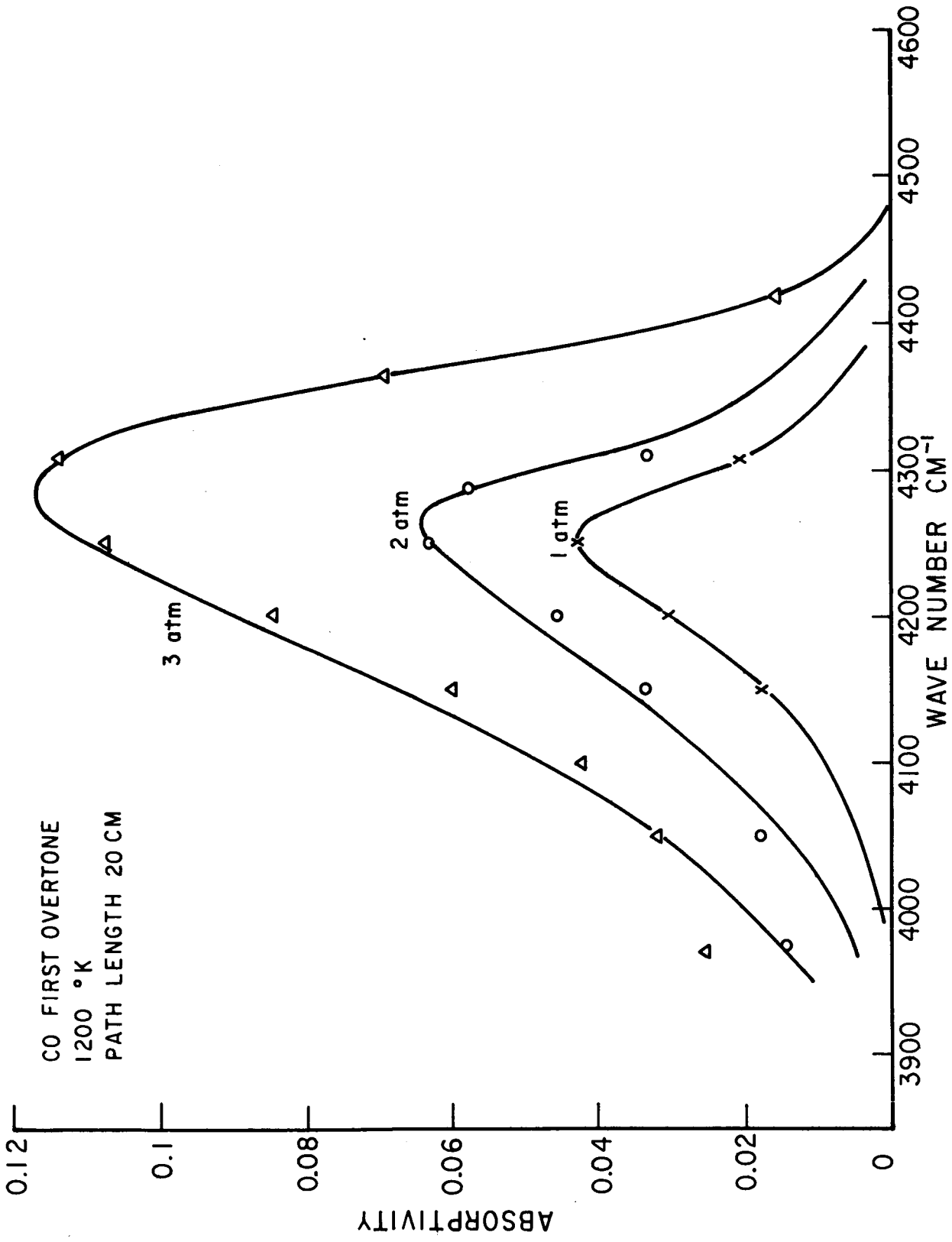
FIG. 4 SPECTRAL ABSORPTIVITY OF FIRST OVERTONE BAND OF CO GAS AT
TEMPERATURE 1200°K AND AT PATH LENGTH 20 CM

Table I-a. Integrated Band Absorptivity of CO
Fundamental at 1200° K (4.67 μ band)

Pressure – atm	path length – cm	Integrated absorption – cm^{-1}
1/2	20	49
1	20	127.4
2	20	233.2
3	20	294
1	10	60
2	10	145
3	10	256.5
1	5	46.6
2	5	119.4
3	5	187.2

Table I-b. Integrated Band Absorption of CO First
Overtone at 1200° K (2.35 μ Band)

1	20	6.8
2	20	13.4
3	20	30.5

Table II. Infrared Radiation Data for CO

Investigators	Apparatus	Design and Interpretation of Optical Conditions	Thermodynamic Conditions	Spectral Range	Optical Region	Forms of Results
S. S. Penner and D. Weber, J. Chem. Phys. 19, 807 (1951)	pressure gas cell	Wilson – Wells – Penner – Weber Method (foreign gas broadening)	room temperature up to 700 psia ≈0.05 cm	fundamental region first overtone region	weak	spectral absorption coefficients and integrated intensities
S. S. Penner and D. Weber, J. Chem. Phys. 19, 817 (1951)	pressure gas cell	Wilson – Wells – Penner – Weber Method (self-broadening)	room temperature up to 700 psia 3.57 and 6.22 cm	first overtone region	weak	integrated intensity
D. Weber and S. S. Penner, J. Chem. Phys. 19, 974 (1951)	pressure gas cell	Wilson – Wells – Penner – Weber Method (self-broadening)	room temperature up to 350 psia 0.0506 cm	fundamental region	weak	integrated intensity
D. E. Burch and D. Williams, Applied Optics 1, 587 (1962)	gas cell of lengths 1.55, 6.35, and 400 cm	Howard – Burch – Williams technique	room temperature 3 – 3000 mm Hg 0.001 – 100 cm	fundamental region first overtone region	weak to strong region	integrated emissivities and their empirical correlations
W. O. Davies, J. Chem. Phys. 36, 292 (1962)	shock tube	absorption measurements under controlled temperatures and total pressures	1160° – 2300° K 1.4 – 3.6 atm 3 cm	4.60 μ 4.67 μ 4.72 μ	transition region	spectral emissivities
C. L. Tien and W. H. Giedt, "Adv. in Thermophys. Prop. at Extreme Temps. and Pres.", 1965	furnace	absorption measurements under controlled thermodynamic conditions	300° and 1800° K 1/4 – 3 atm 10 cm and 20 cm	fundamental region	near-strong region	spectral emissivities and spectral values of $-(\ln T)/P$
R. H. C. Lee and J. Happel, I & EC Fundamentals 3, 167 (1964)	furnace	absorption measurements under controlled temperatures and normalized optical depths	300° to 900° K 1 atm 1.326 to 32.28 cm	fundamental region	strong	correlation of integrated emissivities by Elsasser band model

Table III. Infrared Radiation Data for CO_2 – Room Temperature

Investigators	Apparatus	Design and Interpretation of Optical Conditions	Thermodynamic Conditions	Spectral Range	Optical Region	Forms of Results
A. M. Thorndike, J. Chem. Phys. 15, 868 (1947)	gas cell	Wilson-Wells method	room temp. 1 to 4 atm not reported	4.3 μ region 15 μ region	extended into weak region	integrated intensities
D. F. Eggers and B. L. Crawford, J. Chem. Phys. 19, 1554 (1951)	gas cell (10 cm)	Wilson – Wells method	room temperature 2 atm not reported	3716 cm⁻¹ 3609 cm⁻¹ region 2349 cm⁻¹ region 667 cm⁻¹	extended into weak region	integrated intensities
D. Weber, J. R. Holm and S. S. Penner, J. Chem. Phys. 20, 1820 (1952)	pressure gas cell	Wilson – Penner – Weber Method	room temperature up to 700 psia not reported	3716 cm⁻¹ 3609 cm⁻¹ region 2350 cm⁻¹ region 667 cm⁻¹	weak weak weak not certain	integrated intensities
L. D. Kaplan and D. F. Eggers, J. Chem. Phys. 25, 876 (1956)	gas cell	Curve – of – Growth Method	room temperature 1.25 atm 0.0674 – 0.2631 cm STP	15 μ region	integrated intensity	integrated intensity
J. Overend, M. J. Younquist, E. C. Curtis and B. Crawford, J. Chem. Phys. 30, 532 (1959)	pressure gas cell	Wilson – Penner – Weber Method	room temperature 1000 psia 0.0002 – 0.0012 cm STP	15 μ region	weak region	integrated intensity
J. N. Howard, D. E. Burch and D. Williams, JOSA 46, 237 (1956)	22-m multiple – traversal absorption cell	Howard – Burch – Williams technique	room temperature 1 – 760 mm Hg 5 – 80 cm 5 – 120 cm 0.01 – 20 cm	2.7 μ region 4.3 μ region 15 μ region 1.4, 1.6, 2.0, 4.8, 5.2 μ	strong strong strong	integrated emissivities and their empirical correlations
D. E. Burch, D. A. Gryvnak and D. Williams, Applied Optics 1, 759 (1962)	400 and 3200 cm multiple-traversal cells 1.55, 12.8 cm in length	Howard – Burch – Williams technique	room temperature 40 – 1500 in mm Hg 0.1 – 10 cm STP 10 – 1500 in mm Hg 0.005 – 10 am STP 1 – 1500 mm Hg 0.01 – 1000 cm STP	3716 cm⁻¹ region 3609 cm⁻¹ region 2350 cm⁻¹ region 667 cm⁻¹ region	transition transition transition transition and strong	"

Table IV. Infrared Radiation Data for CO_2 - High Temperature Cells

Investigaotrs	Apparatus	Design and Interpretation of Optical Conditions	Thermodynamic Conditions	Spectral Range	Optical Region	Forms of Results
H. C. Hottel and H. G. Mangelsdorf, Trans. AI Ch E 31, 517 (1935)	the absorbing gas cell is isolated by means of flows of opposite directions in end nozzles	total energy approach	298° - 1320° K - 1640° K 1 atm 0.1 - 51.2 cm	whole spectrum		total emissivities
H. C. Hottel and V. C. Smith, Trans. ASME 57 463 (1935)	"	total energy approach	1640° - 2350° K 1 atm 1.2 - 12 cm	whole spectrum		total emissivities
D. K. Edwards, JOSA 50, 617 (1960)	Hottel - Mangelsdorf system	Howard - Burch - Williams technique	294° - 1390° K 0.5 - 10 atm 0.5 - 1250 cm STP	2.7 μ 4.3 μ 15 μ region 1.4, 1.6, 2.0, 4.8, 5.2, 7.5, 9.4 and 10.4 μ	strong region strong region strong region	integrated emissivities and their empirical correlations
R. H. Tourin, J. Chem. Phys. 20, 1651 (1952)	furnace heated gas cell	preliminary study	up to 1373° K 62 mm Hg not reported	2.7 μ region 4.3 μ		spectral emissivities
R. H. Tourin, JOSA 51, 175 (1961)	furnace	absorption measurements under controlled conditions	300° - 1273° K 50 - 700 mm Hg 0.9 - 12.7 cm	4.3 μ region	strong region	spectral emissivities and integrated emissivities, presented as function of the thermodynamic conditions
R. H. Tourin, Infrared Phys. 1, 105 (1961)	furnace	"	300° - 1273° K 50 - 700 mm Hg 0.9 - 12.7 cm	2.7 μ region (combination bands)	strong region at low temperature but weak region at high temperature	"
R. H. Tourin and H. J Babrov, J. Chem. Phys. 37, 581 (1962)	furnace	to check Beer's law	1273° K 50 - 700 mm Hg 0.9 - 12.7 cm	4.4 μ		It was shown that statistical model applies to CO_2, 4.4 μ at 1273° K
D. E. Burch and D. A. Gryvnak, ASTIA AD 296 016 (1962)	furnace	absorption measurements under controlled conditions	1200° - 1500° K 5 - 1500 mm Hg 0.57 - 7.75 cm	2.7 μ region 4.3 μ	weak region transition region	spectral emissivities
U. P. Oppenheim and Y. Ben-Aryeh, JOSA 53, 344 (1963)	gas cells of different lengths in an electrical furnace	band-model method	1200° K 40 - 1520 mm Hg 1.24 - 150.5 mm	4.3 μ region	weak to strong region	spectroscopic parameters $2\pi\gamma^0/d$ and $S/2\pi\gamma^0$

Table V. Infrared Radiation Data for CO_2 (Shock Tube and Supersonic Burners)

Investigators	Apparatus	Design and Interpretation of Optical Conditions	Thermodynamic Conditions	Spectral Range	Optical Region	Forms of Results
M. Steinberg and W. O. Davies, J. Chem. Phys. 34, 1373 (1961)	shock tube	absorption measurements under controlled temperatures and total pressures	$1200°$ - $2100°$ K 0.26 - 1.05 atm 0.38 cm	4.4 μ	near weak region	absorption coefficients
W. O. Davies, JOSA 54, 467 (1964)	shock tube	emission and absorption measurements under controlled temperatures and normalized optical depths	$5100°$ - $3000°$ K 1 atm 0.04 - 4 cm	4.4 - 5.3 μ	near weak at moderate temp.; weak at high temperature	spectral emissivites
J. C. Breeze and C. C. Ferriso, J. Chem. Phys. 39, 2619 (1963)	shock tube (reflected-shock-wave technique)	temperature broadening as well as pressure broadening of optically thin gas	1200 - $3000°$ K 2.5 atm 0.32 cm	2.7 μ region ($2 \nu_2 + \nu_3$, $\nu_1 + \nu_3$)	weak region	integrated intensity at STP as a function of temperature; the origin of the intensity of this Fermi resonance pair is shown to be the ($\nu_1 + \nu_3$) transition
K. G. P. Sulzmann, JQSRT 4, 375 (1964)	shock tube	band-model method	$1500°$ - $3500°$ K 0.5 - 2 atm 0.198 - 0.762 cm	4.25 μ	weak to near-strong	spectroscopic parameters s/d and s/γ° as functions of temperatures
C. C. Ferriso, J. Chem. Phys. 37, 1955 (1962)	exhaust jet of a supersonic burner	temperature broadening of gas of thin thickness	$1200°$ - $2400°$ K 1 atm 1.5 - 2.4 cm	4.3 μ region	weak for temperature above $2000°$ K not certain for temp. below $2000°$ K	spectral absorption coefficient and integrated intensity
C. C. Ferriso and C. B. Ludwig, JOSA 54, 657 (1964)	"	"	$1200°$, $1500°$, and $1800°$ K 1 atm 0.245 cm STP	2.7 μ region (3100 - 3800 cm^{-1})	weak	spectral emissivites and integrated intensity as a function of temperature