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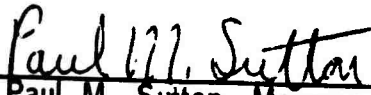
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SCIENTIFIC REPORT
ABSORPTION BY CO₂ BETWEEN 7125 AND 8000 cm⁻¹
(1.25-1.40 Microns)

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ABSTRACT

Transmission spectra in the 7125-8000 cm^{-1} region have been obtained for CO_2 samples with absorber thicknesses as great as 2.18×10^5 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.

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INTRODUCTION AND SUMMARY

The region between 7125 and 8000 cm^{-1} contains several CO_2 absorption bands which are too weak to play a very important part in the radiative transfer in the earth's atmosphere. However, since a large portion of this region contains very little absorption by H_2O and other gases in the earth's atmosphere, CO_2 absorption by the atmospheres of other planets can be studied at ground level with little interference from our own atmosphere. In order to interpret the results of such a study, it is necessary to identify the bands and to know the strengths, widths, and positions of absorption lines.

Courtoy¹ has observed and identified the more important bands in this region and has determined the positions of many of the lines. We have used larger samples in order to study the weaker bands and have determined the strengths of several bands from measurements on samples at high pressures. Besides a listing of the strengths of several of the bands, this report contains detailed results for five representative samples. Included are replotted spectra with several of the bands identified and a table of integrated absorptance versus wavenumber. Tables of transmittance versus wavenumber are available from the authors for workers who require them.

EXPERIMENTAL

Samples of CO_2 were contained in two different multiple-pass absorption cells. The longer one was used at path lengths of 469 and 935 meters and at 1 and 2.5 atm pressure. The shorter one was employed at 14.6 atm with 16.5 and 32.9 meter paths. The absorption cells and sampling procedure have been described previously in considerable detail.^{2,3}

The absorber thickness u was calculated by use of the following equation.

$$u(\text{atm cm}_{\text{STP}}) = p(\text{atm}) L(\text{cm}) [1 + 0.005p]^{273/296}, \quad (1)$$

where p is the CO_2 pressure and L is the geometrical path length. The factor $(273/296)$ accounts for the difference in densities at standard temperature (273°K) and at room temperature (296°K) at which the measurements were made. The quantity $(1 + 0.005p)$ accounts for the non-linearity in the relation between the density of CO_2 and its pressure.

The CO_2 contained traces of H_2O impurity which caused absorption near a few of the CO_2 bands. No absorption by other impurities was observed. It is probably safe to assume that all the isotopes were present in their natural abundances (C^{12} , 98.9%; C^{13} , 1.1%; O^{16} , 99.76%; O^{17} , 0.04%; O^{18} , 0.20%).

Spectra were scanned by the use of a small grating spectrometer enclosed in a vacuum tank. The transmittance of a sample was determined by comparing its spectrum with a background curve scanned over the same region and with the same experimental conditions except that the absorption cell was evacuated. Each spectrum was examined and compared with others as a check for consistency. Spectra of $\text{H}_2\text{O} + \text{N}_2$ were used to determine the contribution of the H_2O impurity. Each spectrum was then replotted and digitized by the method described previously.^{2,3} Pairs of values related to transmittance and wavenumber were punched on IBM cards which served as

input for a computer program used to calculate transmittance and integrated absorbance as a function of wavenumber. The sample parameters for five representative samples scanned with a spectral slitwidth of approximately 1.3 cm^{-1} are given in Table 1. The positions of many of the CO_2 lines given by Courtoy¹ and H_2O lines from an article by Nelson⁴ were used for wavenumber calibration.

TABLE 1
SAMPLE PARAMETERS

Sample No.	p torr	p atm	u atm cm_{STP}	L Path Meters
1	1,900	2.50	2.18×10^5	933
2	1,900	2.50	1.09×10^5	469
3	760	1.00	8.65×10^4	933
4	11,100	14.6	4.76×10^4	32.9
5	11,100	14.6	2.38×10^4	16.5

RESULTS AND DISCUSSION

Table 2 contains a list of all the CO_2 bands in the $7125\text{-}8000\text{ cm}^{-1}$ region which one might expect to absorb appreciably for the samples included in the present investigation. The positions of the centers of several of the bands have been measured by Courtoy.¹ The centers of the other bands were determined from energy levels calculated by Stull, Wyatt, and Plass.⁵

Since, for CO_2 , $\nu_1 \approx 2\nu_2$ ($1388.2 \approx 2 \times 667.4$),¹ bands arising from transitions for which $\Delta\nu_3$ is the same and $2\Delta\nu_1 + \Delta\nu_2$ is constant occur near each other. ($\Delta\nu_1$ is the change in ν_1 , the quantum number associated with ν_1 , etc.) Most of the absorption in the $7125\text{-}8000\text{ cm}^{-1}$ region is due to bands in which $\Delta\nu_3 = 1$, and $2\Delta\nu_1 + \Delta\nu_2 = 8$. The first five bands listed in Table 2 form a group in which $\Delta\nu_1$ varies from 0 to 4, with $\Delta\nu_2$ taking on even values between 0 and 8. The lower energy level involved in the transitions for these five bands is 00^0_0 .

In any theoretical analysis of such a group of bands, it makes little difference which one of the sets of quantum numbers corresponds to a given band. In fact, because of Fermi interactions, it is impossible in some instances to be sure of the proper assignment. For this reason, it has been suggested recently that a new notation be adopted for CO_2 bands. Although the new notation used in this report may be slightly different from the one which eventually will have the most widespread usage, it is certainly similar in some respects. In the new notation, all the energy levels in a group are denoted by three numbers in the following order: the maximum value of ν_1 , the minimum ν_2 , and ν_3 . These three numbers are followed by Roman numeral subscripts I, II, . . ., with I assigned to the highest level, II to the second highest, etc. Table 2 includes both the old and new notations for the energy levels involved in the transitions.

TABLE 2
 CO_2 ABSORPTION BANDS BETWEEN 7125 AND 8000 cm^{-1}

Band Center cm^{-1}	Authority ^a	Upper Level ^b		Remark
		Old Notation	New Notation	
7920.5	SWP	40^0_1	401_{I}	
7734.30	J	32^0_1	401_{II}	
7593.54	C	24^0_1	401_{III}	
7460.37	C	16^0_1	401_{IV}	
7284.22	SWP	08^0_1	401_{V}	
7599.44	C	32^0_1	401_{II}	$\text{C}^{13}_{\text{O}_2^{16}}$ ^c
7481.34	C	24^0_1	401_{III}	$\text{C}^{13}_{\text{O}_2^{16}}$
7332.39	SWP	16^0_1	401_{IV}	$\text{C}^{13}_{\text{O}_2^{16}}$
7758.3	SWP	33^1_1	411_{II}	Lower Level is 01^1_0 (010_{I})
7584.4	SWP	25^1_1	411_{III}	Lower Level is 01^1_0 (010_{I})
7415.2	SWP	17^1_1	411_{IV}	Lower Level is 01^1_0 (010_{I})
7901.5	SWP	13^1_2	212_{II}	
7743.8	SWP	05^1_2	212_{III}	
7981.17	C	02^0_3	103_{II}	$\text{C}^{13}_{\text{O}_2^{16}}$

^a Authority for position of band center. C denotes experimental value from Courtoy.¹ SWP indicates that the band center has been determined from energy levels calculated by Stull, Wyatt, and Plass.⁵

^b The upper level of the transition is given in both the old and new notation. The lower level is 00^0_0 (000_{I}) unless indicated otherwise.

^c Molecular species is $\text{C}^{12}_{\text{O}_2^{16}}$ except as indicated.

Transmittance spectra of the five samples listed in Table 1 are shown in Fig. 1 with the corresponding sample numbers enclosed in squares. Most of the absorption between 7400 and 7800 cm^{-1} is due to the 401_{II} , 401_{III} , and 401_{IV} bands of the most abundant isotopic species, $\text{C}^{12}\text{O}_2^{16}$. The corresponding bands for the $\text{C}^{13}\text{O}_2^{16}$ isotope cannot be seen in our results; the 401_{II} and 401_{III} bands are masked by stronger bands which overlap them, and the 401_{IV} band, whose band center is calculated to be at 7332.39 cm^{-1} , was not observed since it is probably very weak and occurs near some H_2O lines appearing in the spectrum as a result of the impurity in the sample. Absorption by the less abundant isotopes and by weaker bands of $\text{C}^{13}\text{O}_2^{16}$ would, of course, be less and probably not observable in the spectra of samples included in the present investigation.

Evidence of the difference band $411_{\text{II}} \leftarrow 010_{\text{I}}$ can be seen on the high wavenumber side of its associated combination band 401_{II} which occurs 24 cm^{-1} below. (The change in all the quantum numbers are the same for a combination band as for its associated difference band.) The $411_{\text{III}} \leftarrow 010_{\text{I}}$ band is masked by its associated combination band 401_{III} , while slight evidence of the $411_{\text{IV}} \leftarrow 010_{\text{I}}$ band appears just above 7400 cm^{-1} on the low wavenumber side of 411_{IV} . A few H_2O lines near 7400 cm^{-1} make it difficult to determine the true shape of the CO_2 spectrum in this region. The 212_{III} band whose center is at 7743.8 cm^{-1} is probably masked by the stronger 401_{II} band.

The bands near 8000 cm^{-1} and the one near 7300 cm^{-1} are so weak that only the sample having maximum absorber thickness (Sample 1) produced appreciable absorption. There is considerable uncertainty in the spectrum near 7300 cm^{-1} because of possible errors in accounting for absorption by the H_2O impurity. Because of the small amount of absorption in the 7850-8000 cm^{-1} region, the true shape of the spectrum is difficult to determine; the curve of this region in Fig. 1 represents the average of three curves. The transmittance minimum near 7900 cm^{-1} is probably due to the Q-branch of the 212_{II} band, and the two maxima near 7920 and 7980 are probably at the centers of the bands indicated. No absorption other than that shown in Fig. 1 was observed between 7125 and 8000 cm^{-1} .

The 212_{I} band and the remainder of the 103 group for both $\text{C}^{13}\text{O}_2^{16}$ and $\text{C}^{12}\text{O}_2^{16}$ occur at higher wavenumbers and have been discussed previously.⁶

INTEGRATED ABSORPTANCE

Values of the integrated absorptance $\int_{\nu'}^{\nu} A(\nu) d\nu$ are presented in Table 3 for Samples 1-5. The three parts of ν' the table correspond to the three stronger regions of absorption between 7400 and 7800 cm^{-1} . Each column represents the sample indicated at the top. The lower limit of integration, ν' , which is shown at the top of each column, was chosen at a point where there was no absorption. The integrated absorptance between any two wavenumbers listed can be found by subtracting the values tabulated at those two points. In regions where there is structure in the recorded spectra, the integral is tabulated at points midway between the centers of the absorption lines. In other regions where the spectra are smooth, tabulations are made in intervals of 2 or 5 cm^{-1} .

BAND STRENGTHS

The strength, or intensity, of an absorption band is given by

$$S_{\nu} = \int K(\nu) d\nu, \quad (2)$$

where the integration is performed over all ν for which there is appreciable absorption by the band. $K(\nu)$, the absorption coefficient, is related to $T'(\nu)$ the true transmittance that would be observed with infinite resolving power by

$$K(\nu) = -\frac{1}{u} \ln T'(\nu). \quad (3)$$

In regions where two or more bands overlap each other, the value of $K(\nu)$ used in (2) to determine a band strength must include only the contribution by the band of interest. We have shown in a previous report⁷ that under conditions of sufficiently high pressure and high transmittance, $\int \ln T'(\nu) d\nu \approx \int \ln T(\nu) d\nu$, where $T(\nu)$ is the observed transmittance. Thus it is possible to determine the strength of a band, or at least of a region containing overlapping bands, from the spectrum of a sample satisfying these conditions.

From the transmission spectra shown in Fig. 1, we were able to determine $-\frac{1}{u} \int \ln T(\nu) d\nu$ for different spectral regions. We then estimated the contributions of some of the weaker bands in order to calculate the strengths of overlapping stronger bands. The results are summarized in Table 4. For example, $-\frac{1}{u} \int \ln T(\nu) d\nu = 12.2 \times 10^{-5} \text{ atm}^{-1} \text{ cm}^{-1} \text{ STP cm}^{-1}$ for the 7400-7500 cm^{-1} region. We know that at least three bands contribute to the absorption in this region: the 401_{IV} and its associated difference band $411_{IV} \leftarrow 010_I$, as well as the 401_{III} band of $C^{12}O_2^{16}$. The contribution of the latter band is very small ($\sim 0.3 \times 10^{-5}$) and can be estimated from the strength of the corresponding band of $C^{12}O_2^{16}$ by assuming that their strengths are proportional to the abundances of the C isotopes (1.1/98.9). We can also show from quantum theory⁸ that, at room temperature, the strength of a $\Pi \leftarrow \Pi$ difference band such as $411_{IV} \leftarrow 010_I$ is 0.078 times that of the associated combination band 401_{IV} which arises from a transition from the 000_I state. By using this relationship, we were able to show that the strength of the 401_{IV} band is $11.0 \times 10^{-5} \text{ atm}^{-1} \text{ cm}^{-1} \text{ STP cm}^{-1}$. A similar method was used for the 401_{III} band. In order to estimate the strength of the 401_{III} band, we had to assume a value for the 212_{III} band. For lack of anything better we used $0.45 \text{ atm}^{-1} \text{ cm}^{-1} \text{ STP cm}^{-1}$, the value determined for the

TABLE 4
STRENGTHS OF ABSORPTION BANDS

Band Center cm ⁻¹	Upper Level	S_V^* atm ⁻¹ cm ⁻¹ STP cm ⁻¹	
7920.5	401 _I	0.55 ± 0.25 × 10 ⁻⁵	
7734.30	401 _{II}	7.65 ± 0.6 × 10 ⁻⁵	Based on 8.75 × 10 ⁻⁵ for 7675-7790 cm ⁻¹ region
7593.54	401 _{III}	28.6 ± 1.5 × 10 ⁻⁵	Based on 31.1 × 10 ⁻⁵ for 7510-7630 cm ⁻¹ region
7460.37	401 _{IV}	11.0 ± 0.6 × 10 ⁻⁵	Based on 12.2 × 10 ⁻⁵ for 7400-7500 cm ⁻¹ region
7284.22	401 _V	0.55 ± 0.25 × 10 ⁻⁵	
7901.5	212 _{II}	0.45 ± 0.20 × 10 ⁻⁵	
7981.17	103 _{II} C ¹³ O ¹⁶ ₂	0.60 ± 0.20 × 10 ⁻⁵	

*The subscript (STP) is used to emphasize that the strengths were calculated by using absorber thicknesses normalized to standard temperature and pressure. The measurements were made at room temperature 296°K.

212_{II} band. If the actual strength is less than our assumed value, only a few percent error is introduced in our value for the 401_{II} band. It seems unlikely that the 212_{III} band is significantly stronger than we assumed since there is no strong evidence for it in the spectra shown in Fig. 1. Furthermore, Courtoy¹ did not observe it in his high-resolution spectra.

Although there are no overlapping CO₂ bands, the uncertainty in the strength of the 401_V band is large because of errors in accounting for H₂O absorption. Because of the small amount of absorption and overlapping of the bands between 7850 and 8000 cm⁻¹, the strengths of the bands in this region could not be determined accurately. The contribution of each band was estimated by dividing the absorption into portions which seemed consistent with the contour of the spectrum shown in Fig. 1.

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13. ABSTRACT

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