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Harmonic and Combination Bands in CO₂

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The absorption bands of CO₂ at higher frequencies are important for the determination of anharmonic constants which characterize the potential function and for the location of upper levels in the vibration diagram of ν_1 and ν_2 in which resonance interaction appears. Only the odd harmonics are active. The band $3\nu_2$ at 5.0μ has been measured under high resolution and five zero branches

identified, two originating in the normal state and three in the first excited state. The rotational structure of the strongest of these bands at 2078 cm^{-1} is resolved. The band $3\nu_3$ at 1.43μ is a typical doublet. Combination bands near 2μ and 1.6μ are sufficiently resolved to show their contours and to permit for the first time a satisfactory determination of their positions.

PROBABLY no other polyatomic molecule is as completely known in mechanical structure and behavior as is CO₂. The recent very successful formulation of this problem by Adel and Dennison¹ was based in large part upon infrared absorption measurements from this laboratory, including the following which were in progress at that time. The two fundamental bands had already² been located precisely and resolved. For observations upon the less intense harmonic and combination bands we have used an absorption cell seven meters long, with mica windows, filled by displacement with CO₂ to a maximum concentration of about 80 percent. The 4800 line grating used gives good resolution in the region near 5μ and, at shorter wave-lengths, adequate separation to show the contours of the bands but not to resolve their rotational structure.

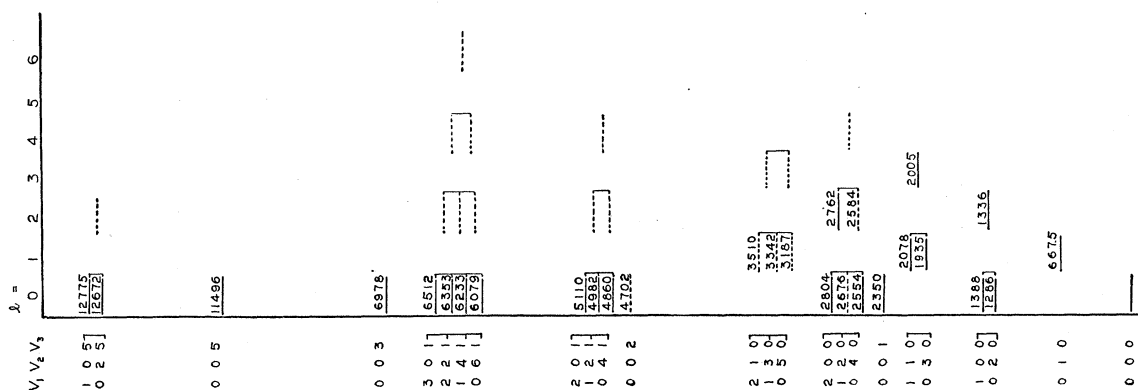
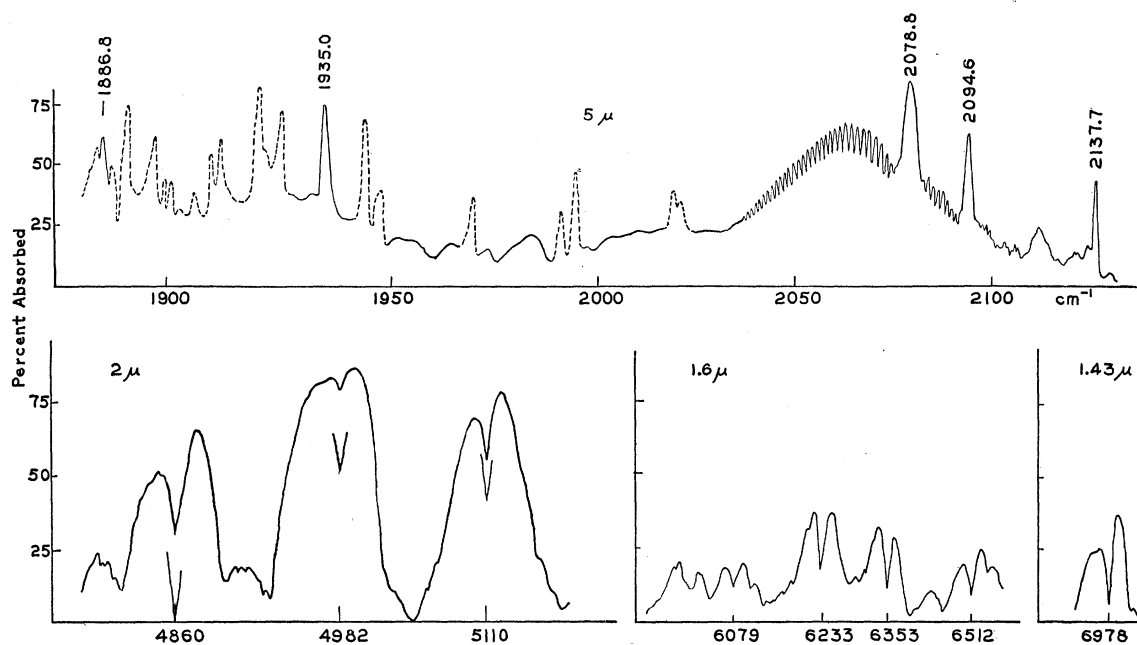
With these measurements a sufficient number of vibrational levels are available to determine completely the arrangement and positions of all the terms, as indicated in Fig. 1. The levels in-

volving V_1 and V_2 occur in groups designated by bracketed quantum numbers at the left of the figure, and, in any one group, the terms with equal l are mixed because of resonance interaction. These interacting levels are connected by brackets. The observed term values are indicated for all levels which have been identified in the spectrum and a few predicted levels are represented by broken lines, the term values in these cases being computed. Absorption bands arise only from transitions for which $\Delta V_2 + \Delta V_3$ is odd. They are of the parallel (doublet) type when $\Delta l = 0$ and perpendicular when $\Delta l = \pm 1$. The Venus bands observed by Adams and Dunham³ determine the three highest levels by transitions from the normal state. For Raman lines $\Delta l = 0$ and ΔV_2 is even, corresponding to transitions between groups in any one column. The groups of degenerate levels may be designated for convenience by the maximum value of V_2 involved. Thus group 2 consists of a pair of interacting levels with $l = 0$ and a single level with $l = 2$. None of the levels of group 5 has as yet been observed. A

¹ Adel and Dennison, *Phys. Rev.* **44**, 99 (1933).

² Martin and Barker, *Phys. Rev.* **41**, 291 (1932).

³ Adams and Dunham, *Pub. A. S. P.* **44**, 243 (1932).

FIG. 1. Diagram of vibrational levels and term values for CO_2 .FIG. 2. Harmonic and combination bands of CO_2 .

careful search was made for the three zero branches corresponding to $(5\nu_2, 3\nu_2 + \nu_1, \nu_2 + 2\nu_1)$ but without success. Their computed positions are 3187, 3342 and 3510 cm^{-1} . They fall in a region of strong water vapor absorption but could have been observed if the maxima had been as great as 5 percent. Apparently a much longer cell would be required to find them.

THE BANDS AT 5μ

Absorption of $(3\nu_2, \nu_1 + \nu_2)$ by the normal molecule produces a pair of perpendicular bands

shown in Fig. 2, with zero branches at 1935 cm^{-1} and 2078 cm^{-1} . A part of the rotation structure of the stronger band at 2078 cm^{-1} has been resolved, mostly in the negative branch which appears to be much more intense than the positive branch. For molecules already excited to the first vibration state the same transition defines three higher levels, namely 2554 and 2804 with $l=0$ and 2762 with $l=2$. These are indicated by the observed lines at 1886, 2137 and 2094 cm^{-1} . There are three other levels in group 4, one with $l=0$, one with $l=2$ and one with

$l=4$. The first two might have been expected here, the positions of the corresponding lines being 2008 and 1917 but apparently these transitions are too weak to be observed. In Fig. 2 the solid lines represent the only absorption attributable to CO₂. The other lines, which have not previously been measured, are probably due to water vapor.

THE BANDS AT 2 μ AND 1.6 μ

Transitions from the normal state to the three levels in group 4 having $l=0$ may be simultaneous with the change $0 \rightarrow 1$ in V_3 , thus yielding three bands near 2 μ , namely $\nu_3 + (4\nu_2, 2\nu_2 + \nu_1, 2\nu_1)$. They are analogous to the well-known pair $\nu_3 + (2\nu_2, \nu_1)$ at 2.7 μ . As indicated in the figure, the centers are observed at 4860, 4982 and 5110 cm⁻¹. Three weaker bands would also be ex-

pected corresponding to transitions from the first excited state but they cannot be located with confidence in the absorption pattern.

A similar set of transitions $\nu_3 + (6\nu_2, 4\nu_2 + \nu_1, 2\nu_2 + 2\nu_1, 3\nu_1)$ with $\Delta l = 0$ gives rise to four bands near 1.6 μ . These are shown at 6079, 6233, 6353 and 6512 cm⁻¹. The pattern is considerably complicated by irregular background and perhaps by weak bands arising from the first excited state.

THE BAND AT 1.4 μ

The position of the band $3\nu_3$ is of interest for the determination of x_{33} , which confirmed the identification of one of the Venus bands as $5\nu_3$. It is a doublet, the center being at 6978 cm⁻¹. This gives the large value -12.7 for x_{33} , indicating the strongly anharmonic character of the vibration ν_3 .