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INFRARED SPECTRA OF VAN DER WAALS COMPLEXES OF
IMPORTANCE IN PLANETARY ATMOSPHERES

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ABSTRACT

It has been suggested¹ that $(\text{CO}_2)_2$ and Ar- CO_2 are important constituents of the planetary atmospheres of Venus and Mars. Here, we present recent results on the laboratory spectroscopy of CO_2 -containing van der Waals complexes which may be of use in the modeling of the spectra of planetary atmospheres. Sub-Doppler infrared spectra have been obtained for $(\text{CO}_2)_2$, $(\text{CO}_2)_3$, and rare-gas- CO_2 complexes in the vicinity of the CO_2 Fermi diad $(\nu_1+\nu_3, 2\nu_2+\nu_3)$ at $2.7 \mu\text{m}$ using a color-center-laser optothermal spectrometer. From the spectroscopic constants the geometries of the complexes have been determined and van der Waals vibrational frequencies have been estimated. The equilibrium configurations are C_{2h} , C_{3h} , and C_{2v} , for $(\text{CO}_2)_2$, $(\text{CO}_2)_3$, and the rare-gas- CO_2 complexes, respectively. Most of the homogenous linewidths for the rovibrational transitions range from 0.5 to 22 MHz, indicating that predissociation is as much as four orders of magnitude faster than radiative processes for vibrational relaxation in these complexes.

INTRODUCTION

The spectral observation² of $(\text{H}_2)_2$ in the atmosphere of Jupiter indicates the presence of weakly bound complexes in planetary atmospheres. Those results led Fox and Kim¹ to estimate the role that other van der Waals complexes play in the spectra of planetary atmospheres. The complexes of $(\text{CO}_2)_2$ and Ar- CO_2 were considered due to the large abundances of CO_2 in the atmospheres of Venus and Mars. Attempts were made to model the contributions of $(\text{CO}_2)_2$ and Ar- CO_2 to the spectra of these planets. A realistic simulation of these spectra, though, requires a substantial amount of information,

including geometries, binding energies, spectroscopic constants, and transition moments for the complexes, which were not known or only incorrectly known at the time. Accurate spectroscopic data are now becoming available for a number of van der Waals complexes through laboratory measurements of rotationally resolved spectra of these complexes. The complexes are typically produced in adiabatic expansions of suitable gas mixtures and then studied using high-sensitivity microwave and infrared spectroscopy.

Here, we will discuss sub-Doppler infrared spectra that have been obtained for $(\text{CO}_2)_2^3$, $(\text{CO}_2)_3^4$, and rare-gas- CO_2^5 complexes using a single-mode color-center laser. A molecular beam of the appropriate complex is formed by seeding a few percent of CO_2 in He or Ar/He and expanding the gas through a pinhole nozzle into a vacuum chamber. The molecular beam energy is monitored using a liquid-He cooled bolometer. Between the nozzle and bolometer, the laser beam is multiply crossed through the molecular beam. The laser excites a vibration in the complex correlating to the $\nu_1 + \nu_3 / 2\nu_2^0 + \nu_3$ Fermi diad in CO_2 . In transit to the bolometer (i.e. in less than ~ 1 ms) the vibrationally excited complex predissociates, leading to a loss of energy detected by the bolometer. In this way a spectrum is recorded by monitoring the bolometer response as a function of laser frequency.

$(\text{CO}_2)_2$

The infrared spectra of the two Fermi diad bands of $(\text{CO}_2)_2$ were recorded near 3611.5 and 3713.9 cm^{-1} , with band origins red shifted by $\sim 1 \text{ cm}^{-1}$ from the monomer origins. The observed nuclear-spin statistical weights and inertial defect are interpreted in terms of a planar C_2h complex [see Fig. 1], in disagreement with previous low resolution infrared results. The nearest neighbor C---O distance is nearly identical to that found in the CO_2 crystal. A centrifugal distortion analysis yields weak bond stretching and symmetric bending frequencies of $32(2)$ and $90(1) \text{ cm}^{-1}$, respectively. The measured transition linewidths of $\sim 2 \text{ MHz}$ give an estimate for the predissociation broadening.

$(\text{CO}_2)_3$

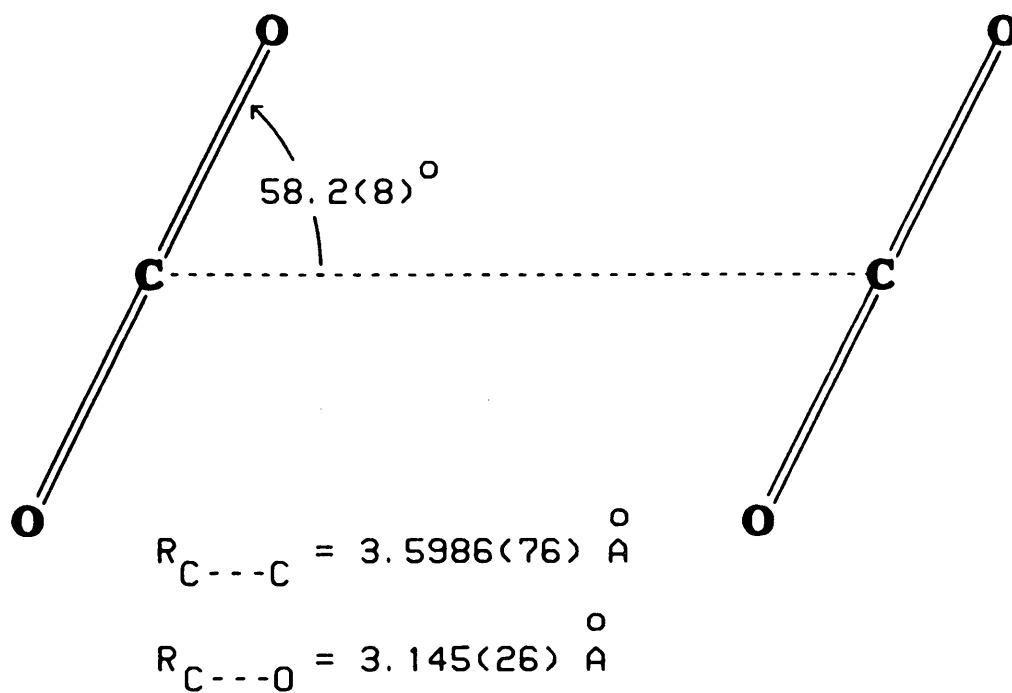
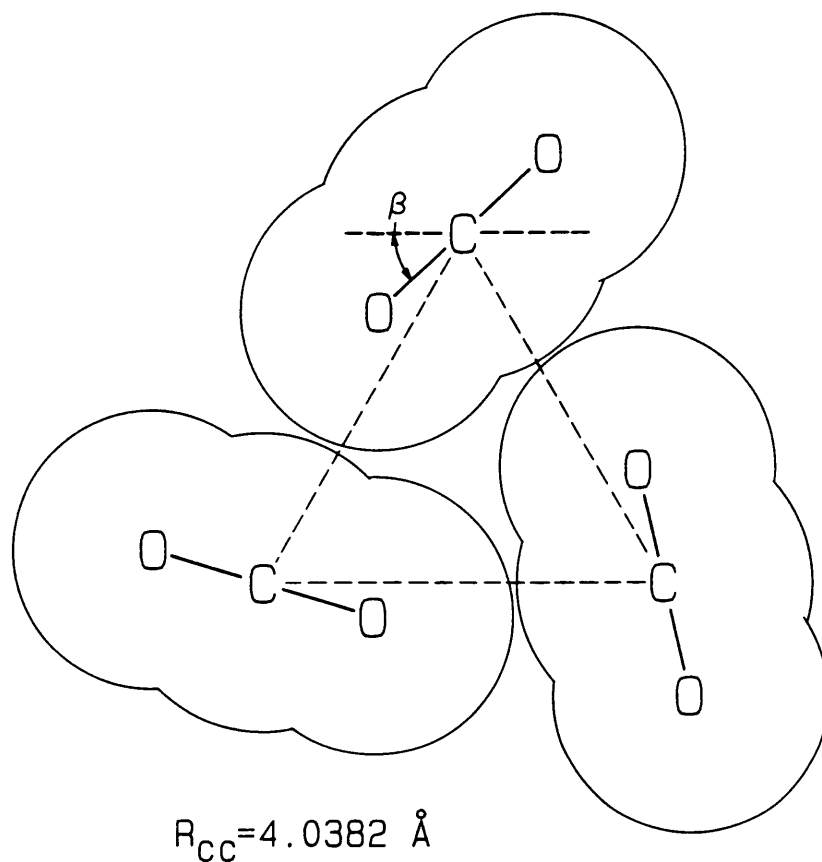


Fig. 1. Structures of CO₂ Dimer and Trimer

The observed spectrum for $(\text{CO}_2)_3$ is shown in Fig. 2. Only the lower frequency Fermi diad band was observed, blue shifted by $\sim 1 \text{ cm}^{-1}$ from the monomer origin. A symmetric top spectrum is seen, with statistical weights depending only on K and a near zero inertial defect, giving a planar C_3h structure for the complex [see Fig. 1]. The C-C separation of 4.0382 \AA is larger than the 3.599 \AA value found in the dimer.

Ne-CO₂, Ar-CO₂, AND Kr-CO₂

Infrared spectra of the $\text{C}_2\nu^6$ Ne-, Ar-, and Kr-CO₂ have been recorded for both Fermi-diad bands of the complex. The band origins for the Ar and Kr complexes are red shifted from that of free CO₂ by $1\text{-}2 \text{ cm}^{-1}$, while for Ne-CO₂ they are blue shifted by $\sim 0.2 \text{ cm}^{-1}$. The predissociation linewidths range from 0.5 to $\leq 5 \text{ MHz}$ except for the upper Fermi-diad band of Ne-CO₂, which shows a broad width of $\sim 22 \text{ MHz}$ arising from near resonant predissociation of $\text{Ne-CO}_2(\nu_1+\nu_3) \rightarrow \text{Ne} + \text{CO}_2(2\nu_2+\nu_3)$.

CONCLUSION

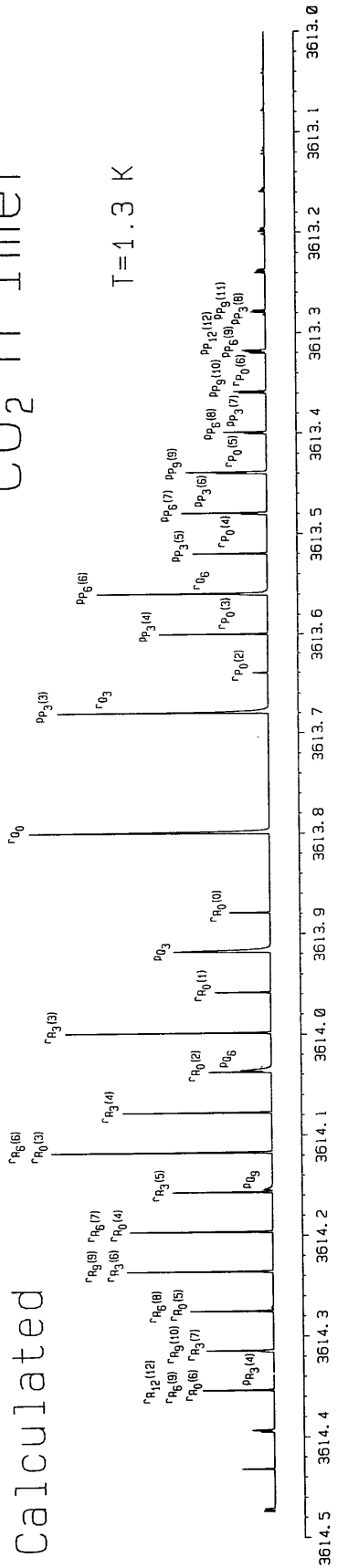
Here, we have summarized spectral results that have been obtained for weakly bound complexes of CO₂. The present data provide valuable information on the spectroscopy and dynamics of these species which should be useful for modeling their spectra in planetary atmospheres.

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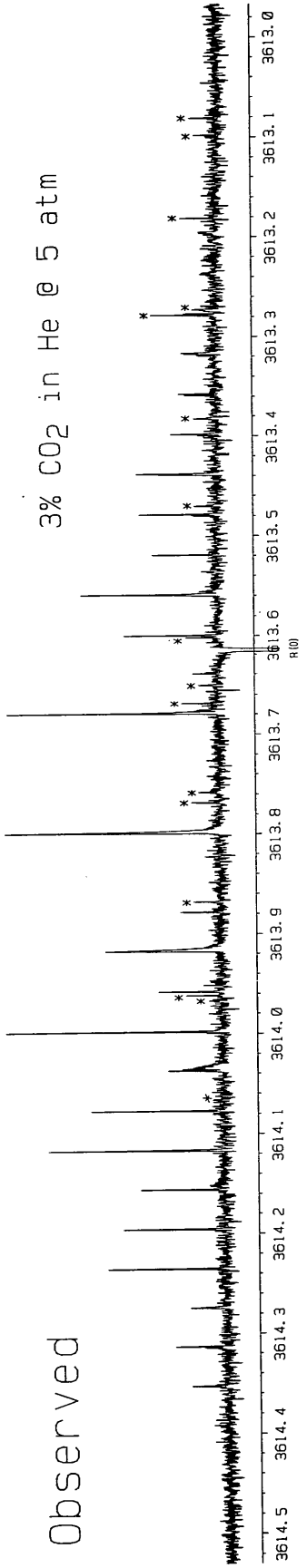
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CO₂ Trimer

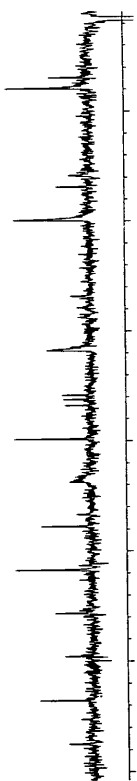
T = 1.3 K



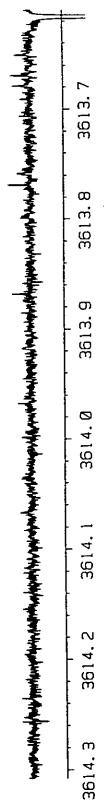
3% CO₂ in He @ 5 atm



3 atm



2 atm



Wavenumber/cm⁻¹

Fig. 2. Observed and calculated infrared spectra of (CO₂)₃ near the 2ν₂+ν₃ vibration of CO₂.