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

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ABSTRACT

It has been suggested[1] that $(CO_2)_2$ 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
$(CO_2)_2$, $(CO_2)_3$, 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 μm 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
$(CO_2)_2$, $(CO_2)_3$, 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 observation[2] of $(H_2)_2$ in the atmosphere of Jupiter
indicates the presence of weakly bound complexes in planetary atmospheres.
Those results led Fox and Kim[1] to estimate the role that other van der Waals
complexes play in the spectra of planetary atmospheres. The complexes of
$(CO_2)_2$ 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 $(CO_2)_2$ 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 $(CO_2)_2$[3], $(CO_2)_3$[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.

$(CO_2)_2$

The infrared spectra of the two Fermi diad bands of $(CO_2)_2$ were recorded near 3611.5 and 3713.9 cm^{-1}, with band origins red shifted by ~ 1 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) cm^{-1}, respectively. The measured transition linewidths of ~ 2 MHz give an estimate for the predissociation broadening.

$(CO_2)_3$

$$R_{CC}=4.0382 \text{ Å}$$

$$58.2(8)^{\circ}$$

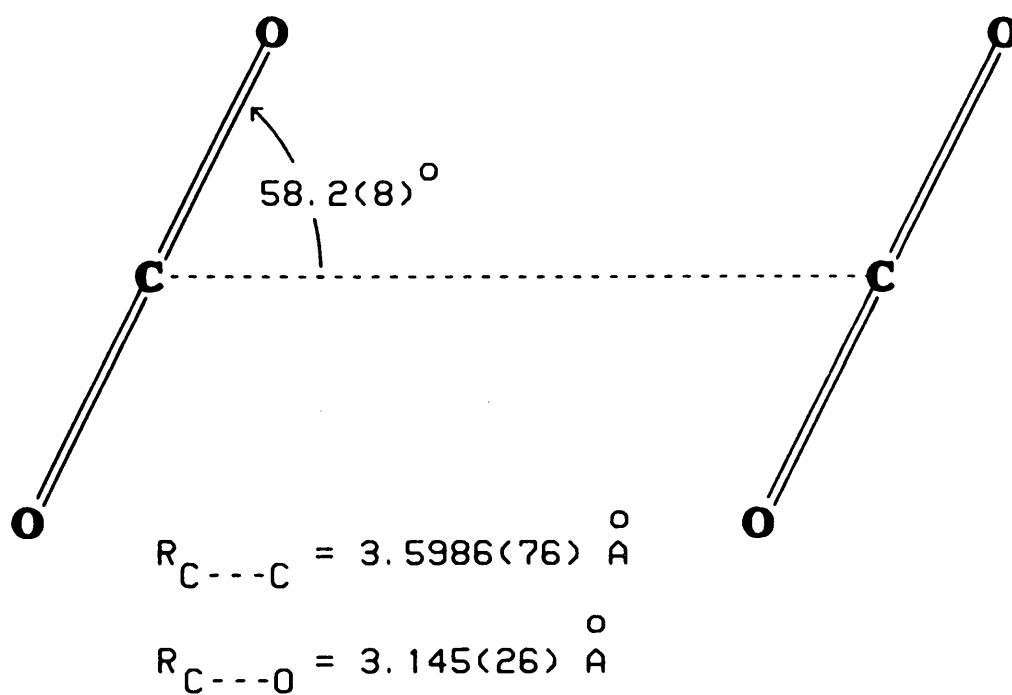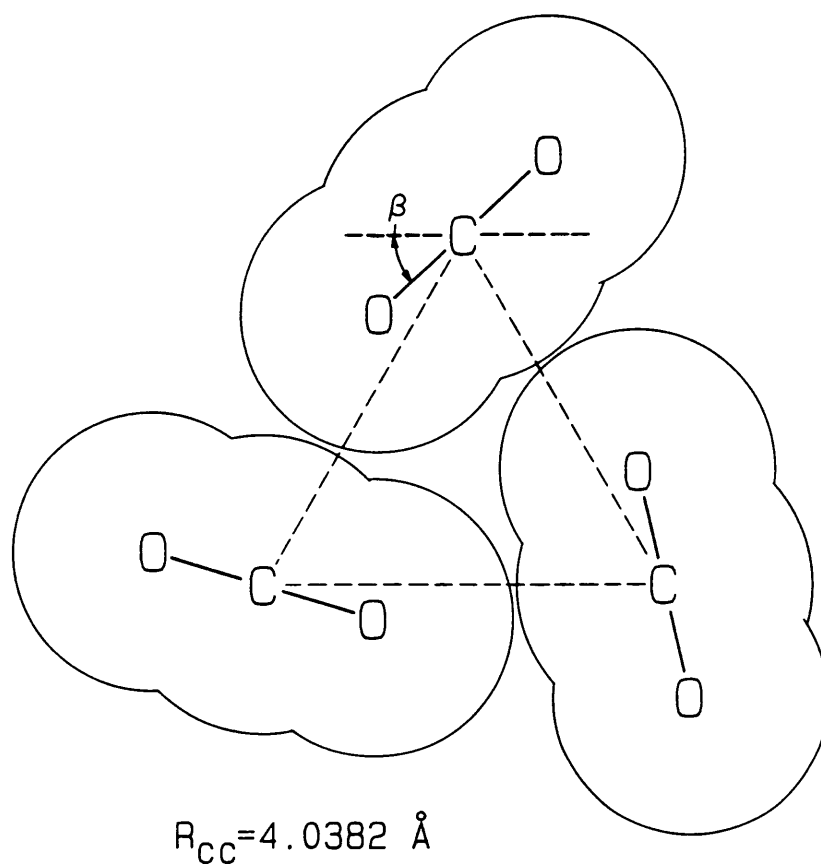$$R_{C---C} = 3.5986(76) \text{ Å}$$

$$R_{C---O} = 3.145(26) \text{ Å}$$

Fig. 1. Structures of CO_2 Dimer and Trimer

The observed spectrum for $(CO_2)_3$ is shown in Fig. 2. Only the lower frequency Fermi diad band was observed, blue shifted by ~ 1 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 Å is larger than the 3.599 Å value found in the dimer.

Ne-CO_2, Ar-CO_2, AND Kr-CO_2

Infrared spectra of the C_{2v}[6] Ne-, Ar-, and Kr-CO_2 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 CO_2 by 1-2 cm^{-1}, while for Ne-CO_2 they are blue shifted by ~ 0.2 cm^{-1}. The predissociation linewidths range from 0.5 to ≤ 5 MHz except for the upper Fermi-diad band of Ne-CO_2, which shows a broad width of ~ 22 MHz arising from near resonant predissociation of Ne-$CO_2(\nu_1+\nu_3)$ → Ne + $CO_2(2\nu_2+\nu_3)$.

CONCLUSION

Here, we have summarized spectral results that have been obtained for weakly bound complexes of CO_2. 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.
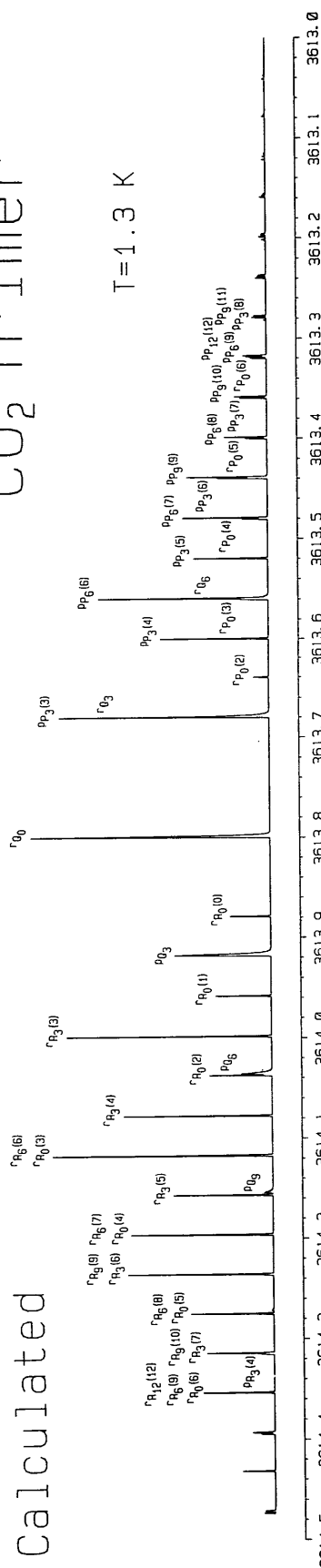
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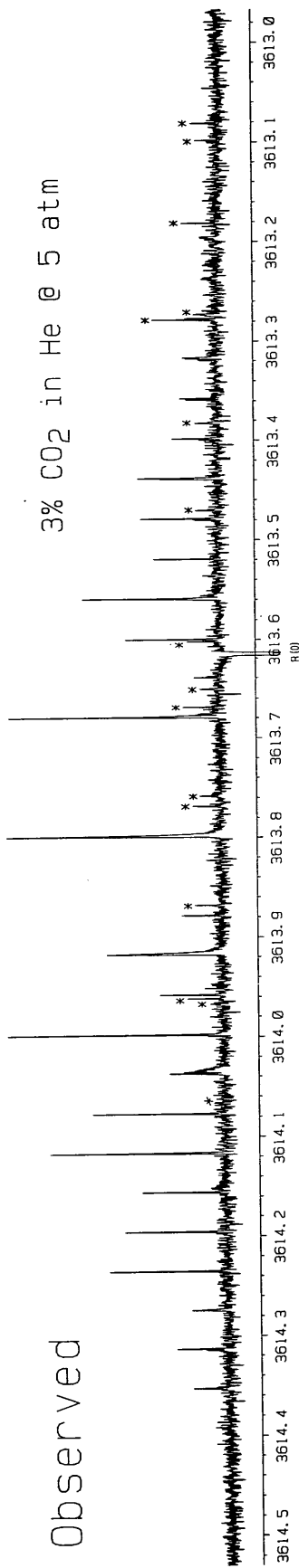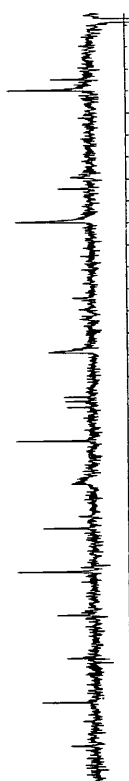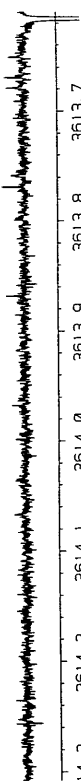Fig. 2. Observed and calculated infrared spectra of $(CO_2)_3$ near the $2\nu_2+\nu_3$ vibration of CO_2.