

HIGH RESOLUTION INFRARED SPECTRA OF CARBON DIOXIDE CLUSTERS $(\text{CO}_2)_N$ IN THE RANGE $N = 6 - 13$

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From 1984 to 1996 there was rapid progress in the spectroscopy of CO_2 dimers and trimers, but since then few high-resolution results have appeared on carbon dioxide clusters. Here we report new results on larger clusters, including assignments of eleven specific bands to $(\text{CO}_2)_6$, $(\text{CO}_2)_7$, $(\text{CO}_2)_9$, $(\text{CO}_2)_{10}$, $(\text{CO}_2)_{11}$, $(\text{CO}_2)_{12}$, and $(\text{CO}_2)_{13}$. The spectra were obtained in the $\text{CO}_2 \nu_3$ region ($\sim 2350 \text{ cm}^{-1}$) by direct absorption using a pulsed supersonic slit-jet expansion and a rapid-scan tuneable diode laser spectrometer. The assignments are based on recent calculations by Takeuchi^a which use the Murthy empirical intermolecular potential.^b

The assignments of $(\text{CO}_2)_6$ and $(\text{CO}_2)_7$ are fairly secure. The hexamer is a symmetric top with S_6 point group symmetry in which all 6 CO_2 monomers are equivalent. It can be thought of as a stack of two planar cyclic trimers. In addition to the main fundamental band with perpendicular selection rules, we also observe one with parallel selection rules, which we believe is a combination band analogous to that observed for the trimer.^c The heptamer is an asymmetric top with no symmetry. The assignments of $(\text{CO}_2)_9$, $(\text{CO}_2)_{10}$ and $(\text{CO}_2)_{11}$ are more tentative, but consistent with their calculated asymmetric top structures. $(\text{CO}_2)_{12}$ is also an asymmetric top, and the rather strong band assigned to it at 2364.34 cm^{-1} has a distinctive Q-branch structure. Finally, $(\text{CO}_2)_{13}$ is calculated to have a remarkable symmetric top structure consisting of a single CO_2 monomer surrounded by an icosahedral cage with S_6 symmetry. We observe three bands with a common ground state and a B-constant of 92.6 MHz, close to the calculated $(\text{CO}_2)_{13}$ value of 94.5 MHz. Interestingly, there is a clear trend for the main cluster band origins to increase (blue-shift) from that of the hexamer at 2353.6 cm^{-1} to those of the tridecamer ($N = 13$) at 2367.7 and 2368.0 cm^{-1} . These bands offer intriguing prospects for learning more about the structures and dynamics of CO_2 clusters in a challenging and important size range.

^aH. Takeuchi, *J. Phys. Chem. A* **107**, 5703 (2008).

^bC.S. Murthy, S.F. O'Shea, and I.R. McDonald, *Mol. Phys.* **50**, 531 (1983).

^cM. Deghany, M. Afshari, N. Moazzen-Ahmadi, and A.R.W. McKellar, *J. Chem. Phys.* **128**, 064308 (2008).

Presentation mode: lecture

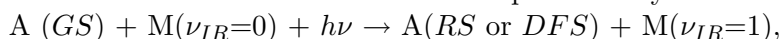
Time required: 15 min

Comment: *lecture is preferred – these are exciting new results on CO2 clusters!*

VIBRATIONALLY INDUCED TRANSITIONS IN SPECTRA OF ATOM-MOLECULE COLLISION PAIRS.

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Spectra of Rg + CF₄, Rg + C₂F₆ (Rg=Xe, Kr) and Na + CF₄ collision pairs display satellite transitions at atom state energies increased by one quantum energy in IR active vibrational mode of molecule ^{a-d}. The process may be written as follows



where *GS*, *RS*, and *DFS* denote respectively the ground, resonance and dipole-forbidden states of the atom and ν_{IR} is an IR active vibrational mode. Satellites of the resonance and dipole-forbidden transitions are essentially differ in spectral shape and intensity implying different intensity borrowing mechanisms

This contribution presents an overview of vibrationally induced transition studies in mixtures of atomic gases with perfluorocarbons. Recent studies of vibrationally induced satellites of molecular transitions in I₂-doped cryogenic C_nF_{2n+2} solids will be discussed as well.

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^aV.Alekseev, N. Schwentner, *Chem. Phys. Lett.* **436**, 327 (2007)

^bV.Alekseev, N. Schwentner, *Chem. Phys. Lett.* **463**, 47 (2008)

^cV.A.Alekseev, 19th International Conference on Spectral Line Shapes, *AIP Conference Proceedings* **1058**, 163 (2008).

^dV.Alekseev, J. Grosser, O.Hoffmann, F. Rebenrost, *J. Chem. Phys.* **139**, 201102-1 (2008).

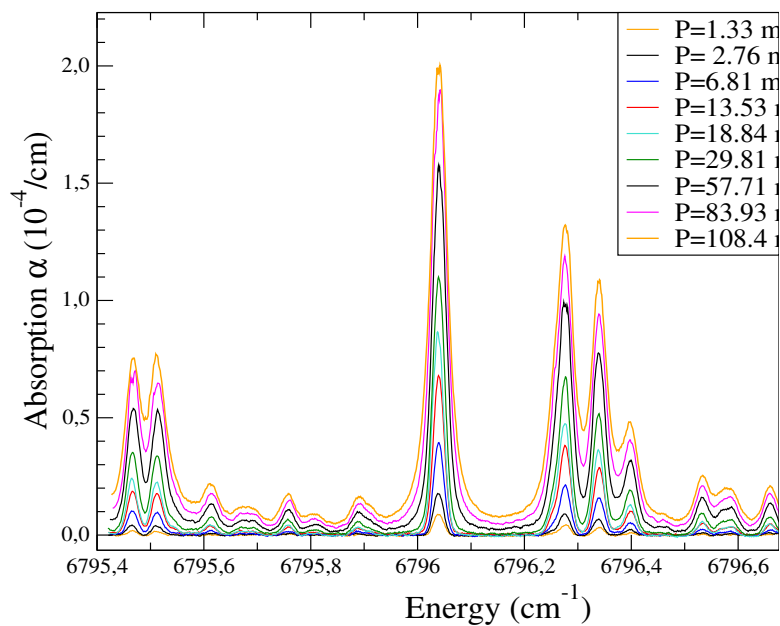
Presentation mode: talk

Collisional broadening study of CH₄ around 1.47 μm using off-axis cavity enhanced absorption spectroscopy.

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On purpose to study the nuclear spin conversion in methane, we have developed a technique to register a part of the absorption spectrum around 1470 nm where transitions of different isomers are present. As the method has to be sensitive enough to study the phenomena with conditions of weak densities (low pressure gas, sublimation, interaction with surfaces), we choose the off-axis cavity enhanced absorption technique. The Doppler effect and collisional broadening is responsible of the transition profiles. We present studies of self and air broadening for some transitions in order to collect data for atmospherical and astrophysical database.

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VERY HIGH SENSITIVITY CW-CRDS OF THE $a^1\Delta_g - X^3\Sigma_g^-$ (0 - 0) AND (0 - 1) BANDS OF OXYGEN NEAR 1.27 AND 1.58 μm : FIRST OBSERVATION OF ELECTRIC QUADRUPOLE TRANSITIONS AND OF THE HYPERFINE STRUCTURE OF THE ^{17}O -CONTAINING ISOTOPOLOGUES

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The CW-Cavity Ring Down Spectroscopy (CW-CRDS) technique has been used to record the $a^1\Delta_g - X^3\Sigma_g^-$ (0 - 0) band of six isotopologues of oxygen near 1.27 μm at room temperature. The achieved sensitivity (noise equivalent absorption $\alpha_{min} \sim 2\text{-}5 \times 10^{-11}$) has allowed for the first laboratory detection of

- (i) extremely weak electric quadrupole transitions with intensity ranging between 1×10^{-30} and 1.9×10^{-28} cm/molecule,
- (ii) the $a^1\Delta_g - X^3\Sigma_g^-$ (1 - 1) hot bands of the of $^{16}\text{O}_2$ and $^{18}\text{O}_2$ species,
- (iii) the partly resolved hyperfine structure of the transitions of the $^{16}\text{O}^{17}\text{O}$, $^{17}\text{O}^{18}\text{O}$ and $^{17}\text{O}_2$ isotopologues.

From the additional recordings of the ^{17}O enriched sample performed by CW-CRDS at liquid nitrogen temperature, the resolution of the hyperfine structure was considerably improved allowing for the first determination of the coupling of the electronic angular momentum with the nuclear spin in the $a^1\Delta_g$ state of the $^{16}\text{O}^{17}\text{O}$

CW-CRDS measurements were also performed in the region of the $a^1\Delta_g - X^3\Sigma_g^-$ (0 - 1) near 1.58 μm with a sensitivity better than 10^{-12} cm^{-1} , extending our previous results and demonstrating very high sensitivity quasi-routine measurements.

Presentation mode: lecture

Time required: 15 min