FAR-INFRARED SPECTRA OF CO_2 CLATHRATE HYDRATE FROSTS; J. C. Landry and A. W. England, Radiation Laboratory, University of Michigan, Ann Arbor, Michigan, USA.

ABSTRACT: As a product of our interest in remote sensing of planetary ices, we have grown frost samples of CO_2 clathrate hydrate by depositing water vapor on a cooled surface and pressurizing the resulting water frost with CO_2 gas. At pressures above the dissociation pressure of the clathrate, the samples exhibit an absorption peak at 75 cm^{-1}. At pressures below the dissociation pressure, the peak disappears. Since the free CO_2 molecule does not have rotational or vibrational absorption in this region, the absorption is attributed to a CO_2 rattling mode within a clathrate cage.

INTRODUCTION

Clathrate hydrates are believed to exist in many places in the solar system. Uranus, Neptune, Mars, and comets are likely places for the presence of clathrate hydrates, but their natural existence has only been confirmed on earth [1]. The most practical way of detecting clathrate hydrates elsewhere in the solar system is probably through remote sensing experiments. In order to design such experiments, it is necessary to know their dielectric properties.

A clathrate hydrate is made up of a host lattice of water molecules that contains cages which incorporate guest molecules. The guests are free to rotate, vibrate, and translate (rattle) within their cages. Rotational and vibrational absorption bands of the guest are similar to those of the free molecule. Consequently, these bands are unsuitable for the remote detection of a clathrate in the presence of the free gas. Rattling modes, however, are unique to the clathrate and may be useful in a detection experiment.

The long term goal of this research is to determine the dielectric properties of carbon dioxide clathrate hydrate in the region of its rattling modes. The CO_2 hydrate is important because it is believed to be a major constituent of the the northern Martian poles during part of the annual cycle. The present paper describes a preliminary study of the absorption of CO_2 frosts.

SAMPLE PREPARATION AND MEASUREMENT

The sample was prepared inside the polyethylene cell shown in Figure 1. One wall of the cell can be conductively cooled through contact with the cold finger of a liquid nitrogen cooled cryostat. The inner face of this wall is covered with copper foil on which the sample is deposited. The temperature of the foil is measured by a platinum resistance temperature detector (RTD) wrapped several times by the foil. A tube connected through the opposite wall of the cell carries in the wires necessary for the temperature measurement. Two additional tube connections allow gas to be flowed through the cell and allow the cell to be evacuated or pressurized.

The cell was mounted on the cold finger of the cryostat and placed in a Bomem DA8 Fourier transform spectrometer. A mercury vapor lamp source, 12 micron mylar beam splitter, and liquid helium cooled silicon bolometer were used to cover the spectral range of 40-200 cm^{-1}. The spectrometer beam entered the sample cell through its non-cooled wall and reflected off the copper foil. All spectral measurements were at 1.0 cm^{-1} resolution.

To prepare a CO_2 clathrate hydrate frost, a water frost sample must first be formed and its presence verified. The cell was evacuated and cooled to 240K, and a reference spectrum taken. Water vapor from a de-ionized water reservoir was allowed to flow through the sample cell so that it deposited a water frost on the cell's cooled face. A second spectrum was taken and ratioed with the reference spectrum to form a transmission spectrum of the frost. By comparing this spectrum with water ice spectra from other sources [2], the presence of the water frost was confirmed.

The cell was pressurized with 1.7 bars of CO_2 gas, which at 240 K is below the clathrate dissociation pressure. (CO_2 clathrate dissociation pressure curves are given in [1] and [2]). A new spectrum of the sample revealed no significant changes in the water ice. The temperature was then lowered to 210 K. where the dissociation pressure of CO2 clathrate is less than 1 bar, but the CO_2 saturation vapor pressure is above 2 bars. The clathrate hydrate formed and another spectrum was taken and ratioed with the previous water frost spectrum. The resulting transmission spectrum repeatedly exhibited the absorption at 75 cm^{-1} shown in Figure 2.

To eliminate the possibility that the absorption was due to CO_2 ice, the temperature was lowered to 190 K where the saturation vapor pressure of CO_2 is below 1 bar. At this low temperature, the sample spectrum shows the lattice mode absorptions of CO_2 ice at 68 cm^{-1} and 111 cm^{-1}[3]. These modes were not observed at 210 K, indicating that CO_2 ice was not present.

DISCUSSION

CO_2 has no permanent dipole moment and therefore does not have strong rotational transitions. Furthermore, its vibrational absorptions occur at frequencies above 600 cm^{-1}. Since the free CO_2 molecule has no strong absorption in the region of 75 cm^{-1}, we attribute the observed absorption to a rattling mode. In order to strengthen this conclusion, a future sample will be prepared using CO_2 gas molecules containing the carbon-13 isotope. Spectra obtained from such a sample should show an isotopic frequency shift in the observed absorption.

According to Mariner 7 radiometric measurements of the north polar region of Mars, surface temperatures reach about 148 K, while the CO_2 partial pressure is 6.5 mbar [1]. We intend to examine clathrate films under these conditions and to extract from their spectra dielectric properties that can be used in remote sensing simulations of the Mars ices.

ACKNOWLEDGEMENTS

This work is supported under NASA Center for Space Terahertz Technology Grant NAGW-1334.

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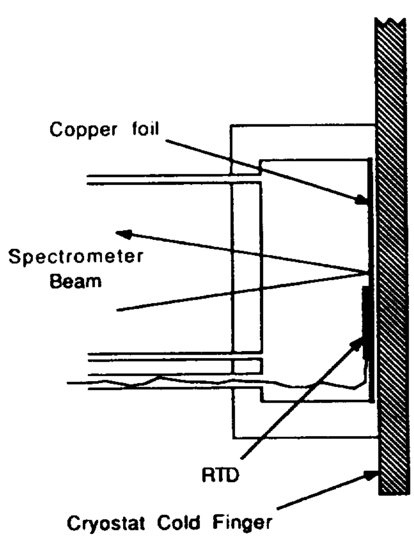

Figure 1: Sample Cell

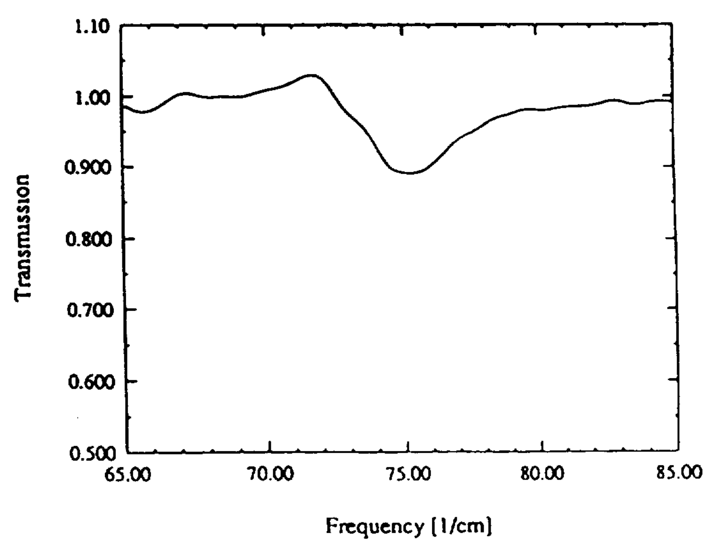

Figure 2: Transmission Spectrum