

MASTER

HIGH PRESSURE STUDIES TO DETERMINE THE EFFECTS OF
VOLUME AND TEMPERATURE ON THE LATTICE DYNAMICS
OF MOLECULAR SOLIDS: N₂, CO₂, CH₄

Progress Report
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ABSTRACT

The temperature dependence of the far infrared spectrum of α -N₂ was studied for a sample at constant volume. The two modes observed near 50 and 72 cm⁻¹ have frequencies which increase slightly with temperature. The integrated intensity of the mode near 50 cm⁻¹ remains constant with temperature, within experimental uncertainty. The Grüneisen parameter of this mode was estimated to be ~ 3 . A study of the volume dependence of the infrared spectrum of α -N₂ is currently under progress.

Two samples of solid CH₄ of different densities were grown. Grüneisen parameters of 2.6 and 3.1 were obtained for the librational mode and one translational mode in phase II. The former indicates an anisotropic intermolecular potential with a strong volume dependence. Changes in the spectrum indicate that the II-III phase transition involves a sudden, simultaneous tetragonal distortion of the lattice and ordering of the orientationally disordered molecules of phase II, with a slow reorientation of the ordered molecules. The librational mode of phase II does not go soft near the transition to the orientationally disordered phase I. The temperature dependence of the linewidth for this mode can be explained by a thermally activated reorientation of the ordered molecules in phase II with an activation energy of 60 cm⁻¹.

A study of the volume and temperature effects on the infrared absorption spectrum of solid methane is presently under progress.

I. PROGRESS SUMMARY

The first experiments carried out last summer did not involve any of the proposed research projects. These experiments were intended to test the experimental set-up without growing a solid. They included collision-induced Raman scattering from fluid methane under pressure and studies of the density dependence of the vibrational mode of nitrogen molecules and the breathing mode of methane molecules in the fluid phase.

The following work on the specific research projects of the original proposal have been carried out or are under progress:

i) A study of the volume and temperature effects on the infrared absorption spectrum of solid nitrogen: A sample of β -N₂ grown at a pressure of 2.6 Kbar on the melting line was taken into the α -phase after annealing. The far infrared spectrum of this sample was studied essentially at constant volume in the temperature range from 13 to 36 K, which is one degree below the α - β transition. The frequencies of the two infrared active modes (around 50 and 72 cm⁻¹) were found to increase with temperature by 1 and 2% in the above temperature range. The large decrease in frequency observed by previous authors for the 50 cm⁻¹ line was ascribed to changes in volume and a Grüneisen parameter of 3 is estimated for this mode. The integrated intensity of this mode was found to remain constant within experimental uncertainty, in sharp contrast with previous results. This results indicate that the quadrupole-induced dipole mechanism fails to predict the volume dependence of the intensity.

A study of the volume dependence of the infrared spectrum of α -N₂ is currently under progress. Two samples have been studied. At least one more sample needs to be studied.

ii) A study of the volume and temperature dependence of the Raman spectrum in phase II of solid methane: Two samples of solid methane were grown at specific points on the melting line so that they would end up in phase II at 20 K with the largest possible difference in pressures - and molar volumes. The line at 34.3 and 39.2 cm^{-1} in the two samples at 20 K was found to have a Grüneisen parameter of 3.2, which supports its previous assignment as a translational mode. The stronger line at 45.0 and 50.3 cm^{-1} was found to have a Grüneisen parameter of 2.6, which is much higher than expected for an octupole-octupole interaction between molecules. This result indicates an anisotropic intermolecular potential with a stronger volume dependence. Changes in the Raman spectrum were consistent with a II-III phase transition involving a sudden, simultaneous tetragonal distortion of the lattice and ordering of the orientationally disordered molecules, with a slow reorientation of the ordered molecules. The librational mode of phase II did not go soft near the transition to the orientationally disordered phase I. The temperature dependence of the librational linewidth could be explained by a thermally activated reorientation of the ordered molecules with an activation energy of 60 cm^{-1} .

iii) A thorough study of the volume and temperature effects on the infrared absorption spectrum in phases II, III, and IV of solid methane has been undertaken by Mr. Bruce Baran, a research assistant, as the subject of his Ph.D. thesis.

II. PERSONNEL

i) Professor Fernando D. Medina, the principal investigator, devoted full time to the project during the summer quarter and half time during the academic year. He will devote half time to the project for the rest of the present academic year.

ii) Mr. Bruce Baran, research assistant, has devoted full time to his research project and will continue to do so for the rest of the present academic year.

iii) Two graduate students were hired during last summer on a full time basis and an undergraduate student is presently working 10-20 hours a week on numerous projects related to the on-going research.

III. PUBLICATIONS

1. F. D. Medina, "Temperature dependence of the far infrared spectrum of α -N₂," J. Chem. Phys., to be published, 15 May 1980.
2. F. D. Medina, "Volume and temperature dependence of the Raman spectrum in phase II of solid CH₄," J. Chem. Phys., to be published, 1 July 1980.
3. F. D. Medina, "High pressure cell for far infrared absorption studies up to 10 Kbar at temperatures from 300 to 10 K," Infrared Physics, to be published.
4. F. D. Medina, "Collision-induced Raman scattering from fluid methane," manuscript in preparation.