

THE FAR INFRARED SPECTRA OF SOLIDS UNDER HIGH PRESSURE
(33-100 μ)*

J. R. Ferraro, S. S. Mitra^{§+} and C. Postmus

Argonne National Laboratory, Argonne, Illinois

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Lippincott and co-workers^{1,2} demonstrated the use of a high pressure diamond cell to study the infrared spectra of solids from 1-15 μ . Later they extended this work to the 35 μ region.^{3,4} Application of the cell for study of liquids has been made by Brasch and Jakobsen.^{5,6} With the use of a Perkin-Elmer #301 spectrophotometer, a modified #301 beam condenser, and a high pressure diamond cell[‡], we have extended the infrared region for use with solids to 100 μ . This communication will discuss the method used, and the results obtained.

The beam condenser was modified by cutting the ellipsoid mirrors to accommodate the diamond cell. The beam condenser with the diamond cell is illustrated in Figure 1. Figure 2 shows the apparatus in place in the #301 spectrophotometer. To allow us to make the alignment of the cell windows in the path of the condensed beam easily and reproducibly, a machine lathe micrometer attachment was used. This allowed freedom in three dimensions.

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§Permanent address: The University of Rhode Island, Electrical Engineering Department, Kingston, Rhode Island.

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‡High Pressure Diamond Optics, Inc., McLean, Virginia.

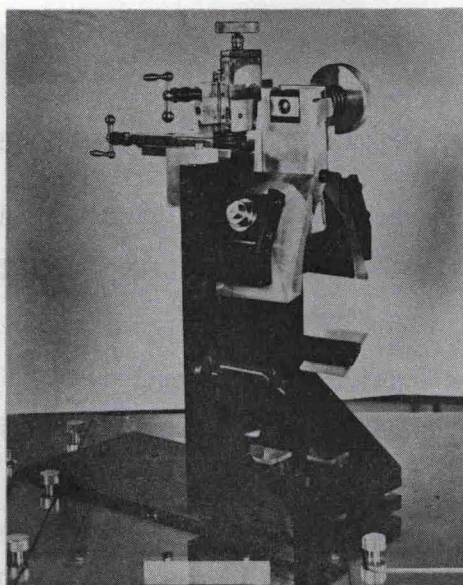


Fig. 1 - High pressure cell mounted in the beam condenser.

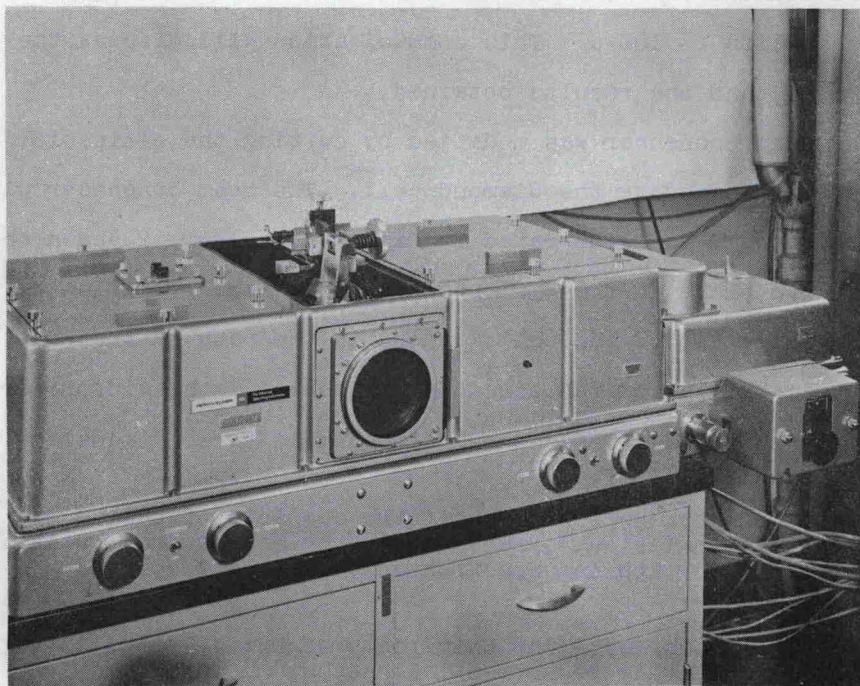


Fig. 2 - High pressure cell in the Perkin-Elmer #301 far infrared spectrophotometer.

To compensate for the large loss in energy the reference beam was attenuated. Attenuation, which simulated the small aperture of the diamond cell (~2 mm), proved to be the most suitable. A diaphragm shutter, such as the type used in a camera worked quite acceptably. A cardboard spacer, with a hole equivalent in size to that of the diamonds, was used in loading the solids in the cell. No attempt was made to optimize the geometry of the optics. Pressures were determined from the calibration of the spring of the high pressure cell.

Only a few results will be discussed. The infrared-active lattice vibration of KBr at about 120 cm^{-1} was shifted to 144 cm^{-1} under a pressure of 35,000 atmospheres, representing a 20% shift toward higher frequencies. Figure 3 illustrates the effect of pressure on the lattice infrared spectrum of KBr with increasing pressure. The ν_4 vibration at about 622 cm^{-1} in Na_2SO_4 shifts 3 cm^{-1} to 625 cm^{-1} under a pressure of 35,000 atmospheres, whereas the lattice vibration at 183 cm^{-1} shifts to 235 cm^{-1} at these pressures. The lattice vibration in NaNO_3 at 212 cm^{-1} splits into two bands under pressure as shown in Fig. 4. One band shifts to 279 cm^{-1} and the other to 224 cm^{-1} at about 35,000 atmospheres.

Changes in intensities and shape of bands for solids under pressure were noted. In some cases spectra washed out completely. In general, absorptions became broader with increasing pressure. In most instances these effects were reversible, and lowering of the pressure brought back the original spectrum.

The high pressure effects on solids appear to be more dramatic and more effective in contracting the lattice in solids, than low temperatures. The temperature dependence of the peak position and half-width of lattice vibrational modes consist of

two parts, (i) the purely volume dependent part obtainable from the Gruneisen equation of state, and (ii) the contribution from the various anharmonic (cubic and higher) terms in the potential energy of the lattice. Often the directions of shifts arising from the two effects may be opposite thus resulting in a small apparent temperature dependence. Such studies on the temperature dependence of the lattice vibrations of LiF and MgO have recently been made.⁷ On the other hand, the pressure dependence of the peak position arises primarily from (i), and thus for the same amount of volume contraction, may be relatively large for certain solids compared to the temperature dependence of the peak position. One of the purposes of the study of the pressure dependence of lattice vibrations is to enable one to estimate the above two contributions separately, when data thus derived are combined in the data on temperature dependence for the same solid. The elucidation of anharmonic forces in dielectric solids thus becomes possible. The present data do not warrant such detailed treatment. Further study is in progress, the results of which will be treated in detail in a forthcoming publication.

Preliminary results have indicated only small minor shifts (if any) for internal modes of vibrations, while large shifts have been observed for external modes (lattice vibrations). This method can thus possibly be a way of distinguishing between the two modes and would simplify the interpretation of the far infrared spectra of solids. Extension of high pressure studies to the infrared region of 100 cm^{-1} , aside from a study of lattice vibrations, makes possible studies of the low-lying hydrogen bonded vibrations in hydrogen bonded systems. In addition other solid state effects in the low energy regions may now be studied under high pressure.

It is anticipated that this work will continue with several modifications of the equipment and techniques as follows:

- (1) Attenuation will be made with a second beam condenser and diamond cell. This will serve to equalize the path lengths in both beams.
- (2) Low temperature and high pressure studies of solids will be made.
- (3) An attempt will be made to optimize the optics geometry.
- (4) Metal foil washers, with smaller holes than the size of the diamond, will be used as spacers between the diamonds. This will prevent observing the solid at the edges of the diamond faces.

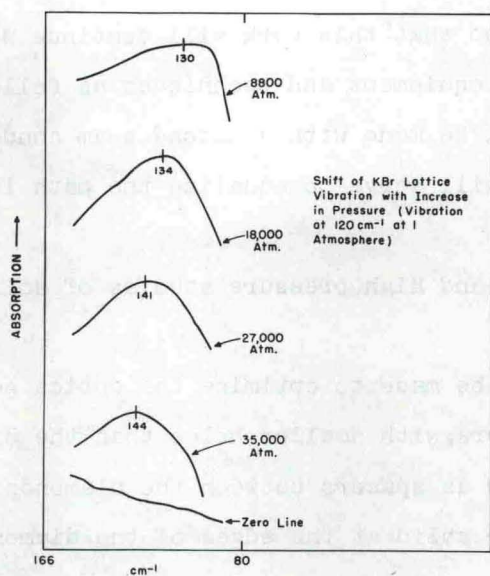


Fig. 3 - Effect of pressure on the lattice vibration of KBr.

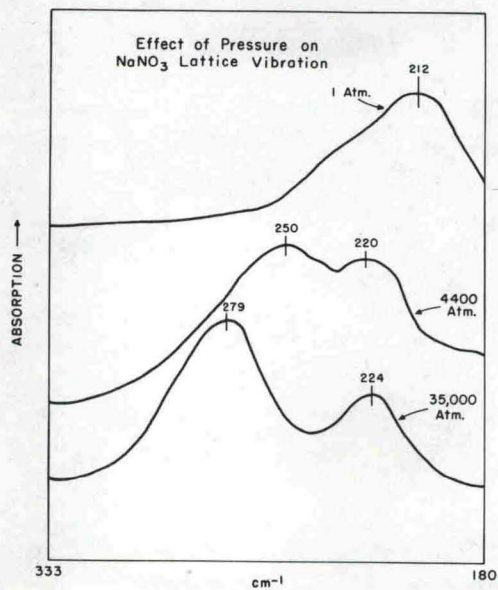


Fig. 4 - Effect of pressure on the lattice vibration of NaNO₃.

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