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HIGH PRESSURE RESEARCH IN THE FAR INFRARED REGION^{*+}

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ABSTRACT

The capability of obtaining vibrational spectra in the low frequency region below 300 cm^{-1} under non-ambient pressures to 80 kbars, is a comparatively new technique. The instrumentation necessary to do this will be reviewed. Studies made with ionic solids and coordination compounds will be discussed. Problems and limitations in the method will be presented.

INTRODUCTION

The first spectroscopic measurements at non-ambient pressures were made by Drickamer. His experiments covered the regions of ultraviolet, visible and near infrared.¹⁻² It is the infrared region that is of concern to us in this paper. In 1956, Drickamer studied the effect of pressure on the vibrational frequency of bonds containing hydrogen to 5.0 microns (2000 cm^{-1}). Extension to 35.0 microns (285 cm^{-1}) was made by Weir, Van Valkenburg, and Lippincott.³⁻⁵ In 1966, the capabilities of making low frequency measurements at high pressures up to 200 microns (50 cm^{-1}) were developed by Ferraro, Postmus and Mitra⁶⁻⁷ using a grating spectrophotometer. Using an interferometer, Gebbie⁸ has reported low

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⁺Presented at the Nato Advanced Study Institute on Far Infrared Properties of Solids, Delft, Netherlands, August 5-23, 1968.

frequency spectra to 1000 microns (10 cm^{-1}), and McDevitt *et al.*⁹ to 40 cm^{-1} . It thus appears that adequate techniques are now available to conduct far infrared studies at high pressure. This is not to say that the ultimate in instrumentation has been reached, however. Many instrumental problems exist and experiments are tedious and time-consuming.

This paper will discuss the present instrumentation and applications of the technique, and in conclusion, will discuss recent high pressure-Raman techniques.

AVAILABLE INSTRUMENTATION FOR FAR INFRARED-HIGH PRESSURE STUDIES

Optical High Pressure Cells

It would be advisable to briefly describe the available instrumentation capable of making low frequency measurements under pressure. A summary of the optical high pressure cells available with their advantages and disadvantages is shown in Table I.

The shock wave techniques can obtain pressures up to 1000 kbars. The shock wave is generated by explosives. The technique would be extremely difficult to use with a scanning spectrophotometer, since the duration of the shock is only of a short time.

The piston-cylinder developed by Drickamer and Balchan¹⁰ for use from 0.2 to 5.0 microns used sapphire windows of $1/2$ inch diameter and $1/2$ inch thickness. These windows proved fragile and Drickamer¹¹⁻¹³ converted to sodium chloride windows thereafter.

Perhaps the most useful cell is the opposed anvil cell developed in recent years by Weir, Van Valkenburg, and Lippincott,³⁻⁵ using diamond anvils. They used type II diamonds which are transparent in the regions of the ultraviolet, visible, and infrared, except for a portion at 4-6 microns where absorption occurs. Pressures up to 200 kbars have been claimed with this cell.¹⁴

Link of Optical Cell with Infrared Spectrophotometer

Table II lists the apparatus in current use for low frequency high pressure studies. The instrumentation using a grating spectrophotometer were developed by Ferraro, Mitra, and Postmus.⁶⁻⁷ The technique is capable of reaching 200μ , and involves the use of a Perkin-Elmer Model No. 301 double-beam grating spectrophotometer, used in double beam operation, a 6x beam condenser and the high

TABLE I
Summary of Available Optical High Pressure Cells

<u>Type of Cell</u>	<u>Pressures</u>	<u>Advantages</u>	<u>Disadvantages</u>
Shock Wave	1000 kbar	1) Highest obtainable pressures	1) Pressure exerted over short time
Piston and Cylinder	200 kbar	1) Largest specimen volumes	1) Not enough optical clarity to permit optical observation or photography
		2) Considered to give hydrostatic pressures	2) Specimen may interact with salt matrix
			3) Must be calibrated with respect to pressures measured in a different type of cell
Opposed Anvils (Diamonds)	200 kbar	1) Micro-quantities of material necessary	1) Pressure gradient exists
		2) Compact--can be used with spectrophotometers	2) Absorption of diamonds from 4-6 μ

TABLE II
High Pressure Apparatus Currently Used for Low Frequency Studies

<u>Workers</u>	<u>Spectrophotometer or Interferometer</u>	<u>Wavelength Range μ</u>	<u>Optical Cell</u>
Weir, Van Valkenburg, and Lippincott ³⁻⁵	Commercial double-beam spectrophotometer with beam condenser	2-35	Diamond Anvil
Jacobsen and Brasch ¹⁵⁻¹⁶	Perkin-Elmer No. 521*	2-35	Diamond Anvil
Ferraro, Mitra and Postmus ⁶⁻⁷	Perkin-Elmer No. 301* Beckman IR-11** Beckman IR-12**	16-200 16-200 2-40	Diamond Anvil " " " "
McDevitt, Witkowski, and Fateley ⁹	FS-520 interferometer	to 250	Diamond Anvil
Bradley, Gebbie <u>et al.</u> ⁸	Michelson interferometer	50-1000	Anvil, quartz window

*With 6x beam condenser.

**With 8x beam condenser, (see L. Basile, et al. Spec. Letters, 1(5), 189 (1968)).

NOTE: For operation to 200 μ with a grating spectrophotometer, a cost of about \$12,000 is necessary for a beam condenser and the diamond cell.

pressure diamond cell of High Pressure Diamond Optics, Inc., McLean, Virginia. Certain modifications were necessary. The size of the ellipsoid mirrors on the beam condenser had to be reduced, to accept the diamond cell. To allow for easy alignment of the cell, a machine lathe micrometer attachment was added to give movement in the x,y,z directions. To allow for more energy for operation below 100 μ , larger diamonds (~ 0.8 sq. mm. area) were used, although above 100 μ diamonds of 0.25 sq. mm. can be used. An expansion scale was also built into the No. 301 spectrophotometer, to amplify weak vibrations. This allows for less compensation in the reference beam and the use of narrower slits. For all of the pressure work a microscope is absolutely essential, to determine if one has a good solid load between the diamonds, and if a phase transition is occurring.

In the interferometer tie-up with the diamond cell, a brass cone light pipe is used (angle $9^{\circ}37'$).⁹ The infrared radiation comes out of the instrument and enters this cone. The cone bends the radiation toward the small opening in the other end (.060" opening). The cone is machined to accept the diamond cell piston. The energy then passes through the diamonds and enters the detector by means of another light pipe.

Calibration of Diamond Cell

It has already been indicated that a pressure gradient exists in the multiple anvil diamond cell. Duecker and Lippincott¹⁷ have demonstrated that the pressure gradient across the diamond face is parabolic, with pressures in the center reaching $1\frac{1}{2}$ times those on the edges. Thus, any measure of pressure in the contact area of the diamond gives only an average pressure.

There are several ways to make a pressure calibration of the cell. These are as follows:

1. One measures the compression of the spring by means of a Dillon force gauge. The contact area of the diamond is determined by means of micro photographs. One then knows the force per unit area or pressure.
2. The use of solids which undergo phase transformations at known pressures (e.g., KBr - 18 kbars; KCl - 20 kbars; NaNO_2 - 14 kbars).
3. Calibration can be made by using nickel dimethylglyoxime, which shows a change in spectral properties with pressure.¹⁷⁻¹⁸

APPLICATIONS

This paper will attempt to present some of the applications of the far infrared-high pressure technique that have thus far been investigated. It will indicate the newest developments in this area, and further point out other applications that are contemplated.

Lattice Vibration Studies

Table III lists some ionic lattice frequencies. Most of the frequencies for the transverse optical lattice modes (ν_{TO}) are found below 300 cm^{-1} . The capability of measuring vibrational spectra in the far infrared region under pressure allows one to study these vibrations for the first time in this manner. The longitudinal mode (ν_{LO}) is more difficult to study in the infrared. At 90° incident radiation it is not normally observed. Berreman¹⁹ observed the longitudinal mode for a thin film of LiF with an oblique incident radiation. Longitudinal optical modes of the silver halides have recently been studied with similar techniques.²⁰ With the diamond cell and the highly converging oblique radiation coming from the beam condenser, the longitudinal modes can be observed. They appear as shoulders on the main intense transverse vibrational bands, and are not easily studied in the infrared, for they are less pressure sensitive than the ν_{TO} , and because of the high frequency shift of the ν_{TO} band, can no longer be observed. In more covalent solids the ν_{TO} is very close to the ν_{LO} . In a homopolar covalent crystal, ν_{TO} may be equal to ν_{LO} . In this instance a very broad absorption is observed, which shows very little frequency shift with pressure.

Figure 1 shows a comparison of several ν_{TO} frequencies with pressure. The ν_{LO} pressure dependence for NaF is shown in Fig. 2. In this system the separation between the ν_{LO} and the ν_{TO} is sufficiently large to make possible a determination of the pressure dependency of both optical modes.

In all cases studied, ionic lattice vibrations shifted toward higher frequency with increasing pressure. The shifts at pressures up to 50 kbars can be considerable. However, not all ionic lattice vibrations will show dramatic shifts, since the compressibility of the solid is involved. The relationship between the change in frequency with pressure is given in equation 1,

$$\gamma\chi\nu = \left(\frac{\partial\nu}{\partial p}\right)_T \quad (1)$$

where γ is the Grüneisen parameter, χ is the isothermal compressi-

TABLE III

Lattice Vibrations for Alkali Halides⁽¹⁾ cm^{-1}

	ν_{TO}
LiF	307
LiCl	191
LiBr	159
NaF	246
NaCl	164
NaBr	134
NaI	117
KF	190
KCl	141
KBr	113
KI	98
RbF	156
RbCl	118
RbBr	88
RbI	77
CsCl ⁽²⁾	99
CsBr ⁽²⁾	74
CsI ⁽²⁾	62

ν_{TO} = Frequency of transverse lattice vibration

1. S. S. Mitra and P. J. Giellisse, "Infrared Spectra of Crystals," AFCRL-69-395, June (1965).
2. C. M. Randall, R. M. Fuller and D. J. Montgomery, Solid State Comm., 2, 273 (1964).

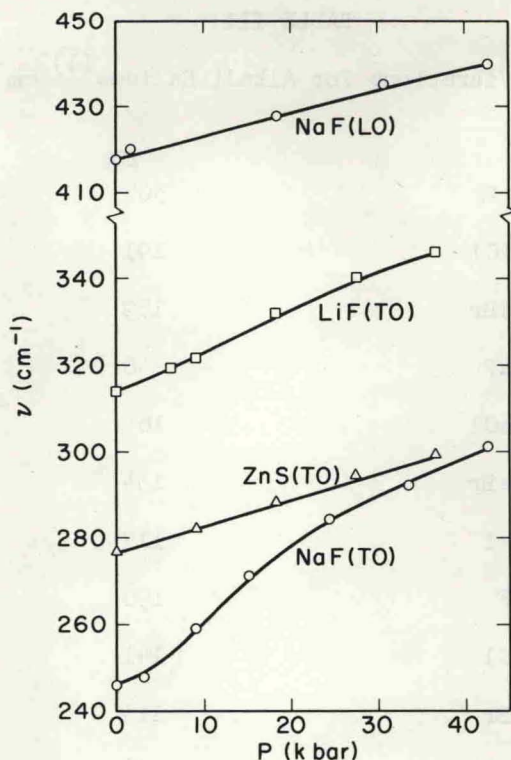


Fig. 1. Pressure Dependencies of Several Lattice Vibrations.

bility of the solid and ν is the frequency of the particular lattice mode. For non-compressible solids it is possible that only small shifts will occur. For example, the lattice modes of zirconia and hafnia failed to show significant shifts at 40 kbars.⁹

The data obtained from studies of the pressure dependency of the $k=0$ lattice vibrations of ionic crystals²¹ when combined with data from studies of these modes with temperature,²² can give a better understanding of the anharmonic interactions in these solids. It is possible to distinguish between the purely volume-dependent contribution and the contribution from various anharmonic terms in the crystal Hamiltonian.²³ Figure 3 shows a plot of $\ln\nu/\nu_0$ vs. $\ln\nu/\nu_0$ for several optic modes. The data has been obtained from pressure and high temperature studies,²¹⁻²³ P-V data from Drickamer²⁴ and from Cline and Stephens.²⁵ It can be observed that the straight line extrapolated from the pressure domain does not coincide with the line obtained from the temperature data. The difference may be attributed to the anharmonic contribution to the frequency shift (known as the "self-energy" shift), and increases steadily with increasing temperature for

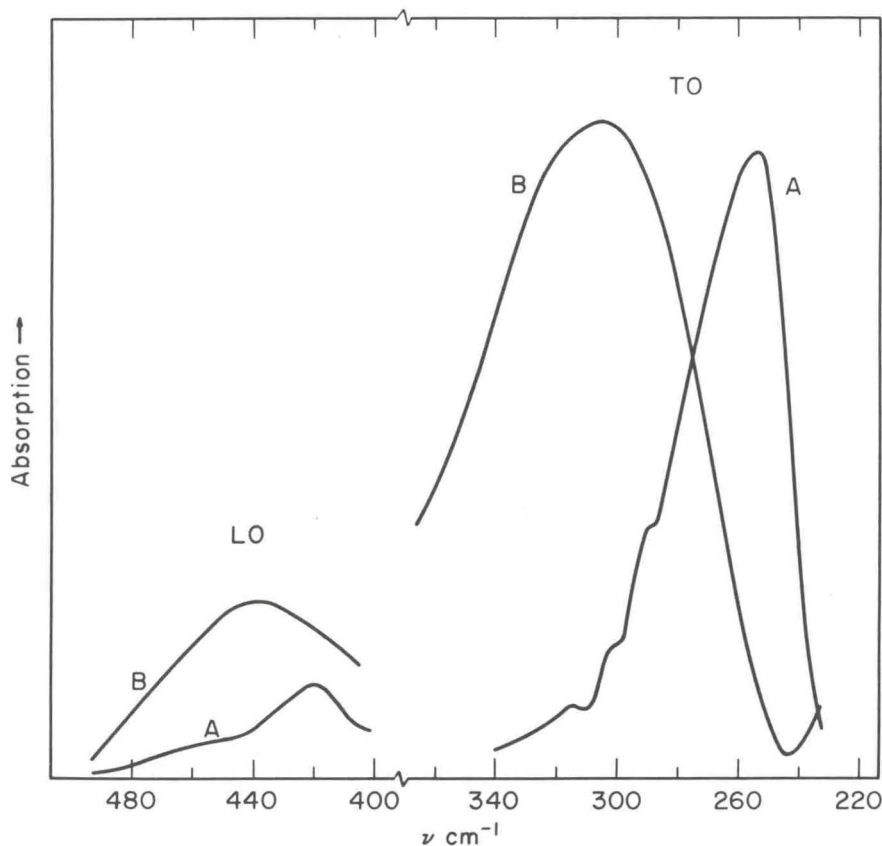


Fig. 2. Comparison of the Transverse and Longitudinal Modes in NaF with and without Pressure.

LiF. A similar analysis was made for KBr and in this crystal the "self-energy" shift is negligible. A similar result was obtained for RbI using other techniques.^{22,26}

The results obtained for the Grüneisen parameters for the long-wavelength optical modes from equation 1 and equation 2,

$$\gamma_j(k) = \frac{\partial \ln \nu_j(k)}{\partial \ln V} \quad (2)$$

are tabulated in Table IV. The agreement with the calculations made from those assuming a rigid-ion model with central forces incorporating repulsion terms of the Born-Mayer [$\exp(-r/p)$] and inverse-power (r^{-n}) type agree well. The results using Cowley's theory give somewhat larger values of γ .

TABLE IV
Gruneisen Parameters for the Long Wavelength Optical Mo

al from Eq. 2	Born-Mayer ²⁷	Calculated r ⁻ⁿ repulsion ²⁸	Cowley ²⁹	C M
2.59	2.44	3.46		
2.95	2.43	3.00		
2.83	2.52	2.95	3.27	
2.46	2.52	2.92		

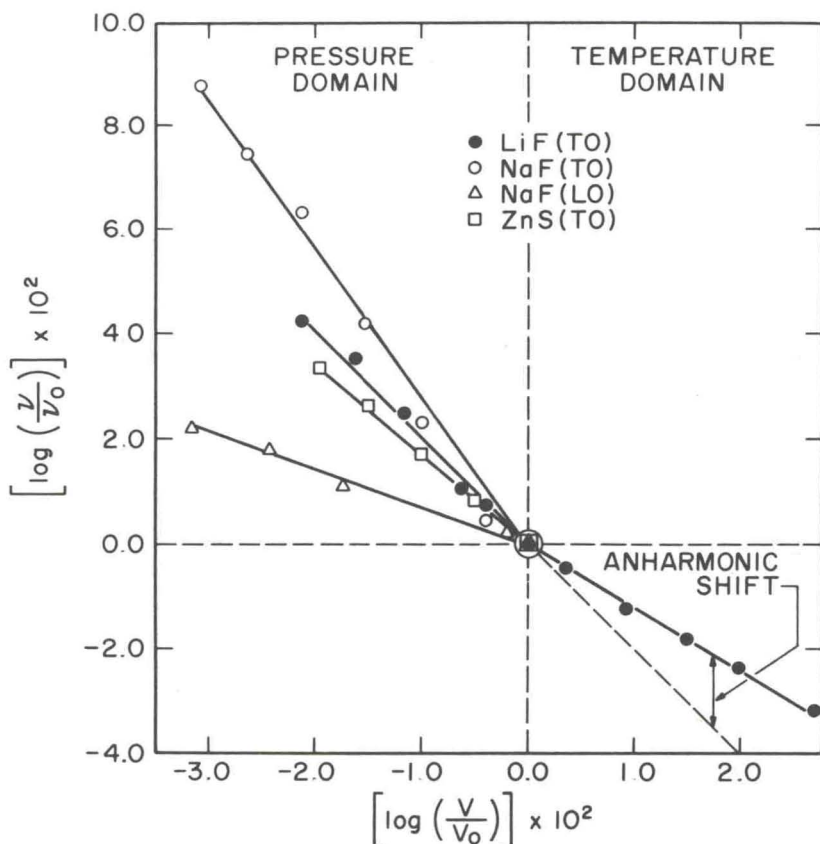


Fig. 3. Plot of $\ln(\nu/\nu_0)$ vs. $\ln(v/v_0)$ for Several Optic Modes.

Pressure dependencies of two phases of a solid can be determined by these techniques.²³ Such studies have been made with KBr²³ and KCl.^{9,23} Figures 4 and 5 show the TO mode of KBr and KCl as a function of pressure. The difficulty of studying phase transitions is illustrated by the figures. The pressure gradient across the diamond anvils prevents the detection of a sharp transition pressure and both phases appear over a range of pressure. The high pressure phase (CsCl structure) appears at 16 kbars for KBr and at 24 kbar for KCl. The conversion to the high pressure phase is complete at 26 kbars and 30 kbars for KBr and KCl respectively. For a limited average pressure range the TO mode of both the low and high pressure phases can be detected, with a gradual decrease in the intensity of the low pressure phase and the in-

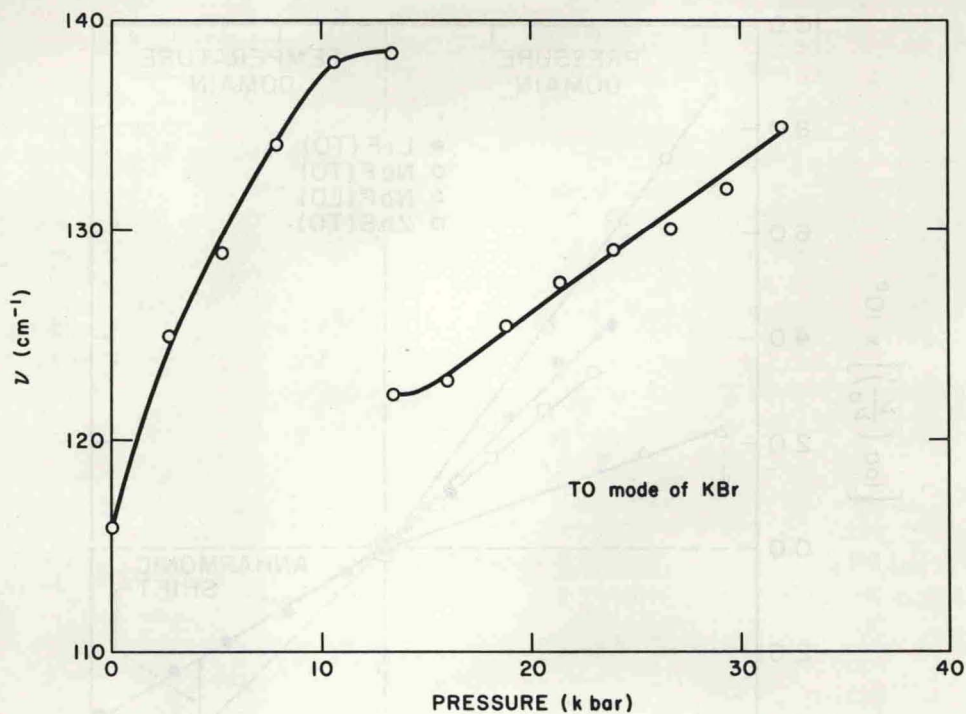


Fig. 4. TO Mode of KBr as a Function of Pressure.

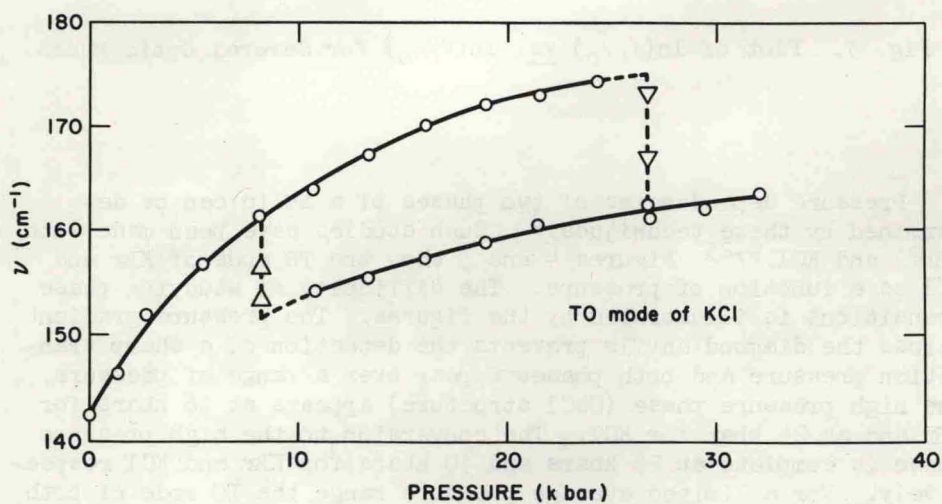


Fig. 5. TO Mode of KCl as a Function of Pressure.

crease in that of the high pressure phase. With a reduction of the pressure, the frequencies of the CsCl phase do not coincide with those determined from increasing pressures (maximum experimental error $\pm 2 \text{ cm}^{-1}$). The low pressure phase does not reappear until 11 and 16 kbars for KBr and KCl respectively. Part of these discrepancies can be attributed to the sluggishness of the system and friction within the cell.

The vibrational frequency decreases at the transition pressure by about 10-12%. The ratio of TO frequency of the CsCl phase to that of the TO frequency in the NaCl phase should equal the square root of the coordination number of each phase; e.g., $\sqrt{6/8}$ or 0.87. The observed ratio for KBr is 0.88 and that of KCl is 0.92.

It has been found³¹ that the $k \sim 0$ TO frequency of the alkali halides of NaCl structure is proportional to $(a/\chi\mu)^{1/2}$, where a is the lattice constant and μ is the reduced mass per unit cell, and χ is the compressibility. The same is true for the CsCl structure. Figure 6 illustrates this. Thus, it may be possible to relate the frequency-pressure data to the structure of the ionic crystal.

Pressure studies with mixed ionic crystals are possible using the diamond cell technique and are now under way.

Certain molecular lattice modes were investigated by McDevitt, Witkowski and Fateley.⁹ The experiments are more difficult to perform, since a thicker sample is needed, and spacers must be used to accomplish this. Molecular lattice vibrations have been observed to also shift toward higher frequency with increasing pressure. It would be expected that their pressure dependencies would be greater than ionic lattice modes due to their greater compressibilities.

Coordination Compounds (Effect of Pressure on Molecular Vibrations)

Whereas certain ionic solids when submitted to pressures show shifts of the optical modes toward higher frequencies, internal modes in other compounds show very little pressure shifts. Nevertheless, certain intensity changes are possible under pressure. For example, a number of coordination complexes having two halides or nitrogens per metal atom would be expected to show an asymmetric and a symmetric stretching vibration. Wherever these two vibrations are resolved into two bands, pressure effects one mode more than the other.³² Figures 7 and 8 illustrate the effect of pressure on the asymmetric and symmetric stretching vibrations of $[\phi_4\text{As}][\text{GeCl}_3]$ and $[\phi_4\text{As}][\text{SnCl}_3]$. The verification as to which is

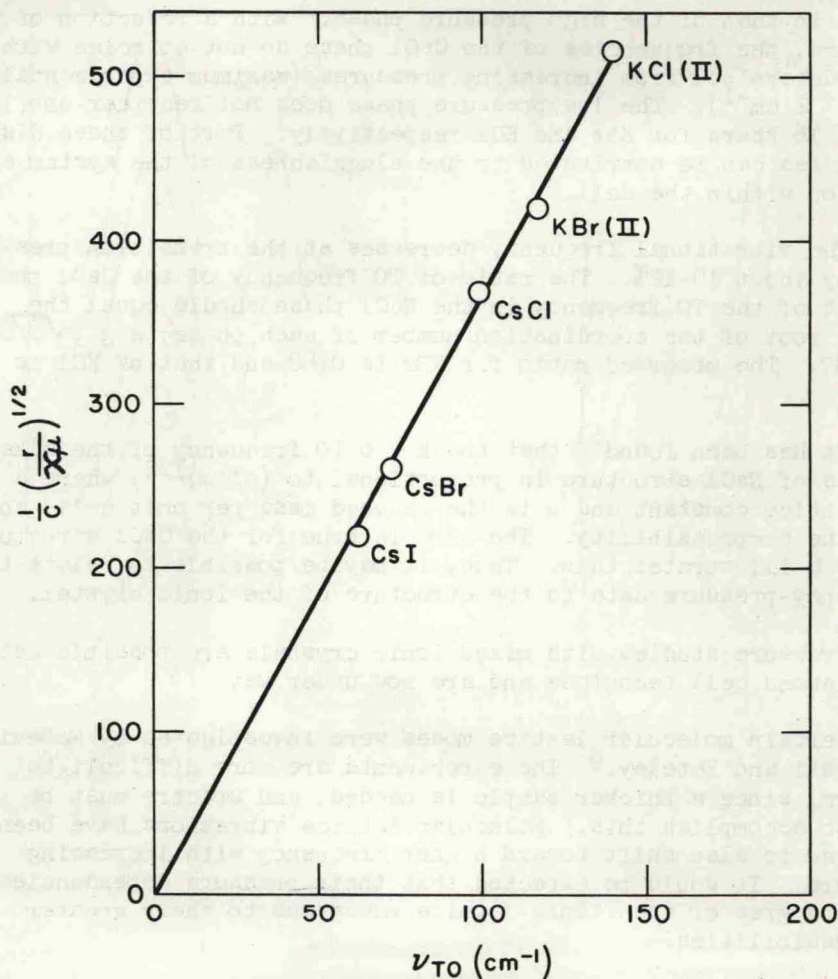


Fig. 6. Plot of TO Mode Frequency vs. $1/c \left(\frac{r}{\chi\mu} \right)^{1/2}$.

low frequency band splits into a doublet, and that the high frequency band decreases in intensity. Under pressure the degeneracy of the F vibration (ν_4) is completely removed. It is concluded that in the spectrum of KMnO_4 at ambient pressure the low frequency band is the E species and the high frequency band is the A_1 species. The results may be attributed to a further lowering of the symmetry of the solid under pressure to C_{2v} and illustrate that pressure can induce symmetry lowering. However, verification of this interpretation can only result when the F vibration (ν_3) is also studied under pressure. It is possible that not all solids will lend themselves to a lowering of the symmetry with the same ease, and one must consider the crystal packing involved for each solid.

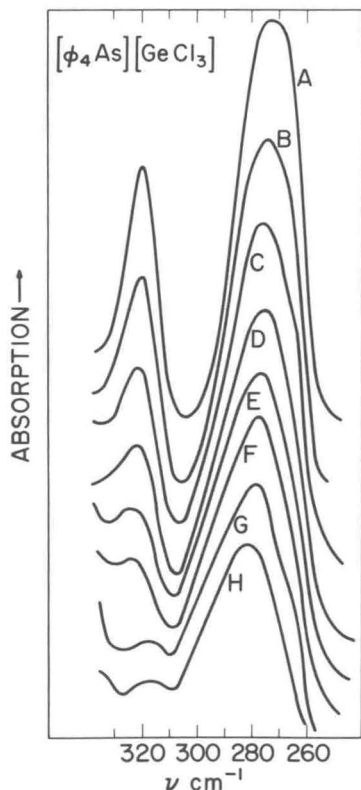


Fig. 7. Low Frequency Spectra of $(\phi_4\text{As})(\text{GeCl}_3)$ with and without Pressure.

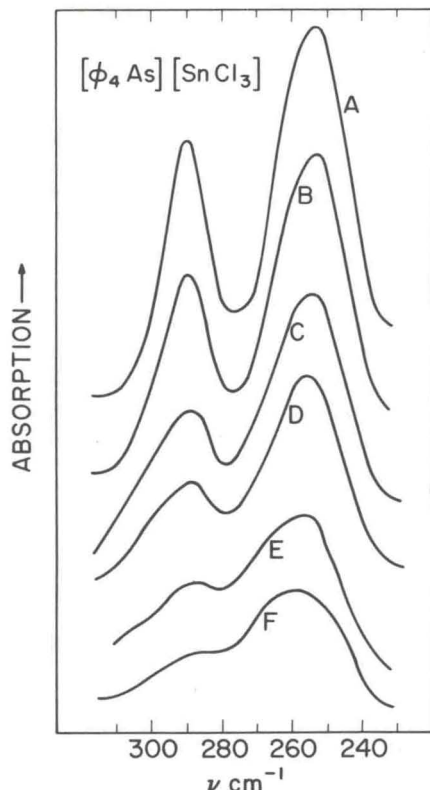


Fig. 8. Low Frequency Spectra of $(\phi_4\text{As})(\text{SnCl}_3)$ with and without Pressure.

The pressure gradient existing in the multiple anvil diamond cell has already been discussed. In an attempt to eliminate as much of the gradient as possible, experiments with molybdenum steel gaskets were made. It has been our experience that applying pressure on a solid with a gasket does not give hydrostatic pressures. However, using a gasket with the solid (HgI), and adding a drop of Nujol and then applying pressure gave what appeared under the microscope to be a single pressure.²⁶ Similar results were obtained recently by Davies¹⁸ with nickel dimethylglyoxime with other organic solvents. Further studies are now under way in our laboratory with other solids and other liquids. The use of a liquid under these conditions, with a freezing point at a known pressure can also give a pressure calibration point besides a hydrostatic pressure.

Discussion

It has been demonstrated that in compressible ionic solids lattice vibrations are pressure sensitive to frequency shift. In all cases studied thus far, the shift is in the direction of higher frequency in agreement with low temperature shifts. However, the pressure shifts may be considerable when compared with the temperature shifts. It is known that the temperature dependence of the peak position and half-width of lattice vibrational modes consist of two contributions: (1) the purely volume dependent contribution; and (2) the contribution from the various anharmonic (cubic and higher) terms in the potential energy of the lattice. Often the directions of shifts in the temperature dependence experiment may be opposite to each other, resulting in a cancellation, and a small overall shift. Apparently molecular lattices, generally speaking, show similar pressure effects. It may be possible in some cases to obtain compressibility data in compressible solids from pressure-frequency measurements (see Equation 1). On the other hand, internal modes which consist of motions involving changes in interatomic distances are not the symmetric mode and which is the antisymmetric mode was made by Raman polarizability data in solution. It is observed that although both peaks diminish in intensity and broaden, the symmetrical vibration (A_1 species) is the most sensitive to pressure. It is important to be able to distinguish between these two modes in making correct far infrared interpretations. The technique is able to do this on powdered or polycrystalline material. Heretofore, only single crystal-dichroism infrared measurements, single crystal or solution-Raman polarizability studies would make this differentiation.

Attempts to induce structural changes in coordination compounds upon the application of pressure to the solids have all failed.³³ Of course, only pressures to about 60 kbars have been used. At these pressures only color changes were observed, similar to those found for nickel dimethylglyoxime.¹⁷⁻¹⁸ These spectral changes with pressure can be observed under the microscope or in a visible spectrophotometer. These changes are not to be confused with any structural changes (e.g., $Td \rightarrow D_{4h}$ etc). It becomes apparent that to determine if any structural changes occur, one should go to solution studies. Such studies are now being initiated.

Newer Developments

Our interest in coordination compounds has motivated us to make a basic study of effects of pressure on the uncomplexed ligands as compared to those in the complexes. Although only preliminary results are available at this time, it appears that some

molecular vibrations involving out-of-plane motions in ligands containing heterocyclic rings (e.g., pyrazine, dipyriddy etc.) are very sensitive to pressure.^{3,4} Some in-plane motions are also sensitive. Thus, motions, generally involving large volume changes, may become pressure sensitive.

Although Lippincott *et al.*^{4,5} examined some inorganic compounds with pressure, no systematic studies have been made in the mid-infrared region and certainly none made in the low frequency region. A systematic basic study of inorganic compounds from 1600-100 cm^{-1} has been commenced. Preliminary results^{2,5} with salts such as K_2SO_4 , K_2CrO_4 , KMnO_4 etc. in the ν_4 region (MO_2 deformation vibration) indicate some pressure sensitivity. For example, the ν_4 (a triply degenerate vibration) vibration in KMnO_4 at $\sim 400 \text{ cm}^{-1}$ is seen as a doublet at ambient pressure. The doublet is attributed to a lowered symmetry (probably to C_{3v}). In this symmetry the two vibrations are the A_1 and E species. Differentiation be-

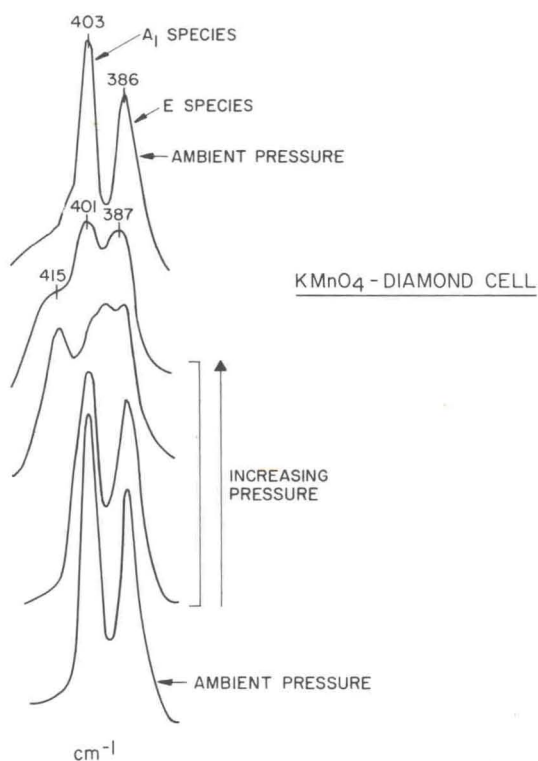


Fig. 9. Low Frequency Spectra of KMnO_4 with and without pressure.

tween the two species is normally difficult. Figure 9 illustrates the effect of pressure on the doublet. It is observed that the similarly effected. No noticeable shifts, or at the most, only slight shifts are observed. The direction of the slight shift may be either a blue or red shift. In hydrogen bonded compounds, studies of the OH stretching vibration has resulted in a red shift.^{5,57} Red shifts were also observed for HgCl_2 and its dioxane complex by Brasch and Jacobsen.³⁸ In most of our studies with internal modes, blue shifts have been observed. The attempts at converting a structural isomer to another having failed in the solid state, indicates that in the pressures used (up to 60 kbars) little effect on the interatomic distances or bond angles occur. However, the results do point to the fact that intermolecular distances are changed (e.g., distance between ions or molecules) under these pressures. It is conceivable that higher pressures are needed to successfully effect the interatomic distances. It should be mentioned, however, that pressure effects appear to be sufficiently large to cause changes in symmetry in a molecule.

The pressure effects on the ionic or molecular lattice modes may be accounted for by the contraction of the solid under pressure, placing ions or molecules closer to each other. Obviously, repulsive and attraction forces in the solid are involved. For internal modes which shift only slightly toward higher frequency the repulsive force must be greater. The shifts of out-of-plane and in-plane vibrations in ring compounds toward higher frequency under pressure, may be attributed to the more energy required to cause the vibration, since the molecules are in closer proximity to each other. Several reasons can be cited for the splitting of bands. The discussion concerns bands with no change in phase occurring with an increase in pressure. One involves the failure to resolve a band into two components at room temperature and ambient pressure. With high pressure this is possible because of the pressure shifts occurring, and one component being shifted a greater amount than the other. Another reason may be due to the removal of degeneracy in degenerate modes. Broadening of all bands occurs and this may be due, at least in part, to the pressure gradient existing in the diamond cell.

The changes in intensities that occur under pressure probably involves large changes in dipole moments for certain modes of vibration. It has been definitely established that other physical effects occurring simultaneously with the electromagnetic effect, can cause changes in the dipole moment for a particular vibration. For example, electrical effects cause dipole moment changes to be non-zero ($\frac{\partial \mu}{\partial Q} \neq 0$) and forbidden frequencies can occur. Pressure effects may cause similar changes, although tending toward $\frac{\partial \mu}{\partial Q} \rightarrow 0$. It has been observed that the A_1 species is particularly sensitive in this regard.

RAMAN-HIGH PRESSURE STUDIES

Raman spectra of gases at high pressures have been obtained.³⁹⁻⁴⁰ The first Raman spectra of micro quantities of solid using the diamond-anvil cell was reported in 1968.⁴¹⁻⁴² The method complements the high pressure-infrared technique and allows a complete vibrational analysis of a molecule to be made at non-ambient pressures.

The instrumentation consisted of a Spectra-Physics Model 125 He-Ne laser (90 mW) with a Spex double monochromator at a slit width of 2 cm^{-1} resolution. Figure 10 shows the schematic diagram of 0° laser excitation. Figure 11 shows the actual apparatus used. Figure 12 shows the Raman spectra for HgI_2 at various pressures. The sample must be contained in a molybdenum steel gasket to build up the thickness of the sample. Best results were obtained for 0° radiation, although 180° radiation may also be used.

The Raman results are important, since the LO mode of crystals showing a first-order Raman spectrum are more intense in the Raman spectra, and thus are more easily studied. In addition, various infrared inactive or infrared weak vibrations may be studied with this technique.

LIMITATIONS OF TECHNIQUES

The above applications have been presented to attempt to illustrate the potential use of the high pressure technique for study of molecules in the low frequency range. The technique is new and much work remains to be done. Further, a better understanding is necessary as to what mechanisms are involved when a material is under pressure stress. More work with gaskets and with hydrostatic pressures is needed. Certainly precautions are necessary when using the average pressures obtained in the diamond anvil cell, and relating these to other pressure data. This is particularly dangerous in attempts to obtain quantitative data such as anharmonic contributions in ionic crystals. For qualitative work, the use of an average pressure appears quite satisfactory. The technique has warranted the attention it has received in the past two years. Although it may never realize all of its potentials ultimately, it has already demonstrated that it is a valuable tool for the chemist, physicist, spectroscopist, and solid-state scientist.

ACKNOWLEDGMENT

The author wishes to acknowledge the valuable contribution of Dr. Clarence Postmus in the aforementioned work.

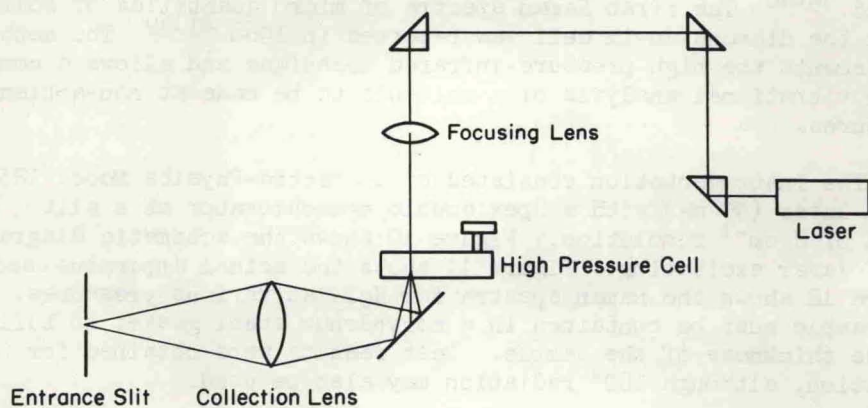


Fig. 10. Schematic Diagram for Laser Raman-High Pressure Experiment.

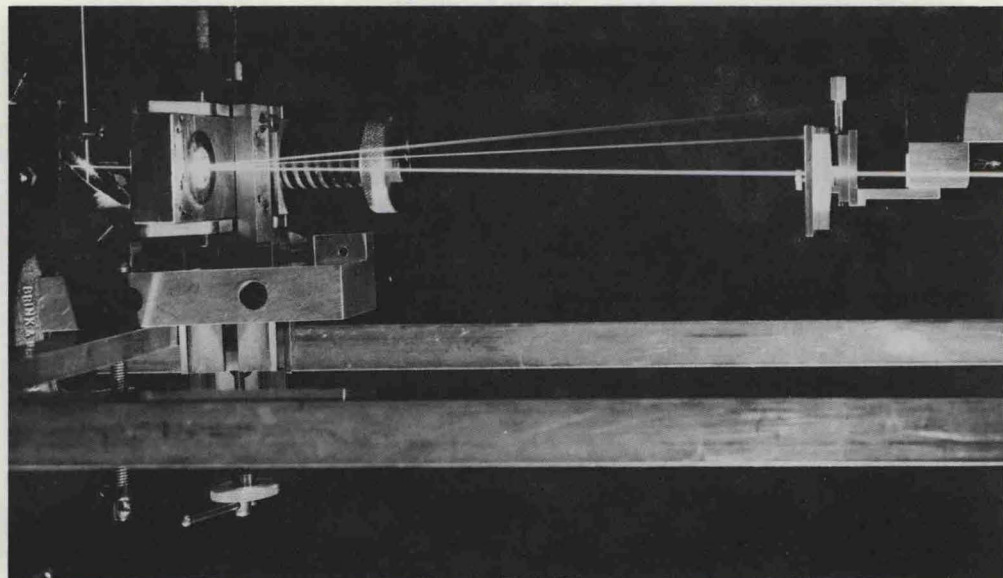


Fig. 11. Apparatus Used in Laser Raman-High Pressure Experiment.

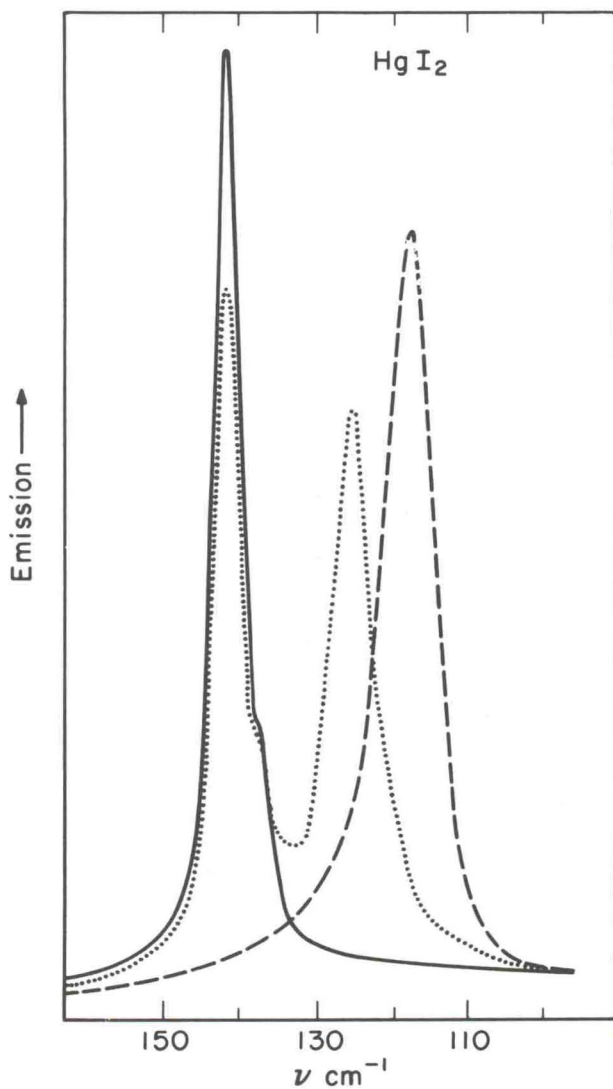


Fig. 12. The Spectra of HgI_2 at Various Pressures.

- Atmospheric pressure (red phase only). Peak at 119 cm^{-1} .
- oooo Intermediate pressure (red and yellow phases present). Peaks at 126 cm^{-1} and 143 cm^{-1} and a weak shoulder at 138 cm^{-1} .
- High pressure (yellow phase only). Peak at 143 cm^{-1} with a weak shoulder at 138 cm^{-1} .

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