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HIGH-PRESSURE VIBRATIONAL SPECTROSCOPY**John R. Ferraro*CHEMISTRY DIVISION
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I. Introduction

The first spectroscopic measurements of molecules under external pressures were made by Drickamer, whose experiments covered the regions of ultraviolet, visible, and near infrared (1, 2). Drickamer studied the effect of pressure on the vibrational frequency in several compounds to 5.0μ (2000 cm^{-1}). Extension to 35.0μ (285 cm^{-1}) was made by Weir *et al.* (3-5). In 1966, the technique of making low-frequency measurements at high pressures

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

of up to $200\ \mu$ ($50\ \text{cm}^{-1}$) was developed by Ferraro *et al.* (6, 7), using a grating spectrophotometer. With the use of an interferometer, Gebbie (8) reported low-frequency spectra to $1000\ \mu$ ($10\ \text{cm}^{-1}$) and McDevitt *et al.* (9) reported spectra to $40\ \text{cm}^{-1}$. Several other high-pressure cells capable of being used in the infrared region have been reported (11-16). It would appear that adequate high-pressure techniques are available to conduct vibrational studies in all regions of the infrared. This is not to say that the ultimate in instrumentation has been reached, however. Many instrumental problems exist, and the experiments are tedious and time consuming.

Contemporary instrumentation, applications of the technique, and, in conclusion, recent high pressure-Raman techniques will be discussed in this chapter. Emphasis is placed on the most recent developments made in the field of high-pressure vibrational spectroscopy.

II. Available Instrumentation for Far Infrared-High-Pressure Studies

A. Optical High-Pressure Cells

It is advisable to describe briefly the available instruments capable of making low-frequency measurements under pressure. A summary of the more important optical high-pressure cells available with their advantages and disadvantages is given in Table I.

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

The piston-cylinder cell developed by Drickamer and Balchan (10) used sapphire windows of 0.5-in. diameter and 0.5-in. thickness in the 0.2 - $5.0\ \mu$ region. These windows proved fragile, and Drickamer (17-19) converted to sodium chloride windows thereafter. Sherman (11) used a similar cell to $400\ \text{cm}^{-1}$.

Perhaps the most useful cell is the opposed anvil cell using diamond anvils, developed recently by Weir *et al.* (3-5). They used type-II diamonds which are transparent in the region of the ultraviolet, visible, and infrared, except for a region of 4 - $6\ \mu$, where major absorption occurs. Pressures up to 200 kbar have been claimed with this cell (20).

B. 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 was developed by Ferraro *et al.* (6, 7). This technique is capable of reaching the

TABLE I
SUMMARY OF AVAILABLE OPTICAL HIGH-PRESSURE CELLS

Type of cell	Pressures (kbar)	Advantages	Disadvantages
Shock wave	1000	1. Highest obtainable pressures	1. Pressure exerted over short time 2. Explosives needed to give shock wave
Piston and cylinder	200	1. Largest specimen volumes 2. Considered to give hydrostatic pressures	1. Not enough optical clarity to permit optical observation or photography 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	1. Only micro quantities of material necessary 2. Compact—can be used with spectrophotometers	1. Pressure gradient exists 2. Absorption of diamonds from 4 to 6 μ

200- μ region, and involves the use of a Perkin-Elmer Model No. 301 double-beam grating spectrophotometer (used in double-beam operation), a 6 \times beam condenser, and the high-pressure diamond cell manufactured by 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 -mm² area) were used, although above 100 μ , diamonds of 0.25 mm² can be used.* An expansion scale was also built into the No. 301 spectrophotometer to amplify weak vibrations. This allowed for less

* For operation to 200 μ with a grating spectrophotometer, the cost of a beam condenser and the diamond cell is about \$7000 (price based on conditions existing in 1969).

TABLE II
HIGH-PRESSURE APPARATUS CURRENTLY USED FOR LOW-FREQUENCY STUDIES

Workers	Spectrophotometer or interferometer	Wavelength range (μ)	Optical cell ^b
Weir <i>et al.</i> (3-5)	Perkin-Elmer No. 621	2-35	Diamond anvil
Jacobsen and Brasch (21, 22)	Perkin-Elmer No. 521 ^a	2-35	Diamond anvil
Ferraro <i>et al.</i> (6, 7)	Perkin-Elmer No. 301 ^a	16-200	Diamond anvil
	Beckman IR-11 ^a	16-200	Diamond anvil
	Beckman IR-12 ^a	2-40	Diamond anvil
McDevitt <i>et al.</i> (9)	FS-520 interferometer	to 250	Diamond anvil
Bradley <i>et al.</i> (8)	Michelson interferometer	50-1000	Anvil, quartz window
Sherman (11)	University laboratory spectrophotometer	25	Piston-cylinder, sapphire, MgO, or fused silica window

^a With 6 \times beam condenser.

^b For a new cell using quartz windows see R. P. Lowndes, *Phys. Rev. B* **1**, 2754 (1970).

compensation in the reference beam and the use of narrower slits. A microscope is absolutely essential in all pressure work to determine whether one has a good solid load between the diamonds and if a phase transition is occurring.

In the interferometer tieup with the diamond cell, a brass cone light pipe is used (angle 9°37') (9). Infrared radiation comes out of the instrument and enters this cone. The cone bends the radiation toward the small opening (0.060-in.) in the other end and 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.

C. Calibration of Diamond Cell

It has already been indicated that a pressure gradient exists in the multiple-anvil diamond cell. Duecker and Lippincott (23) have demonstrated that in compressible solids the pressure gradient is parabolic across the diamond face, pressures in the center reaching 1.5 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 microphotographs, which allows one to determine the force per unit area or pressure.

2. Calibration with an internal calibrant is possible, i.e., solids which undergo phase transformation at known pressures (e.g., KBr, 18 kbar; KCl, 20 kbar).

3. Calibrations can be made by using nickel dimethylglyoxime, which shows a change in spectral properties with pressure, as an internal calibrant (23, 24).

III. Applications

Some of the applications of the far infrared-high-pressure technique that have been investigated thus far will be presented in this section, indicating the newest developments in this area and pointing out other possible applications.

A. Lattice Vibration Studies

Table III lists some ionic lattice frequencies. Most of the frequencies for the transverse optical lattice modes (ν_{TO}) in ionic salts 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. It is not normally observed at 90° incident radiation. Berreman (25)

TABLE III
LATTICE VIBRATIONS FOR ALKALI HALIDES^a

Halide	ν_{TO} (cm^{-1})	Halide	ν_{TO} (cm^{-1})	Halide	ν_{TO} (cm^{-1})
LiF	307	NaI	117	RbCl	118
LiCl	191	KF	190	RbBr	88
LiBr	159	KCl	141	RbI	77
NaF	246	KBr	113	CsCl ^b	99
NaCl	164	KI	98	CsBr ^b	74
NaBr	134	RbF	156	CsI ^b	62

^a S. S. Mitra and P. J. Gielisse (24a).

^b C. M. Randall *et al.* (24b).

observed the longitudinal mode for a thin film of LiF with an oblique incident radiation, and longitudinal optical modes of the silver halides have recently been studied with similar techniques (26). The longitudinal modes can be observed with a diamond cell and highly converging oblique radiation coming from the beam condenser. 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 transverse modes, and because of the high-frequency shift of the ν_{TO} band, can no longer be observed. In more covalent solids ν_{TO} is very close to ν_{LO} . In a homopolar covalent crystal, ν_{TO} may equal 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 ν_{LO} and ν_{TO} is sufficiently large to make possible a determination of the pressure dependence of both optical modes.

In all cases studied ionic lattice vibrations shifted toward higher frequencies with increasing pressure. The shifts at pressures of up to 50 kbar may be considerable; however, not all ionic lattice vibrations show dramatic shifts, since the compressibility of the solid is involved. The relationship between the change in frequency with pressure for simple ionic solids, where the three crystallographic axes are equal, is given in Eq. (1):

$$\gamma\chi\nu = (\partial\nu/\partial p)_T, \quad (1)$$

where γ is the Grüneisen parameter, χ is the isothermal compressibility of the solid, and ν is the frequency of the lattice mode. For noncompressible solids, it is possible that only small shifts will occur. For example, the lattice modes of zirconium and hafnium failed to show significant shifts at 40 kbar (9). It is also possible that the pressure effects may be different in noncubic crystals having different axes parameters, depending on which axis becomes compressible (27, 28).

The data obtained from studies of the pressure dependence of the $k \simeq 0$ lattice vibrations of ionic crystals (29), when combined with data from studies of these modes with temperature (30), may allow one to calculate the anharmonic interactions taking place, and contribute to a better understanding of the lattice dynamics of these solids. It is possible to distinguish between the purely volume-dependent contribution and the contribution from various anharmonic terms in the crystal Hamiltonian (31). Figure 3 shows a plot of $\ln \nu/\nu_0$ vs. $\ln v/v_0$ for several optical modes. The data have been obtained from pressure and high-temperature studies (29-31), P - V data from Drickamer (32), and from Cline and Stephens (33). It can be

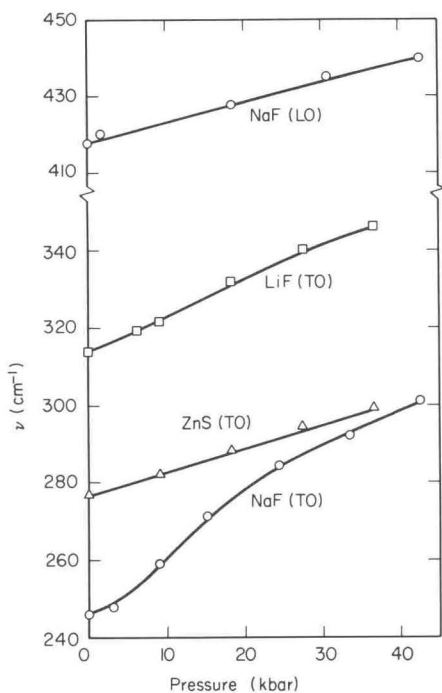


FIG. 1. Pressure dependences of several lattice vibrations.

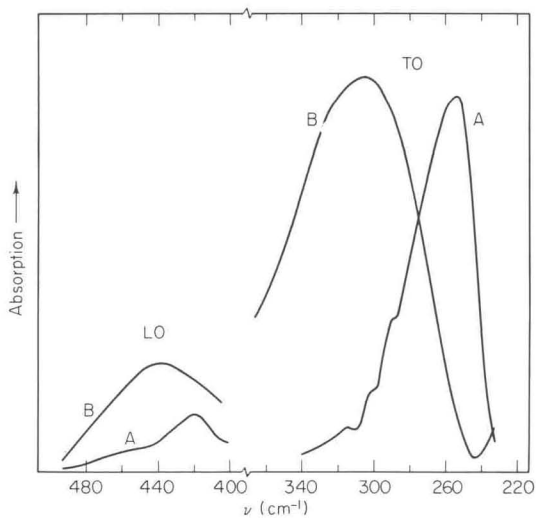


FIG. 2. Comparison of the transverse and longitudinal modes in NaF with and without pressure.

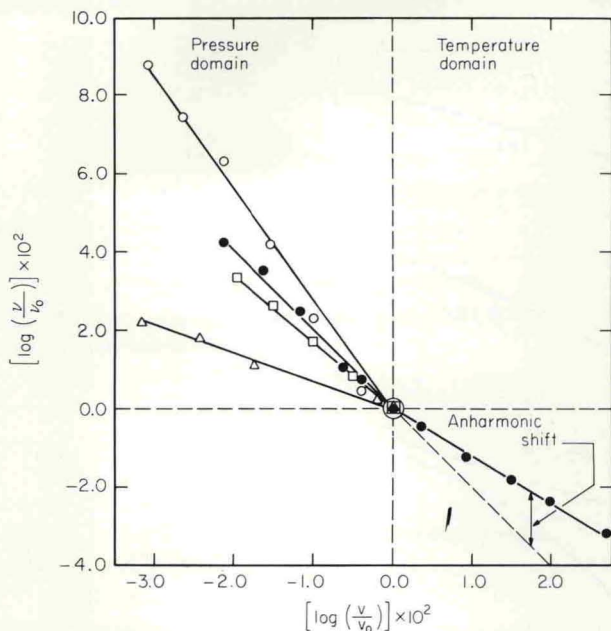


FIG. 3. Plot of $\ln v/v_0$ vs. $\ln v/v_0$ for several optic modes: (●) LiF (TO); (○) NaF (TO); (△) NaF (LO); (□) ZnS (TO).

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), which increases steadily with increasing temperature of LiF. A similar analysis was made for KBr and in this crystal the "self-energy" shift is negligible. Results obtained for RbI using other techniques (30, 34) also indicated negligible "self-energy" shifts.

The results obtained for the Grüneisen parameters for the long-wavelength optical modes from Eqs. (1) and (2),

$$\gamma_{j(k)} = -\partial \ln v_j(k) / \partial \ln V, \quad (2)$$

are given 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 .

The pressure dependences of two phases of a solid can be determined by these techniques (31). Such studies have been made with KBr (31) and KCl (9, 31). Figure 4 shows the TO mode of 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

TABLE IV
GRÜNEISEN PARAMETERS FOR THE LONG-WAVELENGTH OPTICAL MODES

	Experimental		Calculated				
	Eq. (1)	Eq. (2)	Born-Mayer ^a	r^{-n} repulsion ^b	Cowley ^c	Model I ^d	Model II ^d
LiF	2.15	2.59	2.44	3.46			
NaF	2.80	2.95	2.43	3.00			
KBr		2.83	2.52	2.95	3.27	~3.0	~2.6
KCl		2.46	2.52	2.92			

^a From Born and Huang (35).

^c From Cowley (37).

^b From Seitz (36).

^d From Cowley and Cowley (38).

transition pressure and both phases appear over a range of pressures. The high-pressure phase (CsCl structure) appears at 16 kbar for KBr and at 24 kbar for KCl. The conversion to the high-pressure phase is complete at 26 and 30 kbar 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 an increase in that of the high-pressure phase. With the reduction of 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 kbar for KBr and KCl, respectively. Part of these discrepancies can be attributed to the sluggishness of the system and friction within the cell.

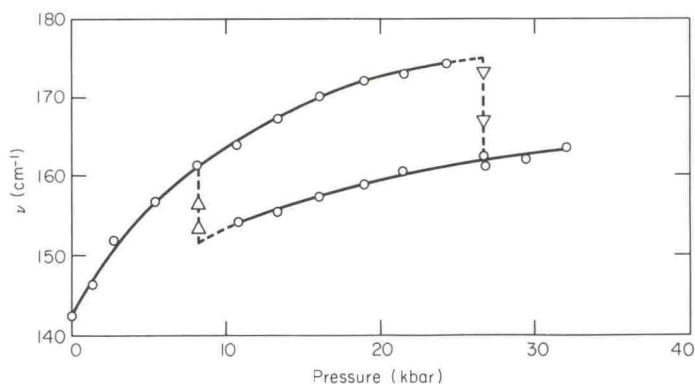


FIG. 4. TO mode of KCl as a function of pressure.

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., $\frac{3}{8}^{1/2}$ or 0.87. The observed ratio for KBr is 0.88 and that of KCl is 0.92.

It has been found (39) that the $k \approx 0$ TO frequency of the alkali halides of NaCl structure is proportional to $(a/\chi\mu)^{1/2}$, where a is the lattice constant, μ is the reduced mass per unit cell, and χ is the compressibility. The same is true for the CsCl structure, as illustrated in Fig. 5.

Pressure studies of mixed crystals have recently been reported for $\text{ZnS}_{1-x}\text{Se}$ (40) and $\text{KCl}_{1-x}\text{Br}$ (41). In both the two-mode system $\text{ZnS}_{1-x}\text{Se}$, and the one-mode system $\text{KCl}_{1-x}\text{Br}$, the pressure dependences of the various mixtures of the mixed crystals parallel those obtained for the pure components. Figure 6 illustrates the pressure dependence of the $\text{KCl}_{1-x}\text{Br}_x$ system.

Certain molecular lattice modes were investigated by McDevitt *et al.* (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 frequencies with increasing pressure. Recent Raman experiments (42) have demonstrated that molecular lattice vibrations are more sensitive to pressure than ionic lattice modes, as expected.

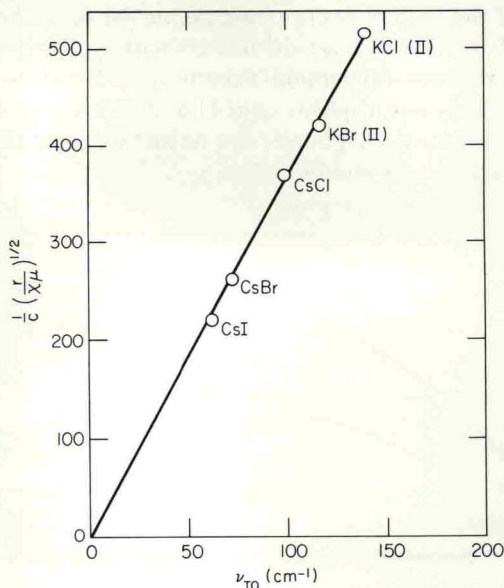


FIG. 5. Plot of TO mode frequency for several CsCl-type salts vs. $1/c(r/\chi\mu)^{1/2}$ (c = velocity of light).

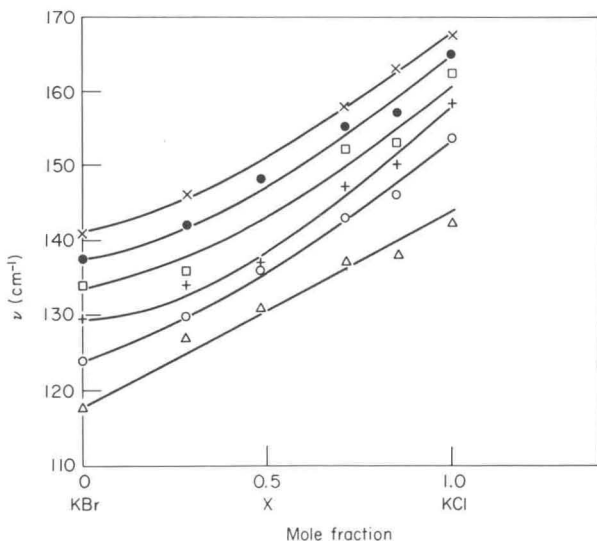


FIG. 6. Pressure dependences of the $\text{KCl}_x\text{Br}_{1-x}$ system: in kilobars (\times) 13.9; (\bullet) 11.1; (\square) 8.3; (+) 5.5; (\circ) 2.8; (\triangle) ambient pressure. Experimental error, $\pm 1 \text{ cm}^{-1}$.

B. Coordination Compounds (Effect of Pressure on Molecular Vibrations)

Whereas certain compressible ionic solids show shifts of the optical modes toward higher frequencies when subjected to external pressure, internal modes in other compounds show very small 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 both an asymmetric and a symmetric stretching vibration. Whenever these two vibrations are resolved into two bands, pressure affects one mode more than another (43). Figure 7 illustrates the effect of pressure on the asymmetric and symmetric stretching vibrations of $[(\text{C}_6\text{H}_5)_4\text{As}][\text{GeCl}_3]$. Although both peaks diminish in intensity and broaden, it is observed that the symmetrical vibration (A_1 species) is most sensitive to pressure. It is important to be able to distinguish between these two modes in making correct far-infrared interpretations. This technique enables one to accomplish this with powdered or polycrystalline material. Previously, only in single-crystal-dichroism infrared measurements, single-crystal, or solution-Raman polarizability studies could this differentiation be made.

Attempts to induce structural changes in coordination compounds upon the application of pressure to the solids have all failed (44). Of course, only pressures of up to about 60 kbar have been used. At these pressures, only

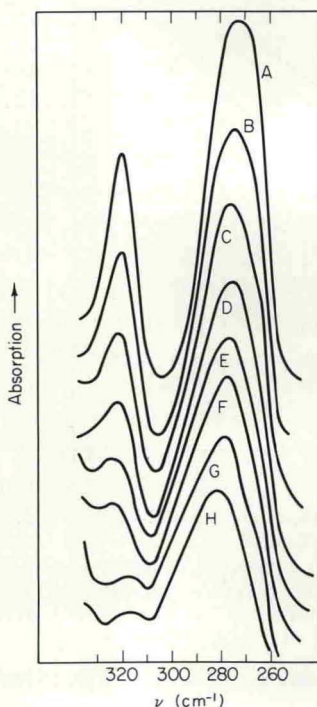


FIG. 7. Low-frequency spectra of $[(C_6H_5)_4As](GeCl_3)$ with and without pressure.

some color changes were observed, which were similar to those found for nickel dimethylglyoxime (23, 24). These involve spectral changes with pressure and can be observed under the microscope or in a visible spectrophotometer. These changes are not to be confused with any structural change (e.g., $T_d \rightarrow D_{4h}$). Thus, one is forced to conclude that it may be necessary to apply pressure in solution, where the added energy of solution may induce the transformation to occur. Such studies are now in progress (44).

C. Recent Developments

A basic study of the effects of pressure on free ligands as compared to the complexed ligands present in several metallic complexes was made recently (45). Some molecular vibrations involving volume expansions were found to be pressure sensitive and this sensitivity was found to be of three types: (1) a shift toward higher frequencies; (2) a drastic decrease in intensity and the disappearance of bands; and, (3) a doubling of some bands.

The behavior of ligands such as 2,2'-bipyridyl and pyrazine (1,4-diazine) under pressure appeared to simulate the effect of complexation of the ligands

with the metal atom. The metal complexes, by contrast, demonstrated negligible pressure effects.

Systematic pressure studies of inorganic compounds in the $1600\text{--}100\text{-cm}^{-1}$ region have also been started. Earlier, Lippincott *et al.* (4, 5) examined several inorganic molecules with pressure in the mid-infrared region, but little if any work has been done in the low-frequency region. Preliminary results (46) with solids in various point-group symmetries (e.g., O_h , T_d , D_{4h} , D_{3h} , C_{3v}) have indicated that external symmetry may be more important than internal (or point-group) symmetry. Certain degenerate vibrations were induced to split, while others did not. The ν_4 (F-type) MnO_2 deformation vibration for KMnO_4 at $\sim 400\text{ cm}^{-1}$ is seen as a doublet at ambient pressure. The doublet has been attributed to a lowered symmetry (probably C_{3v}). Differentiation between the two species is normally difficult. Figure 8 illustrates the effect of pressure on the doublet. It is observed that the 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 higher frequency (ν_3 -F type), under twice the pressure of that used for the ν_4 vibration, failed to split. At ambient

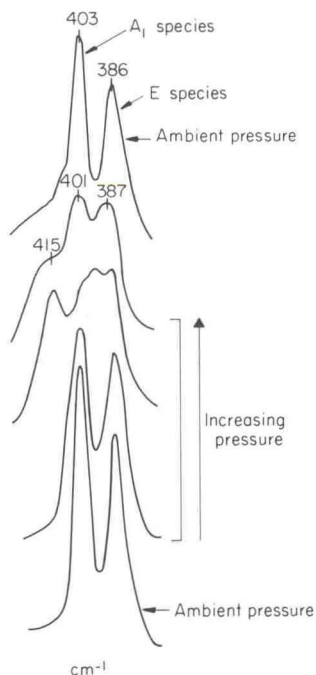


FIG. 8. The behavior of the $\delta(\text{MnO}_2)$ vibration in KMnO_4 with pressure (diamond cell).

pressure, this band is a singlet. The ν_1 vibration, normally forbidden in the infrared, disappears with pressure. Thus, the results cannot be attributed to a further lowering of the symmetry of the solid under pressure. A possible explanation is offered in a later section.

In a recent study of complexes of the type L_2MX_2 (tetrahedral monomer versus octahedral polymer), where M is cobalt, X is halide, and L is pyridine or substituted pyridines, the differentiation of a bridged vibration, $\nu_b(\text{CoX})$, from a terminal vibration, $\nu_t(\text{CoX})$, was made on the basis of pressure measurements (47). The most pressure-sensitive bands (in terms of a blue shift) in the spectrum of the polymer were the $\nu_b(\text{CoX})$ vibrations, which should have pseudolattice-like behavior.

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 experienced that applying pressure on a solid with a gasket does not give hydrostatic pressures. However, using a gasket with the solid HgI_2 , adding a drop of Nujol, and then applying pressure gave what appeared under the microscope to be a single pressure (48). Similar results were obtained recently by Davies (24) with nickel dimethylglyoxime using other organic solvents. Under these conditions, the use of a liquid having a freezing point at a known pressure can also give a pressure calibration point as well as a hydrostatic pressure.

D. Conclusions

Four types of pressure-sensitivity for molecular vibrations have been observed thus far in the course of pressure studies on various modes of vibrations: (1) a broadening and a decrease in peak intensity of vibrations; (2) the doubling of absorption bands; (3) the splitting of degenerate vibrations; (4) frequency shifts in bands. Some of these effects have been observed for both external and internal vibrations.

1. EXTERNAL VIBRATIONS

The effects of pressure on external vibrations have been demonstrated. Both the longitudinal and transverse optical modes are seen to shift in compressible ionic solids. 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. For example, the specific volume of α -quartz shows only a 0.3% decrease from room to liquid-air temperatures (49), and this is smaller than the change occurring upon compression from ambient pressure to 4 kbar (50). Such pressure studies may provide useful information on the amount of anharmonicity existing in solids of this type. Further, it should be possible in some cases to obtain compressibility data in compressible solids from pressure-frequency measurements [see Eq. (1)]. Molecular lattices show similar pressure effects (42).

In addition to the spectral blue shifts, lattice vibrations will broaden and diminish in peak intensity. This appears to be characteristic of all types of vibrations. No quantitative studies have been made to determine the effect of pressure on the integrated intensities of these vibrations. This may prove to be very difficult, since results may not be reproducible because of the pressure gradient existing across the diamond anvil faces. The broadening effects may be connected in part with this pressure gradient, since Raman studies in a hydrostatic cell do not show this pressure broadening of lattice bands (42).

The blue shifts of ionic or molecular lattice modes may result from the contraction of the solid under pressure, causing interionic and intermolecular distances to shorten (2-5, 51). The large pressure effects on compressible lattices are related to the small repulsive forces present in the neighboring ions or molecules.

2. INTERNAL VIBRATIONS

Earlier work indicated that internal modes are affected by pressure, but in a much less dramatic way than the external modes. Frequency shifts are generally small in most cases, either in a blue or red direction. In hydrogen-bonded compounds, studies of the O-H stretching vibration indicated spectral red shifts (5, 52). Red shifts were also observed for HgCl_2 and its dioxane complex by Mikawa *et al.* (53). In most of our pressure studies with internal modes, blue shifts have been observed.

The broadening of bands and decreased peak intensities also occur with pressure. In some cases the symmetrical stretching vibration (A_1 species) is found to be particularly sensitive to pressure (43). This compares favorably with the findings of Nedungadi (54), who studied the temperature dependence of α -quartz and found that the most sensitive vibration was an A_1 -type mode. Pressure dependences of α -quartz produced similar results with the A_1 frequencies more sensitive than the E-type vibration (55). Again, it must be inferred that not all A_1 vibrations are pressure sensitive, as A_1 bending

vibrations and certain A_1 stretching vibrations are not particularly affected at higher frequencies.

Other pressure effects have recently been demonstrated. The $\nu_4(F)$ bending vibration in $KMnO_4$, which is already split into two bands at ambient conditions, proceeds to lose all of its degeneracy with pressure. Studies with ligand ring vibrations in the mid-infrared region have demonstrated that one can also obtain a doubling of vibrations with pressure (45). An attempt to explain these results, at least qualitatively, follows.

(a) *Sensitivity of ν_1 Stretching Vibration to Pressure.* The sensitivity of the ν_1 stretching vibration in various compounds (inorganic and coordination compounds) is especially interesting. By contrast, a symmetrical bending vibration of type A_1 may not be particularly affected (Fig. 7 illustrates the sensitivity of the A_1 species in the metal-chloride stretching region). The intensity of the symmetrical stretch has practically disappeared with pressure, while the asymmetric stretch, although diminished, is still readily observed.

This ν_1 vibration involves an expansion of molecular volume, and these "expansion vibrations" are particularly sensitive to pressure (43). In addition, the dipole moment change for the vibration apparently decreases and this causes a decrease in the intensity. The actual mechanism as to how this is accomplished is obviously unknown at present. Since the intermolecular distances are being diminished, it may be possible to change certain bond angles while the material is under external stress. If the bond angles increase and approach 180° , the dipole moment change for the vibration might approach zero. Carbon dioxide is a case in point, where the bond angle $O-C-O$ is 180° and the ν_1 vibration is forbidden in the infrared spectrum. However, it is observed in the Raman measurements and it would be interesting to observe similar molecules in the Raman experiment with pressure. Water, with a bond angle of $\sim 104^\circ$, shows an infrared-active ν_1 vibration.

(b) *Splitting of Degenerate Vibrations.* The loss of the degeneracy of E or F type vibrations with pressure is possible. The case of $KMnO_4$ has been mentioned. The sensitivity of the ν_4 vibration with pressure while the ν_3 vibration remains unaffected, even at higher pressures, is very interesting. This is not simply a lowering of symmetry of the molecule, for both F species would be expected to split. One would have to conceive of a symmetry in which only ν_4 splits, not ν_3 , and this is virtually impossible. The different behavior must be related to the energy of the vibration. The compound $KMnO_4$ has two molecules per unit cell, and it is possible that the vibrations of one MnO_4 group in the unit cell might couple with the other MnO_4 group. This coupling phenomenon can cause the splitting of degenerate vibrations (Davydov splitting) (56), without a change in symmetry. It is generally believed that coupling occurs more readily in the low-frequency

region of the infrared spectrum. This may cause the lower-frequency ν_4 vibration to split while the higher-frequency ν_3 vibration is unaffected.

(c) *Doubling of Absorption Bands.* In the course of various studies (45) it has been observed that a doubling of bands occurs with pressure. This may be due to a lowered site symmetry induced in the solid state by the external pressure. Alternatively, two accidentally overlapping vibrations may occur at the same frequency. These may be induced to separate because of a difference in the pressure dependences manifested by the two vibrations.

(d) *Lack of Frequency Shift for Internal Modes.* The lack of large frequency shifts for most internal modes in polyatomic compounds is a very useful consequence, for it allows one to distinguish between such a vibration and a lattice mode in a compressible solid. The lack of larger shifts is related to the stronger repulsive forces present in the atoms of these molecules. However, it is dangerous to extrapolate that all internal modes will behave in this manner. The electron density around the various atoms involved may be a very important factor. As the pressure is increased and the atoms or molecules approach each other, the interaction of the electron field increases. For simpler molecules with minimal electronic interaction, such as hydrogen, it may be possible for considerable shifts in frequencies of the internal mode to occur; however, as the electronic fields become more and more complex, the repulsive forces increase and the shifts decrease. Vodar and Vu (57) demonstrated that a shift of $\sim 1 \text{ cm}^{-1} \text{ kbar}^{-1}$ occurs for the pressure-induced $\nu_{\text{H-H}}$ vibration in solid hydrogen. A somewhat lower pressure dependence is found for HCl (57).

E. Raman-High-Pressure Studies

Raman spectra of gases at high pressures have been obtained (58, 59). The first Raman spectra on microquantities of solid using the diamond anvil cell was reported in 1968 (60, 61). This method complements the high-pressure-infrared technique and allows a complete vibrational analysis of a molecule to be made at nonambient pressures.

The apparatus 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 9 shows the schematic diagram of 0° laser excitation; Figure 10 shows the actual apparatus used. Figure 11 shows the Raman spectra of 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.

A recent Raman study (42) using a hydrostatic pressure cell (Daniels

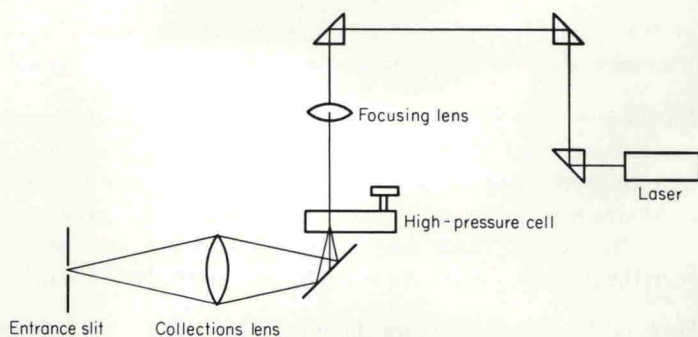


FIG. 9. Schematic diagram for laser Raman-high-pressure experiment.

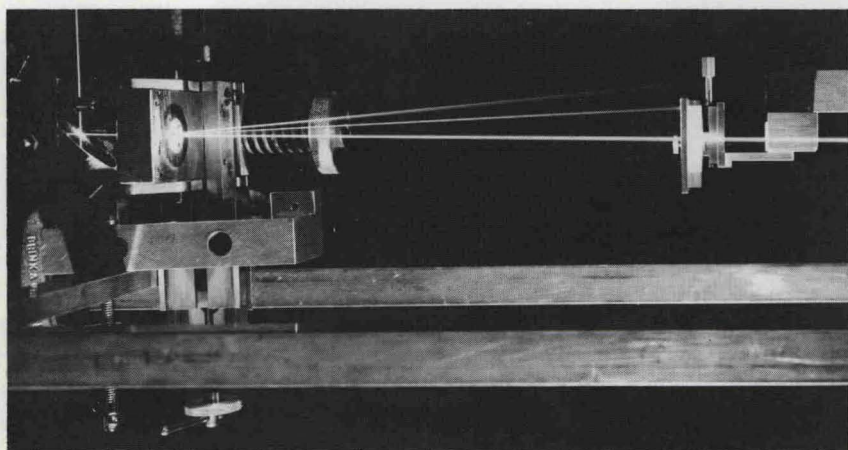


FIG. 10. Apparatus used in laser Raman-high-pressure experiment.

type) (62) was made on studying the phase transition of TII. Walrafen (63) studied the effect of pressure on the intermolecular hydrogen bond bending and stretching Raman intensities of water and solutions of HDO in H_2O . The results were useful in determining a theory for the structure of water. For this study, a Raman cell equipped with windows made of single crystals of sapphire, and an argon-ion laser as the excitation source. Asell and Nicol (55) recently determined the Raman spectrum of α -quartz. A Drickamer-type cell (64) was used for this work with an argon-ion laser. The high-pressure Raman spectra of toluene and isopropylbenzene have also been reported (65).

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.

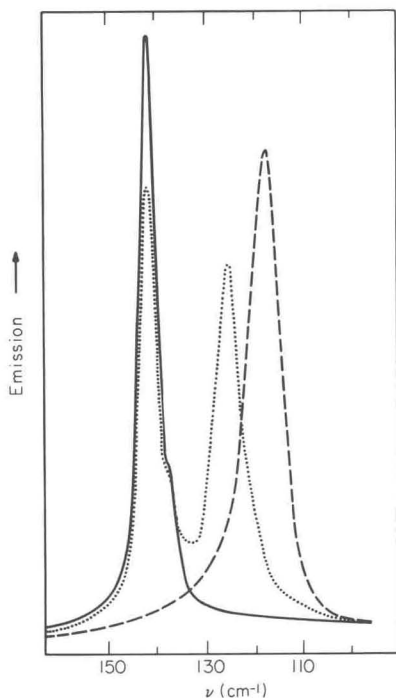


FIG. 11. The spectra of HgI_2 at various pressures: (---) atmospheric pressure (red phase only), peak at 119 cm^{-1} ; (·····) intermediate pressure (red and yellow phases present), peaks at 126 and 143 cm^{-1} and a weak shoulder at 138 cm^{-1} ; (—) high pressure (yellow phase only), peak at 143 cm^{-1} with a weak shoulder at 138 cm^{-1} .

IV. Limitations of Technique

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, and more work with gaskets and with hydrostatic pressures is needed. A problem involving the pressure calibration of the diamond anvil cell merits prime consideration. 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 few years. Although it may never realize all of its potentials ultimately, it has already been demonstrated that this technique is a valuable tool for the chemist, physicist, spectroscopist, and solid-state scientist.

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