

## Studies of infrared absorption spectra of solids at high pressures

E. R. LIPPINCOTT

Department of Chemistry, University of Maryland

and

C. E. WEIR, A. VAN VALKENBURG and E. N. BUNTING

National Bureau of Standards, Washington, D.C.

(Received 5 October 1959)

**Abstract**—Infrared spectra of solids were studied with a diamond pressure cell in the wavelength range 5–15  $\mu$  at pressures between 1 atm and 50,000 atm. The calibration of the cell at the 14,000 atm transition of  $\text{NaNO}_2$  is described. Spectra were studied for aromatic organic compounds, inorganic hydrates, and ammonium halides. In general, band shifts produced by pressure were to higher frequencies and at most 10  $\text{cm}^{-1}$ /10,000 atm. Many bands exhibited large changes in intensity. Occasionally bands increased in intensity or were unaffected but in general a decrease in intensity was observed at elevated pressure. Representative spectra are given, one to a pressure of 160,000 atm. Suggestions for the causes of the frequency shifts are given.

### Introduction

IN AN earlier paper [1] a diamond high-pressure cell was described which was used to obtain infrared spectra in the wavelength region 1–15  $\mu$  to pressures of 30,000 atm. The use of this high-pressure cell was illustrated with studies on calcite. Since then, studies have been made on a wide variety of solid substances, both organic and inorganic. The purpose of this paper is to describe some of these results.

The infrared spectrum of a substance shows a number of changes on application of pressure; these include shifts of absorption bands to both higher and lower frequencies from the positions of the band at 1 atm, the occurrence of new bands, the splitting of degenerate bands arising from a change in selection rules, and changes in apparent band intensity. The shifts in absorption bands observed to date range up to a maximum of  $\pm 10 \text{ cm}^{-1}$  per 10,000 atm pressure with greater shifts sometimes occurring for substances involving systems of hydrogen bonds. With the exception of these latter systems, shifts of frequencies on application of relatively low pressure have not been studied in detail in our work to date. Similarly, the splitting of absorption bands and the appearances of new bands seem to be relatively rare occurrences at pressures below 20,000 atm. However, changes in apparent intensity of many bands were observed at relatively low pressures, i.e. 10,000 atm, with larger changes occurring at higher pressures. Since the magnitude and direction of these intensity changes were unexpected, they will be illustrated and discussed in considerable detail. The change of intensity is specific both with respect to the nature of the substance and the mode of

[1] C. E. WEIR, E. R. LIPPINCOTT, A. VAN VALKENBURG and E. N. BUNTING, *J. Res. Nat. Bur. Standards* A **63**, 55 (1959).



vibration involved. Examples will be given in which the intensity decreases, some in which it increases, and others in which it does not change more than the experimental error. However, the greatest number of cases observed to date have been those which show a decrease in band intensity.

The diamond pressure cell has been used to pressures as high as 160,000 atm and in the wavelength range  $1\ \mu$ – $30\ \mu$ . One example of spectra taken at the higher pressure will be presented and discussed. The data at the longer wavelengths are incomplete at the present time.

### Experimental

The pressure equipment consists of two type II diamonds which are transparent from  $1$  to  $4\ \mu$  and from  $5.2\ \mu$  to beyond  $30\ \mu$  [1]. The specimen is compressed between two flat surfaces ground on the diamonds. The incident beam traverses both diamonds and the specimen parallel to the direction of stress. Pressures have been calculated as force per unit area. Since the sample is held between the diamonds by frictional forces resisting flow in a thin specimen, there is a question as to whether the applied pressure is hydrostatic. Fortunately, the thickness of the specimen retained after extrusion ceases is usually just adequate to obtain a reasonably characteristic spectrum. For organic compounds this thickness is sometimes too small to observe weak bands, while for some inorganic salts it appears somewhat too large in the case of strong bands. The question of the hydrostatic nature of the pressure and the magnitude of the pressure gradients near the edges of the specimen makes it important that the pressure calculated as force per unit area should be checked by a calibration based on a phase change for a given substance at a known hydrostatic pressure.

This type of calibration is surprisingly difficult because most solid–solid transitions appear to produce such small discontinuous changes in the infrared spectrum that they are difficult to identify with present experimental techniques. The calibration point which has been most useful to date has been that for a transition in  $\text{NaNO}_2$  which is found to take place at a hydrostatic pressure of 14,500 atm by a linear interpolation of BRIDGMAN's data [2]. This transition may be studied in the infrared spectrum by observing the behavior of the  $825\ \text{cm}^{-1}$  ( $12.1\ \mu$ ) absorption band of  $\text{NaNO}_2$  corresponding to the nitrite ion bending mode of vibration. The frequency shifts discontinuously to near  $855\ \text{cm}^{-1}$  ( $11.7\ \mu$ ) when this transition takes place. An example of this is illustrated in Fig. 1. In these experiments the pressure was raised to 14,000 atm, lowered a few hundred atmospheres, raised again to 14,000 atm, and the process repeated several times, always approaching the transition from the low pressure direction. This transition served to check the pressure calibration in terms of the applied load and its sharpness furnished evidence that excessive pressure gradients did not exist in the specimen. The absence of appreciable gradients provides evidence that the pressure is reasonably hydrostatic in nature.

The transition was sometimes difficult to initiate but once obtained it was readily reversible. By following the transition with different sets of diamonds it

[2] P. W. BRIDGMAN, *Proc. Am. Acad. Arts. Sci.* **72**, 45 (1937).



was possible to obtain information as to the condition of the diamond surfaces. In some instances the transition was found to occur over a narrow pressure range ( $\pm 300$  atm) with only a single phase present at any time, while in other cases the 855 and 825  $\text{cm}^{-1}$  bands were present simultaneously over a rather wide pressure range indicating the presence of a considerable pressure gradient. This latter situation usually occurred when the diamond surfaces had deteriorated markedly

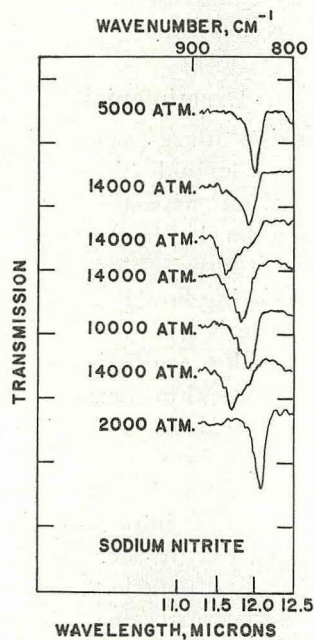


Fig. 1. Behavior of the 825  $\text{cm}^{-1}$  nitrite ion bending frequency for the transition occurring in  $\text{NaNO}_2$ .

with the presence of a number of surface flaws or with diamonds of very small surface area. In such cases it was desirable to regrind the diamond surfaces as described in [1].

Sample handling was accomplished by the techniques described previously [1]. In a typical run, the piston with one of the diamonds was inserted in the bearing and a small quantity of specimen placed on the surface with a spatula. The other piston was inserted and the thrust plate screwed into place. The pressure was then raised to a few thousand atmospheres to produce a film between the diamond faces. The pressure cell was then placed in the focal point of the beam-condensing unit and its position adjusted in the beam to produce a maximum transmission at a wavelength where the specimen had no absorption bands. The pressure was then raised and lowered until no further evidence was found for extrusion of the sample from between the diamond surfaces. The pressure was then raised to the maximum pressure desired and the spectrum run with subsequent runs at successively lower pressures. When the lower pressures were reached, the whole process was repeated by starting at the higher pressures. In most cases the changes which occurred in the spectrum were reversible when run under these conditions.



In a few experiments there was evidence of irreversible changes in the spectrum occurring at the highest pressures (50,000 to 160,000 atm) in that new bands appeared which remained when the pressure was reduced to 1 atm. These irreversible changes may have been caused by a chemical reaction. Examples of these spectra will not be reported until they are investigated further.

Since the diamond faces had an area of from 1 to  $2 \times 10^{-4}$  in<sup>2</sup>, only a portion of the incident i.r. beam could be accepted by the cell. Thus, it was necessary to restrict the reference beam to permit utilization of the full scale of the recorder. This was accomplished by placing a suitable screen (or perforated sheet-aluminum) in the reference beam. The low available energy made it necessary to operate at high gain and to use a slow scanning speed. Scanning speeds used varied from 0.08 to 0.5  $\mu$ /min with a slit program usually from three to four times that for the standard program of the instrument. In studying a given specimen, all instrumental settings were left unchanged. Because of the use of high gains, some of the recorded spectra showed considerable noise.

Errors in reading positions of absorption bands may occur because of the finite rate of scan and the limited amount of energy available. In cases where the exact position of a band was desired, the scanning speed was reduced, or the position was obtained from a manual setting. Since most of the work reported here is not concerned with the quantitative behavior of the frequency shifts, no special effort was made to measure the positions with greater accuracy than that available from the normal scanning rate of the spectrum.

A number of sources of error may affect the intensities of the recorded bands. Among these are the errors associated with the finite slit width, and scanning speeds which are accentuated by the limited amount of energy passing through the small specimen. For a given run under a fixed set of instrument settings, there is the question of error associated with extrusion of the specimen. Also, the material may become increasingly more transparent to infrared radiation at higher or lower pressures depending on the condition of the specimen film. Initially, the powdered specimen is translucent to radiation with considerable scattering. This scattering is usually reduced as the pressure is applied but sometimes increases at higher pressures, presumably because of some sort of phase change. In general, bands tend to broaden at elevated pressures. The finite slit width used would act to increase the apparent intensity of the pressure-broadened bands. Inasmuch as the intensity of most bands decreases at elevated pressures, this source of error produces an effect opposite to that observed.

The effect of the smaller amount of scattering at the higher pressure would be to furnish more energy to the detector with the result that the apparent band intensity would appear slightly greater. In actual practice most, but not all, bands show a decrease in intensity at higher pressures and thus the effect of this source of error is opposite to the observed behavior.

The effect of extrusion of specimen from between the diamond surfaces would produce a decrease in band intensity. However, a loss in intensity through extrusion should not be reversible for the type of materials studied here. The extrusion is generally observed in all experiments as an irreversible, time-dependent, decrease in intensity of *all* bands on the initial application of pressure.



In practice, quantitative intensity measurements were not considered feasible until the flow of specimen from between the diamond surfaces had ceased as shown by reversibility of the band intensities at different pressures. In addition, quantitative data were usually obtained by starting at the maximum pressure with subsequent measurements at successively lower pressures. Additional loss of material would be minimized by this technique. Since the band intensities usually increased at the lower pressures, it would be necessary to postulate a flow of extruded specimen into the pressure cell. Furthermore, a few spectra have been obtained which show that in a given specimen some bands increase in intensity, some decrease, and others show no change as the pressure increases. Such spectra show unmistakably that there is, at the very least, a marked relative intensity change between such bands. In addition, it is believed that the present data illustrate the behavior of the absolute band intensities as a function of pressure.

For obvious reasons no great precision is to be expected in an individual quantitative measurement of absolute intensity but data on the pressure dependence are believed to be qualitatively correct.

The apparent band intensities were calculated from plots of  $\log I_0/I$  vs. wave-number (or wavelength) followed by a graphical determination of the area. All results are given in ratios of the intensity at a given pressure to that at the lowest pressure recorded. In this manner, many problems associated with the computation of integrated intensities have been minimized or cancelled.

Intensity ratios calculated from the integrated expression [3] for band intensities

$$A = [K/cl]\Delta\nu_{\frac{1}{2}} \ln (I_0/I)$$

gave results in essential agreement with those obtained graphically. In this equation  $\Delta\nu_{\frac{1}{2}}$  is the band half-width,  $K$  is a proportionality constant,  $A$  the band area,  $c$  the concentration in moles per/liter and  $l$  the path length in centimeters. In these experiments the product  $cl$ , which is a measure of the quantity of material in the beam, is considered to be constant.

## Results

The following are examples of infrared spectra taken at high pressures for some selected substances. Specimens were obtained from chemically pure analyzed stock supplies. No attempt at further purification was made. The structures of these substances are usually quite complicated and in general it is not possible to interpret the changes which are occurring under pressure in terms of changes in structure.

### *Benzoic acid*

The infrared spectrum of benzoic acid was studied extensively to calculated pressures of 50,000 atm. The results of one typical run are given in Fig. 2. These spectra were taken consecutively on a sample after it had been established that no further extrusion was taking place. The order of recording the spectra at the different pressures was 46,000, 8000, 48,000, 3000 atm, respectively. The spectra

[3] D. A. RAMSAY, *J. Am. Chem. Soc.* **74**, 72 (1952).

have been displaced vertically to prevent confusing overlap of the bands. These spectra serve to illustrate two points. First, the relative shifts of most infrared absorption bands with pressure are small. The shifts here are either to higher frequencies, or are zero within experimental error. For example, there is a definite

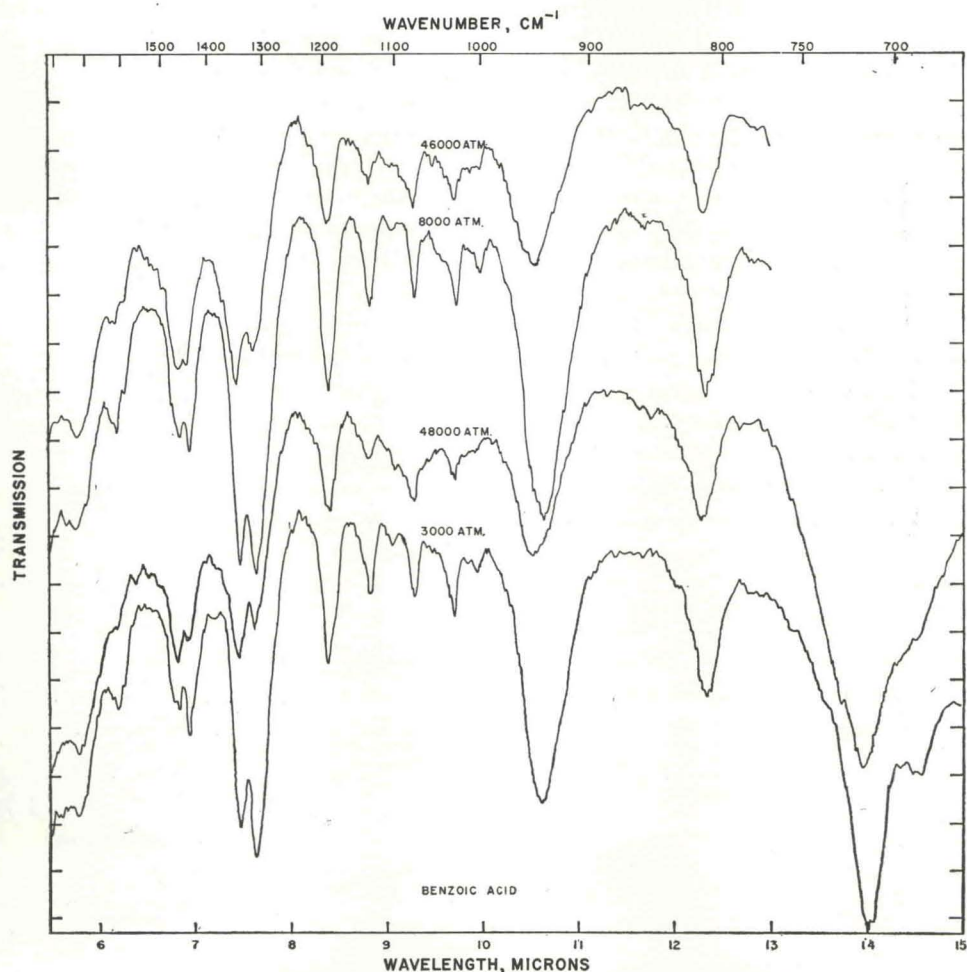


Fig. 2. Infrared spectrum of benzoic acid at calculated pressures 46,000, 8000, 48,000 and 3000 atm, respectively.

shift of a few wavenumbers associated with the 720, 810 and 930  $\text{cm}^{-1}$  bands, respectively. The 720 and 810  $\text{cm}^{-1}$  bands correspond to out-of-plane C—H bending vibration while the 930  $\text{cm}^{-1}$  band is an O—H out-of-plane bending vibration for the acid dimer structure. Secondly, these spectra illustrate that definite changes of intensity occur on the application of pressure and that these changes are specific with respect to different modes of vibration. In particular, some bands show little, if any, change of intensity on the application of pressure while others show large changes in both maximum absorption and apparent band

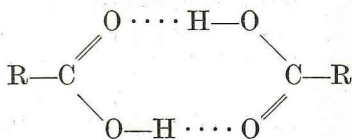


area. The bands which show a marked decrease in intensity are 810, 930, 1000, 1030, 1130, 1195, 1305, 1435 and 1600  $\text{cm}^{-1}$ , respectively. The band areas for the bands at 810, 930 and 1195  $\text{cm}^{-1}$  have been measured graphically in terms of the ratio of the area at high pressure to that at low pressure. The band areas for these peaks decrease by factors of 0.67, 0.5 and 0.67, respectively. Because of the uncertainty of locating the background, no area measurements were made for the other bands. However, it is clear that the decrease is rather large for the 1000  $\text{cm}^{-1}$  band and for the aromatic frequencies near 1600  $\text{cm}^{-1}$ . The least change of intensity seems to occur for the bands at 1455, 1335 and 1070  $\text{cm}^{-1}$ , respectively, but quantitative measurements are not possible because of overlapping. The carbonyl band near 1700  $\text{cm}^{-1}$  cannot be measured quantitatively because it occurs on the shoulder of the strong diamond band where there is only a limited amount of energy. The available data indicate that it shifts to lower frequencies. The bands at 690  $\text{cm}^{-1}$  may increase in intensity but again no reliable measurements could be made because of the shortage of energy. It should be noted that the bands associated [4] with the C—O single bond stretching mode and the coupled O—H bending C—O stretching mode (1195 and 1305  $\text{cm}^{-1}$ , respectively) both show large decreases in intensity.

In some spectra taken at pressures greater than 48,000 atm, there was evidence for a phase change as indicated by the appearance of a band near 860  $\text{cm}^{-1}$ . However, the change was sluggish and could not always be reproduced.

#### *Succinic acid*

The infrared spectrum of succinic acid has been studied to pressures of 50,000 atm. The results of one series of spectra are given in Fig. 3. These curves are spectra taken consecutively on a sample at pressures of 44,000, 6000 and 44,000 atm, respectively, after it was established that a fixed quantity of sample was remaining between the diamond faces. Most of the absorption bands show slight shifts to higher frequencies on application of pressure. The 930  $\text{cm}^{-1}$  hydrogen-bonded out-of-plane O—H deformation frequency gives a relatively large shift of nearly 40  $\text{cm}^{-1}$  to higher frequencies. The carbonyl band near 1700  $\text{cm}^{-1}$  appears to undergo a small but definite shift to lower frequencies. The behavior for these two frequencies may be understood in terms of the effect of pressure on the hydrogen bond structure



An increase of pressure on the sample would have considerably more effect on the relatively weak hydrogen bonds and less effect on the normal covalent bonds for this system. The O  $\cdots$  O hydrogen bond distance would shorten with the result that with increasing pressure the hydrogen bonds would become stronger. This would result in an abnormally high out-of-plane O—H bending frequency

[4] L. J. BELLAMY, *Infrared Spectra of Complex Molecules* p. 172. Wiley, New York (1958).



and a lower carbonyl frequency. The O—H stretching frequency should shift to lower frequencies. This effect has been observed but the O—H stretching frequency was very strong in this specimen and gave essentially one hundred per cent absorption. Examination of the benzoic acid spectra (Fig. 2) shows that the effect of pressure on the out-of-plane bending and carbonyl stretching

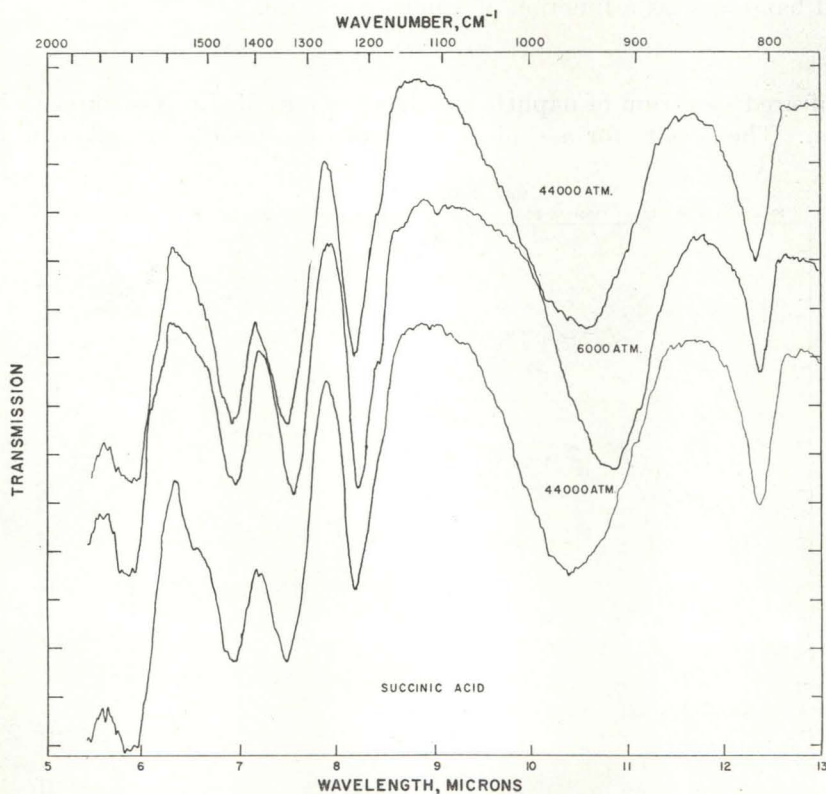


Fig. 3. Infrared spectrum of succinic acid at calculated pressures of 44,000, 6000 and 44,000 atm, respectively.

frequencies may be interpreted in the same manner. In general, most large frequency shifts that have been observed for pressures under 50,000 occurred where hydrogen bonds were present in the structure. Similarly most shifts of frequencies to longer wavelengths that persist above pressures of 10,000 atm have been observed only when hydrogen bonds were present in the structure.

A study of the intensity behavior of the bands in succinic acid on application of pressure was carried out by plotting  $\log I_0/I$  vs. wavelength and calculating the integrated area. The effect of the pressure was then expressed by taking the ratio of these areas. The only bands that were sufficiently free of band overlap to justify integration were the bands near 805, 930 and 1205  $\text{cm}^{-1}$ , respectively. For a change of pressure from 6000 to 44,000 atm these bands show changes in area by factors of 1.26, 1.0, 0.82, respectively. It should be noted that the intensity behavior of the 930  $\text{cm}^{-1}$  O—H out-of-plane band in succinic acid is



considerably different from the corresponding band of benzoic acid where an increase of pressure from 3000 to 48,000 atm changes the band area by a factor of 0.5. The C—O single bond stretching band qualitatively gives the same intensity—pressure dependence in these two acids. Succinic acid is one of the few materials studied to date which shows both definite decreases and increases of integrated band area as a function of applied pressure.

### *Naphthalene*

The infrared spectrum of naphthalene has been studied to pressures as high as 50,000 atm. The results for a typical series of experiments are given in Fig. 4.

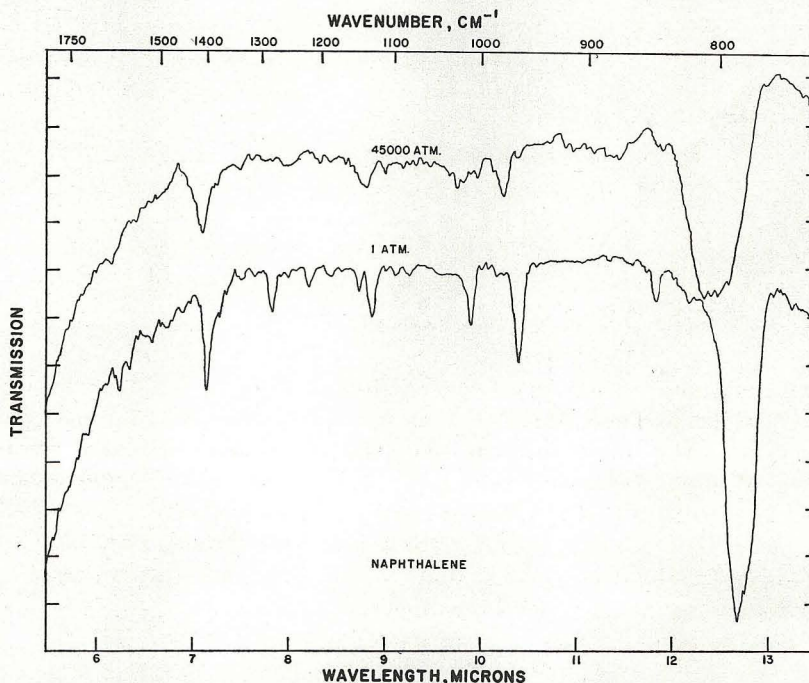


Fig. 4. Infrared spectrum of naphthalene at calculated pressures of 45,000 and 1 atm, respectively.

Considerable difficulty was encountered in obtaining a sufficiently thick film between the diamond surfaces to obtain adequate intensity of most infrared bands. The 45,000 atm spectrum was recorded followed by the equivalent spectrum taken near 1 atm pressure. Spectra taken at intermediate pressures indicate that the shift and broadening of the bands are continuous. There was some evidence for a discontinuous change occurring near 28,000 atm but subsequent runs did not definitely establish a phase change.

The changes which occur in this spectrum are not understood in detail and we will give only a qualitative description of the effects of pressure.

The very strong 782 cm<sup>-1</sup> band is broadened and shifted to 810 cm<sup>-1</sup> at 45,000 atm. The broadening of this band seems to be due to high-frequency



components which appear continuously as the pressure is raised. The integrated band area appears to decrease only slightly with increasing pressure despite the fact that the corresponding absorption maximum decreases rapidly with pressure. This band has been assigned to a  $B_{1u}$  C—H out-of-plane bending mode of vibration [5].

The  $1125\text{ cm}^{-1}$  band is considerably broadened and shifted to  $1136\text{ cm}^{-1}$  while the band area appears to be increased at 45,000 atm. This frequency was assigned as a  $B_{2u}$  in-plane C—H bending frequency.

The  $1387\text{ cm}^{-1}$  ( $7.2\ \mu$ ) band shifts a few wavenumbers to higher frequencies and is slightly broadened as the pressure is increased. This frequency corresponds to a  $B_{2u}$  C—C stretching mode of vibration which involves the central carbon atoms of the fused naphthalene ring.

The  $1510\text{ cm}^{-1}$   $B_{2u}$  multiple bond stretching frequency is broadened and shifted to higher frequencies. The  $1595\text{ cm}^{-1}$  C—C multi-bond stretching frequency is drastically broadened at the higher pressures and it was difficult to locate this absorption in some of the spectra taken at high pressures. In the 1 atm spectrum both the  $1510$  and  $1595\text{ cm}^{-1}$  bands seem to show up poorly in that the band shapes have not completely returned to that observed before the application of pressure. The drastic broadening of these bands probably reflects the effects of compression of the material on the  $\pi$  orbitals of the ring system.

### *Biphenyl*

It was not possible to keep a sufficiently thick sample of biphenyl between the diamond surfaces at high pressures to obtain a spectrum with reasonably intense bands. However, the high intensity of the C—H out-of-plane frequencies characteristic of mono-substituted benzene rings ( $700$  and  $730\text{ cm}^{-1}$ ) made it desirable to study the effect of pressure on these bands. In Fig. 5 the effect of pressure on these bands is illustrated. There was some loss of specimen between the initial run at 12,000 atm and the final run at 8000 atm. A new band appears at  $745\text{ cm}^{-1}$  following the shifting or disappearance of the band at  $730\text{ cm}^{-1}$ . The  $700\text{ cm}^{-1}$  band has a high-frequency component appearing near  $715\text{ cm}^{-1}$ . Since the band at  $700\text{ cm}^{-1}$  has not shifted greatly, it is not clear whether this new band is due to the presence of two phases or whether it is due to a pressure gradient occurring in the specimen. The spectrum taken at 30,000 atm shows the presence of two bands at  $735$  and  $745\text{ cm}^{-1}$ , respectively. Again, this may be due to a true splitting of this band, the presence of two phases, or a pressure gradient. Although no integrations were made, it appears that the areas of these bands (including high-frequency components) do not change significantly with pressure.

### *p-Dichlorobenzene, o-chloro-p-nitrophenol and p-nitrophenol*

The effect of pressure on the infrared spectra of *p*-dichlorobenzene, *o*-chloro-*p*-nitrophenol and *p*-nitrophenol is illustrated in Figs. 6, 7 and 8, respectively. The low-pressure spectra were recorded after the high-pressure spectra.

The high-pressure spectrum for *p*-dichlorobenzene illustrates the usual small

[5] E. R. LIPPINCOTT and E. J. O'REILLY, *J. Chem. Phys.* **23**, 238 (1955).



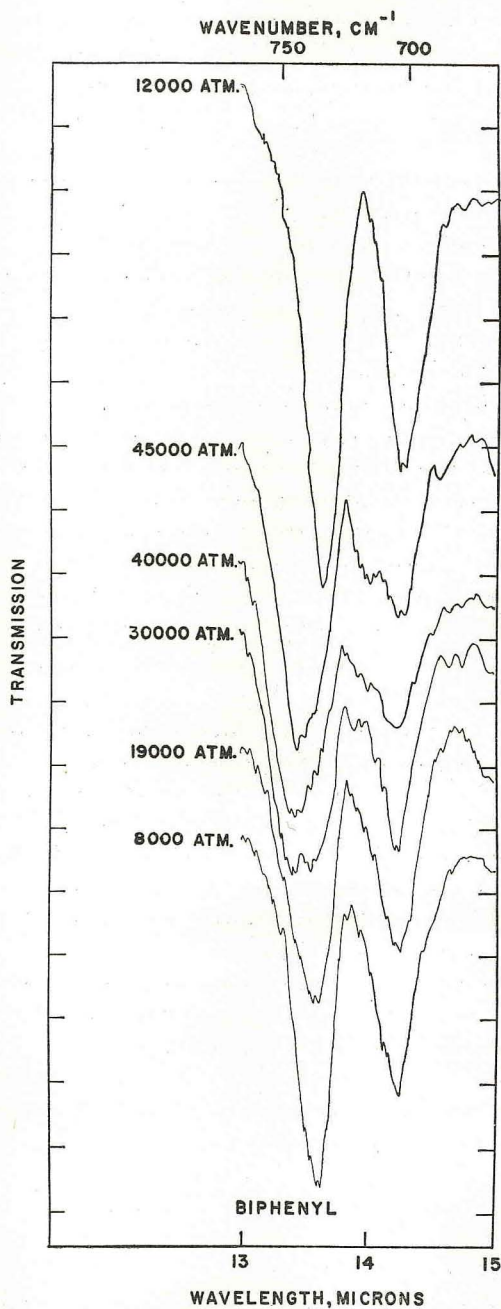


Fig. 5. The effect of applied pressure on the 700 and 730  $\text{cm}^{-1}$  bands of biphenyl.

shift to higher frequencies and the corresponding drop in band intensities. Some of the bands are markedly broadened. The C—H out-of-plane bending frequency near  $815 \text{ cm}^{-1}$ , characteristic of *para*-substitution on the ring, is broadened and



Studies of infrared absorption spectra of solids at high pressures

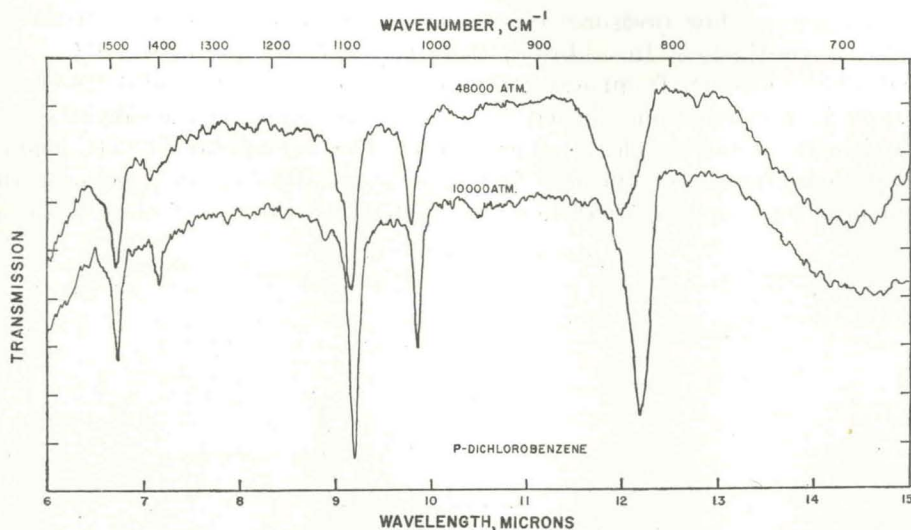


Fig. 6. The effect of applied pressure on the infrared spectrum of *p*-dichlorobenzene.

shifted to higher frequencies by about 15 cm<sup>-1</sup>. The band area is distinctly lower at the higher pressures.

The effect of pressure on the spectrum of *o*-chloro-*p*-nitrophenol is characterized by the appearance of new bands (925 cm<sup>-1</sup> and 1150 cm<sup>-1</sup>) and the disappearance

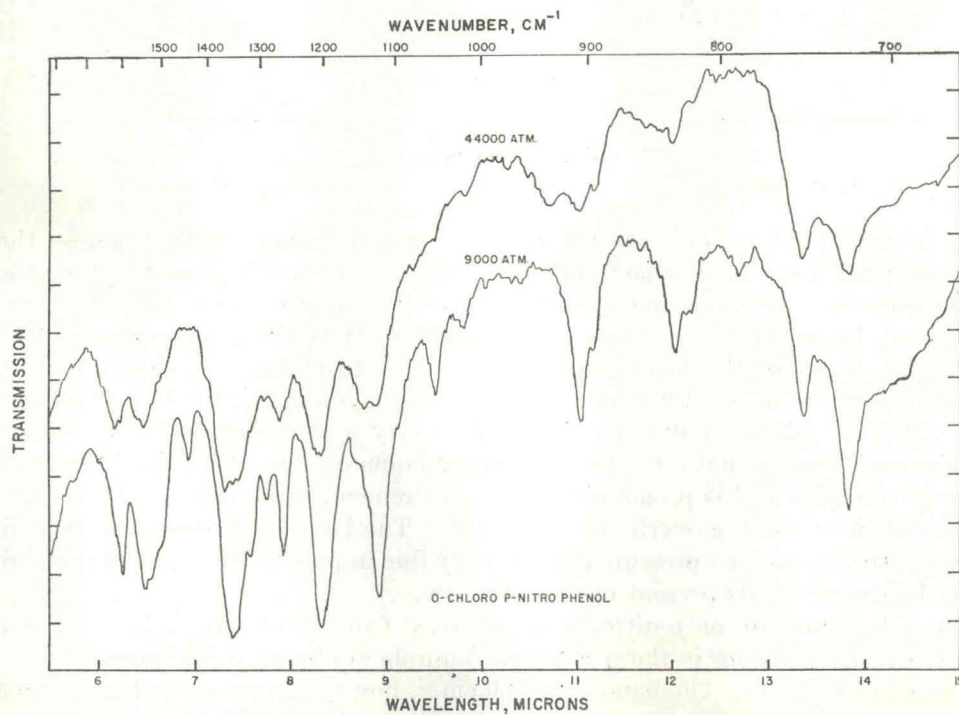


Fig. 7. The effect of applied pressure on the infrared spectrum of *o*-chloro-*p*-nitrophenol.



of bands present at low pressures (for example, see bands near 1015, 1060 and 1450  $\text{cm}^{-1}$ , respectively). In addition, there is the usual loss of band intensity and small shift to higher frequencies. The out-of-plane C—H bending frequency at 830  $\text{cm}^{-1}$  is broadened and shifted to higher frequencies. It appears to consist of more than one band at elevated pressures. The out-of-plane C—H bending frequency characteristic of one free hydrogen atom attached to a benzene ring observed near 900  $\text{cm}^{-1}$  is broadened and appears to consist of more than one

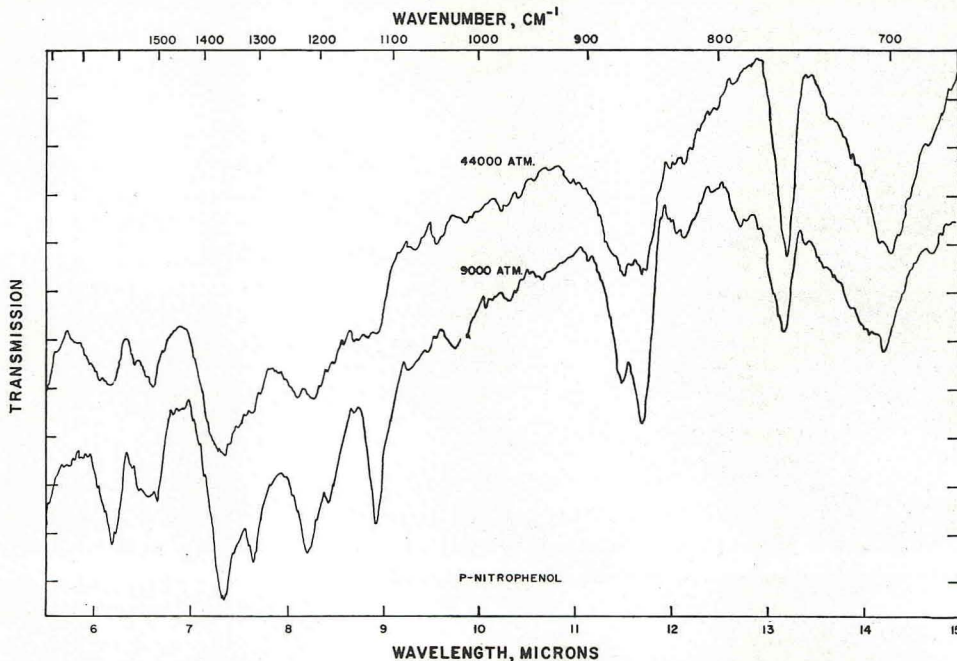


Fig. 8. The effect of applied pressure on the infrared spectrum of *p*-nitrophenol.

component. This may indicate the presence of a pressure gradient across the specimen. The two bands characteristic of the nitro group  $\text{NO}_2$  (anti-symmetric and symmetric stretching modes) which appear near 1545 and 1345  $\text{cm}^{-1}$  are overlapped by aromatic C—C stretching and O—H bending frequencies. The overlapped bands of the nitro group show a shift to higher frequencies and an apparent decrease in band intensity. The C—O single bond stretching frequency near 1200  $\text{cm}^{-1}$  shows a distinct loss of intensity and a slight shift to higher frequencies. The aromatic C—C stretching frequency near 1600  $\text{cm}^{-1}$  shifts to higher frequencies and is broadened. No measurements were made of band areas because of the extensive overlapping of bands. The large changes which occur in this spectrum on applied pressure are probably due in part to the effect of pressure on the hydrogen bonds present in the structure.

When the pressure on *p*-nitrophenol is raised from 9000 atm to 44,000 atm, a number of changes occur in the spectrum. A number of bands have lower intensity at the higher pressure. The band near 760  $\text{cm}^{-1}$ , however, appears to have gained intensity. The antisymmetric stretching frequency for the  $\text{NO}_2$  group observed



near  $1530\text{ cm}^{-1}$  clearly has lost considerable intensity even though it is overlapped by the C—C stretching frequencies. The symmetric stretching frequency of the nitro group observed near  $1350\text{ cm}^{-1}$  is broadened but does not appear to have a greatly reduced intensity. The band at  $1300\text{ cm}^{-1}$  which has been assigned as a C—N single bond stretching frequency by KROSS and FASSEL [6] is almost lost in the shoulder of the  $1350\text{ cm}^{-1}$  band and certainly has considerably reduced intensity. Similarly, the band at  $1210\text{ cm}^{-1}$ , which may be a C—N stretching frequency, has lost considerable intensity, as has also the  $1150\text{ cm}^{-1}$  band. The aromatic C—C stretching frequency near  $1650\text{ cm}^{-1}$  is broadened but seems to have retained much of its band intensity at 44,000 atm.

#### *Ammonium halides*

The only band of the ammonium halides which was sufficiently intense and in a region of the spectrum suitable for studies at elevated pressures was the band corresponding to the degenerate N—H bending vibration observed near  $1410\text{ cm}^{-1}$ . Studies on  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{Br}$  to calculated pressures of 45,000 atm showed that this band did not shift position significantly with pressure. (Possibly a very slight shift to lower frequencies was observed as the pressure was increased.) Graphical integrations of the band area showed that there was no change or only a slight decrease of intensity (within experimental error) to 45,000 atm. Some of the spectra showed evidence of a weak high-frequency component but this could not be resolved with certainty from the main band.

#### *Hydrates*

A number of hydrates were investigated to pressures of 45,000 atm to study the effect of pressure on the H—O—H bending frequency. This frequency appears near  $1630\text{ cm}^{-1}$  in most hydrates. The O—H stretching frequency was not studied because it absorbed too strongly. The application of pressure did not produce any detectable change in the position of the bending frequency for any of the compounds studied. However, there was a definite change of intensity with pressure for a number of hydrates. For  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , the integrated band area increased by a factor of 1.9 as the pressure was decreased from 45,000 to 4000 atm. Similarly, the integrated band intensity for  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  increased by a factor of 1.35 as the pressure was changed from 44,000 to 4000 atm. However, studies on  $\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$  showed that the apparent integrated intensity of the  $\text{H}_2\text{O}$  bending band decreased by a factor of 0.72 as the pressure was changed from 49,000 to 4000 atm. Similar results were found for studies on the  $\text{H}_2\text{O}$  bending frequency in  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ . With  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (gypsum) the water bending band decreased in intensity by a factor of 0.72 when the pressure was decreased from 53,000 to 6000 atm.

#### *Infrared spectra to 160,000 atm*

In order to investigate the performance of the diamond pressure cell at higher pressures, a number of runs were made to calculated pressures as high as 160,000

[6] R. D. KROSS and V. A. FASSEL, *J. Am. Chem. Soc.* **78**, 4225 (1956).



atm. This was accomplished by using diamonds with a small surface area ( $8 \times 10^{-5}$  in<sup>2</sup>) and using a 2/1 lever arm to apply the load of the calibrated spring. Under these conditions, the diamond faces deteriorated after a few runs. The most successful run is illustrated in Fig. 9 which gives the spectrum of *p*-nitrophenol taken at a calculated pressure of approximately 160,000 atm followed by a spectrum taken when the pressure was reduced to 6000 atm. The thinness of the specimen and the lack of energy available at longer wavelengths arising from the small diamond surface area account for the apparent differences in the low-pressure

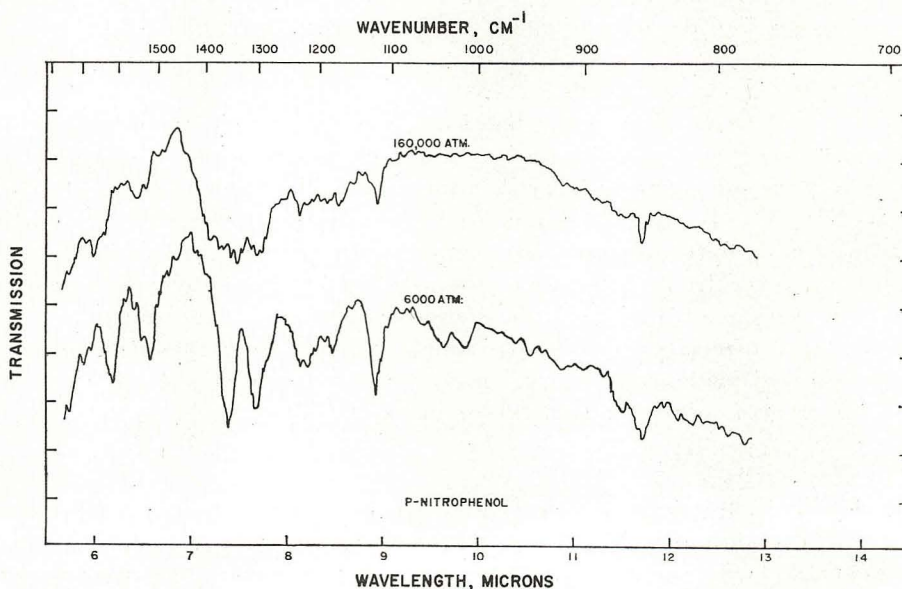


Fig. 9. The infrared spectrum of *p*-nitrophenol at calculated pressures of 160,000 atm and 6000 atm.

spectra of Figs. 8 and 9. Evidence for the high pressure is given by the unusually large shift ( $50\text{--}60\text{ cm}^{-1}$ ) for the aromatic C—C stretching frequency and the large changes of intensity and shape of many of the other bands. For example, the bands near  $1010$  and  $1025\text{ cm}^{-1}$  are completely missing in the high-pressure spectrum while the  $1210\text{ cm}^{-1}$  band has a greatly reduced intensity as do many of the other bands including the  $\text{NO}_2$  antisymmetric stretching frequency. Unfortunately, we do not have any information on the magnitude of the pressure gradients across the specimen, but in any case, the average pressure is very high.

*p*-Nitrophenol was the only sample which gave an infrared spectrum which was essentially reversible from such extremely high to low pressures, before deterioration of the diamonds necessitated a regrinding of the surfaces. Runs on some other compounds to similar pressures gave large changes but a few new bands appeared in the spectrum which did not disappear when the pressure was lowered. These changes were tentatively interpreted as due to a chemical reaction under pressure and will not be discussed here.



### Discussion

In general it has not been possible to interpret the changes in the infrared spectra which occur in application of pressure in terms of the structures of the specific substances. The shift to higher frequencies which is observed at elevated pressures for many bands can qualitatively be interpreted as an increase of the importance of repulsive forces of neighboring molecules as compared to attractive forces as the pressure increases. In cases where shifts to lower frequencies occur, it would appear that attractive forces of neighboring molecules are initially exerting a greater influence on the atoms than the repulsive forces. Most of the shifts to lower frequencies observed to date have been for substances where hydrogen bonds are present in the structure. Such bonds are the result of relatively weak attractive forces between neighbors and it would seem that pressure tends to increase the strength of hydrogen bonds by increasing the attraction. Eventually, there must be some pressure where the repulsive forces become larger than the attractive forces and shifts to higher frequencies should again take place.

If the cases where hydrogen bonds are present in the structure are excluded, it is clear that an applied pressure of the order of 40,000 atm has relatively little effect on the position of most absorption bands. This would indicate that such pressures do not produce significant changes in the bonds responsible for the spectra and that any phase changes that occur do not alter greatly the bond configuration of the molecule, although there may well be a change in space group symmetry of the unit cell. For the organic materials studied here, the decreases in volume at pressures of the order of 40,000 atmospheres is approximately 20 per cent [7]. Since the interatomic distances of atoms involved in the bonds do not change appreciably, there must be a large change in intermolecular distances. The present data indicate that the bonds are relatively insensitive to this change in intermolecular spacing. However, for pressures in excess of 50,000 atm, such changes in structure may occur as is illustrated by the appearance of the spectrum of *p*-nitrophenol recorded at a pressure of 160,000 atm.

The relatively large changes of integrated intensities which occur for pressures up to 50,000 atm suggest that relatively large changes in dipole moment derivatives are occurring for a number of modes of vibration. A discussion of this effect will be presented elsewhere.

---

[7] P. W. BRIDGMAN, *Proc. Am. Acad. Arts. Sci.* **76**, 9 (1945).