# Hydrostatic optical cell with glass windows for 25 kilobar*

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**An optical cell with three glass windows for hydrostatic pressures up to 25 kilobar has been made. Its collecting angle is 13° and it has been used mainly for Raman spectroscopy. The fundamental Raman spectrum of diamond has been recorded.**

## I. INTRODUCTION

High-pressure optical measurements in hydrostatic systems are of course much more useful than those in nonhydrostatic systems at the same pressure, but nonhydrostatic systems are capable of much higher pressures. The purpose of the present paper is to describe a significant increase in the pressure range of hydrostatic optical cells and optical windows. The cell was designed primarily for laser Raman spectroscopy, but can of course be used for absorption, fluorescence, and phosphorescence spectroscopy and could be adapted to infrared spectroscopy.

The earliest high-pressure optical window was Amagat's cone,[1] which was used to 1.5 kilobar, and Wahl[2] managed to reach 4 kilobar with it. This pressure was not exceeded until Poulter[3] invented the packless seal in 1932 and certainly reached 12 kilobar and claimed 30 kilobar. His pressure-transmitting fluid was described as "light paraffin oil," and was shown to transmit pressure to 11 kilobar by observing the liquid-ice VI transition of a sample of water enclosed in a rubber capsule and immersed in the oil. Pressures of 21 kilobar were evidently not generated as the then unknown ice VI-VII transition was not observed. Furthermore, the pressure of the oil was measured by a manganin gauge up to 13 kilobar, but by the force on the pressure-generating piston at higher pressures. It was claimed that pressures of over 20 kilobar were sustained by glass windows covering a circular aperture of 6 mm diameter, but this has not been verified by anyone else, the maximum pressure reported with glass windows being about 12 kilobar.[4] However, shortly after, he reported[5] using diamond windows up to 21 kilobar with water or ether as the pressure-transmitting medium, a pressure that has been exceeded in a hydrostatic windowed pressure vessel only in this work. Recently, sapphire windows have been used up to ~16 kilobar on a 2-mm[6] and up to 6-mm[7] apertures.

It is clear on general grounds that windows made of hard material will withstand any pressure if the aperture is small enough. Unfortunately, the stresses in a window with a packless seal do not seem to have been calculated, and only empirical design is possible at present. For the highest pressures, therefore, the aperture must be as small as possible consistent with the aperture ratio required for the optical experiment. In our cell, the aperture is 800 μm and glass windows covering them withstand 25 kilobar without damage.

The early optical cells were pressurized from an external source, but for the highest pressures it is sometimes more convenient to generate the pressure within the optical cell,[3] particularly when it is to be used not far from room temperature. This has been done here.

## II. THE CELL

The cell was designed primarily for Raman spectroscopy using the Jarrel–Ash 25–300 Raman spectrometer, which has an aperture ratio of 8.7. The laser beam is focusable to a diameter of about 50 μm,[8] and the slit width of the spectrometer will usually be 100 μm, which corresponds to a spectral slit width of ~3 cm$^{-1}$. The source should therefore be magnified at least twice, and the aperture ratio of the collecting optics should be smaller than 4.3. The collecting angle of the spectrometer is 6.6°, and the collecting angle of the cell should be at least 13°. If the angle is less than this, the amount of light passing the slits is proportional to the square of the angle. If the angle is increased beyond this and the magnification increased accordingly, the intensity of light collected increases according to less than the square of the angle because light is lost on the jaws of the slit, but nevertheless, significant gains can sometimes be made. The collecting angle of the cell as made is 13°.

The maximum collecting angle is determined by the ratio of the aperture to the thickness of the window if the sample is close to the window, and the aperture can be decreased at will if the ratio is kept constant. An aperture of 800 μm was chosen as a compromise between small size and ease of alignment. The window thickness is 3.2 mm, which allows a collecting angle of 14.2° if the source touches the window, and 11° if the source is 300 μm from the window. Before the cell was made, a model was tested optically to verify that adequate Raman light could be recovered.

The cell is illustrated in Fig. 1. It is essentially an intensifier with windows, a configuration that appears to have been first used over 40 years ago.[3]

The body A is made of fully hardened type 300 maraging steel and has three crossed bores and six ports. The bore parallel to the long axis is 6.7 mm in diameter at one end and is used for pressurizing the fluid by a tool-steel piston B pushed by a hydraulic jack which is

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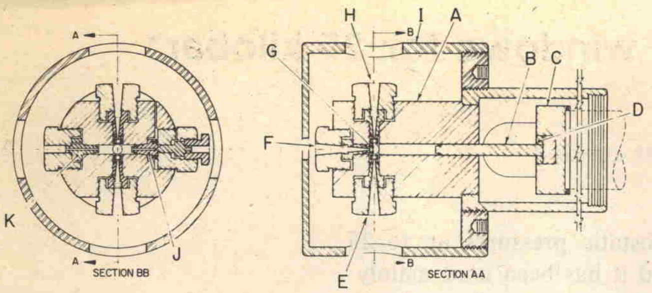

FIG. 1. The hydrostatic optical cell.

not shown. The piston B is centered in its push block C by a centering ring D, which is a close clearance fit in C. The piston can readily be removed for maintenance. The other end of this bore and the two cross bores are 8 mm in diameter. The experimental light beam enters and exits through the two ports E and H on one of the cross bores, and the scattered light, if it is required, is collected through the port F at right angles. The window G of the port F for the scattered light is placed close to the experimental beam so that the maximum light can be gathered. One, J, of the two remaining ports holds a manganin coil for measuring the pressure, and the other, K, has a plug that serves the dual purpose of carrying a holder for a solid sample and providing an inlet for fluid pressure to push back the piston when it is required.

The window assembly is illustrated in more detail in Fig. 2. The windows M used for Raman spectroscopy have been made of optical glass, were 4.8 mm in diameter and 3.2 mm long. Both flat surfaces and the mating surface of the plug were ground optically flat. To assemble, the window M and plug L were carefully cleaned and the window was placed on the plug without sliding or rotation and gently pressed until it started to adhere. It was held in place by screwing the holder N gently home.

The pressure seal for both the plugs and the pressure-generating piston is an unsupported-area wedge-ring seal of modified design[9] that is illustrated in Fig. 2. The rings P are made of either AISI 4340 heat treated to a hardness of 50–52 $R_c$ or of type 300 maraging steel heat treated to 52–54 $R_c$. They are tinned with solder by dipping them in molten solder and throwing them into a metal can so that they rattle around while the solder cools. The excess solder is thrown off and a uniform film is obtained. The purpose of the solder is to increase the sealing properties of the rings and reduce the friction with the walls. The seal does not seal until a pressure of several kilobars has been reached, and so a supplementary seal must be provided. In this cell, O-rings O have been used but they have the disadvantage that they crack when they are pressurized, apparently owing to solvent-induced crazing above the glass transition.[10] As long as the pressure is not reduced below a few hundred bars, the cell can be repeatedly pressurized without changing the O-rings, but if the pressure is dropped to zero, they must be changed. When they are changed, the wedge rings are replaced by freshly tinned rings. Changing the rings is relatively easy, because the gland nuts and plugs can be removed without moving the cell. To prevent pressure that leaks past the seal from acting on the large surface of the head of the window holder, a relief hole Q to the bore was provided. A screw thread R was also provided to facilitate removal of the holder.

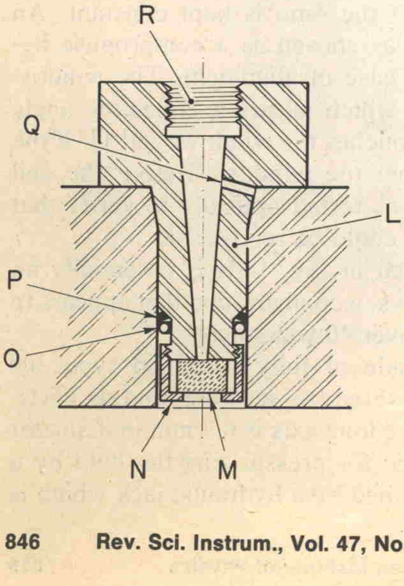

FIG. 2. The window assembly and the pressure seal.

An annealed mild steel tube I in Fig. 1, with four ports around the circumference and a plate, with a fifth port, welded on the end, was used as a safety shield. The shield could be rotated so that the openings were flush with the ports for loading, etc., or the ports were shielded for operation. It was screwed to the cell as illustrated. The optics were protected from a possible breakage of the windows by 6.35-mm-thick Lexan shields. Short bullets from a .220 rifle fired at a range of 1.2 m were stopped.

The manganin coil was calibrated against a controlled-clearance 20-kilobar pressure balance made in this laboratory having a tungsten carbide piston and cylinder.

Because the windows are so small, the cell must be accurately positioned if maximum light is to be collected. It is, therefore, mounted on the cross-slide of a tool carriage that is itself mounted on a small lathe bed. One end of the lathe bed projects into the sample compartment of the spectrometer and the other is clamped to the table of a drill press that is mounted on a plate fitted with wheels and with bolts that act as adjustable legs. The cell is roughly positioned in a horizontal plane by moving the drill press and then fixed in position with the column vertical by means of the adjustable legs of the plate. It is positioned accurately enough in a vertical direction by moving the drill press table. The final horizontal positioning is accomplished by moving the tool carriage and its cross slide. The cell can be rotated about its vertical axis by the compound rest and rotated about the two horizontal axes by means of screws.

Only two or three windows have cracked during three years of operation, and none has failed to hold pressure. The cracks occurred on the inside surfaces of the windows, probably because they were unintentionally heated by a focused laser beam.

It has been used so far for Raman spectroscopy near room temperature. It can undoubtedly be cooled about 100 °C and heated perhaps 200 °C. It should also be useful for absorption, fluorescence, and phosphorescence experiments. The following section describes the results of measuring the Raman spectrum of diamond in the cell.

## III. RAMAN SPECTRUM OF DIAMOND TO 23 KILOBAR

Single-crystal diamonds of gem quality were supplied by Fort Wayne Wire Die, Inc. The Raman spectra were recorded with a Jarrell–Ash model 25–300 Raman spectrometer with a slit width of 2 $\mathrm{cm}^{-1}$, scanning speed 2 $\mathrm{cm}^{-1}\,\mathrm{min}^{-1}$, counting rate $2 \times 10^3\ \mathrm{sec}^{-1}$, and time constant 10 sec, with a Coherent Radiation model 52 argon-ion laser using the 514.5-nm argon line at a power of 1.5 W. The 556.28-nm line of an Ultra-Violet Products neon lamp, which occurs 1363.2 $\mathrm{cm}^{-1}$ lower than the argon-ion exciting line and is only 30 $\mathrm{cm}^{-1}$ from the diamond band, was recorded as a frequency standard with each spectrum of diamond. Three spectral runs were made at each of twelve pressures in the range 0–23 kilobar.

A typical spectrum, one that was run at 22.83 kilobar, is shown in Fig. 3. The signal-to-noise ratio is about 100:1. The frequencies at the maxima of the neon and diamond bands were determined in all thirty-six spectra by drawing the mean frequency of the band edges as a function of intensity and extrapolating the line so obtained to its intersection with the recorded band. The intersection was taken as the peak. The peak frequency so defined could be determined to $\pm 0.1\ \mathrm{cm}^{-1}$ for any one spectrum, and the standard deviation of triplicate determinations of the difference between the neon and the Raman band was $\pm 0.14\ \mathrm{cm}^{-1}$. The half widths were measured directly at several spectral slit widths and were extrapolated to zero slit width.

The frequencies and half widths of the band at various pressures are listed in Table I. The errors of the frequencies are the standard deviations of the triplicate measurements at each pressure, and the errors of the half widths are $\pm 0.1\ \mathrm{cm}^{-1}$.

The frequencies are plotted against pressure in Fig. 4, with error bars indicating the standard deviations. Within the experimental error, the frequency is linear in the pressure, and the least-squares line, using weights proportional to the inverse square of the standard deviations of the individual points, is

$$\nu/\mathrm{cm}^{-1} = (1332.95 \pm 0.13) + (0.296 \pm 0.011)\ p/\mathrm{kilobar}. \quad (1)$$

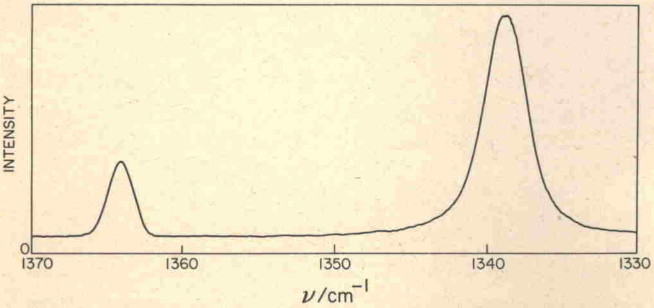

FIG. 3. The fundamental Raman band of diamond at 22.83 kilobar.

TABLE I. Frequencies and half-widths of the fundamental Raman band of diamond at various pressures.

| Pressure (kilobar) | $\nu$ ($\mathrm{cm}^{-1}$) | $\Delta\nu_{1/2}$ ($\mathrm{cm}^{-1}$) |
|---|---|---|
| 0.001 | 1332.92 ± 0.1 | 1.89 ± 0.06 |
| 1.60 | 1333.56 ± 0.07 | 1.87 ± 0.02 |
| 5.17 | 1334.32 ± 0.1 | 1.83 ± 0.1 |
| 6.13 | 1334.65 ± 0.02 | 1.87 ± 0.02 |
| 9.05 | 1335.71 ± 0.14 | 1.87 ± 0.02 |
| 11.70 | 1336.21 ± 0.04 | 1.90 ± 0.07 |
| 13.55 | 1337.00 ± 0.08 | 1.85 ± 0.04 |
| 16.27 | 1337.53 ± 0.06 | 1.83 ± 0.04 |
| 17.28 | 1337.79 ± 0.12 | 1.83 ± 0.02 |
| 20.06 | 1338.77 ± 0.06 | 1.83 ± 0.02 |
| 20.81 | 1338.89 ± 0.04 | 1.86 ± 0.06 |
| 22.83 | 1339.26 ± 0.1 | 1.90 ± 0.06 |

The slope of $0.296 \pm 0.011\ \mathrm{cm}^{-1}\ \mathrm{kilobar}^{-1}$ agrees within the combined error with that of $0.30 \pm {\sim}0.03\ \mathrm{cm}^{-1}\ \mathrm{kilobar}^{-1}$ obtained from Fig. 1 of Mitra *et al.*[11] based on measurements at four pressures in the range 0–9 kilobar. The fractional change of frequency with pressure is

$$(\partial \ln\nu/\partial p)_T = 0.222 \pm 0.008\ \mathrm{Mbar}^{-1}. \quad (2)$$

The change of half width with pressure is $0 \pm {\sim}0.005\ \mathrm{cm}^{-1}\ \mathrm{kilobar}^{-1}$.

The Grüneisen parameter $\gamma$, which is defined as

$$\gamma = (\partial \ln\nu/\partial \ln\rho)_T, \quad (3)$$

can be obtained from the pressure coefficient of the frequency and the compressibility $\kappa$,

$$\gamma = (\partial \ln\nu/\partial p)_T/\kappa. \quad (4)$$

The compressibility of diamond has been measured several times, and although there is a considerable scatter in the values obtained by different workers and different methods, the value $0.226 \pm 0.001\ \mathrm{Mbar}^{-1}$ now seems to be established.[12] From this value and Eq. (4), the Grüneisen parameter is

$$\gamma = 0.98 \pm 0.04. \quad (5)$$

In the zone-center fundamental of diamond, of species $F_{1g}$, alternate (100) planes oscillate in phase with one another, and $\pi$ radians out of phase with the other set of alternate planes. The most elaborate potential that can be analyzed by the data is

$$V = (1/2)k_2(r - r_e) + (1/3!)k_3(r - r_e)^3, \quad (6)$$

where $r$ is the distance between neighboring (100) planes and $r_e$ is the equilibrium distance. To second order in perturbation theory,[13] the frequency in wave numbers of the zone-center oscillation is

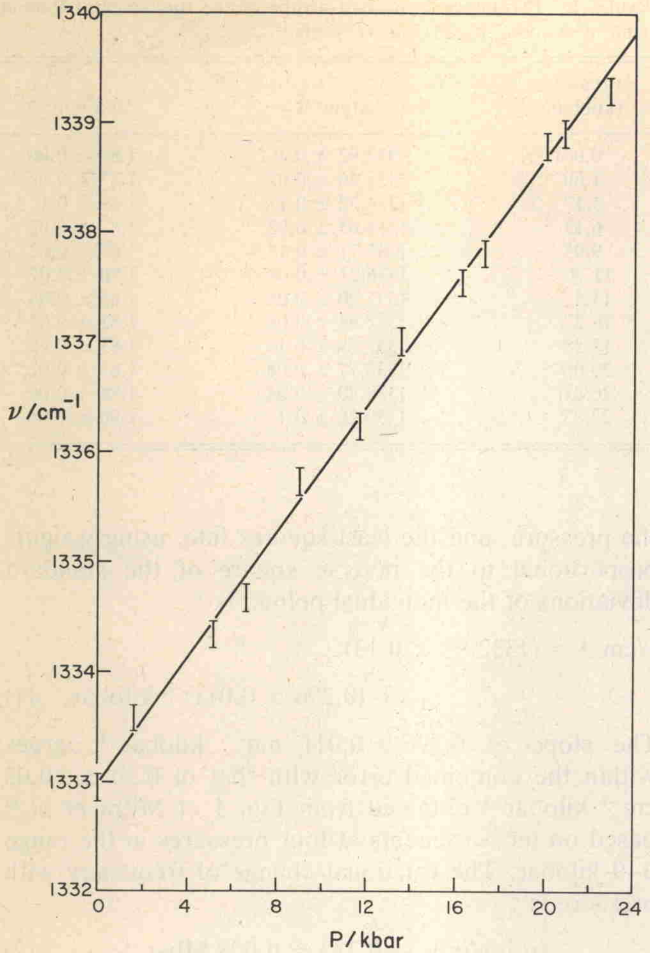

FIG. 4. Effect of pressure on the frequency of the fundamental Raman band of diamond.

$$2\pi c\nu = (k_2/\mu)^{1/2} + (5/24)(k_3/k_2)^2 h/8\pi\mu, \qquad (7)$$

where $c$ is the speed of light, $h$ Planck's constant, and $\mu$ the reduced mass of the oscillation. The effect of hydrostatic pressure is to shift the equilibrium interplanar distance to $r_e' = r_e - \delta$, and when $r_e = r_e' + \delta$ is substituted into Eq. (6) we obtain

$$V = (1/2)(k_2 - k_3\delta)(r - r_e')^2 + (1/3!)k_3(r - r_e')^3, \qquad (8)$$

and the frequency according to second-order perturbation theory is

$$2\pi c\nu = [(k_2 - k_3\delta)/\mu]^{1/2} + (5/24)[k_3/(k_2 - k_3\delta)]^2 h/8\pi\mu.$$

To terms in $(k_3/k_2)^2$

$$\partial \ln\nu/\partial \ln\rho = -k_3 r_0/6k_2, \qquad (9)$$

where $r_0$ is the equilibrium interplanar spacing at zero pressure.

From Eqs. (5) and (9),

$$k_3/k_2 = -6.6 \pm \sim 0.3 \text{ Å}^{-1}, \qquad (10)$$

and from the frequency at zero pressure and Eq. (10),

$$k_2 = 6.28 \text{ mdyn Å}^{-1},$$

$$k_3 = -42 \text{ mdyn Å}^{-2}. \qquad (11)$$

The compressibility is

$$\kappa = 4\sqrt{3}a/k_r,$$

where $a$ is the C–C bond length and $k_r$ the C–C stretching force constant. If other force constants can be neglected,

$$(4/3)k_r = k_2,$$

so that

$$\kappa = (16/\sqrt{3})a/k_2. \qquad (12)$$

From Eqs. (9), (11), and (12),

$$\kappa/\text{Mbar}^{-1} = 0.227 - 0.164 \text{ p/Mbar}.$$

The compressibility at zero pressure agrees well with the best value of 0.226 ± 0.001 Mbar$^{-1}$.[11] There are no experimental values of the compressibility at finite pressures.

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