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Pressure determination in a high-pressure cell for Raman spectroscopy at 4.2 K

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When using Raman spectroscopy for investigating molecular interactions under pressure it is necessary to know the density or the pressure, neither of which can be readily determined in low-temperature experiments. The high-pressure Raman cell used here is of a piston-cylinder type (Jean-Louis and Vu, 1972) with four sapphire windows. It is not suited to density measurements, largely because of the presence of windows. Infrared absorption studies of hydrogen at 4.2 K have been made up to 14 kbar with such a device by Jean-Louis and Vu (1972) in which the pressure was determined from the pressure shift of the energy gap of GaSb immersed in the sample, but this method can be applied only in the infrared range.

The pressure in the sample cannot be estimated directly from the applied load, owing to the large friction in the apparatus, especially at low temperatures, although the friction can be taken into account by making several pressure runs (Bridgman, 1942; Steward, 1956); this provides a means of calibrating a sensor. First, we tried to detect the pressure in the cell by its effect on the Raman librational spectrum of the cell windows, but the sapphire scattering intensity is too weak to allow precise measurements. On the other hand, the window fluorescence, excited by the incident light scattered in the sample, has a fairly high intensity and its spectral pressure shift can be measured with precision; we used it as a pressure sensor. The method resembles that of Barnett *et al.* (1973), which makes use of the R luminescence of a ruby chip placed in the cell. Their pressure sensor was calibrated with the use of fixed points at room temperature, which cannot be applied directly at low temperatures.

The R_1 and R_2 luminescence lines of ruby result from electronic transitions between the doublet state 2E and the 4A_2 state of the chromium ion (Cr^{3+}) in corundum (Al_2O_3). The same lines, although not so wide, are found in the fluorescence spectrum of the sapphire windows of our cell which contain traces of chromium. At 4.2 K only the lower level of 2E is populated in the first step of de-excitation. Accordingly, only the R_1 line is observed in the fluorescence spectrum and is quite sharp. The position, σ , of this R_1 line was used as a pressure sensor after calibration by means of pressure runs employing solid helium to provide hydrostatic environment; with nitrogen, which is not plastic at this temperature one observes splitting of the R_1 line (figure 1). The $\sigma = f(p)$ curves obtained from different pressure cycles were reproducible to within ± 60 bars; correction for friction was made by averaging horizontally between the curves for increasing and decreasing pressure. The calibration curve (figure 2) was taken as the mean value of several experiments. The R_1 line shift is not a linear function of the pressure, as found at normal temperatures for ruby by Barnett *et al.* (1973). The departure from linearity amounts to $\sim \pm 150$ bars, which could be specific to low temperatures,

but could also be due to the complex strain conditions in the windows. The line shift is about $0.84 \text{ cm}^{-1} \text{ kbar}^{-1}$ around 1 kbar, and $0.6 \text{ cm}^{-1} \text{ kbar}^{-1}$ around 9 kbar, which is comparable to literature data for ruby. Thermal stabilisation of the windows is not a major problem, as the R -line temperature coefficient is quite negligible between 4 and 20 K. With account taken of the reproducibility of optical measurements and the inaccuracy associated with the calibration curve, the mean precision of pressure determination is $\sim \pm 200$ bars.

In order to test the method, we have determined the α - γ transition pressure in solid nitrogen at 4.2 K. This phase transition can be detected from a simultaneous record of the low-frequency Raman spectra of both phases. The pressure is applied at ~ 70 K when the solid is still plastic; and the cell is then cooled to 4.2 K. The pressure is determined at 4.2 K from the calibration curve. If the pressure is applied at 4.2 K, it is not hydrostatic, as seen from the Raman spectrum of α - N_2 (figure 3): the lines are broadened, and the double degeneracy of the narrow E_g line is removed and the line is split. Thus under hydrostatic conditions, the α - γ transition occurs at ~ 3.65 kbar (3600 atm). At 3.8 kbar the solid is entirely in its γ phase. According to Swenson (1955) this phase exists at low temperatures above 3500 atm. According to Schuch and Mills (1970) the γ transition at 19.5 K occurs at 3945 ± 70 atm in $^{28}\text{N}_2$ and 3535 atm in $^{30}\text{N}_2$.

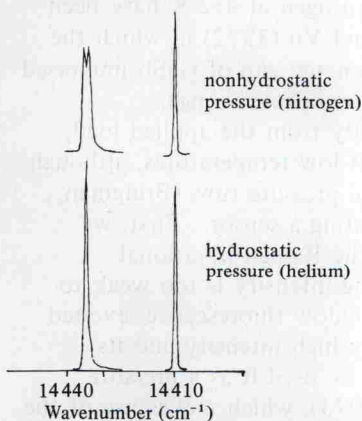


Figure 1. Profile of the fluorescence line of the sapphire window at 8.6 kbar with solid helium and solid nitrogen as the pressure-transmitting medium. The argon line was the reference line.

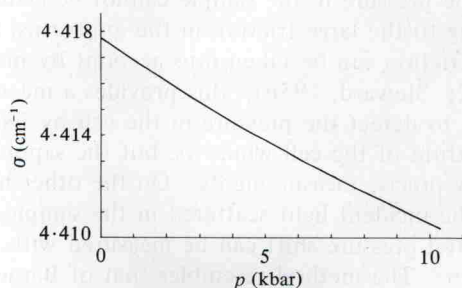


Figure 2. Calibration curve showing the wavenumber of the R_1 fluorescence line of the cell sapphire windows, σ , as a function of pressure in the cell, p .

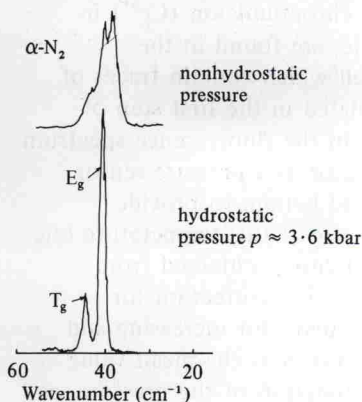


Figure 3. The effect of nonhydrostatic environment on the Raman spectrum of α - N_2 at 7.2 K and 3.6 kbar.