

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

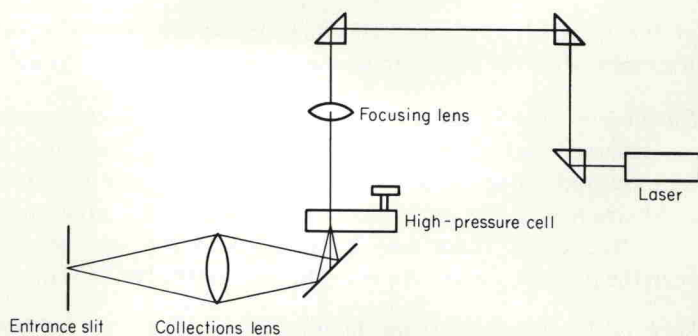


FIG. 9. Schematic diagram for laser Raman-high-pressure experiment.

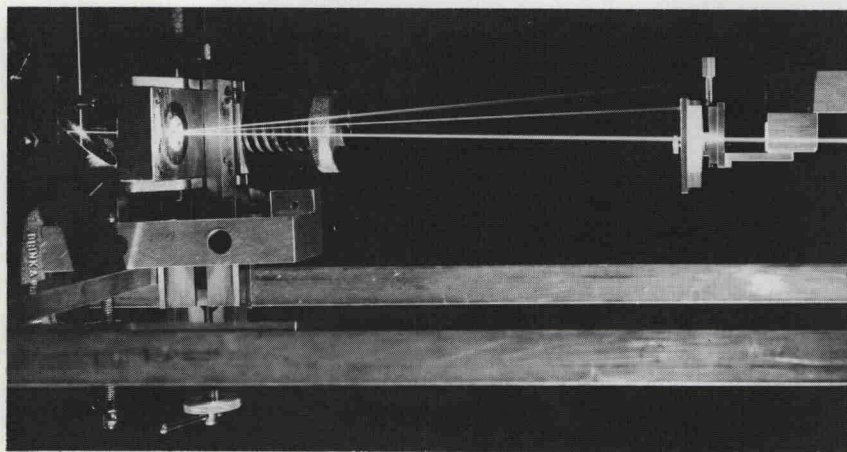


FIG. 10. Apparatus used in laser Raman-high-pressure experiment.

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.