

O—C—O is 180° and the ν_1 vibration is forbidden in the IR 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 ca. 104° , shows an IR-active ν_1 vibration.

(b) *Splitting of degenerate vibrations.* The loss of the degeneracy of *E* or *F* type vibrations with pressure is possible. In some cases this may be due to a lowering of symmetry of the molecule. In other cases, where a molecule may have two or more molecules per unit cell, it is possible that the vibrations in the unit cell might couple, causing a factor group splitting (Davydov splitting) [314].

(c) *Doubling of absorption bands.* In the course of various studies [199] 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 dependencies manifested by the two vibrations. Alternatively, this may be caused by factor group splitting.

(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 may allow 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. Vu et al. [315] demonstrated that a shift of ca. $1 \text{ cm}^{-1} \text{ kbar}^{-1}$ occurs for the pressure-induced $\nu_{\text{H-H}}$ vibration in solid hydrogen. A somewhat lower pressure dependence is found for HCl [316].

(iii) *Functional approach to explain pressure effects*

Recently, Gutmann and Mayer [317] have attempted to explain pressure effects on materials using the functional approach. This is based on a model which considers that pressure acts by increasing the electron donor properties of parts of the systems. In many ways pressure may be considered to play the role of an electron donor. In this way, some of the pressure effects on molecules may be explained.

H. MISCELLANEOUS

Several new pressure conversions of gases to a metallic state are possible in view of existing high-pressure instrumentation. For a discussion on metallic hydrogen, see refs. 318–323. For the possible conversion of xenon to a metallic state, see Ruoff and Nelson [324]. Many of the aforementioned physical tools used with the DAC, including electronic and vibrational spectroscopy, may play a role in the analyses and characterization of these possible new metallic phases.

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