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HIGH-PRESSURE VIBRATIONAL SPECTROSCOPY*

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I. Introduction

The first spectroscopic measurements of molecules under external pressures were made by Drickamer, whose experiments covered the regions of ultraviolet, visible, and near infrared (*1*, *2*). Drickamer studied the effect of pressure on the vibrational frequency in several compounds to 5.0 μ (2000 cm^{-1}). Extension to 35.0 μ (285 cm^{-1}) was made by Weir *et al.* (*3–5*). In 1966, the technique of making low-frequency measurements at high pressures

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of up to 200 μ (50 cm^{-1}) was developed by Ferraro *et al.* (*6*, *7*), using a grating spectrophotometer. With the use of an interferometer, Gebbie (*8*) reported low-frequency spectra to 1000 μ (10 cm^{-1}) and McDevitt *et al.* (*9*) reported spectra to 40 cm^{-1}. Several other high-pressure cells capable of being used in the infrared region have been reported (*11–16*). It would appear that adequate high-pressure techniques are available to conduct vibrational studies in all regions of the infrared. This is not to say that the ultimate in instrumentation has been reached, however. Many instrumental problems exist, and the experiments are tedious and time consuming.

Contemporary instrumentation, applications of the technique, and, in conclusion, recent high pressure-Raman techniques will be discussed in this chapter. Emphasis is placed on the most recent developments made in the field of high-pressure vibrational spectroscopy.

II. Available Instrumentation for Far Infrared–High-Pressure Studies

A. Optical High-Pressure Cells

It is advisable to describe briefly the available instruments capable of making low-frequency measurements under pressure. A summary of the more important optical high-pressure cells available with their advantages and disadvantages is given in Table I.

The shock-wave techniques can obtain pressures of up to 1000 kbar, the shock wave being generated by explosives. The technique would be extremely difficult to use with a scanning spectrophotometer, since the shock is only of short duration.

The piston-cylinder cell developed by Drickamer and Balchan (*10*) used sapphire windows of 0.5-in. diameter and 0.5-in. thickness in the 0.2–5.0 μ region. These windows proved fragile, and Drickamer (*17–19*) converted to sodium chloride windows thereafter. Sherman (*11*) used a similar cell to 400 cm^{-1}.

Perhaps the most useful cell is the opposed anvil cell using diamond anvils, developed recently by Weir *et al.* (*3–5*). They used type-II diamonds which are transparent in the region of the ultraviolet, visible, and infrared, except for a region of 4–6 μ, where major absorption occurs. Pressures up to 200 kbar have been claimed with this cell (*20*).

B. Link of Optical Cell with Infrared Spectrophotometer

Table II lists the apparatus in current use for low-frequency–high-pressure studies. The instrumentation using a grating spectrophotometer was developed by Ferraro *et al.* (*6*, *7*). This technique is capable of reaching the