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HIGH PRESSURE RESEARCH IN THE FAR INFRARED REGION*+

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ABSTRACT

The capability of obtaining vibrational spectra in the low frequency region below 300 cm^{-1} under non-ambient pressures to 80 kbars, is a comparatively new technique. The instrumentation necessary to do this will be reviewed. Studies made with ionic solids and coordination compounds will be discussed. Problems and limitations in the method will be presented.

INTRODUCTION

The first spectroscopic measurements at non-ambient pressures were made by Drickamer. His experiments covered the regions of ultraviolet, visible and near infrared.[1-2] It is the infrared region that is of concern to us in this paper. In 1956, Drickamer studied the effect of pressure on the vibrational frequency of bonds containing hydrogen to 5.0 microns (2000 cm^{-1}). Extension to 35.0 microns (285 cm^{-1}) was made by Weir, Van Valkenburg, and Lippincott.[3-5] In 1966, the capabilities of making low frequency measurements at high pressures up to 200 microns (50 cm^{-1}) were developed by Ferraro, Postmus and Mitra[6-7] using a grating spectrophotometer. Using an interferometer, Gebbie[8] has reported low

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frequency spectra to 1000 microns (10 cm^{-1}), and McDevitt et al.[9] to 40 cm^{-1}. It thus appears that adequate techniques are now available to conduct far infrared studies at high pressure. This is not to say that the ultimate in instrumentation has been reached, however. Many instrumental problems exist and experiments are tedious and time-consuming.

This paper will discuss the present instrumentation and applications of the technique, and in conclusion, will discuss recent high pressure-Raman techniques.

AVAILABLE INSTRUMENTATION FOR FAR INFRARED-HIGH PRESSURE STUDIES

Optical High Pressure Cells

It would be advisable to briefly describe the available instrumentation capable of making low frequency measurements under pressure. A summary of the optical high pressure cells available with their advantages and disadvantages is shown in Table I.

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

The piston-cylinder developed by Drickamer and Balchan[10] for use from 0.2 to 5.0 microns used sapphire windows of 1/2 inch diameter and 1/2 inch thickness. These windows proved fragile and Drickamer[11-13] converted to sodium chloride windows thereafter.

Perhaps the most useful cell is the opposed anvil cell developed in recent years by Weir, Van Valkenburg, and Lippincott,[3-5] using diamond anvils. They used type II diamonds which are transparent in the regions of the ultraviolet, visible, and infrared, except for a portion at 4-6 microns where absorption occurs. Pressures up to 200 kbars have been claimed with this cell.[14]

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 were developed by Ferraro, Mitra, and Postmus.[6-7] The technique is capable of reaching 200 μ, and involves the use of a Perkin-Elmer Model No. 301 double-beam grating spectrophotometer, used in double beam operation, a 6x beam condenser and the high