

VIBRATIONAL STUDIES OF SOLID INORGANIC AND COORDINATION COMPLEXES AT HIGH PRESSURES *

JOHN R. FERRARO

Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439 (U.S.A.)

(Received 1 December 1978)

CONTENTS

| | |
|---|----|
| A. Introduction | 1 |
| (i) Units of pressure | 2 |
| B. Instrumentation for optical measurements at high pressures | 3 |
| (i) Optical high pressure cells | 3 |
| (ii) Optical link of pressure cell with spectrophotometer or interferometer | 10 |
| (iii) Instrumentation for Raman spectroscopy at high pressure | 12 |
| (iv) Optical windows for use at high pressures | 16 |
| C. Pressure calibration | 17 |
| D. Choice of optical regions to use as a probe | 19 |
| E. Vibrational studies at high pressures | 19 |
| (i) Inorganic compounds | 20 |
| (ii) Ionic and pseudo ionic crystals with lattice vibrations | 28 |
| (iii) Coordination compounds | 37 |
| (iv) High-pressure studies of several solids in different symmetries | 44 |
| F. Geological applications | 52 |
| G. Summary | 54 |
| (i) Structural transformations | 54 |
| (ii) Effects on vibrational transitions | 55 |
| (iii) Functional approach to explain pressure effects | 57 |
| H. Miscellaneous | 58 |
| Acknowledgements | 58 |
| References | 58 |

A. INTRODUCTION

The earliest high-pressure studies were made by Amagat [1], but the important and fundamental studies on high pressure were conducted by Bridgman [2-16] who has been called the father of high-pressure chemistry. Bridgman

* Work performed under the auspices of the Division of Basic Energy Sciences of the U.S. Department of Energy. Based on a series of lectures presented at the Universities of Florence and Rome, Italy, May 1978, as Visiting Professor of the Italian Consiglio Nazionale della Ricerche and as NATO recipient of a 1978 Senior Scientist Fellowship Award.

was able to attain pressures to 10^5 atm. His work still finds extensive use today, and his compressibility data as a function of pressure for common liquids was a classical achievement.

There are several books and reviews [3,17–26] on high pressure, some of which cover the history of high pressure comprehensively. It is not intended in this review article to dwell on the history of high pressure to any large degree for fear of being redundant with already published material.

The general effects of pressure on matter have been discussed by Sinn [26].

It is the aim of this review to discuss the effects of pressure to 150 kbar on the vibrational transitions occurring in solid materials such as inorganic compounds and coordination complexes. The magnitudes of these effects are measured by IR and Raman scattering methods. The review restricts itself chiefly with the versatile diamond anvil cell. Electronic transitions have been discussed by Drickamer and Frank [27].

(i) Units of pressure

A brief discussion on the units of pressure is necessary at this point. The international standard (SI) unit of pressure is the Pascal or Newton per square meter. The interrelationships between various units in use today and the SI units are given as follows

$$1 \text{ bar} = 10^5 \text{ N m}^{-2} \text{ (or Pascal)} = 10^6 \text{ dyne cm}^{-2} = 0.9869 \text{ atm} = 1.0197 \text{ kg cm}^{-2}$$

$$1 \text{ atm} = 1.01325 \times 10^6 \text{ dyne cm}^{-2}$$

We will use kbar in this discussion, which corresponds to 10^3 bar, and at extremely high pressures, Mbar, where $1 \text{ Mbar} = 10^3 \text{ kbar}$.

To provide the newcomer with an idea of the magnitude of some of these pressure values, Table 1 has been compiled.

TABLE 1
Naturally occurring pressures [26]

| Pressure (kbar) | Site of occurrence |
|-----------------------|---|
| 1 | Deepest part of ocean — Marianas trench |
| 10 | Crust—mantle interface — Mohorovicic discontinuity |
| 1.37×10^3 | Mantle—core interface — Wichert-Gutenberg discontinuity |
| 3.64×10^3 | Center of earth |
| 1×10^8 | Center of sun |
| 10^{10} — 10^{14} | White dwarf star |
| 10^{17} — 10^{21} | Neutron stars |