High Pressure Molecular Science

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High Pressure Molecular Science

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PREFACE

This monograph contains the proceedings of the NATO-ASI on "High Pressure Molecular Science", held in Il Ciocco, Barga, from September 27 until October 11, 1998, and illustrates new developments in the field of high pressure science. In fact, for chemists, biochemists, physicists and materials scientists, pressure as an experimental variable represents a tool which provides unique information about the microscopic properties of the materials studied. In addition to its use as a research tool for investigating the energetics, structure, dynamics, and the kinetics of transformations of materials at a molecular level, the application of pressure is also being used to modify the properties of materials to preserve or improve their qualities. It is interesting to note how the growth of the high pressure field is reflected in the content of the ASI's dealing with this field. The ASI "High Pressure Chemistry" held in 1977 was followed by the ASI "High Pressure Chemistry and Biochemistry" held in 1986, by the ASI on "High Pressure Chemistry, Biochemistry, and Materials Science" held in 1992, and the coverage of the present ASI also includes new developments and applications to all high pressure fields, in particular to bioscience and biotechnology. In fact, the potential of high pressure techniques in biotechnology has only recently been fully recognized. On the experimental side we have seen advances in static and dynamic high pressure probes. Surely one of the most dramatic changes that has taken place in the last years has been, associated with the development of fast and capable computers, the immense rise of ab-initio molecular dynamics calculations, a means of peering into the ionic and electronic structure of condensed matter.

In view of the teaching character of the ASI, it is natural that the main contribution to this volume presents overviews of the different subfields of high pressure research. The lectures cover the main areas of high pressure applications to materials science, condensed matter physics, chemistry, and biochemistry. In addition, a few contributed papers offer more specialized aspects of various high pressure studies. The contributions to this volume make clear the impressive range of fundamental and applied problems that can be studied by high pressure techniques, and also point towards a major growth of high pressure science and technology in the near future. This ASI focused mainly on advances achieved in the six years since the previous ASI devoted to the high pressure field. We hope that these proceedings will help to establish promising directions for future research on effects of pressure on complex systems.

The editors gratefully acknowledge input of the organizing committee and express their thanks to all lecturers and contributors to this volume for their efforts in preparing their lectures and manuscripts, and to all the participants of the ASI whose enthusiasm convinced us of the importance and excitement of this interdisciplinary area. On behalf of all ASI participants, we express our gratitude for the generous financial support provided by the Scientific Affairs Division of the North Treaty Organization.

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March, 1999

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Chemical, Biophysical, Biochemical, and Biomedical Aspects

HIGH-PRESSURE RAMAN SCATTERING STUDIES OF FLUIDS

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1. Abstract

The field of laser Raman spectroscopy of liquids and gases is reviewed. After introducing the importance of using pressure as an experimental variable in Raman studies of fluids, a brief overview of the experimental techniques is presented. Illustrative examples of specific high-pressure Raman studies deal with the following topics: reorientational motions in liquids, vibrational dephasing, collision-induced scattering, Fermi resonance and Raman frequency noncoincidence effect.

2. Introduction

Laser Raman and Rayleigh scattering experiments on liquids and gases at high pressure continue to provide important and unique information about dynamic processes and intermolecular interactions in liquids.   In high-pressure Raman scattering studies of fluids carried out in our laboratory, the following phenomena were of main interest:

- Reorientational motions
- Vibrational dephasing
- Collision-induced scattering
- Fermi resonance
- Raman frequency noncoincidence effect

The great advantage of Raman experiments lies in the fact that the analysis of Raman lineshapes provides information about the detailed nature of the correlation function - one obtains the time dependence of the correlation function itself and not only an integral.   It is only natural that the Raman experiment also has some limitations, namely, only Raman lineshapes of relatively simple molecules can be analyzed to yield unambiguous results. The general theory of light scattering [1] is

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well established and at this point a few pertinent comments about the Raman experiments are appropriate.

From the experimental polarized and depolarized Raman bandshapes one can obtain the isotropic scattering intensity $I_{iso}(\omega)$ and the anisotropic scattering intensity $I_{aniso}(\omega)$. Only vibrational (nonorientational) processes contribute to $I_{iso}(\omega)$, whereas both reorientational and vibrational processes contribute to $I_{aniso}(\omega)$. This provides the means of separating reorientational processes from vibrational processes and of calculating reorientational and vibrational correlation functions. Assuming vibrational relaxation to be the major nonreorientational broadening mechanism, one can show that

$$I_{iso}(\omega) = \left[I_{VV}(\omega) - 4/3 \ I_{VH}(\omega) \right] / \int \left[I_{VV}(\omega) - 4/3 \ I_{VH}(\omega) \right] d\omega \tag{1}$$

and

$$C_v(t) = \langle Q^\upsilon(0) Q^\upsilon(t) \rangle = \int I_{iso}(\omega) \ \exp(-i\omega t) \, d\omega \tag{2}$$

where $C_v(t)$ is the vibrational correlation function. Similarly, one may write

$$I_{aniso}(\omega) = I_{VH}(\omega) / \int I_{VH}(\omega) \, d\omega, \tag{3}$$

and

$$C_R(t) = \langle Tr \ \beta^\upsilon(0) \beta^\upsilon(t) \rangle = \frac{\int I_{aniso}(\omega) \ exp(-i\omega t) \, d\omega}{\int I_{iso}(\omega) \ exp(-i\omega t) \, d\omega} \tag{4}$$

where $C_R(t)$ is the reorientational correlation function.

During the past two decades, reorientational motions of molecular liquids and gases have been extensively studied by Raman lineshape analysis. High-pressure laser Raman scattering experiments provided conclusive evidence for the need to separate the effects of density and temperature on reorientational processes in liquids. In order to illustrate the large difference between isobaric and isochoric experiments, Figure 1 shows the rotational correlation functions for liquid methyl iodide (CH_3I), a symmetric top molecule. The correlation function describes the reorientation of the CH_3I about axes perpendicular to the main symmetry axis.
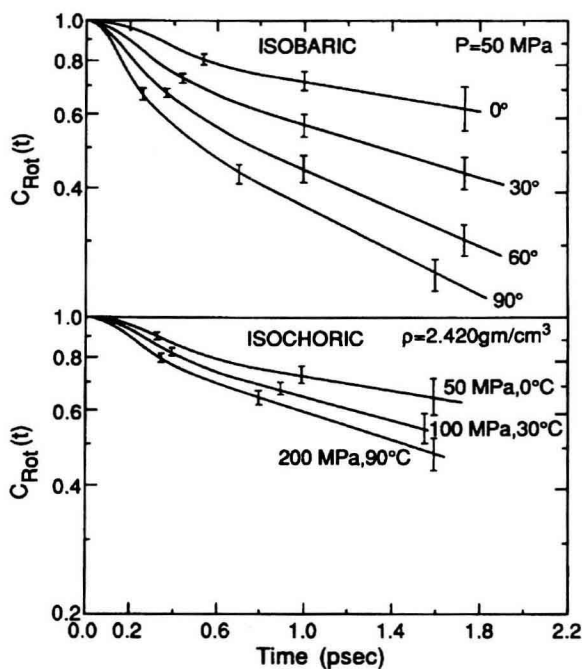
Figure 1. Temperature dependence of the rotational correlation function for liquid methyl iodide (CH_3I) under isobaric and isochoric conditions. (Taken from [2])

As an illustrative example of pronounced density effects on vibrational lineshapes, one can use Figure 2, taken from a study [3] of vibrational relaxation of N_2O which shows the density effects on the normalized intensities of isotropic linewidths of the v_1 band of N_2O.
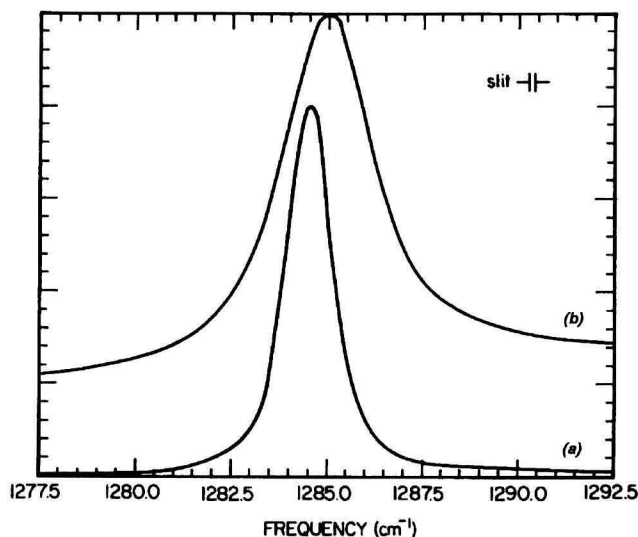
Figure 2. The effect of density on normalized intensities of the isotropic v_1 band (1285 cm^{-1}) of N_2O at 50°C; (*a*) $\rho = 0.53$ g cm^{-3}, (*b*) $\rho = 1.05$ g cm^{-3}. The slit width is also shown.

The overwhelming majority of Raman studies of the dynamic processes in liquids dealt with the investigation of properties of individual molecules by studying the reorientational and vibrational relaxations which reflect only indirectly the influence of intermolecular interactions. Therefore, the problem of collision-induced scattering (CIS) has attracted both theoretical and experimental interest [4, 5]. It has been observed that collisions in dense liquids or gases produce depolarized Rayleigh spectra in fluids composed of atoms or molecules of spherical symmetry. Collision-induced Raman spectra, forbidden by selection rules (symmetry), have been investigated in polyatomic molecular liquids, as well as collision-induced contributions to the allowed Raman bands. The origin of these collision-induced spectra lies in the polarizability changes produced by intermolecular interactions. It is clear that studies of CIS can provide direct information about intermolecular interactions. However, the CIS represents a very difficult theoretical problem because the scattered intensity depends on the polarizability change in a cluster of interacting molecules, and the time dependence of this change is a function of the intermolecular potential.

Studies of intermolecular interactions and Fermi resonance [6] may serve as yet another example of the important role of high-pressure experiments. The Fermi resonance between the v_1 and the first overtone of v_4 have been studied in liquid ND_3 as a function of density and temperature [6]. Figure 3 shows the changes in relative intensities of these Fermi resonance-coupled bands for the extreme density range of our measurements. Since Fermi resonance parameters are sensitive to

intermolecular potential, we can change them by varying temperature and pressure. The transition dipole moments of the $v_1 + 2v_4$ bands are found to vary and the Fermi resonance treatment enables us to estimate the changes in their relative magnitude. The high-pressure experiments provided the spectroscopic information needed for the theoretical analysis of intermolecular interactions in ND_3.
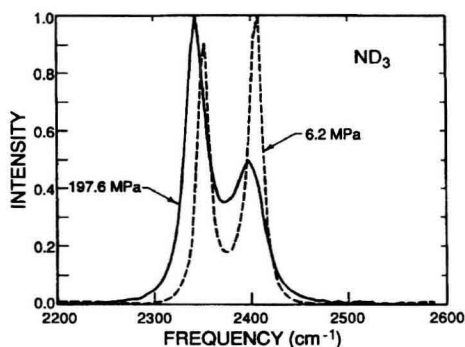

Figure 3. Density effects on the relative intensity of the isotropic $v_1 + 2v_4$ Fermi resonance lines in ND_3. The full line denotes density = 0.730 g cm^{-3} (T=0°C; P = 197 MPa), and the dashed line denotes density = 0.457 g cm^{-3} (T = 100°C; P = 6 MPa).

In the study of symmetric modes in polar liquids by Raman spectroscopy, considerable attention has recently been paid to the noncoincidence effect [5] because Raman measurements of the noncoincidence effect for polar liquid molecules can provide valuable information about the coupling mechanisms of short- and long-range orientational order which arise from the inter- and intramolecular interactions in dense fluid phases. The noncoincidence effect denotes the phenomenon that the peak wavenumbers of the isotropic and anisotropic components of a Raman band do not coincide. The noncoincidence value, δv, is defined as

$$\delta v = v_{aniso} - v_{iso} \tag{5}$$

where v_{aniso} and v_{iso} are the respective anisotropic and isotropic peak wavenumbers. Differences in peak wavenumber start from 0 cm^{-1} in the gaseous phase and increase gradually as the density increases. In the liquid state, normally the wavenumber difference is slight, but for some polar molecules the difference may be as large as 30 cm^{-1} [3]. The origin of the noncoincidence in liquid polar molecules is mainly due to the orientationally dependent intermolecular forces. The intermolecular forces modulate the vibration of a symmetrical mode, changing the oscillator force

constant of this mode. The isotropic component is a measure of the spherically symmetric average of the potential while the anisotropic component reflects the angularly dependent portion of the potential. The noncoincidence effect is primarily associated with symmetric vibrational modes of polar molecules and is very pronounced for the modes which are both Raman active and strongly infrared active.

3. Experimental

The schematic diagram of the experimental setup of the Raman light scattering measurement is shown in Figure 4. All measurements were done with 90° scattering geometry.
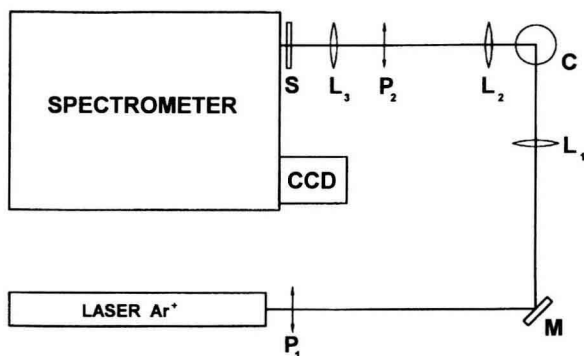

Figure 4. Schematic diagram of the Raman light scattering experimental setup, where P1 is a polarizer, M is a reflection mirror, L1 is a focus lens, C is a Raman sample cell, L2 is a collection lens, P2 is a polarization analyzer, L3 is a focus lens, and S is a polarization scrambler.

The incident radiation is the 4880 Å line from a Spectra-Physica Ar-ion laser. P1 is a polarizer; M is a mirror; L1 is a focus lens used to collect scattered light at 90 degrees. The collection cone angle was kept small ($< 5°$) in order to minimize the errors in the measurements of anisotropic spectra. P2 is a rotatable Glan-Thompson prism used as a polarization analyzer. The VV and VH spectra were obtained with this polarization analyzer set to parallel and perpendicular to the polarization of the incident beam, respectively. L3 (300mm f.l.) is a focus lens used to focus the collected light into the slit of the spectrometer. S is a crystalline-amorphous quartz compensated wedge scrambler which is placed immediately prior to the entrance of the spectrometer and is used to scramble the polarization of the light to ensure

equivalent transmission of different polarized light through the spectrometer. (The need of this scrambler is due to the non-equivalent reflection efficiency of the grating mirrors for different polarized light.) The scattered light was analyzed by a spectrometer (a Spex1403 0.85m double monochromator) and then recorded by a liquid nitrogen-cooled CCD detector (the CCD chip contains 1024x1024 pixels with pixel size: 27μmx27μm) operated at −110°C (manufactured by Princeton Instrument, Inc.). The whole experimental setup was installed on a vibration isolated optic table (manufactured by Newport Corporation).

One important experimental aspect of high-pressure Raman experiments is related to possible problems with stress-induced birefringence by optical windows in the high-pressure Raman optical cell. To introduce the discussion of the stress-induced birefringence, Figure 5 gives a schematic drawing of a high-volume optical cell which can be used for laser scattering experiments on fluids at high pressure.
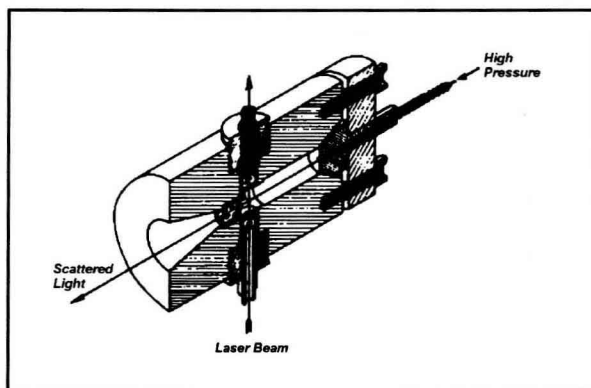

Figure 5. Schematic drawing of high volume optical cell for light scattering experiments at high pressure.

As indicated in the introduction, Raman bandshapes contain information on the orientational and vibrational dynamics of the molecular system. The theoretical basis by which this information may be extracted from the experimental spectra depends on the use of linearly polarized incident radiation and the ability to measure accurately the scattered light in two polarization directions. Lasers, of course, are an excellent source of intense, linearly polarized radiation. However, if the optical cell window material is birefringent, the linearly polarized light will become elliptically polarized, and the results of a bandshape analysis will become questionable. Fortunately, since the most frequently used cell materials such as fused silica and glass are not birefringent, this is usually not a problem for measurements at atmospheric pressure. However, the stress applied to the cell windows in a high-pressure experiment can lead to strain-induced anisotropies which result in a

pressure-dependent scrambling of the polarization. Even though the scrambling is small, it can have a large effect on the I_{VH} band, especially for cases when the depolarization ratio is small. The effect has been known for several years and was studied earlier in our laboratory by Cantor, et al. [7].

Since neglect of the effects of polarization scrambling by optical windows during a high-pressure experiment can lead to erroneous results, the following example [8] stresses the importance of a careful analysis of each specific high-pressure light scattering experiment where polarization measurements are important. In principle, any compound exhibiting a totally polarized band with the depolarization ratio equal to zero can be used as a test liquid to measure the polarization scrambling of the windows. We found particularly useful spherical molecules of T_d symmetry for which the totally symmetrical modes have no anisotropic spectrum and therefore $\rho = 0$. There are many possible choices for the test liquid, but we used tetramethyltin (TMT) as an illustrative example. The spectrum of TMT contains the totally polarized ν_3 (Sn – C symmetrical stretch, A_1) band at 509 cm^{-1}, as well as the depolarized ν_{18} (Sn – C asymmetrical stretch, F_2) band at 530 cm^{-1} which are both very intense and easy to measure.

Since TMT is a spherical molecule of the T_d point group, symmetry demands that the depolarization ratio equal zero for A_1 vibrations such as ν_3. Therefore, any intensity in the ν_3 VH spectrum is due to polarization scrambling. The effects of pressure on the VH spectrum of tetramethyltin is shown in Figure 6. The ν_3 peak can be seen to grow from a small shoulder on the low frequency side of the ν_{18} at 50 MPa to a peak nearly as intense as ν_{18} at 400 MPa.
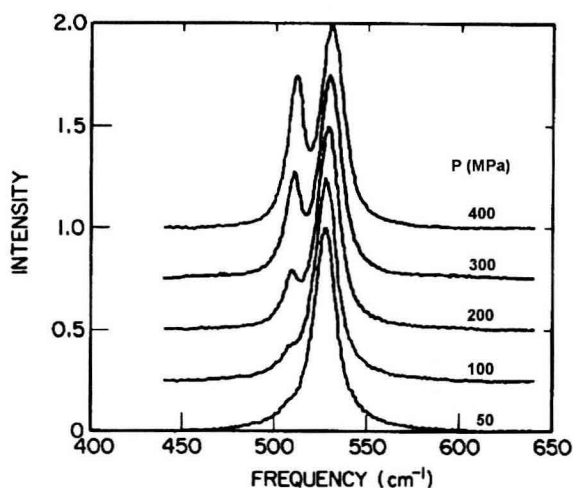

Figure 6. Depolarized spectra of tetramethyltin at different pressures showing the growth of the ν_3 intensity (509 cm^{-1}) produced by polarization scrambling of the float glass window in the high-pressure cell. The strong band at 530 cm^{-1} is the depolarized ν_{18} stretching mode. All measurements were carried out at 90°C.