A technique for obtaining the Raman spectra of liquids and solutions under high pressure

A. R. DAVIS and W. A. ADAMS
Water Science Subdivision, Inland Waters Branch, Department of
the Environment, Ottawa, Ontario, Canada

Abstract—This note describes the design and use of a cell to obtain the Raman spectra of solutions and liquids under high pressure.

THERE IS now a considerable body of literature devoted to the thermodynamic and electrochemical properties of pure liquids and solutions under conditions of high pressure [1–3]. Nevertheless, few attempts have been made to use vibrational spectroscopy to obtain a more detailed understanding of the molecular processes involved. Infrared spectroscopy has been used to study the effects of pressure on solids [4] and liquids [5–7] and, although some attempts have been made to utilise Raman spectroscopy [8–12], the results have usually been qualitative in nature [13–15]. Perhaps the most serious technical difficulty in the use of i.r. spectroscopy at high pressures is the choice of window material.

Sapphire and quartz, which have high mechanical strength, are limited in their transparency in the i.r. region of the spectrum. Diamond is probably the only material that has a suitable combination of mechanical strength and good i.r. transmitting properties. In recording the i.r. spectra of liquids under pressure, it is also necessary to ensure that the pathlength of the cell does not change with pressure [16].

The use of Raman spectroscopy to obtain vibrational spectra under pressure has distinct advantages over i.r. spectroscopy. First, since exciting and Raman scattered radiation both occur in the visible region of the spectrum, sapphire or quartz windows

[1] W. A. ADAMS and K. J. LAIDLER, *Can. J. Chem.* **45,** 123 (1967).
[2] G. J. HILLS, *Chemical Physics of Ionic Solutions* (Edited by B. E. CONWAY and R. G. BARRADAS), Chap. 23. John Wiley, New York (1966).
[3] E. WHALLEY, *Ann. Rev. Phys. Chem.* **18,** 205 (1967).
[4] R. BAYER and J. R. FERRARO, *Inorg. Chem.* **8,** 1654 (1969) and references therein.
[5] R. R. WIEDERKEHR, Ph. D. Thesis. University of Illinois (1957).
[6] E. U. FRANCK, *Ber. Bunsenges. Physik. Chem.* **73,** 135 (1969).
[7] R. J. JAKOBSEN, Y. MIKAWA and J. W. BRASCH, *Appl. Spectry* **24,** 333 (1970).
[8] G. E. WALRAFEN, *Hydrogen Bonded Solvent Systems* (Edited by A. K. COVINGTON and P. JONES), p. 20. Taylor & Francis, London (1968).
[9] S. S. MITRA, O. BRAFMAN, W. B. DANIELS and R. K. CRAWFORD, *Phys. Rev.* **186,** 942 (1969).
[10] O. BRAFMAN, S. S. MITRA, R. K. CRAWFORD, W. B. DANIELS, C. POSTMUS and J. R. FERRARO, *Solid State Commun.* **7,** 449 (1969).
[11] M. NICOL, *J. Opt. Soc. Am.* **55,** 1176 (1965).
[12] J. F. ASELL and M. NICOL, *J. Chem. Phys.* **49,** 5395 (1968).
[13] R. AUMONT, E. DAYAN, B. VODAR, H. VU, G. WIDENLOCHER, *Compt. Rend.* **268,** 1565 (1969).
[14] A. J. MELVEGER, J. W. BRASCH and E. R. LIPPINCOTT, *Appl. Opt.* **9,** 11 (1970).
[15] R. CAVAGNAT, J. J. MARTIN and G. TURRELL, *Appl. Spectry* **23,** 172 (1969).
[16] W. RIGBY, R. WHYMAN and K. WILDING, *J. Phys. E. Sci. Instrum.* **3,** 572 (1970).

may be used. Second, the difficulties posed by pathlength changes due to pressure are no longer a serious problem with Raman spectroscopy, relative to those associated with i.r. spectroscopy.

The following Raman technique was designed to make use of the above facts with a laser as an excitation source, and to incorporate more precise pressure and temperature measurement than previously employed.

EXPERIMENTAL

The experimental arrangement is shown in Fig. 1. The basic cell is an American Instrument Company stainless steel, two-window, 3·0 kbar optical absorption cell (3·5 in. o.d. × 1 in. i.d. × 5 in. long). A two-window configuration, with the
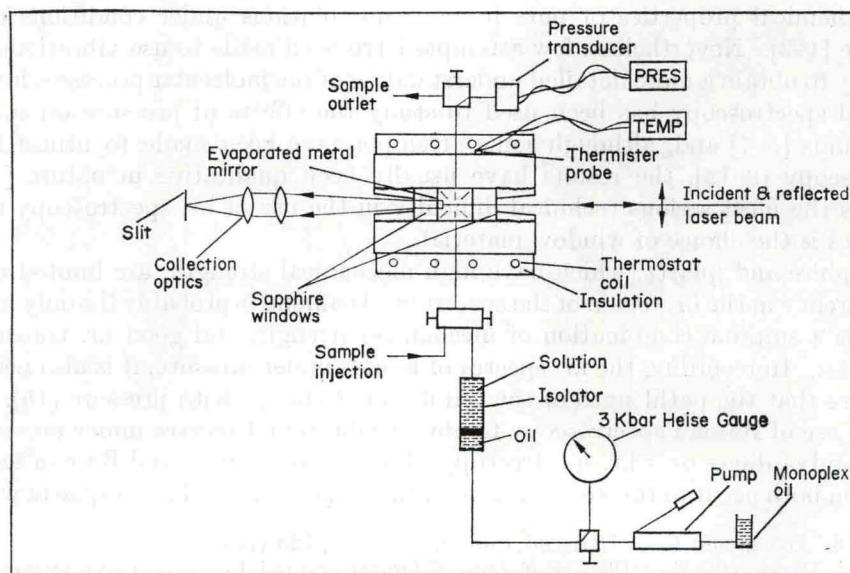
Fig. 1. Schematic diagram of high pressure Raman cell and ancillary measuring equipment.

windows on the same optical axis, is economical to construct and easier to use than one involving three or more windows. This window configuration results in the Raman scattered light being observed at 0° or 180° to the exciting radiation. The technique reported here involves collection of Raman scattered light at 180° to the initial exciting radiation direction. Initially, the laser beam was allowed to pass through the sample and into the spectrometer. This arrangement resulted in the presence of very intense plasma lines obscuring the Raman spectrum. This difficulty was overcome by the use of a small metal mirror evaporated onto the surface of the sapphire window closest to the collection optics. The mirror reflects the laser beam back out of the cell. This procedure not only prevents the direct entry of the exciting beam into the spectrometer, but also increases the Raman intensity, since the laser beam makes two passes through the sample.

The mirror was made by evaporating a 2 mm disc of Inconel onto the window surface next to the sample. The Inconel surface was protected with a half-wave coating of evaporated SiO_2. This arrangement worked very well for organic liquids but electrolyte solutions rapidly dissolved the mirror surface. For studies of these solutions, the mirror was evaporated onto the outside surface of the window. With this arrangement, it is a little more difficult to align the laser beam on the mirror than in the case where the mirror is on the inside.

The windows were further modified by blooming their inside surfaces with a quarter-wave coating of MgF_2 to eliminate reflection of unwanted Rayleigh scattered light into the monochromator.

The temperature of the cell was controlled to $\pm 0.2°C$ by circulating water through the copper coil surrounding the cell. The surface temperature of the cell was measured with a thermistor-meter combination manufactured by Yellow Springs Instruments. After assembly and filling, the cell was completely wrapped, except for the window ports, with strips of $\frac{1}{8}$ in. thick plastic foam to ensure good thermal insulation.

Pressurization of liquid samples was by means of a 3·0 kbar Enerpac hand pump using monoplex hydraulic oil. The pressure in the pump circuit was measured using a 3 kbar bourdon tube gauge manufactured by the Heise Bourdon Tube Company. A gauge isolator was used to avoid contamination of the samples by the hydraulic oil. Isolation is achieved by means of a freely moving piston with oil on one side and sample solution on the other side. Initially it was assumed that the pressure in the pump circuit was the same as that in the bulk of the solution under study. A better procedure is to measure the actual pressure of the solution being studied. This is important because of friction effects between the gauge isolator wall and its piston, and also indicates if the piston has reached the end of the cylinder. In these cases, the pressure indicated by the bourdon gauge would not be that inside the cell. This problem was overcome by using a 3·0 kbar diaphragm strain-gauge pressure transducer, supplied by the Viatran Corporation, in direct contact with the solution under study. The transducer was powered by a stable 20 V source, type LR602FM, supplied by Lambda Electronics Corporation. The change in voltage with pressure was measured with a Hewlett-Packard 3450 A digital voltmeter and the sensitivity was greater than 0·1 bar.

The cell and its holder were mounted in the sample compartment of a Jarrel–Ash 25–300 Raman spectrometer. The necessary transfer and collection optics were those supplied with the instrument for use with 180° excitation. The excitation source was a Coherent Radiation Limited Model 54 Argon ion laser producing 250 mW at 488 nm. The bourdon gauge and pump were mounted external to the spectrometer and connected to the isolator and high pressure cell with 0·125 i.d. high pressure tubing.

RESULTS

The quality of spectra obtained is illustrated by the Raman spectra of CCl_4 shown in Fig. 2. The starred peak is a line originating in the argon discharge. In general, the spectra obtained in this high-pressure cell are of as good a quality as those obtained by conventional Raman sampling arrangements.

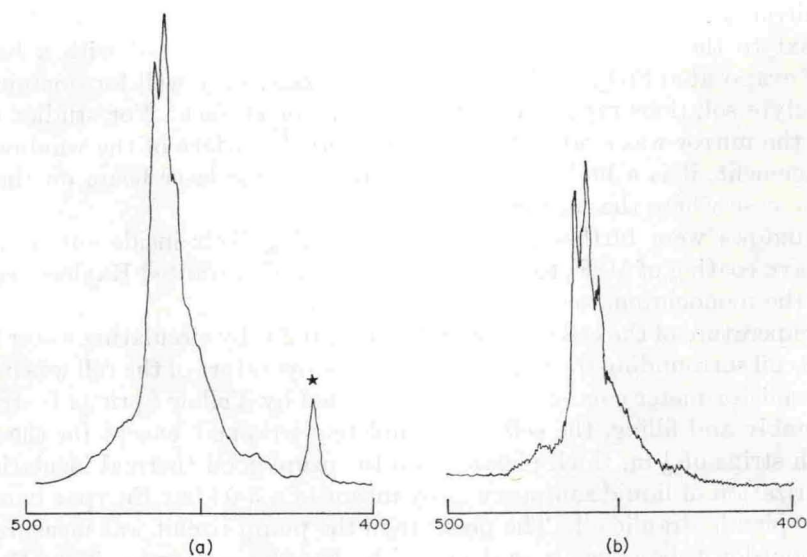A study of the effect of pressure on the Raman spectrum of aqueous thorium

8

Fig. 2. The Raman spectrum of CCl_4 from 400–500 cm^{-1}. Laser wavelength, 488 nm. Laser power, 200 mW. Slit width, 1 cm^{-1}. Full scale intensity corresponds to 2×10^3 counts. Scan speed, 20 cm^{-1}min^{-1}.
(a). Spectrum of CCl_4 contained in the high pressure cell at 0·262 kbar and 24·8°C.
(b). Spectrum of CCl_4 contained in a glass cuvette using 90° collection optics at ambient pressure and 25·0°C.
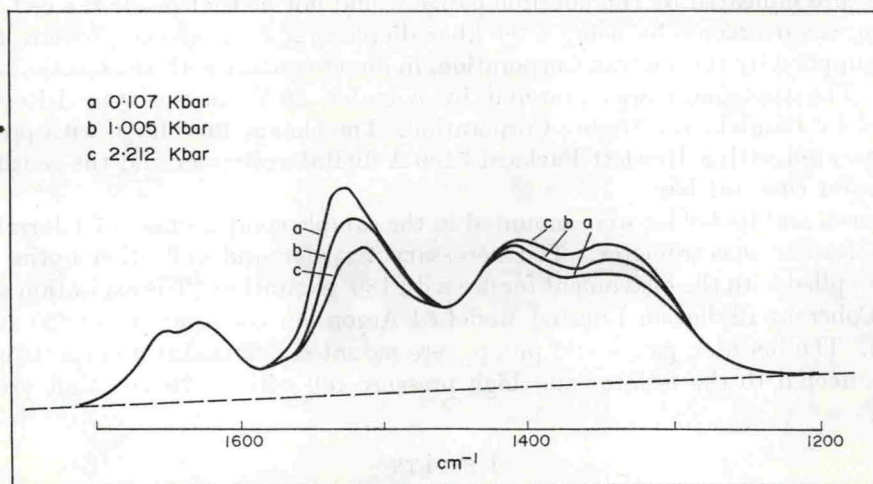
Fig. 3. The Raman spectrum of a 1·05 M aqueous thorium nitrate solution, 1200–1700 cm^{-1}, at various pressures. Laser power 120 mW. Laser wavelength, 488 nm. Slit width, 11 cm^{-1}. Full scale intensity corresponds to 5×10^4 counts/sec. Scan speed, 20 cm^{-1}min^{-1}. Temperature, 25·2°C.

nitrate illustrates how this technique may be used to study the pressure dependence of complex equilibria. Consider the complex equilibrium involving the formation of MX from ions M^+ and X^-. Electrostriction effects will in general lead one to conclude that the sum of the partial molar volumes of the ions will be less than the partial molar volume of the complex species [17]. Therefore, an increase in pressure will favour the dissociation of the complex MX. Conductivity studies tabulated by HORNE support this conclusion, e.g. the ratio of the dissociation constant at 1 kbar relative to the 0·001 kbar value for $FeCl^{2+}$ is 10, and for $MgSO_4$ is 1.5 [18]. The variation of spectral intensity of part of the Raman spectrum of thorium nitrate is shown in Fig. 3. The region between 1200 and 1600 cm^{-1} may be assigned to fundamental modes of vibration of solvated and complexed nitrate ions [19, 20]. The contour between 1200 and 1450 cm^{-1}, which may be ascribed to solvated nitrate ion, increases in intensity with increase in pressure. This effect may be contrasted with the decrease in intensity of the band at 1527 cm^{-1}, ascribed to complexed nitrate ion, with increase in pressure. These observations are interpreted in terms of the dissociation of complex nitrato-thorium species with increase of pressure. Consistent intensity variations are obtained for both rising and falling pressure.

[17] R. A. HORNE, *Marine Chemistry*, p. 166. Wiley-Interscience, New York (1969).
[18] R. A. HORNE, *Advances in High Pressure Research* (Edited by R. S. BRADLEY), Vol. 2, p. 204. Academic Press, London (1969).
[19] D. E. IRISH and A. R. DAVIS, *Can. J. Chem.* **46,** 943 (1968).
[20] A. R. DAVIS and R. A. PLANE, *Inorg. Chem.* **7,** 2565 (1968).