

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.  $\times$  1 in. i.d.  $\times$  5 in. long). A two-window configuration, with the

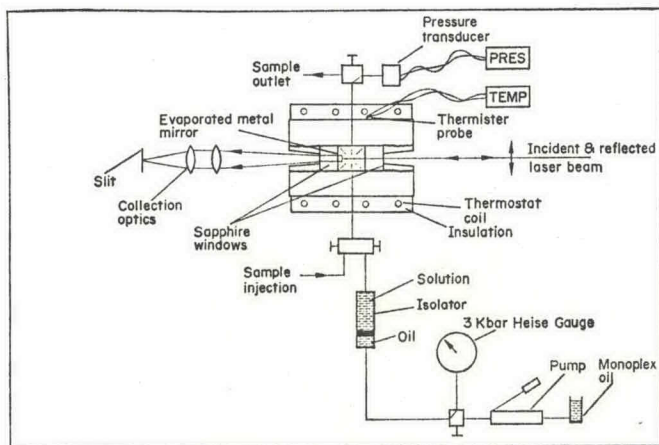


Fig. 1. Schematic diagram of high pressure Raman cell and ancillary measuring equipment.

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  $0^\circ$  or  $180^\circ$  to the exciting radiation. The technique reported here involves collection of Raman scattered light at  $180^\circ$  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  $\text{SiO}_2$ . 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  $\text{MgF}_2$  to eliminate reflection of unwanted Rayleigh scattered light into the monochromator.

The temperature of the cell was controlled to  $\pm 0.2^\circ\text{C}$  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  $\frac{1}{2}$  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  $180^\circ$  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  $\text{CCl}_4$  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