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A cryostatic cell for polarised Raman studies

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Abstract. A low-temperature cell for polarised Raman spectroscopy is described which facilitates the growing of single crystals from the liquid, and the determination of the orientation of the samples with the aid of x-ray diffraction.

1. Introduction

There exist quite a number of substances whose crystalline properties are of interest, but have melting points which lie below room temperature. This fact is generally the source of some experimental problems; in the case of Raman spectroscopy studies, these difficulties are really important. In order to assign an observed band to its proper factor group symmetry species (which is the relevant information one seeks) it is necessary to know its polarisation properties, and these are defined in relation to the principal crystal axes. Therefore one needs to grow a single crystal and know its orientation before performing the polarised Raman experiment. This procedure is performed routinely with substances which are solid at room temperature; it is clear, however, that for liquids the necessity of growing, orienting and recording the spectra of the crystals avoiding manipulation at low temperatures carries considerable complications.

Though many types of cryostats for x-ray diffraction (Odou and More 1975, Maeta *et al* 1976) or Raman scattering experiments (Krauze *et al* 1977, Cavagnat *et al* 1978, Huong and Cornut 1979) have been reported in the literature, none of them seems adequate for both purposes. We have constructed a goniometric low-temperature x-ray/Raman spectroscopy cell which has just been used successfully to obtain the spectra of a single crystal of bromine (Halac and Bonadeo 1982).

2. Description of the cell

Figure 1 shows a schematic drawing of the cell. It consists of two coaxial tubes; the innermost one (2), made of stainless steel, contains the cooling fluid (liquid N_2) and its bottom end is in thermal contact with a specially constructed copper goniometer head (3). There is a vacuum between this tube and the outer one, which forms the body of the cell (1) and is entirely made of bronze. It ends in a cubic structure where only the four edge bars, of about 4 mm diameter, interrupt the incident and diffracted x-rays and visible light in a 360° turn around the cell axis. The corresponding windows are made of 1 mm thick acrylic sheets, glued to the bronze structure with Loctite, which transmit x-rays and visible light. Sufficiently thin glass windows broke under pressure; Mylar, on the other hand, develops tensions that depolarise the light.

There is a circular glass window (7) at the bottom of the cell body for the incident laser light. Two external controls (5) transmit the motions to both arcs of the goniometer head by

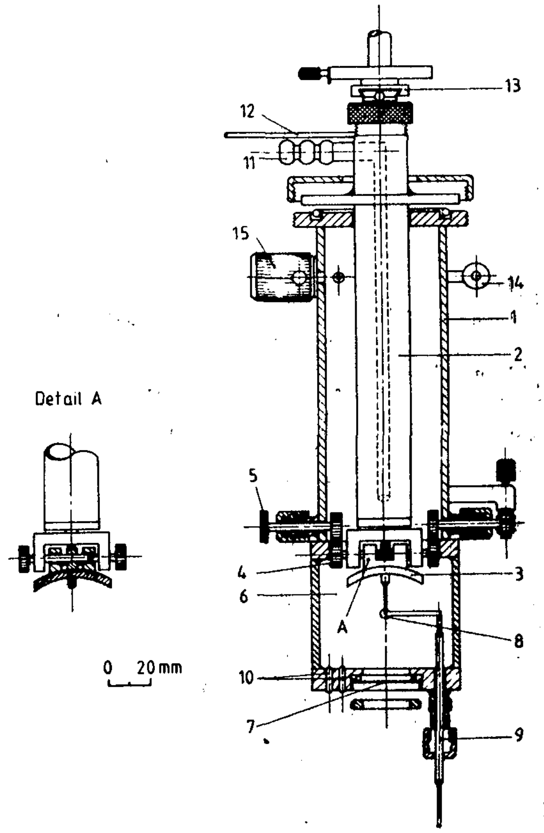

Figure 1. Schematic drawing of the cell: 1, exterior body; 2, liquid N_2 reservoir; 3, sample-holder goniometer with two 30° perpendicular arcs; 4, gear system for transmitting motions to the goniometer from the exterior; 5, gear controls; 6, acrylic windows; 7, glass window; 8, heater resistor; 9, resistor sliding vacuum seal; 10, Kovar seals for thermocouple leads; 11, liquid N_2 inlet in horizontal position; 12, N_2 gas outlet; 13, perpendicular displacement adjusters; 14, vacuum connection; 15, vacuum valve; A, detail shown on left of figure.

means of a gear system (4). The gears were made of Teflon in order to minimise the thermal loss; they are mounted on rotating shafts with O rings, to avoid losing vacuum when they are turned. Similarly, a movable heater resistor (8) is introduced at the base of the cell. It is made of a thin nichrome wire forming a ring around the sample, and can be moved up and down along it.

3. Use and performance

A sealed glass capillary tube contains the sample and is placed in the specimen holder of the goniometer head (3), which is fixed to the bottom of the liquid N_2 reservoir.

After the cell has been evacuated, the single crystal growth is initiated by gradually cooling the sample holder. The heater resistor (8) can be positioned at any height around the sample and allows the control of the thermal gradient along it. If its displacement is adequately controlled, it can eventually act as a zone refiner.

Once the single crystal has been obtained, the cell is mounted in a specially adapted Weissenberg chamber in a horizontal position. The cell axis can be positioned in coincidence with the rotation axis of the chamber by means of

two perpendicular displacement adjusters (13), like those of a conventional goniometer head, located at both ends of the cell.

The orientation of the crystallographic axes is determined by taking oscillation and Weissenberg photographs. The sample alignment may be corrected, between subsequent exposures, by means of the gear controls (4) which transmit the motions to both arcs of the goniometer head. The number of photographs needed for a complete orientation and the exposure times depend on the nature of the sample studied, and of course on the initial position of the crystal. If none of the crystal axes has grown within 15–20° of the capillary tube axis, it is advisable to try a new crystal. The orientation of the samples is complete when the three crystal axes are perpendicular to the pairs of lateral windows and the bottom window (for monoclinic crystals only the unique axis is relevant, and triclinic crystals have only one Raman-active symmetry species).

The cell is mounted on the Raman spectrometer in such a way that each crystal axis is successively perpendicular to the laser beam; this requires the cell to be operated in horizontal and vertical positions. The intensity of the spectrum depends on the inclination of the capillary tube; in particular, if one of the crystal axes is nearly coincident with the capillary axis, the crystal imperfections at the capillary end and the imperfect end of the capillary itself will be in the path of the light for some cell positions, causing partial depolarisation.

The whole procedure from growing one sample to obtaining its polarised Raman spectra is rather cumbersome and may take several days or even weeks; during this time, of course, the cell must be kept filled with the cryogenic liquid automatically.

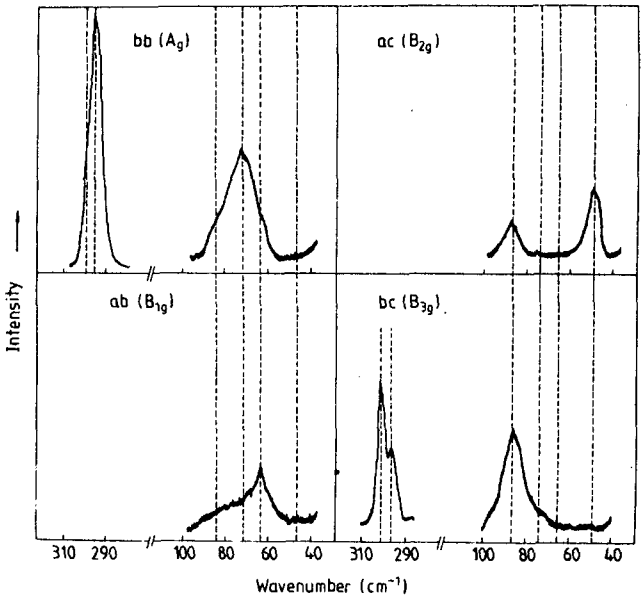

Figure 2. Polarised Raman spectra of a single crystal of bromine.

In figure 2 we show a polarised Raman spectrum of crystalline bromine. The dichroic properties of the bands are clearly observed, although some bands show incomplete polarisation probably due to crystal imperfections or slight misalignment. At the present time, work on the crystals of CS_2 and hexane is in progress.

Acknowledgments

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