A simple, low cost furnace for high temperature Raman measurements

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A simple, low cost furnace for high temperature Raman measurements

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Abstract. The construction of a simple high temperature Raman furnace is presented. This furnace has been operated efficiently in the temperature range from 320 to 700 K.

1. Introduction

Temperature-dependent Raman studies yield a wealth of physicochemical information and many precise reasons exist which justify doing this kind of experiment.

We planned to study the Raman spectra of solid and liquid samples at temperatures above room temperature up to approximately 1000 K. In this paper we present the high temperature furnace built to operate to temperatures of approximately 800 K.

2. Construction details

The furnace is schematically presented in figure 1. It consists of an isolated heater (a) wound on a machined ceramic support (b) which in turn is fastened onto the end plate (c) of a stainless-steel cylinder (d). The cylinder is torch soldered onto a brass cap (e). This sits vacuum tightly (f) on a flat-bottomed Pyrex cylinder (g) of good optical quality. The cap contains the vacuum outlet (h), the feedthroughs (i) for the heater current and an Edwards $\frac{1}{2}$ inch female vacuum connector (k). The sample holder system consists of a stainless-steel tube (l) torch soldered to a modified Edwards $\frac{1}{2}$ inch male brass vacuum connector (m). The other end of the tube is fitted with a beryllium bronze screw (n) which serves to attach the cylindrical sample holder (o) made either from copper or from beryllium bronze. The temperature of the sample is measured with the aid of a copper–constantan thermocouple fixed to the screw (n). It is possible to add another thermocouple a few millimetres off the sample position. Some initial experiments showed that a copper sample support gives a very uniform temperature and the difference between the temperatures of the two thermocouples was less than 2.2 K (under vacuum).

This construction of the sample holder set-up makes it easy to change the sample during an experiment and, at the same time, to keep control over the gas atmosphere inside the furnace. Over this, the stainless-steel tube is perforated in order to facilitate any degassing. Spacers (p) are fastened to this tube. They act as thermal reflectors and as barriers for the dissipative gas circulation.

We have realised two different sample holders. The one (o) displayed in figure 1 was used for powder samples sealed into standard capillary tubes. An axial hole is drilled into the copper cylinder. Its diameter is such that the capillaries can be seated snugly. As our Raman spectrometer is of the 90° scattering geometry variety, the holes shown in figure 1 were machined into the cylinder. The laser beam enters horizontally through a narrow hole in the side of the cylinder whereas the scattered light emerges through the cylindrical cone. The plane through the axes of the holes perpendicular to the cylinder axis is located approximately 13 mm outside the heater support. The holder for single crystals contains a slot and a spring-loaded piston between the two walls. The crystal is pushed towards one wall by the piston. A screw is provided to control the pressure exerted by the spring.

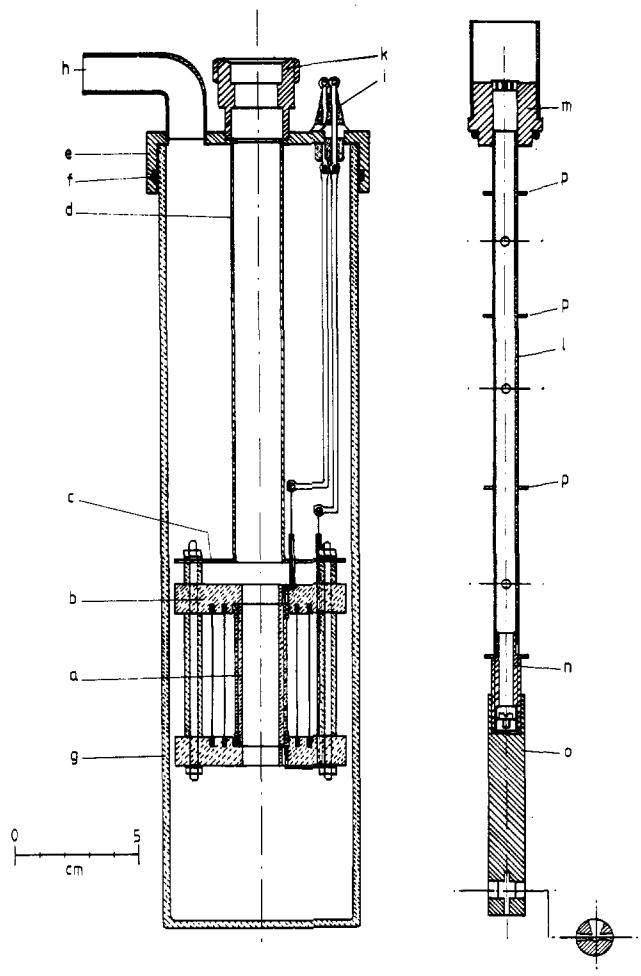

Figure 1. Schematic representation of the Raman furnace. See § 2 for key.

The heater consists of a Kanthal wire with a total resistance of $R = 6.8\ \Omega$ and supporting a maximum current of 8 A. A temperature stabiliser driving an adequate variable voltage transformer is used to heat the device to a given temperature.

Typically, a current of 3 A yields under high vacuum a temperature of about 700 K.

The furnace is built in such a way that it can work under high vacuum or in a controlled inert-gas atmosphere up to ambient pressure. All that is needed is a power supply and a vacuum pump which are available in many laboratories.

The cost of the material used for this construction was evaluated and found to be less than \$100.

3. Experimental applications

Raman measurements have been performed at temperatures between 320 and 600 K without a feedback type power supply. The temperatures were stable within 3 K. Some applications of this furnace are mentioned below.

We have studied previously the infrared and Raman spectra of the single crystal Na_2S between liquid helium and room

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temperature (Montaner *et al* 1979). The Raman active T_{2g} mode (observed at 194 cm^{-1} at 5 K) has been further studied at higher temperatures using the furnace described above. Figure 2 displays the observed experimental linewidth as a function of temperature of this mode. At high temperatures, the linewidth increases strongly. The large experimental error is caused by a significant decrease of intensity. These measurements might be related to the onset of fast ionic conductivity at higher temperatures. Further Raman measurements are in progress in order to obtain more insight into this dynamic behaviour.

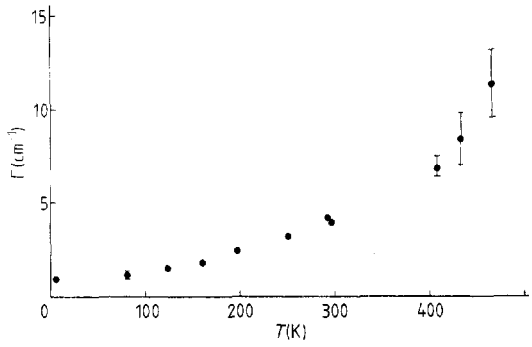

Figure 2. Raman linewidth (FWHM) as a function of temperature of the T_{2g} lattice mode in Na_2S.

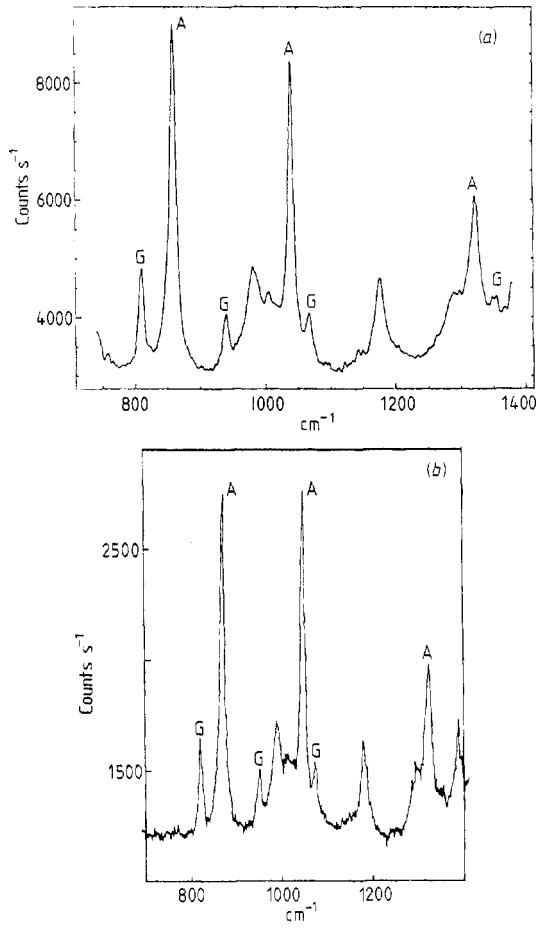

Figure 3. (*a*) Survey Raman spectrum of powdered $C_3H_7NH_3I$ at 347 K. 'G' and 'A' refer to lines pertaining to 'gauche' and 'anti' conformers respectively. Laser: $\lambda = 514.5$ nm, power, 0.2 W. The Raman spectrometer used is laboratory built. It consists of a Spectraphysics Ar-ion laser (model 166), a 1403 Spex double monochromator, a cooled RCA 31034 PM in conjunction with an Ortec photon counting system. The furnace was positioned horizontally in the spectrometer for these experiments. (*b*) Raman spectrum of the same system as (*a*). Sample temperature 302 K, otherwise same conditions apply as in (*a*).

We have recently observed a conformational equilibrium in the solid state in the salts $C_3H_7NH_3X$ with X = Cl, Br and I (Hagemann *et al* 1985). Figure 3 shows parts of the Raman spectrum of powdered $C_3H_7NH_3I$. The lines labelled 'G' pertain to the 'gauche' conformers, and those labelled 'A' to the 'anti' conformer. The evaluation of the intensity ratios of the bands of the 'gauche' isomer with respect to the 'anti' isomer at different temperatures may yield the energy difference between these two conformations. A preliminary value of 0.6 ± 0.3 kcal mol^{-1} has been obtained from spectra at temperatures ranging from 210 to 360 K. The samples seem to decompose at higher temperatures and the large experimental uncertainty is in part due to this but also due to the temperature dependence of the overlap of several lines. Further measurements are in progress to improve the evaluation of this energy difference between 'gauche' and 'anti' conformers in this system.

A quite different experiment with this furnace has been performed by Gâcon *et al* (1984). They have investigated excited state absorption processes in Sm^{2+}-doped BaFCl by analysing the laser-excited anti-Stokes fluorescence at different temperatures up to 650 K. More details are given in their paper (Gâcon *et al* 1984).

Acknowledgment

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