

Use of the FT Raman spectrum of Na_2MoO_4 to study sample heating by the laser

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Abstract

The difference in the FT Raman spectrum of sodium molybdate when it undergoes a crystal transition at about 112°C is used to qualitatively study laser heating effects. Relatively lower laser powers (125 mW) are able to raise the sample temperature by 40°C. Furthermore, large temperature gradients across the sample have been observed.

1. Introduction

Sample heating has always been a problem associated with laser FT Raman spectroscopy. The amount of heating which occurs has proven difficult to quantify as it is dependent on a number of factors. In particular, the effect depends on the sample (thermal conductivity and colour), the length of time in the laser beam and the laser power. A previous study on PTFE [1] estimated a sample temperature rise of about 1°C per 100 mW laser power but this is considered to be an underestimate.

Heating has limited the recording of FT Raman spectra where, for instance, the sample may undergo a phase transition (e.g. melt), may decompose, or may emit radiation as a result of being coloured. In order to record the Raman spectra of some temperature dependent samples, a variety of cells have been devised to keep the sample cool. Alternatively, in some cases it is possible to surround the sample by a good thermal conductor providing an effective heat sink such as a nujol mull between KBr disks. Although these overcome the problem, they do not give any indication of the magnitude of the temperature change encountered.

Sodium molybdate, Na_2MoO_4 , undergoes a fairly sharp non-reversible crystal transition at about 112°C, as confirmed by differential scanning calorimetry [2]. An FT Raman study of the solid over a range of temperatures [3] showed that the transition had occurred when the sample was heated to 100°C in an aluminium heating block. The laser had heated the sample beyond the transition point; a surprising observation as sodium molybdate is a white sample minimising any heating effects and a good scatterer such that only low laser powers are necessary to record a high quality spectrum. This work reports a more detailed study of this transition with respect to sample temperature, laser power and time of laser heating.

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2. Experimental

Standard anhydrous Na_2MoO_4 , purchased from Aldrich Chemicals Ltd. was used as supplied for all the studies described.

All Raman spectra were recorded using a Perkin-Elmer 1760 FT Raman spectrometer. A near infrared laser source was provided by a Spectron c.w. Nd^{3+} :YAG laser with TEM_{00} output at 1064 nm. A solid sample of about 2 mm diameter and 1 mm deep was heated in a Ventacon hot cell. It was estimated that the sample was up to 5°C cooler than the hot cell temperature; the need for the sample to face the collection optics meant there was no thermal contact on the sampling face and heat could be exchanged with the cooler surroundings. Due to the non-reversible nature of the crystal transition, a fresh sample was used for each independent experiment. Each sample was loaded into the hot cell and allowed to stand for about 15 min before use in the spectrometer to ensure temperature equilibration. All spectra were recorded using 1 cm^{-1} resolution.

Three sets of experiments were performed.

(i) The sample was heated to 70°C and the FT Raman spectrum recorded as an average of 5 scans (each spectrum taking about 1.1 min) using laser powers of 50, 125, 250, 375, 500, 625, 750 and 875 mW.

(ii) Using a laser power of 125 mW and a sample temperature of 70°C, the FT Raman spectrum was recorded as an average of 10 to 70 scans incrementing by 10 scans (about 2.2 min) for each spectrum. Additionally, for a sample temperature of 60°C and 375 mW laser power, consecutive time-spectra were recorded as an average of 50 scans using the same sample throughout.

(iii) Spectra were recorded at sample temperatures of 20, 40, 60, 70 and 80°C using 250 mW laser power and averaging 5 scans.

3. Results and discussion

The peak positions for sodium molybdate in the two crystal forms are listed in Table 1. As previously mentioned, the low temperature form exists up to about 112°C. It can be seen that the most notable change between the two spectra is in the ν_1 band and hence this was used as a qualitative measure of the conversion to the high temperature crystal state. There is also a disappearance of the weak combination bands to the high frequency side of ν_4 and ν_2 in the high temperature form.

There is a very significant heating effect due to the laser. This is illustrated in Fig. 1 which shows spectra recorded at five different hot cell temperatures using 250 mW laser power, 1 cm^{-1} resolution and five scans. At room temperature (20°C) there is no transition occurring which is, in fact, true for any laser power used (up to 875 mW). As the temperature is raised, some of the sample has undergone a transition as can be seen by the relative reduction in the peak intensity at 896 cm^{-1} . At 80°C, all the sample has undergone a crystal transition within the time to record a single scan spectrum (0.4 min).

The results from the investigation of varying the laser power are shown in Fig. 2. The global sodium molybdate temperature was maintained at 70°C. As would be expected, when the laser power is increased there is a greater sample heating effect for a given time.

Table 1

Band frequencies for solid Na_2MoO_4 assigned according to the tetrahedral symmetry for the relatively free molybdate ion in solution

Form ^a	ν_1	ν_3	ν_2	ν_4
(a)	891, 896	809, 833, 843	378	302, 320, 330, 340
(b)	890	808	378	302

(a) Low temperature form; (b) high temperature form.

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