CH-4114 beamtime report

Methane beyond the critical point

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We were awarded 9 shifts of beamtime at ID27 in July 2014 to study methane in the supercritical fluid region of the phase diagram, to confirm (or not) recent theoretical predictions of a discontinuous transition between "liquid-like" and "gas-like" states of matter far into the supercritical region on the phase diagram, in principle extending to arbitrarily high P,T. This predicted transition line has been dubbed the "Frenkel line"[1].

Methane is an ideal system to study to verify the existence of the Frenkel line because it has an extremely low critical point (190 K), is of great interest to earth and planetary science, and is optically active; with an extremely strong Raman-active vibron.

In experiments in our laboratory conducted shortly before the beamtime we studied the pressure-induced shift in the Raman-active vibron in methane at ambient temperature whilst unloading pressure from the melting point (1.4 GPa) to zero pressure (figures 1 – 3). We observe a possible transition at 0.2 GPa between a low-pressure regime (< 0.2 GPa) where the vibron frequency does not shift as a function of pressure (as expected for a gas-like phase) and a higher-pressure regime (0.2 – 1.4 GPa) where the vibron frequency does shift as a function of pressure (as expected for a liquid-like phase).

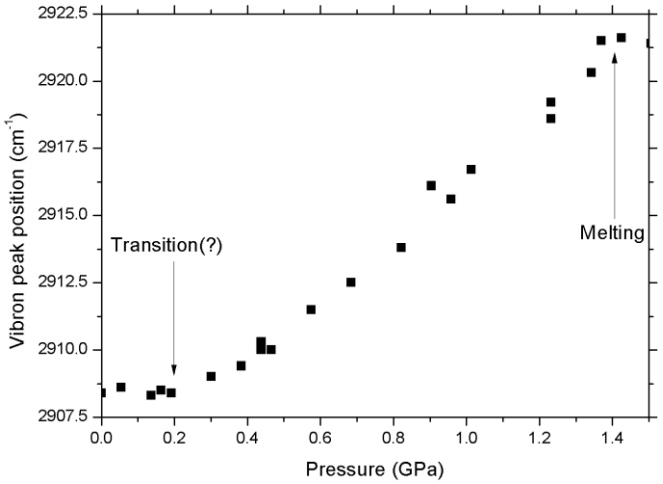

Figure 1. Pressure-induced shift in methane vibron frequency at 300 K, showing possible transition at 0.2 GPa from gas-like phase in which vibron frequency does not shift as a function of pressure, to liquid-like phase in which it does.

The integrated intensity of the vibron is significantly lower in the “gas-like” phase (lower pressure) than in the “liquid-like” phase (higher pressure). There is approximately a 35% decrease in vibron intensity when reducing pressure through the transition at 0.2 GPa (figure 2).

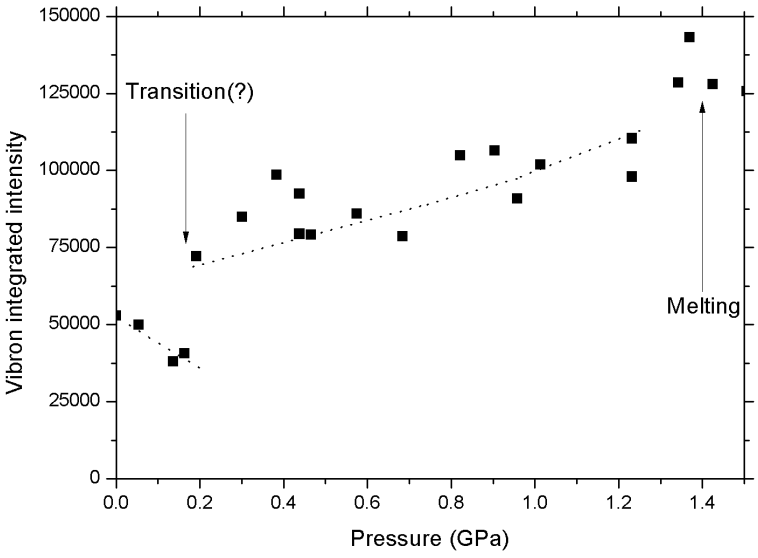

Figure 2. Variation in methane vibron integrated intensity as a function of pressure, showing a discontinuous drop in intensity at ca. 0.2 GPa. Dotted lines are guides to the eye.

If we look at the actual spectra, we can clearly observe the discontinuous decrease in intensity at 0.2 GPa. The 2nd order diamond Raman peak is omitted from this spectrum but is collected as part of the same spectrum as the methane vibron. Monitoring the intensity of this peak and comparing to the methane vibron intensity allows us to verify that the change in vibron intensity is not an experimental artefact. After decreasing pressure through the transition, we then increased pressure and observed the transition to be reversible.

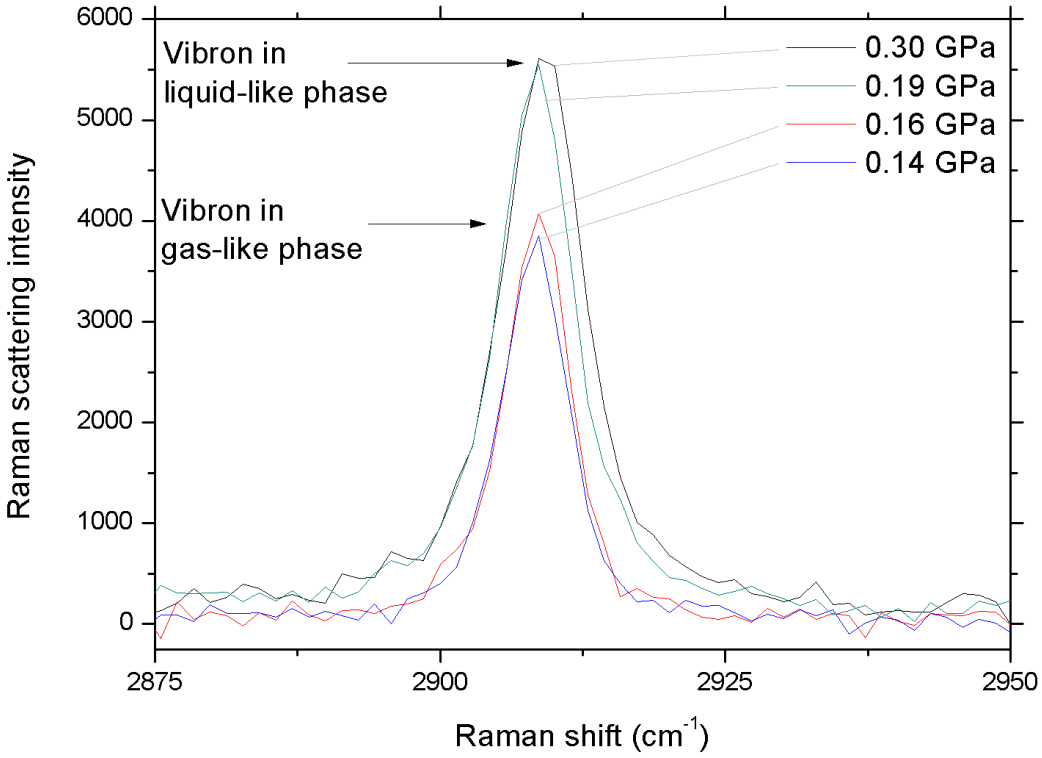

Figure 3. Methane vibron at pressures immediately above and below possible transition from liquid-like to gas-like phase, demonstrating discontinuous change in vibron intensity.

Unfortunately, at the actual beamtime at ID27 we were not able to complete our planned program of work. This was due to problems with the beamline beyond our control; frequent loss of signal in the online optical spectrometer and the X-ray beamstop falling off its mount twice. Time-consuming realignment was required on all these occasions. In total we lost 2/3rds of the beamtime.

However, we were able to perform 2 X-ray diffraction experiments on fluid methane (at 300 K and at 533 K). The data presented here has not been normalized but has had a normalized background subtracted, following the methodology in ref. 2. We have used X-ray diffraction patterns collected from each empty DAC for the background. However, we also collected patterns of methane in the solid phase in the DAC in both experiments. These patterns show the methane to consist of 1 or 2 crystals, so if we prefer we can obtain our background intensity from these patterns, by masking out these spots in Fit2D before integration. We have yet to make a final decision on which method to use for publication.

At 300 K, we reduced pressure from the solid phase into the fluid phase and observed the appearance of a broad peak at relatively low Q as would be expected from a liquid-like phase[3]. However, at extremely low pressure (< 0.30 GPa) we see this peak disappear; to be replaced by an extremely broad and weak peak at even lower Q – barely strong enough to discern from the background. Note that, even at the lowest pressure datapoint (at 0 GPa within experimental error) we can be certain that the methane sample has not escaped. This is because, even at this pressure, we still observed an intense methane vibron at 3000cm^{-1} in the Raman spectrum. Hence the online Raman spectrometer at ID27 is a crucial diagnostic tool for this experiment. Figure 4 shows stacked X-ray diffraction patterns from the same sample at the same set of pressures. Note how the drastic

change in the X-ray diffraction pattern corresponds to a change in the pressure-induced shift of the vibron; just as in the data collected prior to the beamtime (figure 1).

Figure 5 shows a plot of fluid methane vibron frequency vs. pressure for the data collected on the online spectrometer at ID27 at 300 K and figure 6 shows the actual spectra. Note how in this data the intensity jumps several times; a consequence of the repeated alignment issues with the online Raman system at ID27. We have therefore not attempted to plot a graph analogous to figure 2 for this data.

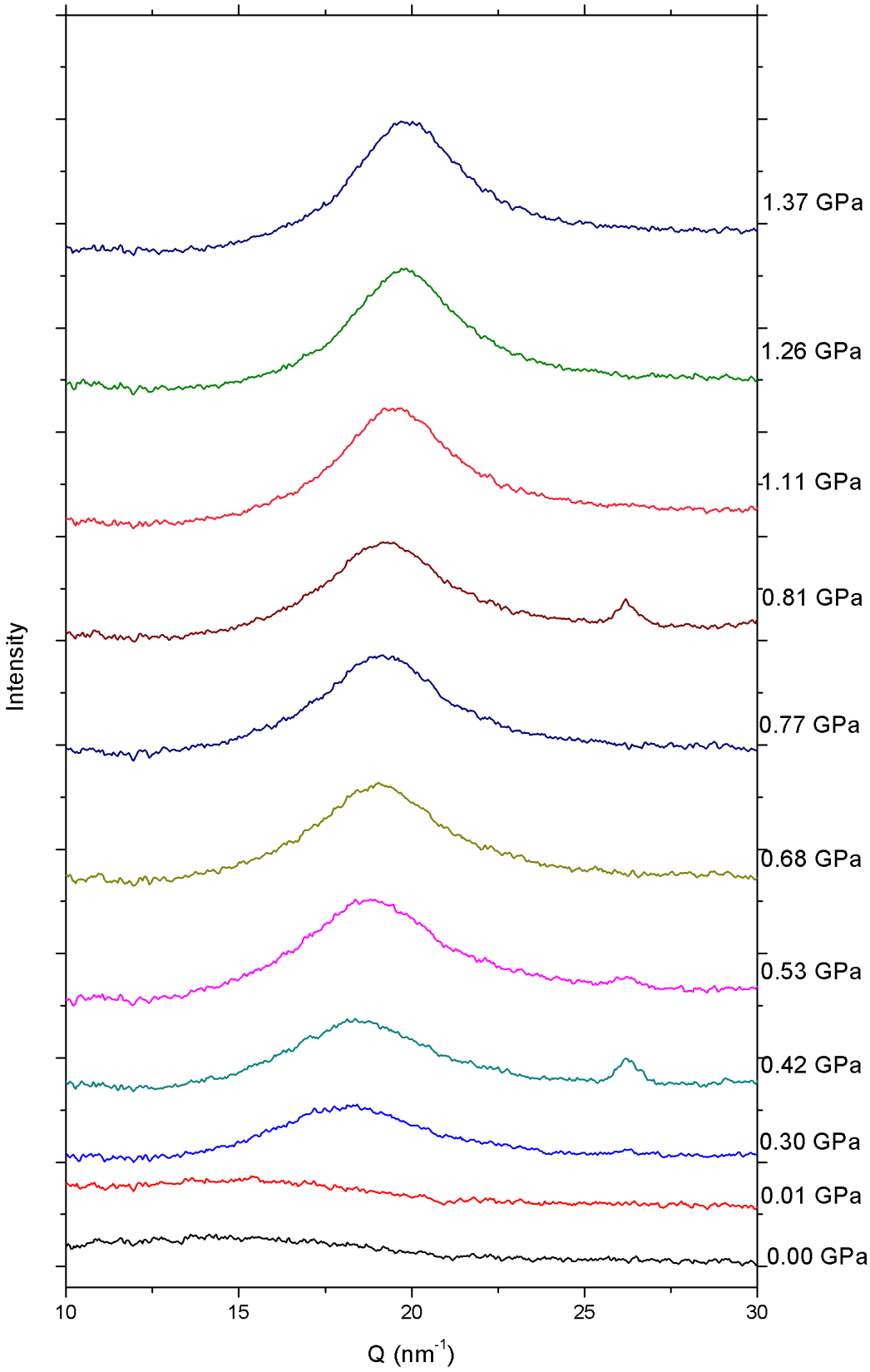

Figure 4. Stacked X-ray diffraction patterns showing peak from fluid methane (liquid-like state) at Q ≈ 17-20 nm^{-1} and its disappearance below 0.30 GPa. Peak occasionally observed at Q ≈ 26 nm^{-1} is experimental artefact not originating from methane.

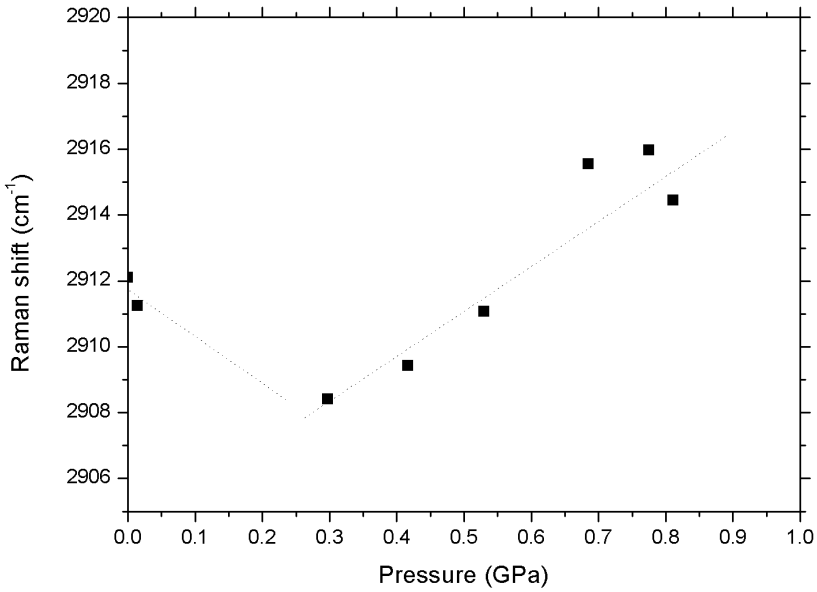

Figure 5. Pressure-induced shift in methane vibron frequency at 300 K (data collected using online Raman spectrometer at ID27), showing possible transition at 0.2 GPa from gas-like phase to liquid-like phase. Dotted lines are simply guides to the eye.

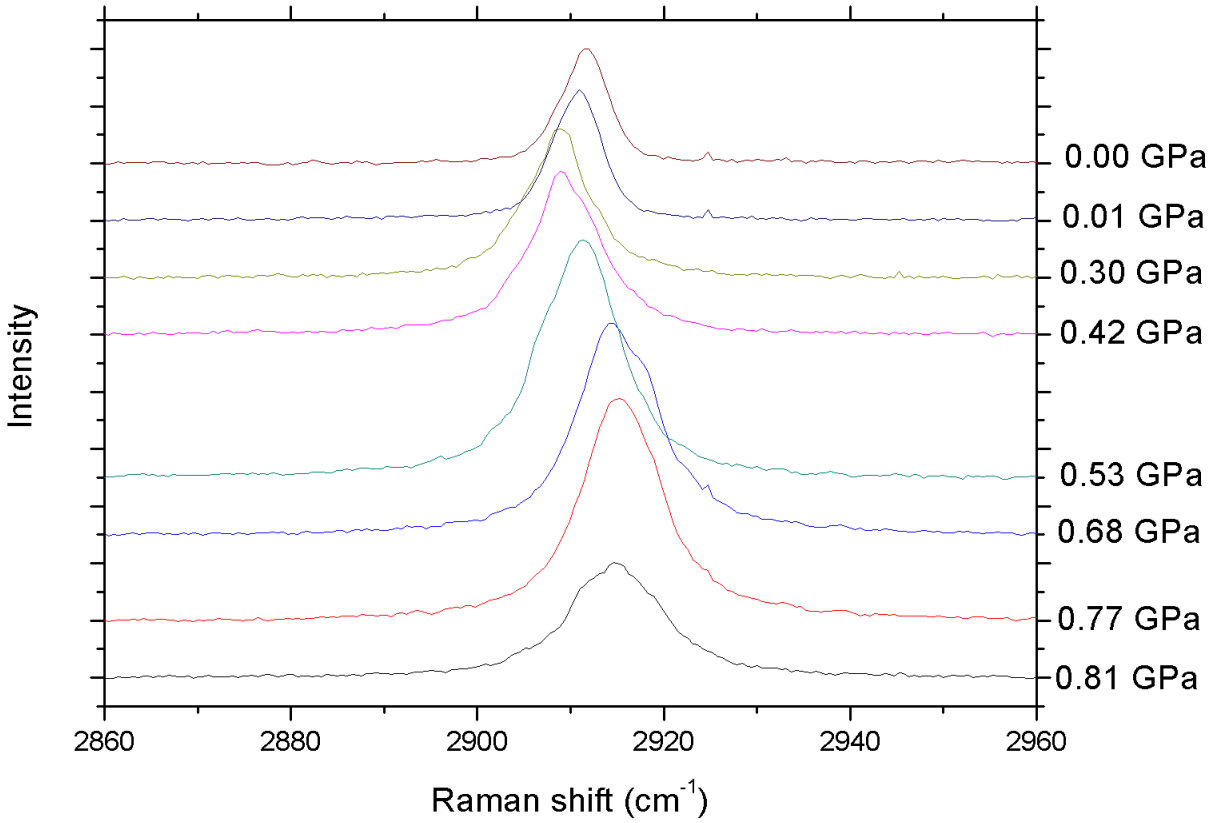

Figure 6. Graph showing methane vibron frequency as a function of pressure at 300 K (data collected using online Raman spectrometer at ID27). Note abrupt change in pressure-induced shift between 0.01 GPa and 0.30 GPa, and multiple jumps in intensity.

We also performed an X-ray diffraction experiment in which we decreased pressure through the region where we expect the Frenkel line to lie at 533 K. Figure 7 is stacked X-ray diffraction patterns at 533 K after background subtraction using the methodology described above.

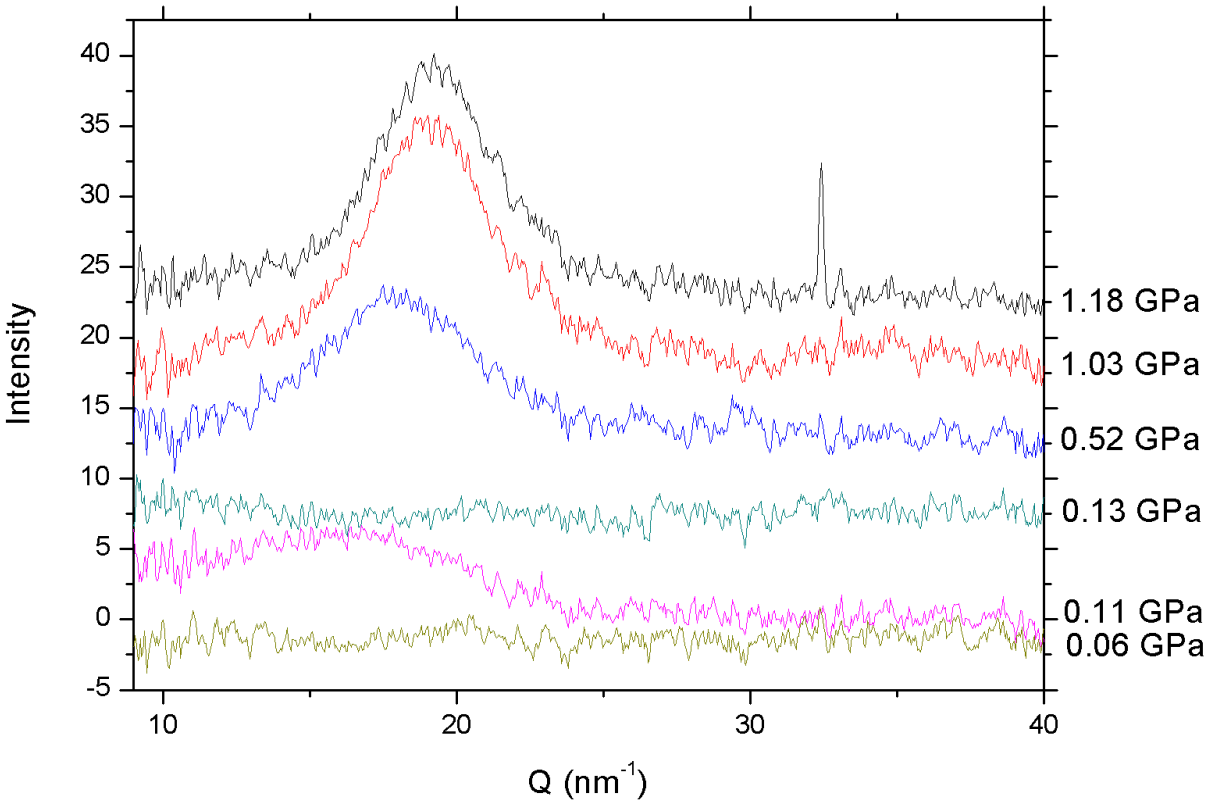

Figure 7. Experiment at 530 K. Stacked X-ray diffraction patterns showing peak from fluid methane (liquid-like state) at Q ≈ 17-20 nm^{-1} and its disappearance below 0.52 GPa. The error in pressure measurement is ±0.06 GPa. Therefore (within error) the curve labelled as 0.11 GPa could be data taken at a higher pressure than the curve labelled as 0.13 GPa. Given that the 0.11 GPa curve exhibits a more pronounced peak, this is likely to be the case.

In this experiment, we again observe the loss of the X-ray diffraction peak characteristic of a liquid-like state as pressure is decreased. Disappearance of this peak commences at 0.5 GPa and is complete by 0.1 GPa. In the experiment at 300 K pressure was measured using the photoluminescence from Ruby, but in the experiment at 533 K pressure was measured using the photoluminescence from Sm:YAG, reported in the literature as being pressure-independent in the temperature range of interest[4].

However the photoluminescence lines from Sm:YAG do become broader and weaker as temperature is increased, leading to errors in pressure measurement. This is exacerbated by the Y1 and Y2 Sm:YAG peaks becoming broader and overlapping significantly at high temperature. The error in the pressure measurements recorded in figure 7 is somewhere between ±0.06 GPa and ±0.1 GPa, a factor that must be borne in mind when interpreting the results.

It was not possible to collect Raman spectra of methane at high temperature whilst the X-ray data shown in figure 7 was being collected. The online spectrometer at ID27 was working at the time (and was used to collect the photoluminescence spectra of Sm:YAG used to measure pressure), but no signal from the methane vibron was observed. We hope that the alignment of the spectrometer can be improved ready for future experiments. Even at high temperature, the methane vibron is a strong Raman peak.

Very recently (figure 8) we collected Raman data on fluid methane at 600 K at the University of Edinburgh. A strong methane vibron was observed. This data will be analysed in preparation for future beamtime allocation at ID27.

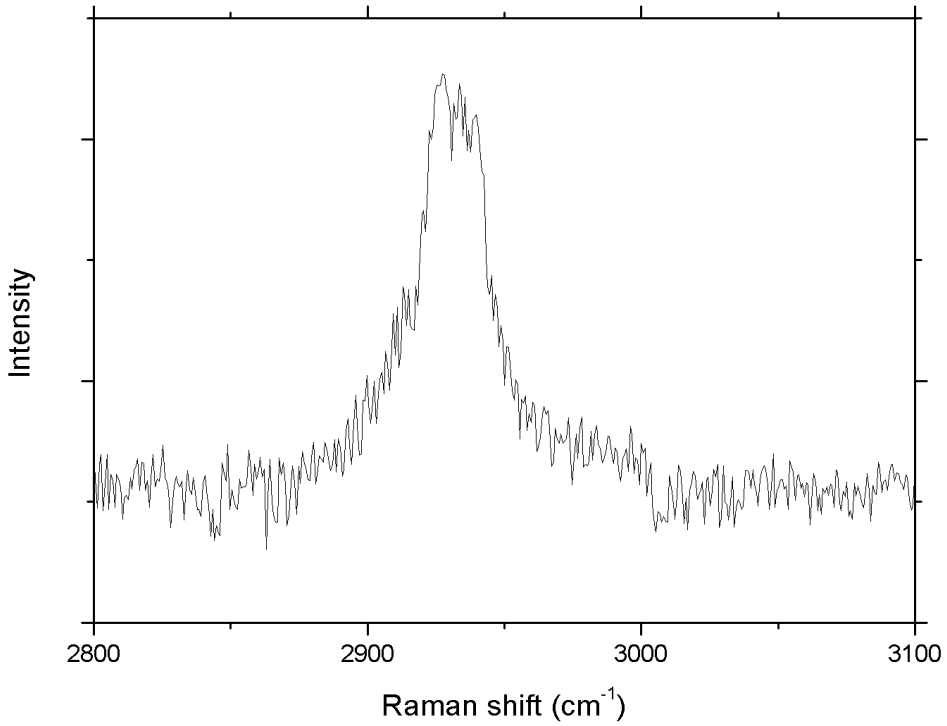

Figure 8. Raman spectrum of methane vibron at 600 K (2 second exposure).

Conclusions

X-ray diffraction and Raman data show evidence for a sharp, nearly discontinuous phase transition in methane at temperatures up to 530 K; nearly 3 x the critical temperature (190 K). To our knowledge, no sharp transition has ever been observed in a supercritical fluid before this far above the critical temperature. Further beamtime has therefore been requested to complete the study.

Note that in some cases information such as recorded pressures etc. has changed since the submission of our follow-up proposal CH-4386. This is because we have had the opportunity to analyse the data in more detail since the submission of this proposal, which had to be written very soon after beamtime CH-4114.

References

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3. J Frenkel, Kinetic Theory of Liquids, Dover (1955)

4. AF goncharov *et al.*, Appl. Phys. Lett. **97**, 094917 (2005)