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Raman Investigation of the Supercritical Mixture He–H_2

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We investigated the vibrational Raman spectrum of H_2 in the binary mixture He–H_2. The Q_1-line was measured between 150 and 350 K for two isobars in the gigapascal region in a mixture of critical composition. The results indicate a broadening of the spectrum due to critical concentration fluctuations.

KEY WORDS: concentration fluctuations; critical line broadening; high pressure; hydrogen–helium; mixtures; Raman spectroscopy.

1. INTRODUCTION

The lineshape of the vibrational Raman spectrum of one of the components in a mixture can be used to probe the influence of critical concentration fluctuations on the local composition. When approaching the critical line of fluid–fluid demixing, the increase in the mean amplitude of the concentration fluctuations can be observed through an increase in the linewidth. This has recently been demonstrated for the mixture helium–nitrogen at high pressures [1].

The relation between linewidth and concentration fluctuations is determined by the *inter*molecular interactions with the neighboring molecules and the *intra*molecular potential of the vibrating molecule [2]. As a consequence the sensitivity of the lineshape to critical fluctuations is system dependent.

In this paper we report our first measurements in a mixture of helium and normal hydrogen of critical composition. They were performed in search for other mixtures displaying critical linebroadening. The mixture

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$He–H_2$ is a good candidate, because the vibrational frequency of H_2 shows a strong dependence on the He concentration [3]. Additional advantages of this system are that the phase diagram of $He–H_2$ is well-known up to high pressures [4] and that above 0.3 GPa and 65 K the critical composition is nearly constant, which facilitates interpretation of the data. Finally, it is worthwhile to study the mixture $He–H_2$ because of its relevance in cosmology and in the physics and chemistry of the giant planets.

2. EXPERIMENTS

To obtain high pressures a diamond anvil cell (DAC) of the wedge type [5] was used. The sample space had a diameter of 110 μm and a thickness of 120 μm at 2.0 GPa. Temperature could be regulated between 140 and 350 K. The gradient over the sample is estimated to be less than 0.1 K, without laser heating.

In a DAC with a certain setting of the piston it is not possible to measure a perfect isochore. When the temperature is varied the expansions in the complete setup result in a change in the sample volume. In practice we measure "quasi-isobars." In a run around 2.0 GPa, for example, the pressure stayed between 1.97 and 2.18 GPa. The pressure was determined with the ruby fluorescence line of a small ruby chip in the sample space [6], with an accuracy of 0.04 GPa. Pressure was measured regularly, and always after a change in temperature larger than 5 K.

The mixture could be observed with a videocamera connected to a microscope. In this way the critical temperature at a given pressure was determined with a relative accuracy of 0.2 K. Subsequently the temperature was raised and Raman spectra were taken.

The spectra were taken in backscattering geometry with an 80-cm triple spectrograph equipped with a CCD detector. The dispersion was 0.3 cm^{-1} per CCD column of 19 μm. During the run at 2.0 GPa the instrumental width was 1.6 cm^{-1}; during the run at 4.25 GPa it was 3.2 cm^{-1}. Spectra were accumulated for 10 to 20 min. Laser powers at the sample between 190 and 250 mW were used for the run at 2.0 GPa, with a few spectra taken at 350 mW. For the run at 4.25 GPa powers between 250 and 350 mW were used. We found no indication for a systematic error in the linewidth as a function of power.

3. RESULTS

A vibrational spectrum of H_2 in 58 mol% He is shown in Fig. 1. The spectra at 2.0 GPa had a peak intensity of 100 counts per s per column against a background of 110 counts per s per column due to fluorescence

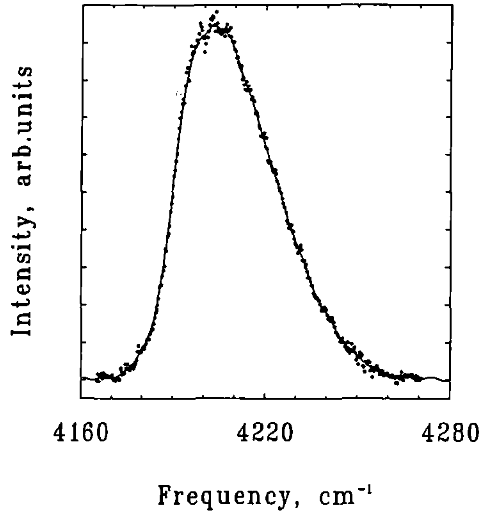

Fig. 1. The Q_1 vibrational spectrum of H_2 in a mixture with 58 mol% He. The smoothed spectrum is given by the solid line.

of the diamonds. At 4.25 GPa the signal was 30 to 55 counts per s per column. The spectra were smoothed with a binomial smoothing method to average out the column to column variation in the response of the detector. The half-maximum (HM) points were then determined, yielding a value of the width (FWHM). There was a systematic error (1 cm^{-1}, 5 cm^{-1}) caused by interference of the diamond fluorescence between the diamond culets, and a statistical error (1 cm^{-1}, 2 cm^{-1}) due to the arbitrariness in the determination of the baseline and the error in determining the maximum. The values in brackets are for the runs at 2.0 and 4.25 GPa, respectively.

Six typical spectra of the 2.0 GPa run are shown in Fig. 2. When the critical line is approached the spectrum broadens and becomes asymmetric with the steeper wing at the low frequency side. Both features were also seen in the 4.25-GPa run, but with larger scatter. The FWHM as a function of temperature is plotted in Fig. 3. To obtain isobars, the widths around room temperature were corrected to the same pressure as close to T_c, using the shift at room temperature of 20 cm^{-1} over 2.25 GPa. The corrections were less than 2 cm^{-1}. It is clearly visible that the linewidth broadens with decreasing temperature and increasing pressure. We interpret the temperature behavior as a critical effect. The broadening with pressure, however, is partly due to noncritical vibrational dephasing, as in N_2 systems [1, 8].

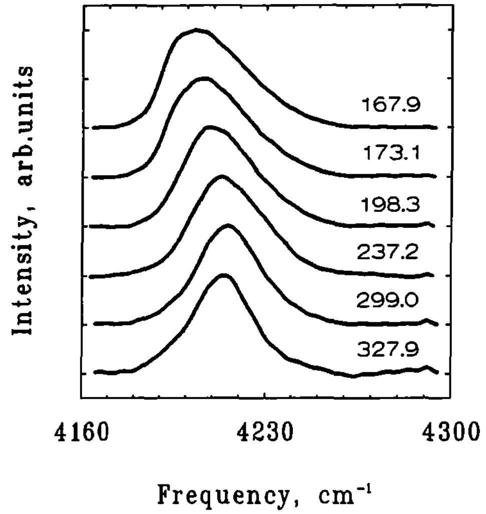

Fig. 2. The Q_1 vibrational line of H_2 along a quasi-isobar around 2.0 GPa. Temperature is given as K. The critical temperature at 1.98 GPa was visually determined to be 166.6 ± 0.2 K. The linewidth (FWHM) changes from 26 cm^{-1} at 327.9 K to 35 cm^{-1} at 167.9 K, near the critical line. Moreover, the spectrum becomes asymmetrical when the critical line is approached.

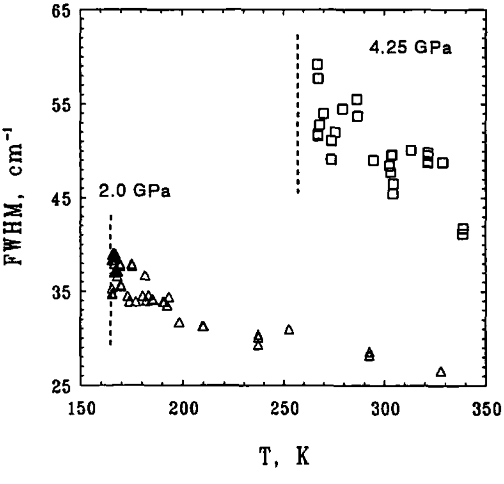

Fig. 3. The width (FWHM) of the Q_1 vibrational line of H_2 in a mixture of 58 mol% He versus temperature along two isobars. Squares, 4.25 GPa; triangles, 2.0 GPa. The critical temperature for each pressure is indicated by a dashed line.

4. DISCUSSION

For the interpretation of the spectra in the mixture of critical composition a comparison should be made with spectra of noncritical mixtures, but these are not yet available. Moreover, the temperature behavior for pure H_2 should be known. At present, there are only data available at room temperature [9, 10] and at liquid nitrogen temperature [11]. They give an indication of the temperature behavior up to 0.51 GPa.

Moulton et al. [10] measured the Q-branch of pure n-H_2 in the fluid phase at room temperature up to 4.6 GPa, which is 0.9 GPa below the solidification pressure of 5.5 GPa [12]. Eggert et al. [11] did the same at 77 K from 0.07 up to 30 GPa, which is far above the solidification pressure of 0.51 GPa [12]. Their data show that the rotation-vibration splitting of the Q-branch of H_2 persists up to high pressures, i.e., throughout the whole fluid phase at 77 K and at least up to 1.3 GPa at room temperature.

This is in contrast with N_2, where due to rotational avaraging the $Q_1(J)$ lines merge to one line, which can be fitted with a Lorentzian above 20 MPa [8, 13]. It should be noticed that this Lorentzian still consists of the summation of an ortho-N_2 and a para-N_2 peak. However, in the analysis of He–N_2 [1] the Q-branch could be considered as one vibrational line.

At room temperature and above 1.3 GPa, the Q-branch of pure n-H_2 also manifests itself as one peak, with above 2.2 GPa a constant width of 12 cm^{-1} [10]. We refer to this single peak as Q_1. As in N_2, however, the spectrum consists at least of one ortho-H_2 (odd J numbers) and one para-H_2 peak (even J numbers). We do not discuss the interpretation of the spectrum in detail here but conclude that measurement of the temperature dependence of the Q-branch of pure fluid H_2 above 0.51 GPa is required.

Considering Fig. 3, there are two features which indicate critical broadening; they are analogous to the critical broadening in He–N_2. First, there is a broadening of the linewidth with decreasing temperature, toward the critical line. At present we can compare this only up to 0.51 GPa with the temperature behavior of pure hydrogen. Table I shows that the width of the resolved $Q_1(1)$ line *narrows* with decreasing temperature along an isobar. The measurements in pure N_2 showed that at pressures in the gigapascal region, the linewidth is nearly constant with temperature [1]. Finally, all existing theories predict a narrowing of the linewidth for decreasing temperature [14]. We conclude therefore that the line broadening is an anomalous effect, which is most probably due to critical concentration fluctuations.

Second, the broadening with pressure along an isotherm is stronger near the critical line at 270 K than further away at 340 K. This is an indication for critical line broadening as well. This pressure behavior is analogous

Table I. The Width (FWHM) of the Q_1 Vibrational Spectrum of H_2 in Pure H_2 and in a Mixture with 58 mol% He

		Pure H_2		
Peak	Pressure (GPa)	At 77 K $(cm^{-1})^a$	At room temp. $(cm^{-1})^b$	$x_{He} = 0.58$ at room temp. $(cm^{-1})^c$
$Q_1(1)$	0.51	1.86	3.5	—
Q_1	2.0	—	12	28
Q_1	4.25	—	12	48

[a] From Eggert et al. [11]; corrected for instrumental width.
[b] From Moulton et al. [10], Fig. 10.
[c] This work.

to that of He–N_2, where the broadening with pressure is also strongest near the critical line [1].

Finally, we note that by admixing helium at room temperature and 2.0 GPa the linewidth broadens with a factor of 2; see Table I. This is most probably due to concentration fluctuations. It is hence plausible to attribute the temperature broadening in the mixture to *critical* concentration fluctuations.

The critical effect apparently stretches out over more than 100 K, which is $0.6T_c$. This order of magnitude is in agreement with the findings in He–N_2 [1] and also with the findings of Chesnoy for pure N_2, where the broadening sets in at about $0.5T_c$ above the critical point [14]. This is in contrast with other critical effects, such as critical opalescence, which is observable only within 1 K from the critical point. Clouter and Kiefte [15] and Chesnoy [14] explain this by the short-range character of the Raman probe. This makes the linewidth sensitive to (critical) fluctuations with wavelengths down to 1 nm, as opposed to critical fluctuations with greater wavelengths ($\sim 0.5\ \mu m$), which cause critical opalescence.

5. CONCLUSION

Going down in temperature to the critical line along isobars at 2.0 and 4.25 GPa, a mixture of helium–hydrogen of critical composition shows a broadening of the Q_1 vibrational line of fluid hydrogen. This is an indication for critical broadening.

To draw more decisive conclusions, measurements should cover the homogeneous phase more completely in terms of composition, temperature, and pressure. Furthermore, the nature of the Q_1-branch of pure H_2 should be well understood.

To avoid the complication of both an ortho and a para component in the spectrum, it could be advantageous to work with heteronuclear molecules.

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