



	<b>Experiment title:</b> High frequency dynamics of supercritical ammonia	<b>Experiment number:</b> HS-2888
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## Report:

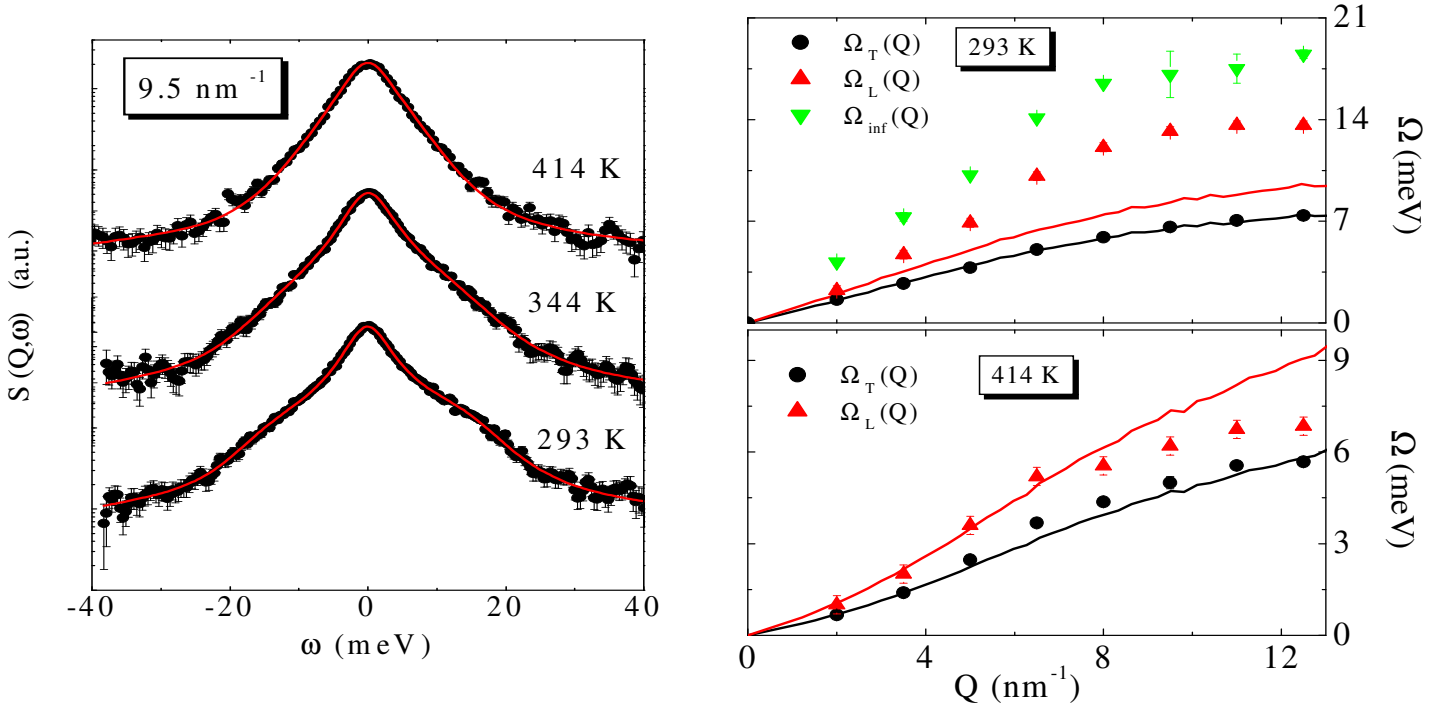
The high-frequency dynamics of liquid and supercritical ammonia was studied by Inelastic X-Ray Scattering (IXS). The sample was embedded in a large volume ( $\sim 0.7 \text{ cm}^3$ ) high-pressure, high-temperature cell. The experimental set-up included also a phase separator, mounted just before the HP cell in order to decouple the cell and the highly corrosive ammonia from the pressure generator. Pressure was applied and changed by nitrogen gas.

The experiment was performed at an incident photon energy of 21.747 KeV, using the silicon (11,11,11) set-up, providing an overall energy resolution of 1.5 meV (FWHM). The chosen thermodynamic states lie on an isobaric path (220 bar), and the investigated temperatures were: 293, 308, 344, 373, 414 and 444 K, while the ammonia critical point is 405 K and 113 bar. For each investigated thermodynamic state, we measured the static structure factor,  $S(Q)$ , and the dynamic structure factor,  $S(Q, \omega)$ , for 10 different transferred momenta,  $Q$ , ranging from 2 to  $15.5 \text{ nm}^{-1}$ , corresponding to 2 different  $Q$ -settings of the 7 meter spectrometer arm. A third  $Q$ -setting ( $Q = 7, 10, 13, 16$  and  $19 \text{ nm}^{-1}$ ) was acquired at 444 K. We accumulated 2 or 3 spectra with an integration time of  $\sim 4\text{h}$  each in order to have sufficient statistics. The contribution of the empty cell was measured as well and yielded a negligible contribution to the signal.

The data were analyzed using a theoretical model based on a viscoelastic function with two exponential decays, one related to the structural relaxation process and the other one related to thermal diffusion. For further details see [1-3]. At high temperature the structural term of the memory function was found to correctly approximated by a  $\delta$ -function. This model function was convoluted with the experimentally determined resolution function. From this viscoelastic analysis, we could derive the value of the isothermal and infinite frequency sound dispersions,  $\Omega_T(Q)$  and  $\Omega_{\text{inf}}(Q)$ . Moreover, from the maxima of the longitudinal current spectrum,  $\omega^2 S(Q, \omega)$ , we could also derive the apparent sound dispersion,  $\Omega_L(Q)$ , that represents the characteristic frequency of sound propagation [1-3]. The value of  $\Omega_T(Q)$  can be also directly deduced from the  $S(Q)$  measurements, through the relation:  $\Omega_T(Q) = (k_B T Q^2 / M S(Q))^{1/2}$ . Our chosen model describes very well the experimental data, as can be appreciated in figure 1.

Figures 2 reports the results concerning the sound dispersion curves at two selected temperatures: 293 K (liquid) and 414 K (supercritical). The black line is the value of  $\Omega_T(Q)$  calculated from the experimentally determined  $S(Q)$ . The agreement with the data as obtained from the fits (black circles) is excellent, especially at low temperature. The red line is the corresponding adiabatic sound dispersion that, according to classical hydrodynamic theory, should be the characteristic frequency of sound propagation. As we can see, at 293 K, the values of  $\Omega_L(Q)$  obtained from our analysis (red triangles) seem to depart from the expected value (red

line) towards the infinite-frequency dispersion (also derived from the fits, green triangles). Such phenomenology has been already observed in different liquid systems. It is usually called “positive sound dispersion” and it is directly related to the structural relaxation [1-3]. In the supercritical phase (414 K) we can no longer observe any positive dispersion and  $\Omega_L(Q)$  closely follows, at low- $Q$ , the adiabatic dispersion. Furthermore, at high- $Q$ , the apparent sound dispersion clearly bends down and seems to join the isothermal one (black line). We think that this feature, recently observed for the first time on  $N_2$  (see report on exp. HS-2681) can be associated to the effect of thermal diffusion that, at high- $Q$ , becomes “faster” than the acoustic wave itself. For more details see also [3].



**Fig. 1 (left):** IXS spectra of liquid and supercritical ammonia at  $Q=9.5 \text{ nm}^{-1}$  and temperatures indicated in the figure. The experimental data (circles) are shown together with their error bars. The red line is the best fit result using the viscoelastic model function.

**Fig. 2 (right):** Dispersion curves of liquid (293 K) and supercritical (414 K) ammonia. The green triangles are the infinite-frequency dispersion, the red triangles represents the apparent dispersion while the black circles are the isothermal sound dispersion (all results obtained from the best fit). The red and black lines represent the isothermal and adiabatic sound dispersions calculated from the experimentally determined  $S(Q)$ . See text for further details.

## References

- [1] U. Balucani et al.; Phys. Rev. E 47, 1677 (1993)
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- [3] T. Scopigno et al.; Rev. Mod. Phys. 77, 881 (2005)