

## Anomalous Behavior of Isotropic Raman Line Shapes near Gas-Liquid Critical Points

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Temperature dependencies of Raman linewidths  $\text{FWHM}(T)$  of the two polarized modes in  $\text{N}_2\text{O}$  have been determined along the coexistence line with mK resolution. Comparing the neat fluid with diluted states of  $\text{N}_2\text{O}$  in Xe (and  $\text{CO}_2$ ), quite opposite behaviors of  $\text{FWHM}(T)$  have been observed when the liquids approach their respective critical temperatures  $T_c$ : While the mixture  $(\text{N}_2\text{O})_{0.05}\text{-Xe}_{0.95}$  shows the well known  $\lambda$ -shaped effect of critical broadening, a unique and sharp density-correlated line narrowing has been observed in the neat state. The gradual switchoff of intermolecular resonance couplings with decreasing density is responsible for this narrowing phenomenon. [S0031-9007(96)01274-4]

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Isotropic Raman line shapes (IRLS)  $J(\omega)_{\text{iso}}$  may show additional (Gaussian) broadening if the liquid-gas critical point  $T_c^{(lg)}$  is reached [1,2]. This so-called critical line broadening (CLB) results in a  $T_c$ -peaked and nearly  $\lambda$ -shaped temperature dependence of the line width  $\text{FWHM}(T)$  (full width at half maximum), which is most pronounced if the fluid follows a path along the critical isochore ( $\rho = \rho_c$ ) [3]. The common interpretation assigns CLB, which is also expected to occur near the consolute point  $T_c^{(ll)}$  of a liquid mixture [4,5], to those modes whose instantaneous frequencies  $\omega(t) = \langle \omega \rangle + \delta \omega(t)$  are modulated by fluctuations of order parameters (density  $\rho$ , concentration  $x$ ) [6,7]. Thus, CLB might reflect the universal power law behavior of three-dimensional thermodynamic systems near  $T_c$  (see [8] for a review). The most significant example of CLB is given by the width of  $\text{N}_2$ , which increases eightfold compared to its low non-critical background value [9,10]. However, it remains an open question whether CLB is universal or not. In addition to  $\text{N}_2$  it has also been observed (counting also minor effects) in  $\text{O}_2$  [2], HD and  $\text{H}_2$  [3], CO [9],  $\text{CO}_2$  (mainly  $\nu_1$ ) [11],  $\text{CH}_4(\nu_1)$  [9,12], and  $\text{H}_2\text{S}(\nu_1)$  [13], whereas CLB was undetectable in  $\text{CF}_4(\nu_1)$  [9] and  $\text{C}_2\text{H}_6(\nu_3)$  [14]. Furthermore, the CLB searches around  $T_c^{(ll)}$  are contradictory, i.e., either a null effect (3-methylpentane-nitroethane) [4] or line broadening by concentration fluctuations ( $\text{He-N}_2, \text{H}_2$ ) [5] were reported. Near  $T_c$  either line broadening or a total insensitivity to critical peculiarities was observed, while line narrowing has never been presented. To elucidate whether CLB might possibly be overlooked by an insufficient approach to  $T_c$ , we studied  $J(\omega)_{\text{iso}}$  of the two polarized modes ( $\nu_1, \nu_3$ ) in  $\text{N}_2\text{O}$  in closest vicinity to  $T_c$  (i.e.,  $|\Delta T^*| \equiv |T/T_c - 1| \gtrsim 10^{-5}$ ) along the critical isochore  $\rho/\rho_c - 1 \equiv \Delta \rho^* \approx 0$ . In a dense state of oscillators intermolecular couplings of both resonant and nonresonant nature contribute to line broadening [15,16]. We therefore compared the neat fluid with

diluted solutions of  $\text{N}_2\text{O}$  in Xe and  $\text{CO}_2$  [17] in order to judge the influence of the couplings on CLB. Solution in a monatomic environment (Xe) removes all of them and additionally narrows the line due to the more isotropic environment [18], whereas isotopic dilution suppresses the resonant contribution alone (here the expensive isotopomers of  $\text{N}_2\text{O}$  are surrogated by  $\text{CO}_2$  [19]).

The Raman line shapes were measured with multi-channel detectors on either a 50 cm focal length triple monochromator Dilor XY (Salzburg, henceforward marked with XY) ( $\nu_3^{\text{neat}}$ ) or a 100 cm double instrument Jobin Yvon U1000 (Jena, marked with U) (all other experiments).  $180^\circ$  (XY) and  $90^\circ$  (U) scattering geometries were used. In both setups, a kernel-in-shell principle (e.g., see [14]) was used for temperature stabilization; i.e., a fine tuned and weakly heated copper kernel containing the sample was surrounded by a more coarsely controlled aluminum shell. Maintenance of  $T_{\text{ke}} - T_{\text{sh}} \lesssim 200$  mK, rms fluctuations  $|\delta T_{\text{ke}}^{XY}| \lesssim 1$  mK and  $|\delta T_{\text{ke}}^U| \lesssim 50$   $\mu\text{K}$  could be achieved over periods of weeks, as was checked with various Pt 100 resistors and thermistors [20]. The improved stability in the U experiments came from  $|\delta T_{\text{sh}}^U| \lesssim 5$  mK compared to  $|\delta T_{\text{sh}}^{XY}| \lesssim 100$  mK and a tenfold greater mass of the kernel ( $m_{\text{ke}}^U = 2.8$  kg). To improve heat conduction, the fluid in the U experiment ( $V^U \approx 2.1$   $\text{cm}^3$ ) was in immediate contact with the (gold-coated) copper, whereas in the XY experiment a sealed thin-walled glass tube was used as the primary container ( $V^{XY} \approx 2$   $\text{cm}^3$ ), fitted firmly into the copper. In both experiments the trial-and-error filling method of [14] was adapted to match the critical density  $\Delta \rho^* = 0$  within 1%. Impurities were  $< 0.3\%$   $\text{N}_2$  [21]. Usually, after reaching the nominal temperature within  $|\delta T| \lesssim 1$  mK, the samples were allowed to equilibrate for  $t_{\text{eq}}^U \gtrsim 0.5$  h or  $t_{\text{eq}}^{XY} \gtrsim 4$  h (because of the intermediate glass wall). Longer equilibration ( $t_{\text{eq}} > 12$  h in both cases) did not change our results. Additionally, they

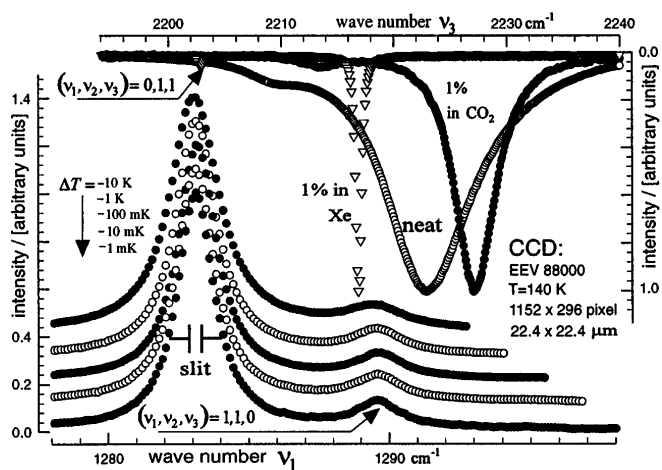


FIG. 1. Polarized CCD Raman spectra of neat and diluted states of liquid  $N_2O$ . Lower part: Temperature dependence of  $\nu_1$  (neat state) near below  $T_c$ , upper part: Solvent dependence of  $\nu_3$  near 218 K. Acquisition times up to 30 min.

were not influenced when, during  $T$  adjustment, the laser beam ( $\lambda_0 = 514$  nm,  $P \lesssim 400$  mW) was (horizontally) directed onto the sample or blocked. Since  $\nu_1$  and  $\nu_3$  are strongly polarized ( $\approx 10^3 : 1$ ), it is sufficient to measure the parallel component for evaluating  $J(\omega)_{iso}$ . The shapes (see Fig. 1) were fitted with inverse polynomials, i.e.,  $J(\omega)_{exp} = [\sum_{n=0}^4 a_n(\omega - \omega_0)^n]^{-1}$ . Except for the critical region in the  $(N_2O)_{0.05}-Xe_{0.95}$  mixture, the  $J(\omega)$  were close to ordinary Lorentzians. In the  $(N_2O)_{0.05}-(CO_2)_{0.95}$  mixture we could only determine  $\nu_3^{N_2O}$  due to strong overlap of  $\nu_1^{N_2O}$  with the tenfold more intense  $2\nu_2^{CO_2}$  mode near  $1285$   $cm^{-1}$ . Figure 2 summarizes the dependencies of FWHM on  $T$  in the different chemical environments. When approaching  $T_c$  from the two-phase region, in the neat liquid the comparatively broad lines ( $\nu_1, \nu_3$ ) narrow. The  $\nu_3$  line in the  $(N_2O)_{0.05}-(CO_2)_{0.95}$  mixture also narrows near  $T_c$ ; however, the overall effect is of smaller magnitude, whereas the well-known CLB effect becomes clearly evident for both lines in the  $(N_2O)_{0.05}-Xe_{0.95}$  mixed fluid.

In Fig. 3, the three data sets showing line narrowing are scaled to their individual  $T_c$  to examine in greater detail the behavior in close proximity to  $T_c$ . In the neat fluid, any indication of CLB is missed. Our highest quality data (i.e., those of  $\nu_1$ ) limit the  $T$  range where such a broadening might exist to  $-10^{-4} \leq \Delta T^* \leq 10^{-5}$  (it is easier to approach  $T_c$  from  $\Delta T > 0$ ). The  $\nu_1$  line (in Fig. 3) most clearly shows that even minor contributions of CLB are not present (even an effect as low as  $0.05$   $cm^{-1}$  would be sufficient to smooth the sharp edge at  $T_c$  [22]).

The  $FWHM(T)$  resemble the temperature dependence of the orthobaric liquid density  $\rho(T)$  near  $T_c$  [21], therefore the underlying broadening mechanism of the IRLS is expected to be highly density correlated. The inset in

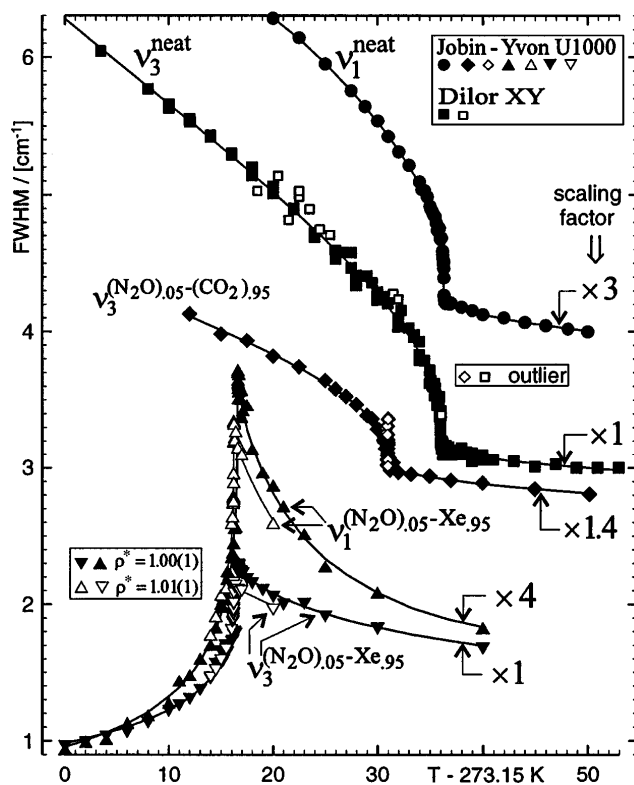


FIG. 2. Line narrowing vs critical line broadening of  $\nu_1^{N_2O}$  ( $\approx 1285$   $cm^{-1}$ ) and  $\nu_3^{N_2O}$  ( $\approx 2220$   $cm^{-1}$ ) in the fluids  $N_2O$ ,  $(N_2O)_{0.05}-(CO_2)_{0.95}$ , and  $(N_2O)_{0.05}-Xe_{0.95}$ . The curves are scaled by appropriate factors to allow an easy comparison. Widths are corrected for finite slits ( $\Delta_{slit}^U, \Delta_{slit}^D = 1.0, 0.5$   $cm^{-1}$ ). The rms fluctuations in  $T$  are  $\leq 1$  mK. If not stated otherwise the critical density has been matched within 1%. Note, that each data set is obtained over periods of weeks in cycles of lowering and raising temperature.

Fig. 3 proves this nearly linear interdependence between half-width and density. To account for the crossover from critical to noncritical temperature dependence of thermodynamic properties a power law expansion is usually used [8], e.g., for the reduced density  $\Delta \rho^*$  along the coexistence line

$$\Delta \rho_{cxc}^* = \pm A |\Delta T^*|^\beta \left[ 1 + \sum_{k=1}^n a_k^{(n)} |\Delta T^*|^{-k\Delta} \right],$$

where  $\beta = 0.326(2)$  is the order parameter exponent of the three-dimensional Ising model and  $\Delta = 0.51(3)$  is the Wegner correction. With  $FWHM \propto \rho$  and  $n = 2$  this expansion is sufficient to characterize the dependencies in Fig. 3. Using  $T_c$ ,  $A$ ,  $\beta$ , and the  $a_k^{(2)}$  as adjustable, and  $\Delta = 0.51$  as fixed, parameters, we obtained a critical exponent of  $\beta_{FWHM} = 0.30(5)$  from our highest quality data ( $\nu_1^{neat}$ ). This result depends somewhat on the choice of  $n$ .  $T_c$  could be fixed in this fit within  $\pm 1$  mK. The noisier data sets in Fig. 3 produce  $\beta_{FWHM} = 0.35(10)$ . Thus, as should be expected, the power law behavior observed for  $FWHM(T)$  is closer to the three-dimensional

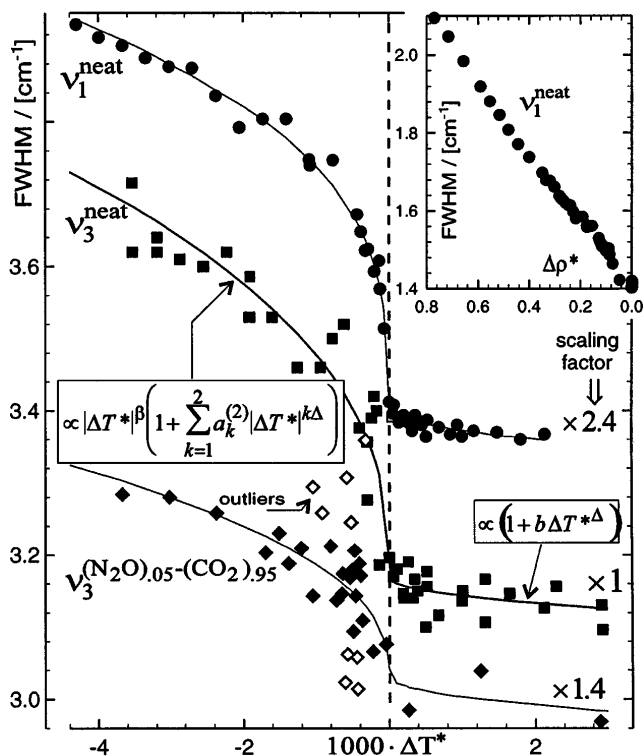


FIG. 3. Line narrowing in the range  $T_c - 1.5 \text{ K} \leq T \leq T_c + 0.9 \text{ K}$ . The full lines are the result of a Wegner expansion (see the expression inside) with fixed  $\Delta = 0.51$ . The highest quality data ( $\nu_1^{\text{neat}}$ ) result in  $\beta = 0.30(5)$ . The inset shows the direct correlation between width and density.

Ising-like behavior of  $\rho(T)$  rather than to the classical mean-field behavior.

What are the reasons for this strong correlation between width and density? Considering the nature of the comparatively broad IRLS of the polarized modes in dense  $\text{N}_2\text{O}$ , it was argued [19] that resonant coupling (RC) between adjacent molecules should be the most effective of the competing broadening mechanisms [15]. However, this conclusion might have been questionable because the authors in [19] were forced to approximate the thermodynamic state dependencies of the individual mechanisms by theoretical expressions which were not well proven experimentally. To avoid any arbitrariness, we studied in detail the  $x$  dependencies of  $J(\omega)^{\nu_1}$  and  $J(\omega)^{\nu_3}$  in liquid mixtures of  $\text{N}_2\text{O}$  with its isotopomers  $^{15}\text{NNO}$  and  $\text{N}^{15}\text{NO}$  as well as  $\text{Xe}$  and  $\text{CO}_2$  [23]. Fortunately, the predictions in [19] were completely confirmed; i.e., chemical as well as isotopic dilution lead to a large line narrowing (see Fig. 1) which has never been observed before in any other liquid. The polarized modes in  $\text{N}_2\text{O}$  are among the rare cases where resonance coupling *dominates* the IRLS of a liquid. Thus, we understand the observed anomalous line narrowing as a switch off of RC, caused by the significant decrease of  $\rho(T)$  for  $T \leq T_c$ . In other words, when RC (as a predominantly two-oscillator process [16]) dom-

inates line broadening, it becomes insensitive to critical fluctuations. The line narrowing observed in the mixture  $(\text{N}_2\text{O})_{0.05}-(\text{CO}_2)_{0.95}$  does not contradict this statement because a residual (nonresonant) interaction between  $\text{N}_2\text{O}$  and  $\text{CO}_2$  (with a similar density dependence as in the neat system) cannot be excluded.

In Fig. 4 the  $\lambda$ -shaped curves of the  $(\text{N}_2\text{O})_{0.05}\text{-Xe}_{0.95}$  mixed fluid are depicted in a log-log plot to show that  $\lim_{\Delta T^* \rightarrow \pm 0} \text{FWHM}(T) = \text{const}$  and  $\lim_{\Delta T^* \rightarrow \pm 0} \partial \text{FWHM}(T) / \partial T = 0$ . It must be stressed that we did not find any indication that  $\text{FWHM}(T)$  diverges near  $T_c$ . At least several among the thousands of individual spectra which were measured (with integration times of 30 s) in the vicinity of  $T_c$  over a period of 1 week would have matched, by chance, the critical temperature even better than  $|\Delta T^*| < 10^{-5}$ . If  $\text{FWHM}(T)$  diverges in this very narrow range, a “sudden” and instantaneous *broadening* of individual spectra would have been observed. This was never the case. The early results in [1] gave first hints that CLB may cross over into a constant width for  $10^{-3} \leq |\Delta T^*| \leq 10^{-2}$ . Mukamel *et al.* [6] have made reference to these experimental observations to justify the results of their hydrodynamic mode-coupling model which predicts  $\lim_{\Delta T^* \rightarrow \pm 0} \partial \text{FWHM}(T) / \partial T = 0$ . Our data in Fig. 4 confirm this proposed flattening of

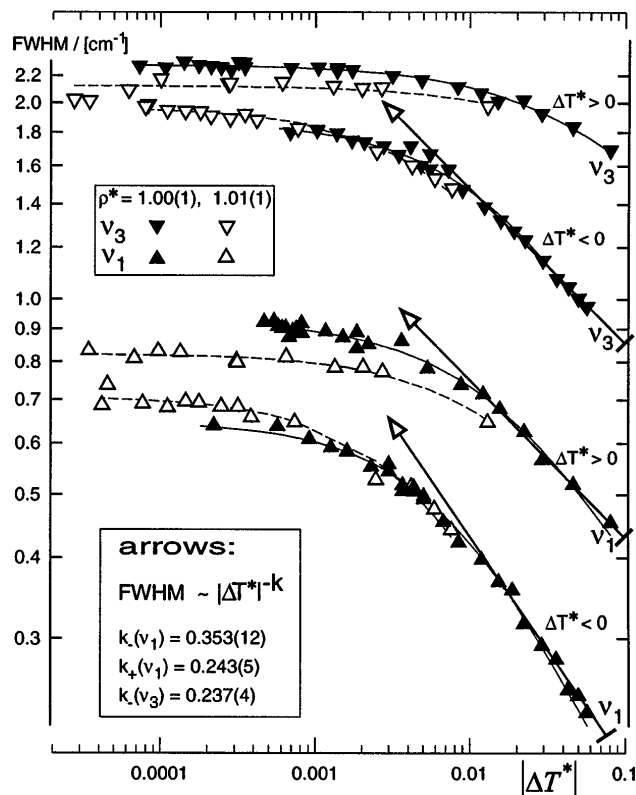


FIG. 4. Critical line broadening of the  $\nu_1$  and the  $\nu_3$  mode in the mixture  $(\text{N}_2\text{O})_{0.05}\text{-Xe}_{0.95}$ . Note the log-log plot. The arrows show the slope resulting from a fitting procedure for  $|\Delta T^*| > 0.01$ , i.e.,  $|\Delta T| \geq 3 \text{ K}$ .

FWHM( $|\Delta T|$ ) as close as  $|\Delta T^*| \geq 10^{-5}$ , i.e., well inside the region between  $T_c$  and the crossover.

In conclusion, our measurements show (1) that the critical dependencies of the purely environmentally induced broadening are completely different from those caused by intermolecular vibrational (resonance) couplings and (2) that any diverging line broadening can be excluded for  $|\Delta T^*| \geq 10^{-5}$ , or more precisely, approaching  $T_c$ , the isotropic linewidth of uncoupled vibrational states increases regressively up to a finite critical width below  $|\Delta T^*| \leq 10^{-3}$ .

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- [20] A 4.7 k $\Omega$  thermistor was used to probe the temperature fluctuations and to control the heater (power  $P < 2$  W). Its characteristic line was fitted (1 K range) to the characteristic line of a Pt 100 resistor. For testing purposes the heat transport between the copper and the fluid was probed by an additional 4.7 k $\Omega$  thermistor immersed in a low vapor pressure liquid (hexane). Equilibration could be called instantaneous in the time scale of our experiment and mK  $T$  resolution; see A. Onuki, H. Hao, and R.A. Ferrell, *Phys. Rev. A* **41**, 2256 (1990), and J. Straub and L. Eicher, *Phys. Rev. Lett.* **75**, 1554 (1995). No effort was made to calibrate the Jena and Salzburg temperature setting devices against each other, therefore a systematic error of  $\pm 100$  mK is expected.
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- [22] Outliers of the  $(N_2O)_{0.05}-(CO_2)_{0.95}$  data set near  $\Delta T^* \approx -5 \times 10^{-4}$  in Figs. 2 and 3 are inadequate to indicate CLB.
- [23] D. Keutel, F. Seifert, and K.-L. Oehme (to be published): Even a small shift of the vibrational energy of the surrounding molecules [i.e.,  $\hbar(\omega_i^{N_2O} - \omega_i^{^{15}N_2O}) < k_B T$ ] decreases the efficiency of the intermolecular coupling to a large extent. Furthermore, the dilution in  $CO_2$  and the two isotopic dilutions are nearly indistinguishable. This justifies our use of  $CO_2$  as a surrogate for the expensive isotopomers  $^{15}N_2O$  and  $N^{15}NO$ . The concentration dependence can be parametrized according to  $FWHM(x_{N_2O}) = A_0 + A_1 x - A_2 x^2$ . For  $\nu_3$  and 218 K we obtain  $A_n\{Xe, N^{15}NO, CO_2\}$  in  $[cm^{-1}]$  as  $A_0 = \{0.36(6), 4.8(1), 3.98(4)\}$ ,  $A_1 = \{10.5(3), 6.4(6), 9.1(2)\}$ , and  $A_2 = \{1.2(3), 1.7(6), 3.5(2)\}$ .