

## Critical Raman line shape behavior of fluid nitrogen\*

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**Abstract:** Isotropic Raman line shapes of simple molecular fluids exhibit critical line broadening near their respective liquid–gas critical points. In order to observe this phenomenon, it is essential that the band position of a given vibrational mode is density-dependent, and that vibrational depopulation processes negligibly contribute to line broadening. Special attention was given to the fact that the isotropic (i.e., nonrotationally broadened) line shape of liquid N<sub>2</sub> is affected by resonant intermolecular vibrational interactions between identical oscillators. By means of the well-chosen isotopic mixture (<sup>14</sup>N<sub>2</sub>)<sub>.975</sub> – (<sup>14</sup>N<sup>15</sup>N)<sub>.025</sub>, the temperature and density dependences of shift, width, and asymmetry of the resonantly coupled <sup>14</sup>N<sub>2</sub> and, depending on the S/N ratio available, of the resonantly uncoupled <sup>14</sup>N<sup>15</sup>N were determined, with up to milli-Kelvin resolution, in the coexisting liquid and gas phases and along the critical isochore, using a highest-resolution double monochromator and modern charge-coupled device detection techniques. Clear evidence was found that vibrational resonance couplings are present in all dense phases studied.

### INTRODUCTION

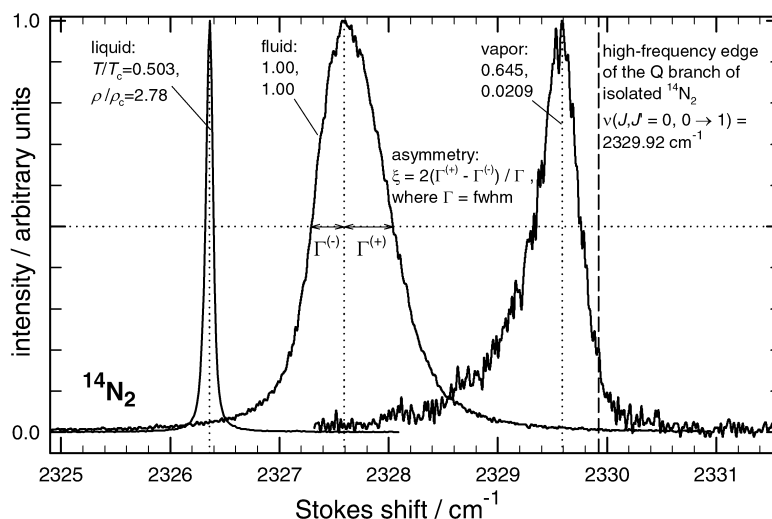
M. J. Clouter and H. Kiefte [1] showed in the late 1970s that the simple fluids N<sub>2</sub>, O<sub>2</sub>, CO, CH<sub>4</sub>, H<sub>2</sub>, and HD exhibit “critical line broadening” (CLB) near their respective liquid–gas critical points, i.e., an impressive additional broadening of their *isotropic* (and therefore rotational invariant) Raman line shapes when approaching the critical point (characterized by its temperature  $T_c$  and density  $\rho_c$ ) along the coexistence line.

Figure 1 exemplifies the Raman line shape  $I(\nu)$  of <sup>14</sup>N<sub>2</sub> measured [3] on the coexistence line in the liquid phase in proximities of the triple point, the critical point  $\{\rho_c = 11.1839(14) \text{ mol l}^{-1} = 0.3133(4) \text{ g cm}^{-3} \text{ at } T_c = 126.192(10) \text{ K [2]}\}$ , and in the vapor phase at the lowest temperature where we could still register a signal with acceptable signal/noise ratio. The most easily accessible line shape parameters which usually are determined as function of temperature, density, or concentration are the line position  $\nu$ , the first moment  $M_1 = \int \nu I(\nu) d\nu / \int I(\nu) d\nu$  (i.e., the center of gravity of a band shape), the full width at half-maximum (fwhm)  $\Gamma$ , and the line asymmetry  $\xi$  (see Fig. 1 for our somewhat arbitrarily chosen definition).

In order to be able to observe the CLB phenomenon for a given vibrational mode it is essential, as we will see, that its band position is strongly correlated with the bulk density  $\rho$  (see Fig. 2). The com-

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**Fig. 1** Raman line shape  $I(\nu)$  of  $^{14}\text{N}_2$  measured on the coexistence line: on the left in the liquid phase in proximity of the triple point, in the middle in proximity of the critical point, and on the right in the vapor phase at the lowest temperature (80 K) where we could still register a signal with acceptable signal/noise ratio. According to the most recent equation of state for  $\text{N}_2$  [2]: critical temperature  $T_c = 126.192(10)$  K, critical density  $\rho_c = 11.1839(14) \text{ mol l}^{-1} = 0.3133(4) \text{ g cm}^{-3}$ .

mon interpretation of CLB is that the instantaneous frequencies  $\omega(t)$  of a vibrational mode are modulated by critical fluctuations of the density appearing in the vicinity of the gas–liquid critical point of a (neat) liquid:  $\omega(t) = \langle \omega \rangle + \delta \omega(t)$ . These density fluctuations manifest themselves macroscopically in the well-known phenomenon of the critical opalescence. Raman line shapes can therefore be sensitive to large-scale density fluctuations, provided that intra- and intermolecular vibrational depopulation processes negligibly contribute to the line-broadening process (see ref. [3] for our more detailed discussion).

Our primary goal was a quantitative comparison of the CLB and its characteristic  $\lambda$ -shaped temperature dependence with theoretical predictions [4,5], which could not be clearly proved up to the present days. Therefore, our intention was to improve the precision of the available experimental database, in order to shed light on a possible relation between CLB and the well-known universal power law behavior of some thermodynamic functions (like density [6], isothermal compressibility, isochoric heat capacity) near critical points,  $F(T) \propto |\Delta T^*|^\lambda$ , with  $\Delta T^* = (T - T_c)/T_c$  being the reduced relative temperature and  $\lambda$  a critical exponent (for a review, see ref. [7]).

## CRITICAL LINE SHAPE BEHAVIOR IN FLUID $\text{N}_2\text{O}$

Our first Raman spectroscopic study on CLB [8] addressed the question if this is really an universal phenomenon, which might sometimes be overlooked due to an insufficient approach to  $T_c$ . In fact, different research groups had observed CLB in  $\text{N}_2$ ,  $\text{O}_2$ , HD,  $\text{H}_2$ , CO,  $\text{CO}_2$ ,  $\text{CH}_4$  [1],  $\text{CD}_4$ ,  $\text{H}_2\text{S}$  [9], but it was undetectable in  $\text{CF}_4$  [1] and  $\text{C}_2\text{H}_6$  [10].

The temperature dependence of the Raman line width of the two polarized vibrational modes  $\nu_1$  and  $\nu_3$  of  $\text{N}_2\text{O}$  was determined along the liquid–gas coexistence line and along the critical isochore with milli-Kelvin resolution: (a) in the neat fluid, where the molecular oscillators are mostly influenced by the resonant intermolecular coupling RC [11]; (b) in  $\text{N}_2\text{O}$  diluted in an  $\text{N}_2\text{O}$  isotopomer (which was approximated by the isoelectronic  $\text{CO}_2$  for budget reasons) in order to (nearly) remove RC; and (c) in  $\text{N}_2\text{O}$  diluted in fluid xenon in order to remove *all* intermolecular couplings, therefore only pure dephasing

PD [12] staying still active. These temperature dependences of the line width showed quite opposite behaviors when approaching the respective critical points. In the cases (a) and (b), an up-to-now unique, highly density-correlated line *narrowing* was observed, ascribed to the gradual switch-off of RC with decreasing density of the fluid (see Figs. 2 and 3 in ref. [8]). In other words, when line broadening is dominated by the resonant intermolecular coupling (which is a predominantly two-oscillator process [11]), it becomes insensitive to critical density fluctuations. Opposite to this, in the case (c) the  $\lambda$ -shaped effect of CLB was observed, the uncoupled  $\text{N}_2\text{O}$  oscillators acting as probes sensing the critical density fluctuations within their environment. In accord with the theoretical predictions [4,5], the isotropic line width of uncoupled  $\text{N}_2\text{O}$  broadens up to a finite width, reached for  $|\Delta T^*| \leq 10^{-3}$  (i.e., the static limit, in which the lifetime of the critical density fluctuations is long compared to the spectral line width [4,18]). As a consequence of the experimental results, any divergence of CLB was to be excluded for  $|\Delta T^*| \geq 10^{-5}$ .

Thus, the fact that critical line *broadening* can only be observed in *uncoupled* systems is the most generalizable result of our  $\text{N}_2\text{O}$  study [8]. In other words, the line shape phenomena observable near critical points are completely different whether resonant or nonresonant vibrational interactions dominate the line broadening.

According to the conclusions reached in our study of CLB in  $\text{N}_2\text{O}$  [8], a quantitative comparison of experimental CLB results with the theoretical predictions [4,5] can therefore be only self-consistent if one can unambiguously discern between resonant and nonresonant contributions to the line broadening, this being only possible when using isotopic mixtures. The well-known advantage of an isotopic mixture is that RC can be gradually switched off by isotopic dilution without changing the chemical environment [13].

## ISOTOPIC DILUTION EXPERIMENTS IN $\text{N}_2$ AND IN $\text{O}_2$

A detailed analysis of the rotational-invariant isotropic scattering is best feasible for the vibrational modes of diatomic molecules, since in this case there are no disturbances from nearby-lying fundamentals, and only small and therefore well-controllable ones from hot bands. The drawback of isotopic mixtures using diatomic molecules is that one has to handle expensive (isotopic mixtures of) cryogenic fluids. The most suitable system for CLB studies is fluid  $\text{N}_2$ , since the width of the  $^{14}\text{N}$ - $^{14}\text{N}$  vibrational mode in the resonantly coupled system ( $\text{N}_2$  in its natural isotopic composition) at the critical point is nearly eight times the minimum width observable around the normal boiling [1]. However, before studying CLB in the isotopic  $\text{N}_2$  system, it was necessary to experimentally determine the influence of RC on its line shape. We therefore first performed dilution experiments to gradually remove RC in the three mixtures attainable from the  $^{14}\text{N}/^{15}\text{N}$  isotopes, and for comparison purposes in the  $^{16}\text{O}_2$ - $^{18}\text{O}_2$  isotopic mixtures [14] (both systems at the normal boiling point of  $\text{N}_2$ ), in order to study concentration-dependent line shape phenomena of the N-N and of the O-O vibrational mode. Associated with these experiments was the question if the *switch-off* of RC in liquid  $\text{N}_2$  at 77 K might have lead to a line *broadening*. This unusual phenomenon, theoretically explained by a destructive interference between different mechanisms which modulate the vibrational coordinate in a neat state [11], remained experimentally unchecked for many years, although molecular dynamics simulation results [15] predicted its existence for  $\text{N}_2$ .

Indeed, the removal of RC leads to quite different behaviors in the  $\text{N}_2$  and the  $\text{O}_2$  systems: the band shifts of the  $\text{N}_2$  systems with dilution are oriented toward higher wavenumbers (which one would generally expect), while in the  $\text{O}_2$  systems they are oriented toward lower ones. We were able to show that the change in position  $\nu_i(T, p, x_i)$  from the completely coupled case (neat liquid,  $x_i = 1$ ) to the completely uncoupled case (infinite dilution,  $x_i \rightarrow 0$ ) becomes invariant under a change of the isotopomer  $i$  ( $^{14}\text{N}_2$ ,  $^{15}\text{N}_2$ ,  $^{14}\text{N}^{15}\text{N}$ , and accordingly,  $^{16}\text{O}_2$ ,  $^{18}\text{O}_2$ ), if we scale  $\nu_i(T, p, x_i)$  according to

$$v_i^* = \frac{v_i(T, p, x) - v_i(J, J' = 0, 0 \rightarrow 1)}{v_i(J, J' = 0, 0 \rightarrow 1)}, \quad (1)$$

where the scaling quantities  $v_i(J, J' = 0, 0 \rightarrow 1)$  are the high-frequency edges of the  $Q$  branches in the isolated oscillators [14].

Additionally, the *switch-off* of RC indeed causes an *increase* of the line width in the  $N_2$  systems (in quantitative agreement with the prediction of ref. [15]), while it causes a *decrease* in the  $O_2$  systems, i.e., which one would generally expect. Moreover, there is nice agreement between the experimental concentration dependence of the line width and its predicted parabolic dependence by the fast modulation model [11]. This confirms that even a *linear* concentration dependence of the line shift allows the observation of a *parabolic* dependence of the width with its maximum at 0.5 units of mole fraction, reflecting the analog dependence of the concentration fluctuations.

The different behaviors in the  $N_2$  and the  $O_2$  systems convincingly show the high sensitivity of the Raman band to details of the intermolecular interactions.

## CRITICAL LINE SHAPE BEHAVIOR IN FLUID $N_2$

The successful measurement of the concentration dependence of the line position and shape at 77 K [14] allowed us to continue with the most demanding part of the experiment, the measurement of the temperature dependence of the line shape parameters of the N–N stretching mode (1) along the coexistence line in the liquid *and* the vapor phase up to the critical point and (2) along the critical isochore up to room temperature [3]. The advantage of using an isotopic system like  $(^{14}N_2)_{0.975} - (^{14}N^{15}N)_{0.025}$  is the possibility to simultaneously observe the resonantly coupled case  $^{14}N_2$  and the uncoupled case  $^{14}N^{15}N$ .

### Experimental

The critical sample was a mixture of composition  $(^{14}N_2)_{0.975} - (^{14}N^{15}N)_{0.025}$  with the reduced density  $\rho^* = \rho/\rho_c = 1.000(5)$  at  $T_c$ , placed in a large heat-capacity “shell-in-shell” construction contained in a liquid nitrogen-cooled bath cryostat (stability  $\pm 200$   $\mu$ K) capable of a temperature range  $74 \text{ K} \leq T \leq 300 \text{ K}$ . In order to extend this temperature range down to 45 K, a closed-cycle Helium cryostat was used, containing in a single-shell construction a second sample consisting of  $(^{14}N_2)_{0.993} - (^{14}N^{15}N)_{0.007}$  (natural abundance) with  $\rho^* = 1.75(5)$  at  $T_c$  (see ref. [3] for a more detailed description).

The Raman spectroscopic experiment was performed under  $90^\circ$  scattering geometry. As excitation source an  $Ar^+$  ion laser in single-mode single-frequency was used, with 250-mW light power at 514.5319 nm. The scattered Raman light was analyzed with the help of a highest-resolution double spectrometer (Sopra DMDP 2000, first stage in single pass, second stage in double pass). The fwhm of the apparatus profile was  $0.050 \text{ cm}^{-1}$  using a 50- $\mu$ m entrance slit. The light detector was a liquid nitrogen-cooled CCD camera, which collects a spectral region of about  $7 \text{ cm}^{-1}$ . Spectra acquisition was done with integration times between 60 and 600 s, and 10 to 15 spectra for each temperature set. In order to compensate for thermal instabilities of the instrument, a continuous calibration of the Raman band positions was necessary, using xenon and krypton spectral lamps.

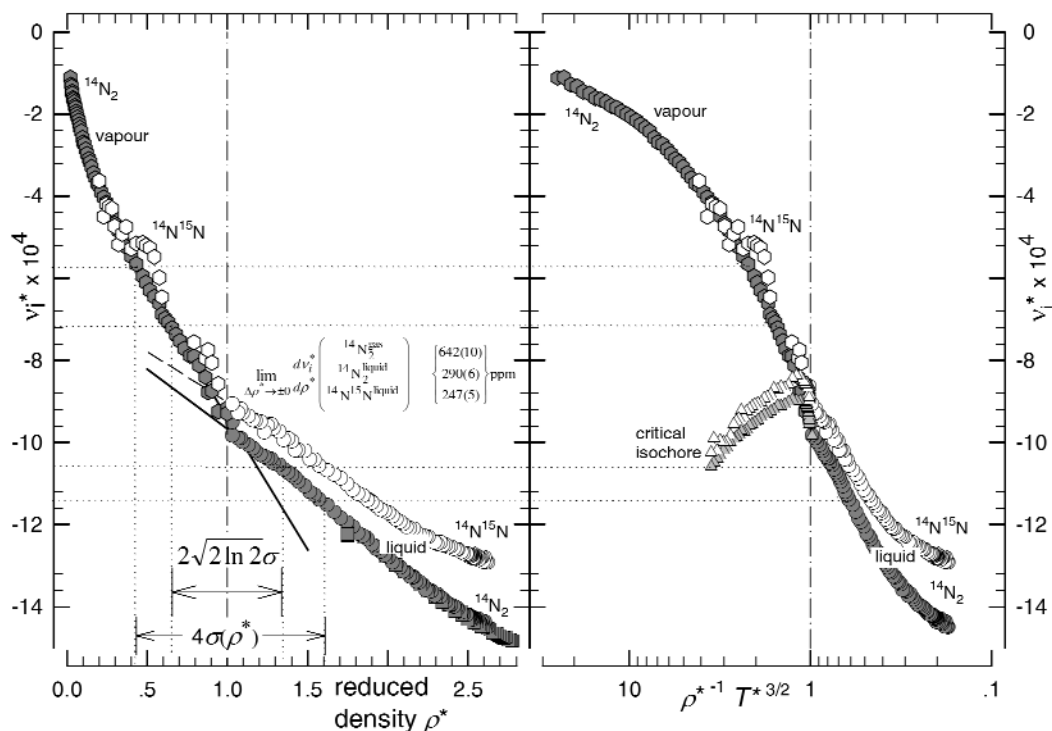
## RESULTS AND DISCUSSION

The temperature and density dependences of the line shift, width and asymmetry of the coupled  $^{14}N_2$  and, depending on the S/N ratio available, of the uncoupled  $^{14}N^{15}N$  were followed in the range  $45 \text{ K} \leq T \leq 300 \text{ K}$  with up to milli-Kelvin resolution (1) in the  $\beta$ -solid phase, (2) in the coexisting liquid and gas phases and (3) along the critical isochore. The results presentend in ref. [3] are evidence more of the temperature dependence under orthobaric conditions, while in the present paper we deal

more with the density dependence, extracted from our original data [3] by converting the temperature dependence to the density dependence  $\rho^{(\text{liquid})}(T)$  and  $\rho^{(\text{gas})}(T)$  using the most recent equation-of-state published in ref. [2].

It is well known that the “isolated binary collisions” and the hydrodynamic models for pure dephasing [12], originally developed for an harmonic oscillator in a repulsive environment, lead (under isochoric conditions) to a  $T^{3/2}$  dependence of the dephasing process, and therefore of the line broadening. Because nitrogen is the most harmonic molecular oscillator, additionally weakly coupling with its surroundings, it seems to be natural to assume that this  $T^{3/2}$  dependence holds true for the noncritical “background” broadening. As was shown in ref. [3] along the critical isochore ( $\rho^* = 1$ ), this is indeed the case. This  $T^{3/2}$  dependence of the “repulsive” dephasing is the reason why we compare the density dependence of the three line shape parameters shift, width, and asymmetry in two different ways: on the left side of Figs. 2, 3, and 4, they are depicted as function of the (reduced) density  $\rho^*(T)$ , and on the right side as a function of  $T^{*3/2}/\rho^*(T)$ , where the  $(\rho^*)^{-1}$ -dependence accounts for the density dependence of the collision rate.

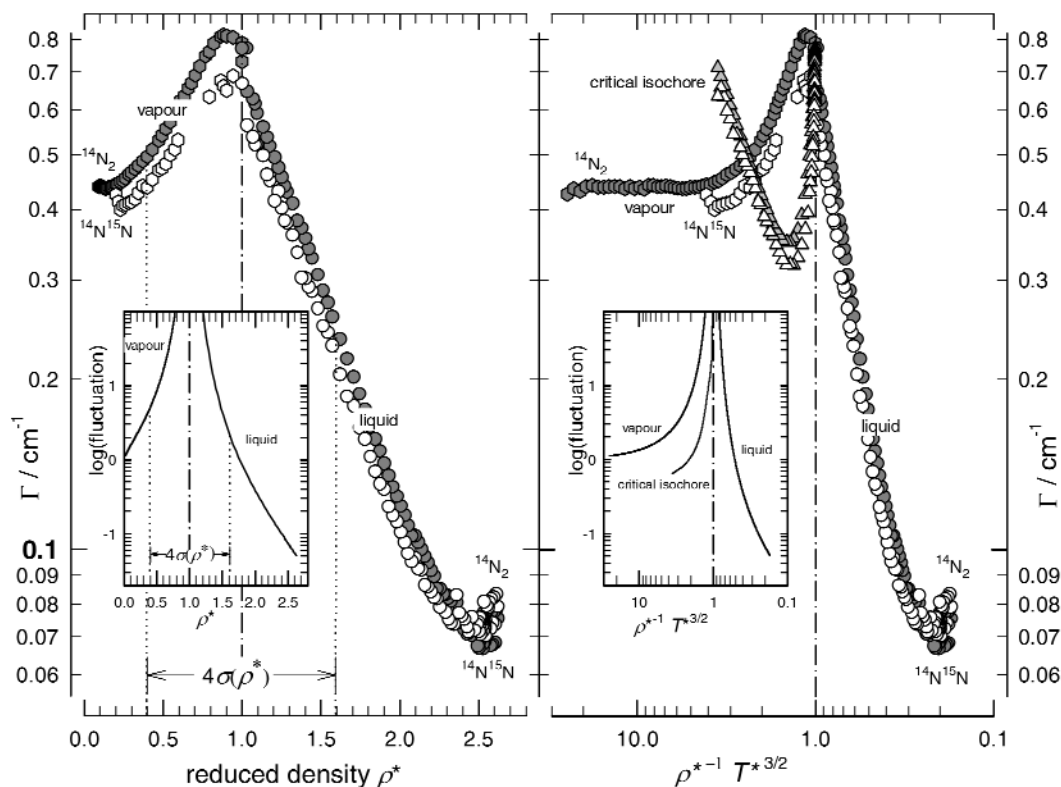
Figure 2 shows the dependence of the scaled line shift  $\nu_i^*$  in the resonantly coupled state  $^{14}\text{N}_2$  and in the uncoupled state  $^{14}\text{N}^{15}\text{N}$  in the coexisting liquid and vapor phase and along the critical isochore. The increasing difference in line shift between the resonantly coupled  $^{14}\text{N}_2$  and uncoupled  $^{14}\text{N}^{15}\text{N}$  with density is the clear evidence that RC is present in all dense phases studied. The comparison of the shift in the coexistence region, Fig. 2, with the shift in the isochoric region of Fig. 2 in ref.



**Fig. 2**  $^{14}\text{N}_2$  and  $^{14}\text{N}^{15}\text{N}$  shift phenomena vs. reduced density  $\rho^* = \rho/\rho_c$  (left) and vs.  $(T^*)^{3/2}/\rho^*$  (right) along the liquid–gas coexistence line and the critical isochore ( $\rho^* = 1$ ). The scaled shifts  $\nu_i^*$  were determined by means of the same procedure adopted in ref. [14] (note that  $\nu_i^* = 1 \times 10^{-4}$  corresponds to a total shift of  $\approx 0.23 \text{ cm}^{-1}$ ). The double arrows indicate the assumed 95 % probability range,  $4\sigma$ , and the fwhm,  $2\sigma\sqrt{2\ln 2}$ , of the density distribution  $P(\rho^*)$  in the static limit. The line width, Fig. 3, and in particular the line asymmetry, Fig. 4, directly reflect the extent of  $P(\rho^*)$  and therefore of the density fluctuations  $\delta\rho^*$  (in this case,  $\delta\rho^* = 0.35$ ).

[3] shows that the line position results more density- than temperature-dependent. We would like to remark that in the coexisting vapor phase, a linear relation  $\log(v_i^*) = a \log(T^{*3/2}/\rho^*) + b$  holds remarkably well. See the left side of Fig. 2; it is noteworthy that the gradients of the shift with density in the different phases behave as  $|dv^*/d\rho^*|_{\text{gas}} \approx 2 * |dv^*/d\rho^*|_{\text{liquid}}$ , and that the line shift in both phases is an approximately linear function of density. Both facts have also been recently observed in an isothermal experiment regarding the line shift of the symmetric C–F stretching mode in supercritical  $\text{CHF}_3$  in proximity of its critical point (see Fig. 3 in ref. [16]).

In Fig. 3, the dependence of the line width for the coexisting densities of the liquid and the vapor phase and along the isochoric region is shown. The previously mentioned unfamiliar phenomenon of a larger line width of the resonantly *uncoupled* states of  $\text{N}_2$  compared to that of the *coupled* states (see the concentration dependence of the line width in Fig. 2 of ref. [14]) has been once more confirmed by the change in width observed in the liquid at around 90 K for the coupled  $^{14}\text{N}_2$  and uncoupled  $^{14}\text{N}^{15}\text{N}$  state (see the temperature dependence of the line width in Fig. 5 of ref. [3]). Figure 3 shows that the change in sign happens at around  $\rho^* \approx 2.4$ , the uncoupled state being broader for  $\rho^* \geq 2.4$ . One may therefore conclude that the (negative) cross-correlations between resonant and nonresonant dephasing mechanisms [11] dominate the always positive auto-correlation terms above a certain threshold density. The density dependence of the line width of the symmetric C–F stretching mode observed in supercritical  $\text{CHF}_3$  in proximity of its critical point (see Fig. 3 in ref. [16]) resembles the behavior presented on the left side of Fig. 3. The broadening effect of  $\text{N}_2$  when moving along the coexistence line from the



**Fig. 3**  $^{14}\text{N}_2$  and  $^{14}\text{N}^{15}\text{N}$  width phenomena vs. reduced density  $\rho^* = \rho/\rho_c$  (left) and versus  $(T^*)^{3/2}/\rho^*$  (right) along the liquid–gas coexistence line and the critical isochore ( $\rho^* = 1$ ).  $\Gamma$  is the full width at half-height of the isotropic Raman band, and in the static limit  $\Gamma$  is a measure of the extent of the density fluctuations  $\delta\rho^*$ . The inset shows the dependence of the thermodynamical density fluctuations  $\langle\Delta N^2\rangle/N$ , calculated from the equation-of-state [2], see also ref. [3].

high-density region to the critical point ( $\rho^* = 1.000(5)$ ,  $|\Delta T^*| \geq 10^{-5}$ ) is about a factor of 10, demonstrating that the nitrogen system is much better suited to study critical line shape phenomena than a more chemically relevant system like  $\text{CHF}_3$ , which is subject to a much more effective *noncritical* background broadening likely caused by strong *intramolecular* couplings, potentially concealing the CLB phenomenon.

The insets in Fig. 3 shows the dependence of the thermodynamical density fluctuations  $\langle \Delta N^2 \rangle / N = N/V k_T k_B T$ , with  $N/V$  being the particle density and  $k_T$  the isothermic compressibility, calculated from the equation-of-state [2] (see also ref. [3]). Note the analog behavior of the line width, apart of the fact that the density fluctuations diverge at the critical point, while the line width attains a constant maximum value. In ref. [3], we have clearly proved, in accordance with the theoretical predictions [4,5], that both the width and the asymmetry converge to a constant maximum value regardless if the critical point is reached from below  $T_c$ , along the coexistence line, or from above  $T_c$ , along the critical isochore, i.e., they do not diverge approaching the critical temperature up to our closest value  $|T/T_c - 1| \approx 10^{-5}$  (see Fig. 7 in ref. [3]). The use of critical exponents resulting from renormalization theory instead of classical exponents resulted in a better description of the cross-over between a compressibility-driven region far from the critical point to a diffusion-driven *static* regime at  $|T/T_c - 1| \leq 10^{-3}$  which causes the saturation of the line-broadening process driven by the critical density fluctuations [4,5].

When approaching the critical point either along the coexistence line or along the critical isochore, the above-mentioned  $\lambda$ -shaped temperature dependence of the width parameters is much more evident in the line asymmetry  $\xi$  than in the usually considered line width (see Figs. 5 and 8 in ref. [3]). The peculiar behavior of  $\xi$  in the liquid and vapor phase for  $|T/T_c - 1| \leq 4 \times 10^{-2}$ , already discussed in ref. [3], can be better appreciated if, as in the present Fig. 4,  $\xi$  is shown as function of  $\rho^*(T)$  or as function of  $T^{*3/2}/\rho^*(T)$ . This extraordinary sensitivity of the line asymmetry to changes of the local environment can be phenomenologically understood if one considers (a) the different gradients  $|dv^*/d\rho^*|$  in the liquid and in the gas phase,  $|dv^*/d\rho^*|_{\text{gas}} \approx 2 |dv^*/d\rho^*|_{\text{liquid}}$  (see Fig. 2), and (b) the asymmetric distribution  $P(\rho^*)$  of density fluctuations  $\delta\rho^*$  around the bulk value  $\langle \rho^* \rangle$ , always directed with the broader wing toward  $\rho^* = 1.0$  [17,18].

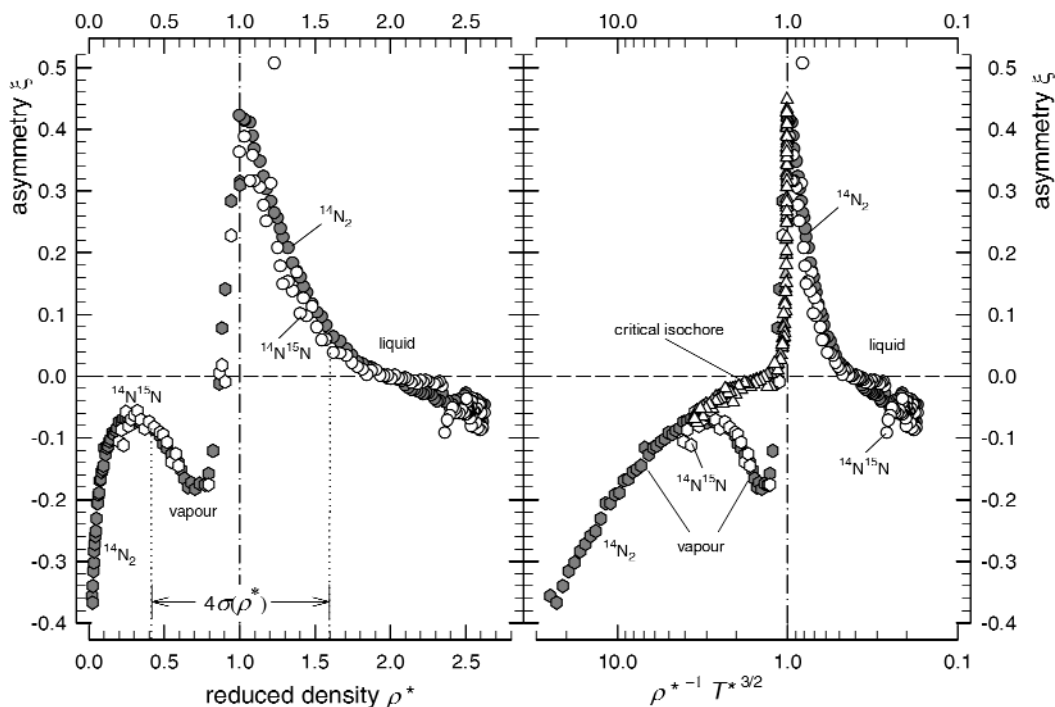
In the liquid phase, the positive asymmetry observable for densities  $\rho^* < 1.6$  is thought to be caused by the increasingly asymmetrical distribution  $P(\rho^*)$  approaching the critical point [17,18], favoring frequencies  $v^*(\rho^*)$  at  $\rho^* < \langle \rho^* \rangle$  compared to those at  $\rho^* > \langle \rho^* \rangle$ . Closest to the critical point,  $P(\rho^*)$  becomes broadest but more symmetric, the density fluctuations now also covering an increasing range of gas-state densities. The latter, having a larger gradient  $|dv^*/d\rho^*|$ , maintains the positive asymmetry.

In the gas phase, the asymmetric distribution of  $\Delta J = 0$  transitions in the  $Q$  branch is reflected by the negative asymmetry at low densities. With increasing density, the magnitude of the negative asymmetry diminishes due to the increasing collision rate. For  $\rho^* > 0.4$ , a further approach to the critical point is accompanied by the increasingly asymmetrical distribution  $P(\rho^*)$  [17,18], favoring frequencies  $v^*(\rho^*)$  at  $\rho^* > \langle \rho^* \rangle$  compared to those at  $\rho^* < \langle \rho^* \rangle$ , leading to the increasingly negative asymmetry. Very close to the critical point ( $|\Delta T^*| \approx 10^{-3}$ ), i.e., as soon as the now more symmetrical  $P(\rho^*)$  also covers liquid densities with  $|dv^*/d\rho^*|_{\text{liquid}} < |dv^*/d\rho^*|_{\text{gas}}$ , the asymmetry is switched to the positive value encountered on the coexisting liquid curve and on the critical isochore.

Some simple assumptions allow one to estimate the magnitude of the average local density fluctuations (also called local density enhancements),

$$\delta\rho^* = \rho^* - \langle \rho^* \rangle. \quad (2)$$

As Fig. 4 shows, the influence of critical density fluctuations is restricted to the range between  $\{\rho^*_{\text{gas}}, \rho^*_{\text{liquid}}\} \approx \{0.4, 1.6\}$ , being equivalent to a temperature range  $|\Delta T^*| \leq 4 \times 10^{-2}$ . If, for simplicity, one assumes that at the critical point  $P(\rho^* = 1.0)$  is a Gaussian with a standard deviation parameter



**Fig. 4** Band asymmetry according to  $\xi = 2(\Gamma^{(+)} - \Gamma^{(-)})/\Gamma$  vs. reduced density  $\rho^* = \rho/\rho_c$  and vs.  $\rho^{*-1} T^{*3/2}$  along the liquid–gas coexistence line and the critical isochore ( $\rho^* = 1$ ), whereby  $\Gamma^{(+)}$  and  $\Gamma^{(-)}$  define the high-frequency and the low-frequency half-width at half-height, and  $\Gamma^{(+)} + \Gamma^{(-)} = \Gamma$ . In the static limit, the band asymmetry directly reflects the extent of the density fluctuations  $\delta\rho^*$ .

$\sigma$ , and that  $\{\rho_{\text{gas}}^*, \rho_{\text{liquid}}^*\} \approx \{0.4, 1.6\} = 4\sigma$  covers 95 % of  $P(\rho^* = 1.0)$ , then the fwhm of  $P(\rho^*)$  is  $2\sigma\sqrt{2\ln 2} = 0.7$ , and therefore  $\delta\rho^* = 0.35$ , a value that compares reasonably well with that presented in ref. [16], but obtained in a different way, and with the theoretically estimated value of ref. [19]. From our value  $\delta\rho^* = 0.35$ , one can determine with the help of Fig. 2 the width and the asymmetry of the line. As reported in ref. [3], the values obtained compare very well with the measured values.

## CONCLUSIONS

Our results clearly demonstrate the exceptional sensitivity of the Raman line shape parameters (shift, width, asymmetry) even of nearly harmonic molecular oscillators to any changes of the intermolecular potential and of the thermodynamic state, provided that intramolecular couplings do not dominate the broadening processes of that band shape.

The influence of critical density fluctuations on the line shape of  $N_2$  is much more manifest in the line asymmetry than in the usually considered line width. In a critical sample,  $\rho/\rho_c = 1.0$ , this influence starts to clearly show itself at  $|T/T_c - 1| \leq 4 \times 10^{-2}$ , and in accord with the theoretical predictions [4,5,20] the static limit is reached for  $|T/T_c - 1| \leq 10^{-3}$ .

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