

## Vibrational Raman Effect: A New Experimental Probe of the Liquid-Vapor Critical Phenomenon

M. J. Clouter and H. Kiefte

*Department of Physics, Memorial University of Newfoundland, St. John's, Newfoundland A1B 3X7, Canada*

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Accurate interferometric line-shape data have been obtained for the pure vibrational ( $\mathcal{Q}$  branch) component in the Raman spectrum of supercritical  $N_2$ . The data were obtained as a function of reduced temperature [ $\epsilon = (T - T_c)/T_c$ ] under isochoric conditions, and analysis of the data clearly shows for the first time that inhomogeneous broadening is dominant when  $\epsilon < 0.001$  at the critical density. It is proposed that in this static dephasing limit it should be possible to extract information pertaining to the statistical distribution of "local" densities within the fluid.

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Observation of a critical anomaly in the vibrational Raman spectrum of supercritical  $O_2$  was reported from this laboratory in 1978.<sup>1</sup> Since it was known that intermolecular interactions were responsible for the sensitivity of this spectrum to changes in bulk density under noncritical conditions, it was suggested that the anomalous behavior reflected the presence of large-amplitude variations in density within the near-critical fluid. Furthermore, knowledge of the operative van der Waals interaction indicated that these density fluctuations were being probed within a previously unexplored range of  $\sim 1$  nm which is short compared to the  $\sim 1$ - $\mu\text{m}$  range characteristic of Rayleigh scattering experiments (for example).

No claim of quantitative accuracy was made in these initial experiments since they were performed under isothermal conditions in an open system and were subject to the criticism that extraneous fluctuations in the mean density of the sample could have contributed to the observed anomaly. This particular element of uncertainty has been eliminated in the presently reported results; the qualitative features of the originally observed effect are confirmed, and the accuracy of the data permits a detailed line-shape analysis which more fully explores the potential importance of this type of experiment as a probe of short-range (clustering) effects in the critical region.  $N_2$  was considered preferable to the chemically active  $O_2$  because constant-density conditions were to be maintained in a relatively small volume over extended periods of time.

Two other independent experiments have been reported, but have produced null results in the sense that no anomalous behavior was observed. Garrabos *et al.*<sup>2</sup> have reported measurements of Raman shifts in the Fermi diad spectrum of  $CO_2$  in the critical region, but no unusual behavior

was detected. However, their spectra were not resolved, and their result is probably not significant, since the present data (as well as those<sup>1</sup> for  $O_2$ ) clearly show that the anomalous excursions in both the shift and width are of the same order as the noncritical linewidth. Wood and Strauss<sup>3</sup> have reported measurements on the resolved spectrum of the C-C stretch mode in near-critical ethane. In this case the identification of possible reasons for the absence of any critical anomaly is precluded by a lack of information regarding the operative relaxation processes, and this applies in particular to energy, or  $T_1$ , relaxation. Their result is analogous to that for  $CF_4$  as already reported by the present authors<sup>4</sup>:  $CF_4$  was found to be the only one of five simple liquids whose vibrational Raman spectrum did not exhibit a sharp increase in width as the critical point was approached along the coexistence line.

The relative importance of energy relaxation versus adiabatic phase ( $T_2$ ) relaxation is potentially crucial in determining whether a particular system should, or should not, exhibit a critical anomaly of the type in question. As has already been emphasized in the literature,<sup>5</sup>  $T_1$  processes are characterized by transition frequencies of order 10 THz, and are not expected to be sensitive to those low-frequency density fluctuations in the hydrodynamic range (of order gigahertz or less) which constitute the critical phenomenon. Consequently, if the structure of a given vibrational Raman spectrum is primarily determined by such ( $T_1$ ) processes, no critical anomaly is expected. The converse argument can, however, apply if adiabatic phase relaxation is dominant, and such is known to be the case for both  $N_2$ <sup>6</sup> and  $O_2$ .<sup>7</sup>

The spectra being presented were obtained in digital form with a scanning Fabry-Perot inter-

ferometer which has been described in a previous publication.<sup>4</sup> The BeCu sample cell had a mass of 1 kg and provided a sample volume of approximately 0.5 cm<sup>3</sup> with optical access appropriate for 90° scattering in the horizontal plane. Isochoric conditions were maintained via an externally activated isolation valve which was incorporated into the body of the cell with a closure point located 5 mm from the scattering volume. The cell was cooled by a closed-cycle cryogenerator, and a temperature stability of ±5 mK was provided by a two-stage controller whose second stage utilized a calibrated Pt thermometer in conjunction with a programmable digital ohmmeter. The beam from a single-mode Ar<sup>+</sup> laser source ( $\lambda = 514.5$  nm) was focused to a diffraction-limited diameter of  $\sim 10$   $\mu\text{m}$  within the scattering volume. It was found that a change in beam power from 15 to 150 mW had no measurable effect on the *anomalous* contribution to the near-critical spectrum at a given temperature control setting and sample density; i.e., although at the highest laser powers the critical opalescence did give rise to a slight decrease in the feedback control current through the cell heaters, there was no evidence of localized heating within the scattering volume.

The critical density was established by the procedure of making small adjustments to the mass of the sample at the highest temperature (126.10 K) where a liquid-vapor interface was easily discernible, the criterion being that, for equal volumes of liquid and vapor, the interface should disappear without vertical movement as the temperature of the isolated sample was slowly raised. As an additional confirmation, it was noted that the independent determination of  $T_c$  obtained in this manner agreed with the most recently measured,<sup>8</sup> and apparently accepted,<sup>9</sup> value (126.20 K) to within the ±5 mK accuracy of the Pt thermometer calibration.

Special precautions were taken to ensure that multiple scattering (i.e., opalescence) and/or possible density gradients within the sample were not contributing to the observed anomaly. Namely, (i) a spatial filter was introduced in the path of the collected light so that the vertical (and horizontal) dimensions of the scattering volume could be effectively reduced in several steps from 1000 to 50  $\mu\text{m}$ , and (ii) the location of the scattering volume was varied over about 80% of the 4-mm vertical extent of the sample. The results obtained were identical in all cases. In addition it must be emphasized that, while the

opalescence is only observable within  $\sim 1$  K of the critical point, the present effects persist for  $T - T_c > 10$  K, and we suggest that this distinctly different behavior is a consequence of the short-range character of the Raman probe; i.e., it is sensitive to the presence of molecular clusters which are orders of magnitude smaller, and which persist much farther from the critical point, than those responsible for the opalescence.

The computerized analysis procedure involved the Fourier transformation of each data set, followed by a deconvolution routine to account for the finite instrument resolution. Separate smoothing functions,  $A(t)$  and  $B(t)$ , were then fitted to the cosine and sine transforms, respectively, and the final processed spectra,  $I(\nu)$ , were generated via inverse transformation with use of the fitted functions. The instrumental resolution (as determined by the interferometer) was adjusted as required to maintain the width of the instrument profile at a level less than 10% of the observed spectral width. The deconvolution process therefore constituted only a minor modification of the observed profile and was largely insensitive to the details of the instrument profile which in all cases was found to be adequately represented by an Airy function of the form  $F(\nu) = c_1(1 + c_2 \sin^2 \nu)^{-1}$ .

A series of  $I(\nu)$  profiles was obtained along the critical isochore at  $\epsilon$  values as listed in Table I. The shape was found to evolve smoothly between the extremes shown in Fig. 1(a) where the temperature dependence of the peak position has been removed. The functional form  $A(t) = a_0 \exp(-a_1 \times t^{1.5})$ , which has recently been proposed by Mukamel, Stern, and Ronis<sup>10</sup> for the case of  $\epsilon \rightarrow 0$ , was found to yield quite good fits at the lowest  $\epsilon$  values but was not applicable at higher temperatures. On the other hand, the form  $A(t) = a_0 \times \exp(-a_1 t - a_2 t^2)$ , which corresponds to a Voigt profile in the frequency domain, was found to fit the data very well at all temperatures and it provides the basis for the present interpretation. The function  $B(t) = b_0 \exp(-b_1 t) \sin(b_2 t)$  was chosen as the simplest one which produced acceptable accuracy in the regenerated  $I(\nu)$  profiles. All essential data pertaining to the spectra in question are listed in Table I.

Attention is now focused on a comparison of the parameters  $a_1$  and  $a_2$  (Table I) which are direct measures of the Lorentzian and Gaussian content, respectively, of the spectral profiles. It is apparent that  $a_1$  shows no consistent trend and, since the range of its variation most prob-

TABLE I. Spectral parameters.

| $\epsilon$           | $a_0$<br>(counts) | $a_1$<br>(GHz) | $a_2$<br>(GHz <sup>2</sup> ) | $b_0$<br>(counts) | $b_1$<br>(GHz) | $b_2$<br>(GHz) | $\Delta\nu^a$<br>(GHz) | FWHM <sup>b</sup><br>(GHz) |
|----------------------|-------------------|----------------|------------------------------|-------------------|----------------|----------------|------------------------|----------------------------|
| $6.9 \times 10^{-2}$ | 0.425             | 4.41           | 3.04                         | 0.002             | 1.01           | 12.1           | 0                      | 11.87                      |
| $3.0 \times 10^{-2}$ | 0.508             | 4.95           | 5.80                         | 0.005             | 2.46           | 12.7           | -0.40                  | 14.59                      |
| $1.4 \times 10^{-2}$ | 0.553             | 4.73           | 9.99                         | 0.022             | 5.68           | 12.6           | -0.92                  | 16.56                      |
| $6.3 \times 10^{-3}$ | 0.586             | 4.81           | 12.38                        | 0.032             | 5.01           | 12.3           | -1.36                  | 17.82                      |
| $3.2 \times 10^{-3}$ | 0.594             | 4.41           | 15.43                        | 0.046             | 4.87           | 12.7           | -1.56                  | 18.66                      |
| $1.6 \times 10^{-3}$ | 0.578             | 3.60           | 18.53                        | 0.047             | 3.92           | 13.3           | -1.44                  | 18.92                      |
| $7.9 \times 10^{-4}$ | 0.614             | 4.01           | 19.78                        | 0.042             | 5.49           | 13.8           | -1.29                  | 19.79                      |
| $7.9 \times 10^{-5}$ | 0.645             | 3.41           | 20.54                        | 0.112             | 6.67           | 12.2           | -1.27                  | 20.98                      |

<sup>a</sup>Change in peak position.<sup>b</sup>Full width at half maximum.

ably reflects the accuracy of the analysis, it can safely be assumed independent of  $\epsilon$ . On the other hand,  $a_2$  exhibits a rather striking increase in

magnitude by a factor of 7, and it is clear that the profile is effectively Gaussian in character at the lowest  $\epsilon$  values.

Given that adiabatic dephasing processes are dominant, this behavior can be understood in terms of the basic idea<sup>11</sup> that two separable contributions can be identified. First, there is the "normal" or "noncritical" contribution associated with those high-frequency (>GHz) fluctuations in density which are presumed not to participate in the critical phenomenon: From Ref. 4 and the present investigation it is clear that in the case of N<sub>2</sub> the result will be a motionally narrowed, Lorentzian component. The second, or "critical," contribution is associated with the low-frequency, hydrodynamic density fluctuations which are responsible for the critical phenomenon in the first instance, and which have been the subject of theoretical investigations in Refs. 10 and 11. While there are differences of opinion<sup>12</sup> as to the correctness of the latter approaches, there appears to be a fair measure of agreement regarding the nature of the corresponding contribution to the spectrum in the limit  $\epsilon \rightarrow 0$ . Namely, because of the critical slowing down process, a static limit is approached where the critical component of the spectrum is inhomogeneously broadened and will reflect the distribution of densities within the fluid. We consequently associate this "critical" contribution primarily with the Gaussian component of  $A(t)$  which in the present case dominates the spectrum at low  $\epsilon$  values because the "noncritical" (Lorentzian) contribution is appropriately small. At the same time it is clear that while  $B(t)$  must also be considered in a similar light, its significance can only be revealed by a more detailed treatment.

In conclusion, it is appropriate to reemphasize that the Raman probe is not directly sensitive to those long-range correlation effects which are

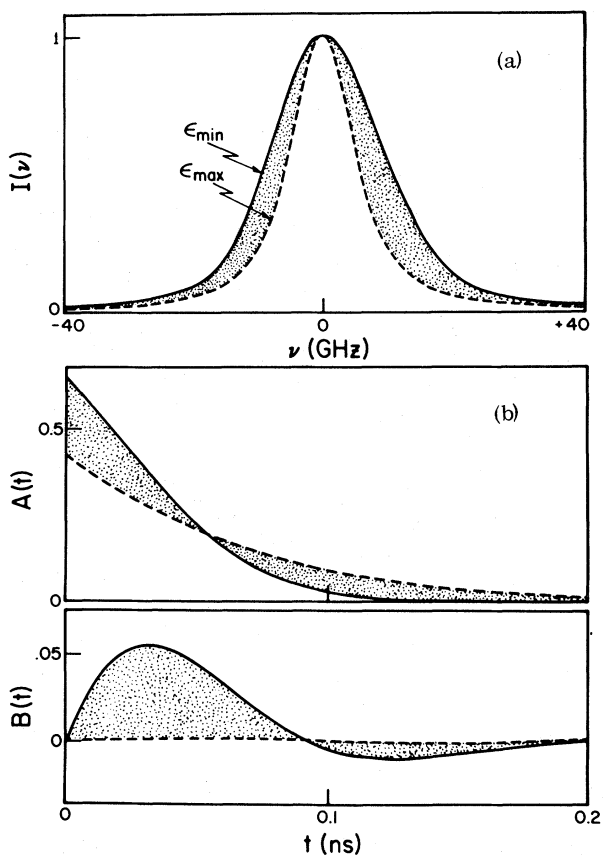


FIG. 1. (a) Pure vibrational Raman spectra of supercritical N<sub>2</sub> as obtained at the critical density and at the extremes of temperature ( $\epsilon$ ) listed in Table I. Each profile was generated from  $\sim 250$  raw data points. The temperature dependence of the peak position has been removed. The gross Raman shift is actually about 69 780 GHz and negative  $\nu$  values correspond to smaller shifts. (b) Cosine transforms,  $A(t)$ , and sine transforms,  $B(t)$ , corresponding to (a).

identified with critical opalescence, and it is in this respect that the experiment is distinct from other techniques which have been applied in the investigation of critical phenomena. Results of the type presented here can provide previously unavailable information of a fine-grained character pertaining to the statistical distribution of local densities in the critical region. A forthcoming publication will concentrate on methods of extracting this information.

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