Local Ordering in Fluid Deuterium

M. J. Clouter, C. G. Deacon, and H. Kiefte
Department of Physics, Memorial University of Newfoundland, St. John's, Newfoundland, Canada A1B 3X7

(Received 21 July 1986; revised manuscript received 17 December 1986)

The vibrational Raman spectrum of D_2 has been found to exhibit a fine structure which is particularly distinct near the liquid-gas critical point ($T_c = 38.3$ K). No such structure was observed in the spectra of either H_2 or HD. The effect is interpreted as arising from a high degree of local ordering in the D_2 system.

PACS numbers: 67.20.+k, 05.70.Jk, 33.70.Jg

Previous observations[1] of the (polarized) vibrational Raman spectrum of N_2 on the critical isochore have revealed that the normal Lorentzian profile undergoes a transformation to a predominantly Gaussian form as the critical point is approached over a temperature range of about 10 K, and that the width of the spectrum also increases by a factor of ~ 2. The effects become less pronounced for densities other than critical, and (for example) disappear completely at twice the critical density. Our interpretation[1] of this critical-region anomaly (as outlined below) emphasizes the potential of such experiments as probes of the state of local order on a scale determined by the ~ 1-nm range of the pair potential, and comparable to the average molecular separation.

The phenomenon can be understood by our regarding the Raman active molecules as anharmonic oscillators whose resonant frequencies are determined to a significant extent by the local fields due to neighboring molecules. In the normal, or noncritical, fluid the effects of spatial variations in the local field are not significant when compared with the dynamical contributions[2] to the spectral width, and so the result is a homogeneously broadened (Lorentzian) profile which reflects only the average effect of the local field via a dependence of the peak frequency on bulk density. However, since the approach to the critical point is characterized by marked increases in the magnitude and lifetime of spatial fluctuations in density, an associated inhomogeneously broadened (Gaussian) contribution may be observable if the dynamical broadening is appropriately small. It turns out that the latter requirement can be satisfied for specific molecular systems (e.g., N_2, H_2) where the normal homogeneous broadening arises primarily from (adiabatic) vibrational dephasing processes as opposed to energy, or population, relaxation. In such cases the near-critical spectrum can be regarded as a superposition of local spectra whose peak frequencies are distributed according to the normal bulk-density dependence. In other words, the spectral profile directly reflects the probability distribution for local density, ρ_{nn}, as determined primarily by the nearest neighbors (nn). On this basis, and as described in detail in Ref. 1, information pertaining to the latter distribution can be extracted from the observed spectrum in a relatively straightforward manner.

Results which are similar to the N_2 case have been obtained from corresponding experiments[3] with H_2 and HD. The overall broadening effect has also been observed in vibrational Raman spectra of near-critical D_2 as reported here, and in this respect the behavior is similar to N_2, H_2, and HD. At the same time, however, the D_2 spectra are very different in that the broadening is accompanied by the appearance of a regular fine structure which is absent in the latter cases. For convenience we concentrate on a comparison of the H_2 and D_2 spectra as shown in Fig. 1. In the case of H_2 the condition of inhomogeneous broadening was established by the determination that the near-critical profile was predominantly Gaussian in character. While this criterion could not be applied for D_2, there is no reason to assume that D_2 and H_2 should differ in this respect. We furthermore emphasize that the assumption of inhomogeneous broadening is the only one underlying the analysis of the D_2 results as described below.

At the temperatures of the D_2 (and H_2) experiments the normal pure vibrational spectrum consists of only two structureless features [cf. Fig. 1(a)] which are designated as $Q_1(0)$ and $Q_1(1)$. The former corresponds to a transition from the molecular ground state to the first excited vibrational state (i.e., $v=0 \rightarrow 1$, $J=0$), and the latter differs only in that one quantum of rotational energy is present ($v=0 \rightarrow 1$, $J=1$). The relative intensities of these features reflects the equilibrium distribution of populations over the rotational states. The spectra were obtained with use of a Fabry-Perot spectrometer,[1] and in the present application it was a matter of coincidence that overlapping of the $Q_1(J)$ profiles was unavoidable when we employed resolution sufficiently high to detect the fine structure. It should be noted, however, that the spectral resolution relative to the width of the $Q_1(0)$ feature(s) is approximately the same for both H_2 and D_2 so that any corresponding fine structure in the H_2 spectrum would easily have been detected. The effect of instrumental width, which was comparable to the width of the fine-structure features in Fig. 1(b), was removed via a Bayesian deconvolution technique.[4] The gross Raman shifts corresponding to $v=0$ in Fig. 1 are approximately

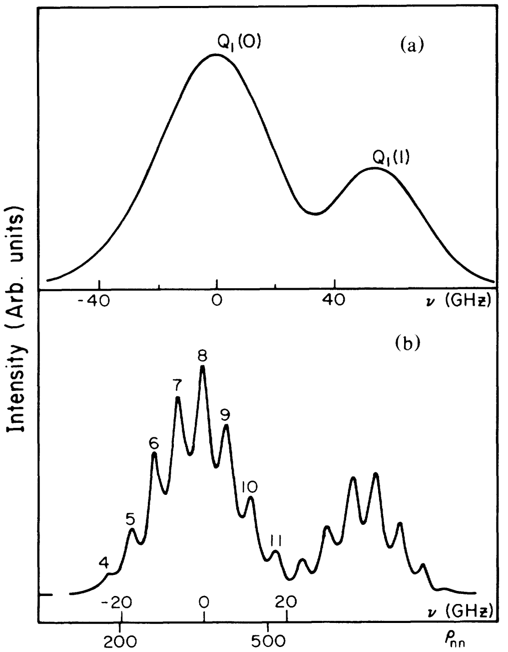

FIG. 1. Vibrational Raman (Q branch) spectra of (a) H_2 and (b) D_2 as obtained at the respective critical densities with $T-T_c \simeq 1$ K. In each case the two vibrational profiles are displayed in adjacent interference orders of the Fabry-Perot spectrometer so that the frequency scales, which are relative to the strongest peaks, apply only to the distribution of intensity in the $Q_1(0)$ features. The fine-structure peaks in (b) are separated by a constant interval of ~ 6 GHz. The scale of local densities ($\rho_{\rm nn}$) is relative to STP and applies only to the $Q_1(0)$ transition of D_2 where the peaks are identified according to nearest-neighbor coordination number (see text).

124.8 and 89.80 THz for H_2 and D_2, respectively.

Discussion of the fine structure in the D_2 spectrum will be restricted to the $Q_1(0)$ feature of Fig. 1(b) because it involves transitions between nondegenerate levels of the D_2 molecule, and one possible source of the observed splitting is thereby eliminated. The number of observed $Q_1(0)$ peaks reached a maximum of eight near the critical point (Fig. 1). However, as was previously the case for analogous results obtained both in Raman scattering[1,2] and in infrared absorption,[5] the basic effect was detected over a wide range of conditions around the critical point. A total of ~ 50 spectra were obtained which revealed (i) that the fine-structure peaks maintained approximately fixed positions and separation (~ 6 GHz) as the temperature was raised from 39 to 60 K on the critical isochore, and (ii) that the number of peaks observed was determined by the overall width of the $Q_1(0)$ profile which decreased by a factor of ~ 3 over the same temperature range. As a consequence, only two such peaks were detectable at $T=60$ K on the critical isochore, and a similar situation applied to the saturated liquid at 35 K.

As implied above, analysis of the D_2 spectra required information regarding the sensitivity of the peak frequency (ν_P, in gigahertz) of the normal-fluid spectrum to changes in the bulk density, since this determines the magnitude of the inhomogeneous broadening.[6] Independent measurements on the $Q_1(0)$ profile were therefore performed along an isotherm at 50 K which yielded $\nu_P = \nu_0 - 0.13\bar{\rho}$, where ν_0 is the free-molecule frequency and $\bar{\rho}$ is the bulk density relative to 4.458×10^{-5} mol cm^{-3} at STP.[7] By use of this linear relation the frequency scale for the inhomogeneously broadened $Q_1(0)$ profile was transformed to a scale of local densities, $\rho_{\rm nn}$, under the above-mentioned assumption[1] that the peak frequencies of the local Raman spectra (which are superimposed to produce the near-critical profile) depend on $\rho_{\rm nn}$ in the same manner that the normal spectrum of the bulk fluid depends on $\bar{\rho}$. This permitted a convenient empirical description of the spectrum in that the positions of the fine-structure peaks could be represented quite accurately by the relation $\rho_{\rm nn} = 48i$, with the values of the integer $i(=4,5,\ldots,11)$ being chosen so that the most prominent peak ($i=8$) corresponded most closely to the mean (critical) density, $\bar{\rho} = \rho_c = 372$. This leads to the first of three conclusions, namely, (I) that the local densities, $\rho_{\rm nn}$, are in some way restricted to this set of preferred values.

It is now relevant to note that changes in the bulk density of normal liquids are achieved[8] primarily via changes in the average nn coordination number, $\bar{z}$, rather than by changes in the average pair separation, $\bar{d}$. By a generalization of this to the case of density fluctuations, it is plausible to consider the observed $\rho_{\rm nn}$ values as indicating an *enhanced* correlation with particular values of z. Support for the existence of this correlation is derived first from model calculations[8] which show that $\bar{z} \simeq 8$ is a reasonable choice for a near-critical fluid, and this is consistent with $i=8$ for the strongest peak [Fig. 1(b)]. The idea also gains more definite support from previous work[9] pertaining to the density dependence of the vibrational Raman shift in the gas phase at higher temperatures. An as intermediate step in their theoretical development, May and co-workers[9] derive an expression for the most important contribution to the frequency shift per nn pair as $\Delta\nu_P = K_{\rm Rep}/d^{12} - K_{\rm Att}/d^6$, where d (as above) is the intermolecular distance. Given the values $K_{\rm Rep} = 2.2\times 10^{-90}$ cm^{11} and $K_{\rm Att} = 2.5\times 10^{-45}$ cm^5 as experimentally determined for D_2 by Looi, Stryland, and Welsh,[10] one can thus calculate the value of d corresponding to a shift per nn pair of 6.0 GHz, as suggested by the experimentally observed splitting. The result is $d = 0.48$ nm, and this compares quite favorably with $\bar{d} = 0.49$ nm which is obtained as an unweighted average of values for simple cubic, bcc, and fcc packing at the critical density ($\bar{\rho} = 372$). It is thus concluded to be most likely (II) that the observed effects reflect a situation where a significant fraction of the local environments is characterized by a well-defined nn distance $d=\bar{d}$, with fluctuations in $\rho_{\rm nn}$ being achieved primarily via variations in the necessarily integral values of z. The peaks of Fig. 1(b) have been identified accordingly; i.e., by putting $i=z$ in the above empirical relation so that $\rho_{\rm nn} \equiv \rho_z = 48z$.

Of the possible mechanisms which might give rise to such ordering we first mention those which can be rejected on reasonable grounds. (1) *van der Waals clusters*: Only the dimers, $(H_2)_2$ and $(D_2)_2$, have so far been observed[11] in infrared absorption at densities $\bar{\rho}<10$, and this is because their lifetime is determined by the collision frequency. The associated spectral features become so broad as to be unrecognizable for $\bar{\rho}>10$, and it appears quite unreasonable to expect any such stable clusters to exist at $\bar{\rho}=372$. Furthermore, the present spectral structure was found to disappear as the density was reduced below the latter critical value. (2) *Resonances associated with the $v=1$ excitation*: Two such effects were considered. First, there is the possibility that a (local) phonon mode can be excited in resonance with the intramolecular vibration on the probe molecule, thereby enhancing the local order. This was rejected because the required phonon frequencies (~100 THz) are extremely high and actually exceed those which are typical of the zone-boundary region in (e.g., metallic) solids. Second, there is the effect of resonant transfer of the $v=1$ excitation between nn molecules. The associated contribution to the pair interaction[12] will, in principle, cause a deepening of the potential well which could in turn promote local ordering (cf. van der Waals clusters) which would not exist under equilibrium conditions. This effect is, however, very small for homonuclear molecules.[12] It is also known[13] that the simultaneous presence of a rotational excitation on the same molecule will severely inhibit the transfer process, and this is inconsistent with the fact that the D_2 fine structure occurs with equal prominence on the $Q_1(1)$ profile as well as the $Q_1(0)$ profile. It is therefore concluded (III) that the ordering is characteristic of the equilibrium fluid.

No firm conclusions have been reached regarding the mechanism responsible for this ordering. One possibility is that it reflects the presence of acoustic modes of high wave number ($k=2\pi/\lambda$) but low frequency (ω). The existence of such modes has recently been the subject of theoretical and computer simulation studies,[14] as well as experimental investigation by neutron scattering.[15] They are associated with the occurrence of a minimum in the dispersion curve (ω vs k) at $k\sigma \sim 6$, or $\lambda \sim \sigma$, where σ is the molecular hard-sphere diameter. This phenomenon, which is well known for the case of liquid He, is now regarded as being potentially significant for fluids in general, and at least one specific model has been proposed.[16] It is clear, however, that in the present context the mechanism is specific to D_2, and must consequently be sensitive to one or more of the isotopic properties listed in Table I. Since quantum effects may be of importance in this respect, the following points are noted. (i) H_2 and D_2 are bosons whereas HD is a fermion. (ii) Given that $\sigma \simeq 0.23$ nm for all three molecules,[12] and that it may constitute a particularly significant length scale, its comparison with the thermal de Broglie wavelength Λ (Table I) is most favorable for D_2. In addition, the fact that the ordering is associated with the critical region must also be emphasized. It is conceivable, for example, that the long correlation times which are characteristic of this region may contribute to the stability of the ordering.

TABLE I. Critical-point properties of the molecular hydrogens (from Ref. 7).

	Mass No.	T_c (K)	Number density n (nm^{-3})	Thermal wavelength[b] Λ (nm)
H_2	2	33.0	9.0–9.4[a]	0.38
HD	3	35.9	9.6	0.30
D_2	4	38.3	10.0–10.4[a]	0.25

[a] Depends on ortho-para ratio.
[b] $\Lambda=(h^2/2mk_BT)^{1/2}$.

In considering alternative experimental probes it is apparent that inelastic neutron scattering is appropriate for investigating the details of the dispersion curve. In addition, an important signature of the effect should be an unusually narrow first peak in the radial distribution function which can be investigated by neutron (or possibly x ray) diffraction techniques. Such experiments, which should be feasible for the D_2 case, have apparently not been performed in the critical region.[17]

The authors wish to acknowledge helpful discussions with C. G. Gray, J. C. Lewis, A. R. W. McKellar, J. V. Sengers, J. A. Tuszynski, J. P. Whitehead, and M. D. Whitmore. We are indebted to E. A. Ballik for supplying the computer code associated with the Bayesian deconvolution process. Special thanks are due to A. Griffin for his critical reading of the revised manuscript. The work was supported by grants from the Natural Sciences and Engineering Research Council of Canada.

---

[1] M. J. Clouter, H. Kiefte, and C. G. Deacon, Phys. Rev. A **33**, 2749 (1986).

[2] D. W. Oxtoby, Adv. Chem. Phys. **40**, 1 (1979); W. G. Rothschild, *Dynamics of Molecular Liquids* (Wiley, New York, 1984).

[3] C. G. Deacon, M. J. Clouter, and H. Kiefte, to be published; P. Staniaszek, M. J. Clouter, and H. Kiefte, to be published. A sample H_2 spectrum has been included in Fig. 1.

[4] T. J. Kennet, P. M. Brewster, W. V. Prestwich, and A. Robertson, Nucl. Instrum. Methods **153**, 125 (1978).

[5] M. J. Clouter and A. R. W. McKellar, J. Chem. Phys. **84**,

2466 (1986).

[6] H. L. Strauss and S. Mukamel, J. Chem. Phys. **80**, 6328 (1984); M. J. Clouter, H. Kiefte, and R. K. Jain, J. Chem. Phys. **73**, 673 (1980).

[7] A. Michels, W. deGraff, T. Wassenaar, J. M. H. Levelt, and P. Louwerse, Physica (Utrecht) **25**, 25 (1959); H. M. Roder, G. E. Childs, R. D. McCarty, and P. E. Angerhofer, *Survey of the Properties of the Hydrogen Isotopes Below Their Critical Temperatures,* U.S. National Bureau of Standards Technical Note No. 641 (U.S. GPO, Washington, D.C., 1973).

[8] J. D. Bernal and S. V. King, in *Physics of Simple Liquids,* edited by H. N. V. Temperley, J. S. Rowlinson, and G. S. Rushbrooke (Wiley, New York, 1968).

[9] J. Fiutak and J. Van Kranendonk, Can. J. Phys. **40**, 1085 (1962), and **41**, 21 (1963); A. D. May, V. Degen, J. C. Stryland, and H. L. Welsh, Can. J. Phys. **39**, 1769 (1961); A. D. May, G. Varghese, J. C. Stryland, and H. L. Welsh, Can. J. Phys. **42**, 1058 (1964); A. D. May and J. D. Poll, Can. J. Phys. **43**, 1836 (1965).

[10] E. C. Looi, J. C. Stryland, and H. L. Welsh, Can. J. Phys. **56**, 1102 (1978).

[11] A. R. W. McKellar and H. L. Welsh, Can. J. Phys. **52**, 1082 (1974); A. K. Kudian and H. L. Welsh, Can. J. Phys. **49**, 230 (1971).

[12] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1967), pp. 990, 157.

[13] J. Van Kranendonk, *Solid Hydrogen* (Plenum, New York, 1983), p. 67.

[14] See, for example, M. J. Zuilhof, E. G. D. Cohen, and I. M. de Schepper, Phys. Lett. **103A**, 120 (1984); W. E. Alley and B. J. Alder, Phys. Rev. A **27**, 3158 (1983), and references contained therein.

[15] I. M. de Schepper, P. Ververk, A. A. van Well, and L. A. de Graaf, Phys. Rev. Lett. **50**, 974 (1983), and Phys. Lett. **104A**, 29 (1984).

[16] M. Héritier, G. Montambaux, and P. Lederer, J. Phys. (Paris), Lett. **40**, L493 (1979), and J. Low Temp. Phys. **42**, 515 (1981).

[17] G. Dolling, P. A. Egelstaff, and R. L. Mills, private communications.