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Negative vibrational shift of nitrogen diluted in xenon at the fluid–solid transition

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It is known from experimental evidence that the Raman shift of nitrogen and nitrogen in argon, measured as a function of the pressure at ambient temperature, reveals a positive jump at the transition from the liquid to the solid phase. Intuitively, this increase is sometimes attributed to the increase of density, but recently it has been shown that the change in order at the transition also plays a role. The present study deals with the behavior of nitrogen diluted in xenon. In this system, even a negative jump is found experimentally. Computer simulations on a model system for the N_2 -Xe mixture make clear that in this case the effect of the change in order is opposite. © 1999 American Institute of Physics. [S0021-9606(99)01006-5]

INTRODUCTION

A positive jump of the Raman frequency of nitrogen has been found experimentally^{1,2} at solidification at ambient temperature in the pure substance as well as in a dilute mixture in argon. It has been remarked elsewhere³ that this increase is due to the increase of density. This seems in contrast with experimental and simulation results in the homogeneous system which reveal an almost constant frequency under isobaric conditions.⁴

It is well known that the vibration frequency of nitrogen molecules, as for many other polyatomic molecules, is influenced by the interaction with surrounding particles. First, the neighboring molecules exert forces on the nitrogen atoms that change the bond length. Because the interatomic force is not harmonic, the change in bond length results in a shift of the frequency. Further, the interaction forces with the surrounding molecules will not be homogeneous, which causes a change in vibration frequency as well. It is interesting to survey this behavior in both phases near the fluid–solid transition. Recent computer simulations² have shown that the interaction between the nitrogen molecules and their surroundings must be regarded in detail to understand the observed results. Simulations at equal density and temperature at both sides of the melting line (thus, one in a metastable phase) still reveal a higher frequency in the solid, for pure nitrogen and for nitrogen in argon, notwithstanding the lower pressure in the latter phase. The radial distribution in line with the molecular axis is essentially for the shift. Although the first peak of the mean, omnidirectional radial distribution function shifts to larger distances in the solid phase, this peak shifts to lower distances for the distribution in line with the molecular axis, both in the case for pure nitrogen as well as for the dilute mixture with argon. A corollary assumption may be that the positive jump in the shift will be less in dilute mixtures of nitrogen with host molecules which are larger in size and consequently crystallize on a larger grid

than nitrogen and argon. Even the occurrence of a negative jump may be possible.

In order to investigate this conjecture, the vibration frequency of nitrogen diluted in xenon at the fluid–solid transition has been determined by means of Raman spectroscopy. In addition, we performed dynamical computer simulations on a corresponding model system. The choice for xenon is evident: it crystallizes at the fluid–solid transition into the same (fcc) structure as argon, but with an $\sim 15\%$ larger intermolecular distance.

EXPERIMENT

At ambient temperature the transition pressure for xenon is only about 0.4 GPa, which is relatively low in comparison to the transition pressure of 1.3 GPa for argon. Also the density around the transition is much less in xenon. Since the measurements have to be performed at low concentrations of nitrogen, these circumstances would lead to relatively weak spectral lines, in particular in the fluid phase. Besides, it is preferable to perform the experiments at pressures which are at least of the same order, as the Raman shift turns out to be directly related to the pressure. Therefore the measurements have been performed at 408 K. At this temperature the transition occurs at $\cong 0.85$ GPa and $\cong 28$ kmol/m³.⁵

High purity gases have been used to prepare a N_2 -Xe mixture with a nitrogen mole fraction of 0.075. Employing the equations of state of N_2 and Xe just below the fluid–solid transition, this leads to a volume fraction of approximately 0.05. The mixture was kept in the gas compressor at 42 bar for several weeks to allow for proper mixing. The high pressure was achieved by using the diamond anvil cell (DAC) technique. The experimental procedure has been described in Ref. 6.

The appearance of a solid phase in the cell can be detected clearly by visual observations through a microscope. The fluid phase is completely transparent. When the pressure is raised above 0.83 GPa a solid–fluid coexistence region is seen in which the amount of solid increases with pressure. In

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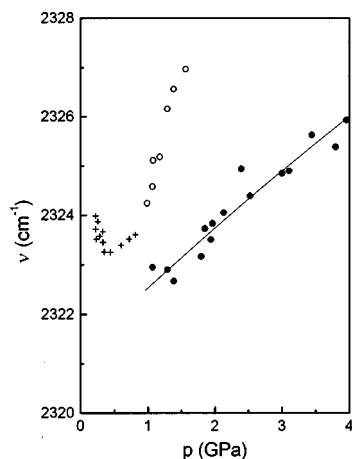


FIG. 1. Experimental results for the Raman shift of the Q branch of nitrogen, diluted in xenon as a function of pressure at 408 K; (crosses) homogeneous fluid phase, (solid circles) solid phase, (solid line) curve fit using Equation (1), (open circles) coexisting fluid phase.

the homogeneous fluid phase, only one single Raman peak has been observed (ν_F). This peak position as a function of pressure shows a minimum value of 2323.2 cm^{-1} at about 0.4 GPa (Fig. 1). Just before the entrance point to the coexistence region at $p=0.81 \text{ GPa}$, this vibrational frequency is 2323.6 cm^{-1} . Above the transition two vibrons are measured, and therefore the spectrum has been fitted by two Lorentzian curves. Since the Raman spectrum consists of two peaks above the transition, it is interpreted as one peak corresponding to N_2 in the fluid phase, and the other peak corresponding to N_2 in the solid xenon phase. The intensity of the high frequency peak ν_F compared with that of the low frequency peak ν_S decreases with increasing pressure, and therefore ν_F is attributed to the Raman mode of N_2 in the fluid phase, and consequently, ν_S to the Raman mode of N_2 in the solid phase. In Fig. 1 it is shown that the frequency ν_F above the transition connects to the frequency which was measured in the homogeneous fluid phase. The change in the slope of ν_F versus the pressure above the transition is due to a continuous change in the concentration of the fluid in the coexistence region to higher nitrogen contents, since the frequency is strongly composition dependent. Above 1.6 GPa the high frequency peak is no longer measurable. Therefore, we can conclude that the usual solid–fluid coexistence region, which occurs in binary mixtures, extends in this case until about 1.6 GPa. At higher pressures the entire sample crystallizes. The Raman frequency ν_S has been measured up to 15 GPa, and has been fitted with the following equation:

$$\nu_S = 2321.27 + 1.28p - 0.025p^2, \quad (1)$$

where ν_S is given in cm^{-1} , p is in GPa, and the standard deviation is 0.25 cm^{-1} . Using Eq. (1) for extrapolation gives a negative frequency shift of $\sim 1 \text{ cm}^{-1}$ at the solid–fluid transition as shown in Fig. 1.

SIMULATIONS

The molecular dynamics (MD) simulations have been performed on a system consisting of 255 xenon model particles and *one* nitrogen particle in a cubic box with periodic

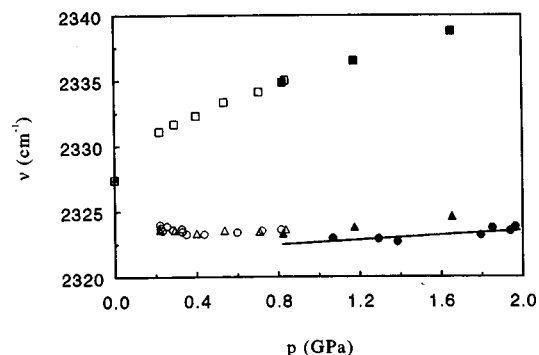


FIG. 2. Raman shift of nitrogen diluted in xenon at 408 K near the solid phase transition: (circles) experimental, (squares) MD results without DC, (triangles) MD results including the DC, (open symbols) fluid phase, (solid symbols) solid phase.

boundaries, allowing for a fcc structure in the solid phase. Note that the experiments have been performed at a volume fraction of 0.05. A linear extrapolation to infinite dilution⁷ does not change the results essentially for the purpose of this investigation. For the intermolecular interactions between the xenon particles the exponential-6 potential model has been adopted. In conformity with previous simulations,^{2,8} the nitrogen molecule was defined as a site–site potential; each site (atom) interacted with the surrounding xenon particles with an exponential-6 potential as well. The parameters for the latter potential have been obtained using the Lorentz–Berthelot rule. The following parameter values have been used:

	ϵ/k_B (K)	r_m (Å)	α
Xe–Xe	231.2	4.45	13
$\text{N}_{\text{atom}}\text{--Xe}$	95.4	4.09	13.75
$\text{N}_{\text{atom}}\text{--N}_{\text{atom}}$	39.4	3.73	14.55

intramolecular N–N distance: 1.094 Å.

The shift has been calculated from the forces acting along the axis of the nitrogen molecule in a way extensively described in previous publications.^{2,8} In short, the influence of the momentary forces and their derivative along the molecular axis on the vibrational frequency is calculated and added to the mean frequency ν_0 of nonrotating, isolated molecules. From the value of ν_0 obtained by Lavorel *et al.*⁹ at ambient temperature and the temperature dependence of the vibration–rotation coupling given by Brueck¹⁰ and Lavorel *et al.*⁹ this zero frequency was determined to 2327.41 cm^{-1} . The results for the shift deviate from the experimental values. It is assumed that this difference is due to the change in the polarizability, and thus to the intermolecular energy at excitation. It is seen in previous work that one can correct for this energy change by the addition of a momentary energy term to the interaction potential, indicated as dispersion correction (DC). Results of the shift without the DC are given in Fig. 2 by squares. In order to lower these frequencies to the experimental results for the dilute mixture in the fluid phase, an energy term between each $\text{N}_{\text{atom}}\text{--Xe}$ interaction has been added. In contrast with simulations for pure nitrogen and mixtures with helium⁸ and with argon² one single term suffices for a good fit all over the fluid phase:

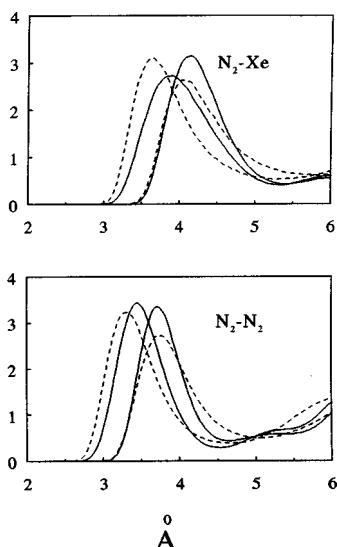


FIG. 3. Simulation results for the pair distribution relative to the center of mass of a nitrogen molecule in the fluid, and in a solid matrix: (upper) in xenon at 408 K, (lower) in nitrogen (Ref. 2) at 296 K; (solid line) solid phase; (dashed line) fluid phase; (left curves) perpendicular on the molar axis; (right curves) in line with the molecular axis.

$$\delta\varphi_{ij} = b/r^6; \quad b = 2700 \text{ K } \text{\AA}^6.$$

For convenience, the same correction has also been used for the simulations in the solid phase, but this does not influence the main conclusions of this paper, because the DC is not involved in the dynamics and therefore has no effect on the structure in the fluid and solid phase. The results are displayed together with the experimental data in Fig. 2.

DISCUSSION AND CONCLUSION

It is seen that, going from the fluid to the solid phase, the experimental results for the shift reveal a *negative* jump of about 1 cm^{-1} , in contrast with the positive jumps in pure nitrogen and argon (respectively, $\approx +1 \text{ cm}^{-1}$ and $\approx +2 \text{ cm}^{-1}$). In order to show this more clearly, the fitted function (1) has been also drawn in Figs. 1 and 2. Note that this function is only slightly convex over the whole pressure range from 1 to 15 GPa; therefore the short extrapolation to 0.83 GPa seems acceptable. The redshift in the fluid phase turns out to be several times more than in pure nitrogen and in dilute mixtures with argon and helium.^{2,8} From Fig. 2 a good correspondence is seen for the value of the shift in the solid phase, and the slope as a function of pressure, obtained

experimentally and by simulations. In addition, the simulations do not reveal a positive jump of the frequency at the transition.

The results of the simulations in the fluid phase without DC are nearly the same as for pure nitrogen and the dilute mixtures mentioned above at room temperature in the same pressure range. Consequently, the DC is largest if the nitrogen is surrounded by xenon molecules, reflecting the high polarizability of xenon.

Two simulations have been performed at $p \approx 0.83 \text{ GPa}$: one in the fluid and the other in the solid phase; evidently one of them is metastable. In both systems the radial distribution of xenon molecules around the nitrogen molecule has been determined in line with the molar axis of the nitrogen as well as in the perpendicular direction. It has been shown in a previous paper that in the case of pure nitrogen and nitrogen in argon,² the first peak *in line* with the molar axis shifts to lower distances from the center of the nitrogen molecule at the transition to the solid phase, resulting in a larger force and consequently, a higher frequency. In Fig. 3 it is seen that this is not the case for nitrogen in xenon: a clear shift of this peak away from the nitrogen molecule is visible, in contrast with pure nitrogen for which the picture has been given as well in the same figure. This means that in the ordered matrix of solid Xe the force exerted on the nitrogen molecule in line with the atomic bond thus need not be higher than in the fluid phase or even may be lower. In that case the resulting vibration frequency will be less as well.

In summary: although the density increases at the fluid–solid transition, the vibrational frequency shows a negative jump in a dilute mixture of nitrogen in xenon. This is due to the change in order, but the effect is opposite that in nitrogen and nitrogen in argon.

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