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Computer simulations of the linewidth of the Raman Q-branch in fluid nitrogen

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By means of molecular dynamical simulations, the width of the Raman line in fluid N_2 is calculated at room temperature and pressures up to the melting line. The results are compared with experimental results for the linewidth and for the dephasing time. Detailed information is given about the relaxation mechanism of the vibrational frequency. For instance, a marked influence of the vibration-rotation coupling is seen, in particular at high pressures. Moreover, the time correlation function of the frequency reveals a long time behavior at high pressures. From a comparison of the simulated change in vibrational frequency as a function of pressure with experimental data for the line shift, an estimate is made for the contribution of the so-called “attractive part” to that shift. © 1995 American Institute of Physics.

I. INTRODUCTION

In recent years the study of the vibrational spectrum of simple fluids has been extended to high pressures. Raman and infrared spectroscopy is used to probe the interaction of the molecule under consideration with the local environment and to study the dynamics of molecular fluids. Meanwhile the change in vibrational frequency and the linewidth (or dephasing time) of nitrogen has been extensively measured at room temperature up to the melting line.^{1–8} Also some data are available for other temperatures.^{9,10} At low pressures there is a red shift of the frequency with a minimum at about 0.14 GPa turning into a blue shift above 1 GPa. The linewidth also shows a minimum but at about 0.5 GPa.

Various investigators^{11–23} have tried to calculate the linewidth and line shift using analytical or computer simulation techniques, as well as a combination of both. In spite of these efforts, it turned out that quantitative agreement is difficult to obtain. The main theoretical models for dephasing are the binary collision model of Fischer and Laubereau,¹¹ the Schweizer and Chandler¹⁶ model, and the hydrodynamic model of Lynden-Bell and Oxtoby.^{13,15}

Levesque *et al.*¹⁹ have carried out a computer simulation of vibrational dephasing in liquid nitrogen near the boiling point. They have investigated the contribution of the various parts of the potential including the vibration-rotation coupling and cross terms. An important conclusion was that the cross terms were essential and that one could not simply calculate separately the effect of different parts of the potential. However, it turned out that as far as the dispersion interaction is concerned the dephasing arises entirely from the bond length dependence of the multipole coefficient. These authors stress that “one needs to know the potential surface very accurately in order to predict quantitatively the vibrational line shape.” The only numerical investigation of the density dependence of the dephasing time has been carried out by Chesnoy and Weis.²⁰ They studied a system of particles interacting by spherical symmetric intermolecular potentials using the method of molecular dynamics. Consequently, they neglected the rotational degrees of freedom.

The main aim of that work was a qualitative analysis and a qualitative comparison with existing theories. Fortunately, recently a very good site–site potential for nitrogen became available.^{22,24,25} Therefore, the aim of the present work is a quantitative calculation by computer simulations of the linewidth for nitrogen at various pressures and a better understanding of the processes contributing to the linewidth.

In Sec. II the method will be described. The contribution of the various mechanisms that influence the frequency, and therefore the linewidth, will be discussed. In contrast with some other investigations²⁰ the vibration-rotation coupling has been included in the calculations throughout. The results are presented in Sec. III. Special attention has been paid to the contribution of various effects to the frequency autocorrelation function. In Sec. IV the results are compared with the experimental data concerning linewidth, dephasing time and line shift. Up to this point the calculations are only based on intra- and intermolecular potentials obtained from literature, without any adjustment to experimental spectroscopic data. In Sec. V the so-called “attractive contribution”¹⁶ is discussed and a new form for this contribution is presented. Finally the results will be compared with other computer simulations or theoretical work in Sec. VI.

II. METHOD

Molecular-dynamical (MD) simulations have been performed on a model system, in order to study the influence of the surrounding molecules on the frequency of a vibrating molecule as a function of pressure and temperature. For practical reasons, a diatomic model was preferred in which the intermolecular forces act on two sites that coincide with the two constituent atoms. It has been shown that the multisite model for nitrogen, given by Etters *et al.*²⁴ leads to rather realistic values, e.g., the equation of state. By omitting the quadrupolar terms, this model was reduced to a two-site model for nitrogen, suitable for our purposes. It turned out that the results for the compressibility with this model are essentially the same as Belak *et al.*^{22,25} obtained with the Etters potential at the densities and the temperature consid-

ered in our work. Moreover, the choice for nitrogen allows for a comparison of the results with experimental data for the Raman shift and the dephasing time available in the literature.¹⁻⁶ The change in vibrational frequency has been calculated from the momentary forces acting on the sites, i.e., the atoms. For the equations of motion used in the simulations, the molecules have been regarded as rigid rotors. Moreover, for the dynamics the same intermolecular potential has been adopted for vibrating and nonvibrating molecules. An experimental study on liquid nitrogen at ambient pressure⁹ showed that, if a resonance coupling is present, its contribution to the linewidth should be less than 10%. A MD study¹⁸ shows that it should be negative, but that the effect should also be less than 10%. It is likely that this fraction will not increase at high pressures²⁶ because a recent experiment with an isotropic dilution on solid N₂ did not reveal any resonance coupling effect on the Raman shift of the ν_2 mode below 20 GPa. This ν_2 mode is the same as the fluid mode along the δ -fluid melting line.²⁷ The reason for this is that the orientational distribution of the molecules, giving rise to ν_2 , are similar to that of the fluid.²⁸ Therefore, no transfer of vibrational energy was taken into account.

As usual with MD simulations, the final results have been obtained as the average of many subsequent momentary observations of the system.

In the first approach, three mechanisms that influence the vibration frequency have been considered.

A. The first order effect by the external forces

External forces, exerted by the surrounding molecules on the sites result in an axial force F_{ax} , relevant for the vibrational motion,

$$F_{ax} = \frac{1}{2} \frac{\mathbf{r}}{|\mathbf{r}|} (\mathbf{F}_2 - \mathbf{F}_1),$$

$$\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1, \quad (1)$$

with $\mathbf{r}_i$ the position of site i and $\mathbf{F}_i$ the total external force acting on site i . F_{ax} would result in a change in the equilibrium bond length. From the values for the harmonic and cubic potential parameters of the intramolecular forces, given by Herzberg²⁹ and Lavorel *et al.*,⁷ the resulting change of vibrational frequency is calculated by

$$d_1 \omega_{vib} = c_1 F_{ax}, \quad (2)$$

with

$$c_1 = 3.807 \times 10^{10} \text{ N}^{-1} \text{ cm}^{-1}.$$

B. The second order effect by the external forces

Because the external force will not be homogeneous, F_{ax} will depend on the bond length r . Thus, the first order derivative

$$f' = \frac{dF_{ax}}{dr} \quad (3)$$

contributes to the harmonic constant of the vibrator, resulting in a frequency change,

$$d_2 \omega = c_2 f', \quad (4)$$

with

$$c_2 = 0.507 \text{ N}^{-1} \text{ m cm}^{-1}.$$

The derivative f' was determined by the differential

$$f' \approx \frac{\Delta F_{ax}(r)}{\Delta r} = \frac{F_{ax}(r + \Delta r) - F_{ax}(r - \Delta r)}{2\Delta r} \quad (5)$$

for each molecule, while all other molecules were kept at there positions. For Δr a value of $0.005 \times 10^{-10} \text{ m}$ was taken. A fourfold of this value did not give any significant change in the results. This fact was regarded as a justification of the linear approach of Eq. (5).

C. The vibration-rotation coupling

A rotation of the molecule results in a centrifugal force that would stretch the bond length and consequently will change the harmonic frequency. Besides, the momentary change in bond length, due to the vibrational motion, will also change the rotational frequency. This well-known vibration-rotation coupling results in a change of the vibrational frequency which is proportional to the rotational energy. Using the potential parameters mentioned above, together with the known values for the atomic masses and the bond length, this effect can straightforwardly be calculated by classical mechanics for the two-site model with the following relation:

$$d_3 \omega_{vib} = c_3 \omega_{rot}^2 \quad (6)$$

with

$$c_3 = -3.073 \times 10^{26} \text{ s}^2 \text{ cm}^{-1}.$$

Resuming, the resulting vibration frequency of each molecule i has been calculated in the simulations by

$$\omega_{i,vib} = \omega_{0,vib} + \sum_{k=1}^3 d_k \omega_{i,vib} \quad (7)$$

with $\omega_{0,vib}$ the frequency of an isolated, nonrotating molecule.

The simulations have been performed on 256 model particles in a cubic box, provided with periodic boundaries. The necessary cutoff of the potential was always chosen as the half of the box length. For simplicity and speed up of the program, simulations have been performed in the NVE ensemble.

The integration of the equations of motion has been performed with the leapfrog algorithm. The elementary time step of integration was fixed at all simulations to $1/6 \times 10^{-14} \text{ s}$. After equilibrium had been established, production runs had been made throughout 36 000 elementary time steps. The analyses of the configurations were made at each 6th step, thus with fixed intervals of 10^{-14} s .

Three topics of interest have been surveyed.

- (1) The mean value for the vibration frequency $\langle \omega_{vib} \rangle$ by averaging Eq. (7) over all particles and time steps.
- (2) The width of the distribution of the momentary individual values of ω_{vib} . This property, commonly called the amplitude of modulation,¹⁵ is defined by

TABLE I. Results for various properties, related with the Raman spectrum of nitrogen at 296 K, obtained by molecular dynamical simulations.

Density (kmol m ⁻³)	Pressure (GPa)	$d\omega_{\text{vib}}$ (cm ⁻¹)	$\Delta/2\pi c$ (cm ⁻¹)	τ_c (10 ⁻¹⁴ s)	FWHM (cm ⁻¹)
18	0.073	-0.47	2.68	...	...
25	0.179	0.67	3.08	13.6	0.486
27	0.231	1.11	3.24	11.1	0.439
29	0.300	1.58	3.44	9.12	0.407
32	0.446	2.52	3.78	6.85	0.369
35	0.643	3.64	4.07	6.17	0.385
37	0.821	4.55	4.35	5.61	0.400
39	1.033	5.56	4.60	5.73	0.457
40	1.157	6.10	4.74	5.57	0.472
41	1.290	6.69	4.87	5.71	0.511
42	1.436	7.28	4.99	5.90	0.554
43	1.596	7.95	5.15	6.08	0.608
44	1.771	8.65	5.29	6.15	0.649
45	1.956	9.39	5.43	6.49	0.721
46	2.163	10.20	5.60	6.84	0.809

$$\Delta = \{\langle \omega_{\text{vib}}^2 \rangle - \langle \omega_{\text{vib}} \rangle^2\}^{1/2}. \quad (8)$$

The brackets denote the averaging over all particles throughout the entire simulation run at equilibrium.

- (3) The time dependence of the momentary vibrational frequency, in terms of the normalized self-correlation function,

$$\Omega(t) = \frac{\langle \omega_{\text{vib}}(0) \omega_{\text{vib}}(t) \rangle - \langle \omega_{\text{vib}}(0) \rangle^2}{\Delta^2}. \quad (9)$$

From this function, the correlation time τ_c was calculated

$$\tau_c = \lim_{t \rightarrow \infty} \int_0^t \Omega(s) ds. \quad (10)$$

For this purpose, the value of ω_{vib} for each molecule was kept in memory for 200 registration steps and the integration (10) has been made over 199×10^{-14} s, making use of a numeric five-point integration rule. Note that one may substitute in Eqs. (8) and (9) the value of $d\omega_{\text{vib}}$ given in Eq. (7), which is the time dependent part of ω_{vib} .

An isothermal series of simulation runs have been made for a temperature of 296 K (± 2 K), covering a density range from 18 kmol m⁻³ to 46 kmol m⁻³, corresponding to pressures from 0.073 GPa up to 2.16 GPa.

III. RESULTS

In Table I, the results are given for the isothermal series. The second column displays the results for the pressure. These values have not been corrected for the long tail interactions beyond the cutoff distance. In fact, these corrections would be too small to be relevant. Under the assumption that the radial distribution function equals unity above the cutoff limit, the correction would be only 1% at the lowest pressure, 0.5% at 1 GPa, and 0.4% at 2 GPa.

The total change in vibration frequency with respect to the frequency of an isolated, *nonrotating* molecule is given in column 3. The simulations reveal separately the values for the constituent terms, mentioned above. It turns out that the

FIG. 1. The change of the vibration frequency $d\omega_{\text{vib}}$ (dots) and the amplitude of modulation (squares) at 296 K as a function of pressure.

second order effect of the external forces has the same sign as the first order effect. Its value is nearly proportional to the first order; gradually decreasing from 19.5% at 0.07 GPa to 18.7% at 2.2 GPa. The contribution of the vibration-rotation coupling was found to be constant, as it ought to be at constant temperature,

$$d_3 \omega_{\text{vib}} = -1.82 (\pm 0.02) \text{ cm}^{-1}, \quad (11)$$

at

$$T = 296 \text{ K}.$$

It is seen that the total change in ω_{vib} as well as the amplitude increases monotonously with the pressure. In column 4 the values for the amplitude have been divided by $2\pi c$, in order to convert them into units of cm⁻¹. The same results are also graphically displayed in Fig. 1. The fifth column of Table I denotes the correlation time, defined in Eq. (10). At the lowest pressure (0.073 GPa) the correlation function (9) converges too slowly to reach the zero limit value after 200×10^{-14} s. The correlation time turns out to have a remarkable behavior. Going from low to high pressures, it falls down rapidly until about 5.6×10^{-14} s at approximately 1 GPa. Above this pressure, a marked increase is seen. In Fig. 2 this is clearly displayed (open circles). Note that this phenomenon is different from the behavior of single variables such as the angular momentum.^{12,14} The fact that the relaxation time is rapidly increasing when the pressure is lowered from ≈ 0.4 GPa puts a limit on the calculations of the line-width, as will be discussed in the next section.

Special attention has been paid to the time behavior of the frequency correlation function $\Omega(t)$. The method of molecular dynamics allows for a separate investigation of the influence of each of the important mechanisms that changes the frequency. A picture with the details of this function is given in Fig. 3. These data deal with the results at 1.15 GPa and 296 K, but can be regarded qualitatively representative for all other simulations. In this figure, the self-correlation of the change of ω_{vib} due to the first and second order effect of the external forces and due to the vibration-rotation coupling have been plotted separately, together with the resulting

FIG. 2. The correlation time τ_c of the vibration frequency as a function of pressure. Open circles, initial MD results; dots, MD results for the refined model.

function. It is seen that the rotational part decays most slowly, while both external force effects are comparable. The final result is a function that rapidly decays within 10^{-13} s, after which a long tail persists. This long-time effect is even more clearly demonstrated in the logarithmic plot of Fig. 4. As has been noted before, the correlation time τ_c defined by Eq. (10) is about at a minimum value at this pressure. Going to lower pressures, the sharp kink at approximately 10^{-13} s is lifted up and becomes less pronounced; meanwhile the long-time tail disappears as well. Going to higher pressures, the initial decay becomes slightly faster, but simultaneously, the tail becomes more pronounced. The latter effect overrules the first one, resulting in an increase of the correlation time. The importance of the vibration-rotation coupling is once more demonstrated in Fig. 5. Performing the simulations without the vibration-rotation coupling leads to a correlation function with essentially another shape; even the kink disappears. A quantitative demonstration of the importance of the

FIG. 4. A semilogarithmic plot of $\Omega(t)$ at 296 K and 1.15 GPa.

vibration-rotation coupling and of the second order external force effect is given in Table II. It is seen that at low pressures, relaxation due to the second order effect is important, but that, at high pressures, rotations play an important role in the relaxation of the vibration. It is also seen that the vibration-rotation coupling has an influence on the amplitude of modulation, especially at the lower densities. Therefore, omitting this coupling would result in a large deviation in the linewidth and its density dependence.

IV. COMPARISON WITH EXPERIMENTAL DATA

The decay of the self-correlation function of the vibrational frequency $\Omega(t)$ and change of ω_{vib} can be related to experimental data for the Raman spectrum of nitrogen.

In the literature, values are available concerning the Q -band shift,^{4,6} the linewidth,^{4,6} and the vibrational decay rate¹⁻³ in nitrogen at pressures which correspond with the pressure range chosen for the simulations.

FIG. 3. The time correlation function for the change in vibration frequency at 296 K and 1.15 GPa. 1, due to the first order effect of external forces only; 2, due to the second order effect of external forces only; R, due to the vibration-rotation coupling only; total, the complete function $\Omega(t)$.

FIG. 5. The MD results for the time correlation function of the frequency, discarding the vibration-rotation coupling (NR) in comparison with the complete function (total).

TABLE II. Deviations of some results of the MD calculations, omitting the 2nd order effect of intermolecular forces and the vibration-rotation coupling.

Pressure (GPa)	Deviation in τ_c no 2nd order	Deviation in τ_c no vib-rot coupling	Deviation in Δ no vib-rot coupling
0.446	+17%	+7%	-11%
1.157	0	+42%	-7%
1.956	-3%	+34%	-4%

A. Dephasing and linewidth

In his treatment of the stochastic theory of the line shape, Kubo³⁰ discusses two opposed situations, namely systems with fast and systems with slow modulation of the frequency by the forces exerted on the vibrator, quantized by

$$\begin{aligned} \text{Fast modulation: } \Delta \cdot \tau_c &\ll 1, \\ \text{Slow modulation: } \Delta \cdot \tau_c &\gg 1. \end{aligned} \quad (12)$$

From the data obtained from the simulations, given in Table I, this modulation criterion can directly be calculated. The result for the isothermal series at 296 K is given in Fig. 6 (open circles). It is seen from these results that, as a first approximation, the system can be considered to be in the fast modulation regime. According to the Kubo-theory the line has a Lorentzian shape and the linewidth, defined as the “full-width at half-maximum” (FWHM) can be calculated with

$$\text{FWHM} = 2\Delta^2 \cdot \tau_c. \quad (13)$$

Numerical values for this property obtained from the simulation are given in Table I, column 6. Experimental values for the linewidth are given by Lavorel *et al.*⁴ and by Scheerboom and Schouten.⁶ Moreover, direct measurements of the vibrational decay time T_2 are performed by Kroon *et al.*¹⁻³ The linewidth is obtained from T_2 by

$$\text{FWHM} = (\pi c T_2)^{-1}. \quad (14)$$

It is clearly seen in Fig. 6 that, going down in pressure, below ≈ 0.2 GPa the domain of fast modulation ends rapidly.

FIG. 6. The “fast modulation criterion” parameter $\Delta \cdot \tau_c$ at 296 K as a function of pressure. Open circles, initial MD simulations; dots, MD results for the refined model.

FIG. 7. The linewidth (FWHM) for the N₂ Q-branch line at 296 K as a function of pressure. Solid line, experimental data by Lavorel *et al.* (Ref. 4); crosses, experimental data from T_2 measurements by Kroon *et al.* (Refs. 1–3); diamonds, experimental results by Scheerboom *et al.* (Ref. 6); open circles, MD results with the initial model; dots, MD results with the refined model.

Consequently, the line shape will be no longer Lorentzian and the linewidth cannot be calculated with Eq. (13). Therefore it must be concluded that our simulations cover the whole density region for nitrogen in the fluid phase at room temperature, where the system is in a fast-modulation regime and the linewidth can be calculated easily.

Figure 7 displays the linewidth at 296 K as a function of the pressure in a comparison between these simulated data (open circles) and experimental data.

B. The line shift

Lavorel *et al.*⁷ determined experimentally the shift for the transition to the first excited vibrational state for an isolated, nonrotating molecule,

$$\omega_{\text{vib},0} = 2329.91 \text{ cm}^{-1}. \quad (15)$$

In order to calculate the simulated shift one has to add $d\omega_{\text{vib}}$,

$$\omega_{\text{shift}} = \omega_{\text{vib},0} + d\omega_{\text{vib}}. \quad (16)$$

A comparison with the experimental data is made in Fig. 8. It is clearly seen that the experimentally determined pressure dependence of the shift is not represented by the calculated change in the vibration frequency (open circles) as given in Eq. (16). Experimentally, the shift initially decreases with increasing pressure and displays a minimum at about 150 MPa, whereas the calculated change always increases.

V. REFINED CALCULATIONS

A serious simplification in our model is the assumption that the intermolecular potential is the same for excited molecules as for molecules in the ground state. It is known for instance, that the polarizability increases at excitation, but it is hard to quantize the effect. A few calculations on this topic concern the change in dispersion forces, often called the attractive contribution.¹⁶ The results turn out to be not very helpful for a quantitative description. Therefore we de-

FIG. 8. The shift of the Q-branch vibration line of N₂ at 296 K as a function of pressure. Solid line, experimental data by Lavorel *et al.* (Ref. 4); squares, experimental data by Scheerboom *et al.* (Ref. 6); open circles, calculated from the change in vibration frequency; dots, results obtained with the refined model.

terminated the change in potential energy at excitation directly from the difference in frequency, i.e., the energy gap, between the simulated and experimental data of the shift.

For this purpose, we determined an intermolecular site-site potential function $\Delta\phi$ which describes the pressure dependence of this energy gap. A suitable functional form turned out to be

$$\Delta\phi = \frac{a}{r^{12}} - \frac{b}{r^6}, \quad (17)$$

with

$$\begin{aligned} a &= 3.75 \times 10^{-115} \text{ cm}^{-1} \text{ m}^{12}, \\ b &= 5.65 \times 10^{-58} \text{ cm}^{-1} \text{ m}^6. \end{aligned} \quad (18)$$

The choice for the inverse 6th power term is obvious, but it was found to be necessary to add another term which reduces the influence of the first one at small distances and takes into account changes in the charge distribution. The choice for an inverse 12th power is—at least partially—traditional. Equation (17) can be rewritten in the Lennard-Jones form,

$$\Delta\phi = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (19)$$

with

$$\begin{aligned} \frac{\epsilon}{k_B} &= 0.30 \text{ K}, \\ \sigma &= 2.95 \times 10^{-10} \text{ m}. \end{aligned} \quad (20)$$

This energy jump $\Delta\phi$ results in a frequency jump $\Delta\omega$,

$$\Delta\omega = \frac{\Delta\phi}{2\pi c}, \quad (21)$$

which is added to the shift, previously obtained with Eq. (16). The quality of the fit of the recalculated values for the shift can be seen in Fig. 8 (dots).

FIG. 9. The energy correction $\Delta\phi$ on the intermolecular site-site interaction (dashed line) compared with the site-site potential energy (solid line). Note that $\Delta\phi$ has been multiplied by 100.

Although the energy jump $\Delta\phi$ has a marked influence on the shift, it barely affects the total potential energy of a molecule. In Fig. 9 a plot is given of the contribution to the intermolecular potential between two sites of different molecules, together with $\Delta\phi$. Note that in this figure the value for $\Delta\phi$ is multiplied by 100 to allow for a visual comparison. At site distances where the attractive forces dominate, ($r > 3.7 \times 10^{-10} \text{ m}$) the value for $\Delta\phi$ is always less than 0.6% of the total potential. At distances where $\Delta\phi$ is positive, the site-site potential is strongly repulsive and dominates $\Delta\phi$ so many orders of magnitude that the precise form of $\Delta\phi$ becomes unimportant. These findings justify the assumption noted in Sec. II that the interaction forces governing the dynamics of the system, may be considered the same for vibrating and nonvibrating molecules. A logical step is now to include $\Delta\omega$ (21) in the calculation of the linewidth and repeat the simulations. This has been done for most of the state parameters chosen for the first simulations. The results are given numerically in Table III. The new results differ in detail with the first ones; the amplitude of modulation increases faster with the pressure, as can be seen in Fig. 10 and the correlation time τ_c is lower, especial between 0.4 and 1 GPa (Fig. 2, dots). The shape of the correlation function $\Omega(t)$ does not change significantly; the description given in Sec. II holds also for the new simulations. It is seen that the minimum in the criterion parameter for the modulation rate, i.e., $\Delta\tau_c$ becomes somewhat more pronounced. Most important is the result for the linewidth; as can be seen in Fig. 7 (dots) the refined simulations reveal more clearly a minimum at $\pm 0.5 \text{ GPa}$, while the pressure dependence above this pressure is conform the experimental data.

VI. DISCUSSION

Levesque *et al.*¹⁹ found an enormous influence of the bond length dependence of the dispersion interaction on the

TABLE III. Results for amplitude of modulation, relaxation time, and linewidth by molecular dynamic calculations, including a so-called "attractive contribution" in the intermolecular potential.

Pressure (GPa)	$\Delta/2\pi c$ (cm ⁻¹)	τ_c (10 ⁻¹⁴ s)	FWHM (cm ⁻¹)
0.179	3.20	13.50	0.521
0.231	3.29	8.72	0.378
0.300	3.62	7.44	0.368
0.446	4.00	5.53	0.334
0.643	4.42	5.28	0.389
0.821	4.73	5.10	0.430
1.157	5.27	5.41	0.566
1.596	5.79	6.03	0.762
1.956	6.18	6.32	0.910
2.163	6.40	6.50	1.004

dephasing time. Moreover, the dependence of the parameter for short range interaction on the vibrational coordinates has not been taken into account because of lack of data. We have shown above (Sec. IV), that it is not possible to get a good agreement with the experimental line shift as a function of pressure if the change in the short range valence interaction is omitted. In our case the total effect of change in bond length is limited probably due to the higher temperature considered in our study. The result of our calculations is in agreement with the experimental data for the linewidth and dephasing times.

Chesnoy and Weis²⁰ neglected the rotational degrees of freedom. Table II shows that this is not correct, even in the case of a qualitative comparison. At 0.45 GPa, where the linewidth shows a minimum, the influence of the vibration-rotation coupling on the correlation time is -7% and on the linewidth +15%. At the highest pressures these numbers are, respectively, -34% and +26%. It should be noted that in liquid nitrogen at the boiling point¹⁹ the role of the vibration-rotation coupling may be considerably smaller. This might be due to the relative low density and temperature (± 28

kmol m⁻³; 76 K) and comparatively very low pressure at the boiling point.

Schweizer and Chandler¹⁶ combined the idea of a binary collision model¹¹ for the repulsive forces with a mean field idea for the slowly varying attractive forces. The quantitative agreement with the experimental linewidth of liquid nitrogen at 76 K was poor and no density dependence was given. Chesnoy and Gale²³ improved the quantitative agreement by adding an adjustable correction factor on the hard sphere model, that deals with the long-range interactions. Oksengorn *et al.*¹⁰ used a soft repulsive interaction model together with adjustable parameters for the influence of the vibration-rotation coupling and of the attractive forces. Nevertheless, they did not obtain acceptable agreement with the experimental results for the density dependence at low temperatures. Lavorel *et al.*⁴ applied this method with more success at room temperature.

The same model was used by Kroon *et al.*¹⁻³ in a limited pressure range. The value for the hard sphere diameter, needed to get agreement with experiment, was not realistic; moreover the results were extremely sensitive for the value of this parameter. The same model has also been used to calculate the shift of the frequency as a function of the pressure or the density (Schweizer¹⁶ and Devendorf¹⁷). The problem is once again the dependence of the intermolecular forces on the bond length. Devendorf and Ben-Amotz¹⁷ have solved this problem by taking into account only the dispersion forces and by stating that the influence of long range dispersive attractive solvent-solute interaction on the frequency shift is proportional to the density, the proportionality constant being fixed empirically. The short range contributions have been omitted. As will be shown in a future publication, this model does not give good results for simple binary mixtures. In our work we have taken into account short range as well as long range dependence on the bond length. These results are in good agreement with both experimentally determined linewidth and line shift. Belak *et al.*²² have determined by constant-pressure Monte Carlo calculations the shift of vibrational frequency of nitrogen in a large pressure and temperature range. They did not obtain the minimum in the shift since they neglected the difference in intermolecular potential for a vibrating and a nonvibrating molecule. Probably due to this effect, they overestimated the frequency. The values at room temperature, deduced from a plot in their paper, are in good agreement with our "repulsive" contribution.

VII. CONCLUSION

We performed molecular dynamical computer simulations on a model system for fluid nitrogen at room temperature, up to the melting line. From these simulations the linewidth of the Raman Q-branch is calculated. In contrast with earlier attempts by others, realistic results have now been obtained which do not depend on ad hoc adjustment of parameters, but are based on the inter- and intramolecular parameters, obtained from other sources. Moreover, the influence of the vibration-rotation coupling on the correlation time is considerable, in particular at high pressures. It is

FIG. 10. The amplitude of modulation calculated from the change in vibration frequency only (open circles) and calculated with the refined model (dots).

shown that the simulations cover the whole fluid range at room temperature where the line shape is Lorentzian.

In combination with the experimental data for the line shift, the calculations give an estimation for the so-called “attractive part” contribution, which is in general very difficult to quantize. In contrast with the importance of the attractive contribution to the shift, it does not change the line-width essentially at the state parameters under consideration.

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