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# Broadening of Vibrational Raman Spectra by Concentration Fluctuations: A Molecular Dynamics Survey[1]

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Molecular dynamics calculations have been performed on model systems for nitrogen and mixtures of nitrogen with other compounds at high pressure and at ambient temperatures. From these simulations the line shape of the Raman *Q*-branch was calculated. A short description of the applied methods is given. Our aim is to investigate whether line broadening, experimentally observed in mixtures, may be at least partially caused by critical fluctuations, as appeared to be the case in nitrogen–helium mixtures. For this purpose it is necessary to investigate first the behavior of a noncritical mixture. We analyzed extensively the results of the mixture of nitrogen in neon at 2.4 GPa and 296 K, which is far away from a critical state. In this system a maximum in the linewidth is seen at equal volume fractions, experimentally as well as in simulations. The details revealed by the simulations allow a comparison with existing models, such as that given by Knapp and Fischer. It is seen that assumptions made in that theory are in clear contradiction with the findings of the simulations.

**KEY WORDS:** linewidth; mixtures; molecular dynamics simulations; nitrogen; Raman spectroscopy.

## 1. INTRODUCTION

During the last decade an increasing amount of information has been obtained by Raman spectroscopy about the vibrational spectra of simple fluids at high pressures. Especially, the Raman *Q*-branch of nitrogen has been chosen in many experimental investigations, in pure substance [1, 2]

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as well as in mixtures [2–6]. In the fluid phase of nitrogen at high pressures only, one spectral line can be observed, which is characterized by its frequency (the "shift") and its shape, e.g., the linewidth, quantized by the full width at half-maximum (FWHM).

Nitrogen is also a favorable substance for studying vibrational behavior at high pressures by means of computer simulations, in particular, molecular dynamics (MD). First, the molecule is relatively simple, is symmetric, and has only one vibrational mode. At moderate temperatures, only a small fraction of the molecules is vibrationally exited (about 0.7% at room temperature). Furthermore, since the rotational energy levels are very close, the rotations can be treated classically, i.e., continuously distributed at equilibrium. Moreover, the vibrational population relaxation is very small and therefore the linewidth is determined mainly by dephasing. Finally, the intramolecular potential as a function of the bond length, as well as the intermolecular potential, is well determined. The nitrogen molecule can be presented very well by a two-site model. Strictly speaking, one should determine simultaneously the vibrational motion of the sites as well as the trajectory of the molecule as a whole. In fact this is not possible. Due to the stiffness of the *intra*molecular force, time steps needed for the simulation of the vibrational motions are orders of magnitude less than those needed for the translations. On the other hand, this stiffness allows a treatment of the molecules as rigid rotors, which simplifies the calculations.

## 2. METHODS AND RESULTS

### 2.1. Pure Nitrogen

Given the low fraction of spontaneously excited molecules, it has been assumed in the simulations that only *one* molecule within the system was excited, but, to improve the statstics, the procedure for calculating the change of the frequency has been performed for all molecules.

In a first approximation one can distinguish three causes for the deviation of the vibrational frequency of a molecule surrounded by other particles from that of an isolated, nonrotating molecule.

(a) The intermolecular forces (of the exponential-6 type) between the molecule under consideration and neighbor molecules will have a resultant component along the axis of the vibrating molecule. As a result, the bond length changes. Because the atom–atom interaction is not purely harmonic, but also includes higher terms, the frequency changes continuously. This is indicated below as the "first-order external contribution" (E1).

(b) Because the external force will not be homogeneous, the axial force will depend on the momentary bond length. Thus, the first-order derivative of the axial force with respect to the bond length contributes to the harmonic constant of the vibrator: the "second-order external contribution" (E2).

(c) Due to centrifugal forces the rotation of a molecule influences the bond length as well, and consequently vibration and rotation influence each other mutually: the vibration–rotation coupling (VR).

An effect that has been neglected is the resonance transfer. The importance of this contribution is thought to be small in the fluid phase [7].

The relation between these momentary forces and the vibration frequency can be determined quantitatively using the well-known *intra*molecular energy function [8], which contains, apart from a harmonic term, also higher-order coefficients. For the purpose of our simulations, only the cubic term is significant.

In our first attempts [7], we simulated a system of nitrogen model particles in the fluid phase at 296 K and at pressures from ±0.07 up to ±2.4 GPa. Details of the simulations are given in Refs. 7, 9, and 10 but it is noted here that the model for the *inter*molecular potential considered a site–site potential between the atoms and a fixed *intra*molecular distance. During each run the following topics have been surveyed.

(a) The mean value for the change of the vibration frequency $\langle \omega_{\mathrm{vib}} \rangle$, i.e., the average over all particles and over all time steps of the sum of E1, E2, and VR.

(b) The width of the distribution of the momentary individual values of $\omega_{\mathrm{vib}}$ by determining the standard deviation, usually called the "amplitude of modulation,"

$$\Delta = \{\langle \omega_{\mathrm{vib}}^2 \rangle - \langle \omega_{\mathrm{vib}} \rangle^2\}^{1/2} \tag{1}$$

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

$$\Omega(t) = \frac{\langle \omega(0)\, \omega(t) \rangle - \langle \omega(0) \rangle^2}{\Delta^2} \tag{2}$$

From this function, the correlation time $\tau_c$ was calculated,

$$\tau_c = \int_0^\infty \Omega(t)\, dt \tag{3}$$

The addition of $\langle \omega_{\text{vib}} \rangle$ to the frequency $\omega_0$ of a nonrotating, isolated molecule [8] gives the simulated shift. For the determination of the line width (FWHM), use has been made of the theory given by Kubo [11]. In this theory, which is quoted more extensively below, an expression is given for the linewidth under the condition that the frequencies are fast modulated, i.e., the system resides in the fast modulation regime

$$\text{FWHM} = 2\Delta^2\tau_c \tag{4}$$

$$\Delta \cdot \tau_c \ll 1 \tag{5}$$

In Fig. 1 both experimental results [1, 2] and results obtained by MD [7] are displayed. A large discrepancy is clearly seen. Experimentally, an initial decrease of the shift with increasing pressure (red shift) is observed, followed by an increase above ca. 0.2 GPa, while the simulations initially performed always gave a blue shift. The most obvious reason for this discrepancy is that the interaction of a particle with its surroundings changes at excitation due to a small change in the potential parameters of the

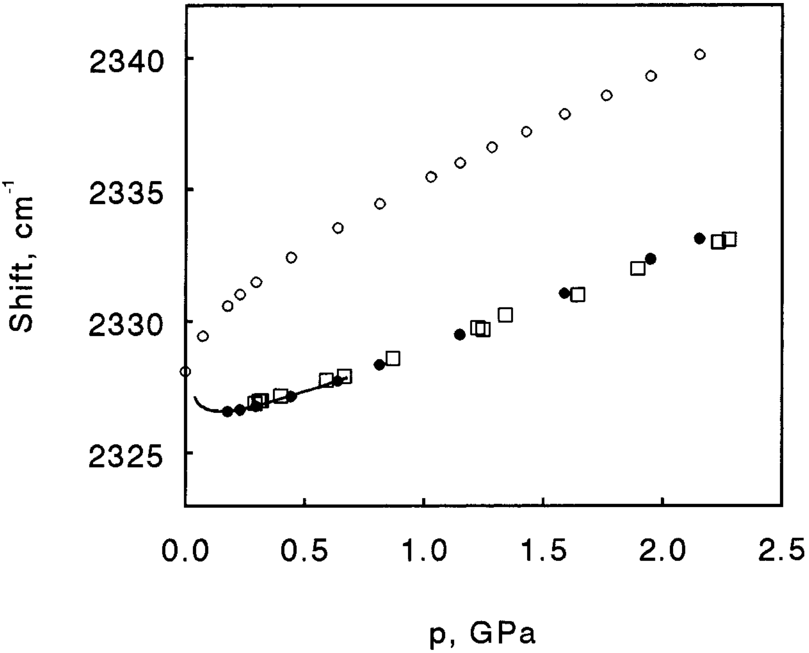

**Fig. 1.** The shift of the $Q$-branch of $N_2$ at 296 K as a function of the pressure. Solid line and squares: experimental results [1, 2]. Open and filled circles: MD results without dispersion correction and with dispersion correction, respectively [7].

excited molecule. In other words, there is a small difference in the solvation energy between an excited and a nonexcited molecule. Although this energy difference is small compared to the total potential energy, it cannot be neglected in calculations of the frequency shift since the energies involved in the shift are very small. This aspect has been neglected in our first approach. However, this energy change is hard to determine theoretically. Therefore, we treated this problem in an opposite way and determined the jump in the dispersion energy between the single excited molecule and the nonexcited molecules from the difference between the preliminary calculations and the experimental data. A suitable way was found by adding a weak intermolecular potential to the ground-state potential between the solute and all solvent molecules, again as a site–site interaction. For this purpose, a Lennard–Jones 12–6 model had been applied. The strength of this potential ($\varepsilon/k_B = 0.3$ K; $\sigma = 2.95$ Å) is two orders of magnitude less than the molecular interaction in the ground state and, therefore, regarded as negligible for the dynamics. It must be emphasized that also the repulsive part of this LJ potential is necessary to obtain a good correction. Nevertheless, the choice for this potential is—at least—traditional; the positioning at the atom sites is somewhat arbitrary as well. It is shown that this correction, indicated as the dispersion correction (DC), plays a dominant role in the mechanisms of relaxation and line broadening. Nevertheless, one must be aware that, due to the method applied, the DC also includes the errors in experiments and simulations, e.g., the neglect of the resonance transfer.

In the second stage of the calculations, the simulations have been repeated, now with the addition of the DC, which now leads to a quantitative correspondence with the experiments. The values for $\Delta \cdot \tau_c$ range from 0.04 to 0.09. Thus, according to Eq. (5) the system may presumably be regarded to be in the fast modulation regime, and consequently, the linewidth FWHM can be calculated with Eq. (4). The results are shown in Fig. 2. The addition of the DC increases the linewidth at pressures above 1 GPa. Considering the experimental uncertainties, the correspondence between experiment and simulation is rather good.

Computer simulations offer a unique possibility to reveal details generally unobservable in experiments. For instance, the various contributions to the correlation, Eq. (2), can be determined. The vibration frequency $\omega_{\text{vib}}$ as a function of time can be written

$$\begin{aligned} \omega_{\text{vib}} &= \omega_0 + \omega(t) \\ \omega(t) &= \omega_{\text{E1}}(t) + \omega_{\text{E2}}(t) + \omega_{\text{VR}}(t) + \omega_{\text{DC}}(t) \end{aligned} \tag{6}$$

with $\omega_0$ the frequency of an isolated, nonrotating molecule.

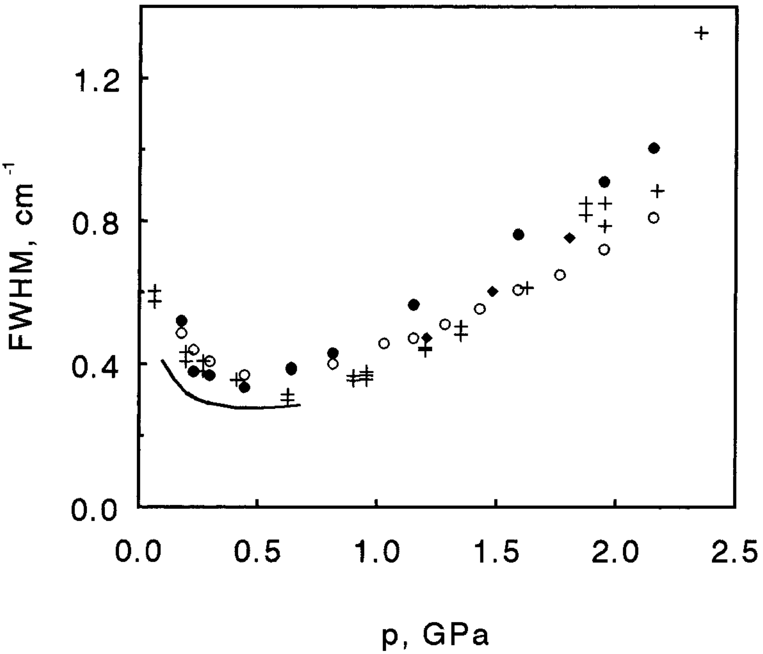

**Fig. 2.** The linewidth (FWHM) for the $N_2$ $Q$-branch at 296 K as a function of the pressure. Solid line and diamonds: experimental results [1, 2]. Crosses: experimental data from $T_2$ measurements [16, 17]. Open and filled circles: MD results without DC and with DC, respectively [7].

Next, the correlation function can be written

$$\begin{aligned} \Omega(t) &= \sum_{\alpha,\beta} \Omega_{\alpha,\beta}(t) \\ \Omega_{\alpha,\beta}(t) &= \{\langle \omega_\alpha(0)\, \omega_\beta(t)\rangle - \langle \omega_\alpha(0)\rangle \langle \omega_\beta(0)\rangle\}/\Delta^2 \end{aligned} \tag{7}$$

where $\alpha$ and $\beta$ denote E1, E2, VR, or DC, and $\Delta$ is again the total amplitude of modulation, Eq. (1).

From these functions the separate contributions to the correlation time can be calculated:

$$\tau_{\alpha,\beta} = \int_0^\infty \Omega_{\alpha,\beta}(t)\, dt \tag{8}$$

$$\tau_c = \sum_{\alpha,\beta} \tau_{\alpha,\beta}$$

In Fig. 3 the total autocorrelation function below 10 ps is shown. The behavior shown is qualitatively representative for all simulations on fluid nitrogen. Three regions can be discerned: an initial rapid decrease, an interval with undulations, and, finally, a smooth decay which approaches an exponential behavior. The complexity of the whole mechanism is demonstrated by Figs. 4a and b, where all 10 contributing functions, 4 diagonal and 6 cross terms, are drawn for fluid $N_2$ just below the transition to the solid $\beta$ phase. Note the importance of the cross-correlations and the partial cancellations due to negative values of the cross-correlations with the VR. Note as well that the latter, according to Eqs. (1) and (7), do not contribute to $\Delta^2$, because in classical statistical physics, rotations and interactions are momentarily independent. Another consequence of the fact that

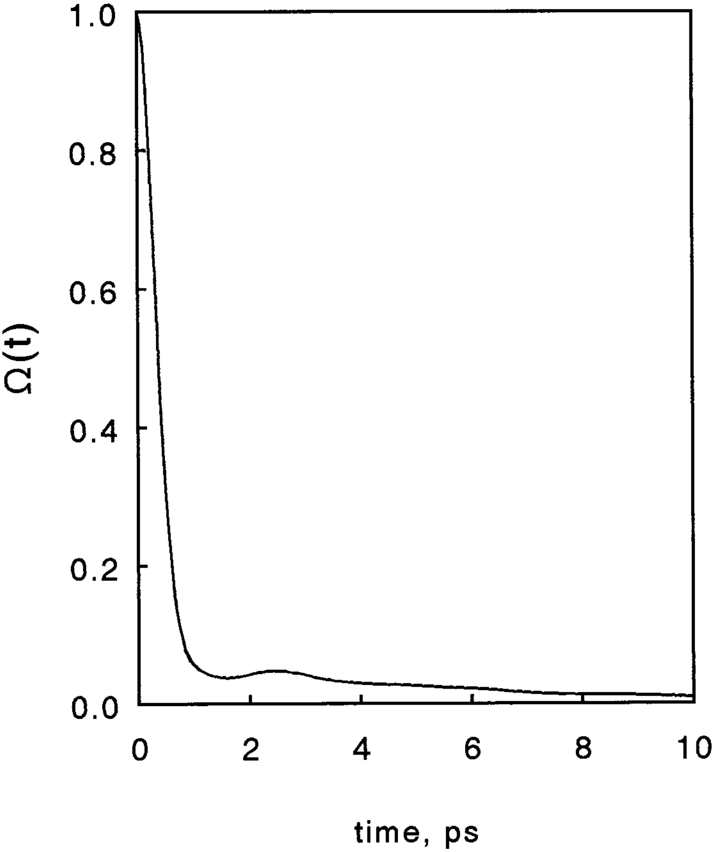

**Fig. 3.** Autocorrelation function of the vibration frequency of $N_2$ at 296 K and 2.4 GPa.

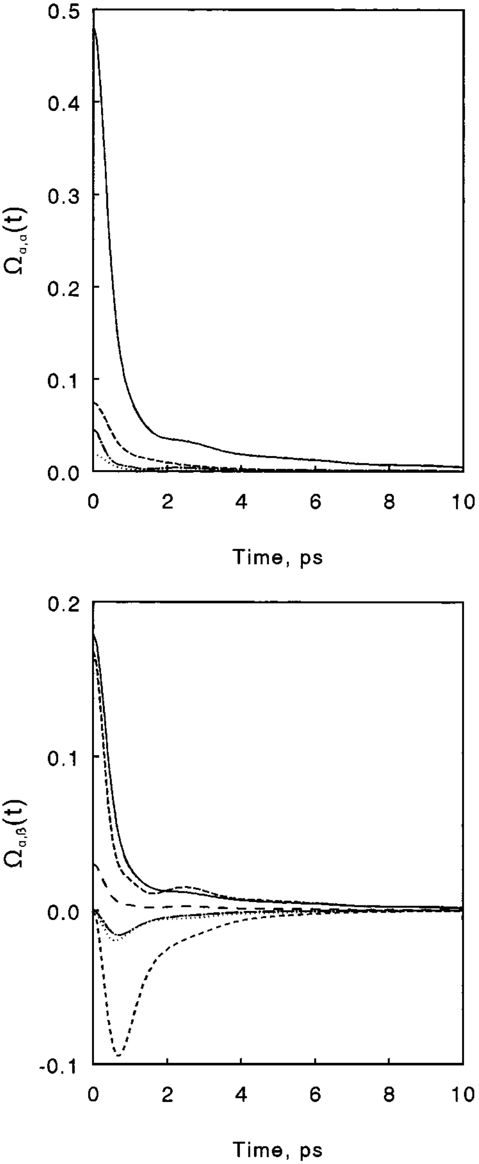

**Fig. 4.** Contributions to the frequency autocorrelation function of $N_2$ at 296 K and 2.4 GPa. (a) Diagonal contributions: $\Omega_{\alpha,\alpha}(t)$. Top-down at $t = 0$: E1_E1; VR_VR; DC_DC; E2_E2. (b) Cross-correlations: $\Omega_{\alpha,\beta}(t) + \Omega_{\beta,\alpha}(t)$. Top-down at $t = <0.5$ ps: E1_E2; E1_DC; E2_DC; E2_VR; VR_DC; E1_VR.

all cross-correlations with VR are negative is the occurrence of negative "correlation times" [Eq. (8)].

## 2.2. Nitrogen in Mixtures

Some years ago our laboratory published results of high-pressure Raman measurements of fluid nitrogen in a mixture with helium [3]. The investigators found a considerable broadening at the critical composition, which was attributed to critical concentration fluctuations. They proposed that on the approach to the critical point, the amplitude of these fluctuations increases and hence an inhomogeneous broadening was achieved. To investigate this proposition, Kooi et al. [6] recently performed similar experiments on mixtures of nitrogen with other compounds, e.g., neon. In contrast with the He–$N_2$ mixture, the Ne–$N_2$ system has no critical demixing line at ambient temperature. Nevertheless, again a clear line broadening was found, although less than in the He–$N_2$ mixture. To reveal the underlying mechanisms and to investigate to what extent critical behavior contributes to the broadening, MD simulations on model systems for both mixtures have been made. In this paper, we discuss primarily the noncritical system Ne–$N_2$, which should be well understood before a critical behavior can be investigated.

It will be clear from the explanation given above that for mixtures one needs, apart from the "unlike" interaction with nitrogen in the ground state, a measure for the "unlike" DC as well. Therefore, simulations have been performed at appropriate pressures and temperatures of one single molecule in a solvent. Similarly as for pure nitrogen, first a series of simulations had to be made without DC. The results for the frequency change with the pressure in various compounds, without DC, relative to the frequency of an isolated molecule are given in Fig. 5. Note that all results are close together and are about the same as for nitrogen in nitrogen and thus nearly independent of the intermolecular interaction. Experimental results for $N_2$ in He are slightly above these MD results, with neon as a solvent slightly below, although an increase with increasing density is always seen ("blue shift"). Experiments with Ar [4] and Xe [5] as solvents show a clear red shift with a maximum of about 2.5 and 4 $cm^{-1}$, respectively. The increase in the DC with the mass of the solvent molecules reflects the higher polarizability of the large molecules: the different behavior in different solvents is due mainly to the DC. A most important conclusion is that, at a given pressure, the shift is determined primarily by the *change* of the intermolecular interaction, at excitation of the molecule under consideration, with the surrounding molecules, and not by the intermolecular forces, acting on the nitrogen molecule in the ground state.

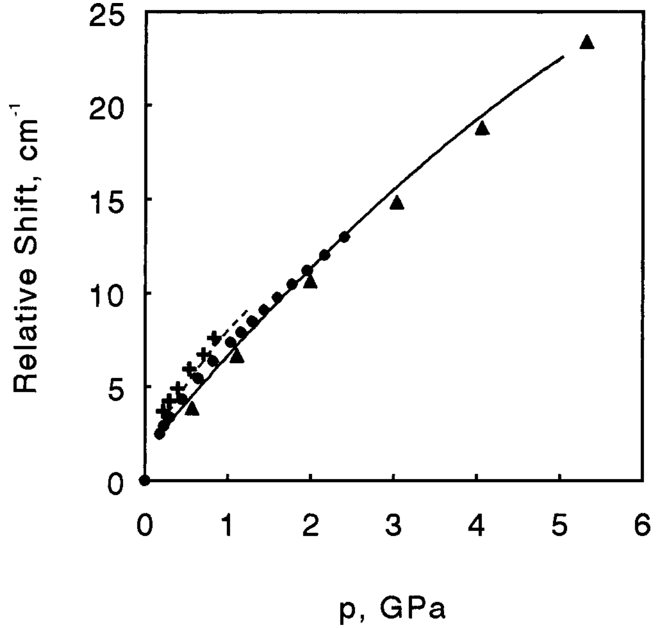

**Fig. 5.** The shift of a single nitrogen molecule in an solvent relative to the frequency of an isolated (undisturbed) molecule, without DC, as a function of pressure. Crosses: in Xe at 408 K. Dashed line: in Ar at 296 K. Solid line: in Ne at 296 K. Triangles: in He at 296 K. Circles: $N_2$ in $N_2$ at 296 K.

Measurements on He–$N_2$ [3] show a maximum in the linewidth at a He mole fraction of ±0.8, which corresponds to a volume fraction of ±0.5. The volume fraction is defined by the ratio of the volumes of the pure components at the same pressure and temperature as the mixture. The measurements by Kooi et al. [6] have been performed on mixtures of $N_2$ with mole fractions of Ne of 0.1, 0.65, and 0.95. In this mixture, the maximum linewidth was seen at a molar fraction of 0.65, corresponding again to a volume fraction of ±0.5. The broadening relative to the average of the linewidth of pure nitrogen and nitrogen at infinite dilution was about a factor of three in helium and a factor of two in neon. It is mentioned above how the DC has been determined for $N_2$ in $N_2$ and for $N_2$ in He and in Ne. Assuming that the DC is pair-additive, we simulated the vibrational behavior of nitrogen at several concentrations in these solvents, at 296 K and 2.4 GPa. Because the shift *without* DC hardly depends on the intermolecular potential, the concentration dependence of the shift is in fact caused only by the contribution of the DC. A remarkable feature is the linear dependence on the volume fraction found for the DC, and thus for the shift itself. Even more remarkable is the observation that *also the amplitude of modulation does not deviate significantly from this linearity.* Problems arise with the determination of the correlation time. In the vicinity of a volume fraction of 0.5, the correlation function $\Omega(t)$ decreases too slowly to perform the numerical integration of Eq. (3), while the random scatter in the correlation function increases with time. This long persisting correlation is exclusively caused by the DC and its cross-correlations. Only by extrapolations, could approximate values for $\tau_c$ be obtained, which are considerably larger than in pure nitrogen. As a consequence, the assumption of fast modulation [Eq. (5)] becomes questionable, and the linewidth may not be determined by Eq. (4). Therefore, a more sophisticated method had to be adopted in these cases.

According to Kubo's theory the line shape $I(\omega)$ can be obtained as the Fourier transform of the relaxation function $\varphi(t)$

$$\varphi(t) = \left\langle \exp\left\{ i \int_0^t dt' \, \omega(t') \right\} \right\rangle \tag{9}$$

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \phi(t) \, dt \tag{10}$$

It is obvious that the linewidth can be determined from Eq. (10), but even more interesting is the possibility to obtain the complete line shape. Near the fast modulation limit, the relaxation tends to be purely exponential and the line becomes Lorentzian, while in the limit of slow modulation, $I(\omega)$ reveals the momentary frequency distribution. Note that Kubo *assumes* in the explanation of his theory that the momentary distribution is Gaussian, but only as a mathematical model. Only in that case does his treatment lead to a Gaussian limit in the slow modulation limit!

Very few calculations of the relaxation function obtained by MD with realistic potential models are known [12–15], and calculations of line shapes are even more scarce [14]. From our experience, it turns out that a straightforward application of this procedure leads to a line image which is seriously blurred by random noise. This is caused mainly by the increase in scatter in $\varphi(t)$ at increasing $t$. It can be seen from the theory, that most information about the line shape is stored in the initial part of the relaxation function. At large times this function approaches an exponential. In our procedure, an exponential function was fitted for large values of $t$ but the initial part was taken without smoothing. In Fig. 6 the experimental results for the FWHM in neon at 296 K and 2.4 GPa are depicted, together with the results of the simulations. First, the linewidth has been calculated as a function of the volume fraction, according to Eq. (4), which assumes a fast modulation and a Lorentzian shape. The large scatter is due to large uncertainties in the values for the correlation time, which in turn are caused by the uncertainties in the extrapolations. Next, the linewidth has been calculated from the Fourier transform of the relaxation function, Eq. (10). For that purpose, an optimal fit with a Voigt profile had been made using the Origin software package. It turned out indeed that only at the extreme compositions does a Lorentzian fit suffice. Moreover, the calculation of the linewidth using Eq. (4) leads to excessive values. The

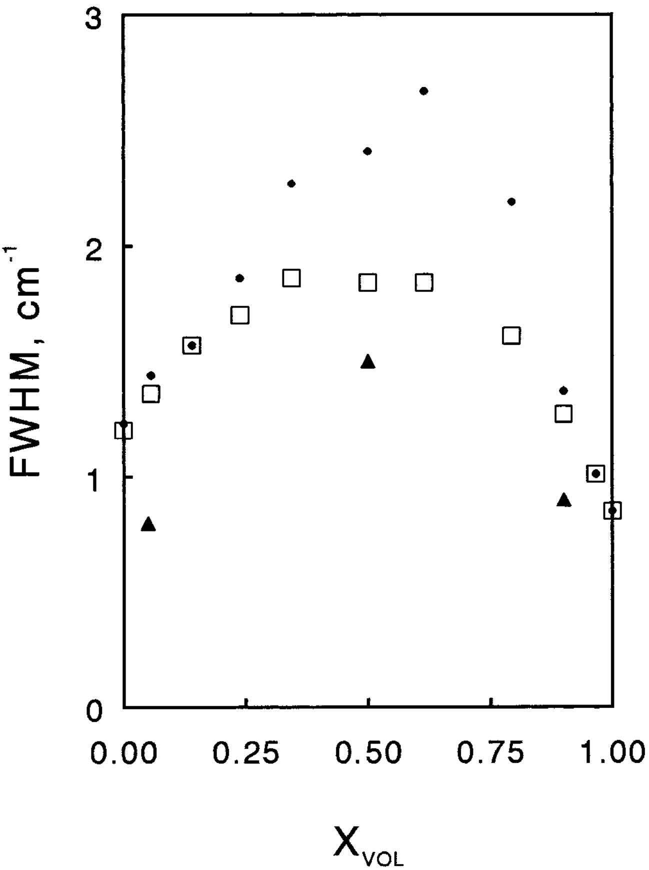

**Fig. 6.** The linewidth at 296 K and 2.4 GPa as a function of the volume fraction of Ne. Circles: calculated by $2\Delta^2\tau_c$. Squares: calculated by Fourier transformation of the relaxation function and Voigt fit. Triangles: experimental.

simulations allow for a quantitative interpretation of the “fast modulation criterion” [Eq. (5)] for this mixture. We have shown elsewhere [10] that this criterion is not unambiguous, but depends on the system under consideration. From Figs. 6 and 7 it can be deduced that for values of $\Delta \cdot \tau_c < 0.1$ the criterion holds, but that already at slightly higher values, significant deviations occur, especially at a high Ne content. Although a systematic discrepancy between the width of the Voigt profile and the experimental values is seen, the simulations describe the composition dependence properly. In Fig. 8 the change in the amplitude of modulation $\Delta$ is plotted as a function of the volume fraction of Ne. It is an important feature that the amplitude $\Delta$ changes only a few percent and does not

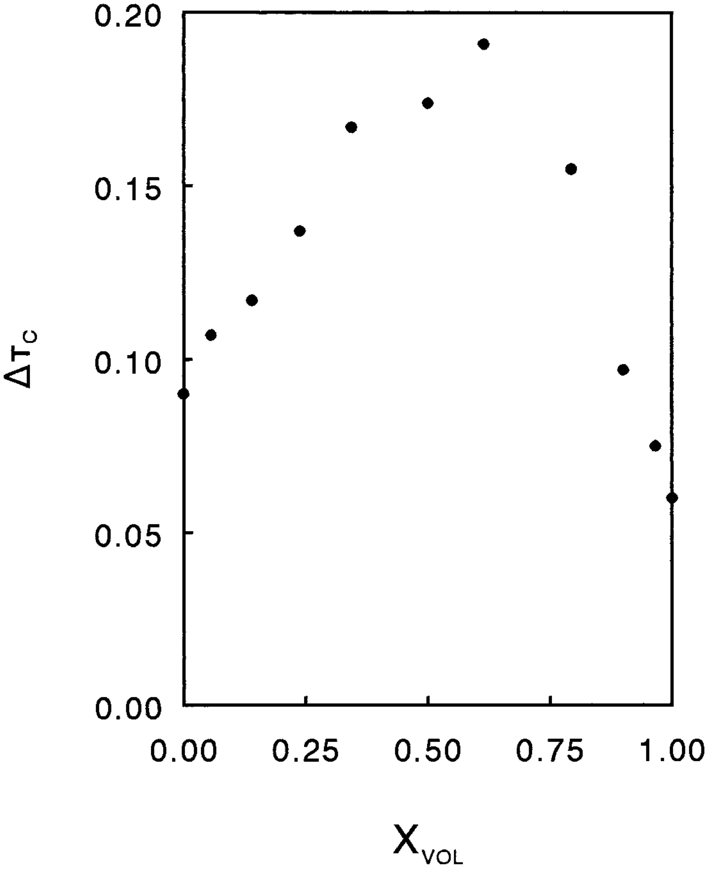

**Fig. 7.** MD results for the Kubo factor $\Delta\tau_c$ for $N_2$–Ne mixtures at 296 K and 2.4 GPa.

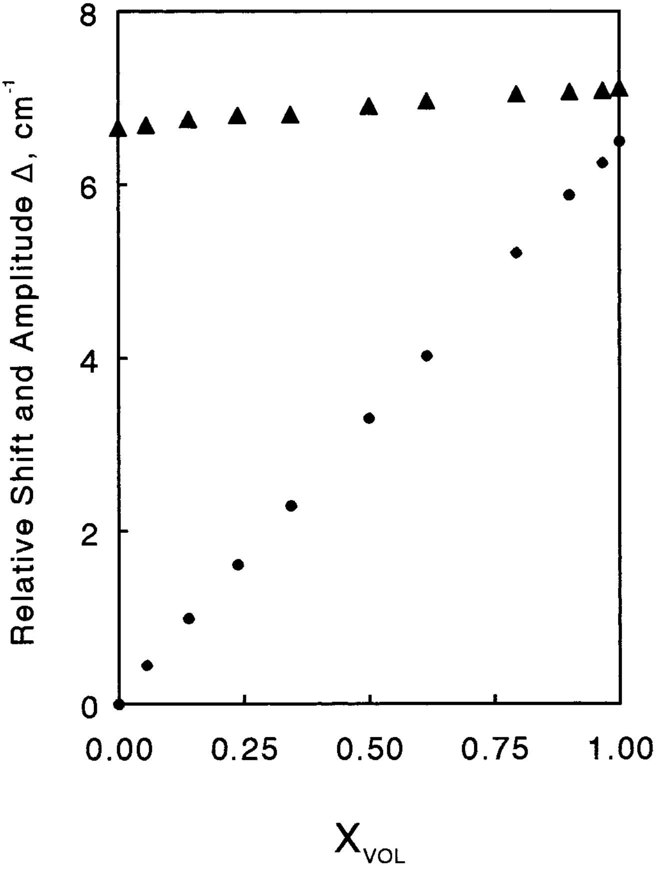

**Fig. 8.** MD results for the amplitude of modulation $\Delta$ (triangles) and the change in vibration frequency with respect to the frequency in pure $N_2$ (circles).

reveal any significant deviation from a linear behavior. Also, the change in the vibration frequency with respect to the frequency in the pure $N_2$ system is depicted in Fig. 8.

In Table I some details are given for the three systems: pure $N_2$, 65% $N_2$ in Ne, and $N_2$ infinitely diluted in Ne, obtained by the simulations. It is seen that the contributions of $\Omega_{\alpha,\beta}(0)$ to $\Omega(0)$ and thus to $\Delta^2$ change gradually from 100% $N_2$ to $\approx 0$% $N_2$. No marked discrepancy is seen at 65%. In contrast, the contribution of the DC to the correlation time at this concentration is 17 times more than in the pure system and 80 times more than in the diluted system, although the initial value $\Omega_{\mathrm{DC,DC}}$ is even less

**Table I.** Amplitude of Modulation, Correlation Time, and Partial Correlation Functions of the Vibration Frequency and Partial Contributions to the Correlation Times in $N_2$–Ne Mixtures at 296 K and 2.4 GPa

| | 0% Ne, $\Delta = 6.63$ | | 65% Ne, $\Delta = 6.92$ | | ≈100% Ne, $\Delta = 7.12$ | |
|---|---|---|---|---|---|---|
| $\alpha, \beta$ | $\Omega_{\alpha,\beta}(0)$ | $\tau_{\alpha,\beta}$ (ps) | $\Omega_{\alpha,\beta}(0)$ | $\tau_{\alpha,\beta}$ (ps) | $\Omega_{\alpha,\beta}(0)$ | $\tau_{\alpha,\beta}$ (ps) |
| E1_E1 | 0.482 | 4.63 | 0.504 | 3.49 | 0.529 | 3.05 |
| E2_E2 | 0.019 | 0.16 | 0.024 | 0.16 | 0.027 | 0.14 |
| VR_VR | 0.075 | 0.77 | 0.068 | 0.61 | 0.064 | 0.48 |
| DC_DC | 0.046 | 0.44 | 0.037 | 7.4 | 0.016 | 0.09 |
| E1_E2 | 0.179 | 1.64 | 0.203 | 1.38 | 0.226 | 1.27 |
| E1_VR | 0 | −1.45 | 0 | −1.17 | 0 | −1.00 |
| E1_DC | 0.169 | 1.47 | 0.137 | 1.23 | 0.114 | 0.61 |
| E2_VR | 0 | −0.25 | 0 | −0.21 | 0 | −0.19 |
| E2_DC | 0.030 | 0.26 | 0.027 | 0.64 | 0.023 | 0.13 |
| VR_DC | 0 | −0.33 | 0 | −0.19 | 0 | −0.11 |
| Total $\tau_c$ | | 7.36 | | 13.3 | | 4.53 |

than in pure nitrogen. The reason is that the function $\Omega_{\mathrm{DC,DC}}(t)$ decays very slowly in this mixture. As a result, the total value of $\tau_c$ is a factor of 2 to 3 larger than the value at the extreme concentrations. In illustration, the correlation functions $\Omega(t)$ are depicted in Fig. 9 in a semilogarithmic plot. It is seen that for pure nitrogen, values above 30 ps are not significant. At infinite dilution, the correlation function becomes negative between 1.7 and 2.4 ps and is not significant above 8 ps. In the 65% mixture, the decay is even too slow to determine the correlation time from direct numerical integration, Eq. (3). An estimate was made by an extrapolation using an exponential fit above 20 ps. The values given in Table I include these extrapolations. Undoubtedly, such extrapolations will increase the uncertainties in the results for $\tau_c$. On the other hand, a long-persisting frequency autocorrelation function is accompanied by a fast-decaying relaxation function, for which an exponential fit at large times can easily be made with only slight uncertainties. Consequently, also for this reason, the method of determination of the linewidth from the relaxation function is the most suitable for this situation.

## 3. DISCUSSION

Knapp and Fischer [18] and Moser et al. [19] developed a theoretical approach to the problem of line broadening in mixtures. In short,

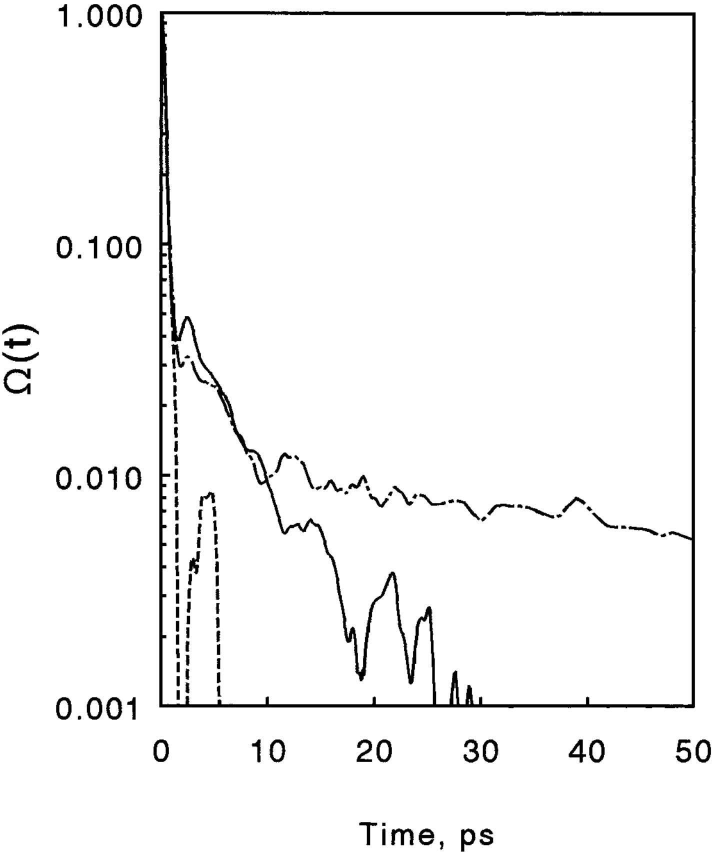

**Fig. 9.** MD results for the frequency autocorrelation function at 296 K and 2.4 GPa. Solid line: pure $N_2$. Dash-dotted line: 65% Ne. Dotted line: $N_2$ infinitely diluted in Ne.

they assume the existence of a few environmental states, formed by a discrete number of possible nearest-neighbor molecules around the vibrating molecule. Each such state is assumed to cause a specific shift with finite width. Due to overlap of these frequencies, one broad line should be seen. This means that the line broadening is attributed to an increase in the amplitude of modulation. Further, it is argued that the influence of diffusion dynamics is small. The simulations discussed above lead to the opposite conclusion: the amplitude depends only very little on the interaction forces with the nearest-neighbor molecules, even at the concentration where the maximum in broadening is seen. Instead, a large increase in the correlation time, caused by the DC, has been found at those concentrations.

The latter strongly indicates the importance of diffusion dynamics. In conclusion, even in systems far away from the critical state, a substantial line broadening is seen. The question then arises whether critical concentration fluctuations will give an extra contribution, as is supposed in Ref. 2 for the system $N_2$–He.

Generally, MD simulations are not considered very suitable for the study of critical behavior. In particular, the systems are too small to enable large fluctuations. Nevertheless, if critical behavior is expected in virtually infinite systems, one may expect that the results of MD simulations should depend on the size of the sample systems. This dependency is the subject of a subsequent study.

## REFERENCES

1. B. Lavorel, B. Oksenkorn, D. Fabre, R. Saint-Loup, and H. Berger, *Mol. Phys.* **75**:397 (1992).
2. M. I. M. Scheerboom, J. P. J. Michels, and J. A. Schouten, *J. Chem. Phys.* **104**:9388 (1996).
3. M. I. M. Scheerboom and J. A. Schouten, *Phys. Rev. E* **51**:R2747 (1995).
4. J. P. J. Michels, M. E. Kooi, and J. A. Schouten, *J. Chem. Phys.* **108**:2695 (1997).
5. M. E. Kooi, J. P. J. Michels, and J. A. Schouten, *J. Chem. Phys.* **110**:3023 (1998).
6. M. E. Kooi, J. P. J. Michels, and J. A. Schouten, *J. Chem. Phys.* **112**:1404 (2000).
7. J. P. J. Michels, M. I. M. Scheerboom, and J. A. Schouten, *J. Chem. Phys.* **103**:8338 (1995).
8. B. Lavorel, R. Chaux, R. Saint-Loup, and H. Berger, *Opt. Commun.* **62**:25 (1987).
9. J. P. J. Michels and J. A. Schouten, *Mol. Phys.* **91**:253 (1996)
10. M. E. Kooi, F. Smit, J. P. J. Michels, and J. A. Schouten, *J. Chem. Phys.* **112**:1395 (2000).
11. R. Kubo, *Fluctuations, Relaxation and Resonance in Magnetic Systems*, D. Ter Haar, ed. (Oliver and Boyd, Edinburgh, 1962).
12. D. W. Oxtoby, D. Levesque, and J. J. Weis, *J. Chem. Phys.* **68**:5528 (1978).
13. D. Levesque, J. J. Weis, and D. W. Oxtoby, *J. Chem. Phys.* **72**:2744 (1980).
14. D. Levesque, J. J. Weis, and D. W. Oxtoby, *J. Chem. Phys.* **79**:917 (1983).
15. N. Gyathri and B. Bagchi, *J. Chem. Phys.* **110**:539 (1999).
16. R. Kroon, M. Baggen, and A. Lagendijk, *J. Chem. Phys.* **91**:74 (1989).
17. R. Kroon, Ph. D. thesis (University of Amsterdam, Amsterdam, 1993).
18. E. W. Knapp and S. F. Fischer, *J. Chem. Phys.* **76**:4730 (1982).
19. G. Moser, A. Asenbaum, and G. Dröge, *J. Chem. Phys.* **99**:9389 (1993).