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# Vibrational Spectra of Nitrogen in Simple Mixtures at High Pressures[1]

**M. E. Kooi,[2,3] L. Ulivi,[4] and J. A. Schouten[2]**

Previous investigations have revealed a considerable difference between the spectral behavior of a molecule in a pure substance and that in a mixture. To gain more insight into the influence of the intermolecular interaction and of the mass of the molecules, we performed high-resolution measurements of the linewidths and peak positions of the vibrational Raman spectrum of pure nitrogen, nitrogen in argon, and nitrogen in helium. The research was carried out at room temperature and at pressures up to the melting line. It turns out that, in contrast with expectation, the linewidth as well as the frequency shift is essentially the same for pure nitrogen as for nitrogen diluted in argon, although both the mass and the potential well depth are quite different. The experimental results show the same tendency as recent computer simulations.

**KEY WORDS:** dilute mixtures; high pressure; high-resolution Raman spectroscopy; line width; nitrogen.

## 1. INTRODUCTION

The characteristic behavior of the vibrational frequency of (diatomic) molecules in the fluid phase as a function of pressure—a red shift at low pressures followed by a blue shift at higher pressures—has been the subject of many experimental and theoretical studies [1–5]. The shift of the frequency with respect to that of an isolated molecule reflects the effect of the average intermolecular forces exerted by the surrounding medium. An

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[2] Van der Waals–Zeeman Institute, University of Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands.

[3] To whom correspondence should be addressed.

[4] Istituto di Elettronica Quantistica, CNR, Via Panciatichi 56/30, 50125 Firenze, Italy.

important aspect is the change in these forces due to the change in bondlength at excitation [6]. Much less attention has been paid to the profile of the spectrum [7]. In a pure component the intermolecular forces establish, in combination with the momentary density distribution, the momentary frequency distribution, whose spread is called the amplitude of modulation. The shape of the *measured* spectrum and its linewidth, however, are affected by the dynamics of the system. In a mixture, also concentration fluctuations play a role [8], in addition to density fluctuations, and the dynamics may be different.

In a previous experimental study on the binary system helium–nitrogen, it has been shown [3] that, in a dilute solution of nitrogen, the shift is much larger than in pure nitrogen and that the red shift does not occur. The linewidth has also been reported for nitrogen and nitrogen in helium, but due to the experimental resolution, the accuracy was limited. Nevertheless, it was clear that the linewidth was smaller in the mixture than in the pure substance.

Calculations using hard fluid theory [9] and computer simulations show that, in diluted solutions of nitrogen in helium, the (positive) bondlength independent contribution of the molecular interaction to the shift is smaller than the experimental value, in contrast with the situation in pure systems. The tendency of the linewidth as a function of pressure, obtained from computer simulations, is the same as in the experiment but the absolute value of the width could not be compared due to the experimental uncertainty. An interesting result is that in the dilute mixture the linewidth is related primarily to the properties of the diluent and, to a much lesser extent, to the interactions between nitrogen and helium molecules. Recently, simulations have been performed for nitrogen diluted in argon [10] and the results have been compared with those of the previous systems. To make the comparison complete, we have carried out a high resolution Raman study of the frequency and linewidth of pure nitrogen and of nitrogen in argon. A useful comparison is possible only if the resolution is higher than in previous measurements. Moreover, some preliminary measurements have been carried out for dilute mixtures of nitrogen in helium.

## 2. EXPERIMENTAL METHOD

The mixtures were prepared in a gas filling system. A mixing time of at least 24 h was taken to allow for proper mixing. All measurements were performed at room temperature. The pressure was generated in a diamond anvil cell (DAC) of the membrane type. For the pressure measurement the ruby method was used, with the scale of Mao et al. [11].

R1 lines of the ruby spectra were measured using a portable spectrometer, which was calibrated using a neon lamp before each measurement. To improve the accuracy of the pressure measurements, the reference wavelength R1 at ambient pressure was measured for each individual ruby chip.

An argon-ion laser with an intracavity etalon was used in single mode operation. We made sure that the power of the laser was low enough during the pressure measurement to prevent heating of the ruby chip. The reference wavelength R1 at ambient pressure was measured with a laser power of 2.5 mW. For the Raman measurements the power of the laser was increased to 300 mW.

A polarization rotator was used to obtain the maximum grating efficiency. The laser was focused into the sample by a microscope objective and, after the DAC, a second microscope objective was placed. The signal was dispersed by a double monochromator and detected by a photomultiplier tube. The double-pass double-monochromator spectrometer (DMDP 2000) described by Mazzacurati et al. [12] was used in the single-pass configuration to increase the efficiency of the instrument. All signals were measured with an entrance slit width of 100 $\mu$m. This leads to an instrumental profile (almost Gaussian) with a width (FWHM) of about 0.11 $\mathrm{cm}^{-1}$.

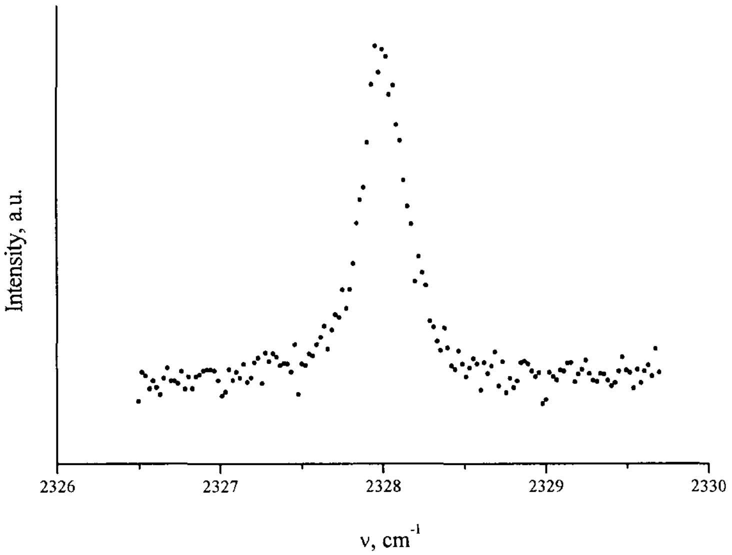

**Fig. 1.** Typical Raman spectrum of $N_2$ in $N_2$–Ar, 6 mol% $N_2$, at 0.6 GPa and 299 K.

Before and after each Raman measurement, the spectrograph was calibrated using the neon lines of 549 and 553 nm, respectively. This gives an accuracy of about 0.1 $cm^{-1}$ in the absolute wave number.

Some additional measurements on pure nitrogen were done using a Dilor *XY* spectrometer in order to extend the measurements on pure nitrogen to the same pressure range as in $N_2$–Ar. The signals were measured with an entrance slit width of 20 $\mu$m, leading to an instrumental profile (almost Lorentzian) with a width (FWHM) of about 0.15 $cm^{-1}$.

The experimental spectra have to be deconvoluted with the experimentally determined resolution function. It turns out that most of the spectra can be better fitted according to the least-squares method with the convolution of the instrumental function and a Lorentzian curve than a Gaussian curve. Therefore, we convoluted several Lorentzians with the resolution function and compared the result with the experimental spectrum. The Lorentzian giving the best agreement with the experiment is used to determine the FWHM. A typical Raman spectrum is presented in Fig. 1.

## 3. RESULTS AND DISCUSSION

With respect to the vibrational frequency of pure nitrogen, the pressure dependence is in good agreement with previous experimental data [1–3] as shown in Fig. 2, but there is a slight systematic deviation toward higher values of about 0.5 $cm^{-1}$ corresponding to about 0.15 GPa. We cannot explain this difference considering the experimental procedure for the frequency as well as for the pressure measurements. However, since we are interested in the *difference* between the pure substance and the dilute mixture, the deviation is not relevant to the further discussion. The frequency of pure $N_2$ as a function of pressure, measured using the Dilor *XY* spectrometer is, within experimental accuracy, in agreement with the frequencies measured with the DMDP 2000. In the high density fluid the frequency is an almost-linear function of pressure from 0.5 to 2.5 GPa.

The linewidth, measured using the DMDP 2000, is plotted in Fig. 3. The scatter in the data is small. In general, the results of this work are in good agreement with those of earlier investigations [2, 3, 13–15]. Our data set forms a good continuation of the accurate work of Lavorel et al. [2]. The values are slightly lower than those of Ref. 3 and of Refs. 13–15. The experimental data obtained from $T_2$ measurements [13–15] show a tendency for a sharper increase near the melting line. In this study we have extended the measurements just into the metastable fluid region to investigate this effect. Our results do not show this tendency, but it turns out that above 1 GPa the linewidth is almost a linear function of pressure.

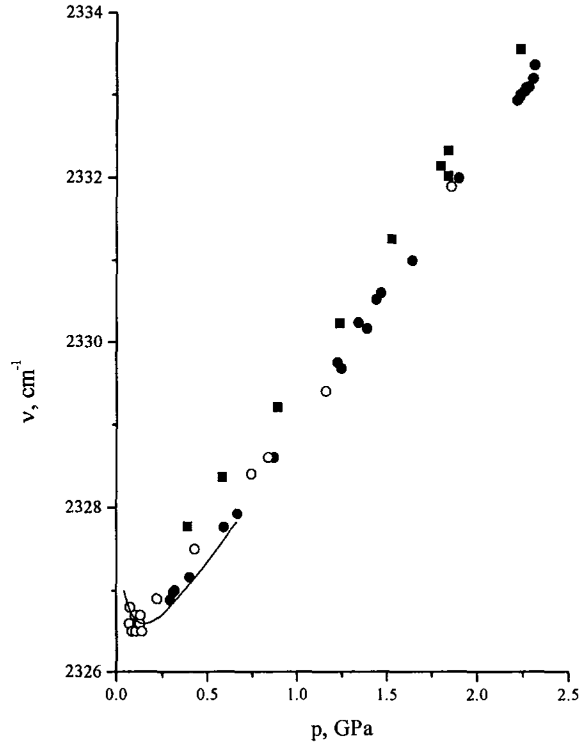

**Fig. 2.** Raman frequency of pure nitrogen at room temperature as a function of pressure. Filled squares, this work (DMDP 2000); open circles, Ref. 1; solid line, Ref. 2; filled circles, Ref. 3.

The linewidth is also measured by the Dilor *XY* spectrometer, in order to extend the measurements to the same low-pressure range as the measurements on $N_2$–Ar. The data are represented in Fig. 3 by open squares. It is shown, in agreement with earlier work of Ref. 2 and Refs. 13–15, that the FWHM as a function of pressure shows a minimum at about 0.5 GPa. The linewidths, obtained from the measurements using the Dilor *XY* spectrometer, are slightly higher than the linewidths obtained from the measurements using the DMDP 2000. The higher instrumental width of the Dilor *XY* spectrometer results in a slightly lower absolute accuracy of the linewidths measured by this setup. A comparison with the values obtained from computer simulations [5] reveals, as before, that the results agree quite well. Simulations performed without the dispersion correction give a slightly lower value for the linewidth.

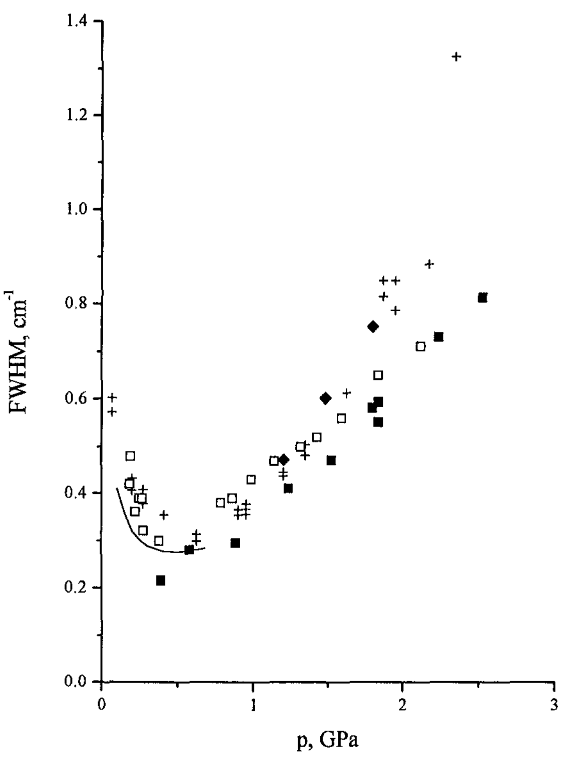

**Fig. 3.** FWHM of the Raman peak of pure nitrogen at room temperature as a function of pressure. Filled squares, this work (DMDP 2000); open squares, this work (DILOR); solid line, Ref. 2; diamonds, Ref. 8; crosses, Refs. 13–15.

The vibrational frequency of nitrogen in the argon–nitrogen mixtures (5.9 mol% nitrogen) is shown in Fig. 4. The value of the frequency is lower than in pure nitrogen (solid line), but the difference is less than 1 cm$^{-1}$. In the case of nitrogen in helium, the frequency was much higher in the mixture than in the pure substance. As mentioned in Section 1, the red shift of the frequency is attributed to the change in bond-length at excitation of the nitrogen molecule and the resulting change in intermolecular interaction. Another way of saying is that the solvation energy for an excited molecule is different from that for a nonexcited molecule. In the case of pure nitrogen, this change is negative. Since the potential depth of helium is very small, the effect is also small, and the red shift is absent. The potential well of argon is 25% deeper than that of nitrogen, and therefore, the observed shift, negative with respect to the pure component, is in agreement

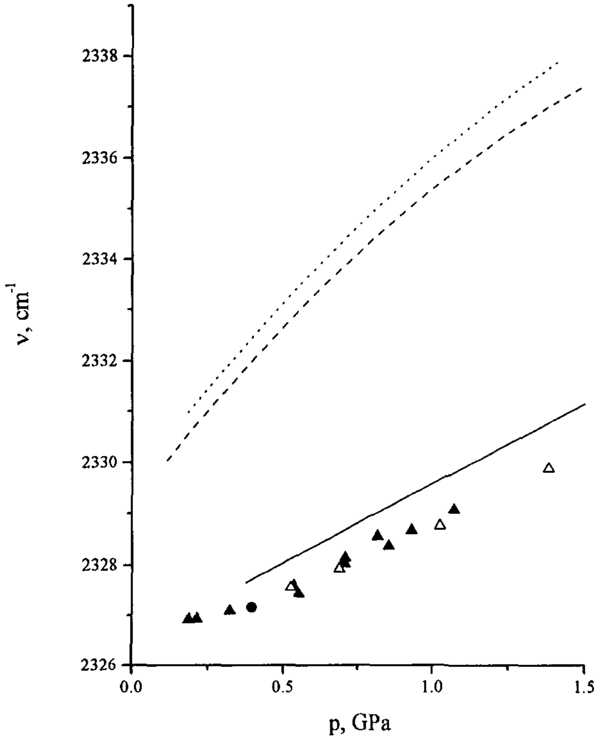

**Fig. 4.** Raman frequency of $N_2$ diluted in Ar and pure $N_2$ as a function of pressure. This work: filled triangles, 5.9 mol% $N_2$; open triangles, 3.0 mol% $N_2$; circle, 2.9 mol% $N_2$; solid line, pure $N_2$ (DMDP 2000). Computer simulations: dashed line, pure $N_2$ [5]; dotted line, $N_2$ diluted in Ar (0 mol%) [10].

with the expected behavior. Figure 4 also shows the results of computer simulations. The frequency, calculated with the bond-length independent potential, is slightly higher for nitrogen in argon than for pure nitrogen. The dispersion correction is about 20% larger for the mixture than for the pure substance.

Measurements were also performed for a mixture with 3 mol% nitrogen. The results coincide with those of 6 mol% nitrogen as far as the frequency is concerned. This would be expected since there is hardly any difference between the frequency of pure nitrogen and that of a 6 mol% mixture and since the frequency changes almost-linearly as a function of the volume fraction [8].

In Fig. 5 the linewidth of nitrogen in argon is given for mixtures with 5.9 and 3.0 mol% nitrogen. The linewidth first decreases as a function of

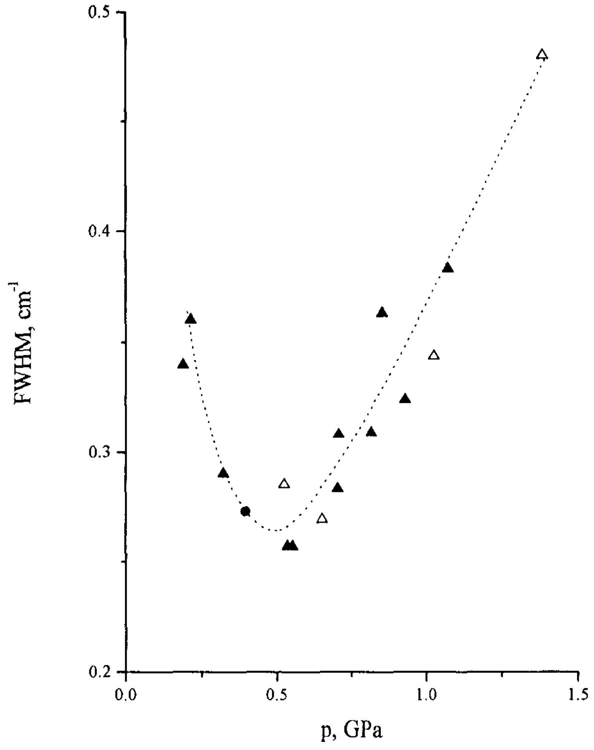

**Fig. 5.** FWHM of the Raman spectrum of $N_2$ diluted in argon. Filled triangles, 5.9 mol% $N_2$; open triangles, 3.0 mol% $N_2$; circle, 2.9 mol% $N_2$.

pressure and then increases via a minimum at about 0.6 GPa. The behavior is the same as for the pure substance. The minimum is at about the same pressure, and the absolute value of the width at a certain pressure is also the same within the experimental accuracy. This is in contrast with the results of nitrogen in helium, in which case the minimum shifts toward about 1 GPa and the linewidth is much smaller than in the pure substance. A detailed analysis of the time correlation's of the various contributions to the vibrational frequency in a dilute mixture, using computer simulations, revealed that the smaller linewidth is due mainly to the smaller mass of helium and the predominantly repulsive interaction between helium atoms [16]. The interaction between helium and nitrogen is almost irrelevant. Since the mass of the argon atom is almost 50% more than that of the nitrogen molecule, and since the argon potential well depth is 25% deeper, one would also expect a difference in linewidth. The two effects might compensate each other, or the rotational degrees of freedom play a role. Meanwhile, simulations have also been performed for argon–nitrogen [9]. The curves for an infinitely dilute mixture and for the pure substance are plotted in Fig. 5. It is interesting to note that the calculated curves also nearly coincide. The calculated lines are broader than the experimental ones.

Actually, the comparison with pure nitrogen and with the simulations should be made only for the infinitely dilute mixture because critical broadening might play a role, as in the case of helium–nitrogen. Therefore, we have also carried out some measurements for a mixture with 3.0 mol% nitrogen. The accuracy is not so high because the signal is very weak. The linewidth is the same within the experimental accuracy.

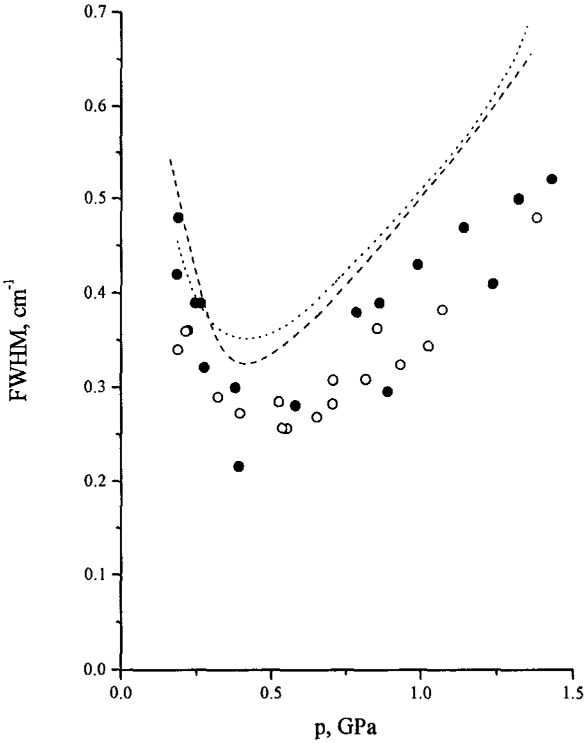

**Fig. 6.** Comparison between the measured and the calculated FWHM of the Raman spectrum of $N_2$ in pure $N_2$ and $N_2$ diluted in Ar. This work: open circles, 5.9, 3, and 2.9 mol% $N_2$; filled circles, pure $N_2$ (DMDP 2000 and DILOR). Computer simulations (with dispersion correction): dashed line, pure $N_2$ [5]; dotted line, $N_2$ diluted in Ar (0 mol%) [10].

Preliminary measurements have been performed for helium–nitrogen. Literature values for the linewidth are not available for pressures below 2.5 GPa, and the data are not very accurate. Data have been collected for mixtures with 4.0 and 3.2 mol% nitrogen. Since the compositions are very close and considering the experimental uncertainty, these data are not suitable for extrapolation to zero concentration. More measurements with a lower nitrogen concentration (2 mol% or less) are in progress. However, if the available data are used to calculate the values for an infinitely dilute mixture, the results indicate a lower value for the linewidth than assumed in Ref. 17. This suggests that the quantitative agreement with the simulations is better.

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