

High-pressure Raman scattering of the stretching mode in nitrogen along the 300-K isotherm

T. Westerhoff, A. Wittig, and R. Feile*

Institut für Physik, Johannes-Gutenberg-Universität, Staudinger Weg 7, D-55099 Mainz, Germany

(Received 27 November 1995; revised manuscript received 6 March 1996)

We present Raman scattering studies of the vibrational band of nitrogen at room temperature between 1 and 31 GPa allowing a detailed line-shape analysis. For the fluid and β phases the vibrational linewidths compare to dephasing rates T_2^{-1} determined by experiments in the time domain. The δ - ϵ transition is unmistakably marked by a drop of the vibrational linewidths around 17 GPa. A further transition into the η phase around 20 GPa proposed from previous Raman results can be ruled out. Additionally, clear evidence is found for a dynamical freezing of the N_2 molecules within the δ phase. [S0163-1829(96)03522-9]

Nitrogen exhibits a large variety of solid phases in the p - T phase diagram essentially determined by Raman and x-ray scattering.¹⁻¹⁰ Recently, Scheerboom and Schouten observed an anomalous behavior of the vibrational frequency shift with decreasing temperature in the high-pressure δ phase of nitrogen,¹¹ which they interpreted as a transition of second order connected with changes in the orientational behavior of the N_2 molecules from a more or less free rotation into an orientationally localized mode. According to their obtained temperature dependence this localization should occur around 10.5 GPa at 300 K.

We have performed Raman scattering studies on the N_2 stretching vibration along the 300 K isotherm in the pressure range from 1 to 31 GPa with two aims. We wanted first to get more detailed information about this localization transition mentioned above, and second to clarify the phase transitions still under discussion along the 300 K isotherm. We will show in the following that the linewidth of the N_2 vibron clearly exhibits anomalies connected with those transitions. This allows a deeper insight into the dynamics of the N_2 molecule in the different high-pressure phases.

High-purity nitrogen gas was filled into a diamond anvil cell (DAC) of Boehler design¹² with a high-pressure gas loading system.¹³ Pressure was determined *in situ* by the ruby fluorescence method after Mao *et al.*¹⁴ on small ruby chips embedded in the sample. The pressure gradient in the sample was determined from locally separated ruby chips and the well known pressure dependence of the N_2 stretching vibration probed at different spots across the sample volume at constant pressure. With these pressure gradients the errors in pressure are estimated to ± 0.1 GPa for $p < 8$ GPa, ± 0.8 GPa for $8 < p < 20$ GPa, and ± 2 GPa for $p > 20$ GPa.

The 514.5 nm emission of an argon ion laser was used as the light source in our experiment. The laser, with a typical power of 200 mW, was focused to 12 μm diameter into the nitrogen sample. Power was reduced to 0.5 mW for the fluorescence measurements on the ruby chips to avoid heating. Backscattered light was analyzed using a Jobin-Yvon U-1000 double monochromator in a standard setup. The collection optics in combination with the 70 μm wide entrance slit of the monochromator resulted in a reduced background scattering from the diamond compared to the N_2 vibron intensity with a signal to background ratio of ≈ 35 . Prior to each measured spectrum a neon discharge lamp was used to

calibrate the frequency and to determine the instrumental resolution function [full width at half maximum (FWHM): 0.6 cm^{-1}].

Vibrational spectra in the fluid ($p < 2.5$ GPa) and β phases ($2.5 < p < 5$ GPa) consist of a single line, and two lines are observed in the δ phase ($5 < p < 16.5$ GPa) corresponding to the two lattice sites a and c as presented in Fig. 1. The low-frequency peak (ν_2) is due to the disks on $6c$ sites, the one higher in frequency (ν_1) is three times lower in intensity and represents spheres on $2a$ sites. The vibrations shift to higher frequency with increasing pressure, and the splitting between ν_1 and ν_2 becomes larger. In addition to the gradual increase of the linewidth with pressure the ν_1 vibron clearly exhibits an anomalous width between 9.3 and 11.2 GPa (double arrow in Fig. 1). Clearly, an asymmetry on the high-frequency side of ν_2 (single arrow in Fig. 1) also can be observed. Above 18 GPa both vibrons become nar-

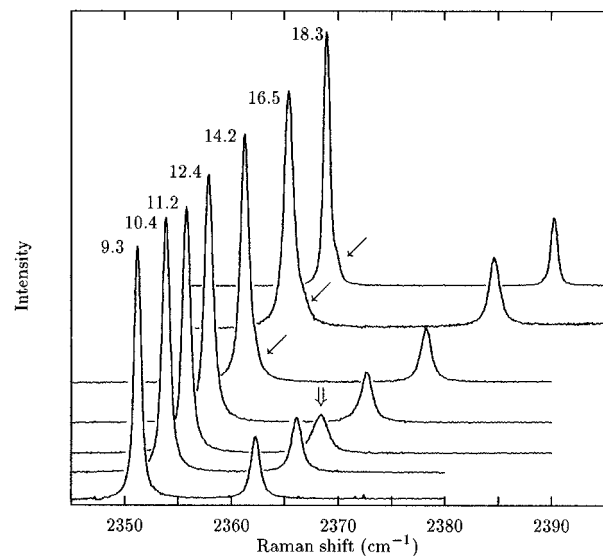


FIG. 1. Polarized Raman spectra of the N_2 stretching vibration at various pressures indicated at the major peak of each spectrum. The baselines of the spectra are shifted along the ordinate proportional to pressure. Single arrows show the splitting of the ν_2 line, and the double arrow the anomalously broadened ν_1 vibron at 11.2 GPa.

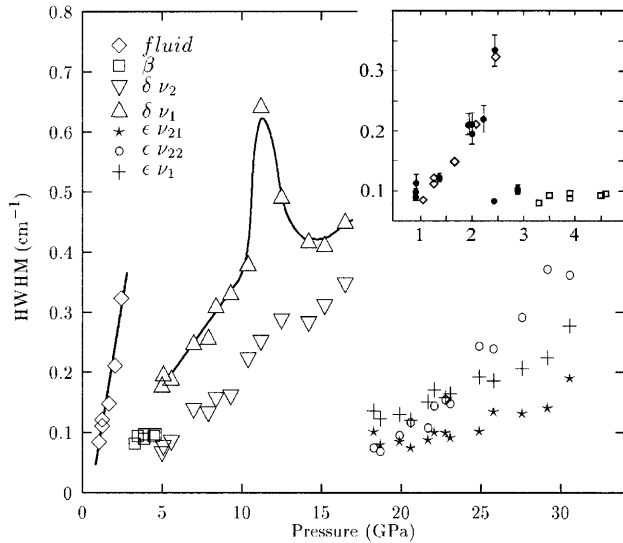


FIG. 2. Half-width (Γ) of the N_2 stretching vibration. Errors in Γ are smaller than the size of the symbols; for the errors in pressure, see text. The inset gives Γ in the fluid (\diamond) and β phases (\square) compared to dephasing rates T_2^{-1} (\bullet) determined with TSRG in Ref. 16, converted according to Ref. 17.

row and the shoulder on the high-frequency side of ν_2 becomes stronger. It separates from the main line (now labeled ν_{21}) into a new line (ν_{22}) above 20.6 GPa in the ϵ phase.

The widths of the vibrational lines were found to be in the same order of magnitude as the width of the resolution function. However, the high quality of the spectra obtained allowed a detailed line-shape analysis of the vibrons in high-pressure nitrogen. The line shape in a standard Marquardt χ^2 algorithm fitting procedure¹⁵ was modeled by convoluting a Lorentzian function with the experimentally determined resolution function. The frequencies for the vibrons obtained from this fitting procedure agree perfectly with literature data.¹⁰ A small step in the frequency at 2.5 GPa and splitting of the vibron at 5 GPa mark the well known fluid- β and β - δ transitions, respectively. The line-shape analysis shows that the above mentioned splitting of the ν_2 vibron into two components (ν_{21} and ν_{22}) reported above 20 GPa^{10,7} is observable in the entire ϵ phase and already in the cubic δ phase above 12 GPa. A kink in the slope of the pressure dependence of the ν_1 vibron is noticeable around 17 GPa.

Further information is obtained from the data of the linewidths [half width at half maximum ((HWHM))] presented in Fig. 2. In the fluid phase the vibron linewidth increases, suddenly dropping at the transition to the solid β phase. This is shown in detail in the inset where the linewidth data are compared with dephasing rates determined by time resolved stimulated Raman gain spectroscopy (TSRG).¹⁶ Just above the β - δ transition the width of the ν_1 vibron is twice that of the ν_2 vibron. With increasing pressure the widths of the two vibrational lines increase further, for the ν_2 vibron relatively more than for the ν_1 vibron. Additionally, in contrast to the nearly monotonic increase of the width of the ν_2 vibron in this pressure region, the width of the ν_1 vibron obviously exhibits an anomaly around 12

GPa. Between 16 and 18.5 GPa the linewidths of both vibrons decrease sharply.

According to Ref. 17 the vibrational energy can be redistributed into other degrees of freedom (T_1 process), or the phase of the vibration can be randomly changed either due to environmental fluctuations or due to the resonant transfer of vibrational energy between the molecules (T_2 process). In liquid nitrogen a lifetime $T_1 = 56$ s is determined¹⁸; extrapolating to 2.4 GPa,¹⁹ values on the order of μ s are expected, still large compared to the dephasing times, which are in the ps range. Thus in nitrogen dephasing is the dominant process for vibrational relaxation.¹⁶ The inset in Fig. 2 shows the perfect agreement between the dephasing rates obtained in the time domain and the data for the linewidths of the N_2 vibrons obtained by spontaneous Raman scattering in this work.

At the β - δ transition the linewidth of the ν_1 vibron is twice as broad as that of ν_2 . A similar behavior is found in Ref. 17 for the linewidths of the two vibrons in the structurally identical γ phase of O_2 . According to Ref. 20 an additional rotational dependent term can contribute to the linewidth, proportional to the rotational diffusion constant D_R . In this respect, a larger value for D_R is expected for the molecules showing three-dimensional orientational degrees of freedom (spheres on site a) than for those molecules which are restricted to reorienting in a planar geometry (disks on site c). This is consistent with our observed linewidths in δ - N_2 . At higher pressures the linewidth Γ_{ν_1} compares to Γ_{ν_2} . In view of Ref. 11 this may indicate that the available phase space for the reorienting molecules on the $2a$ sites becomes more restricted at higher pressures.

The change in the dynamical behavior is also reflected by the anomaly in the pressure dependence of the linewidth of the ν_1 vibron found at a pressure of 12 GPa. This is in accordance with the results of Scheerboom and Schouten,¹¹ who interpreted the anomaly in the temperature dependence of the vibrational frequency, predominantly observed for the ν_1 vibron, as a second-order transition from a more or less free rotation into a localized state for the molecules on the $2a$ sites. They also noted that the x-ray diffraction work of Olijnyk⁹ reporting a softening of the pV data along the 300 K isotherm around 12 GPa can be explained by a jump of the compressibility at the localization transition around 10.5 GPa; however, a proper analysis of Olijnyk's pV data for the δ phase has not been performed yet.²³ We have analyzed these data²² by plotting the negative logarithm of the volume versus pressure and obtained a compressibility of $K = 3.132 \times 10^{-2} (\text{GPa})^{-1}$, which decreases by about 60% at a pressure of ≈ 10 GPa. In terms of the usual arguments for disordered molecular solids²¹ nitrogen has a plastic phase below 12 GPa with a larger compressibility than the frozen phase above.

Additionally, we have performed model calculations^{22,24} in which we obtained single-particle orientational potentials for the N_2 molecules on the two different sites in the cubic δ phase. The results for the pressure dependence of the potential barriers show a clear evidence for a transition from a more or less free rotation to a hindered one for the N_2 molecules on the $2a$ sites. We interpret the orientation localization mentioned by Scheerboom and Schouten as a thermally

excited relaxation process across the barrier. Here freezing is marked experimentally by the crossing of the relaxation rate τ^{-1} and the probing frequency: $\omega\tau \approx 1$. Through the orientation-vibron coupling the crossover from a dynamically disordered state to an orientationally frozen one at our probing frequency is reflected by the anomaly in the vibron width around 12 GPa. For typical phonon frequencies observed in the Brillouin experiment of Grimsditch⁵ the crossover is expected at pressures beyond the stability region of the δ phase.

Figure 2 shows a drop of the linewidth data for all vibrons between 16 and 18.5 GPa. This is correlated with a pronounced hysteresis in the frequency shift in the Brillouin scattering experiment by Grimsditch⁵ around 16.5 GPa at 300 K. Yet his work did not provide any information about the structure of the new phase. X-ray measurements of Olijnyk⁹ gave clear evidence of a phase transition from the cubic δ to the trigonal ϵ phase at a pressure of 16.3 ± 0.5 GPa at room temperature. Schneider *et al.*¹⁰ performed Raman scattering in the pressure range $8 \leq p \leq 54$ GPa and observed three of four lattice modes predicted by group theory and two vibrons in the δ phase. At 18 GPa they found the eight expected lattice modes for the ϵ phase and two vibrational lines. Thus the authors had direct evidence for the δ - ϵ transition from the lattice phonon region but no direct affirmation of this transition in the vibron band. A change in the linewidths of 0.4 cm^{-1} (FWHM) at the δ - ϵ transition (at 9.0 GPa and 173 K) was roughly determined by Scheerboom and Schouten,¹¹ but they were unable to perform a detailed line-shape analysis. The dramatic drop of our linewidth data (HWHM) by values of 0.3 to 0.4 cm^{-1} between 16.5 and 18 GPa in Fig. 2 unmistakably confirms the δ - ϵ phase transition along the 300 K isotherm with data now also from the vibron band.

The splitting of the ν_2 vibron around 20 GPa found in an early work by Reichlin *et al.*⁷ was later also observed by Schneider *et al.*,¹⁰ who therefore concluded that the stability regime of the ϵ phase is rather small, showing a distortion to lower symmetry (η phase) above that pressure. This is, how-

ever, not confirmed in the x-ray work of Olijnyk.⁹ In the δ phase as well as in the ϵ phase three contributions to the Raman signal in the stretching mode region are expected by factor group analysis.⁶ The ν_1 is a single A_{1g} symmetry mode, whereas two modes, with A_{1g} and E_g symmetry contribute to the ν_2 vibron. Eters *et al.*²⁵ calculated a maximal difference of 0.2 cm^{-1} for the two contributions to the ν_2 vibron in the ϵ phase, which they claimed to be too small for experimental observation. We find a splitting of the ν_2 vibron of $\approx 1 \text{ cm}^{-1}$ already at pressures above 12 GPa in the cubic δ phase and for all pressures above the transition in the ϵ phase. Our linewidths increase monotonically with pressure and therefore do not give any evidence for a transition at 20 GPa. The improved resolution of our Raman experiment and the elaborate fitting procedure has allowed us to detect the splitting even at smaller pressures. Since the splitting increases with pressure it then may have been resolvable for the other Raman investigations. Unfortunately, neither Reichlin *et al.*⁷ nor Schneider *et al.*¹⁰ give values for their resolution function and a direct comparison is not possible.

Summarizing, our Raman experiments allowed a detailed investigation of the vibrational line shape of the nitrogen molecule stretching mode under high pressure along the 300 K isotherm. Especially, the pressure dependence of the linewidths unambiguously exhibits the different phase transitions. These data confirm the β , δ , and ϵ phases and clearly indicate strong changes in the orientational dynamics of the molecules at the spherically disordered $2a$ sites in the δ phase. They also exclude the transition to an η phase up to pressures of 31 GPa.

This work was supported by the Deutsche Forschungsgemeinschaft (SFB 262) and the Materialwissenschaftliches Forschungszentrum der Universität Mainz. We thank A. Zerr and R. Boehler for their support in diamond anvil cell high-pressure measurements. We thank K. Binder, A. Loidl, P. Nielaba, M. Müser, E. Sherman, and F. Bruchhäuser for valuable discussions.

*Present and corresponding address: Institut für Festkörperphysik, Technische Hochschule Darmstadt, Hochschulstraße 8, D-64289 Darmstadt, Germany.

¹A. F. Schuch and R. L. Mills, *J. Chem. Phys.* **52**, 6000 (1970).

²R. LeSar *et al.*, *Solid State Commun.* **32**, 131 (1979).

³D. T. Cromer, R. L. Mills, D. Schiferl, and L. A. Schwalbe, *Acta Crystallogr. Sect. B* **37**, 8 (1981).

⁴S. Buchsbaum, R. L. Mills, and D. Schiferl, *J. Phys. Chem.* **88**, 2522 (1984).

⁵M. Grimsditch, *Phys. Rev. B* **32**, 514 (1985).

⁶D. Schiferl, S. Buchsbaum, and R. Mills, *J. Phys. Chem.* **89**, 2324 (1985).

⁷R. Reichlin *et al.*, *Phys. Rev. Lett.* **55**, 1464 (1985).

⁸R. L. Mills, B. Olinger, and D. T. Cromer, *J. Chem. Phys.* **84**, 2837 (1986).

⁹H. Olijnyk, *J. Chem. Phys.* **93**, 8968 (1992).

¹⁰H. Schneider, W. Häfner, A. Wokaun, and H. Olijnyk, *J. Chem. Phys.* **96**, 8046 (1992).

¹¹M. M. Scheerboom and J. A. Schouten, *Phys. Rev. Lett.* **71**, 2252 (1993).

¹²A. Chopelas and R. Boehler, in *High Pressure in Science and Technology*, edited by C. Homan, R. K. McKrone, and E. Whalley, MRS Symposia Proceedings No. 22 (Materials Research Society, Pittsburgh, 1984), p. 275.

¹³R. L. Mills, D. H. Liebenberg, J. C. Bronson, and L. C. Schmidt, *Rev. Sci. Instrum.* **51**, 891 (1980).

¹⁴H. K. Mao, P. M. Bell, J. W. Shaner, and D. J. Steinberg, *J. Appl. Phys.* **49**, 3276 (1978).

¹⁵P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill, New York, 1969).

¹⁶R. Kroon, M. Baggen, and A. Lagendijk, *J. Chem. Phys.* **91**, 74 (1989).

¹⁷H. Kieft, M. J. Clouter, N. H. Rich, and S. H. Ahmad, *Chem. Phys. Lett.* **70**, 425 (1980).

¹⁸S. R. J. Breuck and R. M. O. NAME, Jr., *Chem. Phys. Lett.* **39**, 568 (1976).

¹⁹B. Khalil-Yahyavi, M. Chatelet, and B. Oksengorn, *J. Chem. Phys.* **89**, 3573 (1988).

²⁰B. P. Hills and P. A. Madden, *Mol. Phys.* **35**, 807 (1978).

²¹N. G. Parsonage and L. A. K. Staveley, *Disorder in Crystals*

(Clarendon Press, Oxford, 1978).

²²T. Westerhoff, Ph.D. thesis, Fachbereich Physik, Universität Mainz, 1995.

²³The change of the compressibility is mistakenly assumed positive by the authors; however, their interpretation of the observed

transition as of second-order type due to the jump in the compressibility around 10 GPa is correct.

²⁴T. Westerhoff and R. Feile, *Z. Phys. B* **100**, 417 (1996).

²⁵R. D. Ethers, V. Chandrasekharan, E. Uzan, and K. Kobashi, *Phys. Rev. B* **33**, 8615 (1986).