Kjems and Dolling[74] recently used inelastic neutron scattering to study the lattice dynamics of the $\beta$-phase. They observed two translational modes at $q=0$ and 36 °K having frequencies of 25 and 64 $cm^{-1}$. The low frequency mode splits into two modes for $q \neq 0$ and corresponds to the doubly degenerate $E_{2g}$ mode shown in Table II. This $E_{2g}$ mode is Raman-active and can be identified with the low-frequency line in the Raman spectrum of sample one having a frequency of 25 $cm^{-1}$ at 55 °K. This identification is supported by the large Grüneisen parameter of this line, usually characteristic of translational modes in close-packed molecular crystals. The other translational mode observed by Kjems and Dolling at $q=0$ has too high a frequency to correspond to the other Raman line. Moreover, only one translational mode is expected in the first-order Raman spectrum of an hcp structure. The second Raman line then probably corresponds to a librational mode of $E_{1g}$ symmetry, as expected from Table II. This means that the molecules in the $\beta$ phase are precessing around the $c$ axis.

The high-frequency Raman line could be a two-phonon band. However, this is unlikely since both Raman lines have comparable linewidths and strikingly different temperature dependences. Also, the Grüneisen parameter for this line is somewhat smaller than that of the $E_{2g}$ phonon and closer to those obtained for the librational modes in the $\alpha$ phase. It should be pointed out that the measured Grüneisen parameter for this libration is, as in the $\alpha$ phase, much larger than the value expected for a quadrupolar interaction potential in the quasiharmonic approximation.

The temperature dependence of the frequencies in Table X was fitted to a function of the form given by (6). However, variations in the choice of the frequency at 0 °K had little effect on the fit but drastically changed the characteristic temperature, rendering any results meaningless. Also, no indication of the ordering transition without thermal anomaly suggested by Mandell[48] has been found.

## IV. CONCLUSION

The Raman spectrum of the three known phases of solid nitrogen has been studied in the ranges from 0 to 220 °K and 0 to 10 kbar. A novel method is used in that each sample is grown within a high pressure optical cell which constrains it to nearly isochoric conditions. This method allows the separation of temperature and volume effects.

Two lines in the lattice region and one slightly asymmetrical line in the stretching region have been observed in the Raman spectrum of the $\gamma$ phase. Comparison of experimental and calculated frequencies and relative intensities allows the identification of the low- and high-frequency lines in the lattice region as $E_g$ and $B_{1g}$ librational modes, respectively.

In the $\alpha$ phase, the measured Grüneisen parameters indicate that neither the quadrupolar nor the 6–12 atom–atom interaction potential has the correct volume dependence. The failure to observe any coincidence between the Raman and infrared frequencies supports the assignment of a $Pa3$ structure to the $\alpha$ phase. The temperature dependence of the $E_g$ librational frequency can be explained if this libron is interacting mainly with a $T_u$ phonon through quartic anharmonicity. The temperature dependence of the linewidth of the $E_g$ mode indicates that an $E_g$ libron is combining with another excitation (possibly a $T_g$ libron) to create a third excitation (possibly a $T_u$ phonon).

Two very broad Raman lines are observed in the lattice region of the $\beta$ phase. The low-frequency line can be identified with a translational mode observed in inelastic neutron scattering experiments.[74] The high-frequency line is identified as a librational mode. This implies that the correct structure of the $\beta$ phase is given by the nitrogen molecules precessing at a fixed angle around the crystallographic $c$ axis.

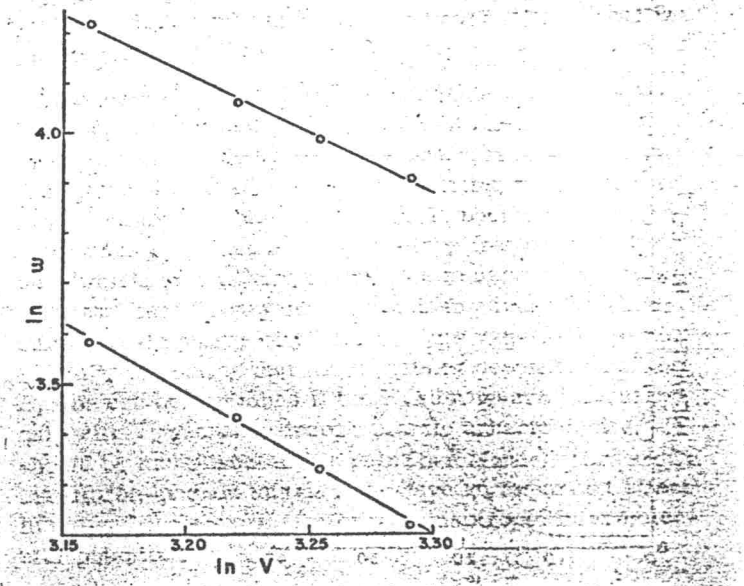


FIG. 11. Plot of $\ln\omega$ versus $\ln V$ for the two Raman lines in the $\beta$ phase where the frequency $\omega$ is in $cm^{-1}$ and the molar volume $V$ is in $cm^3$/mole: ×, experimental points; ——, best fit to a straight line.

TABLE X. Temperature dependence of Raman frequencies in the $\beta$ phase for sample 4.

| $T$ (°K) | Frequencies ($cm^{-1}$) | |
|---|---|---|
| 55 | 36±3 | 68±3 |
| 80 | 34±4 | 67±4 |
| 102 | 32±4 | 67±4 |
| 135 | 30±5 | 66±5 |
| 170 | 26±5 | 66±5 |

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