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Molecular dynamics in crystalline α-nitrogen

Gianni Cardini and Seamus F. O'Shea*
Department of Chemistry, University of Lethbridge, Lethbridge, Alberta, Canada T1K 3M4
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Harmonic lattice-dynamics and classical molecular-dynamics (MD) calculations for crystalline α-nitrogen were used to study a semiempirical potential ($5q$) for the interaction of pairs of nitrogen molecules. The dispersion curves along the special directions of α-nitrogen, and the density of states for the crystal have been calculated in the harmonic approximation, and comparisons made with appropriate experimental data. The effects of increasing temperature at constant volume were studied using MD, mainly through the calculated Raman spectrum. Quite modest shifts relative to the harmonic frequencies were obtained. Further studies with a model potential used by Kobashi in anharmonic perturbation calculations showed similarly modest shifts, contrary to the predictions of perturbation theory. An analysis of the molecular motions showed that for both models the librational amplitudes are large, and we conclude that the perturbation-theory predictions probably overestimate the shifts substantially. Complete reorientations of molecules (flips) were observed in the highest-temperature run for the $5q$ model, but a detailed study failed to reveal a specific mechanism of reorientation.

INTRODUCTION

The theoretical study of the dynamics of molecular crystals by linear[1] and nonlinear[2] methods is now well established. Although many complex systems have been studied with considerable success,[1] some of the simplest continue to pose substantial problems and cannot be considered to be solved in a satisfactory manner. Among these are the various crystal forms of molecular nitrogen, particularly the low-pressure forms α- and β-nitrogen. The fact that nitrogen remains something of an enigma is certainly not due to any neglect; actually quite the opposite is the case. The history of the study of nitrogen is long and has some interesting lessons to teach, even if it is not yet completely clear what those lessons are. The story hinges on the interplay of a number of important aspects of the system.

In order to provide a satisfactory account of the structure and dynamics of the various phases of nitrogen, it would be necessary to have an adequate model for the interactions among nitrogen molecules at ranges varying from the nearest-neighbor spacings in the densest form, slightly less than 4 Å, up to very large separations. Such a potential could be used as the basis for a theoretical study of the dynamics of the crystals, leading to theoretical spectra which would provide a definitive interpretation of the experimentally observed spectra. The dynamical methods employed would necessarily include quantum effects, since the temperature ranges in which many of the experiments are conducted are close to absolute zero ($T < 50$ K). It is also desirable that these methods should be able to handle nonlinearity in the dynamics, since crystalline nitrogen is anharmonic in the disordered phases and probably also in the ordered phases. This is a very stringent set of criteria.

The literature is too voluminous to review comprehensively here, but reviews of early work are available.[3–7] Potential models used were exclusively pair additive, and varied from simple models, such as isotropic Lennard-Jones molecules with embedded electrostatic quadrupoles,[8] diatomic Lennard-Jones[5] (2LJ), and diatomic Lennard-Jones with embedded electrostatics,[6] to elaborate and sophisticated models.[7] A number of purely librational models were also introduced.[9–11] The harmonic approximation was used almost exclusively to treat the dynamics for full potentials, but more elaborate methods were used in the purely librational treatments. As discussed in Scott's review,[3] it proved relatively easy to find parameters which would yield good crystal structures, good binding energies (when modest corrections for many-body forces and zero-point motion were included), and good frequencies for the translational lattice vibrations. The librational modes proved to be a major stumbling block, since neither 2LJ nor 2LJ augmented with quadrupole interactions seemed capable of reproducing the experimental frequencies without creating discrepancies elsewhere. The resolution of this impasse appeared to lie in the roles of both quantum effects[5,9] and anharmonicity[7] in the crystal. The fact that the structure, energy, and translational modes were easily rationalized is due in part to the fact that nitrogen is a weakly anisotropic molecule, and these properties are largely determined by the spherical part of the potential. However, this means that they yield little information about the anisotropy, and because the anisotropic part of the potential is fairly complicated but weak it is difficult to find any bulk measurement that gives direct evidence about it. For example, fluid properties such as virial coefficients can be fitted perfectly well by models which have no anisotropy at all.[12] Spectroscopy offers the only hope, but spectroscopic information dealing with rotational motion alone is restricted to a few high symmetry modes of the ordered crystals,[1,3] α- and γ-nitrogen. Quantum-mechanical treatments of the librations[9–11] indicate that the librational energy-level spacings are large relative to the experimental temperatures in α-nitrogen, but also indicate the presence of a large zero-point anharmonicity. The root-mean-squared amplitude of libration was estimated to be about 18°, a value which seems likely to lead to anharmonicity.

This observation led to a greater emphasis on the dynamical methods.[7,9–11,13–17] The object became to estimate the degree of anharmonicity, and to find a satisfactory dynamical technique which would permit one to obtain reliable anharmonic librational frequencies sufficiently easily that one could use it to determine the quality of proposed models. Neither objective proved easy to achieve. At the same time that this work on dynamics was progressing there were attempts to generate better interaction models both by *ab initio*[18] and semi-empirical[19–21] methods. With the uncertainty that surrounded the dynamical calculations, it remains unclear whether these attempts were, in fact, achieving anything worthwhile.

The object of the new semiempirical models is to give harmonic librational frequencies in better agreement with experiment without either sacrificing the agreement for other properties or using values of the molecular parameters which are incompatible with reliable experimental data. In testing these, the lattice-dynamics calculations were done only for a few high-symmetry points of α-nitrogen, Γ and R, and did not address the question of the density of states; nor was any attempt made to deal with the problem of anharmonicity. The density of states is a relatively straightforward question, requiring only more extensive calculations of the kind already made; these calculations have since been done and we report them here. We tackled the problem of anharmonicity through the use of classical molecular dynamics, a method which is known to be completely anharmonic. However, from the outset it is clear that the results will not resolve the difficulties completely. By going to higher temperatures in the classical system we hope to be able to sample the higher amplitudes which the quantum zero-point motion samples at lower temperatures. The librational frequencies are high enough that thermal excitation is probably small at the temperatures of interest; since the molecular-dynamics (MD) results give the harmonic frequencies in the limit of low temperature, it is not certain that measurable anharmonic shifts will be observed. However, by using the conventional (N,V,E) ensemble we inhibit the phase transition which occurs in the experimental system. α-nitrogen is unable to transform to β-nitrogen so that it is possible to achieve temperatures higher than the experimental transition temperature before the system undergoes rotational melting.

The discussion here is restricted to the effects of temperature on the frequencies of a crystal held at constant volume. This is done for two reasons. First, reliable experimental data are available for the Raman spectrum under these conditions;[22] although the volume used here is that of Kjems and Dolling[6] rather than that of Medina and Daniels,[22] we expect that the qualitative behavior should be very similar. Constant pressure conditions are much more difficult to handle, since an accurate treatment of many-body effects is required in order to get a reasonable value for the molar volume, a quantity to which the frequencies are sensitive. In addition, although studies of the solid phases of nitrogen using constant pressure molecular dynamics have been reported,[23] they concentrate on the structural aspects of the system, and technical difficulties related to the calculation of dynamical data from constant pressure simulations have yet to be resolved.

CALCULATIONS

Lattice dynamics

The standard lattice-dynamical method for rigid linear molecules[1] was used, and the full symmetry of the Pa_3 crystal structure was exploited. The interactions between molecules whose centers were separated by more than 15 Å were neglected, although some calculations were performed using a cutoff of 8 Å in order to be consistent with the MD calculations. The experimental[6] crystal volume ($a = 5.64$ Å) was used throughout. Figure 1

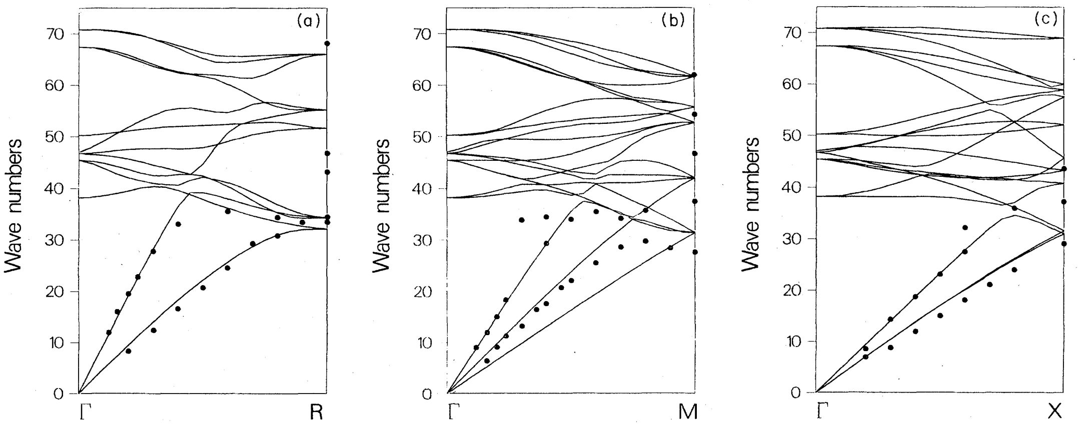

FIG. 1. Dispersion curves for α-nitrogen along the special directions $\Gamma \to M$, $\Gamma \to X$, and $\Gamma \to K$, calculated by harmonic lattice dynamics using the $5q$ model. The dots are the experimental data of Kjems and Dolling[6] obtained by neutron scattering from a crystal of essentially the same volume ($a = 5.644$ Å).

TABLE I. Lattice vibrational frequencies (in cm^{-1}), for α-nitrogen. The experimental values are from Kjems and Dolling.[6]

Mode	LD	MD (5 K)	Expt.
Γ point			
A_u	46		47
E_u	49	(51)	54
T_u	45		48
T_u	66		69
E_g	38	38	32
T_g	46	48	36
T_g	69	70	60
R point			
R_1^-	32	(35)	34
R_{23}^-	34		35
R_{22}^-	68	(67)	68
R_1^+	51	51	44
R^+	54	54	47
M point			
M_1	31	32	28
M_2	42	43	38
M_3	52	54	46
M_4	56	57	54
M_5	62	63	62
X point			
X_1	31	32	29
X_2	41	41	37
X_3	43	43	43

shows the dispersion curves for phonons along the symmetry directions $\Gamma \rightarrow X$, $\Gamma \rightarrow M$, and $\Gamma \rightarrow R$. Also shown are the experimental results of Kjems and Dolling[6] who measured the frequencies by inelastic neutron scattering. For the special points Γ, *X*, *M*, and *R* they combined the reduced zone vector with various Bragg vectors in order to obtain a number of independent measurements of the frequencies; the best-fit values and the corresponding frequencies calculated here are shown in Table I. The data for the Γ and *R* points are of special interest because at these points the translations and librations belong to different irreducible representations; the calculated data for these points have been reported earlier.[20] At general points there are 20 modes which can contribute to the scattering, although not all can be resolved. Even for the special directions only a limited number of the lower frequency branches can be determined (Fig. 5 of Ref. 6). The harmonic results obtained here are in general agreement with the experimental data, Fig. 1 and Table I, but the fit is hardly satisfactory.

The eigenvectors and eigenvalues of the harmonic calculations can be used to estimate the line intensities in the Raman spectrum. Two approaches are commonly used, the simple "oriented gas" model and the more complete local-field approximation. It is known[1] that the local-field approximation gives better absolute intensities, but, for nitrogen at least, the oriented gas model gives reliable relative intensities. We have used both methods, and indeed the relative intensities are similar and in reasonable agreement with experiment, based on values of 1.53 and 2.24 for the parallel and perpendicular polarizabilities, respectively. For the Raman bands at 38, 47, and 71 cm^{-1} the oriented gas values of the relative intensities are 100, 28.4, and 7.73, respectively, and for the local field we obtain 100, 29.0, and 6.78. The corresponding experimental[1] relative intensities are 100, 36, and 4. No absolute intensity measurements are available.

In estimating the density of vibrational states one can use the Chadi-Cohen[24] technique to choose a set of points in **q** space which are optimal, in the sense that for small sets averages over the set converge to averages over the full density of states. However, we have chosen the simpler technique of using a uniform mesh in the interior of the smallest (irreducible) region of the first Brillouin zone ($\frac{1}{32}$ of the full zone) permissible by symmetry. Figure 2 illustrates the one-phonon density obtained in this way with the two largest sample sizes used (640 and 1311 points) and the convergence is clearly satisfactory. With the density of states it is simple to calculate the zero-point energy, and the internal energy, heat capacity, entropy, and Helmholtz free energy as a function of temperature, at fixed volume. Our estimate of the zero-point energy, 1442 J/mol is slightly higher than the figure of 1292 J/mol obtained by Goodings and Henklemann[9] using an interaction model due to Kohin.[25] Our value may be slightly higher than the true value because of the tendency of the $5q$ model to overestimate the librational frequencies; although this can be seen clearly only at the Γ and *R* points, it seems reasonable to assume that the frequencies of mixed modes with substantial librational components at other **q** points suffer a similar fate. The heat capacity, C_v is consistent with the experimental data[3] for C_p up to 30 K, although a detailed comparison is hindered by the lack of accurate data for those thermodynamic quantities necessary to convert C_v to C_p. The volume change is small in this range, but so is the heat capacity, and although one can estimate the difference between C_v and C_p at a given temperature and volume, the correction for the difference in the molar volume between the calcula-

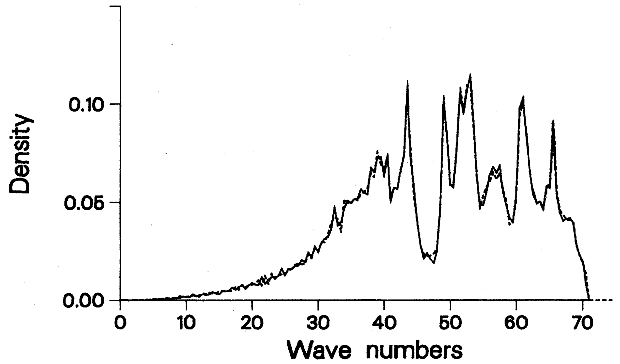

FIG. 2. One-phonon density of states for α-nitrogen calculated in the harmonic approximation using the $5q$ model. The continuous curve represents the results obtained using 1311 points in $\frac{1}{32}$ of the full Brillouin zone, and the dashed curve is for a sample of 640 points in the same volume.

tions and the experiments is difficult to make and subject to large uncertainties. The other thermal properties are also qualitatively correct, but comparison with experiment is equally difficult.

Molecular dynamics

The Verlet algorithm[26] was used with the *atoms plus constraints*[27] method to integrate the equations of motion for systems consisting of either 108 or 256 nitrogen molecules, starting from a *Pa* 3 structure and using a time step of 5×10^{-15} s. Equilibration runs of thousands of time steps were run in each case, and for low-temperature runs the system was first annealed at a higher temperature before being cooled and further equilibrated at the desired temperature. A direct method was used to evaluate the dynamical structure factor:

$$S(\mathbf{q},\omega)=\int \rho(\mathbf{q},t)\rho(-\mathbf{q},t)e^{-i\omega t}dt \ , \tag{1}$$

where $\rho(\mathbf{q},t)$ is the wave-vector—dependent density function defined by

$$\rho(\mathbf{q},t)=\sum e^{i\mathbf{q}\cdot\mathbf{r}_a(t)} \ .$$

The sum over the positions of all atoms, a, in the system is made at a specific instant in time, and the Fourier transform in Eq. (1) displays the time evolution in the frequency domain. $S(\mathbf{q},\omega)$ is directly related to the neutron-scattering measurements, and the peaks in $S(\mathbf{q},\omega)$ calculated from the MD data are the anharmonic predictions for the experimental data shown earlier in Table I and Fig. 1. $S(\mathbf{q},\omega)$ was discussed by Weis and Klein in their pioneering calculation of the dynamics of α-nitrogen by MD.[28] We have chosen to focus our attention on the Raman spectrum, for which extensive data exist.[3]

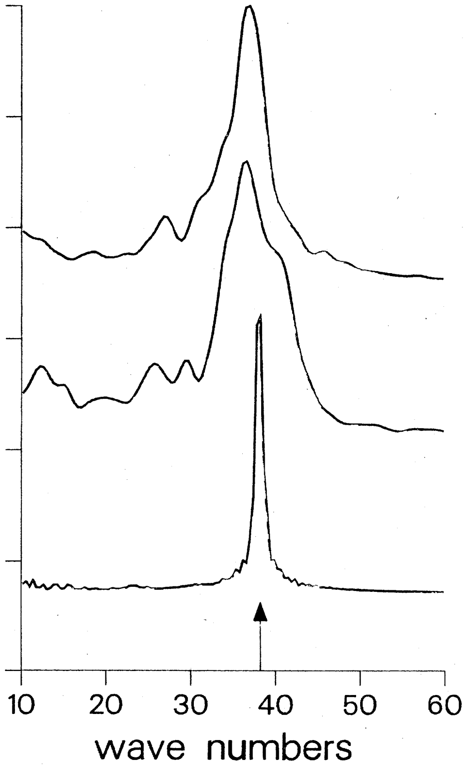

FIG. 3. Raman spectrum for parallel polarization based on harmonic lattice-dynamics (arrow) and molecular-dynamics results. The MD results are for 5, 29, and 40 K, from bottom to top.

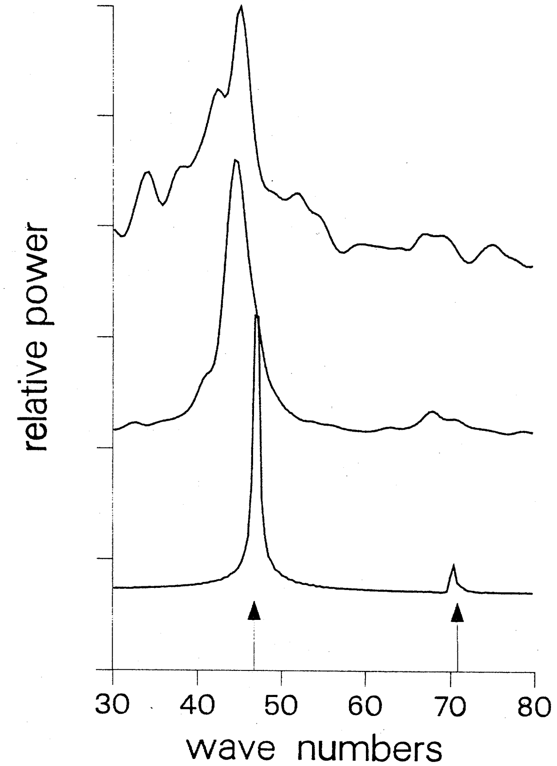

FIG. 4. Raman spectrum for perpendicular polarization based on harmonic lattice-dynamics (arrows) and molecular-dynamics results. The MD results are for 5, 29, and 40 K, from bottom to top.

Figures 3 and 4 show the Raman spectra evaluated from the MD results at three temperatures, 5, 29, and 40 K, and in each case the data on which the spectrum is based were collected during a run of 16 400 time steps. The spectrum can be evaluated either by constructing the time correlation function (TCF) of the anisotropic part of the molecular polarizability in the crystal frame, and evaluating the Fourier transform of that function; or simply by using the square of the absolute value of the discrete Fourier transform of the time-dependent anisotropic polarizability. In constructing the TCF's we used all 16 400 steps to generate a function covering an interval of 8200 time steps (41 ps). Although the frequencies determined both ways coincide to within our estimated resolution, the spectra based on the time correlation functions proved cleaner, with better separation of the peaks from the thermal background, contrary to our expectation. Experience based on the analysis of artificial spectra seems to suggest that this is due to the fact that the various modes in the system have random phases relative to one another. Results were obtained for both parallel (Fig. 3) and perpendicularly (Fig. 4) polarized scattering; the parallel, or diagonal, component displays only one peak, that due to the E_g mode, but the perpendicular, or offdiagonal, component has two peaks due to two T_g bands. In constructing the spectra we have averaged over equivalent components, *xx*, *yy*, and *zz* for the parallel polarization, and *xy*, *xz*, and *yz* for the perpendicular case. At any finite temperature the strict symmetry of the equilibrium structure of the crystal is violated, and some leakage of the translational frequencies into the Raman spectrum is to be expected. In addition, the thermal background due to multiphonon processes increases, and the spectral lines are broadened by local inhomogeneities in structure. In view of these circumstances we investigated many different methods of optimizing the spectral analysis. The simplest option we considered was to use the raw data for the power spectrum, and in the end, aesthetics aside, this may well be the best. Different methods of apodizing[29] the data did not produce the improvement we had hoped for. Even relatively gentle smoothing, such as passing the final spectrum through a Gaussian half-width at half-maximum (HWHM) of 0.8 cm^{-1} blurs details and produces a significant reduction in apparent noise, but also in resolution. Appending zeros[29] in constructing the fast Fourier transform (FFT) gives better plotting resolution without increasing the true resolution, which is limited by the total length of the time correlation function or of the run, depending on the method used. Another technique designed to reduce the noise involves extending the data in the FFT, not by appending zeros, but with the data in reverse order.[30] We used this in calculating the spectra from the TCF, converting the 2^{13} points into 2^{14} through extending the data by folding; this is done so that the zero-time point, e.g., 1, is unique, while points 2 and 2^{14} are equal, as are points 3 and $2^{14}-1$, etc. The resulting spectra were averaged within equivalent groups and smoothed with a Gaussian filter, using a HWHM of 0.2 cm^{-1} for the 5-K spectra, and 0.8 cm^{-1} for the 29- and 40-K spectra. The length of the TCF, 41 ps, gives us a true resolution of about 0.8 cm^{-1} but the filter degrades this, particularly when the HWHM is increased.

The spectra (Figs. 3 and 4) show that the harmonic results, using the same truncation of the potential as was used in the MD calculations, agree well with the Raman spectra for 5 K. At 29 K there is a definite but modest softening relative to these, 2.5—3.5 cm^{-1} at most, but our data do not appear to show any further softening from 29 to 40 K. Both the E_g and lower T_g modes appear, if anything, to suffer a stiffening of less than a wave number, although this is probably beyond our resolution, especially in view of the line shapes. At 5 K the linewidths for both of the two lower frequency bands, E_g and the lower T_g, are slightly below 1 cm^{-1}, and are, therefore, at the limit of our resolution. The published experimental widths[22] for these lines are both 0.8 cm^{-1} at 8 K and a molar volume either of 25.87 or 25.00 cm^3, and the linewidth data for higher temperatures and various volumes in the same range show little, if any, volume dependence. Our data are consistent with these very narrow lines in this temperature range, although our widths should be taken as an upper limit rather than a quantitative prediction. With increasing temperatures the spectra, particularly in the parallel polarization, get progressively noiser, making the problem of determining the frequencies and the assignments more difficult. The E_g band for 29 K shows a pronounced shoulder of unknown origin to the high-frequency side, suggesting a band around 40 cm^{-1}, and a smaller shoulder on the low-frequency side. Both of these features are greatly reduced in the 40-K spectrum, although some intensity remains in the wings of the band. For 40 K these are small enough to be sidebands generated by the data analysis, but that seems much less likely at 29 K. Brith, Ron, and Schnepp[31] reported a shoulder on this band at higher temperatures, but Medina and Daniels[22] make no mention of it in their careful study. The width of the lower T_g band behaves more predictably, being about 4 cm^{-1} at 29 K, and 7 cm^{-1} at 40 K, although there is a possible splitting at the higher temperature. The experimental[22] value is 1.7 cm^{-1} at 18 K and by 33 K it is broadened to the point where neither the frequency nor the width can be measured reliably. The higher T_g band softens and broadens here also, and at both 29 and 40 K the best estimate of the frequency appears to be about 68 ± 1 cm^{-1}, and the linewidth is best described as broad.

MOLECULAR REORIENTATION

During the highest-temperature run for the $5q$ model, molecules occasionally turned completely over, at a rate that averages to one flip per molecule every 80000 time steps. These events provide direct observational data which should be useful in determining the mechanism of reorientation. In the reference configuration each molecule points along a body diagonal of the cube, and this direction can be used as the polar axis of a local coordinate system. A reorientation involves reversing the direction of the molecular axis in this system, and requires that the molecular axis pass through the plane, normal to the polar axis, which contains a hexagonal shell of nearest-neighbor molecules. The remaining six nearest neighbors are found in two triangles, one above the equatorial plane and the other below, and these triangles are reversed so that, in the reference configuration, the molecular centers have inverse symmetry through the central site. For each molecule which turned over we plotted the configuration of this 13-molecule grouping at regular intervals during a period of 200 time steps, 100 on either side of the step in which the axis crossed the equatorial plane. We also plotted the pair interactions between the 12 nearest neighbors and the central molecule, and the total and translational kinetic energy for a symmetrical period of 400 time steps. Similar plots were made for a random selection of molecules *not* undergoing full reorientations, in order to provide a standard against which to judge the features observed during reorientation.

Various aspects of the structure, dynamics, and energetics were considered as possible keys to a mechanism. It seemed likely that the configuration of the molecules in the equatorial plane would be of prime importance. Molecules undergoing reorientation frequently began the process when noticeably displaced from the center of the (approximate) hexagon of neighbors. Surprisingly often, however, they chose to turn over by rotating not through the gap opened in this way, but in a direction perpendicular to the apparently optimum one. The orientation of the molecular axis as it cut the plane seemed also to be a good prospect, but there does not seem to be any preference for orientations which carry the molecule through the crack between adjacent members of the hexagon over those in which the molecular axis lies along a line connecting the centers of two neighboring molecules. Indeed, some cases were observed where the molecule has less angular momentum normal to the plane than in it, so that it goes through in a slow spiral. The displacement of the center of the molecule out of the plane is no more successful as a predictor of those liable to reorientate. Most turn over with their centers more or less in plane, but some are out of plane at the beginning, in the middle, or at the end. The behavior of the neighbors in the triangles does not appear to be any more decisive.

The information gleaned from the pair and kinetic energies is equally confused. Depending on the direction of rotation, the principal barrier to rotation may be due to interactions with the molecules in the triangles or with those in the equatorial plane, and it may be due to a single strongly repulsive pair interaction, or to a number of weaker repulsions. Interactions which sum to 400—500 K above the optimum at some point during the process are common. The sum of 12 pair interactions and the kinetic energy is much less variable than either the potential or kinetic contributions, indicating something approaching local energy conservation. The molecule slows down when climbing barriers, and speeds up when running downhill. Some cases can be seen in which one of the neighbors receives an impulse from outside the group, and transmits it to the molecule in the middle, so that unexpected accelerations are observed occasionally. One of the few characteristics which seems noteworthy is that reorienting molecules tend to have unusual amounts of rotational kinetic energy for at least part of the time, but even here there are exceptions. Another characteristic is that there are cases where the major barrier occurs after the axis has passed through the plane, but no reversals have been observed. One molecule was seen to turn over a second time, but the events seem to be uncorrelated.

The slightly surprising result is that molecules turn over in the solid without apparently seeking out an optimum path. A combination of chance events either provides a low-energy path through the plane, or gives enough rotational energy to storm the barricades. The temperature here is higher than the transition temperature for the $\alpha \rightarrow \beta$ transformation, and one would expect greater selectivity at the lower temperatures at which α-nitrogen is studied experimentally. Nevertheless, the way in which things appear to average out from case to case, e.g., the barrier height being the same whether due to one or many interactions, seems to us to argue against a very specific mechanism or set of mechanisms.

DISCUSSION

The MD results show that increasing the temperature at fixed volume leads to small negative anharmonic shifts for the $5q$ model. At least two interpretations of this observation are possible. One is that the classical motions, even at 40 K, have amplitudes which are too small to sample the anharmonicity in the librational potential. Another is that the amplitudes are large enough, but the anharmonicity leads to small frequency shifts. We have constructed histograms to generate the empirical distributions of angular displacements from the reference directions. Figure 5 illustrates that the amplitudes are substantial, particularly at the higher temperatures. As discussed earlier, we have also detected some molecules making full end-over-end rotations at 40 K, indicating that rotational melting probably occurs at a temperature not much greater than this. In constructing the 40 K distributions plotted in fig. 5, about 10^5 observations were made at an angular deviation of 45°, showing that large excursions are relatively common.

If the amplitudes are large, then the potential must be responsible for the lack of frequency shifts. It is possible that $5q$ accidentally has this attribute, and so we also considered the model used by Kobashi[14] in his study of the librations in α-nitrogen. Simulations similar to those described for $5q$ were used but at the molar volume given by Kobashi, and the results are somewhat surprising. The

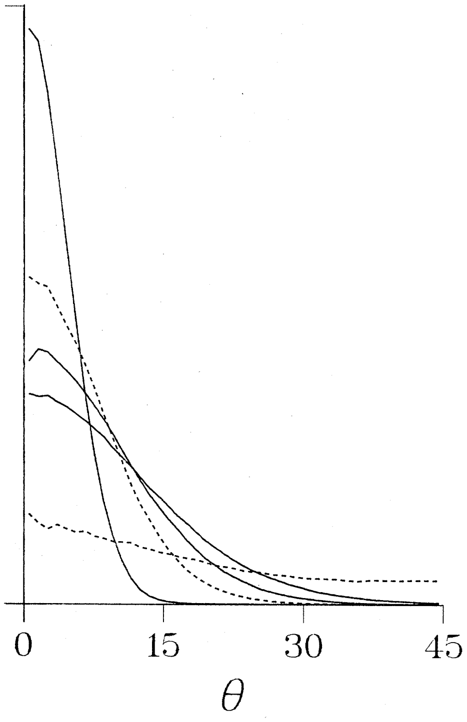

FIG. 5. Empirical probability distributions showing the deviations of the molecular axis direction from the appropriate cube diagonal. The solid curves are for the $5q$ model at temperatures of 5, 29, and 40 K, in order of decreasing intercept at zero deviation. The dashed curves are for Kobashi's model at 10 and 20 K. The latter shows clearly that the system is rotationally melted. The small irregularities near the zero intercept are due to the statistical irregularities resulting from the very small measuring area at small deflection.

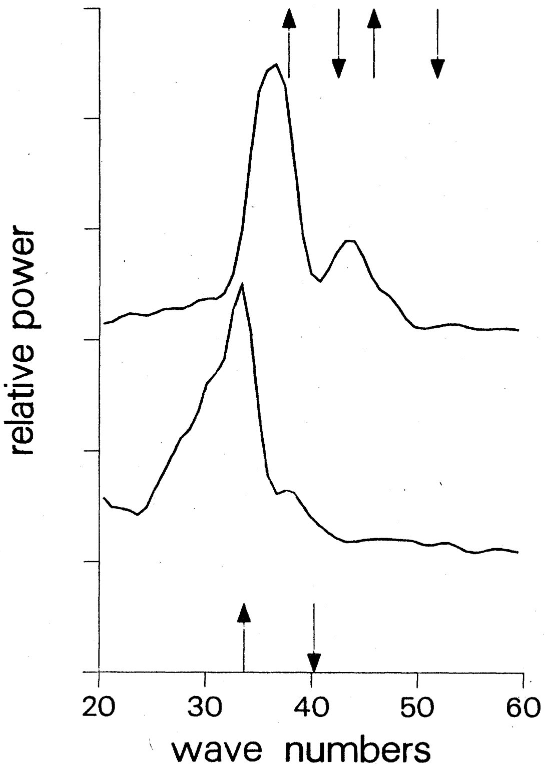

FIG. 6. Computed Raman spectra for the Kobashi model based on molecular-dynamics simulations at 10 K. The lower curve is for parallel scattering and the upper curve is for perpendicular scattering. The upward arrows indicate the corresponding harmonic results, and the downward arrows the anharmonic resonances[14] calculated by perturbation theory for the same temperature and volume.

system is rotationally melted by 30 K, and seems to be in the process of melting at 20 K. At 10 K, the temperature for which Kobashi reported frequencies and linewidths, the system is ordered, and yields acceptable results for the Raman spectra, Fig. 6, and for $S(\mathbf{q},\omega)$, although even at 10 K there is some indication of softening in the orientational structure. Again, the librational motions have appreciable amplitudes (Fig. 5) but the measured frequencies (Fig. 6) are not nearly as different from the harmonic values as perturbation theory would lead us to expect.[14] The results for the linewidths in Kobashi's paper seem reasonable but the frequency shifts may be seriously overestimated. In any case, the situation is very similar to that found with the $5q$ model. Perhaps more significant is the fact that anharmonic shifts obtained from perturbation theory are positive, while those obtained here are negative. A recent summary[1] of anharmonic calculations show that the predicted shifts are predominantly positive, the major exception being a calculation[16] in which a substantial volume increase occurred between harmonic and anharmonic calculations; at constant volume this system also gives positive shifts.[32]

The results presented here lead us to the conclusion that the anharmonic corrections to the librational frequencies in α-nitrogen are overestimated, certainly for Kobashi's potential and possibly for others also. Although we have studied only two models, neither of them particularly good by this evaluation, and have invoked an argument for using higher temperatures in a classical system to mimic important quantum fluctuations, the results do not appear to admit any other interpretation in these cases. Large fluctuations are observed, but large anharmonic shifts are not. Our reservations about the anharmonic theory are strengthened by the results of Weis and Klein,[28] in their calculation they studied the dynamical structure factor of α-nitrogen by MD using a 2LJ model derived from fluid studies.[33] The MD frequencies differed from the quasiharmonic results but by an amount which is significantly smaller than that predicted by perturbation theory, and again the MD values are softer than the quasiharmonic results.

The central difficulty in this entire discussion is that the anharmonic shift is a purely calculational quantity, since neither the harmonic frequency nor the shift is measurable. That being the case, one should, perhaps, direct attention to those consequences of anharmonicity which are measurable, in this case the linewidth. Unfortunately, we are not yet in a position to establish definitive linewidths by MD, and, in any event, the sensitivity of the linewidth to details of the model and the computational method in perturbation theory is probably smaller than it is for the shifts. Furthermore, the determination of linewidths poses greater experimental difficulties than does the determination of frequencies. In spite of that, further study of the linewidths would appear to be the best option available in terms of discussing the role of anharmonicity in this system.

The $5q$ model, although satisfactory in a number of ways, is inadequate even for α-nitrogen alone. The problem of a good pair potential for nitrogen is far from solved,[21] but, if our conclusion is correct, the process of constructing a good model will be significantly simplified (if not made simple) by the fact librational anharmonicity is more likely to be a matter of a few cm^{-1} rather than 10 cm^{-1} or more.

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*Author for correspondence.

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