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Experimental equilibrium crystal structures: Molecular dynamics as a probe for atomic probability density functions

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Abstract

Molecular dynamics simulations using plane-wave DFT calculations have been used along with experimental data to determine the equilibrium crystal structure and thermal anisotropic displacements parameters for ND_3.

1. Introduction

Equilibrium structures, corresponding to theoretical vibrationless states at potential-energy minima, are the ultimate goal of structural chemists. Only by reducing structures to this common denominator can geometric parameters obtained from different experimental and theoretical methods be compared directly.

Thermal motion of atoms in crystals, as in gases and liquids, yields vibrationally-averaged structures, which may yield apparently inaccurate geometric parameters. Atoms generally move along curved trajectories, with apparent bond shortening when determined by diffraction. This has long been understood [1,2], and attempts have been made to counter these structural inconsistencies, including rigid-body analysis of motions [3] (ignoring significant effects of internal molecular vibrations) and classical molecular dynamics (MD) to simulate thermally-averaged structures [4].

Here we demonstrate that, by using MD simulations of a periodic solid, we can follow atomic motions under the influence of vibrational and lattice modes, thence determining the differences between the time-averaged and equilibrium atomic positions. These, applied to nuclear coordinates obtained by neutron diffraction, yield an experimental equilibrium structure. MD trajectory analysis also permits theoretical estimation of the anisotropic displacement parameters (ADPs) of each atom. These important parameters define the thermal motion of the atoms in the crystal in terms of Gaussian probability ellipsoids [5]. We have applied the method to the phase I crystal structure of ND_3. The high symmetry and small cell size make this an ideal case for exploring the potential of MD to simulate crystal structures. The downside to this test case, however, is the low accuracy of the experimental data, which feature a limited $\sin\theta/\lambda$ range and large ESDs [6]. Nevertheless, we present a method for obtaining experimental equilibrium crystal structures and discuss the limitations of sampling adequate phonon dispersion in this case.

2. Calculations

We have applied plane-wave density-functional theory (PW-DFT) to study the time-averaged structure of phase I ND_3, whose structure had previously been determined by neutron powder diffraction [6]. The cubic ($P2_13$) crystallographic unit-cell contains four molecules, with $a = 507.3$ pm and $V = 130.55 \times 10^6$ pm^3 at 77 K. The experimental bond length is 98.8 pm. Starting from the experimental structure and symmetry, the theoretical 0 K equilibrium structure was optimised at ambient pressure using the PW-DFT package CASTEP [7]. The electronic core was described using CASTEP's standard ultrasoft

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pseudopotentials and the PW91 functional was used for both electron exchange and correlation [8]. The plane-wave cut-off energy was 400 eV and a $2 \times 2 \times 2$ Monkhorst-Pack grid was used to sample reciprocal space. During optimisation the unit-cell parameters and atomic positions were alternately optimised until the maximum energy change per atom was less than 5×10^{-7} eV. The optimised cell parameter was 518.46 pm, with rN–D 103.5 pm.

The MD simulations (NVE and NVT ensembles) were run with $P1$ space-group symmetry so that all vibrations were properly represented. The initial temperature of each simulation was chosen to equilibrate at 77 K, the temperature of the original crystallographic experiments. For the NVT ensemble this was facilitated by a Nosé–Hoover chain of five thermostats [9]. Atomic coordinates, velocities and forces were calculated every 0.8 fs for 30 ps for NVE and 50 ps for NVT. As the temperature is stable in most experiments, the NVT ensemble should provide a more realistic picture of the system over time and a more ergodic simulation. The NPT ensemble was not adopted as variable-cell DFT simulations typically require a larger cut-off energy to converge properly. The effect of fixing the cell at its 0 K length is a pressure of approximately 0.1 GPa. Previous studies have suggested that increasing the pressure from ambient to 0.1 GPa results in the lattice modes of ammonia changing by only 5 cm^{-1} [10,11]. The effect of the simulation pressure on the vibrational potential-energy surface (PES) is therefore marginal.

Simulating only a $1 \times 1 \times 1$ cell neglects non-Γ-point phonon modes such as acoustic modes. To determine the effects of phonon dispersion on the equilibrium structure an NVT–MD simulation of a $2 \times 2 \times 2$ cell of ND_3 was performed using the CPMD code. The standard pseudopotentials provided were used at a cut-off energy of 800 eV, with a single k-point and the PBE functional [12]. The geometry was optimised to the same level of convergence as in the $1 \times 1 \times 1$ cell calculations with N–D again 103.5 pm. An NVT Car-Parrinello MD simulation was then performed with a timestep of 0.09 fs. The force, velocity and position of each particle were sampled every 0.9 fs for 15 ps. All MD results are presented in Table 1.

Table 1
Fractional coordinates for ND_3

	Equilibrium	MD averaged	Correction	Experimental [a]	Corrected
NVE ensemble – 1 × 1 × 1 cell					
x_N	0.1935	0.1974(6)	−0.0039(6)	0.2108(11)	0.2069(13)
x_D	0.3460	0.3520(8)	−0.0060(8)	0.3694(6)	0.3634(10)
y_D	0.2712	0.2697(6)	0.0015(6)	0.2694(6)	0.2709(8)
z_D	0.0910	0.0965(8)	−0.0055(8)	0.1141(11)	0.1086(14)
NVT ensemble – 1 × 1 × 1 cell					
x_N	0.1935	0.1974(5)	−0.0039(5)	0.2108(11)	0.2069(12)
x_D	0.3460	0.3519(7)	−0.0059(7)	0.3694(6)	0.3635(9)
y_D	0.2712	0.2698(5)	0.0016(5)	0.2694(6)	0.2710(8)
z_D	0.0910	0.0968(6)	−0.0058(6)	0.1141(11)	0.1083(13)
NVT ensemble – 2 × 2 × 2 cell					
x_N	0.1925	0.1969(23)	−0.0044(23)	0.2108(11)	0.2064(25)
x_D	0.3471	0.3523(25)	−0.0052(25)	0.3694(6)	0.3642(25)
y_D	0.2711	0.2715(27)	−0.0004(25)	0.2694(6)	0.2690(25)
z_D	0.0932	0.0989(27)	−0.0057(27)	0.1141(11)	0.1084(29)

[a] Crystal structure at 77 K [6].

3. Results and discussion

The asymmetric unit of crystalline ND_3 consists of one third of a molecule. The MD trajectory was analysed initially by determining the time-averaged position of each atom in the cell. The values of x_N, y_N and z_N, estimated separately, were averaged to give the single coordinate for nitrogen. The symmetry of the $P2_13$ space-group was used to map each of the time-averaged atomic positions into the asymmetric unit; these were then averaged again to provide the final time-averaged position. The high symmetry of the crystal structure increases our dataset size and, therefore, the accuracy of our average positions. The uncertainties of the time-averaged coordinates were estimated using the central limit theorem [13]; the blocking method [14] was applied to correct for the effects of data correlation.

The differences between time-averaged and equilibrium positions of the N and D atoms, Δx, Δy and Δz, are the corrections to be applied to the experimental structure. Differences between two calculations at the same level of theory should cancel any systematic errors attributable to the theoretical method. Table 1 lists vibrationally-averaged fractional coordinates from the MD simulations, calculated equilibrium coordinates, the correction terms, and the coordinates from the neutron diffraction crystal structure, before and after vibrational correction. The uncertainties of the correction factors are the same as those of the averaged positions, and combine with the experimental uncertainties to give the ESDs of the corrected fractional coordinates. The validity of the DFT PES may be ascertained from the velocity-autocorrelation function of the system, which yields the phonon spectrum by Fourier transformation. This spectrum agrees excellently with experiment [15], and previous constrained MD simulations on NH_3 have also shown the suitability of DFT for modelling thermal motion in ammonia [10]. This Γ-point phonon spectrum does not indicate whether all thermal motions and phonon dispersion have been accurately depicted by the simulations.

As expected, the average deuterium position lies closer to the nitrogen in the vibrationally-averaged structures, for both ensembles, than in the calculated equilibrium structure. The NVE ensemble N–D bond length is 0.41 pm longer in the experimental equilibrium structure than in the experimental time-averaged structure; the NVT ensemble lengthening is 0.54 pm and 0.63 pm from the $1 \times 1 \times 1$ and $2 \times 2 \times 2$ simulations, respectively. The $2 \times 2 \times 2$ simulation yields an experimental equilibrium bond length of 99.4 pm. The ESD of the experimental bond length is 0.9 pm, a relatively large value caused by the limited $\sin\theta/\lambda$ range of the experiment; in contrast, the ESDs