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Inelastic neutron scattering, Raman, vibrational analysis with anharmonic corrections, and scaled quantum mechanical force field for polycrystalline L-alanine

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Abstract

A scaled quantum mechanical harmonic force field (SQMFF) corrected for anharmonicity is obtained for the 23 K L-alanine crystal structure using van der Waals corrected periodic boundary condition density functional theory (DFT) calculations with the PBE functional. Scale factors are obtained with comparisons to inelastic neutron scattering (INS), Raman, and FT-IR spectra of polycrystalline L-alanine at 15–23 K. Calculated frequencies for all 153 normal modes differ from observed frequencies with a standard deviation of 6 wavenumbers. Non-bonded external $k = 0$ lattice modes are included, but assignments to these modes are presently ambiguous. The extension of SQMFF methodology to lattice modes is new, as are the procedures used here for providing corrections for anharmonicity and van der Waals interactions in DFT calculations on crystals. First principles Born–Oppenheimer molecular dynamics (BOMD) calculations are performed on the L-alanine crystal structure at a series of classical temperatures ranging from 23 K to 600 K. Corrections for zero-point energy (ZPE) are estimated by finding the classical temperature that reproduces the mean square displacements (MSDs) measured from the diffraction data at 23 K. External $k = 0$ lattice motions are weakly coupled to bonded internal modes.

Keywords: INS, inelastic neutron scattering; Raman neutron scattering; L-alanine; Crystals; Quantum mechanical force field; DFT, density functional theory; Anharmonic corrections; BOMD, Born–Oppenheimer molecular dynamics; ZPE, zero-point energy; Atomic displacement parameters; Mean square displacements

1. Introduction

Vibrational spectra of molecular crystals obtained from inelastic neutron scattering (INS) measurements contain a substantial amount of information about structure, molecular dynamics, and the potential energy surface [1–3]. INS provides information about the amplitudes of hydrogen atom motions. These motions include external rotational and translational lattice modes of molecules in the unit cell as a whole where vibrational frequencies depend on intermolecular hydrogen bonding, ionic, and van der Waals forces.

Much of this information can be extracted from the INS spectrum by performing an *ab initio* periodic boundary condition (PBC) density functional theory (DFT) calculation of the energy second derivatives and molecular dynamics for the crystal, followed by a scaled quantum mechanical force field (SQMFF) [4] vibrational analysis where the experimental spectra and *ab initio* results are combined using a normal coordinate representation of both internal and external mode motions for the unit cell. The experimental molecular geometry can replace the theoretical optimized geometry at this stage to correct for inadequacies in the predicted structure. The SQMFF is strictly harmonic,

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representing a small area of the potential surface near the minimum energy, so it is necessary to provide corrections for the anharmonic part of the potential surface, and this can be done through a series of first principles molecular dynamics simulations of the crystal performed at several temperatures.

The results consist of experimental information about properties of the molecular solid that go beyond what is provided by frequencies alone:

(1) The potential energy distribution for each vibrational frequency shows the list of motions with their relative energies that contribute to each degree of freedom, and in particular it shows to what extent non-bonded external motions couple with bonded internal modes.
(2) The displacement matrix, in a comparison of the calculated and experimental INS intensities, shows to what extent the calculated harmonic atomic displacements (for Hydrogen atoms) accurately represent the experimental molecular dynamics, and in general to what extent the calculated SQMFF accurately describes the experimental potential surface.
(3) The force constant matrix, representing the rate of change of all harmonic forces with respect to atom displacements, describes the curvature of the potential surface near the energy minimum at every degree of freedom in motion (the diagonal terms) and at every interaction between motions (the off diagonal terms). In particular, it shows what interactions are important. This information can be used to selectively improve the accuracy of molecular mechanics potential functions.
(4) The anharmonic corrections increase the probability that the calculated force constants accurately represent the harmonic part of the potential surface. They can be used to modify the calculated INS intensities so that they more accurately represent the anharmonic molecular dynamics, and to refine the anharmonic terms in the Taylor expansion of a molecular mechanics potential function.
(5) The scale factors represent the corrections required to bring the quantum mechanical force field into agreement with the experimental potential surface. They are known to be transferable with respect to internal modes for isolated molecules, and in principle scale factors obtained from small molecules can be used to correct quantum mechanical calculations on much larger molecules [7,8], even where experimental data is not available. The extension of the SQMFF methodology to crystals is new here, and may provide some correction to the calculated $k = 0$ external lattice modes and to their coupling with low frequency internal modes. However, it should be kept in mind

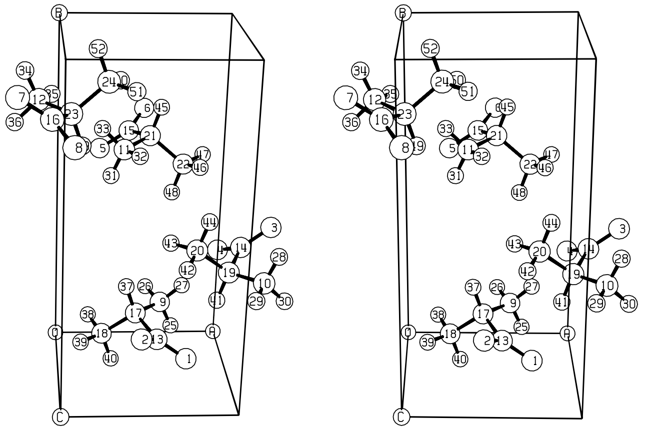

Fig. 1. Divergent stereo Ortep [5] drawing of L-alanine optimized in the 23 K [6] unit cell. Atoms numbered 9, 10, 11, and 12 are Nitrogens.

Table 1
Internal coordinate definitions for the L-alanine crystal molecule 1, and a comparison of the 60 K neutron diffraction, 23 K X-ray diffraction, and DFT optimized geometries[a]

Coordinate	ND[b]	X-ray[c]	DFT	Diff.
$R_1 = \Delta\gamma(C^{13}–O^1)$	1.249	1.248	1.251	0.003
$R_2 = \Delta\gamma(C^{13}–O^2)$	1.270	1.268	1.278	0.010
$R_9 = \Delta\gamma(C^{17}–H^{37})$	1.097	1.125	1.098	−0.027
$R_{13} = \Delta\gamma(C^{17}–C^{18})$	1.529	1.525	1.526	0.001
$R_{17} = \Delta\gamma(C^{17}–C^{13})$	1.538	1.536	1.550	0.014
$R_{21} = \Delta\gamma(C^{17}–N^9)$	1.490	1.488	1.469	−0.019
$R_{25} = \Delta\gamma(C^{18}–H^{38})$	1.097	1.086	1.105	0.019
$R_{26} = \Delta\gamma(C^{18}–H^{39})$	1.104	1.118	1.099	−0.019
$R_{27} = \Delta\gamma(C^{18}–H^{40})$	1.095	1.081	1.103	0.022
$R_{37} = \Delta\gamma(N^9–H^{25})$	1.045	1.044	1.045	0.001
$R_{38} = \Delta\gamma(N^9–H^{26})$	1.059	1.082	1.110	0.028
$R_{39} = \Delta\gamma(N^9–H^{27})$	1.040	1.018	1.043	0.025
$R_{49} = \Delta\theta(N^9–C^{17}–H^{37})$	107.0	107.2	107.2	0.066
$R_{50} = \Delta\theta(C^{13}–C^{17}–H^{37})$	108.3	108.9	107.8	−1.057
$R_{51} = \Delta\theta(C^{18}–C^{17}–H^{37})$	110.5	109.7	110.4	0.623
$R_{52} = \Delta\theta(N^9–C^{17}–C^{13})$	110.1	110.0	111.6	1.668
$R_{53} = \Delta\theta(N^9–C^{17}–C^{18})$	109.8	109.8	109.0	−0.855
$R_{54} = \Delta\theta(C^{13}–C^{17}–C^{18})$	111.1	111.1	110.7	−0.416
$R_{73} = \Delta\theta(O^2–C^{13}–O^1)$	125.7	125.8	125.8	0.041
$R_{74} = \Delta\theta(O^2–C^{13}–C^{17})$	115.9	115.9	113.6	−2.212
$R_{75} = \Delta\theta(O^1–C^{13}–C^{17})$	118.4	118.4	120.5	2.169
$R_{76} = \Delta\omega(C^{17}–$ out of $O^2–O^1–C^{13}$ plane)				
$R_{89} = \Delta\theta(H^{39}–C^{18}–H^{40})$	108.2	108.8	108.7	−0.093
$R_{90} = \Delta\theta(H^{39}–C^{18}–H^{38})$	109.1	109.0	108.5	−0.537
$R_{91} = \Delta\theta(H^{40}–C^{18}–H^{38})$	108.1	108.7	108.3	−0.451
$R_{92} = \Delta\theta(C^{17}–C^{18}–H^{38})$	110.0	109.6	109.0	−0.589
$R_{93} = \Delta\theta(C^{17}–C^{18}–H^{40})$	110.6	110.6	110.4	−0.127
$R_{94} = \Delta\theta(C^{17}–C^{18}–H^{39})$	110.8	110.1	111.8	1.748
$R_{113} = \Delta\theta(H^{26}–N^9–H^{27})$	108.6	109.2	107.1	−2.150
$R_{114} = \Delta\theta(H^{26}–N^9–H^{25})$	108.2	108.5	106.3	−2.244
$R_{115} = \Delta\theta(H^{27}–N^9–H^{25})$	109.9	109.6	109.3	−0.361
$R_{116} = \Delta\theta(C^{17}–N^9–H^{25})$	111.7	111.0	110.1	−0.956
$R_{117} = \Delta\theta(C^{17}–N^9–H^{27})$	108.8	109.4	110.9	1.494
$R_{118} = \Delta\theta(C^{17}–N^9–H^{26})$	109.5	109.0	113.1	4.065
$R_{137} = \Delta\tau(C^{17}–N^9)$				
$R_{141} = \Delta\tau(C^{17}–C^{13})$				
$R_{145} = \Delta\tau(C^{17}–C^{18})$				

[a] Molecule 1 includes atoms numbered 1, 2, 9, 13, 17, 18, 25–27, and 37–40 as shown in Fig. 1. Internal coordinates for molecules 2–4 are identical to those for 1. Symbols: γ = stretch, θ = bend, ω = out-of-plane bend, τ = torsion. Superscript numbers refer to the atom numbering in Fig. 1.

[b] ND, neutron diffraction at 60 K [13].

[c] X-ray, X-ray diffraction of a single crystal at 23 K [6]. The differences on the right are between the X-ray values and the DFT values.