Hydrogen dynamics in solid formic acid: insights from simulations with quantum colored-noise thermostats

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Abstract. With an increase of computational capabilities, \textit{ab initio} molecular dynamics becomes the natural choice for exploring the nuclear dynamics of solids. As based on classical mechanics, the validity of this approach is, in-principle, limited to the high-T regime, whilst low-temperature simulations require inclusion of quantum effects. The methods commonly used to account for nuclear quantum effects are based on the path-integral formalism, which become, however, particularly time consuming when high accuracy methods are used for calculating forces. Recently, new efficient alternative approaches to account for quantum nature of nuclei have been proposed, using so-called quantum thermostats. In this work, we examine the simulations performed with the quantum colored-noise thermostat introduced by Ceriotti [Phys. Rev. Lett., 103:030603, 2009]. We present the tests of portable implementation of the quantum thermostat in the ABIN program, which has been extended to periodic systems through the interface to CASTEP, a leading spectroscopy-oriented plane-wave density functional theory code. The range of applicability of quantum-thermostatted molecular dynamics simulations for the interpretation of neutron scattering data was examined and compared to classical molecular dynamics and lattice-dynamics simulations, using solid formic acid case as a test bed. We find that the approach is particularly useful for the modeling of low-temperature inelastic neutron scattering spectra as well as provides some theoretical estimate for the low-limit of the mean kinetic energy. While finding the quantum-thermostat to seriously affect the dynamic properties of the title system, we illustrate to which extent the unperturbed response can be successfully recovered.
1. Introduction
Molecular dynamics (MD) has evolved into a powerful numerical method to investigate structural and dynamical properties of condensed matter [1]. For an atom, these calculations are, however, only valid in the classical limit, i.e. for temperatures safely above the Debye temperature that signals the onset of quantum effects. The Debye temperature is often of the order of few hundred Kelvins and nuclear quantum effects (NQEs) are thus indeed important over a wide range of temperatures [2,3].

Quantum fluctuations stemming from the Heisenberg uncertainty principle make the energy of a particle at 0 K higher than at the potential energy minimum, leading to a concept of zero point energy (ZPE) (see Fig. 1). While ZPE reflects the quantum nature of atomic motion, it can be approximately accounted for by lattice-dynamics calculations, which, by definition, are based on the quantum harmonic oscillator model.

![Figure 1. Schematic representation of the energy and probability of a mechanical and quantum particle in a harmonic energy well.](image)

In order to capture anharmonic effects from first-principles, a number of static theoretical methods have recently been devised. These approaches are based on calculating vibrational excited states either from vibrational self-consistent field (VSCF) [4–6], the vibrational interaction of configurations (VCI) [7–9] or from perturbation theory (second-order vibrational perturbation theory, VMP2, for example) [10,11]. Despite of a substantial activity in the field [12,13], the use of static methodology in modeling of anharmonic spectra of solids is still practically unworkable for polyatomic molecular systems because of its complexity.

While classical MD simulations in principle do not account for ZPE, they do naturally account for mechanical anharmonicity effects, since no assumption about the shape of the underlying potential energy surface (PES) is imposed. However, if the ZPE is very large (e.g. hydrogenous materials) then the oscillator looks as reaching a higher temperature than the classical spring and so it enters the anharmonic part of the PES. However, in such a case, the low-temperature classical MD simulations do not properly account for anharmonic effects. That is because the particle distribution widths are narrow (see Fig. 1) and the simulations stay near the potential energy minima all the time. In such a way, only the harmonic part of the PES is probed.
Indeed, it has been illustrated that low-temperature \textit{ab initio} Born-Oppenheimer Molecular Dynamics (BOMD) simulations provide vibrational spectra identical to the harmonic ones calculated through the Hessian matrix diagonalization (see references \cite{14} and \cite{15} for an illustration). Above the low-temperature limit, it is necessary to perform the simulations at higher, effective temperature conditions, possibly adjusted to mean square atomic displacements (MSD) found experimentally. For hydrogen atoms this may lead to very high effective temperatures. The problems associated with such a crude approach have been nicely illustrated by Williams et al. \cite{16}. It has been shown that selection of classical effective temperature is a serious problem, stemming from the fact that the measured MSDs only represent a probable upper limit that may be allowed in the BOMD simulation for each atom in the same molecule, whereas the mapping of the quantum system onto the classical one could only be done provided that the temperature is set differently for each mode (or mass). As shown by Van-Oanh et al. \cite{17}, ZPE contributions can be somehow alleviated by preparing the initial conditions for MD simulations in the microcanonical ensemble (NVE) according to semi-classical quantization based on a normal-mode representation. Such an approximation, however, was found to be inefficient for strongly anharmonic cases, suffering from energy relaxation effects and from so-called ‘ZPE leakage’, i.e. a cross-talk between the high-energy and low-energy modes.

An alternative strategy to incorporate NQEs is to place the system in contact with a quantum thermal bath (QTB), where the dynamics follows a generalized Langevin equation (GLE) and the vibrational delocalization is mimicked by a quantum thermostat (QT). In such an approach, the otherwise white noise spectrum of the Fourier Transform of the stochastic force correlation function is filtered (colored) in such a way that it ends up resembling the spectral density of the correlation function for a quantum harmonic oscillator with ZPE contribution included \cite{2,18–20}.

More strictly, in GLE, the particle of unit mass, which position is described by the generalized coordinate $q$, with a conjugate momentum $p$, and being subject to a potential $V'(q)$, yields the following equations of motion:

$$\frac{\dot{q}}{\dot{t}} = p(t)$$

$$q(t) = -V'(q) - \int_{t_{-\infty}}^{t} K(t-s) p(s) ds + \zeta(t)$$

where $\zeta(t)$ is a time-correlation function of the random force and $K(t)$, is the memory kernel, introducing the dependence of the system evolution on its history in terms of a non-Markovian stochastic differential equation \cite{21}. Such definition, however, requires the use of integro-differential equations, leading to a serious numerical challenge. Alternatively, one may map the non-Markovian dynamics onto an equivalent, Markovian dynamics in an extended space $n$, by introducing auxiliary fictitious momenta $s$, linearly coupled to the physical momentum $p$:

$$\left( \begin{array}{c}
\dot{q} \\
\dot{s}
\end{array} \right) = \left( \begin{array}{c}
-V'(q) \\
0
\end{array} \right) + \left( \begin{array}{c}
a_{pp} a_{pp}^T \\
a_{pp} A
\end{array} \right) \left( \begin{array}{c}
p \\
s
\end{array} \right) + \left( \begin{array}{c}
b_{pp} b_{pp}^T \\
b_{pp} B
\end{array} \right) \left( \begin{array}{c}
\xi
\end{array} \right)$$

where $s$ is the vector of $n$ additional degrees of freedom; $\xi$ denotes a $n+1$ dimensional vector of uncorrelated Gaussian numbers \cite{21}; $a_{pp}$ stands for a friction coefficient and $b_{pp}$ denotes the intensity of the random force, both linked by the so-called fluctuation-dissipation theorem ($b_{pp}^2 = 2a_{pp}mkB\tau$).

The matrices in Eq. (2) are related by the so-called drift matrix $C$:

$$A_p C_p + C_p A_p^T = B_p B_p^T$$

where $A_p$ and $B_p$ are the drift and diffusion matrices, respectively.
where $\mathbf{A}_p = \left( a^{pp}_{\mathbf{a}_p, \mathbf{a}_q} \right)$ and $\mathbf{B}_p = \left( b^{pp}_{\mathbf{b}_p, \mathbf{b}_q} \right)$. This allows one to predict the response properties analytically.

For a quantum thermostat, it is, however, required to relax the fluctuation-dissipation theorem, which leads to non-equilibrium GLE dynamics. This may be realized by noting that the kinetic energy distributions of both classical and quantum harmonic oscillator take the form of a Gaussian, with the widths differing only in the standard deviation. While the effective temperature can be defined as:

$$T^* (\omega) = \frac{\hbar \omega}{2 k_B \coth \frac{\hbar \omega}{2 k_B T}}$$  \hspace{1cm} (4)

one can take advantage of GLE dynamics by thermostatting the different vibrational modes present in the system at different effective temperatures $T^*$. In such a way, the kinetic energy distribution with deviation $\sigma_q^2 = \frac{\hbar^2}{2 m \omega \coth \frac{\hbar \omega}{2 k_B T}}$ can be imposed by using purely classical simulations.

Quantum thermostatting has proven to be very efficient for the control and evaluation of static properties in MD simulations. Nevertheless, its use for prediction of dynamical properties of materials, including vibrational spectra or diffusion coefficients, has been found to be limited due to a possible disturbance of these properties induced by the presence of the thermostat. The problem is of particular importance for anharmonic systems, where a strongly coupled thermostat is required to avoid the ZPE leakage.

A remedy to this deficiency has been recently provided by Rossi, Kapil and Ceriotti [21], delivering an analytical scheme to extract the microcanonical velocity-velocity autocorrelation function (VACF) from the quantum-thermostated (GLE) trajectory. It is based on the idea that the exact VACF for a harmonic oscillator of frequency $\omega_0$, coupled to a GLE thermostat is:

$$\Theta (\omega, \omega_0) = C_{qp} (\omega_0) A_{qp} (\omega_0) - 1 \left[ A_{qp} (\omega_0) + \omega^2 \right]_{pp}$$  \hspace{1cm} (5)

where $A$ and $C$ are the drift and the diffusion matrices of the generalized Langevin equation. For the details of the nomenclature and the matrices elements ($[\cdot, \cdot]$), we refer the reader to section 2 of [21]. For a system with a density of states given by $g(\omega)$, the VACF can be written in the harmonic limit as:

$$C_{VV} (\omega) = \int d\omega g(\omega) \Theta (\omega, \omega_0)$$  \hspace{1cm} (6)

Though the result has been derived under a harmonic approximation, the predictions happen to be in excellent agreement with the exact VACF for system as anharmonic as liquid water [21]. It was shown that the post-processing deconvolution of the perturbed spectra can properly recover the unperturbed dynamic properties even in the case of heavily thermostatted cases, i.e. for considerable anharmonic systems [21].

Modeling of anharmonic vibrational dynamics along with nuclear quantum effects is no doubt of great importance for neutron spectroscopy. On the other hand, the aforementioned state-of-the-art ab initio MD approaches are hardly used by the community in the modeling of neutron spectroscopy observables. To meet these needs, we examine here a possible applicability of the quantum-thermostatted molecular dynamics simulations for the prediction of inelastic-neutron-scattering (INS) spectra and neutron Compton scattering (NCS) observables in hydrogen-bonded molecular materials using solid formic acid (FA) as a testbed.

The present paper is organized as follows. First we present the test of quantum thermostat implementation in a molecular dynamics code ABIN, developed by Hollas et al. [22], which we recently interfaced to a leading solid-state plane-wave density functional theory code, CASTEP [23, 24]. We then examine the range of applicability of quantum-thermostatted ab
initio molecular dynamics simulations for the modeling and analysis of neutron-scattering data, with solid FA acting as the reference [25].

2. Research Methodology

2.1. Experimental

The experimental data presented in this paper along with the initial structural models have been published recently in Ref. [25]. In brief, we refer to the low-temperature INS spectrum measured on the inverted-geometry TOSCA spectrometer, located at the ISIS Facility [26]. We further supplement the analysis with the variable-temperature INS spectra collected with the direct-geometry spectrometer HRMECS (Intense Pulsed Neutron Source, Argonne National Laboratory) [27]. NCS experiments were performed at 180 and 240 K on the VESUVIO spectrometer, also located at the ISIS Facility [28–31]. The experimental and data-analysis protocol for VESUVIO measurements is explained in more detail elsewhere [28–35].

2.2. Computational

The ABIN code is a Fortran program performing BOMD [22]. It was designed specifically to deal with NQEs. It can perform path integral MD (PIMD) simulations and also utilizes the recently developed quantum thermostat by Ceriotti [18–20]. ABIN itself handles the propagation of the system according to the Newton equations of motion, while the forces and energies are taken from the external electronic structure programs. The call to the chosen external program is handled via a shell script. Writing a new interface can be done without any changes introduced to ABIN or to the electronic structure code. Therefore, ABIN is very flexible and ideally suited to work with essentially any molecular modelling code. In this communication we present an extension of ABIN including periodic boundary conditions (PBC). To this end, ABIN has been interfaced to CASTEP [23,24] and QUANTUM ESPRESSO [36,37].

In line with our previous study, we employed periodic plane-wave density functional theory (PW-DFT) calculations, using the same numerical settings as defined in Ref. [25]. As a starting point, we used supercells with Z = 24, where the cell volumes were kept fixed to those obtained with the NPT runs at a given effective temperature, that is the temperature relative to the melting point, rather than to the absolute (classical) temperature of the material (see Ref. [25] for more details). The results of the quantum-thermostatted ABIN calculation with CASTEP, were benchmarked with the results of the BOMD simulations obtained using the CP2K code with its own quantum thermostat implementation [38]. The CP2K calculation used a mixed Gaussian and plane-wave approach (GPW) [39]. In both cases exchange and correlation were treated with the Perdew-Burke-Ernzerhof (PBE) functional [40], augmented with semi-empirical dispersion corrections (SEDC). Since both codes employ different SEDC schemes, Tkatchenko and Scheffler (TS) dispersion corrections (PBE-TS) were employed in the CASTEP simulations [41], while the Grimme-D3 scheme with Becke-Johnson damping [PBE-D3(BJ)] was used in the CP2K simulations [42–44]. For CASTEP calculations a plane-wave kinetic-energy cutoff of 900 eV was used along with nonlocal norm-conserving pseudopotentials (NCPPs) [45]. For the CP2K simulations, we employed a valence double-zeta-quality basis set optimized from molecular calculations (DZVP-MOLOPT-SR-GTH) along with the corresponding Goedecker-Teter-Hutter pseudopotentials. The plane-wave cutoff for the finest level of the multi-grid was set to 400 Ry.

The BOMD simulations were performed with an SCF convergence of $5 \times 10^{-8}$ eV threshold per atom. Due to the large size of the real space supercell, the $k$-point grid sampling was reduced to the $\Gamma$ point in both CP2K and CASTEP simulations.

A time step of 0.5 fs was used all throughout the MD runs. While the use of a smaller integration step is recommended for the simulations employing QTs, the use of the standard 0.5 fs step was dictated by a very large computational cost. Use of such an integration step may
potentially result in unphysical blue-shifting of the highest predicted frequencies, estimated at the order of 50 cm$^{-1}$, according to molecular simulations of a FA molecule presented elsewhere [46]. Such a discrepancy might be potentially corrected a posteriori according to Tikhonov [46].

Both the ABIN (CASTEP) and CP2K simulations were run at 50, 180 and 240 K using a strongly-coupled QTs. The thermostats were defined with $N_s = 6$ (the dimension of the drift and the diffusion matrices); $\omega h/kT = 100$ and $N_s = 6$, $\omega h/kT = 50$, for the low- and higher-temperatures simulations, respectively [47]. After a successful equilibration, whose length depended on the temperature and the definition of the thermostat used, production trajectories of 12.5 ps were collected in both the quantum-thermostatted canonical (QT-NVT) and microcanonical (NVE) ensembles. The trajectories were analyzed using the TRAVIS code [48]. Furthermore, direct deconvolution of the QT-NVT trajectory into the microcanonical one (QT-NVT $\rightarrow$ NVE) was performed by the UNWIND code, written by Kapil [49].

A semi-quantitative analysis of the pairwise interactions stabilizing the crystal structure was performed with the help of the Crystal Explorer program [50], employing its internal quantum-chemistry engine, TONTO [51], and following the methodology described in details in Refs. [52] and [53].

3. Benchmarking of quantum-thermostatted molecular dynamics simulations

3.1. The Case Study of Solid Formic Acid

The structure of solid FA, has been extensively investigated both theoretically and experimentally. It has been originally shown to crystallize in an orthorhombic, $Pna_2_1$ structure (see Fig. 2). The structure consists of infinite hydrogen-bonded chains, with FA molecules existing in the trans conformation [54]. The hydrogen-bonded chains are tightly packed in layers. In order to shed more light into the nature of the intermolecular interactions stabilizing the orthorhombic structure of FA, we have performed the analysis of the intermolecular forces within the crystallographic cell [54]. To this end we have used a recently-developed analysis of the pairwise interactions, i.e. energy frameworks scheme, which provides an insight into the anisotropy in the strengths of the crystal packing [52,53]. The analysis of the intermolecular interactions responsible for the $Pna_2_1$ structure reveals three types of attracting forces with a stabilizing energy greater than 5 kJ/mol, namely: the OH···O hydrogen-bond between the FA molecules; the stacking forces tightly packing the chains into the layers; and the inter-chain contacts between the neighboring stacks (see Fig.2). The results of this quantitative analysis are provided in Table 1, where the interaction energies are decomposed into the electrostatic, polarization, dispersion and repulsive terms, reported for two different electronic structure models, namely Møller–Plesset perturbation theory (MP2) and DFT (B3LYP-D2) with the same, 6-31G** basis set. While the calculations refer to the crystallographic structure, and thus to the off-equilibrium geometries with respect to both MP2 and B3LYP-D2 levels of theory, the calculated energy contributions have been scaled appropriately, according to the procedure of Ref. [52]. The scaling factors have been derived from a large molecular training set explored using an CCSD(T)/CBS standard [52].

The energy decomposition derived from both approaches follows the same hierarchy of the intermolecular forces. While standard MP2 (without spin-component scaling) is generally well known for its over-binding tendency [55], one may accept the values provided by the scaled B3LYP-D2 to be more reliable [52]. The stabilization energy of more than 30 kJ/mol classifies the analyzed hydrogen-bond as rather strong, placing the chain attraction well below this energy scale.

Polymorphism in FA has been an object of some controversy, with several reports that could not be further confirmed. For instance, a first-order structural phase transition at 218 K was postulated by Zelsmann et al. [56], based on infrared spectroscopy and differential thermal
Figure 2. Crystal structure of formic acid at 4.5 K (dideutero form), as solved by Albinati [54], with an energy framework projection of the intermolecular interactions present (see Table 1 for a quantitative analysis).

analysis. However, neutron diffraction studies have established that the $Pna2_1$ phase is stable in the 98–278 K range [57]. Recently, using a combination of neutron spectroscopy and $ab$ $initio$ modelling, we have tested the hypothesis, put forward by Zelsmann, on a proton-transfer-driven phase coexistence at high temperatures [25]. Our study has revealed a temperature-induced loosening of the crystal packing, which promotes shearing of the hydrogen bonded chains. In light of the above mentioned energy decomposition, such a scenario seems to be the most plausible one [25].

Table 1. Interaction energies for dideutero-formic acid for the crystal structure solved at 4.5 K by Albinati [54]. $R$ is the distance between the molecular centroids. Decomposition of the total energy into electrostatic, polarization, dispersion and repulsive terms is reported for two energy models (MP2 and DFT+D) [50,51]. The energy terms are scaled appropriately according to Ref. [52].

| Interaction (Symmetry) | $R$ (Å) | Density | $E_{ele}$ | $E_{pol}$ | $E_{dis}$ | $E_{rep}$ | $E_{tot}$ |
|------------------------|---------|---------|---------|---------|---------|---------|---------|
| OH ·· O ($x + 1/2, y + 1/2, z + 1/2$) | 3.63 | MP2 | -68.4 | -10.3 | -6.7 | 41.9 | -43.5 |
|                         |        | B3LYP-D2 | -62.8 | -8.3 | -7.0 | 46.7 | -31.4 |
| Stacking ($-x + 1/2, y + 1/2, z + 1/2$) | 3.63 | MP2 | -8.3 | -0.9 | -4.7 | 2.8 | -11.1 |
|                         |        | B3LYP-D2 | -5.6 | -0.7 | -4.9 | 2.7 | -8.5 |
| Inter ($-x, -y, z + 1/2$) | 4.73 | MP2 | -5.4 | -0.4 | -3.0 | 1.5 | -7.3 |
|                         |        | B3LYP-D2 | -4.2 | -0.3 | -3.1 | 1.5 | -6.1 |

In our previous work [25], we explored the hydrogen dynamics by employing an artificially elevated classical temperature. The primary aim of this work was to re-examine the system with the help of quantum-thermostatted simulations, which is the subject of the next section.
Figure 3. The left panel reports the comparison of hydrogen-projected phonon density of states derived from the classical BOMD simulations in the NVE ensemble (Upper part: NVE) and the quantum-thermostatted MD simulations in the NVT ensemble (Bottom part: QT-GLE), both performed with CASTEP (ABIN) and CP2K codes (see the text for numerical details). The panel on the right depicts a comparison of the highest harmonic frequencies calculated with both codes, with and without inclusion of the semiempirical dispersion corrections.

3.2. The Test of Quantum Thermostat Implementation for Condensed Phase
We have tested the correctness of the QT-NVT BOMD simulations performed using ABIN by comparing the production runs from CASTEP (ABIN) and CP2K simulations. To this end, we have focused on the low-temperature production runs, collected with a target temperature of 50 K. Virtually identical behavior was observed for both CP2K and CASTEP, while the CP2K simulations were characterized by a better performance, owing to the efficient implementation of the wavefunction/density propagation. The low-temperature simulations suffered from a slow-convergence, where at least 25 ps were needed to equilibrate the system with a mean temperature of ca. 450 K (with ± 50 K fluctuations). Using 324 processors (Intel Xeon 2.5 GHz) at the PL-Grid high-performance computing facility PROMETHEUS, these calculations took about 3 months per trajectory (40 ps) at each temperature.

To test the consistency of the predicted dynamic properties we have used the hydrogen-projected density of states obtained with both codes. The left panel of Fig. 3 illustrates the power spectra obtained by Fourier-transform of the velocity-velocity autocorrelation function (VACF) for both classically-initiated microcanonical (Upper - NVE) and quantum-thermostatted canonical ensembles (Bottom - QT-GLE). The results obtained from both codes are indeed consistent, with very similar intensity distributions throughout the whole frequency range, particularly in the quantum-thermostatted case.

One may note a visible difference between the CASTEP (ABIN) and CP2K data, associated with the band positions in the highest-frequency range. Such a difference can be clearly understood through the analysis of the right panel of Fig. 3, presenting harmonic phonon frequencies in the highest-energy spectral edge. This difference stems mainly from different basis-set definitions used in both codes, rather than different SEDC schemes used (see PBE-TS vs the PBE-D3). By comparing the phonon frequencies calculated with the same functional/SEDC scheme (i.e., PBE; PBE-D2, [58]) one may note that the highest-frequencies predicted by CASTEP are much softer (by ca. 10 meV). Such an effect has been extensively studied by Tosoni et al. [59], and proven to stem from the incompleteness of the basis-sets employed. Such a discrepancy might be reduced by extending the basis set size. Unfortunately, the use of any
triple-zeta quality basis set in CP2K along with very high plane-wave kinetic energy cutoff for CASTEP calculations (> 1500 eV) was not possible due to a significant increase in the computational cost anticipated. Nevertheless, as shown earlier, the level of theory selected for the CASTEP simulations ensures an excellent description of the neutron scattering vibrational data [25].

4. Analysis of the Experimental Data

To examine the range of applicability of the quantum-thermostatted molecular dynamics simulations for the interpretation of neutron scattering data, we refer to INS and NCS experiments.

4.1. Inelastic Neutron Scattering

In our previous paper [25], we have extensively explored the proton vibrational dynamics in FA performing harmonic lattice dynamics (HLD) calculations, along with classical BOMD simulations, performed at elevated temperatures. As already mentioned [16], such a crude approach suffers from the fact that the effective nuclear temperature may be different for each different atom. Here, we discuss a possible advantage of employing quantum thermostatting for simulations of INS data.

Figure 4 compares the experimental and theoretical spectra (all the results from CASTEP/PBE-TS/900eV calculations) across the energy transfer range of 2 - 425 meV. One may note a limitation of an indirect-geometry instrument (TOSCA) to explore the range above 225 meV, due to a fixed $Q(E)$ dependence [60,61]. As a consequence, only large momentum transfers are accessible in this range, which suppresses the total intensity via the enhanced Debye-Waller factor and makes the higher-order transitions dominating [60,61]. The latter factor makes the intensities of fundamentals nearly unobservable in this range. Therefore, we supplement the analysis using HRMECS data [27] recorded in a low-momentum transfer regime.

The theoretical spectrum from HLD at 0K was derived from the second derivatives of the energy and simulated with the abINS code [62,63], accounting for the characteristics of TOSCA spectrometer. In the presented BOMD spectra, the intensity across the whole energy transfer range has been suppressed exponentially to mimic the intensity profile induced by an indirect-geometry instrument [60–63]. The HLD spectrum accounting only for the first-order transitions (fundamentals) is presented as a solid line, while the total spectrum accounting for higher-order events (overtones and combination bands) is presented in the logarithmic intensity scale (see the dotted line). The HLD spectrum was discussed in detail in Ref. [25]. A sufficient agreement with the experimental data has been achieved throughout the whole spectral range and will be, hence, treated as a reference.

The classical MD power spectrum refers to the production run (NVE), initiated from the classically-thermostatted (Nosé-Hoover) simulations at low-temperature (50K). The intensity of the resulting power spectrum has been quantum-corrected by means of standard (SA) and harmonic (HA) approximations [64]. In terms of frequency, the 50K classical ab initio BOMD method delivers a virtually identical spectrum to the one from HLD even for highest frequency vibrations. Furthermore, neither the SA-corrected nor HA-corrected spectra can properly reproduce the intensity relations in the lowest-energy transfer range.

On the contrary, the quantum-thermostatted NVT simulations, QT-GLE-NVT, are considerably red-shifted with respect to the classical BOMD simulations, indicating that the simulations enters the anharmonic part of the PES. Since the QT-GLE simulations account for the ZPE contributions, no further quantum corrections were applied here.

One should not forget that a better reproduction of the experimental frequencies by HLD is just a fortuitous effect, thanks to a well-known cancelation of errors due to anharmonicity by pure generalized gradient approximation (GGA) functionals, i.e. PBE-TS. Such a behavior has
Figure 4. Low-temperature experimental spectra of formic acid recorded with the TOSCA and HRMECS (E₀ = 600 meV) spectrometers at 4K and 25K, respectively, along with the set of theoretical ones (CASTEP/PBE-TS/900eV). The theoretical spectra were derived from HLD calculations and from a series of different low-temperature \textit{ab initio} BOMD simulations (hydrogen-projected power spectra, see the text for details). The dotted lines depict the theoretical spectra presented in a logarithmic intensity scale, in order to emphasize weak overtone features and combination bands (see the asterisks in the experimental spectra).

been extensively studied, e.g. by Lin et al. [65], and has been related to improper description of the curvatures of potential energy surfaces. Recently, Pestana et al. have demonstrated similar effects in BOMD simulations of liquid water by comparing the performance of dispersion-corrected GGA with high quality meta-GGA functionals [66]. More proper modeling of the vibrational response would, hence, call for the use of more advanced approximations to the exchange-correlation functional, possibly by employing non-local hybrid functionals. However, in terms of plane-wave DFT at the present stage of development, employing non-local approximations to the exchange-correlation functional is very inefficient, making the use of codes employing atom-centered basis sets more favorable.

One may note a kind of spectral broadening with respect to the classical BOMD power-spectra, presumably due to the thermal fluctuations induced by the quantum-thermostat. This has been confirmed by performing the NVE simulations initiated from the QT-GLE-NVT trajectory (see the NVT NVE panel in Fig. 4), using a single phase-space configuration (see e.g. the bands in the range 100-200 meV). Recently, Tikhonov et al have examined the potential
Figure 5. A mirror-like comparison of the INS spectra of solid formic acid delivered by the simulations accounting for ZPE. The top panel compares the results of simulations in the microcanonical ensemble (MD-NVE, initiated from the quantum-thermostat NVT simulations), with the NVE spectrum directly deconvoluted from the QT-GLE-NVT trajectory [21]. The bottom panel shows the 0K harmonic spectrum derived from the HLD calculations. For the sake of clarity, the band shape in the harmonic spectrum has been adjusted to the one from MD simulations.

ability of the QT-GLE-NVT BOMD simulations to predict the vibrational spectra of small gas-phase molecules at elevated temperatures, finding it inapplicable for this purpose [67]. Such a failure does not hold for the crystal-phase simulations presented here, where the thermal fluctuations do not alter the spectrum so much.

Uncoupling the system from a quantum-thermostat provides some enhancement of the spectral intensity in the lowest-part of the spectrum. This can be understood by a large-friction of the strongly coupled thermostat, which was designed to disturb all the low-frequency modes so as to prevent the ZPE leakage, the effect certainly expected for such a considerably anharmonic solids as FA. As a consequence, in the QT-GLE-NVT simulation the terahertz part of the spectrum is completely smeared out, with all the information on the external modes being lost.

Alternatively, the microcanonical VACF function has been extracted from the quantum-thermostated NVT trajectory according to the analytical scheme introduced by Ross et al. [21]. The deconvolution process corrects at the same time for dynamical disturbances and the frequency-dependent occupations of different normal modes. Such a correction has been applied to deconvolute the QT-GLE-NVT trajectory (see the top panel of Fig. 4). The deconvolution has not reduced the band broadening, but it dramatically affected the intensity relations throughout the whole energy range. Importantly, in the terahertz range all the smeared bands, found in both HLD and classical BOMD spectra, have now been clearly restored. On the whole, this study has shown that such performance opens an exciting possibility of simulating terahertz-INS spectra beyond the harmonic approach.

To summarize the performance of quantum-thermostatted BOMD simulations in the prediction of the INS spectra we refer to Fig. 5. Here, the results of the NVE simulations initiated from the quantum-thermostatted NVT (with only a single phase-space configuration taken) are compared to the ones deconvoluted directly from the QT-GLE-NVT trajectory [21]. While both hydrogen-projected VACF spectra are very similar in terms of anharmonic frequencies, the results differ considerably in terms of the INS intensities, particularly for the
bands below 40 meV and around 165 meV. The most intense spectral feature, predicted at around 35 meV is due to external modes involving hydrogen-bridge stretching modes, O· · ·O, mixed with the out-of-plane librations of FA molecules. The bands at around 165 meV are due to the in-plane CH bending modes, CH (lower band), and due to in-plane hydrogen-bonds deformations, OHO (upper band with a lower intensity). One of the reasons of such a divergence might be the fact that only a single NVT phase-space configuration was used in the subsequent NVE run. The second reason might be a partial loss of the initial population of vibrational modes across the NVE run, an effect particularly probable in the case of an anharmonic system, with a number of coupled modes. Also, it is possible that in the QT-NVT simulations the ZPE leakage could not be completely prevented. However, by noting a reasonable overall distribution of the spectral intensities with respect to the HLD reference (see the bottom panel), the latter effect seems not to be the case here.

To further test the usefulness of the quantum-thermostatted simulations in the modeling of INS observables we continue the discussion by turning into the NCS experiments.

4.2. Neutron Compton Scattering

NCS experiments provide a direct experimental access to the mean kinetic energy $\langle E_K \rangle$ of nuclei, irrespective to the nature (harmonic or not) of their underlying dynamics. In brief, NCS operates within the limits of the so-called impulse approximation (IA) [69], with hundreds of electron-Volt energy transfer $\hbar \omega$ from incident neutrons and up to tens of Å$^{-1}$ of momentum transfer, $Q$. The consequence of the IA is that a time-of-flight (TOF) spectrum measured on VESUVIO consists of separate recoil peaks, each stemming from the longitudinal nuclear momentum distribution (NMD) of each respective nucleus present in the target system, $J_{IA}(y, \hat{Q})$ [69]. Moreover, the intensity of each NCS recoil peak is proportional to the product of the total bound scattering cross-section and the number of atoms under the beam, thus rendering NCS, unlike INS, completely free from the neutron weighting problem, which greatly facilitates the theoretical interpretation of the spectra.

Considering a momentum transfer of a nucleus in direction $\hat{Q}$, the NMD can be defined in terms of Gaussian approximation (GA) as:

$$J_{IA}(y, \hat{Q}) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{exp} \left( \frac{-y^2}{2\sigma^2} \right)$$

where $\sigma^2$ is the second moment of the NMD and $y$ is the so-called West-scaling variable, defined as the projection of an associated radial nuclear momentum $\vec{p}$ onto the direction of the momentum transfer $\hat{Q}$ [69].

For a given nucleus, $\sigma^2$ can be, within the harmonic approximation, further associated with the atom-projected density of vibrational states (AVDOS), $g(\omega)$, according to the following relation:

$$\sigma^2 = \frac{M}{\hbar^2} \int g(\omega) \frac{\omega}{2} \coth \left( \frac{\omega}{2k_B T} \right) d\omega,$$

$g(\omega)$, is determined as the contribution from a given nucleus to the total phonon density of states and defined by the following sum over all $q$ points in the first Brillouin zone (BZ), $N_q$, and over all phonon bands $N_\lambda$:

$$g_n(\omega) = \frac{1}{3N_q} \sum_{q=1}^{N_q} \sum_{\lambda=1}^{N_\lambda} e_n(\lambda, q)^2 \delta(\omega - \omega(\lambda, q))$$

where $e_n(\lambda, q)$ are the polarization vectors for phonon modes $\lambda$ of energy $\omega(\lambda, q)$ [69].
With the second moment of the NMD equal to $\sigma^2$, the mean kinetic energy, $\langle E_K \rangle$, can be defined as:

$$\langle E_K \rangle = \frac{3\hbar^2}{2M} \sigma^2$$  \hspace{1cm} (10)

Equation 8 has been successively used for the analysis of nuclear-dynamics in a number of materials using HLD calculations [69]. Despite the fact that Eq. (8) is derived using the quantum mechanical theory of the harmonic oscillator it can still present a good starting point for the discussion of anharmonic systems. Notably, the average kinetic energy $\langle E_K \rangle$ is equal to the half of the total energy $\langle E \rangle$ only in the harmonic approximation. To this end, two cases of an anharmonic oscillator can be considered: symmetric and asymmetric [70]. In the case of the asymmetric oscillator, described by a potential of the form $V(x) = \frac{1}{2}kx^2 - \frac{1}{3a}x^3$, to first order in the anharmonic parameter, $\delta = Aa/k$, the result is the same as in the case of purely harmonic oscillator [70]. In the second case, described by a potential of the form $V(x) = \frac{1}{2}kx^2 - \frac{1}{4}bx^4$, to second order in the anharmonicity parameter, $\delta = bA^2/k$ with $A$ being the amplitude of the unperturbed harmonic motion, we get:

$$\langle E_K \rangle = \frac{1 - 12/16\delta}{2(1 - 9/16\delta)}$$  \hspace{1cm} (11)

where, perhaps more intuitively, one can introduce a non-dimensional parameter $\epsilon$, equal to first order in $b$ with $-1/32\delta$, where $\epsilon$ is the correction to the classical turning point, $A$, in the spirit of the Wentzel-Kramers-Brillouin (WKB) approximation, i.e., $A \rightarrow A(1+\epsilon)$ with $A = \sqrt{\frac{\hbar \omega}{k}} = \sqrt{\frac{A}{\sqrt{\hbar \omega}}} $ with $\omega$ the characteristic frequency of vibration, $\mu$ reduced mass, and $k$ the force constant for a particular vibration under consideration. Equation (11), in the limit of large anharmonicity of, say, $\delta=0.1$, yields the average kinetic energy being 0.49 of the total energy, thus rendering the anharmonic correction very small for this class of potentials. Thus on the whole, in case of anharmonic symmetric local effective Born-Oppenheimer potential, felt by nuclei which NMDs are under consideration, one can always re-scale the kinetic energy below the harmonic limit, in a spirit which is similar in nature to the application of scaling to $g_n(\omega)$ curves in order to mimic anharmonicity.

As a complementary approach, one may also calculate the mean-kinetic energy for an anharmonic simulation directly from the analysis of the velocity distribution function (VDF). Figure 6 provides some insight into the influence of quantum thermostats on the vibrational energy distribution. By looking at the temperature evolution of the raw QT-NVT spectra (depicted as the solid lines) one may note clearly pronounced blue-shifts throughout the whole energy transfer range, a definitely unexpected effect with increase in temperature. For comparison, the microcanonical spectra deconvoluted from the NVT trajectories are presented as dotted lines. The spectral deconvolution shifts the first moment towards the lower energy transfers leading to correct reproduction of the band positions with respect to the experimental HRMECS reference (see Fig. 7) [27]. While the presence of noise induced by larger thermostat fluctuations at elevated temperatures should not be ignored, the calculations provide an overall reasonable reproduction of the direct-geometry spectrum even close to room-temperature conditions.

Let us now comment on the performance of the QT calculations for the description of the NCS observables. The results of the mean kinetic energy calculations are depicted in Fig. 8 and collected in Table 2, respectively, as referring to classical (HLD) and semi-classical (QT-NVT; QT-NVE) simulations. The results are compared to the experimental data which, however, are only available at 180K and 240 K.

In Fig. 8, the HLD results may serve as a reference, being only slightly above the experimentally observed mean kinetic energy of 147 eV at 240 K. Moreover, taking into account
Figure 6. The variable-temperature proton-VDOS spectra calculated from QT BOMD simulations [25]. The solid lines present the raw power spectra, while the dotted lines presents the NVE spectra deconvoluted from the NVT trajectory according to Rossi et al. [21]. Please note the frequency differences between the solid and dotted curves.

our remark on the possibility of accounting for the anharmonicity in the system by simply scaling the HLD-obtained values of the nuclear kinetic energy by a correction factor derived from the application of the virial theorem to a non-harmonic potential energy curve, we can further say that a \( \frac{\langle E_K \rangle}{\langle E \rangle} \) ratio of 0.4859 would bring the HLD-obtained value into exact agreement with the NCS experiment. This in turn would imply a negative value of the anharmonicity parameter \( \delta \) of -0.0288, which gives a positive quartic term in the potential. A strong disturbance of the nuclear dynamics and the unphysical upward VDOS shifts induced by the quantum thermostat (see Fig. 7) explain why the QT-NVT calculations overestimate the mean kinetic energy at the higher temperature conditions. While a questionable discrepancy of c.a. 10\% between the \( \frac{\langle E_K \rangle}{\langle E \rangle} \) values for the VDF and AVDOS data was noted, both sets of data are noticeably above the HLD reference and the experimental points.

In contrary, the results derived from the AVDOS analysis according to the NVE deconvolution proposed by Rossi et al. [21], brings the mean kinetic energy visibly below the reference data. In order to provide more robust benchmarks, the results were derived from both CASTEP and CP2K calculations. Both computational routes were found to be consistent, where the difference can be clearly attributed to the earlier-discussed differences in predicted VDOSs.

The obtained results provide us with a guess of a lower-limit of \( \frac{\langle E_K \rangle}{\langle E \rangle} \) predicted computationally. Rigorous, direct calculations of nuclear momentum distributions (NMDs) require the use of open-path integral molecular dynamics formalism, which may lead to an unaffordable cost for real-chemistry problems [71, 72]. It motivates the search for less-accurate
Figure 7. The temperature evolution of the INS spectrum of solid formic acid as measured with HRMECS spectrometer and predicted with QT NVT simulations (QT-GLE). The presented spectra were deconvoluted into the microcanonical ones [21, 27]. The calculated energy transfers were semi-empirically scaled by the factor of 1.035.

but more efficient approaches, with the path integral generalized Langevin equation thermostat (PIGLET) as the primary computational route [73].

Table 2. Experimental values (VESUVIO) and first-principles predictions of the standard deviations of NMDs, $\sigma_H$ [Å$^{-1}$] and the mean kinetic energies, $<E_K>$, [meV] of protons in solid FA. The results from Ref. [25] (DINS; HLD) are compared to the present results of simulations with a quantum colored-noise thermostat (QT; see the text for more details). The results were derived both from hydrogen-projected vibrational density of states (PDOS) and from a direct analysis of the velocity distribution function (VDF).

| Temp. [K] | $\sigma_H$ [Å$^{-1}$], $<E_K>$[meV] |
|-----------|-----------------------------------|
| 240       | 4.86± 0.04(147± 2) 4.93 (151.2) 4.97 (153.6) 4.47 (124.1) |
| 180       | 4.76± 0.04(141± 2) 4.92 (150.6) 4.97 (153.5) 4.41 (121.0) |
| LT-LIMIT  | N/A 4.90 (149.4) 4.96 (153.1) 4.73 (139.2) 4.15 (107.0) |
Figure 8. The mean kinetic energy, $\langle E_K \rangle$ [meV] for hydrogen atoms in formic acid as predicted by harmonic lattice dynamics (HLD) and anharmonic quantum-thermostatted simulations (NVT, [25] NVE-Deconv. [21]) and compared to experimental data recorded on VESUVIO spectrometer at 180 and 240 K. [25]

5. Conclusions

We have presented an extension of portable implementation of the quantum-colored noise thermostat towards condensed matter systems by means of ABIN code interfaced to CASTEP. Moreover, we have illustrated how the quantum-thermostated semi-classical simulations can be used in modeling of the INS and DINS response in considerably anharmonic hydrogen-bonded solids, with the case of solid FA.

The physics and chemistry of the crystalline FA is interesting for a multitude of reasons. First and foremost, it is a prominent example of an H-bonded system, where polymorphism had been postulated at a time when no sophisticated tools of computational chemistry and spectroscopy were available. Due to the rapid progress in both of these fields and the flurry of theoretical and experimental activity that followed, often a revision of original phase diagrams of solid molecular crystals is needed [77]. In this context, our previous [32], and present work on solid FA attempts to address the question of the postulated polymorphism by tackling it both experimentally and computationally. The overarching motivation here is that, as suggested by Cazorla and Boronat [77], the nuclear quantum delocalisation of the proton across the hydrogen bond may be easily mistaken for a superposition of two structures, especially when one uses a static probe with an infinite time window as diffraction. To this end, the result of this work seems to corroborate the result of our previous study, strongly suggesting that the nuclear momentum distribution of the proton is consistent with a picture in the direct space of spatial coordinates, in which the proton is quantum-delocalised across the hydrogen bond. In such a picture the distinction between the two formic acid crystal isomorphs, only differing by the position of the proton with respect to the donor and acceptor hydrogen, is lost. As a result, a hypothesis is plausible, in which one single formic acid phase with a single nuclear quantum proton state is present in the crystal, opening a route for extensive ab initio solid-state modeling and benchmarking.
In order to corroborate the hypothesis, a hierarchical series of computational approaches needs to be employed. One has to start from first-principles calculations of the model crystal structures, followed by calculations of the atom-projected vibrational densities of states. This can be further extended towards ab initio MD simulations with a standard thermostating scheme that does not treat the nuclear quantum effect-dictated properties in a special way (e.g. Nose-Hoover thermostat). Finally, employing the nuclear quantum-thermostat with an additional signal post-processing employing the deconvolution of the perturbed spectra in a way that can properly recover the unperturbed dynamic properties [21]. In doing this series of approximations, no convergence towards the experimental results, obtained from the neutron Compton scattering, is guaranteed from the outset, which largely motivated this work. In what we have established herein, the experimental NCS result is bracketed by the results obtained from the traditionally applied thermostated BOMD and the simulations with the nuclear quantum-thermostat with the deconvolution procedure. This result is important by itself as it shows that neither the route towards the optimal thermostating of the BOMD calculations nor the deconvolution procedure are completely optimised yet and further work is necessary to improve the agreement with the experiment. To this end, the NCS method is crucial as an ultimate benchmark of the ab initio results, as it does the comparison on atom-by-atom basis by testing the quality of the experimental data reproduction through the atom-projected VDOS, unlike any other neutron spectroscopic technique.

While NMDs continue to demonstrate its usefulness as benchmarking observables, another source of inspiration and motivation for our work reported here has been the fact that formic acid is an archetypic infinite hydrogen bond chain system and as such represent an ultimate challenge given by nature as far as the computational reproduction of the properties of hydrogen-bonded systems is concerned. Namely, contrary to the hydrogen-bonded systems, which crystalize as crystals of dimers, with benzoic acid and its derivatives given as the prime example, solid FA cannot be approximated computationally as a sum of smaller (dimeric) subsystems. Consequently, an ab initio calculation, at any level of theory and approximation, cannot be broken down into much less complicated lower-dimensional sub-problems. Most importantly in the context of our attempt to establish a hierarchical computational approach towards the high fidelity reproduction of the experimental nuclear momentum distributions, this structural feature of the hydrogen bond network in FA renders any Path Integral Molecular Dynamics calculations practically impossible given the current level of computing power of the high-performance supercomputing. This apparent deficiency can be, however, turned into an opportunity by re-formulating the challenge. Namely, one can still formulate a quest towards an optimal reproduction of nuclear quantum effects by solely resorting to ab initio MD methods and place the centre of gravity of the challenge on the optimal thermostating and deconvolution scheme. To this end, we have found in this work that QT-GLE BOMD simulations can be considered as a particularly useful tool to support the modeling of the INS spectra of molecular materials at low temperatures. Such an approach can be found particularly valuable when combined with the microcanonical spectrum extraction according to Rossi et al. [21]. We have illustrated how the quantum thermostating tends to affect the vibrational density of states at elevated temperatures, leading to an unphysical bias in terms of frequencies. Such a dramatic disturbance can be, however, reduced to a great extent by employing a posteriori corrections [21].

On the whole, this work encourages the use of quantum thermostatting in the modeling of the low-temperature INS spectra in condensed matter systems. A natural extension of this methodology would employ more advanced and accurate approaches, e.g. thermostatted ring-polymer molecular dynamics (TRPMD) [74, 75]. A way of reducing the computational cost of TRPMD has been proposed by Kapil et. al. [78]. It boils down to the the use of multiple time steps in real and imaginary time in which one uses a cheap reference potential which captures well the short ranged part of the potential. The cheap reference is calculated on a large number
of replicas and integrated with a small time step while the difference which contains the ab initio potential is calculated on a small number of replicas and integrated with a long time step.

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