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Thermal Properties of Molecular Crystals through Dispersion-corrected Quasi-harmonic Ab initio Calculations: The Case of Urea[†]

Alessandro Erba,[*a] Jefferson Maul,[a,b] and Bartolomeo Civalleri[a]

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An ab initio quantum-mechanical theoretical framework is presented to compute thermal properties of molecular crystals. The present strategy combines dispersion-corrected density-functional-theory (DFT-D), harmonic phonon dispersion, quasi-harmonic approximation to the lattice dynamics for thermal expansion and thermodynamic functions, and quasi-static approximation for anisotropic thermo-elasticity. The proposed scheme is shown to reliably describe thermal properties of the urea molecular crystal by a thorough comparison with experimental data.

Molecular crystals have increasingly attracted great attention due to their peculiar chemical and physical properties, which make them suitable as high energy-density materials,[1–3] active pharmaceutical ingredients (APIs),[4–6] constituents of opto-electronic devices for their linear and non-linear optical properties,[7–9] etc.

Nonetheless, from a theoretical view-point, they still represent a major challenge to state-of-the-art quantum-chemical methods as many kinds of chemical interactions (covalent intra-molecular, electrostatic, hydrogen-bond, long-range dispersive) need to be accurately described simultaneously. Only in recent years, different theoretical approaches have been devised in order to predict their structural and energetic properties (with the main goal of discriminating between competing polymorphs): from force-field to high-level molecular fragment-based schemes, from periodic dispersion-corrected density functional theory (DFT-D) to periodic many-body wave-function techniques.[10–18] However, once a reliable and balanced description of the various chemical interactions has been achieved by means of any of the above-mentioned quantum-chemical methods, the extension of their applicability to more complex properties of technological and industrial relevance, which would greatly increase their predictiveness, such as mechanical, elastic, optical and thermodynamic responses,[19–22] has to be tackled. Apart from the intrinsic high degree of complexity of the required theoretical techniques and algorithms, the main difficulty is here represented by the fact that most of those properties are largely affected by thermal effects,[23–25] even at room temperature, such as zero-point energy, harmonic and anharmonic thermal nuclear motion, thermal lattice expansion, etc.

Most quantum-chemical *ab initio* methods describe the ground-state of a system at zero pressure and temperature. If the inclusion of pressure on computed structural and elastic properties is a relatively easy task,[16,26–28] this is definitely not yet the case when temperature has to be accurately accounted for. Indeed, we are still far from having effective schemes formally developed and efficiently implemented in a solid state context, particularly so when anharmonic terms to the lattice potential have to be included into the formalism. When the harmonic approximation (HA) to the lattice potential is used, the vibrational contribution to the free energy of the crystal is assumed to be independent of volume. As a consequence, a variety of properties are wrongly described: null thermal expansion, elastic constants independent of temperature as well as the bulk modulus, equality of constant-pressure and constant-volume specific heats, infinite thermal conductivity as well as phonon lifetimes, etc.[29] If the explicit calculation of anharmonic phonon-phonon interaction coefficients remains a rather computationally demanding task,[30,31] with implementations often limited to a molecular, non-periodic context,[32–34] a simpler, though effective, approach for correcting most of the above mentioned deficiencies of the HA is represented by the so-called quasi-harmonic approximation (QHA), which retains the same formal expression of the harmonic Helmholtz free energy F and introduces an explicit dependence of phonon

[a] *Dipartimento di Chimica, Università di Torino and Interdepartmental Centre NIS, Nanostructured Interfaces and Surfaces, Via Giuria 5, 10125 Torino, Italy; E-mail: alessandro.erba@unito.it*
[b] *Laboratório de Combustíveis e Materiais, INCTMN-UFPB, Universidade Federal da Paraíba, CEP 58051-900, João Pessoa, PB, Brazil*

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frequencies $\omega_{\mathbf{k}p}$ on volume.[35] Recent studies have highlighted the improved accuracy of quasi-harmonic calculations for thermal features of inorganic solids when use is made of suitable dispersion-corrected DFT methods.[36–38]

In this Communication, we present a fully-integrated *ab initio* quantum-mechanical theoretical framework for the study of thermal properties of molecular crystals, which is based on: i) use of generalized-gradient and global hybrid functionals, as *a posteriori* dispersion-corrected according to Grimme's D3 proposal;[39,40] ii) efficient use of both harmonic and quasi-harmonic lattice dynamical calculations for the description of phonon dispersion;[41–45] iii) periodic boundary condition calculations with use of an atom-centered Gaussian-type function basis set of triple-ξ quality plus polarization functions;[46,47] iv) use of efficient fully-automated algorithms for the calculation of the fourth-rank elastic tensor of crystals belonging to any space group of symmetry;[48] v) combined use of the quasi-harmonic and quasi-static approximations to include thermal effects on elastic constants;[49,50] vi) full exploitation of both point-symmetry and efficient parallelization of all algorithms at all steps of the calculations.[51,52]

The molecular crystal of urea, belonging to the tetragonal $P\bar{4}2_1m$ space group, is taken as a suitable test-case for a couple of reasons: i) its thermal features (anisotropic thermal lattice expansion,[53–57] single-crystal elastic constants at room temperature,[58–60] thermodynamic properties[61,62]) have been measured in different, independent experimental studies, thus making it the optimal system for benchmarking our computational strategy; ii) a balanced description of most kinds of chemical interactions is required to properly describe it; furthermore, its peculiar molecular chain-like structure (see panel C of Figure 1) leads to a high directionality of the various interactions (from intra-chain electrostatic and hydrogen-bonds to inter-chain dispersive, etc.).

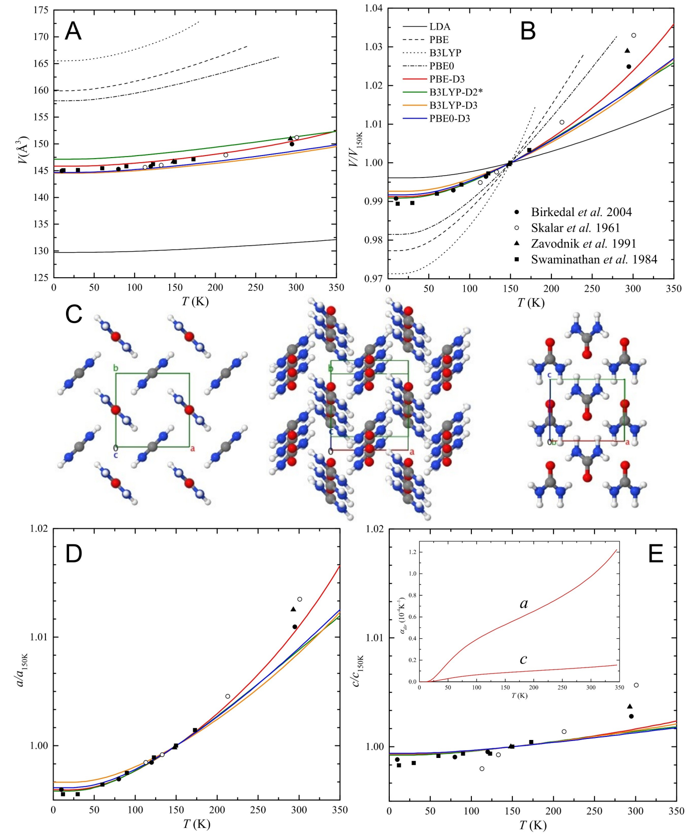

Fig. 1 (color online) Thermal expansion (A,B,D,E) and crystal structure (C) of urea. Absolute (A) and relative to 150 K (B) cell volume as a function of temperature. Directional thermal expansion, relative to 150 K, along the a and c lattice vectors (D,E, respectively). Directional thermal expansion coefficients are given in the inset of panel E. A larger version of the figure is available in the ESI.

In Figure 1, we report the volumetric and directional (i.e. anisotropic) thermal lattice expansion of urea, as measured experimentally (more details in the ESI)[53–57] and as determined by present quasi-harmonic *ab initio* calculations (phonons of the primitive cell evaluated at 7 distinct volumes within QHA), by minimizing F with respect to the volume at each temperature. Several DFT functionals are considered: some non dispersion-corrected and a bunch of -D3 corrected ones. For the global hybrid B3LYP functional, an older dispersion-corrected version is also considered, which was specifically parametrized on molecular crystals (namely, B3LYP-D2*).[15] From $V(T)$ data reported in panel A, all non dispersion-corrected functionals are seen to poorly describe the absolute value of the equilibrium volume of the crystal, with a large overestimation by PBE, B3LYP and PBE0 and a large underestimation by LDA. On the contrary, all -D corrected functionals nicely reproduce the correct volume with deviations from each other always smaller than 1.5%. Let us stress that the sole zero-point motion effect at 0 K (seldom included, along with proper thermal effects, in most *ab initio* studies on the relative performance of different functionals) is that of increasing the volume by about 2.6% for all -D corrected functionals. It follows that any ranking of functionals for the description of structural features of molecular crystals where zero-point and thermal effects are neglected would be rather questionable. In order to better highlight the description of thermal expansion, panel B reports the $V(T)/V(150K)$ ratio as a function of temperature. Non corrected functionals wrongly describe the thermal expansion either by largely over- or under-estimating it; all dispersion-corrected ones give a reliable description of the expansion, with a similar trend with respect to each other, PBE-D3 providing the best description at high temperatures. The anisotropy of the thermal expansion, as obtained by optimizing a and c as a function of the purely internal energy E at different volumes, is documented in panels D and E for -D3 corrected functionals, where the $a(T)/a(150K)$ and $c(T)/c(150K)$ ratios are reported (on the same absolute scale), respectively. The thermal structural response of urea is seen to be rather anisotropic, with a much larger expansion in the ab plane (inter-chain directions) than along c (intra-chain direction), as expected (see also the inset of panel E where directional thermal expansion coefficients $\alpha_x(T) = 1/x(T)[\partial x(T)/\partial T]$ are reported, with x either a or c). All -D3 corrected functionals nicely predict such a strong anisotropic thermal response, with an excellent description of the expansion along a and just a slight underestimation of the small expansion along c. It should be noted that a more accurate optimization of a and c with respect to the free energy F could be considered, which, however, would require a much larger set of calculations to be performed.[63,64]

Table 1 Single-crystal independent elastic constants C_{vu} and bulk modulus K of urea (in GPa) as computed for each functional at 0 K (without zero-point effects) and at room temperature in both the isothermal (T) and adiabatic (S) conditions. Experimental adiabatic constants and bulk modulus at room temperature are also reported for comparison.

	C_{11}	C_{33}	C_{44}	C_{12}	C_{13}	C_{66}	K
B3LYP-D3							
0 K	18.7	80.8	10.6	19.3	11.5	24.1	18.3
293 K (T)	12.3	70.3	8.9	13.5	7.9	17.4	12.5
293 K (S)	13.5	71.5	8.9	14.6	9.1	17.4	13.1
PBE0-D3							
0 K	16.9	75.3	10.3	17.1	10.7	22.1	16.5
293 K (T)	11.0	66.2	8.5	11.7	7.5	15.6	11.1
293 K (S)	11.9	67.0	8.5	12.5	8.4	15.6	11.7
PBE-D3							
0 K	16.7	73.2	9.9	17.5	10.9	22.0	16.5
293 K (T)	10.9	64.2	8.3	12.1	7.7	15.8	11.2
293 K (S)	12.7	66.1	8.3	13.9	9.6	15.8	11.8
Exp.[60] 293 K (S)	11.7	54.0	6.2	10.7	9.2	10.6	11.1
Exp.[59] 298 K (S)	23.5	51.0	6.2	-0.5	7.5	0.5	11.2
Exp.[58] 298 K (S)	21.7	53.2	6.3	8.9	24.0	0.5	11.6

The experimental determination of thermo-elastic parameters of molecular crystals is rather problematic due to general difficulties in growing crystals of adequate size, performing measurements on very soft samples, and dealing with low-symmetry space groups (i.e. high number of independent elastic constants C_{vu} to be determined). From a theoretical point of view, temperature-dependent elastic constants could be obtained as second free energy density derivatives with respect to the strain: $C^T_{vu}(T) = 1/V(T)[\partial^2 F/(\partial\varepsilon_v\partial\varepsilon_u)]$, which, however, would require the costly calculation of phonons at several strained lattice configurations.[65] A simpler way to obtain those thermo-elastic quantities is represented by the quasi-static approximation (QSA),[49,50] which, taking advantage of the $V(T)$ relation obtained through the QHA, consists in evaluating static internal-energy E derivatives at the volume corresponding to the desired temperature: $C^T_{vu}(T) \approx 1/V(T)[\partial^2 E/(\partial\varepsilon_v\partial\varepsilon_u)]$. Let us stress that these elastic constants are isothermal ones, while those commonly measured experimentally are adiabatic ones (i.e. refer to the isentropic limit). To enable a quantitative comparison with the experiment, isothermal constants C^T_{vu} must be transformed into adiabatic ones C^S_{vu}, via the following relation, which involves quasi-harmonic quantities:[66]

$$C^S_{vu}(T) = C^T_{vu}(T) + \frac{TV(T)\lambda_v(T)\lambda_u(T)}{C_V(T)} , \qquad (1)$$

where C_V is the constant-volume specific heat and, in the case of urea, $\lambda_v(T) = -\alpha_a(T)[C^T_{v1}(T)+C^T_{v2}(T)] - \alpha_c(T)C^T_{v3}(T)$.

In Table 1, single-crystal elastic constants of urea are reported as computed at 0 K and at room temperature (in both the isothermal and adiabatic limit) with the -D3 corrected functionals here considered. The corresponding bulk modulus is also reported. Three independent experimental determinations at room temperature are also reported with large discrepancies between each other.[58–60] The effect of temperature is very large, reducing the value of C_{11}, C_{66} and C_{12} by about 30% and that of C_{33} and C_{44} by about 12%. The bulk modulus K is reduced by about 33% when passing from 0 to 293 K (where a reduction of about 12% is due to the sole zero-point motion effect). All -D3 corrected functionals provide a similar description of the anisotropy of the elastic response (i.e. relative values of the different elastic constants), which is a remarkable result given the weak and anisotropic nature of the chemical interactions in urea. The adiabatic correction is relatively small (null by symmetry for the C_{44} and C_{66} constants), always increases the value of the elastic constants, as expected, and acts differently on different elastic constants: C_{11} is increased by 16% while C_{33} by just 3% because of the different thermal expansion along a and c, respectively (see Figure 1). Present calculations provide the first complete and homogeneous set of elastic constants of urea, which allows to amend previous experimental uncertainties on their absolute values.

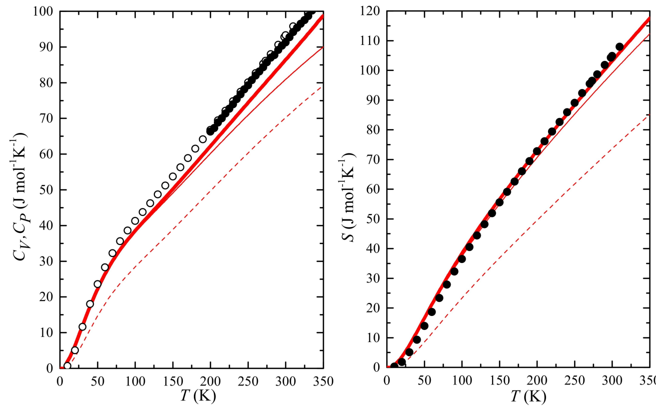

Fig. 2 (color online) Specific heat (left panel) and entropy (right panel) of urea as a function of temperature, as computed at PBE-D3 level and compared with experimental determinations.[61,62] Dashed lines correspond to Γ-only calculations while continuous lines to a converged description of phonon dispersion. Experimental data are constant-presure ones while both constant-volume (thin line) and -pressure (thick line) ones are reported for computed data.

The *ab initio* quantum-mechanical determination of thermodynamic properties of molecular crystals requires the accurate lattice-dynamical evaluation of phonon dispersion (i.e. of out-of-phase intermolecular vibrations). From computed phonon frequencies, harmonic thermodynamic quantities such as the constant-volume specific heat C_V and entropy S can be derived through the vibration partition function within standard statistical mechanics. Experimentally measured specific heats (via calorimetric techniques) refer to the constant-pressure C_P case, which might significantly differ from the C_V one when lattice expansion is large, as in the case of molecular crystals. The QHA offers a way to evaluate such quantity, again enabling a direct comparison with experimental data. The constant-pressure specific heat can indeed be obtained by summing on top of the harmonic constant-volume one the term:

$$C_P(T) - C_V(T) = \alpha^2_V(T)K^T(T)V(T)T , \qquad (2)$$

where α_V is the volumetric thermal expansion coefficient and K^T the isothermal bulk modulus. Such thermodynamic properties of urea are reported in Figure 2 as a function of temperature, as obtained at the PBE-D3 level of theory (thermodynamic properties have been shown to be very insensitive to different choices of DFT functionals).[42,43] A direct space, frozen-phonon, approach is here adopted,[67] which consists in computing phonon frequencies on super-cells of the primitive lattice: a $3\times3\times3$ super-cell is used (i.e. containing 432 atoms), which corresponds to a sampling of phonon dispersion over 27 **k**-points within the first Brillouin zone in reciprocal space. In the right panel, the computed entropy is compared with the experimentally measured one by Andersson *et al.*[61] The dashed line corresponds to a Γ-only calculation of vibration frequencies (i.e. to entirely neglecting the effect of phonon dispersion), while the continuous line to a converged description of phonon dispersion, which confirms the crucial role of collective intermolecular vibrations in predicting reliable thermodynamic properties of molecular crystals. The same consideration also applies to the specific heat case (left panel). Here, we shall note that the correction given in Eq. (2) is essential in order to recover the correct behavior (i.e. slope) of the specific heat at high temperatures when comparing with the experiment (see difference between thin, C_V, and thick, C_P, continuous lines).

To summarize, we have presented a multifaceted *ab initio* theoretical framework for the evaluation of a variety of thermal properties (structural, elastic, thermodynamic) of molecular crystals, which has been implemented into a development version of the CRYSTAL14 program by some of the present authors. The anisotropic thermal expansion, adiabatic single-crystal elastic constants and thermodynamic properties of urea have been shown to be reliably described within the proposed approach. Zero-point and thermal effects (often neglected in quantum-mechanical studies) are documented to be crucial for the accurate prediction of these properties and for a rigorous assessment of the relative performance of different theoretical methods.

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