

## How Accurate Are Simulations and Experiments for the Lattice Energies of Molecular Crystals?

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Molecular crystals play a central role in a wide range of scientific fields, including pharmaceuticals and organic semiconductor devices. However, they are challenging systems to model accurately with computational approaches because of a delicate interplay of intermolecular interactions such as hydrogen bonding and Van der Waals dispersion forces. Here, by exploiting recent algorithmic developments, we report the first set of diffusion Monte Carlo lattice energies for all 23 molecular crystals in the popular and widely used X23 dataset. Comparisons with previous state-of-the-art lattice energy predictions (on a subset of the dataset) and a careful analysis of experimental sublimation enthalpies reveals that high-accuracy computational methods are now at least as reliable as (computationally derived) experiments for the lattice energies of molecular crystals. Overall, this work demonstrates the feasibility of high-level explicitly correlated electronic structure methods for broad benchmarking studies in complex condensed phase systems, and signposts a route towards closer agreement between experiment and simulation.

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Molecular crystals are of central importance to pharmaceuticals [1], organic semiconductor devices [2,3], optoelectronics [4], and medicine [5]. Computational approaches play a central role in molecular crystal research, both in aiding experimental structure determination and in predicting their stability. In particular, the computation of lattice energies is pivotal in crystal structure prediction, as often the relative stabilities of molecular crystals are approximated using static lattice energies rather than finite temperature free energy calculations [6–8].

The most widely used techniques for the calculation of molecular crystals are empirical force-fields and density functional theory (DFT). These techniques have been very successfully applied and have significantly advanced understanding [6,9–14], particularly when modern force-field parametrization and modern DFT exchange-correlation functionals are used. However, despite the success, the accuracy of these methods is not always clear and careful validation is required. Experiment and higher level electronic structure theories are the two obvious sources of validation. However, neither is entirely straightforward as

direct like-for-like comparison with experiment is challenging (see below) and high level electronic structure references are scarce. Indeed, so far each computation of a single lattice energy with a highly accurate correlated method represents a *tour de force* study [15–21], implying a lack of extensive high-accuracy reference values for molecular crystals and periodic solids in general.

Addressing this challenge, recent developments in electronic structure theory enabled accurate and efficient calculations for both surfaces and condensed phases [18,22–24]. Among these, diffusion Monte Carlo (DMC) is very promising for small and large molecules. DMC was shown [18] to deliver lattice energies of molecular crystals at a computational cost comparable to the random phase approximation (RPA) but with the accuracy of the so-called “gold standard” of quantum chemistry, coupled cluster with single, double, and perturbative triple excitations [CCSD(T)]. Specifically, DMC has been successfully applied to study 6 organic molecular crystals [18,21] as well as 13 ice polymorphs [25], providing valuable insights into their energetics.

In this work, we consider the X23 dataset, the most used dataset for the lattice energies of molecular crystals comprising 23 materials. Very recent studies on X23 have shown that near chemical accuracy ( $\sim 4$  kJ/mol) can be achieved with second order Møller-Plesset perturbation theory (MP2) calculations [26], and that coupled-cluster methods achieve subchemical accuracy in the computation

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of the two-body terms [27]. Here, we provide DMC reference computational values for the entire dataset. In addition, when comparison with previous state-of-the-art calculations is possible, we show that different high-accuracy computational methods agree on lattice energies within  $\sim 4$  kJ/mol, which is better than a sometimes larger disagreement among experiments. The feasibility and accuracy of DMC for large molecular crystals open up the road to lattice energies benchmarked directly against computed high-accuracy computational values as well as the production of reference values for more complex condensed phase systems.

We start by elucidating the difference between lattice energy and sublimation enthalpy, which is fundamental to the discussion presented throughout the Letter. In assessing the relative stability of molecular crystals, simulations generally focus on computing the (zero temperature) lattice energy, defined as

$$E_{\text{latt}} = E_{\text{crys}} - E_{\text{gas}}, \quad (1)$$

where  $E_{\text{crys}}$  is the total energy per molecule in the crystal phase, and  $E_{\text{gas}}$  is the total energy of the isolated molecule in the gas phase. However, the physical quantity measured in experiments is the sublimation enthalpy. Experimental estimates of the lattice energy are then obtained by subtracting from measured sublimation enthalpies a computational vibrational term:

$$E_{\text{latt}}^{\text{exp}} = -\Delta H_{\text{sub}}^{\text{exp}}(T) + \Delta E_{\text{vib}}^{\text{comp}}(T), \quad (2)$$

where  $E_{\text{latt}}^{\text{exp}}$  is the experimental lattice energy,  $\Delta H_{\text{sub}}^{\text{exp}}$  is the measured sublimation enthalpy at temperature  $T$ , and  $\Delta E_{\text{vib}}^{\text{comp}}$  is the computational vibrational term, comprising both zero-point energy and thermal effects. It is important to mention here that  $\Delta E_{\text{vib}}^{\text{comp}}$  is challenging to obtain from computation: the need for large periodic cells and the importance of anharmonicity [11,28,29] in molecular crystals mean that this is in general not affordable with reference *ab initio* methods.

Overall, this means that reference lattice energies were so far extrapolated from experiments rather than computed with higher-level methods, which introduces deviations as a result of comparing an experiment at finite temperature to a simulated idealized model system. Moreover, our analysis on the experimental sublimation enthalpy (see below) shows that deviations often larger than the chemical accuracy limit characterize the measured value of  $\Delta H_{\text{sub}}^{\text{exp}}$ . This introduces a (large) uncertainty on  $E_{\text{latt}}^{\text{exp}}$ , which is independent of the (additional) error on the vibrational computational contribution.

In the following, as illustrated schematically in Fig. 1, we show that consensus within chemical accuracy is achieved on the lattice energy among explicitly correlated electronic structure methods, in stark contrast to a sometimes larger disagreement among experiments.

*Consensus of computational methods on lattice energies*—As described in Eq. (2), the experimental estimates of the lattice energy are extrapolated via a computational vibrational term. For the X23 molecular crystals, the term  $\Delta E_{\text{vib}}^{\text{comp}}$  has been previously computed with different

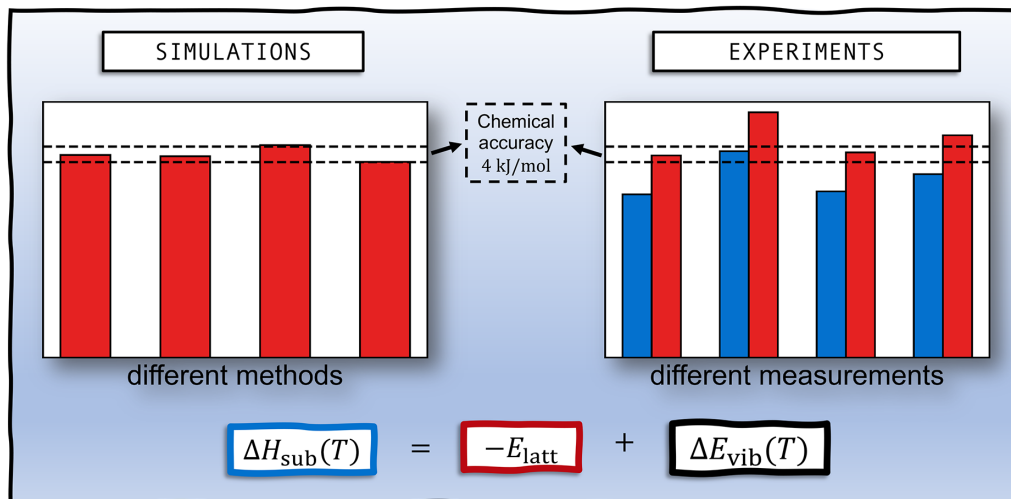


FIG. 1. Schematic of the relation between the sublimation enthalpy  $\Delta H_{\text{sub}}$  and the lattice energy  $E_{\text{latt}}$ . Simulations directly compute the lattice energy. Experimental estimates of the lattice energies  $E_{\text{latt}}^{\text{exp}}$  are obtained by subtracting a computational vibrational contribution  $\Delta E_{\text{vib}}^{\text{comp}}$  from experimentally measured sublimation enthalpies  $\Delta H_{\text{sub}}^{\text{exp}}$ . Lattice energies and sublimation enthalpies are reported with red and blue bars, respectively. The left-hand side illustrates that different high-accuracy computational methods agree on the estimate of the lattice energy within the chemical accuracy limit. This is opposed to the experimental scenario (right-hand side) that can be characterized by larger uncertainties. The difference between the blue and red bars highlights that the lattice energy is the largest contribution ( $\sim 80\%$ ) to the sublimation enthalpy.

approximations in Refs. [30–32]. The most recent one, namely, X23b [30], was obtained using the quasiharmonic approximation, averaging over four DFT functionals and taking into account both electronic and vibrational energy due to thermal expansion, and is therefore used in this work. In each of the previously reported datasets, a single initial value for the sublimation enthalpy was chosen to obtain reference experimental lattice energies. However, as discussed in Ref. [30], the uncertainty on the initial value of the sublimation enthalpy can be larger than  $\sim 5$  kJ/mol. To conduct a careful comparison, we consider all the values of the sublimation enthalpy  $\Delta H_{\text{sub}}^{\text{exp}}$  reported in the literature (except those highlighted as unreliable [33]), corrected with the X23b vibrational energy. The values of  $\Delta H_{\text{sub}}^{\text{exp}}$  as a function of temperature were collected from Refs. [33–36] and are plotted in the Supplemental Material [37]. The vibrational terms  $\Delta E_{\text{vib}}^{\text{comp}}$  were computed at a system specific temperature  $T_{\text{calc}}$  (listed in Table I caption and in [37]). The values of  $\Delta H_{\text{sub}}^{\text{exp}}(T_{\text{calc}})$  at the temperature  $T_{\text{calc}}$  have been extrapolated according to the ideal approximation as described in [37].

The X23 lattice energies computed with DMC are reported in Table I. The lattice energies are computed with fixed-node DMC [48], using the CASINO [49] code. We use energy-consistent correlated electron pseudopotentials [50] (eCEPP) with the most recent determinant locality approximation [51] (DLA) and the ZSGMA [52] algorithm for the time-step convergence. Extensive details on the setup and the convergence of the DMC calculations are reported in the Supplemental Material [37].

In the upper panel of Fig. 2, we plot the DMC lattice energies for each system, highlighting the variability of the X23 lattice energies over a relatively large energy range going from  $-160$  to  $-20$  kJ/mol. The bottom panel shows for each system the difference between the experimental values (black dots) and the DMC lattice energies. The DMC statistical error bars are reported in blue. Lattice energies obtained with RPA + GWSE (red squares) are taken from Ref. [19]. Lattice energies computed with a  $\Delta\text{CCSD(T)}$  method (light green triangles), i.e., energies computed at the complete basis set limit with MP2, and a post-MP2 correction with CCSD(T) at a smaller basis set, are taken from Ref. [20]. The lattice energy of benzene computed with CCSD(T) at the complete basis set limit [CCSD(T)/CBS] using a many body approach (dark green triangle) is taken from Ref. [16].

The range in which the experimentally derived lattice energies vary is often larger than  $\sim 4$  kJ/mol. In Fig. 2, this is evidenced by gold bars—under which the number of available measurements is reported—highlighting a current lack of consensus on the experimental value of the sublimation enthalpy for several molecular crystals. On the other hand, high-accuracy electronic structure methods generally agree within the chemical accuracy limit. Noticeable are the cases of anthracene, benzene,

TABLE I. Lattice energies (kJ/mol) of the X23 molecular crystals computed with DMC. The reported error is the DMC statistical error bar. As discussed later in the Letter, the overall error due to approximations involved in DMC and the DFT geometry optimization is estimated to be  $\sim 2$  kJ/mol. The second column reports the sublimation enthalpy (kJ/mol) at the temperature  $T_{\text{calc}}$ , estimated as the sum of the DMC lattice energy computed in this work and the DFT vibrational energies  $\Delta E_{\text{vib}}^{\text{comp}}(T_{\text{calc}})$  computed in Ref. [30]. The temperature  $T_{\text{calc}}$  is room temperature for every system except: acetic acid ( $T_{\text{calc}} = 290$  K), ammonia ( $T_{\text{calc}} = 195$  K), benzene ( $T_{\text{calc}} = 279$  K), carbon dioxide ( $T_{\text{calc}} = 207$  K) and formamide ( $T_{\text{calc}} = 276$  K). As discussed in the Letter, the overall error on the sublimation enthalpy is estimated to be  $\sim 6$  kJ/mol.

Crystal	(DMC)	(DMC + DFT)
	Lattice energy	Sublimation enthalpy
1,4-cyclohexanedione	$-88.3 \pm 1.0$	79.4
Acetic acid	$-71.7 \pm 0.6$	65.7
Adamantane	$-61.0 \pm 2.3$	50.7
Ammonia	$-38.2 \pm 0.1$	30.7
Anthracene	$-100.2 \pm 0.5$	91.7
Benzene	$-49.8 \pm 0.2$	39.9
CO <sub>2</sub>	$-29.4 \pm 0.2$	26.1
Cyanamide	$-83.6 \pm 0.4$	77.6
Cytosine	$-156.2 \pm 1.0$	149.0
Ethyl carbamate	$-84.2 \pm 1.3$	74.7
Formamide	$-81.0 \pm 1.0$	71.4
Imidazole	$-88.2 \pm 0.8$	79.3
Naphthalene	$-75.5 \pm 0.5$	66.7
Oxalic acid $\alpha$	$-102.6 \pm 1.4$	97.6
Oxalic acid $\beta$	$-102.3 \pm 0.6$	99.0
Pyrazine	$-61.1 \pm 1.1$	53.2
Pyrazole	$-77.3 \pm 0.5$	70.9
Triazine	$-60.5 \pm 0.6$	53.6
Trioxane	$-62.1 \pm 1.9$	53.7
Uracil	$-134.3 \pm 0.7$	127.3
Urea	$-108.5 \pm 0.3$	100.2
Hexamine	$-86.2 \pm 0.6$	76.9
Succinic acid	$-125.2 \pm 0.5$	118.2

naphthalene, and urea, where computational methods agree within  $\sim 4$  kJ/mol, as opposed to the experimental uncertainties ranging from  $\sim 10$  to  $\sim 25$  kJ/mol.

Overall, the “distance” between the experimental range (gold bar) and DMC is always within  $\sim 4$  kJ/mol (with the only exception given by oxalic acid  $\beta$ , where only one experimental measurement is available), qualitatively validating the reliability of our estimates. In addition, we notice that changes to the vibrational contribution (for instance due to the use of a different electronic structure method, or an account of anharmonicity or quantum nuclear effects) would shift the value of all the experimental lattice energies, i.e., the position of the gold bar with respect to the DMC estimate. Including the uncertainty on the vibrational contribution would improve the overlap between the computational and experimental estimates, as

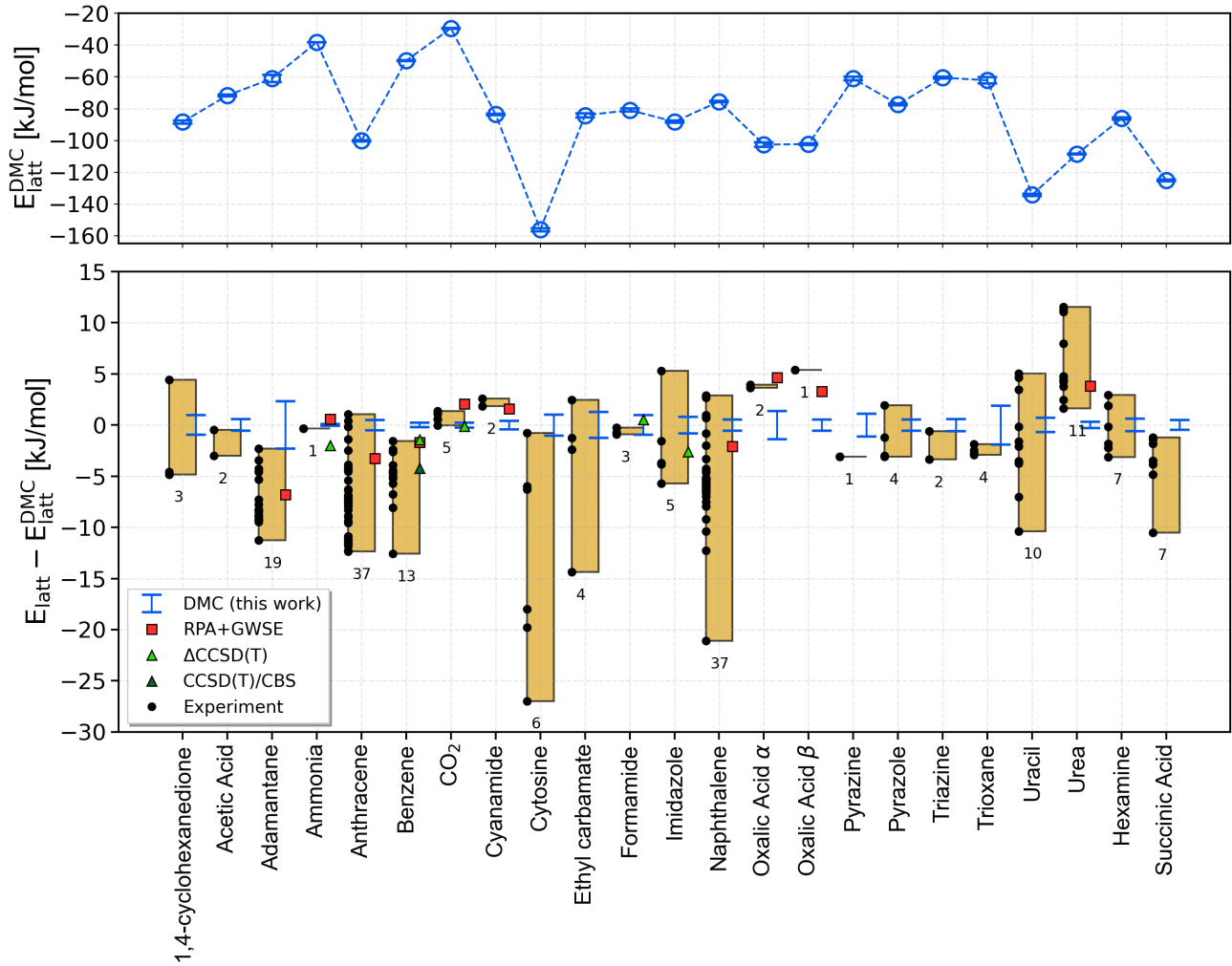


FIG. 2. Performance of computations and experiments on the X23 lattice energies. (Top panel) DMC values of the electronic lattice energy for each system (the dashed line is to guide the eye). DMC has predictive accuracy in a large energy range going from  $-160$  to  $-20$  kJ/mol. (Bottom panel) Difference between experimentally derived lattice energy (black dots) and DMC. The DMC statistical error bar is reported in blue. Experimental lattice energies are obtained by correcting experimental sublimation enthalpies with the most recent vibrational term (X23b), according to Eq. (2). The gold bar highlights the range of existing experimental measurements. The number of available experimental values is reported below each bar. Lattice energies obtained with RPA + GWSE (red squares) are taken from Ref. [19]. Lattice energies computed with the  $\Delta$ CCSD(T) method (light green triangles) are taken from Ref. [20]. The lattice energy of benzene computed with CCSD(T)/CBS (dark green triangle) is taken from Ref. [16].

it is clear from the analysis on the sublimation enthalpies reported later in Fig. 3. Considering the spread in the experimental values of the lattice energy and the additional uncertainty on the necessary vibrational term (discussed below), we suggest that directly computed high-accuracy computational lattice energies have become at least as reliable as experimental ones, and could play a more significant role in benchmarking empirical and *ab initio* methods.

*Comparable uncertainties in experiments and simulations on sublimation enthalpies*—So far we have focused on the performance of experiments and computation on the lattice energy. However, experimental estimates of the lattice energy involve the subtraction of a computational

term. Therefore, we now address the accuracy of experiments and state-of-the-art simulations for sublimation enthalpies.

The experimental sublimation enthalpy,  $\Delta H_{\text{sub}}^{\text{exp}}(T)$ , is directly measured in experiments. Following the same procedure mentioned before and described in the Supplemental Material [37], to allow for comparison with simulations, we extrapolated  $\Delta H_{\text{sub}}^{\text{exp}}$  to the temperature  $T_{\text{calc}}$  at which the vibrational contribution was available [30].

We obtain the computational sublimation enthalpy,  $\Delta H_{\text{sub}}^{\text{comp}}$ , as

$$\Delta H_{\text{sub}}^{\text{comp}}(T_{\text{calc}}) = -E_{\text{latt}}^{\text{DMC}} + \Delta E_{\text{vib}}^{\text{DFT}}(T_{\text{calc}}), \quad (3)$$

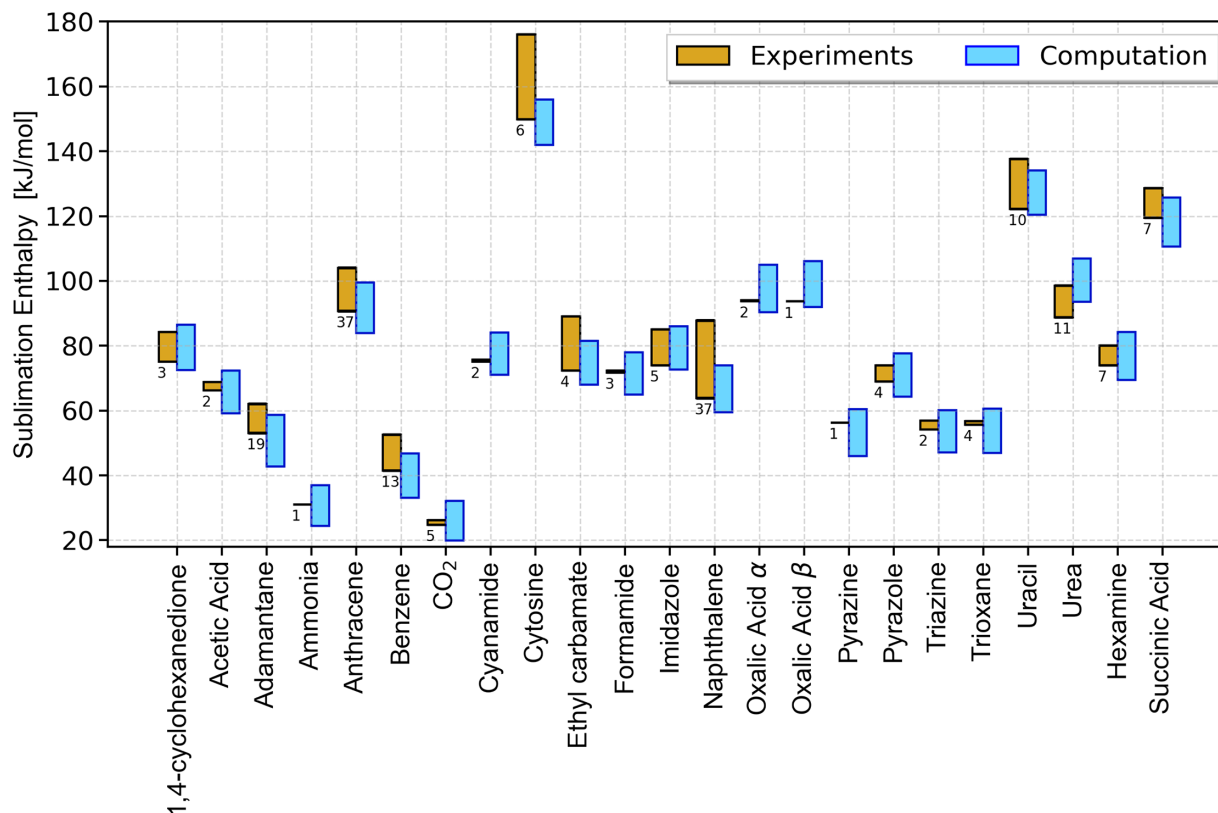


FIG. 3. Comparison of uncertainties for experimental (gold) and state-of-the-art computational (cyan) sublimation enthalpies. The gold bar is due to the spread in the literature sublimation enthalpies, extrapolated to the temperature  $T_{\text{calc}}$  for which the computational vibrational contribution is available [30]. The number of available experimental values is reported below each bar. The cyan bar is due to geometry and methodological approximations used in the computation of electronic lattice energies and vibrational thermal contributions.

where  $E_{\text{latt}}^{\text{DMC}}$  is the DMC lattice energy and  $\Delta E_{\text{vib}}^{\text{DFT}}$  is the DFT vibrational thermal contribution computed in Ref. [30]. The values of  $\Delta H_{\text{sub}}^{\text{comp}}$  are reported in Table I.

The errors on the experimental sublimation enthalpy are due to (1) the spread in the reported measurement; and (2) the correction needed to extrapolate  $\Delta H_{\text{sub}}^{\text{exp}}$  to the target temperature. The range of variation of the computational sublimation enthalpy is due to (1) errors in the computation of the lattice energy and (2) errors in the computation of the vibrational term. The uncertainty on the DMC lattice energy is due to methods limitations (statistical error-bar, nodal surface, finite-size effect) and the considered geometry (optimized with DFT in Refs. [19,32]). We estimate the total error to be  $\sim 2$  kJ/mol, as discussed in the Supplemental Material [37]. Sources of errors on the vibrational contribution are due to the inaccuracy of the DFT potential energy surface (PES) and the considered approximations (anharmonicity). Overall, an uncertainty of the order of  $\sim 4$  kJ/mol on  $\Delta E_{\text{vib}}^{\text{DFT}}$  has to be taken into account when comparing to experiments [30–32]. Finally, we get the total uncertainty by adding the system specific error on  $\Delta E_{\text{vib}}^{\text{DFT}}$  reported in Ref. [30].

In Fig. 3 we plot the estimated range for the X23 sublimation enthalpies in both experiments (gold) and computation (cyan). Different from the lattice energy, it can be seen that state-of-the-art experimental and computational uncertainties for molecular crystals sublimation enthalpies are comparable. Moreover, they are overall larger than the sought after chemical accuracy limit. This poses an interesting question on whether the criterion usually considered to assess the quality of computational approaches is meaningful for current methods. Overall, this work shows that to understand the accuracy of high-level computational methods on sublimation enthalpies, we would need both (1) additional and accurate experimental measurements and (2) to push the application of high-accuracy methods to the computation of fully anharmonic vibrational properties.

*Summary*—This work has focused on lattice energies of molecular crystals. This quantity is not directly measured in experiments and corrections are needed for a direct comparison to simulations. On the other hand, high-accuracy explicitly correlated wave-function methods were so far only applied to a few systems due to the demanding computational cost. Building on recent developments that

enabled accurate and efficient diffusion Monte Carlo for large periodic unit cells, we computed the lattice energies of the X23 molecular crystals with DMC. The analysis of the performance of experiments and state-of-the-art simulations shows that, where direct comparison is possible, different high-accuracy computational methods have now reached consensus on the lattice energies within chemical accuracy. Larger uncertainties characterize instead experimental estimates. Currently no other explicitly correlated method estimates of the lattice energy are available for approximately 50% of the dataset. Therefore, this work provides valuable reference lattice energies for 23 molecular crystals and represents a crucial step toward the calculation of sublimation enthalpies with beyond DFT accuracy.

In fact, we note that routine calculations of molecular crystals with DMC, or beyond DFT methods in general, still require large computational resources. In our case, approximately 1000 CPU hours on the Cambridge Service for Data Driven Discovery (CSD3) are necessary to compute the lattice energy of a solid system with 504 electrons with a statistical error bar of  $\sim 0.5$  kJ/mol (with a time step 0.01 au). The feasibility of the DMC calculations of this work comes indeed with the almost perfect scaling of DMC on modern supercomputers [49]. However, looking forward we note that (i) major hardware improvement is expected with the advent of exascale computing; (ii) consensus within chemical accuracy among explicitly correlated methods has been recently achieved also for surface chemistry [24,53–55]; and (iii) important progress has already been made towards training machine learning potentials at “beyond DFT” accuracy [56–59], as well as the development of foundational models for material chemistry [60,61] potentially requiring minimal data to fine-tune to a higher level of accuracy than the initial training. This suggests that finite temperature simulations with the accuracy of explicitly correlated methods could soon become routine. Overall, this highlights an exciting time for future application of high-accuracy computational methods to complex condensed phase systems. Finally, we have also shown that uncertainties of experimental and state-of-the-art computational sublimation enthalpies are currently comparable in magnitude. Our analysis suggests that the overall accuracy of sublimation enthalpy estimates could benefit from additional experiments as well as the application of higher-accuracy techniques to vibrational properties.

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