Ab initio investigation of intermolecular interactions in solid benzene

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A computational strategy for the evaluation of the crystal lattice constants and cohesive energy of the weakly bound molecular solids is proposed. The strategy is based on the high level *ab initio* coupled-cluster determination of the pairwise additive contribution to the interaction energy. The zero-point-energy correction and nonadditive contributions to the interaction energy are treated using density functional methods. The experimental crystal lattice constants of the solid benzene are reproduced, and the value of 480 meV/molecule is calculated for its cohesive energy.

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I. INTRODUCTION

In the last 50 years, weakly bound solids, including rare-gas solids and organic molecular solids, have been the subject of considerable research interest.[1–3] Many experimental measurements and theoretical predictions of the crystal structures, lattice constants, cohesive energies, lattice dynamics, and phase behavior of weakly bound solids have been published. While experiments can be performed directly on the weakly bound solids, theoretical predictions are often derived from models that build upon pairwise additive interaction energies and include the most important refinements such as nonadditive contributions and zero-point energy. Such information is obtained from calculations on the corresponding weakly bound dimers, trimers, or tetramers. Therefore, a good knowledge of the intermolecular interactions is essential for the reliable theoretical determination of the properties of the weakly bound solids.

Recently, a series of the state-of-the-art theoretical studies on rare-gas solids has been performed using the high-level *ab initio* coupled-cluster method.[4–7] In these studies, the pairwise additive contributions to the interaction energy were represented by empirical potentials, the zero-point-energy (ZPE) corrections were calculated within the harmonic approximation from the pairwise additive contributions, and nonadditive contributions were determined using coupled-cluster calculations with single and double excitations and a perturbative treatment of the triple excitations [CCSD(T)].[8] It was revealed that theoretical predictions of the structural parameters at this level of theory agree with experiment, well within the experimental error bars.

It would be ideal if it were possible to apply the same treatment to weakly bound molecular solids. However, empirical potentials are not always available. Moreover, when the corresponding molecule is relatively large, the high-level *ab initio* methods, such as CCSD(T), are not always affordable. That is why density-functional-theory (DFT) calculations are often performed to determine lattice constants and cohesive energies. On the other hand, predicting the structural parameters of weakly bound molecular crystals using merely the DFT methodology is not straightforward due to the inability of the DFT to account for the dispersion interactions.

In this Brief Report, we present a combined approach to the weakly bound molecular crystals in which the pairwise additive contribution to the interaction energy is calculated at the CCSD(T) level and the ZPE correction and nonadditive contributions are treated purely at the DFT level. We illustrate our approach by calculating the cohesive energy and crystal lattice parameters of solid benzene, the simplest real crystalline system, in which interactions between aromatic molecules can be studied. In a very recent study on the solid-benzene vibrational dynamics,[9] the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional[10] performed extremely well, and its results were in an excellent agreement with the inelastic neutron-scattering spectroscopy data. For precisely this reason, we have selected the PBE functional as a basic DFT tool for our study. The methodology of our approach is described in Sec. II. In Sec. III, the results obtained for the solid benzene are discussed, followed by conclusions in Sec. IV.

II. METHODOLOGY

In general, the interaction energy of a molecular crystal can be expressed as

$$E(\mathbf{a}) = E^{(2)}(\mathbf{a}) + \sum_{n \geq 3} E^{(n)}(\mathbf{a}) + \Delta E_{\mathrm{ZPE}}(\mathbf{a}), \qquad (1)$$

where the 3×3 matrix $\mathbf{a}$ represents lattice parameters, $E^{(2)}$ is a pairwise additive (two-body) contribution, $\sum_{n \geq 3} E^{(n)}$ represents the sum of many-body nonadditive terms, and ΔE_{ZPE} is a zero-point-energy correction. It has been shown that the periodic DFT methods can accurately describe the crystal structure (mutual orientation of molecules) and spectra of molecular solids. On the other hand, the DFT with local density functionals badly fails for binding, and therefore a higher level of theory has to be used for the calculation of cohesive energies and equilibrium lattice constants. Our

computational methodology consists of the following steps: (i) a fixed-volume plane-wave DFT geometry optimization for the given lattice parameters **a**, (ii) a calculation of the two-body term using a coupled-cluster method, and (iii) an estimate of the many-body contributions and a calculation of the ZPE correction at the periodic DFT level. The pairwise additive contribution $E^{(2)}$ represents by far the largest contribution to the total interaction energy, which is the reason why this term was evaluated at the highest level of theory feasible for solid benzene.

A. Plane-wave DFT calculation

The fixed-volume structural optimizations for the solid benzene were performed with the lattice constants obtained from the one-parameter scaling[24] of the experimentally determined unit cell (*Pbca* orthorhombic cell with a =7.355 Å, b=9.371 Å, and c=6.699 Å).[13] The interaction energy of the molecular crystal at different approximation levels was calculated for five values of the scaling parameter (0.95, 0.975, 1.0, 1.025, 1.05). These points were interpolated by a fourth-order polynomial, and minima on the corresponding curves were determined.

The calculations were carried out using the periodic plane-wave DFT with the PBE exchange-correlation functional.[10] The cutoff energy of 800 eV and hard potentials for carbon and hydrogen atoms (ENMAX=700 eV) were employed. The Kohn-Sham equations were solved using a plane-wave basis set by the projector-augmented wave method of Blöchl[11] as adopted by Kresse and Joubert.[12] The Brillouin-zone sampling was carefully checked for convergence with the number of **k** points. The Vienna *Ab initio* Simulation Package[14] was used for all the plane-wave PBE calculations.

B. Calculations of the $E^{(2)}$ term

The CCSD(T) calculations of the interacting benzene pairs in a crystal (for intermolecular center-of-mass distances of less than 10 Å) were carried out with the augmented correlation-consistent valence-double-ζ basis set with polarization functions[15] (AVDZ) using the MOLPRO 2002.6 program suite.[16] The complete basis set (CBS) extrapolation was performed using a simple correlation-energy dependence on the basis-set cardinal number X ($E_X=E_{CBS}+AX^{-3}$).[17] The density-fitting spin-component-scaled MP2 method[18] was employed for the correlation energy extrapolation (using the AVTZ and AVQZ basis sets). The Hartree-Fock energies were calculated using the AV5Z basis on the carbon atoms and the V5Z basis on the hydrogen atoms (the AV5Z* basis set). The CCSD(T)/CBS estimate $E_{CBS}^{CCSD(T)}$ for the benzene dimer was evaluated according to the formula

$$E_{CBS}^{CCSD(T)} = E_{AVDZ}^{CCSD(T)} - E_{AVDZ}^{MP2} + E_{CBS}^{MP2-HF} + E_{AV5Z^*}^{HF}. \quad (2)$$

All the calculated interaction energies were corrected for the basis-set superposition error (BSSE) using the counterpoise correction method of Boys and Bernardi.[19] The $E^{(2)}$ calculations were performed using the benzene geometry of Gauss and Stanton[20] (r_{CC}=1.3915 Å, r_{CH}=1.0800 Å).
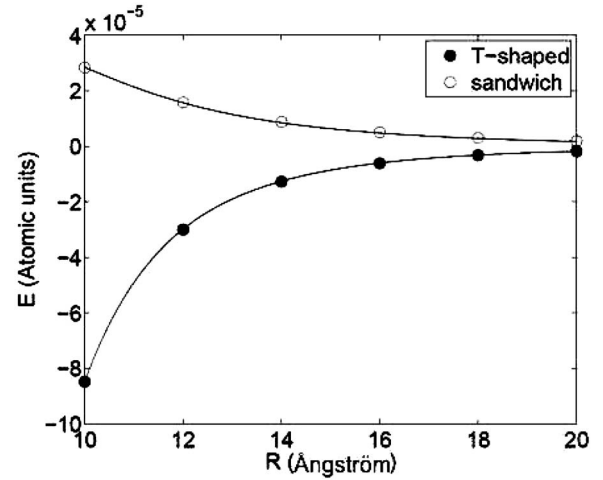

FIG. 1. Asymptotic part of the intermolecular benzene-benzene potential calculated for the sandwich and T-shaped structures.

C. Asymptotic quadrupole-quadrupole and dispersion corrections to $E^{(2)}$

An asymptotic intermolecular benzene-benzene potential was derived from the coupled-cluster data for the sandwich (D_{6h}) and T-shaped (C_{2v}) structures of the benzene dimer. The following functional form of the asymptotic behavior was assumed:

$$E^{asympt} = \frac{\omega Q_{zz}^2}{R^5} - \frac{C_6}{R^6} - \frac{C_8}{R^8}, \quad (3)$$

where R is the distance between the monomer centers of mass, Q_{zz} is an effective (as it includes higher-order electrostatic interactions) quadrupole moment of the benzene molecule, and C_6 and C_8 are isotropic parameters of the dispersion interaction. The angular factor ω describes an angular dependence of the quadrupole-quadrupole interaction for symmetric top molecules[21] ($\omega=-3$ for the T-shaped structure and $\omega=6$ for the sandwich structure of the benzene dimer). One-dimensional CCSD(T)/AVDZ scans through the benzene-dimer potential energy surface were calculated for six points between 10 Å and 20 Å with a step of 2 Å for both structures (see Fig. 1). Then the parameters Q_{zz}, C_6, and C_8 were fitted to the BSSE-corrected CCSD(T)/AVDZ interaction energies of the benzene dimer with the following results: $Q_{zz}=-5.509(5)$ a.u., $C_6=1.66(4)10^3$ a.u., and C_8 =1.7(2)10^5 a.u. Equation (3) was used to calculate the asymptotic correction to the solid-benzene pairwise additive energy for intermolecular distances larger than 10 Å.

D. Plane-wave DFT calculation of many-body and ZPE corrections

The sum of many-body nonadditive terms $\Sigma_{n\geq3}E^{(n)}$ was approximated as the difference between the total crystal energy (without ZPE) and the pairwise additive contribution, both calculated at the the PBE/PW-800 eV level. A simple cubic cell with a lattice parameter of 20 Å was employed for the benzene-pair plane-wave calculations. The calculated benzene-pair interaction energies were in excellent agree-

TABLE I. Two-body, many-body, and ZPE contributions to the total cohesive energy of solid benzene (in meV/molecule).

Model	Level	E_{coh}
Two-body nearest neighbor	CCSD(T)/AVDZ	436
	CCSD(T)/CBS	507
Two-body $R < 10$ Å	CCSD(T)/CBS	571
Two-body including asymptotic correction	CCSD(T)	592
Many-body terms	PBE/800 eV	−68
ZPE correction term[a]	PBE/800 eV	−44 (−38)
Best CCSD(T)+PBE estimate		480 (486)

[a]The value for C_6D_6 is given in parentheses.

ment with the counterpoise corrected benzene-dimer interaction energies obtained from the PBE/AVQZ calculations. The pairwise additive contributions for the intermolecular distances larger than 10 Å were calculated using Eq. (3) with $Q_{zz} = -4.85(3)$ a.u. and $C_6 = 3.87(3)10^2$ a.u. (with C_8 set to zero) obtained by fitting the corresponding PBE/AVQZ data.

The ZPE correction ΔE_{ZPE} was evaluated using zone-centered (Γ-point) harmonic frequencies calculated at the PBE/PW-800 eV level. The sum of many-body and ZPE corrections does not exceed 20% of the total cohesive energy. Hence the relative error introduced in the corresponding calculations is smaller by a factor of 5 compared to the two-body term. Moreover, the importance of the many-body terms increases for shorter intermolecular separations, and thus they should be described reasonably well by DFT. It has been shown by Kearly *et al.*[9] that force constants calculated at the PBE level of theory yield excellent agreement with measured inelastic neutron-scattering spectra. Therefore we believe that the plane-wave PBE calculations should provide fairly accurate estimates of the many-body and ZPE corrections.

III. RESULTS AND DISCUSSION

In Table I, the individual contributions to the cohesive energy of solid benzene are presented, including four approximation levels of the pairwise additive contribution. By comparing the first two rows, it is evident that the basis-set dependence has to be considered very carefully. Our CCSD(T)/CBS estimates can be directly compared with the latest theoretical benchmarks for the benzene dimer. For example, our binding energy for the T-shaped (C_{2v}) benzene-

dimer structure overestimates the best theoretical value, calculated at the QCISD(T)/CBS level,[22] by 0.6%. The same error has to be expected for the two-body contribution in Table I, and our value is thus likely to be overestimated by 4 meV/molecule. It arises from Table I that when taking into account only the nearest neighbors, the two-body contribution is underestimated by 12% even at the CBS limit. The inclusion of the pairs up to 10 Å explicitly [Eq. (2)] and the long-range pairs asymptotically [Eq. (3)] was found to be necessary.

The pairwise additive contribution to the cohesive energy is lowered by the many-body and ZPE-correction contributions thus leading to our best estimates of 480 meV/molecule (C_6H_6) and 486 meV/molecule (C_6D_6) of the solid-benzene cohesive energy. The calculated cohesive energy compares well with the experimental values of the heat of sublimation of 460–560 meV/molecule.[23] Note that by definition the enthalpy of sublimation is equal to the cohesive energy only at the temperature of absolute zero.

The sum of the many-body and ZPE-correction terms forms 17% of the pairwise additive contribution. This is only slightly higher than in the case of the heavier rare-gas solids (Ar, Kr, Xe), where the pairwise additive contributions are lowered by many-body and ZPE contributions as well, and the sums of the many-body and ZPE terms are in the range of 11%−15% of the pairwise additive contributions.[5]

This similarity between solid benzene and heavier rare-gas solids is also apparent when the role of the individual contributions to the crystal lattice constants is examined. The dependence of the lattice constants on the different energetic contributions to binding is shown in Table II, where the ratios of the theoretical lattice constants, calculated at various approximation levels, to the experimental ones are compared

TABLE II. Two-body, many-body, and ZPE contributions to the theory or experiment ratio for the fcc crystal lattice constant of the rare-gas solids (derived from Ref. 5) and solid benzene.

	Ne	Ar	Kr	Xe	C_6D_6 [a]
Two-body term	0.958	0.982	0.980	0.987	0.987
Including many-body terms	0.963	0.989	0.987	0.993	0.993
Including ZPE correction term	1.001	1.000	0.993	0.997	1.000

[a]Relative to the neutron powder diffraction measurement at 4.2 K (Ref. 13).

for the rare-gas solids and deuterated solid benzene. It is obvious that the role of the individual contributions is rather similar, particularly in the case of the heaviest rare-gas solid, solid xenon.

The asymptotic many-body contribution to the interaction energy has been approximated only at the DFT level [because it was beyond our computational possibilities to perform a CCSD(T) calculation on the benzene trimer and tetramer]. From the examination of the results on the deuterated solid benzene (Table II), it seems that this approximation was sufficient for the accurate determination of the crystal lattice constants. However, this might also be caused by a fortuitous cancellation of the terms with different signs, because the asymptotic many-body long-range terms are strongly geometry dependent, and so in other weakly bound molecular solids such an approximation may prove to be insufficient.

IV. CONCLUSION

We have presented a computational strategy for the theoretical determination of the cohesive energy and crystal lattice constants of weakly bound molecular solids. This strategy is based on the high-level *ab initio* [CCSD(T)] calculation of the pairwise additive contribution to the interaction energy, whereas the zero-point-energy correction and nonadditive contributions are treated using the DFT (PBE). Having applied this strategy to solid benzene, we have been able to reproduce its experimental lattice parameters as well as predict its cohesive energy (480 meV/molecule for C_6H_6 and 486 meV/molecule for C_6D_6). Further tests and possible improvements of the proposed computational scheme are desirable, particularly the role of the asymptotic many-body terms in weakly bound molecular solids needs closer attention. More studies on the weakly bound molecular crystals are currently being prepared.

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