

Benchmark Studies of Acetone Interaction on Graphite Surface

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It is often necessary to consider long-range interactions such as dispersion in theoretical calculations, in particular when dealing with graphitic compounds where π - π or CH- π interactions play an important role for adsorption processes. Enabling density functional theory (DFT) to describe such interactions will allow to treat systems large in size compared to systems tractable by expensive *ab initio* methods such as MP2 or coupled cluster (CC). Recently, Tsuneda and coworkers proposed the long-range correction (LC) scheme with the Andersson-Langreth-Lundqvist (ALL) van der Waals correlation functional (LC+ALL) methodology for this purpose [1], and we present here benchmark results of acetone interaction on model systems for a graphite surface, comparing the performance of MP2, CC, LC+ALL, and additionally dispersion-augmented self-consistent-charge density-functional tight-binding (SCC-DFTB-D) methods.

The dispersion energy E_{dis} in SCC-DFTB-D is evaluated by adding the sum of two-center London dispersion term between nuclei α and β separated from each other by a distance $R_{\alpha\beta}$:

$$E_{dis} = - \sum_{\alpha\beta} f(R_{\alpha\beta}) C_6^{\alpha\beta} (R_{\alpha\beta})^{-6},$$

$$f(R_{\alpha\beta}) = [1 - \exp(-3*(R_{\alpha\beta}/R_0)^7)]^4$$

where $f(R_{\alpha\beta})$ is a dumping function to suppress contributions of E_{dis} for small atomic distances where the London dispersion term is not valid. $R_0 = 3.8 \text{ \AA}$ is adopted for all elements of the first row of the periodic table reported by Elstner and coworkers [2]. C_6 is a van der Waals coefficient given from atomic polarizabilities, whose derivation was also described in reference 2. On the other hand, original ALL van der Waals functional was described as follows:

$$E_{vdw}^{ALL} = \frac{6}{(4\pi)^{3/2}} \int_{V_1} \int_{V_2} d^3r_1 d^3r_2 \frac{\rho^{1/2}(\mathbf{r}_1)\rho^{1/2}(\mathbf{r}_2)}{\rho^{1/2}(\mathbf{r}_1) + \rho^{1/2}(\mathbf{r}_2)} \frac{1}{r_{12}^6}$$

where $\rho(r)$ is the total electron density at position r . In actual calculations, this term was calculated with bold approximations to deal with easily and LC-BOP electron density.

As models for the graphite (0001) surface, benzene, coronene, and dicircumcoronene (C₉₆H₂₄) molecules were chosen in this benchmark. One acetone molecule was placed above the central hexagon rings with 6 different initial placement locations (see Figure 1). First, geometry optimization for these systems was performed using RI-MP2/SVP, RI-MP2/QZVPP (only benzene and coronene systems), and SCC-DFTB-D. Second, a single point calculation for the optimized geometry was performed and the interaction energy was evaluated. SCC-DFTB-D, RI-MP2, CCSD, CCSD(T) methods with SVP, TZVPP and QZVPP basis sets were used in this part. The influence of basis set superposition error (BSSE) was evaluated by performing Boys-Bernardi counterpoise correction. Third, using LC+ALL method with Becke 1988 exchange + one-parameter progressive correlation functional (LC-BOP+ALL), a frozen scan of the intermolecular distance between acetone and the

planar π -surface was performed since we have no gradient for LC-BOP+ALL functional. Scanning distances was from 2.5 Å to 3.5 Å with 0.1 Å intervals. We have tested two different μ values, $\mu=0.330$ and 0.470, which is a parameter determining the ratio between the short-range and the long-range part of the two-electron operator in the LC scheme.

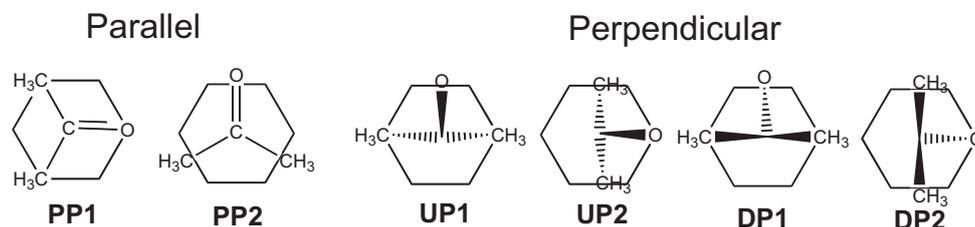


Figure 1. Initial possible conformations of acetone on six membered rings.

For example, SCC-DFTB-D, MP2, and CC calculations suggested that the order of conformation stability is clearly $PP > UP > DP$, which is also the order of the size of contact surface area, while the LC-BOP+ALL frozen scan yields $PP \sim UP > DP$ for benzene-acetone and acetone-coronene systems. This finding is independent on the choice of μ . The interaction energy given by LC-BOP+ALL with small basis set was close to the result of MP2 with large basis set. This is inline with the fact that *ab initio* methods highly depend on the basis set used as opposed to DFT. Table 1 shows SCC-DFTB-D interaction energies for each acetone conformation. We found a size dependency that the larger size of model graphite is the more stable each acetone conformation is. Benzene is too small to cover all of contact surface area of acetone. Therefore, about 10 kJ/mol energy stabilization has observed by changing from benzene to coronene. The difference between coronene

[kJ/mol]		benzene	coronene	dicircumcoronene
PP1	SCC-DFTB-D	-17.37	-28.78	-35.61
	LC-BOP+ALL/SVP (0.330)	-14.11	-29.99	-30.22
	LC-BOP+ALL/SVP (0.470)	-13.11	-26.89	-30.06
PP2	SCC-DFTB-D	-17.20	-41.90	-36.29
	LC-BOP+ALL/SVP (0.330)	-14.33	-29.95	-29.22
	LC-BOP+ALL/SVP (0.470)	-13.44	-26.77	-27.91
UP1	SCC-DFTB-D	-14.16	-27.84	-30.07
	LC-BOP+ALL/SVP (0.330)	-14.66	-30.03	-31.50
	LC-BOP+ALL/SVP (0.470)	-13.67	-26.97	-29.64
UP2	SCC-DFTB-D	-14.44	-28.56	-30.72
	LC-BOP+ALL/SVP (0.330)	-15.26	-29.27	-30.88
	LC-BOP+ALL/SVP (0.470)	-14.68	-26.86	-29.22
DP1	SCC-DFTB-D	-0.18	-9.85	-17.54
	LC-BOP+ALL/SVP (0.330)	2.68	-9.77	-17.00
	LC-BOP+ALL/SVP (0.470)	3.38	-7.85	-15.92
DP2	SCC-DFTB-D	-0.20	-9.86	-17.21
	LC-BOP+ALL/SVP (0.330)	2.71	-9.93	-17.06
	LC-BOP+ALL/SVP (0.470)	3.38	-7.77	-14.77

and dicircumcoronene would come from coronene edge hydrogen atom vs. added hexagonal rings around coronene (carbon atoms). In general, London forces become stronger as the atom becomes larger because of more dispersed electron clouds.

Table 1. Acetone interaction energy [kJ/mol] with SCC-DFTB-D and counterpoise-corrected LC-BOP+ALL/SVP (μ value)

References:

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- [2] M. Elstner, P. Hobza, T. Frauenheim, S. Suhai, E. Kaxiras, J. Chem. Phys. **114**(12), 5149-5155 (2001)