ACCURATE PARAMETRIC FORCE FIELD FOR SIMULATION OF CARBON NANOSTRUCTURE OXIDATION

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Background

Understanding of the microscopic mechanisms of carbon oxidation is very important for coal gasification technology. In this work we develop a tight-binding based parametric force field for description of the potential energy surface (PES) of molecular and atomic oxygen interacting with defect-free carbon skeleton.

Methods

As the first step, the potential energy surface for O and O_2 near defect-free carbon nanostructures with different surface "curvature" (fullerenes, nanotubes and the graphene) is explored in detail using the density functional theory (DFT) approximation (Fig. 1). Then the general tight-binding model [1] is calibrated to reproduce the obtained DFT PES. The calibration is performed to guarantee the correct charge transfer at large interatomic distances [2] and to account for additional short-range exchange-correlation terms, not incuded in the TB model. The last term is constructed as an additive potential $\Delta \boldsymbol{E}$ affecting oxygen and is represented by a $2\boldsymbol{D}$ spline in r_{CO} and r_{OO} coordinates:

$$\Delta \boldsymbol{E}(\mathbf{R}) = \sum_{r_{co}} \boldsymbol{F}_{xc}(\boldsymbol{r}_{co}, \boldsymbol{r}_{oo})$$

$$\boldsymbol{F}_{xc}(\boldsymbol{r}_{co}, \boldsymbol{r}_{oo}) = \boldsymbol{f}_{spline}(\boldsymbol{r}_{co}, \boldsymbol{r}_{oo})$$

$$\boldsymbol{f}_{spline}(\boldsymbol{r}_{co}, \boldsymbol{r}_{oo}) = \sum_{ij}[\, \boldsymbol{f}_{ij} \boldsymbol{L}_{ij}(\boldsymbol{r}_{co}, \boldsymbol{r}_{oo}) + \sum_{k=1}^{3} \boldsymbol{g}_{ijk} \boldsymbol{C}_{ijk}(\boldsymbol{r}_{co}, \boldsymbol{r}_{oo})]$$

$$\Delta \boldsymbol{E}_l = \sum_{lm} \boldsymbol{W}_{lm} \boldsymbol{x}_m, \qquad \boldsymbol{x}_m \equiv \{\boldsymbol{f}_{ij}, \boldsymbol{g}_{ijk}\}_m$$

Least squares minimizaton (linear in $\boldsymbol{x}$):

$$\sum_l (\Delta \boldsymbol{E}_l - \Delta \boldsymbol{E}_l^{TB}) \to \min$$

is applied to find the spline coefficients.

Results

A parametric model is constructed that describes both the singlet and the triplet states of molecular and atomic oxygen near a defect free carbon surface. The predictions of oxydation energies and adsorption sites (Table 1) are in agreement with other DFT calculations and experiments. The parametric model is several orders of magnitude faster than the direct DFT calculation. The extension of the model to the carbon structures with defects like vacancies and edges is in progress.

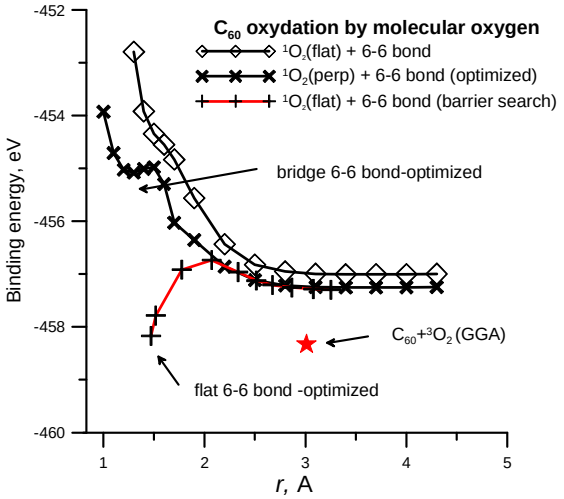

Fig. 1 DFT PES of the atomic/molecular oxygen near a C_{60} molecule..

Table 1Predicted oxygen absorption sites and energies for different defect-free carbon nanostructures

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System	Exothermicity singlet (triplet), eV	Barrier singlet (triplet), eV	Adsorption site
C_{60}+O	3.9 (2.3)	0 (0)	epoxide 6,6
Nanotube 4x4+O	3.2 (1.6)	0 (0)	bridge over perp. bond
Graphene+O	3.0 (1.4)	0 (0)	epoxide C-C
C_{60}+O_2	1.0 (0.06)	0.5±0.1 (1.0)	bridge 6,6
Nanotube 4x4+O_2	0.26 (-0.8)	0.7±0.1 (1.5)	bridge over perp. bond
Graphene+O_2	<-2	>2.0	bridge C-C

References

[1 Froudakis et al. Phys Rev B 68 (2003) 115435
[2] I. Valuev Comput. Physics Comm. 169 (2005) 60.