L10: The van der Waals coefficients between carbon nanostructures and small molecules using time-dependent density functional theory study

The calculations for the present work have been carried out by using scientific computational facility available in both Raja Ramanna Centre for Advanced Technology and Bhabha Atomic Research Centre.

The van der Waals (vdW) interaction and static polarizability play an important role in physics, chemistry and biology and hence it is necessary to calculate these quantities accurately. It is well known that the long range vdW interaction potential between two neutral systems goes as $-1/R^6$ where R is the distance between the two systems and the strength of the interaction is given in terms of coefficient C_6. It is important to study the vdW interactions between the nanostructures since the vdW force plays important role in formation of solid-like structures (rope, bundles etc) and thin films made up of nanostructures. Similary, the vdW interaction is also crucial for physisorption of small molecules on carbon-based nanostructures (CNS) such as carbon nanotubes (CNT) and fullerenes. The study on adsorption of small molecules on CNT is very important since CNT can be used as a potential candidate for storing of small gas molecules such as hydrogen due to large surface-to-volume ratio. The storage of hydrogen on CNT may be further used for making fuel-cells of electric vehicles. CNT can also be used for making gas sensors since their properties can be easily altered by the adsorption of these gases. Here, we employ all-electron time-dependent density functional theory based method to calculate the long range vdW coefficient, C_6, between fullerenes and finite-length CNTs as well as between these CNS and different environmentally important small molecules.

Here, we accurately estimate the strength of the long-range van der Waals interaction, in terms of the C_6 coefficients between these systems, and also compare these values as a function of shape and size of the CNS. We observe that the strength of interaction between the CNTs scales non-linearly with their lengths. Further, the CNTs with larger diameter interact strongly with each other as compared the smaller diameter ones since the former contains more number of carbon atoms per unit length. It is found from our calculations that the values of C_6 and polarizability are about 40 - 50 % lower for the carbon cages when compared with the results corresponding to the quasi-one-dimensional CNT with equivalent number of atoms.

Our calculations are also aimed at exploring the potential of the adsorption of different greenhouse gases, including chlorofluorocarbons (CFC), on the CNS. The percentage reduction of different greenhouse gases in the atmosphere is very important, specially the CFC, since they are both ozone-depleting and also greenhouse gases. We found that these environmentally important gases interact strongly with the carbon nanostructures.

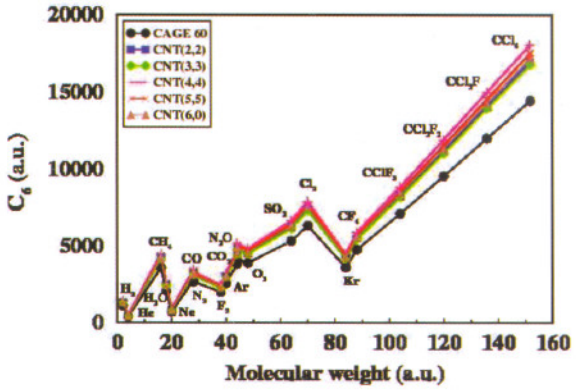

Fig. L.10.1. The vdW coefficient C_6 between different environmentally important small molecules and carbon nanotubes / Fullerenes containing about 60 carbon atoms.

It is also observed that the vdW interaction coefficient for CFCs are much higher as compared to that of other gas molecules. Among the CFCs, Carbon tetrachloride shows very high C_6 values with CNS when compared to their counterparts comprising fluorine atoms. This is due to the presence of the 7 electrons in the valence state for the halogen atoms. However, the fluorine containing CFC show smaller values of C_6 due to the samller size of fulorine atom which leads to more closely bound valence electrons. The results on vdW coefficient C_6 between different environmentally important small molecules and CNS containing about 60 carbon atoms are given in Fig L.10.1. Our estimation of the vdW coefficients based on the ab initio calculations between the CNS and the environmentally important gas molecules can be useful in providing the microscopic understanding in the studies of possible adsorption, specifically physisorption, of these gases on the CNS. *(Ref.: C. Kamal et al, J. Chem. Phys., 131 ,164708, 2009).*

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