Remarkable Effect of Fullerene Confinement on Methane Dimer Formation

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Invoking the B3LYP/6-31++G(d,p) computational level [1], we demonstrate that confinement of methane within the fullerenes' C_{42} and C_{60} voids, which to some extent may imitate the coal pores, results in the formation of the covalently-bonded methane dimer $[H_4C - CH_4]^q$ which C-C bondlength varies between 1.392 and 1.465 Å for C_{42} and C_{60}, respectively (see Fig.1). In the other words, the fullerene's void acts as a nano-reactor.

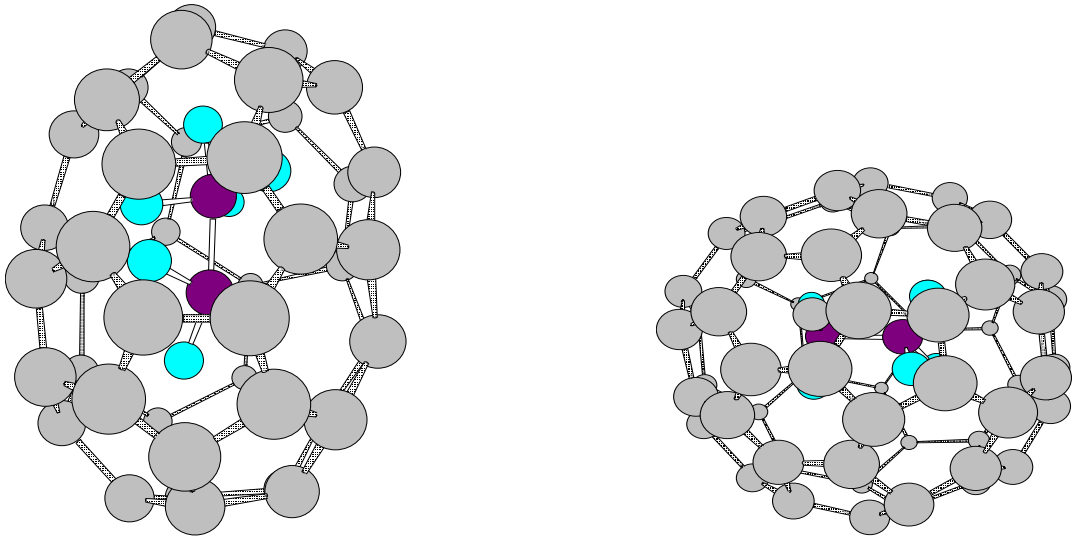

Figure 1. Left panel: The endohedral fullerene $(CH_4)_2@C_{42}$. Right panel: The endohedral fullerene $(CH_4)_2@C_{60}$.

The mechanism of formation of the covalently-bonded dimer of methane molecules which in the gas phase behave in a typical van der Waals manner is the following. The fullerene void that confines two methane molecules features a rather strong electron deficiency [2]. Hence, the molecule being encapsulated into the fullerenes's void is subject to transfer a charge to the fullerene surface – this mechanism that is referred as the ionic model [3] functions for many metallofullerenes since the first experimental isolation of La@C82 in 1991 [4]. We interpret the void electron deficiency within Bader's Atoms-in-Molecules (AIM) theory [5] according to which the one-electron density shows, as in Fig. 2, the minimum indicating the presence of hole. We prove that this minimum is the corollary of the Rolle-Lagrange theorem (theorem of a zero of derivative) [6] which states that if a function f(x) is continuous and differentiable

on the interval (a,b) and f(a) = f(b), there then exists such point x ∈ (a,b) that the derivative f'(x) vanishes, i. e. f(x) reaches the minimum if f'(a) is negative. Since the one-electron density takes the equal Kato's cusps [7] at the carbon atoms of methanes, it obeys the Rolle-Lagrange theorem and hence falls to the minimum which we interpret as the existence of the hole in the fullerene's void. We illustrate this statement in Figure 2. This hole accumulates the charge transfer from the methane molecules to fullerene. Therefore, within this so called hole model, the studied fullerene in Figure 2 can be seen as $[(CH_4)]_2^q@C_{60}^q$ where q = +3. The covalent bond between the charged molecules of methane occurs via the mechanism described in [8] for positively charged benzene molecules.

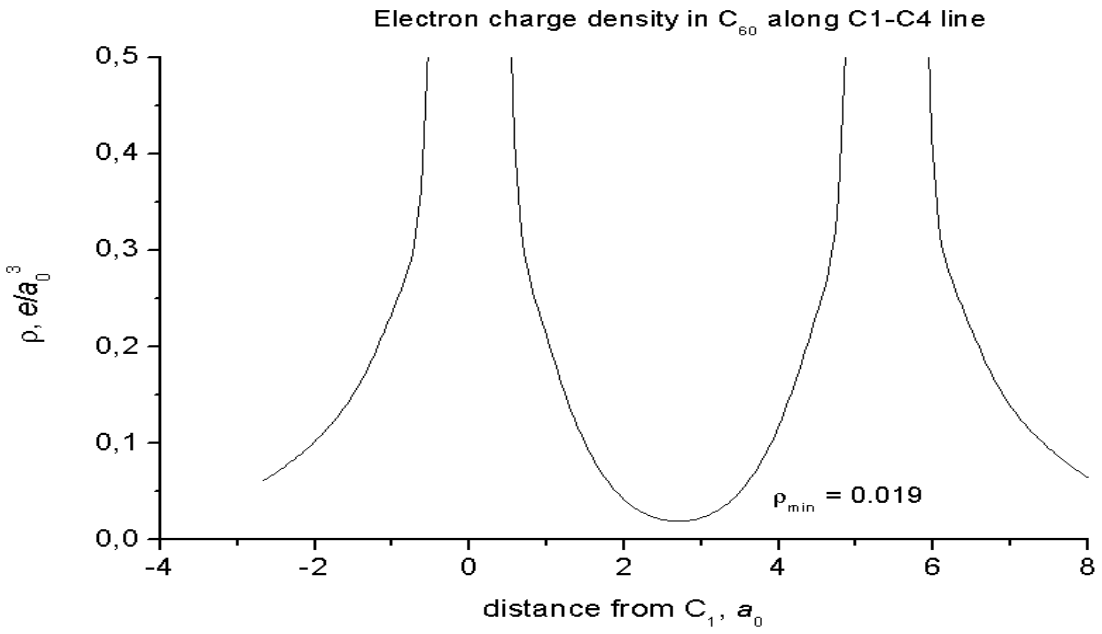

Figure 2. Plot of the one-electron density of $(CH_4)_2@C_{60}$ taken along the C-C bond of the methane dimer.

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