

# COMMENTS

## Comment on “Orbital Interactions between a C<sub>60</sub> Molecule and Cu(111) Surface”

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Recently, Ogawa et al.<sup>1</sup> examined the interaction between Cu clusters and C<sub>60</sub> molecule, to elucidate the nature of the C<sub>60</sub>–Cu(111) bonding and the orientational configuration of a C<sub>60</sub> molecule on a Cu surface. The authors<sup>1</sup> performed partial geometry optimizations for five adsorption models of C<sub>60</sub>–Cu<sub>10</sub> clusters with some geometrical restrictions, and single-point calculations for those of C<sub>60</sub>–Cu<sub>34</sub> clusters at the B3LYP level of theory (see Scheme 1 in ref 1). Large interaction energies were obtained for the edge-atom and 6–6 bond models, and all five models predicted that electron transfer would take place predominantly from C<sub>60</sub> to Cu clusters.<sup>1</sup>

The authors<sup>1</sup> used the LanL2MB basis set, (5s5p5d)/[2s2p1d] basis set for copper and STO-3G for carbon, in the B3LYP calculations. However, it is known that basis set superposition error (BSSE) may be significant when such small-size basis sets are used. We recalculated the interaction energies between the Cu clusters and a C<sub>60</sub> molecule, taking the BSSE into consideration. The C<sub>60</sub> molecule was fully optimized on the Cu<sub>10</sub> cluster with fixed geometries. The BSSE-corrected interaction energy ( $\Delta E$ ) was obtained via<sup>2,3</sup>

$$\Delta E = E_{\text{C}_{60}-\text{Cu}_x}^{\alpha\cup\beta}(\text{C}_{60}-\text{Cu}_x) - E_{\text{C}_{60}-\text{Cu}_x}^{\alpha\cup\beta}(\text{C}_{60}) - E_{\text{C}_{60}-\text{Cu}_x}^{\alpha\cup\beta}(\text{Cu}_x) + E_{\text{rel}}^{\alpha}(\text{C}_{60})$$

where  $E_{\text{rel}}^{\alpha}(\text{C}_{60}) = E_{\text{C}_{60}-\text{Cu}_x}^{\alpha}(\text{C}_{60}) - E_{\text{C}_{60}}^{\alpha}(\text{C}_{60})$  and  $x = 10$  or  $34$ . In the formula, the electronic energy of molecular system  $M$  at geometry  $G$  computed with basis set  $\sigma$  is defined as  $E_G^{\sigma}(M)$ . All calculations were done with the Gaussian03 package.<sup>4</sup>

We started the geometry optimizations from the five structures obtained in ref 1, but in our calculations all the optimized structures converged to the edge-atom model. This discrepancy seems to originate in permitting geometry relaxation for the C<sub>60</sub> molecule in our optimization calculations. For the edge-atom orientation, the interaction energies computed at the B3LYP/LanL2MB level of theory are summarized in Table 1, along with the results in ref 1. The optimized  $R$ , the distance between the center of gravity of the C<sub>60</sub> sphere and the central Cu atom of the first layer of the Cu<sub>10</sub> cluster, is calculated to be 6.111 Å, which is similar to the 6.043 Å in ref 1. The BSSE-uncorrected interaction energies are also similar to the results in ref 1, while there is a slight discrepancy due to the geometry

**TABLE 1: BSSE-Uncorrected and BSSE-Corrected Interaction Energies (in eV) Computed at the B3LYP/LanL2MB Level of Theory**

coordination mode [edge-atom]	uncorrected interaction energy	BSSE	corrected interaction energy
C <sub>60</sub> –Cu <sub>10</sub>	–1.901 (–1.824 <sup>a</sup> )	2.349	+0.448
C <sub>60</sub> –Cu <sub>34</sub>	–3.089 (–3.015 <sup>a</sup> )	3.136	+0.046

<sup>a</sup> The interaction energies in the parentheses refer to the results in ref 1.

relaxation of C<sub>60</sub> in our calculations. The correction energy from the fragment relaxation,  $E_{\text{rel}}^{\alpha}(\text{C}_{60})$ , is very small, i.e., less than 0.03 eV. However, the BSSE-corrected interaction energies show that there is no binding between C<sub>60</sub> and Cu clusters in either the C<sub>60</sub>–Cu<sub>10</sub> or C<sub>60</sub>–Cu<sub>34</sub> cluster models. The calculated BSSE values amount to 2.349 and 3.136 eV for C<sub>60</sub>–Cu<sub>10</sub> and C<sub>60</sub>–Cu<sub>34</sub> cluster models, respectively. The binding, stronger, in the C<sub>60</sub>–Cu<sub>34</sub> cluster model than in the C<sub>60</sub>–Cu<sub>10</sub> cluster model observed in ref 1, may be attributable to the larger BSSE.

The authors<sup>1</sup> reported that the charge transfer takes place predominantly from C<sub>60</sub> to Cu<sub>x</sub> ( $x = 10$  and  $34$ ) clusters, although the experimental result<sup>5</sup> showed that the charge transfer, 1.5–2 e<sup>–</sup> per molecule, takes place in the opposite direction, i.e., from Cu(111) substrate to C<sub>60</sub> molecule. The experimental result was also supported recently by a plane-wave density functional calculation,<sup>6</sup> where the amount of charge transfer is 0.8–0.9 e<sup>–</sup>. We believe that the reverse charge transfer in ref 1 may be attributable to the use of the small basis set.

The authors intended to elucidate the interaction of the C<sub>60</sub>–Cu<sub>x</sub> ( $x = 10$  and  $34$ ) bonding in ref 1, but the majority of their results on binding energies may originate from the BSSE, which is an artificial mathematical effect. It seems that the minimal basis set used in ref 1 is too small to describe reliably the interaction between C<sub>60</sub> and Cu<sub>x</sub> ( $x = 10$  and  $34$ ) clusters. Ruuska et al.<sup>7</sup> showed that the influence of the BSSE correction on the interaction energy of Cu(111)–H<sub>2</sub>O is significant at the ab initio MP2 level of theory. Our results clearly show that BSSE may be considerable, even with density functional calculations, using such minimal basis sets.

## References and Notes

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