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COMMUNICATION

## Strong orbital deformation due to CH- $\pi$ interaction in benzene-methane complex

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**The orbital distribution and composition of the benzene-methane complex have been investigated systemically using *ab initio* calculations for the first time. Surprisingly, we find strong deformation in HOMO-4 and LUMO+2 induced by CH- $\pi$  interaction, extending the general view that nonbonding interaction does not cause orbital change of molecules.**

In the last two decades, the benzene-methane complex has been used as a model system to study CH- $\pi$  interaction, which is considered as weak interaction and has been found to play important roles in determining the physical, chemical, and biological properties of a variety of substances.<sup>1-5</sup> An electronic spectroscopy study demonstrated that a benzene-methane cluster has an on-top structure where the methane molecule is located on the C<sub>6</sub> axis of the benzene moiety to hold the C<sub>3</sub> or a higher symmetry.<sup>6</sup> High-level *ab initio* calculations of the benzene-methane cluster confirmed that the on-top type isomer indicated by the electronic spectroscopy is the most stable structure, with 1.45 kcal/mol binding energy at the CCSD(T)-level calculation<sup>7</sup>. The zero-point energy corrected binding energy (1.13 kcal/mol) agrees well with the experimental value (1.03-1.13 kcal/mol).<sup>8</sup> The calculated decomposed interaction energy indicates that dispersion interaction is significantly important for the attraction in the benzene-methane complex.<sup>7</sup>

In the benzene-methane complex, the dispersion energy contributes most in typical cases, where the CH bond is the hydrogen donor and the C<sub>6</sub>H<sub>6</sub> ring is the CH-acceptor.<sup>9,10</sup> CH- $\pi$  interaction not only reduces the total energy and forms a special configuration of the complex but also changes the properties of the CH and/or  $\pi$  group. In 1955, Pinchas first reported the blue shift of the C-H stretching frequency in the IR spectra of O-substituted benzaldehydes.<sup>11</sup> This phenomenon has since been reported in many experimental<sup>12-</sup>

<sup>14</sup> and theoretical studies<sup>15-18</sup>. Besides the C-H stretching shift effect, CH- $\pi$  interaction can also change the electronic structures of a  $\pi$  group. Li and Chen revealed that considerable band gaps could be opened in the band structures of graphene/CH<sub>4</sub> and silicene/silicane bilayers due to the broken equivalency of two sublattices induced by XH/ $\pi$  (X = C, Si) interactions.<sup>19</sup> A common view is that nonbonding interaction does not involve orbital interaction due to the large distance (> 3 Å) between molecules. To date, there has been no research addressing the impact of CH- $\pi$  interaction on molecular orbitals (MOs).

In the present work, for the first time, we systematically examine the MOs of the benzene-methane complex using *ab initio* calculations. The results reveal that the deformation of MOs occurs not only in deep occupied MO but also in unoccupied MO.

The *ab initio* calculations of structural relaxations and electronic properties were carried out with the Gaussian 09 package.<sup>20</sup> The second-order Møller-Plesset perturbation theory (MP2) was used to explore the configuration and interaction energy in the ground state. MP2 is the most commonly used method for describing intermolecular interactions because it includes electron correlation for capturing dispersion interaction, which approximately accounts for the uncoupled and two-body electron correlations. M06-2X,  $\omega$ B97XD, and CCSD(T) methods were also used for confirmation. The basis set superposition error (BSSE)<sup>21</sup> was corrected for all calculations using the counterpoise method.<sup>22,23</sup> Different basis sets, including 6-311G\*\*, 6-311G+\*\*, 6-311G++\*\*, and cc-pVTZ, were used to explore the basis set effect. Single point calculations were used to show the impact on orbitals of intermolecular interaction based on various methods and basis sets.

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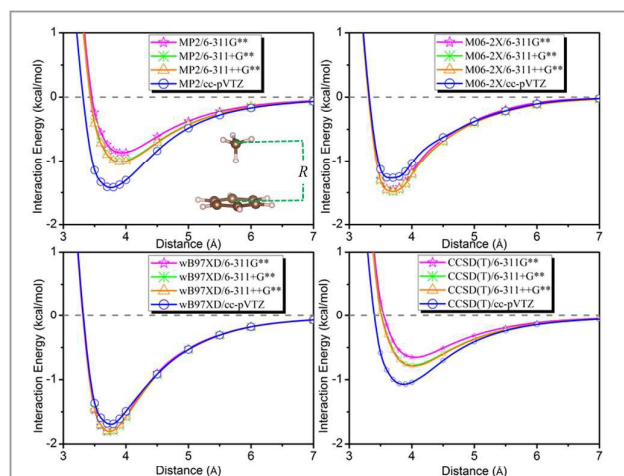


Fig. 1 The BSSE-corrected intermolecular interaction energy of the benzene-methane system considered, calculated using the various methods.

As many experimental and theoretical results have proven that the benzene-methane complex has an on-top type isomer configuration<sup>6–8</sup>, we took this configuration as our model, as shown in Fig. 1. The BSSE-corrected intermolecular interaction energies of the benzene-methane complex, calculated at the MP2, M06-2X, ωB97XD, and CCSD(T) levels of theory using 6-311G\*\*, 6-311G+\*\*, 6-311G+\*\*, and cc-pVTZ, are provided in Fig. 1. For the MP2 calculation, the BSSE-corrected interaction energy is -1.42 kcal/mol with an intermolecular distance  $R$  equal to 3.8 Å using a cc-pVTZ basis set, which is in good agreement with a previous result (-1.45 kcal/mol,  $R=3.8$  Å) at the CCSD(T) level with basis set limit.<sup>7</sup> Using this configuration as the input structure, the BSSE-corrected intermolecular interaction energy is -1.48 kcal/mol after relaxation, and the corresponding distance  $R$  is 3.76 Å. From M06-2X/6-311++G\*\*, ωB97XD/6-311++G\*\*, CCSD(T)/cc-pVTZ calculations, the

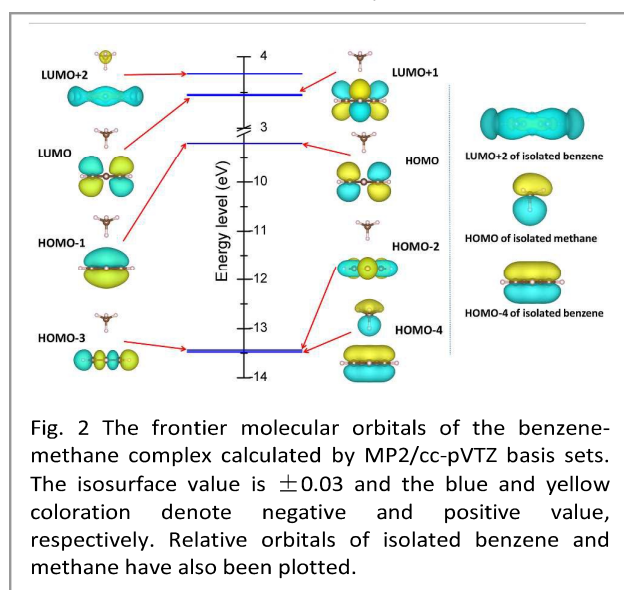


Fig. 2 The frontier molecular orbitals of the benzene-methane complex calculated by MP2/cc-pVTZ basis sets. The isosurface value is  $\pm 0.03$  and the blue and yellow coloration denote negative and positive value, respectively. Relative orbitals of isolated benzene and methane have also been plotted.

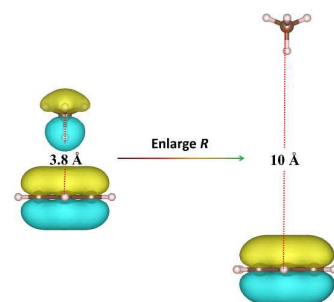


Fig. 3. Frontier occupied orbitals of the benzene-methane complex.  $R$  is the intermolecular distance between the carbon atom of methane and the center of benzene. The isosurface value is  $\pm 0.03$  and the blue and yellow colors denote negative and positive values, respectively.

intermolecular distance remains the same, and the BSSE-corrected interaction energies are -1.48 kcal/mol, -1.84 kcal/mol, and -1.08 kcal/mol, respectively.

The orbital distributions of the benzene-methane complex are plotted in Fig. 2 together with the corresponding energy levels. The results indicate that the orbital distribution of the benzene-methane complex is not a simple superposition of benzene and methane. As shown in Fig. 2, from HOMO-3 to LUMO+1, the contributions only come from the benzene. However, for the HOMO-4 and LUMO+2, the orbitals are localized not only in the benzene but also in the methane. In other words, the HOMO-4 and LUMO+2 are formed by both benzene and methane under CH- $\pi$  interaction. The HOMO-4 of the complex consists of a delocalized  $\pi$  orbital of the benzene and a  $\sigma$  orbital of the methane. Compared with the LUMO+2 of the isolated benzene, the part of LUMO+2 localized in the benzene of the complex has an obvious decrease in distribution. The distribution of the  $\pi$  orbital of benzene in complex is very similar to the HOMO-4 in the isolated benzene. Moreover, the plots of the corresponding MOs of the interacting monomers at a longer distance (10 Å) as shown in Fig. 3 clearly show that the mixture of MOs disappears, which further confirms that the above described orbital deformation is induced by the CH- $\pi$  interaction.

We also check the effect of the method and basis set on the HOMO-4 orbital deformation, as shown in Fig. A1. The results indicate that the HOMO-4 shows almost same distribution for all the considered methods and basis sets except HF/6-311G\*, MP2/6-311G\*, MP4/6-311G\*, and CCSD(T)/6-311G\*, for which the deformed orbital is HOMO-2, shown in Fig. A2. This indicates that although the use of these four methods combined with 6-311G\* basis set reveals the energy level order change, the orbital deformation still remains.

To give a detailed description of the contribution of benzene and methane and confirm the above results, the orbital composition of the benzene-methane complex is listed in Table 1 based on the MP2/cc-pVTZ calculations. The results show clearly that HOMO-4 and LUMO+2 are from the

Table 1. Orbital composition of the benzene-methane complex.

	H-4	H-3	H-2	H-1	HOMO	LUMO	L+1	L+2
CH <sub>4</sub>	20	0	0	0	0	0	0	26
C <sub>6</sub> H <sub>6</sub>	80	100	100	100	100	100	100	74

contributions of both benzene and methane. From HOMO-3 to LUMO+1, the contribution of methane is 0%. However, methane contributes 20% to HOMO-4 and 26% to LUMO+2. Under CH- $\pi$  interaction, the frontier MOs of the complex, from HOMO-3 to LUMO+1, are composed completely by benzene, the deep (HOMO-4) and out (LUMO+2) MOs do not consist of benzene or methane only, but of both. In order to make our results more solid, we use many available methods for the same calculation including Hartree-Fock, hybrid density functionals (B3LYP, HSEH1PBE, etc), and pure density functionals (PBEPBE and B97D), with different basis sets. The calculations further confirm our results, as shown Table A1. The basis set shows little effect and once the level of basis set is higher than 6-31G, the contribution of benzene to the molecular orbital is basically unchanged. And the choice of methods involves a greater impact on the composition of the orbital as seen in the contribution of benzene to the deformed orbital which varies between 40% to 80%. However, the existence of the orbital deformation is clearly not dependent on the choice of methods and basis sets, as observed from results of both isosurfaces and the orbital components.

We further analyze the similarities between the HOMO-4 and LUMO+2 which present strong orbital deformations and find that the orbitals in the isolated molecules which contribute to these two deformed orbitals are very close in energy. We also find that they both involve the contribution from delocalized  $\pi$  or  $\pi^*$  orbital in the benzene. Understandably, delocalization of the  $\pi$  or  $\pi^*$  orbital in the benzene is the necessary condition to facilitate the interaction with the  $\sigma$  orbital in the methane, because of the large distance between the two molecules. Thus, the deformation is determined by two conditions: the delocalization of  $\pi$  or  $\pi^*$  orbital and the closeness in energy between the  $\pi$  or  $\pi^*$  orbital of benzene and  $\sigma$  orbital of methane. We believe similar deformation could be observed in other non-bonding interaction systems including CH- $\pi$  systems if these two conditions are satisfied.

## Conclusions

We have revealed for the first time the deformation of MOs of the benzene-methane complex, a representative weak interaction system. Our *ab initio* calculations based on various methods and basis sets provide the details of the distribution and composition of MOs. From HOMO-3 to LUMO+1, the MOs of the benzene-methane complex are composed of atomic orbitals of benzene. However, HOMO-4 and LUMO+2 are composed of considerable contributions from both benzene and methane. These results indicate that the CH- $\pi$  interaction does not cause changes in all the orbitals but only in some of

the orbitals in the benzene-methane complex. Moreover, the deformed orbital may not be the HOMO. Our results demonstrate that CH- $\pi$  interaction between benzene and methane not only reduces the total energy and forms a stable configuration of the complex, but also affects the distribution and composition of the MOs. This finding enriches our understanding of weak interaction systems.

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