

Theoretical investigation for systematizing surface diradical

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Diradical state is that with two open-shell electrons in pseudo-degenerate orbitals. The state is important for understanding the physical properties originating from strongly correlated intra-/intermolecular electrons [1]. Strongly correlated electrons are the origin of various material functions; hence, novel molecular function will be achieved by immobilising the diradical molecules on surfaces. However, the diradical state of surface-adsorbed molecules (= surface diradical) has not been well studied due to the lack of theoretical and experimental techniques.

In this project, a systematic investigation was performed on the interaction of s- and p-diradical molecules with alkaline-earth metal oxide surfaces. Diradical molecule models with s-orbitals were Au, Ag and Cu dimers with inter-atomic distance where the s-orbitals are pseudo-degenerating. This system was investigated using system B, ohtaka. For the p-orbital diradicals, a real diradical molecule, p-benzyne, was employed. This calculation was performed on system C, kugui. Used programme was VASP. Correction based on the approximated spin projection method to density functional theory calculation with plane-wave

basis (AP-DFT/plane-wave) [2,3], which is a recently developed scheme, was used for the analysis of the diradical states.

Diradical character, y , is a feature value for diradical molecules, and can be utilised to *in silico* design [1]. The effect of surface-adsorption on diradical character (Δy) can be classified into three effects [4], as shown in Fig. 1: namely, the effect of molecular distortion caused by adsorption (Δy_{dis}), the effect of intermolecular interactions (Δy_{coh}), and the effect of molecule-surface interaction (Δy_{surf}). Table 1 summarises Δy values of the p-benzyne adsorption models. Details of the calculated models can be found in the cited article [4]. The absolute values of Δy_{surf} are the largest among three effects. The reason why the y values of p-benzyne is reduced by the molecule-surface interaction is as following:

- (1) Although the computational model is constructed as a physically adsorption of p-benzyne, a slight orbital correlation between the surface ions and the molecule occurs. This causes delocalisation of singly occupied C sp² orbital to the aromatic ring.
- (2) Intramolecular charge polarisation is induced by the charges of the surface ions, and

the spin density is reduced due to the enhanced contribution of the closed-shell resonance structure.

The present study explicitly shows that diradical character of real diradical molecule can be modulated even in weakly adsorbed states, such as physisorption. The results were published from *Physical Chemistry Chemical Physics*, and the paper was selected as the front cover and hot article [4].

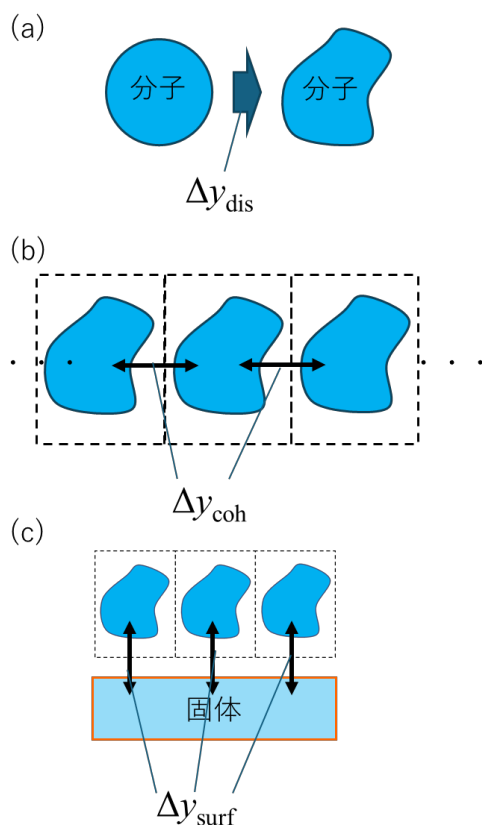


Fig. 1: Schematic views of Δy_{dis} (a), Δy_{coh} (b), and Δy_{surf} (c).

Table 1: Estimated (Δy), (Δy_{dis}), (Δy_{coh}), and (Δy_{surf}) of p-benzyne adsorption models [4]. Negative value indicates the y value of p-benzyne is reduced by the adsorption.

Model	Δy	Δy_{dis}	Δy_{coh}	Δy_{surf}
A	-0.8	+0.2	+0.8	-1.8
B	-5.7	-0.1	-0.6	-5.0
C	-6.0	-0.8	+0.6	-5.7
D	-11.1	-0.7	+0.6	-11.0
E	-5.5	-1.8	+0.6	-4.4

References

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