

Reactivity and Strong Interaction around Ligands of Organometallic Complexes Probed by Collision-Energy-Resolved Excited Triplet Helium Atoms

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Reactivity of collisional ionization (Penning ionization) ($M + \text{He}^*(2^3\text{S}) \rightarrow M^+ + \text{He} + e^-$) is governed by the probability for electron abstraction of an excited helium atom $\text{He}^*(2^3\text{S})$ from respective molecular orbitals (MOs) of the target molecule M . With the collision-energy/electron-energy-resolved two-dimensional measurement of Penning ionization, information on anisotropic interaction potential energy for the spatial region where the corresponding MO extends can be obtained. In order to investigate the electronic structure of organometallic compounds, ultraviolet photoelectron spectroscopy and theoretical calculation of ionization energies have been utilized. In this study, we have investigated anisotropic interaction around the molecule and ionic states by measuring collision energy dependence of partial ionization cross sections (CEDPICS) for each ionic state. Assignments of ionic states are also discussed on the basis of orbital reactivity of Penning ionization, slope of CEDPICS, and calculations by density functional theory (DFT).

Figure 1 shows CERPIES (collision-energy-resolved Penning ionization electron spectra). Figure 2 shows CEDPICS and electron density maps of ferrocene. Negative CEDPICS indicates the effect of attractive interactions around the molecule. The large negative CEDPICS of bands 3,4 can be ascribed to the strong attractive interaction around the cyclopentadienyl (Cp) rings. Since ionic state corresponding bands 1,2 were calculated [1] to be strongly mixed with shake-up states having relation with the $4e_1''$ (d_{xz} , d_{yz}) MO, the large negative CEDPICS can be assigned to the attractive interaction around the Cp rings. The DFT calculations are consistent with the attractive interaction around the Cp ring rather than the Fe atom. Similar anisotropic interaction around the ring was observed for $[(\text{C}_6\text{H}_6)_2\text{Cr}]$.

Reference

[1] K. Ishimura, M. Hada, H. Nakatsuji, *J. Chem. Phys.* **117**, 6533 (2002).

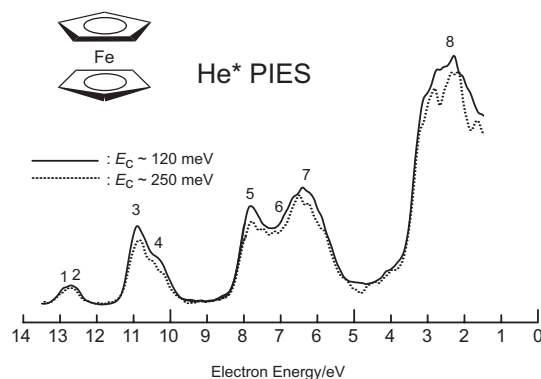


Figure 1. Collision-energy-resolved Penning ionization electron spectra of ferrocene.

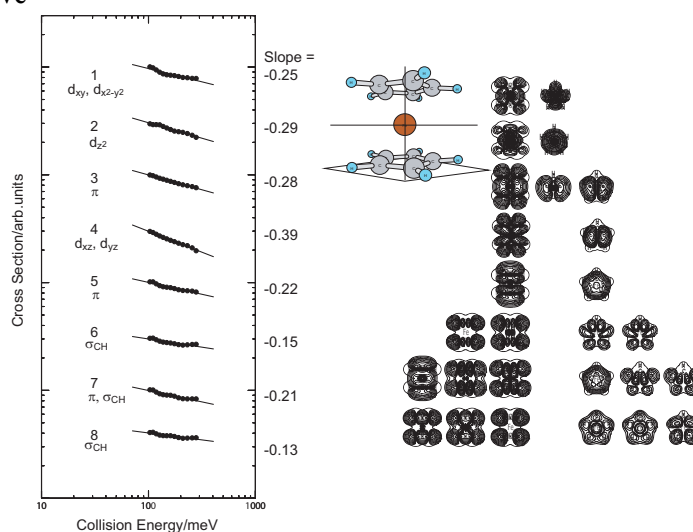


Figure 2. CEDPICS of ferrocene and electron density maps of corresponding MOs