THE LOCAL CORRELATION METHOD AS A TOOL FOR STUDYING THE METALLOPHILIC INTERACTION

L. Magnko[1,2], H. Stoll[1], H.-J. Werner[1]

[1] Theoretical Chemistry, University of Stuttgart, D-70550 Stuttgart, Germany
[2] Dept. of Physical Chemistry, Kazan State Techn. University, Kazan, Russia

Local second-order Møller-Plesset perturbation theory[a] (LMP2) has been used to investigate the metallophilic attraction in the gold, silver and copper compounds $[\text{X-M-PH3}]_2$ (X = H, Cl; M = Cu, Ag, Au). Monomer geometries have been optimized at the B3LYP level and kept frozen in the dimers. Potential energy curves as function of the M-M distance have been computed using a perpendicular orientation of the monomers, which eliminates dipole-dipole interactions. The calculations have been performed using basis sets of augmented correlation-consistent valence-triple-zeta (*aug-cc-pVTZ*) quality.
As expected, the interaction energy curve for gold has the deepest minimum for both ligands, indicating that the Au-Au attraction is stronger than the Ag-Ag and Cu-Cu ones. The interaction energies were found to be -24.91 (Cu), -27.27 (Ag), and -33.34 kJ/mol (Au) for the $[\text{H-M-PH3}]_2$ system and -22.09 (Cu), -30.70 (Ag) and -34.82 kJ/mol (Au) for $[\text{Cl-M-PH3}]_2$. The SCF curves are purely repulsive around the equilibrium geometries. Intramolecular correlation is also repulsive and largest for the gold complex (18.76 and 15.58 kJ/mol for H- and Cl-ligands, respectively). Thus, the above attractive interactions are due to the intermolecular correlation. The analysis of different contributions[b] to the attractive intermolecular interaction shows that for $[\text{X-M-PH3}]_2$ the ionic and dispersion contributions have comparable values, but for $[\text{Cl-M-PH3}]_2$ the dispersion contribution is significantly larger. From the results for the contributions of the different orbital blocks, it becomes clear that the major contributions to the attractive energy component arise from double excitations from the $5d$ and $4d$ shells for gold and silver, respectively. The contributions to the attraction from these $[d, d]$ pair-excitations are 43% ($[5d, 5d]$, Au), 31% ($[4d, 4d]$, Ag) for the system with a hydrogen ligand and 35% (Au) and 27% (Ag) for the one with chlorine. However, a quite different character of contributions has been observed for Cu. In this case the $[3d, 3d]$, [$3d$,Cu-Cl], [$3d$, Cu-P], [$3d$, P-H] and [$3d$, Cl] pair excitations are of similar importance (∼13%, 8%, 11%, 9% and 13%, respectively). But even for copper the sum of $[3d, 3d]$ and $[3d, X]$ pair excitation contributions are 63% ($[\text{H-Cu-PH3}]_2$ and 55% ($[\text{Cl-Cu-PH3}]_2$) of the total interaction energy.

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[a] M. Schütz, G. Hetzer, H.-J. Werner, J. Chem. Phys. **111** (1999) 5691 and references therein

[b] N. Runeberg, M. Schütz, H.-J. Werner, J. Chem. Phys. **110** (1999) 7210