

# Scrutiny of the HSAB principle in some representative acid-base reactions

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A thorough quantitative analysis of the HSAB principle is performed. Complex formation reactions of a typical soft acid,  $\text{Ag}^+$ , and typical hard acid, HF, with the bases  $\text{XH}_3$  ( $X = \text{N}, \text{P}, \text{As}$ ) are studied using the DFT/B3LYP method with the 6-311G\*\* basis set. For the molecules containing  $\text{Ag}^+$  and As, corresponding pseudopotentials are used. Results of the calculations pertaining to the interactions of the hard acid, HF, are robust in comparison to those of  $\text{Ag}^+$ . Correlation and nuclear relaxation effects are important in the case of the interactions of  $\text{Ag}^+$ . Basis set superposition error changes the trend, and the results vary drastically with the quality of the basis set. Pseudopotentials do not introduce any error, and the zero-point energy represents at most 5% of the binding energy. The presence of the solvent, modeled as in Onsager's dipole method and in PCM, does not significantly change the trend. In the exchange reactions, both HSAB and maximum hardness principles are shown to be valid