Supplementary Information (SI) for Reaction Chemistry & Engineering.

Supplementary Information

FF-EP Index: A Practical Index to Accurately Describe the Chemical Reactivity Together with its Calculating Program RAI Calculator

Senzhi Li [a], Hao Zhang [a], Dongdong Qi, *[a], Yongzhong Bian, *[a], Jianzhuang Jiang *[ab]

[a] *Beijing 100083, China Beijing Key Laboratory for Science and Application of Functional Molecular and Crystalline Materials, Department of Chemistry and Chemical Engineering, School of Chemistry and Biological Engineering, University of Science and Technology Beijing, Beijing 100083, China.*

[b] *Guizhou Key Laboratory of Macrocyclic and Supramolecular Chemistry, Department of Chemistry, School of Chemistry and Chemical Engineering, Guizhou University, Guiyang 550025, China.*

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Comparison of Ag^+ and Mg^{2+}

In ESP calculation (**Fig. S1**), the electrostatic potential of Mg^{2+} (hard acid) is “thinner” than Ag^+ (soft acid). In RAI^+ calculation (**Fig. S2**), the value of Mg^{2+} (hard acid) is higher than Ag^+ (soft acid). Based on these two tests, maybe we can get some information about hard/soft acid/base from ESP and RAI functions. To ensure a more balanced comparison between Ag^+ and Mg^{2+}, A well-defined all-electron basis set: dgauss-dzvp[S1-S2] for both Ag^+ and Mg^{2+} was employed in the present calculations.

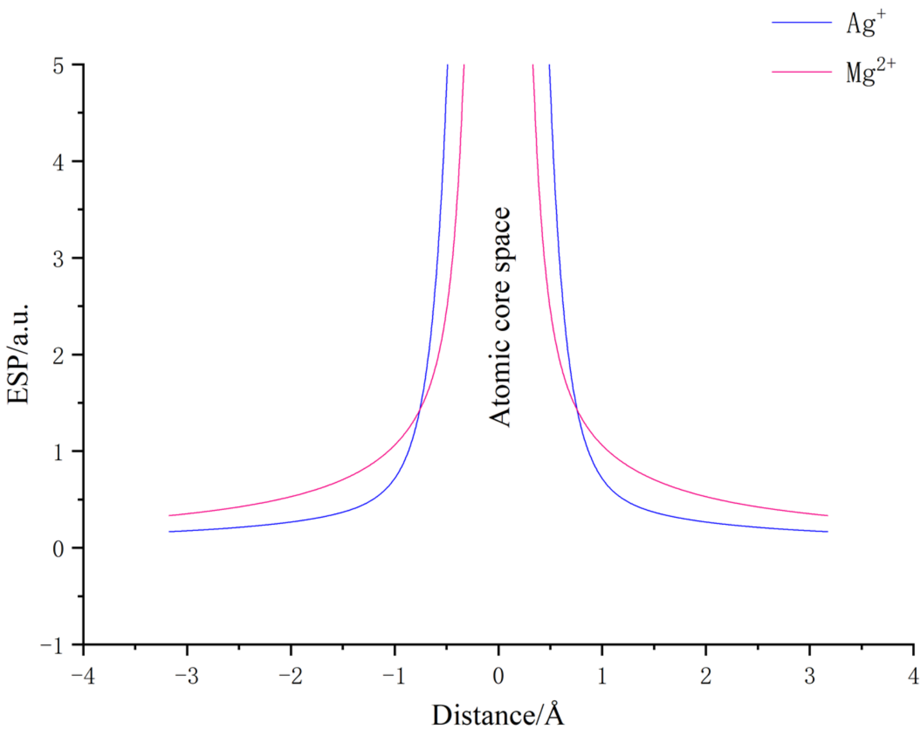

Fig. S1. ESP values of Ag^+ and Mg^{2+} plotted along the z-axis, both Ag^+ and Mg^{2+} are located at the origin.

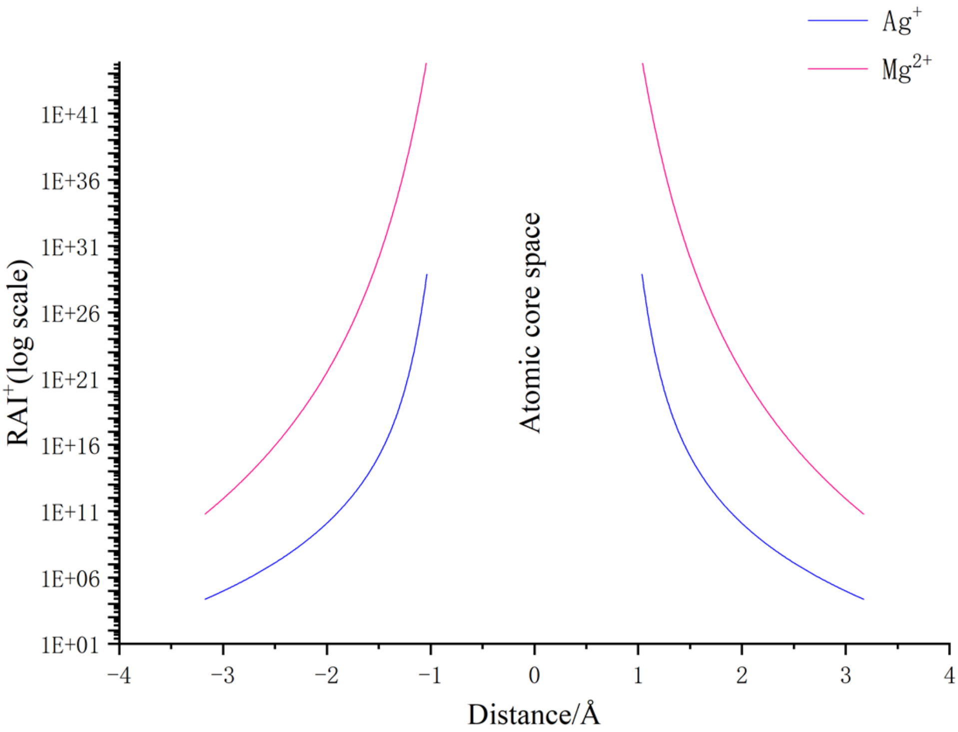

Fig. S2. RAI$^+$ values of Ag$^+$ and Mg^{2+} plotted along the z-axis, both Ag$^+$ and Mg^{2+} are located at the origin. A logarithmic scale is used for RAI$^+$ to facilitate comparison.

Why do we adopt the point charge $q_{attacker}$ to represent the attacking molecule?

To describe the energy change caused by electrostatic interactions when an attacking molecule approaches a target molecule from a special position, $V_{EP}\,q_{attacker}$ is the most appropriate expression. The reason is straightforward: by definition, the V_{EP} is the energy change associated with moving a test charge carrying one unit charge from infinity to a given coordinate. Multiplying V_{EP} by $q_{attacker}$ (the charge of the attacking molecule) thus yields exactly the energy change for moving a point charge with charge $q_{attacker}$ (i.e., the attacking molecule) from infinity to that coordinate, which corresponds perfectly to the process we are aiming to describe. In addition, it is also a reasonable simplification to take the charge directly from the attacking molecule. Nucleophiles generally have lone electron pairs, while electrophiles usually have empty orbitals. Therefore, we extract their common feature in the manner of a negative charge to represent lone electron pairs, and a positive charge to represent the positive charge of the partial atomic core exposed by empty orbitals. For the above reasons, we consider our approximation to be reasonable.

References

(S1) N. Godbout, D. R. Salahub, J. Andzelm and E. Wimmer, *Can. J. Chem.*, 1992, **70**, 560-571.

(S2) C. Sosa, J. Andzelm, B. C. Elkin, E. Wimmer, K. D. Dobbs and D. A. Dixon, *J. Phys. Chem.*, 1992, **96**, 6630-6636.