Molecular Modeling Tools for Reactivity and Kinetics – *Case Examples of Environmental Interest.*

Zoi Salta

Scuola Normale Superiore, Piazza dei Cavalieri 7, 56126 Pisa

zoi.salta@sns.it

Quantum chemical methods [1] have become increasingly powerful and useful for predicting, confirming, or extending the results of experiments. Specifically, the theoretical modeling of gas-phase reactions is central to the understanding of the reaction mechanism involved in a particular reaction system. If experimental results are available, theoretical kinetic analyses can be carried out to test the plausibility of suggested mechanisms, as well as to derive molecular properties of interest from macroscopic measurements. If no information is known regarding a certain reaction system, modeling it theoretically beforehand can aid the experimentalist in predicting a reasonable reaction mechanism and selecting suitable experimental conditions to carry out the investigation.

The modeling of gas-phase reactions (like, for instance, in atmospheric chemistry [2]) has been facilitated by the rapid development of high accuracy quantum mechanical electronic structure methods. These methods are essential for calculating the potential energy surface (PES) of a reaction system. The PES can then be used to derive information about the relative stability, molecular motion, and energy transfer among species on it. Transition State Theory (TST) constitutes a convenient approach for obtaining theoretical canonical rate constants directly from the paths connecting minima (reactants, intermediates, products) and transition states on the PES. Furthermore, it has been shown that the application of Variational Transition State Theory (VTST) results in rate constants which represent the exact upper bounds to the rate constants that would be obtained through extensive classical trajectory calculations.

After an overall presentation of the standard methodologies and their limitations, attention will be given to selected case studies of great importance in environmental chemistry. Thermochemical and kinetic information on the reactions of important organosulfur compounds in the atmosphere [3], oxidation of contaminants of car exhaust gases [4], formation and degradation pathways of ozone depleting substances (ODS) and reaction mechanisms involving water clusters (as an initial attempt to study chemistry in aerosols) will be presented and discussed as an example of application of the aforementioned methods.

References

[1] F. Jensen, *Introduction to Computational Chemistry*, (John Wiley, New York, 2017).

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[3] Z. Salta, J. Lupi, V. Barone, O. N. Ventura, *ACS Earth and Space Chemistry* 4, 3 (2020) 403.

[4] Z. Salta, A. M. Kosmas, M. E. Segovia, M. Kieninger, O. N. Ventura, V. Barone, *Theoretical Chemistry Accounts*, 139:112 (2020).