

Dissection of Polyatomic Reaction Dynamics:



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We discuss recent advances in theoretical characterization of reaction dynamics involving polyatomic molecules. Specifically, we focus on the hydrogen abstraction reactions of water by several atomic radicals, as indicated in the title^[1]. Thanks to recent advances in electronic structure theory and potential energy surface fitting, it has become possible to construct chemically accurate global potential energy surfaces for polyatomic reactive systems such as the ones discussed here. These accurate potential energy surfaces enable detailed dynamical (both quantum and quasi-classical) studies of the reaction dynamics. We report here interesting (and sometimes surprising) dynamical effects revealed by these theoretical studies, focusing on mode specificity and product energy disposal. A simple transition state based model is proposed to explain the observed dependence of reactivity on the initial rotational and vibrational excitations of the reactants and the internal state excitations in the products, some of which are in clear violation of the venerable Polanyi's Rules. This so-called Sudden Vector Projection (SVP) model, which attributes the mode specificity and product energy disposal to the coupling of reactant/product modes with the reaction coordinate at the transition state^[2], is shown to successfully predict most observed mode specificity and product energy disposal.

References:

- [1] Li, J., B. Jiang, H. Song, J. Ma, B. Zhao, R. Dawes, and H. Guo, *J. Phys. Chem. A*, 119, 4667-4687 (2015).
- [2] Guo, H., and B. Jiang, *Acc. Chem. Res.*, 47, 3679-3685 (2014).