

Reaction Dynamics, END and Propagators

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The direct molecular dynamics of reactive systems has been important in establishing the limitations of successful statistical theories, such as, transition state theory and RRKM. Indeed, many reactions have mechanisms and selectivities that are dictated or driven by the dynamics. For instance, it is shown that the selectivity of the $\text{OH}^- + \text{CH}_3\text{ONO}_2$ reaction is determined by the dynamics. This reaction can undergo bimolecular nucleophilic displacement either at the carbon center ($\text{S}_{\text{N}}2@C$) or nitrogen center ($\text{S}_{\text{N}}2@N$) as well as a proton abstraction followed by dissociation ($\text{E}_{\text{CO}2}$) pathway. The experimental ratio $\text{E}_{\text{CO}2} : \text{S}_{\text{N}}2@C : \text{S}_{\text{N}}2@N$ is 0.86 : 0.14 : 0.0 and the RRKM theory is unable to explain these data. Born-Oppenheimer molecular dynamics (BOMD) simulations of quasi-classical trajectories provided qualitative and quantitative reasoning for these experimental observations. The $\text{S}_{\text{N}}2@N$ mechanism is suppressed by the negative electrostatic shielding of the nitrogen center. Whereas, the increase efficiency of the $\text{S}_{\text{N}}2@C$ pathway is explained by the attractive electrostatic interactions between CH_3 and OH^- . The BOMD approach was also employed in the dehydration dynamics of protonated pynacol-like alcohols: $[(\text{CH}_3)_2(\text{R})\text{C}-\text{CH}(\text{OH}_2)\text{CH}_3]^+$, where $\text{R} = \text{CH}_3, \text{CH}_3\text{CH}_2,$ and $(\text{CH}_3)_2\text{CH}$. This reaction has two limiting mechanisms: concerted - where the dissociation of the water molecule is concomitant with the alkyl group migration -, and stepwise - which involves the secondary carbocation, $[(\text{CH}_3)_2(\text{R})\text{C}-\text{CHCH}_3]^+$, intermediate -. The calculated energy profile suggests the concerted mechanism, regardless the electronic structure method employed. However, quasi-classical trajectories starting the reactants yield mainly a stepwise pathway, showing that the transition state region is quite irrelevant for the reaction mechanism. The temporal dependence of synchronicity is also explored in Diels-Alder or [4+2] cycloaddition reactions of symmetric and asymmetric systems by quasi-classical trajectories. It is shown that asymmetric pathways dominate and that the degree of non-synchronicity depends upon the substituents, but from a time-dependent point of view, all reactions are concerted. Also, the strong contribution of the asymmetric trajectories explains the high efficiency of these reactions and, therefore, their usefulness in organic synthesis.

In addition to dynamic effects, some reactions mechanisms also need a proper treatment of couplings between electrons and nuclei. Öhrn and coworkers have shown these couplings are needed to describe the differential cross sections for electron transfer in $\text{H}^+ + \text{H}$ collisions using the electron-nuclear dynamics (END) formalism and the ENDyne program. It is shown that these couplings are also needed to calculate the integral cross sections for electron transfer between $\text{C}^{3+}, \text{O}^{3+}$ or Si^{3+} and H at several energies in good agreement with the experimental data.

Another influence of Öhrn is related to the development of electron propagators to calculate EPR and RMN parameters for open-shell molecules based on a closed-shell reference as well as to directly obtain multiplet splittings for magnetic couplings from the poles of the propagator.

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