

Conformational and Topological Dynamics of Radical Ions in Solution. Experiments and Simulations

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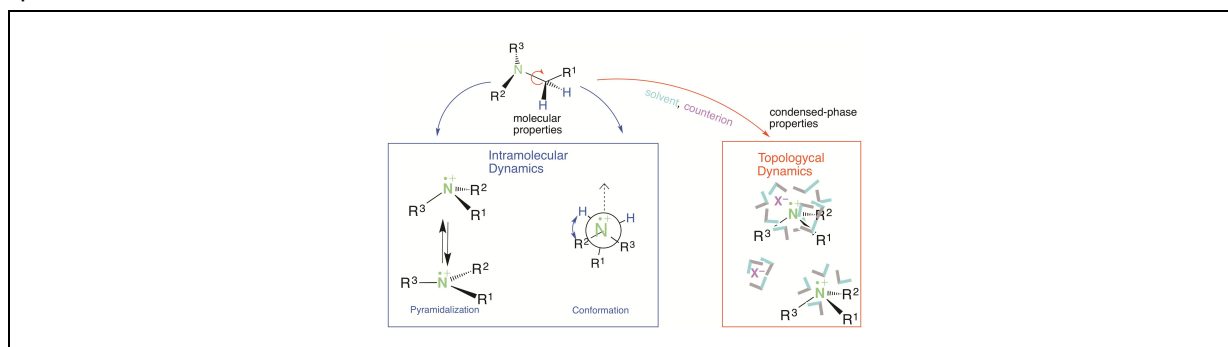
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Dynamic interactions between reactive molecules and their environment, i.e. the solvent and (counter)ions are at the basis of many molecular conversions. In terms of reactive intermediates, radicals play a decisive role in a wide palette of contexts ranging from synthesis to biology.

In solution, these molecular interactions are dominated by diffusive processes generally occur at the nanosecond time scale. Experimentally, this dynamic time scale is ideally matched by EPR spectroscopy ranging from ca. 1 ns to 1 μ s (at X band, ca. 9 GHz). Developments in the theory and analysis of configuration-space networks,^[1] Markov state models^[2] and QM/MM-approaches, together with the increasing power of computers allows now resolving dynamic phenomena at an EPR-compatible time scale even for open-shell systems that require a quantum-mechanical Hamiltonian.

Using EPR data and connecting them to molecular-dynamics simulations we started obtaining detailed insights into charge delocalization and solvent reorganization phenomena at the molecular scale (Fig). Initial results on radical ion pairs will be presented. They indicate unusual views on ion-pairing phenomena.



- [1] a) D. Gfeller, P. De Los Rios, A. Caffisch, F. Rao, *Proc. Nat. Acad. Sci. USA* **2007**, *104*, 1817; b) P. V. Banushkina, S. V. Krivov, *J. Comput. Chem.* **2015**, *36*, 878.
- [2] a) G. Hummer, A. Szabo, *J. Phys. Chem. B* **2014**; b) A. C. Pan, B. Roux, *J. Chem. Phys.* **2008**, *129*, 064107; c) L. Maragliano, E. Vanden-Eijnden, B. Roux, *J. Chem. Theor. Comput.* **2009**, *5*, 2589.