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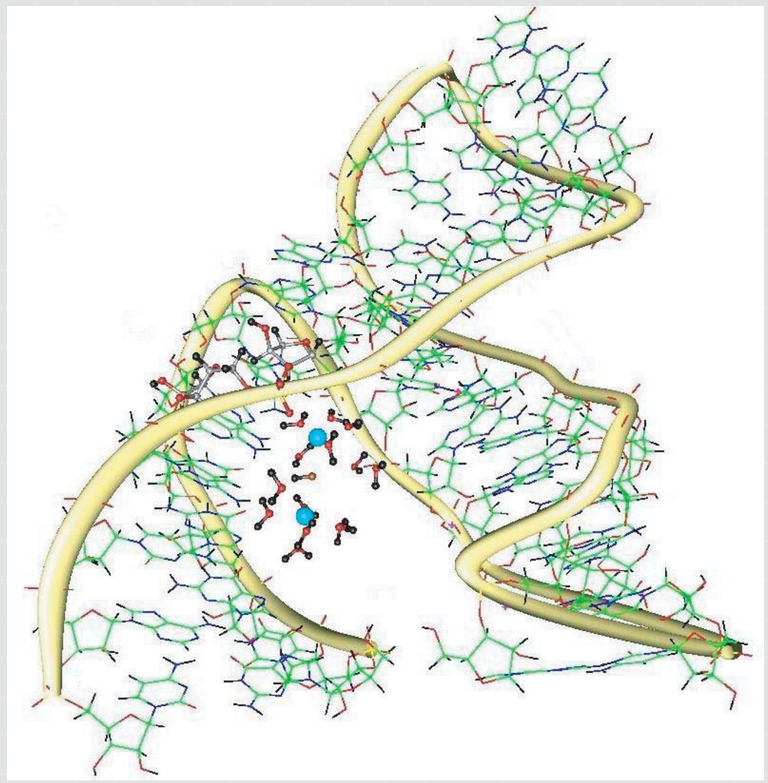
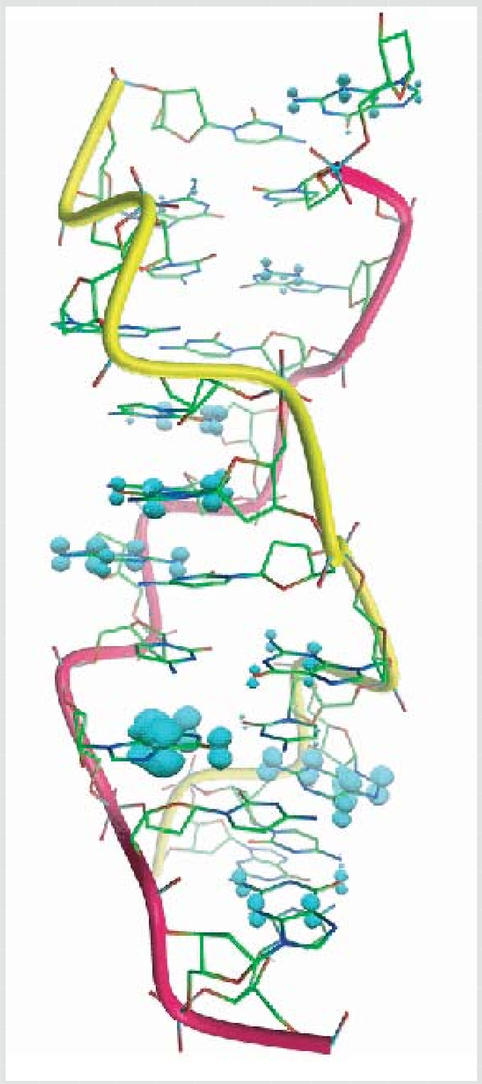
Computational Material and Life Sciences (2)

RNA enzyme catalytic cleavage

The role of metal cations (Mg^{2+}) in the cleavage reaction RNA enzymes is investigated via Car-Parrinello calculations. We find that the action of two metal catalysts is the most efficient way to promote the proton abstraction that triggers the nucleophilic attack and the cleavage of the P-$O^{5'}$ bond. Furthermore, we also find that an OH^- in the coordination shell of Mg^{2+} enhances the proton abstraction and prevents its transfer to the ribozyme, consistently with experiments. This suggests that in real ribozyme systems, the double-metal-ion reaction mechanism in the presence of an OH^- anion is favored with respect to single-metal-ion mechanisms



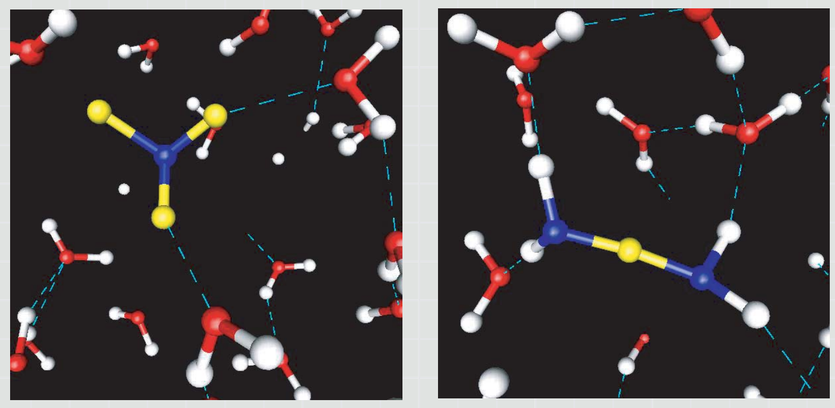
Charge localization in DNA fibers



Charge transfer in DNA is crucial both in a possible use of DNA as a component in nanoelectronics and in the oxidative damage and mutations of DNA. By using Car-Parrinello molecular dynamics, we study the mechanism of charge and electron hole localization in a laboratory realizable radical cation Z-DNA crystal. We find that at room temperature structural deformation are not sufficient to provide an efficient localization mechanism. Instead we find evidence for both an ion-gated and proton-coupled mechanism. Namely, a hole can be localized by two mechanisms: (i) proton shift or (ii) fluctuations in the solvation shell. Between these two scenarios, the proton-coupled charge transfer mechanism seems to provide the best agreement and the key to interpret EPR and H/D substitution experiments.

Density and temperature dependence of Proton Diffusion in Water

First principles studies of an excess proton in water at various thermodynamic states show that above the critical point, contrary to the ordinary liquid state, the disrupted hydrogen bond network destabilizes the Eigen $[H_3O(H_2O)_3]^+$ complex, activating the excess proton in an acid-like way. The proton rapidly explores the connected subnetwork or small clusters, then density fluctuations come into play, making the diffusion depend on two different regimes.



Incomplete Eigen complex ⟷ Zundel complex