

# New Insights into the Dynamics of Molecular Radical Reaction in Helium Droplets

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Helium-solvated peroxy radicals ( $\text{ROO}\bullet$ ) are formed via the *in situ* bimolecular reaction between a hydrocarbon radical and  $\text{O}_2$ . The reactants are captured sequentially through the droplet pick-up technique. Helium droplets are doped with either methyl, ethyl, propyl, propargyl, or allyl radicals via thermolysis of organic precursors in an effusive low-pressure pyrolysis source. Mid-infrared spectra of the peroxy radicals are recorded with species selective beam depletion spectroscopy. Spectral assignments in the CH stretching region are obtained via comparisons to either *ab initio* computations that employ second-order vibrational perturbation theory with resonances (VPT2+K) or via the diagonalization of an effective Hamiltonian represented in a local-mode basis. For peroxy radical systems having multiple conformations, we find only the lowest energy conformer in helium droplets, which is a surprising result. In previous studies of molecular systems exhibiting multiple conformers, the conformer distribution in helium droplets reflected the gas-phase thermal equilibrium distribution in the pick-up region. However, these previously studied systems were not formed through bimolecular chemistry within the droplet; rather, these systems were captured by helium droplets as *intact* molecules. Computations of the ethylperoxy conformer interconversion potential and its dependence on the extent of CO stretch excitation motivates an explanation that is based on an adiabatic funneling mechanism that leads to the exclusive production of the lowest energy peroxy conformer in helium droplets.