Jet-cooled and Matrix-Isolated Radicals: Monitoring Interactions and Reactions through IR Spectroscopy

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Interactions between radicals and solvent molecules are generally of interest, as radicals play an important role in many different fields.[1,2] In this talk, we report investigations on radical complexes at low temperature, with special focus on hydrogen-bonded complexes of nitroxyl radicals with water[3] and alcohols, using FTIR supersonic jet and matrix isolation spectroscopy.[4,5]

The monohydrate of 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO) radical is shown to exhibit a rich conformational and vibrational coupling dynamics, and its detection with a new gas recycling infrared spectrometer revealed its thermal metastability under humid gas conditions.[3] The complexes of the related persistent radical di-tert-butyl nitroxide (DTBN) were also vibrationally characterized, even though DTBN has proven to be less stable than TEMPO, possibly due to its floppier nature. The spectra computed at the unrestricted B3LYP-D3 level and DLPNO-CCSD(T) single point energies supported the assignment of the IR vibrations.

This work also aims to explore the topic of hydrogen-bond interaction between molecules with open-shell configurations and closed-shell molecules for benchmarking purposes.

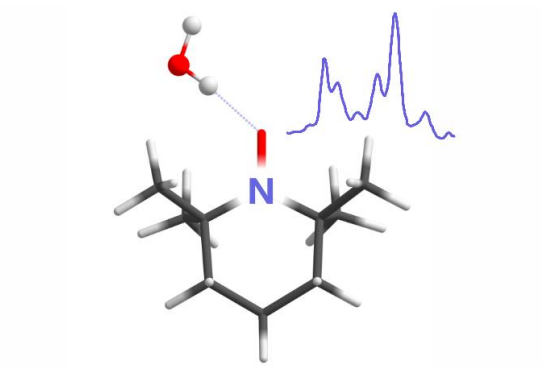

Figure 1. Jet FTIR spectrum of the mono- and dihydrates of TEMPO radical.[3]

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