Vibrational Structure of Macrocyclic Azaannulenes: Supersonic Jet Spectroscopy and DFT Modeling of Porphycene Derivatives

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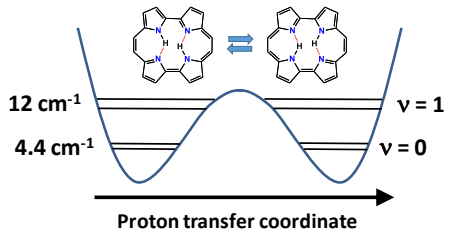
Porphycene derivatives are macrocyclic azaannulenes, which make excellent model systems for studying a proton transfer reaction, one of the most basic chemical reaction.[1,2,3] The process occurs in a reaction center of well-defined geometry formed by four nitrogen atoms. This "nitrogen cavity" is located inside a molecule and isolated from the environment.

Supersonic jet spectroscopy provides insight into the vibrational structure of isolated molecules. Moreover, laser-induced fluorescence (LIF) excitation and single vibronic level fluorescence (SVLF) spectra of porphycenes exhibit splitting of bands into doublets due to coherent delocalization (tunneling) of the inner protons.[4,5] This allows studying the rates of tautomerization reaction, and determining factors which govern the process.



One way to change the barrier for tautomerization, and thereby to tune the tautomerization rates, is modifying the size and shape of nitrogen cavity by peripheral substituents. In this work, we studied a porphycene derivative modified by bulky tert-butyl moieties. Their presence affects the inner proton pathway (H-bond length and angle) and may alter the molecular symmetry of emitting species.

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References:

[1] J. Waluk, *Acc. Chem. Res*. **2006,** 39, 945.
[2] M. Gil, M. Kijak, H. Piwoński, J. Herbich, J. Waluk *Methods Appl. Fluoresc*. **2017**, 5, 014007.
[3] J. Waluk, *Chem. Rev.*, **2017**, DOI: 10.1021/acs.chemrev.6b00328.
[4] J. Sepioł, Y. Stepanenko, A. Vdovin, A. Mordziński, E. Vogel, J. Waluk, *Chem. Phys. Lett.*, **1998**, 296, 549.
[5] Y. Nosenko, J. Jasny, M. Pietraszkiewicz, A. Mordziński, *Chem. Phys. Lett.* **2004**, 399, 331.