Contribution ID: **46** Type: **Contributed talk**

Competition Between NH$\cdots\pi$ Hydrogen Bonding and Charge Resonance Interactions in Aromatic Heterodimer Radical Cations revealed by IR spectroscopy

Monday 15 September 2025 12:40 (20 minutes)

Noncovalent interactions between aromatic dimers, including π-stacking, π hydrogen bonding (H-bonding), and cation-π interactions play an essential role in biological processes. In radical cations, cation-π interactions are stronger than in their neutral counterparts due to the additional electrostatic and inductive effects of the positive charge ($\sim$50 kJ/mol). In charged aromatic dimers, charge resonance (CR), where the positive charge is delocalized over both monomers, is an even stronger force with binding energies of $sim100$ kJ/mol. The strength of the CR depends strongly on the differences between ionization energies (ΔIE) of the interacting monomers. Thus, homodimers such as the pyrrole dimer cation (Py2+) are mostly stabilized by the CR, favoring the sandwich structures. In heterodimers, however, the CR is weakened, allowing NH$\cdots\pi$ H-bonding to compete with the CR, favoring T-shaped structures. Herein, we investigate the binding motifs of the pyrrole+-benzene (Py+Bz) and pyrrole+-toluene (Py+Tol) heterodimers, with ΔIE=1.03 and 0.59 eV, respectively, using infrared photodissociation spectroscopy (IRPD) and density functional theory calculations. Analysis of IRPD spectra of mass-selected Py+Bz and Py+Tol, combined with geometric parameters of intermolecular structures, reveals that NH$\cdots\pi$ H-bonding dominates over the CR interaction for both heterodimers (Figure 1). Furthermore, strongly redshifted NH stretch frequencies enable quantitative evaluation of the NH$\cdots\pi$ H-bond strength.

Keywords

Hydrogen bond: strong, State of system: gas

This abstract is submitted for....

HBond 2025 conference

Primary author: ARILDII, Dashjargal (Technische Universität Berlin)

Co-author: Prof. DOPFER, Otto (Technische Universität Berlin)

Presenter: ARILDII, Dashjargal (Technische Universität Berlin)