

Cryogenic ion vibrational predissociation (CIVP) spectroscopy of a gas-phase molecular torsion balance to probe London dispersion forces in large molecules

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Non-covalent interactions, especially the attractive part of the van der Waals potential – London dispersion forces, had been commonly ignored in organic and organometallic chemistry because individual interactions are small. Nevertheless, the recent recognition that these individually small interactions, whose number rise much faster than does the number of atoms as the molecule gets larger, sum up to "chemically significant" values, i.e. tens of kcal/mol, for organic and organometallic molecules with 50-200 atoms. Molecules in this size-range are typical reagents and substrates for organic synthesis, for which the renewed interest in attractive non-covalent interactions has led to the attribution of reactivity or selectivity to effects of "dispersion energy donors," DEDs, which are then appended as design and control elements, for example, in stereoselective catalysts. Dispersion-corrected quantum chemical computational methods have also proliferated, with DFT-based methods, in particular (but not exclusively), taking a prominent position because of the favorable scaling of performance as the size of the molecule increases.^[1]

Despite the applications in design and control of reactions, as well as the widespread use of computational modeling, there have not been comparably extensive experimental determinations of the interaction energies for molecules with 50-200 atoms in the gas phase, which is necessary to avoid accompanying effects of solvation. Quantitative tests by means of gas-phase bond dissociation energies or gas-phase equilibria are typically restricted to small molecules, for which the desired effects are also correspondingly small. Larger molecules pose technical challenges, whose circumvention has become possible only recently with newly developed experimental methods.

Here we report a gas-phase molecular torsion balance that uses a conformational equilibrium to "weigh" London dispersion against a competing cation- π interaction, for which the readout is the shift in N-H stretching frequency measured by cryogenic ion vibrational predissociation (CIVP) spectroscopy of electrosprayed pyridinium cations in a FT-ICR trap.^[2] While frequency calculations with DFT, assist in the interpretation of the spectra, the observed complex pattern of N-H in spectra comes from a Fermi resonance of the N-H stretch with overtones of in-plane C-H wagging modes, based on the basis of comparison of the spectrum to those for a range of related cations with systematically varied substitution. An equilibrium in favor of the asymmetric conformer would suggest that the dispersion-corrected DFT calculations tested in this work appear to over-estimate significantly the stability of the compact conformations favored by London dispersion in the gas phase.

[1] A. Tsybizova[†], L. Fritsche[†], V. Gorbachev[†], L. Miloglyadova, P. Chen*, *JCP*, **2019**, *just accepted*.

[2] L. Fritsche, A. Bach, L. Miloglyadova, A. Tsybizova, P. Chen, *Rev. Sci. Instrum.*, **2018**, *89*, 063119-1–063119-10.