COLD ION SPECTROSCOPY OF PYRIDINIUM IONS: AN EXPERIMENTAL PROBE TO EVALUATE NON-COVALENT INTERACTIONS IN THE GAS PHASE

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Current quantum chemical methods, such as DFT and coupled-cluster excel at describing the physical properties of small molecular systems. However, they perform quite poorly when used to describe large molecules. We recently demonstrated the generality of this problem when benchmarking different theoretical methods against experimental gas-phase bond dissociation energies values. While theory and experiment agree for small systems, bigger molecules show a large discrepancy. This indicates that certain phenomena are size-intensive and others size-extensive, and that the currently available techniques do not treat all of the phenomena uniformly, which calls into question their transferability to large systems. To overcome this, we must first identify the origin of these difficulties. This will then inform the formulation of better, more accurate computation strategies.

To shed light on the source of these discrepancies, we have designed an independent experiment, one which is not affected by the common mass spectrometric "suspects" such as kinetic shifts. We have measured the infrared spectra of pyridines, quinolones, and pyridinium dimers using a home-made, newly constructed cryogenic FT-ICR mass spectrometer. Our results reveal that the N-H stretching frequency is an excellent probe to test the accuracy of the optimized geometry—and hence dispersion interactions—as it is very sensitive to the spatial proximity of substituents. The pyridinium cations with pendant substituents become exquisitely sensitive molecular torsion balances for the measurement of non-covalent interactions in the gas phase. In addition, we computed the differences in N-H-N frequency for the proton-bound pyridinium dimers and obtained shifts within a range of 500 cm^{-1}, depending on the method/basis-set combination used. IR spectroscopy in the gas phase hence can be used to determine which combination of method and basis-set gives the right answer and for what reasons.