Mapping the force-field of a hydrogen bonded assembly

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Hydrogen-bonding underpins the structure, properties, and dynamics of a vast array of systems spanning a wide variety of scientific fields. From the striking complexity of the phase diagram of H$_2$O and the elegance of base pair interactions in DNA, to the directionality inherent in supramolecular self-assembly at surfaces, hydrogen bonds play an essential role in directing intermolecular forces. Yet fundamental aspects of the H-bond, including the magnitude of the force and binding energy, force constant, and decay length associated with the interaction, have been vigorously debated for many decades. I will discuss how dynamic force microscopy (DFM) using a qPlus sensor can quantitatively map the tip-sample force-field for naphthalene tetracarboxylic diimide (NTCDI) molecules hydrogen-bonded in 2D assemblies. A comparison of experimental images and force spectra with their simulated counterparts from density functional theory calculations shows that image contrast due to intermolecular hydrogen bonds arises fundamentally from charge density depletion due to strong tip-sample interactions. Interpretation of DFM images of hydrogen bonds therefore necessitates detailed consideration of the coupled tip-molecule system: analyses based on intermolecular charge density in the absence of the tip fail to capture the essential physical chemistry underpinning the imaging mechanism.