AN EMPERICAL RELATIONSHIP BETWEEN THE CENTRIFUGAL DISTORTION AND ROTATIONAL CONSTANTS OF ROTORS SOLVATED IN SUPERFLUID HELIUM DROPLETS

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It has been known since the early studies of SF_6 [b] and OCS [c] by Toennies and coworkers that when rotationally resolved spectra of helium solvated rotors are fitted to the standard free rotor Hamiltonians, the resulting effective centrifugal distortion constants are several orders of magnitude larger than what is observed in the gas phase. It was not until Lehmann analyzed the coupling between a planar rotor and a ring of helium atoms in a simple "toy-model"[d] that this behavior was attributed to the increase in the angular anisotropy of the rotor at higher J. While in recent years several high-level Monte Carlo simulations have accurately predicted the values of the effective roational constants a few small molecules in helium, there does not yet exist a general theory or "rule of thumb" that estimates the magnitude of these parameters for any given system. A recent compilation of the spectroscopic parameters of molecules and molecular complexes solvated in helium droplets has revealed that the effective centrifugal distortion constants correlate with the effective rotational constants, scaling nearly quadratically. In this talk, we discuss this phenomenon in the context of the previous theoretical work on helium solvated rotors and compare to the centrifugal distortion constants found in the gas phase.

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