ROTATONAL SPECTRA OF MOLECULES IN SMALL HELIUM CLUSTERS:
PROBING SUPERFLUIDITY IN FINITE SYSTEMS

FRANCESCO PAESANI and K. BIRGITTA WHALEY, *Department of Chemistry and Pitzer Center for Theoretical Chemistry, University of California, Berkeley, CA 94704*.

We present fully quantum calculations of the rotational excitations for different linear molecules solvated by a variable number of ^{4}He atoms and the superfluid response of the latter. Fitting to sets of rotational energy levels allows the effective rotational and distortion constants of the embedded molecules to be extracted as a function of the cluster size. In particular we focus our analysis on clusters containing between $N = 1$ and $N \approx 20$ ^{4}He atoms, i.e., up to a full solvation shell, around the dopant molecule. The size evolution of the spectroscopic constants is discussed with reference to related path integral Monte Carlo calculations that reveal the onset of exchange permutations. We present a linear response formulation of the effective rotational constant that allows for the first time a direct quantitative evaluation of the effect of superfluid response of the helium on the effective rotational constants. We show that the previously characterized transition at small N from van der Waals complexes to a quantum solvated molecule is due to the onset of ^{4}He superfluidity and that this is responsible for the anomalous size dependence of the measured rotational constants.