

PROBING QUANTUM SOLVATION OF ASYMMETRIC ROTORS USING BROADBAND ROTATIONAL SPECTROSCOPY

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Superfluid Helium-4 shows a variety of unique effects. For instance, the effective rotational constants for molecules embedded in ^4He droplets are usually quite different than their gas-phase values. The observed molecular rotational constants shrink with increasing number of He atoms until the "turnaround point," where part of the ^4He density rotationally decouples from a surrounding ^4He superfluid shell, leading to anomalous rotational constants as the number of ^4He atoms increases. Such behavior can appear well below the droplet limit; high-resolution studies of linear molecules embedded in small ^4He clusters containing as few as 6 ^4He atoms reveal superfluidic behavior.^a Although rovibrational spectra of asymmetric top molecules embedded in nanodroplets are routinely acquired using IR techniques, MW spectroscopy of small molecule-(^4He)_n clusters has been limited to linear molecules. In fact, only a small handful of theoretical studies of asymmetric tops embedded in superfluids are currently available.^b The potential experimental complications are foreboding, and are exacerbated by limitations of the Balle-Flygare cavity experiments used in many of the early MW studies.

Thankfully, chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy circumvents some of these limitations. Here, we show exciting new results on ^4He clusters doped with pyridine and benzonitrile. These systems show intriguing and unexplained spectroscopic phenomena and dynamics. In the case of pyridine, we can identify spectroscopic transitions for clusters containing as many as 20 ^4He atoms. We will also describe experimental techniques for sensitivity enhancement to detect such large molecule-doped helium clusters. These techniques, coupled with new efforts to characterize these systems theoretically, should extend generally to studies of more complicated chromophores.

^a[1] Tang, J.; Xu, Y.; McKellar, A. R. W.; Jäger, W. *Science* **2002**, 297, 2030. [2] Dempster, S. P.; Sukhorukov, O.; Lei, Q. -Y.; Jäger, W., *J. Chem. Phys.* **2012**, 137, 174303.

^b[1] Zeng, T.; Li, H.; Roy, P. -N., *J. Phys. Chem. Lett.* **2013**, 4, 18. [2] Zeng, T.; Roy, P. -N., *Rep. Prog. Phys.* **2014**, 77, 046601.