THE ETHYL RADICAL IN SUPERFLUID HELIUM NANODROPLETS: ROVIBRATIONAL SPECTROSCOPY AND AB INITIO CALCLUATIONS

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The ethyl radical has been isolated and spectroscopically characterized in ^{4}He nanodroplets. The five fundamental CH stretch bands are observed near 3 μm and have band origins shifted $< 1\ \mathrm{cm}^{-1}$from those reported for the gas phase species.[a,b] The symmetric CH_2 stretching band (ν_1) is rotationally resolved, revealing nuclear spin statistical weights predicted by G_{12} permutation-inversion group theory. A permanent electric dipole moment of 0.28 (2) D is obtained via the Stark spectrum of the ν_1 band. The four other CH stretch fundamental bands are broadened in helium droplets and lack rotational fine structure. The approximately 1-2 cm^{-1}line widths for these bands are attributed to the homogeneous broadening associated with solvent-mediated rovibrational relaxation dynamics. In addition to these five fundamentals, three A_1' overtone/combination bands are observed and have resolved rotational substructure. These are assigned to the $2\nu_{12}$, ν_4+ν_6, and $2\nu_6$ bands through comparisons to anharmonic frequency computations at the CCSD(T)/cc-pVTZ level of theory.

[a] S. Davis, D. Uy, D. J. Nesbitt. *J. Chem. Phys.* **112**, 1823-1834 (2000).
[b] T. Haber, A. C. Blair, D. J. Nesbitt, M. D. Schuder. *J. Chem. Phys.* **124**, 054316 (2006).