

INFRARED SPECTROSCOPY AND TUNNELING DYNAMICS OF THE VINYL RADICAL IN ^4He NANODROPLETS

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The vinyl radical has been trapped in ^4He nanodroplets and probed with infrared laser spectroscopy in the CH stretch region between 2850 and 3200 cm^{-1} . The assigned band origins for the CH_2 symmetric (ν_3), CH_2 antisymmetric (ν_2), and lone α -CH stretch (ν_1) vibrations are in good agreement with previously reported full-dimensional vibrational configuration interaction calculations.^a For all three bands, *a*-type and *b*-type transitions are observed from the lowest symmetry allowed roconvibrational state of each nuclear spin isomer, which allows for a determination of the tunneling splittings in both the ground and excited vibrational levels. Comparisons to gas phase millimeter-wave rotation-tunneling^b and high-resolution jet-cooled infrared spectra^c reveal that the effect of the ^4He solvent is to reduce the ground and ν_3 excited state tunneling splittings by $\approx 20\%$. This solvent-induced modification of the tunneling dynamics can be reasonably accounted for by assuming either an $\approx 2.5\%$ increase in the effective barrier height along the tunneling coordinate or an $\approx 5\%$ increase in the effective reduced mass of the tunneling particles.

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^cF. Dong, M. Roberts, and D. J. Nesbitt, *J. Chem. Phys.* 128, 044305 (2008)