INRARED SPECTROSCOPY AND TUNNELING DYNAMICS OF THE VINYL RADICAL IN ^{4}He NANODROPLETS

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The vinyl radical has been trapped in ^{4}He 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 ^{4}He solvent is to reduce the ground and ν_3 excited state tunneling splittings by ≈20%. This solvent-induced modification of the tunneling dynamics can be reasonably accounted for by assuming either an ≈2.5% increase in the effective barrier height along the tunneling coordinate or an ≈5% increase in the effective reduced mass of the tunneling particles.

[a] A. R. Sharma, B. J. Braams, S. Carter, B. C. Shepler, and J. M. Bowman, J. Chem. Phys. 130, 174301 2009
[b] K. Tanaka, M. Toshimitsu, K. Harada, and T. Tanaka, J. Chem. Phys. 120, 3604 2004
[c] F. Dong, M. Roberts, and D. J. Nesbitt, J. Chem. Phys. 128, 044305 (2008)