ROTATIONALLY-RESOLVED C-H STRETCH OVERTONE SPECTROSCOPY IN SUBSTITUTED ACETYLENES EMBEDDED IN He CLUSTERS: INTERNAL *VS* EXTERNAL VIBRATIONAL RELAXATION

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The spectra of the first overtone of the acetylenic stretch of propyne, trifluoropropyne, tertbutylacetylene, and trimetylsilylacetylene embedded in helium clusters (T≈0.4 K) have been observed. Rotational resolution has been achieved despite the presence of substantial broadening (linewidths on the order of 0.8–2.0 GHz), and the compression of the spectra due to the increased effective moment of inertia in the superfluid medium. Spectral simulation has allowed to calculate the relavant spectroscopic constants. Center band shifts have been found both to the red (propyne, and trifluoropropyne) and to the blue (tertbutylacetylene, and trimethylsilylacetylene) of the gas phase value. The absolute magnitude of the shifts is between 0.4 and 1.1 cm^{-1}. A comparison of the observed linewidths with their gas phase counterparts suggests that both internal and external relaxation occurs.