ROTATIONALLY-RESOLVED OVERTONE SPECTROSCOPY OF THE ACETYLENIC C-H STRETCH IN HCN AND CH_3CCH IN He CLUSTERS. WHERE DOES THE RELAXATION COME FROM?

C. CALLEGARI, I. REINHARD, A. CONJUSTEAU, K. K. LEHMANN, and G. SCOLES, *Department of Chemisty, Princeton University, Princeton, NJ 08544*.

We have built a new helium cluster isolation spectrometer for IR overtone spectroscopy and here report the first results obtained with it. Rotationally-resolved infrared spectra of the acetylenic C-H stretch first overtones of HCN and $\mathrm{CH_3CCH}$ embedded in He clusters (T=0.4 K) have been obtained. The use of a resonant power build-up cavity enhances the laser intensity effectively seen by the molecules by a factor of 10^3. This has allowed us to obtain S/N ratios in excess of 10^2, even in the presence of considerable broadening. Because of the low temperature, only one line could be seen for HCN, while for $\mathrm{CH_3CCH}$ at least three lines in both the P and R branches have been resolved. Although Intramolecular Vibrational Relaxation (IVR) is not expected for HCN, and is probably not contributing in the case of $\mathrm{CH_3CCH}$ either, measured linewidths range from 1 to 2 GHz. Vibrational, and to a minor extent rotational, relaxation into the superfluid medium is believed to be the cause of the broadening.