VERY SLOW INTRAMOLECULAR VIBRATIONAL ENERGY REDISTRIBUTION IN THE TRANS CONFORMER OF MONOSUBSTITUTED BUTYNES

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We have determined the rate of intramolecular vibrational energy redistribution (IVR) of the acetylenic C-H stretch of three monosubstituted butynes ($HCCCH_2CH_2X$, X= $-CH_3$, Cl, Br). Rotational assignments of the dense high-resolution infrared spectra are accomplished using infrared-microwave double-resonance spectroscopy techniques in an electric resonance optothermal spectrometer. The IVR lifetimes for these compounds are in the 1-5 ns range. This time scale for energy localization in the acetylenic C-H stretch of the trans conformer is about 1000 times longer than the time scale for isomerization predicted by RRKM theory. For the two halogen compounds we have resolved the hyperfine patterns in the highly perturbed excited state via double-resonance measurements. Comparison of the hyperfine patterns for states with the same asymmetric top quantum numbers (J Ka Kc) shows that there are distinct hierarchies in the rovibrational interaction strengths.