

MODE-SPECIFICITY AND NON-RRKM KINETICS IN THE CONFORMATIONAL ISOMERIZATION OF 4-CHLOROBUT-1-YNE

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We have measured the rate of conformational isomerization of 4-chlorobut-1-yne at an energy of 3330 cm^{-1} above the zero-point level through the rotational spectroscopy of single molecular eigenstates. From the spectrum of the $J=3$ - $J=4$ rotational transition of several eigenstates in this energy region we measure a unimolecular conformational isomerization rate of $1.2 \times 10^{10}\text{ s}^{-1}$. This rate is more than two orders-of-magnitude slower than the rate calculated using RRKM theory: $1 \times 10^{13}\text{ s}^{-1}$. Furthermore, from the eigenstate-resolved rovibrational spectrum of the acetylenic C-H stretch we find that there is strong mode-specificity in the isomerization rate. Coherent preparation of the acetylenic C-H stretch of 4-chlorobut-1-yne leads to even slower isomerization with an upper limit of the rate set by the measured rate of intramolecular vibrational energy redistribution: $3.3 \times 10^8\text{ s}^{-1}$.