

## ABSOLUTE CONFIGURATION OF 3-METHYLCYCLOHEXANONE BY CHIRAL TAG ROTATIONAL SPECTROSCOPY AND VIBRATIONAL CIRCULAR DICHROISM

LUCA EVANGELISTI, *Dipartimento di Chimica G. Ciamician, Università di Bologna, Bologna, Italy*;  
MARTIN S. HOLDREN, KEVIN J. MAYER, TAYLOR SMART, CHANNING WEST, BROOKS PATE,  
*Department of Chemistry, The University of Virginia, Charlottesville, VA, USA.*

The absolute configuration of 3-methylcyclohexanone was established by chiral tag rotational spectroscopy measurements using 3-buten-2-ol as the tag partner. This molecule was chosen because it is a benchmark measurement for vibrational circular dichroism (VCD). A comparison of the analysis approaches of chiral tag rotational spectroscopy and VCD will be presented. One important issue in chiral analysis by both methods is the conformational flexibility of the molecule being analyzed. The analysis of conformational composition of samples will be illustrated. In this case, the high spectral resolution of molecular rotational spectroscopy and potential for spectral simplification by conformational cooling in the pulsed jet expansion are advantages for chiral tag spectroscopy. The computational chemistry requirements for the two methods will also be discussed. In this case, the need to perform conformer searches for weakly bound complexes and to perform reasonably high level quantum chemistry geometry optimizations on these complexes makes the computational time requirements less favorable for chiral tag rotational spectroscopy. Finally, the issue of reliability of the determination of the absolute configuration will be considered. In this case, rotational spectroscopy offers a “gold standard” analysis method through the determination of the  $^{13}\text{C}$ -substitution structure of the complex between 3-methylcyclohexanone and an enantiopure sample of the 3-buten-2-ol tag.