

WILL CHIRAL TAG ROTATIONAL SPECTROSCOPY ALWAYS GIVE ACCURATE ENANTIOMERIC EXCESS DETERMINATIONS?

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Chiral tag rotational spectroscopy is a general method for determining the absolute configuration and enantiomeric excess (EE) of a chiral analyte. It is a chiral derivatization method where noncovalent interactions are used to attach a small, chiral molecule to the analyte via cluster formation in a pulsed jet expansion. The addition of a new, known chiral center converts the analyte enantiomers into spectroscopically distinguishable diastereomers. The high spectral resolution in rotational spectroscopy spectrometers makes it possible to fully resolve the diastereomeric chiral tag complex spectra – a favorable situation for quantitative EE measurements. The formula used to determine the analyte EE, when the tag EE is known, is derived under the assumption that transition intensities in the homochiral and heterochiral tag complex spectra are linear in the number densities of the tag and monomer. Using a simple kinetics model, it can be shown that this assumption breaks down in the case where complex formation has reversibility. In this model, chiral recognition, which results from binding energy differences in the homochiral and heterochiral complexes, leads to different dissociation rates of the initial complexes. This kinetics model has been used to explain the enhancement of ^{22}Ne complexes (relative to ^{20}Ne complexes) where the binding energy difference is caused by zero-point vibrational energy differences. If the dissociation rate of the initial collision complex is on the order of the stabilization rate of the complex, then deviations from the derived EE formula are expected in chiral tag rotational spectroscopy. A study of the accuracy of EE determinations using chiral tag rotational spectroscopy in the autotag analysis of trifluoroisopropanol is presented. Quantum chemistry calculations of the binding energy in the homochiral and heterochiral dimers gives an energy difference of about 2 kJ/mol suggesting that deviations from the EE formula could be observed. However, the formula is quantitative across the full EE range. This observation suggests that collision stabilization is rapid compared to the dissociation rate of the initial collision complex for a cluster formed from strong noncovalent interactions.