INVESTIGATION OF THE CHIRO-OPTICAL RESPONSE EVOKED FROM MODEL ORGANIC COMPOUNDS IN THE LIQUID AND VAPOR PHASES

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The chiral nature of molecules and the stereospecificity of molecular interactions play pivotal roles in numerous problems of chemical and biological importance. The molecules (of opposite handedness) comprising an enantiomeric pair long have been known to exhibit wavelength-resolved optical activities of opposite sign; however, definitive correlation of an individual enantiomer with a specific chiro-optical response still requires supplementary information. Likewise, theoretical prediction of optical activity and determination of absolute stereochemical configuration remain formidable challenges, owing in part, to complications introduced by solution-phase environments where the overwhelming majority of laboratory data has been obtained. This presentation will highlight ongoing efforts designed to interrogate the nonresonant optical activity (or circular birefringence) exhibited by isolated (gas-phase) species and to unravel the poorly-understood influence of solvation upon chiro-optical behavior. Heterocyclic organic compounds, including members of the oxirane family, have provided ideal targets for these investigations since their conformational stability and small size make high-level computational studies feasible. Vapor-phase measurements were performed through use of Cavity Ring-Down Polarimetry (CRDP)[a] which builds upon the long-pathlength sensitivity afforded by canonical (pulsed) ring-down techniques. Comparison of gas-phase values for specific polarization rotation with their solution-phase counterparts (obtained in solvents spanning a wide range of chemical properties) has documented pronounced perturbations incurred by the action of nonspecific solvation phenomena. These findings will be discussed in light of recent theoretical analyses, including Monte Carlo simulations to identify weakly-bound solute/solvent complexes and *ab initio* calculations to assess the corresponding chiro-optical response.

[a] T. Müller, K. B. Wiberg, P. H. Vaccaro *J. Phys. Chem. A* **104**, 5959 (2000); T. Müller, K. B. Wiberg, P. H. Vaccaro, J. R. Cheesman and M. J. Frisch *J. Opt. Soc. Am. B* **19**, 125 (2002)