CAVITY RING-DOWN POLARIMETRY (CRDP): RECENT ADVANCES AND NEW MEASUREMENTS

S. M. WILSON, K. B. WIBERG, and P. H. VACCARO, *Department of Chemistry, Yale University, P.O. BOX 208107, New Haven, CT 06520-8107*.

The recent development of Cavity Ring-Down Polarimetery (CRDP) has provided a new scheme for investigating the chiro-optical behavior exhibited by isolated (solvent-free) molecules.[a] Building upon the long-pathlength sensitivity afforded by canonical (pulsed) ring-down techniques, CRDP has the unique ability to probe both circular birefringence (nonresonant polarization rotation) and circular dichroism (resonant differential absorption) in rarefied (gas-phase) environments. Initial efforts have focused on the measurement of nonresonant optical activity parameters for a series of prototypical chiral compounds, with comparison of analogous gas-phase and solution-phase results highlighting the pronounced effects incurred by solvation processes.[b] Ongoing extensions of these studies will be discussed, including attempts to interrogate resonant circular dichroism phenomena as manifest in the differential absorption of circular polarization components. Aside from elucidating the important roles that solvent interactions play in mediating the optical response evoked from chiral solute molecules, information derived from these studies provides a critical assessment for the fundamental validity and practical applicability of burgeoning quantum chemistry calculations designed to predict chiro-optical properties *ab initio*.

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