

## CHIROPTICAL SPECTROSCOPY IN THE VAPOR PHASE

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Electromagnetic radiation propagating through an isotropic chiral medium experiences a complex index of refraction that differs in both real (in-phase) and imaginary (in-quadrature) parts for the right-circular and left-circular polarization states that define the helicity basis. The resulting phenomena of circular birefringence (CB) and circular dichroism (CD) lead to observable effects in the form of dispersive rotation and absorptive elliptization for an impinging beam of plane-polarized light, which commonly are measured under conditions of nonresonant and resonant excitation, respectively. This talk will discuss ongoing efforts designed to elucidate the provenance of electronic optical activity under complementary solvated and isolated conditions, with the latter vapor-phase work made possible by our continuing development of Cavity Ring-Down Polarimetry (CRDP).<sup>a</sup> Molecules of interest include the rigid bicyclic ketone (1*R*,4*R*)-norbornenone, where the spatial arrangement of distal alkene and carbonyl moieties gives rise to extraordinarily large specific rotation (CB) parameters that are predicted incongruously by different quantum-chemical methods; the monoterpene constitutional isomers (*S*)-2-carene and (*S*)-3-carene, which display surprisingly distinct chiroptical properties; and conjugated ketones such as (*S*)-verbenone, where CD probes of weak  $\pi^* \leftarrow n$  absorption bands have been performed at vibronic resolution. The disparate nature of gas-phase and condensed-phase optical activity will be highlighted, with complementary *ab initio* calculations serving to elucidate the structural, chemical, and electronic origins of observed behavior.

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<sup>a</sup>T. Müller, K. B. Wiberg, P. H. Vaccaro, J. R. Cheeseman, and M. J. Frisch, *J. Opt. Soc. Am. B* **19**, 125 (2002); P. H. Vaccaro, "Chapter 1.II.10: Optical Rotation and Intrinsic Optical Activity" in *Comprehensive Chiroptical Spectroscopy*, N. Berova, P. L. Polavarapu, K. Nakanishi, and R. W. Woody, eds. (John Wiley and Sons, Inc., Hoboken, NJ, 2011).