Among the many physicochemical properties used to distinguish chiral molecules, perhaps none has had as profound and sustained an impact in the realm of chemistry as the characteristic interactions that take place with polarized light. Of special note is the dispersive (non-resonant) phenomenon of circular birefringence (CB), the manifestation of which first was reported over two centuries ago and which still is employed routinely – in the more familiar guise of specific optical rotation – to gauge the enantiomeric purity of the products emerging from asymmetric syntheses. Concerted experimental and theoretical efforts designed to probe such electronic optical activity in isolated chiral molecules will be presented, with special emphasis directed towards the marked influence that intramolecular (vibrational and conformational) dynamics and intermolecular (environmental) perturbations can exert upon the intrinsic chiroptical response. Requisite isolated-molecule measurements have been made possible by our continuing development of cavity ring-down polarimetry (CRDP), an ultrasensitive polarimetric scheme that has permitted the first quantitative analyses of optical rotatory dispersion (ORD or wavelength-resolved CB) to be performed in rarefied (gaseous) media. Various technical aspects of CRDP will be discussed to illustrate the unique capabilities and practical limitations afforded by this novel methodology. Comparison of specific rotation values acquired for a broad spectrum of rigid and flexible chiral species under complementary isolated and solvated conditions will highlight the intimate coupling that exists among electronic and nuclear degrees of freedom as well as the pronounced, yet oftentimes counterintuitive, effects incurred by subtle solute-solvent interactions. The disparate nature of optical activity extracted from different surroundings will be demonstrated, with quantum-chemical calculations serving to elucidate the structural, electronic, and environmental provenance of observed behavior. In addition to unraveling basic processes that mediate chiroptical response in condensed media, the vapor-phase ORD benchmarks resulting from these studies afford a critical assessment for computational predictions of dispersive optical activity and for their burgeoning ability to assist in the assignment of absolute stereochemical configuration.