CAVITY RING-DOWN POLARIMETRY (CRDP): A NEW PROBE OF OPTICAL ACTIVITY IN RAREFIED MEDIA

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Cavity Ring-Down Polarimetry (CRDP), a new probe of circular birefringence (nonresonant polarization rotation) and circular dichroism (resonant differential absorption) in rarefied media, has been implemented by incorporating polarization selective components into the light injection optics, stable resonator assembly, and signal detection train of a conventional (pulsed) Cavity Ring-Down spectrometer. The inherent sensitivity of the CRDP scheme far surpasses that attainable by traditional polarimetric instruments and has permitted the first quantitative determination of nonresonant optical activity parameters for a variety of isolated (non-solvated) chiral molecules (α-pinene, β-pinene, cis-pinane, limonene, and propylene oxide). Measured specific rotation values for gas-phase species, when compared with analogous solution-phase results, reveal the pronounced and, oftentimes, counterintuitive perturbations of optical response incurred through complex solvation phenomena (*e.g.*, both the magnitude *and* the sign of circular birefringence can differ between the solution and gas phases). By interrogating isolated molecules in the absence of solvent-induced effects, these experiments provide a critical assessment for ongoing *ab initio* calculations designed to predict optical activity theoretically and to enable the direct assignment of absolute stereochemical conformation through straightforward polarimetric analyses.