Nuclear Velocity Perturbation Theory of VCD and Vibrational Electron Transition Current Density

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Vibrational optical activity (VOA) consists of two major subfields, infrared vibrational circular dichroism (VCD) and vibrational Raman optical activity (ROA) [1]. In differing ways both VCD and ROA depend on the response of electronic motion to nuclear vibrations, and a deeper understanding of these ways is at the forefront of research in VOA. The theoretical basis of ROA can be described within the Born-Oppenheimer (BO) while VCD cannot due to the vanishing of the electronic contribution to the magnetic-dipole transition moment within a non-degenerate electronic ground state [2]. This problem was first resolved conceptually with the complete adiabatic (CA) approximation by including the lowest-order correction to the BO approximation in the form of *nuclear velocities*, and without loss of an adiabatic product wavefunction [3]. This CA wavefunction, calculated by nuclear velocity perturbation (NVP) theory [3,4], provides correlation between nuclear *velocities* and electron *current* density, whereas the BO approximate provides only correlations between nuclear *positions* and electron *probability* density. Subsequently, electron transition current density (TCD) was defined for vibrational transition which allowed visualization of the motion of electron probability density during vibrational transitions [5,6]. More recently, the NVP formalism has been applied to the calculation of vibrational circular dichroism (VCD) [7,8] as an alternative to the established magnetic field perturbation (MFP) formalism available in a variety of commercial quantum chemistry programs. Examples of vibrational electron TCD, including some advanced visualizations [9], will be provided and discussed, as well as directions for future applications of the TCD formalism and VCD more generally.

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