

Theoretical Prediction of Resonance Raman and Resonance Raman Optical Activity Spectra

James R. Cheeseman^a

^a*Gaussian, Inc.*

cheese@gaussian.com

Raman optical activity (ROA), the difference in Raman scattering intensity for left and right circularly polarized light, is a powerful tool for studying chiral molecules and determining the structure of biomolecules in their native environment. Raman optical activity spectra obtained from *ab initio* quantum chemical calculations, using the far-from-resonance approximation (FFR), can often enhance the interpretation of the experimental spectra. The FFR approximation is, however, no longer valid when the incident laser frequency becomes close to the energy of an electronic excited state.

We present a fully analytic derivative extension of a method, first introduced by Jensen and co-workers [1], to compute the resonance vibrational Raman (RR) and Raman optical activity (RROA) of molecules using density functional theory. In this approach, an imaginary empirical damping parameter, corresponding to an effective inverse lifetime of the excited states, is added to the incident frequency. The formalism is the same as the FFR case except the frequency-dependent mixed polarizability tensors and their respective geometric derivatives become complex. The additional work required to handle the complex case increases the computational cost by less than a factor of two. Additionally, this approach is compatible with the two-step procedure in which the force field and Raman/ROA tensors are computed in separate steps, thus allowing for the use of different levels of theory for each step [2].

Preliminary results suggest that this approximate method recovers a significant amount of the resonance effects as the incident frequency approaches an electronic excitation and compares well with vibronic methods when the excited state geometry is similar to the ground state geometry. In the case of a strong resonance with a single electronic state, the calculated RROA obtained using this method is monosignate with the same relative intensities as the parent Raman spectrum, as predicted and observed by Nafie [3-4].

References

1. L. Jensen, J. Autschbach, M. Krykunov and G. Schatz, *J. Chem. Phys.* **127** (2007), 134101.
2. J. Cheeseman and M. Frisch, *J. Chem. Theory Comput.* **7** (2011), 3323.
3. L. Nafie, *Chem. Phys.* **205** (1996), 309.
4. M. Vargck, T. Freedman, E. Lee and L. Nafie, *Chem. Phys. Lett.* **287** (1998), 359.