AN ANALYTICAL DERIVATIVE PROCEDURE FOR THE CALCULATION OF VIBRATIONAL RAMAN OPTICAL ACTIVITY SPECTRA

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Vibrational Raman Optical Activity (VROA) spectroscopy [1] is a powerful tool to unravel the configurations as well as the conformations of molecules [2] and macromolecules [3]. Indeed, the 3N - 6 vibrational degrees of freedom leads to substantial information about the structures, which need theoretical tools for their detailed interpretation. Here we present our latest achievements in elaborating quantum chemistry procedures for the analytical evaluation of the optical molecular responses [electric dipole – electric dipole polarizability (α), electric dipole – electric quadrupole polarizability (A), and the optical activity tensor (G')] as well as of their geometrical derivatives entering into the expressions of the VROA intensities. This analytical algorithm has been developed at the time-dependent Hartree-Fock (TDHF) level using the 2n+1 rule [4] and is implemented in the DALTON quantum chemical package. Although this algorithm does not use the London orbitals, the simulated spectra are similar to the ones calculated combining a numerical differentiation approach with London orbitals but with a speed-up of at least one order of magnitude. These theoretical developments and their implementation will be discussed together with an analysis of the rototranslational sum rules between the different tensors calculated by our scheme [5].

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