AB INITIO MODELING OF ULTRAFAST NONLINEAR OPTICAL SIGNALS IN MOLECULAR SYSTEMS INVOLVING ELECTRONIC TRANSITIONS

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The observation of ultrafast time-resolved molecular dynamics after electronic excitation often relies on the measurement and interpretation of nonlinear optical signals. These signals can be very challenging to interpret without the aid of a theoretical model. A common approach to understand these signals is by using parameterized semi-empirical models that describe the specific process under study. These methods can be very useful and are very flexible but finding appropriate parameter values can be challenging, and the physical interpretation of these parameters can be ambiguous. Ab initio calculations can reduce the number of free parameters. However, available quantum chemistry packages like Dalton, QChem, and others, typically report frequency domain information, and tracking the evolution of the target usually requires the mapping of time onto a nuclear reaction coordinate which may not be observable. Here we present an ab initio approach to modeling time domain ultrafast nonlinear optical signals that addresses these issues by using the Dalton quantum chemistry package to parameterize a general N-level model which is then evaluated using a Liouville space representation. We compare these results to recent Ultrafast Transient Polarization Spectroscopy measurements of nitrobenzene.

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