Abstract Submitted
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On-the-fly ab initio semiclassical dynamics for computing vibrationally resolved electronic spectra[1] JIRI VANICEK, MARIUS WEHRLE, MIROSLAV SULC, SOLENE OBERLI, Ecole Polytechnique Federale de Lausanne, LABORATORY OF THEORETICAL PHYSICAL CHEMISTRY TEAM — We combine the thawed Gaussian approximation (TGA) with an on-the-fly ab initio (OTF-AI) scheme to calculate the vibrationally resolved emission spectra of oligothiophenes with up to five rings as well as absorption and photoelectron spectra of ammonia. The efficiency of the OTF-AI-TGA permits treating all vibrational degrees of freedom on an equal footing even in pentathiophene with 105 vibrational degrees of freedom, thus obviating the need for the global harmonic approximation, popular for large systems. Besides reproducing almost perfectly the experimental emission spectra, in order to provide a deeper insight into the associated physical and chemical processes, we also develop a novel systematic approach to assess the importance and coupling between individual vibrational degrees of freedom during the dynamics. This allows us to explain how the vibrational line shapes of the oligothiophenes change with increasing number of rings. [1] M. Wehrle, M. Šulc, and J. Vaníček, J. Chem. Phys. **140**, 244114 (2014).
[2] M. Wehrle, S. Oberli, and J. Vaníček, J. Phys. Chem. A **119**, 5685 (2015).

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