Accurate Prediction of Vibrational Spectra for 2D Materials from Ab Initio Molecular Dynamics

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We present a highly accurate computational method to calculate vibrational spectra for 2D materials, primarily for covalent-organic frameworks (COFs). IR and Raman spectra are important tools that are frequently used for material characterization. Raman spectroscopy has been especially considered a powerful method to determine a series of structural properties for 2D materials [1]. However, the experimental spectra are often difficult to interpret without aid from theory. The computation of IR and Raman spectra is usually based on the harmonic approximation where molecular vibrations can be determined as normal modes from the second derivatives of the electronic energy with respect to coordinates. Even though this method is more straightforward and computationally less expensive, anharmonic modes cannot be captured. Thus, we employ an AIMD (ab initio molecular dynamics) based approach to include vibrational anharmonicities which play an important role in interlayer interactions. After obtaining the AIMD trajectory, power, IR and Raman spectra can be calculated via a Fourier transformation of the time correlation functions of velocities, dipole moments and polarizability tensors, respectively. We discuss different approaches, such as Wannier localization and density functional perturbation theory (DFPT), to compute dipole moments and polarizabilities [2, 3]. We present the power, IR and Raman spectra we calculated for COF-1, and we compare our AIMD based approach to the spectra obtained via harmonic approximation.

References

[1] L. Liang, J. Zhang, B. G. Sumpter, Q. H. Tan, P. H. Tan, V. Meunier, ACS Nano, 11 (2017) 11777-11802
[2] M. Thomas, M. Brehm, R. Fligg, P. Vöhringer, B. Kirchner, Phys. Chem. Chem. Phys., 5 (2013) 6608–6622
[3] S. Luber, M. Iannuzzi, J. Hutter, J. Chem. Phys., 9 (2014) 094503

Figures

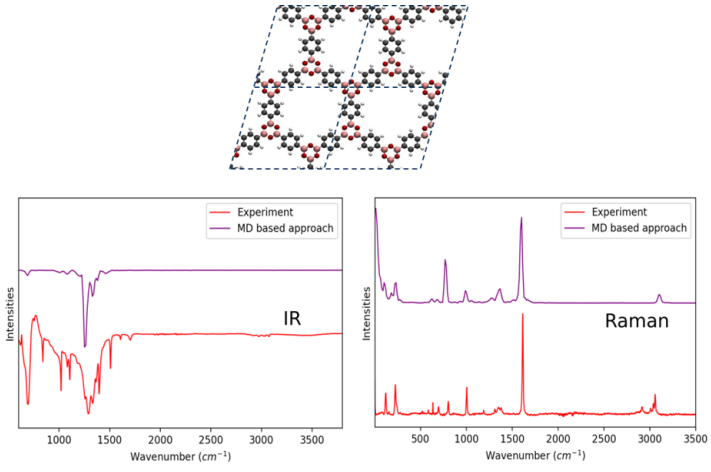

Figure 1: The structure of a single COF-1 layer and the experimental and calculated IR and Raman spectra.