DFT Modelling Of Molecular Crystals: Crystallographic Structures And Raman Spectra

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DFT methods augmented with vdW corrections have been used to predict crystallographic structures and vibrational spectra of a number of molecular crystals. The computed structures and spectra [1,2] are sufficiently accurate to allow for the identification and discrimination of different polymorphs. This is an important result since Raman lattice phonons, detected in the low energy range of the spectrum, are often used as experimental "fingerprints" for polymorph identification. Indeed, the lattice modes, *i.e.*, translations and rotations of the molecules as a whole, display Raman patterns which are characteristic of the crystal packing and therefore of the polymorph. However linking the different spectra to a specific structure requires calibration Raman spectra on a complete set of reference samples, containing only one polymorph and individually identified by X-ray diffraction, which is a complicated and time-consuming task. The finding that appropriate DFT methods yield crystallographic structures and Raman patterns at a level of accuracy (below 5 cm^{-1}) that allows quick and reliable identification of the phase without X-ray measurements on the actual samples [1,2] is, therefore, a major breakthrough that we showcase here for coronene, as a model system. As an added bonus, the computed structures and spectra provide insight into how intermolecular vibrations are affected by the packing motif.

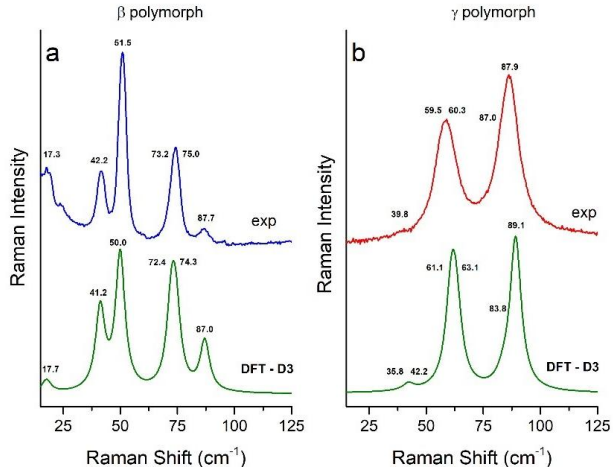

Figure 1: Experimental and calculated Raman spectra of coronene

1. N. Bedoya-Martinez, B. Schrode, A. O. F. Jones, T. Salzillo, C. Ruzie', N. Demitri, Y. H. Geerts, E. Venuti, R. G. Della Valle, E. Zojer, R. Resel;
2. B. Schrode, A. O. F. Jones, R. Resel, N. Bedoya, E. Zojer, R. Schennach, Y. H. Geerts, M. Sferrazza, A. Brillante, T. Salzillo, E. Venuti;