

Supporting electronic structure calculations for high resolution spectroscopy: internal rotors and PAHs as examples

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The combination of high resolution spectroscopy with quantum chemistry calculations has nowadays become a standard. Theoretical molecular parameters are an invaluable help to start the spectral analysis. In turn, the experimental data permit to calibrate the calculations which provide relevant properties of the studied systems as well as reliable estimations about systems of the same class when experiments are missing. Such a complementary is emphasized by some peculiar cases at the edge of both approaches. Indeed, when the limits of the experimental capabilities are reached, the most accurate results may come from previously calibrated calculations and contrarily, the limits of what could be expected from calculations may be evidenced by the experiments. Two recent studies, although having quite different objectives, are good examples of the theory-experiment duality.

Four isomers of the dimethylbenzaldehyde molecule have been analyzed by Fourier transform microwave spectroscopy supplemented by quantum chemical calculations. These isomers represent benchmark species for the development of the theoretical model of asymmetric top molecules containing two nonequivalent methyl tops, exhibiting different barrier heights and coupling terms to methyl internal rotation (the BELGI-Cs-2Tops program).

High resolution spectroscopic data of 16 Polycyclic Aromatic Hydrocarbons (PAHs) and aza-derivatives have been used to calibrate density functional theory (DFT) calculations at the anharmonic level. Unconventionally, the rotational parameters, rather than the vibrational frequencies, are used as reference data to validate the theoretical approach. As consequences, excellent equilibrium geometries for the PAHs family of compounds may be estimated and the accurate rotational parameters will permit to strongly support the rather complicated spectroscopic analysis in the IR/Far-IR region or to account for the rotational structures of the IR bands (e.g. in the AIBs models) when experiments are not possible.