MOLECULES' ROTATION SIGNALS: TORSION, INVERSION, FLEXIBILITY, CHIRALITY

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All molecular system come with their own set of challenges for rotational spectroscopy, theoretically and experimentally: (Multiple) internal interactions might cause complicated energy level schemes and the resulting spectra will be rather difficult to predict theoretically. Experimentally, these spectra are difficult to assess and assign. With today's broad-band microwave (MW) techniques, finding and identifying such spectral features have lost their major drawback of being very time consuming for many molecules. The unrivalled resolution of advanced fast-passage spectrometers, previously only available for narrow-banded MW techniques, now allows to tackle - at the highest precision – very subtle effects.

Historically, (very) low barriers to large amplitude motions leading to (very) large tunnelling splittings often prevented an experimental assessment or if so, their analysis to experimental accuracy. Barriers to large amplitude motions can not only be related to the local atom arrangement but also to the molecular orbital and electron density structure, e.g. chemical information relayed through conjugated π-systems, of the molecule. Theoretically, such systems require calculations at elevated levels, e.g. CCSD(T)/cc-pcVTZ or beyond, but quantitative predictions of the dynamical features often still fall behind those of equilibrium structures. Experimentally, the analysis might require the measurement of tunneling species (in the cm- and mm-wave regions) beyond the torsional ground state to reveal the origin of the observed spectrum and underlying hindering potential.

Furthermore - in the realm of barriers to large amplitude motions - details on internal dynamics and the (stereochemical) molecular structure encode their nature in the coherent signature of molecular rotation spectra obtained after single- and/or double-resonance excitation. Current examples and new directions together with an outlook will be given.