ROTATIONAL SPECTROSCOPY IN THE TIME DOMAIN: NEW TECHNIQUES & CHALLANGES

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Due to the increasing technological importance of small particles as well as basic questions presently being discussed in related sciences, larger molecules and molecular or atomic clusters have also moved into the focus of physical chemistry and spectroscopy. However, larger molecules can impose a number of challenges, theoretically and experimentally.

From the theoretical point of view, e.g., internal large amplitude motions between equivalent potential energy minima lift the degeneracy of the energy levels of a hypothetical rigid molecular system, resulting in a fine structure of the rotational transitions. For larger molecules exhibiting multiple internal motions at low barriers, the resulting spectra will be rather complicated and difficult to assign.

From an experimental point of view, many larger species have low vapour pressures or are unstable at normal conditions, i.e. they have to be transformed into the gas phase or must even be generated in-situ. Pulsed supersonic-jet expansions which can be combined, e.g., with heated, LASER-ablation-, or DC-discharge-plasma sources provide a number of promising possibilities. However, the splitting patterns of, e.g., highly dynamic molecules can be spread quite widely and become difficult to predict. With narrow banded techniques, even though very sensitive, it can become very tedious to locate and identify the spectral features.

The spectroscopic approach that often determines molecular properties such as structure, charge distribution, peculiarities of the chemical bond, details on internal dynamics, etc. with the highest precision uses accurate inertia and interaction information from pure rotational spectra as obtained by microwave spectroscopy. Right now - about a quarter century after the introduction of supersonic-jet resonator Fourier-transform microwave spectroscopy by Balle and Flygare - new exciting technical developments aiming to overcome still existing limitations are expected to pave the way for a promising future of rotational spectroscopy.