HYPERFINE STRUCTURE IN ROTATIONAL SPECTRA OF DEUTERATED MOLECULES: THE HDS AND ND_3 CASE STUDIES

GABRIELE CAZZOLI, CRISTINA PUZZARINI, *Dep. Chemistry 'Giacomo Ciamician', University of Bologna, Bologna, Italy*.

The determination of hyperfine parameters (quadrupole-coupling, spin-spin coupling, and spin-rotation constants) is one of the aims of high-resolution rotational spectroscopy. These parameters are relevant not only from a spectroscopic point of view, but also from a physical and/or chemical viewpoint, as they might provide detailed information on the chemical bond, structure, etc. In addition, the hyperfine structure of rotational spectra is so characteristic that its analysis may help in assigning the spectra of unknown species. In astronomical observations, hyperfine structures of rotational spectra would allow us to gain information on column densities and kinematics, and the omission of taking them into account can lead to a misinterpretation of the line width of the molecular emission lines. Nevertheless, the experimental determination of hyperfine constants can be a challenge not only for actual problems in resolving hyperfine structures themselves, but also due to the lack of reliable estimates or the complexity of the hyperfine structure itself. It is thus important to be able to rely on good predictions for such parameters, which can nowadays be provided by quantum-chemical calculations. In fact, the fruitful interplay of experiment and theory will be demonstrated by means of two study cases: the hypefine structure of the rotational spectra of HDS and ND_3.

From an experimental point of view, the Lamb-dip technique has been employed to improve the resolving power in themillimeter- and submillimeterwave frequency range by at least one order of magnitude, thus making it possible to perform sub-Doppler measurements as well as to resolve narrow hyperfine structures. Concerning theory, it will be demonstrated that high-level calculations can provide quantitative estimates for hyperfine parameters (quadrupole coupling constants, spin-rotation tensors, spin-spin couplings, etc.) and shown how theoretical predictions are often essential for a detailed analysis of the hyperfine structure of the recorded spectra.