DETECTING SPECTRA OF NEW MOLECULES: SYNERGISM WITH THEORY

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The major emphasis of the talk will be on the spectroscopic detection of new, small molecules in the infrared, microwave and millimeterwave regions. There are two cases in which the interplay of experiment and theory is important. The first case occurs when we have observed a spectrum and we want to identify its carrier. This case is important for example in astrophysics or planetology. In the second case we strive to produce a new, short-lived and/or reactive species and want to monitor its occurrence spectroscopically. In both cases high level theoretical calculations have become of great value because they predict reliably either the full spectrum, or some of its features. Moreover, they provide also experimentally inaccessible building blocks of the models which are essential to interpret the spectra and which are employed to deduce physically meaningful molecular parameters.

Some general applications of this strategy will be mentioned, and results of studies performed in the author's laboratory by collaboration with the research group of Professor W. Thiel will be presented. Examples will include rovibrational investigations of halogenophosphines PH_2X, X = F, Cl, Br, I, the detection of difluorovinylidene F_2CC: and some of its derivatives by matrix infrared spectroscopy, and the observation in the gas phase and the determination of the structure of silene $CH_2{=}SiH_2$ by millimeter wave spectroscopy.

Finally the talk is concerned with the aspect of modelling perturbations apparent in high resolution infrared spectra of some fluorohalogenoethyne species, and the elucidation of states that cannot be probed experimentally.

SPECTROSCOPY IN THE TERAHERTZ REGION: NEW DEVELOPMENTS OF EXPERIMENTAL TECHNIQUES

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Extensive developments of high resolution microwave spectroscopy in recent years was initiated by appearance on a world-wide market of series of Russian made ("Istok", Fryazino, Moscow region) backward wave oscillators (BWO) covering the range from tens of Gigahertz up to beyond of Terahertz and series of BWO-based frequency synthesizers in the range 35-178 GHz developed at "Kvarz" (Nizhny Novgorod). Both kind of these sources of microwave radiation - the synthesizers itself and higher frequency BWOs stabilized by use of frequency phase lock technique against the computer controlled synthesizer ideally suit to spectroscopic purposes.

New experimental methods and techniques based on use of aforementioned sources of radiation recently developed by our group will be presented:

In close collaboration with spectroscopy group in Lille the technique developed for frequency stabilization of BWOs was successfully used for stabilization of far infrared laser. The FIR laser working in the range 0.6.- 2.5 THz and serving as radiation source in sideband spectrometer was for the first time stabilized against harmonic of 78-118 GHz synthesizer. The stabilization has considerably increased accuracy of frequency measurements of the spectrometer.

Series of broad-band frequency multipliers for BWOs of 1-3 mm wavelength range has been developed for extension of frequency range of existing sources. Spectral lines are observed on up to 5-th harmonic of fundamental radiation. Developed method of calibration by use of spectral lines with known intensity allows to analyze performance of the multiplier on each separate harmonic.

While working on unstable molecule spectra with phased locked BWO- based Terahertz spectrometer in Lille together with Prague's group new rigorous method of identification if the spectral line belongs to negative or positive ion or neutral molecule based on effect of Doppler shift of frequency has been developed. The method allowed us to identify lines of rotational spectrum of SH^- and SD^- anions which become a first microwave observation of anion spectrum.

Combination of computer controlled microwave source of radiation, spectral line shape processing software and Fabry-Perot cavity with quality factor more than 600000 helped us to develop method of ultralow absorption measurements in dielectrics. The method exceeds level of sensitivity obtained earlier in more than two orders.