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High Resolution Molecular Spectroscopy using synchrotron light source

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High Resolution Molecular Spectroscopy in gas phase is the main source of information about remote objects. High resolution means that vibrational molecular spectra are rotationally resolved. For floppy molecules the spectra can be more complex due to tunneling splitting. The heavier the molecule the smaller are its rotational constants and the spectra may be heavily congested.

The successful recording of high resolution spectra requires that several exeperimental conditions are fulfilled:

- The gas pressure is low, usually below 1 mbar.
- The path length is long; the White-type multiple reflection cells are used.
- The source of IR radiation is stable in time and covers the whole spectral range .
- The noise level is small.

For many years Fourier Transform Infrared Spectrometers are used as the main instrument to record high resolution spectra. The standard spectrometers have resolution of 0.02 cm^{-1}. Typically, about hundred spectra are co-added to improve a signal/noise ratio. The analysis of high resolution spectra requires usually application of advanced software.

Since high resolution spectroscopy brings important information about structure and dynamics of molecules in different vibrational states,there is an obvious expectation to apply this method to heavier molecules and molecules of the complex internal dynamics due to conformation changes. In such cases the experimental requirements become even more demanding, because of two main reasons:

- The density of lines is very high, often exceeding 400 lines/cm^{-1}.
- The pressure broadening of individual lines must be minimized.
- The spectrometer able to record very dense and weak spectra must have following features:
- Stable source of radiation which allows for co-addition of many spectra.
- Source of high power which allows minimization of the gas pressure and study of weak transitions.
- Very long Maximal Optical Path Difference (MOPD) in Michelson interferometer.

These conditions are best fulfilled by Fourier Transform Infrared spectrometers connected to synchrotron light sources. The power of a synchrotron light source in the infrared range is 20 times higher then that of a thermal Globar source. Thus, the aperture can be reduced from 1.5 to 0.9 mm leading to narrower lines. In FTIR spectrometer the resolution is determined through MOPD ($\Delta\nu_u = 0.61/d_{MOPD}$), which in standard spectrometer is equal to 2.5 m. In 8 existing synchrotron setups MOPD is extended to 9.8 m, and in Swiss Light Source up to 11.7 m. Thus, the best unapodized resolution at SLS is 0.00053 cm^{-1} [1].

This feature of the SLS spectrometer allow for analysis of fully resolved spectra of heavy molecules such as naphthalene and indole [2].

New spectrometer allows to study very week transitions in the spectral region which rarely visited using previous IR or mmw experimental techniques. Recently, at SLS the spectrum in the torsional region (26-100 cm^{-1}) of nitromethane was recorded for the first time. The torsional band is extremely weak, four order of magnitude weaker than other fundamental bands. The spectrum is being analyzed with a specialized software LWW (Loomis-Wood for Windows) developed in Poznań. First analysis reveals a number od Q branches. The assignment work is in progress.

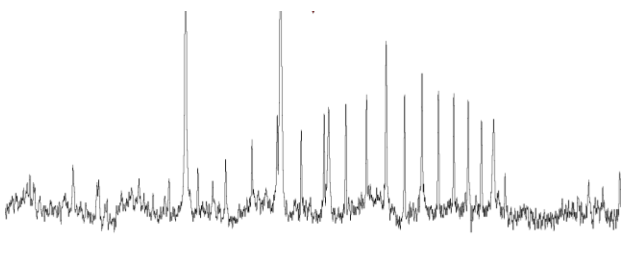

Figure 1. The Q-branch of nitromethane in the spectrum recorded at Swiss Light Source.

[1] S. Albert, K. Keppler Albert, M. Quack in *Handbook of High Resolution Spectroscopy*, Vol. 2 (Eds.: M. Quack, F. Merkt, Wiley, Chichester, 2011, pp. 965–1019).

[2] S. Albert, K. Keppler Albert, P. Lerch, M. Quack, *Faraday Discussions* **150** (2011) 71-99.