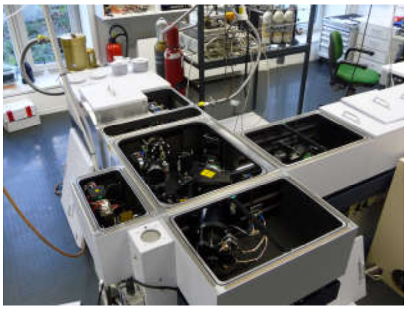
Deutsches Zentrum
für Luft- und Raumfahrt e.V.
in der Helmholtz-Gemeinschaft

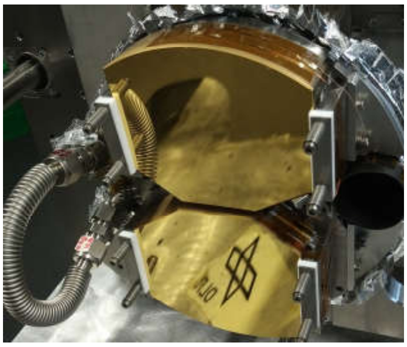
Handout 7/2021

Laboratory Infrared Spectroscopy of Atmospheric Constituents

Bruker IFS 125HR



View into the instrument



View inside the multireflection cell

Background

Remote sensing for determination of the distribution of atmospheric trace gases relies on line parameter spectroscopic databases (e.g. HITRAN, GEISA, or JPL), for line positions, line strengths, pressure broadening parameters or absorption cross sections. The database is mandatory for linking the characteristic spectral signature obtained by remote sensing to the trace gas distribution in the atmosphere. Remote sensing of the atmosphere is carried out from ground-, airplane-, balloon- or satellite-based platforms. The spectroscopic database is mostly obtained from laboratory experiments.
The following sections introduce the infrastructure related to lab spectroscopy of DLR's Remote Sensing Technology Institute.

High Resolution FT Spectrometer

The Fourier Transform (FT) spectrometer at DLR is the commercial high-resolution BRUKER IFS 125HR instrument covering the spectral range from 10 to 40000 cm^{-1} with a maximum resolution of 0.001 cm^{-1} (30 MHz). The instrument can be evacuated to avoid absorption of radiation by water and carbon dioxide in the ambient air. The spectrometer is equipped with a number of highly sophisticated absorption cells covering absorption paths from 0.15 m to 200 m and temperatures from 200 K to 350 K. Several sensitive detectors exist covering the electromagnetic spectrum from FIR to UV. For the MIR region the detector optics was optimized to yield sensitivities up to 10 times higher than standard commercial detectors.

Multireflection cell

The multireflection cell is, amongst others, used for measurements of unstable atmospheric species which are produced in a steady state flow. Since only low average number densities are obtained, a large absorption path is required in order to provide a reasonable absorption for the features of interest. Furthermore, column densities (number density times absorption path length) in the atmosphere, especially for stable species, e.g. H_2O, CO_2, and O_2, can be very large, requiring also large column densities for the laboratory measurements. The large absorption path is realized by a setup applying spherical mirrors, allowing the radiation to pass through the cell several times. The optical setup of the cell mirrors as well as the transfer optics for in- and out-coupling of the radiation from the FT spectrometer was designed by means of a special ray tracing program written at DLR. The cell was optimized for use in the FIR spectral region (10 – 500 cm^{-1}). The maximum absorption path length is 200 m, the base length of the cell 0.8 m and the diameter 0.2 m. Temperatures down to 200 K are achieved by circulating coolant through the double-jacket wall. The cell is unique with respect to its sensitivity for measurement of unstable species in the FIR. Therefore, FIR-FT spectra of species like OH, HO_2, BrO, ClO and Cl_2O_2 could be measured for the first time. It has also been used for H_2O, CH_4, CO, and CO_2.

Coolable short path cells

The short path cell is used for measurements of stable atmospheric species at stratospheric temperatures down to 190 K. The cell exhibits an excellent temperature homogeneity (0.1 K, verified by spectroscopic gas temperature measurements) which is crucial for precision measurements of line strengths and pressure broadening parameters. The absorption path is 0.25 m with an inner diameter of 0.04 m. The window material can be selected according to the required spectral range and chemical stability, e.g. polyethylene for the FIR, or AgCl for the MIR and aggressive gases. The cell body

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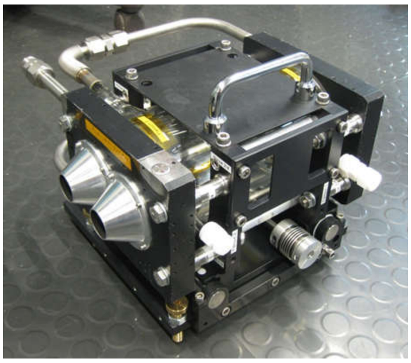

Short path cell

consists of a Duran glass double jacket allowing to flow coolant through the entire length of the cell wall. Windows are mounted to the cell body with good thermal conductivity to further improve temperature homogeneity. The cell has been applied for investigation of the molecules O_3, N_2O_5, $ClONO_2$ for atmospheric remote sensing.
A second short path cell utilizing two window pairs has been developed allowing to cover different spectral regions for the same gas sample. The cell is also mounted inside the sample compartment of the spectrometer and can be move from the outside to select a window pair. It is filled from the outside and flow experiments can be conducted. The cell was applied for $BrONO_2$ and O_3 measurements.

Production of unstable atmospheric compounds

Several atmospheric trace gases are very instable, reactive (mainly radicals) and can neither be bottled nor trapped. Of course, such gaseous compounds cannot be kept in an absorption cell statically but they must be produced in a flow reactor in steady state and pumped through an absorption cell. Between in- and outlet a concentration gradient is achieved invariant in time due to decomposition. The average particle density is low and will decrease with decreasing lifetime. Thus, a multireflection cell with a long absorption path length is required for FT-measurements. In order to obtain line strength data from measured spectra the average particle density is needed. In contrast to stable compounds the particle density cannot be deduced from simple pressure measurements. However, in case of pure rotational transitions located in the FIR the line strength can be calculated from the permanent electric dipole moment of the molecule which is precisely known from Stark measurements. Thus, from FIR measurements the particle density can be derived allowing to obtain line strength data in other spectral regions.
Commonly, the precursors for radicals are atoms of elements like fluorine, chlorine, oxygen or hydrogen which are produced in a microwave discharge in our case. The atomic species are produced in a steady flow reactor with other precursors. The gas flows which are almost entirely inert gas are measured and regulated by means of electronic mass flow controllers. The minimal residence time in the absorption cell is 0.5 s, the total pressure ranges from 5 to 20 hPa. So far, the radicals OH, HO_2, BrO and ClO have been measured, all of these being of atmospheric relevance.

Precision intensity measurements

The extension of the spectroscopic database of atmospheric trace gases requires accurate measurement of spectral intensities and line shapes. Whereas the accurate determination of line positions from FT spectra can be achieved easily, the measurement of intensities is hampered by numerous systematic error sources. These error sources have to be characterised and minimised. Unfortunately, a line intensity standard is not available for the MIR/NIR regions. However, line strengths and thus line intensities can be calculated accurately in case of pure rotational transitions, which can be observed in the FIR region. Thus, the FT measurement of the pure rotational transitions of CO allows accessing and quantifying the systematic error sources. For the first time, line strengths were experimentally determined with a validated accuracy better than 1%. Recently, absolute intensities with accuracies < 0.15% have been obtained for CO_2. This accuracy has not been reached with FT measurements before.

References

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