

REPORT

on

Spectrometer Bruker IFS 120 and 125 HR

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1. Standard Bruker IFS 125 HR

FT-IR absorption spectroscopy is a suitable absolute method for enabling the direct and sensitive detection of the absorption bands of small molecules in a gaseous mixture of unknown composition. The spectrum allows the identification and direct quantification of the detected molecules. Bruker IFS 125 HR apparatus is equipped with MCT (HgCdTe) and InSb nitrogen-cooled semiconductor detectors combined with KBr and CaF₂ beamsplitters. This set up is standardly used in the 680-3500 cm⁻¹ (MCT+KBr) and 1800-5500 cm⁻¹ (InSb+CaF₂) ranges, with a resolution of from 0.002 cm⁻¹ to 0.01 cm⁻¹. 50–300 scans are usually accumulated to obtain reasonable ratio between signal-to-noise and acquisition time. A multipass cell of our own design, with an optical path of 30 m, is used for the measurements.



Fig. 1: The multipass cell together with the spectrometer Bruker IFS 125 HR.

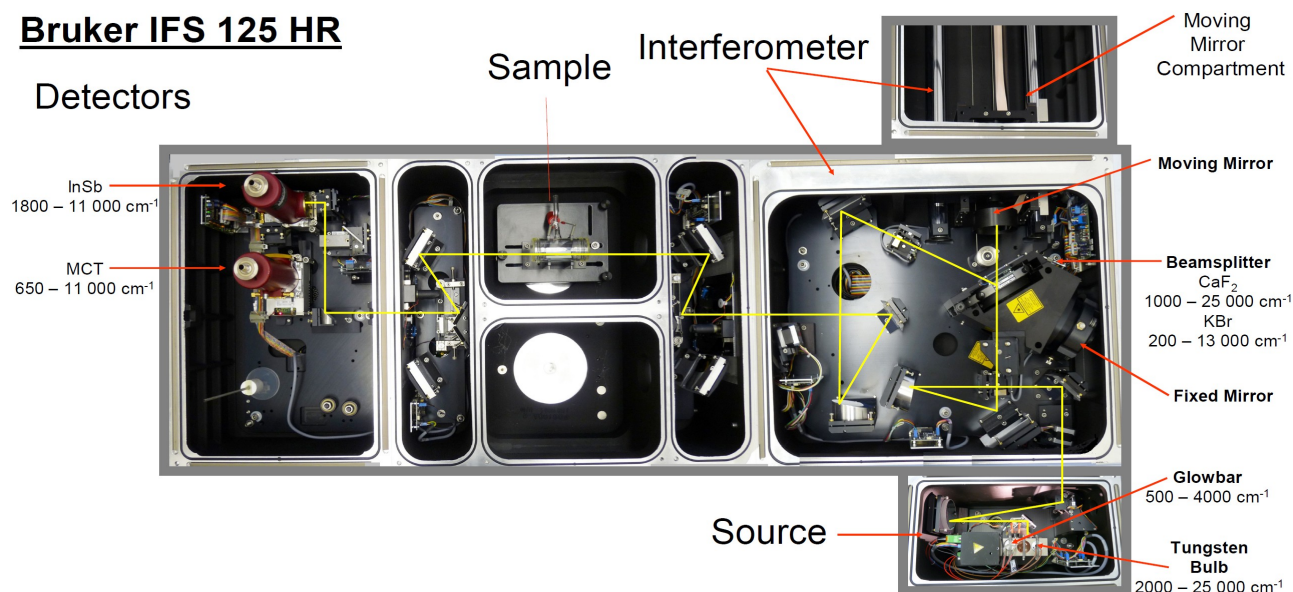


Fig. 2: Bruker IFS 125 HR set-up of optics.

2. Application of the FTIR absorption spectrometry

The absorption set-up of our Bruker IFS 125 HR has been applied to wide range of scientific studies, e.g. qualitative composition of smoke produced by burning of PET, wood, tobacco, fuels (diesel and petrol engines), products of laser spark, discharges, thermal decomposition of molecules (formamide), study of isotopic exchange between TiO₂ and CO₂, HCOOH, N₂O.

The method together with the selected ion flow tube mass spectrometry (SIFT-MS) and gas

chromatography mass spectrometry (GC-MS) have been used for an analysis of *cigarette, cigar and water pipe smoke*. The qualitative and quantitative abundances of detected molecules have been compared based on the sample type. The advantages and disadvantages of the used methods have been discussed in our paper which has already been published in the Czechoslovak Journal of Physics¹. The list of the detected compounds is supplemented by an information about their origin and toxicity.

Additionally, in the next study², samples of *PET material* were combusted in an oven corresponding to the German standard DIN 53 436 at temperatures of 500 °C, 800 °C (in an air flow) and also uncontrolled burning in air. The gaseous products of degradation were analysed using three different analytical methods: high resolution Fourier transform infrared spectroscopy (FTIR), selected ion flow tube mass spectrometry (SIFT-MS) and gas chromatography mass spectrometry (GC-MS). Carbon dioxide, methane, ethylene, acetylene, formaldehyde and acetaldehyde were detected by FTIR. Water, methane, acetaldehyde, ethylene, formaldehyde, methanol, acetone, benzene, terephthalic acid, styrene, ethanol, toluene, xylene, ethylbenzene, naphthalene, biphenyl and phenol concentrations were quantified by SIFT-MS and GC-MS. Additionally, the fumes resulting from combustion were analysed by FTIR which resolves the rotation-vibration structure of the absorption bands of formaldehyde (2779.90 and 2778.48 cm⁻¹) and propane, which was identified from characteristic vibrations of CH₃ groups at 2977.00 and 2962.00 cm⁻¹. The spectra were compared to the reference standards.

In the another study^{3,4} an analysis of the isotopomers was carried out by means of high resolution FTIR spectroscopy. A large-scale plasma was created in *CO-N₂-H₂O gas mixtures* by high-power laser-induced dielectric breakdown. The composition of the mixtures used corresponded to a commentary and/or meteoritic impact into the Earth's early atmosphere. A multiple-centimeter-sized fireball was created by focusing near-infrared laser pulse into the centre of cell. The laser-plasma formation in the mixtures mainly leads to a production of CO₂. The competition of the CO + CO → CO₂ + C and CO + OH → CO₂ + H reactions in the CO₂ production was investigated using ¹⁸O labeled water.

The isotopic composition of the gas phase has been studied in our work⁵ *Oxygen-Isotope Exchange between CO₂ and Solid Ti¹⁸O₂*. In this study the light-induced oxygen-isotope exchange between gaseous CO₂ and solid Ti¹⁸O₂ (anatase) and the spontaneous thermal isotope exchange that takes place between the vacuum-calcined solid Ti¹⁸O₂ and CO₂ were studied by gas-phase high-resolution Fourier transform infrared absorption spectroscopy over a period of several days. The absorption ro-vibrational spectra of all the measured carbon dioxide isotopologues were assigned

and served as the quantification of the time-dependent isotope exchange between the oxygen atoms from the Ti^{18}O_2 solid and the oxygen related to the gaseous CO_2 . The C^{18}O_2 was formed as the dominating final product with a minor content of $\text{C}^{16}\text{O}^{18}\text{O}$. The rate of oxygen-isotope exchange is highly sensitive to the conditions of the titania pretreatment; vacuum-annealed Ti^{18}O_2 at 450°C exhibited a very high spontaneous oxygen exchange activity with gaseous C^{16}O_2 . A mechanism for the $^{18}\text{O}/^{16}\text{O}$ exchange process is discussed at the molecular level. The photocatalytic formation of methane, acetylene and C^{16}O released from the Ti^{18}O_2 surface was observed after irradiation by an excimer laser.

High-resolution FT-IR spectroscopy was also used for the analysis of the products of *formamide dissociation using a high-energy Asterix laser*⁶. In the experiment the detected products of the formamide LIDB dissociation were hydrogen cyanide, ammonia, carbon monoxide, carbon dioxide, nitrous oxide, hydroxylamine and methanol. The molecular dynamics of the process was simulated with the use of a chemical model. The chemistry shared by formamide and the products of its dissociation is discussed with the respect to the formation of biomolecules.

3. Time resolved IFS 120 HR

Time-resolved FT spectroscopy is a wide-spectrum technique used for studying the dynamics of chemical reactions, or the dynamic properties of molecules, radicals and ions in liquid, gas and solid states. The main advantage of TR-FTS lies in obtaining spectra in wide wavenumber intervals. The speed of data acquisition is limited by the duration of the acquisition process and by the band width of the detector. There are basically two methods of obtaining the time-resolved spectra: the continuous scan and the non-continuous, step scan.

A special approach to the time-resolved spectra of phenomena lasting from milliseconds to microseconds is the synchronous scanning FT technique. This method requires the possibility of initiating the reaction in a pulse mode, e.g. using a laser, electric discharge, electron bombardment, a UV discharge lamp, etc. The apparatus carries out a continuous scan and, during the pulse, it reads the signal from the detector corresponding to the position of the mirror and to the time from the beginning of the pulse reaction using the HeNe laser fringe signals generated by the interferometer. This method is called stroboscopic interferometry. After accumulating a sufficient amount of data and scans, the time-shifted interferograms are composed. The time mode is usually from 10 ms to 1 μs .

The continuous scanning principle was the basis for data acquisition by a modified (Bruker IFS

120) spectrometer in our laboratory at the J. Heyrovsky Institute of Physical Chemistry, and a similarly modified spectrometer was used in Okayama (Japan). The data acquisition system can be described as follows:

The position of the traversing mirror of the Michelson interferometer is detected by reading the interference maxima of the HeNe laser emission. The input signal in a cosine function shape is digitally processed into rectangular pulses and becomes the internal standard of the interferometer. The frequency of these rectangular pulses depends on the mirror speed. In the classic measurement mode, the frequency is usually 10 kHz with a pulse duration of 100 μ s. An external processor monitors the beginning of the HeNe laser digital pulse, its order and the zero position of the mirror. During a single pulse, the signal from the detector is read (30 or up to 64 readings), this being the so-called AD trigger. These signals are shifted in time by Δt , where $\Delta t = 1$ or 2, 3 . . . μ s. In this way, a matrix $I(t_k, \delta_i)$ of intensity I in times t_k is acquired for the given optical path difference δ_i (i being the index of the selected optical path difference, from its zero to maximum values). A discharge pulse of variable length can be arbitrarily inserted into the data acquisition process (AD trigger). This process results in 30 to 64 reciprocally time-shifted interferograms.

4. Application of the emission FTIR time resolved spectrometry

Time resolved spectrometry is applied in two different fields in our laboratory: ablation of metals (spectroscopy, theoretical interpretation of the spectra, observation of highly excited atoms) and discharges (spectroscopy, kinetic studies, observation of stable products and unstable radicals or molecular ions). The range of studies is very wide and just several examples are mentioned below.

Time-resolved Fourier transform (FT) spectrometry was used e.g. to study the *dynamics of radical reactions forming the HCN and HNC isomers*⁷ in pulsed glow discharges through vapors of BrCN, acetonitrile (CH₃CN) and formamide (HCONH₂). Stable gaseous products of discharge chemistry were analyzed by selected ion flow tube mass spectrometry (SIFT-MS). Ratios of concentrations of the HNC/HCN isomers obtained using known transition dipole moments of rovibrational cold bands ν_1 were found to be in the range of 2.2-3 %. A kinetic model was used to assess the roles the radical chemistry and ion chemistry play in the formation of these two isomers. Exclusion of the radical reactions from the model resulted in a value of the HNC/HCN ratio two orders of magnitude lower than the experimental results, thus confirming their dominant role. The major process responsible for the formation of the HNC isomer is the reaction of the HCN isomer with the H atoms. The rate constant determined using the kinetic model from the present data for this reaction is $1.13 (\pm 0.2) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$.

Another kinetic study is work focused on the *discharge chemistry of methane*⁸. Time-resolved Fourier transform infrared emission spectroscopy was applied to the study of a pulsed discharge in a He/CH₄ mixture. The dynamics of the formation and decay of acetylene ν_3 (3289 cm⁻¹), methane ν_3 (3019 cm⁻¹) and ν_1 (2917 cm⁻¹), CH radical ground electronic state X²Π_r (2309 cm⁻¹ to 2953 cm⁻¹), C₂ Bernath electronic transition B¹Δ_g - A¹Π_u (3337 cm⁻¹ to 3606 cm⁻¹), molecular hydrogen – emission transitions 5g – 4f and 2p – 2s, atomic hydrogen, and atomic helium were monitored in the 1800–4000 cm⁻¹ region. The time profile of the rotational and vibrational temperature of the CH radical was obtained for a 30 μs time interval during and after the discharge pulse. A kinetic model was used for the study of the chemical dynamics of the formation and decay of the individual fragments and the results from the model were compared to the measured emission spectra.

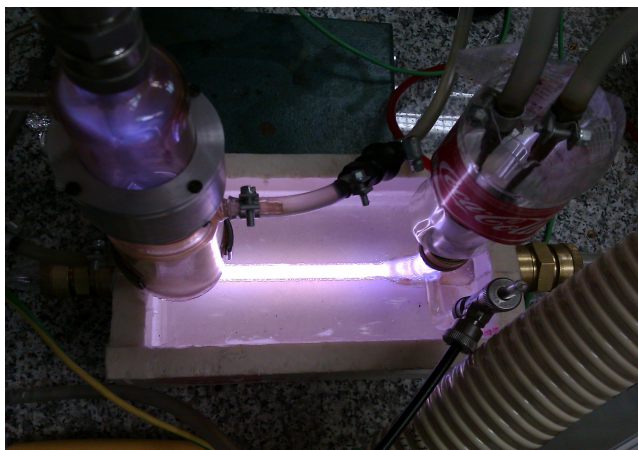


Fig. 3: Glow discharge in formamide+He during the time resolved emission measurement.

The *decomposition of halogenated species CF₃Br and CF₃CHF₂* in the helium discharge plasma⁹ was investigated by the time-resolved high-resolution Fourier transform infrared emission spectroscopy. Contrary to classical pyrolysis we observed a deeper fragmentation of precursors up to atoms and lower molecular species. Excited molecular products CF, CF₂ and C_{F4} achieved the maximal concentration in afterglow. The high concentration of all these species is in agreement with a kinetic model based on radical chemistry. The non-detectable concentration of C_{F3} can be connected with its high reactivity and formation of more stable products, CF₄ and CF₂ by addition or release of fluorine atom, respectively. Other products included HF, HBr, CO and cyano compounds that were produced by secondary reactions with traces of water vapor, atmospheric oxygen and nitrogen present in original industrial samples as impurities.

The ablation studies of metals have been focused on wide range of elements. For example very important metal is Au. Although the Au spectrum has been studied in various spectral domains for several decades, to our knowledge only one experimental study concerning the studied 3- 5 mm IR range is reported. We observed several new strong Au lines in 1800 - 4000 cm⁻¹ domain. The time

decay of the most of strong lines is well described by exponential fitting excepting the 2156.484 cm^{-1} line which demonstrate non-constant decay rate during 30 ms after the laser shot. Some weaker lines demonstrate such a behavior more clearly, their decay is not exponential (and even non-monotonic), so their τ values are estimated in a rough approximation. Such a non-monotonic decay can be due to more complex population kinetics of the atomic Au states in the ablation plasma. We consider most of the observed lines to be due to transitions between the Rydberg $n = 5\dots 10$ states of the valence electron outside the closed-shell $5d^{10}$.

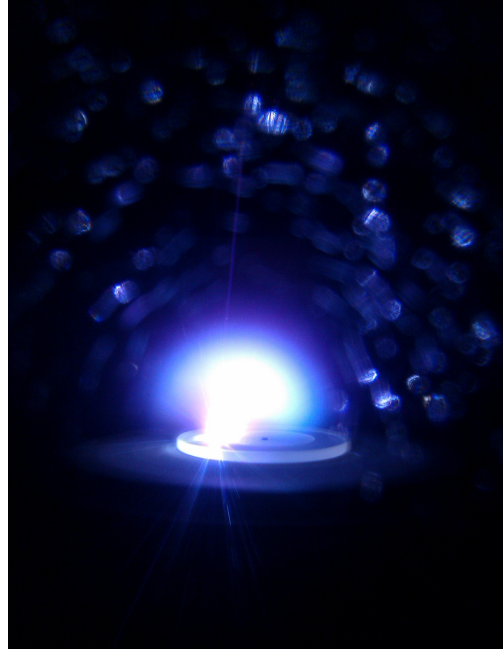


Fig. 4: Ablation plasma formed by the irradiation of RbCl target.

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- 3 Investigation of laser-plasma chemistry in CO-N₂-H₂O mixture using ¹⁸O labeled water. Ferus M, Matulková I, Juha L, Civiš S, *Chemical Physics Letters* 472 (1-3), 14 (2009).
- 4 Oxygen-isotope labeled titania: Ti¹⁸O₂. Kavan L, Zukalová M, Ferus M, Kürti J, Koltai J, Civiš S, *Physical Chemistry Chemical Physics* 13, 11583 (2011).
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- 6 Laser Spark Formamide Decomposition Studied by FT-IR Spectroscopy. Ferus M, Kubelík P, Civiš S, *Journal of Physical Chemistry A* 115, 12132 (2011).
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- 8 The study will be published in the JPC-A in 2012.
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