Impacts of operation condition and fuel type on the chemical composition of soot particles emitted by gasoline and diesel engines

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Context

Ultrafine particles released by internal combustion engines participate to the aerosol loading in dense urban areas subjected to high traffic leading thus to health concerns. Campaigns including simulations and test runs of modern combustion engines offer a powerful tool for the chemical composition determination of particulate emission depending on engine technologies, fuels, operation conditions, and driving cycles.


car particles emission


fog above a Chinese city

Objectives

- Test the effect of conventional/alternative fuels and operation conditions on the chemical composition of particulate emissions (PM);
- Cross-linked analyses using Fourier Transform Infrared (FTIR) spectroscopy and mass spectrometry technique to link functional groups to representative mass fragments;
- Principal component (PCA) and hierarchical clustering (HCA) analyses applied to the mass spectrometry results to outline the subtle composition differences of the exhaust particles produced with different fuels and in various operation conditions.

Sample collection


Diesel **IVECO Tector** engine

- Fuel
  - Diesel (B0)
  - Diesel+30% biodiesel (B30)
  - Biodiesel (FAME, B100)
- Running cycle
  - 1500rpm 30% load (steady-state)
  - Hot WHTC (transient)

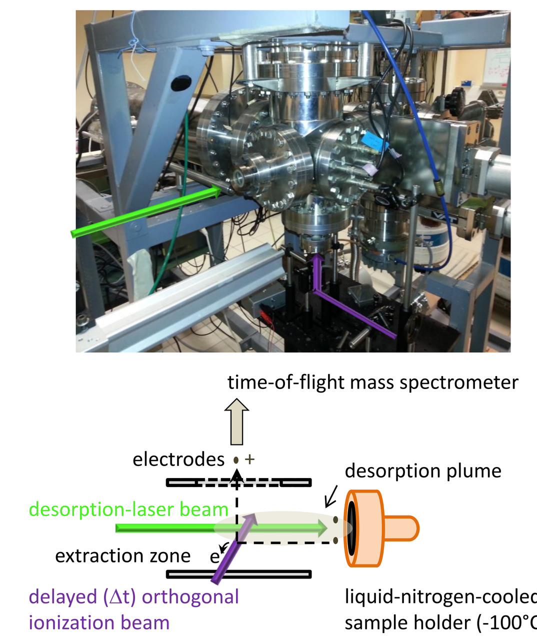

Gasoline **Ford Focus** car - DISI

- Fuel
  - Gasoline (G)
  - Gasoline+15% ethanol (G15%E)
  - Gasoline+ 25 % n-butanol (G25%nB)
- Running cycle
  - Artemis urban
  - Artemis rural
  - Artemis130

Exhaust particles are deposited on quartz paper filters.

Experimental techniques

Surface composition of exhaust particles

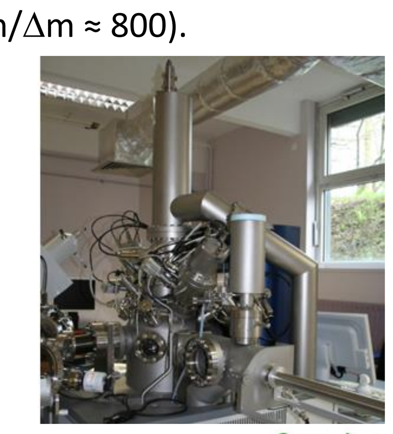


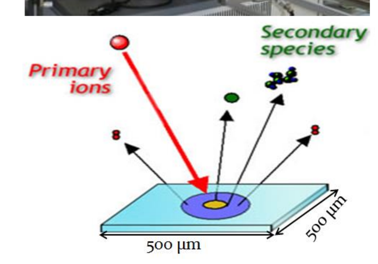
Laser desorption / laser ionization / time-of-flight mass spectrometry (L2MS)

The adsorbed phase of our samples is determined by L2MS. Adsorbed molecules are desorbed by a pulsed laser at 266 or 532 nm, ionized by a second laser at 266 nm (resonant 2-photon ionization – R2PI) or a coherent source at 118 nm (single photon ionization – SPI) and mass-analyzed in the spectrometer ($R = m/\Delta m \approx 800$).

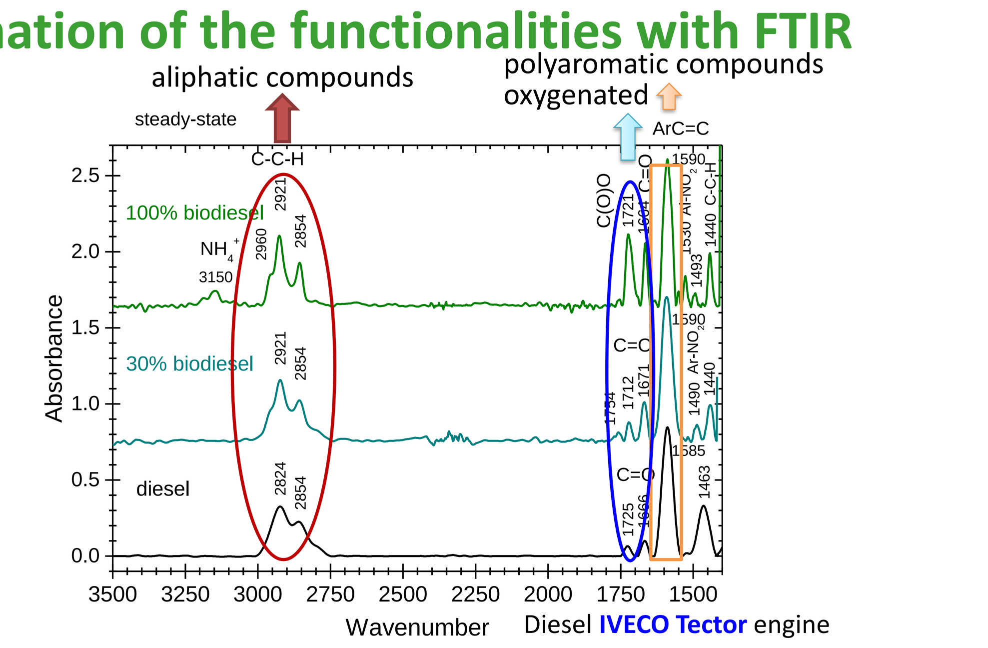
Secondary ion mass spectrometry (SIMS)

The surface can be also probed by a TOF.SIMS[5] instrument (ION-TOF GmbH) at the Regional Platform of Surface Analysis (Lille University). The surface is irradiated by Bi_3^+ ions at 25 keV (1-3 nm penetration depth) inducing the ejection of secondary ions which are mass-analyzed in a spectrometer ($R > 2000$). Positive and negative ions can be detected.





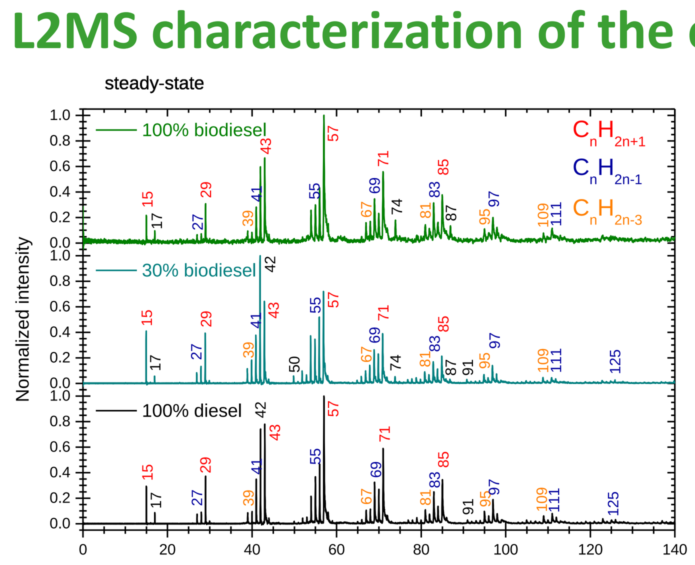
Determination of the functionalities with FTIR



Diesel **IVECO Tector** engine

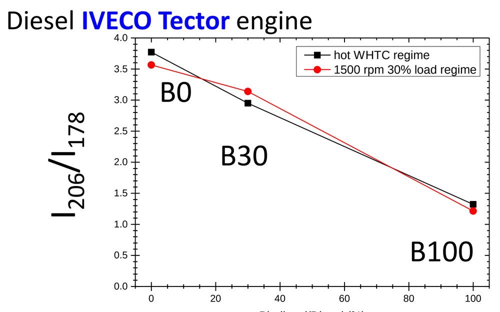
FTIR spectra are dominated by aliphatic and aromatic signatures. Oxygenated bands associated to carbonyl and carboxyl functional groups are increasing with the addition of biodiesel.

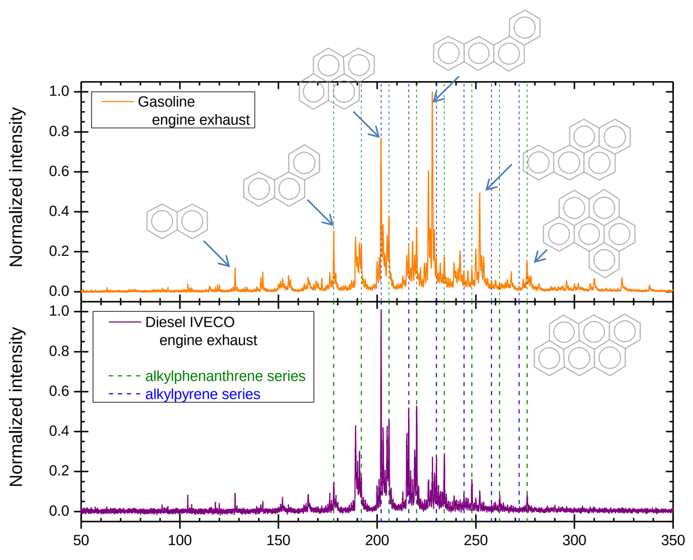
L2MS characterization of the exhaust particles



L2MS spectra with **SPI at 118 nm** are dominated by alkane fragment series. Peaks found at *m/z* 74 and 87 are specific for fragmentation of methyl esters and trace the biodiesel origin of the particles.

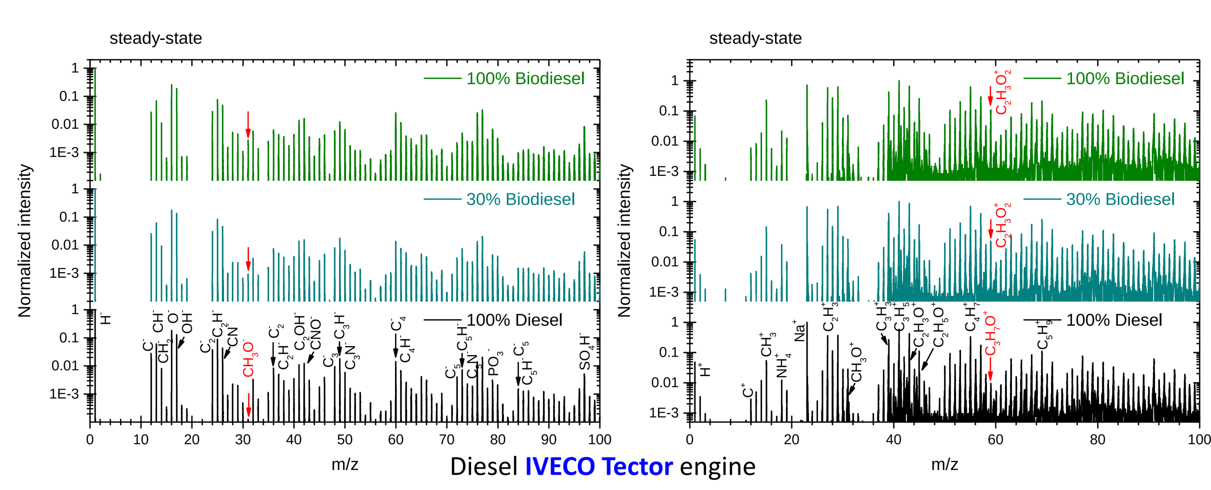
Diesel **IVECO Tector** engine





L2MS spectra with **R2PI at 266 nm** are dominated by polycyclic aromatic hydrocarbons (PAHs) and alkyl-PAHs for gasoline and diesel particles, respectively.
The alkyl-PAHs fraction decreases with biofuel as evidenced by the C2-$C_{14}H_{10}$ to $C_{14}H_{10}$ indicator ratio (I_{206}/I_{178}).

SIMS characterization of the diesel exhaust particles



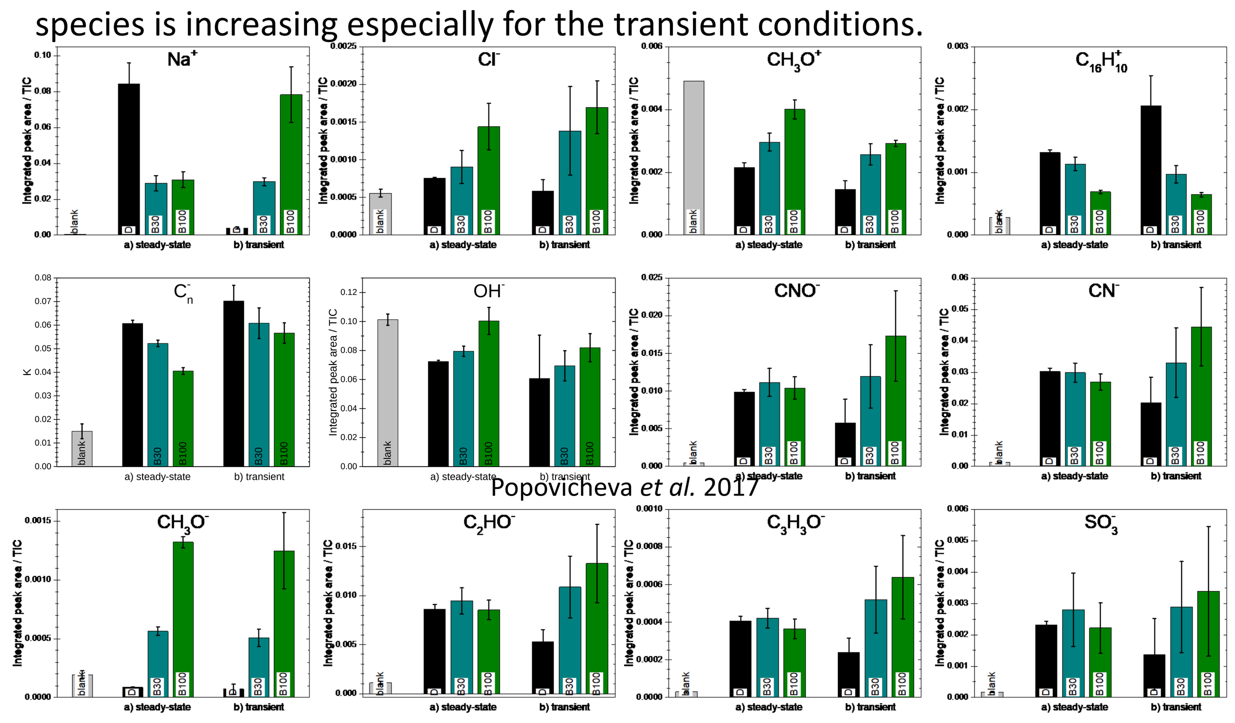
Diesel **IVECO Tector** engine

Negative SIMS spectra are dominated by O^-, OH^-, C_n^- and C_nH^- fragment ions. **Positive SIMS** spectra are characterized by Na^+, $C_nH_m^+$ fragment ions and PAHs. These major species are accompanied by oxygenated and nitrogenized fragments.

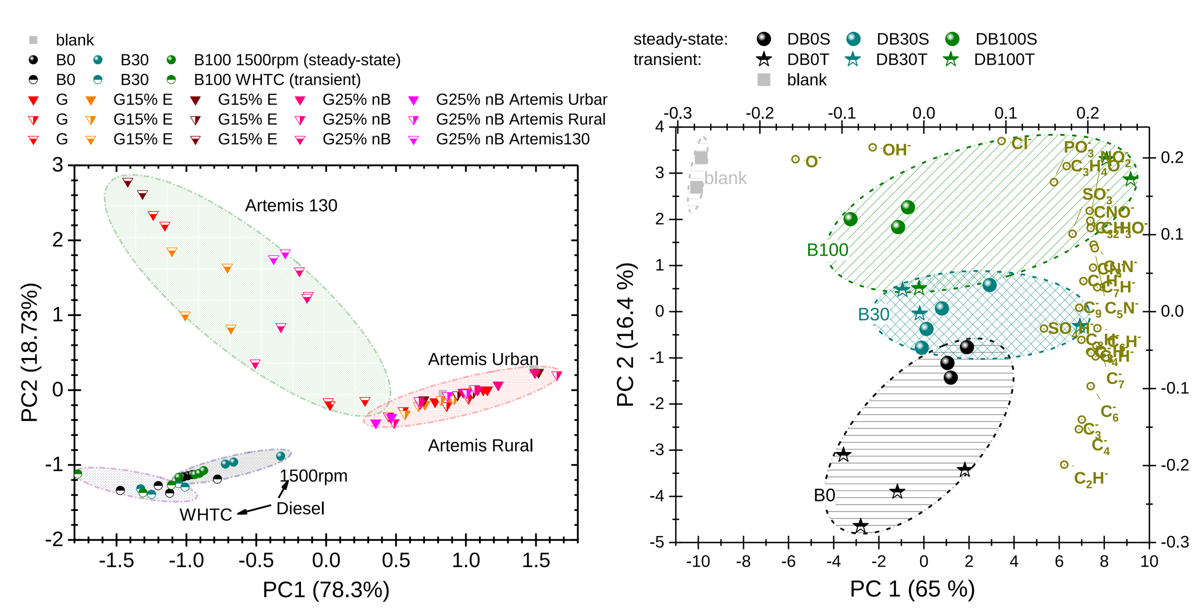
Specific fragments (absent on diesel particles) could be identified for biodiesel soot, especially $C_2H_3O_2^+$ (*m/z* 59) and CH_3O^- (*m/z* 31). $C_2H_3O_2^+$ is associated to methyl esters, acetates or acids. CH_3O^+ and $C_2H_5O^+$ fragments are proposed to be linked to methyl esters or ethers (Scheinmann 2013).

The C_n^- content relative to the total ion count (TIC) is decreasing with the addition of biodiesel. It is proposed to be linked to the elemental carbon (EC) content of the exhaust particles (Pagels *et al.* 2013) and correlates with direct EC measurements.

In the same way, the relative PAH content drop down with the biodiesel addition. In contrast, the relative amount of nitrogenized and oxygenated species is increasing especially for the transient conditions.

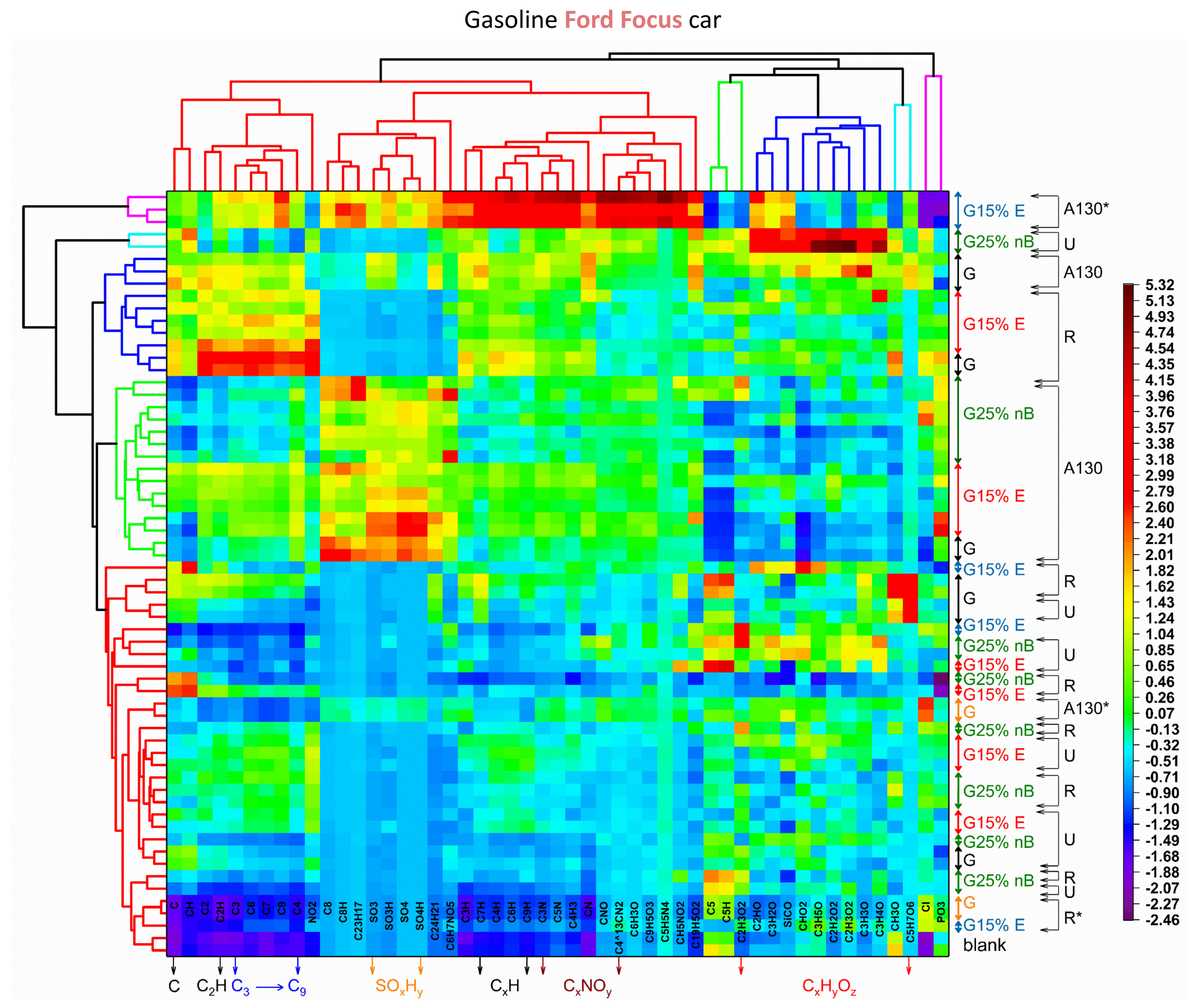


PCA and HCA of the SIMS spectra



PCA and HCA are applied to differentiate the origin of the particles according to the fuels and the operation conditions. It allows to associate spectra having the same spectrometric features and to link them to specific molecules or fragment ions. Heatmap plot with clustering on both samples and mass peaks can help to perform the correlation between sample production conditions and specific chemical compounds.

Gasoline **Ford Focus** car



Ongoing tasks and perspectives

- Development of methods to determine the influence of alternative fuels – **Poster 17 (session 2): L. D. Ngo** – or operating conditions on the surface chemical composition and nanostructure of the particulate emission;
- First step towards the identification of the various intricated combustion sources in dense traffic areas;
- Distinguish, in the context of measurements on vehicle engines (PEMS4Nano, H2020), the different sources of particles (combustion, fuel additives, lubricating oil, mechanical wear, etc.) – **Oral presentation (session 9A): C. Focsa**;
- Use of new laser sources to improve the selectivity and sensitivity of the L2MS technique for ionization (REMPI) and for desorption (infrared OPO) for the detection of specific molecules (aliphatic compounds, oxygenated species, PAH derivatives, PACs, organosulfates);
- Search of correlations between the physical and chemical properties of the soot particles determined by our analysis methods and their role as condensation nuclei as well as their hygroscopic properties (Mermose project, CPER CLIMIBIO, and Labex CaPPA).

Pagels, J., Dutcher, D. D., Stolzenburg, M. R., Mcmurry, P.H., Gälli, M. E., Gross, D. S., Fine-particle emissions from solid biofuel combustion studied with single-particle mass spectrometry: Identification of markers for organics, soot, and ash components, *Journal of Geophysical Research Atmospheres* **118**, 859-870 (2013)
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Scheinmann, F., An Introduction to Spectroscopic Methods for the Identification of Organic Compounds: Mass Spectrometry, Ultraviolet Spectroscopy, Electron Spin Resonance Spectroscopy, Nuclear Magnetic Resonance Spectroscopy (Recent Developments), Use of Various Spectral Methods Together, and Documentation of Molecular Spectra, Elsevier, 22 Oct. 2013