Operando Modulation-Excitation Polarisation-Modulation Infrared Reflection-Absorption Spectroscopy: " Towards Maximised Extraction of Information from IR Spectra "

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Operando spectroscopy is an analytical methodology wherein the spectroscopic analysis of materials accompanies with simultaneous measurement of activity and selectivity during chemical reactions. Since Miguel Bañares coined the term "*operando*" in 2002, its application has made a rapid advance in heterogeneous catalysis. Most of the reported techniques rely on two separated instruments to realise *operando* set-ups, e.g. X-ray or vibrational spectroscopy for materials characterisation and mass spectroscopy for gas-phase analysis. I herein present the first & sole example of a single set-up operando technique by polarisation-modulation IR reflection-absorption spectroscopy (PM-IRRAS) using *p*- and *s*-polarisations and reflectivities (R_p and R_s). R_p + R_s (or R_s) provides spectra of gas-phase components while R_p - R_s allows selective extraction of spectra originating from adsorbed species on catalyst surfaces.

Modulation excitation spectroscopy (MES) was also combined with PM-IRRAS. MES operates under unsteady-state conditions forced by periodic perturbation of the system by changing an external parameter such as concentration, temperature or pH. This transient method enables selective detection of surface molecules responding to an external perturbation, enhancement of the signal-to-noise (S/N) ratio, time-resolution and extraction of kinetic information by phase sensitive detection (PSD).

