

# Identification, thermodynamics and kinetics of surface processes by IR spectroscopy and multivariate analyses

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Despite their prominent role as characterization tools in the fields of adsorption and catalysis, *in situ* / *operando* IR spectroscopies are still most often limited to qualitative investigations or, when quantification is attempted, to determining the number of surface species or sites. Yet, under appropriate experimental conditions, this technique can also provide access to key physicochemical parameters governing the elementary steps of catalytic processes.

Through selected examples, this lecture will highlight the state of the art and the current challenges associated with the quantitative spectroscopic investigation of diffusion, adsorption, and surface reactions occurring on complex heterogeneous surfaces, such as those of working catalysts.

Technologically, *in situ* and *operando* IR spectroscopy are now well established and generally allow the acquisition of high-quality spectra, with excellent spectral and temporal resolution under realistic temperature and environmental conditions. When only spectroscopically distinct surface species are present, and when experimental conditions are carefully optimized, a classical analysis of spectral evolution—for example, monitoring band intensity or area as a function of time, pressure, or contact time—can yield direct access to internal diffusion coefficients [1], adsorption thermodynamics, or intrinsic surface kinetics [2].

However, for most catalytic systems, such a straightforward analysis is not applicable because of the coexistence of multiple adsorbed species, whose spectra and/or concentration profiles are often strongly correlated. In many important cases—particularly for diffusion and adsorption processes—the concentration profiles of several adsorbed species can be approximated by two-parameter models, such as the Langmuir isotherm or fractional uptake curves over time. Under these conditions, the application of the inversion method (2D-IRIS) enables the determination of the distribution of diffusion or adsorption constants, together with the spectral signatures of the corresponding species [3,4].

When the concentration profiles become more complex, a more general methodological framework based on exploratory multivariate analysis and multivariate curve resolutions can be employed. This approach provides both spectra and concentration profiles while accommodating a wide range of constraints—from soft constraints [5,6], to the implementation of hard constraints such as explicit kinetic models [7].

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