Operando Spectroscopy of Catalysts
Exploiting Multi-technique and Modulated Excitation Approaches

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Abstract: Operando spectroscopy combines the in situ determination of material structure by spectroscopy/diffraction techniques with the measurement of material performance, which is conversion/selectivity in the field of heterogeneous catalysis. A central question in operando spectroscopy is whether the signatures visible by the characterization methods are responsible for catalyst performance. Individual analytical methods can provide useful information, but their combination (multi-technique approach) is essential to obtain a complete perspective on molecular reaction mechanisms. This approach must be coupled to experimental protocols and mathematical algorithms enabling the ability to disentangle the contribution of the active structure from the unresponsive one. Here, we report an account with examples from our own research activities in catalysis science.

Keywords: Active species · Liquid phase · N₂O decomposition · Reaction mechanism · SCR

1. Introduction
Operando spectroscopy combines the in situ capability of many modern spectroscopy, diffraction and, lately, microscopy techniques to interrogate the structure of materials in defined environments with the simultaneous measurement of their performance using online analytics.1,11 “It is critical that the activity and kinetic data obtained in an operando reactor agree with those obtained in the corresponding conventional reactor” state Guerrero-Perez and Barnes.2 In a stricter definition, operando spectroscopy studies materials where they operate in reality, which in the case of heterogeneous catalysts is represented by the reactor in which chemical processes take place. While a part of the operando community tackles the key issue of approaching as close as possible reactor conditions in operando experiments, the multi-technique...
approach of the Applied Catalysis and Spectroscopy (ACS) group at the Paul Scherrer Institut (PSI) seeks to obtain the most diverse information on the possible structure of the active phase in catalytic materials.

In situ / operando spectroscopic tools have undoubtedly improved our understanding of chemical reactions. The information delivered by a single technique is, however, generally insufficient to draw a full and reliable description of the process under investigation. Each technique owns the potential to probe specific features (e.g. crystal structure, adsorbed species, electron transfer processes) but may also suffer from characteristic limitations or require special infrastructure. Furthermore, several elementary steps can take place simultaneously but each of them can only be monitored by a single specific technique. The combination of various characterization methods is thus fundamental to derive complementary information and detailed molecular understanding of the process. To this end, we have developed setups that can be easily moved or transported and allow the repetition of the experiments using various techniques and in different places. The setups incorporate the same spectroscopic cell in order to avoid ambiguities introduced by the sample environment. The multi-technique approach undertaken by others, especially at synchrotron facilities, to by-pass this important issue involves the simultaneous measurement of the material structure using two or more techniques in a single experiment. Our approach is more flexible especially when otherwise mutually excluding techniques are used.

Following our approach, we have also developed and systematically used a cell suitable for both gas and liquid phase environments, though further engineering development is required for example to include experiments at elevated pressure. This cell is extremely versatile and was used for X-ray absorption spectroscopy (XAS), infrared spectroscopy in diffuse reflectance (DRIR), X-ray diffraction (XRD), X-ray emission (XES), high-energy resolution off-resonant X-ray spectroscopy (HEROS) and diffuse reflectance ultraviolet-visible spectroscopy (DRUV). It is also intrinsically suitable for experiments in liquid environments and we have pushed this development to the point where using it for DRIFTS to analyze catalysts in contact with liquids has become possible. This should have impact outside the field of heterogeneous catalysis as well. For vibrational spectroscopy (infrared and Raman) and electron spectroscopy (UV), we can use a dedicated cell with a reduced dead volume but with identical design as commercial diffuse reflectance cells to exploit their optimal light throughput.

For obvious reasons, in the case of X-ray photoelectron spectroscopy (XPS) or electron paramagnetic resonance (EPR) the sample environment does not allow for the same spectroscopy cell that we would use in vibrational spectroscopy or XAS. In this case, a second important part of our approach is to exploit systematically single transients or repeated transients according to the (concentration) modulated excitation (ME) scheme to capture structural changes at sufficiently high time resolution to demonstrate reversibility of the experiment and thus to improve its signal-to-noise ratio by averaging several cycles. It thus becomes possible to identify the most active components in a system by obtaining selective information on the portion of the sample that is driven away from equilibrium in response to the single or repeated transient(s). We use phase sensitive detection (PSD) as well as multivariate curve resolution (MCR) to analyze these data and extract responses of species stimulated by the transients and kinetics of spectral components.

The aim of this approach is to uncover the contribution of species that are otherwise overwhelmed by static signals of the unresponsive components of the material. To adhere to the operando definition, the confirmation that these species are catalytically relevant must be then obtained from comparison with reaction rates. In this contribution, we give a survey of our recent activities aiming to combine information from different techniques and to use systematically experiments under dynamic conditions to understand the behavior of catalytic materials.

2. Modulated Excitation (ME)

Many spectroscopic methods used in materials and catalysis research are sensitive to the bulk structure of the material. However, adsorption and reaction processes occur generally at the surface of the material and are sensitive only to the outermost atomic layers. In order to obtain structure-activity relationships between relevant structural motifs and reaction rates it is mandatory to monitor this portion of the material with increased spectral sensitivity and time resolution to be able to follow precisely its changes and the corresponding reaction rate. We have shown that the sensitivity of XRD, a typical long-range order technique sensitive to structure-activity relationships, can be improved using the ME approach introduced first by U. P. Fringeli for biochemical interfaces and then by Bürgi et al. in catalysis. With ME,

![Diagram](image-url)

Fig. 1. Modulated excitation methodology with phase sensitive detection (PSD) and multivariate curve resolution (MCR) algorithms to enhance sensitivity to the presence as well as to the kinetics of signals that are otherwise challenging to observe. The approach is independent of spectroscopy/diffraction technique used. The case of XANES spectra is shown in the scheme.
the minor fraction of the material sampled by XRD that changes within seconds in response to alternating reducing and oxidizing conditions was emphasized providing information beyond what is achievable with static experiments.

The principle of concentration ME is represented in Fig. 1 showing the typical setup for gas phase experiments that we use. In this arrangement, the gas environment is periodically changed by switching between feeds A and B, typically at equal intervals. For complex mixtures, component A is introduced in the main gas stream C containing other components. Feed B contains only an inert gas and is used for flow compensation purposes. During the sequence of alternate changes of the gas environment, the sample is continuously exposed to the selected radiation and spectra are collected with high time resolution to precisely follow structural modifications induced by the variable environment.

This time-resolved data is averaged into one averaged cycle and further subjected to PSD to extract the phase-resolved data. This approach was already reported in this journal,\[23\] but we have since contributed to expand its use to techniques other than IR spectroscopy.\[6–9,14,17b,21\] The phase-resolved data contain only the signals that respond to the external stimulus. Because noise present in the data bears no relation to the phase of the demodulated spectra, the noise as well as other static signals/components are strongly suppressed. We have attempted a didactic description of the meaning of phase-resolved spectra and their interpretation\[16c\] that complements the very instructive work by Urakawa et al.\[16a\] Phase-resolved spectra provide access to kinetic information that is not clearly visible from the corresponding time-resolved data in a classic approach (e.g. by plotting signal intensity against time) and allow detecting signals changing quickly during the modulation sequence.\[22\] This additional kinetic insight is revealed by the sign of the signals of phase-resolved data.\[16c\]

ME data can also be treated by MCR algorithms to extract spectral components and their temporal behavior directly from the time-resolved data (Fig. 1).\[23\] This approach is advantageous because it determines the spectra of the major components present within the system of interest and provides their relative concentrations. It thus delivers more direct information on the structural changes occurring during the ME experiment. The ME-MCR combination is ideal because the modulation sequence defines the mathematical boundaries within which MCR can explore the experimental data. We recently used this approach to investigate elementary steps of the selective catalytic reduction (SCR) of nitric oxide (NO) on Cu–SSZ-13\[23\] and the reaction mechanism of liquid phase dimethyl carbonate synthesis from methanol and CO\(_2\) on ZrO\(_2\).\[23\]

3. Combined DRIFTS-UV-Raman-MS

SCR using NH\(_3\) is the state-of-the-art technology to clean flue gases of mobile and stationary stations.\[26\] Lai et al.\[27\] summarized the key mechanistic aspects of this reaction on V-based catalysts. We have used various spectroscopic methods to study relevant catalytic systems and have demonstrated the level of information that can be obtained by combining the information from each method and the use of the ME approach. Here, we report the benefits of this approach in the case of V\(_2\)O\(_5\)/TiO\(_2\)-type catalysts. The need for transient and ME experiments originates from the observation that IR spectra recorded during SCR on V\(_2\)O\(_5\)/WO\(_3\)-TiO\(_2\) at steady-state deliver information only on species that are static in the given experimental conditions but do not provide useful information with respect to their involvement in the catalytic cycle. It is well known that the IR spectra carry the vibrational modes of NH\(_3\) coordinated in molecular form on Lewis acid sites (LAS) as well as in protonated form (NH\(_4^+\)) on Brønsted acid sites (BAS) in addition to functional groups present at the catalyst surface. At reaction equilibrium, no information on adsorbed NO can be obtained because the reaction follows an Eley–Rideal mechanism with respect to NH\(_3\) and NO.\[28\]

The critical role of adsorbed NH\(_3\) can be better assessed when the catalyst is forced away from equilibrium reaction conditions for some time. We have shown that when adsorbed NH\(_3\) is consumed by dosing of NO, NH\(_3\), coordinated to LAS such as vanadyl species (V=O) reacts prior to NH\(_4^+\) ions even in presence of 2 vol% H\(_2\)O on V\(_2\)O\(_5\)/WO\(_3\)-TiO\(_2\).\[29\] This is observed in Fig. 2a as a fast depletion of the corresponding signal at ca. 1607 cm\(^{-1}\) in the diffuse reflectance IR spectra (DRIFTS) and the evolution of the produced water in the mass spectrometric (MS) data. Other authors have reported comparable reaction rates of the two species on the same type of catalysts, with a preference of NH\(_4^+\) over NO.\[30\]

We have used various spectroscopic methods to study relevant catalytic systems and have demonstrated the level of information achievable with PSD. ‘int.’ stands for the nitramide intermediate.

![Fig. 2. SCR on V\(_2\)O\(_5\)/WO\(_3\)-TiO\(_2\). (a) Temporal evolution of signals corresponding to NH\(_3\) bound to LAS (green) and BAS (red) in the DRIFTS spectra, of the d-d transition at 700 nm indicative of \(\nu^{\pi}\) in the DRUV spectra and the online mass spectrometry data of water (m/z = 19) and NO (m/z = 30). Adapted from ref. [29] with permission from Wiley. (b) Time-resolved spectra obtained in a modulated excitation experiment with NO pulsing in NH\(_3\)/O\(_2\) and representative phase-resolved spectrum (red) demonstrating the level of information achievable with PSD. ‘int.’ stands for the nitramide intermediate.](image-url)
The conclusions obtained from DRIFTS and DRUV were further substantiated by experiments performed using Raman spectroscopy on V_2O_5/TiO_2. Raman spectroscopy records also the vibrational signature of the catalyst.\textsuperscript{[21b]} Despite the different static conditions in various gas environments (O\textsubscript{2}, NH\textsubscript{3} + O\textsubscript{2}, SCR, etc.), the spectra of the catalyst contain a distribution of signals related to the numerous vanadyl groups present. When the SCR reaction is repeatedly switched on and off by sequences of NH\textsubscript{3} pulses, only the Raman signal of specific coordinatively unsaturated vanadyl groups (1031 cm\textsuperscript{-1}) is reversibly perturbed.

Most importantly for the purpose of the operando approach, the intensity of this signal in the PSD data of ME experiments performed at increasing temperature correlates with the reaction rate of SCR measured in the catalytic reactor, confirming that adsorbed NH\textsubscript{3} on LAS in the form of V=O reacts with NO.\textsuperscript{[21b]} This species must then correspond to the species observed by DRIFTS on V_2O_5/WO_3/TiO_2.

The phase-resolved Raman spectra also confirmed that TiO_2 is involved in the exchange of NH\textsubscript{3} with the active sites as the scattering power of the sample changes during the ME experiment.\textsuperscript{[33]} Therefore, Raman spectroscopy confirmed the DRIFTS data with respect to the role of adsorbed NH\textsubscript{3} as molecular storage, despite the different composition of the catalyst.\textsuperscript{[33]}

These experiments show that the combination of spectroscopic techniques together with ME improves our understanding of the reaction mechanism and surface processes as well as to access kinetic information that would remain hidden using a classic experimental approach.

### 4. Combined XAS-EPR-DRIFTS-MS

The usefulness of the multi-technique approach is further showcased for the case of N\textsubscript{2}O activation and decomposition over a Fe-exchanged zeolite catalyst (Fe-FER) that was subjected to periodic exposure to 1000 ppm N\textsubscript{2}O/Ar at 400 °C while recording time-resolved XAS, EPR and DRIFTS spectra in independent but otherwise identical experiments. These series of raw time-resolved spectra were averaged and subjected to PSD to emphasize the contribution of the dynamic (i.e. active) species while suppressing the parts of the spectrum not affected by the perturbation (i.e. spectator species and noise). By using the same equipment and experimental conditions, we were able to monitor the working catalyst under reproducible conditions and thus, merge the results to construct a rationale of N\textsubscript{2}O activation and decomposition.

The averaged operando time-resolved X-ray absorption near edge structure (XANES) spectra measured at beamline SuperXAS of the Swiss Light Source (SLS; Fig. 3a) are mostly static, thus indicating that only a minor fraction of the Fe species is reversibly perturbed by N\textsubscript{2}O. In presence of N\textsubscript{2}O, the absorption edge shifts to higher energy and simultaneously a spectral component is consumed in the rising edge region. This shift occurred because of the intensity loss at 7125 eV (Fig. 3b), evident in the phase-resolved data that we can associate with an Fe\textsuperscript{3+}→Fe\textsuperscript{4+} oxidation promoted by N\textsubscript{2}O.\textsuperscript{[33]} Concurrently, the loss of the spectral feature at 7120 eV suggests that these responsive Fe\textsuperscript{2+} sites possess a distorted square-planar geometry.\textsuperscript{[33]}

This electronic and geometrical response is corroborated by the asymmetric evolution of the pre-edge components (7112 and 7115 eV) indicating that during N\textsubscript{2}O addition the responsive Fe\textsuperscript{2+} sites are consumed i) by undergoing oxidation to Fe\textsuperscript{3+}, ii) because their square-planar structure is distorted towards a less centro-symmetrical coordination in the Fe\textsuperscript{4+} state.\textsuperscript{[33]} This likely occurs upon O-N\textsubscript{2} bond cleavage leaving the O atom on the reduced Fe center during N\textsubscript{2}O activation.\textsuperscript{[34]}

The XANES data is limited by the bulk nature of the technique and the dominant signal of unresponsive oligomeric Fe species. The same experiment was thus repeated using operando EPR to obtain site selective information (Fig. 3c). Being highly sensitive to oxidation state, ligand field and coordination geometry of transition metal ions, EPR provides unique capabilities to disentangle the reactivity among different redox centers in the same material.\textsuperscript{[35]} Despite the heterogeneous Fe speciation comprising isolated Fe species in different cationic environments (Fe\textsuperscript{3+} and Fe\textsuperscript{2+}), oligomeric Fe\textsubscript{3+} (OH)\textsubscript{2} moieties as well as bulk Fe\textsubscript{3+} agglomerates (Fe\textsubscript{3+}nm),\textsuperscript{[36]} the phase-resolved EPR spectra (Fig. 3d) clearly indicate that only Fe\textsubscript{3+} species are reversibly perturbed by the N\textsubscript{2}O pulses. By combining the datasets of the two spectroscopic techniques, the geometry changes observed by XANES can be associated with mononuclear Fe centers in β-cationic position, i.e. a planar 6-membered ring positioned in the FER cavity.\textsuperscript{[37]} The operando EPR data also allowed to strengthen the geometrical information derived from XANES. The reduced 2+ form of Fe\textsuperscript{3+} favors a square-planar geometry\textsuperscript{[38]} and its EPR-active Fe\textsuperscript{3+} square-planar counterpart, supposedly formed upon O-N\textsubscript{2} bond cleavage, exhibits transitions at effective factors of g ~ 6.\textsuperscript{[39]}

The corresponding DRIFTS data (not shown) provide the missing molecular aspect: the presence of the ν\textsubscript{3}\textsuperscript{2} vibrational mode at 3649 cm\textsuperscript{-1} reveals that the activated form of Fe\textsuperscript{3+} is Fe\textsuperscript{3+}-OH. To close the redox cycle, Fe\textsuperscript{3+}-OH reduces to Fe\textsuperscript{2+} in N\textsubscript{2}O-free conditions and is accompanied by desorption of O\textsubscript{2} and water from the catalyst surface evidenced by the on-line MS (not shown).

Precise structural information on the molecular nature, the oxidation state and the environment of active Fe sites was possible only by alloying the evidence from XAS, EPR and DRIFTS experiments. Each technique delivers key information, but individually they do not allow a complete description of the underlying reaction mechanism to be obtained.

### 5. Liquid Phase Reduction of Supported PdO

We use the same multi-technique approach to study also heterogeneous catalysts in liquid environments. For example, we have recently followed the reduction of supported PdO in cyclohexane and the behavior of the reduced catalyst in furfural hydrogenation in 2-propanol.\textsuperscript{[11b, 40]} Identical XANES (beamline SuperXAS of SLS) and high energy XRD (HE-XRD, beamline ID15A of ESRF) experiments with 5 wt% PdO/Al\textsubscript{2}O\textsubscript{3} using our plug flow-like cell\textsuperscript{[4]} revealed that PdO reduction proceeds in two steps, one slower delivering metallic Pd atoms and one faster transforming...
these into Pd hydrides. Differential XRD shows the disappearance of PdO reflections of this commercial Pd/Al₂O₃ (ca. 4 nm particles determined by electron microscopy) and the appearance of reflections at lower angles than expected from reference patterns of metallic Pd. This behavior is associated with the expansion of the Pd lattice due to formation of a hydride phase that can be quantified as PdHₓ (red). Also XAS is capable of providing quantitative information on this process. The high time resolution used to record XAS spectra (0.5 s) enabled us to propose that formation of metallic Pd particles by reduction of PdO follows a nucleation mechanism. From a kinetic perspective, formation of the hydride is characterized by a shrinking core-type mechanism as a result of the fast formation of the hydride phase from the metal nanoparticles (11b).

The two techniques differ in the type of information they deliver but are complementary. Because of the small particles, time-resolved XAS can capture the electronic aspect of the reduction process from the very first moment, while XRD delivers quantitative information once sufficient long range order has been attained within the reduced species.

The Pd hydrides prepared by reduction of PdO/Al₂O₃ can be used to study liquid-phase catalyzed reactions such as furfural hydrogenation (40). Admitting an H₂-saturated 2-propanol solution of furfural to the catalyst at ambient pressure induces the quick consumption of the hydride phase as indicated by the time-resolved XANES data (Fig. 4a). The GC analysis of this operando experiment showed that furfural conversion occurs but also that furan, the product of furfural decarboxylation, is the dominant product. The question then arises why in the presence of furfural and H₂, the hydride phase is consumed completely. Identical IR spectroscopy in attenuated total reflection mode (ATR-IR) using a different cell revealed that CO adsorption on Pd is observed as soon as furfural is admitted to the catalyst as a result of furfural decarboxylation to furan and CO (Fig. 4b). However, CO adsorption does not perturb the hydride phase when it is carried out in the absence of furfural. The hydride phase is also stable from an extended X-ray absorption fine structure (EXAFS) perspective during cyclohexene hydrogenation. MCR analysis of the XAS spectra of Fig. 4a reveals that the hydride phase disappears via a Pd° intermediate and that a third species forms, whose spectrum resembles that of a carbide-like phase (41). Together with the observation that signals of adsorbed CO detected in the operando ATR-IR spectra during furfural hydrogenation differ from those obtained during a CO adsorption experiment (Fig. 4b), we concluded that an adsorbate layer is formed in presence of furfural. This layer contains adsorbed CO as well as, probably, hydrocarbon fragments and does not allow efficient regeneration of the hydride phase causing its rapid consumption. In contrast, cyclohexene hydrogenation appears to proceed efficiently using the surface hydrogen atoms without depletion of the Pd hydride phase.

In collaboration with the ESRF, the University of Torino (Italy) and Chimet S.p.A., we are currently studying the reduction of Pd- and Pt-based catalysts in the presence of various reducing agents and also expanding our multi-technique approach to time-resolved pair distribution function (PDF) (42) because of its ability to measure contributions from different components of the material (e.g. metal nanoparticles, support) simultaneously and in real space, which is ideally complementary to XAS.

6. Current Case Studies Based on a Multi-technique Approach

In our most recent efforts, we have combined IR and HE-XRD measurements to follow processes in gas (catalysis) and liquid phase (materials synthesis).

Due to the desire to produce synthetic aviation fuels through sustainable routes, we are studying molecular aspects of the methanol-to-olefins (MTO) process that is catalyzed by acidic materials such as zeolites (43). Isotopic 13CH₃OH/12CH₃OH switch experiments have played a key role to understand the origin of different olefinic products in this reaction (44). This type of experiment reflects our approach to study materials under transient conditions. Thus, we are using our multi-technique approach together with a transient operando methodology similar to ME and our plug flow-like cell (45) connected to an on-line gas-chromatograph to study the response of zeolite catalysts during methanol pulses. DRIFTS is the analytical tool of choice to follow the accumulation of hydrocarbon species within the pores of different zeolite topologies. The experimental protocol entails short methanol pulses alternated with longer periods of inert gas flow (Fig. 5a). This has two main advantages. Firstly, it allows exposure to the strongly chemisorbed species that are retained by the zeolite and that are essential for the catalytic activity. In IR spectroscopy, their observation is hampered by Fermi resonance between the OH groups of methanol and the hydroxyl groups of the zeolite. In this ME experiment, demodulation becomes challenging because the phase-resolved data would be dominated by these strong signals in response to the methanol pulses. By removing adsorbed methanol by the inert gas flow, we are able to resolve the active hydrocarbon centers. Secondly, we are able to follow the initial phase of the process, before steady-state activity is reached, demonstrating that accumulation of certain species correlates with the initial olefins formation, hence showing the importance of an early formation of a pool of active sites.

The same approach is used to study with sub-second time resolution changes in catalyst structure that reflect the formation of the hydrocarbon species by HE-XRD at beamline ID15A of ESRF (Fig. 5a). For these experiments, the same setup and spectroscopy cell were used in order to reproduce the pulse sequence used in the DRIFTS experiments. A partially reversible expansion and contraction of unit cell volume was observed in each CH₃OH/Ar cycle for different zeolites. This describes the ‘breathing’ and the elastic behavior of the zeolite framework. We also found that the zeolite framework responds to the stimulus in a way that is dependent on the crystallographic direction. Our working hypothesis is that the different activity and stability of zeolite frameworks depends also on their propensity to deform as a result of formation of organic intermediates.
In liquid phase studies, attention must be paid to the selection of a suitable IR technique to avoid signal saturation by the bulk liquid while maintaining sufficient signal from the solutes. We typically use ATR-IR spectroscopy because it intrinsically features low penetration depth and facile implementation in different setups owing to a variety of internal reflection element (IRE) materials and designs. We are using a custom-made batch reactor ATR-IR cell of 25 mL equipped with a ZnSe (30°) IRE at its bottom (Fig. 5b) to monitor the green synthesis process of metal organic frameworks (MOF) in aqueous phase at ambient temperature. For the HE-XRD measurements at beamline ID15A of ESRF, the cell is supplemented by a recirculating sampling loop that allows passing the synchrotron X-ray beam through the reaction mixture outside of the large ATR-IR cell. In principle, even simultaneous IR and XRD/total scattering data collection is feasible in case an IR spectrometer is available at the beamline.

The synthesis proceeds rapidly under the selected conditions and yields a highly crystalline material in 5-10 min. Despite the fast process, we were able to obtain IR data at a time resolution of 1.5 s and HE-XRD data at 50 ms. The ATR-IR spectra reveal the formation of a molecular intermediate and capture crystal nucleation and growth during the synthesis process. The width of the v(C=C) peak of the organic linker strongly correlates with the probability of nucleation as determined by modelling the in situ XRD with a crystal formation and growth model. Therefore, we have shown that we can monitor the evolution of crystallite sizes by IR spectroscopy from the knowledge of the band width and can track the reaction progress in a facile manner.

7. Conclusions

We have used a twofold approach to understand the structure of active sites in heterogeneous catalysts under reaction conditions. Different spectroscopic and diffraction techniques deliver information from different perspectives of material structure and their combination in a multi-technique approach is key to obtain a complete picture. Because catalysis is a surface process, we also need to isolate the information from the portion of the material that is actually responsible for the catalysis. Here, we have shown case studies from our own research topics mainly on catalysis for exhaust gas after-treatment and liquid phase catalyzed reactions, where we use systematically transient methods such as the modulated excitation spectroscopy to resolve this information.

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