Analyzing Zeolites

Two-Dimensional IR Pressure-Jump Spectroscopy of Adsorbed Species for Zeolites**

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Infrared spectroscopy of adsorbed probe molecules is a well established technique for the characterization of surface sites on zeolites and other solid catalysts. Time resolution in modern spectrometers increases the power of the technique for use with complex adsorption systems, with multiple adsorption sites and a microporous structure, by allowing the study of transient systems and of adsorption dynamics out of equilibrium. Step-scan Fourier transform interferometers can easily reach the microsecond timescale if the observation can be repeated with sufficient reproducibility. At this timescale, adsorbed molecules in a zeolite each have their eigen-response frequency to a pressure perturbation or modulation. Using pressure and temperature measurements, Rees and co-workers[1] and Grenier and co-workers[2] have explored the pressure modulation frequencies, indicated the frequencies for given adsorbates on given zeolites, and extracted diffusion kinetic parameters from their results. We

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thought we could use these eigen frequencies to extract spectral information for complex mixtures on surfaces. Thus, several adsorption sites, or several adsorbed molecules in a mixture, would each lead to a specific eigen-response frequency to a pressure modulation, and we could obtain the spectral signature for each individual species on each individual adsorption site. Instead of having to vary the modulation frequency progressively to explore the whole frequency domain, we decided to generate a square pressure wave on the surface (or more exactly a pressure jump), which would be equivalent to the generation of an infinite number of pressure oscillations with different frequencies (Figure 1).

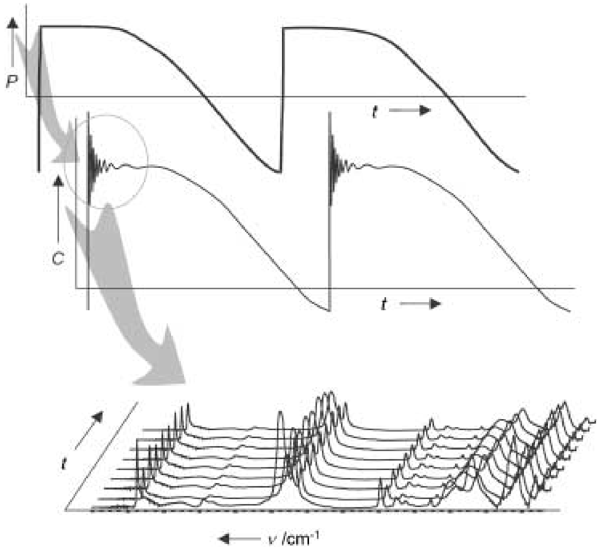

Figure 1. principle of the PJAS-IR method. A pressure jump is generated (top), which leads to a relaxation process by adsorption and diffusion on the surface (middle). The middle graph shows how the concentration *C* of adsorbed species varies following pressure jumps. IR spectra can be recorded for each pressure jump in step or rapid-scan modes (bottom: spectra shown here do not correspond to a specific experiment).

Such a pressure jump can be described as a shift of the adsorption in an excited state, with a relaxation by diffusion and adsorption equilibria. The relaxation process can be followed by fast time-resolved IR spectroscopy. The infrared spectra collected can be analysed by Fourier transform to extract the relaxation processes eigen frequencies, with correlations with the infrared frequencies. The technique is named IR pressure-jump spectroscopy of adsorbed species (PJAS-IR).

Mordenite is an important zeolite as a result of its many industrial applications and its specific pore structure: large 12-membered rings channels (ca. 6.7 × 7.0 Å) which run along the *c* crystallographic axis, with 8-membered-ring side pockets (ca. 3.9 Å free diameter) in the *b* direction. Owing to such different possible locations for catalytic sites, confinement effects are important in mordenites,[3,4] and have been used to tune catalytic activity.[5,6] The location and strength of Brønsted acid sites have long been studied by IR spectroscopy: these sites are due to H^+ ions compensating the charge defects of aluminium atoms in the framework, which leads to very clear ν(OH) vibration bands in the IR spectrum. The ν(OH) band in H-mordenite (H-Mor) has fine structure (Figure 2), in which two main ν(OH) vibration bands are usually identified, for OH groups in the main channels (MC; $\nu(OH_{MC})$ at 3610 cm^{-1}), and in the side pockets (SP) of the structure ($\nu(OH_{SP})$ at 3585 cm^{-1}).[7] Using mainly crystallographic data, Alberti proposed three different OH groups in the structure, at positions O7 in the main channels (OH_{MC}), O2 at the 8-R opening between large channels and side pockets (denoted here as OH_{8R}), and O9 at the end of the side pockets (OH_{SP}).[8] The ν(OH) vibration band for OH_{8R} groups has been identified recently,[9] but remains unclear and can not be seen directly on the spectrum of the fully acidic sample.

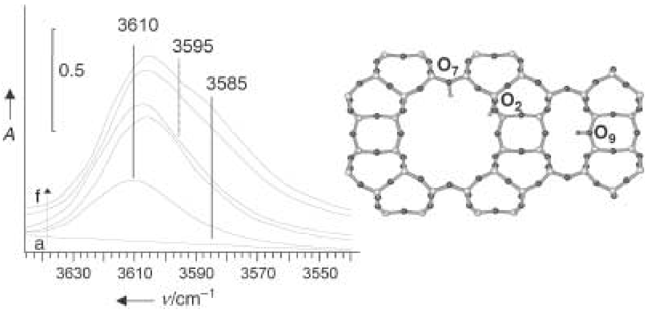

Figure 2. Left: IR room-temperature spectra of Na,H-Mor samples with various sodium contents (a–f, adapted from ref. [9]) showing the fine structure in the ν(OH) vibration region, and right: view of the mordenite framework along the *c* axis, showing the three possible OH groups in H-Mor that were assigned to the three corresponding ν(OH) vibration bands (in ref [10]).

Deuterated acetonitrile is an important probe molecule for acid sites in mordenites,[3,4,6,7,10,11] its properties are strongly influenced by temperature, pressure, and confinement. At room temperature and low coverage, a hydrogen bond is formed between acetonitrile and OH groups. At high coverage, a very strong hydrogen bond is formed between probe molecules (probably dimers) and OH groups in the side pockets.[4] If the pressure is reduced, or if the temperature is risen, this particular hydrogen bond disappears. At very high temperature, acetonitrile is protonated and a nitrilium is formed.[10] The formation of this nitrilium ion seems very much influenced by confinement,[11] and probably takes place in the side pockets, but this has so far not been established.

We studied the acetonitrile adsorption on H-Mor by 2D-PJAS IR, which allowed the measurement of spectroscopic and dynamic features of adsorption in the micropores. The time trace (shown for a given wavenumber at 523 K, Figure 3, top) was obtained for the whole of the mid-infrared (by the first set of Fourier transforms). The pressure jump was detected between 0 and 1 s. The relaxation process on the surface was clearly visible after the pressure pulse: some oscillations and envelopes were visible on the time trace, with intensities rapidly decreasing. The decrease of the baseline from 5 to 8 s was due to the modification of the volume of the cell to prepare for the next jump, at 9 s. The frequencies of the

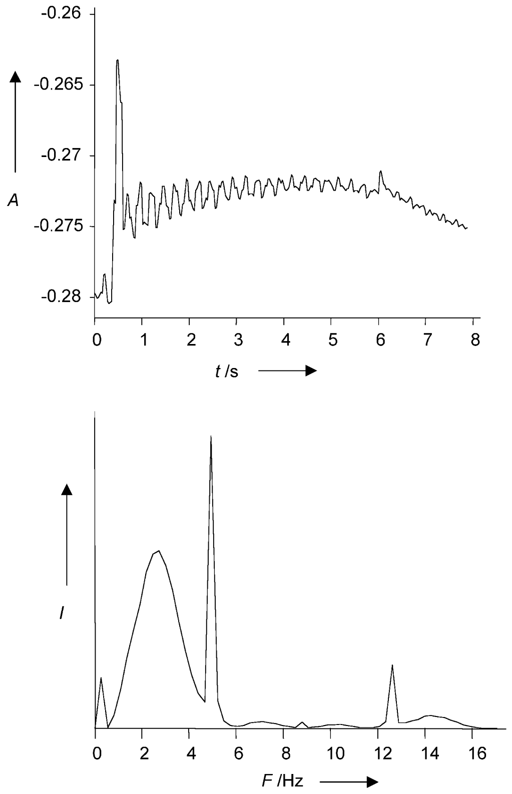

Figure 3. PJAS-IR experiment on H-Mor at 525 K under 78 Pa of acetonitrile (8 cm^{-1} and 28 ms resolution). The data were averaged on 100 pressure jumps. Top: time trace of the IR intensity A at 2295 cm^{-1}; Bottom: corresponding Fourier transform on the first 128 points (3.58 s) after the maximum pressure. F = Fourier frequency, and I = intensity of the Fourier transform.

oscillations were obtained by the second Fourier transforms in the time domain (Figure 3, bottom). Figure 4 shows the whole 2D map.

The Fourier transform in the time domain leads to four main peaks, indicating four oscillation frequencies as a result of the pressure pulse. The two very intense and narrow peaks at 5 and 12.5 Hz (Figure 3, bottom) were also observed in the absence of a sample. They were not damped quickly, and were not affected by surface dynamics on the sample. They were eigen vibration frequencies of the cell itself. The two broad bands at 2.5 and 14 Hz could be observed only in the presence of a solid sample in the cell. Their broadness indicates a rapid relaxation and damping, owing to diffusion and adsorption kinetics on the surface.

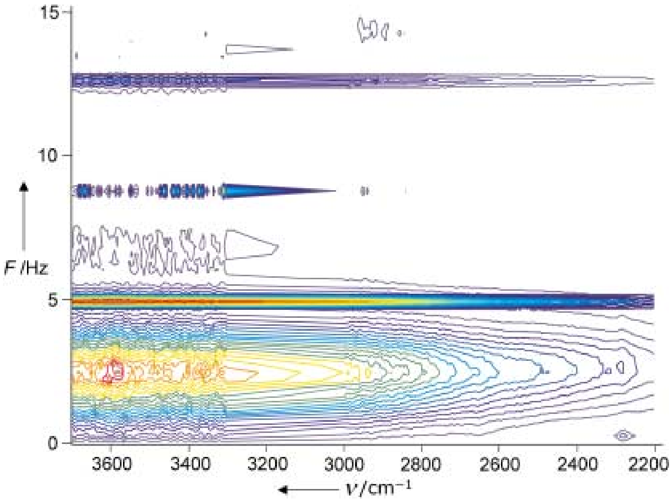

Figure 4. 2D-PJAS-IR spectrum of acetonitrile on H-Mor at 525 K (Fourier intensity contours: blue (minimum), red (maximum), versus pressure response frequency F and infrared wavenumbers).

The experiment was performed at various temperatures: 300, 423, and 523 K. The four peaks in the pressure-response frequency scale were observed in all three experiments. They were at higher frequencies at higher temperatures, because of diffusion and adsorption activation at higher temperature. The two narrow and intense peaks at 5 and 12.5 Hz at 523 K affected all wavenumbers the same way, but the two surface responses at 2.5 and 14 Hz presented a more complex correlation with wavenumber values. The low-frequency response was particularly interesting since it presented a fine structure in the ν(OH) and in the ν(CN) vibration regions (Figure 5). In the ν(OH) vibration region, the three ν(OH) vibration bands of the OH groups in the three possible locations (OH_{MC} 3605 cm^{-1}, OH_{8R} at 3595 cm^{-1} and OH_{SP} at 3585 cm^{-1}) were identified (at points A, B, and C in Figure 5: 2.25 Hz, 2.73, and 2.5 Hz, respectively). This is the first direct IR detection of the three OH groups in H-Mor.

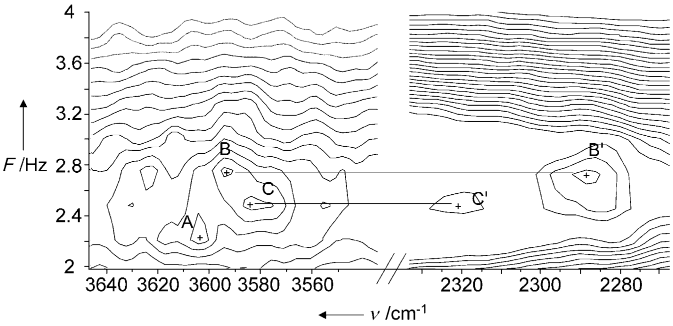

Figure 5. Enlargement of the ν(OH) and ν(CN) regions around 2.5 Hz from Figure 4. The same eigen frequencies for points C and C′ and for points B and B′ indicate correlations between hydrogen-bonded acetonitrile and OH_{8R} (B–B′) and between protonated acetonitrile and OH_{SP} (C–C′).

In the ν(CN) vibration region, at 523 K, two ν(CN) vibration bands were expected: one around 2290 cm^{-1} for the hydrogen bond, and a second one above 2315 cm^{-1} for protonated acetonitrile. They could indeed be observed, at points C′ (2.73 Hz) and B′ (2.5 Hz), respectively. This was a clear indication that protonation of acetonitrile was linked to the OH group in the side pockets, OH_{SP}, and was favored by confinement in this constrained environment.[4] Interestingly, the perturbation of the hydrogen bond by the pressure jump was only detected at the opening of the side pockets (OH_{8R}), and the OH groups in the main channels (ν3605 cm^{-1}) were not involved in the change in the hydrogen bond. This situation is probably due to the number of perturbed sites remaining mostly constant in the main channels during the pressure jump. It had been shown by molecular dynamics simulations[3] that a pressure increase in the main channels allowed a higher proportion of acetonitrile to enter the side pockets: the main channels act as a pipe leading acetonitrile to the side pockets, in which the loading variation becomes important.

When the experiment is performed at room temperature, no difference can be detected between the three OH groups, which give a broad signal in the ν(OH) vibration region. At intermediate temperature, 423 K, the pressure jump leads to the formation of the acetonitrile dimer and the particularly strong hydrogen bond reported in ref.[4] This bond formation also leads to a correlation with the OH_{SP} on the 2D map, which confirms the formation of this specific hydrogen bond in the side pockets only.

In conclusion we have presented a new spectroscopic 2D IR technique for the study of adsorption in micro and mesoporous systems. It is based on µs time-resolved spectroscopy and sudden pressure changes in the infrared cell containing the solid sample and the gas probe molecule. The pressure jump leads to a relaxation process by diffusion and adsorption, which is monitored by IR spectroscopy. The 2D spectrum is obtained by two Fourier transforms in the IR wavelength domain and in the time domain. The potential of the technique was shown by studying probe molecule (acetonitrile) adsorption on mordenite, and confirmed previous studies performed in classical adsorption cells. 2D-PJAS-IR allowed the first direct detection of three distinct OH vibration bands in the IR spectrum of mordenite, and revealed three different interactions with acetonitrile, which depend on the adsorption site. Protonation of acetonitrile at high temperature was shown to take place only in the side pockets.

Experimental Section

A Bruker IFS66s spectrometer was used in the step scan or rapid scan mode. The IR cell allowed in situ heating of the sample in the IR beam, it was connected to a vacuum/gas line. In a typical experiment, the catalyst was activated by in situ heating to 400°C under vacuum (10^{-4} Pa), and the probe molecule (perdeuterated acetonitrile 99.9% pure; Aldrich) was introduced in the cell ($\approx$100 Pa) at room temperature. A 30% pressure jump was applied every 9 s in the cell, and the IR spectrum was recorded at 0.2–30 ms time resolution and 64–8 cm^{-1} spectral resolution, at temperature between 300 and 525 K.

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