

# ***In situ* monitoring of unique switching transitions in the pressure-amplifying flexible framework material DUT-49 by high-pressure $^{129}\text{Xe}$ NMR spectroscopy**

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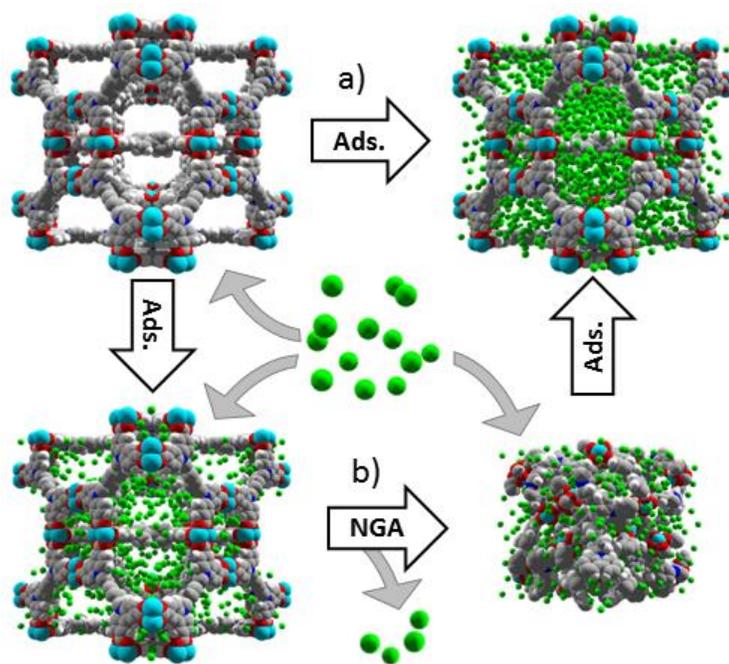
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**ABSTRACT:** Studies of host-guest interactions are especially powerful if the measurements are performed *in situ*.  $^{129}\text{Xe}$  NMR spectroscopy is particularly well-suited since it provides characteristic, structure-sensitive parameters such as the chemical shift and others. The combination of high pressure adsorption of  $^{129}\text{Xe}$  with NMR spectroscopy was used to elucidate the adsorption-induced phase transitions in the recently discovered pressure-amplifying framework material DUT-49, showing unique negative gas adsorption transition (NGA). In the open state, DUT-49<sub>op</sub> exhibits a hierarchical pore system involving both micro- and mesopores. After reaching a critical relative pressure of ca. 0.15, adsorbed xenon induces mesopore contraction resulting in a purely microporous contracted phase. The contraction is accompanied by the release of Xe from the mesopores. Further increase of the pressure initiates the recovery of the mesopores without any indication of a structural intermediate in the NMR spectra. According to the NMR data, the structural transition induced by xenon is obviously a collective, step-wise phenomenon rather than a continuous process. This is the first time NGA has been studied by direct monitoring the guest and its interaction with the host framework.

The pronounced flexibility of special metal-organic frameworks (MOFs) [1-3], so called soft porous crystals, [2,4-14] attracts increasing research interest. Switching between a narrow-pore state and a large-pore state (as observed for MIL-53 series [2,6-8] or transition from closed-pore state to the open-pore state beyond a certain, gas dependent gate-opening pressure (in DUT-8(Ni) [9-12]), are usually accompanied by dramatic increases of the unit cell volume, sometimes exceeding 100%. Apart from the pore volume change, other physical property changes are triggered (optical, magnetic, or dielectric) rendering these materials promising for advanced sensing applications. Moreover, several recent publications (see, e.g., [15-18]) report highly selective adsorption of selected components from gas mixtures by such flexible compounds. Examples are the selective *p*-xylene adsorption from other isomers [15], the low-pressure selectivity of special MOFs for nitric oxide [16] and the enhanced working capacity for natural gas storage applications [19]. Therefore, flexible MOFs are considered to be very promising novel materials also for applications in selective adsorption and catalysis.

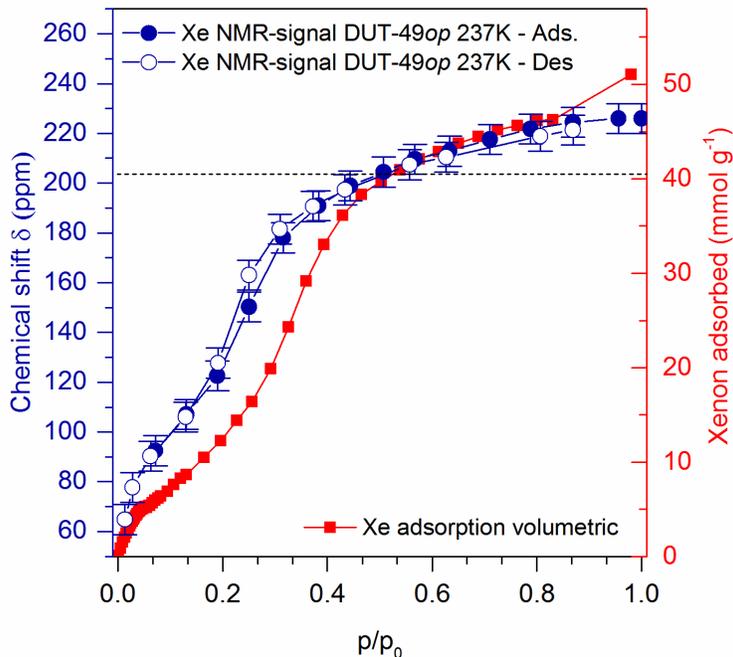
NMR spectroscopy is an efficient tool to monitor the local structure, dynamics, and flexibility of both, the host framework as well as the adsorbed guests like Xe, CO<sub>2</sub>, and others (see [20-28] and references therein). It therefore delivers information which helps developing a fundamental understanding of the processes governing structural transformations in soft porous crystals. Studies of host-guest interactions are particularly powerful if the measurements are performed *in situ*.

Recently, we discovered the pressure-amplifying metal-organic framework DUT-49 [29] (DUT - Dresden University of Technology) with exceptionally high porosity (Fig. 1), showing spontaneous desorption of gas during pressure increase in a defined pressure range (e.g. upon adsorption of methane at temperatures between 91 and 121 K) [30]. This pressure amplification originates from a collapsing metastable state passed during mesopore filling of the hierarchical pore structure (micropore diameters 1.0, 1.7 nm; mesopore diameter 2.4 nm). Structural transformation, i.e., mesopore contraction leads to a purely microporous state and is accompanied by partial gas release (negative gas adsorption, NGA).



**FIGURE 1:** Schematic representation of xenon adsorption process on DUT-49: a) without structural transition and b) with structural transition and NGA. Color code: Xe in green, C in dark grey, Cu in cyan, O in red, H in light grey, N in blue.

Interestingly, a similar NGA transition could be observed at 75 kPa during the adsorption of xenon at 195 K (Fig. S1, S2), which allows studying the NGA by *in situ*  $^{129}\text{Xe}$  NMR spectroscopy. Previous investigations have been focused on elucidating the structural transitions responsible for the unique behaviour while lacking an in depth analysis of the guest dynamics and interaction with the flexible framework. Xe is particularly well-suited to investigate host-guest interactions by NMR since it provides characteristic, structure-sensitive parameters such as the chemical shift, the chemical shift anisotropy, signal intensities, and relaxation times (see [22-24] and references therein).



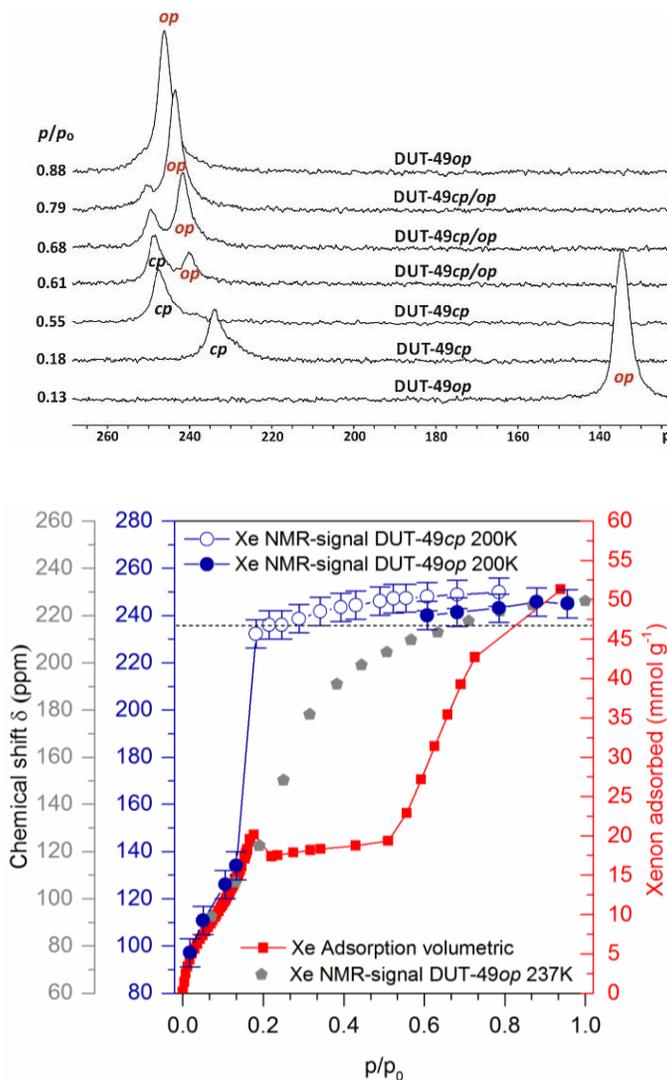
**FIGURE 2:** Chemical shift of adsorbed xenon in DUT-49 measured during adsorption (filled circles) and desorption (open circles) at 237 K in comparison to the adsorption isotherm at 223 K (red squares) measured volumetrically. Chemical shift of bulk liquid xenon is given as dotted line.

Our homebuilt special apparatus [9] allows *in situ* high-pressure NMR spectroscopic studies by applying variable gas pressures up to ca. 30 bar at variable temperatures down to 190 K inside the NMR spectrometer. Gases such as  $^{129}\text{Xe}$ ,  $^{13}\text{CO}_2$ , and  $^{13}\text{CH}_4$  used in our investigations enable us to follow adsorption/desorption process by observing the signals of the adsorbed gases and to correlate these NMR-derived parameters with volumetrically measured adsorption/desorption isotherms.

In previous investigations it was shown that no structural transformation and NGA occurs at higher adsorption temperatures (e.g. at 298 K for methane) [29, 30]. Similar to these findings no hysteresis and no structural transition could be observed for Xe adsorption at 223 and 237 K (Fig 2). Thus an isotherm of the non-flexible DUT-49 was recorded exhibiting the expected shape for a material with micro- and small mesopores. As seen from Fig. 2, the  $^{129}\text{Xe}$  NMR chemical shift of adsorbed xenon in DUT-49 as a function of relative pressure ( $p/p_0$ ) at 237 K exhibits a reversible shape without pronounced hysteresis. The adsorbed xenon rapidly moves inside the pore system giving rise to a single signal at an averaged chemical shift. The chemical shift of adsorbed xenon can be written as

$$\delta = \delta_W + \delta_{\text{Xe-Xe}}(\rho_{\text{Xe}}) \quad (1)$$

assuming that the chemical shift is referenced relative to the gas phase chemical shift extrapolated to zero pressure. The term  $\delta_w$  summarizes all interactions of xenon and the internal surface. The second term describes the influence of xenon-xenon interactions and depends on the xenon density  $\rho_{Xe}$  inside the pores. For low pressures, one can write  $\delta_{Xe-Xe} = \Delta_{Xe-Xe}\rho_{Xe}$ . The parameter  $\Delta_{Xe-Xe}$  is temperature-dependent. The pressure-dependence of the chemical shift should therefore resemble the conventional volumetric adsorption/desorption isotherms since the chemical shift is correlated with  $\rho_{Xe}$ . This is indeed observed (see Fig. 2). Furthermore, it is remarkable that the chemical shift at higher relative pressures significantly exceeds the chemical shift of bulk liquid xenon. This can be explained by the influence of xenon-wall interactions in addition to xenon-xenon interactions. In summary, the observations made at 237 K point on the high mobility of xenon in the open-pore form (*op*) of DUT-49. No indications for framework flexibility are found at this temperature.



**FIGURE 3:** Top:  $^{129}\text{Xe}$  NMR signals of adsorbed xenon on DUT-49 measured at 200 K for various relative pressures during adsorption (*op*: open-pore phase, *cp*: contracted pore phase). Bottom: Chemical shift of adsorbed xenon in DUT-49 at 200 K (blue circles) and 237 K (grey pentagons) measured during adsorption (filled symbols denote to signals of DUT-49*op*, empty symbols to DUT-49*cp*) in comparison to the volumetric Xe adsorption isotherm at 195 K (red squares). Chemical shift of bulk liquid xenon is given as dotted line.

In contrast a remarkably different situation in the pressure-dependence of the adsorbed xenon chemical shift in DUT-49 is observed when adsorption is carried out at 200 K (Fig. 3, selected spectra are shown on top, Fig. S2). After an initial continuous chemical shift increase in low  $p/p_0$  region, a sudden increase from 135 ppm at  $p/p_0 = 0.13$  to 235 ppm at  $p/p_0 = 0.18$  is observed.

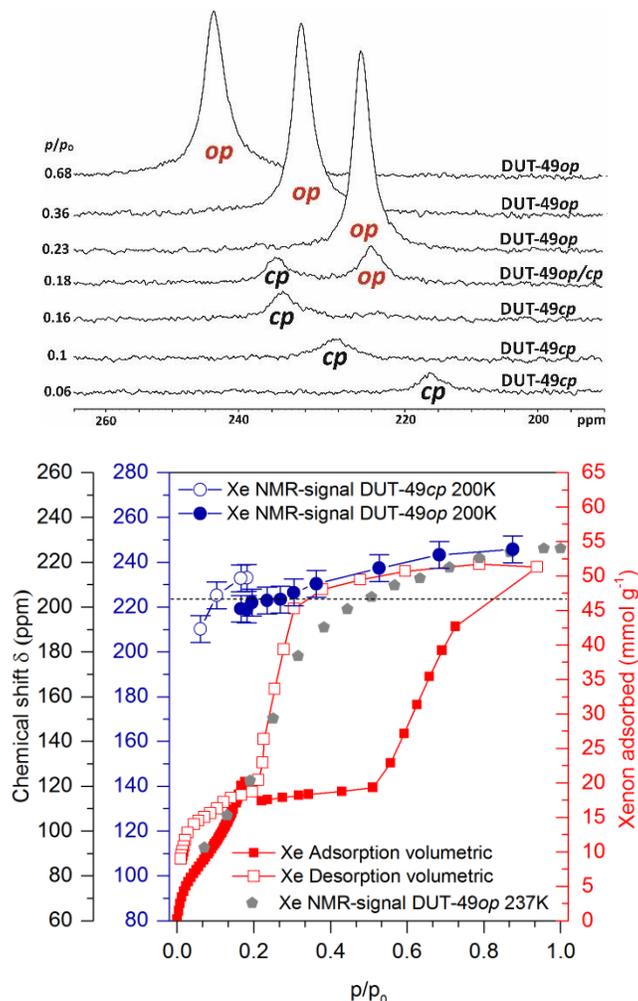
In a rigid MOF, this slight pressure increase should not result in such a dramatic shift especially when compared to the isotherm recorded at 237 K. Furthermore, the signal intensity decreases at  $p/p_0 = 0.18$  compared to 0.13. Accordingly, xenon-xenon interactions cannot be responsible for this huge change in chemical shift. We, therefore, have to conclude that the step-wise increase of the chemical shift indicates a structural transition resulting in an increasing xenon-wall interaction, consequently a xenon density close to the density of liquid xenon is achieved at significantly lower  $p/p_0$  in comparison to the experiment performed at 237 K. To achieve such strong xenon-wall interaction, the average pore size has to decrease drastically. The latter is in accordance with the *in situ* adsorption studies performed with methane at 111 K and Xe at 165 K (Fig. S4, Table S1), showing that the mesopores in DUT-49*op* contract during NGA (by a conformational change of the linkers) and the material becomes purely microporous (DUT-49*cp*). This even results in a negative methane adsorption, i.e., desorption of previously adsorbed methane from the MOF.

Up to a relative xenon pressure of 0.55, the chemical shift and signal intensity only slightly increase according to the plateau in the adsorption isotherm. At  $p/p_0 = 0.61$ , a second signal of adsorbed xenon appears at ca. 240 ppm.

Its intensity continuously increases with rising  $p/p_0$  whereas the signal at higher chemical shift continuously decreases until it disappears at  $p/p_0 = 0.88$ . This indicates a second structural transition (from contracted phase to the open-pore phase) taking place in the relative pressure range between 0.55 and 0.88. The presence of two separate signals corresponding to the *op* and *cp* states reveals that there is no fast exchange of xenon between these two states indicating that the transition is a collective phenomenon taking place in larger domains/crystallites. The coexistence of the two states over a certain relative pressure range shows that the transformation does not take place at the same pressure for all domains/crystallites resulting in a gradual slope of the adsorption isotherm. We do not observe any indication for an intermediate state, i.e., the phase transition seems to be a step-wise switching rather than a continuous process. This structural transition is accompanied by a significant increase of signal intensity whereas the chemical shift only slightly increases. Obviously, the mesopores are restored and immediately filled with xenon at these relatively high pressures (cf. Fig. 4, S5). This explains the relatively high chemical shift which only slightly changes with  $p/p_0$ .

Stepwise pressure release (desorption) reveals a pronounced hysteresis. Down to a relative pressure of 0.23 only one signal is present. However, at  $p/p_0$  between 0.3 and 0.23 a plateau is forming around the chemical shift of liquid bulk xenon in contrast to the expected trend of decreasing chemical shift with decreasing pressure. Again the decrease in porosity by a transition to an intermediate phase can be an explanation of this behaviour.

Obviously, the pore size of DUT-49 is reduced by a structural transition. Consequently, strong Xe-wall and Xe-Xe interactions are maintained even during desorption. Indeed, *in situ* PXRD measurements during desorption of methane indicate the presence of an intermediate phase (*ip*) with a pore diameter in between the pore diameters of *op* and *cp* phases. The fact that only one signal is observed shows that this *op* - *ip* transformation is different from the previously mentioned opening of the structure during adsorption and that it happens simultaneously in all crystallites. At relative pressures lower than 0.23 a second peak at higher chemical shifts is observed indicating the structure transformation to DUT-49*cp*, which was also confirmed by *in situ* PXRD (Fig. S4).



**FIGURE 4:** Top:  $^{129}\text{Xe}$  NMR signals of adsorbed xenon on DUT-49 measured at 200 K for various relative pressures during desorption. Bottom: Chemical shift of adsorbed xenon in DUT-49 at 200 K (blue circles) and 237 K (grey pentagons) measured during desorption (filled symbols denote to signals of DUT-49op, empty symbols to DUT-49cp) in comparison to the volumetric Xe adsorption isotherm at 195 K (red squares, filled symbols denote to adsorption, empty symbols to desorption). Chemical shift of bulk liquid xenon is given as dotted line.

In summary it can be stated that *in situ* high-pressure  $^{129}\text{Xe}$  NMR spectroscopy allows studying the unique phase transitions and NGA in DUT-49 by directly monitoring the adsorbed molecules inducing these transitions. While DUT-49 behaves like a rigid MOF upon Xe adsorption at 237 K, a distinct structural transformation at 200 K can be observed. The transition from open to contracted pore phase which is driven by mesopore to micropore contraction can directly be monitored by an abrupt large change in chemical shift which reflects the higher magnitude of adsorption enthalpy in the cp state. At higher relative pressures, the re-opening of the mesopores in a cp – op transition can be directly monitored by following the individual signals for both phases. A pronounced hysteresis is observed in the desorption experiment, i.e., at stepwise decreasing pressure. At low relative pressure, the material undergoes mesopore contraction in an op – cp transition.  $^{129}\text{Xe}$  NMR spectroscopy thus provides a unique viewing angle from the pore interior revealing a truly collective character of NGA transitions and a two phase co-existence over a certain relative pressure range.

## ASSOCIATED CONTENT

### Supporting Information

Supporting Information: Experimental details concerning the sample preparation, volumetric Xe adsorption experiments, *in situ* PXRD and NMR experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.”

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### Notes

The authors declare no competing financial interests. J. S. and S. Krause. contributed equally to this work.

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