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Experimental Evidence of Selective Heating of Molecules Adsorbed in Nanopores under Microwave Radiation

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Abstract

We have performed in situ quasi-elastic neutron scattering (QENS) measurements on zeolite-guest systems under microwave irradiation, for comparison with corresponding simulations. Both experiment and simulation reveal selective heating of methanol in silicalite, but little to no heating of benzene in silicalite. Effective translational and rotational temperatures extracted from QENS data under microwave heating were found to depend on microwave power. In agreement with simulation, QENS rotational temperatures significantly exceed translational ones at high microwave power, thus providing the first microscopic proof for athermal effects in microwave-driven nanopores.

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Microwave (MW) heating has emerged in the last two decades as a ubiquitous tool in organic [1-4] and materials chemistry [5,6]. Despite its broad technological importance, MW heating remains an unpredictable tool because the detailed physics of MW energy transfer is poorly known. For example, in some cases MW energy speeds up zeolite formation from days to minutes [6] and tunes selectivity of adsorption in zeolites [7], but in other cases a negligible effect is seen. Key to progress in our understanding of MW-driven energy transfer is *in situ* spectroscopy [8], which acts as a microscopic thermometer probing the flow of energy into various motions [9]. Previous MW-driven molecular dynamics simulations suggest that athermal effects – i.e., heating of selected components and degrees of freedom – are possible from continuous MW irradiation of zeolite-guest systems [10,11]. However, no microscopic measurement has been performed to test the predictions of these simulations. In this Letter, we report the first application of *in situ* quasi-elastic neutron scattering (QENS) of zeolite-guest systems subjected to MW irradiation, for comparison with MW-driven molecular simulations, providing an unprecedented picture of selective heating and athermal effects in these systems. We report for the first time experimentally-determined effective rotational and translational temperatures, showing mode-selective excitations from MW heating.

The QENS experiments were carried out at the Institut Laue-Langevin, using the time-of-flight (TOF) spectrometer IN5. The incident neutron wavelength was taken as 5 Å, corresponding to an incident neutron energy of 3.27 meV. After scattering by the sample, neutrons were analyzed as a function of flight-time and angle. The TOF of the scattered neutrons is related to the energy transfer ($\hbar\omega$) and the scattering angle to the wave-vector transfer (Q). The elastic energy resolution, measured with a vanadium

standard, could be fitted by a Gaussian function, whose full-width at half-maximum was almost constant over the entire Q range, around 110 μeV . We used hydrogenated methanol and benzene molecules to take advantage of the large neutron cross-section of hydrogen. Spectra from different detectors were grouped in order to obtain reasonable counting statistics and to avoid the Bragg peaks of the zeolite. The TOF spectra were transformed to an energy scale after subtracting the scattering of the bare zeolite. Three samples contained in cylindrical quartz ampoules were prepared for the neutron experiments: the bare silicalite, silicalite with methanol, and silicalite with benzene. The bare silicalite sample was heated under oxygen flow up to 773 K, and after cooling it was pumped to 10^{-4} Pa while being heated again. The quartz ampoule was sealed on the vacuum line. The two other ampoules were prepared by adsorbing known amounts of methanol or benzene onto the activated zeolite. The concentration of both adsorbates was low, 2 molecules per unit cell.

We used a commercial MW source (20 to 1000 W of power) to generate MW radiation at 2.45 GHz. The temperature was continuously monitored during the experiments using a fibre-optic probe (resolution of 0.1 K) touching the sample vessel wall. The MW radiation was conducted to the sample through a rectangular Aluminum 6061 waveguide of designation WR284 (WG10) with standard dimensions to operate in the fundamental TE₁₀ mode. This waveguide, which constitutes the MW cavity, was connected to the MW power generator through a PTFE vacuum window on one end and was terminated on the other end with a standard rectangular flange supporting, in its center, the sample stand. The sample quartz ampoule, aligned in the neutron beam, was oriented vertically in a 5 mm deep circular recess at the top of a machinable glass ceramic

(MACOR[®]) stand designed to accommodate the fiber-optic temperature probe and to maintain it against the ampoule sidewall. In the conventional heating configuration, a 3 mm diameter cartridge heater was inserted in the stand. The sample chamber containing the MW cavity could be evacuated or flushed with helium. Higher MW powers could be used under helium flow, without a marked rise of temperature, but we found that the temperature within the sample was more accurately measured when the quartz ampoule was under vacuum. Since the runs lasted from 4 to 10 h, we are sure that equilibrium had been reached.

QENS spectra obtained with pure benzene in silicalite showed no dependence on the MW power. On the other hand, the dynamics of methanol is affected by the MW energy, as shown in Fig. 1. The scattering from the hydrogen atoms dominates; because of their large incoherent cross-section, the scattering from the other atoms can be neglected [12]. The hydrogen atoms of a methanol molecule experience several molecular motions: translation, rotation, and vibration, which occur on different time scales. These different molecular motions can then be treated separately. Since the lowest frequency vibration, the methyl torsion, falls well outside the QENS energy range, the vibrational term affects only the elastic intensity through a Debye-Waller factor. For the rotation, we have found that an isotropic rotational diffusion model described well the data and we have assumed that the bond angles and bond lengths of the methanol molecule were not greatly modified upon adsorption, so that we have used a mean radius of gyration of 1.48 Å.

Eight spectra, covering a wide range of wave-vector transfers, were fitted simultaneously using a jump diffusion model [12]. Convolution of rotational and

translational motions with the instrumental resolution gives excellent fits to the experimental spectra. Some comparisons between experimental and calculated spectra are shown in Fig. 2. The averaged self-diffusivities of methanol, D_s , are reported in Fig. 3. At 293 K, without MW or conventional heating, D_s is $1.66 \times 10^{-5} \text{ cm}^2/\text{s}$. This value increases when MW radiation is applied: to $2.07 \times 10^{-5} \text{ cm}^2/\text{s}$ for 50 W, and to $2.63 \times 10^{-5} \text{ cm}^2/\text{s}$ for 100 W. While the absolute errors may amount to 20% (adding up errors due to statistics and to the fitting procedure), one finds from various refinements that the relative error is less, it is estimated to 10% on D_s and 15% on D_R . By monitoring the temperature of the quartz ampoule during the experiments, we found that the sample temperature under vacuum is raised upon MW irradiation, to 308 K with 50 W, and to 328 K with 100W. The effective translational temperature of the molecules under irradiation can be estimated from the D_s values, a calibration being made from conventional heating (Fig. 3). With 50 W, one obtains a temperature of $323 \pm 10 \text{ K}$ (compared with a cell temperature of 308 K), and of $355 \pm 10 \text{ K}$ with 100 W (compared with 328 K). The effective translational temperature of the molecules under MW is therefore higher than the sample temperature.

The rotational diffusion coefficients, D_R , are shown in Fig. 4. One can derive an effective rotational temperature under irradiation, using the conventional heating values as a calibration. For 50 W, there is no influence, within experimental error, but with 100 W, one obtains $385 \pm 10 \text{ K}$, which is much larger than the sample temperature: 328 K.

We simulate these QENS experiments by analyzing energy distributions in MW-heated methanol-silicalite and benzene-silicalite systems. To do this we have simulated steady states of these zeolite-guest systems by irradiation with a classical, monochromatic

MW field, and by removing energy with an Andersen thermostat [13]. We have shown previously that this thermostat approach accurately models the effect of explicit collisions with bath gas particles [14]. We then define effective temperatures as described below for each of the guest's translational, rotational and vibrational motions. This is possible because velocity distributions remain Gaussian even under MW heating, as found in our earlier work [10, 11].

Molecular dynamics (MD) simulations were performed using our in-house program DIZZY [15], following the algorithm previously described by Auerbach and Blanco where the classical force on the i^{th} atom is augmented by $q_i \vec{E}_t$ [10, 11]. Here q_i is the fixed charge assumed for each atom, and $q_i \vec{E}_t$ accounts for the force exerted by the MW field. MWs were modeled using a monochromatic field: $\vec{E}(t) = i \vec{E}_0 \times \sin(\omega t)$, where ω is the frequency, \vec{E}_0 the electric field amplitude, and i the orientation. To speed up the MW effect to MD simulation time (\sim ns), we set the field parameters to: $\omega = 9.4 \times 10^{11}$ Hz, in the blue end of the MW spectrum, and $E_0 = 1$ V/Å, a high field amplitude. Because we do not use a charge-transfer forcefield in the simulations, the use of a very high field strength serves to speed up MW heating without altering its essential properties. We have confirmed this by computing the room-temperature dielectric permittivities (imaginary components) of liquid methanol (11.2) and bare silicalite zeolite (0.01) using the energy balance formula in Ref 16, obtaining excellent agreement with experiments (13.8 and 0.01, respectively [7]).

The simulated systems were equilibrated at 300 K for a total of 10 ps with an Andersen thermostat set to a frequency of one three-dimensional velocity replacement every 10 fs on average. After 10 ps, the MW field was turned on and the systems

evolved to steady states for another 20 ps, at which point we extracted the MW-heated temperatures for the zeolites and the various benzene or methanol motions. In all cases the total simulation time was 0.5 ns. This MD run time was long enough to establish MW heated steady states. These times are considerably shorter than MD times required to compute diffusion coefficients, which was not done in this work.

These temperatures were calculated using the average kinetic energy associated with each type of molecular motion in the following way:

$$R\langle T_k \rangle = \frac{2\langle KE_k \rangle}{DoF_k},$$

where k labels the type of molecular motion, DoF counts the degrees of freedom involved in a given motion, and $\langle \dots \rangle$ is the average calculated from a total of >40 methanol or benzene molecules. Average translational temperatures $\langle T_{trans} \rangle$ were calculated from the center-of-mass kinetic energies of the guest molecules, while vibrational temperatures $\langle T_{vib} \rangle$ were defined from the average intra-molecular potential energies using the virial theorem approximation for harmonic oscillators, namely, that $\langle \text{potential energy} \rangle = \langle \text{kinetic energy} \rangle = RT/2$ for each vibrational mode. Finally, the average rotational kinetic energy was calculated from the difference between the total kinetic energy of the molecule minus the center-of-mass and vibrational kinetic energies. The simulated loadings were chosen to match experimental conditions.

We performed MW-heated simulations on both methanol-silicalite and benzene-silicalite systems. Table 1 shows the average, steady-state temperatures for the different modes for each zeolite-guest system. Our simulations predict that the benzene-silicalite

system heats very little, consistent with the QENS data. This minimal heating is explained by the nonpolarity of benzene, which has a permanent quadrupole but no dipole, giving the electric field little with which to couple. On the other hand, significant heating of methanol in silicalite is observed precisely because of the dipole of methanol (1.7 D in gas phase). This selective heating is an attractive property, allowing the tuning of selective adsorption in zeolites, as predicted by MW-driven grand canonical molecular dynamics simulations reported elsewhere by us [17]. The simulated zeolite temperature increases for the MW-heated methanol/silicalite system, as observed experimentally, through collisional energy transfer with excited methanols, and not through direct MW absorption, as evidenced by the unheated zeolite in the benzene/silicalite system.

As shown in Table 1, the temperature distribution of the methanol molecules follows: $T_{rot} \geq T_{trans} > T_{vib}$ which in turn is much greater than the zeolite average temperature. These results agree extremely well with the experimental data at 100W shown in Figs. 3 and 4, where the rotational diffusivity of methanol produces a higher effective temperature than its translational counterpart. Comparing the simulations with the high MW power experiments is appropriate because of the high MW power assumed in the simulations.

The rotational temperature is the highest in Table 1 because the MW field excites the hindered rotational potential energy of methanol, causing rotational potential energy to pool into rotational kinetic energy. This hindered rotation transfers energy through the host-guest interaction into methanol translational motion, explaining the translational heating in Table 1. Because this is a “second order” effect, translational heating is less

191 than the rotational counterpart. Vibrational heating is the least because of the frequency
192 mismatch between the MW field ($\sim 30\text{ cm}^{-1}$) and intramolecular vibrations.

193 This research has provided the first unambiguous, microscopic evidence for
194 athermal effects in MW-driven zeolite-guest systems. Such progress will help guide new
195 ways to selectively heat heterogeneous materials. Future work will involve extending
196 these QENS measurements to binary and reactive guest phases in nanopores.

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Table 1. Effective, mode-specific temperatures for methanol-silicate and benzene-silicate systems.

	$T_{\text{trans}}(\text{K})$	$T_{\text{rot}}(\text{K})$	$T_{\text{vib}}(\text{K})$	$T_{\text{zeo}}(\text{K})$
Methanol-silicalite	494 ± 73	512 ± 162	421 ± 38	383 ± 19
Benzene-silicalite	305 ± 24	297 ± 26	316 ± 16	301 ± 8

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List of Figures.

Fig. 1. Experimental and calculated (solid lines) QENS spectra obtained under various MW powers for methanol in silicalite: (+) 0 W, (○) 50 W, (▽) 100 W, $Q = 0.415 \text{ \AA}^{-1}$.

Fig. 2. QENS spectra obtained for methanol in silicalite under 50 W of MW power, for different values of the wave vector transfer (a) 0.415, (b) 0.72, (c) 0.95 \AA^{-1} . The plus symbols correspond to the experimental points and the solid lines to the calculated spectra, the dashed lines indicate the contribution from rotational motions.

Fig. 3. Self-diffusivities obtained for methanol in silicalite. The diamond symbol was obtained without MW or conventional heating. The squares were obtained under MW irradiation, D_s increasing when the MW power is raised to 50 and 100 W. The circles correspond to conventional heating, 333 and 393 K.

Fig. 4. Rotational diffusion coefficient for methanol in silicalite. The diamond symbol was obtained without MW or conventional heating. The squares were obtained under MW irradiation, D_R increasing when the MW power is raised to 50 and 100 W. The circles correspond to conventional heating, 333 and 393 K.

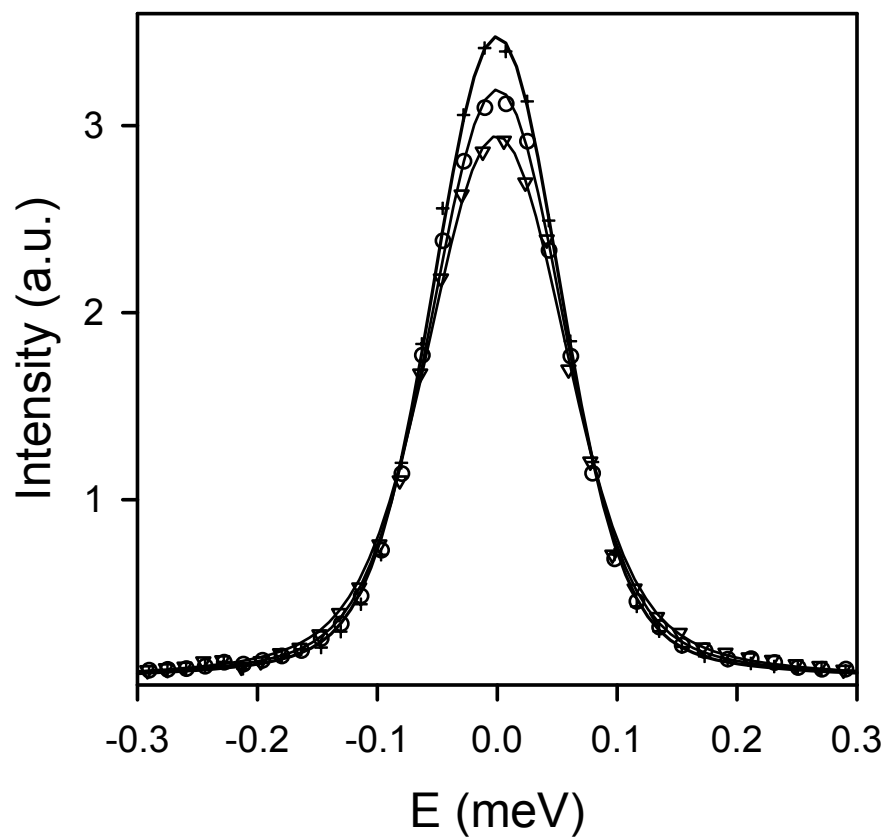


Fig. 1

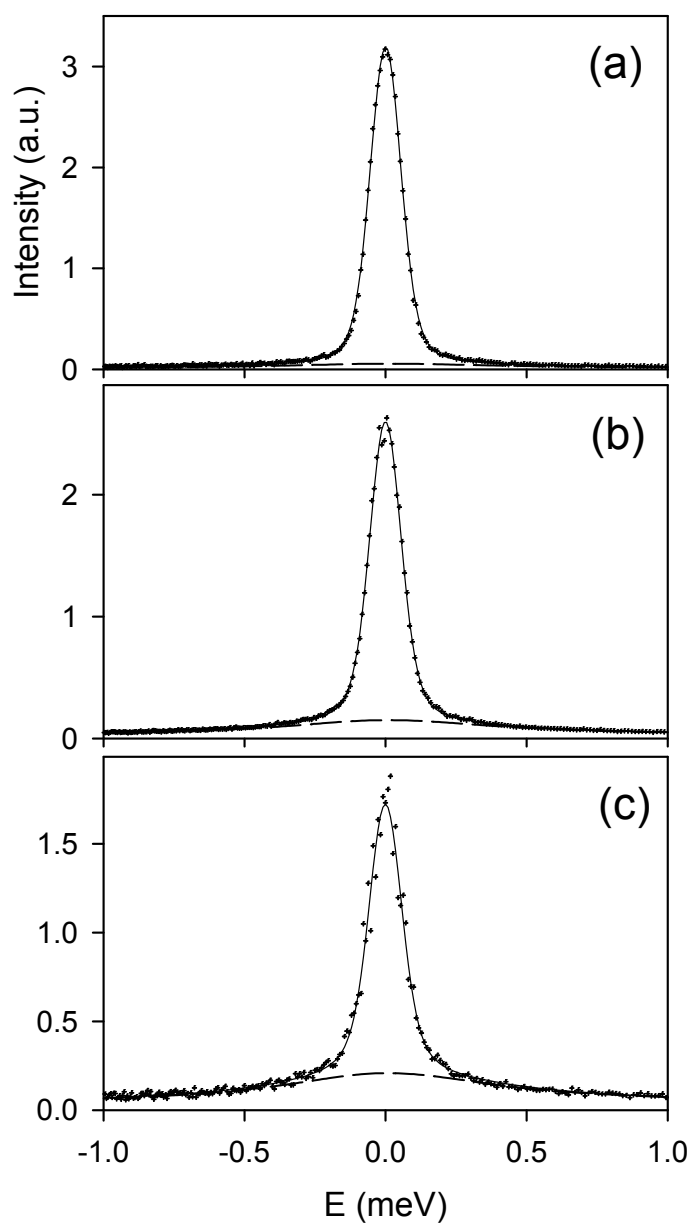


Fig. 2

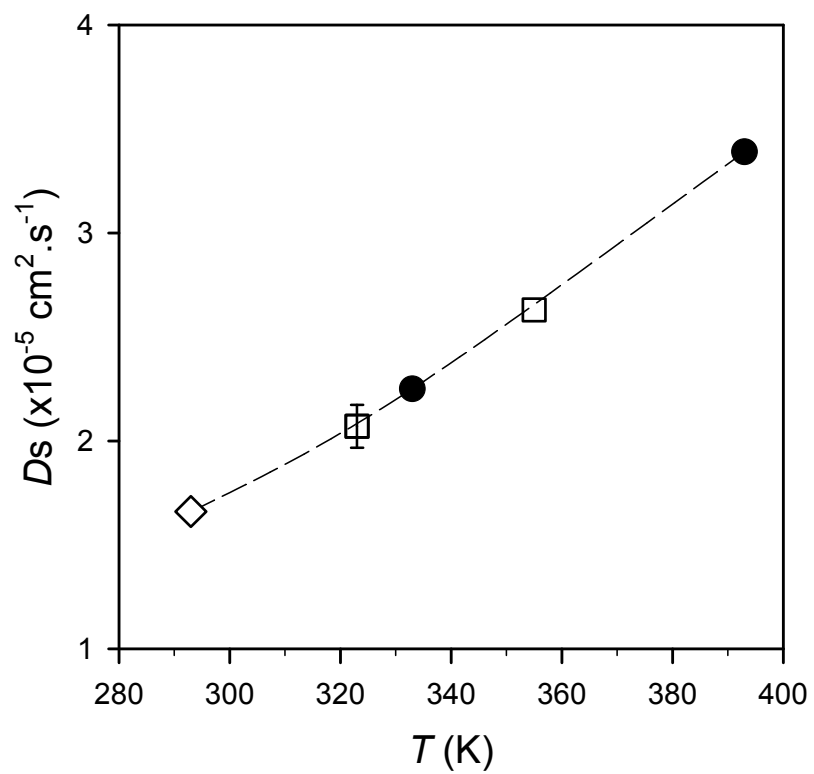


Fig. 3

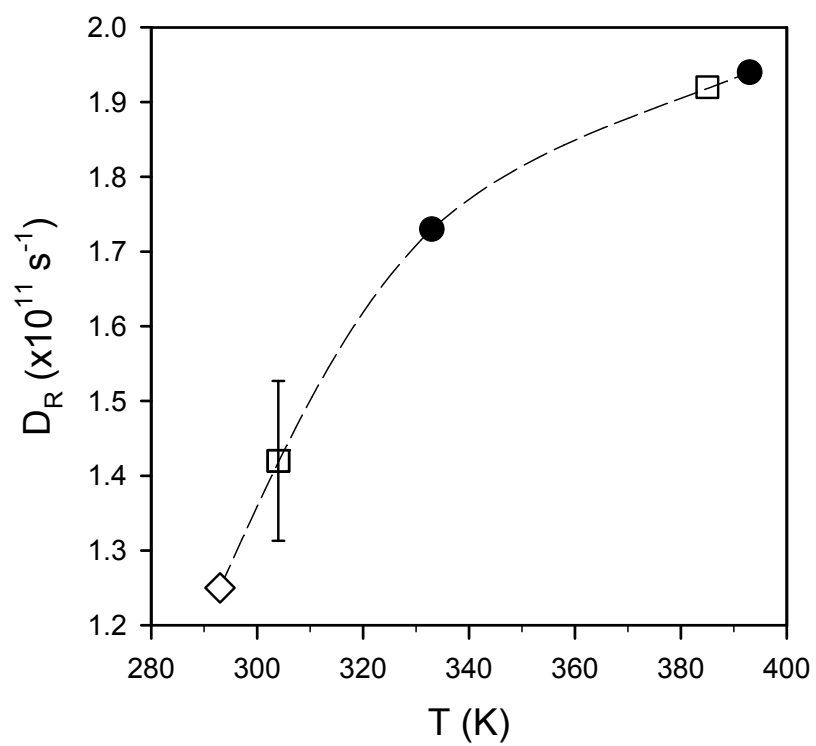


Fig. 4