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In Situ Orientation-Sensitive Observation of Molecular Adsorption on a Liquid/Zeolite Interface by Second-Harmonic Generation

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The inherently surface-specific technique of second-harmonic generation was employed to probe the adsorption of an organic molecule, a hemicyanine dye, on b-oriented silicalite-1 films in situ. Measurements were performed in a purpose-built cell for solution experiments. By measuring at two different polarization combinations of the fundamental and second-harmonic light, the orientation of the adsorbed molecules was measured continuously. It has been observed that the adsorbed molecules gradually align themselves with the straight pores of the zeolite crystallites, thus adsorbing into the pores.

Solid/liquid interfaces are not only abundant in daily life, with examples ranging from paints,¹ soils,² and cosmetics³ to cleaning products,⁴ but also in industry, for example, in heterogeneous catalysis⁵ and fuel cells.⁶ Many industrial catalysts not only have a high surface area at the external surface of the particles but also have mesopores (2-50 nm) and micropores $(\langle 2 nm \rangle)^7$ that contain a large number of active sites that contribute to the overall catalytic activity. For instance, in zeolites, which are crystalline microporous aluminosilicates, the outcome of a reaction is determined by the subtle interplay between adsorption into the pores, diffusion within the pores, and chemical conversion at the sites that are distributed over the crystal.⁸ To understand phenomena such as shape selectivity in zeolite-catalyzed reactions, it is important to study each of these elementary steps.

The kinetics of adsorption from the gas phase into a zeolite can be studied with a series of techniques. The most useful hardly be distilled. That the initial adsorption into the zeolite crystal can indeed be complex has been shown for the gas-phase adsorption of aromatics: fast time-resolved IR spectroscopy has suggested that the molecules first physisorb at the outer crystal surface, followed by a slower adsorption into the pores.9 For liquid-phase adsorption, the techniques available are scarcer and moreover can probe only uptake rates.^{14,15} However, such experiments do not allow us to distinguish between the various steps in an adsorption process. Spectroscopic methods would be particularly suitable to provide insight into the subtleties of an adsorption process because they yield molecular information. However, linear spectroscopic techniques such as UV-vis and IR spectroscopy would also detect contributions of the bulk liquid phase. Even ATR-IR spectroscopy would suffer from significant bulk contributions. Even-order nonlinear optical techniques such as secondharmonic generation (SHG) and sum-frequency generation

of these are IR spectroscopy,9 IR microscopy,10 and inter-

ference microscopy¹¹ because they are capable of providing

molecular or spatially resolved information. Other analysis methods, such as gravimetry¹² and ellipsometry¹³ provide

uptake rate curves from which this information can

harmonic generation (SHG) and sum-frequency generation (SFG) are intrinsically surface-specific techniques in which the interference of most bulk phases is forbidden in the electric dipole approximation and thus nonexistent.^{16,17} Because electronic excitations are more efficient than the vibrational excitations studied by SFG, we used second-harmonic generation in this study. Whereas several studies of organic molecules at a liquid/solid interface by SHG and SFG are

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Figure 1. SEM image of a typical silicalite-1 substrate film.

on hand,¹⁷⁻²² only two real-time kinetic studies of molecular adsorption without the application of an external electric field are available.^{23,24} Here, we report the first in situ adsorption SHG study of an organic molecule on a solid/zeolite interface. Earlier SHG studies on zeolites were ex situ studies of samples that were loaded with dyes outside of the SHG apparatus. Previously, the orientation of molecules adsorbed in zeolites has been studied by various techniques, though only under equilibrium conditions.²⁵⁻²⁷ As will be demonstrated, an additional advantage of the SHG technique is that the orientation of the molecules during the adsorption process can be monitored, which allows insight in the adsorption process itself.

The silicalite-1 films in this study were prepared on a Si wafer, on the basis of a procedure described in the literature.²⁸ In Figure 1, a typical SEM image is presented, which shows that the film consists mainly of b-oriented crystallites with a tablet habit and only a minor fraction of the substrate is not covered with crystallites. Furthermore, few crystals have grown on top of this layer and are tilted over 90° in comparison to the b-oriented crystallites. The XRD pattern, shown in Figure 2, exhibits only (0k0) peaks; this confirms the predominant b orientation of the crystallites.

The SHG experiments were performed with the setup depicted in Figure 3 using a Ti:sapphire laser (Tsunami, Spectra-Physics) which produces ~ 100 fs pulses at 800 nm at a repetition rate of 80 MHz. The polarization of the incoming beam is selected with a half-wave plate $(\lambda/2)$. The fundamental light, with an incident angle of 67.5°, is then focused on the sample, which is placed vertically in a 100 mL octogonal cell (Figure 3); the path length for

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Figure 2. X-ray diffractogram of a typical silicalite-1 substrate film.

both the incoming and the second-harmonic light is 3.62 cm. The angle of 67.5° was chosen because at this angle the direction of both the incoming and the second-harmonic light is perpendicular with respect to the windows. An analyzer is used to select the polarization of the SHG signal, and filters are used to separate the SHG signal from the fundamental and background light. As a detector, a photomultiplier tube (XP2020, Philips) is employed with a lock-in amplifier (SR830, Stanford Research Systems) and chopper (~1 kHz, custom-made) to reduce background noise on top of the signal. The laser output power is measured with a Photodiode (S1722, Hamamatsu) to ensure that it is constant during the measurement. During the adsorption SHG experiments, the cell was filled with 100 mL of 1-hexanol (Acros, 98%) and 1 mL of a 1 mM solution of DAMPI (4-(4-diethylaminostyryl)-1-methylpyridinium iodide, BioChemika, $\geq 97\%$) was injected to obtain a final DAMPI concentration of 10 μ M. In each experiment, we verified that the generated signal was not due to nonlinear scattering processes by performing angledependent measurements. Moreover, a signal was observed only when the focus of the fundamental laser beam coincides with the DAMPI layer, thus it can be concluded that the signal does not originate from the solution through nonlinear scattering processes.

The zeolite substrate films are theoretically treated as azimuthally isotropic. Although the individual silicalite-1 crystallites possess orthorhombic symmetry, azimuthal isotropy of the zeolite substrate films can be expected because individual b-oriented crystallites are positioned randomly on the substrate (Figure 1). This was confirmed by the SHG measurements.

In a substrate-adsorbate system, the second-harmonic intensity is directly proportional to the square of the amplitude of the nonlinear susceptibility $\chi^{(2)}_{tot}$, described by²⁹

$$\chi_{\text{tot}}^{(2)} = \chi_{\text{sub}}^{(2)} + \chi_{\text{int}}^{(2)}(\theta(t)) + \chi_{\text{ads}}^{(2)}(\theta(t))$$
(1)

Therefore, second-harmonic generation can originate from the substrate $(\chi_{sub}^{(2)})$, the interaction between the substrate and adsorbate $(\chi_{int}^{(2)})$, and the adsorbate $(\chi_{ads}^{(2)})$. Because DAMPI exhibits a very large quadratic nonlinearity,³⁰ the terms $\chi_{int}^{(2)}$

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Figure 3. Layout of the SHG system. $\lambda/2$ - half-wave plate for 800 nm; IR filter - filter blocking 400 nm light; blue filter - filter blocking 800 nm light; PMT - photomultiplier tube; PD - photodiode.

and $\chi_{\text{sub}}^{(2)}$ are expected to be negligible with respect to the adsorbate term $\chi_{\text{ads}}^{(2)}$. Hence, only $\chi_{\text{ads}}^{(2)}$ is dependent upon the adsorbate coverage $\theta(t)$ in our system.

In reflection geometry, the effective nonlinear susceptibility, measured at the input and output polarization combinations PP (p input, p output) and SP (s input, p output), takes the forms³¹

$$\chi_{\text{eff, SP}}^{(2)} = L_{ZZ}(2\omega)[L_{YY}(\omega)]^2 \sin\gamma(\chi_{\text{ads}}^{(2)})_{ZYY}$$

$$\chi_{\text{eff, PP}}^{(2)} = +L_{ZZ}(2\omega)[L_{XX}(\omega)]^2 \sin\gamma\cos^2\gamma(\chi_{\text{ads}}^{(2)})_{ZXX} - L_{XX}(2\omega)L_{ZZ}(\omega)L_{XX}(\omega)\sin\gamma\cos^2\gamma(\chi_{\text{ads}}^{(2)})_{XZX} + L_{ZZ}(2\omega)[L_{ZZ}(\omega)]^2 \sin^3\gamma(\chi_{\text{ads}}^{(2)})_{ZZZ} \quad (2)$$

In the above equations, $L_{ii}(\Omega)$ are the Fresnel factors, and γ is the incident angle of the fundamental light. The subindices refer to the laboratory coordinates (X, Y, Z) as depicted in Scheme 1.

Hemicyanine dyes such as DAMPI have one dominant second-order nonlinear polarizability β_{zzz} with z along the long molecular axis.³² The hyperpolarizability β_{zzz} can be related by a coordinate transformation to the different elements of $\chi^{(2)}_{ads}$ in the laboratory coordinates (X, Y, Z) (Scheme 1). If the adsorbate molecules have no preferred direction in the plane and α is the angle between the molecular axis z and the surface normal Z, then^{33,34}

$$(\chi_{ads}^{(2)})_{ZZZ} = N_s \beta_{zzz} \langle \cos^3 \alpha \rangle$$

$$(\chi_{ads}^{(2)})_{ZXX} = (\chi_{ads}^{(2)})_{ZYY} = (\chi_{ads}^{(2)})_{YZY} = (\chi_{ads}^{(2)})_{XZX} = \frac{1}{2} N_s \beta_{zzz} \langle \cos \alpha \sin^2 \alpha \rangle \quad (3)$$

in which N_s is the surface concentration and the brackets refer to the orientational average. We have omitted the local-field factors in the equations because their effect can be included in the Fresnel factors as shown by Zhuang et al.³¹ The ratio of the components of $\chi_{ads}^{(2)}$ allows us to determine the molecular orientation. For this aim, it is convenient to define A as

$$A = \frac{2(\chi_{ads}^{(2)})_{XZX}}{(\chi_{ads}^{(2)})_{ZZZ} + 2(\chi_{ads}^{(2)})_{ZXX}} = \frac{\langle \sin^2 \alpha \cos \alpha \rangle}{\langle \cos \alpha \rangle}$$
(4)

If the orientational distribution can be approximated by a δ distribution, then the tilt angle α can be obtained directly

Scheme 1. Outline of the Experiment^a



^{*a*} Scheme of b-oriented silicalite-1 crystallites on a substrate. The twodimensional pore system, with straight pores normal to the surface and zigzag pores in plane with the substrate, is depicted, as is DAMPI and its behavior as a "nail". The laboratory coordinates X, Y, Z are shown along with the incoming fundamental beam with a frequency of ω and the generated second-harmonic beam with a doubled frequency of 2ω .

through A as $\alpha = \sin^{-1} \sqrt{A}$. Both $(\chi_{ads}^{(2)})_{ZZZ}$ and $(\chi_{ads}^{(2)})_{ZXX}$ can be obtained by measuring at two different polarization combinations, for example, in a PP and an SP configuration.

Because the majority of the zeolite crystallites are b-oriented (vide supra), it is predominantly the straight pores of the zeolite film that are accessible for adsorption, whereas most zigzag pores are inaccessible, as can be seen from Scheme 1. Moreover, the straight pores are oriented along the surface normal. Whereas DAMPI should be able to adsorb into these pores with its stilbazolium moiety,³⁵ the amine head cannot enter because of steric hindrance. In other words, DAMPI behaves as a "nail" (Scheme 1).³⁶ This is an important point because in this case DAMPI can be present only as a monolayer. Because the nonlinearity of the DAMPI layer dominates the observed SHG signal (vide infra), we can treat the generated SHG within the electric dipole approximation. Although in theory electric quadrupole and magnetic dipole contributions could be present, it is well established that they are usually much smaller than the electric dipole response in this type of material.37,38

The adsorption of DAMPI was probed in situ with SHG by collecting both the p-polarized second-harmonic for a

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p-polarized fundamental $(I(2\omega)_{pp})$ and the s-polarized fundamental $(I(2\omega)_{sp})$ (Figure 4a,b). Additionally, the ratio $I(2\omega)_{pp}/I(2\omega)_{sp}$ was recorded (Figure 4c). From eq 3, it is clear that $(\chi^{(2)}_{ads})_{ZZZ}$ will increase with a decreasing value of α (i.e., at a more perpendicular orientation of DAMPI toward the surface and vice versa for $(\chi^{(2)}_{ads})_{ZXX}$). Because $I(2\omega)_{sp}$ probes only the tensor component $(\chi^{(2)}_{ads})_{ZXX}$ and $I(2\omega)_{pp}$ probes both $(\chi^{(2)}_{ads})_{ZXZ}$ and $(\chi^{(2)}_{ads})_{ZXX}$, the ratio $I(2\omega)_{pp}/I(2\omega)_{sp}$ will increase with a more perpendicular orientation of DAMPI.

Before addition of the adsorptive, no SHG signal could be distinguished from the noise. After the addition of DAMPI, a sharp increase in both second-harmonic signals $I(2\omega)_{\rm sp}$ and $I(2\omega)_{\rm sp}$ was observed (Figure 4a,b) indicating the adsorption of DAMPI onto the zeolite. After nearly 2 h, both $I(2\omega)_{\rm pp}$ and $I(2\omega)_{\rm sp}$ stabilize, indicating that the DAMPI adsorption has come to equilibrium. Although the shape of the SHG adsorption curve versus time is similar for $I(2\omega)_{\rm pp}$ and $I(2\omega)_{\rm sp}$, their ratio $I(2\omega)_{\rm pp}/I(2\omega)_{\rm sp}$ changes considerably, as can be seen in Figure 4c: there is a gradual rise in $I(2\omega)_{\rm pp}/I(2\omega)_{\rm sp}$ with time. This seems to indicate that DAMPI slowly positions itself more perpendicularly toward the surface.

In Figure 5, the p-polarized second-harmonic signal at equilibrium is depicted with respect to the polarization angle of the fundamental. The corresponding average tilt angle α was calculated to be 18.8°.⁴⁰ The experiment was repeated twice with other silicalite-1 films from different synthesis batches, resulting in average tilt angles of 22.8 and 13.2° at equilibrium. In correspondence with the former experiment, the gradual rise in the ratio $I(2\omega)_{pp}/I(2\omega)_{sp}$ took place over the course of approximately 2 h. Moreover, the overall shapes of $I(2\omega)_{\rm pp}$ and $I(2\omega)_{\rm sp}$ was similar. However, the temporal fluctuations differed randomly, thus indicating that these are caused by transient inhomogeneous distribution of DAMPI in the solution. In fact, in solvents with low viscosity such as chloroform, such fluctuations are nearly absent. Furthermore, the fluctuations can to some extent be smoothed out by improving the stirring regime in the cell. On the basis of the DAMPI molar absorptivity of 2.59×10^4 L mol⁻¹ cm⁻¹ at 400 nm in 1-hexanol, it can be estimated that about 5% of the generated SHG light is reabsorbed at equilibrium by the solution; however, this does not affect the orientational information gathered from the experiment.

A δ distribution of the molecular orientation was assumed in the calculation of the average tilt angle α . When all adsorbed molecules are present in the straight pores of the b-oriented crystallites, a δ distribution is expected because the pores of a single crystallite all have exactly the same orientation⁸ and the stilbazolium moiety is just able to fit into them.³⁵ However, when the molecules reside on the outer surface, a Gaussian distribution can be expected as a result of the greater extent of orientational freedom. The effect of a deviation from the δ distribution was studied by Simpson and Rowlen,⁴¹ assuming a



Figure 4. Variation of the SHG signal intensity with time after the injection of DAMPI in (a) p-input/p-output polarization configuration ($I(2\omega)_{pp}$), and (b) s-input/p-output polarization configuration ($I(2\omega)_{sp}$). (c) Variation of the ratio $I(2\omega)_{pp}/I(2\omega)_{sp}$ with time after the injection of DAMPI.³⁹

⁽³⁹⁾ Note that in Figure 4b and c occasional gaps can be observed in the experimental data points. During these time periods, no data points where collected. However, these gaps do not influence the overall result.

⁽⁴⁰⁾ Fresnel coefficients were calculated by presenting the interfacial system as a three-layer system, as in Zhuang et al.³¹31 The refractive index used was 1.416 for 1-hexanol and 1.451 for the zeolite film filled with 1-hexanol. The latter was calculated by use of the Lorentz-Lorentz theory⁴⁴ by making use of the experimentally measured refractive index and pore volume of silicalite-1 films made by the same synthesis protocol as ours.¹³13 For the monolayer of DAMPI, the same refractive index as the zeolite film was taken. The local-field factors can be mathematically included in the calculation of the Fresnel coefficient through the refractive index of the monolayer, as is done by Zhuang et al.³¹31 We have adopted the same protocol.

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Figure 5. Variation of the p-polarized second-harmonic signal with the polarization angle of the incoming light. The incoming light is linearly polarized, and the plane of rotation is rotated along the direction of light propagation. A polarization angle of 0° corresponds to p polarization, and a polarization angle of 90° corresponds to s polarization.

Gaussian distribution. They analyzed the deviation of the real average orientation from the apparent tilt angle α with increasing orientational disorder in terms of the root-mean-square width σ . We can derive from their analysis that if the apparent average tilt angle of DAMPI is 18.8° then in fact the orientation and angular distribution of DAMPI is situated in the continuum between $\alpha = 18.8^{\circ}$ with $\sigma = 0^{\circ}$ and $\alpha = 0^{\circ}$ with $\sigma =$ 13.5° (Figure 6). Because we find a very small tilt angle and narrow distribution, it is very probable that at equilibrium most DAMPI molecules are positioned perpendicularly to the surface, and thus in the straight zeolite pores. That DAMPI effectively adsorbs in the pores of the zeolite is further supported by the observation that 2 h is needed to obtain equilibrium because diffusion of the large dye molecules in the narrow 10-membered rings of the MFI zeolite is expected to be slow. In addition, it has been shown that hemicyanine dyes adsorb in the straight pores of silicalite-1 from the liquid phase.^{32,42,43} In the latter case, it has been shown that adsorption needs 4 h to be completed in methanol, which is similar to the time observed here for DAMPI adsorption.⁴² Finally, in previous studies, for the inclusion of a hemicyanine dye in the straight channels of a b-oriented silicalite-1 film, an apparent tilt angle of 11.3° instead of 0° was determined by fluoresence spectroscopy at an angle of 7.7° instead of 0° by SHG.^{32,42}

The SEM picture in Figure 1 shows some overgrowth of a- or c-oriented zeolite crystallites, lying on their (100) or (001) face on the zeolite films. Because the straight pores of these crystallites are parallel to the plane of the film, DAMPI adsorption in these pores could explain a deviation from the average tilt angle from 0° and some orientational disorder. However, we observed no significant influence of the amount of overgrowth on the SHG signal. The sinusoidal pores are accessible at the exposed (100) faces at the discontinuities of the



Figure 6. Plot of the continuum in which the average tilt angle α and the root-mean-square width σ is situated at equilibrium (-) and at the minimum of the $I(2\omega)_{\rm pp}/I(2\omega)_{\rm sp}$ curve (Figure 4c) (—), assuming a Gaussian distribution.

zeolite film and at the overgrown crystallites. DAMPI adsorption has also been studied on ZSM-5, which has the same type of framework as silicalite-1, but contrary to silicalite-1, it contains some isomorphously substituted Al. These experiments have shown that DAMPI has a marked preference for the (010) faces as opposed to the (100) faces.³⁵ Hence, we do not attribute the orientational disorder to the latter faces.

The minimum of the $I(2\omega)_{pp}/I(2\omega)_{sp}$ curve in Figure 4c corresponds to an average tilt angle of 25.0°. If we compare this with the equilibrium state, we see that an 8° change in tilt angle corresponds to a 4-fold difference of $I(2\omega)_{pp}/I(2\omega)_{sp}$. Therefore, it can be concluded that second-harmonic generation, as a second-order technique, is extremely sensitive to orientational information. Furthermore, the apparent tilt angle of 25.0° at minimal $I(2\omega)_{pp}/I(2\omega)_{sp}$ corresponds to the continuum between $\alpha = 25.0^{\circ}$ with $\sigma = 0^{\circ}$ and $\alpha = 0^{\circ}$ with σ = 18.1° (Figure 6). This possibly higher degree of orientational disorder, half an hour after the addition of DAMPI, is in agreement with the conclusion that DAMPI is not yet fully adsorbed in the pores at this stage.

In conclusion, we have for the first time probed adsorption on a zeolite, viz., a b-oriented silicalite-1 film, with secondharmonic generation in situ. Moreover, because of the swift, continuous alternation between $I(2\omega)_{pp}$ and $I(2\omega)_{sp}$, changes in orientation of the adsorptive could be examined in real time. Surprisingly, the adsorption of DAMPI needed on average 2 h to be completed, during which time DAMPI positions itself gradually more perpendicularly toward the surface. It seems therefore that DAMPI inches progressively into the straight pores of silicalite-1. This is in agreement with the study of Jentys et al.⁹ in which it has been shown for several aromatic molecules that these molecules adsorb from the gas phase onto ZSM-5 by first physisorbing on the outer surface, followed by a slower diffusion into the pores. Because molecules in a physisorbed state on the outer surface may retain part of their rotational freedom, the larger tilt angle or larger degree of disorder, as derived from SHG, suggests a physisorbed state at the outer surface. Because secondharmonic generation is uniquely suited to probe the orientation of organic molecules in situ at liquid/solid interfaces, we are currently expanding our approach to other model systems.

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Letter

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