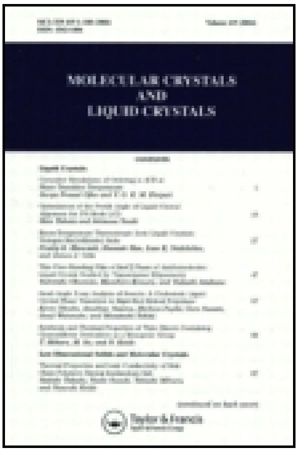

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Dipole Chains in Zeolite Pores: The Effects of Symmetry Breaking

F. Marlow [a] , J. Kornatowski [b c] , B. Reck [d] , I. Leike [a] , K. Hoffman [a] & J. Caro [a]

[a] Institut für Angewandte Chemie, Rudower Chaussee 5, D-12489, Berlin

[b] Institut für Brennstoffchemie, RWTH Aachen, Worringerweg 1, D-52074, Aachen, Germany

[c] Faculty of Chemistry, N. Copernicus University, Gagarina 7, 87-100, Torun, Poland

[d] Bundesanstalt für Materialforschung und - prüfung, Rudower Chaussee 5, 12489, Berlin, Germany

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DIPOLE CHAINS IN ZEOLITE PORES: THE EFFECTS OF SYMMETRY BREAKING

F. MARLOW[1], J. KORNATOWSKI[2], B. RECK[3], I. LEIKE[1], K. HOFFMANN[1]
and J. CARO[1]
[1] Institut für Angewandte Chemie, Rudower Chaussee 5, D-12489 Berlin
[2] Institut für Brennstoffchemie, RWTH Aachen, Worringerweg 1, D-52074
Aachen, Germany, Permanent address: Faculty of Chemistry, N. Copernicus
University, Gagarina 7, 87-100 Torun, Poland
[3] Bundesanstalt für Materialforschung und -prüfung,
Rudower Chaussee 5, 12489 Berlin, Germany

Abstract Dipole molecules become arranged in a highly ordered manner within zeolite pores. They are oriented nearly parallel to the straight channels and aligned collectively into one specific direction. They form arrangements different from the crystallization in the free bulk as well as different from arrangements in amorphous hosts. This polar arrangement results in (i) a lowering of the symmetry of the guest-host system compared to the host, (ii) nonlinear optical effects of second order such as second harmonic generation, (iii) a macroscopic polarization giving rise to pyroelectric effects and (iv) special phase transition phenomena in these one-dimensional systems.

INTRODUCTION

Composites of organic molecules and appropriate host systems are increasingly investigated in fundamental research and material science. The large variety and the ability for aim-depended design might be the reason for that. In this paper we address a special class of these composites, namely organic molecules in inorganic molecular sieves especially zeolites. This class shows an unique property worth noting: Spontaneously, dipolar guest molecules form polar arrangements in the pores of the molecular sieves. This means that all or most of the dipoar molecules point into one specific direction called the polar axis. If the molecular sieve framework was initially inversional symmetric, this symmetry is lost after adsorption of dipolar guests (symmetry breaking).

In the paper, dipole molecules such as p-nitroaniline (pNA) in different molecular sieves (Silicalite-1, $AlPO_4$-5) are investigated. X-ray diffraction delivers a picture of the dipole chains in the molecular sieve structure. The nonlinear optical effects, specially second harmonic generation (SHG) represents the most important experimental consequence of the unique molecular arrangement. These effects could be used in a new kind of nonlinear optical materials. Pyroelectric investigations reveal details of the macroscopic dipolar arrangement. Additionally, a theoretical study attempts to explain the differences in the molecular states of differently prepared intrazeolite dipole chains.

THEORETICAL MODELS

a) Uptake mechanism

In several molecular sieves with straight channels (e.g. $AlPO_4$-5 or Silicalite 1), the experimental findings (XRD, pyroelectricity, SHG) indicate that there are macroscopic regions where the individual dipole moments of the guest molecules point preferentially towards the same direction. This macroscopic polar arrangement is considered to be the result of the following uptake mechanism:

1. Due to sorbate-sorbent interactions, there exists a preference for one of the substituents of the dipolar molecule to be in front whilst entering into the straight channel. For example, it was concluded from pyroelectric studies[11] that the pNA molecules enter the molecular sieve $AlPO_4$-5 with their nitro group in front.
2. When more than one dipole molecule enter a channel, the orientations of the individual molecules start to stabilize each other by dipolar interactions. In some cases the molecules occupy fixed positions in the channel network due to their interaction with the host framework (e.g. in MFI-type structures). However, they keep their polar orientation (brought about by the uptake) regardless their possible steric ability for molecular reorientations in the channel.

It is difficult to give a direct proof for this mechanism. However, the mechanism makes nontrivial forecasts in respect to macroscopic dipole moment. The pyroelectric data meet these forecasts and, therefore, confirm this uptake mechanism.

b) Self-assembling contra Enslaving

Sorbate molecules can occupy specific positions in a molecular sieve channel system depending on combined energetic and entropic effects. For example, adsorbed p-xylene molecules become oriented in an unique way by the pores of ZSM-5. X-ray studies[1] of the "high-coverage" p-xylene/ZSM-5 complex containing 8 p-xylene per u.c. have shown that four p-xylene molecules are located in the channel intersections with their long molecular axes parallel to the straight channels, i.e. in [010] direction. The other four p-xylene molecules are placed in segments of the sinusoidal channels with their molecular axes nearly parallel to [100]. At "low-coverage" (<4 p-xylene per u.c.), only the channel intersections are occupied. Obviously, for sorbate-sorbent systems of weakly interacting sorbate molecules the adsorbate arrangement is the result of the guest-host interaction which competes with the thermal movement. Consequently, the location of a guest molecule in a host molecular sieve becomes a function of temperature and loading. In these cases, the ordering influence of the molecular sieve structure is dominant.

For dipolar molecules, however, the electrostatic dipole-dipole interaction has to be considered additionally as a structure-forming factor. As found by polarization microscopy[2], Raman scattering[3,4], optical second harmonic generation[5-10] and pyroelectric studies[11,12], the dipolar pNA molecules form well aligned molecular chains in the channels of the aluminophosphate molecular sieve $AlPO_4$-5. This host belongs to the structure type AFI[13] having only straight and non-interconnected parallel pores with a diameter of 7.3Å. The encapsulated pNA chains are assumed to be mainly the result of a self-assembling process due to the electrostatic interactions and, to some extent, due to intermolecular hydrogen bonding. Most likely, the molecular periodicity of the pNA chain does not match with the framework periodicity in $AlPO_4$-5. This mismatch becomes energetically possible within AFI type materials, since the walls of $AlPO_4$-5 channels should appear relatively smooth for an aromatic molecule placed in these tubes. However, the situation is more complex in an MFI framework which has an anisotropic bidimensional and bimodal pore system. The straight channels of slightly elliptical cross section are cross-linked by sinusoidal channels.[13] Energy minimization studies show that the channel intersections are preferred sorption sites. This means that the structure formation takes place in a more strongly periodic potential. There, a competition between the ordering influence of the framework and the self-assembling tendency of dipolar guest molecules should be expected. Thus, it is a general question whether the guest molecules form a self-assembled structure or they become "enslaved" by the potential of the framework.

c) Thermodynamics

The intermolecular mean distance within self-assembled dipole chains require a more detailed investigation. Raman spectroscopic investigations of pNA molecules in $AlPO_4$-5 revealed different spectra coming from the pNA molecules in different regions of the crystal: one spectrum similar to that of the free solid pNA, one solution-like spectrum and a mixture of both.[4] It has been supposed that two different states of pNA molecules exist simultaneously within the channels: one state with solid-like chains consisting of closely packed dipoles and another one with more separated but also well aligned molecules.

IR spectroscopic measurements[14] confirmed this assumption. During heating the sample, the IR spectrum was found to change from a solid-like to a solution-like one in a temperature range between 100°C and 200°C where both molecular states exist simultaneously.

The size of the pNA molecule is comparable with the pore diameter of $AlPO_4$-5. Thus, the translational degrees of freedom are restricted to motions parallel to the channels. Therefore, it is reasonable to assume that the dipoles in a channel form a one-dimensional system of aligned dipoles.

It seems to be straightforward to conclude from the above vibrational spectroscopic observations that the different molecular states belong to molecules in different thermodynamic phases in this one-dimensional system. However, phase transitions in one-dimensional systems have a kind of exotic touch. Landau and Lifshitz[15] stated that the existence of separate phases in one dimension is impossible. Later it turned out that this is only correct for systems with short range interactions only. It was shown that there is no phase transition in one-dimensional systems with nearest-neighbor interaction only (independently of the specific form of the interparticle potential).[16] For finite range pair potentials with a cut-off, a proof was given that no phase transition exists.[17] On the other hand, one-dimensional systems with infinite range of interaction were found, which exhibit a phase transition[18,19].

Doubtless, the system under consideration has long range interactions which manifest themselves in macroscopic effects like permanent electric polarization.[11]

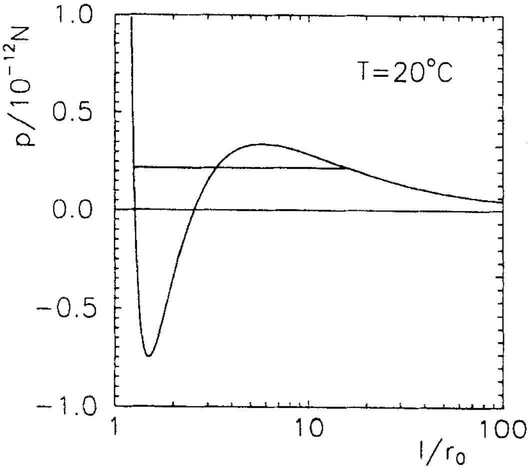

FIGURE 1 The connection between the generalized pressure p (inter-molecular force in the molecular chain) and the mean length l occupied by each molecule at 20°C.[20] This isotherm is unstable and leads to a phase separation indicated by the Maxwell construction. For the calculation the molecular data for the pNA/$AlPO_4$-5 system are used, e. g. the length of the pNA molecule r_0=0.78nm.

It was shown[20] that a model which describes the interaction of dipolar molecules in one-dimensional parallel straight channels leads to a phase transition of the first kind. The equation of state is van der Waals-like. For the actual system pNA in $AlPO_4$-5, the coexistence region covers the chemically relevant conditions, i.e. one has to take into consideration this phase transition in most experiments.

In Figure 1 an example of an isotherm for the one-dimensional system is given. One can see that the system separates itselves into a dense an a dilute phase. These two phases are supposed to be the reason for the experimental observations mentioned above.

X-RAY DIFFRACTION

X-ray diffraction (XRD) allows the structure analysis of periodic molecular arrangements. Guest/host structures can be analysed if the guests become enslaved by the host. The question whether self-assembled structures can also be analyzed by XRD is still open. In the straight channels of $AlPO_4$-5, the dipole molecules are likely to form chains incommensurable with the host framework. If the chains are perfect enough they might result in definite reflections. This has been , however, not observed yet. Here we describe the results on an "enslaved" structure, namely pNA molecules in silicalite 1.[21] The interesting point as compared to other adsorbates is that the dipole chains alter the symmetry of the system. Without dipole guest molecules, silicalite crystals has the Pnma space group, and with pNA guests, the group $Pn2_1a$ has been found.

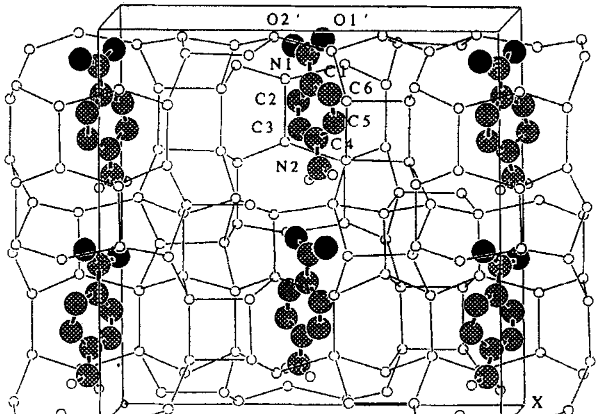

FIGURE 2 pNA in silicalite 1. Result of the refinement of 1252 reflections.

Figure 2 shows the pNA dipole chains in silicalite 1. All nitro groups of the pNA point toward the same direction. The pNA molecules were located in the intersections of the two interconnected pore systems. The molecular axes of the pNA molecules were found to deviate uniformly by 11 from the direction of the straight channels. The symmetry of the loaded molecular sieve crystals is altered by the pNA adsorption which is connected with the loss of inversion symmetry characterizing the unloaded crystals.

PYROELECTRICITY

Pyroelectric studies enable to decide between different mechanisms for the symmetry breaking. The consequences of the uptake mechanism described above and others[5] differ in their resulting macroscopic dipole distribution.

Pyroelectricity results from the reversible temperature dependence of a macroscopic polarization. The sign of the pyroelectric response depends on the temperature coefficient of the polarization (pyroelectric coefficient) and on the sign of the polarization itself. To change the local temperature of a large pNA-loaded $AlPO_4$-5 single crystal, the beam of a He-Ne laser was used, modified by components for focusing and scanning the spot across the crystal.[11] Electrodes were placed at both endings of column-like crystal to measure the pyroelectric current.

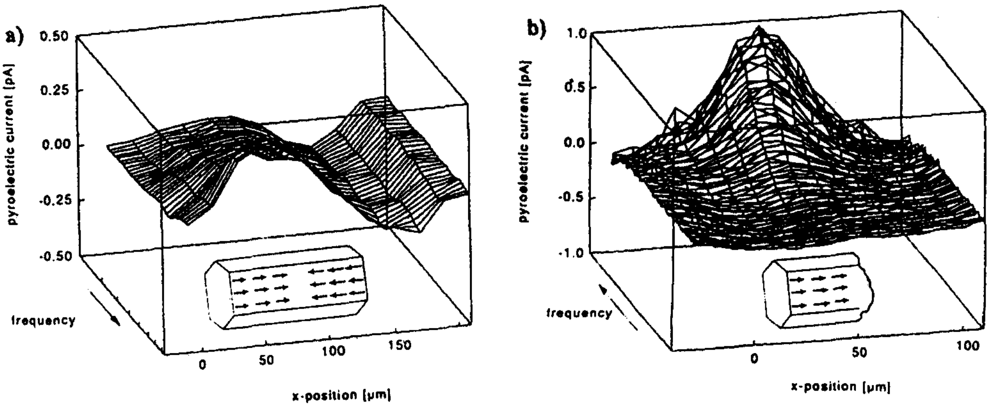

FIGURE 3 The pyroelectric current (real part) as a function of the laser focus position on the sample and the logarithmic frequency of the periodic warming up for a) a pNA-loaded $AlPO_4$-5 single crystal and b) a fragment of a broken crystal. The insert indicates the distribution of dipoles deduced from these results.[11]

The experimental results provide clear evidence for opposite dipole directions in the two halves of the crystal. Scanning with the laser focus over the crystal as shown in Figure 3a, one finds that the pyroelectric current changes its polarity in the middle of the crystal and reaches its maximum value near to the ends of the crystal. However, in the two extreme positions the pyroelectric current is just in the opposite quadrants of the complex plane having opposite signs. We then broke a pNA-loaded crystal in two halves and used one fragment in the pyroelectric measurement. Figure 3b shows a scan over a crystal segment. Correspondingly, here the maximum response is observed for irradiation of the middle of the fragment.

SECOND HARMONIC GENERATION

The SHG on dye loaded molecular sieves is the most interesting consequence of the symmetry breaking in the adsorbate system and has been investigated for a number of guest/host combinations[5-10]. This nonlinear effect of second order is forbidden in systems with inversion centers and, therefore, it indicates directly the symmetry breaking. Furthermore, this effect may point at possible applications for photonic devices.

In detail the nonlinear optical properties are described in previous papers.[5-10] Here we only discuss a special class of composite systems based on MFI type hosts, e.g. silicalite 1. MFI type hosts are of special interest because these crystals -if unloaded- are centrosymmetric.

Qualitatively we found the following results: 1) there is an intensive SHG; 2) the second harmonic radiation is linearly polarized; 3) no SHG has been found if the incident wave propagates into the direction of the straight channels; 4) if the incident wave propagates perpendicular to this channel direction the maximum SHG is generated for incident light polarized parallel to the direction of the straight channels (y-direction, see Figure 2).

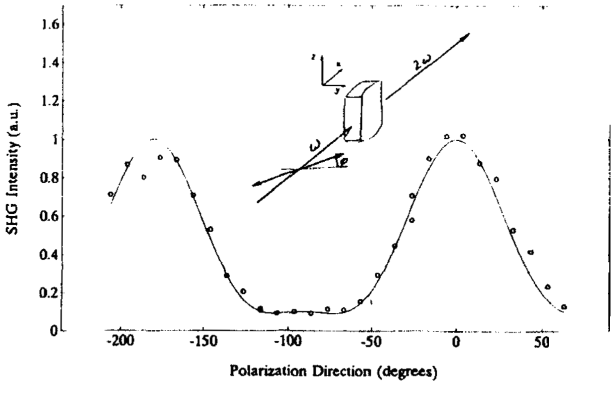

FIGURE 4 Dependence of the SHG intensity on the polarization direction of the incident beam.

Figure 4 shows the dependence of the SHG intensity on the polarization direction of the incident beam. This dependence is quite well fitted by a $\cos^4\varphi$ dependence. Only around the minimum at about 90° it appears a significant deviation from this theoretical dependence. The deviation amounts about 1/10 of the maximum SHG signal. This indicates a small χ_{yzz} component in the susceptibility tensor in addition to the expected χ_{yyy} as main component. The origin for this component is the deviation of the pNA axis from the channel direction.

ABSORPTION SPECTROSCOPY

Linear optical properties are usually considered to be not influenced by inversion symmetry breaking in the system. Arrangements of molecules described by the oriented gas model have a pronounced polarization dependent absorption spectrum, but this does not depend on that whether the arrangement is polar or not. However, if the molecules interact electronically, the effects of interaction on the absorption are strongly dependent on symmetry. The interaction is reflected by shifts and splittings in the spectrum (Davydov splitting). For example, a zigzag chain of slightly tilted molecules has a red-shifted absorption polarized parallel to the chain for a polar arrangement, whereas the unpolar chain with alternating dipole directions exhibits a blue-shifted absorption (polarized parallel to the chain).

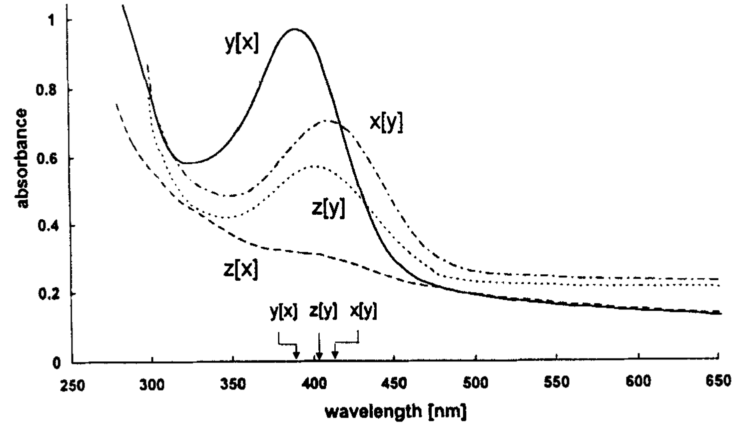

FIGURE 5 The absorption of p-Nitrodimethylanilin in silicalite 1 for different polarizations u=x,y,z and directions v=x,y,z indicated by u[v].

Molecules in molecular sieves show spectral shifts if the molecules are in sufficiently high concentrations. However, the analysis of these shifts is involved since several effects influence them: interaction of molecules within one channel, interaction through the channel walls and the influence of the anisotropic medium on the interaction between two molecules. The spectral shifts in the polarization dependent absorption spectra has

only been recognised, but not well understood yet. Up to now it is only clear that it is not enough to consider the couplings between the molecules within the same channel.
Figure 5 shows the absorption spectrum of pNA in silicalite. One measures slight shifts in the absorption bands dependent on the polarization and the irradiation direction. The shifts differ for polar and unpolar arrangements.

SUMMARY

Special mechanisms of structure formation can act for dipole molecules in molecular sieve pores. They seem to be connected with the uptake in the channels and with the peculiarities of one-dimensional systems. These mechanisms result in stable polar composite structures with typical experimental consequences of symmetry breaking e.g. pyroelectricity and SHG.

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REFERENCES

[1] H. van Koningsveld, F. Tuinstra, H. van Bekkum, J.C. Jansen, Acta Crystallogr., B45, 423 (1989).

[2] F. Marlow, J. Caro, Zeolites, 12, 433 (1992).

[3] F. Marlow, H. Hill, J. Caro, G. Finger, J. Raman Spectrosc., 24, 603 (1993).

[4] W. Hill, F. Marlow, J. Kornatowski, Appl. Spectrosc., 48, 224 (1994).

[5] S.D. Cox, T.E. Gier, G.D. Stucky, J.Bierlein, J. Am. Chem. Soc., 110, 2986 (1988).

[6] S.D. Cox, T.E. Gier, G.D. Stucky, Chem. Mater., 2, 609 (1990).

[7] S.D. Cox, T.E. Gier,.G.D. Stucky, Solid State Ionics, 32/33, 514 (1990).

[8] L. Werner, J. Caro, G. Finger, J. Kornatowski, Zeolites, 12, 658 (1992).

[9] J. Caro, G. Finger, J. Kornatowski, J. Richter-Mendau, L. Werner, B. Zibrowius, Adv. Mat., 4, 273 (1992).

[10] F. Marlow, J. Caro, L. Werner, J. Kornatowski, S. Dähne, J. Phys. Chem., 97, 11286 (1993).

[11] F. Marlow, M. Wübbenhorst, J. Caro, J. Phys. Chem., 98, 12315 (1994).

[12] J. Caro, F. Marlow, M. Wübbenhorst, Adv. Mater., 6, 413 (1994).

[13] W.M. Meier, D.H. Olson, Atlas of Zeolite Structure Types, 3rd ed. (Butterworth-Heinemann, Stoneham, MA, 1992).

[14] F. Marlow, D. Demuth, G. Stucky, F. Schüth, J. Phys. Chem., 99,1306 (1995).

[15] L.D. Landau, E.M. Lifschitz, Statistical Physics, p. 482 (Pergamon Press, New York 1958)

[16] H. Takahashi, Proc. Phys.-Math. Soc. Japan (Nippon Suugaku-Buturigakkwai Kizi, Tokio) 24, 60 (1942).

[17] L. Van Hove, Physica, 16, 137 (1950).

[18] M. Kac, G. Uhlenbeck, P. Hemmer, J. Math. Phys., 4, 216 (1963).

[19] K. Ikeda, T. Takano, Progr. Theor. Phys., 65, 1542 (1981).

[20] I. Leike, F. Marlow, Zeolites, submitted.

[21] G. Reck, F. Marlow, J. Kornatowski, W. Hill, J. Caro J. Phys. Chem., submitted.