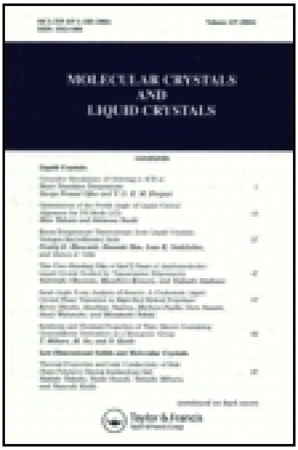

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NONLINEAR OPTICAL EFFECTS ON DYE CONTAINING MOLECULAR SIEVES

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Abstract

Composites of organic molecules and molecular sieves are promising materials for nonlinear optics. In order to achieve different NLO processes in these materials we varied the guest molecules. Paranitroaniline (PNA) and dimethylaminobenzonitrile (DMABN) were investigated in different molecular sieve hosts (AlPO-5, ZSM-5, VPI-5). These two groups of materials studied can be described by qualitatively different models: ensembles of oriented two-level or three-level systems.

In contrast to molecular sieves loaded with PNA which can only mix waves of the same polarization, for the DMABN based materials the mixing of waves of different polarizations is observed.

INTRODUCTION

Composites of organic molecules and molecular sieves are interesting materials for nonlinear optics.[1-4] Potential advantages of these systems are the high nonlinearities of some organic guest molecules, the tunability of the materials by variation of their components and a good optical and thermal resistance of the mineral molecular sieve hosts.

The interesting optical effects of these composites result from the ordering influence of the molecular sieve pores on the guest molecules. The incorporated dye molecules form highly ordered arrangements leading to the following optical properties:

(i) The light absorption becomes strongly anisotropic.[5]
(ii) The birefringence of the molecular sieve crystals is controlled by dye adsorption.[5]
(iii) The crystals show a strong anisotropy in the Raman scattering.[6]
(iv) Such materials can exhibit large nonlinear optical susceptibilities of second order. This results in optical second harmonic generation (SHG) observed for these materials.[1-4,7]

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[1] joined project with the Bundesanstalt für Materialforschung und -prüfung

Whereas the effects (i-iii) result from the alignment of the guest molecules in the pores, the fourth effect is caused by a symmetry breaking in the adsorbate system. Second order nonlinear effects are dipole-forbidden in centro symmetric materials. Therefore, the observation of efficient SHG for PNA loaded zeolite crystals proves a preferential orientation of the adsorbed PNA molecules breaking the inversion symmetry (at least for regions larger than the wavelength of light).

Until now, the occurrence of nonlinear optical (NLO) effects has been reported for a few zeolitic systems.[1-4,7] However, it still remains an open question which concrete NLO processes can be realized by means of these composites. Therefore, in order to achieve different NLO processes we varied the guest molecules using para-nitroaniline (PNA) and dimethylaminobenzonitrile (DMABN) in various molecular sieve hosts ($AlPO_4$-5, ZSM-5, VPI-5).[4,5,8,9] Measurements with these systems showed that there are qualitatively other NLO processes in DMABN based composites than in PNA based ones.

From the molecular point of view, the DMABN or PNA loaded molecular sieves represent two similar groups of materials differing especially in one aspect: whereas PNA has only one relevant excited state in the visible region, two optical transitions are observed for DMABN. Therefore the group based on PNA can be described by a model of an ensemble of two-level systems (ground state and exited state) while three levels are necessary for the description of the other group.

In this paper we compare the SHG (NLO effect of second order) in ordered arrays of two-level and three-level systems. The PNA and DMABN molecules are well described by these models.

THEORETICAL BACKGROUND

The SHG of molecules is described by the hyperpolarizability β. This quantity is connected with the properties of the energy levels of the molecules, especially with the directions of the transition matrix elements. Applying perturbation theory to molecules in the ground state leads to the following β (see e.g. ref.[10]):

$$\beta_{lmn}(-2\omega;\omega,\omega) = \frac{2\pi^2}{\varepsilon_0 h^2} \sum_{rs} \left\{ \frac{\langle 0|P_l|s\rangle\langle s|P_m|r\rangle\langle r|P_n|0\rangle}{(\omega_{0r}-\omega)(\omega_{0s}-2\omega)} + \frac{\langle 0|P_m|s\rangle\langle s|P_l|r\rangle\langle r|P_n|0\rangle}{(\omega_{0r}+\omega)(\omega_{0s}-\omega)} + \frac{\langle 0|P_m|s\rangle\langle s|P_n|r\rangle\langle r|P_l|0\rangle}{(\omega_{0r}+\omega)(\omega_{0s}+2\omega)} \right\}$$

The coordinate indices l,m,n run over all coordinates of the molecular coordinate system (x',y',z'). Let z' be the molecular length axis. ω_{0r} denotes the energy difference (divided by h/2π) between the ground state $|0\rangle$ of the molecule and another state $|r\rangle$. $\langle r|P_m|s\rangle$ is the transition matrix element. ω is the circular frequency of the incident light.

For many molecules, only a few electronic states (denoted by r and s) play a role for the calculation of β. For example in PNA, only one exited state dominates the frequency doubling properties up to 532 nm. This leads to the tensor component $\beta_{z'z'z'}$ which is much greater than all the others (see e.g. ref.[11]).

In DMABN the two lowest excited states (L_a and L_b) are very close in energy. Since these states have transition moments which are perpendicular to each other (with $\langle L_a|P_{z'}|0\rangle \neq 0$ and $\langle L_b|P_{y'}|0\rangle \neq 0$), β differs from zero for some combinations of the coordinate indices y' and z'. One finds that DMABN can have three different non-vanishing components of β ($\beta_{z'z'z'}$, $\beta_{z'y'y'}$, $\beta_{y'z'y'}$).

An ensemble of molecules is described by the nonlinear susceptibility χ which is essentially a superposition of the β of the individual molecules. In the case of perfectly aligned molecules both tensors are the same except for constant factors (For more details see ref.[9,10]). In this case the experimental results can be understood on the basis of β.

ENSEMBLES OF ORIENTED TWO-LEVEL SYSTEMS

It is known from SHG[4], Raman scattering[6] and polarization microscopy[5] that PNA molecules form dipole chains of very well aligned molecules in the straight channels of different molecular sieves. Due to the single optical transition which is polarized parallel to the molecular symmetry axis, the absorption of light by the PNA loaded crystals is highly anisotropic. Therefore, molecular sieve crystals loaded with molecules showing an anisotropy in light absorption (e.g. PNA) act as polarizers.[5] Two-level systems are necessarily anisotropic.

The SHG of such crystals shows a pronounced polarization dependence as well. The generated second harmonic light is fully polarized parallel to the channel direction (z-direction). When the polarization plane of the incident laser light is varied, the second harmonic (SH) intensity reaches a maximum when the crystal is excited parallel to the same direction. The measured values are well fitted by $\cos^4 \Phi$ where Φ is the angle between the z-axis of the crystal and the polarization plane.[3,4]

In our polarization dependent investigations, an individual crystal loaded with dye molecules was positioned in the beam of a ps-Nd:YAG laser[3] as shown in Figure 1.

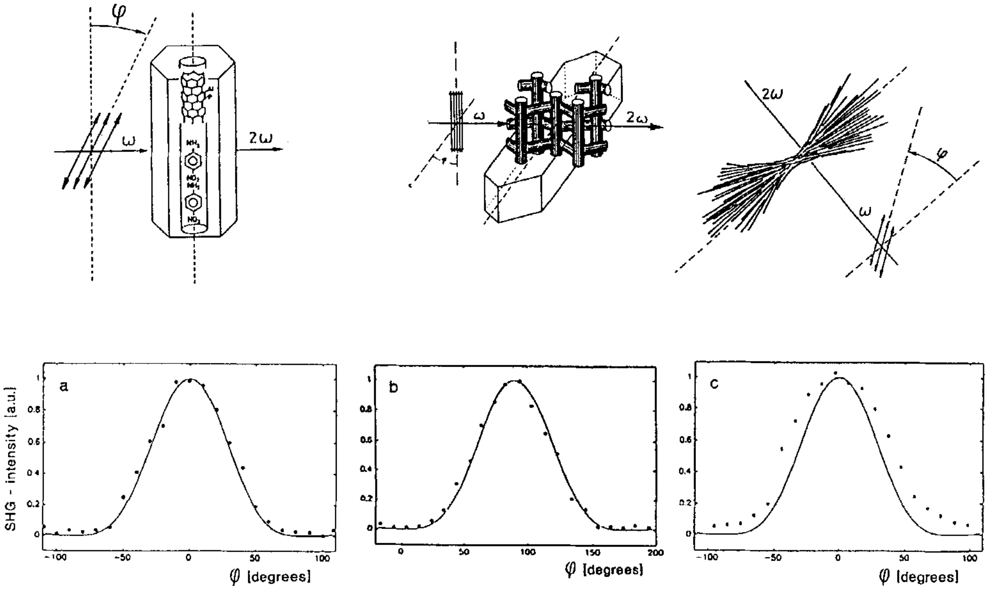

FIGURE 1 Intensity of the SH radiation for PNA in AlPO-5 (a), ZSM-5 (b) and VPI-5 (c) as a function of the polarization direction Φ of the incident light.[3,8]

For $AlPO_4$-5 the pure $\cos^4 \Phi$ behavior is found. Since no SHG was detected at $\Phi = 90°$, the molecular axis of PNA must coincide with the length direction of the crystal (z-axis).

The results obtained for PNA in ZSM-5 are quite similar indicating that only PNA molecules in the straight channels contribute to the SHG. Most likely, the molecules in the sinusoidal channels do not form directed dipole chains.

For PNA in VPI-5, maximum SHG is observed when the light is polarized in the length direction of the needle-like individual crystals. This indicates that the unidimensional pore system containing the PNA dipole chains extends in this direction. Because of the polycrystalline nature of the VPI-5 crystallite, deviations from the $\cos^4\Phi$ behavior are observed, such as especially the non-zero value of the SHG intensity at the minimum of the curve.[8]

ENSEMBLES OF ORIENTED THREE-LEVEL SYSTEMS

Our example for this group of materials is DMABN. Here, the two lowest excited states (L_a and L_b) are closely neighboring. This is important for both the dual fluorescence and the formation of TICT (twisted intramolecular charge transfer) states in DMABN (e.g. ref.[12,13]). Only these states are of relevance in the visible region.

Another consequence of the two close-lying excited states in DMABN is that DMABN can have three different non-vanishing components of β (as mentioned above). All these components were observed in our experiments with the composites based on DMABN.[9]

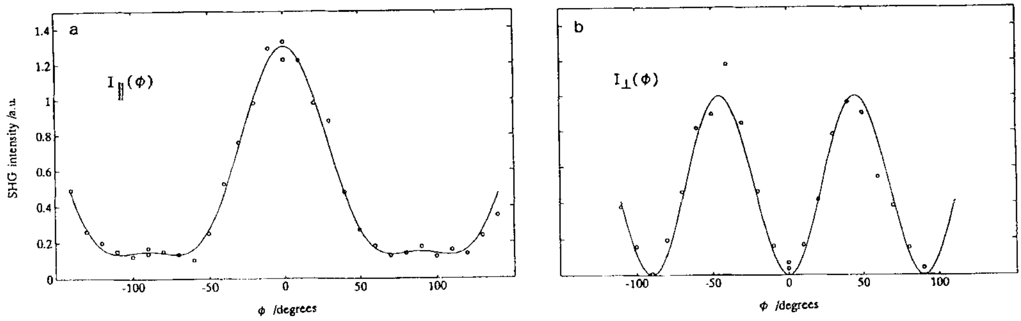

FIGURE 2 Intensity of the SH radiation polarized parallel (a) and perpendicularly (b) to the crystal length axis (z-axis) for DMABN in AlPO-5 as a function of the polarization direction Φ of the incident light. The measured values are well fitted by $I_\parallel(\Phi) = a^2 \cos^4\Phi + b^2 \sin^4\Phi$ and $I_\perp(\Phi) = c\,(\cos\Phi \sin\Phi)^2$.[9]

Contrary to PNA where the SHG is always polarized parallel to the z-direction we found for DMABN in $AlPO_4$-5 (large crystals[14]) that the SH radiation is not linearly polarized in general. The SHG can be divided into two components: $I_{\parallel}$ is polarized parallel to the crystal's length axis (z-axis) and $I_{\perp}$ perpendicularly to the z-axis. Figure 2 shows these two components as functions of the polarization plane of the incident light. Similar to PNA, $I_{\parallel}$ shows a maximum for the excitation parallel to the z-direction ($\Phi=0°$). $I_{\perp}$, however, reaches a maximum for $\Phi=45°$. The ratios of the intensities of the different signals have been determined to

$$I_{\perp}(45) : I_{\parallel}(0) : I_{\parallel}(90) \square 0.88 : 1 : 0.11 .$$

The observed signals $I_{\parallel}(0)$, $I_{\parallel}(90)$ and $I_{\perp}(45)$ are the result of three different SHG processes described by the different tensor components of χ. Schematically, these processes may be represented as follows:

$$\chi_{zzz} : \quad \uparrow + \uparrow = \Uparrow$$

$$\chi_{zyy} : \quad \longrightarrow + \longrightarrow = \Uparrow$$

$$\chi_{yzy} : \quad \longrightarrow + \uparrow = \Longrightarrow$$

In the first process, two photons polarized parallel to the z-axis interact, thus resulting in the generation of a frequency-doubled photon of the same polarization. The second process describes the conversion of two y-polarized photons into a z-polarized one. The third process is the mixing of one z-polarized and one y-polarized photon yielding a y-polarized one.

The SH radiation is found to be elliptically polarized when the electric field of the incident beam and the crystal length axis form any fixed angle between $0<\Phi<90°$. This results from fixed phase relations between the different SHG processes. The SH radiation was divided into two components ($I_{\perp}$ and $I_{\parallel}$), but these components are not independent of each other. Moreover, these two components are caused by different projections of one and the same polarization induced in a single electron system, i.e. in an individual molecule.

CONCLUSIONS

PNA based composites can only be used to mix waves of the same polarization. In DMABN loaded molecular sieves, additionally the mixing of waves of different polarizations occurs. Therefore, one precondition to achieve phase-matching by using birefringence (occurrence of different polarizations of SHG and incident radiation) is fulfilled in DMABN composites. This makes composites which are essentially ensembles of directed three level systems especially interesting for practical applications.

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