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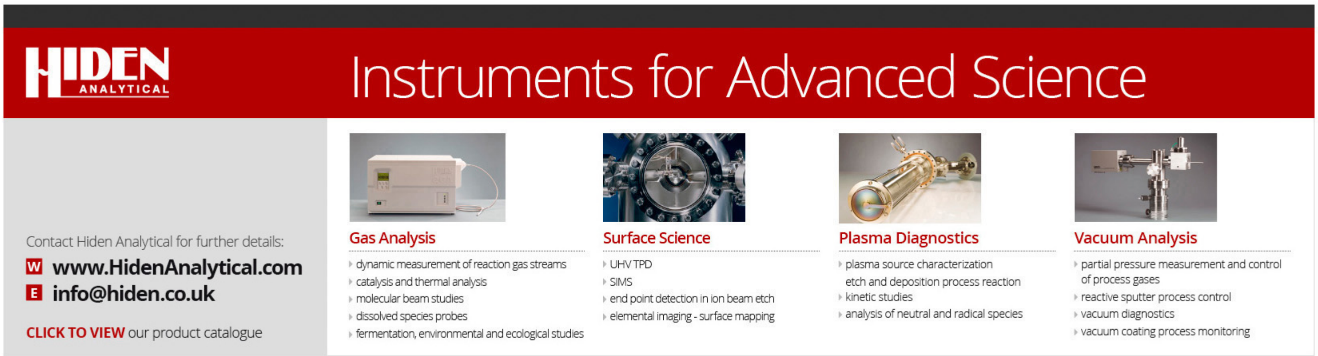
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Polarized adsorption of H_2O on NaCl(100) in air, observed by second harmonic generation

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We have observed a pronounced *m*-symmetry in the azimuthal dependence of optical second harmonic generation in reflection from NaCl(100) in air at room temperature, in spite of the fact that the C_{4v} symmetry of this surface should not exhibit any anisotropy. The observed anisotropy builds up and then disappears again with time of exposure to ambient air. The high solubility of NaCl in water, together with the high polarity of the water molecule, suggests that the dipolar surface hyperpolarization, responsible for second harmonic generation, is caused by adsorbed H_2O at a certain range of coverage. The *m*-symmetry then reflects a macroscopic polarization due to a partially parallel orientation of the adsorbed water molecules. In accord with tentative results of molecular dynamics calculations, this indicates polymerization of water on NaCl(100) at room temperature.

I. INTRODUCTION

Although extensive investigations have been devoted to the problem of H_2O on metals, semiconductors, and oxides,[1] surprisingly little is known about the details of water adsorption on alkali halide crystals,[2–5] albeit its practical interest from several points of view. For instance, the high solubility of the substrates means that condensation of humidity from ambient air is sufficient to irreversibly decompose the surface of alkali halide blanks. Among the open questions, there are, in particular, the orientation and polymerization[6] of H_2O molecules on oriented alkali halide surfaces, which should be influenced by the fact that both the substrate and the adsorbate are of highly dipolar character.

A well-suited technique to study these phenomena is given by optical second harmonic generation (SHG) in reflection from centrosymmetric media,[7] which presents the particular advantage of being applicable to any kind of *in situ* measurements, provided the sample is accessible by light. It is based on the creation of a dipolar hyperpolarization at the surface, reflecting the surface susceptibility, and is therefore a sensitive tool for investigating dipolar adsorbates.[8] Since in dipole interaction the electron motion is directly coupled to the direction of oscillation of the light fields, a rotation of the sample about its normal for fixed light polarizations yields information about geometrical structures at the surface.[9,10] Obviously, this can be readily exploited to investigate the orientation of a highly polar adsorbate like water, in particular, if the orientation of the individual dipole moments is nonrandom and amounts to a macroscopic polarization.

In this contribution, we report on SHG results obtained with polished NaCl(100) surface exposed to air at room temperature. It will be shown that the azimuthal dependence of the respective susceptibility does not correspond to the one expected from geometrical surface structure, but reflects the properties of an adsorbate which, most likely, is water condensed from ambient air.

II. EXPERIMENTAL SETUP

One distinct advantage of the SHG technique is its relatively simple and straightforward experimental realization. As described previously,[10] 6-ns pulses of a frequency-doubled Nd^{3+}–yttrium aluminum garnet (YAG) laser at 532 nm served as the fundamental incident under 45° onto the sample surface, which could be rotated about its normal by means of a stepping motor drive. The intensity was kept below 10 MW/cm^2 in order to avoid parasitic processes such as the ignition of a microplasma at the surface.[11] The reflected second harmonic (SH) radiation was separated by means of color filters and a dispersive prism from the reflected fundamental light and then detected by a solar blind Cs–Te photomultiplier, the signal of which was processed in a gated integrator and stored in a multichannel analyzer. By synchronization between channel number and sample rotation angle quick rotations, each at 0.36°/laser pulse, were superimposed in order to avoid problems from long-time baseline drifts. The polarization of both fundamental and SH was carefully controlled using high-quality Glan prisms with an extinction ratio of $< 10^{-5}$. In order to improve the signal-to-noise ratio, the reflection from the rear surface of the sample was preferred over the front surface reflection, thus taking advantage of a Fresnel enhancement of the applied electric fields.[12] In Fig. 1, the geometrical situation at the sample is schematically indicated.

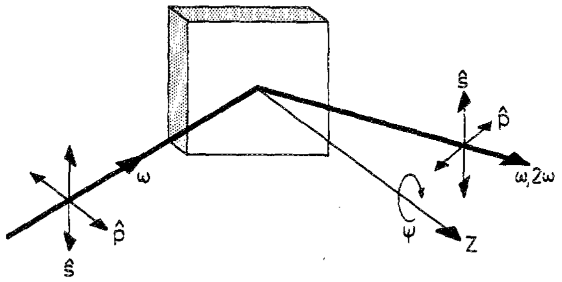

FIG. 1. Principal geometry for SHG in reflection. In the experiment the surface is rotated about its normal Z (azimuthal angle ψ), and the polarization of both fundamental and SH can be varied to any direction between $\hat{s}$ and $\hat{p}$.

III. GENERAL CONSIDERATIONS

As was outlined elsewhere,[10] SHG from a transparent centrosymmetric medium is characterized by two different sources: (i) a dipolar hyperpolarization existing only at the surface, and (ii) a contribution of higher order interactions, i.e., electric quadrupoles or magnetic dipoles coupling to electric field gradients at the surface and in the bulk. We have demonstrated[10] that only the first contribution is able to exhibit an anisotropy upon rotation of the crystal about its normal. Obviously, this can only be probed by electric field components parallel to the surface, i.e., perpendicular to the plane of incidence, whereas field components normal to the surface result in an isotropic contribution to SHG from all sources.

In the following, we will concentrate on the dipolar hyperpolarization

$$P(2\omega) = \hat{\chi}^{(2)}(2\omega)E(\omega)E(\omega), \qquad (1)$$

which is the most sensitive for the investigation of surfaces and adsorbates. As is well known,[7-11] this three-photon interaction vanishes for parity reasons in centrosymmetric media. If both fundamental and SH fields oscillate parallel to the surface (*s*/*s*-polarization, cf. Fig. 1), the whole geometry is reduced to a two-dimensional problem. Thus, at a (100) surface, which is of C_{4v} symmetry, the hyperpolarization vanishes for parity reasons. Only in a fully three-dimensional geometry (e.g., if both fields are parallel, i.e., *p*/*p*-polarization) or at an angle $\neq 90°$ to the plane of incidence (e.g., 45°/45°-polarization, i.e., when the fields have components normal to the surface) the centrosymmetry is lifted and SHG becomes possible, which is, however, isotropic upon crystal rotation. The previously reported[10] result from BaF_2 (100) in Fig. 2(a) confirms this notion. However, from the polished NaCl(100) surface, which had been exposed to ambient air, the result for identical conditions is significantly different, as shown in Fig. 2(b). This deviation from expectation must be attributed to a surface contamination introducing a different symmetry.

IV. RESULTS AND DISCUSSION

Not only for 45°/45°-polarization did we find an unexpected symmetry from NaCl(100) surface exposed to air, but we also found SHG for *s*/*s*-polarization (Fig. 3), in contrast to expectation and the result from BaF_2. In this case, the sample had been exposed to air for a couple of days at a normal laboratory humidity of ~50% and a temperature of ~20 °C. The azimuthal dependence exhibits a pronounced twofold symmetry (it should be kept in mind that for the specific experimental conditions there is a 180° degeneracy for linear light polarizations).

The question arises, what information about the adsorbate can be obtained from the observed symmetry. For an answer, we first have to consider the properties of the dipolar nonlinear susceptibility $\chi^{(2)}$ in Eq. (1). If we assume *m*-symmetry (C_s) in Fig. 3, with the NaCl(010) plane being the mirror plane, only the following *in plane* components of $\chi^{(2)}$ do not vanish[13]:

$$\chi_{111}, \chi_{122}, \text{ and } \chi_{212} = \chi_{221}, \qquad (2)$$

where the subscripts 1 and 2 denote projections of the adsorbate molecular coordinates onto the NaCl$\langle 00\bar{1}\rangle$ and $\langle 010\rangle$ directions, respectively. A transformation in laboratory coordinates (see Fig. 1) then gives for the *s*-polarized SH intensity (in analogy to Refs. 10 and 14):

$$I_{s,2\omega}(\psi)\alpha[-\chi_{111}\sin^3\psi - (\chi_{122} + 2\chi_{212}) \sin\psi\cos^2\psi]^2 I^2_{s,\omega}, \qquad (3)$$

with ψ being the angle between the light polarization and the normal to the mirror plane. The solid line in Fig. 3 is a least-squares fit of $I_{s,2\omega}(\psi)$ to the data, from which we obtain the ratio

$$\frac{\chi_{111}}{\chi_{122} + 2\chi_{212}} = 1.10. \qquad (4)$$

The excellent agreement with the experimental result justifies our choice of *m*-symmetry for the adsorbate.

Similarly, we can model the case of Fig. 2(b), i.e., 45°/45°-polarization. There, we have components of the light fields

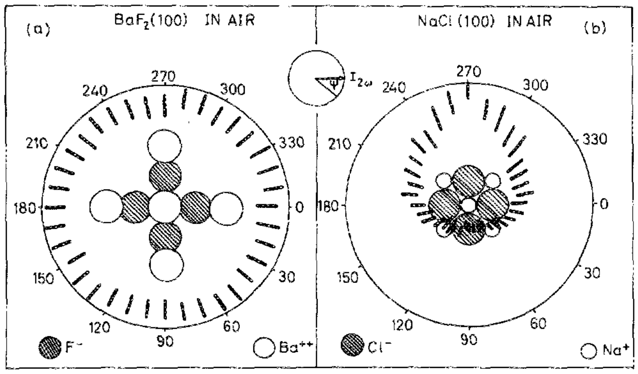

FIG. 2. Polar plots of data for the azimuthal dependence of SHG in reflection from (100) surfaces in air for (a) BaF_2 and (b) NaCl. The fundamental wavelength is at 532 nm, the angle of incidence is at 45° to normal, both polarizations (ω, 2ω) are at 45° to the plane of incidence, the rotation angle ψ is between $e_\parallel$ and $\langle 010\rangle$. The underlaid orientation of the crystal structure was obtained from cleavage.

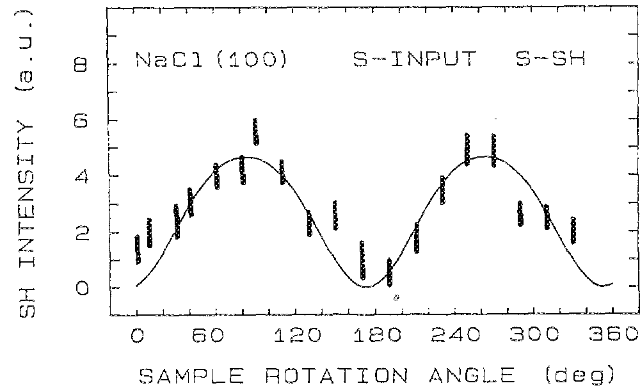

FIG. 3. Azimuthal dependence of SHG in reflection from NaCl(100) in air. Both beams (ω, 2ω) are *s*-polarized and directed at 45° to the surface which is rotated about its normal (rotation angle ψ is between *s* and $\langle 010\rangle$). The solid line is a least-squares fit for *m*-symmetric nonlinear polarization.

both perpendicular and parallel to the surface. Consequently $\chi^{(2)}$ has the following elements (coordinate 3 parallel to the NaCl ⟨100⟩ direction)[13]:

$$\chi_{111}, \chi_{122}, \chi_{133}, \chi_{131} = \chi_{113}, \chi_{223} = \chi_{232},$$
$$\chi_{212} = \chi_{221}, \chi_{311}, \chi_{322}, \chi_{333}, \text{ and } \chi_{331} = \chi_{313}, \qquad (5)$$

which all are operative and lead to a correspondingly more complicated azimuthal dependence. In Fig. 4, the data of Fig. 2(b) are presented in a linear plot together with a calculated curve, where the tensor components were optimized only by eye. Nevertheless, the curve approaches the experimental points so well, that it can be considered as an additional proof that the assumption of *m*-symmetry is correct.

The data reported so far were all obtained from polished NaCl(100) samples which had been exposed to ambient air for a few days. For *fresh* samples (immediately after being taken out of a sealed package), we generally found that they did not exhibit any azimuthal anisotropy of SHG, whatever polarization was used. Only with time of exposure, the *m*-symmetry at the surface developed. In Fig. 5 we have plotted for one particular sample the change in SHG anisotropy with time. The fresh sample, irradiated at 45°/45°-polarization, shows indeed a SH yield independent of the azimuthal orientation, as expected for a (100) surface. After one day of exposure to ambient air, the anisotropy starts to emerge, and after two days it is fully developed. Continuing exposure again reduces the adsorbate specific susceptibility, and for this particular sample the effect vanishes completely after three days. The sequence observed was reasonably reproducible for all samples investigated, whereas the time scale, naturally, depended on humidity and the individual sample.

The *m*-symmetry is extremely well defined even at room temperature. This can be seen in Fig. 6. The lowest set of data [Fig. 6(c)] reproduces the typical twofold dependence on azimuthal orientation for *s*/*s*-polarization (cf. Fig. 3). However, already a small deviation from pure *s*-polarization for either fundamental or SH changes the pattern substantially, as is shown in Fig. 6(b) for a deviation of the fundamental of only $\phi = 3°$. In this case, the oscillation of the electric field is no longer exclusively parallel to the surface and the 180° polarization degeneracy is lifted. A deviation of $\phi = 8°$ [Fig. 6(a)] almost restores the pattern of 45°/45°-polarization (cf. Fig. 5). This sensitivity to even small admixtures of other tensor components is characteristic for *m*-symmetry.

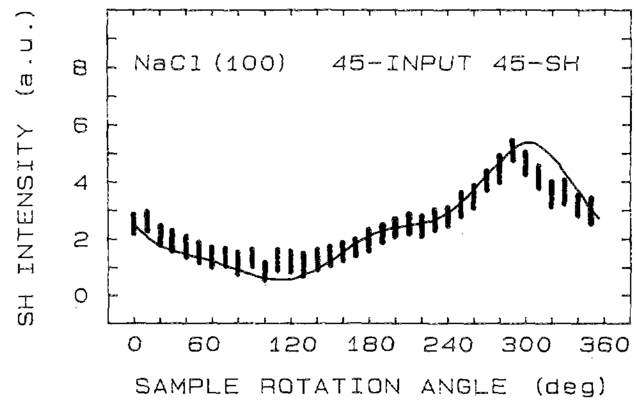

FIG. 4. Azimuthal dependence of SHG from NaCl(100) in air for 45°/45°-polarization [same data as in Fig. 2(b)]. The solid line represents the predicted anisotropy for *m*-symmetry with a particular choice of susceptibility components (see text).

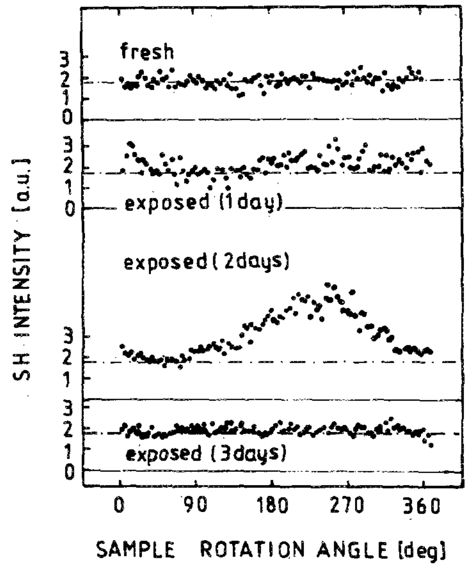

FIG. 5. Development in time of exposure to air of *m*-symmetry on a NaCl(100) surface, recorded with 45°/45°-polarization.

The observed adsorbate-induced *m*-symmetry is equivalent to the assumption that there is a net macroscopic polar-

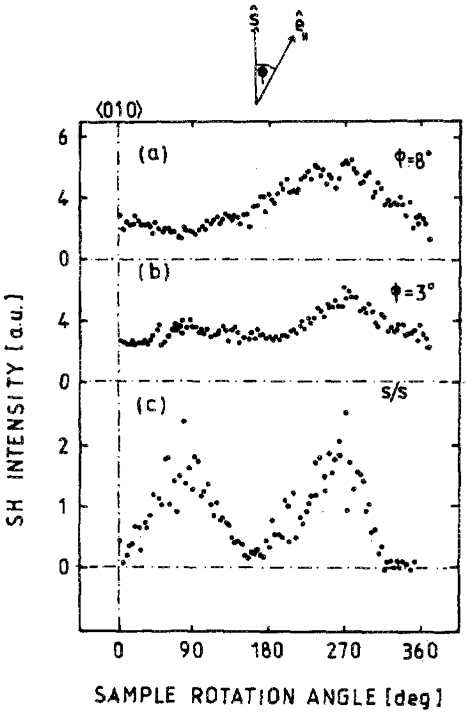

FIG. 6. Variation of the SHG azimuthal pattern when deviating from exact *s*/*s*-polarization. As indicated in the insert, the angle ϕ denotes the deviation of the fundamental field component parallel to the surface ($e_\parallel$) from true *s*-polarization.

ization at the surface which allows for only *one* principal direction of electron motion. In particular the result of Fig. 6 indicates that the direction is inclined with respect to the surface, and all measurements show that its projection onto the surface is along the crystallographic ⟨001⟩ direction. Taking into account the high solubility of NaCl in water, there is strong evidence (cf. Fig. 5) that the polarization is due to adsorbed water molecules with their strong dipole moments. A possible model would be that these link up in such a way that, for a certain coverage, there exists a resulting macroscopic electric polarization[15] on the surface with a projection along the ⟨001⟩ direction. This could be achieved by the formation of H-bridge bonded chains (polymerization) of water molecules. Preliminary results obtained by molecular dynamics calculations support this view. Starting with a coverage of $\frac{1}{4}$ monolayer of arbitrarily oriented and positioned H_2O molecules, we find that after $\sim 3 \times 10^{-11}$ s (i.e., 3×10^4 calculation steps) the average components of the total electric dipole moment parallel and perpendicular to the surface plane are never zero. The calculations were performed for a surface temperature of 100 K, whereas our measurements are carried out at about ~300 K, where correspondingly larger fluctuations are to be expected. Nevertheless, we believe that the electric dipole moments of the water molecules will still not average to zero, even at room temperature.

V. CONCLUSIONS

Using surface SHG we have shown the development of a *m*-symmetry on NaCl(100) exposed to ambient air for a few days. Because of the large solubility of NaCl in water and because of the large dipole moment of the H_2O molecules, we interpret the data as indicating polarized water adsorption. Although the measurements were carried out at room temperature, polymerization of water in chains would provide an explanation for the observed adsorbate-related *m*-symmetry. The fact that the latter vanishes again after several days of exposure to air must be taken as evidence that full coverage of the surface with H_2O is reached and an icelike network is formed which no longer results in a preferential orientation of the water dipoles.

Further work is required to confirm the observations reported in this contribution. In our laboratory experiments on Raman scattering, aimed to identify the adsorbate as water molecules, are under way, as well as experiments on SHG under ultahigh vacuum conditions with well controlled H_2O adsorption, in order to shed more light on the dynamics of the process. Finally, the molecular dynamics calculations have to be refined and extended to give a more detailed understanding.

ACKNOWLEDGMENTS

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