Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Study of Single Crystal Surface with Second-Harmonic Generation : p-Nitroaniline

Hiroyuki Kobayashi [a] & Masahiro Kotani [a]
[a] Faculty of Science, Gakushuin University, Mejiro, Tokyo, 171, Japan

Version of record first published: 24 Sep 2006.

To cite this article: Hiroyuki Kobayashi & Masahiro Kotani (1994): Study of Single Crystal Surface with Second-Harmonic Generation : p-Nitroaniline, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 252:1, 277-281

To link to this article: http://dx.doi.org/10.1080/10587259408038233

Mol. Cryst. Liq. Cryst. 1994, Vol. 252, pp. 277–281
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

STUDY OF SINGLE CRYSTAL SURFACE WITH SECOND-HARMONIC GENERATION : *p*-NITROANILINE

HIROYUKI KOBAYASHI AND MASAHIRO KOTANI
Faculty of Science, Gakushuin University, Mejiro, Tokyo 171, Japan

Abstract We study cleaved surface of a single crystal of *p*-nitroaniline by laser microprobe technique with SHG detection. The surface is scanned with a tightly focused beam from a Q-switched Nd:YAG laser, while SHG is monitored. There is a strong variation of the SH intensity, although angular as well as polarization dependence indicates well-ordered alignment of molecules on the surface. Possible origin of this inhomogeneity is discussed.

Keywords: p-nitroaniline, second harmonic generation, single crystal surface

Introduction

It has been recognized that generation of optical second-harmonic (SHG) can be a powerful tool for studying surfaces [1]. SHG is forbidden in a medium which has an inversion symmetry. Since surface lacks inherently a center of inversion, any second-harmonic signal originated from a centrosymmetric medium should come from the surface and should bear information of the surface. This is an optical method and can be applied to many surfaces and interfaces, including those of insulating media.

Molecular solids are unique in that orientation of molecules which constitute the solids is an important parameter. SHG is especially suited for studying orientation of molecules. Here we report a SHG study of crystal surface of a highly nonlinear compound, *p*-nitroaniline (*p*-NA).

The crystal structure of *p*-NA has an inversion symmetry [2] (see Fig.1) and hence SHG from the bulk is forbidden. However, SHG can be observed when a

cleaved surface is irradiated with a 1.06 μ m pulse from a Q-switched Nd:YAG laser [3]. The cleaved surface is (101) plane. The SH intensity is the largest, when the fundamental is incident normal to the surface. The SH is polarized parallel to X (see Fig.1), irrespective of the polarization of the incident beam. Measurements with various incident angles and with various polarizations indicate that a large nonlinear polarization oscillates along the surface, while the SH component normal to the surface is small. The only dominating component is χ_{xxx}, which has a magnitude of 2×10^{-13} cm^2/esu. This is nearly two orders of magnitude smaller than the nonlinearity expected from a perfect monolayer [3]. In order to get more insight into the surface generation of SH, we studied the surface with a laser microprobe technique with SH detection.

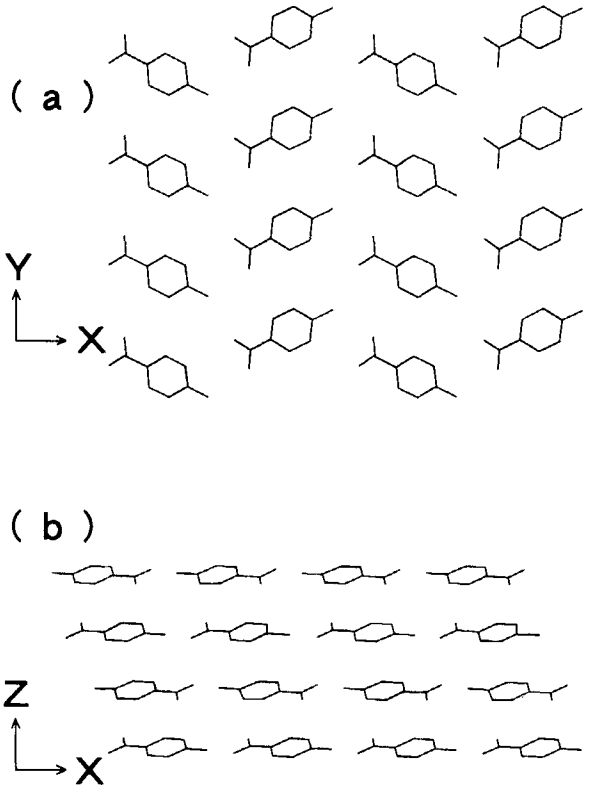

Fig.1 Molecular arrangement in *p*-nitroaniline crystal.
(a) The model structure of the outermost layer of a cleaved surface. (b) Drawing of the crystal structure projected down Y axis. The crystal structure is an alternating stack of molecular sheets as in (a) and identical sheets with reversed polarity.

Experimental

An experimental arrangement for SH microprobe study is shown in Fig.2. A beam from a small Q-switched Nd:YAG laser was focused on a cleaved surface of a *p*-NA crystal and the intensity of the SH at 532 nm was monitored as the beam traverses across the surface. The laser beam waist had a diameter of ca. 10 μ m. The energy of the laser pulse was reduced to 0.1 mJ / pulse. At this intensity no damage of the surface was detected. The sample was fixed on a two-axis translator which was driven by stepping motors, controlled by a computer. The fundamental and SH components were separated with dichroic mirrors. The intensity of the transmitted SH was measured with a photomultiplier. The signal from the photomultiplier was digitized with a 12 bit transient digitizer and was averaged with a microcomputer. The spatial resolution was ca. 5 μ m.

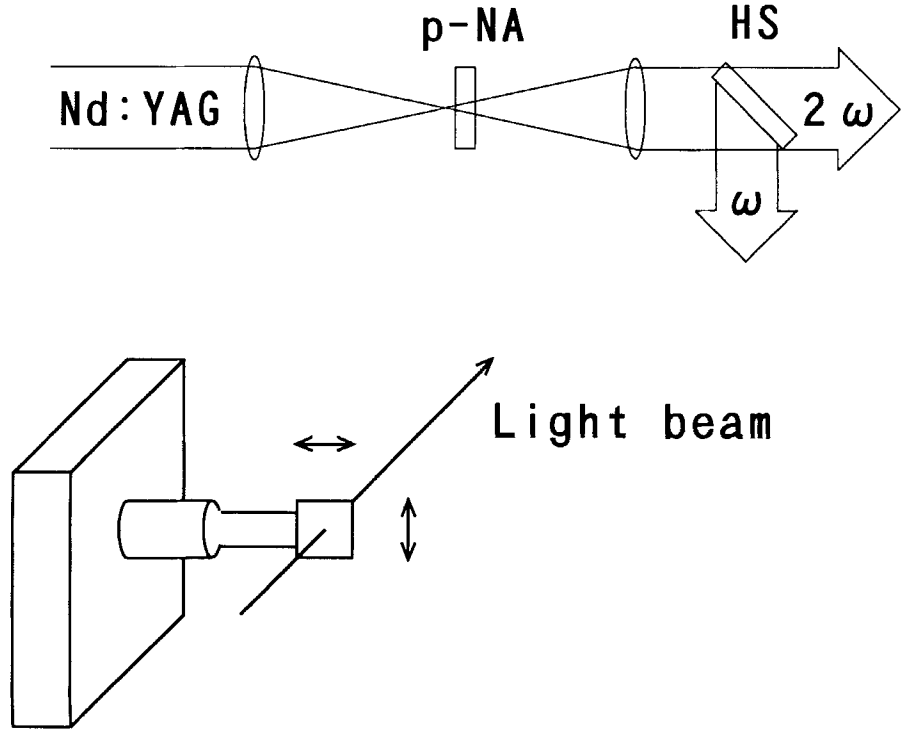

Fig.2 Experimental arrangement.
The sample can be moved in 1 μ m steps in the vertical plane. HS: Dichroic mirror which transmits the second-harmonic and reflects the fundamental.

Results and discussion

A two-dimensional scan with a laser beam has disclosed that the surface of a cleaved *p*-NA single crystal is not homogeneous in generating SH (Fig.3). There are spots at which the SH intensity is stronger by 2-3 orders of magnitude compared to the surrounding area. We observed that the freshly cleaved surface is relatively homogeneous while the number of spots which give strong SH increases in the course of a few days after the cleavage. The SH is polarized parallel to X both in the "hot" spots and in the surroundings which indicates that molecules are well aligned in both areas. There are two possible origins of the "hot" spots.

One possibility is that irregularities such as etch pits are responsible for the high SHG efficiency. Boyd et al. [4] have noted that the intensity of the SH can be sensitive to the surface defects since it is proportional to the fourth power of the local electric field. We could observe that 2-3 weeks after its cleavage the surface became rough and many etch pits developed on the surface. This formation of pits may be the result of slow evaporation of the surface molecules at room temperature, i.e.: thermal etching.

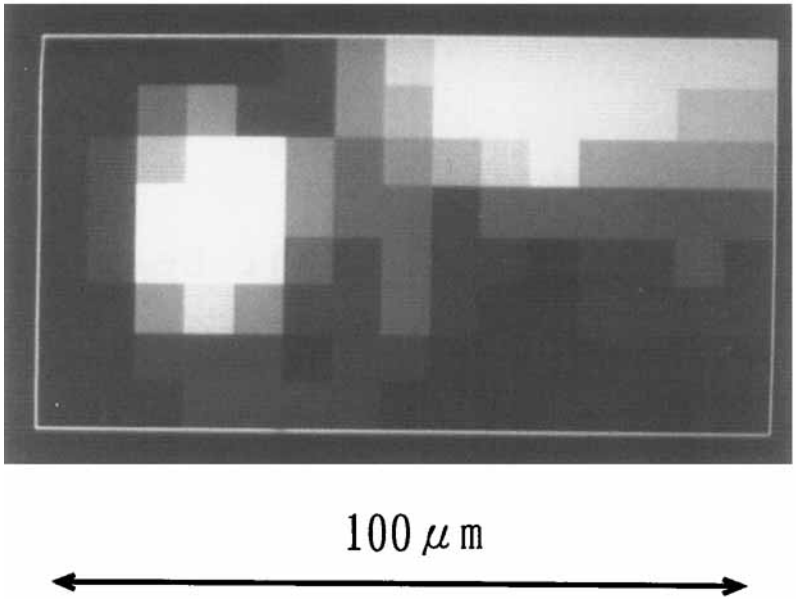

Fig.3 Image of a cleaved surface with second-harmonic.
Intensity in white spots is stronger than in the surrounding area.

The other possible origin of the inhomogeneity is closely associated with the structure of a *p*–NA crystal. The crystal structure can be regarded as a stack of sheets of molecules. Each sheet is polar, with its dipole moment directed to either of two opposite directions along the sheet (see Fig. 1a). The crystal structure is made up by stacking such sheets in alternating order (even–numbered sheets with their dipole pointing to the right and odd–numbered sheets to the left) so that it is centrosymmetric. The top layer is polar and SHG is possible with normal incidence. If however, the surface has a step of one molecular thickness, the areas on both sides of the step have opposite polarity and generate SH with a phase difference of π . If a large number of such steps exist within the focal spot of the laser the intensity of SH observed will be small, since the contributions from areas of differrent polarity tend to cancel each other. The spatial fluctuation of the SH intensity observed may indicate that the size of a single domain in which molecules are aligned unidirectionally is comparable to the size of the focal spot of the laser.

Acknowledgement

The authors wish to thank the Japan Securities Scholarship Foundation for financial support.

References

[1] Y. R. Shen, *Nature* 337, 519 (1989).
Y. R. Shen, *Annu. Rev. Phys. Chem.* 40, 327 (1989).
[2] K. N. Trueblood, E. Goldish, and J. Donohue, *Acta Cryst.* 14, 1009 (1961).
[3] H. Kobayashi and M. Kotani, *Chem. Phys. Lett.* (submitted)
[4] G. T. Boyd, T. R. Shen, and T. W. Hänsch, *Opt. Lett.* 11, 97 (1986).