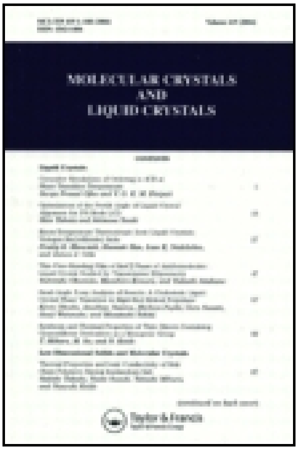

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Second Harmonic Generation in the Benzimidazole Crystal

A. Bree [a] & R. Zwarich [a]
[a] Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada, V6T 1Y6

Version of record first published: 22 Sep 2006.

To cite this article: A. Bree & R. Zwarich (1990): Second Harmonic Generation in the Benzimidazole Crystal, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 186:1, 99-105

To link to this article: http://dx.doi.org/10.1080/00268949008037198

Mol. Cryst. Liq. Cryst., 1990, vol. 186, pp. 99–105
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

SECOND HARMONIC GENERATION IN THE BENZIMIDAZOLE CRYSTAL

A. BREE and R. ZWARICH
Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6.

Abstract Two different types of second harmonic generation have been observed in a benzimidazole single crystal. A 'normal' type of harmonic is observed well away from any material resonance when the entering and outgoing beams have orthogonal polarizations in order to achieve phase-matching. A second type of harmonic generation is found near resonance with the first excited electronic state when the entering and outgoing beams have the same polarization.

INTRODUCTION

Benzimidazole (BZ) is an example of a molecule of low symmetry (C_s) in a crystal of higher symmetry (C_{2v}). The high symmetry of the solid links the principal directions of the optical indicatrix to the orthorhombic crystal frame. In the case, as here, where there is no centre of inversion second harmonic generation (SHG) and two-photon absorption (TPA) may both contribute to population of an excited state[1]. They may be distinguished in the semi-classical model by regarding TPA as occurring through a complex susceptibility ($\chi^{(3)}$), whether phase-matching is possible or not, and by treating SHG as arising through constructive interference of real polarizations through ($\chi^{(2)}$). If 2ω is near a material resonance, then the amplitude of the excited state wave function is derived from a combination of a phase-matched $\chi^{(2)}$ and a non-phase-matched $\chi^{(3)}$ part. In BZ we find evidence for pre-resonant as well as resonance-enhanced SHG, the enhanced signal being observed near the electronic origin of the lowest energy absorption system at 35 844 cm^{-1} where TPA is also found.

NON-RESONANT SHG

BZ forms an orthorhombic crystal ($Pna2_1$) with four molecules in each unit cell[2]. There is perfect (100) cleavage. Thus *bc* sections were easily prepared from melt-grown ingots. Refractive indices were measured at room temperature with the electric vector of light parallel to *b* and *c* in two ways: (i) The Becke immersion method was used at the sodium D line and at the 514.5, 488.0 and 476.5 nm lines of an argon ion laser. (ii) The angle of minimum deviation (δ_m) for monochromatic light passing through a wedge of BZ with known wedge angle (α), as measured under a microscope, was determined and the refractive index (n) was found using[3]

$$n = \frac{sin\frac{1}{2}(\delta_m + \alpha)}{sin\frac{1}{2}\alpha} \tag{1}$$

This second method had the advantage that frequency doubled light from a Nd/YAG pumped dye laser could be used, extending the measurements into the near UV. The results of these refractive index measurements are shown in Figure 1. Our values do not agree with those listed by Winchell[4].

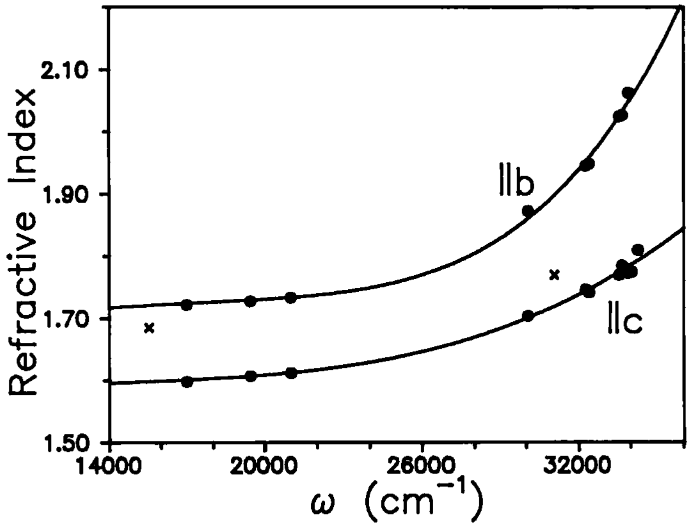

FIGURE 1. Dispersion of the refractive indices, n_b and n_c, of benzimidazole at room temperature.

The appearance of SHG is restricted strongly by the phase-matching condition[1] that the refractive index at the fundamental (ω) and at the harmonic frequency (2ω) be the same, so that the two beams may pass coherently through the medium. From Figure 1, we see that the phase-matching condition

$$n_b(\omega) = n_c(2\omega) \tag{2}$$

is reached for $\omega = 15\ 533\ \mathrm{cm}^{-1}$. This feature, that the harmonic is polarized at right-angles to the fundamental, is common in the use of commercial frequency doubling crystals. In our case, a blue spot was easily seen on a sheet of bond paper, used as a fluorescent screen, when the doubled beam was passed through a Corning 7-54 filter to remove the fundamental. A check with polaroid showed that the SHG behaviour was as predicted, i.e., a signal was observed only when the fundamental was parallel to *b*, and then the doubled beam was polarized parallel to *c*. This observation of SHG confirms the correctness of our refractive index values.

With a 12 mJ pulse at the fundamental frequency ω, a 0.085 mJ pulse was produced at 2ω in a BZ crystal 1.09 cm thick. For a rough comparison, the same fundamental pulse energy was passed through a 1 cm thick commercial KD*P crystal to produce a 0.24 mJ output pulse. Since the SHG signal should scale with the crystal length for perfect phase-matching, BZ and KD*P have a comparable doubling efficiency, although the useful range of BZ is reduced by ultraviolet absorption.

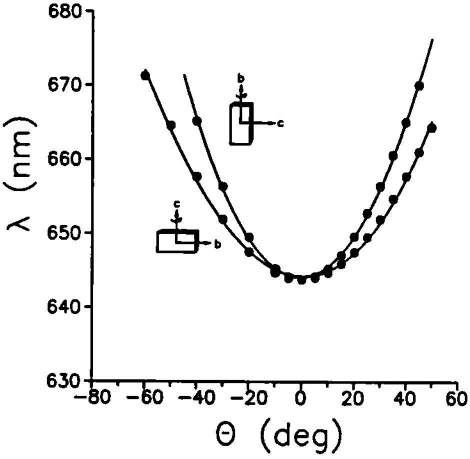

FIGURE 2. The effect of rotating a *bc* section of BZ on the laser wavelength that gives maximum SHG intensity.

Angle-tuning experiments were carried out in which a 1.18 mm, cleaved *bc* section of BZ was rotated about either the *b* or *c* axis with the phase-matching wavelength being found by tuning the dye laser. The results of these experiments are displayed in Figure 2 and demonstrate that it is SHG being observed.

The data from the angle-tuning study may be used to estimate the refractive index of BZ when the electric vector vibrates along the third crystal axis *a*. The estimates for n_a at ω and 2ω are shown as crosses on Figure 1.

RESONANT SHG

A less usual resonant SHG is illustrated in Figure 3.

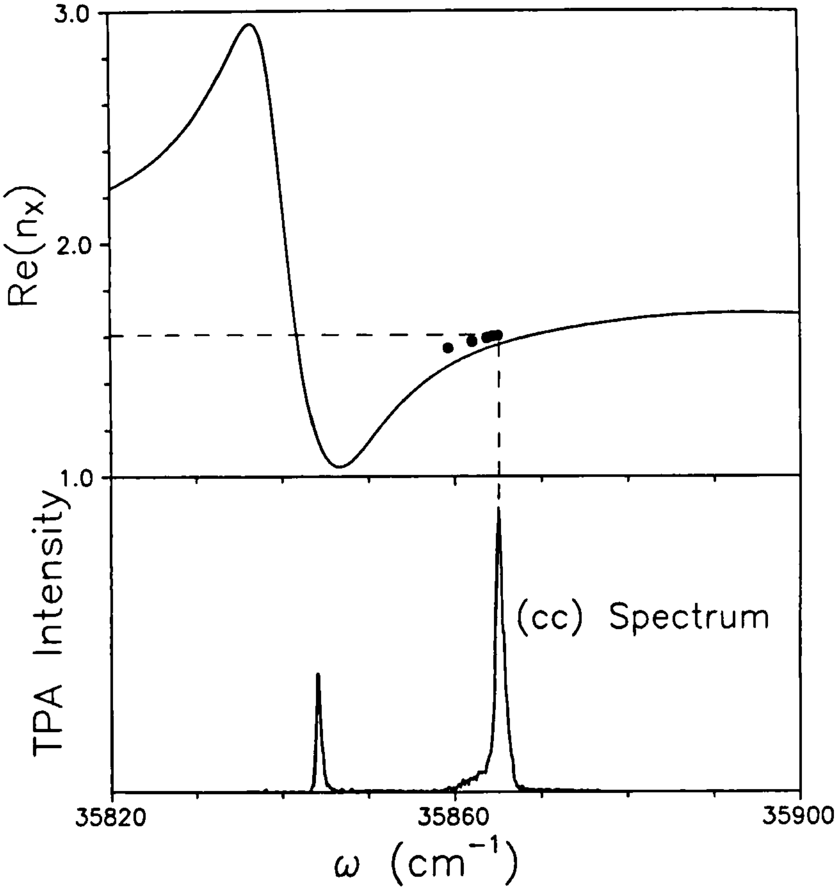

FIGURE 3. The dispersion of the real part of the complex refractive index parallel to *c* (upper panel), and the (*cc*) polarized two-photon excitation spectrum of benzimidazole at 1.8 K.

The lower panel of Figure 3 depicts the (*cc*) polarized TPA of a BZ crystal held at 1.8 K, the absorption event being detected by the observation of the resulting fluorescence. A doublet, at 35 844 and 35 865 cm^{-1}, is observed in which the lower energy component is the emitting state in fluorescence. Each member of the doublet is sharp, having a full-width at half-maximum of 0.47 and 0.70 cm^{-1} for the lower and higher energy component, respectively. The width of the narrower of these two lines is probably limited by the exciting dye laser which has a nominal linewidth of 0.3 cm^{-1}. In the higher energy region of the TPA spectrum, no similar doublets are observed; this doublet structure is a feature seen only at the origin.

The upper panel of Figure 3 illustrates an attempt to model the dispersion of the real part of the refractive index using parameters found in fitting the observed *c* polarized reflection spectrum[5] measured at 1.8 K to an equation of the form

$$\epsilon(\omega) = \epsilon_0 + \sum_j \frac{\omega_j^2 f_j}{\omega_j^2 - \omega^2 - i\omega\gamma_j} \tag{1}$$

where f_j, ω_j and γ_j are the oscillator strength, transition frequency and homogeneous linewidth of the jth transition in the crystal. ϵ_0 is a background term meant to include the contributions from higher energy transitions, and was chosen to be 2.56, the square of the refractive index in Figure 1. We set n as $\sqrt{\epsilon(\omega)}$, and the full line in the Figure represents the values for Re(n) found in fitting the reflection spectrum.

The appearance of the 35 865 cm^{-1} line in the TPA spectrum can now be accounted for as a resonant (or near-resonant) SHG effect. The dashed line on Figure 3 represents the value $n_c = 1.603$ observed at room temperature at $\omega = 17932$ cm^{-1} (see Figure 1). Figure 3 shows that phase-matching can occur near 35 865 cm^{-1} when both the incident and outgoing radiation is *c* polarized. The apparent phase-match is not precise, and this is attributed to imprecision in the fitting procedure.

To check this idea, angle-tuning experiments were carried out in which the vertical axis *b* was the rotation axis. The frequency of the upper component of the doublet did change with angle (while the lower energy component did not), and the observed dependence is shown in Figure 4. The frequency red shifts with increasing angle of rotation because the value of n_a is greater at 2ω than at ω. The small part of the n_c dispersion curve in the region of the second harmonic was mapped out from the angle-tuning data. These values are shown as the full circles in Figure 3.

The line at 35 865 cm^{-1} is strongest by far in the (cc) spectrum. This happens because the harmonic intensity is resonantly enhanced, 2ω falling at the edge of the weak phonon sideband of the 35 844 cm^{-1} origin. Any SHG formed in this way is promptly absorbed and the process is detected by fluorescence. We believe that the intensity at 35 844 cm^{-1} is largely due to $\chi^{(3)}$(TPA). This frequency corresponds to the center of the absorption band and any SHG contribution is small because the effective crystal thickness for the process is of the order of the reciprocal of the absorption coefficient. Certainly, this line shows no angle-tuning behaviour at all. On the other hand, the intensity at 35 865 cm^{-1} arises almost entirely through the $\chi^{(2)}$(SHG) term. Any contribution from a two-photon absorption process should follow the shape of the absorption band contour, found also in fitting the reflection spectrum[5], and this would provide only a broad background (following the shape of the phonon sideband).

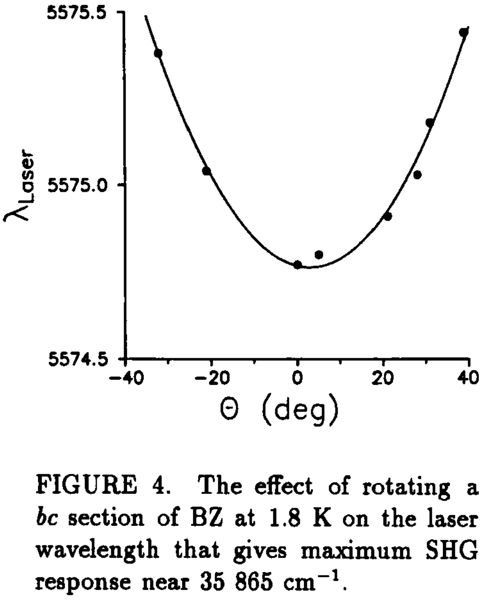

FIGURE 4. The effect of rotating a bc section of BZ at 1.8 K on the laser wavelength that gives maximum SHG response near 35 865 cm^{-1}.

The width (0.70 cm^{-1}) of the SHG peak at 35 865 cm^{-1} is surprisingly narrow, and is attributed to the rapid dispersion of the refractive index. If the phase-matching condition $n_c(2\omega) = n_c(\omega)$ is not met, the output power is reduced by a factor[6]

$$F = \frac{sin^2(2\pi\omega l[n(2\omega) - n(\omega)])}{2\pi\omega l[n(2\omega) - n(\omega)]} \tag{2}$$

where l is the crystal thickness and ω is in cm^{-1}. The data in Figure 3 give a calculated width of 0.02 cm^{-1} for the SHG peak when the full crystal thickness of about 0.1 cm is used. A close fit to the observed linewidth is found when the effective crystal thickness is reduced to about 30 μm, and this is a reasonable estimate for the reciprocal of the absorption coefficient in the phonon sideband.

ACKNOWLEDGEMENT

We are grateful for financial support from the National Sciences and Engineering Research Council of Canada.

REFERENCES

1. N. Bloembergen, *Nonlinear Optics* (W.A. Benjamin, Inc., Reading, 1965); T.P. McLean, *Interaction of Radiation with Condensed Matter* (International Atomic Energy Agency, Vienna, 1977).
2. A. Escande and J.L. Galigne, *Acta Cryst.*, **B 30**, 1647 (1974).
3. F.A. Jenkins and H.E White, *Fundamentals of Optics* (McGraw-Hill, New York, 1957).
4. A.N. Winchell, *The Optical Properties of Organic Compounds* (Academic, New York, 1954), p205.
5. A. Bree and R. Zwarich, *J. Chem. Phys.*, **90**, 5901 (1989).
6. A. Yariv, *Introduction to Optical Electronics* (Holt, Rinehart and Winston, New York, 1971).