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Interferometric Enhancement of Surface-Generated Second-Harmonic Radiation

G. Marowsky and A. Gierulski

Max-Planck-Institut für biophysikalische Chemie, Abteilung Laserphysik, D-3400 Göttingen, Fed. Rep. Germany

G. A. Reider and A. J. Schmidt

IAEE, Abteilung für Quantenelektronik und Lasertechnik, Technische Universität, A-1040 Wien, Austria

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Abstract. Greatly improved second-harmonic emission has been obtained from dye monolayers adsorbed at quartz etalons. Two different types of interferometers have been studied in terms of the SH signal from dye coverage versus harmonic background emission. The phasematching-like conditions for constructive interferometric enhancement and the concomitant spatial and spectral emission characteristics are discussed in detail.

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It is a well-known fact that second-harmonic (SH) generation cannot occur in centrosymmetric media for symmetry reasons within the electric dipole approximation [1]. However, this symmetry considerations do not hold at the surface of isotropic media and for thin layers covering such a surface. SH generation from dye monolayer coverages adsorbed on fused silica substrates has been demonstrated recently by Shen and coworkers [2]. SH emission from dye coated surfaces of a plane-parallel plate has been studied in [3]. In either case it has also been shown that SH generation can be considerably enhanced if the harmonic light is at resonance with the S_0-S_2 transition of the dye molecules. However, SH signals from single dye-covered surfaces are rather small, typically 10^4 photons per pulse, if laser radiation with an energy of a few millijoules is focused to 10^{-3} cm^2, an energy density close to the damage threshold of synthetic quartz samples. It is the purpose of this contribution to show that this signal level can be increased by several orders of magnitude, using multiple-beam interferences.

Experimental

All experiments have been performed by focusing the radiation of an excimer pumped dye laser (Lambda Physik FL 2000 [4]) of 4 mJ pulse energy and 10 ns pulse duration onto thin quartz slabs of etalon quality. With 1.5 mm in thickness and 45 mm in length (Fig. 1) interference of SH waves originating from up to 30 internal reflections of the fundamental wave could be observed. To permit adequate coherence the laser bandwidth was narrowed down to 0.1 cm^{-1} by an intracavity etalon.

The square dependence of the SH intensity versus intensity of the fundamental had been previously established by alternation of the dye laser output or changing the focusing conditions. To achieve highest SH signals by multiple-beam interference spatial overlap of the SH radiation from consecutive internal reflections of the fundamtental is essential. In fact, highest signals have been obtained by focusing the 4 mJ dye laser energy on 4 mm^2 cross section of the entrance face of the etalon. Highest directionality with considerably lower power levels has been obtained with unfocused fundamental radiation. Experiments with shorter etalons indicated that the N^2 law (N: number of reflections) is valid for up to the first 10 reflections, whereas further reflections add additively, as described in [3].

Details of the experimental arrangement are shown in Fig. 1. Besides interferometric enhancement by superposition of the various SH contributions inside

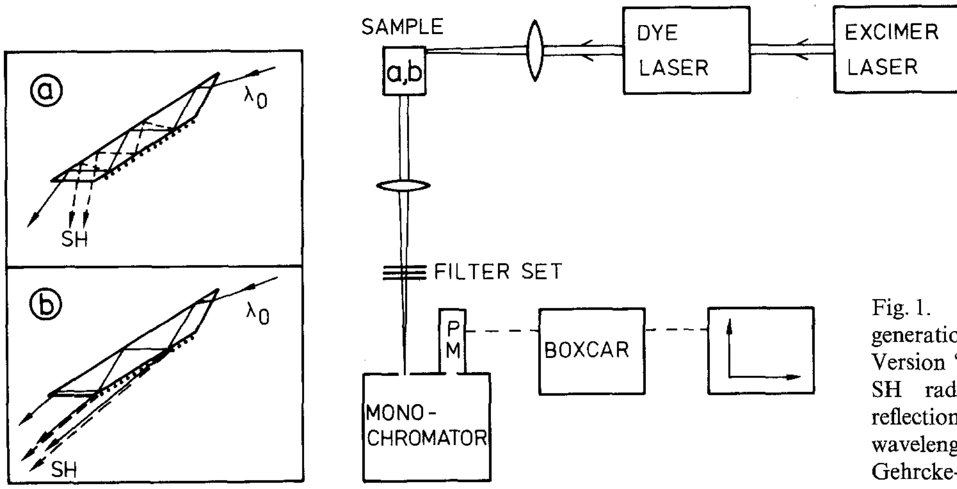

Fig. 1. Experimental set-up of SH generation at dye-covered etalon surfaces. Version "a": intra-etalon superposition of SH radiation generated by multiple reflection of the fundamental of the wavelength λ_0, version "b": Lummer-Gehrcke-type interferometric arrangement

the quartz etalon (version "a") a Lummer-Gehrcke-type interferometer [5] has also been studied (version "b"). In the latter case the fundamental leaves the etalon under grazing angle together with the SH radiation generated in the surface dye layer. The collinear propagation allows convenient analysis of the UV signal with a monochromator, shielded with an appropriate set of filters, and a multiplier-boxcar combination.

Results

As dye coverage monolayers of sulforhodamine 101 have been chosen, since this dye exhibits a higher spectral enhancement than the previously studied dyes rhodamine 110 and rhodamine 6G [2, 3]. For this dye the peak of the spectral enhancement coincides with the S_0-S_2 absorption of sulforhodamine 101 in liquid solution. Figure 2 shows an absorption spectrum together with spectral details of the S_0-S_2 absorption and SH enhancement in the spectral region between 340 and 400 nm on an enlarged scale.

The superposition of SH contributions from a large number of phase-matched sources leads also to build-up of a considerable signal from the quartz background. Figure 3 shows for comparison Maker-fringe type [1] oscillations in the SH intensity from the pure, uncovered quartz substrate (lower trace) and form the dye monolayer (upper trace) versus angle of incidence. Both signals were recorded with p-polarized light. Under an angle of incidence of 45° the number of oscillations was limited to 10 due to the change in the number of reflections upon rotation of the quartz plate. The magnitude of the background signal strongly depended on the nature of the polarization of the incident light. For convenience p-polarization has been chosen in order to normalize the SH output data by a well-defined quartz-signal. Excitation with s-polarized light reduced the quartz-background typically by two orders of magnitude and thus it

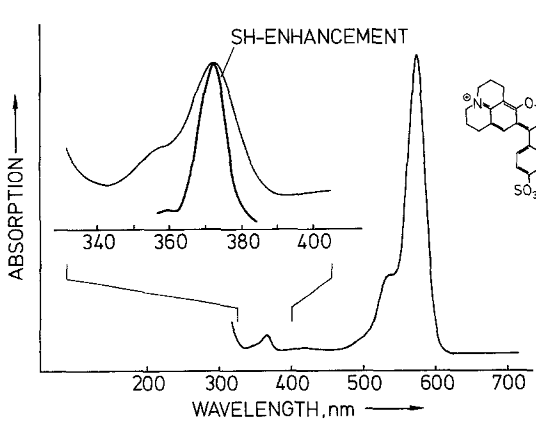

Fig. 2. Absorption spectrum of sulforhodamine 101 in methanolic solution. On enlarged scale: S_0-S_2 absorption and concomitant SH enhancement

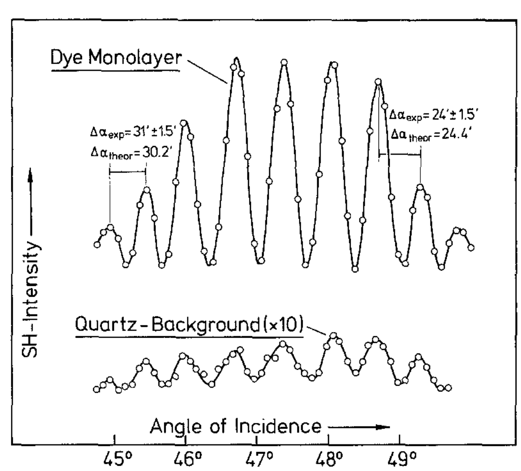

Fig. 3. Maker-fringe-type oscillations of SH intensity of dye monolayer and quartz-background for p-polarized excitation

became close to the noise limit of our detection system.

The background contributions of both versions are compared in Fig. 4, showing chart recorder traces obtained by boxcar averaging of 1000 laser pulses for each case. It is apparent from this figure that the Lummer-Gehrcke interferometer is superior in total SH output. The SH intensities of the dye coverage refer to a single coverage, whereas the background signal inevitably comprises contributions of both surfaces. According to [6] this quartz background signal is due to surface effects rather than to electric-quadrupole and magnetic-dipole contributions from the bulk. Compared with the SH signal from a single dye-covered surface, constructive multiple-beam interference typically resulted in a signal-enhancement of a factor 10^3.

The spacing of the Maker-fringe type oscillations of the SH intensity (Figs. 3 and 6) will be described with reference to the optical schematic of Fig. 5. In principle this angle- and wavelength-dependent spacing results from an evaluation of the phasedifference along B–C by comparison of the optical pathlengths $\overline{OB}$ and $\overline{OAC}$. The experimental findings suggest, however, that it is sufficient to assume equal phases at points A and B. In fact, due to the high dispersion of fundamental and SH wavelength the interference pattern resulting from the phasedifference along $\overline{AC}$ is superimposed by a very fast modulation which is beyond the wavelength resolution of our setup. With

$$\overline{AC} = m \cdot \left(\frac{\lambda_0}{2n'}\right) \tag{1}$$

(m an integer and n' the index of refraction at $\lambda_0/2$) a phasematching-type condition for constructive interference can be established for both, intensity modulation due to changes in the angle of incidence (Fig. 3) and due to variation of the fundamental wavelength λ_0 (Fig. 6). With $n' \cdot \sin\alpha' = n \cdot \sin\alpha$ according to [7], the modulation shown in Fig. 3 occurs due to a change $\Delta\alpha$ in the angle of incidence α:

$$\Delta\alpha = \frac{\lambda_0/2n}{a \cdot \cos\alpha + \frac{da}{d\alpha} \cdot \sin\alpha}, \tag{2}$$

$$a = h \cdot (\tan\alpha - \tan\alpha'). \tag{2a}$$

Variation of the wavelength $\Delta\lambda$ leads to a modulation of the SH intensity (Fig. 6) with

$$\Delta\lambda = \lambda_0^2/(\lambda_0 + an \sin\alpha). \tag{3}$$

In either case, $\Delta\alpha$ and $\Delta\lambda$ describe the angle- and wavelength-dependent separations between successive maxima of the SH modulation. Both modulations have been used to check the calculated frequencies. For

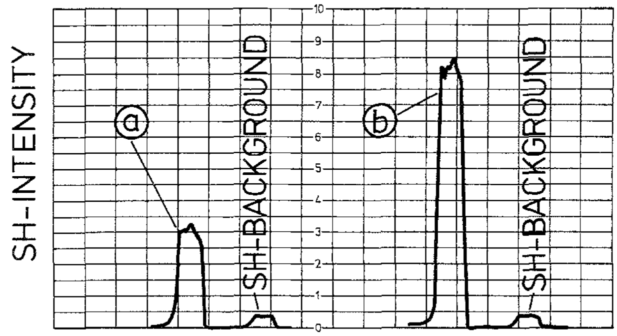

Fig. 4. Chart recorder traces of SH intensity of versions "a" and "b" of Fig. 1 together with background signal

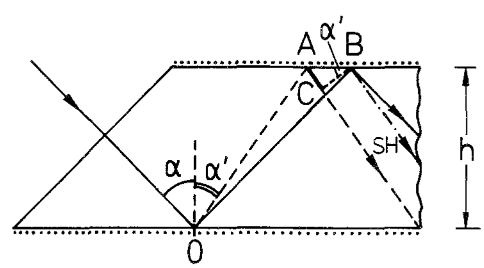

Fig. 5. Optical schematic of SH generation by superposition of SH contributions from successive reflections of fundamental at dye-covered surface of quartz plate (h: plate thickness)

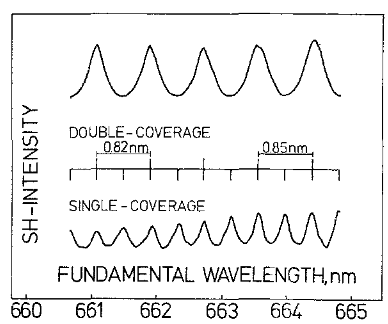

Fig. 6. Maker-fringe type oscillations for single- and double-coverage of quartz etalon with dye monolayer

modulations due to angular changes in α experimental values $\Delta\alpha_{exp} = 31' \pm 1.5'$ and $24' \pm 1.5'$ have been derived from Fig. 3, which compare well with the data calculated from [2], $\Delta\alpha_{theor} = 30.2'$ and $24.4'$, respectively. A similar comparison has been performed upon wavelength variation. At the spectral positions indicated (Fig. 6) $\Delta\lambda_{exp} = 0.82 \pm 0.05$ nm and 0.85 ± 0.05 nm has to be compared with $\Delta\lambda_{theor} = 0.82$ nm and 0.85 nm, respectively, as calculated from [3]. In either case the agreement is good, in particular when considering the other results of Fig. 6: a coverage of both quartz surfaces halves the modulation frequency or doubles the effective free spectral range (FSR) and doubles the number of successive reflections.

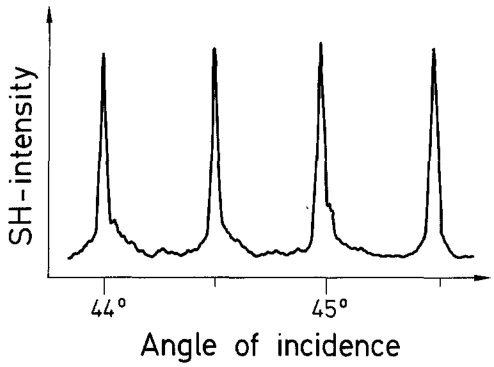

Fig. 7. High directionality obtained from multiple-beam interferences of SH radiation generated by incidence of unfocused dye laser radiation

Conclusions

It has been shown that the relatively small SH signals, obtained from dye-covered surfaces of quartz slabs, can be enhanced by constructive interference due to multiple reflections by a factor of up to 1000. This strong enhancement allows for the first time the quantitative study of sub-monolayer coverages, or less SH effective dyes or experiments without $S_0 - S_2$ spectral amplification. In addition, SH signals have been obtained from unfocused dye laser beams with this technique (Fig. 7), revealing the high degree of directionality of this intra-etalon generated UV radiation.

References

1. N. Bloembergen: *Nonlinear Optics* (Benjamin, New York 1977)
2. T.F. Heinz, C.K. Chen, D. Ricard, Y.R. Shen: Phys. Rev. Lett. **48**, 478 (1982)
3. G.A. Reider, A.J. Schmidt, G. Marowsky: Opt. Commun. **47**, 223 (1983)
4. The dye laser FL 2000 was kindly left to our disposal by Dr. R. Vehrenkamp, Lambda Physik, Göttingen
5. M. Born, E. Wolf: *Principles of Optics*. 4th ed. (Pergamon Press, London 1970)
6. H. W. K. Tom, T. F. Heinz, P. Ye, Y. R. Shen: In *Laser Spectroscopy* VI, ed. by H.P. Weber, W. Lüthy, Springer Ser. Opt. Sci. **40** (Springer, Berlin, Heidelberg, New York 1983)
7. N. Bloembergen, P.S. Pershan: Phys. Rev. **128**, 606 (1962)