PHYSICAL REVIEW B VOLUME 58, NUMBER 24 15 DECEMBER 1998-II

Phase-sensitive detection technique for surface nonlinear optics

K. J. Veenstra,* A. V. Petukhov,† A. P. de Boer, and Th. Rasing
Research Institute for Materials, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands
(Received 4 September 1998)

We have developed a simple technique to measure the phase of the weak surface optical second-harmonic response to excitation with femtosecond laser pulses that uses the principle of spectral interference. This approach is necessary for the study of surfaces under (ultrahigh) vacuum conditions, where the conventional method fails due to the dispersion in optical windows. As a demonstration, we have applied the technique to clean Ni(110) in UHV and to a Rh/Co/Cu multilayer in air. We have determined the phase with an accuracy of 5° which is comparable to the conventional method. [S0163-1829(98)50548-6]

Optical second-harmonic generation (SHG) has attracted significant attention due to its high sensitivity to the electronic, magnetic, geometric, etc., structure of surfaces and interfaces.[1–4] The surface sensitivity stems from the fact that SHG is dipole forbidden in the bulk of centrosymmetric media but is allowed at interfaces where the centrosymmetry is lifted. In surface SHG experiments only the intensity of the generated harmonic light is usually measured. The phase of the second-harmonic (SH) light does, however, often contain valuable information for a correct interpretation of the experimental data. Furthermore, phase-sensitive measurements are especially useful in surface-specific second-harmonic generation where the response mainly originates from a thin surface region so that the optical phase is directly related to the phase of the components of the surface second-order susceptibility $\chi^{(2),S}$. As an example the phase may give direct information about molecular orientation on surfaces[5] and in liquid crystals.[6] In magnetization-induced second-harmonic generation (MSHG), phase information is needed to evaluate the relative size of the odd (magnetic) and even (nonmagnetic) tensor elements.[7–9]

The phase of the SH response can be determined by employing an interference technique originally introduced by Chang *et al.*[10] This method, however, is not compatible with, for example, ultrahigh vacuum (UHV) experiments when femtosecond lasers are used. The reason is the dispersion of the optical windows ($\Delta n_{\text{glass}} \sim 10^{-2}$), causing a too large time delay ($\tau \sim 1$ ps) between the fundamental and SH pulses that destroys the interference. For studying clean surfaces, UHV conditions are nevertheless unavoidable, leading to a demand for an alternative approach. In this paper we show that by making use of spectral interferometry,[11,12] phase-sensitive measurements in UHV are readily accessible. We believe our technique to be easy, accurate, and reliable.

When a SH (2ω) and a fundamental (ω) pulse (described by their amplitudes E_{SH} and E_f) propagate through air, the relative phase Φ between E_{SH} and E_f^2 gradually changes,

$$\Phi(d) = \Phi_0 + \delta\Phi = \Phi_0 + \frac{4\pi\Delta n_{\text{air}}}{\lambda} d, \tag{1}$$

where $\Delta n_{\text{air}} = n(2\omega) - n(\omega) \sim 10^{-5}$ is the dispersion of the ambient air, d is the distance the two pulses travel through air, and λ is the wavelength of the fundamental pulse. By using an additional SHG source (reference) at position d in the path of the beam, interference can be observed in the detected total SH signal

$$I_{2\omega,\text{tot}}(d) = I_{2\omega,s} + I_{2\omega,r} + 2\alpha\sqrt{I_{2\omega,s} I_{2\omega,r}}\cos[\delta\Phi(d) + \Phi_0], \tag{2}$$

where $I_{2\omega,s}$ and $I_{2\omega,r}$ are the SH signals generated by the sample and the reference, respectively. The spatial coherence is described by the coherence parameter α. This interference, however, disappears if the reference SH pulse and the sample SH pulse arriving at the detector do not overlap in time. As is shown in Fig. 1, this occurs when the femtosecond fundamental and reference SH pulses also have to travel through a relatively strong dispersive element like an optical window of a UHV system. For example, the dispersion of a few mm thick fused quartz UHV window causes a total delay of order 1 ps between the fundamental and SH light. Instead of compensating the delay in a complicated optical setup, our approach is to use this delay to obtain the phase information from the spectrum of the generated second-harmonic light.

In the time domain the optical field at the detector of two SH pulses with a delay τ can be described by the function

$$E_{\text{SH}}(t) = E_1 g(t) e^{-i2\omega_0 t} + E_2 g(t-\tau) e^{-i2\omega_0 t + i\Phi} + \text{c.c.}, \tag{3}$$

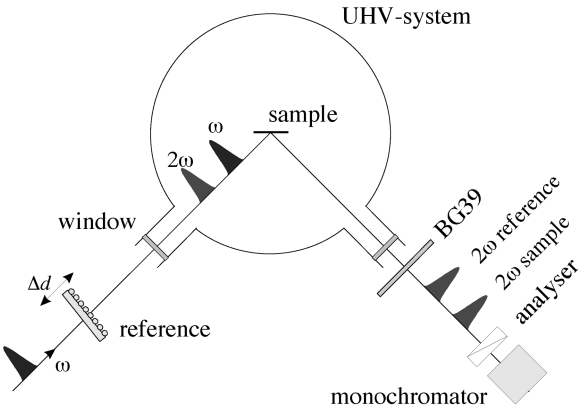

FIG. 1. Sketch of the experimental setup. The SH pulse from the reference is delayed with respect to the fundamental laser pulse due to the dispersion of the window.

where $E_i g(t)$ describes a slowly varying envelope with amplitude E_i $(i=1,2)$. The fast oscillating part of the pulses and their relative phase Φ are contained in the exponentials. Using the so-called ''time-shifting'' identity, $g(t-\tau) \Leftrightarrow G(\Omega) e^{i\Omega\tau}$, where $g(t) \Leftrightarrow G(\Omega)$ and the Fourier transformation is denoted by $\Leftrightarrow$, the measured spectrum at the detector is given by

$$I(2\omega_0+\Omega) \propto |G(\Omega)|^2 [(E_1^2+E_2^2 + 2\alpha E_1 E_2 \cos(2\omega_0\tau+\Omega\tau+\Phi)], \quad (4)$$

where Ω denotes the deviation of the frequency from the central frequency $2\omega_0$ within the spectrum of the SH pulse. The first term in the cosine, $2\omega_0\tau$, is a fixed number whereas the second, $\Omega\tau$, leads to beatings with a period $2\pi/\tau$ in the spectrum of the SH light. The phase of the beatings is directly related to the phase Φ of the response from the sample. Thus, the phase information can be easily recovered just by using a spectrometer with a resolution of better than 0.25 nm (with a second-harmonic wavelength of 400 nm and a delay of 1 ps). Note that no additional components are needed such as, e.g., delay lines (which would be needed to recover the interference in the time domain) or a Mach-Zender interferometer (which is often needed to observe spectral interference[13,14]).

To demonstrate our technique we have studied the SH-response from a Ni(110) single crystal in a UHV system with fused quartz windows as shown in Fig. 1. A Ti-sapphire laser was used to generate the fundamental 80 fs light pulses with a repetition rate of 80 MHz. The average power at the sample was about 400 mW with a spot diameter of approximately 150 μm. The polarization combination for the fundamental and the second-harmonic beam could be chosen by using a Babinet-Soleil compensator and an analyzing polarizer. The reference source is a glass slide covered on one side by a thin poled polymer film with a high second-order nonlinearity. It was placed outside the UHV chamber as shown in Fig. 1. For the detection of the harmonic light we used a monochromator, with a resolution of 0.125 nm, in combination with a charge-coupled device (CCD) camera. A color filter (BG39) was used to filter out the fundamental light. A magnetic field could be applied along the easy $(\bar{1}11)$ axis of the Ni crystal that was in the optical plane of incidence.

In Fig. 2(a) the measured spectrum of the second-harmonic light generated by the nickel sample and the reference is displayed. The spectrum clearly shows the spectral interference oscillations as expected from Eq. (4). From the raw data it is, however, difficult to accurately determine the relative phase. Therefore, we apply a Fourier analysis to the data. First, the Fourier transform $f(t)$ of the (shifted) SH spectrum $F(\Omega)=I(2\omega_0+\Omega)$ is calculated, where $2\omega_0$ is a certain frequency close to the center of the spectrum. In the inset $f(t)$ is shown, which is proportional to the autocorrelation function

$$f(t) \propto \int_{-\infty}^{+\infty} \mathcal{E}(t') \mathcal{E}^*(t'-t) dt' \quad (5)$$

of the overall envelope $\mathcal{E}(t)=E_1 g(t)+E_2 g(t-\tau) e^{i\Phi}$ at the entrance of the spectrometer. The autocorrelation function (5) possesses one central peak around $t=0$ and two satellites

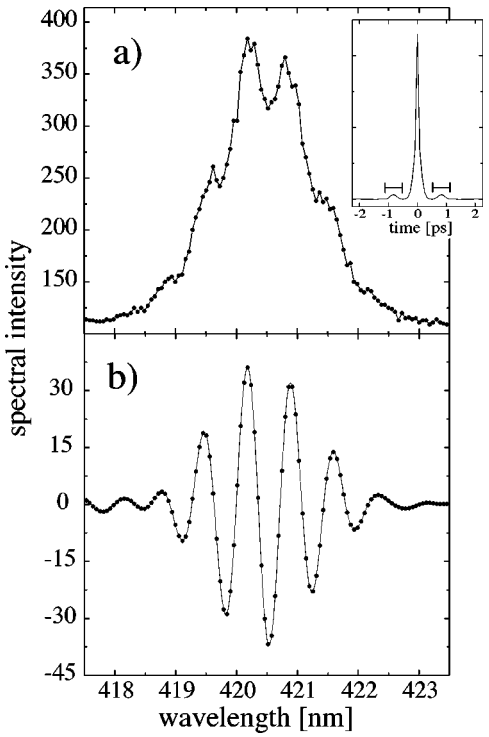

FIG. 2. Illustration of the data treatment procedure. (a) The original (as measured) SH spectrum. Inset: autocorrelation function $f(t)$; the horizontal bars show the windows used to calculate the oscillating part $\delta I(\Omega)$ of the spectrum, which is displayed in (b).

at $t=\pm\tau$, which contain the information on the oscillatory part in the raw data. The inverse Fourier transform is then exclusively applied to those parts of the autocorrelation function that contain the two satellites [the chosen windows are marked in the inset by horizontal bars]. As is displayed in panel (b), this procedure results in the oscillating part $\delta I(\Omega)$ of the spectrum only. The overall spectrum of the SH light and most part of the random noise are removed. The relative phase Φ is defined as the phase of $\delta I(\Omega)$ relative to $2\omega_0$ (note that the phase depends on the choice of $2\omega_0$). The estimate of the phase Φ and of the error $\Delta\Phi$ is made by finding eight zeros of the $\delta I(\Omega)$ function, from which six evaluations of Φ are performed. A typical error bar of the phase evaluation from our spectra is found to be $\Delta\Phi=\pm 5°$, which is comparable to the accuracy that is usually achieved using the technique of Chang *et al.* for weak surface SH response.[10,15] We have verified that within a few degrees the evaluation of the phase is not sensitive to the numerical parameters used in the Fourier analysis.

In order to study the reliability of the results as obtained by the phase-determination method described above, two test experiments were performed. In the first experiment the relative phase Φ was determined for 12 different positions d of the reference in air. According to Eq. (1), the phase delay $\Phi(d)$ between SHG from the sample and the reference is a linear function of d. As shown in Fig. 3, our evaluation of the relative phase Φ closely follows this expected linear dependence. The standard deviation from the straight line is found to be 8°, which is comparable with the estimate of the phase evaluation error $\Delta\Phi$ given above. We note that the reference translation is not a necessary step for the phase determination but is only used here as a test of the technique.

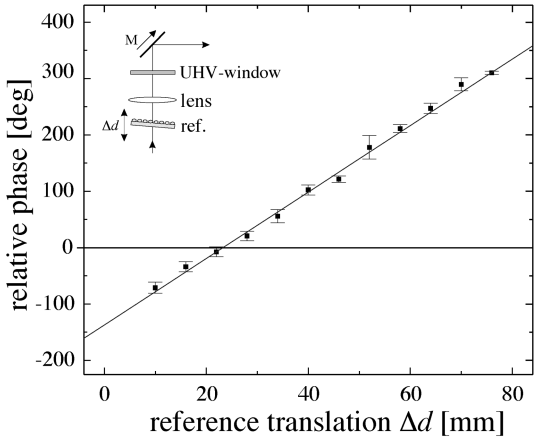

FIG. 3. Variation of the measured phase Φ as a function of the reference translation Δd. The inset shows the relative positions of the lens, the reference SH source, the window, and the sample.

In the second experiment the phase of the MSHG response from a Rh/Co/Cu multilayer was measured. In the longitudinal geometry the *s*-polarized SHG from this isotropic sample should be odd in the magnetization so that reversal of the magnetization direction must change the phase of the response by 180°.[15] In contrast to the experiment with the clean nickel sample, this experiment was performed in air. As indicated in the inset of Fig. 4, a 3 mm thick glass plate was used to introduce the time delay τ between the SHG response from the sample and the reference. In addition to that, the relative position of the lens and the reference was reversed (see the inset in Fig. 4), therefore in this setup no delay was introduced by the lens. The interference oscillations measured for opposite directions of the magnetization are shown in Fig. 4. The phase change introduced by the magnetization reversal is found to be $\Phi(-M)-\Phi(+M) = 176° \pm 5°$, in excellent agreement with the expected π shift.

As in conventional phase measurements, the strength of the interference depends on the ratio between the signals generated by both SH sources and on the coherence parameter α that is present in Eqs. (2) and (4). In addition to the laser beam parameters and the quality of the optical components like the UHV window, the coherence α can be affected by, for instance, the fact that the focal length F of the lens is slightly different for the fundamental and the SHG light. As a result, in the first experiment (Fig. 3), the curvature of the phase front of the fundamental light after the lens differs from that of the SHG light from the reference. If the difference in the focal lengths δF is comparable or larger than $F^2\lambda/d^2$, where d is the beam diameter before the lens, the phase shift between E_{SH} and E_f^2 essentially varies within the beam cross section and thus leads to a loss of contrast in the interference pattern. In the first experiment the lens was put between the reference and the sample, in order to allow for the reference translation in air. The effect of the frequency dependence of the focal length then led to a relatively low value $\alpha \sim 0.2$ of the coherence factor. In the second experiment (Fig. 4) there was no lens between the sample and the reference and a much higher coherence factor $\alpha \sim 1$ was found.

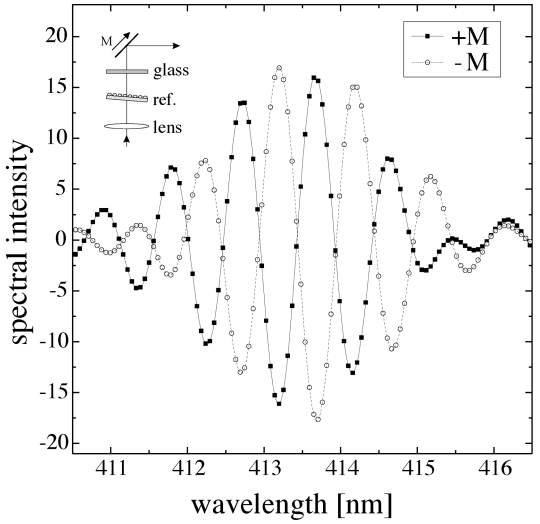

FIG. 4. Spectral interference from a Rh/Co/Cu multilayer for two opposite magnetization directions. The inset shows the relative positions of the lens, the reference SH source, the window, and the sample.

The method was also applied to measure the phase change of the SH response from a clean Ni(110) sample induced by magnetization reversal. The magnetic asymmetry measured in an MSHG experiment in a fixed polarization configuration is[8]

$$A = \frac{I(+\mathbf{M}) - I(-\mathbf{M})}{I(+\mathbf{M}) + I(-\mathbf{M})} = \frac{2|\chi_{\mathrm{odd}}/\chi_{\mathrm{even}}|}{1+|\chi_{\mathrm{odd}}/\chi_{\mathrm{even}}|^2}\cos\Phi, \qquad (6)$$

where χ_{odd} and χ_{even} are linear combinations of odd (magnetic) and even (nonmagnetic) tensor elements and corresponding Fresnel factors. In the p_{in} p_{out} geometry with $\mathbf{M}\|(111)$ being in the optical plane of incidence we have measured a phase change of $17 \pm 4°$ and an asymmetry $A = 0.10 \pm 0.02$ giving, for this particular configuration, $\chi_{\mathrm{odd}}/\chi_{\mathrm{even}} = 0.052 \pm 0.011$.

In conclusion, we have shown that spectral interference can be used to perform phase-sensitive measurements in surface second-harmonic generation. The major advantage of the method is its applicability in setups where sample and reference are necessarily separated by an optical window (for instance, for samples mounted in a UHV chamber or in a cryostat). In the conventional technique such a window would cause the interference (of femtosecond laser pulses) to disappear. In addition, using our method it is not necessary to vary the phase delay between reference and sample by translating the reference along the path of the beam like in the conventional method. Instead, phase information is obtained directly from the spectrum of the second-harmonic light. We have demonstrated the feasibility of the technique by performing experiments on Ni(110) in UHV and a Rh/Co/Cu multilayer in air.

We would like to thank A.F. van Etteger for useful discussions and technical assistance. Part of this work was supported by the Stichting Fundamenteel Onderzoek der Materie (FOM), Stichting Toegepaste Wetenschap (STW), and by the TMR network NOMOKE.

*FAX:+31 24 3652190. Electronic address: veenstra@sci.kun.nl
†On leave from the Insitute of Crystallography, Moscow, Russia.

[1] Y. R. Shen, *The Principles of Nonlinear Optics* (Wiley, New York, 1984).
[2] G. L. Richmond, J. M. Robinson, and V. L. Shannon, Prog. Surf. Sci. **28**, 1 (1988).
[3] T. F. Heinz, in *Nonlinear Surface Electromagnetic Phenomena*, edited by H. E. Ponath and G. I. Stegman (Elsevier, Amsterdam, 1991), Chap. 5, p. 353.
[4] Th. Rasing, J. Magn. Soc. Jpn. **22**, 1 (1998).
[5] K. Kemnitz, K. Bhattacharya, J. M. Hicks, G. R. Pinto, K. B. Eisental, and T. F. Heinz, Chem. Phys. Lett. **131**, 285 (1986).
[6] R. Stolle, M. Loddoch, G. Marowsky, G. Berkovic, F. H. Kreuzer, and H. Leigeber, Langmuir **11**, 3251 (1995).
[7] H. A. Wierenga, M. W. J. Prins, D. L. Abraham, and Th. Rasing, Phys. Rev. B **50**, 1282 (1994).
[8] R. Vollmer, M. Straub, and J. Kirschner, Surf. Sci. **352**, 937 (1996).
[9] J. Hohfeld, E. Matthias, R. Knorren, and K. H. Bennemann, Phys. Rev. Lett. **78**, 4861 (1997).
[10] R. K. Chang, J. Ducuing, and N. Bloembergen, Phys. Rev. Lett. **15**, 6 (1965).
[11] L. Lepetit, G. Chériaux, and M. Joffre, J. Opt. Soc. Am. B **12**, 2467 (1995).
[12] W. J. Walecki, D. N. Fittinghoff, A. L. Smirl, and R. Trebino, Opt. Lett. **22**, 81 (1997).
[13] P. Martin *et al.*, Phys. Rev. B **55**, 5799 (1997).
[14] M. F. Emde, W. P. de Boeij, S. Pshenichnikov, and D. A. Wiersma, Opt. Lett. **22**, 1338 (1997).
[15] R. Stolle, K. J. Veenstra, F. Manders, Th. Rasing, H. A. M. van den Berg, and N. Persat, Phys. Rev. B **55**, R4925 (1997).