附件一

# 行政院國家科學委員會補助專題研究計畫 □成果報告 ■期中進度報告

（計畫名稱）

## 發展紅外線/可見光合頻波成像顯微術以研究表面催化反應

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執行期間：97 年 3 月 1 日至 98 年 7 月 31 日

計畫主持人：重藤真介
共同主持人：
計畫參與人員：

成果報告類型(依經費核定清單規定繳交)：■精簡報告　□完整報告

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執行單位：國立交通大學應用化學系

中 華 民 國 97 年 5 月 29 日

# Development of infrared–visible sum-frequency generation (SFG) imaging microscope: Toward applications to surface catalytic reactions

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## Abstract (English)

Our objective is to develop an infrared (IR)–visible sum-frequency generation (SFG) microscope that is applicable to investigating surface catalytic reactions and molecular chirality at surfaces and interfaces. This technique combines molecular specificity of SFG spectroscopy with high spatial resolution. Originally we had planned to use the existing femtosecond (fs) laser system at Institute of Molecular Science, NCTU. However, we came to know that a picosecond (ps) laser system at Institute of Atomic and Molecular Sciences could be transferred to NCTU for our project. The benefit of using this laser system is twofold: 1) In contrast to the fs laser system, the ps laser will be available exclusively for this project, so that we will have more running time. 2) The ps laser system is capable of generating a wider range of mid-IR generation (2.3–18 μm, i.e., 600–4000 cm$^{-1}$). Thus vibrational transitions in the finger-print region as well as in the CH-stretch region can be observed with that ps laser. We are now preparing for the transfer of the lasers so that we can start constructing an SFG imaging microscope as soon as possible.

## Keywords (English)

Sum-frequency generation, microspectroscopy, surface catalytic reaction, molecular chirality

## 中文摘要

此計畫的目標是發展紅外線/可見光合頻波成像顯微術，使其能適合研究表面及介面的表面催化反應和分子對掌性。此技術結合高分辨空間率及紅外線/可見光合頻波成像顯微術的分子專一性。原先我們計畫使用交大分子科學研究所的飛秒雷射系統，然而後來得知可以轉借中研院原分所的皮秒雷射系統支援我們的計畫。使用這台雷射系統有兩項優點：1、此皮秒雷射可以專門支援本計畫，因此我們將有更多執行實驗的時間；2、皮秒雷射能產生範圍較廣的中紅外產生波(2.3–18 μm, i.e., 600–4000 cm$^{-1}$)，因此可以用來觀察指紋區及 CH-拉伸區的振動遷移。我們預計將這台雷射及早搬運至交大以開發紅外線/可見光合頻波成像顯微術。

# 中文關鍵詞

合頻波、顯微光譜術、表面催化反應、分子對掌性

# Report Content

## *1. Introduction*

Surfaces are ubiquitous in nature. They play vital roles in solvent extraction, catalytic reactions, chemical reactions in cells, and so forth. However, compared to the long history of studies on the bulk such as liquids or solutions, fundamental understanding of those surfaces from a molecular viewpoint is still scant. We know far less about dynamical behavior of reacting species involved in surface catalytic reactions and molecular chirality at surfaces.

IR–visible sum-frequency generation (SFG) spectroscopy, initiated by Shen et al. [1] in 1987, is a powerful technique to measure vibrational spectra at surfaces. Because this technique is based on a second-order nonlinear optical process [2,3], the vibrational information obtained is inherently surface-specific. In addition, SFG spectroscopy has recently proven both experimentally and theoretically to have the ability to probe molecular chirality in the bulk and monolayers [4–7]. However, a vibrational spectrum obtained with conventional SFG technique is the one that is spatially averaged.

The objective of this project is to develop an SFG imaging microscope that enables us to study surfaces with high spatial definition [8,9]. SFG microspectroscopy can be applied to a variety of molecular systems of interest, ranging from the dehydration reaction of formic acid on $TiO_2$(110) surface to chirality of proteins at surfaces. Probing molecular chirality at surfaces with SFG microscope was not included in our initial proposal. The PI had a chance to discuss this issue with Prof. Y. R. Shen at Berkeley, and came to the idea that SFG microspectroscopy will also be powerful for detecting molecular chirality at surfaces with high spatial resolution. It has the potential to provide higher sensitivity than circular dichroism (CD) and Raman optical activity (ROA) techniques [10]. Therefore we will focus our interest on probing molecular chirality as well.

## *2. Method*

The principle of IR–visible SFG spectroscopy is schematically shown in Fig. 1. The target surface is irradiated with a narrowband IR pulse and a narrowband visible pulse, and the SF signal is generated in the phase-matched direction. To fulfill the phase-matching condition and get sufficient SF signal, both the visible and mid-IR pulses are incident upon the surface with angle of 60 to 70 degrees from the surface normal. In this scheme, since a narrowband mid-IR pulse is used, we need to scan the wavelength of the mid-IR pulse to obtain a vibrational spectrum. This could be regarded as a disadvantage over the multiplex SFG method presented in the original proposal. However, the spectral resolution achieved with ps narrowband pulses and tunability of the mid-IR laser will outweigh the disadvantage, causing no essential problem to the project.

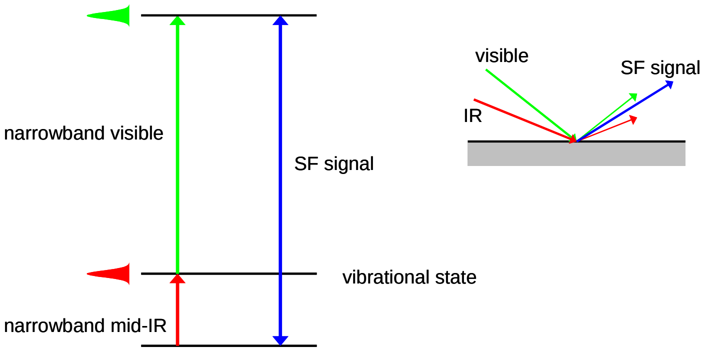

**Fig. 1** Principle of IR–visible sum-frequency generation (SFG) spectroscopy

Chiral SFG spectroscopy is based on the tensorial nature of the second-order nonlinear susceptibility $\chi^{(2)}$. To selectively probe the optically active molecular response of a chiral medium, one would choose specific input/output polarization combinations in SFG. The chiral elements of $\chi^{(2)}$, which change signs when the molecular chirality is switched (i.e., different enantiomer), can be selectively probed with *SPP, PSP*, and *PPS* polarization combinations [11]. Here *SPP* represents polarization combination of the SF signal, visible input pulse, and mid-IR input pulse, respectively.

### *3. Progresses*

The project began in the end of March. In the original grant proposal, we planned to use an existing fs Ti:sapphire laser/amplifier system at the Institute of Molecular Science (IMS) in NCTU. Figure 2 shows photos of the ps laser system that we currently plan to transfer from IAMS. It is an EKSPLA Nd:YAG laser and an OPG/DFG system, where OPG stands for optical parametric generation and DFG difference frequency generation. The Nd:YAG laser operated at 20 Hz produces 25 ps pulses at three different output wavelengths: 1064 nm (fundamental), 532 nm (the second harmonic), and 355 nm (the third harmonic). The typical pulse energy of the fundamental is <25 mJ. The 1064 and 355 nm pulses are used to

**Fig. 2.** Pictures of the EKSPLA laser system at IAMS. Left: picosecond Nd:YAG laser. Right: OPG/DFG part, which generates mid-IR light in the range of 2.3–18 μm (600–4000 $cm^{-1}$).

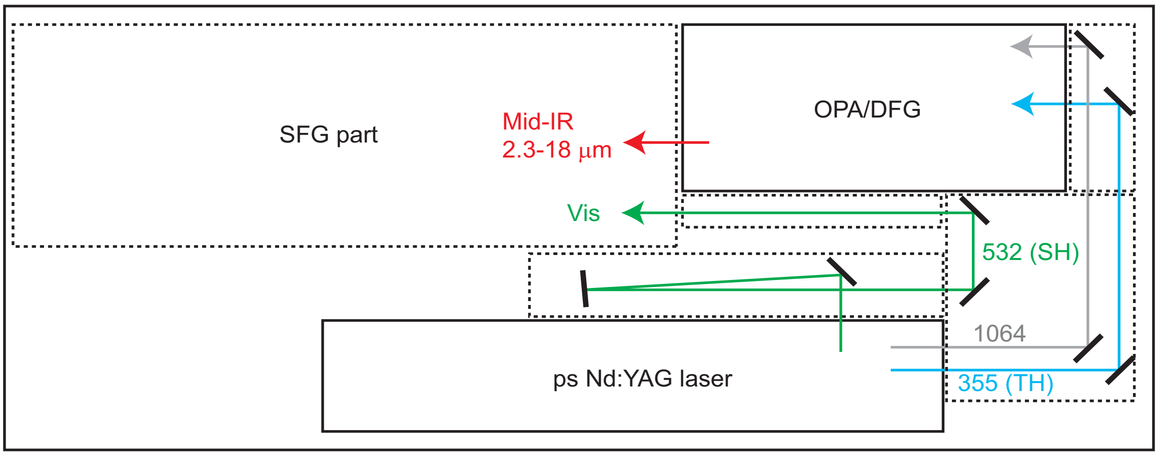

**Fig. 3.** Layout of the laser system after transferred to NCTU.

pump the OPG/DFG unit to generate tunable mid-IR pulses basically in the 2.3–18 μm range with >50 μJ pulse energy, 25 ps pulse duration, and ~6 $cm^{-1}$ bandwidth. The spectral coverage of the mid-IR light is wide enough to study vibrational transitions in the finger-print region as well as the CH-stretch region.

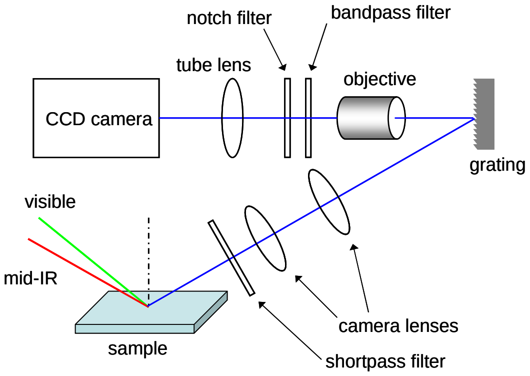

**Fig. 4.** Optical layout of the SFG imaging microscope

Figure 3 illustrates our current plan of the layout of the laser system on a 1.2 m × 3.0 m optical table. In the SFG part, we will align optics to guide the input beams and the SF signal (see Fig. 4). We will purchase the optical table, together with optics such as microscope objectives and tube lenses.

To facilitate efficient development of a new experimental setup, a well-trained personnel is definitely needed. We thus have been recruiting for a research assistant (RA) who has a master degree or higher (http://www.ac.nctu.edu.tw/app/news.php?Sn=230). Unfortunately no candidate has applied so far, but we hope that around the end of this semester, we will be able to have an RA with interest in developing the state-of-the-art nonlinear spectroscopic apparatus.

## References

[1] X. D. Zhu, H. Shur, and Y. R. Shen, *Phys. Rev. Lett.* **35**, 3047 (1987).

[2] S. Mukamel, *Principles of Nonlinear Optical Spectroscopy*, Oxford University Press, New York, USA, 1995.

[3] Y. R. Shen, *The Principles of Nonlinear Optics*, Wiley, New York, USA, 1984.

[4] M. A. Belkin and Y. R. Shen, *Int. Rev. Phys. Chem.* **24**, 257 (2005).

[5] N. Ji, V. Ostroverkhov, M. Belkin, Y. J. Shiu, and Y. R. Shen, *J. Am. Chem. Soc.* **128**, 8845 (2006).

[6] M. Oh-e, H. Yokoyama, S. Yorozuya, K. Akagi, M. A. Belkin, and Y. R. Shen, *Phys. Rev. Lett.* **93**, 267402 (2004).

[7] S. Cheon and M. Cho, *Phys. Rev. A* **71**, 013808 (2005).

[8] D. M. P. Hoffmann, K. Kuhnke, and K. Kern, *Rev. Sci. Instrum.* **73**, 3221 (2002).

[9] K. Cimatu and S. Baldelli, *J. Am. Chem. Soc.* **128**, 16016 (2006).

[10] L. D. Barron, *Molecular Light Scattering and Optical Activity*, Cambridge University Press, Cambridge, UK, 1982.

[11] M. A. Belkin, T. A. Kulakov, K.-H. Ernst, L. Yan, and Y. R. Shen, *Phys. Rev. Lett.* **85**, 4474 (2000).

## Self-Evaluation of the Progress

There was a change in the project regarding what laser system we will use for our study. Initially we planned to perform the research sharing with the fs Ti:sapphire laser/amplifier system (Coherent) installed at IMS with another research group. In April, we were offered to use a ps Nd:YAG laser equipped with an OPG/DFG unit (EKSPLA) installed at IAMS would be available for our project. We decided to take this offer, partly because this laser system was designed especially for SFG studies, and partly because we would be the only possible user of the laser system. The change in the laser system does not affect the essential part of the project, and we anticipate no serious delay caused by this. We will complete the transfer and reinstallation of the laser system and development of the SFG microscope by the end of this year. If we succeed in hiring an RA, then it will accelerate the development. In summary, although there was the change in the laser system that we use, we believe the project is being in progress with no problem, considering that it has been just two months or so since the project was approved.