

# Detection of molecular orientation by using surface plasmon resonance in the near infrared region

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## Introduction

In the past decade, substantial studies have been conducted on surface plasmon resonance (SPR). SPR, that is resonance between light and collective oscillation of free electrons in a thin metal film, has been receiving much attention and is becoming widely used in the field of biochemistry in chemical sensors due to its high sensitivity to refractive index.<sup>1</sup> However SPR is also sensitive to absorption, which is the imaginary part of a complex refractive index and we call this phenomenon absorption-sensitive SPR. Needless to say, the absorption spectrum is characteristic for the molecule. If a SPR condition meets the target molecular absorption, the SPR signal is largely modified by the presence of the absorption.<sup>2</sup> Therefore, this phenomenon can be used for enhancement of absorption spectra with low intensity, such as near infrared (NIR) spectra. We have demonstrated some methods for absorption enhancement in the NIR region.<sup>3-5</sup> Absorption-sensitive SPR is able to enhance the absorptivity about 100 times compared with total reflection measurements without a metal film. Moreover, it is expected that absorption bands due to functional groups, whose dipole moments are parallel to the polarisation of the incident beam, are particularly enhanced, because SPR is excited by only P-polarised light. This paper explains the property of absorption-sensitive SPR in the NIR region, and the principle of molecular-orientation detection, taking a uniaxially stretched polyethylene film.

## Materials and methods

An FT-NIR spectrometer (MPA, Bruker Optics, Ettlingen, Germany) was used to obtain NIR spectra of SPR. The sample was held on a homemade Kretschmann configuration SPR attachment, which consists of a LASF15-N hemicylinder (an internal reflection element, IRE) and a 16nm thick gold film.<sup>3</sup> The incident beam from the FT-NIR spectrometer was polarised by a polariser (SPFN-30C-26, Sigma-Koki, Tokyo, Japan) with a 90°-rotation holder. The S, P and non-polarised light were used as incident light. The angle of incidence was set to 56°. In order to demonstrate the molecular-orientation detection, a uniaxially stretched polyethylene (PE) film was used as a sample and compared with a 201 layered Langmuir-Blodgett (LB) film of Cd

arachidic acid.<sup>6</sup> To guarantee a high signal-to-noise ratio within a limited amount of time (*ca* 30 sec), 16 interferograms were co-added with a spectral resolution of  $2\text{ cm}^{-1}$ . All experimental data shown in this paper were obtained by using the same gold film.

## Results and discussion

In Figure 1, a Kretschmann configuration, which is very typical for SPR sensing is illustrated with the directions of polarisation of the incident and reflected beams.

It is a little known fact that S polarised light perfectly reflects on the surface of the IRE, while on the other hand, P polarised light is absorbed in the sample material on the gold film. In other words, P polarised light is only active for absorption-sensitive SPR. Therefore it is important to select the loading direction for anisotropic samples. For the uniaxially stretched PE film, two directions: parallel and perpendicular to the direction of the incident beam were tested.

The SPR peak is enhanced by absorption when these peaks overlap with each other. In the case of a water-based sample, full width at half maximum (FWHM) of the SPR peak is about  $300\text{ cm}^{-1}$ . As shown in Figure 2, however, the SPR peak for PE is so broad (FWHM  $> 1000\text{ cm}^{-1}$ ) that enhanced absorption peaks of PE can be directly compared with transmittance spectra, because of the low dispersion characteristic of PE.

Figure 2 shows SPR spectra obtained by using P, S and non polarised lights and a corresponding total reflection spectrum without a gold film. It is confirmed that a broad SPR peak centred at  $6000\text{ cm}^{-1}$  enhances the overtones (*ca*  $5800\text{ cm}^{-1}$ ) and combination (*ca*  $4300\text{ cm}^{-1}$ ) peaks of PE. The inactivity of S polarised light for SPR is also confirmed in Figure 2. Figure 3 compares two loading directions of the stretched PE film: parallel and perpendicular to the P polarised incident light.

The enhanced absorption spectra of the two directions were quite similar because almost all peaks are due to C-H vibrations along the direction of “out of plane” (OP, see Figure 1).

If alkyl chains vertically stood on the surface, different spectra would be obtained. Arachidic acid LB film, previously reported by us, is possible material because the alkyl chains of the mole-

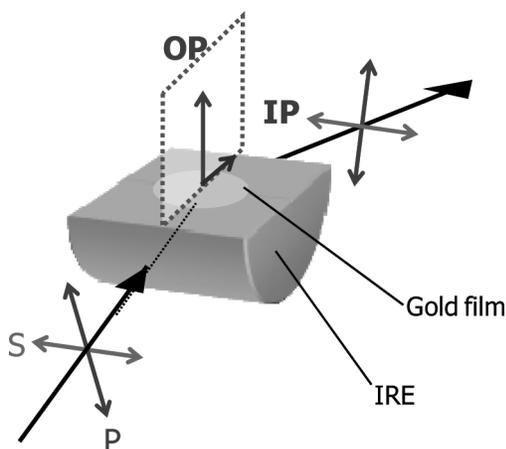
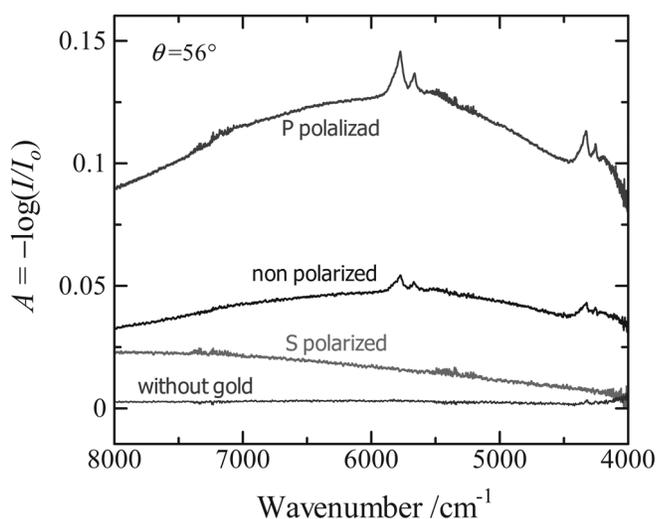


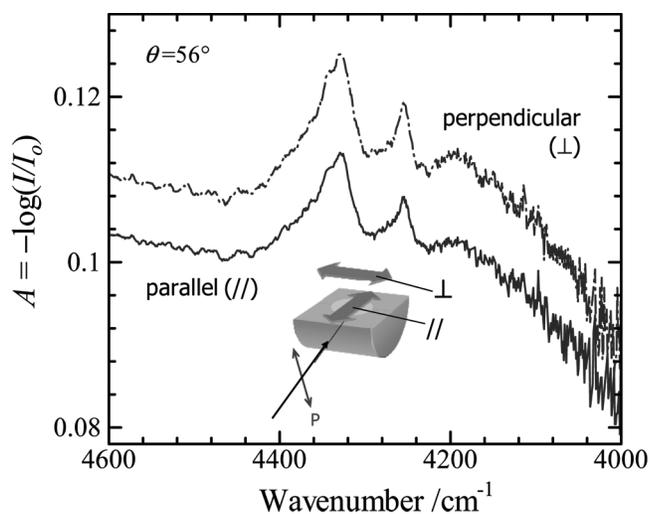
Figure 1. Polarisation direction for the Kretschmann configuration.



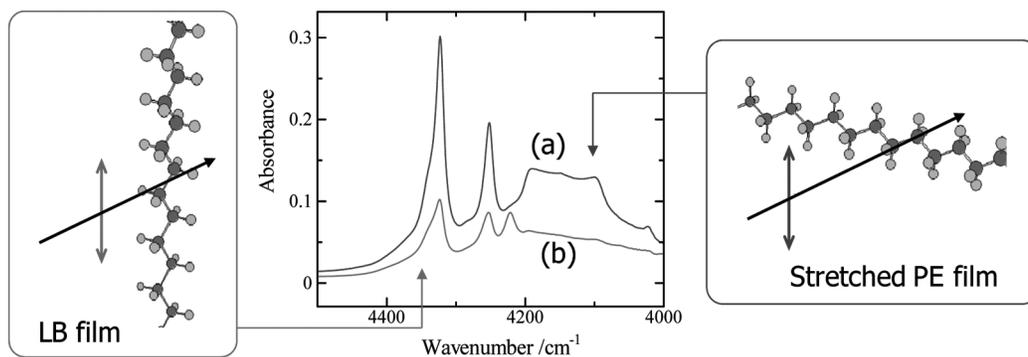
**Figure 2.** SPR spectra obtained by using P, S and non polarised lights and a corresponding total reflection spectrum without a gold film.

cules are perpendicularly arranged to the gold surface.<sup>6-8</sup> The direction of the electric vector of the surface plasmon is corresponding to that of OP direction. Therefore, for the LB film, the vibrational modes along the direction of the main chain of the molecules are only active for absorption transitions. Figure 4 summarises the typical spectra of (a) stretched PE film and (b) LB film.

Taking into account the fact that the sharp band at  $4222\text{ cm}^{-1}$  is assigned to a combination of asymmetric stretching and wagging modes,<sup>9</sup> the enhanced NIR spectrum of the PE film was



**Figure 3.** The enhanced absorption spectra of the stretched PE film for two loading directions, which are parallel and perpendicular to the P polarised incident light.



**Figure 4.** Typical NIR spectra of alkyl chain in combination band with schematic pictures of molecular directions of (a) uniaxially stretched PE film and (b) LB film.

complementary to the result of the LB film. This method will be particularly valuable for the assignment of unconfirmed combination bands.

## Conclusion

From the findings, we can safely conclude as follows. (1) P polarised light is only active for absorption-sensitive SPR measurement. (2) The enhanced NIR spectrum of stretched PE film by SPR was consistent with the result of LB film. (3) Activity for In-plane (IP) mode is negligibly small. The absorption-sensitive SPR method is based on the opposite geometry of well-known reflection absorption spectroscopy (RAS) method, which is frequently used in the mid IR region. Therefore, the method proposed in this paper will help determination of molecular direction where absorption is weak, and this may be one of the standard reflection measurements as RAS.

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