

# Development of Otto-ATR Raman spectroscopy for thin lubricant films

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**ABSTRACT** – In this study, Raman scattering signals from molecules in a thin lubricant film were measured by using a newly developed tribotester with the Otto-attenuated total reflection (ATR) configuration. This system employs a point contact between a transparent dove prism (N-SF11) and an aluminum ball. From the electric field enhancement effect based on the Otto-ATR configuration, a high sensitivity measurement of Raman scattering signals was realized under shearing of thin lubricant films.

## 1. INTRODUCTION

Raman spectroscopy has been known as one of the most important measuring techniques used in tribology [1]. In particular, in-situ Raman spectroscopy based on the attenuated total reflection (ATR) configuration has a powerful potential for understanding the mechanism of lubrication [2]. The direct measurements of the Raman spectrum at contact regions allow us to identify physical and chemical structures of lubricant films.

In this study, we developed a new tribotester with an in-situ Raman spectroscopy, based on the Otto-ATR configuration. The advantage for using the Otto-ATR configuration in Raman measurement systems is its signal enhancement effect resulting from the surface plasmon resonance (SPR). In addition, the measurement of SPR signals allows obtaining additional information about physical structures of adsorbed thin lubricant films, such as their film thickness, and density.

As a first step, this paper discussed the possibilities of the developed in-situ Raman spectroscopy. Using two types of test oils (n-hexadecane or n-hexadecane containing 1.0 wt% oleic acid), Raman spectrum was measured under shearing condition.

## 2. EXPERIMENTAL DETAILS

### 2.1 Experimental Apparatus

A photograph of an experimental setup developed in this study is shown in Figure 1. This system employs a point contact between a copper ball ( $\phi = 25.4$  mm) and the lower face of a dove prism (made of BK7). A normal load was applied by using a restitution force of a coil spring. A sliding speed can be controlled by adjusting a rotation speed of an AC servomotor that is connected to the copper ball via a flexible coupling.

For Raman measurements, an attenuated total reflection (ATR) is utilized as illustrated in Figure 2. A collimated green laser beam (wavelength: 532 nm, maximum power: 100 mW) was focused at the lower

face in the contacting region, and Raman scattering signals at the region were condensed by an objective lens tube system and recorded by a spectrometer. In addition, images of the contact region were also captured by using a CCD camera.

The ATR configuration developed corresponds to a well-known Otto configuration for SPR. The use of the copper surface allows to excite the SPR under optical wavelengths. A polarizing plate was fixed between the laser diode and the first objective lens, because the laser light to excite SPR should be polarized parallel to the incident plane (i.e., p-polarized).

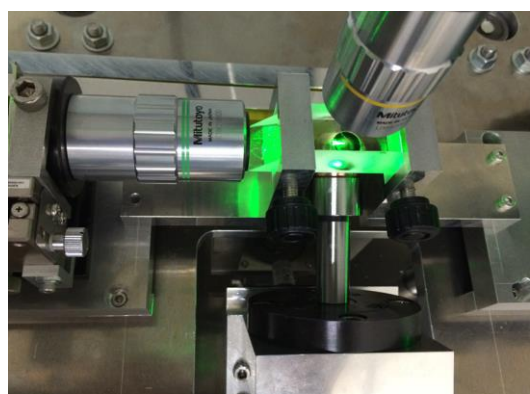


Figure 1 Photograph of experimental setup.

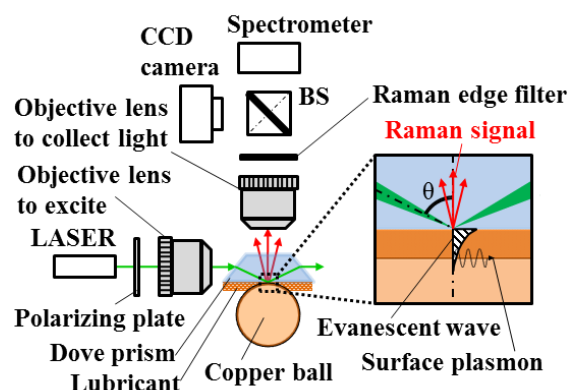


Figure 2 Schematic of ATR configuration.

### 2.2 Experimental Procedure

First, test oil (i.e., n-hexadecane or n-hexadecane with 1.0 wt% oleic acid) was filled in the contact point between the prism and ball, and then a normal load of 37 N was applied. After waiting scheduled time, the ball was rotated with a constant rotating speed; the surface

velocity of the ball was set to be 25.0 mm/s under all conditions. Before and after rotating roller, the Raman signals were recorded in each acquisition time and averaging times.

### 3. RESULTS AND DISCUSSION

Figure 3 shows the results of the Raman spectra of n-hexadecane and oleic acid, which was measured at the outside of the contact region with an enough large film thickness. Several peaks are clearly observed in the spectrum; these peaks include the intensities resulting from C-H, C-C stretching modes, respectively.

Figure 4 shows the results of Raman spectrum. From above, Figure 4(a) shows the Raman spectrum of n-hexadecane under non-shearing (non-rotating) condition. Figure 4(b) also shows the Raman spectrum of n-hexadecane with 1.0 wt% oleic acid under the stationary condition. Figure 4(c) is the Raman spectrum of n-hexadecane with 1.0 wt% oleic acid under shearing condition.

From the comparison between Figure 3 and Figure 4(a), it was found that the developed Otto-ATR system has an enough sensitivity to find spectrum peaks even if the film thickness has a small value. The film thickness in the stationary condition will correspond to the level of surface roughness, i.e., 0.3  $\mu\text{m}$ . However, as shown in Figures 4(a) and (b), it is difficult to recognize the difference between Raman spectrum peaks with or without oleic acid. In shearing condition, Fig. 4(c), the spectrum has a different trend compared to the results in situational conditions, Figures 4(a) and (b). It implies that the system has a potential to observe the structure changes in molecule due to shearing.

As described above, the developed system has a high ability for in-situ Raman spectroscopy. For more quantitative discussion, however, the enhancement of measuring accuracy is required. The optimization of optical systems will be a key to discuss the mechanism of lubricant dynamics.

### 4. CONCLUSION

Using a developed tribotester with the Otto-ATR configuration, the Raman scattering signals from thin lubricant films were directly measured under shearing conditions. These results provided a high possibility to realize in-situ Raman spectroscopy under thin film lubrication conditions.

### 5. REFERENCES

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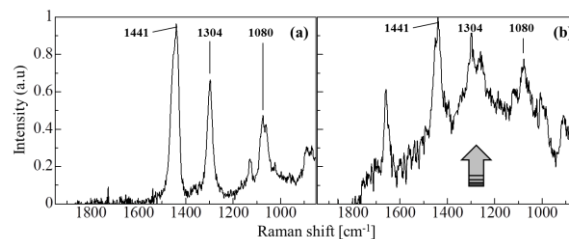


Figure 3 Raman spectrum (a) lubricant: n-hexadecane, acquisition time: 6 s, averaging times: 10, (b) lubricant: oleic acid, acquisition time: 0.2 s, averaging times: 300.

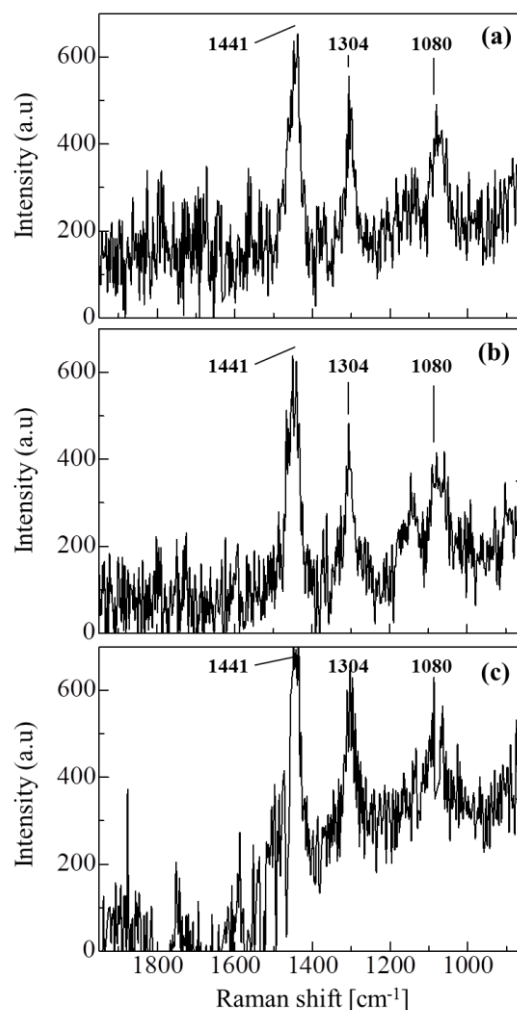


Figure 4 Results of Raman spectrum: (a) lubricant: n-hexadecane, acquisition time: 6 s, averaging times: 50, (b) lubricant: n-hexadecane with 1.0wt% oleic acid, acquisition time: 6 s, averaging times: 50, and (c) surface speed 25.0 mm/s, lubricant: n-hexadecane with 1.0 wt% oleic acid, acquisition time: 6 s, averaging times: 50.