Water molecules on the liquid superlubricity interfaces achieved by phosphoric acid solution

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Abstract: The superlubricity mechanism of phospholipid molecules on biological surfaces and interfaces has been receiving much attention. Since the superlubricity can be achieved with a phosphoric acid aqueous solution, the interaction of the phosphate group with the water molecule is considered to be the key to bio-lubrication. However, no direct evidence has been offered to distinctly interpret the underlying mechanism of superlubricity, due to the limitations in the method for the detection of interfacial molecules, especially water molecules on the interface. By using sum-frequency generation (SFG) vibrational spectroscopy, which is extremely sensitive to interfacial molecules, the authors were able to explore the underlying microscopic mechanism for superlubricity in a phosphoric acid system, which might be related to interfacial water molecules. By trapping the phosphoric acid aqueous solution between silicon nitride and silica surfaces, they discovered that phosphoric acid could exercise a great influence on the ordered structure of interfacial water molecules, contributing to SFG spectral changes in the broad O–H bond stretching region. This work directly revealed the interfacial interaction between water and phosphoric acid molecules in liquid superlubricity interfaces, which could shed new light on the microscopic mechanism of liquid superlubricity.

1 Introduction

There are many relatively sliding surfaces in the living body, and the coefficient of friction between them will affect the health function of the biosurfaces, especially the synovial joint [1, 2]. Healthy articular cartilage surfaces possess superlubricity properties in the synovial fluid, with a coefficient of friction <0.01 at pressures up to some 100 atmospheres [3]. As a major component of all cell membranes, phospholipid molecules are widely present in articular cartilage surfaces and synovial fluids, so they are considered to be a key component of joint lubrication [4–6]. Although phospholipid molecules exhibit excellent lubricating properties in systems such as water or synovial fluid [7–10], the lubrication mechanism research is still lacking at the molecular level. A phospholipid molecule generally consists of two hydrophobic fatty acid ‘tails’ and a hydrophilic ‘head’ consisting of a phosphate group. If the structure of water molecules near the phosphate group can be observed, it will greatly help to understand the mechanism of biosurface lubrication.

Furthermore, in recent years of liquid superlubricity research, a series of aqueous solutions containing phosphoric acid have been reported to achieve ultra-low coefficients of friction between a Si3N4 ball and a SiO2 disc [11, 12]. This phenomenon was explained by the effect of a strong hydrogen bond network formed by phosphoric acid and water molecules [11]. This report speculated that the ultralow friction was attributable mainly to hydrogen bond effects and somewhat to dipole–dipole effects. However, there were no direct detection methods to demonstrate a detailed and accurate molecular structure of the phosphoric acid interface during the rubbing process, which was the most crucial aspect and urgently needed to be determined.

During the superlubricity of both phospholipid and phosphoric acid, the molecular structure near the phosphate group was fundamental to understanding its mechanism. Generally, Raman spectroscopy and infrared (IR) spectroscopy were applied to characterise the molecular structure to a great extent. For instance, Zhang observed the orientation behaviour of liquid crystal molecules in a confined area by use of Raman scattering [13]. Jiang reported the surface-induced torsional alignment of polydimethylsiloxane chains on the mica surface by confocal Raman scattering [14]. However, the above methods were not able to purely detect an interfacial molecular structure without any bulk signal. Interfacial molecular information could be entirely obtained by using nonlinear interface spectroscopy. Sum-frequency generation (SFG) vibrational spectroscopy is a second-order nonlinear optical process in which infrared and visible beams at frequencies νIR and νVis, respectively, overlap in a medium and generate an output beam at the frequency νSFG = νIR + νVis [15]. Theoretically, as a nonlinear optical process, the SFG signal does not generate in inversion-symmetric bulk on the condition of the electric dipole approximation but exists at interfaces where inversion symmetry disappears. The SFG process is extremely interface-selective and interface-sensitive, which is greatly beneficial for defining the interfacial microstructure, orientation, conformation etc. SFG has been generally used in various fields, such as chemistry, physics, biology and environmental sciences. By real-time SFG detection of Langmuir monolayers and interfacial water, the relationship between the microscopic structures of Langmuir films and the arrangement of interfacial water molecules has been demonstrated [16]. It was also reported that SFG could also be used to investigate the conformation of molecular chains in polymer solutions [17]. Moreover, the SFG spectra of water molecules in diverse solutions such as methanol [18, 19], surfactant solution [20, 21], electrolyte solution [22] etc. showed different water molecular structures. Here, SFG vibrational spectroscopy is used to analyse specific interfacial chemical bonds with the aim of demonstrating the interfacial structure at the molecular level, which could offer direct evidence of the mechanism of superlubricity.

In this work, the friction between a Si3N4 ball and a SiO2 disc across phosphoric acid aqueous solution was conducted on a
universal micro-tribotester-3 (UMT-3). When ultralow friction was achieved, we explored the SFG spectra of the phosphoric acid aqueous solution near the contact region on the SiO₂ disc when ultralow friction was achieved. To investigate the role of phosphoric acid in the rubbing process, we also measured SFG spectra for phosphoric acid solutions with different concentrations and diverse acid solutions for comparison. Based on our experiments, during the superlubricity, the microscopic structural transformation could be clearly observed, which was extremely beneficial for demonstrating the underlying mechanism of superlubricity.

2 Experimental

2.1 Materials

Highly purified water (Thermo TKA, TOC 2 ppb, 18 MΩ cm) was used for preparing solutions and cleaning the specimens. Phosphoric acid aqueous solutions with different pH values were prepared by diluting phosphoric acid (85 wt%) with highly purified water. The phosphoric acid used in the tests is a commercial product with purity >99%. In addition, hydrochloric acid and hyaluronic acid were used to prepare 0.001 mol l⁻¹ reference solutions.

In the tribological experiments, the upper samples were silicon nitride ceramic spheres with a mean surface roughness (Ra) of ∼20 nm (diameter: 3.969 mm). Ra was measured by a white light interferometer (MICROXAM-3D, measuring range 46.3 μm × 61.8 μm). The lower samples were glass discs with an initial mean surface roughness of 5 nm.

2.2 Tribological experiment

The tribological experiment was performed on a rotary sliding tester (UMT-3, CETR) using 0.1646 mol l⁻¹ phosphoric acid solutions (pH value: 1.5). The applied load was 300 g, which corresponded to a Hertzian contact pressure of up to 700 MPa. The spinning speed was maintained at 180 rpm corresponding to a linear speed of ∼56 mm/s, while the rotating radius was 3 mm.

The test method was the same as that described in the early literature [17]. After a running-in period, superlubricity was achieved with a friction coefficient of 0.004. Then, the rubbed samples were used for SFG measurements.

2.3 SFG measurements

Before the rubbing test, SiO₂ prisms needed further clean. First, the SiO₂ prisms were completely immersed in toluene solution for 10 min, then they were well cleaned in an ultrasonic bath with acetone and ethanol, each for 5 min. Finally, after being washed by ultrapure water and dried by compressed nitrogen, they were cleaned in a plasma cleaner (PDC-32G-2, Harrick Plasma) for 5 min.

In this work, all measurements were conducted by a SFG setup along with a monochromator, which was connected to a charge-coupled device (CCD). CCD was used to collect and detect the SFG signal generated from the overlap of infrared and visible beams temporally and spatially, as shown in Fig. 1. The polarisation of IR, visible and generated beams could be changed by a half wave disc. S polarisation meant vertical to the incident plane, while P polarisation meant parallel to the incident plane. Different polarisation combinations led to different intensities of the SFG signal. Therefore, all experiments used the SSP polarisation combination (SFG: S, Vis: S, IR: P). The recorded intensity was baseline subtracted and normalised by the spectrum of gallium arsenide that was recorded before each measurement.

3 Results and discussion

3.1 SFG spectra of the superlubricity interfaces

First, we conducted the friction test between a Si₃N₄ ball and a SiO₂ disc across the phosphoric acid aqueous solution on a UMT-3 and explored the SFG spectra of two points near the contact region of the residues by using the picosecond SFG setup. Fig. 2a shows the evolution of the friction coefficient with time, and ultralow friction was obtained under the lubrication of the phosphoric acid solution (pH = 1.5). Fig. 2b shows the detailed measurement point in the contact region of the Si₃N₄ ball and SiO₂ disc across phosphoric acid. Point A referred to the edge of the track and point B represented the centre of the track, where the IR beam and the visible beam both crossed the silica disc and finally overlapped temporally and spatially. SFG spectra in the O–H bond stretching region of both measurement points are shown in Fig. 2c. The spectra at point A displayed the 3200 cm⁻¹ peak of ‘ice-like water’ [23]. Moreover, the SFG signal of the residues in the centre of the track (point B) nearly totally disappeared after the friction process. To verify the existence of a phosphoric acid solution in the centre of the friction track, we also recorded the spectrum of the residues in the 1000–1200 cm⁻¹ region, and the 1025 and 1150 cm⁻¹ peaks are present in Fig. 2d, as we expected. These two peaks could be assigned to P=O symmetric (1170 cm⁻¹) and P=O asymmetric (1010 cm⁻¹) stretching vibrations [24, 25].

In pure water, water molecules presented a relatively ordered molecular arrangement. In solution, the interaction between phosphoric acid and water molecules would destroy the ordered molecular arrangement [26]. This experiment provided evidence of the combination of phosphoric acid and water molecules under superlubricity conditions.

3.2 Effect of concentration of the phosphoric acid solution

Subsequently, we investigated the internal relationship between SFG intensity and the concentration of a phosphoric acid solution by...
could see that the spectra mainly exhibited two prominent peaks at the SFG signal. The difference between the two spectra might be due to the prism to form a relatively ordered structure, which could enhance the untreated one [27].

network of the water on a plasma-treated silica surface than on an untreated silica surface due to a stronger hydrogen bonding function of time. The tests were performed with a 300 g load at a 56 mm/s velocity.

In the 1000–1200 cm$^{-1}$ range, it was reported that ‘ice-like water’ was dominated on plasma-treated silica surfaces due to a stronger hydrogen bonding network of the water on a plasma-treated silica surface than on an untreated one [27].

At the interface of liquid and solid, water molecules adsorbed on the prism to form a relatively ordered structure, which could enhance the SFG signal. The difference between the two spectra might be due to the different levels of plasma-treating. Prolonged plasma-treating could obtain a stronger ice-like water structure [27]. With the concentration of phosphoric acid increasing, the SFG intensity of the two O–H stretching peaks actually kept decreasing, and finally disappeared at 13.3 mol L$^{-1}$. We assumed that this result could be attributed to the breakdown of the water structure at the liquid/solid interface. If the O–H chemical bonds are disordered and unsystematic on the prism surface, their SFG signals would be destroyed by each other.

3.3 SFG spectra of different acid solutions

To confirm the above assumption, we also studied the SFG spectra in the O–H stretch region of different acid solutions absorbed on SiO$_2$ prisms. With the measuring method shown in Fig. 1a, we obtained the SFG spectra of pure water and three acid solutions shown in Fig. 3. (The spectrum of phosphoric acid in Fig. 4 differs from that in Fig. 3 due to the different degrees of plasma-treating [27].)

By calculating the ratio of ice-like water peak intensity ($I_1$) at 3200 cm$^{-1}$ to water-like peak intensity ($I_2$) at 3400 cm$^{-1}$, and comparing the $(I_1/I_2)$ ratios of the three acid solutions, we discovered that this ratio apparently was not governed by the pH value. This result indicated that the pH value had little effect on the spectra in the O–H stretching region. However, it was clear that the $(I_1/I_2)$ ratio of phosphoric acid was the smallest of these four systems, and the other three ratios did not vary much during the same situation. This might be attributable to a stronger interaction between phosphoric acid molecules and water molecules, resulting in a more ice-like and less liquid-like water structure.

3.4 Interaction between phosphoric acid and water

These three experiments indicated that the interaction between phosphoric acid and water played an important role in the molecular arrangement. The molecular structure of phosphoric acid aqueous solution on the interface was discussed above.

What occurred during the friction process at the molecular level? What factor was most crucial to the formation of the superlubricity state? In this work, we mainly focused on the effect of phosphoric

![Fig. 2](image-url) Tribological experiments of phosphoric acid solution

a Friction coefficient of phosphoric acid (pH = 1.5, concentration 0.1646 mol L$^{-1}$) as a function of time. The tests were performed with a 300 g load at a 56 mm/s velocity.
b A schematic diagram of the SFG from phosphoric acid solution residue in the contact region and the optical image of residues after friction (A: track edge, B: track centre).
c SFG spectrum for phosphoric acid solution residue in the contact region on the SiO$_2$ disc in the O–H stretching region.
d In the 1000–1200 cm$^{-1}$ range.

![Fig. 3](image-url) SFG spectra of pure water and phosphoric acid–water mixtures with different concentrations as indicated at the solid–liquid interface. Phosphoric acid concentration ranged from $3 \times 10^{-4}$ to 13.3 mol L$^{-1}$

![Fig. 4](image-url) SFG spectra of

a Pure water and different acid solutions with the same concentration (0.001 mol L$^{-1}$)
b phosphoric acid
c hydrochloric acid
d hyaluronic acid. The red solid line is a Gaussian fit to the SFG spectra.

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acid hydration. From the experimental data and analysis presented above, we proposed a model for the molecular structure of the phosphoric acid aqueous solution in Fig. 5 to illustrate the interaction between phosphoric acid and water molecules.

As shown in Fig. 5a, pure water molecules presented an ordered arrangement at the liquid/solid surface, which generated strong O–H stretching peaks in SFG spectra. However, hydration played an important role in the phosphoric acid aqueous solution. From Figs. 5b and c, it could be inferred that once phosphoric acid was added to pure water, phosphoric acid molecules would gradually combine with water molecules and began to break up the regular structure of interfacial water molecules, contributing to the decrease of SFG peak intensity in the broad O–H stretching region. More phosphoric acid molecules hydrated as the acid concentration rose and finally formed a totally disordered arrangement of water molecules when the acid concentration reached 13.3 mol l\(^{-1}\). In that case, no SFG peak could be found in the O–H stretching region. Moreover, when phosphoric acid dissolved in pure water, the solution would ionise hydrogen ions, which would influence the surface charge of SiO\(_2\). We knew that superlubricity was achieved only if the pH value of the original phosphoric acid solution is 1–1.5 [11, 28]. However, when the pH value was lower than the pH\(_{\text{pzc}}\) (a pH value of zero surface charge, \(\approx 2\) for SiO\(_2\) [29]), the SiO\(_2\) surface would be positively charged so that it would attract oxygen atoms rather than hydrogen atoms. In addition, phosphoric acid and water might form hydrogen bonds, which could break the regular water molecular arrangement. With the switching of the surface charge and increasing concentration of phosphoric acid, the original, ordered interfacial molecular arrangement was gradually destroyed. By comparing Fig. 5c with Fig. 5d, the chemical transformation during the superlubricity might be confirmed, i.e., the rubbing period probably accelerated the hydration of phosphoric acid, which is why the SFG intensity of the phosphoric acid residue in the centre of the friction track entirely disappeared. Fig. 2c displayed a completely different SFG signal during the friction track, while the concentration of the phosphoric acid solution in the two measured points was nearly identical after the equal time of evaporation. Therefore, evaporation of water during the onset of superlubricity did not account for the nulled SFG signal. The ultralow friction might be attributable to the hydration of phosphoric acid molecules.

4 Summary

The water structure in phosphoric acid solution during the friction process was further investigated in this work. By comparing SFG spectra of different acid aqueous solutions at the liquid/solid surface, it was confirmed that phosphoric acid possessed stronger hydration ability, which could break hydrogen bonds between water molecules. In aqueous phosphoric acid solution, the intensity of the peaks at 3200 and 3400 cm\(^{-1}\) both decreased with increasing phosphoric acid concentration, indicating the enhancement of hydration of phosphoric acid. In addition, a molecular structure model of the phosphoric acid aqueous solution was proposed, offering a theoretical basis for the hydration occurring in the aqueous solution.

There existed some apparent distinction between SFG spectra for phosphoric acid at the edge and the centre of the friction track, i.e. phosphoric acid in the friction track possessed a weaker peak intensity at 3200 and 3400 cm\(^{-1}\), which was explained by the accelerated hydration of phosphoric acid molecules because of the friction process.

All these experimental results suggested that hydration of phosphoric acid played an important role during the friction. Most of the previous literature [11, 12] about liquid superlubricity only speculated the lubricating mechanism from the perspective of the whole lubricating film. As SFG spectroscopy is superior to other common methods, such as Raman and IR spectroscopy, in the interface molecular structure, this work focused on the liquid/solid interface of the lubricating film. According to these observations and analyses, the underlying molecular structure of phosphoric acid solution at the liquid/solid interface has been revealed, which is of great significance to understand the mechanism of superlubricity and liquid lubrication.

Furthermore, in tribological studies, lubricants often involve complex heterogeneous solutions. The synergistic effects of lipids, proteins, hyaluronic acid, and water would become an important mechanism for the lubrication of articular cartilage. We believe that SFG spectroscopy can be applied to biosurface and bio-tribology. In the future, we are devoted to the development of the SFG measurement system for obtaining in situ information on the interface molecular structure of lubricating films.

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