Applications of sum-frequency generation vibrational spectroscopy in friction interface

Zhifeng LIU^{1,3}, Mengmeng LIU¹, Caixia ZHANG^{1,3,*}, Hongyan CHU^{1,3}, Liran MA^{2,*}, Qiang CHENG^{1,3}, Hongyun CAI³, Junmin CHEN³

¹ Institute of Advanced Manufacturing and Intelligent Technology, Beijing University of Technology, Beijing 100124, China

² State Key Laboratory of Tribology, Tsinghua University, Beijing 100084, China

³ Beijing Key Laboratory of Advanced Manufacturing Technology, Beijing University of Technology, Beijing 100124, China

Received: 05 June 2020 / Revised: 25 October 2020 / Accepted: 19 November 2020

© The author(s) 2020.

Abstract: Sum-frequency generation (SFG) vibrational spectroscopy is a second-order nonlinear optical spectroscopy technique. Owing to its interfacial selectivity, SFG vibrational spectroscopy can provide interfacial molecular information, such as molecular orientations and order, which can be obtained directly, or molecular density, which can be acquired indirectly. Interfacial molecular behaviors are considered the basic factors for determining the tribological properties of surfaces. Therefore, owing to its ability to detect the molecular behavior in buried interfaces *in situ* and in real time, SFG vibrational spectroscopy has become one of the most appealing technologies for characterizing mechanisms at friction interfaces. This paper briefly introduces the development of SFG vibrational spectroscopy and the essential theoretical background, focusing on its application in friction and lubrication interfaces, including film-based, complex oil-based, and water-based lubricating systems. Real-time detection using SFG promotes the nondestructive investigation of molecular structures of friction interfaces *in situ* with submonolayer interface sensitivity, enabling the investigation of friction mechanisms. This review provides guidance on using SFG to conduct friction analysis, thereby widening the applicability of SFG vibrational spectroscopy.

Keywords: SFG vibrational spectroscopy; film-based lubricating systems; complex oil-based lubricating systems; water-based lubricating systems

1 Introduction

Sum-frequency generation (SFG) vibrational spectroscopy is an interface spectroscopy technique based on the second-order nonlinear optical effect principle. Under an electric field caused by a weak light beam, the polarization (P) of the material can be identified as a function of the optical input field, i.e., $P = \epsilon_0 \tilde{\chi}^{(1)} \bar{E}$, where ϵ_0 is the vacuum permittivity, $\tilde{\chi}^{(1)}$ is the first-order linear polarizability, and $\bar{E}$ is the intensity of the corresponding electric field [1, 2]. The first ruby laser developed in 1960 enabled the development and growth of SFG vibrational spectroscopy. Thereafter,

the application of this spectroscopic technique has expanded significantly in various fields.

In 1961, Franken et al. [3] irradiated a quartz crystal with a 694.2 nm laser light and observed two beams in the exit region: One with a wavelength of 694.2 nm and the other 347.1 nm. This was the first experiment in which a light source of wavelength λ produced a beam of wavelength 2λ ; this phenomenon is known as second-harmonic generation (SHG). The discovery of SHG signaled the birth of nonlinear optics. Such studies laid the theoretical foundation for SHG and SFG [4]. In 1987, SFG vibrational spectroscopy of organic molecules adsorbed onto a substrate was first

* Corresponding authors: Caixia ZHANG, zhang-cx15@bjut.edu.cn; Liran MA, maliran@tsinghua.edu.cn

reported by Hunt et al. [5, 6] at the University of California, Berkeley, USA. This was the foremost study pertaining to SFG vibrational spectroscopy applied to a gas–solid interface. The outcomes of the aforementioned studies resulted in the merits of SFG gradually surpassing those of SHG for surface studies, with the introduction of mid-infrared (IR) beams to excite a monolayer of molecules and the detection of vibrational-resonance-enhanced SFG signals. This initiated the application of SFG vibrational spectroscopy in the fields of surfaces and interfaces. Thereafter, the application of this spectroscopic technique has extended from gas–solid interfaces to various solid–solid interfaces, laying the foundation for *in situ* and real-time detection of the molecular characteristics of friction interfaces. In 1993, Du et al. [7] first measured the SFG spectrum of a pure water surface under SSP (the polarization directions of the SFG, visible (VIS), and IR beams). Because the hydrogen-bond structure of water surfaces is complex, many problems related to hydrogen bonds remain to be solved. Based on Ref. [7], several researchers have successively conducted SFG studies regarding pure water surfaces [8–16]. In 1994, Du et al. [17] studied the SFG spectra of the quartz–water interface at different pH values. Subsequently, the SFG vibrational spectroscopy of the quartz–water interface was extensively investigated [18–20]. Water is a natural (and environment-friendly) biological lubricant with a large heat storage capacity exceeding those of artificial oil lubricants [21]. Owing to the development of SFG vibrational spectroscopy, various hydrophilic and hydrophobic solid–liquid interfaces have been investigated [22–25]. The first study regarding a film-based friction interface using SFG vibrational spectroscopy was conducted in 1995 [26]. In 2009, Nanjundiah et al. [27] used SFG vibrational spectroscopy to prove that an uneven water layer exists in a nanoscale space where two friction pairs are in contact during water lubrication. In 2016, a complex oil-based friction interface was studied using SFG vibrational spectroscopy [28]. More frictional interfaces are expected to be analyzed using SFG vibrational spectroscopy in the future.

Friction is primarily a behavioral characteristic of a surface or interface. SFG vibrational spectroscopy is used to detect the microscopic characteristics of an

interface in real time. Information regarding the molecular density, orientation, conformation of the surface, and interface molecules can be obtained directly or indirectly from the polarization, frequency, and signal intensity of SFG spectra. Furthermore, SFG vibrational spectroscopy can be used to monitor the dynamic processes of a system in real time [29]. Over the past few decades, this technique has become fundamental for determining the molecular behavior at friction interfaces and has facilitated the understanding of the interfacial mechanism of lubrication. This review briefly introduces the basic theory pertaining to this technique and then summarizes the contributions of SFG vibrational spectroscopy to friction studies.

2 Theory

SFG is a coherent second-order nonlinear optical process. An SFG beam with a frequency of ω_{SFG} is generated in a direction determined based on the phase-matching condition when an IR beam with a tunable frequency ω_{IR} and a visible beam with a constant frequency ω_{VIS} are simultaneously incident at an interface and overlap in space and time. The frequencies must satisfy the following equation: $\omega_{\text{SFG}} = \omega_{\text{IR}} + \omega_{\text{VIS}}$. In an SFG experiment, the frequency of the IR beam is continuously and automatically adjusted within the required range. When the frequency of the IR beam reaches the vibrational frequency of the molecules at the surface or interface, the corresponding SFG signal undergoes resonance enhancement. Consequently, the vibrational peaks of molecular groups become evident in the SFG spectra [2, 30].

Interface selectivity is the most prominent feature of SFG vibrational spectroscopy. The bulk material with central symmetric molecules does not contribute to the SFG signal owing to the formation of a centrosymmetric structure. Because the forces arising from the two different phases of interfacial molecules differ, the interfacial molecules lose their central symmetry and therefore contribute to the SFG signal [31, 32]. The interfacial selectivity of SFG is derived from the interfacial selectivity of the effective second-order nonlinear polarizability $\chi^{(2)}$. For centrosymmetric media, $\chi^{(2)} = 0$; hence, such media cannot generate SFG signals. For interfaces between different media,

the central symmetry is broken, i.e., $\chi^{(2)} \neq 0$, which produces SFG signals. This is also the origin of the interfacial selectivity of SFG [30].

SFG comprises two main experimental configurations. When visible and IR beams approach from opposite sides, the beams are considered to have counter-propagating geometry, as illustrated in Fig. 1(a). When both beams approach the interface from the same side, the beams are considered to have a co-propagating geometry. Figure 1(b) illustrates the noncollinear case of this geometry. In addition, a special case of collinear geometry arises when the two pump beams have the same angle of incidence [33]. The co-propagating geometry is widely used because it can prevent interference in the surface layer signal caused by the uneven local distribution of the medium. The corresponding change in the molecular vibrational energy levels is shown in Fig. 1(c). This can be interpreted as a continuous process of IR absorption and anti-Stokes Raman scattering [1, 2, 34, 35].

In the co-propagating geometry, the SFG intensity reflected from a surface can be expressed as shown in Eq. (1) [2]:

$$I(\omega_{\text{SFG}}) = \frac{8\pi^3 \omega_{\text{SFG}}^2 \sec^2 \beta_{\text{SFG}}}{c^3 n_1(\omega_{\text{SFG}}) n_1(\omega_{\text{VIS}}) n_1(\omega_{\text{IR}})} |\chi_{\text{eff}}^{(2)}|^2 I_{\text{IR}} I_{\text{VIS}} \quad (1)$$

where β_{SFG} is the reflection of the SFG beam with respect to the interface normal, $\sec \beta_{\text{SFG}}$ is the secant of angle of β_{SFG} and $n_1(\omega_i)$ ($i = \text{IR, VIS, and SFG}$) denotes the refractive indices of the three beams in

medium 1. In a system, $\frac{8\pi^3 \omega_{\text{SFG}}^2 \sec^2 \beta_{\text{SFG}}}{c^3 n_1(\omega_{\text{SFG}}) n_1(\omega_{\text{VIS}}) n_1(\omega_{\text{IR}})}$ is a constant; I_{IR} and I_{VIS} are the intensities of the IR and visible input beams, respectively; $\chi_{\text{eff}}^{(2)}$ is the effective second-order nonlinear susceptibility. When the frequency of the IR beam is equal to the vibrational frequency of the surface molecules, $\chi_{\text{eff}}^{(2)}$ can be written as shown in Eq. (2) [2, 30, 36, 37]:

$$\chi_{\text{eff}}^{(2)} = \chi_{\text{NR}}^{(2)} + \sum_q \frac{A_q}{\omega_{\text{IR}} - \omega_q + i\Gamma_q} \quad (2)$$

where $\chi_{\text{NR}}^{(2)}$ is the nonresonant signal of the sample; A_q , ω_q , and Γ_q are the amplitude, frequency, and line width of resonance q , respectively. Equation (2) can be used to fit the experimental spectra. The exact values of A_q , ω_q , and Γ_q can be obtained via fitting to quantitatively compare the vibrational intensities of different functional groups.

At an isotropic interface, only seven nonzero components of the second-order nonlinear polarizability exist: $\chi_{ijk}^{(2)}$, $\chi_{xxx}^{(2)} = \chi_{yyz}^{(2)}$, $\chi_{xzx}^{(2)} = \chi_{yzy}^{(2)}$, $\chi_{zxx}^{(2)} = \chi_{zyy}^{(2)}$, and $\chi_{zzz}^{(2)}$ [2, 35, 38]. Only four combinations of input and output beams in all polarizations can be used to measure the sum-frequency signal, which is determined by the nonzero second-order nonlinear optical susceptibility at an isotropic interface. These four combinations are SSP, SPS, PSS, and PPP, as shown in Eqs. (3)–(6). In the combinations, P means that the polarization direction of the photoelectric field is

Fig. 1 (a) Co-propagating geometry for SFG at an interface, (b) counter-propagating geometry for SFG at an interface, (c) SFG energy level diagram, and (d) molecular orientation of C–CH₃ group.

perpendicular to the incident light in the incident plane, and S indicates that the polarization direction of the photoelectric field is perpendicular to the incident plane. The three letters in the combinations represent the polarization directions of the SFG, VIS, and IR beams, respectively [2, 30, 35].

$$\chi_{\text{eff,ssp}}^{(2)} = L_{yy}(\omega_{\text{SFG}})L_{yy}(\omega_{\text{VIS}})L_{zz}(\omega_{\text{IR}})\sin\beta_{\text{IR}}\chi_{yyz}^{(2)} \quad (3)$$

$$\chi_{\text{eff,spS}}^{(2)} = L_{yy}(\omega_{\text{SFG}})L_{zz}(\omega_{\text{VIS}})L_{yy}(\omega_{\text{IR}})\sin\beta_{\text{VIS}}\chi_{yzy}^{(2)} \quad (4)$$

$$\chi_{\text{eff,pss}}^{(2)} = L_{zz}(\omega_{\text{SFG}})L_{yy}(\omega_{\text{VIS}})L_{yy}(\omega_{\text{IR}})\sin\beta_{\text{SFG}}\chi_{zyy}^{(2)} \quad (5)$$

$$\begin{aligned} \chi_{\text{eff,ppp}}^{(2)} = & -L_{xx}(\omega_{\text{SFG}})L_{xx}(\omega_{\text{VIS}})L_{zz}(\omega_{\text{IR}})\cos\beta_{\text{SFG}}\cos\beta_{\text{VIS}}\sin\beta_{\text{IR}}\chi_{xxz}^{(2)} \\ & -L_{xx}(\omega_{\text{SFG}})L_{zz}(\omega_{\text{VIS}})L_{xx}(\omega_{\text{IR}})\cos\beta_{\text{SFG}}\sin\beta_{\text{VIS}}\cos\beta_{\text{IR}}\chi_{xzx}^{(2)} \\ & +L_{zz}(\omega_{\text{SFG}})L_{xx}(\omega_{\text{VIS}})L_{xx}(\omega_{\text{IR}})\sin\beta_{\text{SFG}}\cos\beta_{\text{VIS}}\cos\beta_{\text{IR}}\chi_{zxx}^{(2)} \\ & +L_{zz}(\omega_{\text{SFG}})L_{zz}(\omega_{\text{VIS}})L_{zz}(\omega_{\text{IR}})\sin\beta_{\text{SFG}}\sin\beta_{\text{VIS}}\sin\beta_{\text{IR}}\chi_{zzz}^{(2)} \end{aligned} \quad (6)$$

where $L(\omega_i)$ is the corresponding Fresnel coefficient; it is used to correct the photoelectric field because the original intensities of the incident and outgoing beams are not consistent with the intensities of the beams in the surface region.

Nonlinear susceptibility is not a simple sum of the hyperpolarizability of all molecules. The overall susceptibility of an interface is the sum of all molecular hyperpolarizabilities projected onto a specific coordinate system considering molecular orientations. The hyperpolarizability $\beta_{ijk}^{(2)}$ of each molecule is typically defined in molecular coordinates (a, b, c) . The effect of the hyperpolarizability of the local field can be attributed to the interfacial refractive index. The $\chi_{ijk}^{(2)}$ of a material is the ensemble average of the hyperpolarizability of each molecule that is projected onto the lab frame multiplied by the number density of molecules. This can be written as shown in Eq. (7) [2, 30]:

$$\chi_{ijk}^{(2)} = N_s \sum_{ijk=xyz} \langle R_{ii'}R_{jj'}R_{kk'} \rangle \beta_{i'j'k'}^{(2)} \quad (i'j'k' = a, b, c) \quad (7)$$

where N_s is the number of molecules with a second-order nonlinear response on the surface. The angled brackets denote the ensemble averages. R is the matrix for transformation from the molecular coordinate system (a, b, c) to the laboratory coordinate system

(x, y, z) and can reflect the molecular orientation information of the interface. The methyl group is presented as an example because it is the most typical functional group in SFG spectra. A schematic diagram of the molecular orientation is shown in Fig. 1(d), which includes three components. The first is the tilt angle θ between the group principal axis and the interface normal, whose value range is $(0, \pi)$; the second is the rotation angle Ψ around the normal direction of the interface, whose value range is $(0, 2\pi)$; the final is the twist angle Φ of the molecular principal axis, whose value range is $(0, 2\pi)$ [2, 35]. Changes in the molecular orientation at the friction interface are among the most significant molecular behaviors that can be directly correlated with the tribological properties of a material.

3 SFG vibrational spectroscopy for investigating friction interfaces

SFG vibrational spectroscopy is an effective technique for investigating buried interfaces. This technique has been used in numerous studies pertaining to buried interfaces, including liquid–solid [39–44] and solid–solid interfaces [44–50]. Friction is a typical interface behavior. Because SFG vibrational spectroscopy can detect friction-induced changes in the interface molecular behavior in real time and *in situ*, the molecular regulatory mechanisms of different lubricating systems can be determined. We can improve the lubrication effects of lubricating systems by adjusting the molecular structure in these systems. Herein, the applications of SFG vibrational spectroscopy in friction interfaces are reviewed. They include the molecular behavior of lubrication interfaces in film-based, complex oil-based, and water-based lubricating systems. The corresponding experimental configurations are shown in Fig. 2. Excellent results were obtained and are described below.

3.1 Friction interface behaviors in film-based lubricating system investigated via SFG vibrational spectroscopy

In 1920, Hardy [51] introduced the concept of “boundary lubrication”, in which a monolayer can reduce the coefficient of solid–solid sliding friction by an order

Fig. 2 Experimental configurations of SFG vibrational spectroscopy in different lubricating systems. (a) Film-based lubricating system (where I denotes patches of organic film transferred to counterface in friction, II denotes orientation changes of interface molecules in friction, and III denotes disorder of interfacial molecules in friction); (b) complex oil-based lubricating system (I denotes interaction between base oil and friction modifier molecules and II denotes interaction between different friction modifier molecules); and (c) water-based lubricating system (I represents the lubrication effect of the water layer and II represents the effect of ions on water lubrication).

of magnitude. Ultrathin organic films represent film-based lubricating systems [52, 53]. Although the friction-reducing properties of organic films are well known, the molecular basis for boundary lubrication remains poorly understood, preventing the design of effective boundary lubricating films [54]. In addition, because contact and stress are the basis and premise of friction, investigations regarding changes in interface molecules during contact and stress are important for designing effective boundary lubrication films. SFG vibrational spectroscopy has been used to investigate molecular changes in organic films under contact and stress [55, 56]. The principal effect of contact and stress is a considerable loss of the resonant SFG signal, i.e., the state of molecules at the interface changes significantly under contact and stress. Possible explanations for the loss of the SFG signal can be summarized into three points, as shown in Fig. 2(a).

The patches of organic film transferred to the counterface may contribute the decrease in the SFG signal level. Many studies support this conclusion, as shown in Fig. 3. In this case, the SFG signal cannot be fully recovered after the stress is released. The results of compression experiments on ultrathin organic films have been used to formulate models for understanding

lubrication [57]. In 1998, Fraenkel et al. [52] investigated an Langmuir–Blodgett monolayer in contact with a quartz lens using SFG vibrational spectroscopy. It was speculated that the reduction in the SFG intensity after the release of stress may be due to the transfer of ordered patches of the organic film to the counterface. Based on the aforementioned study, Beattie et al. [58, 59] conducted an in-depth study regarding a monolayer at the interface between a sapphire prism and a fused silica lens. The results shown in Fig. 3(a) support the results of Ref. [52]. Furthermore, Beattie et al. [59] further confirmed that organic film patch transfer is a real phenomenon, of which the sketches are shown in Fig. 3(b). It is speculated that the transfer of monolayer patches to the counterface in contact is a viscoelastic process, owing to the incomplete recovery of the SFG signal upon shock unloading [60]. The self-assembled monolayer was compressed by laser-driven shock waves. The response to shock loading and unloading was monitored using SFG vibrational spectroscopy, as shown in Fig. 3(c). This viscoelastic process is irreversible and causes an increase in friction.

Self-assembled monolayer (SAM) molecules in the order of 10%–20% undergo a viscoelastic process [60]. Researchers believe that SFG signal loss in elastic

Fig. 3 Analysis of contact and stress-induced transfer of organic film patches using SFG vibrational spectroscopy. Reproduced with permission from Ref. [59], © American Chemical Society 2006; Ref. [60], © American Chemical Society 2005. (a) Incomplete recovery of SFG signal after stress release; (b) confirmation of organic film patch transfer; and (c) patches related to monolayer transferred to counterface during viscoelastic process.

processes indicates intermolecular order loss. Therefore, changes in molecular orientation caused by friction may be the second reason for the decrease in the SFG signal level. The corresponding experimental configuration is shown in Fig. 4(a). In some cases, orientation changes occur at the terminal group of the molecule under the action of stress [26, 51, 61, 62]. Based on a hydrocarbon chain with a methyl group (which is the terminal group in this example), the loss of methyl resonances in the SFG spectra under stress is not accompanied by the vibrational characteristics of methylene groups. This suggests that orientation changes only occur at the terminal group of the molecule [51]. This differs from the disorder typically observed in SFG spectra [63, 64]. Orientation changes occurring at the terminal group of the molecule are reversed after the release of stress, as shown in

Fig. 4(b). This effectively reduces the friction damage. In addition, the local molecular interpenetration from two friction pairs during the friction process is another reason contributing to changes in molecular orientation, as shown in Fig. 4(c). The molecular orientation angle can be obtained by combining the second-order nonlinear polarizability, which is written as a functional formula of the orientation angles obtained through an Eulerian coordinate transformation, using experimental data. Furthermore, the local molecular interpenetration can be reversed when stress is released. However, the molecular orientation caused by local molecular interpenetration at the interface significantly increases the friction coefficient, as demonstrated by Yurdumakan et al. [65, 66].

As mentioned above, the patches of organic film transferred to the counterface and changes in molecular

Fig. 4 Analysis of contact-and-stress-induced molecular orientation changes at interface via SFG vibrational spectroscopy. Reproduced with permission from Ref. [51], © American Chemical Society 2003; Ref. [65], © American Chemical Society 2007. (a) Corresponding experimental configuration; (b) orientation change in terminal group of molecule; and (c) change in molecular orientation due to interpenetration.

orientation, which caused by friction, are two important reasons for the decreasing of SFG signal level. In addition, friction causes disordered interfacial molecules, which may be the third reason for the decrease in the SFG signal level. The corresponding experimental configuration is illustrated in Fig. 5(a). Such a significant structural change would result in the appearance of a large number of molecules with gauche defects at the interface. For a hydrocarbon chain with a methyl group, the ratio of the peak intensities of methylene and methyl can be used to describe the accumulation of gauche defects in the films, considering the correlation between methylene stretching and the conformation of the hydrocarbyl chain [67, 68]. However, the mechanism of recovery of the SFG signal after the force is released remains unclear. When the stress is constant, the resulting molecular defects can self-heal after the force is released; this can be proved by the similar SFG spectra of the sample before and after contact, as shown in Fig. 5(b). Moreover, this can account for the considerable resistance of the SAM toward mechanical stress [68]. However, the SFG signal can only be recovered partially after the release of stress when the sliding

process is accompanied by a variable force, as shown in Fig. 5(c). This indicates that gauche defects caused by a variable force are irreversible [69].

Based on the results of the aforementioned studies pertaining to film-based lubricating systems using SFG vibrational spectroscopy, changes in interface molecular behavior caused by friction can be classified into three categories. The first type of change arises as patches of film are transferred to the counterface; this can be proved by the incomplete recovery of the SFG signal after the release of stress. The transferred patches of film destroys part of the organic film, resulting in increased friction. In addition, friction results in a change in the interface molecular inclination. This change cannot be determined directly from the spectra. Information regarding the interface molecular orientation can be obtained by connecting the molecular coordinate system with the laboratory coordinate system through the Euler matrix. The last type of change is the increase in the number of molecules with gauche defects; this can be proven from the ratios of peak intensity for different groups in the SFG spectra. Defects caused by a constant stress can generally self-heal after the release of stress, unlike

Fig. 5 Analysis of stress-induced molecular ordering changes at an interface via SFG vibrational spectroscopy. Reproduced with permission from Ref. [68], © American Chemical Society 2014; Ref. [69], © American Chemical Society 2014. (a) Corresponding experimental configuration; (b) self-healing mechanism of defects induced by stress; and (c) non-healing of defects induced by variable force.

defects caused by a varying stress. Monitoring the molecular behavior using SFG improves the analysis of lubrication mechanisms.

3.2 Friction interface behaviors in complex oil-based lubricating systems investigated via SFG vibrational spectroscopy

Compared with those based on pure base oil, complex oil-based lubricating systems are used more widely. The addition of certain compounds to the base oil can effectively reduce friction and wear. These compounds are known as friction modifiers [70, 71]. The reduction in friction and wear is attributable to two aspects at the molecular level: the interaction between the base oil and friction modifier molecules, and the interaction between different modifier molecules. These interactions are shown in Fig. 2(b). The changes in interface molecular behavior during the friction process can be analyzed via SFG vibrational spectroscopy.

The interaction between the base oil and friction

modifier molecules can reduce the friction coefficient in the sliding processes [28, 72, 73]. The experimental configuration is shown in Fig. 6(a). Such interactions exhibit different forms under static and dynamic conditions, as shown in Fig. 6(b). Under static conditions, the base oil molecules on the friction modifier adsorption film form an all-trans structure without gauche defects; this can be proven by the disappearance of the features of methylene in the SFG spectra. This disappearance occurs owing to the interaction between the terminal groups of the base oil and friction modifier molecules, resulting in the formation of an interdigitated structure. In addition, it has been discovered that different characteristic peaks appeared in the SFG spectra under different sliding directions, signifying that the friction modifier caused the base oil molecules to be oriented along the sliding direction under dynamic conditions. Consequently, the friction coefficient in the sliding process reduced. The molecular structure of the friction modifier is an important factor

affecting the interaction between the friction modifier and base oil. It affects the friction coefficient [74–76], as shown in Fig. 6(c). Fatty acids such as stearic acid, elaidic acid, and oleic acid are typical oiliness additives that have been widely used as friction modifiers [77–80]. The presence of double bonds in the alkyl chains generates many gauche defects, producing a special conformation that breaks the local symmetry of the alkyl chain. Such conformations increase the friction coefficient compared with that of a carbon chain structure without double bonds. In addition, the position of the double bond in the carbon chain affects the number of molecules with gauche defects. However, the position of the double bond does not significantly affect the friction coefficient. The tilt angle of the friction modifier molecule in the adsorbed film is another important factor affecting the interaction between the friction modifier and base lubricant. This was corroborated by Watanabe et al. [81] through a combination of SFG vibrational

spectroscopy and macroscopic friction experiments. The larger the tilt angle of the friction modifier molecule, the lower is the friction coefficient, as shown in Fig. 6(d).

In addition to the interaction between the friction modifier and base oil molecules, when two or more friction modifiers are added to the base oil, the molecules of the different friction modifiers interact with each other, thereby changing the friction and wear, as shown in Fig. 7(a). Casford et al. [82] discovered from SFG spectra that when a lubricant contains two modifiers, its adsorption film structure differs significantly from that of a lubricant containing only one modifier, as shown in Fig. 7(b). An in-depth study was conducted on this basis, as shown in Fig. 7(c) [83]. Co-operative behavior was observed between different friction modifier molecules. Such behavior can change the molecular configuration of the interface, thereby effectively reducing the friction coefficient. This can be proven by the change in the intensities of methyl

Fig. 6 Analysis of interfacial structures regulated by interaction between base oil and friction modifier molecules using SFG vibrational spectroscopy. Reproduced with permission from Ref. [28], ©American Chemical Society 2016; Ref. [74], © Springer Science Business Media New York 2016; Ref. [81], © American Chemical Society 2014. (a) Experimental configuration; (b) effect of friction modifier under static and dynamic conditions; (c) effect of friction modifier's molecular structure; and (d) effect of tilt angle of friction modifier molecule.

Fig. 7 Analysis of interfacial structures regulated by interaction between different friction modifier molecules via SFG vibrational spectroscopy. Reproduced with permission from Ref. [82], © The Author(s) 2016; Ref. [83], © The Author(s) 2020. (a) Experimental configuration; (b) different interface structures of single and mixed modifier systems at the interface; and (c) formation of mixed modifier complex at the interface.

and methylene peaks in the SFG spectra. Notably, the friction coefficient of the mixed friction modifiers decreases faster than that of a single friction modifier as the temperature increases, owing to the co-operative behavior. Another postulation is that different friction modifiers in the complex oil-base lubricating system may form a mixed modifier complex at the interface. The formation of the mixed additive complex at the interface can reduce the temperature at which the maximum ordered adsorption of the single friction modifier occurs. Because the maximum ordered adsorption of the friction modifier can significantly reduce the friction coefficient, when the maximum effective adsorption temperature of the single friction modifier is high, the formation of the mixed additive complex facilitates the reduction in friction and wear.

In summary, the friction and wear in complex oil-based lubricating systems are lower than those in pure oil-base lubricating systems owing to the different

interfacial molecular structures, which can be monitored via SFG vibrational spectroscopy. Two reasons for this phenomenon are as follows. First, the interaction between friction modifier and base oil molecules enables the base oil molecules to form an all-trans structure without gauche defects under static conditions. This can be proven by the disappearance of group peaks with local symmetry in the spectra. Furthermore, the presence of a friction modifier can cause the base oil molecules to change their molecular orientation along the sliding direction. This can reduce friction and wear during sliding. In addition, different modifier molecules in the complex oil-base lubricating system exhibit cooperative behavior. This can significantly reduce the friction coefficient by changing the molecular structure of the interface and by rendering the temperature of maximum ordered adsorption for a mixed friction modifier lower than that for a single friction modifier. This can be proven by the changes

in the intensities of methyl and methylene peaks in the SFG spectra.

3.3 Friction interface behaviors in water-based lubricating system investigated via SFG vibrational spectroscopy

Water has been used as a biological lubricant, and its environmental friendliness renders it superior to artificial oil lubricants [84]. SFG vibrational spectroscopy can be used to reflect the uniformity and stability of water layers in the friction process through changes in the state of water at the interface. Moreover, SFG vibrational spectroscopy can be used to predict the effect of adding ions on friction, as shown in Fig. 2(c). Typically, the SFG intensity spectrum of water exhibits three characteristic bands centered at 3,200, 3,400, and 3,550 cm^{-1} . The molecular interpretation of these peaks is debatable. However, based on the more typically accepted interpretation, the bands at 3,200 and 3,400 cm^{-1} can be attributed to strongly bonded and more loosely bonded DDAA molecules, respectively. The band at 3,550 cm^{-1} is assigned to the donor-bonded OH stretches of three-coordinate DDA and DAA water molecules. Here, D and A denote the donor and acceptor hydrogen bonds, respectively, with which a water molecule connects to its nearest neighbors [85]. It is noteworthy that the strongly bonded water molecules, which are typically known as “ice-like” water molecules, are not easily squeezed out by pressure during friction. However, the more loosely bonded water molecules, which are known as “liquid-like” water molecules, are easily squeezed out during friction [27, 86–90].

Studies have shown that liquids confined in nanospaces exhibit properties that are different from those of bulk liquids, owing to liquid structuring induced by the restricted molecular motion of liquids in nanospaces and by the interactions of liquids with solid surfaces [91]. When two friction pairs are rubbed in pure water, the existence of water at the friction interface can be proven by the appearance of peaks in the OH stretching region of the SFG spectrum. The friction coefficient in such cases may be lower or higher than that of dry friction; nonetheless, it cannot be lower than that of oil lubricants [27]. It has been proven that water at the frictional interface cannot

easily form a uniform and stable water layer, resulting in its relatively high friction coefficient [27, 89]. The corresponding model is shown in Fig. 8(a). To obtain a uniform and stable water layer at the interface, which will not be forced out of the interface during friction, it is necessary to regulate the structure of the interface water must be regulated. Real-time SFG vibrational spectroscopy analysis can be extremely helpful in this context.

Two effective methods can be used to obtain a uniform and stable water layer in the friction process. The first is to enhance the surface hydrogen bonding environment; this can be achieved by increasing the content of surface hydroxyl through special treatments such as thermal [92–94] or plasma treatment [87, 95–97]. The intensity of the peak at 3,200 cm^{-1} in the SFG spectra corresponding to the interface hydroxyl of the treated friction pair can be enhanced significantly compared with that before treatment. An increase in the proportion of ice-like water will increase the thickness of the water layer at the interface and its bearing capacity, thereby reducing friction and wear [87], as shown in Fig. 8(b). In addition, Noguchi et al. [90] discovered that the higher the pressure, the lower was the intensity of the ice-like water peak and the stronger was the liquid-like water peak in SFG spectra. Hence, the water layer can be extruded from the frictional interface more easily. Another method is to control the characteristics of the electrostatic force to improve the bearing capacity of the water layer in the friction process. This can be achieved by changing the surface charge [98, 99], which can be controlled using specific methods such as adding a surfactant to the water [86, 100] and modifying the surface of the friction pair [90]. In such cases, a significant amount of ice-like water appears at the friction interface, and relevant studies have shown that a highly coordinated ice-like water layer between two surfactant-covered surfaces can withstand confinement pressures and reduce sliding friction, as shown in Fig. 8(c) [86, 90].

Since ions are widespread in nature and particularly in biological systems, they should be considered when water is used as a lubricant for friction. Our previous studies demonstrated that salt ions can regulate the lubrication characteristics of water [101, 102]. Hofmeister, or “specific ion” effects have

Fig. 8 Lubrication effect of water layer using SFG vibrational spectroscopy. Reproduced with permission from Ref. [27], © American Institute of Physics 2009; Ref. [86], © The Authors 2016; Ref. [87], © American Chemical Society 2013; Ref. [89], © American Chemical Society 2018; Ref. [90], the PCCP Owner Societies 2008. (a) Existence of water layer between two friction pairs proven by appearance of OH stretching region in SFG spectra; (b) effect of surface hydrogen bonding environment; and (c) characteristics of electrostatic force controlled by the surface charge.

been with us for 150 years, as shown in Fig. 9(a) [103, 104]. The ions on the left can form a stable hydrogen bond network structure with the surrounding water molecules, and these ions are known as “kosmotropes”. The ions on the right are weak in binding to water molecules and break the original hydrogen bond network in the water; these ions are known as “chaotropes”. As a typical ion effect, the Hofmeister series has been discovered in many systems that use SFG vibrational spectroscopy [105–109]. For kosmotropic anions, Marcus [110] observed a linear correlation between the degree of dehydration difficulty and the hydration Gibbs free energy of the anions. This indicates that the effect of ions may be

correlated with the hydration Gibbs free energy of the ions [111]. In terms of the form of influence on friction, ionic effects can be classified into two types, i.e., perturbation to the hydrogen bond environment and effect on molecular chains.

For substrates without surface modifications, this ion effect is manifested as a disruption in the hydrogen bond environment of the original system and the formation of a new hydrogen bond environment, as shown in Fig. 9(b). Ions primarily disturb the original hydrogen bond environment by screening the surface charges. Based on a negatively charged surface as an example, cations behave as counterions and are expected to be closer to the interface than anions.

Compared with monovalent cations, divalent cations produce a more oriented interfacial solvent. This is accomplished by charging the interface to yield a longer SFG-active region. The addition of divalent cations can not only destroy the original hydrogen bond network by screening the interface charge, but also actively rearrange the interfacial hydrogen bonding network at the negatively charged interface [112]. The SFG signal of the interfacial water with divalent cations in the OH region is stronger than that of a monovalent cation, signifying that the ability of cations to form a new hydrogen bond environment is affected by the valence state. In addition, Tuladhar et al. [108] discovered that the degree of perturbation of ions in the interfacial hydrogen bond environment is affected by the size of the ions.

For surfaces with organic films, the effect of ions on the molecular chain in the film must be considered

in the friction process. Some studies have shown that the addition of monovalent cations does not change the conformation of the molecular chain of the modified film. Instead, the direction of the interfacial water molecules changes owing to the screening effect of charges, which can be directly reflected by the phase change in SFG spectra [113]. The addition of divalent cations removes the SFG signal component of the interface water molecules, suggesting that the interfacial hydrogen bond environment is completely destroyed. It is believed that a divalent cation can interact with two intrachain or interchain charges and form a jointing point [113, 114]. However, such polymer-ion complex models are not suitable for all systems. Feng et al. [115] highlighted that the addition of divalent cations can cause the head groups and terminal groups of the molecular chains to reorient, resulting in more orderly main chains of the molecules.

Fig. 9 Effect of ions on water lubrication analyzed via SFG vibrational spectroscopy. Reproduced with permission from Ref. [108], © American Chemical Society 2018; Ref. [112], © American Chemical Society 2019; Ref. [113], © American Chemical Society 2013; Ref. [115], © Biophysical Society 2017. (a) Schematic diagram of Hofmeister series and different properties of kosmotropes and chaotropes in aqueous solution; (b) perturbation to interfacial hydrogen bond environment by ions; and (c) effect of ions on molecular chains.

Two different polymer-ion complex models are shown in Fig. 9(c). Notably, the bonding ratio between the bare ions and the interface charged functional groups is closely related to the valence state of the ion. This binding ratio is plausible in terms of charge neutralization [116]. The interaction between such adsorption ions (K^+ , Na^+ , Ca^{2+} , Mg^{2+} , and La^{3+}) and the head groups has been demonstrated to induce a blue shift in the peak of the adsorbed groups in SFG spectra [117–120]. The analysis of ion effects using SFG vibrational spectroscopy will be beneficial for determining the mechanism of water lubrication.

Based on the analysis above, the two characteristic peaks in the OH range of the SFG spectra at 3,200 and 3,400 cm^{-1} were used to characterize the state of the interfacial water. These two peaks corresponded to the ice-like and liquid-like water, respectively. A water layer that primarily comprises ice-like water cannot be squeezed out easily during friction and can provide satisfactory lubrication; by contrast, liquid-like water is easily extruded. Two methods can be used to enhance the uniformity and stability of the water layer in the friction process: enhancing the hydrogen bonding environment of the friction interface; and controlling the characteristics of the electrostatic force between two friction pairs, which can be monitored via SFG vibrational spectroscopy. In addition, the effect of ions on the interfacial hydrogen bond environment [43, 108–110, 114, 115, 120–123] and the molecular chains at the interface [113, 114] were discovered to be related to friction and wear, based on changes in the corresponding water peaks, the order degree of the molecular chain, and the orientation angle of the group, as reflected in the SFG spectra. Hence, SFG-based analysis can be beneficial for investigating the regulation of water lubrication using ions.

4 Conclusions

SFG vibrational spectroscopy has become a widely useful optical tool for the analysis of buried interfaces, particularly for different friction interfaces. The advantages of SFG vibrational spectroscopy have been demonstrated through the achievements of many research groups worldwide. Herein, the application

of SFG in investigating three different lubricating systems was reviewed: (1) For a film-based lubricating system, the interface molecular behavior changes caused by friction can be classified into three categories through SFG analysis, including the transfer of film patches to the counterface, change in interface molecular inclination, and increase in the number of molecules with gauche defects. The molecular information extracted from SFG spectra including the degree of SFG signal recovery after the release of stress, changes in the molecular chain tilt angle, and molecular chain order degree can reveal the lubrication mechanism. (2) For a complex oil-based lubricating system, the addition of a friction modifier can significantly reduce the friction coefficient owing to the interaction between the base oil and friction modifier molecules as well as the interaction between different friction modifier molecules. The interaction between the different components in the complex oil-based lubricating system was proven by the change in SFG signal intensities in contrasting experiments. This can reveal the lubrication mechanism of complex oil-based lubricating systems. (3) For a water-based lubricating system, interfacial hydrogen bonding is clearly reflected in SFG spectra. The stronger the intensity of the ice-like water peak in an SFG spectrum, the stronger is the hydrogen bond network of water molecules; consequently, the harder it is to squeeze water molecules out of nanospaces during the sliding process, hence a reduction in friction. Moreover, the addition of ions changed the interface hydrogen bond environment and the stability of the modified film. Therefore, the effect of ions on water friction can be predicted based on the changes in the strong and weak hydrogen bond peaks in SFG spectra before and after ion addition.

SFG has been applied to many different interfaces, and many macroscopic phenomena have been explained at the molecular level; this is expected to continue in the future. However, the wider application of SFG vibrational spectroscopy is hindered by some obstacles. First, some restrictions exist regarding the selection of samples. The samples should be transparent to IR, visible, and SFG beams to ensure the successful input and output of the beams, such that SFG spectra of different friction interfaces can be obtained. Another barrier is the peaks in SFG spectra. SFG vibrational

spectroscopy does not yet offer the same detailed and standard spectral analysis as IR spectroscopy. However, SFG vibrational spectroscopy will continue to contribute positively to studies pertaining to friction-related interfaces. Further development of laser technology will increase the sensitivity and reliability of SFG spectrometers. In addition, the coordination of SFG vibrational spectroscopy and molecular dynamics analysis presents considerable potential in revealing friction interfaces in unprecedented detail. Many other tools, including various spectroscopic and microscopic techniques, can be combined with SFG vibrational spectroscopy to compensate for the disadvantages and restrictions imposed by the separate techniques. We expect the applications of SFG vibrational spectroscopy to expand significantly in the future.

Acknowledgements

The authors appreciate the funding supported by the National Natural Science Foundation of China (51705010, 51675297, and 51527901), the Beijing Natural Science Foundation (3192003), the General Project of Science and Technology Plan from Beijing Educational Committee (KM201810005013), the Tribology Science Fund of State Key Laboratory of Tribology (STLEKF16A02, SKLTKF19B08), and the training program of Rixin talent and outstanding talent from Beijing University of Technology.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made.

The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- [1] Prylepa A, Reitböck C, Cobet M, Jesacher A, Jin X, Adelung R, Schatzl-Linder M, Luckeneder G, Stellnberger K H, Steck T, *et al.* Material characterisation with methods of nonlinear optics. *J Phys D: Appl Phys* **51**(4): 043001 (2018)
- [2] Zhang C. Sum frequency generation vibrational spectroscopy for characterization of buried polymer interfaces. *Appl Spectrosc* **71**(8): 1717–1749 (2017)
- [3] Franken P A, Hill A E, Peters C W, Weinreich G. Generation of optical harmonics. *Phys Rev Lett* **7**(4): 118 (1961)
- [4] Bloembergen N, Pershan P S. Light waves at the boundary of nonlinear media. *Phys Rev* **128**(2): 606 (1962)
- [5] Hunt J H, Guyot-Sionnest P, Shen Y R. Observation of C–H stretch vibrations of monolayers of molecules optical sum-frequency generation. *Chem Phys Lett* **133**(3): 189–192 (1987)
- [6] Zhu X D, Suhr H, Shen Y R. Surface vibrational spectroscopy by infrared-visible sum frequency generation. *Phys Rev B* **35**(6): 3047–3050 (1987)
- [7] Du Q, Superfine R, Freyse E, Shen Y R. Vibrational spectroscopy of water at the vapor/water interface. *Phys Rev Lett* **70**(15): 2313–2316 (1993)
- [8] Shen Y R, Ostroverkhov V. Sum-frequency vibrational spectroscopy on water interfaces: Polar orientation of water molecules at interfaces. *Chem Rev* **106**(4): 1140–1154 (2006)
- [9] Richmond G L. Molecular bonding and interactions at aqueous surfaces as probed by vibrational sum frequency spectroscopy. *Chem Rev* **102**(8): 2693–2724 (2002)
- [10] Gopalakrishnan S, Liu D F, Allen H C, Kuo M, Shultz M J. Vibrational spectroscopic studies of aqueous interfaces: Salts, acids, bases, and nanodrops. *Chem Rev* **106**(4): 1155–1175 (2006)
- [11] Gan W, Wu D, Zhang Z, Feng R R, Wang H F. Polarization and experimental configuration analyses of sum frequency generation vibrational spectra, structure, and orientational motion of the air/water interface. *J Chem Phys* **124**(11): 114705 (2006)
- [12] Baldelli S, Schnitzer C, Jane Shultz M, Campbell D J. Sum frequency generation investigation of water at the surface of H₂O/H₂SO₄ and H₂O/Cs₂SO₄ binary systems. *Chem Phys Lett* **287**(1): 143–147 (1998)
- [13] Viswanath P, Motschmann H. Oriented thiocyanate anions at the air–electrolyte interface and its implications on interfacial water—A vibrational sum frequency spectroscopy study. *J Phys Chem C* **111**(12): 4484–4486 (2007)
- [14] Tyrode E, Johnson C M, Kumpulainen A, Rutland M W, Claesson P M. Hydration state of nonionic surfactant

- monolayers at the liquid/vapor interface: Structure determination by vibrational sum frequency spectroscopy. *J Am Chem Soc* **127**(48): 16848–16859 (2005)
- [15] Du H, Liu J, Ozdemir O, Nguyen A V, Miller J D. Molecular features of the air/carbonate solution interface. *J Colloid Interface Sci* **318**(2): 271–277 (2008)
- [16] Sovago M, Campen R K, Wurpel G W H, Müller M, Bakker H J, Bonn M. Vibrational response of hydrogen-bonded interfacial water is dominated by intramolecular coupling. *Phys Rev Lett* **100**(17): 173901 (2008)
- [17] Du Q, Freysz E, Shen Y R. Vibrational spectra of water molecules at quartz/water interfaces. *Phys Rev Lett* **72**(2): 238 (1994)
- [18] Gurau M C, Kim G, Lim S M, Albertorio F, Fleisher H C, Cremer P S. Organization of water layers at hydrophilic interfaces. *Chemphyschem* **4**(11): 1231–1233 (2003)
- [19] Li I, Bandara J, Shultz M J. Time evolution studies of the H₂O/quartz interface using sum frequency generation, atomic force microscopy, and molecular dynamics. *Langmuir* **20**(24): 10474–10480 (2004)
- [20] Kim J, Kim G, Cremer P S. Investigations of polyelectrolyte adsorption at the solid/liquid interface by sum frequency spectroscopy: Evidence for long-range macromolecular alignment at highly charged quartz/water interfaces. *J Am Chem Soc* **124**(29): 8751–8756 (2002)
- [21] Urbakh M, Klafter J, Gourdon D, Israelachvili J. The nonlinear nature of friction. *Nature* **430**(6999): 525–528 (2004)
- [22] Kataoka S, Gurau M C, Albertorio F, Holden M A, Lim S M, Yang R D, Cremer P S. Investigation of water structure at the TiO₂/aqueous interface. *Langmuir* **20**(5): 1662–1666 (2004)
- [23] Nihonyanagi S, Ye S, Uosaki K, Dreesen L, Humbert C, Thiry P, Peremans A. Potential-dependent structure of the interfacial water on the gold electrode. *Surf Sci* **573**(1): 11–16 (2004)
- [24] Liu W T, Shen Y R. Surface vibrational modes of α -quartz(0001) probed by sum-frequency spectroscopy. *Phys Rev Lett* **101**: 016101 (2008)
- [25] McFearin C L, Beaman D K, Moore F G, Richmond G L. From franklin to today: Toward a molecular level understanding of bonding and adsorption at the oil–water interface. *J Phys Chem C* **113**(4): 1171–1188 (2009)
- [26] Du Q, Xiao X D, Charych D, Wolf F, Frantz P, Shen Y R, Salmeron M. Nonlinear optical studies of monomolecular films under pressure. *Phys Rev B* **51**(12): 7456–7463 (1995)
- [27] Nanjundiah K, Hsu P Y, Dhinojwala A. Understanding rubber friction in the presence of water using sum-frequency generation spectroscopy. *J Chem Phys* **130**(2): 024702 (2009)
- [28] Watanabe S, Nakano M, Miyake K, Sasaki S. Analysis of the interfacial molecular behavior of a lubrication film of n-dodecane containing stearic acid under lubricating conditions by sum frequency generation spectroscopy. *Langmuir* **32**(51): 13649–13656 (2016)
- [29] Wang H F, Velarde L, Gan W, Fu L. Quantitative sum-frequency generation vibrational spectroscopy of molecular surfaces and interfaces: Lineshape, polarization, and orientation. *Annu Rev Phys Chem* **66**(1): 189–216 (2015)
- [30] Zhang C, Myers J N, Chen Z. Elucidation of molecular structures at buried polymer interfaces and biological interfaces using sum frequency generation vibrational spectroscopy. *Soft Matter* **9**(19): 4738–4761 (2013)
- [31] Wang H F. Sum frequency generation vibrational spectroscopy (SFG–VS) for complex molecular surfaces and interfaces: Spectral lineshape measurement and analysis plus some controversial issues. *Prog Surf Sci* **91**(4): 155–182 (2016)
- [32] Shiratori K, Morita A. Theory of quadrupole contributions from interface and bulk in second-order optical processes. *Bull Chem Soc Jpn* **85**(10): 1061–1076 (2012)
- [33] Jena K C, Hung K K, Schwantje T R, Hore D K. Methyl groups at dielectric and metal surfaces studied by sum-frequency generation in co- and counter-propagating configurations. *J Chem Phys* **135**(4): 044704 (2011)
- [34] Humbert C, Noblet T, Dalstein L, Busson B, Barbillon G. Sum-frequency generation spectroscopy of plasmonic nanomaterials: A review. *Materials* **12**(5): 836 (2019)
- [35] Xiao M Y, Lu T Y, Lin T, Andre J S, Chen Z. Understanding molecular structures of buried interfaces in halide perovskite photovoltaic devices nondestructively with sub-monolayer sensitivity using sum frequency generation vibrational spectroscopy. *Adv Energy Mater* **10**(26): 1903053 (2020)
- [36] Ge A M, Rudshiteyn B, Videla P E, Miller C J, Kubiak C P, Batista V S, Lian T Q. Heterogenized molecular catalysts: Vibrational sum-frequency spectroscopic, electrochemical, and theoretical investigations. *Acc Chem Res* **52**(5): 1289–1300 (2019)
- [37] Shen Y R. Phase-sensitive sum-frequency spectroscopy. *Annu Rev Phys Chem* **64**(1): 129–150 (2013)
- [38] Casford M T L, Davies P B. The structure of oleamide films at the aluminum/oil interface and aluminum/air interface studied by sum frequency generation (SFG) vibrational spectroscopy and reflection absorption infrared spectroscopy (RAIRS). *ACS Appl Mater Interfaces* **1**(8): 1672–1681 (2009)
- [39] Wang L, Nihonyanagi S, Inoue K I, Nishikawa K, Morita A, Ye S, Tahara T. Effect of frequency-dependent Fresnel factor on the vibrational sum frequency generation spectra for liquid/solid interfaces. *J Phys Chem C* **123**(25): 15665–15673 (2019)
- [40] Jubb A M, Hua W, Allen H C. Organization of water and atmospherically relevant ions and solutes: Vibrational sum frequency spectroscopy at the vapor/liquid and liquid/solid interfaces. *Acc Chem Res* **45**(1): 110–119 (2012)

- [41] Zou X Q, Wei S, Jasensky J, Xiao M Y, Wang Q M, Brooks C L III, Chen Z. Molecular interactions between graphene and biological molecules. *J Am Chem Soc* **139**(5): 1928–1936 (2017)
- [42] Zaera F. Surface chemistry at the liquid/solid interface. *Surf Sci* **605**(13–14): 1141–1145 (2011)
- [43] Lyu Y Q, Wang Y R, Wang S N, Liu B, Du H. Potassium hydroxide concentration-dependent water structure on the quartz surface studied by combining sum-frequency generation (SFG) spectroscopy and molecular simulations. *Langmuir* **35**(36): 11651–11661 (2019)
- [44] Chen Z. Investigating buried polymer interfaces using sum frequency generation vibrational spectroscopy. *Prog Polym Sci* **35**(11): 1376–1402 (2010)
- [45] Lu X L, Li B L, Zhu P Z, Xue G, Li D W. Illustrating consistency of different experimental approaches to probe the buried polymer/metal interface using sum frequency generation vibrational spectroscopy. *Soft Matter* **10**(29): 5390–5397 (2014)
- [46] Xiao M Y, Jasensky J, Zhang X X, Li Y X, Pichan C, Lu X L, Chen Z. Influence of the side chain and substrate on polythiophene thin film surface, bulk, and buried interfacial structures. *Phys Chem Chem Phys* **18**(32): 22089–22099 (2016)
- [47] Fang Y, Li B L, Yu J C, Zhou J, Xu X, Shao W, Lu X L. Probing surface and interfacial molecular structures of a rubbery adhesion promoter using sum frequency generation vibrational spectroscopy. *Surf Sci* **615**: 26–32 (2013)
- [48] Lu X L, Xue G, Wang X P, Han J L, Han X F, Hankett J, Li D W, Chen Z. Directly probing molecular ordering at the buried polymer/metal interface 2: Using P-polarized input beams. *Macromolecules* **45**(15): 6087–6094 (2012)
- [49] Lu X L, Shephard N, Han J L, Xue G, Chen Z. Probing molecular structures of polymer/metal interfaces by sum frequency generation vibrational spectroscopy. *Macromolecules* **41**(22): 8770–8777 (2008)
- [50] Lu X L, Xue G, Wang X P, Han J L, Han X F, Hankett J, Li D W, Chen Z. Directly probing molecular ordering at the buried polymer/metal interface 2: Using P-polarized input beams. *Macromolecules* **45**(15): 6087–6094 (2012)
- [51] Sir William Bate Hardy—Collected Scientific Papers. Rideal EK, Ed. Cambridge: Cambridge University Press, 1936.
- [52] Fraenkel R, Butterworth G E, Bain C D. *In situ* vibrational spectroscopy of an organic monolayer at the sapphire–quartz interface. *J Am Chem Soc* **120**(1): 203–204 (1998)
- [53] Hsu S M, Gates R S. Effect of materials on tribochemical reactions between hydrocarbons and surfaces. *J Phys D: Appl Phys* **39**(15): 3128–3137 (2006)
- [54] Bhushan B, Israelachvili J N, Landman U. Nanotribology: friction, wear and lubrication at the atomic scale. *Nature* **374**(6523): 607–616 (1995)
- [55] Duffy D C, Friedmann A, Boggis S A, Klenerman D. Surface vibrational spectroscopy of lubricants adsorbed at the iron–water interface. *Langmuir* **14**(22): 6518–6527 (1998)
- [56] Huang J Y, Song K J, Lagoutchev A, Yang P K, Chuang T J. Molecular conformation and nanomechanics of self-assembled alkylsiloxane monolayers. *Langmuir* **13**(1): 58–64 (1997)
- [57] Salmeron M. Generation of defects in model lubricant monolayers and their contribution to energy dissipation in friction. *Tribol Lett* **10**(1): 69–79 (2001)
- [58] Beattie D A, Haydock S, Bain C D. A comparative study of confined organic monolayers by Raman scattering and sum-frequency spectroscopy. *Vib Spectrosc* **24**(1): 109–123 (2000)
- [59] Beattie D A, Fraenkel R, Winget S A, Petersen A, Bain C D. Sum-frequency spectroscopy of a monolayer of zinc arachidate at the solid–solid interface. *J Phys Chem B* **110**(5): 2278–2292 (2006)
- [60] Lagutchev A S, Patterson J E, Huang W T, Dlott D D. Ultrafast dynamics of self-assembled monolayers under shock compression: Effects of molecular and substrate structure. *J Phys Chem B* **109**(11): 5033–5044 (2005)
- [61] Berg O, Klenerman D. Effects of mechanical compression on the vibrational spectrum of a self-assembled monolayer. *J Appl Phys* **90**(10): 5070–5074 (2001)
- [62] Kveskin S J, Komvopoulos K, Somorjai G A. Molecular restructuring at poly(n-butyl methacrylate) and poly(methyl methacrylate) surfaces due to compression by a sapphire prism studied by infrared–visible sum frequency generation vibrational spectroscopy. *Langmuir* **21**(8): 3647–3652 (2005)
- [63] Li Y Y, Feng R J, Lin L, Liu M H, Guo Y, Zhang Z. Ordering effects of cholesterol on sphingomyelin monolayers investigated by high-resolution broadband sum-frequency generation vibrational spectroscopy. *Chin Chem Lett* **29**(3): 357–360 (2018)
- [64] Wang L, Ishiyama T, Morita A. Theoretical investigation of C–H vibrational spectroscopy. 1. modeling of methyl and methylene groups of ethanol with different conformers. *J Phys Chem A* **121**(36): 6687–6700 (2017)
- [65] Yurdumakan B, Nanjundiah K, Dhinojwala A. Origin of higher friction for elastomers sliding on glassy polymers. *J Phys Chem C* **111**(2): 960–965 (2007)
- [66] Kurian A, Prasad S, Dhinojwala A. Unusual surface aging of poly(dimethylsiloxane) elastomers. *Macromolecules* **43**(5): 2438–2443 (2010)
- [67] Reitböck C, Glowacki E, Stifter D. Sum-frequency generation vibrational spectroscopy investigations of phosphonic acids on anodic aluminum oxide films. *Appl Spectrosc* **72**(5): 725–730 (2018)

- [68] Meltzer C, Paul J, Dietrich H, Jäger C M, Clark T, Zahn D, Braunschweig B, Peukert W. Indentation and self-Healing mechanisms of a self-assembled monolayer—A combined experimental and modeling study. *J Am Chem Soc* **136**(30): 10718–10727 (2014)
- [69] Ghalgaoui A, Shimizu R, Hosseinpour S, Álvarez-Asencio R, McKee C, Johnson C M, Rutland M W. Monolayer study by VSFS: *In situ* response to compression and shear in a contact. *Langmuir* **30**(11): 3075–3085 (2014)
- [70] Xu S H. Preparation and tribological behaviour of poly(methyl methacrylate) (PMMA) microcapsules containing friction modifiers. *J Microencapsul* **37**(4): 314–323 (2020)
- [71] Hu W J, Xu Y H, Zeng X Q, Li J S. Alkyl-Ethylene amines as effective organic friction modifiers for the boundary lubrication regime. *Langmuir* **36**(24): 6716–6727 (2020)
- [72] Oh-E M, Lvovsky A I, Wei X, Kim D, Shen Y R. Nonlinear optical studies of surface structures of rubbed polyimides and adsorbed liquid crystal monolayers. *Mol Cryst Liq Cryst Sci Technol Sect A Mol Cryst Liq Cryst* **364**(1): 427–434 (2001)
- [73] Pagliusi P, Chen C Y, Shen Y R. Molecular orientation and alignment of rubbed poly(vinyl cinnamate) surfaces. *J Chem Phys* **125**(20): 201104 (2006)
- [74] Koshima H, Iyotani Y, Peng Q L, Ye S. Study of friction-reduction properties of fatty acids and adsorption structures of their Langmuir–blodgett monolayers using sum-frequency generation spectroscopy and atomic force microscopy. *Tribol Lett* **64**(3): 34 (2016)
- [75] Koshima H, Kamano H, Hisaeda Y, Liu H J, Ye S. Analyses of the adsorption structures of friction modifiers by means of quantitative structure-property relationship method and sum frequency generation spectroscopy. *Tribol Online* **5**(3): 165–172 (2010)
- [76] Wood M H, Casford M T, Steitz R, Zarbakhsh A, Welbourn R J L, Clarke S M. Comparative adsorption of saturated and unsaturated fatty acids at the iron oxide/oil interface. *Langmuir* **32**(2): 534–540 (2016)
- [77] Fry B M, Moody G, Spikes H A, Wong J S S. Adsorption of organic friction modifier additives. *Langmuir* **36**(5): 1147–1155 (2020)
- [78] Massoud T, de Matos R P, Le Mogne T, Belin M, Cobian M, Thiébaud B, Loehlé S, Dahlem F, Minfray C. Effect of ZDDP on lubrication mechanisms of linear fatty amines under boundary lubrication conditions. *Tribol Int* **141**: 105954 (2020)
- [79] Zachariah Z, Nalam P C, Ravindra A, Raju A, Mohanlal A, Wang K Y, Castillo R V, Espinosa-Marzal R M. Correlation between the adsorption and the nanotribological performance of fatty acid-based organic friction modifiers on stainless steel. *Tribol Lett* **68**(1): 11 (2020)
- [80] Zhang Y J, Wei L P, Hu H Y, Zhao Z Y, Huang Z Q, Huang A M, Shen F, Liang J, Qin Y B. Tribological properties of nano cellulose fatty acid esters as ecofriendly and effective lubricant additives. *Cellulose* **25**(5): 3091–3103 (2018)
- [81] Watanabe S, Nakano M, Miyake K, Tsuboi R, Sasaki S. Effect of molecular orientation angle of imidazolium ring on frictional properties of imidazolium-based ionic liquid. *Langmuir* **30**(27): 8078–8084 (2014)
- [82] Casford M T L, Davies P B, Smith T D, Bracchi G L. The adsorption of synovene on ZDDP wear tracks: A sum frequency generation (SFG) vibrational spectroscopy study. *Tribol Lett* **62**(1): 11 (2016)
- [83] Casford M T L, Puhan D, Davies P B, Bracchi G L, Smith T D. Thermal behaviour of synovene and oleamide in oil adsorbed on steel. *Tribol Lett* **68**(2): 52 (2020)
- [84] Kim H J, Kim D E. Water lubrication of stainless steel using reduced graphene oxide coating. *Sci Rep* **5**: 17034 (2015)
- [85] Ye S J, Ma S L, Wei F, Li H C. Intramolecular vibrational coupling in water molecules revealed by compatible multiple nonlinear vibrational spectroscopic measurements. *Analyst* **137**(21): 4981–4987 (2012)
- [86] Dhoptkar N, Defante A P, Dhinojwala A. Ice-like water supports hydration forces and eases sliding friction. *Sci Adv* **2**(8): e1600763 (2016)
- [87] Kasuya M, Hino M, Yamada H, Mizukami M, Mori H, Kajita S, Ohmori T, Suzuki A, Kurihara K. Characterization of water confined between silica surfaces using the resonance shear measurement. *J Phys Chem C* **117**(26): 13540–13546 (2013)
- [88] Meister K, Strazdaite S, DeVries A L, Lotze S, Olijve L L C, Voets I K, Bakker H J. Observation of ice-like water layers at an aqueous protein surface. *PNAS* **111**(50): 17732–17736 (2014)
- [89] Defante A P, Nyarko A, Kaur S, Burai T N, Dhinojwala A. Interstitial water enhances sliding friction. *Langmuir* **34**(13): 4084–4094 (2018)
- [90] Noguchi H, Hiroshi M, Tominaga T, Gong J P, Osada Y, Uosaki K. Interfacial water structure at polymer gel/quartz interfaces investigated by sum frequency generation spectroscopy. *Phys Chem Chem Phys* **10**(32): 4987–4993 (2008)
- [91] Tsukahara T, Morikawa K, Mawatari K, Kitamori T. Structure and dynamics of water and nonaqueous solvents confined in extended nanospaces characterized by NMR spectroscopy. *Bunseki Kagaku* **64**(4): 261–271 (2015)
- [92] Zhang C X, Liu Y H, Wen S Z, Luo J B. Insight into the formation mechanism of durable hexadecylphosphonic acid bilayers on titanium alloy through interfacial analysis. *Colloids Surfaces A: Physicochem Eng Aspects* **447**: 51–58 (2014)

- [93] Park Y J, Song H J, Kim I, Yang H S. Surface characteristics and bioactivity of oxide film on titanium metal formed by thermal oxidation. *J Mater Sci: Mater Med* **18**(4): 565–575 (2007)
- [94] Wang S, Liu Y H, Zhang C X, Liao Z H, Liu W Q. The improvement of wettability, biotribological behavior and corrosion resistance of titanium alloy pretreated by thermal oxidation. *Tribol Int* **79**: 174–182 (2014)
- [95] Xiao H, He B H, Li J R. Surface modification of natural fibers by plasma for improving strength properties of paper sheets. *Holzforschung* **69**(8): 1001–1008 (2015)
- [96] Vargas Gonzalez LR, Walsh SM, Pappas DD. Control of the interfacial properties of ultrahigh-molecular-weight polyethylene/magnesium hybrid composites through use of atmospheric plasma treatment. *Polymer Composites* **33**(2): 207–214 (2012)
- [97] Calchera A R, Curtis A D, Patterson J E. Plasma treatment of polystyrene thin films affects more than the surface. *ACS Appl Mater Interfaces* **4**(7): 3493–3499 (2012)
- [98] Xie G, Luo J, Liu S, Guo D, Zhang C. “Freezing” of nanoconfined fluids under an electric field. *Langmuir* **26**(3): 1445–1448 (2010)
- [99] Xie G X, Luo J B, Guo D, Liu S H. Nanoconfined ionic liquids under electric fields. *Appl Phys Lett* **96**(4): 043112 (2010)
- [100] Dionne E R, Badia A. Electroactive self-assembled monolayers detect micelle formation. *ACS Appl Mater Interfaces* **9**(6): 5607–5621 (2017)
- [101] Zhang C X, Liu Y H, Liu Z F, Zhang H Y, Cheng Q, Yang C B. Regulation mechanism of salt ions for superlubricity of hydrophilic polymer cross-linked networks on Ti₆Al₄V. *Langmuir* **33**(9): 2133–2140 (2017)
- [102] Zhang C, Liu Z, Liu Y, Ren J, Cheng Q, Yang C, Cai L. Novel tribological stability of the superlubricity poly (vinylphosphonic acid) (PVPA) coatings on Ti₆Al₄V: velocity and load independence. *Applied Surface Science* **392**: 19–26 (2017)
- [103] Parsons D F, Bostrom M, Lo Nostroc P, Ninham B W. Hofmeister effects: Interplay of hydration, nonelectrostatic potentials, and ion size. *Phys Chem Chem Phys* **13**(27): 12352–12367 (2011)
- [104] Kunz K, Henle J, Ninham B W. ‘Zur Lehre von der Wirkung der Salze’ (about the science of the effect of salts): Franz Hofmeister’s historical papers. *Curr Opin Colloid Interface Sci* **9**(1–2): 19–37 (2004)
- [105] Weißenborn, Braunschweig. Specific ion effects of dodecyl sulfate surfactants with alkali ions at the air–water interface. *Molecules* **24**(16): 2911 (2019)
- [106] Kobayashi T, Kemna A, Fyta M, Braunschweig B, Smiatek J. Aqueous mixtures of room-temperature ionic liquids: entropy-driven accumulation of water molecules at interfaces. *J Phys Chem C* **123**(22): 13795–13803 (2019)
- [107] Rock W, Qiao B F, Zhou T C, Clark A E, Uysal A. Heavy anionic complex creates a unique water structure at a soft charged interface. *J Phys Chem C* **122**(51): 29228–29236 (2018)
- [108] Tuladhar A, Piontek S M, Frazer L, Borguet E. Effect of halide anions on the structure and dynamics of water next to an alumina (0001) surface. *J Phys Chem C* **122**(24): 12819–12830 (2018)
- [109] Dewalt-Kerian E L, Kim S, Azam M S, Zeng H B, Liu Q X, Gibbs J M. pH-dependent inversion of hofmeister trends in the water structure of the electrical double layer. *J Phys Chem Lett* **8**(13): 2855–2861 (2017)
- [110] Marcus Y. Thermodynamics of solvation of ions .5. gibbs free-energy of hydration at 298.15-K. *J Chem Soc, Faraday Trans* **87**(18): 2995–2999 (1991)
- [111] Ma S L, Tian K Z, Ye S J. The dehydration dynamics of a model cell membrane induced by cholesterol analogue 6-ketocholestanol investigated using sum frequency generation vibrational spectroscopy. *Sci China Chem* **58**(7): 1176–1186 (2015)
- [112] Piontek S M, Tuladhar A, Marshall T, Borguet E. Monovalent and divalent cations at the α -Al₂O₃(0001)/water interface: How cation identity affects interfacial ordering and vibrational dynamics. *J Phys Chem C* **123**(30): 18315–18324 (2019)
- [113] Hu D, Yang Z, Chou K C. Interactions of polyelectrolytes with water and ions at air/water interfaces studied by phase-sensitive sum frequency generation vibrational spectroscopy. *J Phys Chem C* **117**(30): 15698–15703 (2013)
- [114] Schulze-Zachau F, Bachmann S, Braunschweig B. Effects of Ca²⁺ ion condensation on the molecular structure of polystyrene sulfonate at air–water interfaces. *Langmuir* **34**(39): 11714–11722 (2018)
- [115] Feng R, Lin L, Li Y, Liu M, Guo Y, Zhang Z. Effect of Ca²⁺ to sphingomyelin investigated by sum frequency generation vibrational spectroscopy. *Biophys J* **112**(10): 2173–2183 (2017)
- [116] Pittler J, Bu W, Vaknin D, Travesset A, McGillivray D J, Lösche M. Charge inversion at minute electrolyte concentrations. *Phys Rev Lett* **97**(4): 046102 (2006)
- [117] Tang C Y, Huang Z S, Allen H C. Binding of Mg²⁺ and Ca²⁺ to palmitic acid and deprotonation of the COOH headgroup studied by vibrational sum frequency generation spectroscopy. *J Phys Chem B* **114**(51): 17068–17076 (2010)
- [118] Huang Z S, Hua W, Verreault D, Allen H C. Salty glycerol versus salty water surface organization: Bromide and iodide surface propensities. *J Phys Chem A* **117**(29): 6346–6353 (2013)

- [119] Tang C Y, Allen H C. Ionic binding of Na^+ versus K^+ to the carboxylic acid headgroup of palmitic acid monolayers studied by vibrational sum frequency generation spectroscopy. *J Phys Chem A* **113**(26): 7383–7393 (2009)
- [120] Sung W, Krem S, Kim D. Binding of trivalent ions on fatty acid langmuir monolayer: Fe^{3+} versus La^{3+} . *J Chem Phys* **149**(16): 163304 (2018)
- [121] Hu D, Yang Z, Chou K C. Interactions of polyelectrolytes with water and ions at air/water interfaces studied by phase-sensitive sum frequency generation vibrational spectroscopy. *J Phys Chem C* **117**(30): 15698–15703 (2013)
- [122] Sung W, Avazbaeva Z, Kim D. Salt promotes protonation of amine groups at air/water interface. *J Phys Chem Lett* **8**(15): 3601–3606 (2017)
- [123] Götze L, Parry K M, Hua W, Verreault D, Allen H C, Tobias D J. Solvent-shared ion pairs at the air–solution interface of magnesium chloride and sulfate solutions revealed by sum frequency spectroscopy and molecular dynamics simulations. *J Phys Chem A* **121**(34): 6450–6459 (2017)

Zhifeng LIU. He received his Ph.D. degree in mechanical engineering from Northeastern University, Shenyang, China. He is the team leader of the Institute of Advanced

Manufacturing and Intelligent Technology, Beijing University of Technology. His research interests include heavy-duty machine tool, superlubricity, robot, and assembly technology.

Mengmeng LIU. She received her B.S. degree from Applied Technology College of Soochow University, China. She is currently

a graduate student at the Beijing University of Technology, China. Her research interests include superlubricity and the control of smart surface and interface.

Caixia ZHANG. She received her Ph.D. degree in mechanical engineering in 2015 from Tsinghua University, Beijing, China. After then, she joined Beijing Key Laboratory

of Advanced Manufacturing Technology, Beijing University of Technology. Her research interests include biotribology, superlubricity, and surface and interface analysis.

Hongyan CHU. She received her Ph.D. degree in mechanical design and theory in 2003 from Beijing University of Technology. Now she works in the Institute of Advanced

Manufacturing and Intelligent Technology, Beijing University of Technology. Her research interests include intelligent manufacturing technology, surface and friction characteristics, and contact dynamics of viscoelastic material.

Liran MA. She received her Ph.D. degree in 2010 in the Department of Precision Instrument and Mechatronics from Tsinghua University, China. Following a postdoctoral period at the Weizmann Institute of Science in Israel, she is now working as an associate professor in the State Key Laboratory

of Tribology, Tsinghua University. Her interests in tribology have ranged from aqueous lubrication and hydration lubrication to the liquid/solid interface properties. She was elected as the Young Chang Jiang Scholar in 2015. Her current research interests are tribology and surface & interface science. She has published over 60 papers indexed by SCI.

Qiang CHENG. He is a professor at the Institute of Advanced Manufacturing and Intelligent Technology, Beijing University of Technology. He received his Ph.D.

degree in mechanical engineering in 2009 from Huazhong University of Science and Technology, Wuhan, China. His research interests include wear modelling and validation, interface engineering, precision retaining ability design, etc.

Hongyun CAI. He received his B.S. degree from Anhui Agricultural University, China, in 2018. He is currently a graduate student at the

Institute of Advanced Manufacturing and Intelligent Technology, Beijing University of Technology, China. His research interests include nanotribology and molecular dynamics simulation.

Junmin CHEN. He received his B.S. degree from the Luoyang Institute of Science and Technology, China, in 2019. He is currently a graduate student at the Institute of Advanced

Manufacturing and Intelligent Technology, Beijing University of Technology, China. His research interests include biotribology, superlubricity, surface and interface analysis, and triboelectric nanogenerator.