Probing polymer surfaces and interfaces using sum frequency generation vibrational spectroscopy – a powerful nonlinear optical technique

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Sum frequency generation (SFG) vibrational spectroscopy has been proved to be a powerful technique which substantially impacts on many research areas in surface and interfacial sciences. This paper reviews the recent progress of applying this nonlinear optical technique in the studies of polymer surfaces and interfaces. The theoretical background of SFG is introduced first. Current applications of SFG in polymer science are then described in more detail to demonstrate the significance of this technique. Finally, a short summary is presented on this relatively new but widely applicable spectroscopic technique.

Keywords sum frequency generation vibrational spectroscopy, SFG, nonlinear optical technique, surface and interface, polymer

1 Introduction

Polymer is one of the most widely used materials, with a variety of applications in coatings, biomedical implants, microelectronic devices, and composites etc. In these applications, the polymer surface and/or interfacial properties are extremely important. These properties are determined by the molecular structures of the surface or interface. Therefore in order to optimize the surface/interfacial properties in these applications, it is necessary to fully understand the polymer surface/interfacial structure-property relationships, after characterizing the polymer surface and interfacial molecular structures. Many surface-sensitive techniques have been developed in the past several decades, including the attenuated total reflection infrared spectroscopy (ATR-IR) [1,2], surface enhanced Raman scattering (SERS) [3,4], X-ray photoelectron spectroscopy (XPS) [5–7], secondary ion mass spectroscopy (SIMS) [6,7], and near edge X-ray absorption fine structure (NEXAFS) spectroscopy [8,9], etc. Even though excellent research results have been reported by using these techniques in the studies, each technique has some weaknesses in surface/interface characterizations. Some of the above techniques lack the desired surface sensitivity (e.g., ATR-IR), while others need a high-vacuum environment to operate, which prevents the in situ characterization (e.g., XPS, SIMS, and NEXAFS). SERS requires special metal surfaces or particles to enhance the signal, which cannot be applied to investigate many different surfaces or interfaces.

In the last twenty years, a second-order nonlinear optical spectroscopy, sum frequency generation (SFG) vibrational spectroscopy has been developed into a powerful technique to probe the molecular structures of various surfaces and interfaces in situ. The first SFG paper was published in 1987, examining the adsorption of methanol and pentadeca-noic acid monolayers on the glass and water [10]. After that, tremendous progress has been made in the development of SFG theoretical description, instrumentation, data analysis, and applications [11–26]. Nowadays SFG becomes a widely used technique by a large number of research groups to study polymer surfaces and interfaces, catalysis, biochemical processes, self-assembled monolayers, and small molecular liquids, ionic liquids, water structures on surfaces and at interfaces. SFG is a nonlinear optical technique and a molecular vibrational spectroscopy. Therefore scientists carrying out SFG research are required to have some background knowledge in nonlinear optics and molecular spectroscopy. Fortunately, there have already been excellent books/review articles introducing such background knowledge. This paper is a general introduction of SFG vibrational spectroscopy using concise language (hopefully without losing its essence), emphasizing on practical applications of the technique in polymer studies. The recent advances of SFG studies on the molecular structures of polymer surfaces and interfaces are presented. For more detailed understanding, readers are strongly recommended to look into many SFG review articles [13–26].

2 Theoretical background

As a second-order nonlinear optical technique, an SFG process involves two incoming photons and one output
photon. As shown in Fig. 1, in an SFG experiment, a visible beam with a fixed frequency and an infrared beam with a tunable frequency temporally and spatially overlapped at a surface or an interface. Besides the two naturally reflected beams with respect to the input visible and infrared beams, a third reflected beam (SFG signal) with its frequency being the sum of the visible and infrared frequencies may also be generated, especially when the input infrared frequency is tuned over a vibrational resonance of the surface/interfacial molecules. SFG signal is contributed by molecules on surfaces/at interfaces, due to the selection rule of the SFG process, which will be discussed further below. An SFG spectrum is obtained by plotting the intensity of the SFG signal beam versus the input infrared frequency, which is a vibrational spectrum like an infrared absorption spectrum.

Figure 1  A schematic SFG sample geometry

2.1 Theory

Interaction of photon(s) with a molecule can induce a dipole moment with different orders, depending on the number of photon(s) interacting with the molecule [27]. The induced dipole moment can be written as an expanded power series, as shown in Eq. (1) [27]. The first term in each order in this polynomial defines the polarizability of each order, describing the relationship between the corresponding induced dipole moment and the interacting photon(s). Sequentially, the first order, second order, and third order polarizability..., are defined. In this equation, SFG corresponds to the second item and is a second-order nonlinear optical process.

$$\bar{\mu}_{in} = a_{ij} \bar{E} + \beta_{ijk} \bar{E}_1 \bar{E}_2 + \gamma_{ijkl} \bar{E}_1 \bar{E}_2 \bar{E}_3 + \ldots.$$  (1)

When SFG is used to detect the molecular vibration, it is easy to use a schematic energy level diagram to describe this process, as shown in Fig. 2. When a resonance is reached in an SFG process, a photon in the infrared frequency range ($\omega_1$) matching the vibrational transition energy brings the vibration from the ground state to the first excited state. Another photon in the visible frequency range ($\omega_2$) then continues to pump the molecule to a virtual electronic state. The molecule coming back from the virtual electronic state to the ground state generates a third photon in the visible range, with the energy conservation ($\omega = \omega_1 + \omega_2$). It can be recognized immediately from Fig. 2 that an SFG process can be regarded as a combination of an infrared absorption process and an anti-Stokes Raman scattering process. Therefore, it is easy to understand that the SFG hyperpolarizability (a second-order polarizability) can be written as the product of the infrared transition dipole moment and Raman polarizability with respect to the normal coordinate of the vibration, as shown in Eq. (2) [28], where $\omega_0$ is the surrounding medium dielectric constant; $\omega_q$ is the angular frequency of the $q$th vibrational mode.

$$\beta_{ijk} = \frac{1}{2\epsilon_0\omega_q} \frac{\partial a_{ij}}{\partial Q_q} \frac{\partial \mu_k}{\partial Q_q}.$$  (2)

Figure 2  A schematic energy level diagram for an SFG process

In the macroscopic scale or from the experimental viewpoint, it should be noted that, SFG can only detect a collection of hyperpolarizabilities of a large number of molecules on surfaces or at interfaces, which is called the second-order nonlinear optical susceptibility ($\chi^{(2)}_{ijk}$), as shown in Eq. (3) [11,27], where $N_s$ is the number density of molecules in the detected surface/interfacial area and the bracket indicates an average over all orientations of the molecules. The collection of the induced dipole moments is called “polarization”, as shown in Eq. (4) [11,27].

$$\chi^{(2)}_{ijk} = N_s \langle\beta_{ijk}\rangle,$$  (3)

$$\vec{P}_{in} = \chi^{(2)}_{ijk} \bar{E}_1 \bar{E}_2.$$  (4)

It is vitally important that, $\chi^{(2)}_{ijk}$ is a polar tensor, which means that it changes sign under an inversion operation. In a centro-symmetric medium, nothing should change under an inversion operation. This indicates that $\chi^{(2)}_{ijk}$ for a medium with