Vibrational spectra and molecular dynamics of hydrogen peroxide molecules at quartz/water interfaces

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ABSTRACT

The influence of H_2O_2 on the water vibration at quartz interface was examined using sum-frequency generation (SFG) spectroscopy, and the effect of H_2O_2 concentration has been systematically studied. Further, the number density and radical distribution of water molecules, H_2O_2 molecules, and quartz surface silanol groups were calculated using molecular dynamics (MD) simulation to provide molecular level interpretation for the SFG spectra. It is concluded from this study that the hydrogen peroxide molecules prefers to donate H-bonds to the in-plane silanol groups rather than accepting H-bonds from out-of-plane silanol groups, as evidenced by the strengthening of the peak located at 3400 cm^{-1} assigned to "liquid-like" hydrogen-bonding network. The SFG results have been supported by the MD calculation results, which demonstrate that the relative intensity of the peak located at 3400 cm^{-1} to that of located at 3200 cm^{-1} increases monotonously with the increase in the number of hydrogen peroxide in the first hydration shell of silanol.

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1. Introduction

Hydrogen peroxide, H_2O_2, is one of the environmentally friendly ('green') oxidants whose degradation products are oxygen and water, and has been widely used in many industrial fields, such as water treatment [1], ozone decomposition [2], heterogeneous catalytic reactions [3,4], and skin disinfection [5].

However, H_2O_2 is not stable due to its tendency to disproportionate exothermally into molecular oxygen and water under the influence of catalytic impurities (e.g., metal ions), elevated temperatures, pH levels, solar radiation, and airborne particles. In this regard, continuous efforts have been made to design new compounds for safe storage and handling of H_2O_2. Some of the more successful compounds include solid peroxohydrates, which are used mainly as bleaching agents in washing powders [6], and urea–hydrogen peroxide (1:1) adduct, which is used in hair bleaching, skin disinfection, teeth whitening, and as an efficient oxidant in organic synthesis [7,8].

Recently, a new method, sol–gel technique, featuring the incorporation of H_2O_2 into a silica xerogel matrix was successfully developed for the safe handling and storage of H_2O_2 [9,10]. A large number of researches have been reported in terms of the stability of hydrogen peroxide in silica gel, focusing on the release and reaction activity of hydrogen peroxide [10–12]. However, limited studies have been reported with respect to the interaction between hydrogen peroxide and silica gel from the molecular level, which is of great importance for in-depth understanding of the properties of hydrogen peroxide incorporated in silica xerogel. Spectroscopic techniques including IR spectrum and Raman, as well as molecular simulations have been utilized to examine the structure of hydrogen peroxide on the surface of silica gel [9]. It is generally agreed that the fundamental structure of silica consists of three dimensional tetrahedral SiO_4 units arranged in a variety of siloxane structures, both linear and cyclic, with hydrophilic hydroxyls on the surface [13]. Any hydrogen-bonding sensitive molecule close to the silica surface would be anchored to its surface by hydrogen bonds, and the hydroxyl functions, Si–OH, are believed to be responsible for the adsorption properties of silica [14,15]. Owing to its favorable geometry, hydrogen peroxide may form a relatively strong hydrogen bond with the oxygen atom in the siloxane bridge, Si–O–Si. Further, the presence of H_2O molecules, strongly linked to H_2O_2, facilitate the generation of cluster geometry by forming a less strained ring, thus reinforcing the hydrogen bonding network, as

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well as the binding of hydrogen peroxide to silica surface [9]. Nevertheless, previous studies generally focus on the interpretation of interfacial structure based on indirect spectra examination due to the limitation of the experimental methods, and direct observation of H_2O_2-silica interaction still remains a challenge, which could be resolved by performing surface sensitive spectroscopic examination. In this regard, sum-frequency generation (SFG) spectroscopy would provide valuable information for further understanding of the influence of H_2O_2 on silica interfacial phenomena.

SFG spectroscopy is based on a second-order nonlinear optical process that is forbidden in media with inversion symmetry, thus, it is highly interface-sensitive [16]. It has been recognized as an ideal tool for the investigation of liquid/solid interfacial phenomena [17]. Examination of hydrophilic quartz surface has provided rich information with respect to surface water structures and water—quartz interactions. It has been well established that the SFG peak located at 3200 cm^{-1} corresponds to the well-ordered, tetrahedrally coordinated, symmetric O—H stretching mode, defined as the ice-like band because of the internal O—H and intermolecular H-bond O—H$\cdots$O network are close to those encountered in ice. And the assignment of the 3400 cm^{-1} band is generally attributed to more randomly oriented (asymmetric) O—H stretching vibrations (liquid-like hydrogen-bonding network) [18].

Interpretation of SFG spectra of complex system is quite challenging due to the difficulty to resolve the contribution from different molecular vibrations observed in the spectra. Molecular simulation in this regard could serve as a complimentary method for the determination of interfacial water geometries and contributions of modeled molecules to SFG spectra. The silica—water interface had been examined using density functional theory based molecular dynamics simulations [19]. It has been pointed that the silanol groups on the water/quartz interface can be separated into two families, naming out-of-plane and in-plane. The out-of-plane silanols donate a strong and a short H-bond to a nearby water molecule, which is responsible for intensification of the 3200 cm^{-1} vibrational band observed in SFG experiments. The in-plane silanols, however, accept one H-bond from a nearby water molecule. These water molecules are not strongly bound to the surface, and they are responsible for the liquid-like O—H band in the SFG spectrum, localizing in around the 3400 cm^{-1} [19].

Interactions between hydrogen peroxide and water molecules have been extensively studied using computational methods, focusing on the structural of H_2O_2-$(H_2O)_n$ complexes [20,21]. However, fundamental researches on the silica-H_2O_2 interactions are limited. In view of the forgoing, the purpose of this study is to systematically study the influence of H_2O_2 on the water vibration at quartz interface using SFG spectroscopy and molecular dynamics (MD) simulation, providing fundamental information for better understanding of the $H_2O_2/SiO_2/H_2O$ surface interactions.

2. Methods

2.1. SFG spectroscopy

A picosecond Nd:YAG laser (PL2251, Ekspla) was used to pump an optical parametric generation/optical parametric amplification/difference frequency generation (OPG/OPA/DFG) system to generate tunable infrared radiation in the 2.3—10 μm range. The second harmonic output of the YAG (yttrium-aluminum-garnet) laser (532 nm) was the source of the visible beam. The two beams are about 4.0 and 6.0 mJ, respectively, and they were introduced to co-focus on the quartz sample surface to generate SFG signal (Fig. 1). The produced SFG beam was reflected from the quartz surface and filtered through irises and a monochromator,
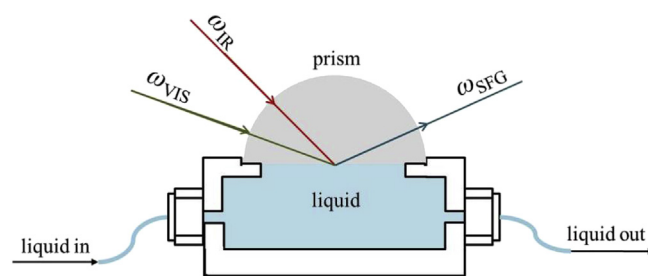

Fig. 1. Experimental setup for SFG studies of the structure of hydrogen peroxide solution at a quartz prism surface.

eventually being detected by a photomultiplier tube. The SFG signals were normalized to the intensities of the visible and the infrared beam.

The prism was fixed on top of the cell using screws as illustrated in Fig. 1, and the amount of liquid in the cell was about 2 mL. All measurements were carried out at constant temperature (22 ± 1 °C). The incident angle of the visible light was about 70°, which is close to the critical angle of total reflection (θ_c) of quartz/water (72°) so that a strong surface field can be generated. The incident angle of the infrared light was set at 50°, which is far from θ_c in order to avoid a large change in the Fresnel factor when the IR frequency is scanned in the absorption range of the OH stretching vibration of water [22].

The output/input polarization combination for the spectra is s output, s visible input, and p infrared input, respectively. This polarization combination (ssp) is sensitive only to the vibrational mode normal to the surface of the isotropic media. The following equations express the SFG intensity (I_{SFG})

$$I_{SFG} \propto \left| \chi_{NR}^{(2)} + A_0 \exp(i\varphi)/(\omega - \omega_0 + i\Gamma_0) \right|^2$$

where ω is the infrared frequency, $\chi_{NR}^{(2)}$ is the non-resonant contribution to the surface non-linear susceptibility, and ω_0, A_0, φ, and Γ_0 are the resonant frequency, transition amplitude, phase difference between the resonant and non-resonant terms and homogeneous width, respectively [16,23—25].

Before each experiment, the hemicylindrical fused quartz prism was cleaned in "piranha" solution (3:1 v/v concentrated H_2SO_4/30% H_2O_2; Caution: extremely oxidative and should be handled carefully) for 30 min and then rinsed thoroughly with deionized water. It was then dried at 110 °C for 5 min and irradiated in a UV/ozone cleaner for 30 min. At the beginning of each experiment, the SFG spectrum of pure water/quartz interface was measured to confirm that the quartz surface was contamination free. Following that, the SFG spectra of the interface in contact with the H_2O_2 solutions (concentrations of 0.5 M, 1.0 M, 1.5 M, and 2.0 M) were measured sequentially from the lowest concentration to the highest concentration. For each solution with a particular concentration, the cell and quartz prism were rinsed thoroughly with the solution before spectroscopic measurements to guarantee that the bulk solution in the cell had the desired electrolyte concentration.

All SFG spectra were normalized to the SFG signal reflected from a quartz crystal in order to reduce the effects of laser fluctuation, change of beam overlap, and IR absorption (~10%) of the fused quartz window. A nonlinear least-squares routine was used to fit the SFG spectra [22]. The quality of the fit was evaluated by r^2 values (>0.98), and the best fits are shown as solid lines in the SFG spectra presented in the following sections.