

Ethylenediamine at Air/Liquid and Air/Silica Interfaces: Protonation Versus Hydrogen Bonding Investigated by Sum Frequency Generation Spectroscopy

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The adsorption process on mineral oxide surfaces is one of the most important factors influencing the migration and distribution of contaminants in the environment. Although there have been numerous studies carried out at the macroscopic scale, there is a lack of molecular-scale interfacial information. The molecular-scale information is often crucial for the determination of sorption mechanisms. In this study, sum frequency generation spectroscopy (SFG), a surface specific vibrational spectroscopy, has been employed to investigate the adsorption of ethylenediamine ($\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2$, EDA) onto the amorphous SiO_2 surface and EDA protonated products at air/liquid interfaces. The SFG spectra of EDA adsorbed on the silica surface and the singly protonated EDA solution are similar in both CH and NH stretching regions. These spectral similarities indicate that EDA molecules are strongly chemisorbed to the silica surface through the protonation of one EDA amine group by surface silanol OH groups, thereby forming a $(\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_3)^+(\text{O}-\text{Si}\equiv\text{O})^-$ surface complex. The SFG results also indicate that the surface acidity of the silanol OH groups ($\text{p}K_a$ ($\text{HOSi}\equiv\text{O}$)) is between the two $\text{p}K_a$ values of EDA (in the range of 7.56–10.71) at the air/silica interface.

Introduction

The adsorption of organic compounds onto mineral oxide surfaces plays a critical role in several environmental processes including aqueous geochemistry and heterogeneous atmospheric chemistry (1). Adsorption is an important process that determines the environmental fate of many pollutants. It influences the transport of contaminants in aqueous environments. For example, naturally occurring mineral oxides can sequester heavy metal contaminants in groundwater, an important natural attenuation type process (1). In addition, adsorption influences transformation and degradation processes, such as the heterogeneous reactions of trace atmospheric gases on mineral aerosols in the troposphere and the interactions between ionic species and oxides in aqueous systems (1, 2). The aim of this study is to provide molecular level information of organic adsorption onto mineral oxide surfaces to elucidate adsorption mechanisms. This type of information has the potential to play a key role in predicting contaminant fate.

Ethylenediamine ($\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2$, EDA) and similar molecules 1,3-diaminopropane and 1,4-diaminobutane are of considerable industrial importance and have been employed in a wide variety of applications such as chelating agents for metal ions and corrosion inhibitors in metal/liquid systems (3, 4). EDA is the representative model in the studies for the diamine classification of pollutants. However, EDA itself is of environmental interest although it has been shown not to be carcinogenic or genotoxic (5, 6). Approximately 100 000–500 000 tons of EDA are produced in the world annually (4). Among the different equilibrium conformations of EDA, the more stable NCCN conformers in the vapor-phase were found to be either *cis* or *gauche* but not *anti* by an IR study (7). Moreover, numerous theoretical studies on EDA suggest that EDA is a molecule in which intramolecular hydrogen bonds form (7, 8). The lowest energy conformers of EDA have a *gauche* NCCN arrangement, stabilized by intramolecular hydrogen bonding (7, 8). In addition, the dimer structures of EDA can be described in terms of a general hybridization model of the hydrogen bonding (9).

Many theoretical and experimental studies have been completed on the adsorption of chemical compounds with amine groups onto silica surfaces (10–16). Infrared spectroscopy has been widely used to study the adsorption of amine compounds onto silica surfaces (11, 15, 16). ^{13}C NMR spectroscopy was also used to observe the interactions between the adsorbed amines and the surface acid sites of silica based on the chemical shift differences between the free and the adsorbed molecules (13). Adsorption kinetics of polyamidoamine dendrimers onto silica surfaces was investigated with total internal reflection fluorescence correlation spectroscopy (14). X-ray photoelectron spectroscopy (XPS) was employed to understand the interactions between the adsorbed amine compounds and the silica surfaces as well as the amounts and structures of the adsorbed amines (11, 12).

Two possible mechanisms of amine compound adsorption onto the silica surface have been suggested as shown from infrared diffuse reflectance spectral studies and XPS studies (10, 11): (1) Amine groups form hydrogen bonds with the surface silanol groups; (2) Amines are chemisorbed onto the silica surface through protonation reactions. In this study, vibrational sum frequency generation (SFG), a surface specific spectroscopy that provides direct molecular level information, is used to evaluate the possible mechanisms of ethylenediamine adsorption onto the silica surface.

The second-order optical technique of SFG has been shown to be a powerful and versatile spectroscopic tool for surface and interface studies (17–22). SFG has a number of advantages. SFG is highly surface selective and applicable to all interfaces accessible by the incident and exigent frequencies, typically visible and infrared light (17, 23, 24). Additionally, SFG is sensitive to submonolayer coverage (17, 25). The submonolayer sensitivity together with the high surface specificity allows spectroscopic study of the interface even if the associated bulk absorbs in the same spectral region, and SFG can, therefore, be used to monitor surface reaction kinetics (17, 23, 26). Another advantage of SFG is that most pressure ranges are accessible (24, 27) and, as a result, SFG can be used under ambient conditions. Moreover, surface orientation of the adsorbed molecules can be obtained by the analysis of SFG spectra (28). The SFG intensity is proportional to the square of surface number density and the surface orientation. The details of SFG theory can be found in the literature (29–32).

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Experimental Section

Chemicals. Ethylenediamine (redistilled, 99.5+%), ethylenediamine dichloride (98%), and hydrochloric acid (37.5%) were purchased from Aldrich and used as received. Solutions were prepared using Nanopure water with a resistivity of 18.3 M Ω cm. All solutions were only in contact with glass and polytetrafluoroethylene throughout sample preparation.

Sum Frequency Generation Experiments. The laser system used to obtain the sum frequency generation spectra has been previously described (33). Briefly, the system uses a pulsed 10 Hz Nd:YAG laser that pumps a KTP–KTA-based LaserVision OPG/OPA (optical parametric generator/amplifier). Doubling the 1064 nm pulses (29 ps) produces a 532 nm visible beam with energy of ≤ 1.1 mJ/pulse at the sample surface. The mid-infrared beam generated is tunable from 2500 to 4000 cm^{-1} with a bandwidth of 4–8 cm^{-1} and energy of 250–650 μJ /pulse at the sample surface, depending on the spectral region. The visible and infrared beams are overlapped at the interface spatially and temporally. The resulting sum frequency light is collected using a cooled CCD camera (DV412, Andor Technology). The polarization is ssp or sps for the sum frequency, visible and infrared light beams, respectively. The s polarized light has its electric field vector perpendicular to the plane of incidence, while the p polarized light has its electric field vector parallel to the plane of incidence. Only the ssp spectra are shown in this paper (the sps spectra are shown in the Supporting Information).

The infrared-grade fused amorphous silica plates were purchased from Quartz Plus Inc. Crystals were heated in a muffle oven at 900 $^{\circ}\text{C}$ for more than 12 h before experiments to remove organics from the surface. After the silica plates were cooled to room temperature (297 ± 2 K), they were placed under ambient conditions for half an hour before SFG experiments were performed to ensure equilibrium with water vapor in the air (relative humidity $50 \pm 3\%$). Relative humidity was measured by a traceable hygrometer (Fisher Scientific) with an accuracy of $\pm 0.2\%$. The scanning SFG spectra were obtained before and after organic adsorption. The adsorption experiment was performed by placing the silica plate into a sealed bottle with saturated EDA vapor (vapor pressure 11.4 mmHg (34)) for 30 min, and was then purged with carbon free dry air (<1 ppm CO_2 and water vapor) from FT-IR purge gas generator (Parker Balston, model 75–62NA) for the specified amount of time. The scanning SFG spectra were obtained in ambient conditions (relative humidity $50 \pm 3\%$) over several hours.

The SFG spectra presented in this paper are the average of at least two replicate spectra. To ensure the stability of the SFG system and to confirm the reproducibility of the spectra, water spectra were obtained at the beginning and the end of each experiment. The spectra shown here are normalized to the infrared beam intensities and the frequencies (wavenumbers) are calibrated by using the 3700 cm^{-1} peak that is the free OH stretch of surface water for ease of comparison and interpretation. An arbitrary unit, which equals the SFG intensity (CCD counts) divided by the infrared intensity, is used in the SFG spectra.

Surface Tension. The surface tension values of ethylenediamine aqueous solutions were obtained by using a DeltaPi Tensiometer (Kibron Inc.). Neat water (Nanopure, with a resistivity of 18.3 M Ω cm) was used for calibration. All measurements were completed at a constant temperature (297 ± 2 K). Estimation of the surface mole fractions according to the surface tension values (35–37) is described in the Supporting Information.

Results and Discussion

Ethylenediamine at the Air/Liquid Interface. SFG spectra from air/liquid interfaces of EDA solutions were acquired to

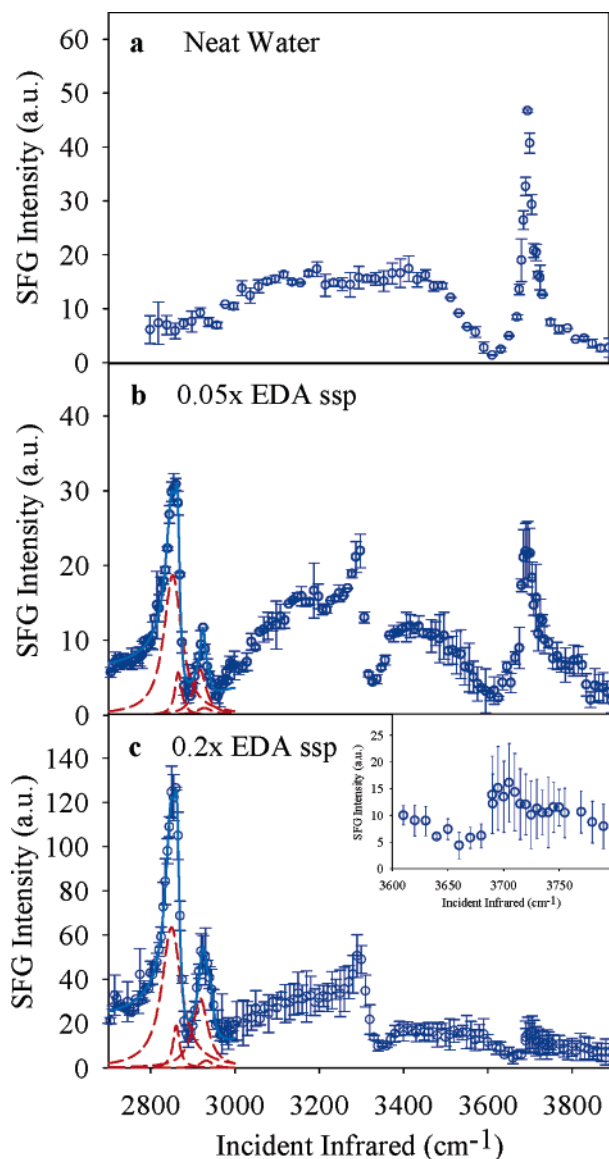


FIGURE 1. SFG spectra of (a) neat water; (b) 0.05 m.f. ethylenediamine at the air/liquid interface; (c) 0.2 m.f. ethylenediamine at the air/liquid interface; inset of (c) the free OH peak expanded. Dark blue circles indicate experimental data with error bars; blue solid lines indicate overall fits; red dashed lines indicate Lorentzian component peaks.

establish reference systems of vibrational frequencies to compare against the SFG spectra from the air/silica interfacial adsorption studies. The ssp-polarized SFG spectra of EDA aqueous solutions at air/liquid interfaces are shown in Figure 1b–c. The spectrum of neat water is shown in Figure 1a for comparison. Of importance to this study are the neat water assignments of the 3700 cm^{-1} peak to the free OH of surface water, and the 3000 cm^{-1} to 3600 cm^{-1} region to the hydrogen-bonded stretching region of surface water (assignment details of this region are found in the recent literature (38)). Although vibrational frequencies of infrared, Raman, and SFG spectra do not exactly correspond with one another, these frequencies are generally within a few wavenumbers (24, 27, 39). Thus, the peak assignments of SFG spectra in the present study are based upon Raman and infrared spectra from the literature (3, 40, 41). In the CH stretching region (2700–3000 cm^{-1}), the peak around 2860 cm^{-1} is assigned to the CH_2 symmetric stretching (CH_2 -SS) modes, and the peak around 2920 cm^{-1} is attributed to the CH_2 antisymmetric stretching (CH_2 -AS) modes (40, 41). To obtain accurate CH peak positions, the

TABLE 1. Curve-fitting and Orientation Calculation (42–44) Results of SFG Spectra (details in the Supporting Information)

	CH ₂ -SS (cm ⁻¹)		CH ₂ -AS (cm ⁻¹)		A(SS)	A(AS)	A(SS)/A(AS)	χ _{SS} /χ _{AS}	cos (θ)	θ (degrees)
	peak 1	peak 2	peak 3	peak 4						
0.05 m.f. EDA	2852.6	2866.0	2917.7	2928.3	1501.6	368.4	4.076	2.019	0.7278	43 ± 5
0.2 m.f. EDA	2849.8	2861.2	2918.0	2932.4	5429.6	2057.3	2.639	1.625	0.6445	50 ± 3
0.07 m.f. singly protonated EDA	2849.6	2872.0	2900.9	2917.6	1134.9	1248.6	0.9089	0.9534	0.06211	86 ± 4
0.05 m.f. EDD (doubly protonated EDA)	2858.8	2882.6	2914.8	2934.0	601.8	638.6	0.9424	0.9708	0.1473	82 ± 2
silica with EDA (5 min purging)	2852.0	2881.0	2918.9	2932.8	505.7	171.2	2.954	1.719	0.6689	48 ± 6
silica with EDA (24 h purging)	2848.7	2872.1	2906.8	2932.0	1290.0	1353.7	0.9529	0.9762	0.1647	81 ± 7

^a A(SS): the area of CH₂-SS peaks; A(AS): the area of CH₂-AS peaks; χ_{SS}: the second-order macroscopic susceptibility of CH₂-SS; χ_{AS}: the second-order macroscopic susceptibility of CH₂-AS.

SFG spectra of 0.05 mole fraction (m.f.) and 0.2 m.f. EDA aqueous solutions were fitted using Lorentzian profiles in the CH stretching region (see the Supporting Information). The component peaks are shown as dashed lines in Figure 1. The frequencies (ω) of the component peaks are listed in Table 1.

The SFG spectra can provide information about the orientation of surface molecules. Based on the SFG intensity ratios of the CH₂ symmetric and antisymmetric stretching modes, the average orientation angles of methylene groups were calculated (42–44), as listed in Table 1 (calculations are shown in the Supporting Information). According to the orientation calculations, the average tilt angle of CH₂ groups for the 0.05 m.f. EDA solution surface is 43° ± 5° from the surface normal, while this tilt angle for 0.2 m.f. EDA is 50° ± 3°. Thus, the CH₂ orientation angle of the 0.2 m.f. EDA solution surface and that of the 0.05 m.f. solution surface are similar.

The NH stretching frequencies overlap with the hydrogen-bonded OH stretching frequencies of water, as shown in Figure 1. According to previous assignments for infrared and Raman spectra (3, 40, 41), there are two NH stretching peaks at ~3300 cm⁻¹ and ~3360 cm⁻¹ that overlap with the broad hydrogen-bonded OH stretching bands of water. The ~3300 cm⁻¹ and ~3360 cm⁻¹ peaks are assigned to the NH₂ symmetric stretching (NH₂-SS) and NH₂ antisymmetric stretching (NH₂-AS) modes, respectively. The dip observed in the SFG spectra is due to the destructive interferences between NH₂-SS and NH₂-AS modes and/or between the NH stretching modes of EDA and the hydrogen-bonded OH stretching modes of water. Since the NH stretching and the hydrogen-bonded OH stretching modes have contributions to the intensities in the 3000–3600 cm⁻¹ region and the peaks are relatively broad compared to the peaks of the CH stretch, it is difficult to deconvolute the contributions of each vibrational stretching mode. One solution to this problem, although not within the scope of this study, could be studying the SFG spectra of N-deuterated EDA aqueous solutions (ND versus NH vibrations). (ND stretching peaks lie in the 2300–2550 cm⁻¹ region, and these peaks are not affected by vibrational modes of water (3).)

In the SFG spectra shown in Figure 1a–c, a peak at 3700 cm⁻¹ is assigned to the free OH stretch of water molecules (45). The SFG intensities of the free OH peak are reduced in the 0.05 m.f. and 0.2 m.f. EDA solutions from that of neat water. Since the SFG response is proportional to the square of the interfacial number density and is related to the orientation of surface molecules, the concentrations of EDA at the interface were estimated through surface concentration analysis based on the surface tension measurement results. The calculated surface mole fractions (m.f._s) are approximately 0.08 m.f._s and 0.3 m.f._s, for 0.05 m.f. and 0.2 m.f. EDA solutions, respectively (refer to the Supporting Information). Therefore, the mole fraction of the surface water molecules for the 0.08 m.f._s EDA and the 0.3 m.f._s EDA are 0.9 m.f._s H₂O and 0.7 m.f._s H₂O, respectively. The square root of the SFG

intensity ratio from the free OH peak in the 0.05 m.f. EDA and 0.2 m.f. EDA spectra (Figure 1b, c, and c inset) is 1.3. This corresponds to the mole fraction ratio of surface water (0.9/0.7 = 1.3), indicating that the orientation of the free OH does not change significantly in the interfacial region of the 0.2 m.f. EDA solution compared to that of the 0.05 m.f. solution. This is approximately consistent with the SFG spectra with the sps polarization combination (shown in the Supporting Information). Although the surface tension and the resulting surface number density calculations reveal that there are less water molecules in the surface region relative to the bulk, the surface of the EDA solutions is still water-rich.

Ethylenediamine at the Air/Silica Interface. The SFG spectra of the amorphous SiO₂ surface before and after exposure to EDA vapor are shown in Figure 2a–c. As discussed in previous work (33, 46), at ambient conditions with relative humidity (RH) at around 50%, the SFG spectrum of silica at the air/silica interface (Figure 2a) shows low-intensity hydrogen-bonded OH stretch bands in the 3000–3600 cm⁻¹ region, whereas, a sharp, high-intensity isolated silanol OH stretching peak is observed at ~3750 cm⁻¹. This suggests that at 297 K and 50% RH, water molecules only cover a limited portion of the hydrated silica surface in islandlike formations, and that the isolated silanol OH groups are present as the major surface species. After exposure to EDA vapor, the significant SFG responses from the CH and NH stretching modes in Figure 2b and c suggest the adsorption of EDA molecules to the silica surface. The suppression of the silanol OH peak reveals that the adsorption occurs through the interaction between the surface silanol OH groups and the amine groups of the EDA molecules.

SFG spectra of the silica surface after being exposed to EDA vapor and being purged with organic free air for 5 min and then for 24 h are shown in Figure 2b and c, respectively. One would expect that there should be less EDA molecules on the silica surface after longer purging times, and, as a result, the SFG response might decrease after 24 h purging compared to 5 min purging. However, the peak intensities obtained after 24 h purging have increased by a factor of about 4 in both the CH and the NH stretching regions compared to the peaks in the spectrum obtained after 5 min purging.

A possible scenario to explain the differences between Figure 2b and c is that there is a liquidlike layer on the silica surface after the initial EDA adsorption, and this layer persists when purging for 5 min. The liquidlike layer may reevaporate or transform irreversibly into other states after longer purging time due to drying of the silica surface (47). The SFG spectra with 5-minute purging and 24-hour purging may reveal two different stages of adsorption respectively: a physisorbed (metastable precursor) stage where the interactions are largely due to van de Waals forces, and a chemisorbed stage where the interactions between the sorbant and the sorbate are much stronger (47). The differences of the spectral features (peak intensity, position, ratio etc.) between the short and the long purging times suggest that the liquidlike layer is

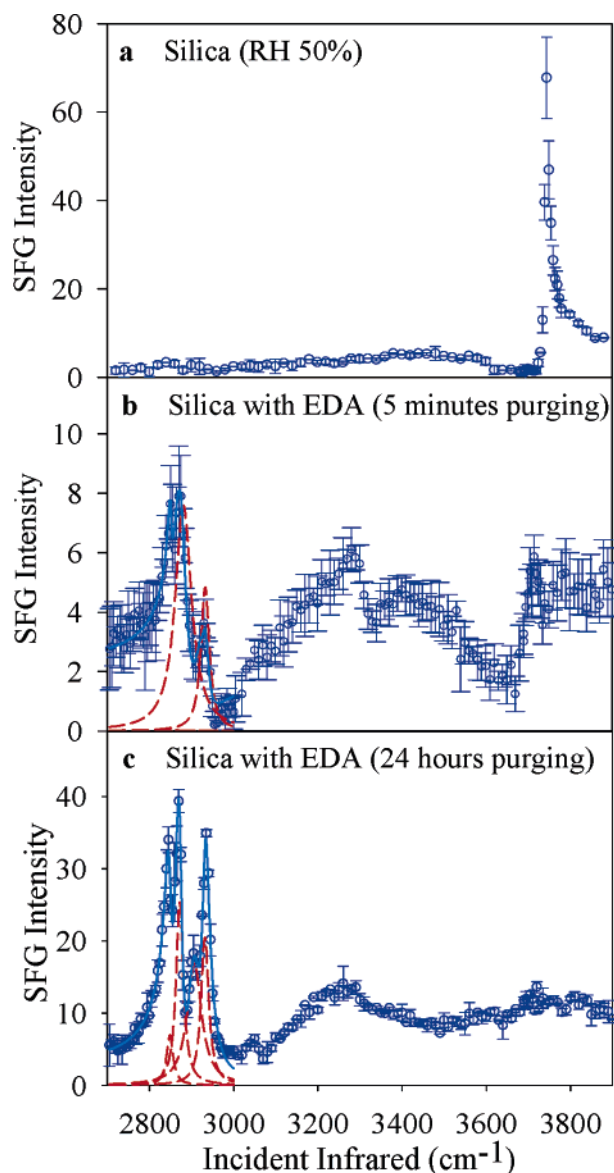


FIGURE 2. SFG spectra of amorphous SiO_2 at the air/solid interface: (a) before exposure to ethylenediamine; (b) after exposure to ethylenediamine vapor and purged with organic free air for 5 min; (c) after exposure to ethylenediamine vapor and purged for 24 h. Dark blue circles indicate experimental data with error bars; blue solid lines indicate overall fits in the CH region; red dashed lines indicate Lorentzian component peaks.

removed and only strongly adsorbed EDA remains upon drying. Another possibility is that the surface EDA molecules change their coordination upon purging. However, it is beyond the scope of this work to fully elucidate the liquidlike state, as further described below.

The persistence of the EDA molecules on the silica surface after longer purging times indicates that EDA uptake by silica is at least partially irreversible. Under the purging condition with 24 h, the adsorption–desorption process reaches equilibrium since there is no significant spectral change observed after purging for times greater than 24 h (spectra not shown here). Consequently, the SFG spectrum of silica exposure to EDA with the 24-hour purging time reveals the adsorption mechanism between EDA molecules and the SiO_2 surface. To elucidate the adsorption mechanism, the 24-hour purging spectrum was compared to spectroscopic signature frequencies of other carefully chosen systems.

Adsorption Mechanism: Hydrogen Bonding Versus Protonation. There are four possible adsorption mechanism

scenarios as shown in Figure 3. In scenario I, there is a liquidlike aqueous layer on the silica surface. In scenario II, the amine groups of EDA form hydrogen bonds with the surface silanol OH groups, with the amine group acting as a proton acceptor and the silanol group being a proton donor. In scenarios III and IV, the amine groups of EDA molecules are protonated by the surface silanol OH groups and form $(\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_3)^+(\text{O}-\text{Si}\equiv)^-$ complexes through ionic bonds. In scenario III, only one of the two amine groups of the EDA molecule is protonated ($\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_3^+$), while both of the amine groups are protonated ($^+\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_3^+$) in scenario IV. In all four scenarios, water can coexist on the surface (recall $\sim 50\%$ RH).

EDA is a medium-strong base with $\text{p}K_{a1} = 10.71$, $\text{p}K_{a2} = 7.56$ for its conjugate acids (as shown in Equations 1 and 2),



while the reported $\text{p}K_a$ values for surface silanol OH groups are generally less than 9.0 (48–52). The interaction between the silanol functional groups on the silica surface and EDA can be described as an acid–base reaction because the acid–base (Bronsted) reaction can take place when the $\text{p}K_a$ of the acid is smaller than that of the conjugate acid of the base. In other words, the adsorption mechanisms in scenarios III and IV are highly probable for EDA adsorption to the silica surface.

In this study, the SFG spectra of aqueous EDA solutions were used to establish three reference systems: doubly protonated EDA, singly protonated EDA, and isolated EDA. The doubly protonated EDA solution was prepared using ethylenediamine dichloride ($\text{C}_2\text{H}_8\text{N}_2\text{Cl}_2$, EDD) and water. The singly protonated EDA solution was prepared by controlling the pH of the EDA solution with aqueous HCl to be 9.07 (95% of EDA molecules are singly protonated EDA at this pH as determined by the acidity constants, see the Supporting Information). The isolated (nonprotonated) EDA solution was prepared as a 0.05 m.f. EDA aqueous solution. Amine groups in EDA molecules are expected to be the functional groups interacting with the silica surface sites. However, the NH stretching peaks overlap with OH stretching peaks and are generally broadened due to the hydrogen bonding with neighboring water molecules, and therefore, NH stretching peaks are not used as a spectral reference. In this study, the CH stretching peaks were used to reveal the interaction between the sorbate molecule and the sorbant surface since these peaks are well separated from other spectral features. Recall that the vibrational frequency provides information on the chemical bond and is influenced by the chemical environment (53). Previous studies (46, 53) have successfully established a spectral reference system in the CH stretching region to study the adsorption of piperidine on silica and alumina surfaces. A similar approach was applied to elucidate the viability of the adsorption mechanisms for the present study.

Figure 4 shows SFG spectra in the CH stretching region with the overall spectral fits for reference systems and EDA adsorbed silica surfaces (Figure 4a, also see the Supporting Information for the SFG spectra with the deconvoluted component peaks). The CH_2 –SS peaks were chosen as the spectroscopic reference in this study since they are better separated relative to the CH_2 –AS peaks from the OH and the NH stretching peaks, and therefore have minimal spectral interference. There are three significant differences observed for the CH_2 –SS peaks after protonation for the reference aqueous EDA solutions (Figure 4a). First, the CH_2 –SS peak splits into two prominent peaks for both singly and doubly protonated EDA aqueous solutions. This reveals that pro-

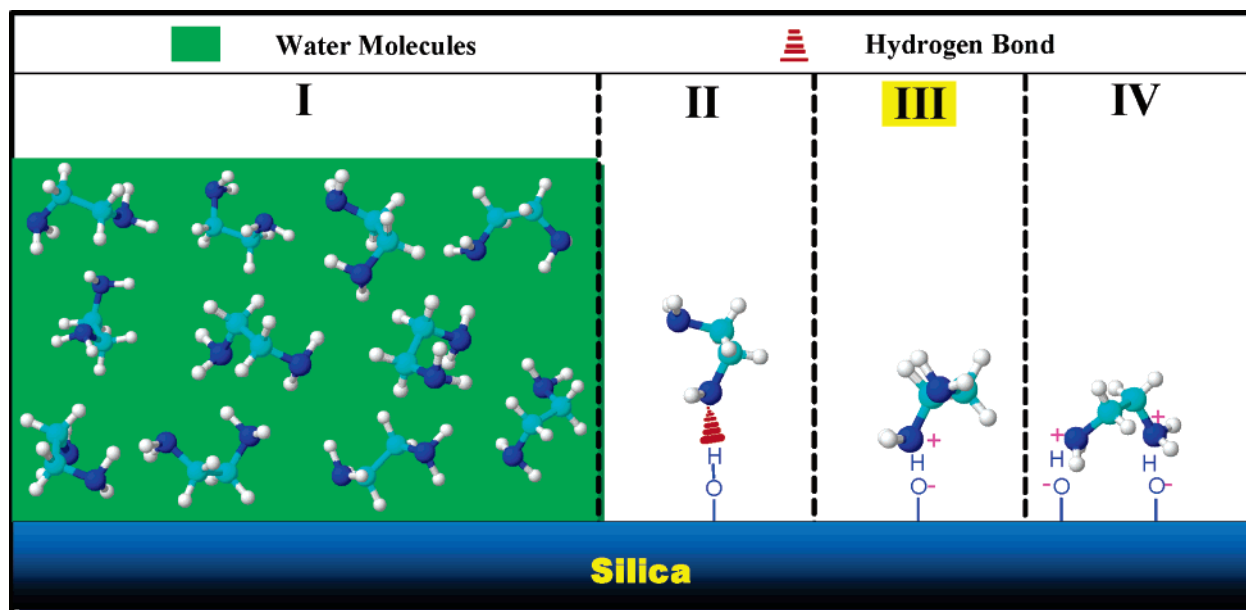


FIGURE 3. Schematic representation of adsorption scenarios: (I) liquidlike aqueous layer; (II) hydrogen bonding of EDA with a surface silanol group; (III) singly protonated EDA by a surface silanol group; (IV) doubly protonated EDA by two surface silanol groups. In all four scenarios, water can coexist on the surface.

tonation changes the distribution of the EDA conformations in the interfacial region. Second, due to the protonation, the orientation of the EDA molecules changes significantly. Assuming C_{2v} symmetry for the CH_2 groups in EDA and that the bond angle is 109.5° , orientation calculations show that the average tilt angle of the CH_2 groups in EDA molecules is $43 \pm 5^\circ$ (0.05 m.f. EDA solution) and $50 \pm 3^\circ$ (0.2 m.f. EDA solution), and this angle changes to $86 \pm 4^\circ$ (0.07 m.f. singly protonated EDA solution) and $82 \pm 2^\circ$ (0.05 m.f. doubly protonated EDA solution) after protonation, as listed in Table 1 (see the Supporting Information for details of calculations). Third, the peak position of the CH_2 -SS blue shifts from $\sim 2861 \text{ cm}^{-1}$ for the 0.2 m.f. EDA aqueous solution to $\sim 2872 \text{ cm}^{-1}$ for the singly protonated EDA aqueous solution and, eventually, to $\sim 2883 \text{ cm}^{-1}$ for the doubly protonated EDA aqueous solution (Figure 4b–c, Table 1). This result is consistent with previous studies, which revealed that protonation causes a blue shift of the CH_2 -SS peak for piperidine in aqueous solution as well as on silica and alumina surfaces (46, 53).

Compared to the reference spectra, the SFG spectrum of EDA adsorbed onto the silica surface with 5 min purging (Figure 4a) has the spectral features of several species. The peak position of the probe peak (Figure 4b) in the SFG spectrum with 5 min purging ($\sim 2881 \text{ cm}^{-1}$) is close to that from the doubly protonated EDA solution ($\sim 2882 \text{ cm}^{-1}$); however, orientation results show that the surface CH_2 has a similar average orientation angle ($\sim 48^\circ$) to that of the isolated EDA solution ($\sim 43^\circ$) (see Table 1). One explanation is that with the 5-minute purging time, EDA molecules form a liquidlike aqueous layer on the silica surface (scenario I of Figure 3), and this liquidlike layer together with the underlying liquid/silica interface has contributions to the SFG response.

After 24 h purging for the EDA adsorbed silica surface (Figure 4a), the SFG response is from the interfacial EDA-silanol complex. The SFG spectrum of EDA adsorbed to the silica surface after 24 h purging reveals the splitting feature of the CH_2 -SS peak and a similar average CH_2 orientation angle ($\sim 81^\circ$) compared to that of the reference systems of singly and doubly protonated EDA solutions. Both features strongly suggest that EDA molecules adsorbed on the silica surface are protonated by the silanol groups. In addition, the probe peak position ($\sim 2872 \text{ cm}^{-1}$) is nearly the same as that

of the singly protonated EDA aqueous solution ($\sim 2872 \text{ cm}^{-1}$) as shown in Table 1 and Figure 4b–c. Therefore, the adsorption of EDA molecules onto the silica surface occurs via protonation of an amine group by a silica surface silanol site as shown in scenario III of Figure 3 and Figure 4c.

In this study, we have also shown that EDA is an effective surface acidity probe molecule ($\text{p}K_{a1} = 10.71$ and $\text{p}K_{a2} = 7.56$), and that SFG spectroscopy results reveal that the surface acidity constant of silanol OH groups ($\text{p}K_a(\text{HOSi}\equiv)$) from an amorphous silica surface is in the range of 7.56–10.71. This is consistent with previous studies. Eienthal et al. showed that the planar fused silica surface had a $\text{p}K_a$ value of 4.5 for 19% of the silanols and a $\text{p}K_a$ value of 8.5 for 81% of the silanols based on the second harmonic results (51). By using the bond-valence methods, Bickmore et al. predicted the $\text{p}K_a$ values of the silica surface were 7.74 and 10.45 (50).

Environmental Implications. A mechanistic interpretation of diamine adsorption onto mineral oxide surfaces has been presented in this study. The molecular-scale spectroscopic results indicate that ethylenediamine molecules are strongly chemisorbed (through ionic forces) to the silica surface through the protonation of one amine group by surface silanol OH groups, thereby forming a $(\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_3)^+(\text{O}-\text{Si}\equiv)^-$ surface complex. Additionally, the surface acidity of the amorphous silica has been quantified to be in the range 7.56–10.71. Serving as a proxy for the interactions between organic pollutants and mineral oxide surfaces, this molecular-scale study of diamine molecule adsorption onto the silica surface enables us to have a more thorough understanding of diamine pollutant fate on soil and atmospheric particles. Furthermore, detailed information of the adsorption mechanism helps to guide the development of adsorption models, the prediction of pollutant migration in the natural environment, and the design of more efficient remediation methods for pollutant-contaminated natural systems.

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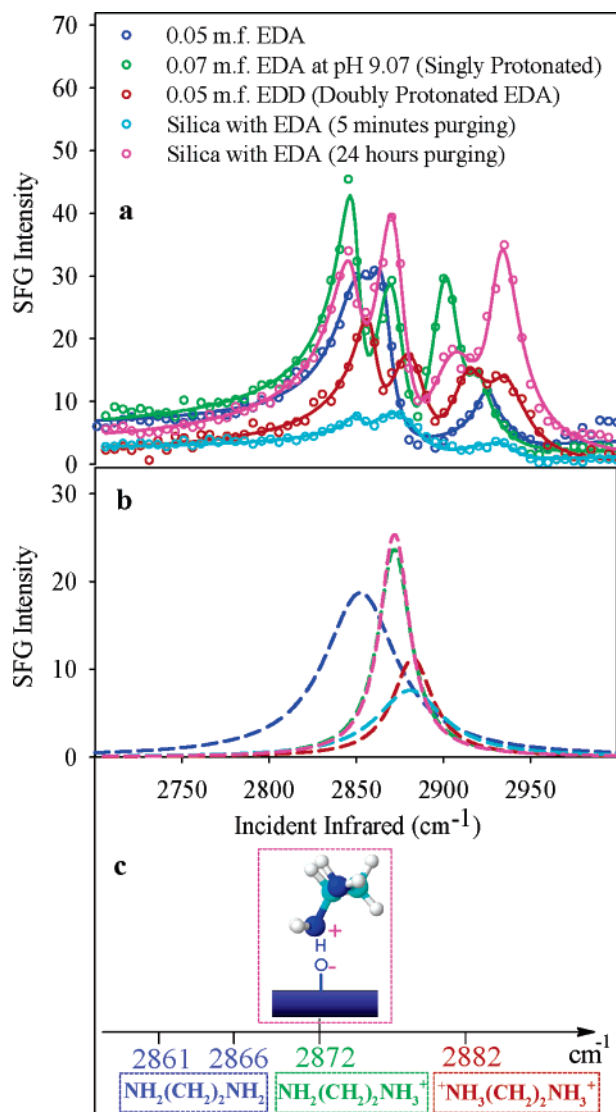


FIGURE 4. (a) SFG spectra in the CH stretching region of 0.05 m.f. ethylenediamine at the air/liquid interface, 0.07 m.f. singly protonated ethylenediamine at the air/liquid interface, 0.05 m.f. ethylenediamine dichloride at the air/liquid interface, ethylenediamine at the air/silica interface with 5 min purging, and ethylenediamine at the air/silica interface with 24 h purging. Circles indicate experimental data; blue solid lines indicate overall fits. (b) Probe peaks for the reference systems and ethylenediamine adsorbed silica surfaces. (See Supporting Information regarding equations for fitting which give rise to SFG component peak positions.) (c) Probe peak frequencies in the reference systems and the adsorption mechanism.

Supporting Information Available

Details of curve-fitting, orientation angle calculations, surface concentration calculations, and sps SFG spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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