Identification of Al_{13} on the Colloid Surface Using Surface-Enhanced Raman Spectroscopy

Ning Li,^{†,§} Chengzhi Hu,[‡] Xiaoning Fu,^{||} Xiufang Xu,^{||} Rui Liu,^{⊥,Ⓟ} Huijuan Liu,^{*,†,§} and Jiuhui Qu^{‡,§}

[†]State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, [‡]Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, and [⊥]State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, P.R. China

[§]University of Chinese Academy of Sciences, Beijing 100049, P.R. China

^{||}Department of Chemistry, Nankai University, Tianjin 300071, P.R. China

Supporting Information

ABSTRACT: Al_{13} is the most active polymeric Al species responsible for coagulation at the solid–liquid interface, whereas the detection techniques for Al_{13} at the interface are currently limited. In this study, for the first time, the identification of Al_{13} on the silicon dioxide-based colloid surface was realized by using surface-enhanced Raman scattering (SERS), which is an ideal surface method sensitive for single-molecule detection. The high purity Al_{13} salts were prepared by an electrolysis procedure followed by precipitation or metathesis. $\text{Al}_{13}\text{-Cl}_n$ was determined to be feasible for the Raman detection as it exhibited more noticeable signals in comparison to $\text{Al}_{13}\text{-(SO}_4)_p$ and $\text{Al}_{13}\text{-(NO}_3)_m$. The peak of $\text{Al}_{13}\text{-Cl}_n$ at 635 cm^{-1} could be the major characteristic peak of Al_{13} , and the other two peaks at 300 and 987 cm^{-1} could be accessorial evidence for the identification. Further, the identification of Al_{13} adsorbed on the surface of Ag and gold-core/silica-shell colloids was confirmed by the SERS response at the above three wavenumbers with a higher signal-to-noise ratio than the normal Raman scattering. According to the least-squares fitting computed Raman spectra, each of the characteristic peaks was associated with specific vibrational modes.

INTRODUCTION

Coagulation as a common water treatment technology is a reaction process of the coagulants and particulates proceeding at the solid–liquid interface. During coagulation, the aluminum (Al) hydrolyzed products can act as a highly effective coagulant for the removal of charged colloidal particulates and organics, which would aggregate into large flocs and could be removed by the following sedimentation or filtration treatment.^{1–3} The Al_{13} polycation, $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ (Al_{13}^{7+}) (i.e., Keggin- Al_{13}), is confirmed to be the most active polymeric Al species responsible for the coagulation.¹ Particularly, the production and persistence of the active Al_{13} on the colloid surface were assumed to play a dominant role in the coagulation.^{3,4} However, no direct evidence for the Al_{13} on the colloid surface was reported.^{1,3} Therefore, identification of the Al_{13} aggregates at the solid–liquid interface is desirable for understanding the coagulation of Al salts.

It has been reported that in aqueous solutions, the aluminum-27 nuclear magnetic resonance spectroscopy (^{27}Al -NMR), ferron colorimetric method, and electrospray ionization-mass spectrometry can be applied for the determination of Al species.^{5–8} As for the flocs containing Al_{13} , X-ray photoelectron spectra and solid-state ^{27}Al -NMR were used for the identification.^{2,3} In fact, it is recognized that the

hydrolyzed polymeric Al species adhered to the surface of colloids substantially affect the coagulation mechanism.¹ However, the detection technique for the Al_{13} formed on the colloid surface is currently limited. Recently, Raman scattering techniques have attracted vivid interests because they can distinguish different species and molecules based on the characteristic “fingerprint” spectra with minimal sample pretreatment.^{9–11} For instance, the monomer $\text{Al}(\text{OH})_4^-$ containing only tetrahedron coordinated Al (Al_{IV}) in the aluminate solution at high pH can be well identified by a strong band at 620 cm^{-1} corresponding to the Al–O stretching mode, and the dimeric or oligomeric aluminum species were characterized by two bands at 535 and 695 cm^{-1} .¹² In addition, flat Al_{13} , $[\text{Al}_{13}(\text{OH})_{24}(\text{H}_2\text{O})_{24}]^{15+}$, is constructed upon a repeated set of cubane-like moieties arrayed in a lattice of edge shared with an octahedra Al (Al_{VI}) core (Figure S1). The Raman study of flat Al_{13} revealed that the region from 200 to 900 cm^{-1} and 900 to 1300 cm^{-1} exhibited the $\text{Al}_{\text{VI}}\text{-O}$ vibrations and hydroxo group vibrations, respectively, which defined the

Received: November 12, 2016

Revised: February 8, 2017

Accepted: February 10, 2017

Published: February 10, 2017

Figure 1. (a) The optimized geometry of Al_{13} and (b) the structure of ϵ -Keggin-like Al_{13} shown in a polyhedral representation.

fingerprints for flat Al_{13} ,^{13,14} Al_{13}^{7+} , the most common polynuclear species in the coagulation process, has not been studied by Raman techniques so far.^{15,16}

Particularly, surface-enhanced Raman spectroscopy (SERS) as a promising surface analytical technique appeared more attractive for the ultrasensitive detection down to the single-molecule level since it can provide an increased sensitivity (enhancement factor as high as 10^8 to 10^{12}) with the nanoscale metal substrates.^{17,18} It was speculated that the electromagnetic field enhancement arising from localized surface plasmon resonance and the chemical enhancement due to charge transfer might be responsible for the increased scattered intensity.^{19–21} Through SERS analysis, the slight changes in molecular structure can be detected.²² The optimized geometry and structure of Al_{13} are shown in Figure 1. It has an ϵ -Keggin-like structure of T_d symmetry, which is characterized by a AlO_4 tetrahedron center surrounded by 12 octahedrally coordinated Al sharing edges and oxygens ($-\text{O}-$, $-\text{OH}$, and $-\text{OH}_2$). The unique vibrational structure of Al–O bonds makes Raman and SERS a promising method for the detection of Al_{13} on the colloid surface. The nanoscale metals such as Ag and Au have been widely used as substrates in the SERS analysis for a better detection of the organic and inorganic contaminants, pathogens, and nanomaterials in environmental samples.¹¹ Considering that SiO_2 is the dominant component of the clay mineral widely dispersed in natural water,²³ the Au core was coated with an ultrathin SiO_2 shell which was used to simulate the natural particle surface. Both Ag and Au-core/ SiO_2 -shell (Au/SiO_2) colloids are used as the substrates for investigating the SERS spectrum and characteristic peaks of Al_{13} .

In the present work, a SERS method for the detection of Al_{13} on the colloid surface was established. The results showed that the Raman and SERS can act as an ideal method to identify Al_{13} species in solids, solutions, and on the surface of colloids. A detailed structural-mode assignment was given based on the geometry optimization and frequency calculation of Al_{13}^{7+} using density functional theory (DFT) calculations. The spectroscopic observations of Al_{13} on the colloid surface may be helpful to further understand the hydrolysis reaction of Al salts in some specific cases and optimize the strategies for the productivity of Al_{13} during coagulation.

MATERIALS AND METHODS

Preparation of Al_{13} Salts. PACl with the total Al concentration of 0.55 mol/L was prepared by the electrolysis process as reported by Liu et al.²⁴ Then, it was purified to obtain Al_{13} salts ($\text{Al}_{13}(\text{SO}_4)_p$, $\text{Al}_{13}(\text{NO}_3)_m$, and $\text{Al}_{13}\text{Cl}_n$) by sulfate precipitation, nitrate metathesis, and the ethanol-acetone

precipitation method (see the Supporting Information for details). The solid Al_{13} was obtained by air-drying at room temperature and then placed onto the clear glass slides for the Raman detection. The Al_{13} solution with a concentration of 0.50 mol Al/L was prepared by redissolving the solid $\text{Al}_{13}\text{Cl}_n$ in ultrapure water and was transformed onto the as-prepared silicon wafers, followed by the spectral acquisition using a confocal Raman spectroscopy system. The silicon wafers were chosen as the substrate for placing the samples during the detection procedure due to the fact that it provides less spectral overlaps than other substrates such as glass and mica plate (see details in Figure S2 in the Supporting Information).

Preparation of Ag Colloids and Au/SiO_2 Particles. The aqueous solution of Ag colloids was prepared by the reduction of silver nitrate with hydroxylamine hydrochloride.²⁵ The colloids were produced by the fast addition of 10 mL of hydroxylamine hydrochloride/sodium hydroxide (1.5×10^{-2} / 3×10^{-2} mol/L) solution to 90 mL of 1.11×10^{-3} mol/L silver nitrate solution.

It was reported that the optimum size of coinage metals (Ag, Au, and Cu) for SERS enhancement ranged from 10 to 100 nm.²⁶ Au nanoparticles with a diameter of about 50 nm were synthesized as cores following Frens' method, on which the ultrathin SiO_2 shells were coated to form Au/SiO_2 nanoparticles.^{27–30} In a typical synthetic procedure for Au/SiO_2 nanoparticles, 1.25 mL of a freshly prepared 1 mmol/L (3-aminopropyl)trimethoxysilane aqueous solution was dropwise added to the 250 mL of Au sol under vigorous magnetic stirring for 15 min to ensure the complete complexation of the amino groups with the gold surface. Subsequently, 10 mL of 0.54 wt % sodium silicate solution, the pH of which was adjusted to 10–11 by the successive addition of cation exchange resin, was added to the sol under vigorous stirring. After stirring for another 15 min at the temperature of 90 °C, 100 mL of the as-prepared solution was added into 400 mL of ethanol. Growth of the additional shell was accomplished by the dropwise addition of 400 μL of ammonia and 60 μL of tetraethyl orthosilicate. The reaction system was then stirred for 15 min and allowed to remain undisturbed for at least 12 h. Finally, the product was washed and dried at the room temperature to obtain Au/SiO_2 particles.

Adhesion of Al_{13} on Ag Colloids and Au/SiO_2 Particles. The Al_{13} solutions were prepared by dissolving $\text{Al}_{13}\text{Cl}_n$ in ultrapure water. The Ag substrate was found to be unstable over time due to the aggregation of Ag colloids.³¹ Hence, 10 μL of the as-prepared Ag colloid solution was mixed with isovolumic Al_{13} solution (0.01 mol Al/L) transferred on the prepared silicon wafers and then was dried for Raman

analysis immediately. In the case of Au/SiO₂, Au/SiO₂ was used as the model colloid for the simulated adsorption of Al₁₃ onto the colloid surface in natural water. Hence, a certain amount of as-prepared particles was added to the flasks containing 40 mL Al₁₃ solution with different concentrations (10⁻², 10⁻³, 10⁻⁴, 10⁻⁵, 10⁻⁶, and 0 mol Al/L), which covers the common dosage of Al coagulant in the coagulation process (several tens to thousands of micromoles per liter). After shaking for 24 h (stirring rate, 160 rpm; temperature, 25 ± 1 °C) for a sufficient adsorption process, the mixture was filtered through an ultrafiltration membrane, and then the dried Au/SiO₂ with a thin layer was spread onto the silicon wafer for Raman detection. The adsorption efficiency of Al on the Au/SiO₂ surface was determined by the difference in Al₁₃ concentration in solution before and after adsorption.

Analytical Methods. Raman spectra were obtained by using a confocal Raman spectroscopy system (Renishaw InVia Raman microscope, Renishaw PLC) equipped with a Leica microscope with 10, 50, and 100 × objectives and 532 nm laser lines as the excitation source with a 5 mW laser power. Every signal was measured by taking 6 accumulations with an exposure time of 10 s. To increase the signal-to-noise ratio, spectra were acquired using the SERS technique. The total Al concentration is determined by the inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer Co.), and the purity of Al₁₃ product is determined by ²⁷Al-NMR (Avance III 500 MHz, Bruker) and the solid-state ²⁷Al NMR (Avance III 400 MHz, Bruker). The morphology and mean size of the synthesized core-shell particles are measured by transmission electron microscopy (TEM, FEI F20) and scanning electron microscopy (SEM, JSM 6301), respectively.

Computational Methods. The geometry optimization for Al(H₂O)₆³⁺, Al(OH)₄⁻, Al₂Cl₆, and Al₁₃ and the frequency analysis for Al₁₃ were carried out using DFT on the B3LYP level with a 6-31G(d) basis set.^{32–35} The Cartesian coordinates of the models are listed in Tables S3–S6 in the [Supporting Information](#). The frequencies were corrected by using frequency scaling factor 0.9614.³⁶ All calculations were carried out with Gaussian 09.³⁷ To identify the individual vibrational modes consisting of each of the peaks in the SERS spectra of Al₁₃, the least-squares fitting computed Raman (LSFC-Raman) spectra were created from the computed frequencies and intensities of the Al₁₃ model.^{13,38} More details on the calculation and the method for selecting Gaussian functions are listed in the [Supporting Information](#).

RESULTS AND DISCUSSION

Verification of Pure Al₁₃ by NMR. For the Raman detection of Al₁₃, the high purity Al₁₃ salts, Al₁₃-(SO₄)_p, Al₁₃-(NO₃)_m, and Al₁₃-Cl_n, were chosen as the target analytes due to the fact that they can inhibit the interference of monomeric, dimeric, oligomeric, and other Al species. First, the purity of Al₁₃ in PACl, Al₁₃-(NO₃)_m, and Al₁₃-Cl_n was characterized by the liquid ²⁷Al-NMR, and the results are shown in [Figure 2](#). The peak at the chemical shift of 0 ppm in PACl is assigned to the monomeric Al species, which disappeared in the samples of Al₁₃-(NO₃)_m and Al₁₃-Cl_n, revealing that no monomeric Al species existed after purification. The peaks at 63 and 80 ppm are attributed to the resonance of the central Al atom in the structure of Al₁₃ and the inner standard Al(OH)₄⁻, respectively. The yield of Al₁₃ in PACl is determined to be 65.7%, while the contents of Al₁₃ in both Al₁₃-(NO₃)_m and Al₁₃-Cl_n are calculated to be more than 98% of the total Al concentration

Figure 2. ²⁷Al-NMR spectra of PACl (total Al concentration: 0.55 mol/L), Al₁₃-Cl_n (total Al concentration: 0.50 mol/L), and Al₁₃-(NO₃)_m (total Al concentration: 0.50 mol/L).

after purification. The purity of Al₁₃-(SO₄)_p cannot be measured by the liquid ²⁷Al-NMR directly because it was an insoluble polymer, while Al₁₃-(SO₄)_p is believed to have the same purity with Al₁₃-(NO₃)_m due to Al₁₃-(NO₃)_m being prepared from Al₁₃-(SO₄)_p by a metathesis method with Ba(NO₃)₂. The solid-state ²⁷Al NMR spectrum of Al₁₃-(SO₄)_p is provided in [Figure S3](#). The purified Al₁₃ solution was freeze-dried into the solid, and redissolution of the solid exhibited no significant decrease in Al₁₃ purity, which was consistent with the previous research.³⁹ The results suggest that other than Al₁₃, there is no trace of other Al species during Raman detection.

Identification of the Characteristic Peaks for Al₁₃ in Solid and Aqueous Solution by Raman. Considering that the anions of Al₁₃ salts may affect the identification of the vibrational modes in Al₁₃, the Raman spectra of solid Al₁₃-(SO₄)_p, Al₁₃-(NO₃)_m, and Al₁₃-Cl_n are compared with those of solid Na₂SO₄, NaNO₃, and AlCl₃, respectively. Al₁₃-Cl_n is compared with AlCl₃ rather than NaCl due to the fact that the Cl is monatomic and there is only one kind of Raman-active mode in NaCl, the external lattice mode,⁴⁰ which is helpless for the assignment of the Raman signals of Al₁₃-Cl_n. It is observed that the spectrum of Al₁₃-Cl_n is quite different from that of AlCl₃ ([Figure 3a](#)). As for the solid Al₁₃-Cl_n salts, no investigation on the bonding mode of Al₁₃ with Cl atom was reported. However, the Br, which also belongs to the halogen family, has been reported to intersperse among interstices between the tetrahedrons and octahedrons of the polyaluminum and has fixed positions after the formation of strong hydrogen bonds between OH and Br.⁴¹ Additionally, the Al atoms in Al₁₃ have a saturated bonding structure with OXs (X stands for -Al, -H, and -H₂) as shown in [Figure 1](#), so no bonds between Al and the anionic groups can be formed. Hence, it can be rationally deduced that Cl atoms are combined with Al₁₃ by forming hydrogen bonds with OH instead of the Al-Cl bond. Thereby no signal associated with Cl exists in the spectrum of the solid Al₁₃-Cl_n. The three bands in Al₁₃-Cl_n, a sharp one at 300 cm⁻¹, a broader one at 635 cm⁻¹, and a smaller one at 987 cm⁻¹, can be accordingly assigned to the vibrational modes of Al-OXs or the hydroxo group. Although these Raman peaks are not too strong, their signal-to-noise ratios are statistically significant. By contrast, only one prominent band located at 305 cm⁻¹ appears in the spectrogram of solid AlCl₃, which can be attributed to the stretching vibration of the Al-Cl bond.^{42,43} The Raman

Figure 3. (a) Raman spectra of solid AlCl_3 and $\text{Al}_{13}\text{-Cl}_n$. (b) Raman spectra of solid NaNO_3 and $\text{Al}_{13}\text{-(NO}_3)_n$ and the fitting curve for $\text{Al}_{13}\text{-(NO}_3)_n$. (c) Raman spectra of solid Na_2SO_4 and $\text{Al}_{13}\text{-(SO}_4)_p$.

spectrum of the solid AlCl_3 which is characteristic of a centrosymmetric Al_2Cl_6 molecule is calculated and provided in Figure S4. The strong peak appears at 314 cm^{-1} in the calculated Raman spectrum, which is nearly identical to 305 cm^{-1} in the experimental spectrum and 308 cm^{-1} in the study of Edwards et al.⁴³

As for NaNO_3 , the three peaks centered at 724, 1066, and 1384 cm^{-1} correspond to the ν_4 , ν_1 , and ν_3 modes of NO_3 , respectively (Figure 3b).¹⁴ In the Raman spectrum of $\text{Al}_{13}\text{-(NO}_3)_n$, the Raman peaks of Al_{13} at 300 and 635 cm^{-1} could be observed clearly. On the basis of the peak fitting results, the weak peak at 1014 cm^{-1} and the strong sharp peak at 1053 cm^{-1} are assigned to Al_{13} (hydroxo group bending vibrations at 987 cm^{-1} in $\text{Al}_{13}\text{-Cl}_n$) and NO_3 (ν_1 NO_3 symmetric stretching mode at 1066 cm^{-1} in NaNO_3), respectively. The shifts of the two peaks may arise from the interaction of the hydroxo group in Al_{13} with the NO_3 group.

In the spectrum of Na_2SO_4 (Figure 3c), four bands at 454, 645, 991, and 1150 cm^{-1} are characteristics of the ν_2 , ν_4 , ν_1 , and ν_3 modes of SO_4 , respectively.⁴⁴ While in the spectrum of $\text{Al}_{13}\text{-(SO}_4)_p$, four bands at the similar wavenumber values of 454, 616, 988, and 1087 cm^{-1} are observed, and the band at 300 cm^{-1} is considered to be related to the vibration mode of Al_{13} . For $\text{Al}_{13}\text{-(SO}_4)_p$, the characteristic peaks of Al_{13} at 635 and 987 cm^{-1} are close to the ν_4 and ν_1 modes of SO_4 , respectively. It was reported that SO_4 had a large Raman cross section which would result in the characteristic peaks with high intensity,^{21,45} whereas the intensity of the Al_{13} spectra was relatively feeble owing to the high symmetry and small polarizabilities of the

Al_{13} nanocluster. Therefore, the peaks of Al_{13} at 635 and 987 cm^{-1} are overlapped by the modes of SO_4 due to their similar positions and the high intensity of the peaks related to SO_4 . The applicability for $\text{Al}_{13}\text{-(NO}_3)_n$ and $\text{Al}_{13}\text{-(SO}_4)_p$ is excluded in this study, because $\text{Al}_{13}\text{-Cl}_n$ exhibits more noticeable characteristic peaks at 300, 635, and 987 cm^{-1} , which could be successfully used for the identification of Al_{13} . The subsequent detection of Al_{13} was thereby based on $\text{Al}_{13}\text{-Cl}_n$.

Raman analysis of $\text{Al}_{13}\text{-Cl}_n$ aqueous solution transferred onto the silicon wafer was investigated, and the results are presented in Figure 4. No obvious changes were observed in the band

Figure 4. Raman spectrum of $\text{Al}_{13}\text{-Cl}_n$ (Al_{13}) aqueous solution (total Al concentration: 0.50 mol/L) on the silicon wafer. Inset shows the Raman spectrum of the silicon wafer.

frequencies between the solid and aqueous solution of Al_{13} . For $\text{Al}_{13}\text{-Cl}_n$ in the aqueous solution, it is believed that Cl is in the bulk solution or the electric double-layer of Al_{13} as a free anion, which would not contribute to the Raman signals. The strong band at 520 cm^{-1} and the broad band near 987 cm^{-1} are related to the silicon wafer (shown in the inset). As mentioned above, AlCl_3 has a vibrational band at 305 cm^{-1} , and the silicon wafer has one around 987 cm^{-1} , so it is unreliable to distinguish Al_{13} based on the two bands. The Raman band at 635 cm^{-1} could be the major characteristic peak for the effective identification of Al_{13} , and the signals at 300 and 987 cm^{-1} could be accessorial evidence.

Identification of Al_{13} on the Surface of Colloids by SERS. To investigate the feasibility of SERS for detecting Al_{13} on the colloid surface, two nanoparticles (Ag and Au/ SiO_2) were chosen as the substrates for evaluation due to the fact that the nanoscale metal substrates (e.g., Ag and Au) are almost essential for enhancing the Raman signals of the target molecules.^{19,27} As illustrated in Figure 5a, three obvious bands at 300, 635, and 987 cm^{-1} corresponding to Al_{13} are observed after adding Al_{13} into Ag colloids, suggesting that SERS exhibited an excellent response for Al_{13} . The peak area at 635 cm^{-1} is more than half of the strongest peak at 520 cm^{-1} , which is roughly considered as the spectral feature belonging to the silicon wafer. The signal-to-noise ratio of Al_{13} species is substantially increased in the SERS compared to that in the normal Raman. Since the Raman bands of Al_{13} in the SERS spectrum using Ag colloids and the normal Raman spectrum are similar in their positions, and no chemical bonds or charge-transfer were validated between the Ag and Al_{13} , the chemical enhancement cannot be supported. The electromagnetic

Figure 5. (a) SERS spectra of Ag colloids and Al₁₃ (0.01 mol Al/L) on Ag colloids. The inset shows the fitted peak areas of two samples. (b) SERS spectra of Au/SiO₂ and Al₁₃ adsorbed on the surface of Au/SiO₂ particles.

enhancement, which should be a nonselective amplifier for Raman scattering by all molecules adsorbed on the surface of substrates, is likely to be responsible for the enhanced Al₁₃ spectra. In addition, two new weak bands at 475 and near 520 cm⁻¹ appeared in SERS, which would be analyzed subsequently.

The identification of various amounts of Al₁₃ adsorbed on the surface of Au/SiO₂ colloids by SERS is shown in Figure 5b. The mean size of Au/SiO₂ nanoparticles is approximately 50 nm (Figure S5a), and the thickness of silica shell is about 2–4 nm (Figure S5b). The adsorption efficiencies of Al₁₃ on Au/SiO₂ (dosage of 1 g/L) are determined, and the amounts of Al₁₃ on per unit weight of Au/SiO₂ are calculated to be 0.13 × 10⁻², 0.98 × 10⁻³, 1.0 × 10⁻⁴, 1.0 × 10⁻⁵, and 1.0 × 10⁻⁶ mol/g for the initial Al₁₃ concentration of 10⁻², 10⁻³, 10⁻⁴, 10⁻⁵, and 10⁻⁶ mol Al/L, respectively (Table S1). For a better comparison, the Raman spectrum of Au/SiO₂ treated by the ultrapure water placed on the silicon wafer is also provided as a blank control. The bare Au/SiO₂ (0 mol Al/g) yielded no signals in SERS except the peaks related to the silicon wafer. In the presence of Al₁₃ species, three obvious vibrational bands at 300, 635, and 987 cm⁻¹ can be found, demonstrating the successful identification of vibrational modes of Al₁₃ adsorbed onto the particle surface with enhanced Raman signals. These Raman

features, especially the peaks at 300 and 635 cm⁻¹, strongly increased in intensity with increasing the amounts of Al₁₃ adsorbed on the Au/SiO₂ particle surface and were still observable with the low Al₁₃ amounts of 10⁻⁶ mol Al/g. Considering that the common dosage of Al salts is higher than 10⁻⁵ mol Al/L,³ the concentration range investigated in this study can cover most cases in coagulation treatment processes. Therefore, the SERS approach has the potential to be applied in the identification of the Al₁₃ species on the colloid surface. To further examine the quantitative ability of this method, the linear calibration curves are presented in Figure S6. The result indicates a less-than-ideal linear correlation, which is probably due to the nonuniform distribution of the solid samples on the silicon wafer as observed by the microscopy, inhomogeneous hot spot densities, analyte polarizability, or the inhomogeneity and irreproducibility of the noble-metal substrate. In the case of Au/SiO₂, the Au core is used to generate a large field enhancement, and the inert silica shell prevents the core from direct contact with Al₁₃ molecules, ensuring that there are no chemical interactions between Al₁₃ and Au.⁴⁶ The adsorption of Al₁₃ on the Au/SiO₂ surface depends on the electrostatic attraction.^{47,48} Hence, the electromagnetic enhancement should be the enhancement mechanism for Au/SiO₂ colloids. On the basis of the obtained results, SERS is proved to be a reliable method to identify Al₁₃ on the surface of Ag and Au/SiO₂ colloids with a higher peak intensity.

Theoretical Analysis for Al₁₃ Identification. It is known that the vibrational modes are related to the species and structures.⁴⁹ The characteristic Raman signals of Al₁₃ can be assigned to the vibration of bonds related to the Al₁₃ molecule structure. The molecule of Al₁₃ ions is considered to be symmetrical, assuming that the Al₁₃ group is free with Cl⁻. As shown in Figure 6a, Al_{IV}-O, Al_{VI}-OAl_{IV}, Al_{VI}-OH, Al_{VI}-OH₂, and O-H (or -H₂) are believed to be the dominant chemical bonds. The LSFC-Raman spectra of Al₁₃ adsorbed on the Ag and Au/SiO₂ colloid surface were created to associate all the Raman peaks with specific vibrational modes. During the hydrolysis process of Al coagulants, different kinds of monomers such as Al(H₂O)₆³⁺ and Al(OH)₄⁻ may polymerize to dimeric or oligomeric aluminum species and further to form multimetric species like Al₁₃ and flat Al₁₃, although their reaction conditions are generally different.^{13,50} As a result, the Al_{VI}-O bond in Al(H₂O)₆³⁺ (Figure 6b) and the Al_{IV}-O bond in Al(OH)₄⁻ (Figure 6c) are the structural units of Al₁₃ or flat Al₁₃. The Raman signals of the Al-O bonds in Al(H₂O)₆³⁺, Al(OH)₄⁻, and flat Al₁₃ were used as the assistance and supplementary of LSFC results for the assignment of vibrational peaks of Al₁₃.

The experimental SERS spectra, associated LSFC-Raman spectra, and constituent vibrational modes of Al₁₃ adsorbed on Ag and Au/SiO₂ colloids are shown in Figure 6d. It is observed that the spectra of Al₁₃ on the two kinds of colloids are similar, as well as their corresponding vibrational modes. The LSFC-Raman spectra are composed of 156 unique vibrational modes (the coefficients of the component Gaussian functions are listed in Table S2 in the Supporting Information). The LSFC Raman spectra of Al₁₃ samples, incorporating the vibrations of the aforementioned various bonds, correlate well to the experimental spectra over the entire frequency range of 260–1100 cm⁻¹. The peaks from 260 to 900 cm⁻¹ in the Raman spectra of Al₁₃ are found to be mainly associated with the Al-O vibrational modes, and the positions of these bands are in agreement with recent Raman studies of the Al-O bands in the

Figure 6. (a) Schematic diagram of the bonds in Al_{13} , the optimized geometry of (b) $\text{Al}(\text{H}_2\text{O})_6^{3+}$ and (c) $\text{Al}(\text{OH})_4^-$, and (d) LSFC-Raman spectra that depict the contributions of each type of vibrational modes of Al_{13} on the surface of Ag and Au/SiO_2 colloids (concentration of Al_{13} with Ag colloids: 0.01 mol Al/L; amounts of Al_{13} absorbed onto Au/SiO_2 : 0.13×10^{-2} mol Al/g).

flat Al_{13} which contains only Al_{VI} .^{13,14} The band at 300 cm^{-1} is accordingly assigned to the $\text{Al}_{\text{IV}}\text{-O}$, $\text{Al}_{\text{VI}}\text{-OAl}_{\text{IV}}$ bending, and $\text{Al}_{\text{VI}}\text{-OH}_2$ stretching vibrations. The previous study of the $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-H}_2\text{O}$ system also supported the assignment of the region below 350 cm^{-1} to the $\text{Al}\text{-O}$ bending vibrations.¹² The low-intensity band at 475 cm^{-1} in the SERS spectra of Al_{13} , which is insensitive for the normal Raman method, is associated with the $\text{Al}_{\text{VI}}\text{-OH}$ stretching vibrations. This result is consistent with the previous report that the peak at 478 cm^{-1} was attributed to the metal-oxygen ($\text{Al}_{\text{VI}}\text{-O}$) symmetric stretch of the *flat* Al_{13} cluster.¹⁴ For the peak near 520 cm^{-1} , it is observed that $\text{Al}_{\text{IV}}\text{-O}$, $\text{Al}_{\text{VI}}\text{-OAl}_{\text{IV}}$, $\text{Al}_{\text{VI}}\text{-OH}$, and bonds in the silicon wafer all contribute spectral intensity to this region. Because they partially overlap with the intense peak at 520 cm^{-1} of the silicon wafer, there is considerable uncertainty in the precise identification of Al_{13} on the basis of this region.

The most dominant features in the region from 550 to 1100 cm^{-1} are the peaks located around 635 and 987 cm^{-1} . The peak at 635 cm^{-1} is assigned to the stretching vibrations of $\text{Al}_{\text{IV}}\text{-O}$ and $\text{Al}_{\text{VI}}\text{-OH}$ and bending vibrations of $\text{Al}_{\text{VI}}\text{-OH}_2$. The $\text{Al}_{\text{IV}}\text{-O}$ stretching vibrations have been reported to be located at 620 cm^{-1} in the Raman spectrum of $\text{Al}(\text{OH})_4^-$.^{51,52} While in this study, the peak corresponding to the $\text{Al}_{\text{IV}}\text{-O}$ vibrational mode in Al_{13} is resolved to be located around 660 cm^{-1} . It is recognized that the position of a Raman band, which relates to the corresponding bond force constant, basically depends on

electronic structure and bonding.⁵³ The 40 cm^{-1} blue shift of the $\text{Al}_{\text{IV}}\text{-O}$ band in Al_{13} reveals an overall increase in the extent of $\text{Al}_{\text{IV}}\text{-O}$ bonding. Due to the fact that the electron donor H atom was replaced by the Al-octahedrons, the electron density of $\text{Al}_{\text{IV}}\text{-O}$ in Al_{13} is more uniform than that of $\text{Al}(\text{OH})_4^-$, resulting in the decrease in the polarity of the $\text{Al}_{\text{IV}}\text{-O}$ bond, and thereby the blue shift in the frequency. Jackson and co-workers recently reported that the region from 900 to 1300 cm^{-1} exhibited resolved bridging hydroxo group vibrations that collectively define fingerprints for the *flat* Al_{13} clusters.¹⁴ Computations in this study also reveal that hydroxo group bending vibrations dominate in the region from 900 to 1000 cm^{-1} . These give rise to a broad signal around 987 cm^{-1} . The spectra of the parent monohydrate salts and other polymeric species with the similar structure have been reported in the previous studies.^{13,14,54-56} By contrast, the obtained results show that Al_{13} exhibits unique vibrational characteristics and reveal the reliability of Raman spectrum for the detection of the Al_{13} molecule.

Potential Application. The interactions between coagulants and colloids are known to play a vital role in the coagulation process. Particularly, the production and persistence of active Al_{13} species on the colloid surface have a significant impact on the treatment performance. In this study, SERS is proposed as an effective analytical method for the identification of Al_{13} species on the surface of colloids. The

findings may shed some light on understanding of the real coagulation process by clarifying the behaviors of Al_{13} at the solid–liquid interface. It may also help to optimize the realistic water purification process upon the optimization of the selection, dosing mode, and dosage of the coagulants and the regulation of reaction conditions (pH, basicity, temperature, etc.). Moreover, the established method is considered to have the application potential in the study of the geochemical cycle of Al, due to the fact that Al_{13} plays an important part in the process in the nature system. In some cases, the applications of the detection method may be limited due to the interferences by some anions, thus the inhibition of the interferences needs to be further investigated. However, the foreseeable applications can be realized in the simulated water systems for investigating the migration and transformation of Al_{13} on the colloid surface and for providing some references for the Al coagulation in a realistic water treatment process.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b05721.

Preparation of $\text{Al}_{13}(\text{SO}_4)_p$, $\text{Al}_{13}(\text{NO}_3)_m$, and $\text{Al}_{13}\text{Cl}_n$, SEM and TEM images of the Au/ SiO_2 particles, Raman spectra of silicon wafers, glass, and mica plate, solid-state ^{27}Al NMR spectrum of the pure $\text{Al}_{13}(\text{SO}_4)_p$, calculated Raman spectrum of the solid AlCl_3 , discussion on the enhancement factor, quantitative detection of Al_{13} adsorbed on the Au/ SiO_2 surface, least-squares fitting procedure and the Cartesian coordinates for $\text{Al}(\text{H}_2\text{O})_6^{3+}$, $\text{Al}(\text{OH})_4^-$, and Al_{13}^{7+} , as well as the coefficients of all the component Gaussian functions of the LSFC-Raman of Al_{13} (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*Phone: 86-010-62849128. Fax: 86-010-62923541. E-mail: hjliu@rcees.ac.cn.

ORCID

Rui Liu: 0000-0001-6353-6193

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by the National Science Fund for Distinguished Young Scholars of China (Grant No. 51225805). The authors sincerely thank Prof. Jingfu Liu and Ms. Fanglan Geng at RCEES for their generous experimental assistance.

■ REFERENCES

- (1) Lin, J. L.; Chin, C. J. M.; Huang, C. P.; Pan, J. R.; Wang, D. S. Coagulation behavior of Al_{13} aggregates. *Water Res.* **2008**, *42*, 4281–4290.
- (2) Lin, J. L.; Huang, C. P.; Chin, C. J. M.; Pan, J. R. The origin of $\text{Al}(\text{OH})_3$ -rich and Al_{13} -aggregate flocs composition in PACI coagulation. *Water Res.* **2009**, *43*, 4285–4295.
- (3) Hu, C. Z.; Liu, H. J.; Qu, J. H.; Wang, D. S.; Ru, J. Coagulation behavior of aluminum salts in eutrophic water: Significance of Al_{13} species and pH control. *Environ. Sci. Technol.* **2006**, *40*, 325–331.
- (4) Zhao, H.; Liu, H. J.; Hu, C. Z.; Qu, J. H. Effect of Aluminum speciation and structure characterization on preferential removal of disinfection byproduct precursors by aluminum hydroxide coagulation. *Environ. Sci. Technol.* **2009**, *43*, 5067–5072.
- (5) Bertsch, P. M.; Thomas, G. W.; Barnhisel, R. I. Characterization of hydroxy-aluminum solutions by aluminum-27 nuclear magnetic resonance spectroscopy. *Soil Sci. Soc. Am. J.* **1986**, *50*, 825–830.
- (6) Buffle, J.; Parthasarathy, N.; Haerdi, W. Importance of speciation methods in analytical control of water treatment processes with application to fluoride removal from waste waters. *Water Res.* **1985**, *19*, 7–23.
- (7) Parker, D. R.; Bertsch, P. M. Identification and quantification of the “ Al_{13} ” tridecameric polycation using ferron. *Environ. Sci. Technol.* **1992**, *26*, 908–914.
- (8) Zhao, H.; Hu, C. Z.; Liu, H. J.; Zhao, X.; Qu, J. H. Role of aluminum speciation in the removal of disinfection byproduct precursors by a coagulation process. *Environ. Sci. Technol.* **2008**, *42*, 5752–5758.
- (9) Kusic, D.; Kampe, B.; Rosch, P.; Popp, J. Identification of water pathogens by Raman microspectroscopy. *Water Res.* **2014**, *48*, 179–189.
- (10) Ghosal, S.; Macher, J. M.; Ahmed, K. Raman microspectroscopy-based identification of individual fungal spores as potential indicators of indoor contamination and moisture-related building damage. *Environ. Sci. Technol.* **2012**, *46*, 6088–6095.
- (11) Halvorson, R. A.; Vikesland, P. J. Surface-enhanced Raman spectroscopy (SERS) for environmental analyses. *Environ. Sci. Technol.* **2010**, *44*, 7749–7755.
- (12) Johnston, C. T.; Agnew, S. F.; Schoonover, J. R.; Kennedy, J. W.; Page, B.; Osborn, J.; Corbin, R. Raman study of aluminum speciation in simulated alkaline nuclear waste. *Environ. Sci. Technol.* **2002**, *36*, 2451–2458.
- (13) Wang, W.; Liu, W. M.; Chang, I. Y.; Wills, L. A.; Zakharov, L. N.; Boettcher, S. W.; Cheong, P. H. Y.; Fang, C.; Keszler, D. A. Electrolytic synthesis of aqueous aluminum nanoclusters and in situ characterization by femtosecond Raman spectroscopy and computations. *Proc. Natl. Acad. Sci. U. S. A.* **2013**, *110*, 18397–18401.
- (14) Jackson, M. N.; Wills, L. A.; Chang, I. Y.; Carnes, M. E.; Scatena, L. F.; Cheong, P. H. Y.; Johnson, D. W. Identifying nanoscale M_{13} clusters in the solid state and aqueous solution: vibrational spectroscopy and theoretical studies. *Inorg. Chem.* **2013**, *52*, 6187–6192.
- (15) Akitt, J. W.; Farthing, A. Aluminium-27 nuclear magnetic resonance studies of the hydrolysis of aluminum (III). Part 4. Hydrolysis using sodium carbonate. *J. Chem. Soc., Dalton Trans.* **1981**, 1617–1623.
- (16) Hu, C. Z.; Liu, H. J.; Qu, J. H. Preparation and characterization of polyaluminum chloride containing high content of Al_{13} and active chlorine. *Colloids Surf., A* **2005**, *260*, 109–117.
- (17) Le Ru, E. C.; Etchegoin, P. G. Quantifying SERS enhancements. *MRS Bull.* **2013**, *38*, 631–640.
- (18) Stiles, P. L.; Dieringer, J. A.; Shah, N. C.; Van Duyne, R. R. Surface-Enhanced Raman Spectroscopy. *Annu. Rev. Anal. Chem.* **2008**, *1*, 601–626.
- (19) Haynes, C. L.; McFarland, A. D.; Van Duyne, R. P. Surface-enhanced Raman spectroscopy. *Anal. Chem.* **2005**, *77*, 338A–346A.
- (20) Kneipp, K.; Kneipp, H.; Itzkan, I.; Dasari, R. R.; Feld, M. S. Ultrasensitive chemical analysis by Raman spectroscopy. *Chem. Rev.* **1999**, *99*, 2957–2975.
- (21) Campion, A.; Kambhampati, P. Surface-enhanced Raman scattering. *Chem. Soc. Rev.* **1998**, *27*, 241–250.
- (22) Guo, H. Y.; Zhang, Z. Y.; Xing, B. S.; Mukherjee, A.; Musante, C.; White, J. C.; He, L. L. Analysis of silver nanoparticles in antimicrobial products using surface-enhanced Raman spectroscopy (SERS). *Environ. Sci. Technol.* **2015**, *49*, 4317–4324.
- (23) Liew, Y. M.; Heah, C. Y.; Mond, M. A. B.; Kamarudin, H. Structure and properties of clay-based geopolymer cements: A review. *Prog. Mater. Sci.* **2016**, *83*, 595–629.
- (24) Liu, H. J.; Qu, J. H.; Hu, C. Z.; Zhang, S. J. Characteristics of nanosized polyaluminum chloride coagulant prepared by electrolysis process. *Colloids Surf., A* **2003**, *216*, 139–147.

- (25) Leopold, N.; Lendl, B. A new method for fast preparation of highly surface-enhanced Raman scattering (SERS) active silver colloids at room temperature by reduction of silver nitrate with hydroxylamine hydrochloride. *J. Phys. Chem. B* **2003**, *107*, 5723–5727.
- (26) Moskovits, M. Surface-enhanced Raman spectroscopy: a brief retrospective. *J. Raman Spectrosc.* **2005**, *36*, 485–496.
- (27) Lu, Y.; Yin, Y.; Li, Z. Y.; Xia, Y. Synthesis and self-assembly of Au@ SiO₂ core-shell colloids. *Nano Lett.* **2002**, *2*, 785–788.
- (28) Li, J. F.; Huang, Y. F.; Ding, Y.; Yang, Z. L.; Li, S. B.; Zhou, X. S.; Fan, F. R.; Zhang, W.; Zhou, Z. Y.; Wu, D. Y.; Ren, B.; Wang, Z. L.; Tian, Z. Q. Shell-isolated nanoparticle-enhanced Raman spectroscopy. *Nature* **2010**, *464*, 392–395.
- (29) Stöber, W.; Fink, A.; Bohn, E. Controlled growth of monodisperse silica spheres in the micron size range. *J. Colloid Interface Sci.* **1968**, *26*, 62–69.
- (30) Frens, G. Controlled nucleation for the regulation of the particle size in monodisperse gold suspensions. *Nature, Phys. Sci.* **1973**, *241*, 20–22.
- (31) Ingram, J. C.; Pemberton, J. E. Investigation of the quenching of surface enhanced Raman scattering from pyridine on copper and silver electrodes by underpotential deposition of lead. *Langmuir* **1992**, *8*, 2040–2048.
- (32) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- (33) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785–789.
- (34) Becke, A. D. A new mixing of Hartree-Fock and local density-functional theories. *J. Chem. Phys.* **1993**, *98*, 1372–1377.
- (35) Qian, Z.; Feng, H.; Yang, W.; Bi, S. Theoretical investigation of water exchange on the nanometer-sized polyoxocation AlO₄Al₁₂(OH)₂₄(H₂O)₁₂⁷⁺ (Keggin-Al₁₃) in aqueous solution. *J. Am. Chem. Soc.* **2008**, *130*, 14402–14403.
- (36) Scott, A. P.; Radom, L. Harmonic vibrational frequencies: an evaluation of Hartree-Fock, Møller-Plesset, quadratic configuration interaction, density functional theory, and semiempirical scale factors. *J. Phys. Chem.* **1996**, *100*, 16502–16513.
- (37) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; et al. *Gaussian 09*, Revision D.01; Gaussian, Inc.: Wallingford, CT, 2013.
- (38) Wang, W.; Chang, I. Y.; Zakharov, L.; Cheong, P. H. Y.; Keszler, D. A. [Sc₂(μ-OH)₂(H₂O)₆(NO₃)₂](NO₃)₂: aqueous synthesis and characterization. *Inorg. Chem.* **2013**, *52*, 1807–1811.
- (39) Shi, B. Y.; Li, G. H.; Wang, D. S.; Tang, H. X. Separation of Al₁₃ from polyaluminum chloride by sulfate precipitation and nitrate metathesis. *Sep. Purif. Technol.* **2007**, *54*, 88–95.
- (40) Pasternak, A.; Cohen, E.; Gilat, G. Calculation of second-order Raman scattering for KBr, NaCl, and MgO crystals. *Phys. Rev. B* **1974**, *9*, 4584–4592.
- (41) Sun, Z.; Wang, H.; Feng, H.; Zhang, Y.; Du, S. Crystal structure of [Al₄(OH)₆(H₂O)₁₂][Al(H₂O)₆]Br₁₂: A new polyaluminum compound. *Inorg. Chem.* **2011**, *50*, 9238–9242.
- (42) Alves, C. C.; Campos, T. B. C.; Alves, W. A. FT-Raman spectroscopic analysis of the most probable structures in aluminum chloride and tetrahydrofuran solutions. *Spectrochim. Acta, Part A* **2012**, *97*, 1085–1088.
- (43) Edwards, H. G. M.; Farwell, D. W.; Johnson, A. F. FT-Raman spectroscopic study of aluminum(III) chloride in acetonitrile and dichloromethane solutions containing water. *J. Mol. Struct.* **1995**, *344*, 37–44.
- (44) Dong, J. L.; Li, X. H.; Zhao, L. J.; Xiao, H. S.; Wang, F.; Guo, X.; Zhang, Y. H. Raman observation of the interactions between NH₄⁺, SO₄²⁻, and H₂O in supersaturated (NH₄)₂SO₄ droplets. *J. Phys. Chem. B* **2007**, *111*, 12170–12176.
- (45) Dudik, J. M.; Johnson, C. R.; Asher, S. A. Wavelength dependence of the preresonance Raman cross-section of CH₃CN, SO₄²⁻, ClO₄⁻ and NO₃⁻. *J. Chem. Phys.* **1985**, *82*, 1732–1740.
- (46) Li, J. F.; Tian, X. D.; Li, S. B.; Anema, J. R.; Yang, Z. L.; Ding, Y.; Wu, Y. F.; Zeng, Y. M.; Chen, Q. Z.; Ren, B.; Wang, Z. L.; Tian, Z. Q. Surface analysis using shell-isolated nanoparticle-enhanced Raman spectroscopy. *Nat. Protoc.* **2013**, *8*, 52–65.
- (47) Lin, J.; Huang, C.; Chin, C. M.; Pan, J. R. Coagulation dynamics of fractal flocs induced by enmeshment and electrostatic patch mechanisms. *Water Res.* **2008**, *42*, 4457–4466.
- (48) Ma, X.; Zeng, G.; Zhang, C.; Wang, Z.; Yu, J.; Li, J.; Huang, G.; Liu, H. Characteristics of BPA removal from water by PACl-Al₁₃ in coagulation process. *J. Colloid Interface Sci.* **2009**, *337*, 408–413.
- (49) Jin, X. Y.; Yan, Y.; Shi, W. J.; Bi, S. P. Density functional theory studies on the structures and water-exchange reactions of aqueous Al(III)-oxalate complexes. *Environ. Sci. Technol.* **2011**, *45*, 10082–10090.
- (50) Tang, H. X.; Xiao, F.; Wang, D. S. Speciation, stability, and coagulation mechanisms of hydroxyl aluminum cluster formed by PACl and alum: A critical review. *Adv. Colloid Interface Sci.* **2015**, *226*, 78–85.
- (51) Moolenaar, R. J.; Evans, J. C.; McKeever, L. Structure of the aluminate ion in solutions at high pH. *J. Phys. Chem.* **1970**, *74*, 3629–3636.
- (52) Watling, H. R.; Fleming, S. D.; van Bronswijk, W.; Rohl, A. L. Ionic structure in caustic aluminate solutions and the precipitation of gibbsite. *J. Chem. Soc., Dalton Trans.* **1998**, 3911–3917.
- (53) Schlucker, S.; Singh, R. K.; Asthana, B. P.; Popp, J.; Kiefer, W. Hydrogen-bonded pyridine-water complexes studied by density functional theory and Raman spectroscopy. *J. Phys. Chem. A* **2001**, *105*, 9983–9989.
- (54) Watling, H. Spectroscopy of concentrated sodium aluminate solutions. *Appl. Spectrosc.* **1998**, *52*, 250–258.
- (55) Rudolph, W. W.; Mason, R.; Pye, C. C. Aluminium(III) hydration in aqueous solution. A Raman spectroscopic investigation and an ab initio molecular orbital study of aluminium(III) water clusters. *Phys. Chem. Chem. Phys.* **2000**, *2*, 5030–5040.
- (56) Lu, B.; Jin, X.; Tang, J.; Bi, S. DFT studies of Al-O Raman vibrational frequencies for aquated of aluminium species. *J. Mol. Struct.* **2010**, *982*, 9–15.