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Infrared Spectra of Alkylphosphonic Acid Bound to Aluminium Surfaces

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Summary: The infrared absorption (IR) spectrum of alkyl phosphonic acid adsorbed on the α-Al_2O_3 (0001) surface has been calculated by means of a density-functional based tight-binding method. Thereby mono-dentate, bi-dentate and tri-dentate bonding of the acid to the surface have been considered. In addition, experimentally obtained Fourier Transform Infrared Spectra (FTIR) of octadecylphosphonic acid (ODPA) on the natural surface of aluminium have been included. The absence of the P=O band in the experimental surface spectrum and in the calculated spectrum of the tridentate adsorption complexes showed that adsorption of (alkyl)phosphonic acids on aluminium favours tridentate bonding, where the acid is bound to the surface via three symmetric P–O–Al bonds.

Keywords: adsorption; alkyl phosphonic acid; aluminium; infrared spectroscopy; tridentate bonding

Introduction

Aluminium has found a wide use in industrial and technical applications. The air-formed oxide film on pure aluminium is a natural protection against corrosion. However due to the presence of intermetallic inclusions the aluminium surface has to be further protected by coatings to enhance its properties and durability in wet or humid conditions. As an alternative to the traditional inorganic pre-treatment with chromium compounds[1] the formation of highly hydrophobic, stable, self-assembled monolayers (SAMs) of alkyl phosphonic acids on the aluminium surface is applied.[2] Thereby, the adsorption of the alkyl phosphonic acids on the aluminium surface is proposed to proceed via an acid-base condensation reaction mechanism in three steps resulting in tridentate complexes,[3] where the phosphonic acid head group is bound to the air-formed oxide film via three symmetric P–O–Al bonds. Evidences for this have been shown experimentally by Inelastic Tunneling Spectroscopy[4–6] and by FTIR Spectroscopy.[2,7] In this work we confirm this proposition by means of density-functional based calculations of the vibrational spectra of phosphonic acid ($HPO(OH)_2$) adsorbed on an aluminium surface model. Since the actual aluminium surface is mostly amorphous,[8–10] we decided to base our model on the hydroxyl terminated (0001) surface of corundum (α-Al_2O_3). In addition, experimentally obtained FTIR spectra of ODPA ($C_{18}H_{37}PO(OH)_2$) on the natural surface of aluminium have been included for comparison.

Experimental Section

Materials

Octadecylphosphonic acid (ODPA) was synthesized according to Michaelis-Arbusov method.[2] All solvents used were of analytical quality grade and procured from commercial sources.

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Substrates were p-doped silicon wafers evaporated with 300 nm aluminium. Before use the substrates were cleaned ultrasonically for 10 min in chloroform, acetone, and ethanol, respectively.

Sample Preparation

Immersion from solution was carried out under ambient laboratory conditions. Pretreated substrate samples were coated with ODPA by immersing the substrate in a 1 mmol ethanolic solution for 1 h. The samples were carefully rinsed with ethanol and dried in a stream of argon.

IR Spectroscopy

For detecting the Infra-Red spectra Unicam RS 1000 FT-IR spectrometer was used. For measuring the bulk spectra of ODPA and its Al-salt the samples were prepared by dispersing the substances into KBr-pellets.

Absorption-Reflection-IR spectra of the adsorbed samples were measured using a MTC-detector and FT-80 unit from Spectra Tech Inc. All spectra consist of 500–1000 scans at a resolution of 4 cm^{-1} and were normalised to the pre-treated substrate samples.

Computational Details

All calculations have been performed using a self-consistent charge density-functional based tight-binding method (SCC-DFTB).[11,12] Before calculating the vibrational frequencies all structures and molecules have been optimised with the conjugate gradient algorithm until the root

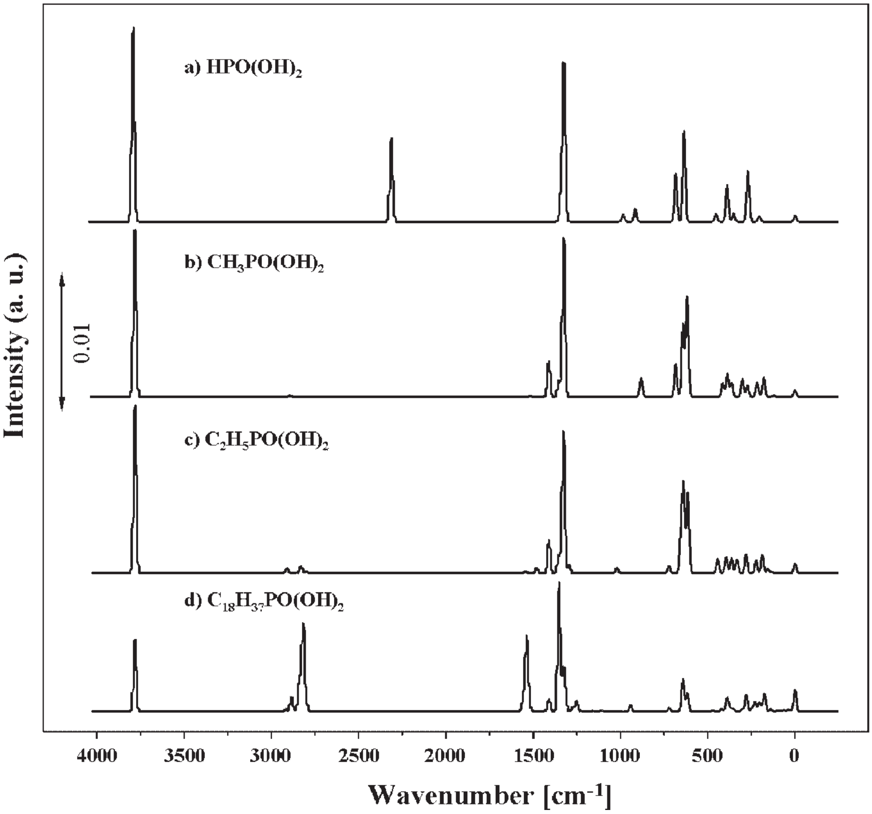

Figure 1.

Calculated IR spectra of a) phosphonic acid, $HPO(OH)_2$, b) methylphosphonic acid $CH_3PO(OH)_2$, c) ethylphosphonic acid, $C_2H_3PO(OH)_2$ and d) octadecylphosphonic acid, $C_{18}H_{37}PO(OH)_2$ (ODPA).

mean square force was less than 10^{-4} a.u. For the surface structures periodic boundary conditions and the Γ-point approximation have been included. The periodic surface slab has been derived from the optimised bulk structure of α-Al_2O_3. The size of the simulation cell was $2 \times 2 \times 1$ (hexagonal) bulk unit cells in direction of the lattice parameters a, b (= a) and c, respectively. A minimum vacuum distance of 50 Å was added to the cell to avoid self-interaction. The optimised (0001) surface of α-Al_2O_3 has been then used to construct the adsorption complexes. Thereby, we considered mono-dentate, bi-dentate and tri-dentate binding modes of the phosphonic acid. For each coordination the surface was covered with the maximum number of molecules and the preferred adsorption sites on the surface have been used.[13] The phosphonic acids were added on both sites of the slabs in order to minimize artificial dipoles.

Results and Discussion

Initially, we have calculated the vibrational frequencies of the free $HPO(OH)_2$ molecule (Figure 1a). The bands attributed to the OH, PH and P=O stretches at 3795, 2314, and 1324 cm^{-1} were of strong intensity and could be clearly identified. Their frequencies agree very well with other theoretical[14] and experimental[4,6,15] results. However, the IR frequencies calculated for the P–O stretching modes at 683 and 636 cm^{-1} were more than 200 cm^{-1} red-shifted with respect to the experimental and theoretical results, which range from 840 to 1030 cm^{-1} depending on the applied method and experimental conditions. The P–O vibrational modes are usually shifted to higher wavenumbers in the condensed phase spectra compared to the gas phase spectra. We also found that in these two bands not only the P–O vibrations but also the vibrations of the whole molecule were

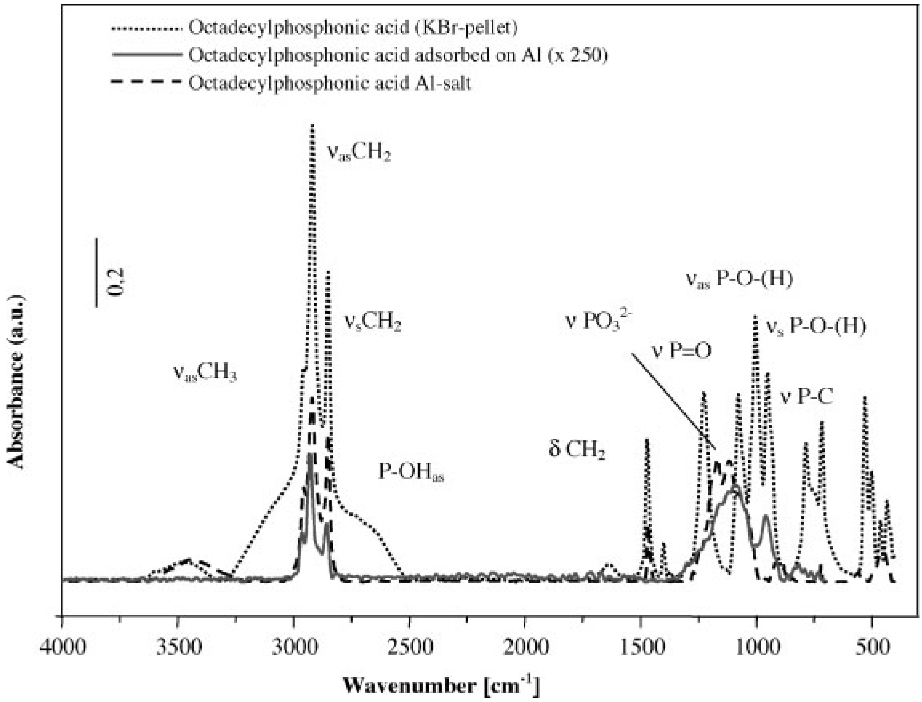

Figure 2.
FTIR Spectra of ODPA and its aluminium salt (KBr pellets) and polarised external reflectance spectrum of ODPA on AlMg1 for comparison.

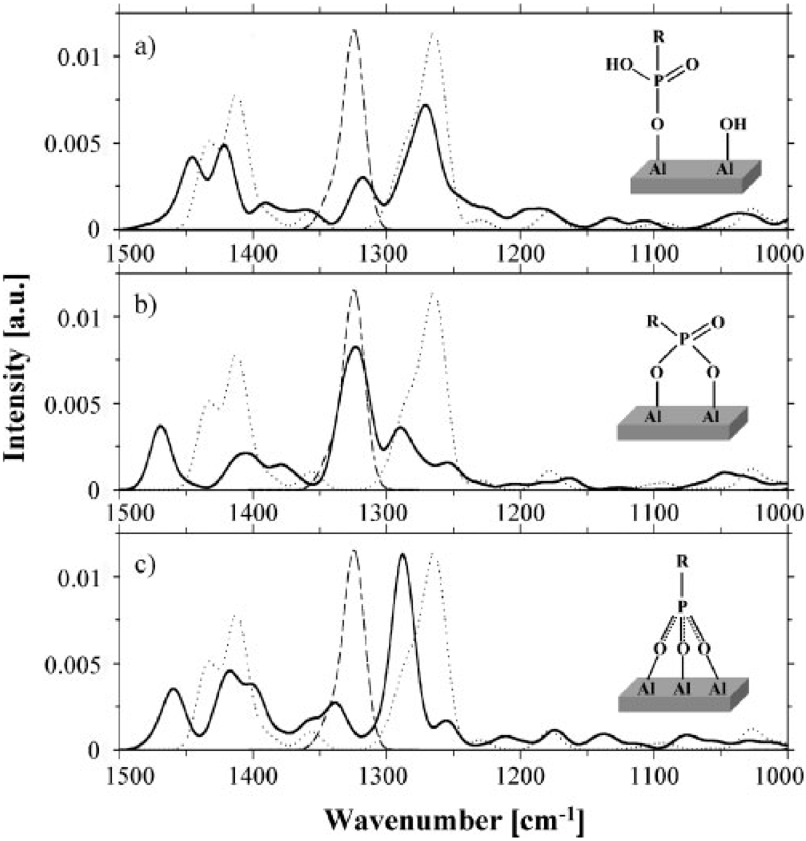

Figure 3.
Calculated IR spectra of phosphonic acid ($HPO(OH)_2$) bound to the α-Al_2O_3 (0001) surface (solid line) in comparison with the free acid (dashed line) and the free Al_2O_3 surface (dotted line).

involved. Thus, vibrations attributed to bands lower than 1250 cm^{-1} are complex and will not be included in the discussion of IR spectra of the adsorption complexes.

It is obvious from Figure 1b–d that by changing to alkyl phosphonic acids the bands attributed to the OH and P=O stretches are still clearly present at the same positions. The P-H band is absent and additional bands attributed to the CH_2 vibrational modes in the region of 2750–3000 cm^{-1} and around 1500 cm^{-1} are observed, which become more intensive with increasing chain length. Despite the deviation in the relative intensity and position of the P–O modes the agreement is reasonable well between the calculated (Figure 1d) and the experimental (Figure 2, dotted line) IR spectra of ODPA.

Figure 2 shows the FTIR spectra of ODPA (dotted line) and its aluminium salt (dashed line) in KBr as well as the surface spectrum (solid line) of ODPA adsorbed on aluminium from a 10^{-3} M ethanolic solution. The absorbance intensities of the surface spectrum were multiplied by 250 to enable comparison with the KBr spectrum. The surface spectrum is similar to the KBr spectrum of the aluminium salt. The characteristic P–OH vibrations of the free phosphonic acids at 2700 and 2300 cm^{-1} are not present in the surface spectrum.

The P–O stretching vibrations are shifted to higher wavenumbers. The P=O stretching vibration at 1225 cm^{-1} and the mentioned P–OH bands are absent in the spectra of the aluminium salt and in the spectra of the adsorbed species. However, the bands attributed to the resonance stabilized PO_3^{2-} group are present, which are supposed to correspond to the stretches of three symmetric P–O–Al bonds in the surface spectra. The experimental data indicate that the adsorption of ODPA on the aluminium surface favours tridentate complexes. Other authors came to the same conclusions.[2,4–7]

The IR spectra of mono-dentate, bi-dentate and tri-dentate adsorbed phosphonic acid on the α-Al_2O_3 (0001) surface (solid line) calculated with SCC-DFTB are shown in Figure 3a–c.

For comparison the spectra of the free phosphonic acid molecule (dashed line) and the free surface (dotted line) are included. It is obvious that the IR spectra of the adsorption complexes are mainly dominated by the vibrations of the α-Al_2O_3 (0001) surface. However, the surface spectrum does not show any bands in the region of the P=O stretching mode. Thus, the strong bands at about 1320 and 1325 cm^{-1} in the spectra of the mono-dentate and the bi-dentate bound $HPO(OH)_2$ molecule respectively, could be clearly attributed to the P=O mode. Evidences for this assignment are also shown in Figure 4a and b. There the PVDOS (projected vibrational density of states) of the P atom (dashed line) are comparative high in the corresponding regions indicating that its participation in the vibration attributed to these bands is high.

In contrast the P=O stretch vibration is absent from the spectra of the tri-dentate adsorption complex and PVDOS of the

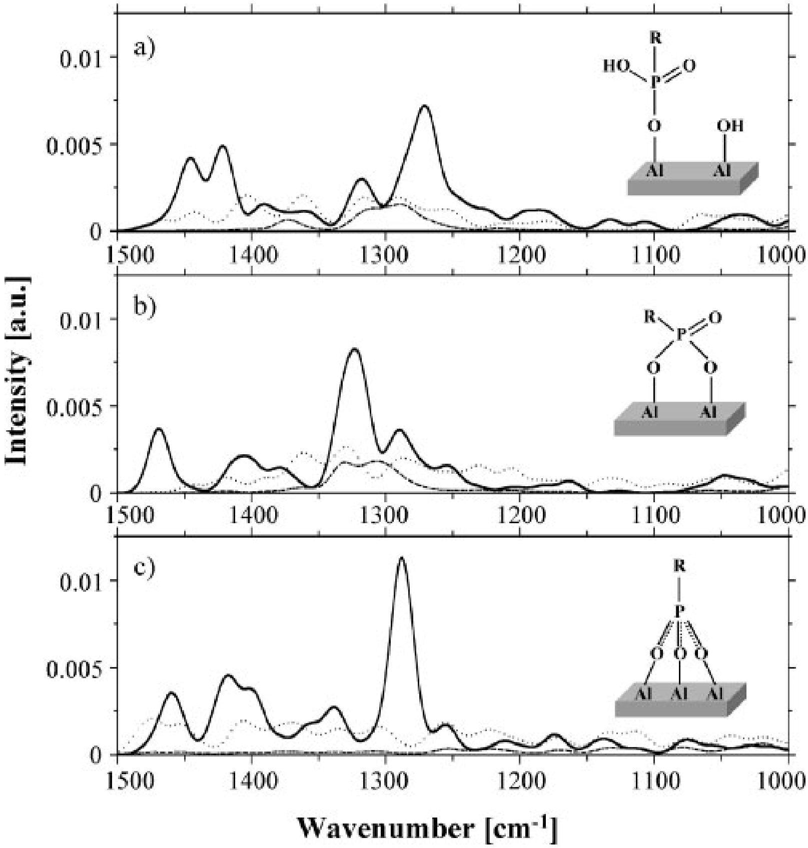

Figure 4.
Calculated IR spectra of phosphonic acid ($HPO(OH)_2$) bound to α-Al_2O_3 (0001) surface (solid line) and the corresponding PVDOS of the P (dashed line) and the Al (dotted line) atoms.

P atom is negligible in the region of frequencies higher than 1250 cm^{-1} (see Figures 3c and 4c). Thus, we can conclude from our theoretical result that the absence of the P=O mode in the experimental spectra is a strong hint that adsorption of phosphonic acids on aluminium surfaces favours tridentate complexes.

Conclusion

In this work we have used a density-functional based tight-binding method SCC-DFTB to calculate the infrared absorption spectra of $HPO(OH)_2$ adsorbed on the α-Al_2O_3 (0001) surface. Initially, we calculated the vibrational frequencies of the free acid to identify the position of the P=O stretching band, which were in very good agreement with other experimental and theoretical results. In case of the adsorption complexes we studied monodentate, bi- dentate and tridentate bonding of $HPO(OH)_2$ to the aluminium surface. We found that the band attributed to the P=O stretching mode is absent in the spectra of tri-dentate bonding, but could clearly be identified in the spectra of mono-dentate and bi-dentate adsorption complexes. In addition, experimentally obtained FTIR spectra of ODPA on aluminium have been included for comparison. There the P=O band is absent as well. Thus, we can state that adsorption of phosphonic acids on aluminium surfaces favours tridentate complexes, where the acid is bound to the surface via three symmetric P–O–Al bonds.

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