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Raman study of vibrational dynamics of aminopropylsilanetriol in gas phase

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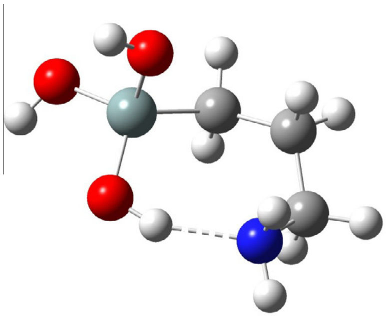
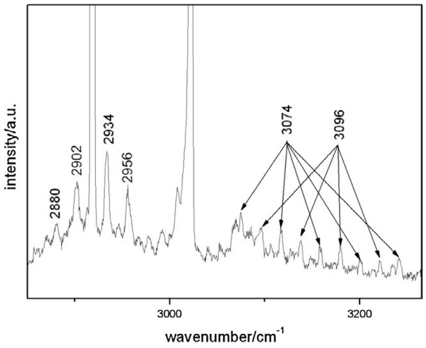
HIGHLIGHTS

- Gas phase Raman spectrum of aminopropylsilanetriol was recorded at room temperature.
- The assignment of the molecular spectrum based on the DFT calculation is presented.
- Ring like *gauche* conformation with intramolecular hydrogen bond was confirmed.
- High frequency periodic structure was observed.
- It is the result of the coupling between anharmonic proton motion and NH_2 stretchings.

GRAPHICAL ABSTRACT





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ABSTRACT

Raman spectrum of aminopropylsilanetriol (APST) in gas phase has been recorded at room temperature in macro chamber utilizing two-mirror technique over the sample tube. Unlike predominantly *trans* molecular conformation in condensed phase, the spectra of vapor show that the molecules are solely in *gauche* conformation with intramolecular hydrogen bond N···H—O which reduces the molecular energy in respect to *trans* conformation by 0.152 eV. The assignment of the molecular spectra based on the DFT calculation is presented. The strong vibrational bands at 354 cm^{-1}, 588 cm^{-1} and 3022 cm^{-1} are proposed for verifying the existence of the ring like, hydrogen bonded structure. Special attention was devoted to the high frequency region, where hydrogen bond vibrations are coupled to stretchings of amino and silanol groups.

Introduction

Aminopropylsilanetriol (APST) is one of the most frequently used organofunctional silane coupling agents. This molecule also emerges through the hydrolysis of other alkoxysilanes as a product of hydrolysis. Because of its two functional groups located at the opposite molecular sites, it can react with organic polymers as well as with inorganic substrates and fillers. During the solidification different kinds of networks can be formed. Lots of effort has been made in order to establish the conditions which enable forming the desired structure. Ishida et al. [1] investigated the structure of aminofunctional coupling agents by FTIR and Raman spectroscopy. Raman scattering was also used to study the conformational changes of aminopropylsilyl segments depending on the concentration and pH of solutions [2,3]. The influence of temperature and electromagnetic radiation, as well as of the substrate on which the solidification takes place, was also investigated [4]. Handke and co-workers [5] used FTIR to study different ladder-like oligosiloxane structures. Conformational stability and vibrations of APST has been investigated using DFT calculations [6,7], but the vibrational spectra were recorded only for

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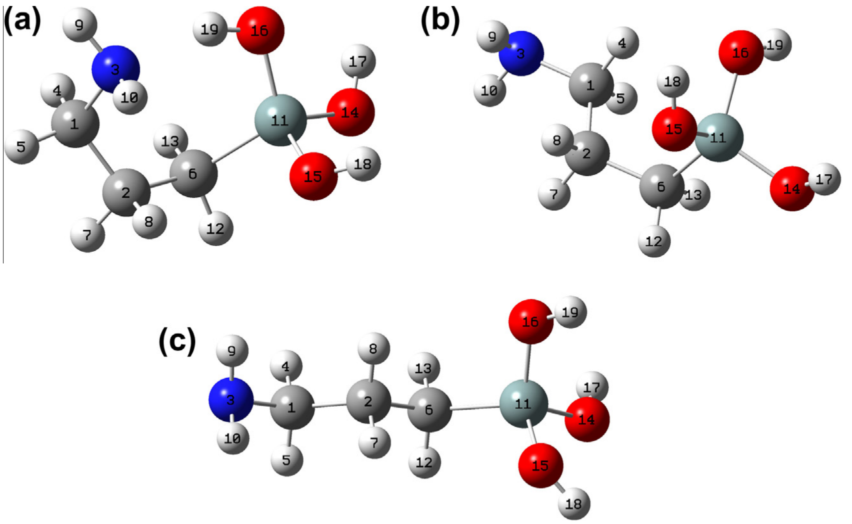

Fig. 1. Conformations of APST:(a) $APST_{HB}$ – *gauche* conformation with hydrogen bond, (b) $APST_{gauche}$ – *gauche* conformation without hydrogen bond, and (c)$APST_{trans}$ – *trans* conformation.

water solution and condensed, polymerized structure. According to these investigations there are two possible conformations of the propyl chains, the *trans* and the *gauche* one. In the water environment, where hydrogen bonds are formed between APST and water molecules, the most stable conformation is the *trans* one which enables formation of ladder structure during the polymerization process. The question arises what happens when APST evaporates from the solution and does it prefer to form *gauche* conformation with the intramolecular hydrogen bond N···H—O which stabilizes the structure (Fig. 1). In this work we present Raman spectrum of APST in vapor phase at room temperature, as well as DFT calculation of the total potential energy depending on the position of the proton between O and N atoms. The complete assignment of the vibrational spectrum of APST in gas phase ($APST_{HB}$), based on the calculation for the molecule in its most stable state, is given. We also present the possible explanation of the high frequency band structure that is based on vibrational dynamics considerations of intramolecular hydrogen bonds of Madsen et al. [8] and Dwyer et al. [9].

Experimental

In order to get Raman spectra of evaporated APST molecules at room temperature following procedure was used: sample tube $\Phi = 4$ mm was filled with 25% water solution of APST, frozen in liquid nitrogen bath and then connected to the vacuum line in order to remove the air above the solid sample. After evacuation the tube was sealed and left at room temperature. Raman spectra of liquid sample and of the vapors above the solution were recorded at room temperature in macro chamber under 90° scattering geometry in the horizontal plane with triple grating spectrometer Horiba Jobin Yvon model T64000. The spectra were excited by 514.5 nm line of the Coherent INNOVA-400 argon ion laser. Laser power at the sample was 70 mW. For the gas sample we used two mirror technique (one mirror is reversing the incident laser beam into itself, another is opposite to the collimating optics; together close to quadruplation), with the accumulation time of 300 s and spectral width of 3.52 cm^{-1}. This procedure enabled us to get Raman spectra of APST in vapor phase at room temperature revealing the fine structure in the high frequency region. Recorded spectra of vapor (Fig. 2) differ quite seriously from those of solution and solid phase and we undertook DFT study in order to explain the differences.

Calculation

In this study the density functional theory using the Becke's three-parameter exchange functional in combination with the

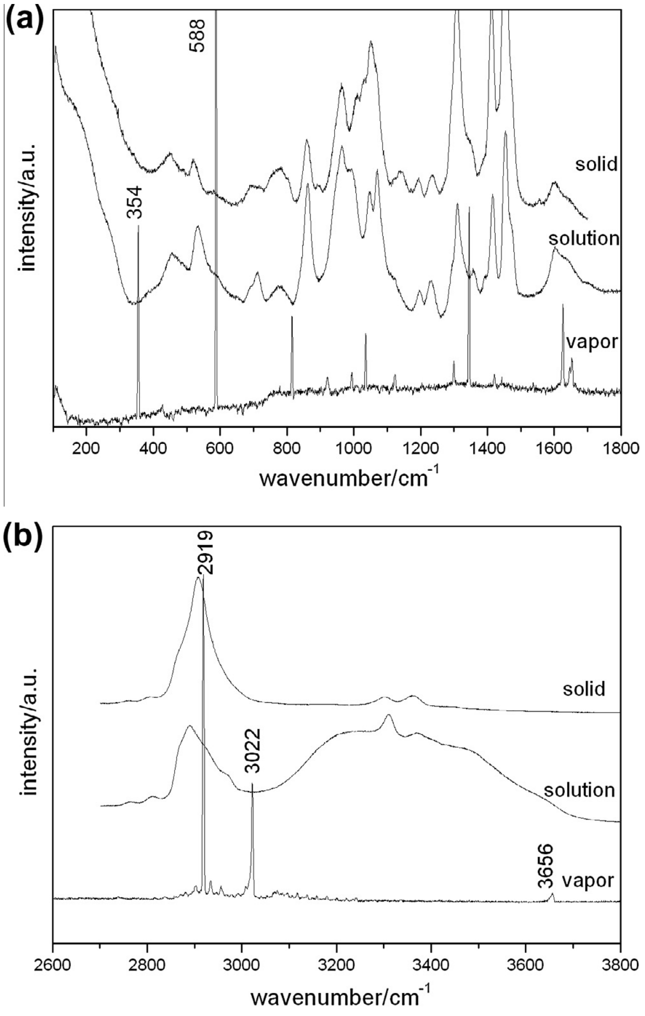

Fig. 2. Raman spectra of APST solid, solution and gas phase. (a) 100–1800 cm^{-1} and (b) 2600–3800 cm^{-1}.