Density functional study of gamma-aminopropyltriethoxysilane

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Abstract. Density functional theory calculations using Becke’s three-parameter exchange functional in combination with the Lee-Young-Parr correlation functional (B3-LYP) and standard 6-311+G(d,p) basis set were carried out to study the conformational stability and vibrational spectra of gamma-aminopropyltriethoxysilane. Calculations reveal the existence of two stable conformers trans and gauche. The calculated energy for the gauche conformation was found to be 608 cm⁻¹ above the minimum energy of the trans conformation. Temperature dependence of Raman spectra of liquid APTES and DFT calculation enabled us to identify the vibrational bands characteristic for both conformers. It has been shown that there is an increase in the population of gauche conformer with increasing temperature.

1. Introduction

Aminofunctional organosilanes, such as gamma-aminopropyltriethoxysilane (APTES) provide superior bonds between inorganic substrates and organic polymers. The structure of silane layers on the surfaces are strongly influenced by the conformation of APTES molecule in liquid. The number of molecules in different conformations depends on temperature. Since Raman intensities are proportional to the population, we investigated relative intensities of the vibrational bands characteristic for different conformers and their changes with temperature. Recently, it has been shown that a density functional theory can be applied as a general approach to the structural and vibrational problems of silanols [1]. Therefore, we have performed DFT calculations of structure and vibrational spectra of APTES. The comparison of theoretical spectra with the experimental data enabled us to assign the characteristic vibrational bands of different APTES conformers.

2. Experimental

97% APTES (NH₂CH₂CH₂CH₂Si(OCC₂H₅)₃) was purchased from ABCR Company. The Raman spectra of APTES from 3500 – 50 cm⁻¹ were recorded on a Dilor Model Z24 triple monochromator coupled with an IBM AT computer (Fig. 1). The 514.5 nm line of a Coherent INNOVA-165 Model argon ion laser was used for excitation. The spectral resolution was 5 cm⁻¹. The sample was cooled and heated in a liquid nitrogen variable temperature cryo-termostat Janice model VPF-700 equipped with Lake Shore temperature controller model 31S-T1. During each spectral record temperature stability was ±0.05 degrees. Temperature has been changed between 79 and 383 K. The boiling temperature of APTES is 488 K.
3. Results and discussion

DFT calculations were carried out by using the Gaussian.98 program suite [2]. The full geometry optimization of APTES, Cartesian force constants, IR intensities, Raman scattering activities and vibrational frequencies were calculated using B3-LYP correlation functional and 6-31G(d,p) basis set.

According to the calculations there are two stable conformers *trans* and *gauche* (Fig. 2) with SiCCC torsion angle of 178.67° and 71.37°, respectively. The predicted energy of the more stable *trans* conformer is 608 cm⁻¹ less than the energy of *gauche* conformer.

The analysis of Raman spectra shows that the relative intensity of several bands change with temperature (Fig. 3). The wavenumbers of these bands are conformation sensitive and for this reason the changes in relative intensities of conformer pairs of bands correspond to temperature induced
changes of conformation. A vibrational assignment of those bands is based on the normal coordinate analysis and scaled DFT force-constants expressed in local symmetry coordinates. Scaling factors were transferred from aminopropylsilanetriol [1]. In the temperature range between 79 and 383 K APTES molecule is still in its ground state and DFT calculations can be used to study vibrational spectra.

From the normal coordinate analysis the band at 1228 cm$^{-1}$ assigned as CH$_2$ wagging coupled with CH$_2$ and NH$_2$ rocking belongs to gauche conformer. For the trans conformer the corresponding fundamental is observed at 1190 cm$^{-1}$ and assigned to the CH$_2$ twisting mixed with CH$_2$ and NH$_2$ rocking vibrations. Although the intensity of both bands decreases with the temperature raise their relative intensities change in favour of 1228 cm$^{-1}$ band.

The band observed at 1076 and 1095 cm$^{-1}$ show similar behaviour. According to the calculated potential energy distribution they represent CO stretching vibrations in ethoxy groups of trans and gauche conformers, respectively. The normal mode analysis depicted the band observed at 867 cm$^{-1}$ as a characteristic vibration of gauche-APTES described in terms of CH$_3$ rocking, CC and SiO stretching vibrations. The intensity of that band increases with temperature in comparison to the other surrounding bands.

The normal modes observed at 640 cm$^{-1}$ in trans-APTES is interpreted in terms of SiC and SiO stretching. The fundamental at 620 cm$^{-1}$ in spectra of gauche-APTES has the same character and exhibit relative increase in intensity after heating of the sample.

![Figure 3. Temperature dependence of Raman spectra](image-url)
It has been shown that there is an increase in the population of gauche-APTES conformers at the expense of the trans one on heating the sample. According to the statistical thermodynamics, the ratio of the gauche to trans conformer is governed by relation

\[ \frac{n_g}{n_t} = \exp\left(\frac{-\Delta G}{R \cdot T}\right), \]

where \( n_g \) and \( n_t \) are the number of molecules in gauche and trans conformations, \( \Delta G \) is the Gibbs free energy difference between the two conformers [3]. From DFT calculation \( \Delta G = 4.1 \text{ kJmol}^{-1} \).

![Figure 4. Changes in ratio of the gauche to trans conformation with temperature](image)

The change of number of trans and gauche conformers with temperature can be seen from Fig 4. At very low temperature all molecules are in trans conformation. The amount of gauche conformation increased with increasing temperature to 35% at the boiling temperature. Temperature dependence of Raman spectra shows the same qualitative behaviour.

**References**

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