

UDC 544.77.023.5:544.18

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QUANTUMCHEMICAL CALCULATION OF ^{29}Si NMR SPECTRUM OF SILICON DIOXIDE FULLERENE-LIKE MOLECULES

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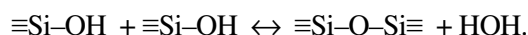
^{29}Si NMR spectra of fullerene-like hollow oligomers of silicic acid were calculated by the density functional theory method using hybrid exchange-correlation functional B3LYP, 6-311+G(2d, p) basis set and GIAO procedure. It is shown that fullerene-like molecule $(\text{SiO}_2)_{20}(\text{H}_2\text{O})_{10}$ gives an intensive signal in the range from -102 to -105 ppm.

Keywords: silicic acids, fullerene-like molecules, ^{29}Si NMR spectra, density functional theory

INTRODUCTION

There are many synthesized silica structures nowadays, such as silica films, nanotubes, nanospheres, nano-sized amorphous silica. They are industrially important materials widely used in catalysis, ion exchange, chromatographic separation; they are potentially important for synthesis of special-purpose materials. However, some physical and chemical aspects of silica nanoparticles formation have not yet been fully explained. The structure of crystalline and amorphous silica modifications is determined by peculiarities of the stage of formation of primary particles. There are still some questions despite considerable progress in theoretical and experimental study of nucleating stages. The mechanisms of primary particles condensation of the molecular level during the process of synthesis, thermodynamic and kinetic parameters of the stages of primary particles during that process have not yet been fully explained.

Most of silica materials are obtained by using sol-gel and hydrothermal method of synthesis. Polycondensation of orthosilicic acid molecules is the main chemical process during all the stages of the method, and we can write it down schematically using equation:



Experiment shows [2] that at the initial stages of synthesis in solution during the first hours of sol-gel synthesis different oligomers are forming. The formed oligomers are: dimers, linear trimers and

tetramers, cyclic trimers and tetramers, prismatic hexamers, cubic octamers and other oligomers with more elaborated structure.

The complexity in study of silicate solution and silica solutions is different comparing to polymeric hydrocarbon compounds because of the only fact – any change of solution (pH, T , concentration) immediately leads to the changes in the polymer composition. Thereby, all the clearness in definition of polymer composition in solution of silicic acid has been not yet achieved. That is why so important to study the structure and properties of silica molecular forms which can be formed at the initial stages of synthesis.

A powerful tool to identify species present in silicic acid solutions is ^{29}Si nuclear magnetic resonance spectroscopy (NMR) which allows making conclusions about polymer structure in solutions without changing its state. NMR spectra encode allows identifying specific polymeric forms of silicic acids and their content in solution [3]. We can determine a type of connection Q^0 , Q^1 , Q^2 , Q^3 and Q^4 (Fig. 1) depending on how many siloxane bonds (Si-O-Si) are at particular silicon atom according to ^{29}Si NMR spectroscopy. A silicon atom of orthosilicic acid coincide with Q^0 type of connection; silicon atoms included in dimer or end link of more elaborated structures refer to Q^1 ; the Q^2 type describe silicon atoms located in cycle or inside chain; Q^3 – silicon atoms in places of chains branch; Q^4 – silicon atoms connected with four bridging oxygen atoms. Though the type of connection is certain characteristic, it is still indirect; and that fact does not give us an

unambiguous statement about anionic composition of silica solution.

According to the papers work [3–5], chemical shift values δ (relative to tetramethylsilane TMS) for Q^0 coincide with the range of -66 to -73 ppm in ^{29}Si NMR spectrum. There are Q^1 and $Q^{2\Delta}$ (Δ indicates that the core Q^2 is a link of threefold cycle) signals located in the range of -76 to -83 ppm. The signals of the other silicon atoms of Q^2

type included in larger chains or cycles are shifted relatively $Q^{2\Delta}$ in direction of a strong magnetic field (of -86 to -91 ppm). The signals of Q^3 atoms appear in the range of -95 to -101 ppm. The $Q^{3\Delta}$ signals are shifted in Q^3 for about 10 ppm in to a low magnetic field and can be placed on Q^2 from the side of a strong magnetic field. The Q^4 groups provide a wide band in the range of -103 to -120 ppm in spectrum.

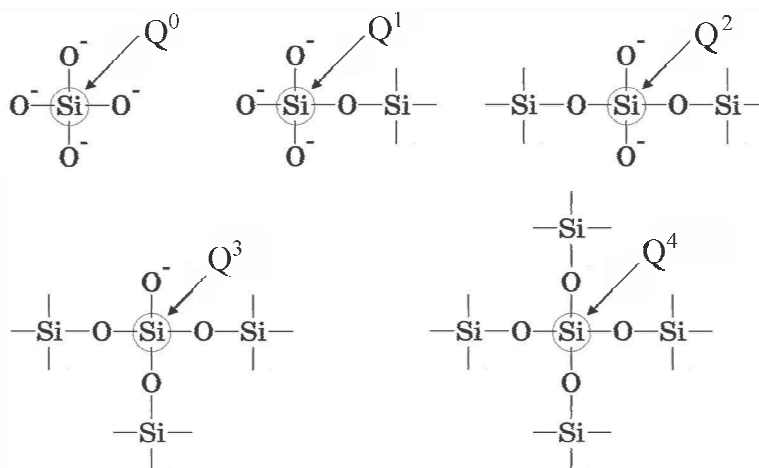


Fig. 1. Silicon atoms with different types of connection

The results obtained prove that it is not always possible to receive from experimental ^{29}Si NMR spectra unambiguous and reliable information about the structure of created silicic acids. In order to make an exact analysis of correlation between structure and ^{29}Si NMR spectrum, we use *ab initio* quantum chemical calculations which will allow obtaining detailed information about the structure of silicic acids at the atomic level. It will provide also more information about the factors which have influence on the value of chemical shifts in the structure because of different types of silicic atoms [6, 7].

In the paper [8] we made earlier an analysis of possible formation of hollow oligomers of spherical single-frame structure $[\text{HOSiO}_{1.5}]_N$ ($N=8, 20, 24, 28, 36, 60$) (Fig. 2) in silicic acid solutions using DFT method using hybrid exchange-correlation functional B3LYP and 6-31 G** basis set, polarizable continuum model. It shows the formation of hollow spherical silicon dioxide molecules to be energetically advantageous comparing to its reverse reaction of hydrolysis. In this paper we have been calculated ^{29}Si NMR spectra of a fullerene-like molecule $[\text{HOSiO}_{1.5}]_{20}$. We consider that we can prove the possibility of

formation of fullerene-like structures in solution during synthesis of silicon dioxide based systems by researching the influence of polysilicic acid degree of condensation N ($N=2, 4, 8, 10, 20$) on calculated ^{29}Si NMR spectra. Besides that, such researches allow defining relations between chemical shift and structural characteristics including polymer composition of the systems mentioned above.

COMPUTATIONAL METHOD

^{29}Si NMR spectra were calculated according to Gaussian 09 (D. 01) program using density functional theory (the functional B3LYP, basis set 6-311+G (2d, p) and GIAO (Gauge invariant atomic orbitals) method for the optimized structures related to DFT approach (B3LYP/6-31G(d, p)/PCM without symmetry restrictions). ^{29}Si chemical shifts were calculated according to TMS. The paper [4] has proved counting symmetry to reduce accommodation of calculated and experimental data.

RESULTS AND DISCUSSION

In the references below we can find experimental [5] and theoretically calculated [6]

isotropic chemical shifts for the ortho-, di-, cyclic tetra-, octa- and decasilicic acids. The size of shifts can serve as a point of reference for proving the

method of calculation NMR spectra of silicic acids to be chosen properly.

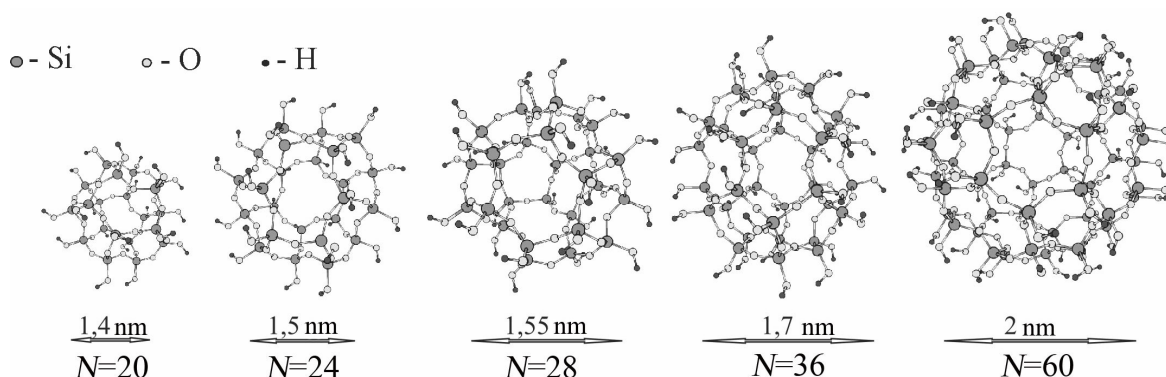


Fig. 2. Optimized structures of silicic acid molecules $[\text{HOSiO}_{1.5}]_n$ (n – polymerization degree)

In the paper [4] using an example of neutral molecule of orthosilicic acid H_4SiO_4 ($\delta = -71.2$ ppm) and an anion H_3SiO_4^- ($\delta = -65.9$ ppm), calculated NMR ^{29}Si isotropic chemical shifts has been shown to differ in 6.3 ppm. However, when we count the influence of environment and presence of counterions for deprotonated particle, the differ between shifts reduces to 0.1 ppm. Correlations received agree well with experiment [4]. The change of pH environment has a low influence on the position of a signal of particular oligomeric species members. With increasing of pH we see their deprotonation. Therefore quantum-chemical calculations of ^{29}Si NMR spectra of the studied systems have been made only for molecules of silicic acid. We can see in Table ^{29}Si NMR chemical shifts of silicic acids. The Table proves that chosen method of calculation show with satisfaction accuracy

positions of ^{29}Si NMR spectra peaks for mono-, di- and cyclic tetrasilicic acids. We can see a bit more deviation from the experimental values for frame structure octa- and decasilicic acids.

There are 4 silanol groups in silicic acid molecules, namely isolated silanol group (Fig. 3 *a*), a silanol group with hydrogen atom involved in hydrogen bonding (Fig. 3 *b*), a silanol group with electron-donor oxygen atom (Fig. 3 *c*), and a group of oxygen and hydrogen atoms involved in hydrogen bonding (Fig. 3 *d*). The exact value of ^{29}Si NMR chemical shift in spectrum depends on the type of silicon atoms silanol groups include. For $\text{H}_6\text{Si}_2\text{O}_7$ disilicic acid, in NMR spectrum we can see two signals respond to Si atoms with different types of silanol groups: -77.85 and -78.62 ppm related to the type of silanol groups *b* and *c* respectively (Fig. 3).

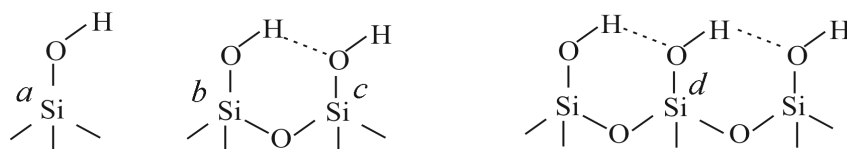


Fig. 3. Types of silanol groups in silicic acid structure

Every silicon atom for tetrasilicic acid molecule with cycle structure is characterized by the same chemical environment (one free hydroxyl group (Fig. 3 *a*) and one is involved in a hydrogen







bonding of type *d* (Fig. 3)). Therefore only one line of $\delta = -86.45$ ppm is observed in ^{29}Si NMR spectrum.

Silicon atoms of $\text{H}_8\text{Si}_8\text{O}_{20}$ octasilicic acid molecule with frame-like structure have only one isolated hydroxyl group, which gives single signal

$\delta = -109.5$ ppm in ^{29}Si NMR spectrum. There are type *a*, *b* and *c* silanol groups in $\text{H}_{10}\text{Si}_{10}\text{O}_{20}$ frame-like structure decasilicic acid (Fig. 3) which continue their signals in ^{29}Si NMR spectrum in the range of $-112.16 - -106.74$; $-99.01 - -99.32$ and 101.08 ppm respectively. Molecules of fullerene-like $\text{H}_{20}\text{Si}_{20}\text{O}_{50}$ silicic acid in the range of $(-98.00 - -101.08$ ppm) give signals of type *b* silanol groups; chemical shifts in the range of $-101.47 - -102.17$ ppm

related to silicon atoms included into silanol groups with electron-donor and proton-donor features (type *d*); for silanol group silicon atoms which have oxygen atoms involved in hydrogen bonding (type *c*) – in the range of $-103.28 - -107.47$ ppm (Fig. 3). Comparing the spectra of different silicic acids shows signals of all the molecules with frame-like structure to be in the only range of the spectrum ($\delta = -98 - -113$ ppm) (Fig. 4).

Table. ^{29}Si NMR chemicals shifts (ppm) for silicic acids

Silicic acid	Structure *	Q^n	$-\delta$		
			$-\delta$ (TMS) calc.	$-\delta$ (TMS) exp. [4]	$\Delta\delta = \delta(\text{exp.}) - \delta(\text{calc.})$
H_4SiO_4		Q^0	68,79	71,3	2,51
$\text{H}_6\text{Si}_2\text{O}_7$		Q^1	77,85; 78,62	79,81	1,96; 1,19
$\text{H}_8\text{Si}_4\text{O}_{12}$		Q^2	86,45	87,29	0,84
$\text{H}_8\text{Si}_8\text{O}_{20}$		Q^3	109,53	98,61	-10,92
$\text{H}_{10}\text{Si}_{10}\text{O}_{25}$		Q^3	99,01 – 112,16	98,45	-0,56 – -13,71
$\text{H}_{20}\text{Si}_{20}\text{O}_{50}$		Q^3	98,00 – 106,95	–	–

* \bullet - atom Si, $\bullet\text{---}\bullet$ - bridge Si–O–Si, silanol groups of silicic acid are not shown (number of hydroxyl groups in silicic acids is determined by the number of hydrogen atoms)

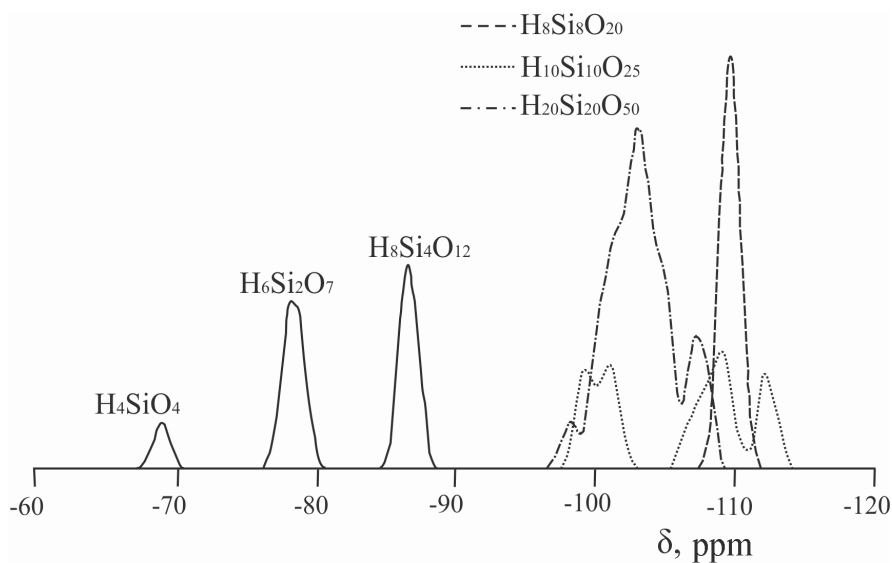


Fig. 4. ^{29}Si NMR spectra calculated for silicic acid molecules with $n = 1, 2, 4, 8, 10, 20$

We can clearly see the positions of the lines related to isolated silanol groups ($\delta = -106 - 113$ ppm) and hydrogen bonded silanol groups ($\delta = -98 - -107$ ppm). It is hard to recognize a type of hydrogen bonded silanol groups because the ranges of their signals for different silicic acids with frame-like structure are overlapping.

CONCLUSIONS

Comparing of ^{29}Si NMR spectra of different silicic acids ($n = 1, 2, 4, 8, 10, 20$) proves the signals of all the frame-like structure molecules to belong to the one range of the spectrum ($\delta = -98 - -113$ ppm). We can clearly see the positions of the lines from isolated silanol groups ($\delta = -106 - 113$ ppm) and hydrogen bonded silanol groups

($\delta = -98 - -107$ ppm). $(\text{SiO}_2)_{20}(\text{H}_2\text{O})_{10}$ fullerene-like molecule gives an intensive signal in the range of $-102 - -105$ ppm. The results obtained from the analysis of ^{29}Si NMR spectra for silicic acids ($n = 1, 2, 4$) and for frame-like structure silicic acids ($n = 8, 10, 20$) could be helpful in assigning signals of unknown silica structures in ^{29}Si NMR spectra.

ACKNOWLEDGEMENTS

We thank Prof. Vladimir M. Gun'ko (Chuiko Institute of Surface Chemistry of National Academy of Sciences, Ukraine) for having provided access to GAUSSIAN 09 (D.01) program which was used for NMR spectra calculation.

Квантовохімічний розрахунок ^{29}Si ЯМР спектрів фулереноподібних молекул діоксиду кремнію

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Методом функціоналу густини з гібридним обмінно-кореляційним функціоналом B3LYP та базисним набором 6-311 + G(2d, p) з використанням методу GIAO розраховано ^{29}Si ЯМР-спектри фулереноподібних пустотілих олігомерів кремнієвої кислоти. Показано, що фулереноподібна молекула $(\text{SiO}_2)_{20}(\text{H}_2\text{O})_{10}$ дає інтенсивний сигнал в області $-102 - -105$ м.д.

Ключові слова: кремнієва кислота, фулереноподібні молекули, ^{29}Si ЯМР-спектри, теорія функціонала густини

Квантовохимический расчет ^{29}Si ЯМР спектров фуллереноподобных молекул диоксида кремния

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Методом функціонала щільності з гібридним обмінно-кореляційним функціоналом B3LYP і базисним набором 6-311 + G(2d, p) з використанням методу GIAO розраховано ^{29}Si ЯМР спектри фулереноподібних пустотілих олігомерів кремнієвої кислоти. Показано, що фулереноподібна молекула $(\text{SiO}_2)_{20}(\text{H}_2\text{O})_{10}$ дає інтенсивний сигнал в області $-102 - -105$ м.д.

Ключевые слова: кремниевая кислота, фуллереноподобные молекулы, ^{29}Si ЯМР-спектры, теория функционала плотности

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Received 30.03.2015, accepted 23.04.2015