PHYSICS AND CHEMISTRY OF SOLIDSTATE
V. 18, № 1 (2017) P. 111-116
DOI: 10.15330/pcss.18.1.111-116

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 18, № 1 (2017) С. 111-116

PACS: 544.77.023.5:544.18

ISSN 1729-4428

O. Filonenko, V. Lobanov, A. Grebenyuk

The Hollow Spherical Silica Molecule $(SiO_2)_{20}(H_2O)_{10}$: Theoretical Calculations of the IR spectrum

A.A. Chuiko Institute of Surface Chemistry, National Academy of Sciences, 17, General Naumov Str,
Kyiv 03164, Ukraine. E-mail: filonenko_ov@ukr.net

The IR spectrum of hollow spherical molecule $(SiO_2)_{20}(H_2O)_{10}$ have been calculated within harmonic approximation using density functional theory method (exchange-correlation functional B3LYP and basis set 6-31G (d, p)) and an assignment have been made of the frequencies to the forms of vibrations. It has been shown that the theoretically calculated spectrum of molecule $(SiO_2)_{20}(H_2O)_{10}$ is consistent with the experimental spectra of nanospheres, so the molecule $(SiO_2)_{20}(H_2O)_{10}$ and its higher homologues can be used in quantum-chemical calculations of the properties of synthesized hollow nanospheres (d ≈ 290 nm).

Keywords: hollow spherical silica molecule; IR-spectroscopy; density functional theory.

Article acted received 20.02.2017; accepted for publication 05.03.2017.

Introduction

Recently, a significant interest has been increased to examination of the materials composed of the hollow nanospheres, due to their possible potential use as containers for drug delivery, carriers of catalysts, and microreactors [1-3]. Among these materials, hollow silica nanospheres attract a high attention due to their low cost, unique mechanical properties, high thermal stability, highly developed surface, porosity, good biocompatibility and low toxicity. Development of new methods for the synthesis of such nano- and microstructures of SiO_2 and examination of their structures today are actual problems.

In most cases, hollow silica nanospheres are obtained using template synthesis methods based on the deposition of spherical nanoparticles (Fig. 1, a) on solid surfaces which define a shape and size of the nanomaterial, the molecules of organic substances, the surface of spherical aerosol droplets or emulsions playing the role of geometric templates. Spherical SiO_2 nanoparticles are obtained, as a rule, by the sol-gel method due to hydrolysis of tetraethoxysilane (TEOS) in a water-ethanol medium in the presence of ammonium hydroxide, by so-called Stöber–Fink–Bohn technique. The hydrolysis of TEOS involves two main stages: the hydrolysis itself of TEOS up to the formation of silicic acid and further polycondensation of its monomers to bulk silica. When the reaction ends, the organic template is removed by chemical or heat treatment, so leaving inorganic thin hollow nanospheres composed of silicon dioxide [4].

Most articles concerning hollow silica nanospheres are focused on the methods for their preparation and on experimental studies of their properties. There are few theoretical studies on the structure and spectroscopic characteristics of such silica materials available in the literature. The elucidation of the relationships between molecular structures and physic-chemical properties of the materials is one of the most important areas in materials science, because the knowledge of the structure at the atomic level is a prerequisite for creating materials with desired properties.

Today it is known that during the first hours of the sol-gel synthesis by the hydrolysis of TEOS silica acid monomers are formed; their subsequent polymerization results in the formation of the nuclei with diameter of ~2 nm. The crystallization nuclei have a spherical shape, as polymer chains formed as a result of condensation of branched polysiloxane chains are fold into spherical particles of silica due to minimization of surface energy. Depending on the synthesis conditions, the sizes of nuclei can reach 10-15 nm due to addition of silica acid monomers (Fig. 1b). So the initial nanoparticles of SiO_2 are formed. When the critical size (specific for the concrete synthesis conditions) is achieved, primary particles begin to aggregate, so forming a larger species [5]. The structures of nuclei (small particles with diameter of ~1-2 nm) formed due to polymerization of silica acid monomers are still unclear. The existence of

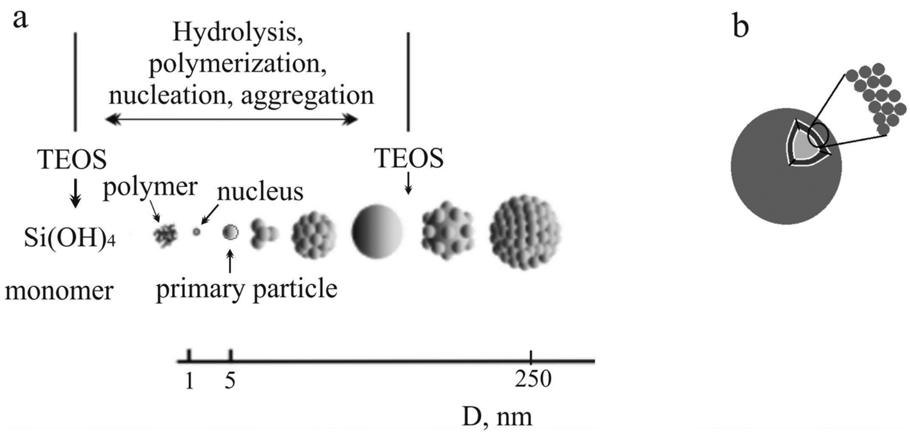

Fig.1. a) scheme of the formation of colloidal SiO_2 microparticles [5]; **b)** probable structure of a hollow silica nanosphere [1].

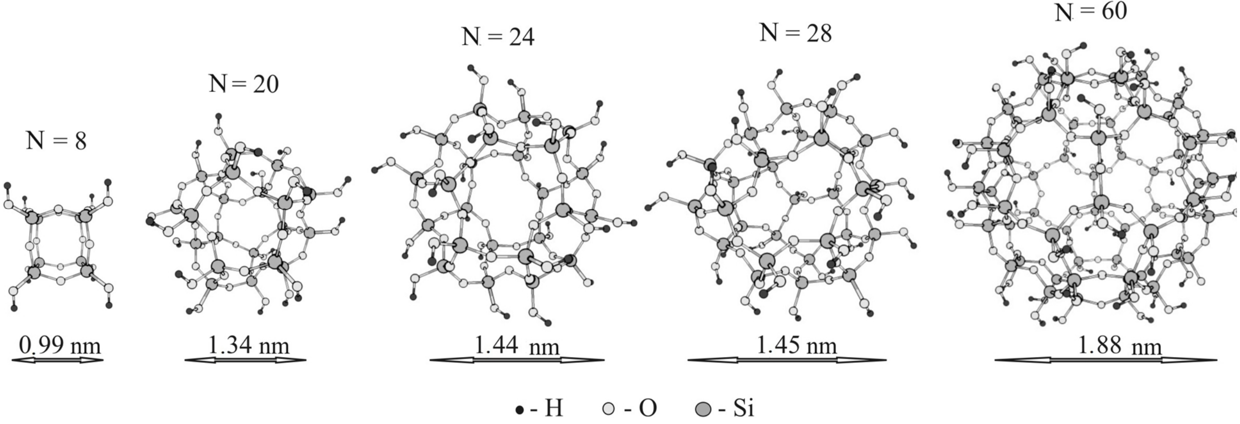

Fig. 2. Equilibrium spatial structure of the hollow spherical silica molecule $(SiO_2)_N(H_2O)_{N/2}(SiO_2)_N(H_2O)_{N/2}$.

such siloxane structures $(RSiO_{1.5})_n$, (R = H, CH_3; n = 8, 10, 12, ...) [6], so-called oligomeric silsesquioxanes does not exclude probable formation of hollow spherical polysiloxane molecules due to the polycondensation of silica acid. For example, in [7] theoretically a possibility was proved of the formation of hollow spherical molecules of silicic acids $(SiO_2)_N(H_2O)_{N/2}$ (N = 8, 20, 24, 28, 36, 60) (Fig. 2) as intermediates in the hydrothermal and sol-gel synthesis of silica materials.

In this paper, IR spectra of molecules $(SiO_2)_N(H_2O)_{N/2}$ are calculated, the smallest size of representatives with N = 8 and 20 being taken as examples. A comparison of the IR spectra of experimentally obtained hollow silica nanospheres available elsewhere [8] with theoretically calculated vibrational spectra of cell-like silicon dioxide molecules can give evidence of their existence as a crystallization cores in the synthesis of spherical silicon dioxide molecules in general, and of hollow SiO_2 nanospheres in particular.

In addition, since the real structure of hollow spheres of silicon dioxide is quite complicated, it is necessary to find an effective model for examination of the properties of such systems using quantum-chemical calculations in order to reproduce the experimental data with satisfactory accuracy.

I. Models and methods of calculation

1.1. The structures of $(SiO_2)_N(H_2O)_{N/2}$ molecules.

The building blocks of hollow molecules $(SiO_2)_N(H_2O)_{N/2}$ with frame structure, as well as those in case of crystalline and amorphous silica polymorphs, are silicon-oxygen tetrahedra (Fig. 2). The molecular skeleton is a polyhedron with silicon atoms in vertices, each of them bears a hydroxyl group. The oxygen atoms of siloxane bonds are situated in the middle of Si···Si distances.

1.2. Computational method.

Frequencies and normal vibrational modes of molecules $(SiO_2)_8(H_2O)_4$ and $(SiO_2)_{20}(H_2O)_{10}$ were found as eigenvalues and eigenvectors respectively of mass-weighted Hessian obtained within the DFT/B3LYP/6-31G (d,p) approximation by means of the program package GAMESS-US [9]. A scaling factor for theoretically calculated frequencies was taken into consideration, which is usually used in calculations within the harmonic approximation the frequencies of normal vibrations by the method mentioned above, its value being equal to 0.96 [10]. The frequencies of normal vibrations in the IR spectra found theoretically were visualised by means of the Chem Craft program [11]. When designing spectra from the frequencies obtained,

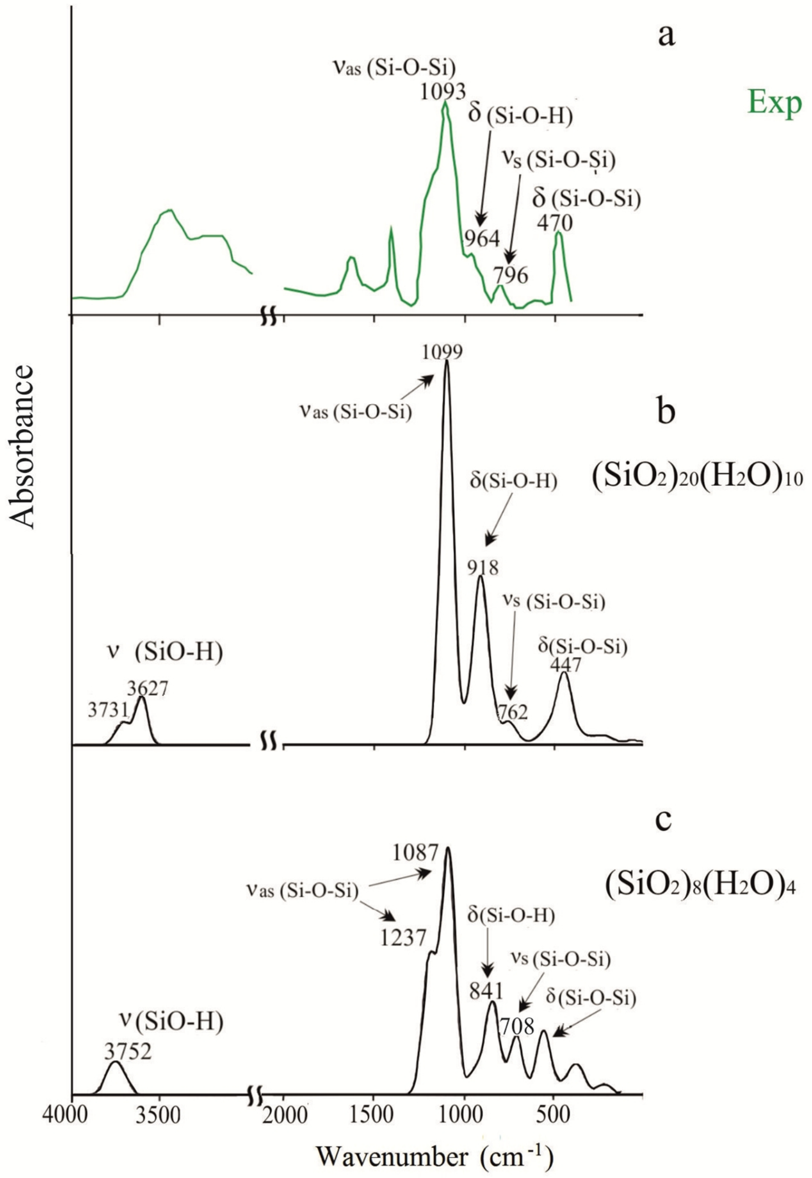

Fig. 3. Experimental (a) IR spectrum of the hollow nanospheres of silicon dioxide [8]; the calculated (b) IR spectrum of the molecule $(SiO_2)_{20}(H_2O)_{10}$ and the calculated (c) IR spectrum of the molecule $(SiO_2)_8(H_2O)_4$.

the Loretzian broadening of the bands was taken into consideration with band width on ½ height of 60 cm^{-1}.

II. Results and discussion

The method of infrared spectroscopy is widely used for the study of systems based on silicon dioxide. The presence of characteristic bands for various silicon-oxygen groups gives an opportunity of their identification. Thus, for three-dimensional structures, the absorption caused by antisymmetrical vibrations of atoms of the Si–O–Si fragments is observed within the region of 980–1200 cm^{-1}: for cristobalite 1104–1204 cm^{-1}, for quartz 980–1200 cm^{-1}, for quartz glass 1085 - 1150 cm^{-1}, for coesite 1040 - 1225 cm^{-1} [12, 13].

For two-dimensional structures, for example silica films, the atomic vibrations of Si–O bonds are related to the bond within 1008–1195 cm^{-1} [14, 15].

For the IR-spectra of one-dimensional hollow silica nanorods with internal diameter of 10 nm, wall thickness of 10–15 nm, and length of up to 150 nm, the bands are characteristic related to stretching antisymmetrical vibrations of Si–O–Si atoms with a maximum at 1077 cm^{-1}, stretching vibrations of Si–OH at 800 cm^{-1}, and bending vibrations of the triatomic group Si–O–Si at 470 cm^{-1} [16].

For oligomeric silsesquioxanes $(RSiO_{1,5})_n$ where the silicon-oxygen skeleton is an octameric close cell (n=8), the stretching antisymmetrical vibrations of Si–O–Si atoms give an absorption band with maximum at 1140 cm^{-1} (R=H) or 1117 cm^{-1} ($R=CH_3$). The maximum of absorption band related to the bending vibrations of the atoms of Si–O–Si cell, irrespective of the nature and size of the substituent R, is at 465 cm^{-1} [17]. For the $(HSiO_{1,5})_n$ (n = 10) adsorbed on the Si(100)-2×1 surface, the stretching asymmetrical vibrations of Si–O–Si atoms become apparent at 1180 cm^{-1} [18]. In the IR-spectra of siloxanes having the structures with open octameric cells and of ladder-like silsesquioxanes, the antisymmetrical stretching vibrations of Si–O–Si atoms in the $(Si–O)_4$ rings are related to 1050–1085 cm^{-1} [13, 19, 20].

In [21-23], the diapason of 500–800 cm^{-1} in the IR-spectra of zeolites and cyclosilicates was shown to relate to the vibrations of silicon-oxygen rings. Such a band was entitled ring one. When n increases in $(SiO)_n$ rings, the ring band is shifted to the lesser wavenumber, namely, the spectral regions of 700 - 720, 650, and 600 - 630 cm^{-1} are related to the vibrations of three-, four-, and six-membered rings respectively. The vibrations of the five-membered rings in the zeolites of 5-1 structural group (they contain chains of five-membered rings) are related to the band in the region of 520 - 560 cm^{-1} [24, 25].

There are natural crystalline modification of silica - mineral melanophlogite with gross formula $46 \cdot SiO_2 \cdot 6M^{14} \cdot 2M^{12}$ (M^{14} = CO_2, N_2; M^{12} = CH_4, N2) [26] as well as artificially synthesized ZSM-39 (dodecacil-3C) with gross formula $136 \cdot SiO_2 \cdot 16M^{12} \cdot 8M^{16}$ (M^{12} = N_2, CH_4; M^{16} = $N(CH_3)_3$, CO_2) [27] with polyhedral cavities, their frames being identical to those of silicic acids $(SiO_2)_{20}(H_2O)_{10}$, $(SiO_2)_{24}(H_2O)_{12}$. These compounds belong to the family of pentacils – zeolites. Their structures, along with other structural elements, are formed also by five-membered rings which can be ascertained using infrared spectroscopy. Thus, for melanophlogite, there are characteristic bands at 1118 and 795 cm^{-1} related to the asymmetric and symmetric stretching vibrations of atoms in the bridge links Si–O–Si of five-membered rings. For ZSM-39, corresponding bands are at 1090 and 790 cm^{-1} [25]. The absorption band in the spectra of both melanoflogite and ZSM-39 near 550 см$^{-1}$ is absent because the five-membered rings are united with formation of polyhedral hollows not chains.

In [8], due to combination of sol-gel and Stober methods, in presence of cetyltrimethylammonium bromide with TEOS as a silica precursor, hollow silica nanospheres were synthesized with wall width of ~110 nm and internal diameter of ~290 nm. As a template, carboneous spheres were used with diameter of 300 nm, finally eliminated by calcination at 550 °C during 5 hours. There are some absorption bands in the IR-spectra of hollow multiwall silica nanospheres obtained, namely 470, 796, 964, and 1093 cm^{-1}, related to bending vibrations of atoms in the triatomic fragment Si–O–Si, stretching symmetrical vibrations of the atoms of siloxane bonds, bending Si-O-H vibrations, and assymetrical stretching vibrations of the atoms of Si–O–Si fragment, respectively (Fig. 3, a). Besides, a band at 1626 cm^{-1} is available in the spectrum related to the bending vibrations of H–O–H atoms, so detecting the presence of free or adsorbed water. The bands in the region of 3300–3500 cm^{-1} are related to the stretching vibrations of the atoms of O–H bonds of the adsorbed water molecules forming hydrogen bonds with a silanol group of the surface of nanoparticle.

The hollow spherical molecule $(SiO_2)_{20}(H_2O)_{10}$ (its IR-spectrum is simulated in this work) consists of 90 atoms. The skeleton of its cell is formed only by five-membereed rings and has a structure similar to that of fullerene C_{20} molecule (namely, its silicon atoms, as carbon ones, are in the vertices of a dodecahedron). It is characterized by 264 normal vibrational modes. The frequencies obtained for the most intensive normal vibrations of $(SiO_2)_{20}(H_2O)_{10}$ molecule are given in the Table. In order to simplify a comporison with the experimental spectra, the program Chem Craft was used, each line is approximated by Lorentz functions. The spectrum obtained is given in Fig. 3.

The theoretically calculated vibrational spectrum of a

Table 1

Calculated IR wavenumbers (cm^{-1}) and intensities (conventional units) of $(SiO_2)_{20}(H_2O)_{10}$ molecule

Wavenumber (cm^{-1})	Intensity	Vibrational assignmen	Structural origin
3762 3720	2.8 2.9	ν SiO–H	Isolated silanol
3648	5.7	ν SiO–H	Mono hydrogen bonded silanol
3628 3602	7.7 6.0	ν SiO–H	Mono + two hydrogen bonded silanol
1106 1094 1092	43.1 45.4 48.0	ν_{as}(Si–O–Si) + δ(Si–O–H)	
921 918	32.7 43.7	δ(Si–O–H) + ν(Si–O)	All silanols
838 769	5. 2 5. 9	ν_s(Si–O–Si) + δ(Si–O–H)	Vibrations of five-membered rings
446	8.2	δ(Si–O–Si)	“Breathing” mode of silicon-oxygen skeleton
440	8.1	Twisting vibrations of OH groups around Si–OH + δ(Si–O–Si)	

hollow spherical molecule $(SiO_2)_{20}(H_2O)_{10}$ (Fig. 3 b) with the frame formed by only the five-membered rings and a structure similar to that of the fullerene C_{20} molecule contains an intense band in the area of 1099 cm^{-1} related to asymmetric stretching vibrations of the atoms of Si–O–Si bonds and a low intensity band at 762 cm^{-1} related to symmetric vibrations of these bonds. The above mentioned vibrational frequencies of the molecule $(SiO_2)_{20}(H_2O)_{10}$ are in good agreement with those experimentally obtained for melanophlogite and ZSM-39 [25]. This indicates the possible presence of molecules $(SiO_2)_{20}(H_2O)_{10}$ in solution. Such molecules can also be regarded as secondary building units in the synthesis of the above mentioned pentasils.

In addition, in the IR spectrum of the molecule $(SiO_2)_{20}(H_2O)_{10}$ a wide absorption band is available in the range of 3600 to 3800 cm^{-1} with peaks at 3627 and 3731 cm^{-1}, due to stretching vibrations of the atoms of O–H bonds of silanol group with hydrogen atom involved in hydrogen bonds with the oxygen atom of adjacent silanol group and those of the atoms of O–H bonds of free silanol groups, respectively. For molecule $(SiO_2)_{20}(H_2O)_{10}$, these frequencies are slightly shifted towards higher values of wave number as compared to the corresponding values for the H-bonded silanols on silica surface ($\nu_1 = 3510$ та $\nu_2 = 3715$) [28]. Near 918 cm^{-1}, there is an absorption band attributed to the bending vibrations of silanol group, rather close to that of Si–O–H group (964 $cm^{\,1}$) in the infrared spectra of large diameter hollow multiwall silica nanospheres with surfaces, according to the authors [27], covered with hydroxyl groups. There are no bonds in the regions of 3300–3500 and of 1626 cm^{-1}, as the calculation has been carried out for the isolated molecule, but these bands denote the presence of the molecules of free or adsorbed water in the samples of synthesized hollow nanospheres.

It is seen from the above data that the theoretically calculated spectrum of molecule $(SiO_2)_{20}(H_2O)_{10}$ is consistent with the experimental spectrum of hollow nanospheres. In our opinion, the molecule $(SiO_2)_{20}(H_2O)_{10}$ and its homologues can be used as models in the study of the properties of the synthesized hollow nanospheres, having great scientific and practical interest [1–3], primarily as possible containers for long-term storage and targeted delivery of drugs.

In [29, 30], to study the properties of nanoscale silica, cell octamer $(SiO_2)_8(H_2O)_4$ is used as a model. From the calculated spectra of molecules $(SiO_2)_{20}(H_2O)_{10}$ and $(SiO_2)_8(H_2O)_4$ (Fig. 3 b, c) it is seen that more accurate experimental spectrum hollow nanospheres SiO_2 is reproduced by a molecule with N = 20. In its spectrum, there are bands of all the major frequencies that occur in the experimental spectrum. In the spectrum of molecule $(SiO_2)_8(H_2O)_4$ there is no splitting of the band caused by stretching vibrations of atoms of the O–H bonds of silanol groups (in the range of 3600-3800 cm^{-1}) due to equivalence of all the silanol groups in the structure of octamer cell. In the structure of the hollow spherical molecule $(SiO_2)_{20}(H_2O)_{10}$, both isolated and hydrogen bound silanol groups are available, similarly to the surface of SiO_2 nanoparticles. This fact supports once more the advisability of use hollow spherical molecules as models for examination of the properties of hollow SiO_2 nanospheres.

Conclusions

The results of calculations of the frequencies, forms, and intensities of the normal vibrations of atoms of the molecule $(SiO_2)_{20}(H_2O)_{10}$ have shown a fairly good agreement with the experimental spectrum of hollow nanospheres of silicon dioxide. Therefore, in our opinion, the molecule $(SiO_2)_{20}(H_2O)_{10}$ and its homologues are suitable models for examination of the properties of synthesized hollow nanospheres, which are of great scientific and practical interest, especially as possible containers for long-term storage and targeted delivery of drugs.

Filonenko O.V. – Ph.D., young researcher;
Lobanov V.V. – Prof., Dr.Chem.Sci.,Head of the Lab. of Quantum Chemistry and Chemical Physics of Nanosystems;
Grebenyuk A.G. – Ph.D., senior researcher.

[1] Y. Liu, X. Chen, J.H. Xin, J.Mater Sci. 41(16), 5399 (2006).
[2] Y. Le, M. Pu, J.-F. Chen, Materials Research Bulletin 41(9), 1714 (2006).
[3] Y. Le, M. Pu, J.-F. Chen, Journal of Non-Crystalline Solids 353(2), 164 (2007).
[4] N.M. Gorsd, L.R. Pizzio, M.N. Blanco, Procedia Materials Science 8, 567 (2015).
[5] V.M. Masalov, N.S. Sukhinina, E.A. Kudrenko, G.A. Emelchenko, Nanotechnology 22(27), 275718 (2011).
[6] W.-D. Cheng, K.-H. Xiang, R. Pandey, J. Phys. Chem. B. 104(29), 6737 (2000).
[7] O. Filonenko, V. Lobanov, Chemistry, Physics, Technology of Surface 4(3), 260 (2013).
[8] X. Guo, X. Liu, B. Xu, T. Dou, Colloids and Surfaces A. 345(1-3), 141 (2009).
[9] M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T.Elbert, M.S.Gordon, J.H.Jensen, S.Koseki, N.Matsunaga, K.A.Nguyen, S.J.Su, T.L.Windus, M.Dupuis, J.A.Montgomery, J. Comput. Chem. 14(11), 1347 (1993).
[10] A.P. Scott, L. Radom, J. Phys. Chem. 100(41), 16502 (1996).
[11] G.A. Zhurko, http://www.chemcraftprog.com.
[12] Y. Liang, C.R. Miranda, S. Scandolo, J. Chem. Phys. 125(19), 194524 (2006).
[13] M.Sitarz, W. Jastrzebski, P. Jelenr, E. Długonr, M. Gaweda, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 132, 884 (2014).
[14] P. Innocenzi, Journal of Non-Crystalline Solids 316(2,3), 309 (2003).

[15] M. Heyde, S. Shaikhutdinov, H.-J. Freund, Chemical Physics Letters 550, 1 (2012).
[16] G. Fu, A. He, Y. Jin, Q. Cheng, J. Song, BioResources 7(2), 2319 (2012).
[17] E.S. Park, H.W. Ro, C.V. Nguyen, R.L. Jaffe, D.Y. Yoon, Chem. Mater. 20(4), 1548 (2008).
[18] J.N. Greeley, M.M. Banaszak Holl, Inorg. Chem. 37(23), 6014 (1998).
[19] N. Hu, Y. Rao, S. Sun, L. Hou, P. Wu, S. Fan, B. Ye, Applied Spectroscopy 70(8), 1328 (2016).
[20] A. Kolezynɾski, W. Jastrzebski, W. Szczypka, A. Kowalewska, M. Nowacka, M. Sitarz, Journal of Molecular Structure 1044, 314 (2013).
[21] M. Sitarz, M. Handke, and W. Mozgawa, Spectrochimica Acta A 56(9), 1819 (2000).
[22] M. Sitarz, M. Handke, W. Mozgawa, Spectrochimica Acta Part A 55(14), 2831 (1999).
[23] M. Kryl, W. Mozgawa, W. Jastrzebski, K. Barczyk, Microporous and Mesoporous Materials 156, 181 (2012).
[24] M. Krol, W. Mozgawa, W. Jastrzebski, J Porous Mater 23(1), 1 (2016).
[25] J.C. Jansen, F.G. Gaag, H. Bekkum, Zeolites. 4(4), 369 (1984).
[26] H. Gies, Zeitschrift fur Kristallographie. 164, 247 (1983).
[27] H. Gies, Zeitschrift fur Kristallographie. 167, 73 (1984).
[28] B.C. Bunker, D.M. Haaland, T.A. Michalske, W. L. Smith, Surf. Sci. 222(1), 95 (1989).
[29] I. Roggero, B. Civalleri, P. Ugliengo, Chem. Phys. Lett. 341(5), 625 (2001).
[30] J. Sauer, J.-R. Hill, Chem. Phys. Lett. 218(4), 333 (1994).

О.В. Філоненко, В.В. Лобанов, А.Г. Гребенюк

Порожниста сферична молекула діоксиду силіцію $(SiO_2)_{20}(H_2O)_{10}$: теоретичні розрахунки ІЧ-спектру

Інститут хімії поверхні ім. О.О. Чуйка Національної академії наук України, вул. Генерала Наумова 17, Київ, 03164, Україна, e-mail: filonenko_ov@ukr.net

Методом функціоналу густини з гібридним обмінно-кореляційним функціоналом B3LYP і базисним набором 6-31G(d, p) в гармонічному наближенні розраховано інфрачервоний спектр порожнистої сферичної молекули $(SiO_2)_{20}(H_2O)_{10}$ та виконано віднесення частот у відповідністю з формою коливань. Показано, що теоретично розрахований спектр молекули $(SiO_2)_{20}(H_2O)_{10}$ узгоджується із експериментальним спектром наносфер, а тому молекулу $(SiO_2)_{20}(H_2O)_{10}$ та її вищі гомологи можна використовувати при квантовохімічних розрахунках властивостей синтезованих порожнистих наносфер ($d \approx 290$ нм).

Ключові слова: порожнисті сферичні молекули діоксиду силіцію, ІЧ-спектроскопія, метод функціоналу густини.