Quantum Chemical Simulation of Relaxation and Thermally Stimulated Processes: a Vibration Excitation-relaxation Stochastic Optimization

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A new method for theoretical examination of thermal inter-conversions via the space structure vibration excitation-relaxation stochastic optimization method has been proposed. The software to perform implementation of the methodology has been developed and tested on a silica $27SiO_2$ cluster. A set of thermodynamically probable space structures of amorphous silica particles and temperatures of their inter-conversions has been simulated. The simulated space structures have been verified by comparison of calculated inelastic neutron scattering spectra of different highly dispersed silicas with experimental ones.

Key words: Quantum Chemistry; Semi-empirical Method; Silica; Thermo-chemical Processes; PM3.

1. Introduction

Amorphous silicas obtained by gas phase processes are widely used in modern optics [1]. Amorphous matter [2 – 4] can be considered as a branching graph, the nodes corresponding to space structures (considered as constitutional isomers) refering to the local energy minima. The minima are separated by energy barriers, significant for constitutional isomer isolation but low enough to enable time-expanded permanent relaxation processes. The temperature is a driving force of the aforementioned process. The standard quantum chemical (QC) computational procedure does not consider the temperature. In the present work it has been introduced into the QC simulation as stochastic deviation of atoms around their equilibrium positions. In order to determine the pathways of the graph branching, an effective methodology and corresponding software has been developed.

The starting object, chosen for the verification of the methodology, is a $27SiO_2$ silica cluster formed by the condensation of $27SiO_2$ molecules and simulated by the QC technique in [2].

In [2] the graph branching and the results of the $27SiO_2$ simulation are discussed in line with experimental inelastic neutron scattering (INS) spectra of different silicas, which have been collected in order to verify the simulations.

2. Experimental

2.1. Materials

The silica glass was produced by Alcatel, France. Commercial high purity amorphous fumed silica (HDK®) was supported by Wacker Chemie GmbH, Germany. The fumed silica samples were heated in air at 1273 K for 6 h and then cooled at room temperature in air to purify them from organic impurities. Silica fume was supported by ELKEM ASA (purity 98% mass).

2.2. Methods

The INS spectra of all samples were measured in the frequency range $10 – 10000$ cm^{-1}, using the inverted geometry time-of-flight spectrometers KDSOG and NERA, installed in an IBR-2 nuclear pulse reactor at the Joint Institute for Nuclear Research, Dubna, Russia [5]. All spectra were recorded at 10 K to reduce the Debye-Waller factor. Pyrolytic graphite analyzers with a resolution of ca. $2 – 3\%$ $\Delta E/E$ (NERA) or $4 – 8\%$ $\Delta E/E$ (KDSOG) have been used. The finely ground

samples of known weights (approximately 185 g) were uniformly loaded into aluminium foil sachets and mounted onto a centrestick which was placed in a closed-cycle refrigerator. The samples were then stored for cooling to 10 K, and the INS spectra were recorded.

COSPECO software [16] has been used to simulate the INS spectra. The experimental spectra have been used to solve the inverted vibration problem for the QC simulated clusters.

3. Methodology and Computation Methods

3.1. Vibration Excitation-relaxation Stochastic (VERS) Optimization Methodology. Cluster Approximation

The thermal motion of atoms might be considered as relative atomic deviations from certain equilibrium positions. In the current work this process is assumed to be completely stochastic, the vector of each atomic deviation being independent of vibrations of other atoms. Since the fluidity of amorphous matter can be treated as that of a liquid [7], the number of subsequent excitations must be examined in order to simulate the thermal process correctly. Also, one can assume that the time of the thermal excitation is much smaller than that of the thermal relaxation process inside the node. Thus, these two processes might be considered separately.

The majority of the space structure optimization methodologies and software (MOPAC [8], Gaussian [9] and GAMESS [10]) are related to the local minimum search, while the global minimum search is based on the empirical potentials [11, 12] or the high-level *ab initio* derived potential [13]. The methodology proposed in the present article is intermediate between the aforesaid ones.

Semi-empirical (PM3) quantum chemical software "QuChem" has been used for the local structure optimization of the system under study. The starting cluster for the simulation is one of the local minima, which is preliminarily defined by standard local optimization methods [2]. A stochastic shift is applied to the Cartesian coordinates of each atom in the examined cluster at its local minimum space structure. The value of the shift can be defined in two ways, using amplitude random distribution or impulse random distribution by (1) and (2), respectively:

$$X'(i) = d(s - d/2)X(i), \qquad (1)$$

$$X'(i) = [d(s - d/2)X(i)]/m_i, \qquad (2)$$

where $X(i)$, $X'(i)$ are the starting and the shifted Cartesian coordinate of the atom i, d is the input maximal deviation, s the randomly distributed number ranging from 0 to 1, and m_i the atomic mass of the atom i.

The aforementioned procedure may invoke collisions between atoms, which lead to unconvergency during the QC self-convergence field computations. In order to prevent this, the approachment of atoms to less than 0.5 Å is prohibited.

After complete coordinate randomization an excited ("shacked") structure is put into the 'QuChem' program for the local optimization by the PM3 method. Then a preliminary optimization of 100 – 150 steps is performed. The partly optimized, i.e. relaxed space structure is used for the next coordinate randomization procedure. The excitation-relaxation cycle is repeated up to the preset number of steps.

Each step of the excitation-relaxation cycle is stored in the individual directory, where the optimization is continued up to a gradient limit in order to localize the energy minimum with high accuracy. $\Delta_f H$ is QC evaluated for the space structure, corresponding to the energy minimum. The two-step procedure, including the excitation-relaxation cycle and the localization of the energy minimum, has shown high efficiency.

The coordinate randomization can be considered in a term of thermal vibrations. The difference between the heat of formation for the starting structure ($\Delta_f H_0$) and the heat of formation of the "shacked" structure ($\Delta_f H_{excited}$) might be understood as the additional energy of the vibrational degree of freedom or heating of the system under study. Henceforth the standard enthalpy of formation $\Delta_f H^0_{298.15}$ is denoted as $\Delta_f H$. Since individual molecules or clusters are considered, rotation and translation degrees of freedom can be neglected.

In this case the following formula is proposed to estimate the temperature increment, referring to transition into the excited state:

$$\Delta T = (T_{excited} - 298 \text{ K}) = (\Delta_f H_{excited} - \Delta_f H_0)/R, \quad (3)$$

where $R = 1.9872$ kcal mol^{-1} K^{-1} is the gas constant and $\Delta_f H$ is in kcal mol^{-1}. Since the parameters of semi-empirical methods, like AM1 and PM3, are defined at 298 K, the ΔT value shows the excess over 298 K.

But it is necessary to take into account that the $T_{excited}$ is not the temperature of the macroscopic system but only the excess of internal energy on the vibrational degree of freedom. So the relation between the

estimated ΔT and the thermal vibrations may qualitatively simulate the real system.

3.2. The Criteria for the Structure Analysis of Optimized Clusters

The following three criteria were used for the structural analysis of the clusters, corresponding to the energy minimum, obtained on the second step of the two-step procedure (see Section 3.1.).

1.) The Wiberg index for the bond (W_{AB}) as measure of the bond order distribution analysis [14] is determined basing on the value of the interaction between the atomic orbitals of two atoms. The corresponding equations for the semi-empirical Neglected Differential Overlapping quantum chemistry methods were discussed in [15].

2.) The coordination number of the atom is defined as an integer number of significant chemical bonds with neighbor atoms.

An atomic index, i.e. the sum of Wiberg indexes for each atom (W_i), is used in order to determine the significant chemical bonds. W_i is defined by summing W_{AB} over B neighbors around A. The atomic index W_i is independent of the type of atom. It reflects the atomic valence, i. e., the number of electrons participating in the covalent bonds between the atom i and neighboring ones. From the QC point of view one can define W_i as a coordination number of the atom i. The bond AB is considered as significant if $W_{AB} \geq (W_i/N)$, where N is the number of neighboring atoms around the atom i. This approach was used for plotting the atomic valence distribution function.

3.) The relative volume (V_R) of a cluster was used to estimate the cluster volumetric changes at each step of the VERS optimization through the formula

$$V_R = V/V_0, \qquad (4)$$

where V is the volume of the VERS simulated cluster calculated by the formula

$$V = \left(\frac{1}{n} \sum_i^n \sum_j^n r_{ij} \right)^3 . \qquad (5)$$

V_0 is the volume of the starting $27SiO_2$ cluster equal to 303.2 Å^3, r_{ij} is the interatomic distance, and n the number of atoms in the cluster. Formula (5) allows to find the relation between volumes of different clusters without direct volume calculation.

4.) The vibrational characteristics of the clusters have been analyzed in order to verify QC simulated models, using experimentally recorded and theoretically simulated INS spectra applying the COSPECO software [16].

4. Results and Discussion

The silica cluster $27SiO_2$ has previously been simulated by the condensation of 27 free silicon dioxide molecules using the QC PM3 method [2]. The cluster has been verified by comparison of the simulated radial distribution function and vibration spectra with the experimental data. The structure of the cluster in the first local minimum is shown in Figure 1.

VERS simulations have been performed with maximal atomic deviations d of 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 Å. $\Delta_f H$ versus the stochastic step is plotted in Figure 2. The step zero denotes the starting $27SiO_2$ cluster.

The VERS simulation for $d = 0.2$ Å leads to $\Delta T = 400$ K according to (3). The $\Delta_f H$ dynamics versus the number of excitation-relaxation cycles is shown in Figure 2a. One can see that after some ineffective cycles the criterion function for minimization of $\Delta_f H$ decreases. The VERS simulations with higher d cause constitutional changes in the cluster structure, i.e. the chemical reaction.

Summarizing the results of the VERS simulations, one can conclude that its procedure is controlled by 2 parameters, namely the maximal atomic deviation (d) and the number of optimization steps for each point. The parameters correspond to the value of the heating and the rate of relaxation, respectively. It should be mentioned that the rate of heat dissipation is compatible with the rate of relaxation. The different conditions of thermal treatment can be simulated by varying the parameters.
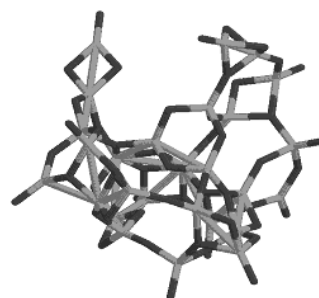

Fig. 1. Starting cluster $27SiO_2$ at the first local minimum. Black, O; gray, Si.

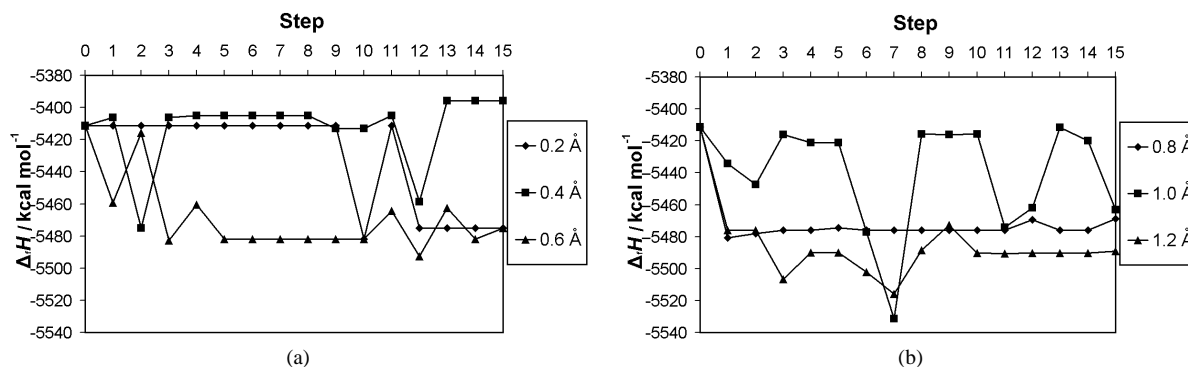Fig. 2. The standard heat of formation ($\Delta_f H$) for the cluster $27SiO_2$ vs. the stochastic step (a) for $d = 0.2 - 0.6$ Å and (b) for $d = 0.8 - 1.2$ Å.
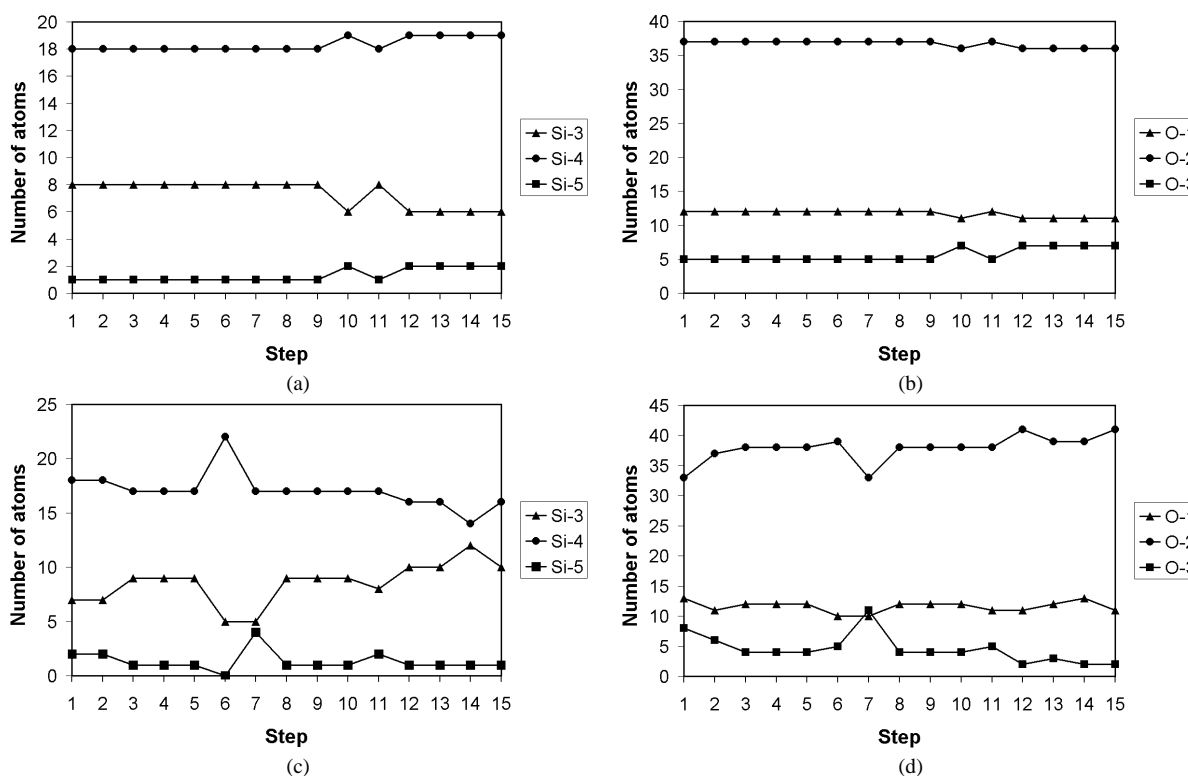

Fig. 3. Silicon and oxygen coordination numbers for the cluster $27SiO_2$ vs. the stochastic step number (a, b) for $d = 0.2$ Å and (c, d) for $d = 1.0$ Å.

According to [16] the chemical reaction (corresponding to the "minimum to other minimum" transitions in the terms of the potential energy surface conception) depends not only on the initial energy of the heating but also on the distribution of the energy excess on the vibration degrees of freedom (corresponding to the directions of atomic displacements in the framework of the VERS methodology). Sometimes the

heating may be distributed on the vibration degrees of freedom in such a way that no chemical reaction occurs. Since the atomic displacements are stochastic in the framework of the VERS methodology, this distribution is not controlled.

If the number of optimization steps is relatively small, the heat energy during the VERS optimization can be accumulated. In this way the chemical reac-
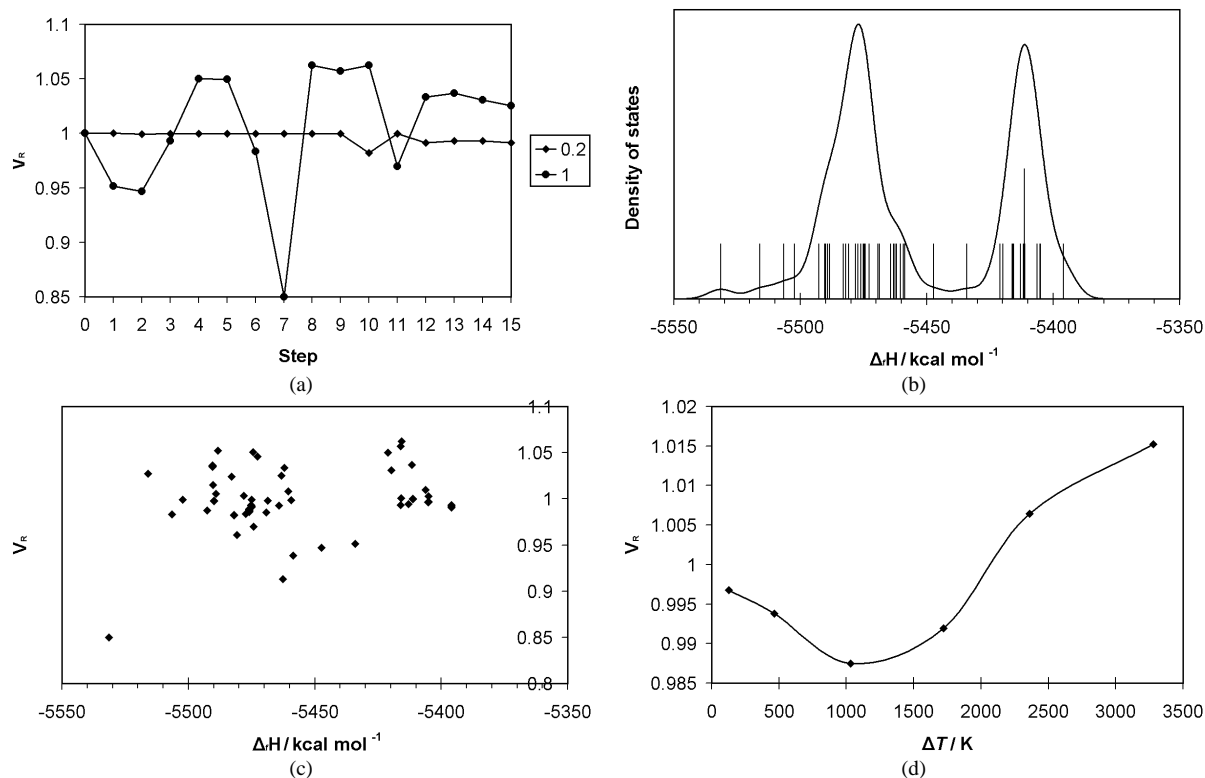
Fig. 4. The statistical properties for the system under study. (a) The relative volume of the 27SiO$_2$ cluster (V_R) vs. the stochastic step for $d = 0.2$ Å and $d = 1.0$ Å. (b) The density of states as a function of the standard heat of formation ($\Delta_f H$) for the cluster 27SiO$_2$. (c) The relative volume of the 27SiO$_2$ cluster (V_R) vs. the standard heat of formation ($\Delta_f H$). (d) The relative volume of the 27SiO$_2$ cluster (V_R) vs. the temperature increment (ΔT), referring to the transition into the excited state.

tion might occur even when the energy barrier is higher than the $\Delta_f H$ increase on each cycle of the VERS procedure. But this measure is effective only to some extend, since the accumulation of the energy on the vibration degree of freedom is limited by the capacity of the vibrational levels of freedom referring to the cluster size.

The distribution of coordination numbers of the Si and O atoms is observed as was shown in [2]. The silicon atoms may be 3-, 4- and 5-fold coordinated, while the oxygen atoms are 1-, 2- and 3-fold coordinated. The one-fold coordinated oxygen atoms are typical for the surface and correspond to the active centers, which cause the high chemical activity of the CVD silica protoparticle [3, 4]. The bond orders between one-fold coordinated O and corresponding Si atoms (W_{Si-O}) are in a range of $1.427 \leq W_{Si-O} \leq 1.545$. Thus the surface one-fold coordinated O atoms are quasi-double bonded with Si atoms, containing no dangling bonds. The coordination number 2 is characteristic for the ordinary

silicon-oxygen compounds like quartz and cristobalite. Coordination number 3 is typical for high-pressure silica, e.g. stishovite and coesite. The change of the coordination number distribution (for Si and O atoms) at the VERS optimization is illustrated in Figure 3.

Only three types of the coordination numbers for Si atoms (3, 4 and 5) have been observed, except for step 7 at $d = 1.0$ Å, through the VERS optimization with all d values examined. The local $\Delta_f H$ minimum at step 7 ($d = 1.0$ Å) shows that it is the most stable among all studied clusters, and this structure contains one six-fold coordinated Si atom.

The coordination number 2 was not observed for the stable silica cluster structures. This Si atom configuration was detected only by the VERS procedure but not in any local minimum. The two-fold coordinated Si atoms tend to react with the neighboring atoms, increasing the coordination number. Consequently, the two-fold coordinated Si atoms may exist for a long time in specific conditions, but not in the bulk of the
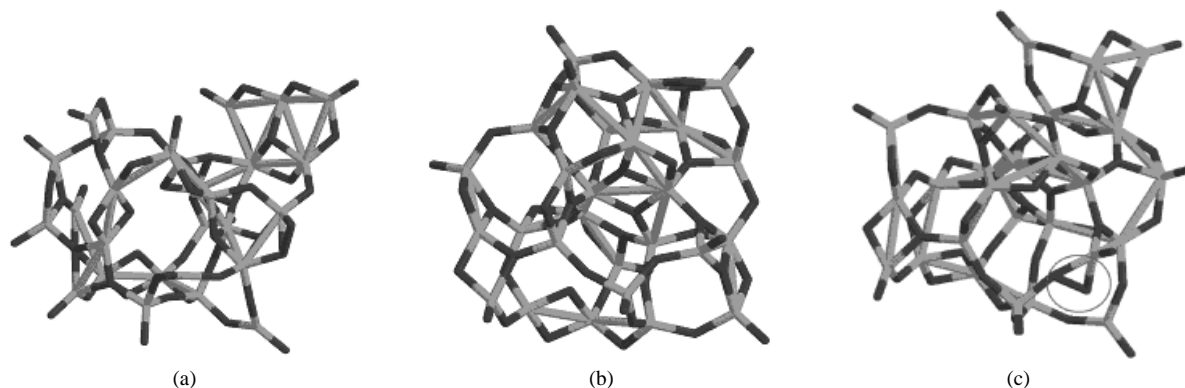
(a)   (b)   (c)

Fig. 5. Stochastically generated during VERS optimization 27SiO$_2$ clusters with maximal standard heat of formation ($\Delta_f H$) (a) at #(13−0.4) Å, (b) with minimal $\Delta_f H$ at #(7−1.0) Å, and (c) at #(11−1.0) Å with a marked oxygen deficient center.

silica. Analyzing Figs. 2a and 3, one can conclude that decreasing $\Delta_f H$ is accompanied by coordination number changes and structural reorganization of the 27SiO$_2$ cluster. This can be clearly seen in Figure 4. V_R and $\Delta_f H$ change symbately, and the $\Delta_f H$ minima correspond to the minima of V_R.

The structure of the cluster under examination at step N and $d = x$ is denoted as #$(N − x)$ Å. Two structures of the silica clusters 27SiO$_2$, which correspond to the extremes on the $\Delta_f H$ curve, are shown on Fig. 5a (maximal, #$(13 − 0.4)$ Å) and Fig. 5b (minimal, #$(7 − 1.0)$ Å). A spongy and disordered structure (Fig. 5a) is characteristic for the 27SiO$_2$ cluster with maximal $\Delta_f H$ (−5395.91 kcal/mol) in contrast to the compactly packed one (Fig. 5b) with minimal $\Delta_f H$ (−5531.50 kcal/mol). The V_R value of the cluster #$(13 − 0.4)$ Å (0.9919) is more than one of the cluster #$(7 − 1.0)$ Å (0.8499). The VERS simulations illustrate the mechanism of the small silica particle sintering into the silica glass, and can explain why the silica glass decreases the volume and increases the density at the annealing.

Atypical fragments like "non-bridged" oxygen atoms or oxygen deficient centers can be observed in some structures obtained by the VERS simulations. The fragments are widely discussed as one of the oxygen defects in silica optical glass [17]. These defects can act as the luminescence quenching centers. The defects are chemically active groups, responsible for the optical glass reactivity, the generators of additional absorption bands in electronic spectra of silica optical glass and are the sources of nonlinear effects. The formation of these defects is still questionable. The VERS methodology enables explaining the way of the defect

formation. Consequently, this methodology can be a valuable tool in the elucidation of the mechanism of glass defect formation.

As the d increases up to 0.8 Å (refering to $T_{excited} \sim$ 1473 K) (Fig. 4) V_R decreases and the vibrationally excited cluster stabilizes thermodynamically. This corresponds rather well to the experimental temperature of sintering of amorphous silica occurring at $T = (1373 − 1573)$ K [18]. Further increase of d up to 1.2 Å leads to an increase of V_R, which reproduces the melting silica.

Therefore, the VERS simulation of silica heating from 298 to 3473 K gives the models for slightly relaxed highly amorphous silica (fumed silica), sintered silica (at about 1473 K) and fused silica, i.e. silica glass (high temperature, relaxed structures). Aforementioned models can be further used for simulation of chemical reactions as it has been already done for fumed silica [2, 4], vibrational spectra and physical properties of different silica forms.

The INS spectra of the theoretical models have been simulated in order to verify the results. The 27SiO$_2$ cluster at point #$(7 − 1.0)$ Å (Fig. 5b), at the starting point (Fig. 1), and at the starting point after reaction with water reported in [2] has been used to simulate the spectra of silica glass (Fig. 6b), of silica fume (Fig. 6c) and of fumed silica (Fig. 6d). The good coincidence between calculated for the small clusters and experimentally registered INS spectra confirms that the VERS methodology leads to reasonable results.

5. Summary

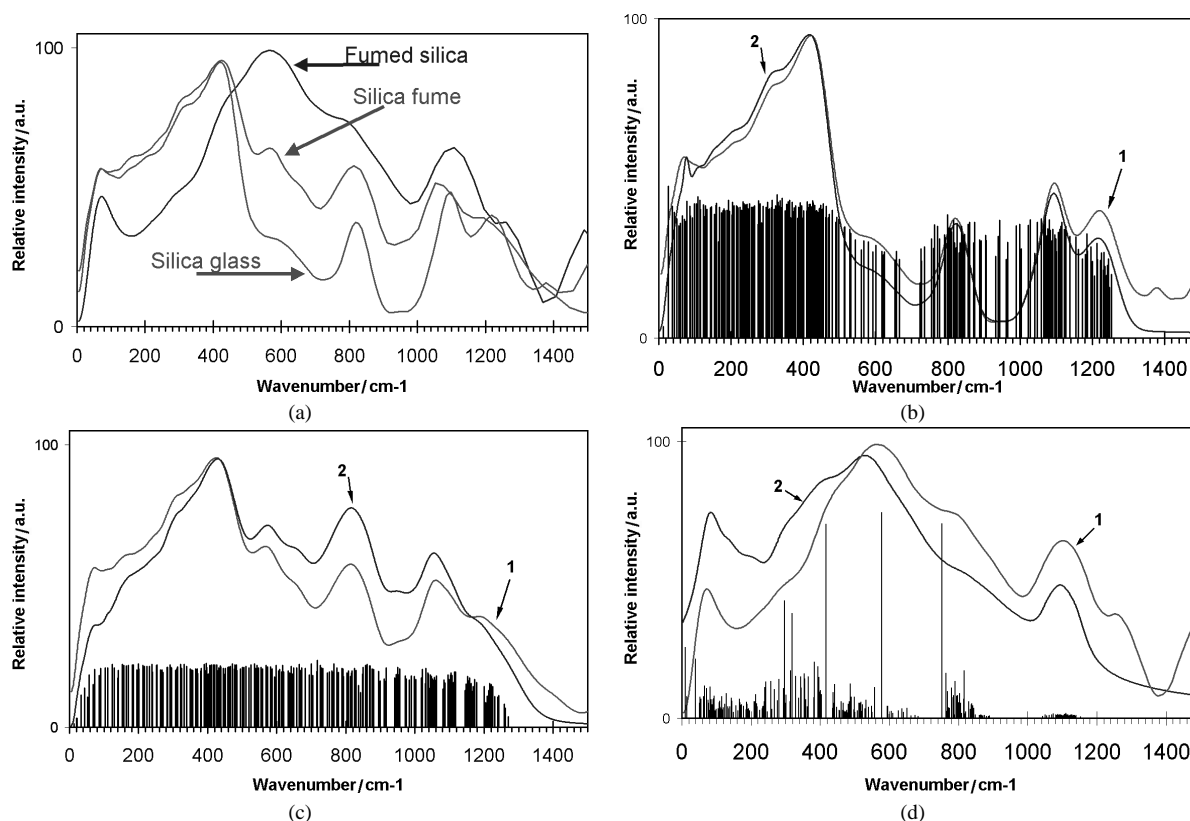The approach has been proposed to simulate thermo-chemical processes with QC methods. The

Fig. 6. Experimental and quantum chemically simulated inelastic neutron scattering (INS) spectra of silica glass, silica fume and fumed silica. (a) Experimental INS spectra for the silicas. (b) INS spectra calculated for the dense packed silica $27SiO_2$ cluster at #$(7 - 1.0)$ Å (1) and experimental one (2) for the optical silica glass. (c) INS spectra calculated for the initial silica cluster $27SiO_2$ (1) and experimental one (2) for the silica fume. (d) INS spectra calculated for the $27SiO_2$ silica cluster reacted with H_2O (1) and experimental (2) for the fumed silica. Delta-function of vibrational modes are represented as thin solid sticks in all figures.

methodology of the VERS procedure, which may be implemented into any computational model, has been developed and tested on the silica $27SiO_2$ cluster at heating. The thermal, chemical, and structural properties of amorphous substances can be studied applying the VERS procedure as a tool. The clusters obtained on different stages of heating can reproduce the relative volume, the coordination number distribution and the INS spectra of real objects, e.g. fumed silica, silica fume and silica glass.

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