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Chemically-bound xenon in fibrous silica†

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High-level quantum chemical calculations reported here predict the existence and remarkable stability, of chemically-bound xenon atoms in fibrous silica. The results may support the suggestion of Sanloup and coworkers that chemically-bound xenon and silica account for the problem of “missing xenon” (by a factor of 20!) from the atmospheres of Earth and Mars. So far, the host silica was assumed to be quartz, which is in contradiction with theory. The xenon-fibrous silica molecule is computed to be stable well beyond room temperature. The calculated Raman spectra of the species agree well with the main features of the experiments by Sanloup *et al.* The results predict computationally the existence of a new family of noble-gas containing materials. The fibrous silica species are finite molecules, their laboratory preparation should be feasible, and potential applications are possible.

It is well known that the atmospheres of Earth and Mars are depleted in Xe by a factor of 20 in relation to other noble gases.¹ Over 99% of Xe was degassed from the Earth's mantle.² The “Missing Xenon” issue is a mystery of nature that modern chemistry is trying to solve, and in view of this the possible existence of chemically-bound xenon species in natural environments is receiving attention by researchers in several laboratories.^{3–6} Considering the fact that Earth's core is unlikely to be the xenon reservoir,^{7,8} several explanations have been suggested. A recent one proposed by Sanloup *et al.*⁹ states that missing xenon might be bound in quartz like minerals. Arguments were presented claiming that the missing xenon issue cannot be explained by entrapment in ices¹⁰ or water clathrates.¹¹ Models of early escape from the atmosphere¹² and sediments¹³ also encounter major difficulties, Sanloup's theory seems at present to be the most likely explanation.

Sanloup and coworkers successfully trapped some xenon in α -quartz under high pressure but no details on microscopic structure or bonding were reported. This motivated several studies. Brock and Schrobilgen synthesized XeO_2 ¹⁴ and showed that it may under some conditions behave very similarly to SiO_2 , which supports Sanloup's results but proposed that the xenon insertion mechanism is rather endothermic and not necessarily spontaneous. The DFT calculations by Probert¹⁵ found possible geometries in quartz for xenon entrapment, but no chemical bonding was demonstrated for the noble gas atoms.

In this work we explore the possibility of chemically-bound xenon atoms in a finite silica molecule. Xe-silica chemical bonding is calculated and its stability determined. Microscopic and bonding properties and their possible relevance to the “missing Xe” issue are discussed later. The predictions made here introduce a new family of noble-gas compounds with very interesting properties.

The problem with Xe-quartz bonding is the nature of neighborhood Xe prefers. Among the most stable known Xe compounds we find linear structures (noble gas hydrides, XeF_2), planar squares (XeF_4 , XeO_2) or octahedral geometries (XeF_6) while the quartz environment is enforcing tetrahedral-like structure which seems to be incompatible with Xe orbitals, therefore, not stable. There are very few known cases of Xe compounds with tetrahedral coordination, of which XeO_4 is the most established.¹⁶ However, XeO_4 is thermodynamically unstable, and decomposes spontaneously. There is no case of well established, thermodynamically stable tetrahedrally coordinated Xe.

Thus, there are strong reasons for exploring systems other than quartz for possible binding of Xe in silica. A large variety of different forms of SiO_2 are found in nature. This, combined with the striking similarities between SiO_2 and XeO_2 , leads to at least one possible solution.

In searching for possible embeddings of Xe in silica, non-crystalline silicates can and should be considered. Different polymorphs of silica, amorphous silica and other systems are sufficiently present in nature to be considered. Here, a finite silica molecule will be examined for the binding of Xe atoms. It may not only give the answer to the “Missing Xenon” problem, but also suggest the existence of a new and very interesting family of noble-gas compounds.

The first noble-gas compound was prepared by Bartlett, in a celebrated paper from 1962.¹⁷ Since then, fluorine atoms,

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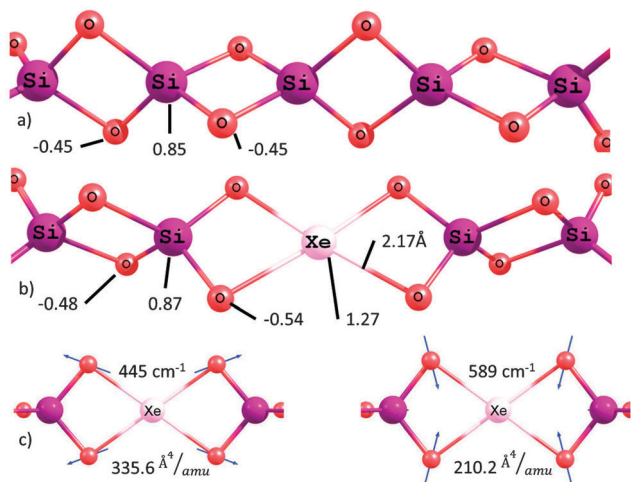


Fig. 1 (a) Geometry of fibrous silica chain, numbers on atoms represent partial charges from NBO analysis (b) geometry of fibrous silica chain substituted with Xe, numbers on atoms represent partial charges from NBO analysis and the number for bond is its length in angstroms (c) vibrations associated with the most characteristic Raman peaks for fibrous silica substituted with Xe together with Raman intensities.

or other highly electronegative elements, were involved in the great majority of the noble-gas compounds that were prepared. Among the important recent developments in noble-gas chemistry is the family of noble-gas hydrides, prepared by Räsänen and coworkers.^{18–23} These species have presented a bonding motif that does not require always elements of highest electronegativity. The compounds predicted here share much in common with regard to the bonding motif with the known noble-gas compounds, but introduces new structures, and higher stability.

Of the variety of different silicates that are significantly present in terrestrial environments, we consider here fibrous silica.²⁴ Fibrous silica has a structure similar to SiS_2 where every silicon atom is connected to another silicon atom through two Si–O–Si bridges making long chains as shown in Fig. 1. This environment offers a great advantage over quartz for binding to Xe. When looking at the single chain of fibrous silica (see Fig. 1) Si atoms have tetrahedral geometries. If a single Si atom is replaced with a Xe atom, one side of the chain can twist making a planar square neighborhood for Xe and keeping tetrahedral neighborhood for all Si atoms.

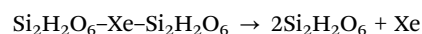
The equilibrium structure of the Xe substituted fibrous silica molecule, the pathway and energetics of the decomposition of the species were computed. These calculations throw light on the chemical stability of the compound. Calculations of decomposition, which is a bond-breaking process are computationally demanding. Thus, standard DFT calculations are not reliable for this purpose. Therefore, for reliable, accurate calculations of the decomposition the coupled cluster CCSD(T) method was used. This method is known to give satisfactory results up to the transition state even for the homolytic bond breaking.²⁵ To confirm the reliability of the results, we compared them with the multireference method MCQDPT, which treats homolytic bond breaking more rigorously,²⁶ but which is computationally too demanding for a calculations of the whole process. The high level of calculation we carried out set a

limit on the size of the molecule that could be considered. We used a short chain of fibrous silica with 5 silicon atoms and OH terminations on both sides of the chain. The middle Si atom was removed and replaced with a Xe atom, yielding the model system of the present study.

The structure formed by replacing the middle Si atom with Xe has a minimum energy geometry with Xe bound to oxygens as shown in Fig. 1b. Bond order analysis shows that there are four equivalent single Xe–O bonds and the Xe atom has a very large positive charge in this structure. The charges on silicon atoms remain basically unchanged in Xe insertion. There is also no sign of any interaction between the OH termination of limited fibrous silica chain with the Xe neighborhood indicating that the size of the chain is not important.

In considering the stability of this molecule, it seems that there are two likely channels for its decomposition (Fig. 2).

One channel is the 3-body channel similar to the known 3-body channel for decomposition of noble gas hydrides.^{22,23} In this case it follows the equation:



The barrier for this decomposition is $45.2 \text{ kcal mol}^{-1}$ according to CCSD(T) method. CCSD(T) overestimates the barrier for 3-body decomposition. To check if this happens also here we performed single-point energy calculations with an appropriate method (MCQDPT) on geometries taken from CCSD(T) calculation. The barrier is then slightly decreased to $\sim 42 \text{ kcal mol}^{-1}$. The barrier is slightly smaller, but remain very high for noble gas compounds. Such a barrier suffices for room temperature stability of the compound.

A more intuitive channel for decomposition is the one where either a Xe atom or xenon oxide is formed and shorter fibrous silica chain is recreated in a 2-body channel. Computationally, however, we could not find a decomposition path where xenon oxide is a direct product. However, there is a channel for Xe atom leaving the system and shorter fibrous chain is obtained with two peroxide defects as in Fig. 3. Peroxide Si–O–O–Si linkages were already proposed as an intermediate for formation of Xe compounds with silica structures.¹⁴

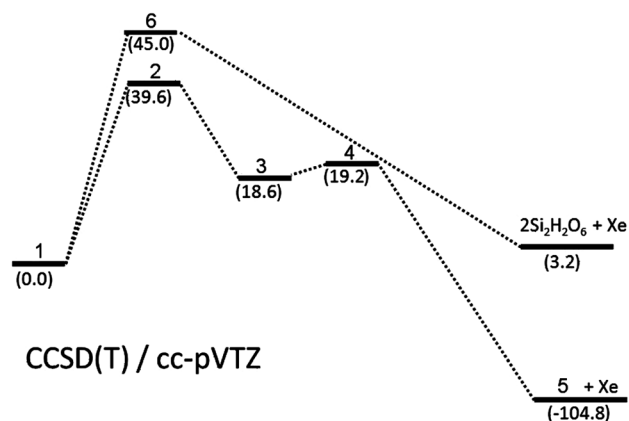


Fig. 2 Energy diagram for decomposition of fibrous silica substituted with Xe. The numbers correspond to the relative energies in kcal mol^{-1} .

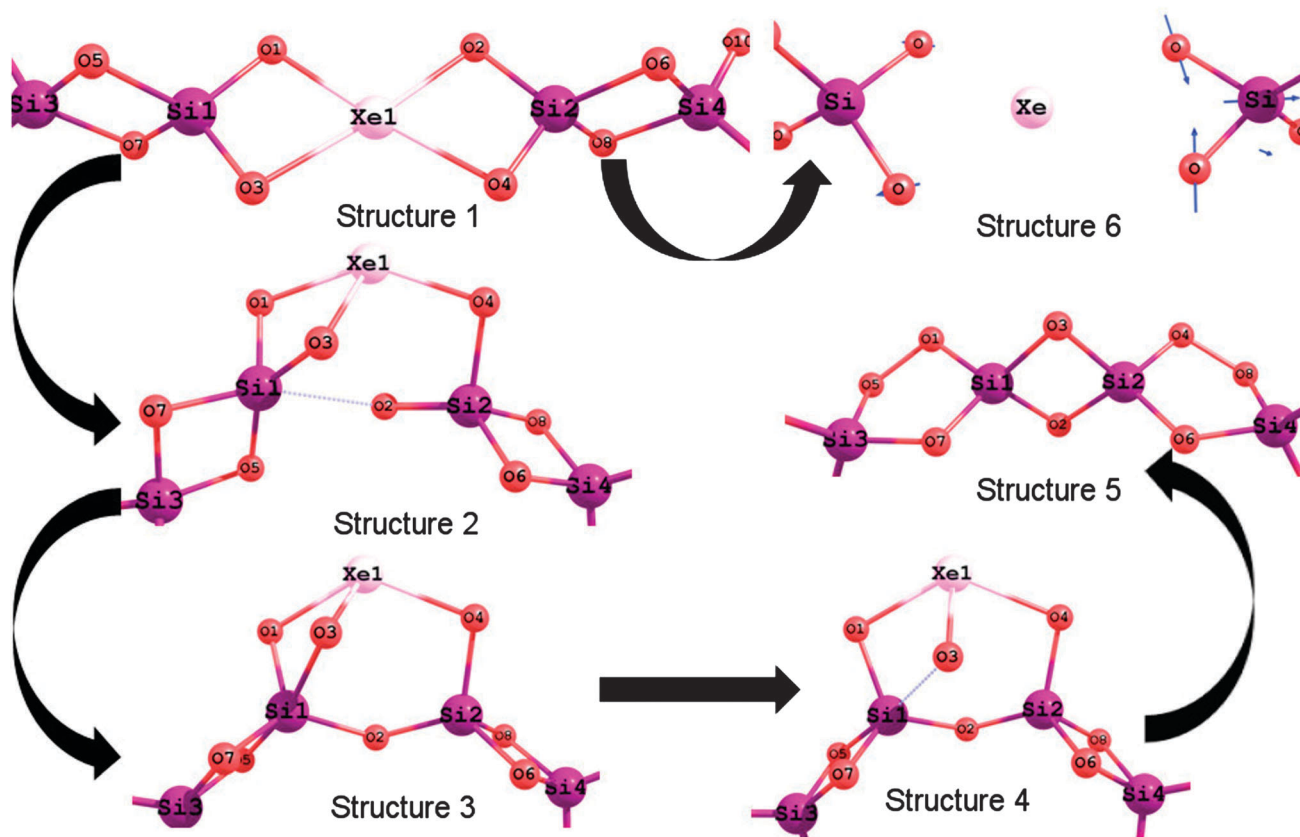


Fig. 3 Stationary points for decomposition of fibrous silica substituted with Xe.

The barrier for this channel is equal to $39.6 \text{ kcal mol}^{-1}$ by the CCSD(T) method and with a correction from MCQDPT it is even higher ($40.8 \text{ kcal mol}^{-1}$). Thus the barrier for 2B channel is lower than the 3B channel but it still guarantees very high stability even at room temperature. According to transition state theory this fibrous silica molecule substituted with xenon has practically infinite lifetime at 300 K. Since the decomposition is highly exothermic, the compound should be classified in principle as metastable rather than stable, but for all practical purposes it is expected to behave as thermodynamically stable material at room temperature.

In view of the stability of the predicted compounds, calculations of spectroscopic features that may serve as signatures for identification are obviously of interest. We computed the Raman spectrum of the compound, and compared with calculations of common silicates. Two peaks were found that are characteristic for chemically-bound Xe in the fibrous silica. These correspond to the two vibrations shown in Fig. 1c. Similar frequencies has been found in Sanloup's experiment on quartz.⁹ Especially the lower frequency vibration, initially assigned to XeO_4 , and later reassigned to XeO_2 ¹⁴ seems to fit even better a Xe atom bound in a chain. Even though Sanloup's measurements were done on α -quartz this agreement suggest an interesting explanation to the "missing xenon" issue. Fibrous silica is known to exist in nature.^{27,28} It is a matter of speculation at this stage how such Xe-silica compound may have formed in Earth's crust from Xe gas. It could be that the conditions of formation were of high temperature and pressure

that prevailed when the Earth was young. This is compatible with the ideas of Sanloup and coworkers for other silicates. However, while high pressure and temperature may have provided the activation mechanism in the formation stage, it should be stressed that high pressure is not required for the existence of Xe in fibrous silica. Interesting recent work by Sanloup and coworkers²⁹ demonstrates the formation and stability of new Xe-water compounds at high pressure. These compounds, however, require pressures at the GPa range for their existence.

In conclusion, using high level methods of quantum chemistry we predict that chemical bonding between xenon and fibrous silica is stable at ambient temperatures and pressures. It seems that the stability of Xe-silica compounds is a matter of forming a planar square surrounding of oxygens for Xe atom. High stability of such bonding between silicates and Xe is very promising in the search for xenon containing silicates in nature as well as in the pursuit of new noble gas compounds between Xe and silicates in the laboratory. These will be stable at room temperatures. Finally, the high stability of xenon binding inside silicates supports the explanation of Sanloup *et al.* for the missing xenon. In this respect, the agreement between the Raman spectrum computed for the predicted compound and that measured by Sanloup *et al.* is very encouraging and future Raman calculations on large clusters of silica with xenon defects could be very useful in searching and identifying xenon in silica materials.

Room temperature stability of these species is predicted here only for unimolecular decomposition channels. High stability in

respect to unimolecular decomposition channels may not always suffice for long lifetimes in real environments where decomposition may follow bimolecular channels involving other silicates or water. However, unimolecular channel is the most important for the molecule to exist and very often unimolecular stability is sufficient for further experimental studies on isolated species.

The predicted Xe compound is a finite-size molecule, yet the results suggest that there is a whole family of species with Xe bound in fibrous silica segments of different lengths. Our findings suggest little interaction between the Xe atom and the termination of the silica chain, and all of these are expected to be stable at room temperature. Experiments in Xe matrices at very high pressures may be a possible approach for the preparation of those compounds, and for studying their properties. There is the intriguing possibility that Xe–fibrous silica compound may serve for storage of Xe at high densities and at room temperatures, for which potential technological applications exist.³⁰

Methods

Most of quantum chemical calculations presented here are done using CCSD(T) method with Dunning's cc-pVTZ^{31,32} basis set. For stationary points additional single point calculations were carried in order to confirm the reliability of CCSD(T) for the barriers. Additional single point calculations were done using MCQDPT^{33–36} method with active space constructed from 12 electrons in 12 orbitals. CCSD(T) calculations were done using numerical forces and NWChem³⁷ code for obtaining single point energies. Frequencies were obtained calculating Hessians by numerical differentiation also with CCSD(T)/cc-pVTZ and were corrected on anharmonicity using only the diagonal approximation for selected modes.³⁸ Partial charges and bond orders were calculated using NBO^{39,40} analysis. In all calculations the internal coordinates were used.

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