



## Ab Initio Calculation $^{29}\text{Si}$ NMR Chemical Shift Studies on Silicate Species in Aqueous and Gas Phase

Seyed Naser Azizi\*, Salma Ehsani Tilami, Fatematozzahra Mosavi

Analytical Division, Faculty of Chemistry, University of Mazandaran, Babolsar, Iran, P.O.Box: 47416-95447. Tel: + 98 1125342380, Fax: + 98 1125342350,

\*Corresponding author E-mail address: [azizi@umz.ac.ir](mailto:azizi@umz.ac.ir)

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**Abstract:** Nowadays NMR spectroscopy becomes a powerful tool in chemistry because of the NMR chemical shifts. Hartree–Fock theory and the Gauge-including atomic orbital (GIAO) methods are used in the calculation of  $^{29}\text{Si}$  NMR chemical shifts of various silicate species in the silicate solution as initial components for zeolite synthesis both in gas and solution phase. Calculations have been performed at geometries optimized at the  $\text{AM}_1$  semi-empirical method. The GIAO-HF calculations were carried out with using different basis sets: 3-21G, 6-31G, 6-311G, 6-31G (d,p), 6-311G (d,p), 6-311G (2d,p) and 6-31G (2d,p). To demonstrate the quality of the calculations the calculated chemical shifts,  $\delta$ , were compared with the corresponding experimental values for the compounds in study. The results, especially with 6-311G (2d, p) are in agreement with experimental values. Also the calculated chemical shifts on gas phase have more agreement than solution phase.

**Key words:** GIAO, HF,  $\text{AM}_1$ , and  $^{29}\text{Si}$  Chemical shift

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### 1. Introduction

Over the last four decades, techniques have been developed that have proved NMR spectroscopy to be a powerful method for both solution and solid samples. With regard to zeolites, thirteen NMR-active nuclei have been utilized in obtaining information on their structural features. The most directly relevant nuclei in zeolite studies have been  $^{29}\text{Si}$  and  $^{27}\text{Al}$ , although other nuclei, including  $^1\text{H}$ ,

$^{13}\text{C}$ , and  $^{17}\text{O}$ , may also provide framework or structural information about zeolites [1]. Identification of the silicate species present in solution plays a key role and  $^{29}\text{Si}$  NMR spectroscopy proved to be a powerful technique for this purpose [2, 3]. However, extracting information about individual events using only experimental data is difficult, the chemistry of silica species has also been studied extensively using theoretical techniques [3]. In this

study chemical shifts of four silicate species are calculated with HF theory at different basis sets in both gas and aqueous phase.

## 2. Theory

To simplify writing the various silicate species that can occur in solution, an abbreviated notation has been utilised to describe the structures. The use of "Q-units" was first proposed by Engelhardt et al. [4, 5] and they have been used by most investigators in later studies. In this notation, Q represents a silicon atom bonded to four oxygen atoms forming a tetrahedron. The superscript  $i$  indicates the connectivity, i.e. the number of other Q units attached to the  $\text{SiO}_4$  tetrahedron under study. Thus  $\text{Q}^0$  denotes the monomeric orthosilicate anion  $\text{SiO}_4^{4-}$ ,  $\text{Q}^1$  end-groups of chains,  $\text{Q}^2$  middle groups in chains or cycles,  $\text{Q}^3$  chain-branching sites and  $\text{Q}^4$  three-dimensionally cross-linked groups.

The notation  $\text{Q}^n$  for silicon in silicate solutions, and  $\text{q}^n$  for aluminium in aluminosilicate solutions, is well established and will therefore be used throughout this work. It should be remembered that the  $^{29}\text{Si}$  signal for each Q-unit is shifted by ca. 10 ppm to lower frequency when the number of siloxane bridges is increased by one.

Hartree-Fock self-consistent field (HF-SCF) approximation is the most of currently available quantum chemical methods for calculating NMR chemical shift [6-10]. The NMR shift calculations at the HF-SCF level are suitable for a wide range of chemical applications [11]. The problem of calculating the NMR chemical shift is twofold. First, the chemical shielding tensor  $\sigma$  is formally a second-order property. Such quantities are more difficult to

calculate than the corresponding first-order properties whose computation at correlated levels is nowadays a routine matter [12].

The second difficulty in the computation of NMR chemical shifts is the gauge-invariance problem which plagues all calculations of magnetic properties. When applied to a molecular system, the magnetic field  $B$  appears in the Hamiltonian only in form of the vector potential  $A$  whose origin, the so-called gauge origin, is not fixed. As long as the complete basis sets is used in quantum chemical calculations, the results are independent of the choice of the gauge origin. This is no longer true for calculations with truncated (finite) basis sets.

Despite the gauge-origin problem, a relatively large number of conventional (common gauge origin and, therefore, gauge dependent) NMR shift calculations using finite basis sets have been reported at SCF [13] and correlated levels [14-16]. To minimize the gauge-error, very large basis sets have to be employed and such calculations are restricted to small molecules. Although there is value in these calculations with respect to calibration, the chosen approach to the gauge-origin problem is not appropriate for investigating magnetic properties of medium sized or large molecules. More satisfying solutions to the gauge origin problem have been offered by approaches in which introduce local gauge origins to define the vector potential [16].

Within quantum chemical NMR shift calculations, this idea was first adopted by Ditchfield in his gauge-including atomic orbital (GIAO) method [6] in which each atomic orbital has its own local gauge origin placed on its center. The efficiency of the GIAO method has been significantly improved [8, 9, 10] and applications to large molecules at the SCF level

are now routinely possible. The GIAO method is conveniently formulated in terms of explicitly field dependent orbital. [6].

In this paper, The GIAO-SCF method applied for calculations of the  $^{29}\text{Si}$  NMR chemical shifts for silicate species by Gaussian Software. The GIAO methods for calculating the NMR chemical shifts utilize the following explicitly field-dependent basis function [6]:

$$\chi_{\mu}(\mathbf{B}) = \exp\left[\frac{-i}{2C}(\mathbf{B} \times \mathbf{R}_{\mu}) \cdot \mathbf{r}\right] \chi_{\mu}(0) \quad (1)$$

Where  $\chi_{\mu}(0)$  denotes the usual field-independent atomic orbital and the  $\mathbf{R}_{\mu}$  is their centers. At the SCF level the expression for the chemical shielding tensor of the nucleus N is given as:

$$\sigma_{ij}^N(\text{scf}) = \left[ \frac{d^2 E(\text{scf})}{dB_i dM_{Nj}} \right]_{B=0} \quad (2)$$

With  $B$  as the external magnetic field and  $M_N$  is the magnetic moment of the nucleus N. Equation (1) for the shielding tensor can be more explicitly written as:

$$\sigma_{ji}^N(\text{scf}) = \sum_{\mu\nu} D_{\mu\nu}^{\text{scf}} \frac{\partial^2 h_{\mu\nu}}{\partial B_i \partial M_{Nj}} + \sum_{\mu\nu} \frac{\partial D_{\mu\nu}^{\text{scf}}}{\partial B_i} \frac{\partial h_{\mu\nu}}{\partial M_{Nj}} \quad (3)$$

As the SCF density matrix and  $h_{\mu\nu}$  as the one electron Hamiltonian in the AO  $D_{\mu\nu}^{\text{scf}}$  with representation (for detail see reference [17]).

### 3. Calculations

#### 3.1. Hartree-Fock (HF) and Density Function Theory (DFT) chemical shifts

In order to predict accurate NMR chemical shifts for  $^{29}\text{Si}$ , it is necessary to access the accuracy of the available methods using lower levels of theory. Thus, a method is desired which will produce accurate chemical shifts at a reasonable cost. To obtain NMR properties in Gaussian, four levels of theory MP2, DFT, HF and Hybrid Function can be used. DFT method is not relative to Magnetic field [13] since for calculations NMR is not used.

The MP2 method is not used for two reasons one in the same conditions MP2 needs more CPU time in calculation[3], Secondly MP2 calculations in essence need larger basis sets. These problems and the relative large species in our study cause an excess of time and needs an advanced computer instead of PC.

The NMR shielding tensors are another property that can be computed in the context of a single point energy calculation. Such a calculation is requested by including the NMR keyword in the route section for the job in Gaussian [17] for example HF/6-31G\*\* NMR. We would run this job on silicate species at HF level using three Basis sets {6-31G\*\*, 6-31+G\*\* and 6-311+G (2d, p)}.

The output of each calculation gives the predicted value for each atom in the molecule in turn. Shielding constants reported in experimental studies are usually shifted relative to the standard compound, often tetramethylsilane (TMS).

In order to compare the predicted values with experimental results, we also need to compute the absolute shielding value for the TMS, using exactly the same model chemistry (level of theory, basis set, and method of geometry optimization). To obtain the predicted shift for the silicon atoms in species, we subtract its absolute value from that of the reference molecule.

The above mentioned GIAO methods have been implemented into Gauss view 03 and all calculations were performed using this program and Hyperchem. The calculations have been performed at geometries optimized at AM1 semi-empirical method. The GIAO-SCF calculations have been performed at the three basis sets and at Hartree-fock (HF) level.

On a comparative basis, the relative shielding constant  $\Delta\sigma_x$  (i.e. chemical shift  $\delta_x$ ) is defined as  $\delta_x = \Delta\sigma_{x(\text{reference})} - \Delta\sigma_{x(\text{species})}$  where  $\sigma_{x(\text{TMS})}$  and  $\sigma_{x(\text{species})}$  are isotropic chemical shielding constant,  $\sigma_{\text{iso}}$ , of nucleus  $x$  in the silicon species and interference molecule respectively.

The  $^{29}\text{Si}$  chemical shielding for TMS have also been calculated as reference.

### 3.2. The $^{29}\text{Si}$ isotropic chemical shift ( $\delta$ ppm) calculations

The  $^{29}\text{Si}$  isotropic chemical shifts ( $\delta$  ppm) have been calculated for the silicate species in figure 1 using Hartree-Fock Self-Consistent-Field (HF-SCF) theory and the Gauge Including Atomic Orbital (GIAO). The molecular geometries of the species of figure 1 were fully optimized at the AM1 semi empirical method at the three basis sets: 6-31G\*, 6-31+G\*\* and 6-311+G(2d, p) ( see figure 2).

All these calculations were carried out with Gaussian 03 programs. GIAO isotropic  $^{29}\text{Si}$  chemical shifts are given in table 1. In this table  $^{29}\text{Si}$  values is relative to TMS the normal standard is used as the reference for  $^{29}\text{Si}$ , i.e.  $\delta = (\delta_i - \delta_{\text{TMS}})$ , in order to compare directly with the experimental values [18,19]. In this study, the calculated values are compared with the estimated Hartree-Fock limits for the silicate species in figure 1.

The total range of calculated  $^{29}\text{Si}$  chemical shifts as the same of observed in the  $^{29}\text{Si}$  spectra of silicate and silicic acid solutions extended from about -60 to about -120 ppm. i.e. about 60 ppm. Within this range, five well separated subdivisions have been found which correspond to the five possible  $Q^n$  building units.

The peak of the monomeric silicate anion  $Q^0$  calculated value appears at the low field side, followed in a regular sequence by the  $Q^1$  to  $Q^4$  units shifted by about 10 ppm to high field for each newly formed SiOSi bond as the same as observed sequence values [18,19]. The results show that, second nearest  $Q^n$  neighbors and cyclization effects will affect the chemical shifts.

The results of chemical shift calculations are summarized in table 1 and 2. Note that we present relative shifts rather than absolute chemical shielding. Absolute value can be obtained with the chemical shielding given for the chosen reference compound.

There are several reasons for reporting relative shifts. First, only relative shifts are determined in the gas phase NMR measurements. The shielding constants are obtained only after converting the relative shifts to the absolute scale using the known shielding of at least one molecule.

The latter can be obtained from experimentally measured spin rotation constants, which yield the required paramagnetic contribution, and a theoretical calculation of the diamagnetic contribution. The uncertainty in absolute NMR shielding scale depends on the accuracy with which these values can be determined and is in some cases large, e.g. about 15 ppm for  $^{29}\text{Si}$   $Q^3$  unit at the 6-311+G (2d, p) basis set.

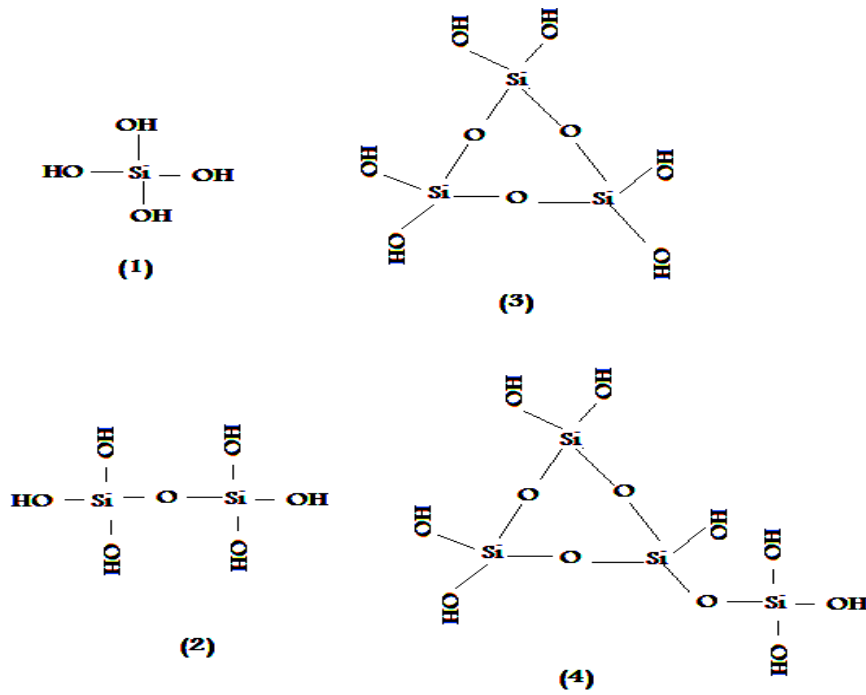


Figure 1: Silicate species in silicate solution

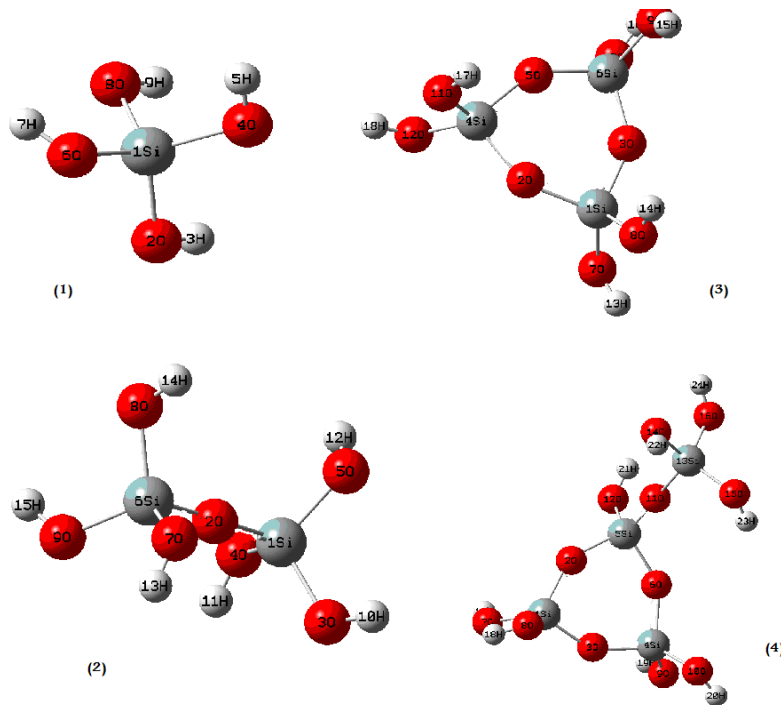


Figure 2: Optimized geometries of silicate species in gauss view

Table1: Calculated and experimental  $^{29}\text{Si}$  chemical shifts in aqueous phase

method number	3-21g	6-31g	6-311g	6-31g(2d,p)	6-311g(2d,p)	6-31g(d,p)	6-311g(d,p)	Experimental
1	-21.62	-28.52	-23.91	-56.78	-59.76	-49.19	-49.43	-73
2								
Si 1	-6.38	-29.76	-27.37	-73.29	-77.54	-64.78	-68.92	-82
Si 5	-5.36	-31.15	-27.74	-72.25	-77.31	-64.89	-68.47	-82
3								
Si 1	-40.54	-39.88	-35.92	-79.87	-84.42	-72.04	-75.48	-83
Si 4	-40.52	-38.40	-33.51	-80.84	-85.53	-73.16	-76.97	-83
Si5	-30.45	-39.33	-34.65	-80.86	-85.49	-73.13	-76.88	-83

Table2: Calculated and experimental  $^{29}\text{Si}$  chemical shifts in Gas phase

method number	3-21g	6-31g	6-311g	6-31g(2d,p)	6-311g(2d,p)	6-31g(d,p)	6-311g(d,p)	Experimental
1	-12.42	-56.80	-21.44	-88.90	-58.05	-47.36	-47.10	-73
2								
Si 1	-26.27	-26.98	-23.56	-72.70	-76.16	-63.42	-66.74	-82
Si 5	-28.24	-29.46	-24.77	-71.50	-75.50	-63.49	-65.83	-82
3								
Si 1	-29.26	-36.59	-41.01	-80.65	-84.51	-72.33	-74.92	-83
Si 4	-28.32	-38.44	-31.03	-81.58	-85.40	-73.37	-26.25	-83
Si5	-29.93	-38.39	-34.18	-81.77	-85.49	-73.49	-76.29	-83
4								
Si 1	-19.31	-26.80	-22.46	-74.02	-77.00	-64.45	-66.82	-83
Si 4	-49.24	-54.23	-51.64	-93.13	-99.97	-85.96	-91.38	-80
Si5	-27.47	-36.10	-33.30	-79.94	-84.90	-70.97	-75.55	-76
Si 13	-29.16	-37.34	-33.89	-80.42	-84.71	-72.18	-75.50	-83



Second, in chemical applications of NMR spectroscopy only relative shifts are measured and used for the interpretation of obtained spectrum.

Therefore, it seems natural to explore the computational requirements of NMR shift calculations with respect to relative shifts rather than to absolute shielding constants, we will discuss in the following mainly relative shifts, but comment in addition on the absolute shielding constants of our chosen reference compound TMS. Absolute shielding constants are also discussed for some silicate species.

#### 4. Result and discussion

The chemical shifts of the silicate species were calculated with standard Gaussian 03 program. Calculations have been performed with using different basis sets: 3-21G, 6-31G, 6-311G, 6-31G (d,p), 6-311G (d,p), 6-311G (2d,p) and 6-31G (2d,p) by RHF methods. In these methods, with the above basis sets, a geometry optimization was first performed for the molecule and for TMS.

The NMR shielding tensors were computed with the GIAO (gauge independent atomic orbital) method. Calculations have been performed at geometries optimized at the AM<sub>1</sub> semi-empirical method and for aqueous phase with pcm model.

Figure 1 shows some of silicate species in silicate solution and Tables 1 and 2 give calculated <sup>29</sup>Si chemical shifts which were obtained by NMR theoretical methods respectively in aqueous and gas phases. The results of the chemical shift calculations with the small basis sets are not accurate but the bigger basis sets specially 6-311G (2d,p) are in reasonable agreement with the experimental values.

Also the calculated chemical shifts in gas phase have more agreement than aqueous phase. Figure 2 shows the optimized geometry of silicate species in gauss view.

#### 5. Conclusion

The results of the chemical shift calculations with the small basis sets are not accurate. The results, especially with 6-311G (2d, p) are in reasonable agreement with the experimental values. The formation of three membered rings apparently causes some deshielding compared to chains or larger rings. Also the calculated chemical shifts on gas phase have more agreement than solution phase.

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