



Trade Science Inc.

January 2008

Volume 7 Issue 4

# Analytical CHEMISTRY

An Indian Journal

Full Paper

ACAJ, 7(4) 2008 [192-198]

## A study on the $Q^n(mAl)$ complexes by $^{29}Si$ NMR chemical shift calculation

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Received: 28<sup>th</sup> November, 2007 ; Accepted: 3<sup>rd</sup> December, 2007

### ABSTRACT

Valuable insights into  $Q^n(mAl)$  complexes can be achieved when the NMR results are combined with the calculated data.  $^{29}Si$  NMR chemical shift calculation has been used to investigate the  $Q^n$  local structures about the Si in a series of aluminosilicate solutions. By using the gauge-including atomic orbital method at the self-consistent-field and Hartree-Fock theory levels, the *ab-initio* calculations of the  $^{29}Si$  NMR chemical shifts for non cyclic or chain form oligomers of  $Q^n$  units of aluminosilicate species have been performed. The GIAO-HF-SCF calculations were carried out using, three different basis sets: 6-31G\*\*6-31+G\*\* and 6-311+G(2d,p). This data convincingly shows the right sequence of aluminosilicate anions through the different structures  $Q^n$ - $q^1$  connectivity. The results, especially with 6-31+G\*\* and 6-311+G(2d,p), with a few exceptions are satisfactory. Theoretical calculations of NMR spectroscopic properties can be very helpful and can provide the missing information.

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### KEYWORDS

GIAO;  
HF;  
DFT;  
 $^{29}Si$  Chemical shift, NMR;  
Zeolite;  
Aluminosilicate.

### INTRODUCTION

In the last three decades, techniques have been developed which prove NMR spectroscopy to be a powerful method for solution and solid samples. The NMR chemical shift,  $\delta$ , must be ubiquitous parameter, allows for distinguishing magnetically in equivalent nuclei in a molecule. Beyond distinguishing one nucleus from another, in fact it can reveal information regarding the chemical surroundings of a nucleus. In liquid, or gas, the molecules are freely tumbling so one does observe an average chemical shift (isotropic chemical shift)<sup>[1]</sup>. Regard to the zeolites thirteen active NMR nuclei have been utilized in obtaining information on structural features of zeolites. The most directly relevant nucleus in zeolite studies has been  $^{29}Si$  and  $^{27}Al$ , though other nuclei including  $^1H$ ,  $^{13}C$ ,  $^{23}Na$ ,  $^{17}O$ ,  $^{129}Xe$ ,  $^2H$ ,  $^7Li$ ,  $^{11}B$ ,

$^{15}N$ ,  $^{19}F$ , and  $^{205}Tl$  may also provide framework or structural information about the zeolite. Because of the NMR chemical shifts, nowadays, the NMR spectroscopy becomes a powerful tool in chemistry. There are a lot of experimentally NMR chemical shift data but theoretical studies with special emphasis on the aspects relevant to the zeolites are still poor.

In principle, NMR spectroscopy is uniquely capable of detecting and characterising  $^{27}Al$  and  $^{29}Si$  centres in aqueous solutions, but its application is hindered by the low solubility of aluminosilicate under many circumstances, the quadruple effect of Al and the exchange process. They consist of 2-12  $SiO_4$  units and include chains, rings, and cages. The peak of the monomeric silicate anions,  $Q^0$ , appears at the high-frequency side of the spectrum followed in a regular sequence by the  $Q^1$  to  $Q^4$  units shifted by about 10 ppm to low fre-

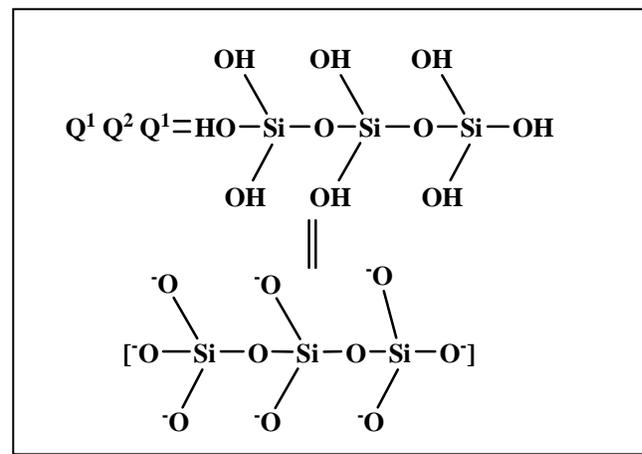
quency for each newly formed Si-O-Si bond, but in the case of q-units substitution the  $^{29}\text{Si}$  resonance is shifted by only ca. 5 ppm to lower frequency, e.g. from  $q^0$  to  $q^{1-6}$ . These five well-separated subdivisions for five possible  $Q^n$  building units<sup>[3,4]</sup> and the difference in chemical shifts in the case of q substitution as well as have been examined by the theoretical methods.

The calculated  $^{29}\text{Si}$  isotropic chemical shifts ( $\delta$  ppm) of the chain form silicate have been employed for investigation of the effect of  $q^1$  unit (aluminate ion) substitution in the silicate solution.  $^{29}\text{Si}$  NMR shifts have also been used to characterize the structure of aluminosilicate anions. This task in experimental work is complicated by the fact that  $^{29}\text{Si}$  peaks from aluminosilicate species are much broader than those for purely silicate species and by the absence of many well-defined aluminosilicate structures to base peak assignments. As a consequence, only a fragmentary picture of the interactions of aluminate and silicate anions have been achieved thus far<sup>[7]</sup>. Hence a range of  $^{29}\text{Si}$  chemical shifts for each  $Q^n$  (mAl) units in aluminosilicates have been obtained in experiment, for example see figure 2 for the  $q^4$  species. Furthermore, the purpose of this study is calculation  $^{29}\text{Si}$  chemical shifts in different  $Q^n$ - $q^1$  connectivity and is to investigate for the silicate monomer the dependence of the  $^{29}\text{Si}$  NMR chemical shift on the Al substitution and comparing the data of  $Q^n$   $^{29}\text{Si}$  chemical shifts of the silicate to the aluminosilicate.

### Notation and methods

To simplify writing the various silicate and aluminosilicate species that can occur in solution, an abbreviated notation (presentation) has been utilized to describe the structures. The use of "Q-units" was first proposed by Engelhardt et al.<sup>[8-9]</sup> and they have been used by most investigators in latter studies. In this notation, Q represents a silicon atom bonded to four oxygen atoms forming a tetrahedron  $[(\text{Si}(\text{OH})_4)]$ , and n in  $Q^n$  units indicates the number of siloxane bridges to a given silicon centre. With this notation the extent of ionisation is ignored; therefore, the full structure corresponding to a given abbreviated notation may be either completely ionised or entirely as the protonated form, or at any stage in between. Thus,  $Q^0$  denotes the monomeric orthosilicate anion  $\text{SiO}_4^{4-}$  or  $\text{Si}(\text{OH})_4$ ,  $Q^1$  end-groups,  $Q^2$  middle groups in chains or cycles,  $Q^3$  chain-branch-

ing sites and  $Q^4$  three-dimensionally cross-linked groups. For example, the linear trinuclear silicate species would be represented as:



For aluminosilicate solutions a similar notation can be introduced to deal with species containing aluminium as well as silicon. The notation dealing with the silicate sites is the same as above (i.e. as for silicate solutions). The only difference is in the way the number of aluminium atoms involved in the species in question is indicated. For instance, the prismatic hexamer with one aluminium will be denoted as  $Q^3_6(1\text{Al})$ , and the cubic octamer with two aluminium sites will be shown as  $Q^3_8(2\text{Al})$ . For individual silicon sites the number of bridges to aluminium is similarly indicated, e.g.  $Q^2(1\text{Al})$ ,  $Q^3(2\text{Al})$  etc. In the case of individual aluminium sites, the notation is similar to that for silicon. An aluminium site is indicated as "q" (rather than Q for the silicon sites). For such a site, linkage to one siloxane bridge is denoted  $q^1$ . In the same way, if it links to 2, 3 and 4 siloxane bridges it is indicated as  $q^2$ ,  $q^3$  and  $q^4$  respectively. If aluminium has no siloxane bridge, as for the aluminate anion,  $\text{AlO}_4^{5-}$ , it is represented as  $q^0$ . Therefore  $q^0$ ,  $q^1$ ,  $q^2$ ,  $q^3$  and  $q^4$  are  $\text{Al}(\text{OOSi})$ ,  $\text{Al}(\text{1OSi})$ ,  $\text{Al}(\text{2OSi})$ ,  $\text{Al}(\text{3OSi})$  and  $\text{Al}(\text{4OSi})$  respectively. Under Lowenstein's rule, it is unnecessary to introduce a notation for aluminium sites with aluminoxy bridges. According to Lowenstein's rule Al-O-Al Bridge is forbidden in aluminosilicate species. For the detail definition of the notation of the species see the references<sup>[3-6]</sup>.

The notation  $Q^n$  for silicon in silicate solutions, and  $q^n$  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

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TABLE 1: Data of calculated and experimental values of  $^{29}Si$  chemical shifts [ $\delta$  (ppm)] and absolute deviations or errors for  $Q^n$  units of aluminosilicate species, which obtained with three basis sets 6-311+G(2d, p), 6-31+G\*\* and 6-31G\*\*

Species no.	$Q^n$	Methods						$-\delta_{exp.}^*$
		HF/6-311+G(2d, p)	HF/6-31G**	HF/6-31+G**	Experiment <sup>a</sup>	$I\delta_{cal.} - \delta_{exp.}$	$I\delta_{cal.} - \delta_{exp.}$	
1	$Q^0$	73.7	2.4	64.2	7.1	67.0	4.3	71.3
2	$Q^1$	87.8	8.0	74.5	5.3	76.2	3.6	79.8
	$Q^1$	87.8	8.0	74.5	5.3	76.2	3.6	79.8
3	$Q^1$	72.6	2.4	62.1	12.9	66.1	8.9	75.0
	$Q^1$	87.5	9.2	74.5	5.3	76.1	3.2	79.3
4	$Q^1$	88.1	8.8	75.4	5.3	77.7	1.6	79.3
	$Q^2$	101.2	13.0	85.0	3.2	87.5	0.7	88.2
5	$Q^1$	85.8	6.5	71.9	7.4	75.0	4.3	79.3
	$Q^2$	87.9	2.9	75.1	9.9	78.1	6.9	85.0
6	$Q^2$	81.5	1.5	70.3	9.7	73.2	6.8	80.0
	$Q^1$	87.4	8.2	74.3	4.9	76.1	3.1	79.2
7	$Q^1$	87.5	8.3	74.5	4.7	76.4	2.8	79.2
	$Q^1$	88.1	8.9	75.6	3.6	78.0	1.2	79.2
	$Q^3$	110.4	*	96.4	**	100.1	**	95-101
8	$Q^1$	85.6	6.4	73.1	6.1	75.6	3.6	79.2
	$Q^1$	86.3	7.1	73.5	5.7	75.9	3.3	79.2
9	$Q^3$	98.8	3.8	82.6	12.4	86.8	8.2	95.0
	$Q^1$	87.5	8.3	74.0	5.2	76.4	2.8	79.2
	$Q^3$	94.7	4.7	79.9	10.1	83.7	6.3	90.0
10	$Q^3$	89.4	4.4	77.7	7.3	79.1	5.9	85.0
	$Q^1$	85.6	6.4	74.1	5.1	76.6	2.6	79.2
	$Q^1$	85.8	6.6	74.1	5.1	76.6	2.6	79.2
11	$Q^1$	87.7	8.5	74.1	5.1	76.8	2.4	79.2
	$Q^1$	87.8	8.6	75.2	4.0	77.2	2.0	79.2
	$Q^4$	125.2	*	104.2	**	108.6	**	103-120
12	$Q^1$	86.6	7.4	74.5	4.7	76.3	2.9	79.2
	$Q^1$	88.0	8.8	75.1	4.1	77.6	1.6	79.2
	$Q^1$	88.2	9.0	75.6	3.6	77.2	2.0	79.2
13	$Q^4$	114.2	*	94.9	**	99.0	**	95-105
	$Q^1$	83.3	4.1	75.5	3.7	75.8	3.4	79.2
	$Q^1$	86.7	7.5	74.0	5.2	75.8	3.4	79.2
14	$Q^4$	102.9	*	85.9	*	90.0	*	92-99
	$Q^1$	84.6	5.4	71.2	8.0	73.4	5.8	79.2
	$Q^4$	99.7	*	84.2	*	88.9	**	88-94
15	$Q^4$	97.6	*	82.1	*	85.8	**	83-87

\*Out of the experimental range; \*\*In the range of experimental values; (a) All experimental values taken from references 3-6, 14

$Q$ -unit is shifted by ca. 10ppm to lower frequency when the number of siloxane bridges is increased by one, but in the case of  $q$ -units (i.e. aluminium sites) the  $^{27}Al$  resonance is shifted by only ca. 5ppm to lower frequency, e.g. from  $q^0$  to  $q^{1-6}$ .

The  $^{29}Si$  isotropic chemical shift ( $\delta$  ppm) calculations to the chain form silicate solutions for investigation

Figure 1: Non cyclic or chain form silicate and aluminosilicate species that have been investigated. Each line represents a Si-O-Si or Si-O-Al linkage

Prese- ntation	Species number	Prese- ntation	Species number
1	$Q^0$	2	$Q^1-Q^1$ $Q^1(0Al)$
3	$Q^1-Q^1$ $Q^1(1Al)$	4	$Q^1-Q^2-Q^1$ $Q^2(0Al)$
	$Q^1-Q^2-Q^1$ $Q^2(1Al)$	6	$q^1-Q^2-q^1$ $Q^2(2Al)$
7	$Q^1-Q^3-Q^1$ $Q^1$ $Q^3(0Al)$	8	$Q^1-Q^3-Q^1$ $Q^1$ $Q^3(1Al)$
9	$Q^1-Q^3-Q^1$ $Q^1$ $Q^3(2Al)$	10	$Q^1-Q^3-Q^1$ $Q^1$ $Q^3(3Al)$
11	$Q^1-Q^4-Q^1$ $Q^1$ $Q^4(0Al)$	12	$Q^1-Q^4-Q^1$ $Q^1$ $Q^4(1Al)$
13	$Q^1-Q^4-Q^1$ $Q^1$ $Q^4(2Al)$	14	$q^1-Q^4-q^1$ $Q^1$ $Q^4(3Al)$
15	$Q^1-Q^4-Q^1$ $Q^1$ $Q^4(4Al)$		

of the effect of  $q^1$  unit (aluminat ion) substitution in the silicate solution have been employed. As well, in the present study,  $^{29}Si$  NMR chemical shift calculation has been used to investigate the  $Q^n$  local structures about the Si in a series of aluminosilicate and as well as silicate species. This convincingly shows the different chemical shift in different  $Q^n-q^1$  connectivity (see TABLE 1).

Hartree-Fock self-consistent-field (HF-SCF) theory and the gauge-including atomic orbital (GIAO) methods have emerged in recent years as a promising alternative to conventional *ab-initio* methods in quantum chemistry. Nowadays, calculations of NMR (nuclear magnetic resonance) chemical shielding constants are familiar with the theoretical chemist. Most of the current available quantum chemical methods for calculating NMR chemical shifts are based on the Hartree-Fock self-consistent-field (HF-SCF) approximation and the gauge-including atomic orbital (GIAO) methods [10-13]. Hartree-Fock calculations of magnetic properties are difficult for small molecules, today to be carried out routinely for large systems. Recently some workers

have reported *ab-initio* calculations of  $^{29}\text{Si}$  NMR chemical shifts for various silicate species which are precursors for <sup>[13]</sup>

Based on the reasons pointed out in previous paper<sup>[13]</sup> the HF level theory is chosen for our calculations. Owing to the increasing availability of *ab-initio* programs for the calculation of nuclear shielding, the *ab-initio* literature on shielding of larger systems is increasing rapidly. Most of these calculations have been restricted to the Hartree-Fock level. In this work, the GIAO-SCF method applied using gaussian software for calculations of the  $^{29}\text{Si}$  NMR chemical shifts for  $Q^n$  units of 15 compounds with various chain forms aluminosilicate species of figure 1.

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 (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. On a comparative basis, the relative shielding constant  $\Delta\sigma_x$  is defined as  $\delta_x = \sigma_{(\text{reference})} - \sigma_{x(\text{species})}$  where  $\sigma_{(\text{TMS})}$  and  $\sigma_{x(\text{species})}$  are isotropic chemical shielding constant,  $\sigma_{\text{iso}}$ , of reference and nucleus x respectively. GIAO isotropic  $^{29}\text{Si}$  chemical shifts for silicate and aluminosilicate are given in TABLE 1 for the 15 molecules in study.

## RESULTS AND DISCUSSION

Corresponding calculated  $^{29}\text{Si}$  NMR shift investigations of aluminosilicates, as the same as the results for  $Q^n$  unit shifts of silicate solutions<sup>[13]</sup> have shown that possible influences in obtaining accurate chemical shifts are: the basis set effects, the theory levels, optimization effects, the degree of condensation of silicate species and as well the substitution aluminate to silicate species and the effect of atoms in the second co-ordination sphere, bond distances and angles, and the degree of condensation of the tetrahedral groups under consideration<sup>[15-17]</sup>. The theory levels HF and DFT(B3PW91 and B3LYP) dependence of  $^{29}\text{Si}$  chemical shifts, in  $Q^1$  units of species in silicate solutions have been determined in our previous work<sup>[13]</sup>. It has been shown that, the accuracy for the HF by a same basis set will produce less error than the DFT levels, and or the HF level

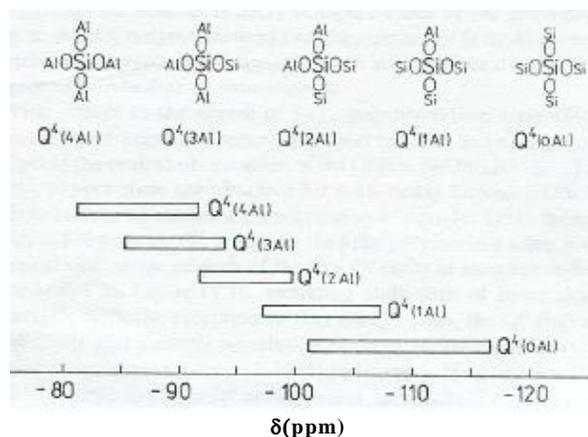


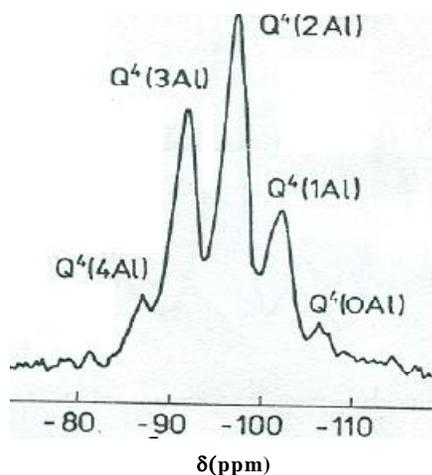
Figure 2 : Range of  $^{29}\text{Si}$  chemical shifts of  $Q^n(\text{mAl})$  units in aluminosilicates (reprinted from reference 4)

of predicted  $^{29}\text{Si}$  chemical shifts are much closer to experiment than both at the B3LYP and B3PW91 level of theory, as well B3PW91 provides a significant improvement over B3LYP level. Hence, HF level is chosen for the present investigations. According to this, the  $^{29}\text{Si}$  isotropic chemical shifts ( $\delta$ ppm) have been calculated for the various silicate and aluminosilicate species in figure 1 by using the HF with the three basis sets 6-31G\*\*, 6-31+G\*\* and 6-311+G(2d, p). The calculated  $^{29}\text{Si}$  chemical shifts for the  $Q^1$  to  $Q^4$  linked to the  $q^1$  aluminate units of 15 different molecules in figure 1, summarized in TABLE 1 together with the available experimental gas phase data<sup>[3-6,18]</sup>. The GIAO isotropic  $^{29}\text{Si}$  chemical shifts are relative to TMS, which the normal standard is used as the reference for  $^{29}\text{Si}$ . As we can see the two later basis sets provide a significant improvement over the HF/6-31G\*\* in predicting the  $^{29}\text{Si}$  chemical shifts in species studied here. The results for  $^{29}\text{Si}$  isotropic chemical shifts at the HF/6-31+G\*\* level are sufficiently accurate to aid in experimental peak assignments.

As the same results as the experimental  $^{29}\text{Si}$  NMR chemical shifts of silicate and silicic acid<sup>[2-6]</sup>, the calculated values of  $Q^0$ , appears at the high-frequency followed in a regular sequence by the  $Q^1$  to  $Q^4$  units shifted by about 10ppm to low frequency for each newly formed Si-O-Si bond (see TABLE 1 for the species no. 2, 4, 7 and 11), but in the case of Al-O-Si i.e. aluminium atom substitution, there are more subtle structural influences on the Si shielding.

The replacement of one or more Si atoms by Al

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**Figure 3:**  $^{29}\text{Si}$  NMR spectrum of the whole set of  $Q^4(\text{mAl})$  peaks (reproduced from refs.4)

atoms in the outer coordination sphere of a  $Q^n$  unit results in significant low-field shifts (i.e. less negative  $\delta$  values) as the same as experiment. In general, each substitution  $\text{SiOSi} \rightarrow \text{SiOAl}$  brings about a deshielding of ca. 5ppm for the central silicon atom<sup>4)</sup> see figure 3 and the calculated data in TABLE 1. As shown in TABLE 1, those sequences can readily be seen in the calculated  $^{29}\text{Si}$  NMR, especially from the calculated data of 6-31+G\*\* basis set. Characteristic shift ranges of the five  $Q^4(\text{mAl})$  [i.e.  $\text{Si}(\text{OSi})_{4-m}(\text{OAl})_m$ ] units in framework silicates have been established from a large body of shift data measured in various types of zeolitic and non-zeolitic aluminosilicates (see figure 3). The different  $Q^4(\text{mAl})$  shift ranges partly overlap are shown in figure 2. G.Engelhardt and coworkers<sup>14)</sup> by using some special condition in experimental work, have found the distinct types of  $Q^4(\text{mAl})$  structural units, which have assigned by the  $^{29}\text{Si}$  NMR spectrum and those shifts in assignments well confirmed by the calculated data see figure 2 and the data in TABLE 1. As we know with the exception of that for  $Q^4$  units, the  $Q^3(\text{mAl})$ ,  $Q^2(\text{mAl})$  and  $Q^1(\text{mAl})$  units in the tetrahedral sheet of chain form silicates in experiment overlap significantly and we cannot have a good resolution such as the  $Q^4(\text{mAl})$  structural units, but by the calculation method in a similar way, the  $Q^3(\text{mAl})$ ,  $Q^2(\text{mAl})$  and  $Q^1(\text{mAl})$  units in the tetrahedral sheet of chain form silicates can be studied for example the chemical shifts  $Q^2$  of the species numbers 4,5, and 6 or as well as  $Q^3$  of species numbers 7,8,9 and 10 (see figure 1 and TABLE 1).

Clearly, a detailed knowledge of the calculated

chemical shifts of the various  $Q^n(\text{mAl})$  structural groups can provides an important basis for obtaining further information on the aluminosilicate structure, especially on silicon, aluminium ordering of the framework. The theoretical values derived on the basis of the three methods exhibit right sequence of the different lines in all cases. The calculated changes for the  $Q^n(\text{mAl})$  complexes in comparison with the free aluminium  $Q^n$  molecules are more significant in chemical shift value. For this complex the total region of calculated shifts agrees well with the experimental results. The calculations differ especially with respect to the various silicones. The theoretical values are in fair agreement with experimental  $^{29}\text{Si}$  NMR shifts (see TABLE 1).

By closer look at the data in TABLE 1 and the species in figure 1, the following results also could be obtained:

Firstly, there are, beyond the immediate Al co-ordination with oxygen atoms, more subtle structural influences on the Si shielding. In particular, in addition to the directly-bonded oxygen atoms, the Al contribute to the deshielding of the Si and the molecular symmetry is affected as the same as experimental work. In substitution: one or more silicon may replace with aluminium, which can lead in principle to  $q^n$  with any value of n (eq. 1).



Structural variation in the siloxane skeleton will have a marked influence upon the chemical environment of the silicon nuclei in the structure, and this will be reflected to the  $^{29}\text{Si}$  NMR chemical shift in experimental and as well as in calculated values.

Anyway, it might be because of the quadruple effects, molecular asymmetric and line broadening and the other effects, due to the effect of the Al atoms, it hindered and we could not see for example these differences in each site of  $Q^1$ ,  $Q^2$  and  $Q^3$  chemical shifts in spectrum, for example all of  $Q^1$  in different species observed at the ca. 79. 2 ppm, but these effects are reflected in the three sets of calculated data for the different aluminosilicate species (see TABLE 1). We believe within these effects  $Q^1$  chemical shifts must be differed both within and between the different species (see  $Q^1$  values of different species in TABLE 1). For showing the effect of aluminate substitution, it could be com-

**TABLE 2 : Statistical data for  $^{29}\text{Si}$  chemical shifts calculated at the three basis sets and the same level of theory HF, which obtained from the data of TABLE 1**

Statistical measures	Methods		
	HF/6-311+G (2d, p)	HF/6-31+G**	HF/6-31G**
Minimum error	2.4	1.2	3.6
Maximum error	9.2	8.9	12.9
Mean absolute error	7.4	3.2	5.5
Standard deviation	7.8	3.7	5.9
RMS error	7.6	3.6	5.8

pared the  $^{29}\text{Si}$  chemical shifts of  $\text{Q}^n$  in between species, for example species nos. 2 to 3 for  $\text{Q}^1$  unit, 4 to 5, 6 for  $\text{Q}^2$  and 7 to 8-10 for  $\text{Q}^3$  units and 11 to 12-15 for the  $\text{Q}^4$  units. Comparing the experimental data of samples except of the species no.3 and 5 on which the deshielding effect of aluminate is obvious, in the other cases the deshielding effects except in some instance is not quite clear in experiment, but in the all calculated chemical shifts these deshielding effects are quiet clear. In addition, it has been shown from  $^{27}\text{Al}$  NMR spectra of aluminosilicates that replacement of Al with Si in the second co-ordination sphere of Si site causes, in general, a low-frequency shift of about 5ppm<sup>[7]</sup>, comparing to the value of ca. 10 ppm for Si. The deshielding effect in some extent is also obvious for example for the  $\text{Q}^1$  units within species, for example  $\text{Q}^1$  in species numbers 8, 12 and 13. This effect is well established in this work.

As discussed above, there are variety species which are linked to the  $\text{Q}^1$  unit and affected the  $\text{Q}^1$  shifts, and the NMR could not detect this effects separately, and they might be appearing in one site, perhaps the NMR machine detected them at average in other word within the above mentioned reasons made some unexpected experimental data, for example for the  $\text{Q}^1$  chemical shifts which are listed in TABLE 1. Therefore in such a situation, theoretical calculations of spectroscopic properties can be very helpful and from the calculated data could be obtained some missing information

From the data of TABLE 1 we emphasized that in addition to the basis sets and theory levels the accuracy also depends on  $\text{Q}^n$  units i.e. in the same condition the accuracy will change from the  $\text{Q}^0$  to the  $\text{Q}^4$  units as well to the size of species, though in some extent, there is alternative approach. For example in one level of theory and basis set might be the best result for the  $\text{Q}^0$  unit

approached but it might be not yielded for the some of the  $\text{Q}^1$  units, for better understanding on the effect of basis set in calculations of chemical shifts the statistical data of TABLE 1 has been calculated and shown in TABLE 2. Regarding the statistical data, only the 6-31+G\*\* basis set gives results with RMS and standard deviation less than ca. 4 for all investigated molecules. However, for the reasons pointed out above, it would be difficult to decide which approach yields better results in the whole  $\text{Q}^n$  unit ranges in different species at least for the used condition.

## CONCLUSION

The  $^{29}\text{Si}$  NMR calculations can provide structural information about the environment of Si nuclei for aluminosilicates through using the data of both calculated and the experimental chemical shift. As the same as experimental values five separated subdivisions have been found which correspond to the five possible  $\text{Q}^n$  building units, followed in a regular sequence by the  $\text{Q}^1$  to  $\text{Q}^4$  units shifted by about 10 ppm to high field for each newly formed SiOSi bond. Substitutions Al to the  $\text{Q}^n$  apparently cause some deshielding compared with  $\text{Q}^1$  to the  $\text{Q}^n$  linkage similar to the experimental values. The results of  $^{29}\text{Si}$   $\text{Q}^1$  chemical shift calculations with the 6-31G\*\*, 6-31+G\*\* and 6-311+G(2d, p) basis sets specially 6-31+G\*\* basis set are in reasonable agreement with the experimental values. All of the results for the  $^{29}\text{Si}$  isotropic chemical shifts at the HF/6-31+G\*\* level are reasonable accurate to aid in experimental peak assignments.  $^{29}\text{Si}$  chemical shifts for aluminosilicate species are shown in TABLE 1 sights into the  $\text{Q}^n(\text{mAl})$  complexes can be achieved when the NMR results are combined with the calculated data. Moreover, in many cases calculated NMR data can be helpful in proving or disproving distinct structural features of  $\text{Q}^n$  units deduced from studies by experimental methods.

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