Comparative quantum chemical studies in the framework of Gaussian approximations of the acidic characteristics of the simplest zeolite clusters and of the sulfuric acid molecule

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Different variants of the Gaussian approximation, giving the energetic characteristics of molecules with chemical accuracy (±2 kcal mol^{-1}), are applied to calculations of the deprotonation energy of the sulfuric acid molecule in the gas phase as well as to the simplest clusters modeling the bridging hydroxyl groups in zeolites. The conclusion is made that the bridging hydroxyls are more acidic than the sulfuric acid molecule. The estimated range of deprotonation energy in zeolites (275±15 kcal mol^{-1}) is in good agreement with experimental data and with results of *ab initio* calculations for extended models including several tens of atoms. The effects of the quality of the basis set and electron correlation on deprotonation energy are also discussed.

Keywords: acidity, zeolite catalysts, sulfuric acid, *ab initio* calculations, deprotonation energy.

Measuring the acidic and basic strength of isolated molecules has became nowadays a routine procedure due to the considerable improvements in ion cyclotron resonance and high pressure mass spectrometry techniques.[1,2] At the same time direct measurements of the absolute acidity of heterogeneous acid catalysts are still impossible. That is why the acidic strength of acidic sites in heterogeneous acid catalysts is usually estimated by measurements of the adsorption/desorption of probe molecules. The acidic strength of surface sites in solid materials can be estimated by microcalorimetry or temperature-programmed desorption methods using the heat of chemisorption of simple bases with known proton affinity.[3,4] The relative strengths of acidic sites in solid acids is also estimated by the frequency shift of the OH-group stretching vibration induced by its interaction with an adsorbed molecule of a base.[5,6] A comparison of these data with results for molecules with known deprotonation energies makes the estimation of the absolute acidity of surface hydroxyl groups possible.

The objective of this paper is a comparative quantum chemical study of the acidic characteristics of simplest molecular models of bridging hydroxyl groups in zeolites and sulfuric acid molecule in gas phase using high level *ab initio* methods.

Calculation Methods

The absolute acidity of the AH molecule is defined as the change in the Gibbs' free energy in the deprotonation reaction:

$$AH \rightarrow A^- + H^+,$$

$$\Delta G^\circ_{DP} = \Delta H^\circ_{DP} - T\Delta S^\circ_{DP}.$$

The enthalpy of this reaction is called the heterolytic bond dissociation energy or the deprotonation energy of the AH molecule. In quantum chemical calculations the deprotonation energy, ΔE_{H^+}, is usually calculated as the difference in the total energies of the anion A$^-$ and the neutral molecule AH at their equilibrium geometries[7], *i.e.*

$$\Delta E_{H^+} = E(A^-) - E(AH).$$

Analogously the absolute acidity of molecule B is defined as having the reverse sign of the standard free energy of the process:

$$B + H^+ \rightarrow BH^+.$$

With the opposite sign the enthalpy of the protonation reaction is called the absolute proton affinity of basic molecule B. Usually it is calculated as the difference in the total energies of the neutral and protonated molecules. Thus, according to the above given definitions, the proton affinity of the anion is equal to the deprotonation energy of the neutral molecule, and the deprotonation energy of the cation is equal to the proton affinity of the neutral molecule.

The calculations were carried out using the «Gaussian-92»[8] program and the recently introduced Gaussian-1[9] and Gaussian-2[10] additive procedures. It was shown by the authors of these approaches that for the simplest

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ion-molecular processes they result in data comparable to experimental values. The difference between experimental and calculated values is usually not more than 2 kcal mol^{-1}.[11]

The Gaussian-1 approximation, hereinafter designated as G1, gives results comparable in accuracy to those obtained at the QCISD(T)/6-311+G(2df) level (quadratic configuration interaction method with perturbative inclusion of triple excitations)[12] but requires considerably lower computation costs.

The total energy in the G1 approximations calculated by the formula:

$$E(\mathrm{G1}) = E_0 + \Delta E(+) + \Delta E(\mathrm{2df}) + \Delta E(\mathrm{QCI}) + \\ + \Delta E(\mathrm{HLC}) + \Delta E(\mathrm{ZPVE}),$$

where: E_0 is the total energy of the system, calculated at MP4/6-311G**//MP2(full)/6-31G*, $\Delta E(+)$ is a correction for diffuse functions, ΔE(2df) is a correction for the higher polarization on non-hydrogen atoms, ΔE(QCI) is a correction for correlation beyond fourth order perturbation theory using a quadratic configuration interaction, and ΔE(HLC) is an empirical correction taking into account the remaining basis set deficiencies and the correlation connected with higher orders. The last term is a zero point vibrational energy correction calculated at the HF/6-31G* level using scaled factor 0.8924.[13]

The Gaussian-2 approximation, G2, is a further development of the G1 technique. The total energy in this case is calculated by the formula:

$$E(\mathrm{G2}) = E(\mathrm{G1}) + \Delta + 1.14\ n_{\mathrm{pair}},$$

where n_{pair} is the number of valence pairs, and Δ is a term taking into account a correction connected with the inclusion of a third set of polarization d-functions for non-hydrogen atoms and a second set of p-functions for hydrogen atoms. This correction is calculated by the formula:

$$\Delta = E[\mathrm{MP2/6\text{-}311{+}G(3df,2p)}] - E[\mathrm{MP2/6\text{-}311G(2df,p)}] - \\ - E[\mathrm{MP2/6\text{-}311{+}G(d,p)} + E[\mathrm{MP2/6\text{-}311G(d,p)}].$$

It is necessary to emphasise that the G2 approximation, in comparison with G1, requires only one additional calculation at the MP2/6-311+G(3df,2p) level because all necessary data are automatically obtained from G1 calculations. In addition, a further modification of G2 approximation was proposed by the authors of these techniques. It is called G2(MP2)[14] and is based only on second order Moeller—Plesset perturbation theory. In the framework of the G2(MP2) approximation it is necessary to carry out only two calculations at the QCISD(T)/6-311G(d,p) and MP2/6-311+G(3df,2p) levels. The total energy in the G2(MP2) approach is calculated by the formula:

$$E[\mathrm{G2(MP2)}] = E[\mathrm{QCISD(T)/6\text{-}311G(d,p)}] + \Delta(\mathrm{MP2}) + \\ + \Delta(\mathrm{HLC}) + \Delta E(\mathrm{ZPE}),$$

where: $\Delta(\mathrm{MP2}) = E[\mathrm{MP2/6\text{-}311{+}G(3df,2p)}] - E[\mathrm{MP2/6\text{-}311G(d,p)}]$, and Δ(HLC) is calculated as in G2 theory. The G2(MP2) approach provides substantial savings in computational time and disk storage.

All three variants of Gaussian approximation described above, as well as the recently introduced G2(MP2,SVP) approach,[15] which provides substantial savings in computational resources without reducing the accuracy of calculations were used in this paper. The last scheme makes it possible to apply Gaussian approximation to larger systems. The total energy in the G2(MP2,SVP) approach is calculated by the formula:

$$E[\mathrm{G2(MP2,SVP)}] = E[\mathrm{QCISD(T)/6\text{-}31G(d)}] + \\ + E[\mathrm{MP2/6\text{-}311{+}G(3df,2p)}] - E[\mathrm{MP2/6\text{-}31G(d)}].$$

It can be seen from this formula that the most time-consuming stage in the G2(MP2) approach is replaced by a calculation at the QCISD(T)/6-31G(d) level, which is nowadays possible for rather extended systems.

Results and Discussion

The deprotonation energies and proton affinities of water and methanol molecules calculated using differ-

Table 1. Deprotonation energies (ΔE_{H^+}) and proton affinity (PA) of H_2O and CH_3OH molecules calculated using different variants of Gaussian theory (values in parentheses are obtained using 6d functions)

Method	H_2O		CH_3OH	
	ΔE_{H^+}	PA	ΔE_{H^+}	PA
G1	388.0 (387.1)	164.1 (164.8)	380.2 (380.2)	177.9 (178.2)
MG1	388.5 (387.5)	163.4 (163.4)	380.4 (380.3)	178.1 (178.3)
G2	388.6 (388.6)	163.9 (164.4)	381.4 (381.5)	178.6 (178.7)
G2(MP2)	389.1 (389.0)	163.1 (163.2)	381.6 (381.6)	178.7 (178.8)
G2(MP2,SVP)	388.6 (386.5)	162.9 (163.0)	381.5 (381.6)	178.6 (178.7)
G2(MP2,SVPP)[a]	389.0 (388.9)	163.2 (163.3)	381.7 (381.7)	178.8 (178.9)
Эксперимент[б]	389.6±0.4[1]	165.0±0.5[21]	381.3±0.5[22]	181.7[1]

[a] Since we are dealing with splitting (formation) of OH bonds, an additional set of polarization functions was used for hydrogen atoms. Total energy in the G2(MP2,SVPP) approach was calculated by the formula
$E[\mathrm{G2(MP2,SVPP)}] = E[\mathrm{QCISD(T)/6\text{-}31G(d,p)}] + E[(\mathrm{MP2/6\text{-}311{+}G(3df,2p)}] - E[\mathrm{MP2/6\text{-}31G(d,p)}]$.

[b] Data from papers[1,21,22].

ent variants of Gaussian approximation are listed in Table 1.

It follows from these data that the deprotonation energies and proton affinities of water and methanol molecules are very well reproduced by the G1, G2 and G2(MP2) approximations. The maximum deviation of deprotonation energies from their experimental values is not more than 2 kcal mol^{-1}. The results obtained are also in a good agreement with other high level theoretical studies.[18,19] The application of the G2(MP2,SVP) approach does not reduce the accuracy (maximum deviation from G2(MP2) results is only 0.5 kcal mol^{-1}). At the same time, application of the G2(MP2,SVPP) approach results in further improvement of agreement with experimental data.

Thus, the above-described modifications of the G1 and G2 approximations do considerably reduce computational efforts without reducing the accuracy of calculations and consequently extend the capabilities of the G1 and G2 approximations, making possible their application to systems of considerably larger size.

Figure 1 depicts the structures considered: the 3 simplest cluster models for the bridging hydroxyl group in zeolites, their deprotonated forms, and the sulfuric acid molecule, along with its anion and protonated sulfuric acid. Cluster **1** is widely used in quantum chemical studies of different properties of isolated bridging hydroxyls[20,21] in zeolites, and clusters **2** and **3** are the simplest models that take into account the basic site conjugated to the neighboring hydroxyl group. They are also widely used in studies of the mechanisms of acid-base reactions on zeolites.[22,23] It should be mentioned that calculations for cluster **1** in the framework of the modified G1 approach have been performed earlier,[24] however, the conformer used did not correspond to the local minimum but resembled a transition state for rotation of hydrogen atoms around the Al—O bond.

The MP2(full)/6-31G* geometries of the structures studied and of their deprotonated forms (for sulfuric acid also for the protonated form) are listed in Table 2. It follows from these data that the deprotonation of sulfuric acid results in considerable elongation of the S—O bond and remarkable lengthening of the S=O bond. At the same time protonation results in slight shortening of all the bonds (S—O and S=O). A detailed analysis of the potential energy surface of sulfuric acid

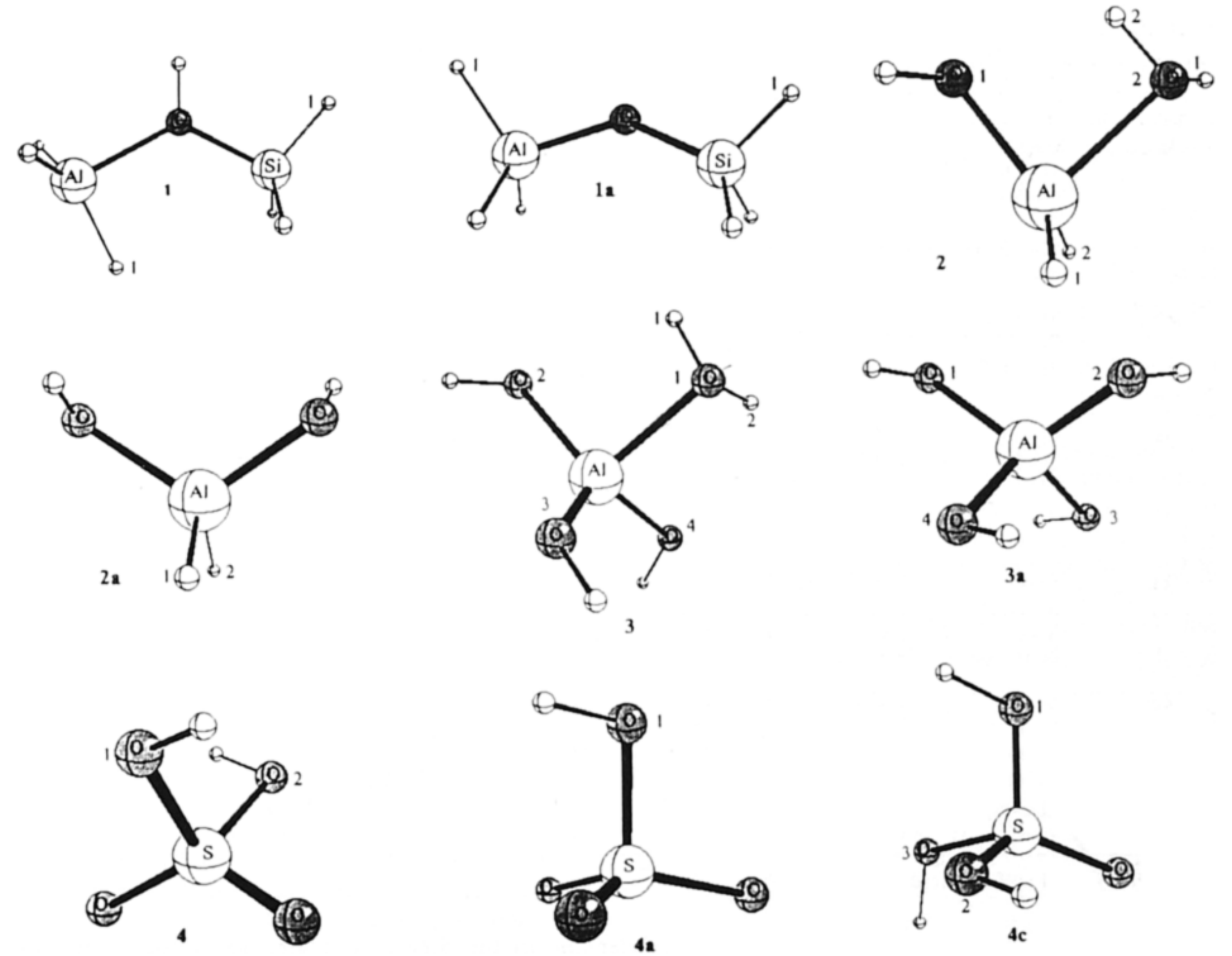

Figure 1. Cluster models of zeolite catalysts (**1—3**), their deprotonation form (**1a—3a**), the H_2SO_4 molecule (**4**), the HSO_4^- anion (**4a**), and the $H_3SO_4^+$ cation (**4c**).

Table 2. Geometry of clusters **1—3**, the H_2SO_4 (**4**) molecule, and their deprotonated forms (**1a—4a**)

Cluster	Bond	*d*/Å	Bond angle	ω/deg	Dihedral angle	φ/deg
1	O—H	0.973	H—O—Si	117.2	H(1)—Si—O—H	0.0
	Si—O	1.725	Si—O—Al	124.1	H(1)—Al—O—H	0.0
	Al—O	2.013	H—Si—O	108.7	H—Si—O—H(1)	118.8
	Si—H	1.472	H(1)—Si—O	104.3	H—Al—O—H(1)	119.4
	Si—H(1)	1.481	H—Al—O	101.6		
	Al—H	1.602	H(1)—Al—O	93.6		
	Al—H(1)	1.608				
2	Al—O(1)	2.027	O(1)—Al—O(2)	84.5	H—O(1)—Al—O(2)	133.5
	Al—O	1.768	H—O(1)—Al	120.4	H(1)—O(2)—Al—O(2)	108.9
	O(1)—H	0.966	H(1)—O(2)—Al	113.1	H(2)—O(2)—Al—O(2)	−1.2
	O(2)—H(1)	0.974	H(2)—O(2)—Al	93.1	H(1)—Al—O(2)—H(2)	191.8
	O(2)—H(2)	0.986	H(1)—Al—O(2)	108.6	H(2)—Al—O(2)—H(2)	314.0
	Al—H(1)	1.594	H(2)—Al—O(2)	99.0		
	Al—H(2)	1.598				
3	O(1)—H(1,2)	0.979	O(1)—Al—O(2)	91.7	O(3)—Al—O(1)—O(2)	117.4
	O(2,3)—H	0.967	O(3)—Al—O(4)	121.3	O(4)—Al—O(1)—O(2)	240.8
	Al—O(1)	1.984	O(1)—Al—O(3)	113.8	H(1)—O(1)—Al—O(2)	359.8
	Al—O(2)	1.743	H(1)—O(1)—Al	100.7	H(2)—O(1)—Al—O(2)	109.9
	Al—O(3)	1.730	H(2)—O(1)—Al	101.3	H—O(2)—Al—O(1)	134.6
	Al—O(4)	1.747	H—O(2)—Al	118.1	H—O(3)—Al—O(1)	81.5
			H—O(3)—Al	119.4	H—O(4)—Al—O(1)	166.5
			H—O(4)—Al	121.1		
4	S—O(1)	1.620	H—O(1)—S	107.9	O(1)—S—O(1)—O(2)	92.2
	S—O(2)	1.443	O(1)—S—O(1)	101.6	H—O(1)—S—O(1)	83.3
	H—O(1)	0.98	O(2)—S—O(2)	125.0		
			O(1)—S—O(2)	106.5		
1a	Si—O	1.611	Si—O—Al	138.8	H(1)—Si—O—H	180.0
	Al—O	1.824	H(1)—Si—O	111.8	H—Al—O—H	0.0
	Si—H(1)	1.502	H—Si—O	115.2	H—Si—O—H(1)	119.1
	Si—H	1.503	H(1)—Al—O	107.5	H—Al—O—H(1)	120.1
	Al—H(1)	1.642	H—Al—O	108.6		
	Al—H	1.642				
2a	Al—O(1,2)	1.801	O(1)—Al—O(2)	112.6	H—O(1)—Al—O(2)	108.7
	O(1,2)—H	0.969	H—O(1,2)—Al	108.7	H(1)—O(2)—Al—O(2)	71.3
	Al—H(1,2)	1.649	H(1)—Al—O(2)	105.4	H(1)—Al—O(2)—H	46.9
			H(2)—Al—O(2)	110.0	H(2)—Al—O(2)—H	169.1
3a	Al—O	1.790	O(1)—Al—O(2)	117.6	H—O(1,2)—Al—O(2,1)	93.7
	O—H	0.969	O(1)—Al—O(3)	105.6	O(4)—Al—O(1)—O(2)	242.6
			H—O—Al	106.9	O(3)—Al—O(1)—O(2)	117.4
					H—O(3)—Al—O(1)	23.7
					H—O(4)—Al—O(1)	148.9
4a	S—O(1)	1.696	H—O(1)—S	103.3	H—O(1)—S—O(2)	111.4
	S—O(2)	1.470	O(1)—S—O(2)	101.4		
	S—O	1.479	O(2)—S—O	115.4		
	O(1)—H	0.975				
4c[a]	S—O	1.424	O—S—O(1)	111.6	O—S—O(1)—H	186.5
	S—O(1)	1.552	O—S—O(2)	119.8	O(2)—S—O(1)—H	314.5
	S—O(2)	1.560	O—S—O(3)	115.3	O(2)—S—O(1)—H	58.4
	S—O(3)	1.574	H—O(1)—S	114.9	H—O(2)—S—O(1)	179.4
	H—O(1)	0.99	H—O(2)—S	114.1	H—O(3)—S—O(1)	93.5
	H—O(2,3)	0.991	H—O(3)—S	112.4		

[a] Protonated sulfuric acid.

and of its anion and cation was carried out using different basis sets in our previous paper[25]. The deprotonation of model zeolitic clusters causes a remarkable increase in the Si(H)OAl angle and considerable shortening of the Al—O and Si—O bond lengths. The formally coordinative Al—O bond undergoes the greatest shortening.

Table 3. Deprotonation energy of clusters **1—3** and the H_2SO_4 molecule calculated at different levels

Method	**1**	**2**	**3**	H_2SO_4	
	ΔE_{H^+}			ΔE_{H^+}	PA
3-21G//3-21G	324.7	345.8	350.3	327.8	186.3
6-31G*//6-31G*	316.5	335.0	335.4	325.1	175.5
MP2/6-31G*//6-31G*	313.7	332.4	332.9	319.5	172.0
MP2/6-31+G**//6-31G*	315.3	328.8	326.2	315.5	167.5
MP2(FU)/6-31G*	313.4	332.9	333.4	320.0	172.1
MP4/6-311G**[a]	319.0	337.1	337.9	327.0	179.5
MP3/6-311G**[a]	321.3	338.4	339.0	327.4	181.1
MP2/6-311G**[a]	317.6	335.7	336.7	324.8	177.7
MP2/6-311+G**[a]	315.7	328.7	327.0	317.5	174.8
MP2/6-311G(2df,p)[a]	310.3	330.5	333.5	323.3	176.4
QCISD(T)/6-311G**[a]	319.7	337.4	338.3	327.3	180.3
MP2/6-311+G(3df,2p)[a]	309.1	325.1	325.2	315.6	172.9
MG1	303.2	317.1	317.7	311.4	170.0
G2(MP2)	303.7	318.7	319.0	310.9	169.4
G2(SVP)	303.9	318.6	318.8	310.5	169.1
G2(SVP)*	304.7	319.0	319.1	310.8	169.5
Experiment[b]				313.6±2	169.0

[a] At geometry obtained at the MP2(full)/6-31G* level.

[b] Data of paper[26].

Table 4. Stretching, in-plane and out-of-plane bending vibrations of the OH[a] bond in model clusters

Cluster	ν(OH)	δ(SiOH)	γ(OH)
$H_3SiO(H)AlH_3$	3640	1068	374
$HO(H)Al(H)_2OH$	3665, 3553	1598	200, 390
$HO(H)Al(OH)_2OH$	3647, 3556	1600	247, 317
$H_3SiO(H)Al(H)_2OSiH_3$	3600	1050	315
$H_3SiO(H)Al(OH)_2OSiH_3$	3624	1049	330
Experement[b]	3520— 3630[30,31]	1060[30] (1090[32])	360— 420[29]

[a] Scaled (0.892) values of frequencies are given.

[b] Experimental values are taken from papers[29—32].

All the structures considered correspond to the local minima on the potential energy surfaces of the investigated structures.

The deprotonation energies of the systems under investigation calculated at the MG1 and MG2 levels are compared in Table 3 with the data obtained at different levels of approximation using geometries optimized at the SCF and MP2 levels. The deprotonation energies of sulfuric acid calculated using modified Gaussian approximations are very close to each other. The maximum deviation from the experimental data is within the uncertainty of its experimental determination. The proton affinity of sufuric acid calculated in the framework of the Gaussian approaches is also in a good agreement with its experimental value (maximum deviation is less than 1 kcal mol^{-1}).

At the same time it should be pointed out that the deprotonation energy of sulfuric acid calculated at the SCF level using the 3-21G and 6-31G* basis sets is considerably (13—15 kcal mol^{-1}) overestimated. Taking the electron correlation in the framework of second order Moeller—Plesset perturbation theory with the 6-31G* basis set at geometry obtained at the SCF level using the 6-31G* basis set (calculation at MP2/6-31G**//6-31G*) into consideration results in considerable improvement in the agreement with experimental data. An additional set of diffuse functions (calculation at the MP2/6-31+G**//6-31G* level) results in further improvement of agreement with experimental data. Further improvement in the quality of the basis set, *i.e.* using the tri-exponent 6-311G** basis set and taking into account the electron correlation effects in higher orders of Moeller—Plesset perturbation theory does not result in significant improvement of agreement with experimental data. An additional set of diffuse functions, as in the case of the 6-31G* basis set, leads to considerable reduction of the difference between the calculated and measured values of the deprotonation energy.

As it has already been mentioned above, direct measurements of deprotonation energies in zeolites are impossible. The data obtained for the model zeolitic clusters make it possible to estimate the order of these values. We assume that cluster **1** slightly better describes the properties of the isolated OH-group than clusters **2** and **3**. As was shown in Refs. 27 and 28 this cluster describes the spectroscopic features of the bridging hydroxyl group (stretching, in-plane and out-of-plane bending vibrations, anharmonicity of OH-vibration, *etc.*) in close agreement with experimental data, while the data for clusters **2** and **3** differ remarkably (Table 4). It follows from Table 3 that the deprotonation energy of cluster **1** is 6—10 kcal mol^{-1} lower and for clusters **2** and **3** is 7—10 kcal mol^{-1} higher than that of the sulfuric acid molecule. To analyze the effect of the size of a cluster on its acidic characteristics we have carried out the calculations for more extended clusters **5** and **6** (Fig. 2), which might be considered as clusters **2** and **3** with two of the boundary hydrogen atoms replaced with an SiH_3 fragment. Such clusters are also widely used in quantum chemical modeling of bridging hydroxyls in

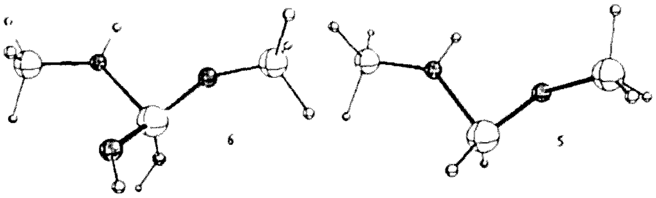

Figure 2. Extended models (**5**, **6**) the bridging OH group in zeolites.

Table 5. Deprotonation energies of model clusters **1**—**3**, **5**, **6** calculated using the 3-21G and 6-31G* basis sets (corrected for ZPVE values are given in parentheses)

Cluster	3-21G	6-31G*
1	324.7 (315.2)	316.5 (309.0)
2	345.8 (336.6)	335.0 (326.4)
3	350.3 (341.4)	335.4 (326.3)
5	322.5 (314.2)	312.5 (304.3)
6	329.4 (320.9)	314.0 (305.5)

zeolites. The deprotonation energy for clusters **1**—**3** and for the more realistic models $H_3SiO(H)Al(H)_2OSiH_3$ (**5**) and $H_3SiO(H)Al(OH)_2$—$OSiH_3$ (**6**) calculated using the 3-21G and 6-31G* basis sets are listed in Table 5. The values obtained using a zero point energy correction are given in parentheses.

It can be seen from Table 5 that the deprotonation energies obtained at the SCF level using the 6-31G* basis set with a zero point energy correction for clusters **1**, **5** and **6** are close to the corresponding data obtained with the Gaussian approaches but are remarkably lower than those for clusters **2** and **3**. It follows from the analysis of the data in Tables 5 and 6 that the calculations for clusters **5** and **6** at higher levels of the approximations should decrease the deprotonation energy by approximately 5 kcal mol^{-1}, *e.g.* the values of the deprotonation energy for zeolitic clusters **5** and **6** should be equal to 300±5 kcal mol^{-1}. Further extension of the cluster also decrease the deprotonation energy by ≈ 10 kcal mol^{-1}. Taking into account the fact that the acidity of the bridging hydroxyl groups is influenced by a number of factors (for the H-form of zeolites, mainly by the Si/Al ratio and the geometry of the zeolite's framework) it is possible to give an approximate evaluation of the range of deprotonation energies in zeolites. Quantum chemical calculations[33—36] indicate that increasing the SiOAl angles at both neighboring bridges (bonded and unbonded with the proton) increases the acidity (decreases the deprotonation energy) by approximately 15—20 kcal mol^{-1}. Increasing the Si/Al ratio also results in considerable changes in the acidity of the bridging OH-groups. Estimations[37] show that the increase in acidity (the decrease in deprotonation energy) in passing from zeolites containing little silica to those containing large amounts of silica is approximately 20 kcal mol^{-1}. Taking into account the fact that according to X-ray data zeolites containing large amounts of silica have a higher range of TOT (T = Si, Al) angles than those containing little silica, *i.e.* the increase in the acidity induced by increasing the Si/Al ratio includes a corresponding change in the acidity due to a change in the structural parameters, it is expected that change in the energy of deprotonation of zeolites should be in the range of 25—30 kcal · mol^{-1} depending on their composition and structure. Hence, the deprotonation energies for zeolitic catalysts should fall in the range of 275±15 kcal · mol^{-1}.

Table 6. Mulliken charges on the hydrogen atom of the OH group, (q(H)/e), the OH stretching vibration frequencies, (ν(OH)/cm^{-1}), the OH bond lengths, (d(OH)/Å), and the deprotonation energies, (ΔE_{H^+}/kcal mol^{-1}), in structures studied and in other OH containing molecules calculated at the HF/6-31G* level

Molecule	q(H)	$\nu(OH)^a$	d(OH)	$\Delta E_{H^+}{}^b$
LiOH	0.405	4252	0.938	457.0
HOH	0.434	4190,4072	0.947	429.3
CH_3OH	0.437	4117	0.946	408.5
FOH	0.476	4070	0.952	378.6
H_3SiOH	0.464	4146	0.946	376.4
HCOOH	0.466	4041	0.953	363.8
F_3SiOH	0.490	4150	0.946	350.7
F_3COH	0.478	4092	0.950	349.2
3	0.516	4098,3996	0.954	335.4
2	0.515	4118,3991	0.956	335.0
CH_3OSO_2OH	0.503	4038	0.954	323.2
H_2SO_4	0.506	4036, 4031	0.954	321.3
1	0.512	4093	0.951	316.5
5	0.520	4045	0.954	314.0
6	0.521	4073	0.952	312.5
$CH_3OH_2{}^+$	0.556	3941,3874	0.964	189.8
$CH_3OH_2SO_3{}^+$	0.557	3915,3903	0.963	184.7
$H_3SO_4{}^+$	0.566	3894,3879,3873	0.965	174.9
H_3O^+	0.585	3885,3774	0.969	170.7

[a] Unscaled values are given. [b] Deprotonation energies are given without the ZPVE correction.

The values obtained are in a good agreement with the theoretical results for extended cluster models and with experimental estimations. The calculations using split-valence plus the polarization basis set performed at the SCF level for extended cluster model of the bridging hydroxyl group in faujasites, $H[Si_{10}AlO_{14}(OH)_{16}]$, which includes 14 silicon/aluminium/oxygen tetrahedra, give a value of the deprotonation energy equal to 275±6 kcal mol^{-1}.[38] For a model cluster that includes up to 24 silicon/aluminium oxygen tetrahedra the value of the deprotonation energy is equal to 295 kcal mol^{-1} [39]. Experimental estimates[5,6,40] of deprotonation energy are equal to 265—280 kcal mol^{-1} for H-ZSM-5 zeolites and 275—280 kcal mol^{-1} for HY zeolites.

In conclusion let us discuss the relation between deprotonation energy of the systems studied and the other characteristics of the OH group (stretching vibration frequency, charge on the bridging proton, and OH bond length). The corresponding data obtained for the studied systems as well as for other hydroxyl-containing molecules are listed in Table 6. Analysis of the given data indicates that the qualitative trends in the charges on the hydrogen atom of the bridging OH group, the OH bond lengths, and the stretching vibration frequencies are in agreement with the trends in the deprotonation energies. However, there is no distinct correlation between these parameters and it is impossible to recommend the values listed in Table 6 for the acidity estimates because the values of d(OH) and ν(OH) depend crucially on such factors as the possibility of the formation of intermolecular hydrogen bonds and the geometry of the framework in the case of zeolites. The charge on the hydrogen atom of the OH group has slightly better characteristics, however in this case it is also necessary to choose related systems for comparison.

Thus, the high level *ab initio* calculations of the acidic characteristics of the sulfuric acid molecule and the simplest clusters modeling zeolites carried out in this paper in combination with the *ab initio* results for more realistic models of zeolites point the fact that the acidity of the bridging hydroxyls in zeolites is higher than that of isolated sulfuric acid molecule in the gas phase. The estimated range of the deprotonation energies in zeolitic catalysts is in good agreement with experimental estimates and with *ab initio* results for extended models that include several tens of atoms.

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