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chemisorption of CO or H$_2$. As is usually the case with other systems, there is some uncertainty in the stoichiometry of titration. However, the merit of this type of titration procedure is to provide a standard that permits an easy comparison between the work of different investigators. Hence, consistency, reproducibility, and convenience should be attributes of the procedure. For molybdenum and molybdenum carbides, both CO and H$_2$ chemisorption methods appear to satisfy the requirements. The recommended procedures are summarized as follows: (i) For molybdenum carbides, CO chemisorption at 196 K with the stoichiometry of one CO per surface Mo atom is recommended. For molybdenum, CO chemisorption at RT with the stoichiometry of two CO per surface Mo atom is better. (ii) For both Mo and carbides, H$_2$ chemisorption while cooling the sample from 620 K to RT and

the stoichiometry of one H per surface Mo atom are recommended. The estimation of particle size by chemisorption is difficult due to the presence of polymeric carbon. The success by CO chemisorption in the present study should be considered rather extraordinary. The XRD could be used for unsupported molybdenum carbides. Yet it is difficult to apply to small particles on a support, alumina in particular. The TEM is the best method for the purpose.

Interaction of NH$_3$ with a Zeolitic Proton: Ab Initio Quantum-Chemical Cluster Calculations

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The interaction of NH$_3$ and a zeolitic cluster as well as the protonation of NH$_3$ by zeolitic protons are studied by quantum-chemical calculations on small clusters at different levels of approximation. The focus of the paper is on a comparison of results obtained by the different methods. The clusters are studied at the SCF level as well as at the correlated level. Electron correlation is included through second-order Møller–Plesset perturbation theory. The basis-set superposition error (BSSE) was avoided by using the counterpoise scheme. Monodentate singly bonded NH$_3$, that is NH$_3$ being attached to one oxygen atom, forms a strong hydrogen bond with the zeolitic OH group. This bond has a strength of 60 or 67 kJ/mol, depending on the geometry of the zeolitic cluster. This value is approximately half the experimentally found heat of desorption. For this case, the O···N distance is found to be very short (2.74 or 2.73 Å) and the intermolecular O–H–N stretching frequency is calculated to be 185 or 193 cm^{-1}. The latter values agree reasonably with experimental data. Upon complexation with NH$_3$, the OH stretching frequency shows a red shift of 551 cm^{-1}. Proton transfer from the zeolitic cluster to NH$_3$ is calculated to be unfavorable by 52 kJ/mol, as long as NH$_4^+$ is considered to be monodentate coordinated. The description of the hydrogen-bonded form is only slightly dependent on the basis set used. However, the proton-transfer energy does strongly depend on the basis set used. Electron correlation makes the proton transfer more favorable. The BSSE has a large influence on the description of the structures, especially if electron correlation is included. Although electron correlation has a nonnegligible effect on the proton-transfer energy, some conclusions can be drawn from SCF calculations on doubly and triply coordinated NH$_4^+$. The computed energy of adsorption now is approximately twice that computed for the hydrogen-bonded and singly coordinated NH$_3$ and close to experimentally observed values of ammonia adsorption. From these results, it follows that these adsorption modes are prefered over the singly bonded form. These forms are preferred because of the favorable electrostatic stabilization of NH$_4^+$ when bonded to the cluster by two or three hydrogen bonds.

Introduction

The acidic hydroxyl group in zeolites has been the object of much research. Of particular interest is the interaction between the hydroxyl group and adsorbed bases, like NH$_3$. Experimental infrared measurements and desorption experiments provide some information on the interaction between the acidic zeolitic hydroxyl group and NH$_3$.[1-14] The acidic hydroxyl group has also been studied extensively by quantum mechanical methods.[15] Still the details of the adsorption process and the process of proton transfer are not fully explained. In particular, from these experiments and calculations, it is not clear how the NH$_3$ or the NH$_4^+$ is bonded and which properties influence the acidity of a zeolite. We have started a project to study the proton transfer and the binding of the NH$_4^+$ cation to the zeolite by means of quantum-chemical calculations.

From a theoretical point of view, two questions have to be answered: first the choice of the adsorption site model, relating

to chemical structural aspects and second the technical questions of the computational approach and accuracy. As sketched in

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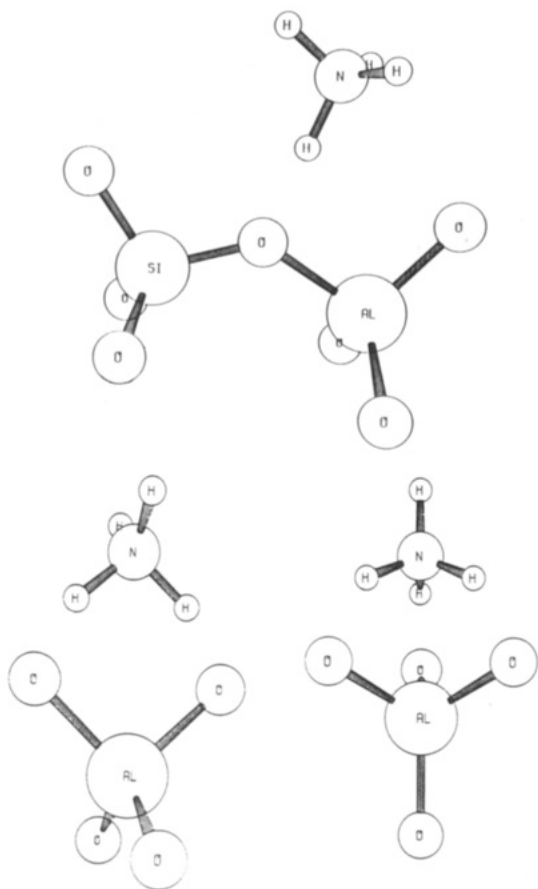
Figure 1. The three possibilities for the coordination of NH_4^+: (a, top) singly (b, bottom left) doubly and (c, bottom right) triply bonded.

Figure 1, the ammonium ion can in principle bind in three different ways to the $Al(OH)_4^-$ tetrahedron in the zeolite lattice. Paukshtis et al.[16] concluded from semiemperical calculations that the NH_4^+ ion is stable when its doubly bound to the zeolite lattice. On the other hand, Allavena[17] suggests that the singly bonded structure is most stable, but that the long-range electrostatic field due to the ionic lattice is responsible for the stabilization of the NH_4^+ cation. This raises the issue of the validity of the cluster approach to study the site locations in zeolites. Apart from this important question, one has also to consider the consequences of computational choices. The accuracy of the computational method is dependent on the basis set and the use of the electron correlation.

In this paper, we will report the first part of our study, mainly dealing with the NH_3 species being singly bonded to the cluster. As a model for the zeolitic acidic site binding to NH_3, a small cluster containing a bridging OH group, $H_3SiOHAlH_3$, is studied. The size of this system is small enough to perform a comparative study of different quantum-chemical approximations. This will provide a benchmark for reference of later studies on more extended systems that as a consequence cannot be done with the same rigor of calculation as employed here. In later studies, effects due to long-range electrostatic interactions and cluster embedding will be reported. Chemically the relative adsorption energies of the singly, doubly and triply bonded NH_4^+ are of course of great interest. Therefore some results, calculated on the SCF level, for doubly and triply bonded NH_4^+ also will be given.

The ab initio calculations for the singly bonded NH_3 were performed at two levels. The lowest level is the SCF level. Electron correlation is obtained by using second-order Møller–Plesset perturbation theory (MP2).[18] The basis set superposition error (BSSE) will be avoided by using the full counterpoise correction (CPC).[19,20] The basis sets used are a split-valence basis set augmented with polarization functions, 6-31G(d), and a larger basis set containing diffuse functions on hydroxylic oxygen 6-311+G(d,p).

Survey of Experimental Data

The adsorption process of NH_3 onto zeolitic hydroxyls can be followed by adsorption and desorption experiments and by infrared measurements. Heats of desorption of ammonia from zeolites, at zero coverage, have been measured by several research groups, and it appears that the results are quite dependent on the type of zeolite and on their pretreatment. Auroux and Vedrine[6] used microcalorimetry to measure the heats of adsorption. On the H and Na forms of zeolite Y, they found these heats to be 120 and 140 kJ/mol. Other authors used temperature-programmed desorption experiments to determine the heats of adsorption. Tsutsumi et al.[7] found heats of adsorption ranging from 100 to 130 kJ/mol on HY zeolites; Schirmer et al.[8] reported a distribution of adsorption energies with a maximum around 40 kJ/mol for the adsorption of ammonia on zeolite NaH–Y. Post and van Hooff[9] found heats of desorption on ZSM-5-type zeolites ranging from 73 to 169 kJ/mol, depending on the site of adsorption. For different types of zeolites H–rho and H–erionite, Shannon et al.[10] measured heats of adsorption between 140 and 190 kJ/mol. Dima and Rees[11] recently found heats of adsorption ranging from 97 to 153 kJ/mol.

Additional infrared measurements can give detailed information on the adsorption state. With far-infrared measurements at $NaNH_4^+$–Y, Ozin et al.[1] found a mode at 169 cm^{-1} which was assigned to the NH_4^+ vibration in the zeolite α-cage. Stock et al.[2] assigned bands at 204 and 174 cm^{-1}, measured in zeolite X and Y, to NH_4^+···lattice modes; the two bands were assigned to different cation sites. In a later experiment on a NH_4^+-Y zeolite, Ozin et al. found the NH_4^+···lattice modes to give a broad band in the range 164–193 cm^{-1}.[3] At 423 K, Hegde et al.[4] assigned the broad band in the 3000–3400-cm^{-1} region to be N–H stretching modes. The bending modes were found to give broad bands at 1450 and 1700 cm^{-1}.[5]

Changes in the lattice vibrations of the zeolite upon ammoniation indicate that calculations predicting NH_3 being the stable species instead of NH_4^+ should be considered with care. If the lattice stretching vibrations in the Si–O stretching region of NaY,[12] NH_4Y, and HY[13] are compared, one notes that the former two are almost equivalent whereas the latter is different.

Methods

For singly bonded ammonia, a useful way to model the zeolite acidic site is a bridging OH group in a cluster with the formula SiH_3OHAlH_3. In this cluster, the dangling bonds of the T atoms (Si and Al) are saturated by hydrogens. Using this cluster, the protonation of NH_3 and the hydrogen bond formation to NH_3 will be compared. Also the infrared frequencies and their shifts upon complexation will be calculated. Different methods will be used. The simplest one is the SCF method. The SCF calculation can be followed by a second-order Møller–Plesset calculation[18] this is denoted SCF/MP2. If the result of a calculation is corrected for the BSSE by the counterpoise correction,[19,20] the calculation is denoted SCF/CPC, the notation for a SCF/MP2/CPC calculation then is evident.

The calculations are split in two sets. In the first set, a 6-31G(d)/STO-3G basis set is used and the geometries are fully optimized. The basis set denoted as 6-31G(d)/STO-3G has a

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6-31G(d)[21] basis set on all atoms and a STO-3G[22] basis on the dangling bond hydrogens. In the second set of calculations, the geometries are kept fixed, and the results obtained with the 6-31G(d)/STO-3G basis sets are compared to those obtained with a much larger basis set: 6-311+G(d,p)/STO-3G.[21-23] In this larger basis set, the hydrogens that saturate the dangling bonds have a STO-3G basis.[22] The other hydrogens, aluminum, and silicon have a 6-31G(d,p) basis.[21] The nitrogen has a 6-311G(d,p) and the hydroxyl oxygen a 6-311+G(d,p) basis.[23] On the hydroxyl oxygen, diffuse functions were included because the calculated proton affinity of oxygen anions appears to be sensitive to these functions.[24] The smaller basis set used on the dangling bond hydrogens will have little effect on the proton-transfer energy.[25] By comparison of the small basis set results with the results obtained with the larger one, the validity of the use of this smaller basis set can be tested.

Little is known about the flexibility of the lattice surrounding the acidic site. In the calculations with fixed geometry, it is assumed that the T-atoms are constrained in their movements in the lattice. If the geometry is optimized, the T-atoms are assumed to have no geometrical constraints. The latter calculations have the disadvantage of using more computer time but have the advantage that much more complete infrared and Raman spectroscopic properties can be obtained from the calculations.

The large basis set calculations were performed with the GAMESS,[26] ATMOL,[27] and INTACAT[28] program packages on an APOLLO 10000 and a Cyber 205. The small basis set calculations were executed on an Alliant FX-8 using Gaussian88.[29] In the small basis set, the MP2 calculations were done with frozen cores.

In the first set of calculations, the $OSiAlH_7$, $OSiAlH_6^-$, NH_3, and NH_4^+ molecules are fully geometry optimized, with the restriction that the former two are kept in a C_s symmetry. The complex of the SiOAl hydride cluster with the ammonia molecule is constructed by alligning the O–H bond with the C_3 symmetry axis of NH_3. For several hydrogen bonds formed between acidic XH and NH_3, little or no deviation from linearity has been reported.[30-32] These geometries will be the starting geometries for the interaction energy and normal mode calculations. The geometries are optimized in the same basis set that will be used in the further calculations: 6-31G(d)/STO-3G. The normal modes are calculated at the SCF level using the force method with analytical first derivatives provided by the Gaussian88 package. In addition, the interaction energy and the intermolecular
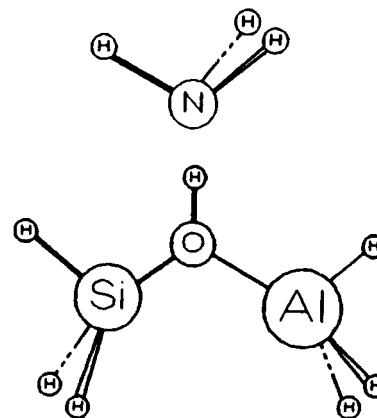
Figure 2. The silicon aluminum hydride cluster interacting with ammonia. The bond lengths and angles for the ionic and covalent form are given in Table I.

TABLE I: The Geometrical Parameters[a]

parameter	covalent structure	ionic structure	parameter	covalent structure	ionic structure
R_{N-H}	1.01	1.03	∠H–N–H	106.7	109.471
R_{O-H}	0.96		∠H–N–O	112.1	109.471
R_{O-Si}	1.67	1.60	∠Si–O–Al	129.1	136.73
R_{O-Al}	1.85	1.82	∠H–O–Si	118.1	118.1

[a] The parameters are given in angstroms and degrees; the ∠H–N–O is the angle the NH bond makes with the C_3 axis. The O–H distance in the ionic structure is equal to the O–N equilibrium distance minus the N–H bond length (1.03 Å).

stretching frequency will be calculated from the intermolecular potential curve. This curve is generated by choosing a number of equidistant (0.1 Å) O–N points around the minimum. At each fixed O–N distance, all internal coordinates, except the ones that determine the position of the dangling bond proton, are optimized. At this reoptimized geometry, a single-point SCF/MP2/CPC calculation of the interaction energy is performed. From the minimum in the curve, the final interaction energy is calculated, and the curvature yields the intermolecular stretching frequency. The intermolecular frequency is calculated in this way because it allows us to study this vibration at the SCF/MP2/CPC level and because the normal modes give the modes a gas-phase complex would have, whereas for this frequency it is more desirable to picture NH_3 as vibrating against a lattice with infinite mass. However, we cannot exclude the possibility of this vibration to couple with other low-frequency modes.

In the second set of calculations, the geometries of the interacting particles are kept fixed. The Si and Al positions are taken from force field calculations on a 1:1 Si/Al Na-faujasite.[33] The hydrogens that saturate the dangling bonds are put in the direction of the missing oxygens in the second shell of atoms with respect to the bridging OH group, with a Si–H bond length of 1.615 Å and a Al–H bond length of 1.480 Å. To minimize geometrical artifacts, the positions of the cluster hydroxyl oxygen atom and proton were optimized at the SCF/6-21G level with d functions on oxygen only. NH_3 and NH_4^+ were taken in their experimental geometry.[34,35] The interaction energy has been calculated for the covalent structure, which consists of the acidic form of the SiAl–hydride cluster hydrogen bonded to the NH_3 as well as for the ionic structure that consists of the anionic form of the SiAl–hydride complexed to a NH_4^+ cation. In both the covalent and the ionic complexes the C_3 axis of the NH_3 species was taken along the O–H bond. In Figure 2 and Table I, the geometrical parameters for both the covalent and the ionic systems are given.

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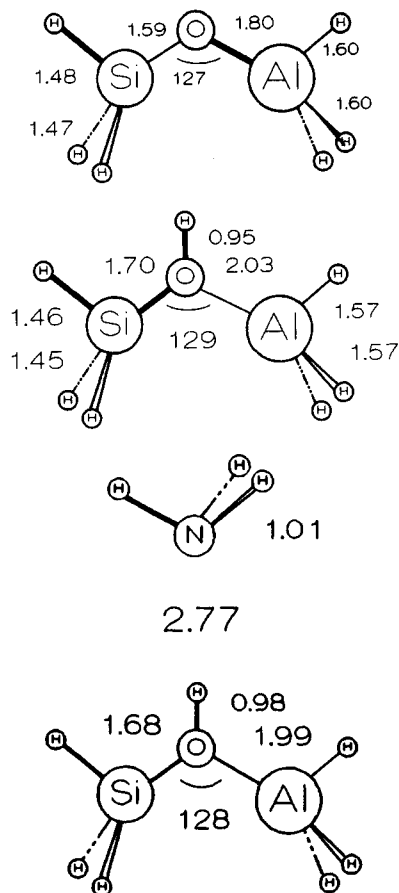(35) Ibers, J. A.; Stevenson, D. P. *J. Chem. Phys.* **1958,** *28,* 929.

Figure 3. Results of optimizations.

These parameters are kept fixed in this second set of calculations; thus this set of calculations will be denoted as the rigid geometry calculations.

The optimum energies for the covalent and the ionic structures are determined by optimizing the O–N distance at the SCF/MP2/CPC level, keeping the monomer geometries fixed. As mentioned above, this calculation will be carried out in a small and a large basis set. The first set has the advantage that the calculations require little computer time; the second is of higher quality and may be expected to yield the proton affinity within 7 kJ/mol at the MP2 level.[24] On comparison of the difference in proton affinities between OH⁻ and NH₃, it is seen that electron correlation calculated at the MP2 level gives a proper value of the correlation energy contribution to the proton-transfer energy. MP2 behaves well in comparison to other methods for calculation of electron correlation.[36] The larger basis set may be expected to give the energy of the interaction of NH₃ with the cluster with a precision of 3 kJ/mol.[37]

For the covalent system, the adsorption energy equals the binding energy of NH₃ to the zeolitic cluster; for the ionic species, the total adsorption energy should be calculated by the following formula.

$$\Delta E^{ads} = \Delta E^{bind} + \Delta E_\infty^{PT}$$

ΔE_∞^{PT} denotes the proton-transfer energy at infinity. The formula means that the total adsorption energy is thought of as being built from a proton transfer at infinity followed by binding of the NH₄⁺ cation to the zeolite lattice. To compare in a fair way the adsorption energies for the doubly and triply bonded system, the ΔE_∞^{PT} used was equal to the ΔE_∞^{PT} for the H₃SiOHAlH₃ system to eliminate the (small) difference in proton affinity for the different clusters.

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TABLE II: Total Energies (in hartrees)[a]

structure	SCF energy	structure	SCF energy
OSiAlH₇	−609.732 998	NH₄⁺	−56.511 865
OSiAlH₆⁻	−609.201 621	OSiAlH₇···NH₃	−665.926 384
NH₃	−56.171 677	OSiAlH₇···NH₃*	−665.916 245

[a] The total energies (in hartrees) of the fragments in their optimized geometries as shown in Figure 3. The optimization was performed in the 6-31G(d)/STO-3G basis. The optimization for * started from the ionic structure.

TABLE III: Scaled Harmonic Frequencies in the Optimized Geometry for the Singly Bonded NH₃[a]

description of mode	complex	neutral fragments	ionic monomers
OH bend in plane	1251	1001	
OH stretch	3115	3666	
NH deformation	1161/1599/1604	1407/1636	1106/1614
N–H stretch	3210/3325/3329	3095/3224	3199/3317

[a] All frequencies are in cm⁻¹.

TABLE IV: The Hydrogen Bond in the Optimized Geometry[a]

method	R_{N-O}	ΔE^{bind}	ν_{inter}
SCF/MP2/CP	2.74	−59.5	185
SCF/CP	2.82	−48.6	194
SCF/MP2	2.64	−77.5	227
SCF	2.77	−57.1	184

[a] The equilibrium distances are given in angstroms, the binding energies in kJ/mol, and the frequencies in cm⁻¹.

Results

In the first set of calculations, the geometries of the fragments were fully optimized at the SCF level using the 6-31G(d)/STO-3G basis. The complex was optimized completely except for the dangling bond hydrogens. These hydrogens were assigned similar positions in the acidic and in the anionic form. The results of the optimizations are given in Figure 3, and the accompanying total SCF energies in Table II. Inspection of the OH and NH bond lengths shows that the lowest total energy is obtained with the acidic proton attached to the zeolitic cluster. To determine whether there was also a minimum on the NH₄⁺ side, the complex was also optimized starting from the ionic structure, that is from the complex of the anionic silicon aluminum hydride and the ammonium cation. The ionic structure did not appear to be a local minimum: the result of the optimization was a structure with only minor differences from the optimizations started at the neutral monomers (these differences are due to the position of the dangling bond hydrogens which were kept fixed). Thus in this model also no proton transfer takes place.

The full set of harmonic frequencies was calculated at the SCF level for all fragments and for the optimized complex. The frequencies and their shifts upon deprotonation and complexation can give additional information about the nature of the structures. A few selected frequencies are given in Table III. To make the comparison with experiment more convenient, the SCF normal mode frequencies are scaled by 0.89, the generally used correction factor.

The intermolecular modes for the OSiAlH₇···NH₃ system were all mixed modes; they appeared at 62, 91, 135, 217, 280, and 379 cm⁻¹. The most striking shift in frequencies upon complexation is the shift in the OH stretching mode; it has a red shift of 551 cm⁻¹. Like the elongation of the bond length by 0.03 Å, it signals the weakening of the OH bond when forming the hydrogen bond. When the N–H modes are examined, it can be seen that starting from the NH₃ structure the frequencies shift toward the values in the NH₄⁺ cation.

In Table IV, the binding energies and the intermolecular frequencies as calculated from the potential energy curve are given.

Results for the fixed-geometry cluster calculations are presented in Tables V and VI. For the largest basis set the binding energy, the intermolecular frequency, and the proton-transfer energy as

TABLE V: **Characteristics of the Systems in the Rigid Geometry Calculated in a Large Basis**

method	R_{NO}		ΔE^{ads}		$\nu_{intermolecular}$	
	coval	ionic	coval	ionic	coval	ionic
SCF/MP2/CPC	2.73	2.53	−67.0	−15.4	193	275
SCF/CPC	2.79	2.55	−59.7	4.8	181	278
SCF/MP2	2.64	2.48	−87.7	−15.2	227	281
SCF	2.76	2.53	−69.4	−5.0	223	276

a The bondlengths are in angstroms, the binding energies in kJ/mol, and the frequencies in cm^{-1}.

calculated from the potential energy curve and the formula given in the Methods are given in Table V. The ΔE_{∞}^{PT} was −445.2 kJ/mol at the SCF level and −435.6 kJ/mol at the MP2 level.

In the first and second rows of Table V, the bond lengths and binding energies are given. Proton transfer is unfavorable in all cases. Furthermore the inclusion of electron correlation stabilizes the ionic structure by 13 kJ/mol. For the ΔE_{∞}^{PT}, this stabilization was 10 kJ/mol. The counterpoise correction hardly affects the proton-transfer energy because the correction is almost equal in the covalent and ionic systems. To compare the results obtained in a different basis set, the calculations were repeated in the 6-31G(d)/STO-3G basis with the same geometries. The results of these calculations are given in Table VI. The ΔE_{∞}^{PT} was −494.6 kJ/mol at the SCF level and −492.2 kJ/mol at the MP2 level for this small basis set. The small basis set clearly overestimates the proton-transfer energy.

When Tables V and VI are compared, it is seen that the binding energy for the hydrogen-bonded cluster is quite well described by the small basis set: it is within 2 kJ/mol from the one obtained in the larger basis set. The intermolecular stretching frequency shows a somewhat larger deviation. However, the ionic structure is poorly described by the small basis set. The adsorption energy deviates 39 kJ/mol from the ones obtained with the larger basis set at the SCF/MP2/CPC level and 11 kJ/mol from ones at the SCF level. The effect of the CPC on the optimum R is the same as in the large basis set, the influences on the absorption energies are now larger, due to the incompleteness of the small basis set.

On comparison of the geometries in Table III and the covalent structure of Table VI, the influence of the geometry optimization can be estimated. It is seen that the binding energies are about 11 kJ/mol higher in a fixed geometry.

Although the study of the coordination of the doubly and triply bonded NH_4^+ is still at an early stage, some results at the SCF level are useful. To model the adsorption sites as pictured in Figure 1, we used an $Al(OH)_2H_2$ and an $Al(OH)_3H$ cluster to describe the doubly and triply bonded NH_4^+, respectively. For these clusters, we used the 6-311+G(d,p)/STO-3G basis set. The geometries were completely optimized; the result of the geometry optimizations is that NH_3 was converted to NH_4^+. The doubly bonded complex has an Al–N distance of 3.41 Å and a N–O distance of 2.56 Å; for the triple bonded structure, these distances were 3.0 and 2.7 Å.

The heats of desorption for these two structures were calculated to be −110 and −112 kJ/mol, respectively. However, we wish to emphasize that these are SCF results, and as shown, they can result in enhanced protonation energies. These results are fully in agreement with the experimental results; proton transfer is found, and the heat of adsorption agrees perfectly with experimentally found values. These results clearly disagree with the semiempirical calculations of Paukshtis et al.[16]

Discussion

When the clusters in the optimized geometry are compared, it is seen from Figure 3 that the anionic structure has a Si–O bond length shortened by 0.11 Å and a Al–O bond length shortened by 0.23 Å. The Si–O–Al angle has become somewhat larger. After deprotonation, the anion is stabilized by strengthening the Si–O and especially the Al–O bonds. In the protonated form, aluminum forms a very weakly bonded complex with the bridging oxygen atom whereas in the anionic form it forms a bond that

is comparable to the Al–O bond in $Al(OH)_4^-$. The stabilization of the anion by strengthening the Si–O and Al–O bonds is in agreement with earlier cluster calculations.[38] After adsorption of NH_3, that is when the hydrogen bond is formed, the geometrical parameters of the cluster are slightly shifted toward the anionic values. The Si–O and Al–O bonds shorten; the N–H bonds lengthen. The $\angle_{SiOAl}$ gets larger, and the $\angle_{HNH}$ widens. These changes are similar to those found experimentally for zeolite RHO: compared to the hydrogen form of the zeolite, the ammonia form has a smaller T–O–T angle; T can be aluminum or silicon; the average T–O distance only shows minor changes.[39,40] The NH_3 also undergoes changes on the formation of the hydrogen bond. The frequency of the N–H stretching modes shifts into the region where the N–H stretching of the NH_4^+ adsorbed in zeolites is found experimentally. Moreover the OH stretching frequency shifts into the same region.

The binding energy, for the hydrogen-bonded NH_3, calculated in the optimized geometry is 60 kJ/mol, and is 67 or 69 kJ/mol in the fixed geometry, depending on the basis set used. The experimental heat of adsorption is 110 ± 40 kJ/mol,[6-11] with a large spread, dependent the type of zeolite. The much better agreement found for doubly or triply coordinated molecules supports the view that the NH_3 species is adsorbed in the latter modes. From crystallographic data, it is known that cations always have a high coordination number in the zeolite.[41]

The second set of calculations, performed with the large basis set, enables a comparison of the results obtained at the different levels of theory, and the effect of geometry optimization can be studied. One observes that electron correlation included at the MP2 level increases the strength of the hydrogen bond by about 8 kJ/mol. Without the counterpoise correction, the interaction energy is overestimated by 20 kJ/mol at the MP2 level. Because of the opposing effects of the BSSE and the absence of correlation, the binding energies found at the SCF level compare well with the values found at the SCF/MP2/CPC level: they are the same within 2.5 kJ/mol. The lengths of the hydrogen bonds react in a way similar to the different methods as do the energies. If the counterpoise correction is omitted, then the hydrogen bond is found too short, and if electron correlation is included, then the bond length also shortens. The value found at the SCF level is within 0.03 Å of the value found at the SCF/MP2/CPC level.

When the proton-transfer energies, that is the difference in energy between the ionic and covalent structures are compared, the counterpoise correction hardly changes the difference in energy between the two systems, not even at the MP2 level. This can be explained by the only minor changes in geometry. However the inclusion of electron correlation does make a difference: it stabilizes the ionic form about 13 kJ/mol more than it does the covalent form. This is far less than the effect of electron correlation calculated by Sauer et al. on the bond between H_2O and a zeolitic cluster.[42] This possibly relates to the large changes in geometry found in these calculations; then the BSSE could play an important role. No BSSE correction was applied in these cluster calculations.

Compared to other hydrogen bonds, the cluster NH_3 bond is very strong and short. For example, the $H_2O–NH_3$ bond has a strength of 24.0 kJ/mol with an O–N distance of 3.01 Å.[30] The hydrogen bonds of NH_3 with strong acids are comparable to the one between NH_3 and the zeolitic OH group; the CPC uncorrected SCF/MP2 values for the $H_3N–HCl$ and $H_3N–HF$ bonds are 46.15 and 63.30 kJ/mol.[43] Ugliengo et al.[44] found a hydrogen bond with a strength of 36.5 kJ/mol at the SCF/MP2 level, without BSSE correction, for the $SiH_3OH–NH_3$ system. Geerlings

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TABLE VI: Characteristics of the Systems in the Rigid Geometry Calculated with the Small Basis Set[a]

method	R_{NO}		ΔE^{bind}		$\nu_{intermolec}$	
	coval	ionic	coval	ionic	coval	ionic
SCF/MP2/CPC	2.72	2.56	−68.5	23.6	211	508
SCF/CPC	2.77	2.54	−59.3	38.6	190	348
SCF/MP2	2.64	2.54	−89.7	−35.5	227	535
SCF	2.73	2.52	−68.4	5.6	204	364

[a] The bondlengths are in angstroms, the binding energies in kJ/mol, and the frequencies in cm⁻¹.

et al.[45] found an interaction energy of 56.2 kJ/mol for NH₃ and a zeolitic cluster with the same stoichiometry as used in this paper, with a 3-21G basis set at the SCF level. At this level, a O–N distance 2.69 Å was found.

A striking result is that the zeolitic cluster does not transfer its proton to the base ammonia if the NH₃ is only singly coordinated. When the geometries are optimized, the ionic structure is not even a local minimum, and in the rigid geometry approach, the ionic structure is 51.6 kJ/mol higher in energy than the covalent structure.

The results of the calculations as described in this work are not in agreement with the results found by Allavena et al.[17,38] They found that the ion pair structure was 13 kJ/mol lower in energy than the covalent structure. No details of the calculation are available for further comparison.

Absence of proton transfer to the NH₃ in the singly coordinated structure agrees with gas-phase reactions of NH₃ with strong acids. In absence of a solvent, HCl and HF do not transfer their proton to NH₃.[31,43] To transfer the proton, the ionic products of the transfer should be stabilized. This stabilization is not present in these small cluster calculations which therefore resemble gas-phase reactions. Solvation effects are necessary to stabilize charge separation. The cation can become stabilized by hydrogen bonding with other coadsorbed species. Such complexes have been shown experimentally for a water zeolite system.[46] The interaction of the cation with another NH₃ is large enough to favor proton transfer.[32] Our result that NH₄⁺ doubly or triply coordinated to negatively charged oxygen atoms becomes energetically favored agrees with early ideas by Kazansky[47] that the cations generated by proton transfer have to be stabilized by solvation by the zeolite wall.

Stabilization of the cation form may occur when long-range effects due to the Madelung potential are included in the calculations. Several approaches have been used to embed the cluster into the Madelung field of the zeolite. The results found differ considerably. Allavena et al.[17] reported that the ionic structure

was stabilized by 196 kJ/mol by applying the electric field of the zeolite onto the cluster calculations. By imposing the Madelung potential on the position of the acidic site, however, polarization effects of the cluster were not taken into account. Vetrivel et al.[48] simulated the field by a limited number of point charges. This simulation overestimated the deprotonation energy, probably because of the stoichiometry of the cluster. A deprotonation energy of 634 kJ/mol was found. The excellent agreement with the experiment for the computed NH₃ adsorption energies when adsorbed doubly or triply coordinated might indicate that long-range effects could be of minor importance compared to the difference in energy when site coordination is varied. However, other chemical differences in zeolites might be due to the differences in electrostatic field.

Conclusion

For the singly bonded configuration, the zeolitic cluster does not transfer its proton to the NH₃ molecule. Proton transfer is unfavorable by 52 kJ/mol. Although there is a strong interaction between the NH₄⁺ cation and the anionic cluster, the ionic reaction products are not stabilized enough to favor the ionic structure. Monocoordinated NH₃ forms a strong hydrogen bond with the cluster; this bond has a strength of 60, 67, or 69 kJ/mol, depending on the basis set and the geometry of the cluster. These calculated interaction energies are too small compared to the experimentally observed desorption energy of 110 ± 45 kJ/mol. SCF calculations of NH₃ adsorbed with a double or triple coordination indicate that this adsorption mode of NH₃ is the preferred one and now NH₄⁺ is a stable ion.

When a large basis set is used, inclusion of electron correlation stabilizes the ionic state by about 13 kJ/mol relative to the value without electron correlation. Without the counterpoise correction, the binding energy of NH₃ or NH₄⁺ is overestimated by about 10 kJ/mol at the SCF level and by about 22 kJ/mol at the MP2 level. About half of the MP2 binding energy is a BSSE effect. The smaller basis set used does not seem able to aptly describe the ionic structures. The difference between the covalent and the ionic structure is then grossly overestimated.

Registry No. NH₃, 7664-41-7.

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