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# Theoretical Calculations of the Proton Affinities of *n*-Alkylamines, *n*-Alkyl Thiols, and *n*-Alcohols and the Ammonium Affinities of the *n*-Alcohols

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The B3LYP/6-31+G(d,p) method was used to calculate the proton affinities of *n*-alkylamines, *n*-alkyl thiols, and *n*-alcohols and the ammonium affinities of the *n*-alcohols up to C-18. These affinities and the gas-phase acidities of the *n*-alcohols were all found to correlate linearly with the quotient $n/(n + 1)$, where $n$ is the number of carbon atoms in the alkyl chain. This correlation leads to a limiting value of $\Delta H$ for very long alkyl chains: for the amines, thiols, and alcohols, the calculated maximum proton affinities $\mathrm{PA}_{298,\mathrm{max}}(\mathrm{RX})$ were 938.7, 828.2, and 816.9 kJ mol$^{-1}$, respectively. The maximum ammonium affinity, $-\Delta H_{298,\mathrm{max}}$, of the *n*-alcohols is 115.1 kJ mol$^{-1}$.

## 1. Introduction

In selecting an appropriate reactant gas for chemical-ionization mass spectrometry (CIMS), it is useful to know the proton affinity (PA) of the analyte. If a reactant gas with a much lower PA is selected, the proton transfer is followed by fragmentation, whose extent depends on the size of the PA difference.[1] On the other hand, reactant gases with higher PA's often form adducts with the analyte through cationic hydrogen bonds; the difference in PA's of reactant gas and analyte determines the size of this complex, which may contain a large number of molecules of the reactant gas.[2,3] Obtaining a simple mass spectrum requires the formation of a monoadduct $[\mathrm{M} + \mathrm{X}]^+$ and the avoidance of multiple adducts $[n\mathrm{M} + m\mathrm{X}]^+$.

The majority of experimentally determined PA's have been obtained either by relative methods, kinetic or thermokinetic, or from gas-phase equilibrium constants based upon some absolute standard that is accessible over ionization threshold measurements or theoretical calculations.[4] These experimental methods require very complex equipment.[5−7]

Theoretical calculation of PA's and of possible adduct complexes gives access to absolute values. The necessary semiempirical and ab initio procedures and density functional theories (DFT) have been available for a long time, and molecular energies calculated with G3,[8] G3(MP2),[9] and DFT/B3LYP[10,11] are in very good agreement with experimental values. Ab initio methods are preferred for calculating the structure of molecules, but for large molecules methods such as G3(MP2) exceed computer capacity. For this reason the present work has made use of the DFT/B3LYP method developed by Becke, Lee, Yang, and Parr and contained in the software package GAUSSIAN98.[12]

No theoretical determinations of the PA's of higher *n*-alkyl compounds of amines, thiols, and alcohols, of the ammonium affinities of the *n*-alcohols, or of their dependence on the length of the carbon chain have been reported previously, although the results of some experimental and theoretical investigations of lower *n*-alkyl compounds have been published.[2,13−15] This article reports the calculation of the relevant energy values of these industrially important intermediates, so that they can aid in the selection of the reactant gas in GC−CI-MS studies.

Both natural and technical amines, alcohols, and thiols consist mainly of even-numbered *n*-alkyl compounds. For this reason the emphasis of the calculations was placed upon these homologues. Since the first three odd-numbered *n*-alkyl compounds exercise a nonnegligible influence upon the later calculations, they were also taken into consideration.

## 2. Calculation Method

The molecular energies were calculated by means of the standard hybrid density functional method DFT/B3LYP, which has repeatedly been shown to be highly efficient.[16,17] DFT/B3LYP is an approximation to the three-parameter adiabatic connection method (ACM) of Becke[10] and consists of a combination of Slater,[18] Hartree−Fock,[19] and Becke[10] exchange functions with the local correlation function of Vosko, Wilk, and Nusair (VWN)[20] and the nonlocal one of Lee, Yang, and Parr (LYP).[9] The basis set 6-31G was extended with a simply diffuse (+)[21] and a (d,p) polarization function.[22]

The linear, all-anti form was selected as the geometric basis in optimizing the structures of all the alkyl compounds. The possibility that significant contributions to the average structure in the gas phase are made by forms in which the hydrocarbon chain is coiled about the charged end of the molecule[23] had to be ignored, since there is not enough information in the literature to allow a decision about that and the number of starting geometries is huge.

## 3. Proton Affinity

The proton affinity of molecules is generally defined as the negative reaction enthalpy of the bimolecular protonation (eq 1). Equation 2 was used to calculate the absolute proton affinities.[24−26]

$$\mathrm{A} + \mathrm{H}^+ \rightarrow \mathrm{AH}^+ \qquad -\Delta H \tag{1}$$

$$\mathrm{PA(A)} = -\Delta H = -\Delta E_{\mathrm{elec}} - \Delta\mathrm{ZPE} + \Delta E_{\mathrm{v}}(T) + C \tag{2}$$

$\Delta E_{\mathrm{elec}}$ represents the electronic energy difference between the protonated and unprotonated forms, $\Delta$ZPE the difference in the

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**TABLE 1: Comparison of Proton Affinities Calculated with G3 und B3LYP (kJ mol$^{-1}$)**

| alcohol | $PA_{298}G3^a$ | $PA_{298}B3LYP^b$ | $PA_{298}Ref^c$ |
|---|---|---|---|
| $CH_3OH$ | 755.1 | 753.2 | 754.3 |
| $C_2H_5OH$ | 777.7 | 773.0 | 776.4 |
| $C_3H_7OH$ | 785.4 | 779.7 | 786.5 |

[a] $PA_{298}$ calculated with G3: additivity approximation to determine the QCISD(T)/G3large; G3large is modified 6-311+G(3df,2p) basis set. [b] $PA_{298}$ calculated with B3LYP/6-31+G(d,p). [c] Reference value from Hunter and Lias.[4]

**TABLE 2: Proton Affinities of *n*-Alkylamines, *n*-Alkyl Thiols, and *n*-Alcohols (kJ mol$^{-1}$)**

| compound | $PA_{298}B3LYP^a$ | $\Delta E_{corr}(n)$ | $PA_{298}Cal^b$ | $PA_{298}Ref^c$ | $diff^d$ |
|---|---|---|---|---|---|
| $CH_3NH_2$ | 897.8 | −1.1 | 896.7 | 899.0 | −2.3 |
| $C_2H_5NH_2$ | 910.0 | 0.7 | 910.8 | 912.0 | −1.2 |
| $C_3H_7NH_2$ | 915.1 | 2.4 | 917.5 | 917.0 | 0.5 |
| $C_4H_9NH_2$ | 918.1 | 3.8 | 921.9 | 921.5 | 0.4 |
| $C_5H_{11}NH_2$ | 919.7 | 5.0 | 924.7 | 923.5 | 1.2 |
| $C_6H_{13}NH_2$ | 920.6 | 6.1 | 926.7 | 927.5 | −0.8 |
| $C_8H_{17}NH_2$ | 921.4 | 7.9 | 929.3 | 928.9 | 0.4 |
| $C_{10}H_{21}NH_2$ | 921.8 | 9.2 | 931.0 | 930.4 | 0.6 |
| $C_{12}H_{25}NH_2$ | 922.1 | 10.2 | 932.2 | | |
| $C_{14}H_{29}NH_2$ | 922.2 | 10.9 | 933.1 | | |
| $C_{16}H_{33}NH_2$ | 922.3 | 11.6 | 933.8 | | |
| $C_{18}H_{37}NH_2$ | 922.4 | 12.2 | 934.6 | | |
| $CH_3SH$ | 769.2 | −1.5 | 767.7 | 773.4 | −5.7 |
| $C_2H_5SH$ | 786.0 | 1.9 | 787.9 | 789.6 | −1.7 |
| $C_3H_7SH$ | 792.9 | 5.0 | 797.9 | 794.9 | 3.0 |
| $C_4H_9SH$ | 796.2 | 7.6 | 803.8 | 801.7 | 2.1 |
| $C_5H_{11}SH$ | 798.1 | 9.8 | 807.9 | | |
| $C_6H_{13}SH$ | 799.2 | 11.7 | 810.9 | | |
| $C_8H_{17}SH$ | 800.2 | 14.5 | 814.8 | | |
| $C_{10}H_{21}SH$ | 800.7 | 16.5 | 817.2 | | |
| $C_{12}H_{25}SH$ | 800.9 | 17.8 | 818.7 | | |
| $C_{14}H_{29}SH$ | 801.1 | 18.8 | 819.9 | | |
| $C_{16}H_{33}SH$ | 801.2 | 19.8 | 821.0 | | |
| $C_{18}H_{37}SH$ | 801.3 | 21.2 | 822.4 | | |
| $CH_3OH$ | 753.2 | 0.2 | 753.5 | 754.3 | −0.8 |
| $C_2H_5OH$ | 773.0 | 3.0 | 776.0 | 776.4 | −0.4 |
| $C_3H_7OH$ | 779.7 | 5.5 | 785.2 | 786.5 | −1.3 |
| $C_4H_9OH$ | 783.7 | 7.7 | 791.4 | 789.2 | 2.2 |
| $C_5H_{11}OH$ | 785.9 | 9.7 | 795.7 | | |
| $C_6H_{13}OH$ | 787.6 | 11.5 | 799.1 | | |
| $C_8H_{17}OH$ | 788.1 | 14.5 | 802.6 | | |
| $C_{10}H_{21}OH$ | 788.5 | 16.7 | 805.3 | | |
| $C_{12}H_{25}OH$ | 788.8 | 18.4 | 807.2 | | |
| $C_{14}H_{29}OH$ | 788.9 | 19.6 | 808.5 | | |
| $C_{16}H_{33}OH$ | 788.9 | 20.5 | 809.4 | | |
| $C_{18}H_{37}OH$ | 789.0 | 21.2 | 810.2 | | |

[a] $PA_{298}$ calculated with B3LYP/6-31+G(d,p). [b] Sum of $PA_{298}B3LYP$ and $\Delta E_{corr}(n)$. [c] Reference value from Hunter and Lias.[4] [d] Difference between $PA_{298}Cal$ and $PA_{298}Ref$.

zero-point energies, and $\Delta E_v(T)$ the change in the occupation of the vibrational levels as a function of the temperature. The correction $C$ is made necessary by the assumption that the translational and rotational changes behave classically.

Polarization interactions are still a challenge for DFT functionals. The B3LYP functional augments the Becke gradient correction for the exchange and Lee−Yang−Parr correlation functional with a small amount of HF exchange. While this improves the performance for bond dissociation energies, it does not do anything for polarization interactions, for which traditional correlation such as MP2 is still needed.

Curtiss et al.[8] and Hammerum[27] have demonstrated that proton affinities obtained with the G3 method agree well with experimental values for small molecules. To compare B3LYP and G3 for the molecules in question here, G3 calculations of the 298 K proton affinities were carried out for the primary alcohols C-1 to C-3. The results are shown in Table 1 along with experimental values cited in a recent critical evaluation by Hunter and Lias and generally taken as standard.[4,28] The good agreement of the G3 and experimental values is obvious.

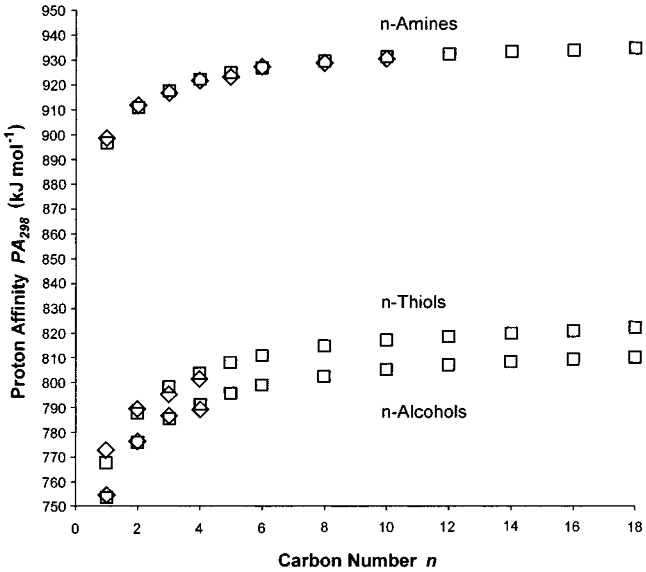

**Figure 1.** Calculated $PA_{298}$ of the alkyl compounds as a function of carbon number $n$ (□ = this work; ◇ = literature values).

A comparison of the energy values obtained by means of B3LYP with energies found in the literature and those calculated by G3 showed that this DFT method is applicable to small molecules. As expected, the deviation of B3LYP from the experimental and G3 values increases with the size of the molecule, and for *n*-alkyl compounds with 10 or more atoms a correction to the B3LYP values becomes necessary. As in all DFT models, the main problem here is to determine the correct polarization, exchange, and correlation energies for the molecular systems. The difference observed with the larger molecules can be interpreted as a correction $\Delta E_{corr}$ to the correlation component of the electronic energy. An empirical correlation function $\Delta E_{corr}(n)$, dependent on carbon-chain length $n$, was therefore determined from the difference between the experimental proton affinities in the literature[4] and those calculated here; it was added to the $\Delta E_{elec}$ term in $PA_{298}B3LYP$. This correlation function is dependent upon the type of quantum-mechanical model used and must therefore be calculated for each of these models. In the work here a simple polynomial of third degree was used to calculate $\Delta E_{corr}(n)$, the use of polynomials of higher degree not leading to any improvement in the correlation. The 298 K proton affinities of the alkyl amines, thiols, and alcohols calculated with B3LYP are listed in Table 2 and plotted in Figure 1. Table 2 includes the literature values and empirical corrections $\Delta E_{corr}(n)$.

The average difference between the zero-point energies of the protonated and unprotonated forms was determined as 39.9 kJ mol$^{-1}$ for the amines, 27.2 kJ mol$^{-1}$ for the thiols, and 32.7 kJ mol$^{-1}$ for the alcohols. To calculate the gas-phase basicity ($GB = -\Delta G_{298}$), the following arithmetically averaged entropies of protonation $\Delta S_p(T)$ were determined for the *n*-alkyl compounds: amines, $-$ 4.7 J mol$^{-1}$ K$^{-1}$; thiols, +4.3 J mol$^{-1}$ K$^{-1}$; alcohols, +7.0 J mol$^{-1}$ K$^{-1}$. As entropy of the proton $S^o(H^+,T)$ a recommended value of 108.95 J mol$^{-1}$ K$^{-1}$ was used.[29]

Figure 1 suggests that the calculated PA's of the *n*-alkyl compounds approach a limit. When the *x*-axis is redefined as $n/(n + 1)$, a linear function is obtained (Figure 2). Equation 3 expresses this linear relationship between the PA's of the *n*-alkyl

**TABLE 3: Calculated Parameters of Eq 3 for *n*-Alkylamines, *n*-Alkyl Thiols, and *n*-Alcohols (kJ mol$^{-1}$)**

| RX | HX | $I_{298}$ | $PA_{298}(HX)$ | $PA_{298}(HX)Ref^{a}$ | diff[c] | $PA_{298,max}(RX)^{d}$ |
|---|---|---|---|---|---|---|
| *n*-amines[b] | $NH_3$ | 76.8 ± 1.9 | 860.5 ± 1.5 | 853.6 | 6.9 | 937.3 ± 3.4 |
| *n*-amines | $NH_3$ | 84.2 | 854.5 | 853.6 | 0.9 | 938.7 |
| *n*-thiols | $H_2S$ | 121.2 | 707.0 | 705.0 | 2.0 | 828.2 |
| *n*-alcohols | $H_2O$ | 125.8 | 691.1 | 691.0 | 0.1 | 816.9 |

[a] Hunter and Lias.[4] [b] Parameters for all amines up to $C_{10}$ except $C_7$ and $C_9$ from Hunter and Lias.[4] [c] Difference between $PA_{298}(HX)$ and $PA_{298}(HX)Ref$. [d] Largest possible $PA_{298}(RX)$: Sum of $I_{298}$ and $PA_{298}(HX)$.

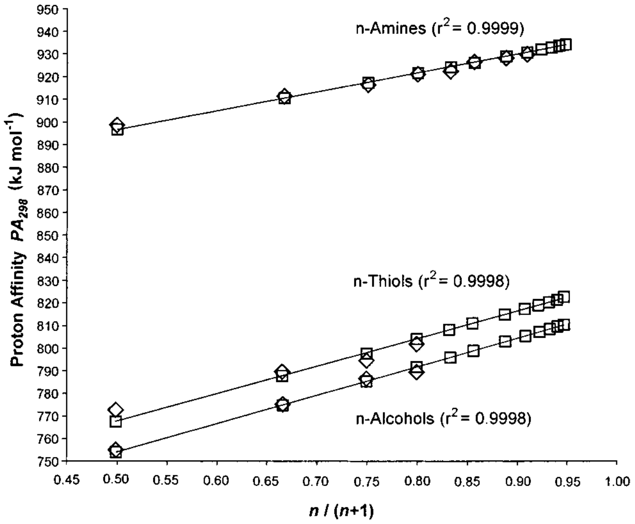

**Figure 2.** Calculated $PA_{298}$ of the alkyl compounds as a function of $n/(n + 1)$ (□ = this work; ◇ = literature values).

compounds and their carbon number.

$$PA(RX) = I\left(\frac{n}{n+1}\right) + PA(HX) \qquad n \geq 0 \qquad (3)$$

Here the constant term PA(HX) corresponds to a value of zero for *n* and may be regarded as the proton affinity of the basis molecule ($NH_3$, $H_2S$, $H_2O$). The calculated parameters $I_{298}$ and $PA_{298}(HX)$ of eq 3 are shown in Table 3. In the case of the parameters determined from literature values of the *n*-alkylamines, *n*-heptyl and *n*-nonylamine were left out of consideration to allow better comparison with the calculated parameters. When *n* is very large, eq 3 reduces to a simple sum, which represents the maximum proton affinity $PA_{298,max}(RX)$ of the homologous series (Table 3).

It is clear from a consideration of eq 3 that each additional carbon atom contributes less to the PA of the molecule than the one before. This contribution of further C-units follows the series $^1/_2$, $^1/_6$, $^1/_{12}$, $^1/_{20}$, $^1/_{30}$, $^1/_{42}$, $^1/_{56}$, etc., as described by eq 4.

$$\Delta PA(I) = \frac{I}{n(n+1)} \qquad n \neq 0 \qquad (4)$$

In the early 1980s Holmes described an empirical relationship between the reciprocal of the total number of atoms $n_{atom}$ of carbenium ions and either ionization energy IE or the enthalpy of formation $\Delta H_f$.[30] It is possible to transform eq 3 to reflect Holmes's relationship (eq 5).

$$PA(RX) = K\frac{1}{n_{atom}} + PA_{max}(RX) \qquad n \geq 0 \qquad (5)$$

The relationship of eqs 3 and 5 to Holmes's empirical principle shows that these correlations have a common physical basis. Unlike eq 3, however, eq 5 has a negative slope *K* and an intercept corresponding to $PA_{298,max}(RX)$. The quotient of the slopes *K* and *I* is always −3, independent of the functionality of the alkyl chains, so that the functional group appears to be equivalent to a simple atom. The significance of this observation is not clear.

The questions arose in this context as to what physicochemical meaning might be attached to the parameter $I_{298}$ and whether eq 3 can be applied to other thermodynamic characteristics of molecules in the gas phase. The gas-phase enthalpy of acidity ($\Delta H_{acid}$, eq 6) of the *n*-alcohols provided a ready test of the latter question, for experimental acidities of the *n*-alcohols C-1 to C-10 have been published.[31] Insertion of the literature data into eq 3 led to values of −(83.8 ± 1.1) and (1638.2 ± 0.9) kJ mol$^{-1}$ for $I_{298}$ and $\Delta H_{acid,298}(H_2O)$ with a certainty measure of $r^2 = 0.9984$. The experimental value for $\Delta H_{acid,298}(H_2O)$ is 1636.2 kJ mol$^{-1}$.[32]

$$BH \rightarrow B^- + H^+ \qquad + \Delta H \qquad (6)$$

Whether this behavior of the enthalpy of acidity of the alcohols is generally valid cannot be stated with certainty, for nonlinear trends of $\Delta G_{acid}$ have been observed under equilibrium conditions.[33] The latter data are, however, relatively recent and not yet confirmed. A reviewer of this article pointed out that the acidities of ammonia and hydrogen sulfide also do not fall on the straight lines calculated from the *n*-alkyl homologues.[28] Calculations with G3 (not presented here) confirm this. Despite these examples, the strong correlation with $n/(n + 1)$ in several series suggests that other homologous series be investigated.

In all the *n*-alkyl molecules calculated in this work the heteroatom substituent can be understood as an electron sink. With increasing length of the alkyl chain, the electron density in the substituent increases, and it should assume a limiting value with a sufficiently long chain. One can thus regard *I* as a maximum inductive effect or polarization. The influence of the *n*-alkyl chain on the electron density in the substituent and thus on any available nonbonding electron pairs would lead to an analogous relationship between $n/(n + 1)$ and the energy of any hydrogen bonds formed.

The good agreement of experimental values in the literature with the PA values calculated here for the all-anti form of the alkyl chains suggests that the former were obtained for structures with almost completely stretched alkyl chains. An alkyl chain held coiled about the charged, protonated terminal functional group by a field effect cannot, however, be excluded with certainty; the effect of such conformations on the energy is not known. A theoretical calculation of PA for such systems is very difficult because of the huge number of conformations that would have to be considered.

## 4. Ammonium Affinities of the *n*-Alcohols

In studies of CI-MS with $NH_3$ as reactant gas, the only molecule that has so far received both experimental and theoretical attention is $H_2O$.[7,34,35] The adducts of the *n*-alcohols up to propanol (eq 7) in time-of-flight mass spectrometry (TOF-MS) have been described, but the ammonium affinities of these

**TABLE 4: Ammonium Affinities of *n*-Alcohols and $H_2O$ ($-\Delta H$ in kJ mol$^{-1}$)**

| compound | $-\Delta H_{298}$B3LYP[a] | $\Delta E_{corr}(n)$ | $-\Delta H_{298}$Cal[b] | $-\Delta H_{298}$Ref[c] | diff[d] |
|---|---|---|---|---|---|
| $H_2O$ | 86.2 | −0.6 | 85.6 | 86.2 | 0.6 |
| $CH_3OH$ | 97.7 | 0.0 | 97.7 | 98.2 | 0.5 |
| $C_2H_5OH$ | 101.1 | 0.6 | 101.7 | 104.0 | 2.3 |
| $C_3H_7OH$ | 103.7 | 1.1 | 104.8 | 106.4 | 1.6 |
| $C_4H_9OH$ | 105.5 | 1.5 | 107.0 | 108.1 | 1.0 |
| $C_5H_{11}OH$ | 106.5 | 1.9 | 108.4 | 109.2 | 0.7 |
| $C_6H_{13}OH$ | 107.1 | 2.3 | 109.4 | 110.1 | 0.7 |
| $C_8H_{17}OH$ | 107.9 | 2.9 | 110.8 | 111.0 | 0.2 |
| $C_{10}H_{21}OH$ | 108.1 | 3.3 | 111.5 | 111.7 | 0.2 |
| $C_{12}H_{25}OH$ | 108.3 | 3.7 | 112.0 | 112.2 | 0.1 |
| $C_{14}H_{29}OH$ | 108.4 | 3.9 | 112.3 | 112.5 | 0.2 |
| $C_{16}H_{33}OH$ | 108.6 | 4.1 | 112.7 | 112.7 | 0.0 |
| $C_{18}H_{37}OH$ | 108.7 | 4.2 | 112.9 | 112.9 | 0.0 |

[a] $-\Delta H_{298}$ calculated by B3LYP/6-31+G(d,p). [b] Sum of $\Delta H_{298}$B3LYP and $\Delta E_{corr}(n)$. [c] Calculated with eq 8 and the PA's of the *n*-alcohols as calculated above. [d] Difference between $\Delta H_{298}$Cal and $\Delta H_{298}$Ref.

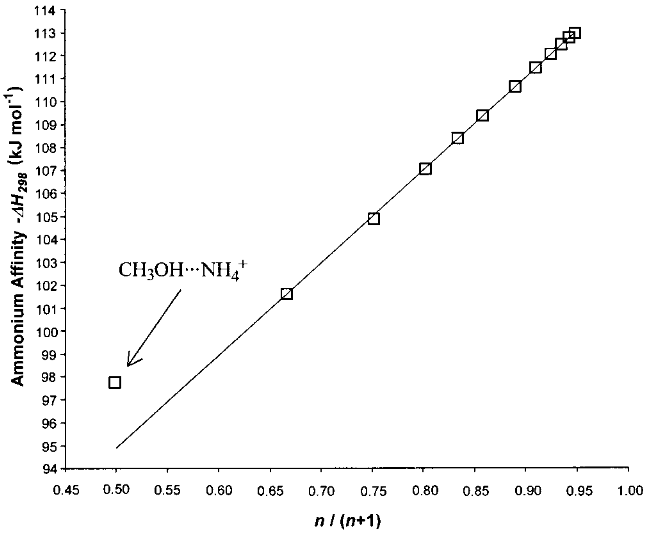

**Figure 3.** Calculated ammonium affinities $-\Delta H_{298}$ of the *n*-alcohols as a function of $n/(n + 1)$.

alcohols are yet to be determined.[2] The amount of energy liberated in the reaction of alcohols with ammonium ions determines the stability of the adducts formed, and the $-\Delta H_{298}$ values in Table 4 indicate that these contain strong hydrogen bonds.[36]

$$n\text{ROH} + \text{NH}_4^+ \rightleftarrows [n\text{ROH}\cdots\text{NH}_4]^+ \qquad n = 1-4 \quad (7)$$

In this work the O···HN bond energy was calculated by eq 2, the energy of $NH_4^+$ always being taken into consideration.

The desired linear correlation of the value of $-\Delta H_{298}$ with $n/(n + 1)$ could be obtained by multiplying the function $\Delta E_{corr}(n)$, discussed above, by an empirical scaling factor of 0.2. This is justified by the fact that the inductive effects on the hydrogen bond and the PA are similar, so that the $\Delta E_{corr}(n)$ determined above requires only an appropriate scaling factor. The liberated hydrogen bond energy calculated in this way is listed in Table 4 and displayed in Figure 3 as a function of $n/(n + 1)$. Equation 8, which Meot-Ner derived on the basis of experimental data from 48 quite diverse simple bimolecular adducts,[2,7] allows a comparison of this hydrogen bond energy with the calculated ammonium affinities.

$$\Delta H_{298}\ (\text{kJ mol}^{-1}) = (125.60 \pm 6.38) - (0.26 \pm 0.03)\Delta\text{PA}_{298} \quad (8)$$

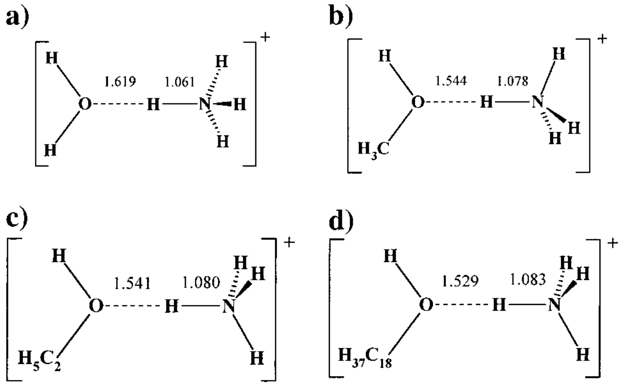

**Figure 4.** Structures of the ammonium adducts of (a) water, (b) methanol, (c) ethanol, and (d) octadecanol as determined by B3LYP/6-31+G(d, p) (bond distances in angstroms).

$\Delta PA_{298}$ here is the difference in the proton affinities of the molecules participating in the hydrogen bond. For this equation the PA's of ammonia (see Table 3) and the *n*-alcohols calculated above were used.

$\Delta$ZPE is 7.3 kJ mol$^{-1}$ for $H_2O$ and amounts on the average to 4.2 kJ mol$^{-1}$ for the alcohol adducts. To determine $-\Delta G(T)$ the following entropies were calculated: $S^o(NH_4^+, T) = 206.7$ J mol$^{-1}$ K$^{-1}$ and $\Delta S_A(T) = 69.8$ J mol$^{-1}$ K$^{-1}$ (this latter value is an arithmetically averaged entropy of formation of the $NH_4^+$ adducts of the *n*-alcohols).

Except for $H_2O$ and $CH_3OH$, the ammonium affinities can be calculated quite accurately with eq 3. The parameters calculated for this equation were $I_{298} = 40.3$ kJ mol$^{-1}$ and $-\Delta H_{298}(H_2O) = 74.8$ kJ mol$^{-1}$. The maximum ammonium affinity $-\Delta H_{298,max}$, obtained in analogy with the proton affinity of the *n*-alcohols, amounts to 115.1 kJ mol$^{-1}$.

The theoretically determined geometrical structures of the $[ROH\cdots NH_4]^+$ adducts are comparable to that of the water cluster $H_5O_2^+$.[37] In the calculated adducts (Figure 4) the bridging hydrogen is asymmetrically arranged between ROH and $NH_3$; the group O···HN is always linear, and the vector of the dipole moment of ROH coincides with the hydrogen bond. With increasing carbon-chain length the distance between O and HN decreases asymptotically toward 1.527 Å. Figure 4 shows that the optimized structures of $H_2O$ and $CH_3OH$ differ considerably from those of the higher alcohols, and this apparently accounts for the deviation of the hydrogen-bond energies calculated for $H_2O$ and $CH_3OH$ (Table 4) from the values predicted by eq 3, which amounts to 10.9 kJ mol$^{-1}$ for $H_2O$ and 2.8 kJ mol$^{-1}$ for $CH_3OH$. Meot-Ner's equation (eq 8) does not take structural differences into account, but the energies obtained from it correlate well with those calculated here (Table 4).

## 5. Conclusion

The quality of the calculation method used here is confirmed by the good agreement of the calculated proton affinities of the *n*-alkylamines, the *n*-alkyl thiols, and the *n*-alcohols with the values found in the literature. Equation 3, derived from these values, makes it possible to determine the proton affinities of all homologues without complex measurements and calculations, and the characterization of these series by the parameters *I* and PA(HX) can serve to simplify extensive existing data collections. While only the experimental determination of a number of the energies predicted by the calculations in this work can ultimately confirm eq 3, it can be regarded as already verified to a certain extent by the literature values of PA for the *n*-alkylamines and the enthalpy of the gas-phase acidity of the *n*-alcohols. It is important to determine to what extent the equation can also be applied to other homologous series.

The calculated PA's make it clear that $NH_3$ is an appropriate reactant gas for the formation of so-called "quasi-molecular ions" (clusters) of thiols and alcohols in CIMS. $NH_3$ cannot form corresponding clusters with *n*-alkylamines; only gases with very large PA's, such as trimethylamine, can be used in this case.

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