of about 480 cm\(^{-1}\) in the fundamental frequency of the \(\text{O}_2\) molecule (assuming that the \(\nu_1(\text{A}_1)\) normal mode is dominated by the O–O stretching). The same effect is found by theory since the calculated \(\nu_2(\text{A}_2)\) frequencies are reduced roughly 570 cm\(^{-1}\) with respect to the SCF calculated value for the fundamental frequency of \(\text{O}_2\) (15\(^{2}\) symmetry).

The next step was to calculate the fundamental frequencies at the CI level. Unfortunately, when calculations were carried out at the distorted \(C_2\) geometries needed to calculate the second derivatives, it was found that some of these geometries were more stable than the one corresponding to the \(C_2\) minimum. This fact was also observed in the RHF open-shell calculations for the allyl radical\(^{[16-21]}\) as well as for CI calculations carried out for the HCO_2 radical.\(^{[22]}\) This doublet instability has been examined in ref 18–22 and it was found to be due to the “shape” of the MOs obtained through RHF calculations. Inclusion of electron correlation effects by means of CI calculations is unable to recover the correct MOs and up to now it seems that the only solution comes from MC–SCF calculations.

On the other hand, it is also known\(^{[21]}\) that the Nesbet approximation for open-shell systems often gives correctly the symmetric structure. This is probably due to the fact that this method uses a pseudo-closed-shell system with fractional occupation,\(^{[23]}\) the final energy being corrected by adding a nonvariational term.

Thus, we have not determined the vibrational frequencies of these group 13 superoxides due to the doublet instability, but work is in progress to obtain MC–SCF results for the nonempirical pseudopotentials used here.

**Conclusion**

In this work, the optimized geometries and dissociation energies for the \(\text{MO}_2\) superoxides (\(\text{M} = \text{Ga}, \text{In}, \text{and} \text{Tl}\)) have been determined at the SCF and CI levels. It is shown that these molecules have a high degree of ionic character and their molecular structures must be interpreted on the basis of both covalent and ionic valence bond states.

Vibrational frequencies calculated at the SCF level by using the Nesbet approximation\(^{[15]}\) to treat the open shells can be summarized as follows. The \(\nu_2(\text{A}_1)\) frequencies of \(\text{GaO}_2\), \(\text{InO}_2\), and \(\text{TIO}_2\) are in agreement with experiment. The same holds for the \(\nu_3(\text{B}_1)\) frequencies of \(\text{GaO}_2\) and \(\text{InO}_2\), while a discrepancy is found for \(\text{TIO}_2\). On the other hand, a systematic deviation has been found for the \(\nu_1(\text{A}_1)\) frequencies which is found to be due to the electron correlation effects.

Unfortunately, all the molecules studied here exhibit doublet instability which prohibits calculation of the fundamental frequencies at the CI level. Since this problem can generally be solved at the MC–SCF level,\(^{[22]}\) work is now being carried out to develop an MC–SCF version of the PSHONDO–CIPSI package.

Finally, it should be pointed out that recent experimental work carried out by Sonchik et al.\(^{[24]}\) suggests a nonsymmetrical AIO molecule, contrary to the earlier work of Serebrennikov et al.\(^{[25]}\) which predicted a \(C_2\) structure. A theoretical study of the \(\text{Al}_2\) \((\text{C}_2)\) and \(\text{AlOO} (\text{C}_3)\) molecules will be reported in a forthcoming paper.\(^{[26]}\)

**Acknowledgment.** The authors thank the theoretical group of the Laboratoire de Physique Quantique de l'Université Paul Sabatier de Toulouse, France, for making available the computer programs used here as well as details concerning the pseudopotentials and basis sets. The calculations were carried out on the IBM 3083 computer at the Centre de Calcul of the Universitat de Barcelona and its financial support is gratefully acknowledged.

**Registry No.** \(\text{GaO}_2\), 51199-55-4; \(\text{InO}_2\), 12600-43-0; \(\text{TIO}_2\), 67657-12-9.

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### Theoretical Determination of Molecular Structure and Conformation. 17. On the Existence of \(\text{FH}_2^-\), \(\text{OH}_3^-\), \(\text{NH}_4^-\), and \(\text{CH}_5^-\) in the Gas Phase

**Dieter Cremer* and Elfi Kraka**

*Lehrstuhl für Theoretische Chemie, Universität Köln, D-5000 Köln 41, West Germany*

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Ab initio calculations (HF/6-31G* and MP2/6-31++G**) carried out for \(\text{FH}_2^-\), \(\text{OH}_3^-\), \(\text{NH}_4^-\), and \(\text{CH}_5^-\) indicate that these ions are most stable in the form of \(\text{AH}_n\)-solvated \(\text{H}^+\) ions. Theoretical binding energies (42, 26, 15, and 6 kcal/mol) decrease with increasing polarity of the AH bond. Apart from \(\text{CH}_5^-\), all \(\text{H}^+\)-\(\text{AH}_n\) complexes can rearrange via internal proton transfer to \(\text{AH}_n^-\)-\(\text{H}^+\) complexes which are 2–15 kcal/mol less stable than the former. Investigation of the various dissociation channels of \(\text{AH}_n^-\)- ions reveals that \(\text{NH}_4^+\), \(\text{OH}_3^-\), and \(\text{FH}_2^-\) are sufficiently stable in the gas phase to be detected by mass spectrometry.

**I. Introduction**

Recent investigations by Nibbering and co-workers\(^{[1-3]}\) have provided convincing evidence that \(\text{H}_2\text{O}^-\) and \(\text{NH}_4^+\) are relatively long-lived species in the gas phase.\(^{[4]}\) They can be generated in a Fourier-transform ion cyclotron resonance mass spectrometer by oxidation of formaldehyde with \(\text{OH}^+\) and \(\text{NH}_2^-\), respectively. The first step in the formation of the electron-rich hydrides most probably involves a collision complex between the ion \(\text{AH}_n^-\):
(OH\textsuperscript{−}, NH\textsubscript{3}\textsuperscript{−}) and the neutral which then decomposes by successive proton and hydride transfer to carbon monoxide and AH\textsubscript{n+1}− (H\textsubscript{2}O\textsuperscript{−}, NH\textsubscript{3}\textsuperscript{−}).\textsuperscript{1−3} 

AH\textsubscript{n+1}− + H\textsubscript{2}CO \rightarrow [AH\textsubscript{n+1}−...H\textsubscript{2}CO] \rightarrow [AH\textsubscript{n}...H\textsubscript{CO}−] \rightarrow AH\textsubscript{n+1}− + CO \quad (1)

The hydride transfer occurs either in the complex AH\textsubscript{n}...H\textsubscript{CO}− (A = O) or after its decomposition (A = N). Deuterium-labeling experiments indicate that the hydrogen atoms of H\textsubscript{2}O\textsuperscript{−} and NH\textsubscript{3}\textsuperscript{−} are not equivalent. Therefore, their structure has been described as a hydride ion solvated by a water or an ammonia molecule.\textsuperscript{1−3}

Stimulated by these fascinating observations we have carried out ab initio calculations in order to investigate the association between molecules AH\textsubscript{n} for A = F, O, N, C (1–4, Figure 1) and an H\textsuperscript{+} ion (5). Association can lead to a type I AH\textsubscript{n+1}− complex shown in Scheme I (see also Figure 1, 6–9). Type I complexes may rearrange to type II complexes (Figure 1, 10–13) which are composed of H\textsubscript{2} (14) and anions AH\textsubscript{n+1−} (15–18). Thus complexes I and II can be considered as possible intermediates of the proton-transfer reaction

AH\textsubscript{n} + H\textsuperscript{+} \rightarrow AH\textsubscript{n+1}− + H\textsubscript{2} \quad (2)

Accordingly, a theoretical investigation of complexes AH\textsubscript{n+1}− inevitably entails an exploration of the potential energy surface of reaction 2.

A priori it is difficult to say whether a solvated H\textsuperscript{−} is more stabilized in complex I or in the bifurcated structure of complex III (Scheme I and 23–25 in Figure 1), which has been suggested by Nibbering and co-workers for H\textsubscript{2}O\textsuperscript{−}.\textsuperscript{1,2} If n ≥ 3, the AH\textsubscript{n} molecule may even direct three AH bonds at an approaching H\textsuperscript{−} ion thus leading to the trifurcated structure IV of scheme I (26, 27, Figure 1). An alternative to complex II is the T-shaped complex V (Scheme I and 19–22 in Figure 1) with both hydrogens of H\textsubscript{2} being at equal or similar distance from the negatively charged atom A. Finally, one can consider structures with the H\textsuperscript{−} ion approaching AH\textsubscript{n} (A = F, O, N) on its electron lone pair side. It is easy to see that these structures are highly destabilized due to electron pair-electron pair repulsion. If, however, the incoming H\textsuperscript{−} ion possesses sufficient energy, the highly symmetrical structure VI of Scheme I (28–31, Figure 1) can be adopted. In case of A = F or C, VI corresponds to the transition state (TS) of the Sn2 reaction

H\textsuperscript{−} + AH\textsubscript{n}−H \rightarrow HAH\textsubscript{n+1}− + H\textsuperscript{−} \quad (3)

In order to give an account of the relative stability of complexes I–VI, we have determined the equilibrium geometries, energies, and charge distributions of 1–31 (Figure 1). On the basis of the analysis of these data the following questions are answered in this work: (1) What does the energy profile of proton transfer reaction 2 look like? (2) Which of the possible ion–neutral complexes is

Figure 1. MP2/6-31++G** geometries of 1–31. 32–35 correspond to calculated transition-state geometries of proton-transfer reaction 2. Starred values denote HF/6-31G* values. The angle r determines the degree of nonpolarity for pyramidal molecules.
actually observed in experiment? (3) Does there exist a long-lived ion–neutral complex CH4 and NH3? (4) What are the forces dominating the stability of complexes AHm+?μ?

Before representing our results it is interesting to note that some of these questions have been dealt with already 20 years ago by Ritchie and King. In three pioneering ab initio studies on proton-transfer reactions these authors calculated the minimum energy path of (2) for A = H, O, N, and C with basis sets including already flat s,p functions in order to correctly describe the tail behavior of the anion MOs. Although their final results differ from ours, partially due to incomplete optimization and partially due to the difficulty of getting reliable estimates of correlation energies in the mid-sixties, their calculated energy profiles are in qualitative accord with ours.

Apart from this early work only scattered theoretical investigations on AHm+μ (A = O, N, C, H) can be found in the literature. Most of them consider the transition state of the S2 reaction between CH4 and H+μ. Kari and Csizmadia have calculated D2h-symmetrical H30- at the Hartree-Fock level employing a DZ+P basis set. They find H30- to be unstable by 825-833 kcal/mol relative to the dissociation products H2O and H+. A much lower value of about 30 kcal/mol has been calculated in the case of the H+ ion. These authors have termed such a basis set 6-31++G**. Apart from the 6-31++G** basis we have also employed two other basis sets with diffuse functions at H in order to improve the description of charge polarization in an H2 molecule approached by an anion. The corresponding geometries and relative energies differ, however, only slightly from those obtained with the 6-31++G** basis. AH bond lengths are underestimated at the HF/6-31G* and HF/6-31++G** level. At the same time their polar character is overestimated yielding H atoms which are charged too positively. As a consequence, electrostatic H,H interactions and, hence, binding energies of solvated H+ ions are also underestimated at this level of theory. Consideration of correlation corrections reverts this trend. For example, application of second-order Möller–Plesset (MP2) perturbation theory leads to AH bond lengths somewhat longer than experimental values.

Accordingly, electrostatic interactions and binding energies of AHm+μ complexes are underestimated at the MP2 level. In view of these trends we have reoptimized all molecular geometries considered in this work at the MP2/6-31++G** level of theory in order to get upper bounds to AH bond distances and lower bounds to true binding energies of complexes AHm+μ. The location of the transition state of reaction 2 has been determined by increasing R(A,H2) of I stepwise and optimizing all remaining parameters. The maximum of the resultant energy curve E(R) has been evaluated by applying simple interpolation techniques and by reoptimizing the transition-state geometry for the corresponding R(A,H2) value.

III. Results and Discussion

In Figure 1 optimized MP2/6-31++G** geometries are depicted. In those cases (6, 9, 22) where no equilibrium geometries have been found at this level of theory, HF/6-31G* parameters are given (for other HF/6-31G* geometries see Table 1).
At the MP2/6-31++G** level the HF molecule electron-acceptor ability of A and is contrary to the A-H bond distance \( R(\text{H}1,\text{H}2) \) decreases from C to F. At the same time the bond length \( R(\text{A},\text{H}2) \) increases relative to that in the free \( \text{AH} \), (H2). Hydrogen atom H2 is pulled toward the H- ion the more \( \text{PA} \) values in hartree. aEnergy of complex 10 is given.

<table>
<thead>
<tr>
<th>molecule</th>
<th>HF/6-31G*</th>
<th>MP2/6-31+**//HF/6-31G*</th>
<th>MP2/6-31++G**//HF/6-31G*</th>
</tr>
</thead>
<tbody>
<tr>
<td>FH (1)</td>
<td>-100.02 91</td>
<td>-100.21 80</td>
<td>-100.19 73</td>
</tr>
<tr>
<td>OH2 (2)</td>
<td>-76.01 75</td>
<td>-76.23 61</td>
<td>-76.20 51</td>
</tr>
<tr>
<td>NH3 (3)</td>
<td>-56.18 34</td>
<td>-56.39 63</td>
<td>-56.35 52</td>
</tr>
<tr>
<td>CH4 (4)</td>
<td>-40.19 17</td>
<td>-40.37 41</td>
<td>-40.33 33</td>
</tr>
<tr>
<td>H+ (5)</td>
<td>-0.42 44</td>
<td>-0.50 33</td>
<td>-0.50 33</td>
</tr>
<tr>
<td>FH-H+ (6)</td>
<td>-100.49 79</td>
<td>-100.79 23</td>
<td>-100.79 23</td>
</tr>
<tr>
<td>OH-H+ (7)</td>
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<td>-76.76 69</td>
<td>-76.73 68</td>
</tr>
<tr>
<td>NH2-H+ (8)</td>
<td>-56.36 21</td>
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<td>-56.87 44</td>
</tr>
<tr>
<td>CH2-H+ (9)</td>
<td>-40.63 13</td>
<td>-40.87 73</td>
<td>-40.84 73</td>
</tr>
<tr>
<td>H2 (14)</td>
<td>-1.11 83</td>
<td>-1.15 77</td>
<td>-1.12 77</td>
</tr>
<tr>
<td>F (15)</td>
<td>-99.35 48</td>
<td>-99.62 07</td>
<td>-99.60 07</td>
</tr>
<tr>
<td>OH- (16)</td>
<td>-75.32 60</td>
<td>-75.60 31</td>
<td>-75.58 31</td>
</tr>
<tr>
<td>NH3- (17)</td>
<td>-55.47 08</td>
<td>-55.73 52</td>
<td>-55.70 52</td>
</tr>
<tr>
<td>CH2- (18a)</td>
<td>-39.46 79</td>
<td>-39.68 90</td>
<td>-39.70 90</td>
</tr>
<tr>
<td>CH2- (18b)</td>
<td>-39.46 16</td>
<td>-39.68 12</td>
<td>-39.68 12</td>
</tr>
</tbody>
</table>

All values in kcal/mol. \( \sigma \) denotes the deviation of theoretical \( \Delta E_p \) values from experimental \( \Delta H_r \) values. \( \Delta H_r = \text{PA}(\text{AH}_{-1}) - \text{PA}(\text{H}) \). The proton affinity of \( \text{H}^- \) is 400.4 kcal/mol. Reference 33.

Calculated absolute and relative energies are summarized in Tables II (HF and MP2 energies), III (energies \( \Delta E_r \) of the proton-transfer reaction 2), IV (relative energies of complexes I and II), and V (relative energies of complexes III–VI).

**Geometries.** The following trends become obvious by inspection of the data of Figure 1. (1) In type I complexes atoms A, H2, and H1 are in a linear or an almost linear arrangement which is in line with the results obtained by Ritchie and King.5,6 The distance \( R(\text{H}1,\text{H}2) \) decreases from C to F. At the same time the bond length \( R(\text{A},\text{H}2) \) increases relative to that in the free \( \text{AH} \), molecule by 0.002 (A = C), 0.021 (N), 0.054 (O), and 0.157 Å (F). Hydrogen atom H2 is pulled toward the H- ion the more polar the \( \text{AH}^+ \) bond becomes. This trend has to do with the electron-acceptor ability of A and is contrary to the A-H bond strength.16 At the MP2/6-31++G** level the HF molecule

looses a proton without barrier upon \( \text{H}^- \) approach while at the HF/6-31G* level 6 represents a local minimum of the \( \text{FH}^- \) energy surface. In 7 and 8 the HAH angles are smaller than in 2 and 3 which is probably due to electrostatic attraction between \( \text{H}^- \) and the more distant H3 (\( \text{H}^+ \)) atoms.

(2) In type II complexes changes of the geometrical parameters for a variation of A from F to C are less regular. If appropriate levels of theory are compared, the nonbonded distance \( R(\text{A},\text{H}2) \) is 0.1-0.6 Å larger than \( R(\text{A},\text{H}1) \) in I. The bond distance \( R(\text{A},\text{H}2) \) is slightly lengthened by 0.016–0.024 Å. Somewhat unexpected 10, 11, and 12 adopt highly symmetrical geometries, namely, \( \text{C}_n \) (10, 11) and \( \text{C}_6 \) (12). However, the potential energy surface is rather flat in the direction of \( \text{AH}^+ \) bending. An energy increase \( < 0.6 \) kcal/mol has the \( \text{H}_2(\text{AH}_{-1}) \) molecule swinging back and forth by more than 50°, e.g.

At the HF/6-31G* level, 11a and 12a are more stable than 11 and 12, probably due to significantly shorter \( R(\text{A},\text{H}2) \) distances.

(3) In type III and type IV complexes the same dependence of nonbonded distances \( R(\text{H}1,\text{H}2) \), etc. on the polarity of the AH bond is found as in I. Again, the \( \text{AH}^+ \) angles are smaller than in the free \( \text{AH} \) molecules. In this way electrostatic attraction between \( \text{H}^- \) and the positively charged \( \text{H}^+ \), \( \text{H}^+ \), etc. atoms is increased.

(4) Type V complexes contain essentially nondeformed \( \text{AH}^+ \) and \( \text{H}_2 \) molecules which seem to associate rather loosely at distances of \( 3-4 \) Å. 19 and 21 were found only when the H basis was augmented with flat p functions.

(5) Highly symmetrical arrangements of the H atoms around A lead to considerable lengthening of AH distances which are largest for those structures corresponding to the transition states of a \( \text{S}_2 \) reaction (28, 31). Contrary to previous calculations our \( \text{OH}^- \) (29) prefers a pyramidal (\( \text{C}_2 \)) rather than a planar (\( \text{D}_2 \)) geometry \( (E(29b) = -3.4 \text{ kcal/mol}) \).

**Energies.** Energies \( \Delta E_p \) of the proton-transfer reaction 2 are a measure of the relative proton affinity (PA) of 15–18 using \( \text{H}^+ \) as a reference:

\[
\Delta H_r = \text{PA}(\text{AH}_{-1}) - \text{PA}(\text{H}) = \Delta E_p
\]

Three situations can be distinguished (Figure 2a–c): (a) For anions \( \text{AH}_{-1}^- \) (neutrals \( \text{AH} \)) with a larger PA value (lower acidity) proton-transfer reaction 2 is endothermic \( (\Delta H_r, \Delta E_p > 0) \); (b) for anions with comparable PA values reaction 2 is thermoneutral \( (\Delta H_r, \Delta E_p = 0) \); (c) for anions (neutrals) with lower PA values (larger acidity) reaction 2 is exothermic \( (\Delta H_r, \Delta E_p < 0) \). According to the experimental PA and \( \Delta H_r \) values listed in Table III situation (a) applies to A = C, situation (b) to A = N although the reaction is slightly endothermic (by 3 kcal/mol), and situation (c) to A = O and F.

---

HF/6-31G* energies reproduce experimental \( \Delta H \) values satisfactorily (mean deviation \( \sigma = 2.1 \) kcal/mol) due to a consistent description of PAs. The value of \( \sigma \) is twice as large for MP2/6-31G++ energies. At both levels of theory deviations \( \sigma \) become more negative for a variation of A from C to F. This is a result of decreasing \( \sigma \) in AH\(_2\) and AH\(_2\)\(^-\), respectively.17 Similar errors are involved in calculated energy differences \( \Delta E_{\text{II-I}} \) between type I and type II complexes (Figure 2). In order to take this into account all calculated \( \Delta E_{\text{II-I}} \) values are corrected by the appropriate \( \sigma \) values of Table III.

Theoretical energy differences \( \Delta E_{\text{I}}, \Delta E_{\text{II}}, \) and \( \Delta E_{\text{III-I}} \) (Table IV) reveal that in all cases considered type I complexes are more stable than type II complexes. However, \( \Delta E_{\text{III-I}} \) becomes relatively small when going from A = C to A = F. In the latter case, 6 and 10 probably possess similar energies with 6 being slightly more stable. Type III and type IV complexes are only 1–3 kcal/mol less stable than type I complexes (Table V). They correspond to transient points of an H\(^-\) ion rapidly moving on the hydrogen “face” of an AH\(_m\) molecule between the most favorable positions close to H\(^2\), H\(^3\), etc. Contrary to I–IV, the binding energy of type V complexes (relatively to the dissociated products) is vanishingly small. Thus, they will be considered as thermoneutral, and (c) exothermic proton transfer.

On the basis of the energies given in Tables IV and V it can be concluded that it is sufficient to consider just type I and type II complexes as intermediates of the proton-transfer reaction 2. All relevant energy parameters needed to construct the energy diagrams of Figure 2 are given in Table IV. Calculated \( E_a \) barriers (Figure 2) have been corrected by \( \sigma \) values in the same way as \( \Delta E_{\text{II-I}} \) differences. Apart from A = C, the calculated intrinsic barriers \( E_a \) for proton transfer are all smaller than the solvation energy \( \Delta E_{\text{I}} \) of an H\(^-\) ion. If 6, 7, or 8 are formed from AH\(_2\) and H\(^-\), they will possess sufficient energy to surmount the central barrier and rearrange to the H\(_2\)-solvated anions AH\(_2\)\(^-\). This process can be facilitated by proton tunneling through the central barrier.

For A = O and F the excess energy of type I complexes suffices to overcome even the binding energy of type II complexes, \( \Delta E_{\text{II-I}} \), and to yield as dissociation products H\(_2\) and AH\(_2\)\(^-\). A further decrease in relative energy is calculated (Table V). Hence, the relatively low energy of 30 can be considered as being the result of charge distribution to five atoms. Since negative charge resides in the \( \sigma^+ \) and AH\(_2\) bond in 28–31 (0.337, 0.069, 0.034, and 0.497 \( \AA \)) relative to those of parent compounds 1–4 (Figure 1) is a good indicator of the extent of charge distribution and the resultant relative energy.

![Figure 2](image-url)  
Figure 2. Energy profile of reaction 2 for an (a) endothermic, (b) thermoneutral, and (c) exothermic proton transfer.

**Table IV: Relative Energies of Complexes I and II and Intrinsic Barriers to Proton Transfer**

<table>
<thead>
<tr>
<th>Complexes</th>
<th>HF/6-31G*</th>
<th>MP2/6-31G**</th>
<th>MP2/6-31G**</th>
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</thead>
<tbody>
<tr>
<td>I</td>
<td>( \Delta E_I )</td>
<td>( \Delta E_{II} )</td>
<td>( \Delta E_{III-I} )</td>
</tr>
<tr>
<td>II</td>
<td>( \Delta E_{II} )</td>
<td>( \Delta E_{III-I} )</td>
<td>( \Delta E_{IV} )</td>
</tr>
</tbody>
</table>

**Table V: Relative Energies of Complexes I and II (MP2/6-31G**//MP2/6-31G**)**

<table>
<thead>
<tr>
<th>A</th>
<th>IV, trifurcated</th>
<th>IV, bifurcated</th>
<th>V, T-shaped</th>
<th>VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>19</td>
<td>0</td>
<td>28</td>
<td>37.9</td>
</tr>
<tr>
<td>O</td>
<td>20</td>
<td>-0.3</td>
<td>29a</td>
<td>21.1</td>
</tr>
<tr>
<td>N</td>
<td>21</td>
<td>0</td>
<td>30</td>
<td>1.3</td>
</tr>
<tr>
<td>C</td>
<td>22</td>
<td>-0.5</td>
<td>31</td>
<td>54.5</td>
</tr>
</tbody>
</table>

17 This has to do with the fact that a given basis set level a spherical F\(^-\) ion is easier to describe than linear F-H, linear OH\(^-\) in turn easier than bent H\(_2\)O, and nearly "spherical" CH\(_4\) easier than pyramidal CH\(_4\)\(^-\). For NH\(_3\) and NH\(_2\) the same basis set errors can be expected thus yielding the lowest \( \sigma \) values.

\( \text{PA}(X') > \text{PA}(H^+) \)

\( \text{PA}(X') < \text{PA}(H^+) \)

\( \text{PA}(X') = \text{PA}(H^+) \)

\( \text{PA}(X') = \text{PA}(H^+) \)

\( \text{PA}(X') < \text{PA}(H^+) \)

\( \Delta E_{\text{I}} > 0 \)

\( \Delta E_{\text{II}} < 0 \)

\( \Delta E_{\text{III-I}} > 0 \)

\( \Delta E_{\text{IV}} > 0 \)

\( \Delta E_{\text{V}} > 0 \)

\( \Delta E_{\text{VI}} < 0 \)

\( \Delta E_{\text{II-I}} < 0 \)

\( \Delta E_{\text{III-I}} > 0 \)

\( \Delta E_{\text{IV}} > 0 \)

\( \Delta E_{\text{V}} > 0 \)

\( \Delta E_{\text{VI}} < 0 \)

\( \Delta E_{\text{II-I}} < 0 \)

\( \Delta E_{\text{III-I}} > 0 \)

\( \Delta E_{\text{IV}} > 0 \)

\( \Delta E_{\text{V}} > 0 \)

\( \Delta E_{\text{VI}} < 0 \)

\( \Delta E_{\text{II-I}} < 0 \)
Figure 3. Calculated difference electron density distributions $\Delta \rho(r)$ (e/Å$^3$) for H$_3$O$^-$ complexes 7 (a) and 11 (b). Parts c and d show the corresponding difference concentration distributions $\Delta (\nabla^2 \rho(r))$ (e/Å$^5$). Dashed (solid) contour lines correspond to negative (positive) $\Delta \rho(r)$ values. In the case of $\Delta (\nabla^2 \rho(r))$ they indicate charge concentration (depletion).

The degree of charge polarization can also be assessed by inspection of the difference electron density distributions, which reflect the change in $\rho(r)$ upon complex formation. In Figure 3 contour line diagrams of $\Delta \rho(r)$ are shown for H$_3$O$^-$ complexes 7 and 11. In the case of 7 (Figure 3a) the charge of the incoming H$^-$ ion contracts and pushes the electron density from H$_2$ toward the O atom where it builds up in front of the nucleus. There is a decrease of electron density in the bond OH$_2$ coupled with an increase of $\rho(r)$ at the position of nucleus H$_3$. Thus, the density pattern of complex 7 reveals alternating changes in $\rho$ along the atom chain H$^1$, H$^2$, O, and H$^3$. This is equivalent to a charge transfer within the H$_2$O molecule from H$_2$ toward H$^3$, which increases the electrostatic attraction between ion and molecule. Figure 3a contains also information about the possible fate of 7 in a collision reaction. According to $\Delta \rho(r)$, there will be a heterolytic cleavage of the OH$_2$ bond and the formation of an oxygen lone pair, which will polarize the newly formed H-H bond. Atom H$^1$ will swing into the axis H-H$_2$O where there is a significant accumulation of electron density behind the O nucleus.

Figure 3b, in turn, contains information about the fate of complex 11. There is a slight polarization of the density of the OH$_2$ bond. The procomplex consists of the noninteracting complex partners (ion and neutral) kept at the geometry of the complex.

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$\rho(r)$ values are obtained by using the classical equation $\rho(r) = q \cos \theta / r^2 - a \rho_0 / 2r = \rho(r)_{\text{virial}}$ with $q = 1$ e, $\rho_0 = 1.85$ D (H$_2$O), and $\rho_0 = 1.47$ D (NH$_3$). 

In order to make an assessment of the various interactions in complexes 6-13, we have calculated atomic monopole (charges), dipole, and quadrupole moments employing the virial partitioning method. Contrary to the Mulliken population analysis, this method provides reasonable gross atomic charges even when basis sets with diffuse GTF's are used.

Due to the fact that the maximum of the radial distribution of a diffuse GTF is far removed from its location, a Mulliken population analysis leads to unreasonable values in the case of basis sets with flat s,p GTF's. For example, Mulliken charges suggest a large transfer of negative charge from H$^+$ to AH$_n$.
TABLE VI: Experimental Solvation Enthalpies of Some Anions

<table>
<thead>
<tr>
<th>anion</th>
<th>neutral</th>
<th>Cl⁻</th>
<th>F⁻</th>
<th>OH⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>FH</td>
<td>21.8</td>
<td>38.5</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>OH₂</td>
<td>14.4</td>
<td>23.3</td>
<td>22.5</td>
<td></td>
</tr>
<tr>
<td>NH₃</td>
<td>10.5</td>
<td>12.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Values (in kcal/mol) from ref 24-27. The PA values of the anions are 333 (Cl⁻), 371 (F⁻), 391 (OH⁻), and 400 kcal/mol (H₂). Estimates from differences in binding enthalpies between CH₃OH·H⁻ (41.3), CF₃CH₂OH·F⁻ (39.1), and OH₂·F⁻ and the binding enthalpies found for CH₃NH₂·H⁻ (31.2) and CF₃CH₂NH₂·F⁻ (28.1 kcal/mol).

OH⁻ ion equivalent to a charge transfer from H⁺ toward O⁻. This leads to a higher total density in the region of the electron lone pair pointing at H₂. The H₂ molecule is strongly polarized. A considerable amount of electron density is shifted from H² toward H⁻. Again, the calculated difference density reveals that the neutral (H₂) will undergo heterolytic bond cleavage under the impact of an approaching OH⁻ ion.

Analysis of the Laplace concentration of ρ(r), V²ρ(r), provides further insight into the electronic structure of ion–neutral complexes 7 and 11. Molecular regions where the electron density concentrates more in the complex than in the procomplex are indicated by negative values of Δ(V²ρ(r)) (dashed contours in parts c and d of Figure 3); those where electron density concentrates less possess positive values of Δ(V²ρ(r)) (solid contours in parts c and d of Figure 3). The contour line maps in parts c and d of Figure 3 clearly show the development of a new O lone pair in 7 and the polarization of this lone pair toward H₂ in 11. They also reveal that the concentration of charge at H⁻ and in the nonbonding area of the O atom of 7 is partially due to a depletion of electron density in regions further remote from the nuclei of complex 7. Obviously, electron density at the H⁻ ion becomes less diffuse if solvation by H₂O takes place. A similar contraction of charge can be found for H⁻ in complex 11.

Qualitatively similar difference maps of ρ(r) and V²ρ(r) are obtained for complexes I and II with A = F, N₃, or C₄, only that the degree of charge polarization decreases in the series 6–9 and 10–13 which can be quantitatively determined by the calculated atomic multipole moments. We conclude that the binding energies of type I and type II complexes are dominated by attractive electrostatic forces resulting from charge polarization. Polarization of the electron density of an AH bond by H⁻ increases with the acidity of AH which in turn is proportional to the electron-acceptor ability of A. Polarization of the electron density of a H₂ molecule increases with the amount of electron charge located at A in AH⁻: The actual binding energies ΔE₁ and ΔE₁ are essentially a result of electrostatic attraction and overlap repulsion.

IV. Chemical Relevance of Results

As discussed in section II, the two sets of energy data shown in Table IV provide upper and lower bounds to the true stabilities of the complexes. In Table IV, the energy of type I is substantially lower than that of type II, which is consistent with the experimental observations made by Diercksen and Kraemer. This is in line with similar theoretical calculations and experimental results reported by other groups.

As for ΔE₂, binding energies ranging from 4 to 10 kcal/mol have been found for a variety of ion–H₂ complexes in the gas phase. Again, HF/6-31G* values are generally lower than the corresponding values of other basis sets. Hence, it seems reasonable to base the following discussion on reasonable ΔE₂ values for F⁻·H₂ and OH⁻·H₂ with normal DZ+P basis sets at the HF level. As for ΔE₂, binding energies ranging from 4 to 10 kcal/mol have been found for a variety of ion–H₂ complexes in the gas phase. Again, HF/6-31G* values are generally lower than the corresponding values of other basis sets. Hence, it seems reasonable to base the following discussion on reasonable ΔE₂ values for F⁻·H₂ and OH⁻·H₂ with normal DZ+P basis sets at the HF level.

Figure 4. Energy profile of the S₂ reaction for A = C.
Generation of stable AH\textsubscript{1+}- complexes by collision of AH\textsubscript{3} and H\textsuperscript{+} is not possible under the experimental conditions of an ion cyclotron resonance spectrometer since these processes lead to considerable excess energies which cannot be dissipated by collisions with other molecules. Accordingly, AH\textsubscript{1+}- complexes will immediately decompose. If, however, the formation of ions AH\textsubscript{1+} occurs as in reaction 1 via a collision complex AH\textsubscript{1+}-CH\textsubscript{2}O, then the collision partner can carry away most of the excess energy, thus yielding stable AH\textsubscript{1+}- complexes.

\[ \text{AH}\textsubscript{1+} + \text{CH}_2\text{O} \rightarrow \text{AH}_n + \text{CHO}^- \]  
(4)

\[ \text{AH}^- + \text{CHO}^- \rightarrow \text{AH}_{n+1}^- + \text{CO} \]  
(5)

\[ \Delta\Delta H(4) \text{ and } \Delta\Delta H(5) \text{, which yield } \Delta\Delta H(1) \text{, the reaction enthalpy of (1) (see Table VII). A qualitative representation of the energy profile of the formation of NH}_4^- \text{ via reaction 1 is shown in Figure 5.} \]

Since reaction 4 is exothermic for A = N\textsubscript{2}, generation of NH\textsubscript{4}^- can occur via either path a or b shown in Figure 5. Experimentally, it is found that path a is preferred.\textsuperscript{3} In case of A = O only path b is possible because of \( \Delta\Delta H(4) > 0 \). Accordingly, CHO\textsuperscript{-} ions can only be observed when generating NH\textsubscript{4}^-\textsuperscript{1+} \text{NH}_4^-/CO and OH\textsubscript{3}/CO are formed with excess energies of 16-18 kcal/mol, which have to be partially absorbed by CO to make detection of AH\textsubscript{1+} ions possible.

In the case of A = C, proton transfer from CH\textsubscript{3}O to CH\textsubscript{3}\textsuperscript{-} is exothermic by 15 kcal/mol. Only a part of this excess energy (~5 kcal/mol\textsuperscript{36}) is necessary to have CHO\textsuperscript{-} decompose to CO + H\textsuperscript{+} (\( \Delta\Delta H = -2 \text{ kcal/mol} \)), a reaction which is not possible for the other systems considered because of \( \Delta\Delta H(4) \geq 0 \) (Table VII). Alternatively, CH\textsubscript{3} is formed via path b as a short-lived intermediate which decomposes immediately due to its relatively low stability of 6 kcal/mol.

In the case of A = F one might argue that the difference in acidities of HF and CH\textsubscript{2}O is far too large and, hence, reaction 4 far too endothermic (31 kcal/mol, Table VII) to permit formation of the complex HF-CHO\textsuperscript{-}. If, however, this complex is stable by at least 36 kcal/mol relative to HF and CHO\textsuperscript{-}, then its formation would be exothermic by an energy amount (~5 kcal/mol) probably sufficient to allow hydride transfer and the formation of HF\textsuperscript{7} via path b. HF solvation energies of anions range from 20 (HF-Cl\textsuperscript{-}) to 40 kcal/mol (HF-H\textsuperscript{+}, Table IV). Accordingly, there is a limited chance that HF\textsuperscript{7} can be observed as a collision product of F\textsuperscript{-} and CH\textsubscript{2}O in the ion cyclotron resonance spectrometer.

\textbf{Note Added in Proof:} After this work had been finished Prof. P. v. R. Schleyer brought to our attention that he and his coworkers have also performed HF and MP calculations on NH\textsubscript{4}-.\textsuperscript{35} Their results are in accord with ours. Prof. H. Budzikiewicz informed us of the detection of a spurious CH\textsubscript{5}- ion in a quadrupole mass spectrometer set up for negative chemical ionization.\textsuperscript{36} Our theoretical results helped to identify the "pseudonegative" ion as CH\textsubscript{5}-.\textsuperscript{4}

\textbf{Acknowledgment.} It is a pleasure to acknowledge fruitful discussions with Prof. H. Budzikiewicz. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. All calculations have been carried out at the Rechenzentrum der Universität Köln.

\textbf{Registry No.} H\textsubscript{2}, 1333-74-0; OH\textsubscript{3}, 12325-19-8; NH\textsubscript{4}+, 12325-21-2; CH\textsubscript{3}+, 12316-54-0; H\textsuperscript{+}, 12184-88-2; F\textsuperscript{-}, 16984-48-8.

\textsuperscript{36} Poppe, A.; Schröder, E.; Budzikiewicz, H., to be submitted for publication.