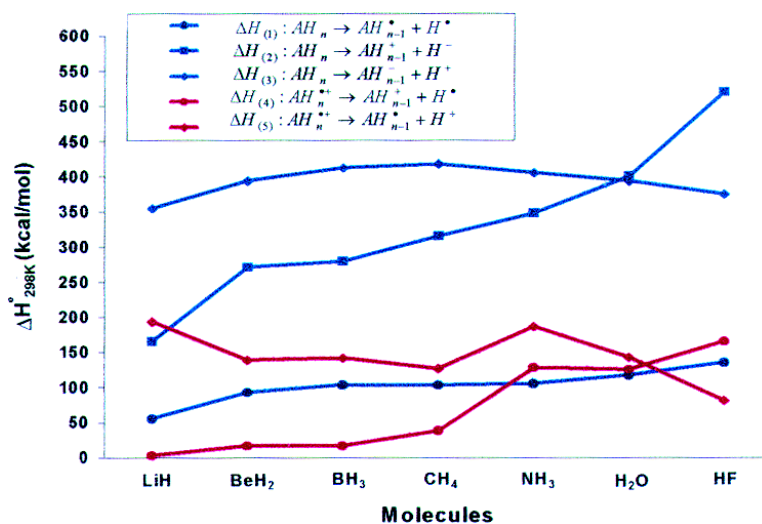Article

Gas Phase Dissociation Energies of Saturated AH Radical Cations and AH Neutrals (A = Li–F, Na–Cl): Dehydrogenation, Deprotonation, and Formation of AH⁻ – H Complexes

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Gas Phase Dissociation Energies of Saturated $AH_n^{\cdot+}$ Radical Cations and AH_n Neutrals (A = Li−F, Na−Cl): Dehydrogenation, Deprotonation, and Formation of $AH_{n-2}^{\cdot+}$ − H_2 Complexes

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Abstract: The dissociation energies corresponding to the two possible A−H cleavages of $AH_n^{\cdot+}$ (A = Li−F and Na−Cl) radical cations (loss of a H^+ and loss of a $H^{\cdot}$) have been computed at the CCSD(T)/6-311++G(3df,2pd) level of theory and compared to those of their neutral precursors. Removing an electron from AH_n decreases dramatically its deprotonation energy, especially for the $AH_4^{\cdot+}$ molecules ($CH_4^{\cdot+}$ and $SiH_4^{\cdot+}$), which become one of the most acidic species of the row, their acid character being only exceeded by $FH^{\cdot+}$ and $ClH^{\cdot+}$, respectively. However, dehydrogenation energies only decrease for the systems on the left side of the row (up to $CH_4^{\cdot+}$ and $SiH_4^{\cdot+}$) for which the electron is removed from a A−H bonding orbital. Nevertheless, the loss of hydrogen is the more favorable cleavage in all cases except $FH^{\cdot+}$. Ionization of SiH_4 leads to a Jahn−Teller distorted structure that corresponds to a $SiH_2^{\cdot+}$ − H_2 complex. Other $AH_{n-2}^{\cdot+}$ − η_2H_2 complexes in the doublet spin state have also been found to be stable for A = Be, Mg, Al, and P, the hydrogen molecule complexes being more stable than their corresponding $AH_n^{\cdot+}$ radical cations, for Be, Mg, and Al.

I. Introduction

Radical cations, generated by the removal of one electron from a neutral molecule, are important intermediates in many oxidative reactions of biological importance.[1] These species exhibit a very rich and varied chemistry because in the ionized state, they can evolve via many different chemical reactions such as electron transfer, proton transfer or molecular rearrangements. Such a varied chemistry is due to the changes produced in the charge and spin when an electron is removed from a system. On one hand, ionization creates a positive charge that introduces large electrostatic effects, whereas, on the other hand, the deficit of one electron modifies, directly and indirectly, the strength of covalent bonds. Such effects result in unusual structures and reactivities, which are often significantly different from those of their neutral precursors.

For example, the thermodynamics of the keto−enol isomerization is reversed upon ionization, the enol structure becoming more stable in the ionized system.[2,3] This tautomerism may occur spontaneously for 1,5 transfers[2] or may become very favorable in 1,3 transfers[3] if the reaction proceeds through proton transport catalysis.[4] Moreover, intermolecular proton transfer reactions are also strongly affected by ionization[5−9] in such a

way that in many cases these reactions occur spontaneously, leading to the so-called distonic radical cations,[10] species in which the charge and the spin lie on different sites. This is due to an increased acidity of the ionized system ($AH_n^{\cdot+}$) and to the fact that the proton transfer reaction does not imply a separation of charge but just the transfer of a positive charge.

In solution, the loss of a proton is usually favored over the loss of a hydrogen atom due to the large solvation energy of

(1) See, for example: (a) Steenken, S. *Chem. Rev.* **1989**, *89*, 503. (b) Stubbe, J.; van der Donk, W. A. *Chem. Rev.* **1998**, *98*, 705. (c) Stadtman, E. R. *Annu. Rev. Biochem.* **1993**, *62*, 797. (d) Easton, C. J. *Chem. Rev.* **1997**, *97*, 53. (e) Steenken, S. *Biol. Chem.* **1997**, *378*, 1293. and references therein.
(2) (a) Gebicki, J.; Bally, T. *Acc. Chem. Res.* **1997**, *30*, 477. (b) Marcineck, A.; Adamus, J.; Gebicki, J.; Platz, M. S.; Bednarek, P. *J. Phys. Chem. A* **2000**, *104*, 724. (c) Marcineck, A.; Adamus, J.; Huben, K.; Gebicki, J.; Bartczak, T. J.; Bednarek, P.; Bally, T. *J. Am. Chem. Soc.* **2000**, *122*, 437.

(3) (a) van der Rest, G.; Nedev, H.; Chamot-Rooke, J.; Mourgues, P.; McMahon, T. B.; Audier, H. E. *Int. J. Mass Spectrom.* **2000**, *202*, 161. (b) Mourgues, P.; Chamot-Rooke, J.; van der Rest, G.; Nedev, H.; Audier, H. E.; McMahon, T. B. *Int. J. Mass Spectrom.* **2001**, *210/211*, 429. (c) Rodríguez-Santiago, L.; Vendrell, O.; Tejero, I.; Sodupe, M.; Bertran, J. *Chem. Phys. Lett.* **2001**, *334*, 112. (d) Trikoupis, M. A.; Terlouw, J. K.; Burgers, P. C. *J. Am. Chem. Soc.* **1998**, *120*, 12 131.
(4) (a) Bohme, D. K. *Int. J. Mass Spectrom. Ion Processes* **1992**, *115*, 95. (b) Gauld, J. W.; Audier, H.; Fossey, J.; Radom, L. *J. Am. Chem. Soc.* **1996**, *118*, 6299. (c) Chalk, A. J.; Radom, L. *J. Am. Chem. Soc.* **1997**, *119*, 7573. (d) Gauld, J. W.; Radom, L. *J. Am. Chem. Soc.* **1997**, *119*, 9831.
(5) (a) Ceulemans, J. *Acc. Chem. Res.* **2002**, 35, 523.
(6) (a) Sodupe, M.; Oliva, A.; Bertran, J. *J. Phys. Chem. A* **1997**, *101*, 9142. (b) Re, S.; Osamura, Y. *J. Phys. Chem. A* **1998**, *102*, 3798. (c) Kim, H.-T.; Green, R. J.; Qian, J.; Anderson, S. L. *J. Chem. Phys.* **2000**, *112*, 5717. (d) Feng, Y.; Liu, L.; Fang, Y.; Guo, Q.-X. *J. Phys. Chem. A* **2002**, *106*, 11 518. (e) Baciocchi, E.; Bietti, M.; Chiavarino, B.; Crestoni, M. E.; Fornarini, S. *Chem.- A Eur. J.* **2002**, *8*, 532. (f) Li, Y.; Liu, X.; Wang, X.; Lou, N. *Chem. Phys. Lett.* **1997**, *276*, 339.
(7) (a) Sodupe, M., Oliva, A., Bertran, J. *J. Am. Chem. Soc.* **1995**, *117*, 8416. (b) Sodupe, M., Oliva, A., Bertran, J. *J. Am. Chem. Soc.* **1994**, *116*, 8249.
(8) (a) Rodríguez-Santiago, L.; Sodupe, M.; Oliva, A.; Bertran, J. *J. Am. Chem. Soc.* **1999**, *121*, 8882. (b) Rodríguez-Santiago, L.; Sodupe, M.; Oliva, A.; Bertran, J. *J. Phys. Chem. A* **2000**, *104*, 1256.
(9) (a) Hutter, M.; Clark, T. *J. Am. Chem. Soc.* **1996**, *118*, 7574. (b) Bertran, J.; Oliva, A.; Rodríguez-Santiago, L.; Sodupe, M. *J. Am. Chem. Soc.* **1998**, *120*, 8159. (c) Turecek, F.; Wolken, J. K. *J. Phys. Chem. A* **2001**, *105*, 8740. (d) Li, X.; Cai, Z.; Sevilla, M. D. *J. Phys. Chem. B* **2001**, *105*, 10 115.
(10) (a) Stirk, K. M.; Kiminkinen, L. K. M.; Kenttämaa, H. I. *Chem. Rev.* **1992**, *92*, 1649. (b) Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1984**, *106*, 5805.

the proton. In fact, C−H bonds in radical cations have been found to be very acidic in solution, these species often being superacids with large negative pK_a.[11] However, the increase of acidity of N−H and O−H acids in $AH_n^{\cdot+}$ radical cations has been found to be significantly smaller than for C−H compounds and so, the acidity order in $AH_n^{\cdot+}$ radical cations is quite different from that observed for the neutral species.[11b] These observations are in agreement, for example, with the fact that glycyl radical $(NH_2CHCOOH)^{\cdot}$ is the observed species upon irradiation of glycine (NH_2CH_2COOH) in solution, even at low pH.[12] That is, the most favorable structure is the one that arises from the deprotonation of CH_2. Preliminary calculations in gas phase for glycine radical cation have shown that the deprotonation energy from the C is smaller than from the N or the O atoms. Although this is partly due to the large stability of glycyl radical because of captodative effects,[1d] the fact that, in general, the relative acidity of C−H, N−H, and O−H bonds change dramatically when going from the neutral molecules to their radical cations makes interesting a theoretical study.

In the gas phase, however, the loss of a hydrogen atom to lead $A^+ + H^{\cdot}$ may be a more favorable pathway than the loss of the proton $(A^{\cdot} + H^+)$ because the charge is better delocalized in the A^+ fragment.[13] Because both the proton-transfer reaction and the loss of the hydrogen atom play a crucial role in many biochemical processes, the effect of ionizing radiation and oxidizing agents in these two dissociation energies is of great interest.

In this paper, we report the gas phase A−H dissociation energies in $AH_n^{\cdot+}$ (A = Li−F and Na−Cl) radical cations and compare them to those of their neutral counterparts. In addition to the nonmetal hydride compounds, typically found in biological systems, we have also included the metal-hydride ones in order to analyze the trends along the whole row. It must be mentioned that whereas many theoretical studies have been performed both for neutral[14,15] and ionized systems,[14,16−19] to our knowledge, no theoretical study has systematically analyzed the resulting changes in the $AH_{n−1}−H$ dissociation energies of

these systems upon ionization. The observed trends are simply explained in terms of the nature of the HOMO orbital from which the electron is removed and from the stability of the radical and cations that are formed. We expect that this systematic study will help understand how radical cations evolve in many relevant biological reactions as well as to interpret mass spectrometry experiments.

II. Methods

Radical cations are open shell systems and, so, their theoretical study present some specific methodological problems. Unrestricted post Hartree−Fock calculations, such as the Møller−Plesset MP_n ones, may suffer from spin contamination which can lead to a slow convergence of the Møller−Plesset perturbation expansion[20] and as a consequence to the determination of nonreliable geometries and energies. Moreover, there are examples in the literature in which MP2 finds spurious minima on low contrast potential energy surfaces.[21] On the other hand, although for some radical cations density functional methods have been shown to perform much better than UMP2,[6a,9b] in some specific very symmetrical situations they can lead to an overstabilization of the radical cation.[22] Because of that, in the present work geometry optimizations have been carried out using both the post Hartree−Fock MP2 and the nonlocal hybrid three parameter B3LYP[23] density functional method, with a double-ζ plus diffuse and polarization 6-31++G(d,p) basis set.

It has been observed that in almost all cases, the optimized geometries are very similar with both methods. The only exceptions are the $MgH_2^{\cdot+}$ and $CH_4^{\cdot+}$ molecules for which the MP2 and B3LYP optimized geometries are significantly different. Because of that these two systems will be discussed in more detail in the following Results and Discussion section.

For the geometries considered, the results obtained have shown that the spin contamination is small in the UMP2 calculations, since the S^2 expectation value (0.75−0.78) of the UHF reference wave function is close to 0.75, the value corresponding to a pure doublet spin state.

Dissociation energies have been computed using the extensively correlated coupled cluster singles and doubles method with a perturbative estimate of triple excitations, CCSD(T),[24] using the enlarged 6-311++G(3df,2pd) basis set, at the B3LYP optimized geometries. For $MgH_2^{\cdot+}$ and $CH_4^{\cdot+}$ CCSD(T) calculations have been carried out both at the MP2 and B3LYP geometries. MP2 and CCSD(T) calculations have been performed correlating the valence electrons, except for alkali and alkaline-earth containing systems for which CCSD(T) energies

(11) (a) Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 2473. (b) Bordwell, F. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1989**, *111*, 1792. (c) Zhang, X.; Bordwell, F. G. *J. Org. Chem.* **1992**, *57*, 4163. (d) Zhang, X.-M.; Bordwell, F. G. *J. Am. Chem. Soc.* **1994**, *116*, 4251.

(12) Rega, N.; Cossi, M.; Barone, V. *J. Am. Chem. Soc.* **1997**, *119*, 12 962.

(13) Simon, S.; Sodupe, M.; Bertran, J. *J. Phys. Chem. A* **2002**, *106*, 5697.

(14) See for example (a) Pople, J. A.; Head-Gordon, M.; Fox, D. J.; Raghavachari, K.; Curtiss, L. A. *J. Chem. Phys.* **1989**, *90*, 5622. (b) Curtiss, L. A.; Jones, C.; Trucks, G. W.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1990**, *93*, 2537. (c) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(15) (a) Smith, B. J.; Radom, L. *J. Phys. Chem.* **1991**, *95*, 10 549. (b) De Proft, F.; Langenaeker, W.; Geerlings, P. *Int. J. Quantum. Chem.* **1995**, *55*, 459. (c) Smith, B. J.; Radom, L. *Chem. Phys. Lett.* **1995**, *245*, 123. (d) Gronert, S. *J. Am. Chem. Soc.* **1993**, *115*, 10 258. (e) Gronert, S. *Chem. Phys. Lett.* **1996**, *252*, 415. (f) Hinde, R. J. *J. Phys. Chem. A* **2000**, *104*, 7580. (g) Martin, J. M. L. *Chem. Phys. Lett.* **1997**, *273*, 98.; (h) Laidig, K. E.; Streitwieser, A. *J. Comput. Chem.* **1996**, *17*, 1771.

(16) (a) Kella, D.; Vager, Z. *J. Chem. Phys.* **1995**, *102*, 8424. (b) Paddon-Row: M. N.; Fox, D. J.; Pople, J. A.; Houk, K. N.; Pratt, D. W. *J. Am. Chem. Soc.* **1985**, *107*, 7696. (c) Frey, R. F.; Davidson, E. R. *J. Chem. Phys.* **1988**, *88*, 1775. (d) Signorell, R.; Sommavilla, M.; Merkt, F. *Chem. Phys. Lett.* **1999**, *312*, 139. (e) Rasul, G.; Surya Prakash, G. K.; Olah, G. A. *Proc. Natl. Acad. Sci.* **1997**, *94*, 11 159. (f) Ericksson. L. A.; Lunell, S.; Boyd, R. J. *J. Am. Chem. Soc.* **1993**, *115*, 6986. (g) Boyd, R. J.; Darvesh, K. V.; Fricker, P. D. *J. Chem. Phys.* **1991**, *94*, 8083. (h) Wetmore, S. D.; Boyd, R, J.; Ericksson, L. A.; Laaksonen, A. *J. Chem. Phys.* **1999**, *110*, 12 059. (i) Knight L. B.; Steadman, J.; Feller, D.; Davidson, E. R. *J. Am. Chem. Soc.* **1984**, *106*, 3700.

(17) (a) Frey, R. F.; Davidson, E. R. *J. Chem. Phys.* **1988**, *89*, 4277. (b) De Proft, F.; Geerlings, P. *Chem. Phys. Lett.* **1996**, *262*, 782. (c) Caballol, R.; Catala, J. A.; Poblet, J. M. *Chem. Phys. Lett.* **1986**, *130*, 278.

(18) (a) Bauschlicher, C. W. *Chem. Phys. Lett.* **1993**, *201*, 11. (b) Ricca, A.; Bauschlicher, C. W. *Chem. Phys. Lett* **1998**, *285*, 455.

(19) (a) Curtiss, L. A.; Pople, J. A. *J. Phys. Chem.* **1988**, *92*, 894. (b) Curtiss, L. A.; Pople, J. A. *J. Phys. Chem.* **1987**, *91*, 155. (c) Curtiss, L. A.; Pople, J. A. *J. Phys. Chem.* **1987**, *91*, 3637. (b) Patil, S. H.; Tang, K. T.; *J. Chem. Phys.* **2000**, *113*, 676. (c) Petrie, S. *J. Phys. Chem. A* **2002**, *106*, 5188.

(20) Handy, N. C.; Knowles, P. J.; Somasundram, K. *Theor. Chim. Acta.* **1985**, *68*, 87. (b) Gill, P. M. W.; Pople, J. A.; Radom, L.; Nobes, R. H. *J. Chem. Phys.* **1988**, *89*, 7307.

(21) (a) Barrientos, C.; Largo, A. *J. Mol. Struct. (THEOCHEM)* **1995**, *336*, 29. (b) Petrie, S. *Int. J. Quantum. Chem.* **2000**, *76*, 626.

(22) (a) Sodupe, M.; Bertran, J.; Rodríguez-Santiago, L.; Baerends, E. J. *J. Phys. Chem. A* **1999**, *103*, 166. (b) Braïda, B.; Hiberty, P. C.; Savin, A. *J. Phys. Chem. A* **1998**, *102*, 7872.

(23) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648; (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785 (c) Stephens, P. J.; Devlin, F. J.; Chablowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11 623.

(24) (a) Bartlett, R. J. *Annu. Rev. Phys. Chem.* **1981**, *32*, 359. (b) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

have been computed including also the outermost inner-shell electrons in the correlation space. Previous studies have shown the importance of correlating such outermost inner shell in the calculation of binding energies for systems of this kind.[19c,25] Thermodynamic corrections have been obtained at the B3LYP level assuming an ideal gas, unscaled harmonic vibrational frequencies, and the rigid rotor approximation by standard statistical methods.[26]

The A−H dissociation energies have been computed with respect to the ground state of the fragments. We have considered the singlet spin state for the AH$_{n-1}^+$ molecules in all cases except F$^+$, OH$^+$, NH$_2^+$, Cl$^+$, and SH$^+$, for which the triplet is the ground-state multiplicity. For AH$_{n-1}^-$, all species have been shown to have a singlet ground state, with the exception of BH$_2^-$ (isoelectronic with *CH*$_2$), for which the triplet state was found to be somewhat lower in energy than the singlet one.

The use of CCSD(T) method with a large basis set, at the B3LYP geometries and including thermodynamic corrections from B3LYP frequency calculations is expected to provide accurate numbers for determining dissociation energies. In fact, after the explosion of density functional methods, several studies have reported the good performance of a G2 modified methodology in which the MP2 geometries and HF frequencies are substituted by the B3LYP ones and the QCISD(T) calculations are replaced by CCSD(T) ones.[27] The comparison of the computed values with the known experimental data (mainly for neutral systems) shows the good behavior of these strategies because, for example, the computed deprotonation enthalpies of neutral systems agree to 2−3 kcal/mol with the experimental ones in all cases except BeH$_2$ for which the difference is 6.8 kcal/mol.[28] The present results agree also very well with previous very accurate theoretical studies.[15c,f−g,18b,19c] Because the goal of this paper is not to calibrate the methodology used or to critically evaluate the experimental values, but instead to use an accurate enough approach to provide trends and a physical insight of the effects of ionization in the dissociation energies of the AH$_n$ systems, we have not included the experimental values in the present work.

Net atomic charges and spin densities have been obtained using the natural population analysis of Weinhold et al.[29] All calculations have been performed with the Gaussian 98 package.[30]

(25) (a) Ma, N. L.; Siu, F. M.; Tsang, C. W. *Chem. Phys. Lett.* **2000**, *322*, 65. (b) Petrie, S. *J. Phys. Chem. A* **1998**, *102*, 6138.
(26) McQuarrie, D. *Statistical Mechanics*; Harper and Row: New York, 1986
(27) (a) Mebel, A. M.; Morokuma, K.; Lin, M. C. *J. Chem. Phys.* **1995**, *103*, 7414. (b) Bauschlicher, C. W.; Partridge, H. *J. Chem. Phys.* **1995**, *103*, 1788.
(28) NIST Chemistry WebBook, NIST Standard Reference Database Number 69, March 2003, Eds. P. J. Linstrom and W. G. Mallard" (http://webbook.nist.gov).
(29) (a) Weinhold, F.; Carpenter, J. E. *The structure of small molecules and ions*; Plenum: New York, 1988. (b) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.
(30) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; and Pople, J. A. *Gaussian 98*, Gaussian, Inc., Pittsburgh, PA, 1998.

III. Results and Discussion

First, we will briefly present the homolytic and heterolytic dissociation energies of the neutral AH$_n$ (A = Li−F, Na−Cl) systems. Second, the two possible A−H cleavages of the AH$_n^{·+}$ radical cations (loss of a H$^+$ and loss of a H) will be presented and compared to those of the neutral parents. Finally, the H$_2$ elimination from the AH$_n^{·+}$ radical cations will be analyzed.

Neutral Systems. The dissociation energies (D_0) and the reaction enthalpies (ΔH_{298K}^0) corresponding to the following three cleavages

$$AH_n \rightarrow AH_{n-1}^· + H^· \tag{1}$$

$$AH_n \rightarrow AH_{n-1}^+ + H^- \tag{2}$$

$$AH_n \rightarrow AH_{n-1}^- + H^+ \tag{3}$$

for systems with A belonging to the second (A = Li−F) and third row (A = Na−Cl) are given in Table 1. The variation of these three enthalpies across the second and third row systems are shown in Figures 1 and 2, respectively.

A simple thermodynamic cycle shows that, at 0 K, the enthalpies of these three reactions can be related through the ionization energies (IE) and electron affinities (EA) of AH$_{n-1}^·$ and H$^·$.
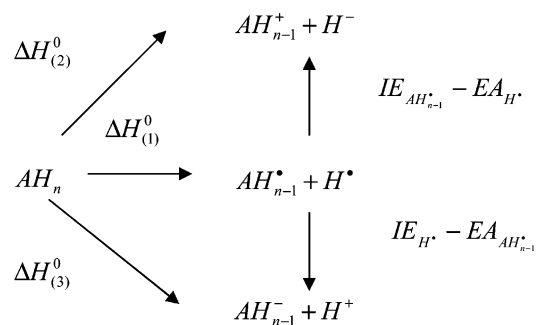
$$\Delta H_{(2)} - \Delta H_{(1)} = IE_{AH_{n-1}^·} - EA_{H^·}$$
$$\Delta H_{(3)} - \Delta H_{(1)} = IE_{H^·} - EA_{AH_{n-1}^·}$$

These relations allow us to understand not only the enthalpy differences of the three reactions considered but also their variations along the row. First, it can be observed in Table 1 that for the two rows, the gas phase AH$_{n-1}$−H homolytic dissociation (eq 1) is clearly preferred over the heterolytic ones (eqs 2 and 3). This is not surprising considering that charge separation in gas phase is energetically very costly given that in all cases the ionization energies of AH$_{n-1}^·$ and H$^·$ are much larger than the electron affinities of H$^·$ and AH$_{n-1}^·$, respectively.

It can be observed in Figures 1 and 2 that whereas the homolytic dissociation enthalpy, in general, increases smoothly along the row, the heterolytic dissociation enthalpy corresponding to the loss of a hydride increases drastically when going from left to right of the row. That is, the $\Delta H_{(2)} - \Delta H_{(1)} = IE_{AH_{n-1}^·} - EA_{H^·}$ difference becomes larger as the atomic number of *A* increases. This is due to an increase of the
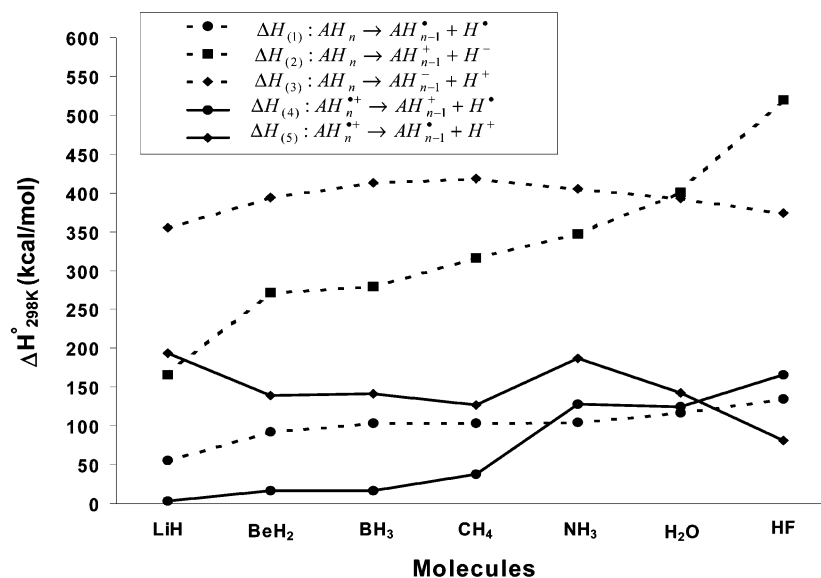
Figure 1. Reaction enthalpies, ΔH_{298}^0, corresponding to different A–H cleavages in neutral AH_n and radical cations $AH_n^{\cdot+}$ (A = Li–F) systems.

Table 1. Dissociation Energies, D_0,[a] and Reaction Enthalpies, ΔH_{298K}^0,[b] Corresponding to Different *A-H* Cleavages in Neutral AH_n (A = Li–F, Na–Cl) Systems at the CCSD(T)/6-311++G(3df,2pd)// B3LYP/6-31++G(d,p) Level[c]

	$AH_n \rightarrow AH_{n-1}^{\cdot} + H^{\cdot}$		$AH_n \rightarrow AH_{n-1}^{+} + H^{-}$		$AH_n \rightarrow AH_{n-1}^{-} + H^{+}$	
system	D_0	ΔH_{298K}^0	D_0	ΔH_{298K}^0	D_0	ΔH_{298K}^0
LiH	54.9	55.8	165.6	166.5	354.4	355.3
BeH$_2$	92.1	93.3	271.1	272.2	393.5	394.6
BH$_3$	102.3	103.8	278.4	279.6	411.4	412.9
CH$_4$	101.8	103.4	314.3	315.7	416.6	418.1
NH$_3$	103.7	105.2	346.0	347.6	403.8	405.3
H$_2$O	115.8	117.0	399.5	400.7	392.1	393.3
HF	134.2	135.0	519.3	520.2	373.6	374.5
NaH	42.4	43.2	147.0	147.8	343.5	344.4
MgH$_2$	69.1	70.1	215.4	216.5	363.3	364.4
AlH$_3$	82.3	83.7	231.8	233.2	372.1	373.5
SiH$_4$	89.1	90.5	262.2	263.6	372.7	374.1
PH$_3$	79.5	80.9	291.1	292.6	367.6	369.0
H$_2$S	88.4	89.6	310.5	311.7	352.1	353.3
HCl	101.1	102.0	381.6	382.5	334.8	335.7

[a] Includes zero point energy computed from the unscaled harmonic B3LYP frequencies. [b] Includes zero point energy computed from the unscaled harmonic B3LYP frequencies and thermal corrections for translational, rotational and vibrational energies determined at 298 K. [c] Energies in kcal/mol.

electronegativity of atom A along the row which leads to larger $IE_{AH_{n-1}^{\cdot}}$. However, the deprotonation enthalpy shows a maximum at CH$_4$ and SiH$_4$. Such variation can be explained from the electron affinity of $AH_{n-1}^{\cdot}$, which starts increasing significantly from NH$_3$ and PH$_3$. As a consequence, the curve representing $\Delta H_{(3)}$ along the row crosses that of $\Delta H_{(2)}$ at H$_2$O for the second row systems and at ClH for the third one (see Figures 1 and 2). Such crossing can again be understood considering the ionization energy of $AH_{n-1}^{\cdot}$ and H$^{\cdot}$ and the electron affinities of H$^{\cdot}$ and $AH_{n-1}^{\cdot}$, because $\Delta H_{(3)} - \Delta H_{(2)} = (IE_{H^{\cdot}} - IE_{AH_{n-1}^{\cdot}}) + (EA_{H^{\cdot}} - EA_{AH_{n-1}^{\cdot}})$. The loss of a hydride will be more favorable if $\Delta H_{(3)} - \Delta H_{(2)} > 0$, whereas the loss of a proton will be preferred if $\Delta H_{(3)} - \Delta H_{(2)} < 0$. Considering that the $IE_{H^{\cdot}}$ (13.60 eV)[28] and $EA_{H^{\cdot}}$ (0.754 eV)[28] are constant along a row, the preference for one reaction or another arises from the changes on the $IE_{AH_{n-1}^{\cdot}}$ and $EA_{AH_{n-1}^{\cdot}}$. The dominant term is the variation of the $IE_{AH_{n-1}^{\cdot}}$ which increases signifi-

cantly from left to right of the row (from 5.39 eV for Li$^{\cdot}$ to 17.42 eV for F$^{\cdot}$ and from 5.14 eV for Na$^{\cdot}$ to 12.97 eV for Cl$^{\cdot}$).[28] Thus, it is not surprising that the loss of the proton becomes more favorable when the ionization energy of $AH_{n-1}^{\cdot}$ becomes larger than that of $H^{\cdot}$. Moreover, the highest electron affinities of $AH_{n-1}^{\cdot}$ correspond to systems on the right side with larger atomic numbers Z_A, which also favors the loss of a proton over the loss of a hydride.

In summary, it is observed that for all systems, except H$_2$O, HF, and HCl, the loss of a hydride (2) is more favorable than the deprotonation process (3). In solution, however, deprotonation becomes much more favorable due to the high solvation energy of the proton.

All dissociation enthalpies of AH_n systems with A belonging to the second row are larger than those of the third row molecules. This trend can be explained considering that when going down from the second to the third row, the size of the central atom A increases resulting in a weakening of the A–H bonds.

Radical Cations. Removing an electron from the neutral AH_n systems to lead to the corresponding $AH_n^{\cdot+}$ radical cations induces significant changes on the structure of the molecule and on the A–H dissociation energies. As a general trend, it is observed that ionization of AH_n induces a lengthening of the A–H bonds. This lengthening is more important for systems on the left side of the row, from LiH to CH$_4$, and from NaH to SiH$_4$, because the electron is removed from a A–H bonding orbital. The largest increases are found for LiH (0.670 Å) and NaH (0.737 Å). For systems on the right side of the row the increase is, in general, smaller because the electron is removed from a lone pair and so, the effect of ionization is indirect. For *NH$_3$* the increase is very small (0.013 Å) and for PH$_3$ the distance does not increase but slightly decreases (−0.019 Å). This is due to the changes in pyramidalization of the systems upon ionization, because NH$_3$ becomes planar and PH$_3$ diminishes significantly its degree of pyramidalization, which allows shorter A–H distances.

For some systems the HOMO orbital is degenerate and so, the removal of one electron leads to a Jahn–Teller distortion
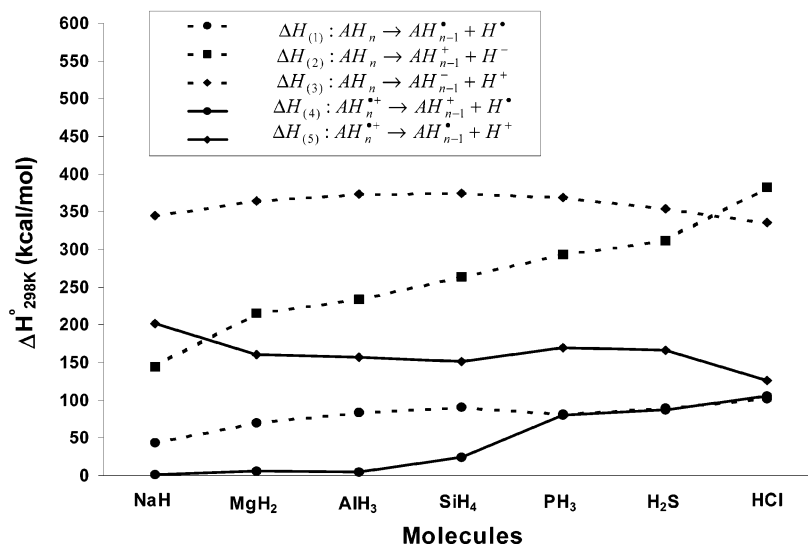
Figure 2. Reaction enthalpies, ΔH^0_{298}, corresponding to different A–H cleavages in neutral AH_n and radical cations $AH_n^{\cdot+}$ (A = Na–Cl) systems.
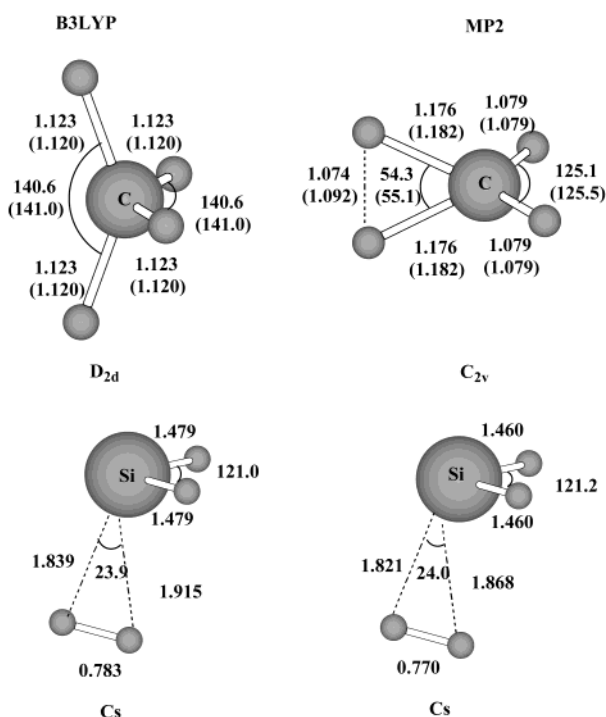

Figure 3. B3LYP and MP2 optimized geometries of $CH_4^{\cdot+}$ and $SiH_4^{\cdot+}$ radical cations with the 6-31++G(d,p) basis. Values in parentheses correspond to the larger 6-311++G(3df,2pd) basis. Distances are in Å and angles in degrees.

which results in a decrease of symmetry. This is the case for BH_3, AlH_3, CH_4,[16] and SiH_4.[17] For BH_3 and AlH_3, the symmetry is reduced from D_{3h} to C_{2v}, whereas for CH_4 and SiH_4, the symmetry changes from T_d to C_{2v} and C_s, respectively. These Jahn Teller distortions produce important variations on the HAH angles, especially for $CH_4^{\cdot+}$ and $SiH_4^{\cdot+}$, which present structures significantly different from those of their neutral precursors. Figure 3 shows the optimized geometrical parameters of these radical cations, both at the B3LYP and MP2 levels. First, it can be observed that whereas for $SiH_4^{\cdot+}$ both B3LYP and MP2 methods provide similar results, for $CH_4^{\cdot+}$ the results obtained at these two levels of theory are quite different. As found previously,[16h] at the B3LYP level the minimum energy

structure of $CH_4^{\cdot+}$ has D_{2d} symmetry with equal C–H bonds, whereas at the MP2 one it has C_{2v} symmetry, with two C–H bonds longer ($\sim$0.1 Å) than the other two. It should be mentioned that at the B3LYP level, the C_{2v} structure is found to have an imaginary frequency, whereas at the MP2 one, the D_{2d} structure is a second-order saddle point. To analyze if such differences arise from the limitations of the basis set used, we have also optimized the two structures using the larger 6-311++G(3df,2pd) basis set. The optimized values are given in parentheses in Figure 3. It can be observed that the results are very similar with the two basis sets and so, differences arise from the different treatment of electron correlation with the two methods.

Because previous studies for other radical cations have shown that density functional methods tend to overstabilize symmetrical situations,[22] we have explored these molecules in more detail, and performed single points CCSD(T) calculations at the two geometries. Results have shown that the CCSD(T) energy is 2.9 kcal/mol lower when the MP2 geometry is used. Therefore, we expect for this particular case the MP2 geometries to be more accurate than the B3LYP ones. Moreover, experimental studies support a C_{2v} symmetry structure for $CH_4^{\cdot+}$.[16d,i]

It can be observed in Figure 3 that in the C_{2v} structure of $CH_4^{\cdot+}$, the angle defined by the two longer C–H bonds is quite small (54.3°), which leads to a significantly short H–H distance (1.074 Å). A similar structure has been found for the isoelectronic $BH_4^{\cdot}$ radical,[31] for which the H···H interaction is interpreted as a one electron bond similar to that found in $H_2^{\cdot+}$. This is confirmed also in our calculations since the net positive charge on this fragment is 0.80. $CH_4^{\cdot+}$ can thus be viewed as the interaction of CH_2 ($^3B_1$) with $H_2^{\cdot+}$. The interaction of the $3a_1$ orbital of CH_2 with the σ_g of $H_2^{\cdot+}$ forms a three-center-two electron bond. The open shell orbital has b_1 symmetry and remains mainly localized at the carbon atom, although there is a slight delocalization due to its interaction with the σ_u^* orbital of $H_2^{\cdot+}$. Accordingly, the spin density at the carbon atom is 0.81. Thus, because positive charge and spin density lie at different sites, this radical cation presents a certain distonic character.[10]

(31) Andrews, L.; Wang, X. *J. Am. Chem. Soc.* **2002**, *124*, 7280.

Table 2. Dissociation Energies, D_0,[a] and Reaction Enthalpies,[b] ΔH^0_{298K}, Corresponding to Different A−H Cleavages in $AH_n^{\cdot+}$ (A = Li−F, Na−Cl) Radical Cations at the CCSD(T)/6-311++G(3df,2pd)//B3LYP/6-31++G(d,p) Level[c]

system	symmetry (state)	$AH_n^{\cdot+} \rightarrow AH_{n-1}^+ + H^\cdot$		$AH_n^{\cdot+} \rightarrow AH_{n-1}^\cdot + H^+$	
		D_0	ΔH^0_{298K}	D_0	ΔH^0_{298K}
$LiH^{\cdot+}$	$C_{\infty v}$ ($^2\Sigma^+$)	2.4	3.1	192.5	193.2
$BeH_2^{\cdot+}$	C_{2v} ($^2B_2$)	16.4	17.4	138.3	139.2
$BH_3^{\cdot+}$	C_{2v} ($^2B_2$)	15.7	16.7	140.5	141.8
$CH_4^{\cdot+}$	C_{2v} ($^2B_1$)[d]	37.1	38.4	125.3	126.8
$NH_3^{\cdot+}$	D_{3h} ($^2A_2''$)	126.4	127.9	185.0	186.5
$H_2O^{\cdot+}$	C_{2v} ($^2B_1$)	124.0	125.2	141.3	142.4
$HF^{\cdot+}$	$C_{\infty v}$ ($^2\Pi$)	164.4	165.3	80.2	81.1
$NaH^{\cdot+}$	$C_{\infty v}$ ($^2\Sigma^+$)	1.3	1.9	197.6	198.3
$MgH_2^{\cdot+}$	$C_{\infty v}$ ($^2\Sigma^+$)[e]	4.9	5.5	159.4	160.0
$AlH_3^{\cdot+}$	C_{2v} ($^2B_2$)	4.0	5.1	155.4	156.5
$SiH_4^{\cdot+}$	C_s ($^2A'$)	22.8	23.8	150.6	151.6
$PH_3^{\cdot+}$	C_{3v} ($^2A_1$)	79.2	80.6	168.5	169.9
$H_2S^{\cdot+}$	C_{2v} ($^2B_1$)	85.9	87.1	164.7	165.9
$HCl^{\cdot+}$	$C_{\infty v}$ ($^2\Pi$)	104.2	105.1	124.6	125.5

[a] Includes zero point energy computed from the unscaled harmonic B3LYP frequencies. [b] Includes zero point energy computed from the unscaled harmonic B3LYP frequencies and thermal corrections for translational, rotational and vibrational energies determined at 298 K. [c] Energies in kcal/mol. [d] MP2 optimized geometry. B3LYP calculations provide D_{2d} symmetry and a $^2B_2$ electronic state. See text. [e] MP2 geometry. B3LYP calculations provide $D_{\infty h}$ symmetry and a $^2\Sigma_u^+$ electronic state.

The optimized structure for $SiH_4^{\cdot+}$ is very different from that of $CH_4^{\cdot+}$. In this case, the distance between the two hydrogens (0.770 Å) of the elongated Si−H bonds clearly correspond to that of H_2. Therefore, this species can be viewed as the interaction between $SiH_2^{\cdot+}$ radical cation and neutral H_2. Natural population analysis confirms this fact because the charge and spin mainly lie on the SiH_2 fragment.

The cleavage of A−H in $AH_n^{\cdot+}$ can be produced either by losing a hydrogen atom to form the AH_{n-1}^+ cation or by losing a proton to form a neutral radical $AH_{n-1}^\cdot$

$$AH_n^{\cdot+} \rightarrow AH_{n-1}^+ + H^\cdot \tag{4}$$

$$AH_n^{\cdot+} \rightarrow AH_{n-1}^\cdot + H^+ \tag{5}$$

The A−H dissociation energies (D_0) and enthalpies (ΔH^0_{298}) of the $AH_n^{\cdot+}$ systems with A atoms belonging to the second (A = Li−F) and third row (A = Na−Cl) are given in Table 2. The reaction enthalpies corresponding to processes (4) and (5) for the second and third row systems have been included in Figures 1 and 2, respectively. As for the neutral systems, CCSD(T) calculations have been performed at the B3LYP geometries except for $CH_4^{\cdot+}$ and $MgH_2^{\cdot+}$, for which the MP2 geometries have been considered. As mentioned, the optimized MP2 geometry for $CH_4^{\cdot+}$ is expected to be more accurate than the B3LYP one. For $MgH_2^{\cdot+}$ the two methods differ also significantly, because the B3LYP optimization lead to a structure that has $D_{\infty h}$ symmetry with two equal Mg−H distances (1.799 Å), whereas the MP2 one provided a $C_{\infty v}$ structure with one short (1.653 Å) and one long (2.301 Å) Mg−H distance. At the MP2 level, the symmetric $D_{\infty h}$ structure was found to have an imaginary frequency of σ_u symmetry. As for $CH_4^{\cdot+}$, using the larger basis set does not change the results and CCSD(T) calculations seem to indicate that the MP2 geometry is more accurate.
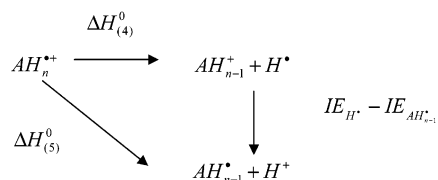
First of all, it can be observed that the reaction enthalpy corresponding to the loss of a hydrogen atom is very small for

the systems on the left side of the row; that is, from $LiH^{\cdot+}$ to $CH_4^{\cdot+}$, and from $NaH^{\cdot+}$ to $SiH_4^{\cdot+}$. This was to be expected considering that the radical cation is obtained from removing an electron from a A−H bonding orbital. The reaction enthalpy is particularly small for the first three systems because the HOMO orbital has a bonding character with an important contribution of the 1s orbitals of the hydrogen atoms and so, the spin density in the radical cation mainly lies on the hydrogen atoms. For example, $LiH^{\cdot+}$ can be viewed as the interaction of Li^+ with $H^\cdot$. As we move from left to right across the row, the contribution of the atomic orbitals of A to the molecular A−H bonding orbitals becomes more important, the spin density on A increases and consequently the loss of $H^\cdot$ becomes more difficult. For the second row systems, one can observe an important gap between $CH_4^{\cdot+}$ and $NH_3^{\cdot+}$ so that the reaction enthalpy starts increasing significantly. The values obtained are even larger than those found for the homolytic dissociation of their neutral counterparts. This is due to the fact that now the electron is removed from a nonbonding orbital. The creation of a positive charge on AH_n, which is mainly localized on the central atom A, induces a stabilization of the molecular bonding orbitals. Consequently, the loss a hydrogen atom becomes energetically more costly than for the neutral systems (see Figure 1). In these cases, for which the electron is removed from a nonbonding orbital, the loss of a hydrogen atom is a real homolytic dissociation process. For the third row systems, we observe a similar behavior, the homolytic dissociation energy of the radical cation being only larger than that of the neutral molecule in the case of ClH.

The reaction enthalpy corresponding to the loss of a proton in $AH_n^{\cdot+}$ also experiences important changes, both qualitatively and quantitatively, compared to the analogous reaction in the neutral systems. First, it is observed that all deprotonation energies become much smaller when the system is ionized. Second, results show that, whereas for the neutral species the largest deprotonation enthalpy correspond to the AH_4 systems (CH_4 and SiH_4), for the radical cations, the $AH_4^{\cdot+}$ molecules ($CH_4^{\cdot+}$ and $SiH_4^{\cdot+}$) present the second smallest deprotonation energies of the row. That is, neutral CH_4 and SiH_4 are the less acidic species of the second and third row, respectively, but the corresponding radical cations, $CH_4^{\cdot+}$ and $SiH_4^{\cdot+}$, are one of the most acidic species, their acid character being only exceeded by $FH^{\cdot+}$ and $ClH^{\cdot+}$. Again, this can be understood considering the nature of the HOMO orbital from which the electron is removed. From $LiH^{\cdot+}$ to $CH_4^{\cdot+}$, and from $NaH^{\cdot+}$ to $SiH_4^{\cdot+}$, the HOMO orbital is a A−H bonding orbital with an increasing contribution of the orbitals of *A* and thus, the protonic character of the H atoms in $AH_n^{\cdot+}$ increases from left to right with the consequently decrease of the deprotonation energy. There is only one exception, $BeH_2^{\cdot+}$ and $BH_3^{\cdot+}$ which have very similar deprotonation energies. As mentioned, starting from $NH_3^{\cdot+}$ and $PH_3^{\cdot+}$, the electron is removed from a nonbonding orbital and so, the increase of acidity is an indirect effect, due to the polarization of the A−H bonds produced by the presence of a positive charge. Because of that, although the deprotonation energies also decrease when going to the right of the row, (from $NH_3^{\cdot+}$ to $FH^{\cdot+}$, and from $PH_3^{\cdot+}$ to $ClH^{\cdot+}$) there is an important gap between $CH_4^{\cdot+}$ and $NH_3^{\cdot+}$ or between $SiH_4^{\cdot+}$ and $PH_3^{\cdot+}$. It must be remarked that for these three last systems of the row the deprotonation reaction is a real heterolytic process. In all

cases, however, the important decrease of the AH$_n^{\cdot+}$ deprotonation energy compared to that of the neutral AH$_n$ system is due to the presence of the positive charge, which induces a stabilization of the A atomic orbitals, and as a consequence increases the positive charge on the H atoms. Variations along the row depend on whether the electron is removed from a bonding or from a nonbonding orbital.

The reaction enthalpies of the two possible cleavages can be related through the ionization energies of H$^\cdot$ and AH$_{n-1}^\cdot$.

$$AH_n^{\cdot+} \xrightarrow{\Delta H^0_{(4)}} AH_{n-1}^+ + H^\cdot$$
$$\Delta H^0_{(5)} \searrow \qquad \downarrow IE_{H^\cdot} - IE_{AH_{n-1}^\cdot}$$
$$AH_{n-1}^\cdot + H^+$$

Thus, $\Delta H^0_{(5)} = \Delta H^0_{(4)} + IE_{H^\cdot} - IE_{AH_{n-1}^\cdot}$. From this relation, it is clear that the loss of a hydrogen atom will be more favorable than the loss of the proton if $IE_{H^\cdot} - IE_{AH_{n-1}^\cdot} > 0$; that is, when the ionization of AH$_{n-1}^\cdot$ is less energetically costly than that of H$^\cdot$. This is the situation at the beginning of the row. However, as we move across the row the $IE_{AH_{n-1}^\cdot}$ starts increasing significantly and so, the loss of a proton becomes more favorable. It can be observed in Figure 1 that the two curves cross between H$_2$O$^{\cdot+}$ and FH$^{\cdot+}$. For the third row systems, the effect of ionization on the deprotonation energy is in general smaller and thus, the two curves do not cross although they get quite close for ClH$^{\cdot+}$.

Changes in acidities produced by ionization have important consequences. On one hand, all species become much more acid than neutral HF or ClH. The decrease of deprotonation energy upon ionization ranges from 161 to 293 kcal/mol for the second row systems and from 146 to 222 kcal/mol for the third row ones, the largest decreases corresponding to CH$_4^{\cdot+}$ and FH$^{\cdot+}$ and to SiH$_4^{\cdot+}$ and ClH$^{\cdot+}$, respectively. The increase of acidity as well as the presence of the positive charge will lead to strong hydrogen bonds between AH$_n^{\cdot+}$ radical cations and a proton acceptor molecule, like for example water. Moreover, if the proton affinity of water is larger than the deprotonation energy of AH$_n^{\cdot+}$, the proton-transfer reaction leading to the distonic AH$_{n-1}^{\cdot+}$ − H$_3$O$^+$ species may be a spontaneous process. As a matter of fact, previous calculations on HOH$^{\cdot+}$ − OH$_2$, NH$_3^{\cdot+}$−OH$_2$, and FH$^{\cdot+}$−OH$_2$ have shown that the proton transfer process occurs spontaneously for H$_2$O$^{\cdot+}$ and FH$^{\cdot+}$ but not for NH$_3^{\cdot+}$.[7b] We have performed additional calculations to complete the whole row and observed that the proton transfer occurs for all the other systems except LiH$^{\cdot+}$. This behavior is in agreement with the fact that both LiH$^{\cdot+}$ and NH$_3^{\cdot+}$, have a larger deprotonation energy than the proton affinity of water (165.0 kcal/mol).[28]

On the other hand, ionization changes the relative acidity of these species. That is, the relative acidity of neutral CH$_4$, NH$_3$, and H$_2$O systems is as follows

$$CH_4 < NH_3 < H_2O$$

whereas that of the corresponding radical cations is as follows

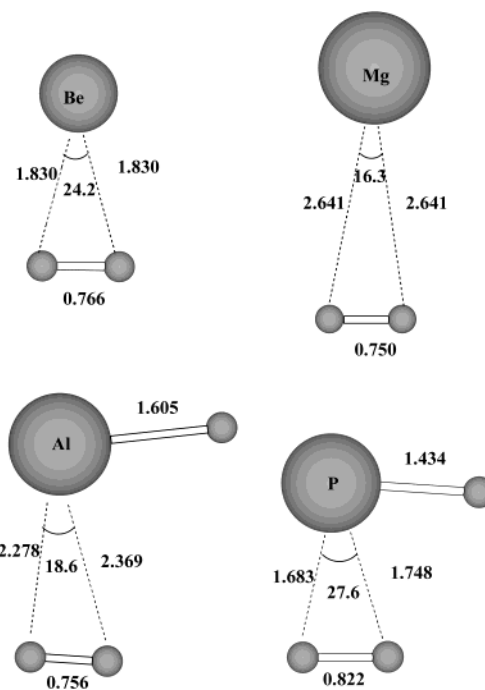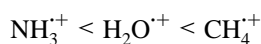$$NH_3^{\cdot+} < H_2O^{\cdot+} < CH_4^{\cdot+}$$

Figure 4. B3LYP optimized geometries of AH$_{n-2}^{\cdot+}$ − H$_2$ (A = Be, Mg, Al, and P) hydrogen molecule complexes. Distances are in Å and angles in degrees.

This order is in perfect agreement with the order found experimentally for the analogous PhOH, PhNH$_2$, and PhCH$_3$ systems,[11] both for neutral and radical cation species. Moreover, these relative orders are the same in gas-phase as in solution which indicates that the variations observed upon ionization are due to the changes produced on the intrinsic electronic properties of the molecule, as shown by the present calculations. The increase of acidity by solvation is larger for the neutral systems than for the radical cations because in the first case deprotonation process implies the creation of two ionic species. However, the deprotonation reaction in the radical cations implies just the transfer of a positive charge. Nevertheless, because the changes on the intrinsic acidity due to ionization are much more important than the solvation effects, radical cations, especially those derived from hydrocarbon compounds, often become superacid species with large negative pK_a.[11]

H$_2$ Elimination in AH$_n^{\cdot+}$ Systems. As seen in the previous section, ionization of SiH$_4$ leads to the formation of a SiH$_2^{\cdot+}$ − η_2H$_2$ complex from which H$_2$ can easily be eliminated. This raises the question of whether other radical cations could also form similar species. Because of that, we explored the possibility of having AH$_{n-2}^{\cdot+}$ − η^2H$_2$ structures for all species from BeH$_2^{\cdot+}$ to H$_2$O$^{\cdot+}$ and from MgH$_2^{\cdot+}$ to H$_2$S$^{\cdot+}$. We have restricted the study to surfaces with a doublet spin multiplicity, the same as the AH$_n^{\cdot+}$ species. Figure 4 shows the geometrical parameters of the localized minima and Table 3 shows the relative energies of these AH$_{n-2}^{\cdot+}$ − H$_2$ structures with respect to the AH$_n^{\cdot+}$ ones. Moreover, Table 3, shows the relative energy of the AH$_{n-2}^{\cdot+}$ + H$_2$ asymptote, which corresponds to the elimination of H$_2$.

It can be observed in Table 3 that for the second row systems, the AH$_{n-2}^{\cdot+}$ − H$_2$ hydrogen complex is only found for BeH$_2^{\cdot+}$. For the remaining systems, the optimization of a hydrogen molecule complex in the doublet spin state collapsed to the

Table 3. Relative Enthalpies,[a] ΔH^0_{298K}, of $AH^{\cdot+}_{n-2} - H_2$ and $AH^{\cdot+}_{n-2} + H_2$ with Respect to $AH^{\cdot+}_n$ in kcal/mol[b]

system	$AH^{\cdot+}_n$	$AH^{\cdot+}_{n-2} - H_2$	$AH^{\cdot+}_{n-2} + H_2$
BeH_2	0.0	−23.9	−15.5
BH_3	0.0		28.9
CH_4[c]	0.0		56.9
NH_3	0.0		170.1
H_2O	0.0		219.9
MgH_2[c]	0.0	−53.4	−51.5
AlH_3	0.0	−25.9	−22.3
SiH_4		0.0	12.3
PH_3	0.0	37.3	61.1
H_2S	0.0		114.0

[a] Includes zero point energy computed from the unscaled harmonic B3LYP frequencies and thermal corrections for translational, rotational and vibrational energies determined at 298K. [b] Calculations have been restricted to the doublet spin state. [c] Calculations performed at the MP2 geometries.

$AH^{\cdot+}_n$ compound. In contrast, for the third row systems, the hydrogen molecule structure is found in all cases except $H_2S^{\cdot+}$.

The hydrogen molecule complex is the global minimum for $BeH^{\cdot+}_2$, $MgH^{\cdot+}_2$, $AlH^{\cdot+}_3$, and $SiH^{\cdot+}_4$. The fact that the first three structures were not obtained upon removing one electron from the corresponding neutral precursors is due to the existence of a significant energy barrier between $AH^{\cdot+}_n$ and $AH^{\cdot+}_{n-2} - H_2$, which arises from a change in the electronic state. For instance, $[Mg - H_2]^{\cdot+}$ has a $^2A_1$ ground state, that results from the interaction of $Mg^{\cdot+}$ ($3s^1$) with neutral H_2, whereas $[HMgH]^{\cdot+}$ (at the B3LYP level) has a $^2\Sigma^+_u$ ground state which reduces to a $^2B_2$ state in C_{2v} symmetry. The crossing point between the two electronic states occurs at an HMgH angle of about 40°, the energy barrier from $[HMgH]^{\cdot+}$ being 12.7 kcal/mol.

Within a row, the relative stability of the hydrogen molecule complex $AH^{\cdot+}_{n-2} - H_2$ with respect to $AH^{\cdot+}_n$ decreases as the atomic number increases. Moreover, the comparison between A = Be and Mg seems to indicate that $AH^{\cdot+}_{n-2} - H_2$ becomes more stable as we move down on a group. Thus, the relative stability of $AH^{\cdot+}_{n-2} - H_2$ with respect to $AH^{\cdot+}_n$ appears to be related with the energy cost of the $A^+ - H^{\cdot}$ cleavage, which is very small for the left row systems. This is not surprising considering that the formation of $AH^{\cdot+}_{n-2} - \eta^2H_2$ requires the cleavage of two $A^+ - H^{\cdot}$ bonds of $AH^{\cdot+}_n$.

For the $AH^{\cdot+}_{n-2} - H_2$ (A = Al, Si, and P) complexes, both deprotonation and dehydrogenation reactions can take place either from one of the $AH^{\cdot+}_{n-2}$ bonds or from the complexed $\eta2 - \eta^2$ molecule. To analyze whether the obtained products are different or not we have performed calculations for A = Al and Si, for which $AH^{\cdot+}_{n-2} - \eta^2H_2$ is the ground-state structure. Results have shown that when the loss of a $H^{\cdot}$ or a H^+ occurs from the $\eta^2 - H_2$ interacting molecule, the obtained fragments are AH^+_{n-1} or $AH^{\cdot}_{n-1}$, respectively. Thus, for A = Al the deprotonation and dehydrogenation enthalpies from $AH^{\cdot+}_{n-2} - \eta^2H_2$ become 25.9 kcal/mol larger than from $AH^{\cdot+}_n$.

Instead, if deprotonation or dehydrogenation is produced from one of the $AH^{\cdot+}_{n-2}$ bonds, the obtained products are $AH^{\cdot}_{n-3} - \eta^2H_2$ or $AH^+_{n-3} - \eta^2H_2$, respectively. That is, the complexed hydrogen molecule is retained upon dissociation. Both for A = Al and Si, the $AH^{\cdot}_{n-3} - \eta^2H_2$ structures that result from deprotonation are 15.1 and 38.4 kcal/mol less stable than the corresponding $AH^{\cdot}_{n-1}$ ones and so, the loss of a proton from one of the $AH^{\cdot+}_{n-2}$ bonds is energetically more costly than from the interacting $\eta^2 - H_2$ molecule and, at least for these

two systems, the hydrogen atoms of the complexed $\eta^2 - H_2$ molecule are more acidic than the $AH^{\cdot+}_{n-2}$ ones.

In contrast, dehydrogenation of $AH^{\cdot+}_{n-2} - \eta^2H_2$ from one of the $AH^{\cdot+}_{n-2}$ bonds can be more favorable than from the complexed $\eta^2 - H_2$ molecule depending on the system. For A = Al, the $AH^+_{n-2} - \eta^2H_2$ complex is 11.3 kcal/mol more stable than AH^+_{n-1}. However, for A = Si, the reverse trend is observed, the AH^+_{n-1} structure being more stable by 29.1 kcal/mol.

The energy difference between the two last columns of Table 3 give the strength of the interaction between $AH^{\cdot+}_{n-2}$ and the H_2 molecule. It can be observed that such interaction increases from left to right in a row. The computed values for $AH^{\cdot+}_{n-2} - H_2$ (A = Mg, Al, Si, and P) are 1.9, 3.6, 12.3, and 23.8 kcal/mol, respectively. This increasing interaction energy agrees with the optimized $AH^{\cdot+}_{n-2} - H_2$ structures, given that the H_2 distance increases and the $A\cdots H_2$ distances decrease from $Mg^{\cdot+} - H_2$ to $PH^{\cdot+} - H_2$ (see Figures 3 and 4). Such strengthening correlates with the charge transfer from H_2 to $AH^{\cdot+}_{n-2}$, which increases in the same direction: 0.02 for $Mg^{\cdot+} - H_2$, 0.04 for $AlH^{\cdot+} - H_2$, 0.18 for $SiH^{\cdot+}_2 - H_2$ and 0.28 for $PH^{\cdot+} - H_2$. This was to be expected considering that the larger the charge transfer from the occupied σ_g orbital of H_2 to the unoccupied orbitals of $AH^{\cdot+}_{n-2}$ radical cation, the shorter the $A\cdots H_2$ distances.

For Si and P, the strength of the $AH^{\cdot+}_{n-2} - H_2$ interaction is similar to that found in transition metal dihydrogen complexes, first discovered by Kubas et al. in 1984,[32] and now extensively studied.[33,34] However, transition metal dihydrogen compounds differ from the ones studied in the present work, $AH^{\cdot+}_{n-2} - H_2$, in the fact that in addition to the donation from the filled $H_2(\sigma_g)$ orbital to the empty $M(d_\sigma)$ orbital, there is also a back-donation from filled $M(d_\pi)$ orbitals to the empty $H_2(\sigma_u^*)$ one. If this back-donation is strong enough, then the bond of the hydrogen molecule is broken and one obtains the classical dihydride complex. Because oxidation of transition metal complexes will reduce the metal to H_2 back-donation, one may expect that the stability of the hydride compound will be disfavored with respect to that of the nonclassical dihydrogen complex. In fact, a experimental study of the $Cp^*MoH_3(dppe)$ compound has shown that its oxidation induces the H_2 reductive elimination from the polyhydride complex.[35]

IV Conclusions

The dissociation energies corresponding to the two possible A−H cleavages of $AH^{\cdot+}_n$(A = Li−F and Na−Cl) radical cations (loss of a H^+ and loss of a $H^{\cdot}$) have been computed at the CCSD(T)/6-311++G(3df,2pd) level of theory and compared to those of their neutral precursors. Moreover, the H_2 elimination from the $AH^{\cdot+}_n$ radical cations has also been analyzed. The results obtained have lead to the following conclusions.

(32) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984,** *106*, 451.
(33) Maseras, F.; Lledos, A.; Clot, E.; Eisenstein, O. *Chem. Rev.* **2000,** *100*, 601 and references therein.
(34) (a)*Recent Advances in Hydride Chemistry*, Eds. M. Peruzzini, R. Poli, Elsevier: Amsterdam, **2001**, (b) Kubas, G. J. *Metal Dihydrogen and σ-bond complexes. Structure, Theory and Reactivity. Modern Inorganic Chemistry*; Flacker, J. P., Ed.: Kluwer Academic: New York, 2001.
(35) (a) Pleune, B.; Morales, D.; Meunier-Prest, R.; Richard, P.; Collange, E.; Fettinger, J. C.; Poli, R. *J. Am. Chem. Soc.* **1991**, *121*, 2209. (b) Poli, R. *Recent Advances in Hydride Chemistry*; Peruzzini, M., Poli, R., Eds.; Elsevier: Amsterdam, 2001, 139**.**

Removing an electron from a AH$_n$ neutral system changes significantly the gas phase A−H dissociation energies: the deprotonation energy is significantly reduced in all cases, whereas the dehydrogenation energy shows an important decrease only for systems on the left side of the row, for which the electron is removed from a A−H bonding orbital. Nevertheless, the loss of hydrogen is still more favorable than the deprotonation process in all cases except FH$^{\cdot+}$.

Deprotonation energies are much smaller and so, acidities much larger, for the AH$_n^{\cdot+}$ radical cations than for the neutral precursors. Moreover, ionization changes the relative order of acidity of AH$_n$ systems. The most remarkable result is that, whereas for the neutral systems the less acidic species are the AH$_4$ compounds (CH$_4$ and SiH$_4$), for the radical cations, the AH$_4^{\cdot+}$ molecules (CH$_4^{\cdot+}$ and SiH$_4^{\cdot+}$) are one of the most acidic species of the row, their acid character being only exceeded by FH$^{\cdot+}$ and ClH$^{\cdot+}$, respectively. Thus, AH$_n^{\cdot+}$ radical cations, especially hydrocarbon radical cations, will easily deprotonate in the presence of proton acceptor molecules. The superacidic behavior found experimentally in solution for these radical cations is a consequence of the intrinsic electronic changes produced upon ionization.

AH$_{n-2}^{\cdot+}$ − η^2H$_2$ complexes in the doublet spin state have been found to be stable for A = Be, Mg, Al, Si, and P. These hydrogen molecule complexes are more stable than their corresponding AH$_n^{\cdot+}$ radical cations only for Be, Mg, and Al, the stability of AH$_{n-2}^{\cdot+}$ − η^2H$_2$ decreasing from left to right in a row. For SiH$_4$, the Jahn Teller distorted species found upon ionization corresponds already to the SiH$_2^{\cdot+}$ − H$_2$ complex and thus, formation of the hydrogen molecule complex is a spontaneous process. The extrapolation of the present results to transition metal hydride systems suggest that their oxidation might induce the formation of the nonclassical transition metal hydrogen molecule complexes, from which H$_2$ may be easily eliminated. In solution, however, other reactions such as deprotonation may compete with the H$_2$ reductive elimination.

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