
**PROPERTIES AND REACTIVITY OF FIRST AND SECOND ROW
HYDRIDES. INTRODUCTORY REMARKS, ISOMERIZATIONS,
AND INVERSION BARRIERS OF THE AH_2 , AH_3 , AH_4
AND RELATED SYSTEMS**

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In this paper and in the following parts of this series chemical reactivity and physical characteristics of hydrides of the first (LiH, BeH₂, BH₃, CH₄, NH₃, H₂O, HF) and second (NaH, MgH₂, AlH₃, SiH₄, PH₃, H₂S, HCl) row atoms of the Periodic System are discussed in terms of nonempirical quantum chemical characteristics. Semiquantitative features and tendencies rather than quantitative aspects of reactivity are investigated, which permits one to use rather modest theoretical methods. Besides the members of the mentioned series also radicals, ions, and radical ions thereof will be treated. In this part isomerizations of "unnatural" ionic hydrides (cations derived from electron-deficient and anions derived from electron-rich hydrides, e.g., LiH⁽⁺⁾ and LiH₂⁽⁺⁾ or HF⁽⁻⁾, H₂F⁽⁻⁾) are studied. One or two van der Waals ions derived from all these systems represent thermodynamically rather stable forms. Relations between structure and inversion barriers have been studied for bent triatomic (C_{2v}), pyramidal tetraatomic (C_{3v}) and tetrahedral pentaatomic (T_d) molecules and ions. Inversion barriers increase when passing from the first-row C_{2v} and C_{3v} hydrides to higher-row analogues; both decrease (e.g., CH₄ → SiH₄) as well as increase (e.g., BH₄⁽⁻⁾ → AlH₄⁽⁻⁾) were calculated for transitions of T_d hydrides.

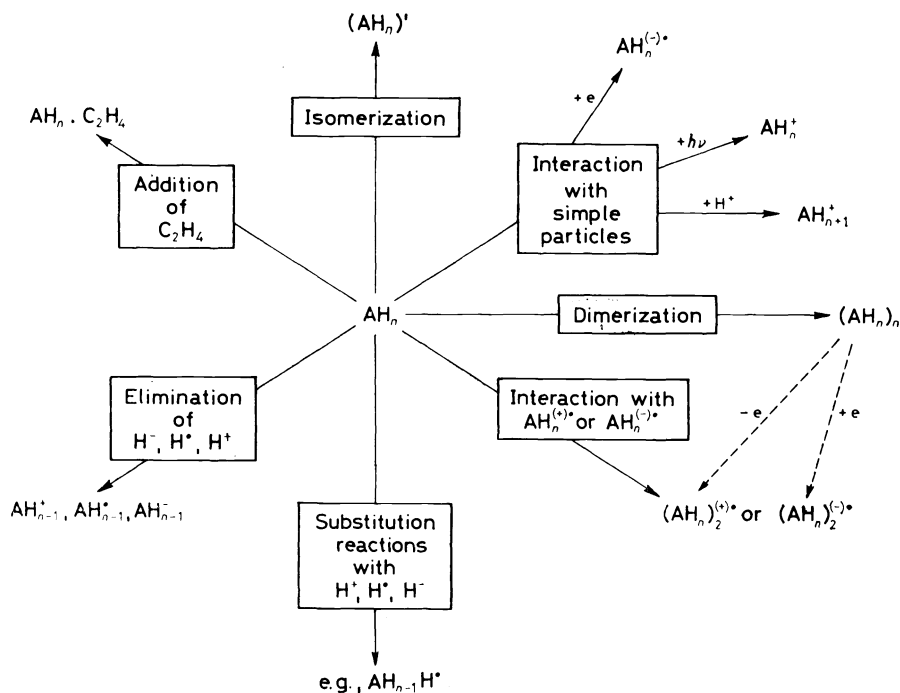
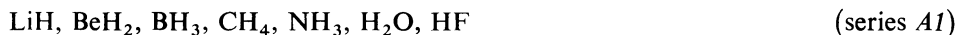
Hydrides of atoms of the first and second rows of the Periodic System represent suitable systems for investigating prototypes of fundamental chemical transformations. Isomerizations, additions, dimerization and related processes, substitutions, eliminations, proton, hydrogen atom and hydride transfer and acid-base equilibria can be investigated by means of interactions between the AH_n hydrides and radical ions, radicals, and ions derived from them with partners like H⁺, H[•], H⁻, H₂, H₂O, and C₂H₄. These processes represent a very rich source of information on chemical reactivity. There are additional reasons supporting the choice of these systems for such a study: they are very well suited for quantum chemical and statistical mechan-

ical studies and, even more importantly, relatively numerous experimental data are available.

The main attention of the set of papers of this series will be paid to regularities of physical properties and chemical reactivity in the series rather than to characteristics of the individual members of the series. Being primarily interested in qualitative features and tendencies in series of related systems allows us to use rather moderate, standard types of quantum chemical methods. Only in some special cases results of more sophisticated calculations are used.

THEORETICAL

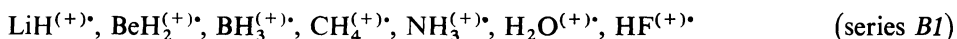
The hydrides under study are the following:



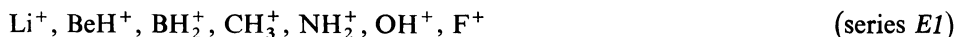
SCHEME 1

Outline of processes under study

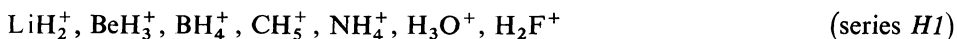
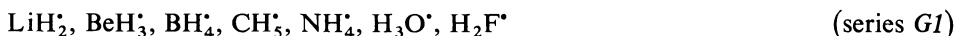
For the sake of simplicity, the next series are represented only by the derivatives of the first row atoms:



as well as the corresponding radical anions (series *C1*); furthermore



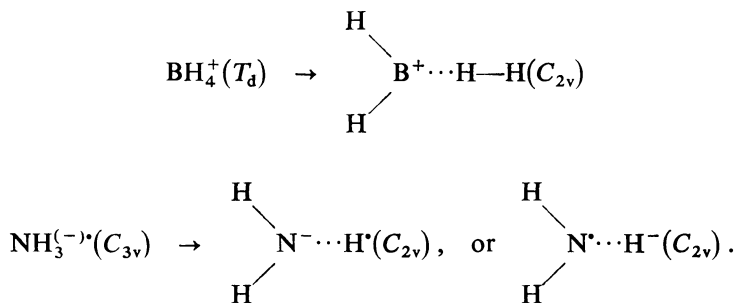
and the corresponding anions (series *F1*). Finally the following series will be investigated



and the corresponding anions (series *I1*). The analogous series of the second row atoms are *B2*, *C2*, *D2*, *E2*, *F2*, *G2*, *H2*, and *I2*. The processes treated, outlined in Scheme 1, are as follows.

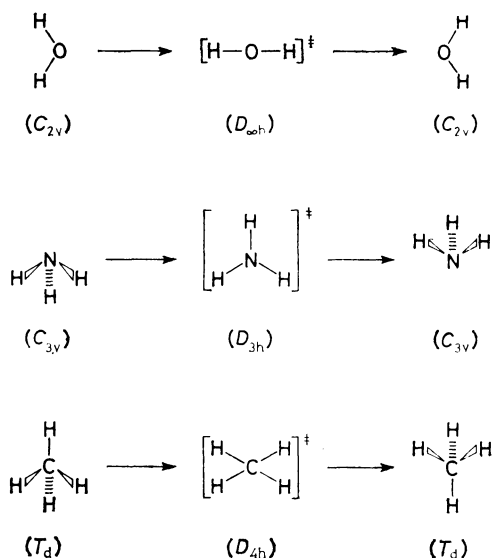
Isomerizations

Some hydrides, especially their ions and radical ions are sometimes metastable when possessing structures of the parent hydrides (series *A1* and *B1*) and although they are formally analogous, they pass rapidly into, e.g., van der Waals species. This can be illustrated for example by the isomerizations:



In general, natural hydrides possess relatively deep minima on the potential energy surfaces (P.E.S.) while unnatural hydrides are unstable and either decompose into fragments or isomerize into van der Waals species (see below).

To this group of processes belong also inversions. Products of these transformations are identical with reactants (except for chiral compounds); the activated complexes assume a linear or planar form (Scheme 2).

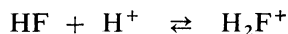


SCHEME 2

Additions

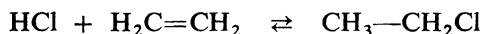
We consider two processes.

a) Additions of a proton to molecules and radicals of series *A* and *B* (as well as to other systems), e.g.,



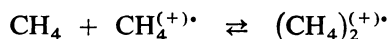
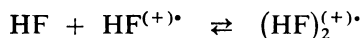
Enthalpy and Gibbs energy changes at 300 K of this process are called proton affinity and gas basicity, respectively. Moreover, addition of an H atom, H^- , and metal cations is topical.

b) Addition of ethylene to the members of our series, in particular to series *A*, e.g.,

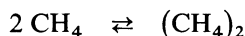
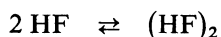


Dimerization and Related Processes

We are mainly interested in interactions between hydrides of the *A* series with their own radical cations, e.g.,

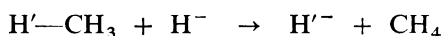


In order to get more general information, also comparison will be made with the well-known dimer formation, e.g.,



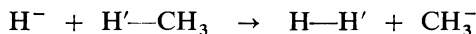
Substitutions

Nucleophilic, electrophilic, and radical substitutions can be studied especially for members of series *A* with H^- , H^+ , and H^\cdot as substituting agents. One can use the following process as an example of an $\text{S}_{\text{N}}2$ reaction:



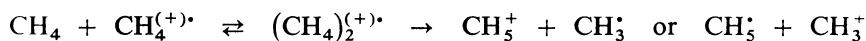
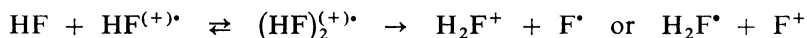
Eliminations

These reactions can be viewed as alternative or parallel processes to the just mentioned substitutions. Elimination related to the above mentioned substitution reaction proceeds as:



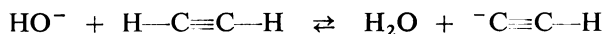
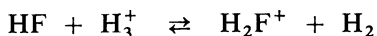
Proton and Hydrogen Atom Transfer

Our main concern deals with the radical cation dimers already mentioned in connection with dimerization and related processes. The products of the following processes are either formed by direct processes (proton or hydrogen atom transfer) or via long-lived dimeric radical cations



Acid-Base Equilibria

Members of the series *A*, *D*, and *F* will be considered as proton acceptors; equilibria with proton donors ranging from H_3^+ to H_2 (via, e.g., H_2O and C_2H_2) will be studied. The following processes can serve as examples:



In the following papers we do not intend to discuss strictly separately processes of the above mentioned types. This is mainly because some reactions under study can be considered as processes belonging to different classes. Nevertheless, all the reactions studied will be labeled in terms of the above given classification.

Survey of Literature

Unnatural systems. Chemical literature on hydrides of the first- and second-row elements is vast and, therefore, only rather recent studies, having direct relation to our work, will be mentioned.

Systematic theoretical studies of atomization energies of neutral hydrides (series *A1* and *A2*) have been done¹. Moreover, enthalpies of formation of sets of cations and radical cations (series *B1* and *B2*, *E1* and *E2*), as well as ionization potentials and electron affinities of the parent molecules were calculated nonempirically by using extended basis sets²⁻⁴.

LiH_2^+ is a van der Waals cation possessing a C_{2v} structure⁵. This cation as well as NaH_2^+ was studied by Dixon et al.⁶

Although the LiH_2^- anion is formally not "unnatural", it is proper to mention that a linear ($D_{\infty h}$) structure was found (highly correlated⁷ CEPA wave function) with a very long Li—H bond, $R_e = 1.74 \text{ \AA}$. In a recent study by Kalcher⁸ several minima on P.E.S. of $\text{CH}_4^{(-)}$, $\text{SiH}_4^{(-)}$, CH_5^- , and SiH_5^- were investigated.

Ionization energies of NH_4^- isomers were studied by using propagator theory; this has been extended to the analogous C, O, F systems⁹. The NH_4^- anion was observed experimentally¹⁰ and it was characterized as a complex of H^- with NH_3 which is in accordance with a theoretical study¹¹. Later it was shown by means of calculations with very extensive basis sets that besides a $\text{H}_2\text{NH}\cdots\text{H}^-$ a T_d structure (minimum) exists; the former structure is by 9.7 kcal/mol* more stable. Removal of an electron from the $\text{H}_2\text{NH}\cdots\text{H}^-$ structure leads to a shallow van der Waals minimum for the $\text{H}_2\text{NH}\cdots\text{H}^\bullet$ radical.

On the basis of highly correlated wave functions, the $\text{O}^-\cdots\text{H}_2$ and $\text{OH}\cdots\text{H}^-$ structures were suggested¹² for $\text{H}_2\text{O}^{(-)}$.

Structure and reactivity of H_3O^- was studied carefully by Chałasiński et al.¹³ The barrier separating $\text{OH}_2\cdots\text{H}^-$ and $\text{HO}^-\cdots\text{H}_2$ amounts to 2.5 kcal/mol; the structure of the activated complex is similar to that of $\text{HOH}\cdots\text{H}^-$.

* 1 kcal/mol = 4.184 kJ/mol.

Theoretical as well as experimental attention was paid to the remarkable dications of the H_4O^{2+} and H_4S^{2+} type¹⁴ (vide infra). A tendency to form dications from monocations was discussed in a mass-spectrometrical study¹⁵.

The molecular structures of H_2F^- , H_3O^- , NH_4^- , and CH_5^- were theoretically investigated (MP2/6-31 + G** basis set). $\text{H}^- \cdots \text{AH}_n$ structures can rearrange to $\text{H}_2 \cdots \text{AH}_{n-1}^-$ complexes which are 2–15 kcal/mol less stable than the former isomers¹⁶.

Although “unnatural” radicals (e.g., as series $\text{H}_2\text{F}^\bullet$, $\text{H}_3\text{O}^\bullet$, NH_4^\bullet , CH_5^\bullet) are not a subject of our study, it is expedient to mention theoretical and experimental studies on them. Their chemistry is closely related to the chemistry of the corresponding unnatural anions. Attention was recently paid to $\text{H}_2\text{F}^\bullet$, $\text{H}_3\text{O}^\bullet$, NH_4^\bullet (ref.^{17–20}), CH_5^\bullet (ref.²¹), and HNe^\bullet (ref.¹⁷) radicals.

A very shallow van der Waals minimum (about 2 kcal/mol) at 2.1 Å was localized on a potential curve of $\text{HCl}^{(-)\bullet}$ (ref.²²).

Inversion barriers. The Walsh method is well-suited for qualitative analysis of molecular shapes²³. A valuable summary of this subject is available in the third chapter of a book by Pearson²⁴ where older literature on inversion barriers is also summarized (see also refs^{25–27}) for CH_3^- , PH_3 , and NH_3 , respectively.

It is well known that the role of polarization functions for a correct theoretical description of inversion barriers is crucial²⁸. It seems, however, that tendencies in, e.g., isoelectronic series and when passing from first-row systems to analogous second-row systems are correctly described with mere DZ basis sets. Most of the attention has been paid to inversions of pyramidal molecules of the AX_3 type^{29,30}. Špirko and coworkers have paid intense attention^{31–35} to theoretical studies of inversion barriers and to various other aspects of the inversion problem. The vibration-inversion-rotation Hamiltonian was improved by allowing for anharmonicity³² and applied to the NH_3 and PH_3 molecules. In order to make the search for the spectra of H_3O^+ and CH_3^- easier, their rotation-inversion-vibration energies were calculated using nonempirical surfaces³¹. The inversional double-minimum potential function of pyramidal molecules and ions (C_{3v}) were studied by using nonempirical (MP2) and CNDO/2 potentials (NH_3 , PH_3 , AsH_3 ; CH_3^- , SiH_3^- , GeH_3^- ; H_3O^+ , H_3S^+ , H_3Se^+)³⁴. Inversion of PH_3 was studied on the basis of 93 points of the ground state potential energy surface³⁵. Effective inversion potential functions of PH_3 , AsH_3 , and SbH_3 were obtained on the basis of the Frost–Musulin reduced potential³³.

Schleyer and coworkers³⁶ studied theoretically structural features of the isoelectronic series BH_4^- , CH_4 , NH_4^+ , and AlH_4^- , SiH_4 , PH_4^+ . In the former series there is a clear barrier maximum with methane; in the latter series there is a significant barrier increase when passing from AlH_4^- via SiH_4 to PH_4^+ . Unfortunately the published values do not permit one to make a definite comparison when passing from first row

to the second row representatives, but there is reliable indirect evidence that passing from BH_4^- to AlH_4^- , from CH_4 to SiH_4 and from NH_4^+ to PH_4^+ is connected with a very large, large, and small barrier decrease, respectively.

In a study on pyramidal inversion in a series of silyl anions³⁷ (HSiH_2^- , $\text{SiH}_3\text{SiH}_2^-$, HCO.SiH_2^- , $\text{BH}_2\text{SiH}_2^-$) it was shown that the 6-31G* inversion barrier decreases from 34.7 to 0.7 kcal/mol (i.e. the barrier is extremely sensitive to substitution) and, moreover, they differ only slightly from the 3-21G values.

Edge inversion in a series CF_4 , SiF_4 , GeF_4 , and SnF_4 was carefully studied theoretically³⁸ and a decrease from 128.9 to 37.2 kcal/mol (MP2/DZ+P) was found. It is useful to realize that for CF_4 the D_{4h} structure lies above the C—F bond dissociation energy. Furthermore, the same authors proposed a new inversion mechanism ("edge inversion of a tetrahedron") for substituted tricoordinate pyramidal systems³⁹ which was proved experimentally⁴⁰.

The tetrahydridosulfonium dication, H_4S^{2+} , was studied experimentally⁴¹ and it was shown⁴² that its calculated inversion barrier is extremely high (244.6 kcal/mol) and, amazingly, by a factor of 2.5 higher than that of the barrier for the oxygen analogue, H_4O^{2+} .

CNDO (UHF) inversion barriers of T_d - D_{4h} equilibria in ML_4^{2-} complexes of the first row transition metals suggest tendencies which are worth-mentioning⁴³. Barrier height increases as follows: $\text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+}$ and for ligands $\text{F}^- < \text{Cl}^- < \text{Br}^-$. The barriers for MF_4^{2-} , MCl_4^{2-} , and MBr_4^{2-} amount to 24–48, 29–67, and 60–105 kcal/mol, respectively. According to a CI study⁴⁴, the bent Ni_3 system (90°) is by 1.8 kcal/mol more stable than the linear form.

CALCULATIONS

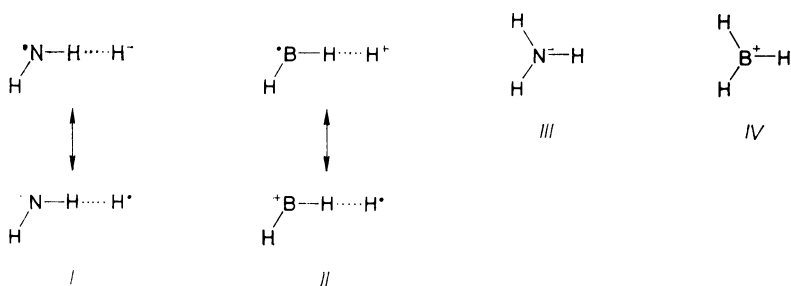
Statistical mechanical treatment and vibrational analysis have been done analogously to/those in our previous papers (e.g., refs^{45,46}). Molecular constants necessary for such calculations have been obtained from quantum chemical calculations; in general data have been calculated for completely optimized structures. Unless stated otherwise, optimization was performed for the basis set for which total energy was calculated. Nonempirical Hartree–Fock as well as beyond Hartree–Fock calculations have been performed along standard lines by using HONDO VI (ref.⁴⁷), GAUSSIAN 86 (ref.⁴⁸), and MICROMOL (ref.⁴⁹) programs. Because numerous computational data required for this series of papers is available in accessible literature (e.g., refs^{50,51}), we do not consider it expedient to publish any intermediate values unless they were obtained at a higher level or by using a special basis or when finding (very rare) a discrepancy with the literature.

Results of some higher level calculations are presented in Appendices I–IV.

RESULTS AND DISCUSSION

Van der Waals Species Derived from Unnatural Hydrides

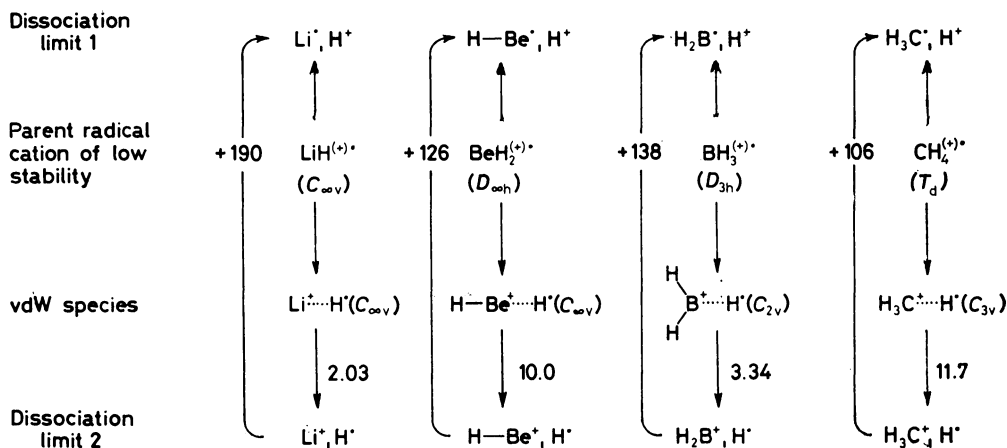
The parent systems (e.g., BeH_2 , NH_3 , H_2S) and the systems derived from them by abstracting H^+ , H^\cdot or H^- are thermodynamically stable systems. Their potential energy surfaces possess a single deep minimum, or a pair of minima separated by an energy barrier as typical for systems possessing two equivalent inversion structures. When passing to systems richer by one or two hydrogen atoms (or proton or hydride ion), van der Waals species are formed, having shallow, flat minima. These systems are frequently associated with several minima, mutually separated by low barriers. Also the radical anions derived from the electron-rich parent systems (e.g., $\text{NH}_3 \rightarrow \text{NH}_3^{\cdot-}$) and the radical cations derived from electron-deficient systems (e.g., $\text{BH}_3 \rightarrow \text{BH}_3^{\cdot+}$) are unstable van der Waals systems represented by formulas *I* and *II* rather than species possessing structures *III* and *IV*. We call all systems like this unnatural hydrides.



In Schemes 3–7 the 6-31G* (unless stated otherwise) reaction energies are presented for vdW isomers of unnatural systems belonging to series *HI* and *II*. Specifically, Schemes 3–7 concern the radical cations derived from electron-deficient molecules, the radical anions derived from electron-rich molecules, species resulting from protonation of electron-deficient and from attachment of H^- (“hydridation”) to electron-rich molecules, respectively. In all instances the parent species are mentioned (with structure of the corresponding natural system, e.g., the T_d form of NH_4^- in analogy to the same form of NH_4^+), two possible dissociation limits and one (or two) van der Waals species.

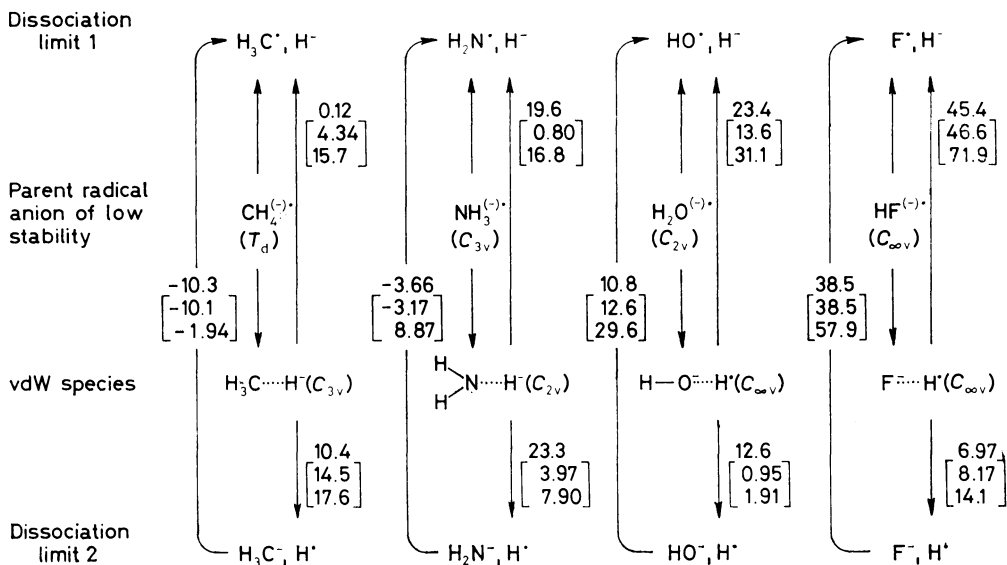
With the radical cations in Scheme 3 only one type of van der Waals cation was located. Dissociation limit 2, i.e. the limit including the hydrogen atom is strongly favoured. The van der Waals cations are stabilized with respect to the dissociation limit 2 by 2 to 12 kcal/mol.

With the radical anions of Scheme 4 also a single van der Waals anion was obtained. Being mainly interested in trends and qualitative features, we begin with the



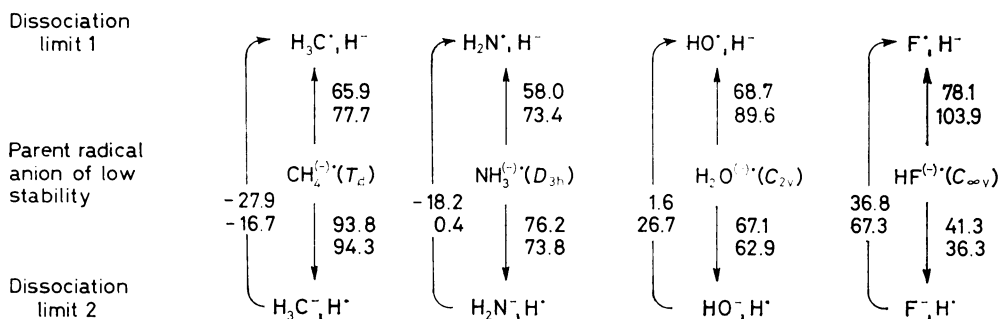
SCHEME 3

6-31G* energy changes (kcal/mol) accompanying transformation of isomers of radical cations formed by removal of an electron from LiH, BeH₂, BH₃, and CH₄



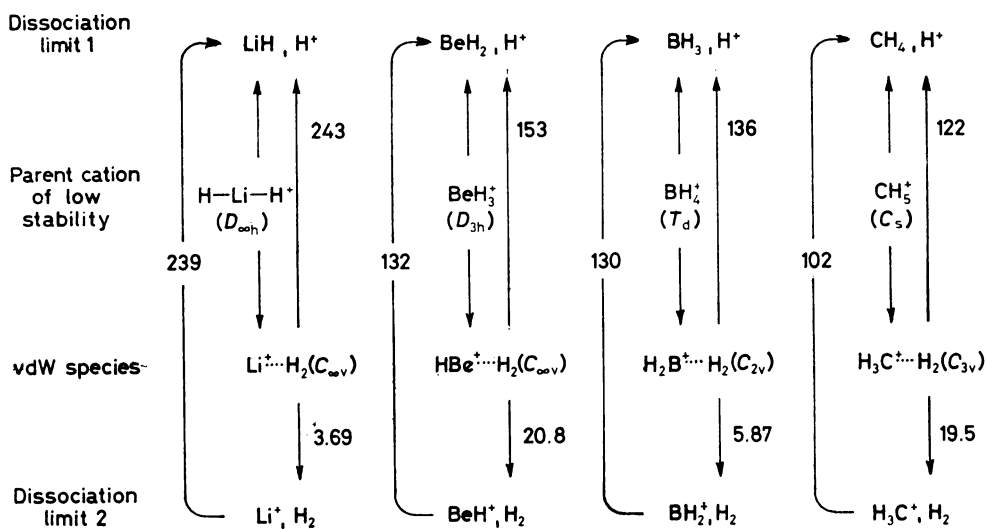
SCHEME 4

6-31G* energy changes (kcal/mol) accompanying transformations of isomers of radical anions formed by electron attachment to CH₄, NH₃, H₂O, and HF. 6-31G** and CCD/6-31G** values are presented in parentheses



SCHEME 5

6-31++G**//6-31G** and MP4/6-31++G**//6-31G** energy changes (kcal/mol) accompanying transformations of the radical anions formed by electron attachment to CH₄, NH₃, H₂O, and HF

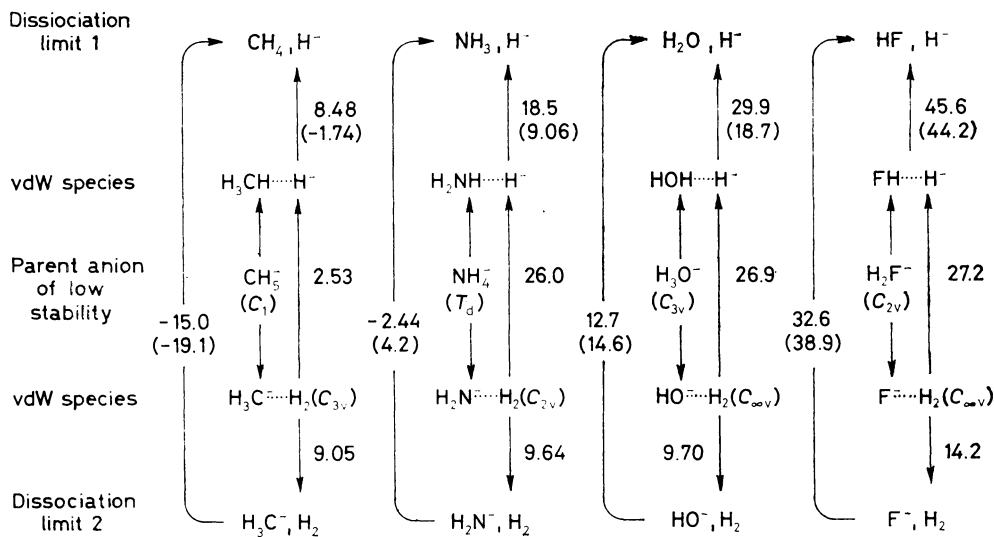


SCHEME 6

6-31G* energy changes (kcal/mol) accompanying transformations of isomers of cation formed by proton attachment to LiH, BeH₂, BH₃, and CH₄

6-31G* energy characteristics. The van der Waals species include H⁻ in case of CH₃ and NH₂, while in case of HO and F the hydrogen atom is included. In accordance with this, CH₄⁽⁻⁾ and NH₃⁽⁻⁾ tend to dissociate into H₃C[•] and H⁻ and H₂N[•] and H⁻, while H₂O⁽⁻⁾ and HF⁽⁻⁾ will decompose into HO⁻ and H[•] and F⁻

and H^{\cdot} . All the van der Waals anions are stabilized with respect to the dissociation limit 1 (2) by 0.1 to 45 kcal/mol (7 to 23 kcal/mol). Roughly speaking the tendencies remain unchanged when passing to 6-31G** and CCD/6-31G** levels but, of course, the absolute values of ΔE change significantly. At the 6-31++G**//6-31G** and MP4/6-31++G**//6-31G** levels minima were found for $CH_4^{(-)}$, $NH_3^{(-)}$, and $HF^{(-)}$ (Scheme 5) but again the overall picture reminds of that which is seen in Scheme 4.



SCHEME 7

6-31G* energy changes (kcal/mol) accompanying transformation of isomers of anions formed by interaction of CH_4 , NH_3 , H_2O , and HF with H^{\cdot} . MP2/6-31++G** values in parentheses are taken from ref.¹⁶

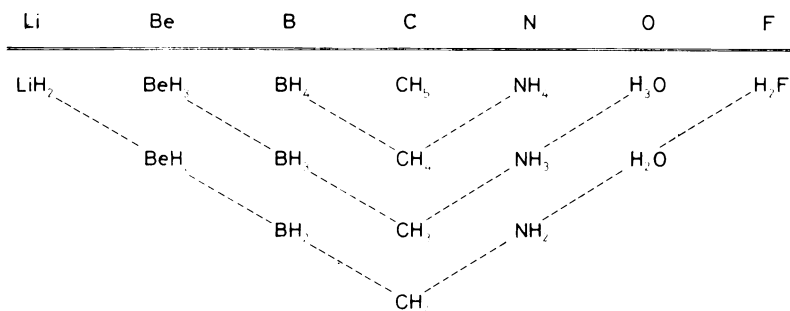
The cationic van der Waals species in Scheme 6 are stabilized by 3.7 to 21 kcal/mol with respect to the dissociation limit 2 (including H_2) which is much more stable than the dissociation limit 1 (including H^{\cdot}). The overall situation is similar to that described in Scheme 1.

Although the anions included in Scheme 7 are the only one for which two types of van der Waals anions are available, there is a great deal of similarity with anions described in Schemes 4, 5. In spite of the fact that the 6-31G* basis set is definitely not suitable for describing anions, it is worth-mentioning that semiquantitative energy features are (except the sign of the dissociation energy of $H_3CH\cdots H^{\cdot}$) in good agreement with MP2/6-31++G** energies of Cremer and Kraha¹⁶.

Inversion of Hydrides and Inversion Barriers

Inversion processes are important not only in connection with chemical reactivity (e.g., Walden inversion during S_N2 substitution reaction, or inversion of chiral species, enantiomers) but also in connection with molecular spectroscopy. Specifically, the already mentioned inversions of bent XH_2 , pyramidal XH_3 , and tetrahedral XH_4 systems are the subject of our interest. Again, we are interested in structural trends rather than in accurate calculations of inversion barriers. However, in case of a few prominent systems also a higher level of calculation is used.

In order to make our orientation easier, the potential candidates for a study are arranged on the basis of the Periodic System (Scheme 8); an analogous scheme is valid for the hydrides of the second row atoms. Calculated inversion energy barriers are given in Table I.



SCHEME 8

Survey of XH_2 , XH_3 , and XH_4 based on the Periodic System. The individual types are connected by dotted lines

Walsh diagrams represent a good basis for interpreting the behaviour of simple bent triatomic (AH_2), pyramidal tetraatomic (AH_3) and tetrahedral pentaatomic (AH_4) species. It is true, however, that attention has been focused for years mainly on the inversion of C_{3v} pyramidal systems. For discussion of tendencies and for semiquantitative estimates inclusion of MP correlation energy (through the second or forth order) is not important but the role of polarization function has been realized for many years.

Passing from the first-row to the analogous second-row systems is accompanied by significant increase of inversion barriers with $AH_2(C_{2v})$ and $AH_3(C_{3v})$ systems (${}^3CH_2 \rightarrow {}^1SiH_2$, $NH_2 \rightarrow PH_2$, $H_2O \rightarrow H_2S$; $CH_3^- \rightarrow SiH_3^-$, $NH_3 \rightarrow PH_3$, $H_3O^+ \rightarrow H_3S^+$); the opposite is true for the ${}^1CH_2 \rightarrow {}^3SiH_2$ transitions in the first electronically excited state (Fig. 1). Analogous transitions for T_d systems are connected either with a significant barrier decrease ($BH_4^- \rightarrow AlH_4^-$, $CH_4 \rightarrow SiH_4$) or an increase

TABLE I

Inversion energy barriers ΔE at 0 K in kcal/mol. Systems related to the first-row hydrides are followed by systems related to the second-row hydrides

Empir. formula	System (R)	Symmetry		Method ^{a,b}	ΔE
		R	act. complex		
Systems related to the first-row hydrides					
BeH ₂	BeH ₂ ⁽⁻⁾ *	C _{2v}	D _{∞h}	6-31G*	12.49
BH ₂	BH ₂ [•]	C _{2v}	D _{∞h}	6-31G*	11.23
CH ₂	³ CH ₂	C _{2v}	D _{∞h}	6-31G*	8.40
				MP4	7.41
	¹ CH ₂	C _{2v}	D _{∞h}	6-31G*	37.93
				MP4	40.11
NH ₂	NH ₂ [•]	C _{2v}	D _{∞h}	3-21G	33.76
				6-31G*	38.60
	³ NH ₂ ⁺	C _{2v}	D _{∞h}	3-21G	0.36
				6-31G*	0.92
H ₂ O	H ₂ O	C _{2v}	D _{∞h}	6-31G*	37.51
				MP4	37.32
				6-311++G**	31.70
				MP2	32.24
				MP3	32.93
				MP4(DQ) CCD	32.89 32.91
	H ₂ O ⁽⁺⁾ *	C _{2v}	D _{∞h}	3-21G	14.16
				6-31G*	22.94
H ₂ F	H ₂ F ⁺	C _{2v}	D _{∞h}	3-21G	9.67
				6-31G*	18.50
BH ₃	BH ₃ ⁽⁻⁾ *	C _{3v}	D _{3h}	3-21G	0.59
				6-31G*	1.23
CH ₃	CH ₃ ⁻	C _{3v}	D _{3h}	6-31G*	12.98
				6-31+G*	3.13
NH ₃	NH ₃	C _{3v}	D _{3h}	6-31G*	6.53
				6-311++G*	4.61
				MP2	5.06
				MP3	5.37
				MP4(DQ) CCD	5.41 5.42

TABLE I
 (Continued)

Empir. formula	System (R)	Symmetry		Method ^{a,b}	ΔE
		R	act. complex		
H ₃ O	H ₃ O ⁺	C _{3v}	D _{3h}	6-31G*	1·74
				6-31G**	0·89
				MP2	1·48
				MP3	1·49
				MP4(DQ)	1·52
				CCD	1·53
				6-311++G**	1·03
				MP2	1·66
				MP3	1·68
				MP4	1·69
CCD	1·70				
BH ₄	BH ₄ ⁻	T _d	D _{4h}	6-31G*	
				DZ+P(HU-DU)	161·90
CH ₄	CH ₄	T _d	D _{4h}	6-31G*	171·13
				MP2	168·85
				6-311++G**	155·20
				MP2	141·25
				MP3	143·42
				MP4(DQ)	144·45
CCD	144·64				
NH ₄	NH ₄ ⁺	T _d	D _{4h}	6-31G*	132·74
Systems related to the second-row hydrides					
SiH ₂	¹ SiH ₂	C _{2v}	D _{∞h}	6-31G*	77·61
				MP4	74·70
	³ SiH ₂	C _{2v}	D _{∞h}	6-31G*	28·51
				MP4	25·35
PH ₂	PH ₂ [*]	C _{2v}	D _{∞h}	RHF 3-21G	72·76
				RHF 6-31G*	130·68
H ₂ S	H ₂ S	C _{2v}	D _{∞h}	6-31G*	223·91
				DZ+P(HU-DU)	223·23
				6-311++G**	130·20
				MP2	124·08
				MP3	124·42
				MP4	119·97
				CCD	123·31
	H ₂ S ⁽⁺⁾ *	C _{2v}	D _{∞h}	6-31G*	21·86

TABLE I
 (Continued)

Empir. formula	System (R)	Symmetry		Method ^{a,b}	ΔE
		R	act. complex		
SiH ₃	SiH ₃ [•]	C _{3v}	D _{3h}	3-21 G 6-31 G*	5·05 7·69
	SiH ₃ ⁻	C _{3v}	D _{3h}	6-31 G*	34·71
PH ₃	PH ₃	C _{3v}	D _{3h}	3-21 G	30·67
				6-31 G*	32·60
				6-311++G**	35·95
				MP2	35·12
				MP3	36·94
				MP4(DQ) CCD	35·96 36·05
H ₃ S	H ₃ S ⁺	C _{3v}	D _{3h}	3-21 G	19·49
				6-31 G*	33·30
				DZ(HU-DU)	18·79
				6-31 G**	
				MP2	30·57
				MP3	31·02
				MP4(DQ)	31·26
				MP4(SDTQ)	31·31
				CCD	31·36
				6-311++G**	31·21
				MP2	31·09
				MP3	31·60
				MP(DQ)	31·81
				CCD	31·89
AlH ₄	AlH ₄ ⁻	T _d	D _{4h}	DZ+P(HU-DU)	54·14
SiH ₄	SiH ₄	T _d	D _{4h}	6-31 G*	93·47
				MP4	96·00
				6-311++G**	93·54
				MP2	93·95
				MP3	93·65
				MP4 CCD	93·56 93·22
PH ₄	PH ₄ ⁺	T _d	D _{4h}	6-31 G*	153·81

^a Unless stated otherwise, UHF procedure has been used for open-shell systems. ^b HU-DU stands for Huzinaga-Dunning basis set.

($\text{NH}_4^+ \rightarrow \text{PH}_4^+$, $\text{H}_4\text{O}^{2+} \rightarrow \text{H}_4\text{S}^{2+}$). The reason for these tendencies is not obvious and therefore the dependence of orbital energies on the valence angle (in the region 90° – 180° , 100° – 120° , and 108° – 90° for C_{2v} , C_{3v} , and T_d species, respectively) was investigated. The STO-3G calculations for four angles in the mentioned regions were performed for pairs H_2O , H_2S ; NH_3 , PH_3 , and CH_4 , SiH_4 . The results obtained suggest that it is the course of the highest occupied MO (HOMO) which might be responsible for the observed trends, e.g., the observed decrease of inversion barrier when passing from CH_4 to SiH_4 . In Fig. 2 the results concerning the pair CH_4 – SiH_4 are presented for illustration; the energy of the HOMO increases more rapidly with CH_4 than with SiH_4 and the difference for the T_d – D_{4h} transition amounts to 82 kcal/mol. The energy difference between CCD energies of inversion between CH_4 and SiH_4 is equal to 52 kcal/mol.

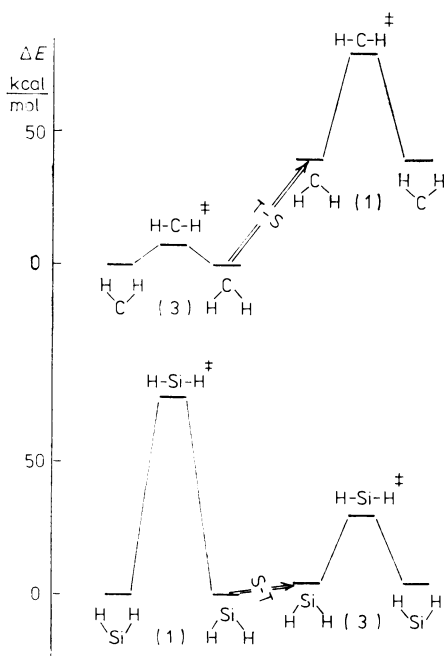


FIG. 1

Schematic picture of inversion barriers (MP4/6-31G*) of carbene and silene in their electronic ground states ($^3\text{CH}_2$, $^1\text{SiH}_2$) and lowest excited states ($^1\text{CH}_2$, $^3\text{SiH}_2$)

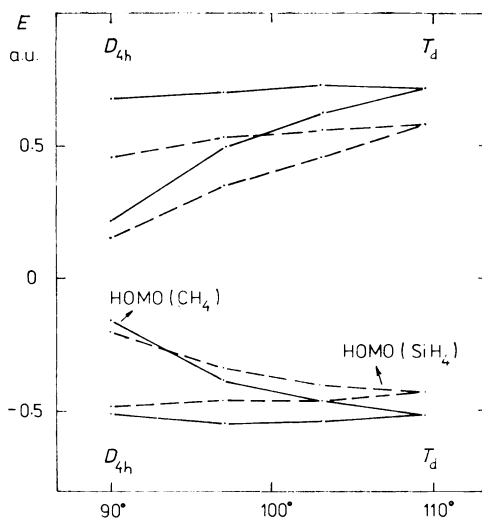


FIG. 2

Dependence of STO-3G orbital energies of the two highest occupied and two lowest free orbitals on valence angle for passing from T_d structures ($\alpha = 108^\circ$) to D_{4h} structures ($\alpha = 90^\circ$, activated complex): methane (—), silane (---)

In the isoelectronic series $\text{CH}_3^- \rightarrow \text{NH}_3 \rightarrow \text{H}_3\text{O}^+$ and $\text{SiH}_3^- \rightarrow \text{PH}_3 \rightarrow \text{H}_3\text{S}^+$ a barrier decrease is observed. This is understandable because the higher is the occupancy of the n -orbital the higher is the resistance against planarization. In the $\text{BH}_3^{(-)'} \rightarrow \text{CH}_3^* \rightarrow \text{NH}_3^{(+)}$ series the central system is planar and the two other systems possess a very small barrier. In the series of tetrahedral species an increase and a subsequent decrease ($\text{BH}_4^- \rightarrow \text{CH}_4 \rightarrow \text{NH}_4^+$) and a decrease ($\text{AlH}_4^- \rightarrow \text{SiH}_4 \rightarrow \text{PH}_4^+$) are observed.

In spite of the extensive attention which has been paid to the inversion barriers of molecules, accurate spectroscopic values are available only for NH_3 and H_3O^+ . Unfortunately, the calculated barrier heights for PH_3 and H_3S^+ are too high to be spectroscopically attainable. It was shown recently that CEPA-1 gave very good agreement with experimental values for NH_3 (ref.⁵²) and H_3O^+ (ref.⁵³) as obtained by Špirko et al.^{31,32} The experimental values for NH_3 and H_3O^+ amount to 1 834 and 672 cm^{-1} , respectively; the CCD/6-31G** (CEPA-1 (refs^{52,53})) are equal 1 891 and 595 cm^{-1} (1 874 and 679 cm^{-1}).

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APPENDIX I

Hartree-Fock (H.F.), MPn, and CCD energies (a.u.) of radical anions (geometries optimized in the given basis sets)

Anion	Sym.	Basis set	Energy				
			H.F.	MP2	MP3	MP4(SDTQ)	CCD
CH ₄ ⁽⁻⁾	C _{3v}	6-31G**	39·99380	40·15570	40·17312	40·18053	40·17596
	T _d	6-31++G**	40·15881	40·32782	40·34631	40·35281	40·34843
NH ₃ ⁽⁻⁾	C _{2v}	6-31G**	55·98853	56·18003	56·19018	56·19678	56·19239
	D _{3h}	6-31++G**	56·14797	56·34537	56·35651	56·36326	56·35805
H ₂ O ⁽⁻⁾	C _{∞v}	6-31G**	75·83240	76·02737	76·03118	76·03600	76·03325
	C _{2v}	6-31++G**	75·98987	76·19794	76·20188	76·20985	76·20399
HF ⁽⁻⁾	C _{∞v}	6-31G**	99·86173	100·04776	100·04777	100·05270	100·04979
	C _{∞v}	6-31++G**	99·98313	100·17945	100·17793	100·18691	100·18026

APPENDIX II

Optimized geometries of the radical anions included in Table I: Bond lengths (*R*, *R'*) in Å, bond angles (*A*) in degrees

Anion	Sym.	Basis set	Bond lengths and bond angles
CH ₄ ⁽⁻⁾	C _{3v}	6-31G**	<i>R</i> = 1·0937, <i>R'</i> = 2·0478, <i>A</i> = 109·30
	T _d	6-31++G**	<i>R</i> = 1·0856
NH ₃ ⁽⁻⁾	C _{2v}	6-31G**	<i>R</i> = 1·8354, <i>R'</i> = 1·0185, <i>A</i> = 127·75
	D _{3h}	6-31++G**	<i>R</i> = 0·9918
H ₂ O ⁽⁻⁾	C _{∞v}	6-31G**	<i>R</i> = 0·9575, <i>R'</i> = 2·1674
	C _{2v}	6-31++G**	<i>R</i> = 0·9508, <i>A</i> = 140·54
HF ⁽⁻⁾	C _{∞v}	6-31G**	<i>R</i> = 1·6352
	C _{∞v}	6-31++G**	<i>R</i> = 0·9225

APPENDIX III

Hartree-Fock (H.F.), MPn, and CCD 6-31++G**//6-31++G** energies (a.u.) of decomposition products of anions involved in Appendix I

Species	Sym.	H.F.	MP2	MP3	MP4(SDTQ)	CCD
H [•]	—	0.49880	0.49880	0.49880	0.49880	0.49880
H ⁽⁻⁾	—	0.48707	0.50363	0.50828	0.51039	0.51135
CH ₃ [•]	D _{3h}	39.56679	39.69652	39.71394	39.71867	39.71651
CH ₃ ⁻	C _{3v}	39.51056	39.68196	39.69464	39.70366	39.69676
NH ₂ [•]	C _{2v}	55.56849	55.71591	55.73130	55.73589	55.73346
NH ₂ ⁻	C _{2v}	55.52768	55.73177	55.73495	55.74681	55.73787
OH [•]	C _{∞v}	75.39336	75.54091	75.55237	75.55674	75.55427
OH ⁻	C _{∞v}	75.38419	75.60213	75.59580	75.61075	75.59998
F [•]	—	99.37165	99.49882	99.50669	99.51087	99.50825
F ⁻	—	99.41859	99.62385	99.61363	99.62975	99.61770

APPENDIX IV

Hartree-Fock (H.F.), MPn, and CCD/6-311++G**//6-31G** energies (a.u.) for bent, pyramidal, tetrahedral, linear, and planar molecules and ions

Species	Sym.	Energy				
		H.F.	MP2	MP3	MP4(DQ)	CCD
H ₂ O	C _{2v}	76.05341	76.27431	76.27723	76.27912	76.27927
	D _{∞h}	76.00290	76.22294	76.22475	76.22670	76.22682
H ₂ S	C _{2v}	398.70219	398.84755	398.86649	398.86890	398.86822
	D _{∞h}	398.49471	398.64981	398.66821	398.67691	398.67171
NH ₃	C _{3v}	56.21472	56.41514	56.42611	56.42752	56.42780
	D _{3h}	56.20737	56.40707	56.41755	56.41890	56.41917
PH ₃	C _{3v}	342.47803	342.61311	342.63554	342.63857	342.63892
	D _{3h}	342.42074	342.55714	342.57667	342.58126	342.58147
CH ₄	T _d	40.20915	40.37952	40.39854	40.40048	40.40082
	D _{4h}	39.96182	40.15443	40.16999	40.17029	40.17032
SiH ₄	T _d	291.25331	291.37233	291.39557	291.40188	291.40036
	D _{4h}	291.10424	291.22261	291.24633	291.25279	291.25180
H ₃ O ⁽⁺⁾	C _{3v}	76.33258	76.54917	76.55566	76.55709	76.55732
	D _{3h}	76.33094	76.54653	76.55298	76.55439	76.55461
H ₃ S ⁽⁺⁾	C _{3v}	398.98160	399.13054	399.15211	399.15439	399.15464
	D _{3h}	398.93187	399.08099	399.10176	399.10370	399.10382