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A Comparison of Model Chemistries

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Abstract: The energies of 166 molecules, radicals, anions, and cations have been calculated using four recently developed model chemistries: G2, G2(MP2), CBS-4, and CBS-Q. The results of these calculations are compared with the experimental heats of formation, bond dissociation energies, gas phase acidities, and proton affinities. Both G2 and CBS-Q reproduce the known heats of formation of molecules with an average error of only 1 kcal/mol. The bond dissociation energies (BDE) derived from G2, CBS-Q, and CBS-4 also agree with the experimental data with an average error of only 1 kcal/mol. The BDE for several series (HX, CH_3X, $CH_2{=}CHX$, $HC{\equiv}CX$, and CH_3COX, where X is a first- or second-row substituent) were compared, and it was found that the coordinately unsaturated substituents (Li, BeH, BH_2, Na, MgH, and AlH_2) gave essentially the same effect in each series. Differences were found with the substituents having lone pairs (NH_2, OH, F, PH_2, SH, and Cl). It was possible to correlate a wide variety of bond dissociation energies using a Pauling-type relationship based on electronegativity differences. Gas phase acidities and proton affinities also were examined, and were equally well reproduced.

1. Introduction

A model chemistry is a theoretical construct that is used in estimating the structure, energy, and other properties of molecules. The G2 model[1] developed by Pople et al. is an example of a well-studied model chemistry that has been applied with much success to a variety of chemical problems.[2] It is essentially QCISD(T)/6-311+G(3df,2p) calculated using the MP2/6-31G* geometries plus the zero-point energy and a higher level correction. It has been applied to a number of molecules having up to four non-hydrogen atoms, but it is not generally practical for larger molecules. A modification, G2(MP2),[3] has been developed which gives essentially the same results but with fewer computational steps. It is possible to use it to study compounds with up to six non-hydrogen atoms.

A different approach has been taken by Ochterski, Petersson, and Montgomery,[4] making use of a complete basis set (CBS) extrapolation of the second-order energy.[5] Their models take advantage of the fact that order-by-order contributions to chemical energies, and thus the number of significant figures required for a given accuracy, generally decrease with increasing order of perturbation theory.[4] Concomitantly, the computational demands increase rapidly for the higher orders of perturbation theory. These two complementary trends were combined to design two efficient computational models which employ progressively smaller basis sets for the higher orders of perturbation theory.

The less computationally intensive of the two models is CBS-4 which is practical for up to 12 non-hydrogen atoms. This model starts with a HF/3-21G* geometry, then uses a large basis set HF calculation (6-311+G(3d2f,2df,p)). This notation is a simple extension of standard basis set notation to indicate there is an extra d and f function on elements sodium though argon. The CBS extrapolation is applied to an MP2/6-31+$G^{\dagger\dagger}$ calculation. Here, the dagger (†) symbol indicates that the polarization functions have been taken from the 6-311G** basis set. Finally, the authors use an MP4(SDQ)/6-31G calculation to approximate higher than second order effects. This model also has corrections for zero-point energy and spin contamination and a size-consistent higher order correction.

The CBS-Q model uses larger basis sets at every level of theory and is practical for systems with up to six non-hydrogen atoms. Equilibrium geometries are calculated at the MP2(FC)/6-31$G^{\dagger}$ level, while the CBS extrapolation is based on a MP2/6-311++G(3d2f,2df,2p) calculation. Higher order contributions are estimated with two calculations: MP4(SDQ)/6-31+G(d(f),d,p), where the "(f)" indicates that there are f polarization functions on the elements phosphorus through argon, and QCISD(T)/6-31+$G^{\dagger}$. Again this model has corrections for zero-point energy, spin contamination, and higher order effects. Both CBS-Q and CBS-4 have been found to reproduce the energies in the G2 test set[1] with relatively small errors, 1.0 and 2.0 kcal/mol mean-absolute deviation from experiment, respectively.[4]

We have obtained the CBS-4, CBS-Q, G2(MP2), and G2 energies for a variety of organic compounds, cations, anions, and radicals in the course of other studies and additional calculations have been carried out to complete the set. It was then of interest to see how well the methods reproduce experimental data, and when the latter are not available, to see how good an internal consistency exists between the methods. The calculated total energies for 166 compounds, radicals, anions, and cations are given in the supporting information, and the compounds are listed in Table 1.

Although the total energies derived from the different methods differ somewhat, they generally still lead to essentially the same

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Table 1. Calculated Enthalpies of Formation[a]

	ΔH_f(0K)				ΔH_f(298K)			ΔH_f(0K)				ΔH_f(298K)	
compd	CBS-4	CBS-Q	G2(MP2)	G2	calc	obs	compd	CB-4	CBS-Q	G2(MP2)	G2	calc	obs
LiH	36.1	33.7	33.1	32.7	33.0	33.6 ± 0.1	$CH_2{=}PH$	28.0	29.5	30.3	30.3	28.3	
BeH_2	43.4	40.4	41.3	40.3	40.3		$CH_2{=}S$	27.5	27.8	27.7	28.7	27.8	
BH_3	27.4	26.7	26.6	25.8	24.9	25.5 ± 2.5	$H_2C{=}O$	−25.8	−26.0	−27.6	−27.0	−27.9	−26.0 ± 0.1
CH_4	−16.7	−15.8	−16.2	−16.7	−18.6	−17.8 ± 0.1	$HCONH_2$	−43.0	−43.3	−44.5	−44.0	−46.3	
NH_3	−8.1	−8.3	−9.2	−9.1	−10.8	−11.0 ± 0.1	CH_3CHO	−38.8	−37.2	−38.7	−38.5	−40.9	−39.7 ± 0.1
H_2O	−56.8	−57.2	−58.2	−57.4	−58.1	−57.8 ± 0.0	CH_3COLi	−15.2	−14.7	−16.5	−16.4	−18.4	
HF	−65.8	−66.1	−66.8	−66.2	−65.9	−65.1 ± 0.2	CH_3COBeH	−3.6	−4.2	−4.0	−4.6	−6.8	
NaH	35.7	33.9	34.0	32.3	32.1		CH_3COBH_2	−10.1	−11.8	−12.7	−12.9	−15.6	
MgH_2	43.1	38.5	39.6	38.3	37.8		CH_3COCH_3	−51.0	−48.1	−49.0	−49.1	−52.9	−51.9 ± 0.2
AlH_3	34.0	31.4	31.9	31.0	29.4		CH_3CONH_2	−54.0	−52.8	−53.7	−53.5	−57.2	−57.0 ± 0.2
SiH_4	8.3	9.2	9.9	9.8	7.4	8.2 ± 0.5	CH_3COOH	−101.0	−100.8	−102.6	−101.8	−105.0	−103.4 ± 0.4
PH_3	2.8	3.2	4.2	3.9	2.0	1.3 ± 0.4	CH_3COF	−104.5	−104.2	−106.0	−105.4	−107.7	−105.7 ± 0.8
H_2S	−5.1	−4.9	−4.9	−4.1	−4.8	−4.9 ± 0.2	CH_3CONa	−6.9	−8.2	−9.7	−9.5	−11.6	
HCl	−23.2	−22.9	−23.3	−22.4	−22.1	−22.1 ± 0.1	CH_3COMgH	0.8	−2.2	−1.8	−2.7	−5.1	
HCN	35.1	32.3	31.5	31.3	31.5	32.3 ± 2.0	CH_3COAlH_2	−10.9	−11.1	−10.7	−11.0	−14.4	
CH_3Li	28.3	27.6	27.2	26.5	24.9		CH_3COSiH_3	−23.8	−22.0	−22.0	−21.7	−25.6	
CH_3BeH	27.1	25.2	26.0	24.5	22.6		CH_3COPH_2	−31.8	−29.5	−29.2	−29.0	−32.7	
CH_3BH_2	11.7	12.3	12.2	10.9	8.4		CH_3COSH	−44.3	−41.6	−42.9	−41.6	−44.3	−41.8 ± 2.0
CH_3CH_3	−18.3	−15.8	−16.1	−16.8	−20.6	−20.0 ± 0.1	CH_3COCl	−59.0	−57.4	−58.8	−57.7	−59.9	−58.0 ± 0.2
CH_3NH_2	−2.1	−0.5	−1.7	−1.9	−5.5	−5.6 ± 0.2	P_2	34.9	35.1	35.9	36.1	35.7	34.3 ± 0.5
CH_3OH	−45.6	−45.7	−47.8	−46.8	−49.4	−48.2 ± 0.1	Na_2	35.3	34.2	31.8	32.2	31.6	34.0 ± 0.3
CH_3F	−54.7	−55.2	−56.6	−56.4	−58.3		$BeH^{\bullet}$	83.0	81.2	82.8	81.9	82.7	
CH_3Na	30.1	31.5	28.6	28.1	26.3		$BH_2^{\bullet}$	79.8	79.7	80.1	79.3	79.4	
CH_3MgH	32.8	29.5	29.5	29.1	26.9		$CH_3^{\bullet}$	35.3	35.9	36.2	35.7	35.1	35.0 ± 0.1
CH_3AlH_2	20.1	18.5	18.9	17.8	15.0		$NH_2^{\bullet}$	46.3	46.2	45.9	45.7	45.0	45.1 ± 0.3
CH_3SiH_3	−4.4	−1.0	−1.8	−2.1	−6.0	−7.0 ± 2.0[b]	$OH^{\bullet}$	9.5	8.9	8.8	9.0	9.0	9.4 ± 0.1
CH_3PH_2	−3.1	−1.5	−0.3	−0.6	−4.2		$MgH^{\bullet}$	59.4	56.3	58.2	57.2	57.4	
CH_3SH	−5.0	−3.6	−3.6	−2.9	−5.4	−5.5 ± 0.2	$AlH_2^{\bullet}$	64.9	63.5	64.6	64.1	63.4	
CH_3Cl	−19.4	−18.8	−19.2	−18.6	−20.5	−19.6 ± 0.1	$SiH_3^{\bullet}$	46.8	48.5	49.6	49.5	48.1	47.9 ± 0.6
$CH_3CH{=}CH_2$	6.6	9.8	9.7	9.0	5.4	4.8 ± 0.2	$PH_2^{\bullet}$	31.6	32.7	34.2	33.8	32.9	33.1 ± 0.6
$CH_3C{\equiv}CH$	44.1	46.4	48.2	47.4	45.6	44.2 ± 0.2	$SH^{\bullet}$	33.8	33.8	34.2	34.4	34.4	34.2 ± 0.7
CH_3CN	21.1	20.4	20.2	19.8	18.1	17.7 ± 0.1	$CH_3CH_2^{\bullet}$	30.0	32.6	33.2	32.4	29.9	28.9 ± 0.4
CH_3NO_2	−14.8	−16.2	−18.5	−17.4	−20.5	−17.8 ± 0.2	$CH_2{=}CH^{\bullet}$	71.7	72.8	74.4	73.6	72.6	71.6 ± 0.8
CH_3OCH_3	−40.1	−40.2	−42.0	−41.8	−46.1	−44.0 ± 0.1	$HCC^{\bullet}$	135.5	136.3	138.5	137.8	138.9	135.1 ± 0.7
CH_3SCH_3	−8.3	−5.5	−5.7	−5.1	−9.2	−8.9 ± 0.2	$CN^{\bullet}$	110.5	106.2	106.7	106.5	107.3	105.5 ± 1.1
propane	−22.8	−18.7	−19.1	−20.0	−25.4	−25.0 ± 0.1	$HCO^{\bullet}$	10.2	9.4	8.6	9.2	9.3	10.0 ± 0.2
cyclopropane	11.0	18.5	18.3	17.6	13.5	12.7 ± 0.1	$CH_3CO^{\bullet}$	−2.2	−1.0	−1.5	−1.4	−2.9	−2.4 ± 0.3
$CH_2{=}CH_2$	14.0	15.5	15.3	14.8	12.8	12.5 ± 0.1	$CH_3Be^{\bullet}$	66.8	66.0	67.3	66.0	65.0	
$CH_2{=}CHLi$	53.9	53.9	53.7	53.0	51.6		$CH_3BH^{\bullet}$	63.3	64.5	64.6	63.4	62.0	
$CH_2{=}CHBeH$	55.6	54.6	55.5	54.0	52.2		$CH_3NH^{\bullet}$	46.0	46.5	46.2	45.7	43.1	
$CH_2{=}CHBH_2$	36.0	37.3	37.3	36.0	33.4		$CH_3O^{\bullet}$	9.2	7.0	6.8	6.7	4.9	4.1 ± 0.9
$CH_2{=}CHNH_2$	16.7	18.5	17.8	17.5	13.9		$CH_3Mg^{\bullet}$	48.6	47.1	49.1	47.8		
$CH_2{=}CHOH$	−27.1	−26.7	−27.5	−27.3	−30.0	−29.8 ± 2.0[c]	$CH_3AlH^{\bullet}$	51.2	51.0	52.3	51.6	49.5	
$CH_2{=}CHF$	−32.3	−32.1	−33.1	−33.0	−35.0	−33.2 ± 0.4	$CH_3SiH_2^{\bullet}$	34.5	37.7	38.9	38.6	35.7	
$CH_2{=}CHNa$	56.4	55.7	55.5	54.9	53.3		$CH_3PH^{\bullet}$	24.5	26.9	28.8	28.3	25.7	
$CH_2{=}CHMgH$	60.6	58.1	59.6	57.9	55.9		$CH_3S^{\bullet}$	29.8	30.6	31.5	31.6	29.9	29.8 ± 0.4
$CH_2{=}CHAlH_2$	46.2	46.1	46.6	45.5	42.7		$H_2BCH_2^{\bullet}$	54.1	54.5	55.0	53.7	51.9	
$CH_2{=}CHSiH_3$	23.9	26.6	27.4	27.0	23.4		$H_2NCH_2^{\bullet}$	38.1	39.7	39.8	39.6	37.0	
$CH_2{=}CHPH_2$	22.7	25.1	26.7	26.3	22.9		$HOCH_2^{\bullet}$	−1.7	−2.1	−2.6	−2.2	−3.8	−4.1 ± 0.8
$CH_2{=}CHSH$	18.6	20.9	22.7	23.4	21.0		$H_2AlCH_2^{\bullet}$	68.8	66.9	65.1	63.9	61.9	
$CH_2{=}CHCl$	4.5	6.6	6.4	7.0	5.1	[8.9 ± 0.3][d]	$H_3SiCH_2^{\bullet}$	44.6	46.3	47.9	47.5	45.0	
$CH_2CHCHCH_2$	28.1	32.0	32.3	31.5	28.0	26.3 ± 0.2	$H_2PCH_2^{\bullet}$	45.6	46.8	46.3	45.8	43.4	
$CH_2{=}CHC{\equiv}CH$	68.0	72.0	75.5	74.7	73.0	72.8 ± 0.4	$HSCH_2^{\bullet}$	29.8	38.9	39.9	40.6	39.2	36.3 ± 2.0
$CH_2{=}CHCN$	48.6	47.8	48.1	47.6	46.0	43.2 ± 0.4	$H_2C{=}CHBe^{\bullet}$	94.4	95.7	97.4	96.0		
$HC{\equiv}CH$	57.7	56.3	56.5	56.0	56.1	54.5 ± 0.2	$H_2C{=}CHBH^{\bullet}$	88.2	91.0	92.0	90.7		
$HC{\equiv}CLi$	69.7	69.2	69.4	68.7	69.1		$H_2C{=}CHCH_2^{\bullet}$	39.8	43.1	45.6	44.6	41.9	
$HC{\equiv}CBeH$	78.6	78.3	80.1	78.8	79.2		$H_2C{=}CHNH^{\bullet}$	51.7	53.4	55.1	54.4		
$HC{\equiv}CBH_2$	71.1	69.8	71.2	69.9	69.2		$H_2C{=}CHO^{\bullet}$	6.9	5.9	5.6	5.6	3.9	2.5 ± 2.2
$HC{\equiv}CNH_2$	62.5	62.5	62.7	62.4	60.8		$H_2C{=}CHSiH_2^{\bullet}$	59.1	63.0	66.5	66.2		
$HC{\equiv}COH$	24.1	22.2	23.2	23.4	22.7		$H_2C{=}CHPH^{\bullet}$	43.7	47.6	51.4	50.7		
$HC{\equiv}CF$	25.3	27.5	25.0	25.1	25.4		$H_2C{=}CHS^{\bullet}$	44.9	47.6	50.8	50.8		
$HC{\equiv}CNa$	73.9	75.7	71.6	71.0	71.6		$2\text{-}C_3H_7^-$	22.6	27.1	27.8	26.8	22.8	21.5 ± 0.4
$HC{\equiv}CMgH$	77.6	78.0	80.3	78.7	78.9		$c\text{-}C_3H_5^-$	68.4	74.9	74.1	76.4	73.3	
$HC{\equiv}CAlH_2$	73.2	72.7	72.2	73.3	72.3		CH_3^-	33.9	37.0	34.5	34.1	33.2	33.2 ± 0.7
$HC{\equiv}CSiH_3$	55.6	57.5	59.8	59.5	57.6		NH_2^-	27.4	29.4	27.8	28.1	27.4	27.3 ± 0.4
$HC{\equiv}CPH_2$	59.0	61.2	63.4	63.1	61.4		HO^-	−34.6	−32.1	−34.3	−33.9	−33.0	−32.8 ± 0.1
$HC{\equiv}CSH$	60.1	61.1	62.8	63.6	63.1		F^-	−65.0	−59.6	−61.0	−61.7	−61.2	−59.3 ± 0.3
$HC{\equiv}CCl$	52.1	51.0	54.2	54.8	55.2		SiH_3^-	17.7	16.9	17.7	16.8	15.5	14.7 ± 2.0
$HC{\equiv}CCN$	87.1	88.6	91.9	91.4	92.0		PH_2^-	4.7	3.3	5.9	5.0	4.1	6.4 ± 2.0
$CH_2{=}BH$	56.6	56.3	56.2	55.2	54.3		HS^-	−18.9	−21.0	−19.1	−18.7	−18.7	−19.1 ± 2.0
$CH_2{=}NH$	23.8	22.1	22.7	22.6	20.7		Cl^-	−56.2	−57.1	−54.9	−54.6	−54.1	−53.4 ± 0.2
$CH_2{=}AlH$	82.9	80.6	81.0	80.5	79.4		CH_3O^-	−32.5	−29.2	−31.5	−31.1	−33.0	−32.4 ± 0.2
$CH_2{=}SiH_2$	46.5	48.1	48.2	48.5	46.3		CH_3S^-	−12.6	−13.2	−11.6	−11.4	−13.2	−14.3 ± 2.2

Table 1 (Continued)

	ΔH_f(0K)				ΔH_f(298K)			ΔH_f(0K)				ΔH_f(298K)	
compd	CBS-4	CBS-Q	G2(MP2)	G2	calc	obs	compd	CB-4	CBS-Q	G2(MP2)	G2	calc	obs
CN^-	16.1	16.1	15.4	14.9	15.7	18.0 ± 2.0	NH_4^+	155.2	155.3	154.3	154.3	151.6	151 ± 3
$C_2H_5^-$	34.4	38.9	37.0	36.6	33.9	35.1 ± 2.2	H_3O^+	148.7	146.0	144.6	145.5	143.8	141 ± 3
$C_2H_3^-$	54.1	57.9	56.7	56.9	55.8	56.2 ± 0.6	FH_2^+	191.2	185.9	184.4	185.2	184.5	184 ± 3
C_2H^-	66.4	68.0	66.2	66.0	66.8	66.8 ± 0.6	PH_4^+	181.1	182.8	183.3	183.7	180.8	178 ± 3
2-$C_3H_7^-$	27.4	32.9	31.7	30.9	26.5	28.2 ± 2.2	H_3S^+	193.2	194.4	192.6	194.2	192.5	190 ± 3
c-$C_3H_5^-$	56.3	65.7	64.3	63.8	60.7	59.0 ± 2.2	ClH_2^+	211.0	211.3	209.0	210.5	209.8	207 ± 3
allyl$^-$	30.0	33.8	33.2	32.9	30.4	30.4 ± 0.4	$C_2H_3^+$	267.1	269.5	268.2	267.7	266.8	266 ± 3
CH_2CHO^-	−39.2	−36.5	−37.9	−37.7	−39.3	−39.6 ± 2.2	$C_2H_5^+$	227.7[e]	226.4	225.6	225.0		
HCO^-	1.5	2.6	1.0	1.4	1.5	2.7 ± 0.2		219.5[f]	220.4	219.1	218.6	215.7	215.6 ± 1.0

[a] Heats of formation are given in kcal/mol. Unless otherwise stated, experimental heats of formation of organic compounds are taken from Pedley (Pedley, J. B. *Thermochemical Data and Structures of Organic Compounds*; Vol. 1, Thermodynamics Research Center: College Station, TX, 1994; Vol. 1), of inorganic compounds are taken from the JANAF Thermochemical Tables (ref 6), of radicals are taken from ref 17, and of ions are taken from refs 17 and 16. [b] Doncaster, A. M.; Walsh, R. *Int. J. Chem. Kinet.* **1981**, *13*, 503. Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246. [c] Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* **1982**, *104*, 2648. [d] It has been suggested that the reported enthalpy of formation for vinyl chloride is significantly in error: Wiberg, K. B.; Rablen, P. R. *J. Am. Chem. Soc.* **1993**, *115*, 9234. [e] Open cation. [f] Bridged cation.

heats of atomization or formation, bond dissociation energies, and heats of reaction. The remainder of this summary will be concerned with how well the several methods reproduce experimental data. The heats of formation are probably the more important of these quantities, for the others may be derived from them. These quantities are obtained by first calculating the heats of atomization making use of the calculated energies of the atoms that are involved.

Table 2. Calculated Heats of Formation and Atomization of Elements, kcal/mol

a. Heats of Formation of Atoms in the Gas Phase, 0 K

element	molecule	G2	CBS-Q	APNO	recommended
beryllium					75.8 ± 0.8
	Be_2	75.6	75.5	76.6	
	BeF_2	74.1	74.6	75.1	
	average	74.8	75.1	75.8	
	MAD[a]	0.7	0.5	0.8	
boron					136.2 ± 0.2
	BF_3	136.3	135.3	135.7	
	HBF_2	136.0	135.5	136.3	
	average	136.2	135.4	136.0	
	MAD[a]	0.1	0.1	0.3	
silicon					108.1 ± 0.5
	SiH_4	108.9	108.8		
	Si_2H_6	108.1	108.4		
	average	108.5	108.6		
	MAD[a]	0.4	0.2		

b. Heats of Atomization, kcal/mol

element	molecule	G2	CBS-Q	APNO	$\Delta_f H$ (obs)
beryllium	Be_2	0.3	0.3	2.4[a]	150.8 ± 1.5[c]
	BeF_2	301.4	301.8	302.3	−190.3 ± 1.0[c]
boron	BF_3	462.4	461.4	462.4	−271.2 ± 0.2[d]
	HBF_2	399.2	398.6	399.4	−174.5 ± 0.8[c]
silicon	SiH_4	305.0	304.8		10.5 ± 0.5[c]
	Si_2H_6	503.0	503.5		23.0 ± 0.4[e]

[a] Mean absolute deviation. [b] Petersson, G. A.; Shirley, W. A. *Chem. Phys. Lett.* **1989**, *160*, 494. [c] Reference 6. [d] Reference 14. [e] Pedley, J. P.; Iserad, B. S. *CATCH Tables*; University of Sussex, 1972, 1976.

2. Heats of Formation

Although the heats of formation of most atoms are generally well-known,[6] there are a few elements, most notably beryllium, boron, and silicon, that have unusually large experimental error bars of 1.2, 1.2, and 1.9 kcal/mol, respectively.[6] Further, for boron[7] and silicon[8] different values have been proposed that are substantially (1.9−2.4 kcal/mol) larger than those published in commonly referenced compilations.[6] The large error bars, and general disagreement over which value is correct, limit the confidence which can be placed in the model chemistries, even though the models generally are accurate to 0.5−2.0 kcal/mol. Clearly, more accurate heats of formation of gaseous atoms are needed. Unfortunately, it is not possible to determine the heats of formation of beryllium, boron, and silicon atoms directly using model chemistries, since the reference states for these elements are crystals. Instead, we have determined the heats of formation for these atoms using a few well-established heats of formation for small molecules, and the atomization energies calculated by G2[1] and by Montgomery, Ochterski, and Petersson's improved CBS-QCI/APNO and CBS-Q model chemistries.[4,9] The improved APNO model, which is defined only for the elements hydrogen through neon, is highly accurate, reproducing the experimental results from the first-row subset of the G2 test set with a 0.7 kcal/mol root-mean-square deviation. In developing this model the authors attempted to ensure that various components of the total energy were converged to 1 mH accuracy.

The atomization energies calculated using these three models were used in conjunction with experimental heats of formation for small molecules at 0K to determine the heats of formation of the atoms. In Table 2 the atomization energy of the molecule is given for each model, along with the heat of formation of one of the atoms calculated from the atomization energy. If a molecule has more than one kind of element, it is used to calculate the heat of formation of an atom of the less accurately known element. The data provided by the APNO model for the heats of formation of beryllium and boron will be used, since it is the most accurate of the three. G2 and CBS-Q will be used to verify Schaefer's heat of formation of silicon.

The computational data for beryllium are somewhat inconclusive, due to the relatively large experimental error bars for the heats of formation for beryllium dimer and BeF_2. Using the APNO results for Be_2[10] and the improved APNO results for BeF_2, we conclude that the heat of formation of beryllium atom is 75.8 ± 0.8 kcal/mol, which is consistent with the experimental heats of formation of both molecules.

The heat of formation of the boron atom has been the source of some discussion in the literature. One of the more commonly referenced values is 133.3 kcal/mol.[6] This is close to the Mar

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Table 3. Calculated Energies of Atoms and Heats of Formation

element	CBS-4	CBS-Q	G2(MP2)	G2	$\Delta_fH(0K)^a$
H	−0.503 35	−0.499 82	−0.500 00	−0.500 00	51.63 ± 0.001
Li	−7.436 58	−7.432 03	−7.432 22	−7.432 22	37.7 ± 0.2
Be	−14.628 78	−14.620 44	−14.623 51	−14.622 34	75.8 ± 0.8
B	−24.606 35	−24.601 62	−24.602 72	−24.602 05	136.2 ± 0.2
C	−37.788 25	−37.785 15	−37.783 90	−37.784 32	169.98 ± 0.10
N	−54.524 51	−54.520 26	−54.516 31	−54.517 98	112.5 ± 0.1
O	−74.992 92	−74.987 09	−74.978 68	−74.982 03	58.99 ± 0.02
F	−99.650 77	−99.642 26	−99.628 94	−99.632 82	18.50 ± 0.07
Na	−161.850 53	−161.845 98	−161.846 17	−161.846 18	25.7 ± 0.2
Mg	−199.652 92	−199.642 91	−199.646 20	−199.645 14	35.0 ± 0.2
Al	−241.935 55	−241.928 70	−241.929 95	−241.930 97	78.8 ± 1.0
Si	−288.931 95	−288.931 14	−288.930 02	−288.933 25	108.1 ± 0.5
P^b	−340.813 68	−340.816 95	−340.813 87	−340.818 22	75.4 ± 0.2
S	−397.651 29	−397.656 90	−397.646 99	−397.654 95	65.58 ± 0.07
Cl	−459.676 01	−459.682 91	−459.666 72	−459.676 64	28.59 ± 0.002

[a] kcal/mol. [b] White phosphorus.

and Bedford[11] value of 132.9 ± 0.7 kcal/mol that is recommended by Nordine and Shiffman.[12] However, Ruscic et al. recommend a larger value of 136.2 ± 0.2 kcal/mol,[7] which was determined by Storms and Mueller.[13] To confirm one of the values, we calculated the atomization energy of BF_3 (462.4 kcal/mol) using the improved APNO model. The experimental heat of formation of BF_3 is given as −271.2 ± 0.2 kcal/mol.[14] These two values yield a heat of formation for the boron atom of 135.7 ± 0.7 kcal/mol, in agreement with the Storms and Mueller value. We also used the same models to determine the atomization energy of HBF_2. The APNO atomization energy of HBF_2 is 399.4 kcal/mol, which yields a heat of formation for boron of 136.3 kcal/mol, again in excellent agreement with the Storms and Meuller value. Both the CBS-Q model and G2 theory support these results, predicting the same heat of formation of boron to within 1 kcal/mol. Schlegel and Harris[15] reported G2 heats of formation for the sequence BH_mCl_n (n, m = 1, 2, 3) that also are consistent with the Storms and Mueller value for $\Delta_fH°$ of the boron atom.

Silicon is the third element where there is some discrepancy regarding the atomic heat of formation. Unfortunately, the APNO model is not defined for the silicon atom, so it is not useful here. However, Grev and Schaefer[8] very carefully determined the heat of formation of the silicon atom to be 108.1 kcal/mol, using the heat of formation of silane. The CBS-Q model and G2 theory give the heat of formation of the silicon atom from silane as 108.8 and 108.9 kcal/mol, respectively; both models are in agreement with Grev's results. We obtained heats of formation for the silicon atom of 108.4 and 108.1 from disilane (Si_2H_6) for the CBS-Q model and G2 theory, respectively, again in agreement with Schaefer's results. We suggest error bars of 0.5 kcal/mol based on the close agreement of the G2 and CBS-Q values with Grev's results.

In summary, we recommend heats of formation of beryllium, boron, and silicon atoms of 75.8 ± 0.8 (APNO), 136.2 ± 0.2 (expt), and 108.1 ± 0.5 (Grev and Schaefer) kcal/mol, respectively.

Table 4. Deviation between Experimental and Calculated Energies (kcal/mol)

	model			
	CBS-4	CBS-Q	G2(MP2)	G2
a. Heats of Formation (89 Compounds, Radicals, and Ions)				
av dev	−0.76	0.40	−0.03	0.00
rms dev	2.59	1.51	1.55	1.35
wt rms dev	2.09	1.13	1.45	1.08
b. M−H Bond Dissociation Energies (18 Compounds)				
av dev	0.14	0.03	1.03	0.71
rms dev	1.41	0.91	1.32	1.11
wt rms dev	1.09	0.77	1.18	0.90
c. C−X Bond Dissociation Energies (18 Compounds)				
av dev	0.67	−0.02	1.41	0.81
rms dev	1.53	1.55	1.95	1.44
wt rms dev	1.34	1.20	1.84	1.27
d. Gas Phase Acidities (16 Compounds)				
av dev	1.25	0.26	0.64	0.39
rms dev	2.64	1.65	1.59	1.33
wt rms dev	1.97	1.30	1.11	0.92
e. Proton Affinities (8 Compounds)				
av dev	−0.88	−1.26	−0.21	−0.49
rms dev	2.76	1.59	1.08	1.21
wt rms dev	2.27	1.53	0.98	1.12

The heats of formation of all the atoms used in this study are included in Table 3. These experimental heats of atomization of the elements in their normal states are then compared to the calculated heats of converting the compounds into the atoms in the gas phase. The difference between these quantities gives the heat of formation of the compounds from the elements. The energies thus obtained are given in Table 1, which also gives the experimental heats of formation when they are known. The heats of formation of the ions at 298 K are based on the convention used by Lias et al.,[16] where the integrated heat capacity of the electron is taken as zero.

The internal consistency between the methods may be examined by calculating the average of the absolute values of the deviations between their predictions of $\Delta_fH°(0K)$. This average is 1.6 kcal/mol between the related CBS-4 and CBS-Q models, 0.6 kcal/mol between the G2(MP2) and G2 models, and 0.9 kcal/mol between the CBS-Q and G2 models. Thus, the internal consistency is fairly satisfactory in all cases.

The change in heat of formation on going from 0 to 298 K was estimated using the HF/6-31G* calculated vibrational frequencies scaled by 0.893, and the $\Delta_fH°(298K)$ derived from the G2 energies are recorded in Table 1 along with the available experimental data. The data in the table allow the $\Delta_fH°(298K)$ for the other model chemistries to be obtained. The deviations between the calculated and observed energies are summarized in Table 4. The average deviation (the average of the signed

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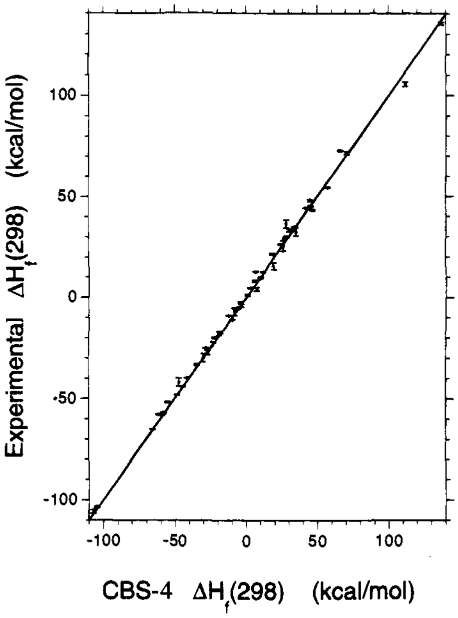

Figure 1. Relationship between the experimental and CBS-4 heats of formation. The line is drawn with a unit slope.

deviations) should be zero if the deviations were randomly scattered, and it is quite small for all models except CBS-4, and even here it is less than 1 kcal/mol. The rms deviations are quite small for the CBS-Q and G2 models, and somewhat larger for the others. Since the standard deviations for the experimental data vary considerably, it seemed appropriate to weight the deviations from the experimental values by the reciprocal of their standard deviations. The weighted rms deviations are about 1 kcal/mol for both CBS-Q and G2, and with CBS-4 that gives the largest deviation as only 2 kcal/mol (Figure 1).

The rms errors in the calculated heats of formation for the CBS-4, CBS-Q, G2(MP2), and G2 models and the present data (2.0, 1.0, 1.6, and 1.1 kcal/mol) are comparable to the corresponding rms errors in the atomization energies of the G2 test set (2.0, 1.0, 1.6, and 1.5 kcal/mol, respectively).[4] Since there is little overlap between the present set and the G2 test set, the close agreement of the rms errors indicates that both sets provide useful measures of the reliability of the models for application to chemical studies. In addition, it is likely that the small deviations between experimental and calculated heats of formation will in large measure cancel when used in isodesmic reactions.

We have examined several elementary chemical reactions: bond dissociation energies of bonds to hydrogens; bond dissociation energies of C−X bonds; gas phase acidities; and proton affinities of neutral molecules. In each of these cases, good experimental data have become available, allowing a detailed comparison with the calculated values. In addition, where experimental data are not available, the calculated energies will serve as good estimates of the quantities in question.

3. Bond Dissociation Energies

The X−H bond dissociation energies that may be derived from the data in Table 1 are summarized in Table 5a. Much of the available data have been summarized by Berkowitz, Ellison, and Gutman,[17] and that for propene has recently been determined by Davico et al.[18] These data are included in the table. There is remarkably good agreement between experiment and theory (Table 4). This suggests that the calculated dissociation energies for the bonds that have not been studied experimentally may be used with confidence in their accuracy.

Knowing the experimental heats of formation of radicals and of the compounds from which they are arrived, it is possible to obtain experimental values of the bond dissociation energies for bonds not involving hydrogens. These energies also may be calculated from the data in Table 1, and they are compared with the experimental values in Table 5b. Again, there is very satisfactory agreement between the calculated and experimental values (Table 4). The performance of the relatively inexpensive CBS-4 model is particularly encouraging.

Comparing the combined rms errors in the calculated M−H and C−X bond dissociation energies for the CBS-4, CBS-Q, G2(MP2), and G2 models (1.2, 1.0, 1.5, and 1.1 kcal/mol) with the corresponding rms errors in the calculated heats of formation (2.0, 1.0, 1.6, and 1.1 kcal/mol, respectively) for the CBS-Q, G2(MP2), and G2 models, we note surprisingly similar values. One might expect the dissociation energy of just one bond to be easier to calculate than the total dissociation energies for all bonds in a molecule, but only the CBS-4 model gives better results for bond dissociation energies than for heats of formation.

Having this set of data provides an opportunity to examine trends in dissociation energies. The values for HX, MeX, CH^2=CHX, HC≡CX, and CH_3COX where X includes all of the first- and second-row substituents are summarized in Table 6. Plots of one set of dissociation energies against another generally appear to be scattergrams.

However, if one chooses subsets of substituents, some patterns appear. Figure 2 shows the correlation of the RX bond dissociation energies with those for HX where the X's are the coordinately unsaturated substituents, Li, BeH, BH_2, Na, MgH, and AlH_2. The correlations are good, and the slopes of the lines are about the same (1.20 for MeX, 1.20 for CH_2CHX, 0.91 for HC≡CX, and 0.93 for CH_3COX). The similarity of the slopes is remarkable. There cannot be any π interactions in the HX series, methyl can give a small π interaction, and vinyl might be expected to give a large π interaction. These expectations are not born out by the data. The order of the substituents, X, is the order of increasing electronegativity. But, this is not the only effect since the bond dissociation energies drop on going to X = CH_3. This implies that the hybridization of the bond from X is also important. The bonds from the above substituents would be expected to have a high degree of s character, which would decrease on going to X = CH_3.

The main difference is found in the intercepts, where the ethynyl compounds give the largest intercept, which is followed by vinyl and methyl. This is, of course, the order of decreasing s character, and it is well-known that higher dissociation energies are associated with high s character (cf. vinylacetylene and acrylonitrile in Table 5b).

Another group of substituents are those that have lone pairs, and probably have similar hybridization for their bonds: NH_2, OH, F, PH_2, SH, Cl. Figure 3a shows the correlation between the HX dissociation energies and those for MeX and CH_2=CHX. Again, the slopes of the lines are about the same (0.75 for MeX and 0.85 for CH_2=CHX), and the intercepts correspond to the difference in s character. Figure 3b gives the corresponding data for the ethynyl and acetyl compounds. Now, the slopes are quite different (0.46 for HC≡CX and 1.16 for CH_3COX).

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Table 5. Bond Dissociation Energies, kcal/mol[a]

compd	bond	CBS-4	CBS-Q	G2(MP2)	G2	obs	
						0 K	298 K
			a. X−H bonds				
LiH	Li−H	53.3	55.6	56.2	56.6		
BeH_2	Be−H	91.2	92.4	93.1	93.3		
BH_3	B−H	104.1	104.6	105.1	105.2		
CH_4	C−H	103.6	103.3	104.0	104.0	103.3 ± 0.1	104.7 ± 0.1
NH_3	N−H	106.0	103.3	104.0	106.7	106.7 ± 0.3	108.2 ± 0.3
H_2O	O−H	117.9	117.8	118.7	118.1	118.1 ± 0.1	119.3 ± 0.1
HF	F−H	135.9	136.2	136.9	135.3	135.1 ± 0.2	136.4 ± 0.2
NaH	Na−H	41.6	43.5	44.5	45.0		
MgH_2	Mg−H	67.9	69.4	70.2	70.5		
AlH_3	Al−H	82.5	83.7	84.4	84.7		
SiH_4	Si−H	90.1	90.9	91.3	91.3	90.4 ± 0.8	91.7 ± 0.5
PH_3	P−H	80.5	81.1	81.7	81.5	82.5 ± 0.5	83.9 ± 0.5
H_2S	S−H	90.6	90.3	90.7	90.2	89.9 ± 0.7	91.2 ± 0.7
HCl	Cl−H	103.4	103.2	103.5	102.7	102.2 ± 0.0	103.2 ± 0.0
HCN	C−H	127.0	125.5	126.8	126.8	124.8 ± 0.4	126.1 ± 0.4
C_2H_6	C−H	99.9	100.0	100.9	100.8	99.5 ± 0.5	101.0 ± 0.4
C_2H_4	C−H	109.3	108.9	110.7	110.4	109.7 ± 0.8	111.2 ± 0.8
C_2H_2	C−H	129.5	131.6	133.7	133.5	131.5 ± 0.7	132.8 ± 0.6
C_3H_8	2-C−H	97.0	97.4	98.4	98.5	97.1 ± 0.4	98.6 ± 0.4
c-C_3H_6	C−H	109.0	108.4	107.4	110.4		
propene	C−H(Me)	84.9	85.0	87.5	87.3	87.2 ± 0.4	88.6 ± 0.4
H_2CO	C−H	87.6	87.1	87.9	87.9	86.6 ± 0.2	88.0 ± 0.2
CH_3COH	C−H	88.3	87.8	88.7	88.7	87.9 ± 0.3	89.4 ± 0.3
CH_3BeH	Be−H	91.3	92.4	93.0	93.1		
CH_3BH_2	B−H	103.2	103.8	104.0	104.1		
CH_3BH_2	C−H	94.0	93.8	94.4	94.4		
CH_3NH_2	N−H	99.7	99.2	99.5	99.2		
CH_3NH_2	C−H	91.8	91.9	93.1	93.1		
CH_3OH	O−H	106.5	104.3	105.6	105.0	103.0 ± 0.9	104.2±0.9
CH_3OH	C−H	95.6	95.3	96.2	96.2		
CH_3MgH	Mg−H	67.4	69.2	70.1	70.4		
CH_3AlH_2	Al−H	82.8	84.1	85.0	85.3		
CH_3SiH_3	Si−H	90.6	90.4	92.2	92.3		
CH_3PH_2	P−H	79.2	79.9	80.7	80.5		
CH_3SH	S−H	86.4	85.8	86.7	86.1	86.1 ± 0.5	87.4 ± 0.5
$CH_2{=}CHBeH$	Be−H	90.4	92.7	93.3	93.7		
$CH_2{=}CHBH_2$	B−H	103.8	105.3	106.3	106.3		
$CH_2{=}CHNH_2$	N−H	86.6	86.6	88.9	88.5		
$CH_2{=}CHOH$	O−H	85.7	84.2	84.8	84.6		
$CH_2{=}CHSiH_3$	Si−H	86.9	88.0	90.7	90.8		
$CH_2{=}CHPH_2$	P−H	72.7	74.1	76.3	76.0		
$CH_2{=}CHSH$	S−H	77.9	78.4	79.7	79.0		
			b. X−Y Bonds				
CH_3Li	C−Li	44.7	46.0	46.8	47.0		
CH_3BeH	C−Be	91.2	91.9	93.0	93.1		
CH_3BH_2	C−B	103.4	103.2	104.2	104.1		
CH_3CH_3	C−C	88.9	87.5	88.5	88.3	88.0 ± 0.2	89.4 ± 0.3
CH_3NH_2	C−N	83.7	82.5	83.8	83.3	83.9 ± 1.5	85.7 ± 1.5
CH_3OH	C−O	90.4	90.5	92.2	91.5	90.5 ± 0.3	92.2 ± 0.2
CH_3F	C−F	108.4	109.5	111.3	110.7	108.2 ± 2.0	109.6 ± 2.0
CH_3Na	C−Na	30.9	32.4	33.3	33.4		
CH_3MgH	C−Mg	61.8	62.7	65.0	63.9		
CH_3AlH_2	C−Al	80.1	80.8	81.9	82.0		
CH_3SiH_3	C−Si	86.5	85.4	87.6	87.3	88.4 ± 2.1	89.6 ± 2.1
CH_3PH_2	C−P	70.0	70.0	70.7	70.2		
CH_3SH	C−S	74.1	73.2	74.0	73.0	73.0 ± 0.7	74.4 ± 0.8
CH_3Cl	C−Cl	83.3	83.2	84.0	83.0	82.0 ± 0.2	83.3 ± 0.3
CH_3CN	C−C	124.7	121.6	122.7	122.5		
CH_3NO_2	C−N	57.7	58.4	61.3	61.0		
$CH_2{=}CHLi$	C−Li	55.5	56.7	58.5	58.3		
$CH_2{=}CHBeH$	C−Be	99.1	99.4	101.7	101.5		
$CH_2{=}CHBH_2$	C−B	115.6	115.2	117.2	116.9		
$CH_2{=}CHCH_3$	C−C	100.4	98.9	100.9	100.4	100.3 ± 0.9	101.5 ± 0.9
$CH_2{=}CHNH_2$	C−N	101.3	100.5	102.4	101.8		
$CH_2{=}CHOH$	C−O	108.3	108.4	110.7	109.9	108.9 ± 2.2	110.7 ± 2.2
$CH_2{=}CHF$	C−F	122.5	123.4	126.0	125.1	122.4 ± 0.9	123.8 ± 0.9
$CH_2{=}CHNa$	C−Na	41.0	42.8	50.9	44.4		
$CH_2{=}CHMgH$	C−Mg	70.4	71.0	73.0	72.9		
$CH_2{=}CHAlH_2$	C−Al	90.4	90.2	92.4	92.1		
$CH_2{=}CHSiH_3$	C−Si	94.6	94.7	96.6	96.0		
$CH_2{=}CHPH_2$	C−P	80.7	80.4	81.9	81.0		
$CH_2{=}CHSH$	C−S	87.0	85.7	85.9	84.6		
$CH_2{=}CHCl$	C−Cl	95.8	94.8	96.6	95.3		
$CH_2{=}CHCH{=}CH_2$	C−C	115.4	113.6	116.5	115.7	115.4 ± 1.2	116.9 ± 1.2
$CH_2{=}CHC{\equiv}CH$	C−C	139.2	137.1	137.4	136.7		
$CH_2{=}CHCN$	C−C	133.5	131.2	133.0	132.6	134.1 ± 2.3	135.6 ± 2.3
CH_3CHO	C−C	84.3	82.5	83.5	83.4		

Table 5 (Continued)

compd	bond	CBS-4	CBS-Q	G2(MP2)	G2	obs 0 K	obs 298 K
			b. X−Y Bonds				
$HCONH_2$	C−N	99.5	98.9	99.0	98.9		
CH_3COLi	C−Li	50.8	51.4	52.7	52.7		
CH_3COBeH	C−Be	84.4	84.4	85.2	85.2		
CH_3COBH_2	C−B	87.7	88.5	91.3	90.9		
CH_3COCH_3	C−C	84.1	82.9	83.7	83.5	82.3 ± 0.5	84.2 ± 0.5
CH_3CONH_2	C−N	98.2	97.9	98.1	97.8	97.9 ± 1.5	100.1 ± 1.5
CH_3COOH	C−O	108.3	109.0	109.9	109.5	108.0 ± 0.7	110.3 ± 0.6
CH_3COF	C−F	120.8	121.4	122.9	122.5	120.5 ± 0.9	122.3 ± 0.9
CH_3CONa	C−Na	30.5	32.9	33.8	33.8		
CH_3COMgH	C−Mg	56.4	57.5	58.4	58.5		
CH_3COAlH_2	C−Al	73.6	73.6	73.8	73.8		
CH_3COSiH_3	C−Si	68.4	69.5	70.0	69.8		
CH_3COPH_2	C−P	61.3	61.1	61.9	61.5		
CH_3COSH	C−S	75.9	74.3	75.5	74.3	71.6 ± 2.2	73.6 ± 2.1
CH_3COCl	C−Cl	85.4	85.0	85.9	85.0	83.1 ± 0.5	84.6 ± 0.4
$HC{\equiv}CLi$	C−Li	103.6	104.8	106.9	106.8		
$HC{\equiv}CBeH$	C−Be	140.0	139.2	141.2	141.0		
$HC{\equiv}CBH_2$	C−B	144.2	146.2	147.5	147.2		
$HC{\equiv}CCH_3$	C−C	126.7	125.8	126.6	126.2	124.1 ± 0.7	125.7 ± 0.7
$HC{\equiv}CHNH_2$	C−N	119.3	119.9	121.7	121.1		
$HC{\equiv}CHOH$	C−O	120.9	123.0	124.1	123.4		
$HC{\equiv}CHF$	C−F	128.7	127.2	132.0	131.2		
$HC{\equiv}CNa$	C−Na	87.3	86.5	92.6	92.6		
$HC{\equiv}CMgH$	C−Mg	117.3	114.6	116.4	116.4		
$HC{\equiv}CAlH_2$	C−Al	127.2	127.1	130.9	128.6		
$HC{\equiv}CSiH_3$	C−Si	126.7	127.3	128.3	127.7		
$HC{\equiv}CPH_2$	C−P	108.2	107.8	109.4	108.5		
$HC{\equiv}CSH$	C−S	109.3	108.9	109.9	108.7		
$HC{\equiv}CCl$	C−Cl	112.0	113.9	112.9	111.7		
$HC{\equiv}CCN$	C−C	158.9	157.7	153.4	153.0		

[a] The calculated dissociation energies are for 0 K.

Table 6. Summary of G2 Bond Dissociation Energies, kcal/mol, 0 K

X	Y: H	CH_3	$CH_2{=}CH$	$HC{\equiv}C$	CH_3CO
H	104.0	104.0	110.4	133.5	88.7
Li	56.6	47.0	58.3	106.8	52.7
BeH	93.3	93.1	101.5	141.0	85.2
BH_2	105.2	104.1	116.9	147.2	90.9
CH_3	104.0	88.3	100.4	126.2	83.5
NH_2	106.4	83.3	101.8	121.1	97.8
OH	118.1	91.5	109.9	123.4	109.5
F	135.3	110.7	125.1	131.2	122.5
Na	45.0	33.4	44.4	92.6	33.8
MgH	70.5	63.9	72.9	116.4	58.5
AlH_2	84.7	82.0	92.1	128.6	73.8
SiH_3	91.3	87.3	96.0	127.7	69.8
PH_2	81.5	70.2	81.0	108.5	61.5
SH	90.2	73.0	84.6	108.7	74.3
Cl	102.7	83.0	95.3	111.7	85.0

The large slope for the acetyl compounds is a result of the polarity of the C=O bond. Electronegative substituents will increase the positive charge at carbon and will strengthen the C=O bond, leading to an extra term in the stabilization.[19] The ethynyl compounds have the smallest range of dissociation energies.[20]

The linear relationships between the R−X and H−X bond dissociation energies are of interest in themselves since they clearly indicate a consistency of bonding in these simple monovalent species. However, insight into the nature of this consistency can be gained by examination of the relationship to Pauling's electronegativity interpretation of covalent and ionic contributions to bonding:[21]

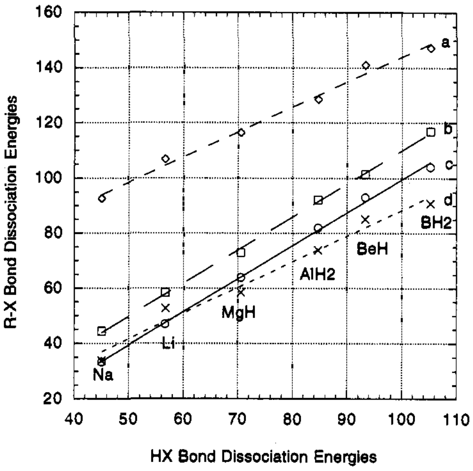

Figure 2. Relationship between the RX and HX bond dissociation energies for the coordinately unsaturated substituents X = Na, Li, MgH, AlH_2, BeH, and BH_2. The lines correspond to (a) $HC{\equiv}CX$, (b) $CH_2{=}CHX$, (c) CH_3, and (d) CH_3COX.

$$D_0(\mathrm{A-B}) = {}^1/_2[D_0(\mathrm{A-A}) + D_0(\mathrm{B-B})] + (23\ \mathrm{kcal/mol})(\chi_\mathrm{A} - \chi_\mathrm{B})^2 \quad (1)$$

where χ_A is the electronegativity of atom A. If we apply this approximation to both D_0(H−X) and D_0(R−X), we obtain:

$$D_0(\mathrm{R-X}) = D_0(\mathrm{H-X}) + {}^1/_2[D_0(\mathrm{R-R}) - D_0(\mathrm{H-H})] - (23\ \mathrm{kcal/mol})\,(\chi_\mathrm{R} - \chi_\mathrm{H})(2\chi_\mathrm{X} - \chi_\mathrm{R} - \chi_\mathrm{H}) \quad (2)$$

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[19] Wiberg, K. B.; Hadad, C. M.; Rablen, P. R. *J. Am. Chem. Soc.* **1992**, *114*, 8644.

[20] Wiberg, K. B.; Rablen, P. R. *J. Am. Chem. Soc.* **1993**, *115*, 9234.

[21] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; eq 3-12 on p 92.

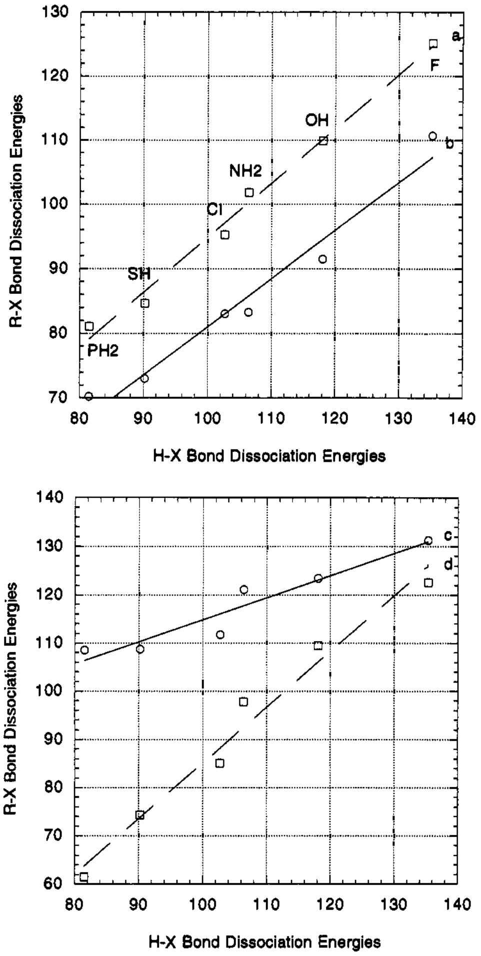

Figure 3. Relationship between the RX and HX bond dissociation energies for the substituents bearing lone pairs X = PH_2, SH, Cl, NH_2, OH, and F. The lines in part a corresponds to (a) $CH_2{=}CHX$ and (b) CH_3X, and those in part b correspond to (c) $HC{\equiv}CX$ and (d) CH_3COX.

The first two terms of this expression would give lines of unit slope with intercept $\frac{1}{2}[D_0(R{-}R) - D_0(H{-}H)]$ in Figures 2 and 3. The large intercepts for the ethynyl radical in Figures 2 and 3b are thus a consequence of the inherent covalent bond strength of this radical [$D_0(HCC{-}CCH)$ = 164.8 kcal/mol]. The electronegativities of the four organic radicals are all slightly greater than that of hydrogen ($\chi_H = 2.20$), making ($\chi_R - \chi_H$) a small positive number. The quantity ($2\chi_X - \chi_R - \chi_H$) is negative and approaching zero from left to right for X = Na, Li, MgH, AlH_2, BeH, and BH_2 in Figure 2, but it is positive and approaching zero from right to left for X = PH_2, SH, Cl, NH_2, OH, and F in Figure 3. The third term of eq 2 will therefore reduce the slopes of the lines in Figures 2 and 3. This effect is greatest for the ethynyl radical ($\chi_{HCC} = 2.82$; *vide infra*). The major qualitative trends exhibited in Figures 2 and 3 can thus be rationalized with Pauling's electronegativity relationship.

In order to further examine the validity of eq 1, we have determined the entire set of 171 bond dissociation energies between all possible pairs of the 18 monovalent radicals from Table 6. The CBS-Q calculated values for these D_0's (Table 7) can be fit to within 7.31 kcal/mol rms error by adjustment of the electronegativities of these monovalent groups. If we instead use Paulings' alternative geometric mean expression:[22]

$$D_0(A{-}B) = [D_0(A{-}A)D_0(B{-}B)]^{1/2} + (30\ \text{kcal/mol})(\chi_A - \chi_B)^2 \quad (3)$$

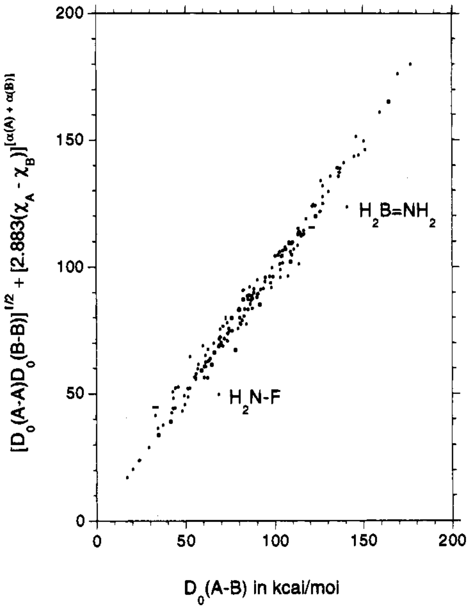

Figure 4. Relationship between the CBS-Q calculated bond dissociation energies and the values estimated from eq 4.

the rms error is reduced to 6.30 kcal/mol. At this point we noted that the largest errors was associated with bonds to the species with the largest polarizabilities (*i.e.* HCC, H_2P, HS, and Cl). The strength of the bonds of ethynyl to both Li and F was underestimated by eq 3. We therefore introduced a new empirical "polarizability parameter", α, to attenuate the energetic effect of differences in electronegativities:

$$D_0(A{-}B) = [D_0(A{-}A)D_0(B{-}B)]^{1/2} + |2.883(\chi_A - \chi_B)|^{[\alpha(A)+\alpha(B)]}\ \text{kcal/mol} \quad (4)$$

The parameter, 2.883, was selected to give $\chi_H = 2.20$ and $\chi_F = 3.98$, so that the electronegativities of the organic radicals in Table 7 could be compared directly with the Pauling scale.[23] The inclusion of the empirical "polarizability parameters", α(A), in eq 4 reduced the rms error to 4.73 kcal/mol. The exponential attenuation by α(A) + α(B) was more effective than multiplication by α(A) + α(B) which led to an rms error of 5.23 kcal/mol.

The agreement between eq 4 and the *ab initio* CBS-Q bond dissociation energies is striking (Table 7 and Figure 4). The two largest discrepancies occur in $H_2B{=}NH_2$ (for which the B=N double bond readily explains the extra *ab initio* bond strength) and $H_2N\text{-}F$ (for which we see no obvious explanation). If we omit these two species, the rms error is reduced to 4.21 kcal/mol. One could hardly expect any better correlation since π-electron stabilizing effects (e.g., acetamide, etc.) and lone pair repulsion (e.g., F_2 and N_2H_4) have not been explicitly considered. Although the group electronegativities, χ_A, and the polarizability parameters, α(A), in Table 7 (obtained by a least-squares fit of the dissociation energies) can adjust to partially account for π interactions, since electronegative species have lone pairs and electropositive species have empty orbitals, these effects undoubtedly still account for much of the 10 kcal/mol scatter in Figure 4.

The strength of the chemical bond between any two monovalent radicals can be interpreted as arising from covalent and ionic components. The covalent component depends on only one parameter per radical, $D_0(A{-}A)$. The ionic component depends on both the electronegativity, χ_A, and the polarizability

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[22] Reference 21; eq 3-11 on p 91.

[23] Allred, A. L. *J. Inorg. Nucl. Chem.* **1961**, *17*, 215.

Table 7. Calculated CBS-Q Bond Dissociation energies, D_0, of monovalent species (kcal/mol)

	H	Li	BeH	BH$_2$	CH$_3$	NH$_2$	OH	F	H$_2$C═CH	HC≡C	CH$_3$CO	Na	MgH	AlH$_2$	SiH$_3$	Ph2	SH	Cl
χ_A	2.200	0.980	1.365	1.664	2.393	3.657	3.841	3.980	2.362	2.821	2.223	0.936	1.357	1.424	1.829	2.553	2.989	3.295
α (Å)	1.000	0.523	0.764	0.859	0.883	1.320	1.533	1.678	0.977	1.711	1.006	0.380	0.649	0.730	0.873	1.332	1.675	1.793
H	104.5	55.6	92.4	104.6	103.3	106.1	117.8	136.2	108.4	131.6	87.8	43.3	69.4	83.7	90.9	81.1	90.3	103.2
		56.4	91.0	106.4	95.9	107.6	118.8	135.7	109.1	135.6	87.7	48.1	72.3	83.3	89.4	77.4	89.3	101.1
Li		23.9	42.3	44.4	46.0	72.4	103.0	136.6	56.7	104.8	51.4	20.2	34.8	41.6	49.9	52.4	80.5	113.2
			42.5	52.3	52.6	79.8	105.8	137.2	59.7	101.5	48.7	20.4	33.7	39.4	45.6	52.1	82.9	112.6
BeH			71.7	82.5	91.9	121.6	147.7	176.9	99.4	139.2	84.4	34.5	55.2	66.3	76.3	79.3	106.6	135.6
				87.1	84.9	115.5	144.1	179.9	96.2	140.8	77.4	36.3	56.5	66.0	74.7	75.6	107.0	139.0
BH$_2$				104.0	103.2	141.0	151.2	169.7	115.2	146.2	88.5	33.9	59.5	76.0	84.8	87.5	113.2	126.0
					98.8	123.5	146.2	176.0	112.1	151.2	89.8	44.7	68.9	79.9	88.4	83.5	108.3	133.8
CH$_3$					87.5	82.5	90.5	109.5	98.9	125.8	82.9	32.4	62.7	80.8	85.4	70.0	73.2	83.2
						90.8	94.7	102.4	99.7	121.7	80.5	44.6	67.5	77.7	83.1	70.1	77.9	83.6
NH$_2$						63.9	62.7	68.9	100.5	119.9	97.9	52.5	86.0	109.8	102.2	75.8	65.7	61.4
							56.2	49.7	104.3	115.6	93.8	64.5	92.2	104.7	104.7	79.5	69.9	62.4
OH							49.2	48.3	108.4	123.0	109.0	80.4	113.3	130.3	122.9	88.5	69.0	56.1
								43.0	109.8	119.7	106.0	83.8	115.1	129.6	124.0	91.4	71.7	57.9
F								37.6	123.4	127.2	121.4	111.0	145.2	159.4	150.6	110.3	81.8	60.9
									120.0	131.9	123.8	107.0	143.5	160.9	149.4	109.7	78.9	56.5
H$_2$CCH									113.6	137.1	94.0	42.8	71.0	90.2	94.7	80.4	85.7	94.8
										138.8	91.6	50.7	76.5	88.1	94.2	79.9	89.0	96.0
HC≡C										164.8	116.3	86.5	114.6	127.1	127.3	107.8	108.9	113.9
											114.2	85.4	113.4	127.5	124.8	96.4	101.9	101.2
CH$_3$CO											73.7	32.9	57.5	73.6	69.5	61.1	74.3	85.0
												41.5	61.6	70.8	75.4	65.0	75.7	87.3
Na												17.2	29.6	34.8	41.6	43.1	68.7	98.2
													28.8	33.7	39.0	44.2	69.0	91.7
MgH													44.5	51.4	59.0	61.2	86.9	116.6
														52.0	59.2	60.7	86.8	112.8
AlH$_2$														60.5	68.4	70.9	97.3	121.9
															68.5	68.8	96.3	124.3
SiH$_3$															74.7	69.9	87.3	109.7
																69.3	88.4	109.0
PH$_2$																55.9	65.4	78.1
																	61.1	67.1
SH																	62.9	64.7
																		61.5
Cl																		59.0

[a] The empirical estimate from eq 4 is given below the *ab initio* value for each dissociation energy.

parameter, α(A). These three parameters are sufficient to describe the bond energies of monovalent radicals to within ±5 kcal/mol. Changes in hybridization and variable bond orders make the energies of multiple bonds substantially more complex.

The consistently large energies of bonds to the ethynyl radical are a consequence of all three effects. First, D_0(HCC−CCH) is very large (164.8 kcal/mol). Second, the electronegativity of the ethynyl radical, 2.82, provides strong ionic bonding to both metals (χ_{Li} = 0.98) and halogens (χ_F = 3.98), compensating for their weak covalent bonding [D_0(Li−Li) = 56.4 kcal/mol, D_0(F−F) = 37.6 kcal/mol]. Finally, the polarizability of the triple bond [α(HCC) = 1.71] increases the energy of the ionic bonding.

4. Gas Phase Acidities

A large body of information on gas phase acidities has become available in recent years.[16−18] The energies of the anions given in Table 1 permit the calculation of these energies, and they are compared with the experimental values in Table 8. Again, it is seen that there is very good agreement among the model chemistries, and between the calculated and experimental values. Both G2(MP2) and G2 give weighted rms deviations of only 1 kcal/mol (Table 4). The relatively large average and rms errors for the CBS-4 model are probably related to the error in the CBS-4 energy for the hydrogen atom (Table 3).

One might expect the rms errors on the calculated gas phase acidities for the CBS-4, CBS-Q, G2(MP2), and G2 models (2.0, 1.3, 1.1, and 0.9 kcal/mol) to be comparable to the corresponding rms errors in the electron affinities of the G2 test set (3.2, 1.67, 2.4, and 1.6 kcal/mol, respectively).[4] However, we find that both G2 models give significantly better results when restricted to closed shell ions involved in gas phase acidities, whereas the CBS models show less improvement when restricted to closed shells.

5. Proton Affinities

The proton affinities of some neutral compounds have been measured in the gas phase,[24] and may be calculated from the data in Table 1. The data are compared in Table 9. The experimental data are for 298 K, and would be reduced by about 1.4 kcal/mol on going to 0 K (cf. the differences in Table 8). The deviations between the calculated and experimental proton affinities are again quite small (Table 4), and in fact considerably smaller than the estimated uncertainties in the measurements.

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(24) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

Table 8. Gas Phase Acidities, kcal/mol[a]

compd	CBS-4	CBS-Q	G2(MP2)	G2	obs (0 K)	obs (298 K)
CH_4	418.0	418.0	416.1	416.2	415.0 ± 0.7	416.4 ± 0.7
NH_3	403.0	403.0	402.3	402.6	402.6 ± 0.4	404.0 ± 0.4
H_2O	389.7	390.4	389.3	388.9	389.5 ± 0.1	390.8 ± 0.1
HF	368.2	371.7	371.1	369.8	370.1 ± 0.2	371.5 ± 0.2
SiH_4	376.8	372.9	373.1	372.4	370.8 ± 2.0	372.2 ± 2.0
PH_3	369.5	365.4	367.2	366.5	369.4 ± 2.0	370.8 ± 2.0
H_2S	353.8	349.1	351.2	350.9	349.7 ± 2.0	351.1 ± 2.0
HCl	334.6	331.2	333.8	333.3	332.0 ± 0.3	333.4 ± 0.1
HCN	348.5	349.1	349.3	349.0	349.7 ± 0.5	351.1 ± 0.5
C_2H_6	420.2	419.9	418.5	418.7		
C_2H_4	407.5	407.6	406.8	406.9	408.0 ± 0.6	409.4 ± 0.6
C_2H_2	376.3	377.0	375.1	375.4	376.6 ± 0.6	378.0 ± 0.6
2-C_3H_8	417.7	416.9	416.2	416.3		
c-C_3H_6	412.8	412.8	411.3	411.6		
propene	390.9	389.3	388.9	389.3	389.9 ± 0.4	391.3 ± 0.3
CH_3OH	380.6	381.8	381.1	381.0	380.1 ± 0.2	381.5 ± 0.1
CH_3SH	359.8	355.7	357.4	356.9	355.5 ± 2.2	356.9 ± 2.2
CH_3CN	373.0	373.6	373.2	373.2	371.5 ± 2.1	372.9 ± 2.1
CH_3CO_2H	345.7	346.1	346.1	345.7	347.3 ± 3.0	348.7 ± 3.0

[a] The calculated energy changes are for 0 K. The 298 K data were taken from (a) ref 17, (b) ref 18, and (c) ref 16. The change in energy on going from 298 to 0 K was taken from ref 6 when available and was taken as 1.4 ± 0.2 kcal/mol for the other cases.

Table 9. Proton Affinities, kcal/mol[a]

compd	CBS-4	CBS-Q	G2(MP2)	G2	obs (0 K)	obs (298 K)
NH_3	204.4	202.6	202.5	202.5	202.6	204.0 ± 3.0
H_2O	161.2	162.6	163.1	163.1	161.5	166.5 ± 2.0
HF	110.6	113.8	114.7	114.5	116	117 ± 5
PH_3	189.4	186.3	186.8	186.2	187.2	188.6 ± 2.0
H_2S	169.2	166.6	168.5	167.7	168.8	170.2 ± 2.0
HCl	133.5	131.7	133.6	133.0	133.4	134.8 ± 2.0
$H_2C{=}CH_2$ op[b]	154.3	154.4	155.1	155.3		
$H_2C{=}CH_2$ br[c]	161.8	160.4	161.6	161.7	161.2	162.6 ± 1.0
$HC{\equiv}CH$	149.1	152.1	153.7	153.6	151.9	153.3 ± 3.0

[a] The calculated energy changes are for 0 K. The experimental data were taken from ref 24. The difference in proton affinity between 0 and 298 K was assumed to be 1.4 kcal/mol. [b] To give the open ethyl cation. [c] To give the bridged ethyl cation.

6. Summary

We report the calculated energies for 166 atoms, molecules, radicals and ions using the CBS-4, CBS-Q, G2(MP2) and G2 theoretical models. Comparison with the available experimental heats of formation, bond dissociation energies, gas phase acidities, and proton affinities consistently gives rms errors in the range of 1 to 2 kcal/mol for all theoretical models. The CBS-Q and G2 models give the most reliable heats of formation (±1.1 kcal/mol rms error) and bond dissociation energies (±1.0 kcal/mol rms error). However, the most reliable gas phase acidities are obtained from the G2 (±0.92 kcal/mol rms error) and G2(MP2) (±1.11 kcal/mol rms error) models. Although the CBS-4 model is somewhat less reliable for heats of formation (±2.1 kcal/mol rms error) and gas phase acidities (±2.0 kcal/mol rms error), this relatively inexpensive model provides bond dissociation energies (±1.2 kcal/mol rms error) that are comparable in accuracy to the most expensive calculations.

The energies of a number of additional compounds were calculated using the CBS-Q model giving the bond dissociation energies for the series of R−X bonds where R = H, CH_3, $CH_2{=}CH$, $HC{\equiv}C$ and $CH_3C{=}O$ and X = Li, BeH, BH_2, NH_2, OH, F, Na, AlH_2, PH_2, SH and Cl. They follow simple linear relationships. These bond dissociation energies along with the R−R′ and X−X′ BDE's fit a modified Pauling electronegativity relationship to within ±4.7 kcal/mol rms error.

7. Calculations

All calculations were carried out using Gaussian-93.[25]

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Supporting Information Available: An extended Table 1 including the calculated total energies (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS, can be downloaded from the Internet: see any current masthead page for ordering information and Internet access instructions.

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