Ab initio Determination of the Proton Affinities of Small Neutral and Anionic Molecules*

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The proton affinity of a molecule in the gas phase is a fundamental measure of its basicity and is the factor controlling the course of many ion-molecule reactions. In this article, *ab initio* molecular orbital theory at the MP4/6-311 ++ G(3*df*, 3*pd*) level of theory is demonstrated to predict proton affinities (PA's) for small neutral and anionic bases to within 2 kcal mol^{-1}. Furthermore, the errors are random, indicating that there are likely no systematic errors in either the experimental or theoretical PA's. Also, this level of theory is used to calibrate less sophisticated theoretical models which are suitable for larger molecules; the MP4/6-311 ++ G(2*d*, 2*p*) and MP2/6-311 ++ G(*d*, *p*) theoretical models should be particularly useful. A procedure for predicting the vibrational frequencies for anions is proposed and applied to CH_3^-, NH_2^-, OH^-, and CN^-.

INTRODUCTION

The gas phase *proton affinity* (PA) of a molecule, B, is the negative of the room temperature enthalpy change for the reaction

$$B + H^+ \rightarrow BH^+, \qquad PA \equiv -\Delta H_{298} \qquad (1)$$

It is a quantitative measure of the basicity of B and is crucial for understanding the fundamental nature of acid-base interactions and for predicting the course of ion-molecule reactions which occur in solution, in mass spectrometers, in interstellar space, and in the upper atmospheres of the earth, Jovian planets, and Saturn's moon Titan.[1] For example, tentative identification of HOC^+ was recently made[2] in the interstellar molecular cloud Sgr B2 located near the center of the Milky Way galaxy. This species is a metastable isomer of the abundant interstellar molecule HCO^+ According to models of gas-phase interstellar chemistry,[3] the predominant formation reaction for these isomers is proton transfer from protonated H_2 to CO, reactions 2.

$$CO + H_3^+ \rightarrow HCO^+ + H_2 \qquad (2a)$$

$$CO + H_3^+ \rightarrow HOC^+ + H_2 \qquad (2b)$$

One test of the proposed identification is comparison of the observed abundance of HOC^+ with theoretical estimates.[4,5] Clearly, any theory of the interstellar HOC^+ abundance depends on the energetics of reactions 2*a* and 2*b*, that is on the relative proton affinities of H_2, CO on carbon, and CO on oxygen.

Experimental determinations of *relative* proton affinities for bases B_i,

$$B_1 + B_2H^+ \rightarrow B_1H^+ + B_2, \qquad \Delta H_{298} = PA(B_2) - PA(B_1), \qquad (3)$$

are performed using several mass spectrometric techniques: high pressure mass spectrometry, ion cyclotron resonance, and sundry flow methods.[1] With these techniques, a scale of relative PA's for compounds which are more basic than water is established. Putting the scale on an absolute basis requires independent determination of the exothermicity of reaction 1 for at least one, but preferably several, bases on the scale. This has proven to be a more difficult problem than measuring the relative PA's, but a self-consistent scale of *absolute* proton affinities for compounds more basic than water is now emerging.[6] A separate scale exists where the base, B, is an anion.[7] Here, putting the scale on an absolute basis is easier because of the availability of accurate electron affinity and

This work is dedicated to Professor John Pople in honor of his contributions to computational chemistry and his 60th birthday.

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bond strength measurements which, when combined with the ionization potential of the hydrogen atom, provide the proton affinity of a negative ion via a thermochemical cycle, given below. Neutral molecules that are less basic than water are less studied than either the anions or the more basic neutrals and thus their proton affinities are not as well determined. In one of two published studies, Bohme, Mackay, and Schiff (BMS)[8] measured the PA's of some very low basicity compounds relative to the oxygen atom, which they used as their absolute reference. In the second study, McMahon and Kebarle (MK)[9] connected the very low basicity compounds studied by BMS to the proton affinity scale at water choosing the PA of ethylene as their standard. These two studies lead to very different values for the PA's of low-basicity compounds. For example, BMS place the PA of carbon monoxide at 141.4 kcal mol^{-1} while MK recommend a value of 145.6 kcal mol^{-1}.

Numerous *ab initio* molecular orbital studies of protonation have been made,[5,10–14] most of them involving positive rather than negative ions, and recently reviewed.[15] Several of the recent ones claim to determine PA's as accurately as experiment.[5,10b,10d] In some cases, theory provides PA data that cannot be obtained with the normal experiments; a case in point is the oxygen PA of CO, reaction 2*b*. In several recent papers, Pople and coworkers have developed a theoretical model which they used to compute the heats of formation of the neutral one-heavy-atom molecules AH_n (where A is Li to Cl) to an accuracy of ±2 kcal mol^{-1}.[10b,16] In this article, we use related theoretical models to compute the PA's for some one- and two-heavy-atom neutral and anionic bases. The goals of our calculations are:

1. To explore the effect of diffuse functions in the basis set on vibrational frequencies for anions
2. To compare PA's computed at the MP4SDTQ/6-311++G(3*df*, 3*pd*) level of theory with experiment to validate the theoretical model and attempt to resolve the controversy over the compounds of low PA
3. To examine the dependence of the computed PA's with respect to changes in the basis set and the basis set superposition error
4. To compute PA's with a variety of less sophisticated theories and calibrate these relative to MP4SDTQ/6-311++G(3*df*, 3*pd*)

METHODS AND RESULTS

We compute the PA, eq. 1, using the formulas:

$$\mathrm{PA} \equiv -\Delta H_{298} \tag{4a}$$

$$\Delta H_{298} = \Delta E^{\mathrm{elec}} + \Delta E^{\mathrm{vib}}_{298} + \Delta E^{\mathrm{rot}}_{298} + \Delta E^{\mathrm{trans}}_{298} + \Delta(pV)_{298} \tag{4b}$$

The Gibbs free energy change, the negative of the gas phase *basicity*, is computed using

$$\Delta G_{298} = \Delta H_{298} - T\Delta S_{298}. \tag{5}$$

The electronic energy change for the proton transfer reaction, ΔE^{elec}, is computed using *ab initio* molecular orbital theory. Geometries optimized using configuration interaction theory with all double substitutions (CID) and a polarized, split valence basis set [either 6-31G(*d*), 6-31G(*d*,*p*),[17] or, for the anions, 6-31+G(*d*) which includes diffuse functions[18]] were used for these calculations and are listed in Table I. (Some of these have been published before and are included here for completeness.[20]) This level of wave function gives geometrical parameters that are in very good agreement with experiment.[20b] ΔE^{elec} is computed at these geometries for several basis sets up to the largest, 6-311++G(3*df*, 3*pd*),[21] which is a valence-triple-split basis[22] with diffuse functions on all atoms, three sets of *d* and a set of *f* functions on the nonhydrogen atoms, and three sets of *p* and a set of *d* functions on the hydrogen atoms. Correlation energies were computed with complete fourth order Møller-Plesset perturbation theory, MP4, which includes contributions from single, double, triple, and quadruple substitutions.[23] The frozen-core approximation was used, i.e., the 1s atomic orbitals on the nonhydrogen atoms were not correlated. The electronic energies are given in Supplemental Table S1 (see Appendix) and the derived values for ΔE^{elec} are in Supplemental Table S2. The vibrational energies, $\Delta E^{\mathrm{vib}}_{298}$, were computed using standard statistical mechanical formulas and vibrational frequencies computed[24] at the HF/6-31G(*d*) level of theory and multiplied by 0.89. Vibrational frequencies so computed have been shown to

Table I. Theoretical geometries. (Bond lengths in Ångstroms, angles in degrees.)

Molecule	Point Group	Geometry[a]
CH_3^-	C_{3v}	r(CH) = 1.103, ∢(HCH) = 109.8
NH_2^-	C_{2v}	r(NH) = 1.031, ∢(HNH) = 103.4
OH^-	$C_{\infty v}$	r(OH) = 0.972
CN^-	$C_{\infty v}$	r(CN) = 1.180
CH_4	T_d	r(CH) = 1.091
NH_3	C_{3v}	r(NH) = 1.016, ∢(HNH) = 106.3
H_2O	C_{2v}	r(OH) = 0.996, ∢(HOH) = 104.3
HF	$C_{\infty v}$	r(HF) = 0.931
CO	$C_{\infty v}$	r(CO) = 1.133
HCN	$C_{\infty v}$	r(CH) = 1.067, r(CN) = 1.154
N_2	$D_{\infty h}$	r(NN) = 1.104
O_2	$D_{\infty h}$	r(OO) = 1.206
CH_5^+	C_s	r_1 = 1.090, r_2 = 1.103, r_3 = 1.143, r_4 = 1.194, α = 129.0, β = 80.2, θ = 45.3, ξ = 118.2
NH_4^+	T_d	r(NH) = 1.027
OH^+	$C_{\infty v}$	r(OH) = 1.038
H_3O^+	C_{3v}	r(OH) = 0.987, ∢(HOH) = 111.6
H_2F^+	C_{2v}	r(HC) = 0.981, ∢(HFH) = 111.7
HCO^+	$C_{\infty v}$	r(CH) = 1.088, r(CO) = 1.109
HOC^+	$C_{\infty v}$	r(OH) = 0.986, r(CO) = 1.158
$HCNH^+$	$C_{\infty v}$	r(CH) = 1.081, r(NH) = 1.015, r(CN) = 1.136
N_2H^+	$C_{\infty v}$	r(NH) = 1.036, r(NN) = 1.097
O_2H^+	C_s	r(OH) = 1.005, r(OO) = 1.230, ∢(HOO) = 112.1

[a]All geometries were computed at the CID/6-31G(d) level of theory except HCO^+, HOC^+, and O_2H^+ which are at CID/6-31G(d,p) and the anions which are CID/6-31 + G(d). The parameters defining the CH_5^+ structure are given in ref. 19.

be in very good agreement with experiment for neutral[25] and positively charged[26] molecules with as many frequencies that are too low as are too high, leading to a cancellation of errors. The accuracy of scaled HF/6-31G(d) vibrational frequencies has not been demonstrated for negative ions, however. Since diffuse functions have a significant effect on computed equilibrium geometries[18] and presumably on the vibrational frequencies as well, we have computed vibrational frequencies for several anions with the 6-31G(d) basis set and the diffuse function augmented 6-31+G(d) basis. These are presented in Table II where the basis set dependence is clearly demonstrated. The HF/6-31+G(d) frequencies, scaled by 0.89, were used to derive the various thermodynamic quantities for the anions. The rotational and translational energies, ΔE_{298}^{rot} and ΔE_{298}^{trans}, were computed classically. The pressure-volume work term, $\Delta(pV)_{298}$, was computed using the ideal gas law, and, for reaction 1, is $-RT$ where R is

Table II. Computed vibrational frequencies of anions (cm^{-1}).[a]

Molecule		HF/6-31G(d)	HF/6-31 + G(d)
CH_3^-	a_1	2852	3045
		1230	880
	e	2849	3109
		1630	1577
NH_2^-	a_1	3299	3481
		1747	1663
	b_2	3328	3555
OH^-	σ	3739	3969
CN^-	σ	2360	2330

[a]These have not been scaled and are thus not appropriate for comparison with experiment. (see text.)

Table III. Theoretical thermodynamic quantities.[a]

Molecule	Zero-point energy (kcal/mol)	E_{298} (kcal/mol)	S_{298} (cal/deg-mol)
CH_3^-	16.919	18.758	46.223
NH_2^-	11.068	12.849	45.067
OH^-	5.050	6.531	41.110
F^-	0.0	0.889	34.767
CN^-	2.965	4.446	46.980
CH_4	26.682	28.485	44.442
NH_3	20.665	22.463	45.893
O	0.0	0.889	36.437
H_2O	12.832	14.612	44.991
HF	5.545	7.026	41.436
CO	3.103	4.585	47.150
HCN	10.047	11.630	47.982
N_2	3.509	4.990	45.687
O_2	2.543	4.025	48.851
CH_5^+	31.026	33.279	53.450
NH_4^+	29.756	31.548	44.351
OH^+	4.267	5.748	43.539
H_3O^+	20.513	22.339	46.139
H_2F^+	11.186	12.969	45.480
HCO^+	10.106	11.660	48.055
HOC^+	7.763	10.125	54.051
$HCNH^+$	17.037	18.738	48.965
N_2H^+	10.084	11.699	48.228
O_2H^+	8.186	9.980	55.091

[a]Computed for an ideal gas at STP with scaled HF/6-31G(d) vibrational frequencies (HF/6-31 + G(d) for anions) and classical rotations and translations.

the gas constant. Table III contains zero-point vibrational energies, internal energies,

$$E_{298} = E_{298}^{vib} + E_{298}^{rot} + E_{298}^{trans} \quad (6)$$

and entropies,

$$S_{298} = S_{298}^{vib} + S_{298}^{rot} + S_{298}^{trans} \quad (7)$$

computed using the methods just described. All calculations were performed for an ideal gas at a pressure of 1 atm and a temperature of 298.15 K. Thermodynamic quantities for

proton transfer reactions (1) are displayed in Table IV. The electronic energy change, ΔE^{elec}, has been broken into a Hartree-Fock (HF) and a correlation component,

$$\Delta E^{elec} = \Delta E^{HF} + \Delta E^{corr} \quad (8)$$

Included among the bases, B, are some with PA's greater than those of water to assess the theory, some of low PA to resolve the experimental controversy described above, and some anions to assess the applicability of the theory to negatively charged systems.

Besides computing the electronic energy at the MP4SDTQ/6-311++G(3*df*, 3*pd*) level of theory (generally we will write MP4SDTQ as simply MP4), calculations were performed at several lower levels to provide guidance in the choice of a theoretical model when MP4/6-311++G(3*df*, 3*pd*) is impractical. These include Hartree-Fock self-consistent-field (SCF) theory and second (MP2), third (MP3), and complete fourth (MP4) order Møller-Plesset perturbation theory[23] with a series of basis sets of increasing complexity. These are split-valence polarized 6-31G(*d*,*p*)[17], and the valence-triple-split polarized basis 6-311G(*d*,*p*).[22] The latter is extended[21] through the addition of diffuse functions, 6-311++G(*d*,*p*), and by expansion of the polarization space to double polarization (2*d*, 2*p*), single polarization with *f* functions on non-hydrogen atoms and *d* functions on hydrogen (*df*, *pd*), double polarization with *f*'s and *d*'s (2*df*, 2*pd*), and finally triple polarization with *f*'s and *d*'s (3*df*, 3*pd*). The computed total energies and ΔE^{elec} for these methods are in the Supplemental Tables S1 and S2 (see Appendix).

DISCUSSION

The data in Table II demonstrate that diffuse functions have an effect on the computed vibrational frequencies as large as several hundreds of wavenumbers for negatively charged molecules. For neutral molecules and for cations, adding diffuse functions has a negligible effect as does adding diffuse functions to the hydrogen atoms of the anions. Most of the frequencies become larger when diffuse functions are added, the exceptions being bending motions in CH_3^- and the stretch in CN^-. (This is consistent with the bond shortening that is observed in theoretical equilibrium geometries when diffuse functions are added to the basis set.[18]) This leads to an increase in the molecule's zero-point vibrational energy with the net effect on the proton affinity being an increase which, for the small anionic bases studied here, is less than 0.5 kcal mol^{-1}. We have chosen to use the 6-31+G(*d*) frequencies scaled by 0.89 as the basis for our thermochemical calculations. This leads to frequency predictions that are in reasonable accord with published *ab initio* values for cyanide,[28] 2052 cm^{-1}, and for hydroxide,[29] 3639 cm^{-1}, and it is consistent with the procedure used for the cations and neutral molecules. The factor of 0.89 was derived by comparing theoretical and experi-

Table IV. Theoretical thermodynamic quantities for B + $H^+ \rightarrow BH^+$ (kcal mol^{-1}).[a]

Base[b]	ΔE^{HF}	ΔE^{corr}	ΔH_0	ΔH_{298}	$-T\Delta S_{298}$	ΔG_{298}
O_2	−114.0	9.4	−98.9	−100.1	5.9	−94.2
OC	−113.0	6.2	−102.2	−102.8	5.7	−97.1
HF	−121.7	0.3	−115.7	−116.9	6.5	−110.4
O	−119.9	−1.5	−117.2	−118.1	5.6	−112.4
N_2	−120.8	−2.6	−116.8	−118.2	7.0	−111.2
CH_4	−130.6	−2.3	−128.5	−129.5	5.1	−124.5
CO	−144.4	−4.4	−141.8	−143.2	7.5	−135.7
H_2O	−174.7	3.4	−163.6	−165.1	7.4	−157.7
HCN	−180.0	4.4	−168.6	−170.0	7.5	−162.5
NH_3	−215.5	3.9	−202.5	−204.0	8.2	−195.8
CN^-	−355.9	−0.5	−349.3	−350.7	7.5	−343.2
F^-	−383.5	5.9	−372.0	−372.9	5.8	−367.2
OH^-	−407.6	9.8	−390.0	−391.2	6.6	−384.6
NH_2^-	−422.1	9.7	−402.8	−404.3	7.5	−396.7
CH_3^-	−433.5	7.8	−415.9	−417.5	8.3	−409.2

[a]Computed with data from Table S2 at the MP4/6-311++G(3*df*, 3*pd*) level, except CH_4 and O_2 which are MP4/6-311++G(2*df*, 2*pd*), and data from Table III.
[b]"OC" designates protonation of carbon monoxide on oxygen, "CO" on carbon.

mental frequencies for neutral molecules[25] and it has been shown to be effective in the computation of cation frequencies as well.[26] Unfortunately, no gas-phase vibrational frequencies for negative ions have been reported thus no direct experimental justification for using this procedure for anions is available. However, the methods that have been developed for measuring the spectra of cations[30] are equally applicable to anions and the availability of such spectra will allow our proposed scheme to be tested. In the meantime, the scaled 6-31 + G(d) frequencies should be useful to the spectroscopists as a guide in finding the first anion vibrational band.

Experimental and theoretical proton affinities are compared in Table V. Of the levels of theory used, agreement versus experiment is best at MP4/6-311++G(3df, 3pd). For neutral bases, the experimental values are from the recent compilation of Lias et al.[6] This critical compilation of measured proton affinities is the most recent and complete; for a uniform comparison it is best to use experimental PA's from a single source. For anionic bases, the values are those computed by Bartmess et al.[7] with the thermodynamic cycle

$$\mathrm{AH} = \mathrm{A} + \mathrm{H}, \qquad \Delta H_{298} = DH(\mathrm{A} - \mathrm{H}) \quad (9)$$

$$\mathrm{A} + \mathrm{H} = \mathrm{A}^- + \mathrm{H}^+, \qquad \Delta H_{298} \simeq \Delta H_0 = IP(\mathrm{H}) - EA(\mathrm{A}) \quad (10)$$

$$\mathrm{AH} = \mathrm{A}^- + \mathrm{H}^+, \qquad \Delta H_{298} = PA(\mathrm{A}^-) \quad (11)$$

$$PA(\mathrm{A}^-) \simeq DH(\mathrm{A\text{-}H}) + IP(\mathrm{H}) - EA(\mathrm{A}) \quad (12)$$

where DH(A-H) is the homolytic A-H bond dissociation energy, IP(H) is the ionization potential for the hydrogen atom, and EA(A) is the electron affinity for the molecule A. The bond strengths were updated using data from the 1982 JANAF tables.[31] For the bases of low PA the values of BMS and of MK are also given in Table V. The agreement between theory and experiment is excellent, the mean absolute error is 1.0 kcal mol^{-1} for these 14 bases; all except CH_4 are within 2 kcal mol^{-1} of the experimental value. (The PA's of methane and of molecular oxygen were computed with the 6-311 ++ G(2df, 2pd) basis set. The mean absolute error with experiment using this basis at the MP4 level is 1.5 kcal mol^{-1} with the largest absolute error being 3.6 kcal mol^{-1}. Thus, if the experimental PA for methane is correct, it seems reasonable to expect that the MP4/6-311 ++ G(3df, 3pd) PA will be in error by less than 2 kcal mol^{-1}.) Furthermore, the theoretical PA's are equally distributed between those that are larger and those that are smaller than the experimental values, indicating that either there are no systematic errors in either

Table V. Theoretical and experimental proton affinities (kcal mol^{-1}).

Base[a]	Theory[b]	Experiment[c]	BMS[d]	MK[e]
O_2	100.1	100.9 ± 0.5	100.4 ± 0.4	
OC	102.8			
HF	116.9	117. ± 1		120.4
O	118.1	116.3 ± 1	116.1 ± 0.2	120.7
N_2	118.2	118.2 ± 1	117.4 ± 0.7	122.0
CH_4	129.5	132.0 ± 1	130.5 ± 2	134.7 ± 1
CO	143.2	141.9 ± 2	141.4 ± 0.4	145.6 ± 1
H_2O	165.1	166.5 ± 2		
HCN	170.0	171.4 ± 2		
NH_3	204.0	204.0 ± 3		
CN^-	350.7	349.4 ± 1.8		
F^-	372.9	371.3 ± 0.7		
OH^-	391.2	390.7 ± 0.4		
NH_2^-	404.3	405.0 ± 2.1		
CH_3^-	417.5	416.9 ± 0.9		

[a]"OC" designates protonation of carbon monoxide on oxygen, "CO" on carbon.
[b]From Table IV.
[c]For neutral bases taken from ref. 6, for anions from Table I of ref. 7 with updated bond strengths from ref. 31, for cyanide the value relative to SH^-, ref. 27, was used along with the PA for SH^- computed as for the other anions from ref. 7.
[d]Reference 8.
[e]Reference 9.

set of PA's or that systematic errors are in the same direction in the theoretical and experimental results. The *ab initio* proton affinities are in substantially better accord with the values recommended by BMS for the low end of the PA scale than with the more recent data of MK. The mean absolute differences are 1.4 and 3.5 kcal mol^{-1}, respectively.

The basis set superposition error (BSSE)[32] is a potential source for systematic error in the computed proton affinities. Except in the complete basis set limit, the basis set describing the protonated species for reaction (1), BH^+, is better than that used for the conjugate base, B, leading to proton affinity predictions that are too large. An upper limit to the magnitude of the BSSE can be estimated using the Boys-Bernardi counterpoise method.[32a] While it doesn't provide a sufficiently accurate accounting of the BSSE to be used to correct the computed PA,[32d] it should give some indication of the magnitude of the effect. We computed the BSSE using the counterpoise method for the protonations of hydrogen fluoride and of hydroxide with a variety of basis sets at the HF and the MP4 levels of theory, Table VI. The effect is much larger at the correlated MP4 level than at the HF level; even for the larger basis sets where it has converged to 0.4 kcal mol^{-1} at the HF level it is in the range of 2–4 kcal mol^{-1} at the MP4 level. This clearly could lead to a significant systematic error in the theoretical proton affinities. Furthermore, the size of the error is relatively insensitive to additions to the basis set beyond 6-311 ++ G(2*d*, 2*p*). The excellent agreement between theory and experiment displayed in Table V, in particular the lack of evidence for systematic error, can be explained in light of the BSSE by one or more of the following:

1. The BSSE is significantly smaller for the 6-311 ++ G(3*df*, 3*pd*) basis set than the upper limit estimated with the counterpoise procedure. In part, this may be because the BSSE is expected to be largest for compounds containing electronegative atoms like oxygen and fluorine.
2. The theoretical PA's are indeed systematically too large, but so are the experimental values by an equal amount, so that the effect is not apparent.

Table VI. Counterpoise estimates of the basis set superposition error in the PA as a function of basis set (kcal mol^{-1}).

Basis	HF/H_2F^+ HF	HF/H_2F^+ MP4	OH^-/H_2O HF	OH^-/H_2O MP4
6-31G(*d*,*p*)	1.9	4.5	6.0	11.2
6-311G(*d*,*p*)	1.4	5.0	8.4	16.3
6-311 ++ G(*d*,*p*)	0.4	3.4	0.4	5.2
6-311 ++ G(*df*,*pd*)	0.5	4.8	0.5	6.2
6-311 ++ G(2*d*, 2*p*)	0.4	2.2	0.4	4.0
6-311 ++ G(2*df*, 2*pd*)	0.4	2.5	0.4	4.1
6-311 ++ G((3*df*, 3*pd*)	0.4	1.9	0.4	3.0

3. The BSSE error in the theoretical PA's is counteracted by other deficiencies in the theoretical model of equal magnitude but opposite sign.

Determining the relative importance of these factors must wait, in part, for further refinements in the experimental data. However, it seems more likely that 1 and 3 provide the explanation rather than 2.

Proton affinities computed with less sophisticated models are compared with the MP4/6-311 ++ G(3*df*, 3*pd*) level of theory in Table VII. The mean and maximum absolute differences are given at each level of theory for all thirteen compounds, including neutral and anionic bases, and for the eight neutral compounds only. The table is ordered for increasing mean error for the complete set of compounds, including anions, although the order is roughly the same if the anions are excluded. In particular, the diffuse functions are as necessary for good agreement with experiment for the neutral bases as they are for the anions. This is consistent with the notion[16a] that the diffuse functions are needed for a proper description of lone pairs as all of the molecules studied are lone pair bases. (Note that CH_4 and O_2 are not included in this comparison.) For the better methods, the anions are as well described as are the neutrals. However, as the overall level of agreement with the MP4/6-311 ++ G(3*df*, 3*pd*) model decreases, the discrepancy between the level of agreement for neutral and anionic bases increases, until for the basis sets which exclude diffuse functions there is a very large difference indeed. This reflects the greater difficulty of describing the negative ions, although the best methods do so well. The even-powered orders of perturbation theory, MP2

Table VII. Comparisons of ΔE^{elec} computed with various theoretical models relative to MP4/6-311 + + G(3*df*, 3*pd*) (kcal mol^{-1}).

Procedure	Basis	All Bases Mean	All Bases Max	Neutral Bases Mean	Neutral Bases Max
MP4	6-311 + + G(3*df*, 3*pd*)	0.0	0.0	0.0	0.0
MP4	6-311 + + G(2*d*, 2*p*)	0.7	1.8	0.8	1.8
MP2	6-311 + +G(2*df*, 2*pd*)	0.7	2.9	1.0	2.9
MP4	6-311 + + G(2*df*, 2*pd*)	0.9	2.0	0.4	0.8
MP2	6-311 + + G(3*df*, 3*pd*)	1.1	2.8	1.1	2.8
MP2	6-311 + + G(*d*, *p*)	1.3	3.7	1.4	3.7
MP2	6-311 + + G(2*d*, 2*p*)	1.4	4.8	1.6	4.8
MP4	6-311 + + G(*d*, *p*)	1.5	3.5	1.2	2.9
MP2	6-311 + + G(*df*, *pd*)	1.9	3.4	1.4	2.4
MP3	6-311 + + G(2*d*, 2*p*)	2.1	6.2	1.1	2.3
MP3	6-311 + + G(3*df*, 3*pd*)	2.2	6.1	1.2	2.8
MP3	6-311 + + G(2*df*, 2*pd*)	2.8	7.4	1.4	2.7
MP4	6-311 + + G(*df*, *pd*)	2.9	4.9	2.2	3.5
MP3	6-311 + +G(*d*, *p*)	3.3	7.9	1.9	3.7
HF	6-311 + + G(2*d*, 2*p*)	4.5	9.9	3.3	5.3
HF	6-311 + + G(*d*, *p*)	4.6	9.8	3.7	5.4
HF	6-311 + + G(3*df*, 3*pd*)	4.6	9.8	3.3	6.2
HF	6-311 + + G(2*df*, 2*pd*)	4.6	9.9	3.4	6.0
MP3	6-311 + + G(*df*, *pd*)	4.7	10.4	2.9	4.6
HF	6-311 + + G(*df*, *pd*)	4.8	10.1	3.7	6.8
HF	6-311G(*d*, *p*)	11.7	31.8	4.2	6.9
MP2	6-311G(*d*, *p*)	12.2	35.3	3.3	7.2
MP4	6-311G(*d*, *p*)	13.2	37.0	3.9	8.1
MP3	6-311G(*d*, *p*)	13.3	37.2	4.1	8.3
HF	6-31G(*d*, *p*)	15.3	36.6	5.6	8.6
MP2	6-31G(*d*, *p*)	16.0	41.5	4.2	8.7
MP3	6-31G(*d*, *p*)	17.1	42.0	5.4	9.3
MP4	6-31G(*d*, *p*)	17.3	43.2	5.5	9.4

and MP4, are in general superior to the odd orders, HF and MP3. For several of the basis sets, the MP2 results are comparable to the much more expensive fourth order results with the same basis set. The MP4/6-311 ++ G(2*d*, 2*p*)and MP2/6-311 ++ G(*d*, *p*) levels of theory would appear particularly cost-effective for the computation of proton affinities; the mean absolute errors relative to experiment (for all compounds) are 1.3 and 1.9 kcal mol^{-1} with the maximum absolute error being 3.6 and 5.9 kcal mol^{-1}, respectively. A similar comparative analysis of theoretical models has been performed[33] for calculations on the H_2F and H_2CO potential energy surfaces. Those data are compared with the PA data in Table VIII. The most striking differences are for the methods that do not include diffuse functions; while they are essential in the PA calculations, they do not play as crucial a role on the neutral surfaces.

Table VIII. Comparison of the performance of various theoretical models on charged and neutral surfaces (kcal mol^{-1}).[a]

	Method	Ions	Neutrals
3(a)	HF/6-31G(*d*, *p*)	5.0	13.5
4(a)	MP2/6-31G(*d*, *p*)	5.6	5.0
5(a)	MP4/6-31G(*d*, *p*)	16.9	5.2
6(a)	MP4/6-311 ++ G(*d*, *p*)	1.5	2.0
7(a)	MP4/6-311 + + G(*df*, *pd*)	2.9	0.7
8	MP4/6-311 + + G(2*df*, 2*pd*)	0.8	0.4
9	MP4/6-311 + + G(3*df*, 3*pd*)	0.0	0.0

[a]Using the numbering and the "neutral" results on H_2F and H_2CO from ref. 33 and the "ions" results from this work.

CONCLUSIONS

1. The addition of diffuse functions to the basis sets used to describe negative ions generally increases the computed vibrational frequency by as much as several hundreds of wavenumbers. This has a small but significant effect on the computed thermochemistry for protonation of these small anions; the effect could be larger for bigger molecules with more vibrational degrees of freedom. The frequencies reported here can be used by spectroscopists as a guide in their efforts to detect infrared

spectra of gas-phase anions. Such a detection will provide the final test of the applicability of the scaling factor of 0.89 to the HF/6-31+G(d) frequencies.

2. The *ab initio* proton affinities are in excellent agreement with the experimental values with the theoretical PA's being both larger and smaller than the experimental results. The mean absolute error is 1.0 kcal mol^{-1} and all of the MP4/6-311++G(3df, 3pd) values are within 2 kcal mol^{-1} of experiment. Theory supports the assignments of Bohme, MacKay, and Schiff[8] relative to those of McMahon and Kebarle[9] for the low-PA bases. The level of agreement between theory and experiment is as good for the anionic as for the uncharged bases.
3. The basis set superposition error apparently does not lead to systematic errors in the computed proton affinities. This is probably because of a cancellation of the BSSE with other deficiencies in the theoretical model but conceivably could be due to a fortuitous agreement with a systematic error in the experimental PA's.
4. Diffuse functions are crucial for achieving good agreement between theory and experiment for these proton affinities, and the even orders of perturbation theory are generally superior to the odd orders. The MP4/6-311++G(2d, 2p) and MP2/6-311++G(d, p) levels of theory should be particularly useful for computing proton affinities in larger systems.

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APPENDIX

Table S1. Total energies, E^{elec} (hartrees).

	Basis	HF	MP2	MP3	MP4
CH_3^-	6-31G(d,p)	-39.4684754	-39.6265078	-39.6425810	-39.6488033
	6-311G(d,p)	-39.4941739	-39.6668352	-39.6829866	-39.6904388
	6-311++G(d,p)	-39.5180880	-39.6984931	-39.7119833	-39.7216602
	6-311++G(df,pd)	-39.5192760	-39.7167860	-39.7298902	-39.7398864
	6-311++G(2d,2p)	-39.5208813	-39.7159338	-39.7290348	-39.7393191
	6-311++G(2df,2pd)	-39.5216181	-39.7322929	-39.7451330	-39.7557369
	6-311++G(3df,3pd)	-39.5216411	-39.7356285	-39.7481575	-39.7593095
NH_2^-	6-31G(d,p)	-55.4833955	-55.6685340	-55.6788207	-55.6846818
	6-311G(d,p)	-55.5038903	-55.7023382	-55.7109223	-55.7194331
	6-311++G(d,p)	-55.5411557	-55.7556605	-55.7572627	-55.7718816
	6-311++G(df,pd)	-55.5422911	-55.7773684	-55.7795416	-55.7942994
	6-311++G(2d,2p)	-55.5444078	-55.7773119	-55.7782550	-55.7938212
	6-311++G(2df,3pd)	-55.5454635	-55.7970806	-55.7985803	-55.8143261
	6-311++G(3df,3pd)	-55.5458725	-55.8021205	-55.8030450	-55.8198701
OH^-	6-31G(d,p)	-75.3324966	-75.5260633	-75.5301606	-75.5347296
	6-311G(d,p)	-75.3610786	-75.5735859	-75.5749698	-75.5832385
	6-311++G(d,p)	-75.4050289	-75.6401713	-75.6309089	-75.6501120
	6-311++G(df,pd)	-75.4062818	-75.6638694	-75.6558836	-75.6748923
	6-311++G(2d,2p)	-75.4067944	-75.6639623	-75.6542412	-75.6742442
	6-311++G(2df,2pd)	-75.4078752	-75.6854458	-75.6770031	-75.6969687
	6-311++G(3df,3pd)	-75.4084434	-75.6921867	-75.6831801	-75.7046989
F^-	6-31G(d,p)	-99.3504820	-99.5266066	-99.5275062	-99.5307477
	6-311G(d,p)	-99.4028924	-99.6132607	-99.6112153	-99.6170987
	6-311++G(d,p)	-99.4456557	-99.6786867	-99.6668982	-99.6844252
	6-311++G(df,pd)	-99.4456557	-99.7000308	-99.6899182	-99.7069904
	6-311++G(2d,2p)	-99.4456557	-99.7038310	-99.6921524	-99.7097732
	6-311++G(2df,2pd)	-99.4456557	-99.7248163	-99.7150205	-99.7324085
	6-311++G(3df,3pd)	-99.4456557	-99.7321343	-99.7219881	-99.7411325
CN^-	6-31G(d,p)	-92.2849035	-92.5622113	-92.5632143	-92.5834355
	6-311G(d,p)	-92.3179994	-92.6108890	-92.6090828	-92.6334553
	6-311++G(d,p)	-92.3336964	-92.6336960	-92.6293066	-92.6564839
	6-311++G(df,pd)	-92.3360010	-92.6623307	-92.6589054	-92.6864914
	6-311++G(2d,2p)	-92.3368380	-92.6555680	-92.6514013	-92.6795181
	6-311++G(2df,2pd)	-92.3390441	-92.6815266	-92.6782068	-92.7065639
	6-311++G(3df,3pd)	-92.3399730	-92.6867994	-92.6829839	-92.7119558

	Basis	HF	MP2	MP3	MP4
CH_4	6-31G(d,p)	-40.2015584	-40.3645472	-40.3827702	-40.3886301
	6-311G(d,p)	-40.2088937	-40.3792322	-40.3982974	-40.4050505
	6-311++G(d,p)	-40.2090354	-40.3796369	-40.3986892	-40.4054775
	6-311++G(df,pd)	-40.2102771	-40.3991637	-40.4179186	-40.4250602
	6-311++G(2d,2p)	-40.2119516	-40.3936525	-40.4119535	-40.4193883
	6-311++G(2df,2pd)	-40.2126152	-40.4107326	-40.4289305	-40.4366597
	6-311++G(3df,3pd)	-40.2124042	-40.4119051	-40.4297993	-40.4377123
NH_3	6-31G(d,p)	-56.1949383	-56.3831765	-56.3959298	-56.4014027
	6-311G(d,p)	-56.2098126	-56.4087660	-56.4205213	-56.4280451
	6-311++G(d,p)	-56.2140185	-56.4154634	-56.4263655	-56.4345699
	6-311++G(df,pd)	-56.2155772	-56.4392064	-56.4507041	-56.4593406
	6-311++G(2d,2p)	-56.2173618	-56.4334096	-56.4436741	-56.4528498
	6-311++G(2df,2pd)	-56.2183956	-56.4540602	-56.4648389	-56.4743751
	6-311++G(3df,3pd)	-56.2185010	-56.4567801	-56.4671187	-56.4770579
O	6-31G(d,p)	-74.7839336	-74.8800367	-74.8932179	-74.8959730
	6-311G(d,p)	-74.8052114	-74.9181454	-74.9308731	-74.9333269
	6-311++G(d,p)	-74.8073964	-74.9217813	-74.9344308	-74.9372398
	6-311++G(df,pd)	-74.8085119	-74.9370255	-74.9506584	-74.9535890
	6-311++G(2d,2p)	-74.8080594	-74.9351744	-74.9487932	-74.9523101
	6-311++G(2df,2pd)	-74.8092071	-74.9500366	-74.9647066	-74.9684261
	6-311++G(3df,3pd)	-74.8093404	-74.9524213	-74.9669835	-74.9709351
H_2O	6-31G(d,p)	-76.0225389	-76.2197426	-76.2260063	-76.2312043
	6-311G(d,p)	-76.0457548	-76.2637382	-76.2681148	-76.2761362
	6-311++G(d,p)	-76.0521621	-76.2748232	-76.2773566	-76.2871780
	6-311++G(df,pd)	-76.0546191	-76.3025384	-76.3063814	-76.3164849
	6-311++G(2d,2p)	-76.0554299	-76.2961889	-76.2981049	-76.3091345
	6-311++G(2df,2pd)	-76.0570823	-76.3197332	-76.3227493	-76.3340687
	6-311++G(3df,3pd)	-76.0579992	-76.3241962	-76.3267565	-76.3386409
HF	6-31G(d,p)	-100.0105750	-100.1945380	-100.1962240	-100.2013220
	6-311G(d,p)	-100.0454280	-100.2668510	-100.2667630	-100.2738630
	6-311++G(d,p)	-100.0519570	-100.2786690	-100.2765200	-100.2860300
	6-311++G(df,pd)	-100.0546940	-100.3071250	-100.3067450	-100.3163320
	6-311++G(2d,2p)	-100.0542470	-100.3028760	-100.3004410	-100.3109370
	6-311++G(2df,2pd)	-100.0558060	-100.3272890	-100.3265220	-100.3371950
	6-311++G(3df,3pd)	-100.0567540	-100.3326000	-100.3314350	-100.3428660
CO	6-31G(d,p)	-112.7369100	-113.0204920	-113.0184500	-113.0421570
	6-311G(d,p)	-112.7674110	-113.0746830	-113.0700270	-113.0982460
	6-311G(d,p)	-112.7674110	-113.0746830	-113.0700270	-113.0982460
	6-311++G(d,p)	-112.7690470	-113.0780640	-113.0729580	-113.1018720
	6-311++G(df,pd)	-112.7739520	-113.1115270	-113.1079130	-113.1367840
	6-311++G(2d,2p)	-112.7731000	-113.1006580	-113.0954670	-113.1249490
	6-311++G(2df,2pd)	-112.7765150	-113.1299970	-113.1260910	-113.1555410
	6-311++G(3df,3pd)	-112.7789060	-113.1367190	-113.1324900	-113.1623660
HCN	6-31G(d,p)	-92.8758728	-93.1649982	-93.1660892	-93.1871842
	6-311G(d,p)	-92.8979174	-93.1996539	-93.1986070	-93.2232696
	6-311++G(d,p)	-92.8995232	-93.2026244	-93.2011129	-93.2262507
	6-311++G(df,pd)	-92.9024682	-93.2318909	-93.2313503	-93.2568806
	6-311++G(2d,2p)	-92.9028225	-93.2221549	-93.2203866	-93.2466817
	6-311++G(2df,2pd)	-92.9061585	-93.2501555	-93.2494010	-93.2759173
	6-311++G(3df,3pd)	-92.9071637	-93.2541772	-93.2528905	-93.2799196
N_2	6-31G(d.p)	-108.9417230	-109.2535530	-109.2477430	-109.2715660
	6-311G(d,p)	-108.9681960	-109.2964220	-109.2870170	-109.3159040
	6-311++G(d,p)	-108.9704200	-109.3009350	-109.2908490	-109.3205840
	6-311++G(df,pd)	-108.9727330	-109.3315400	-109.3225630	-109.3526420
	6-311++G(2d,2p)	-108.9757000	-109.3228850	-109.3131900	-109.3440940
	6-311++G(2df,2pd)	-108.9793160	-109.3520700	-109.3435910	-109.3745520
	6-311++G(3df,3pd)	-108.9803280	-109.3570920	-109.3481600	-109.3796350
O_2	6-31G(d,p)	-149.6150660	-149.9476870	-149.9431410	-149.9632860
	6-311G(d,p)	-149.6553840	-150.0234710	-150.0158200	-150.0418130
	6-311++G(d,p)	-149.6598850	-150.0294820	-150.0217150	-150.0486860
	6-311++G(df,pd)	-149.6638190	-150.0691360	-150.0639130	-150.0914230
	6-311++G(2d,2p)	-149.6661880	-150.0619470	-150.0539620	-150.0830640
	6-311++G(2df,2pd)	-149.6711210	-150.1012760	-150.0957430	-150.1253850
	6-311++G(3df,3pd)	-149.6726680	-150.1079600	-150.1024870	-150.1327740
CH_5^+	6-31G(d,p)	-40.4052428	-40.5746701	-40.5937803	-40.5996906
	6-311G(d,p)	-40.4156538	-40.5898628	-40.6098428	-40.6165952
	6-311++G(d,p)	-40.4159237	-40.5903603	-40.6103481	-40.6171198
	6-311++G(df,pd)	-40.4173312	-40.6110188	-40.6308526	-40.6380293
	6-311++G(2d,2p)	-40.4194244	-40.6030130	-40.6220067	-40.6293125
	6-311++G(2df,2pd)	-40.4207009	-40.6216710	-40.6407331	-40.6483796

	Basis	HF	MP2	MP3	MP4
NH_4^+	6-31G(d,p)	-56.5447906	-56.7336339	-56.7480067	-56.7533069
	6-311G(d,p)	-56.5580400	-56.7550727	-56.7688609	-56.7758178
	6-311++G(d,p)	-56.5584534	-56.7556729	-56.7694784	-56.7764554
	6-311++G(2d,2p)	-56.5614249	-56.7703909	-56.7835151	-56.7911698
	6-311++G(df,pd)	-56.5598495	-56.7796023	-56.7940529	-56.8014921
	6-311++G(2df,2pd)	-56.5624466	-56.7911068	-56.8048103	-56.8128460
	6-311++G(3df,3pd)	-56.5619307	-56.7927602	-56.8060948	-56.8143314
OH^+	6-31G(d,p)	-74.9740892	-75.0746527	-75.0892991	-75.0930789
	6-311G(d,p)	-74.9963131	-75.1143531	-75.1288157	-75.1323998
	6-311++G(d,p)	-74.9972221	-75.1153599	-75.1298481	-75.1334703
	6-311++G(df,pd)	-74.9984192	-75.1319236	-75.1472958	-75.1510961
	6-311++G(2d,2p)	-74.9989321	-75.1268684	-75.1417610	-75.1459285
	6-311++G(2df,2pd)	-74.9996817	-75.1415314	-75.1571924	-75.1615352
	6-311++G(3df,3pd)	-75.0004244	-75.1445274	-75.1600757	-75.1644716
H_3O^+	6-31G(d,p)	-76.3082426	-76.5059493	-76.5137428	-76.5190655
	6-311G(d,p)	-76.3297581	-76.5482415	-76.5544357	-76.5620467
	6-311++G(d,p)	-76.3305579	-76.5499224	-76.5559165	-76.5638557
	6-311++G(df,pd)	-76.3338487	-76.5794548	-76.5867985	-76.5951122
	6-311++G(2d,2p)	-76.3332797	-76.5678119	-76.5733342	-76.5821644
	6-311++G(2df,2pd)	-76.3352864	-76.5919778	-76.5985606	-76.6077021
	6-311++G(3df,3pd)	-76.3364553	-76.5960391	-76.6022812	-76.6116772
H_2F^+	6-31G(d,p)	-100.2124670	-100.4017580	-100.4036200	-100.4098010
	6-311G(d,p)	-100.2408590	-100.4685230	-100.4691130	-100.4769100
	6-311++G(d,p)	-100.2418660	-100.4707050	-100.4709890	-100.4794180
	6-311++G(df,pd)	-100.2475910	-100.5041850	-100.5063310	-100.5149730
	6-311++G(2d,2p)	-100.2460850	-100.4939470	-100.4938410	-100.5032250
	6-311++G(2df,2pd)	-100.2488470	-100.5202640	-100.5217600	-100.5313680
	6-311++G(3df,3pd)	-100.2506570	-100.5251790	-100.5263650	-100.5363030
HCO^+	6-31G(d,p)	-112.9666610	-113.2635250	-113.2572480	-113.2837960
	6-311G(d,p)	-112.9969520	-113.3163310	-113.3077390	-113.3385410
	6-311++G(d,p)	-112.9975960	-113.3177050	-113.3089830	-113.3400320
	6-311++G(2d,2p)	-113.0017730	-113.3379400	-113.3288950	-113.3605640
	6-311++G(2df,2pd)	-113.0064570	-113.3692470	-113.3617010	-113.3933130
	6-311++G(3df,3pd)	-113.0089870	-113.3753390	-113.3674880	-113.3994560
	6-311++G(df,pd)	-113.0031200	-113.3516120	-113.3445090	-113.3754300
HOC^+	6-31G(d,p)	-112.9207680	-113.1929960	-113.1993530	-113.2206370
	6-311G(d,p)	-112.9464110	-113.2411040	-113.2455550	-113.2699230
	6-311++G(d,p)	-112.9472110	-113.2424530	-113.2469470	-113.2714190
	6-311++G(2d,2p)	-112.9497820	-113.2633020	-113.2671670	-113.2923240
	6-311++G(2df,2pd)	-112.9562640	-113.2955370	-113.3005630	-113.3255950
	6-311++G(3df,3pd)	-112.9590470	-113.3024430	-113.3071510	-113.3325960
	6-311++G(df,pd)	-112.9549490	-113.2786930	-113.2844770	-113.3087860
$HCNH^+$	6-31G(d,p)	-93.1642325	-93.4477360	-93.4530216	-93.4720760
	6-311G(d,p)	-93.1844227	-93.4799081	-93.4834857	-93.5057865
	6-311++G(d,p)	-93.1848564	-93.4807732	-93.4843821	-93.5067200
	6-311++G(df,pd)	-93.1898293	-93.5116696	-93.5162250	-93.5387905
	6-311++G(2d,2p)	-93.1882256	-93.4989901	-93.5017688	-93.5250606
	6-311++G(2df,2pd)	-93.1931364	-93.5288779	-93.5327961	-93.5562207
	6-311++G(3df,3pd)	-93.1940618	-93.5325604	-93.5358785	-93.5597825
N_2H^+	6-31G(d,p)	-109.1337700	-109.4511900	-109.4473120	-109.4721030
	6-311G(d,p)	-109.1610340	-109.4943800	-109.4874770	-109.5169800
	6-311++G(d,p)	-109.1622420	-109.4961320	-109.4892730	-109.5188680
	6-311++G(df,pd)	-109.1664100	-109.5279900	-109.5220380	-109.5519710
	6-311++G(2d,2p)	-109.1666250	-109.5156430	-109.5084470	-109.5392540
	6-311++G(2df,2pd)	-109.1722080	-109.5469270	-109.5409840	-109.5717490
	6-311++G(3df,3pd)	-109.1728770	-109.5514800	-109.5449150	-109.5762850
O_2H^+	6-31G(d,p)	-149.7953780	-150.1083210	-150.1140830	-150.1341820
	6-311G(d,p)	-149.8362150	-150.1849700	-150.1888340	-150.2129020
	6-311++G(d,p)	-149.8389700	-150.1880740	-150.1921590	-150.2163850
	6-311++G(df,pd)	-149.8440320	-150.2301930	-150.2364320	-150.2612770
	6-311++G(2d,2p)	-149.8476860	-150.2204710	-150.2240380	-150.2501390
	6-311++G(2df,2pd)	-149.8527250	-150.2598450	-150.2653910	-150.2920580

Table S2. Computed values of ΔE^{elec} (kcal mol^{-1}).

Base	Basis	HF	MP2	MP3	MP4
CH_3^-	6-31G(d,p)	-460.02	-463.13	-464.48	-464.25
	6-311G(d,p)	-448.49	-447.04	-448.86	-448.43
	6-311++G(d,p)	-433.58	-427.42	-430.91	-429.10
	6-311++G(df,pd)	-433.61	-428.20	-431.74	-429.95
	6-311++G(2d,2p)	-433.65	-425.28	-428.54	-426.75
	6-311++G(2df,2pd)	-433.61	-425.73	-429.09	-427.29
	6-311++G(3df,3pd)	-433.46	-424.37	-427.74	-425.70
NH_2^-	6-31G(d,p)	-446.50	-448.45	-449.99	-449.75
	6-311G(d,p)	-442.97	-443.29	-445.28	-444.66
	6-311++G(d,p)	-422.23	-414.03	-419.87	-415.84
	6-311++G(df,pd)	-422.49	-415.31	-421.16	-417.32
	6-311++G(2d,2p)	-422.29	-411.71	-417.56	-413.55
	6-311++G(2df,2pd)	-422.27	-412.26	-418.08	-414.19
	6-311++G(3df,3pd)	-422.08	-410.81	-416.71	-412.39
OH^-	6-31G(d,p)	-433.01	-435.29	-436.65	-437.04
	6-311G(d,p)	-429.64	-433.08	-434.96	-434.80
	6-311++G(d,p)	-406.08	-398.25	-405.65	-399.77
	6-311++G(df,pd)	-406.84	-400.77	-408.19	-402.61
	6-311++G(2d,2p)	-407.03	-396.73	-404.03	-398.40
	6-311++G(2df,2pd)	-407.38	-398.02	-405.21	-399.79
	6-311++G(3df,3pd)	-407.60	-396.59	-403.85	-397.80
F^-	6-31G(d,p)	-414.21	-419.13	-419.63	-420.79
	6-311G(d,p)	-403.20	-410.13	-411.36	-412.13
	6-311++G(d,p)	-380.46	-376.49	-382.54	-377.51
	6-311++G(df,pd)	-382.18	-380.96	-387.07	-382.37
	6-311++G(2d,2p)	-381.90	-375.91	-381.71	-377.24
	6-311++G(2df,2pd)	-382.88	-378.06	-383.72	-379.51
	6-311++G(3df,3pd)	-383.47	-376.80	-382.43	-377.59
CN^-	6-31G(d,p)	-370.84	-378.25	-378.31	-378.86
	6-311G(d,p)	-363.90	-369.46	-369.93	-370.11
	6-311++G(d,p)	-355.06	-357.01	-358.81	-357.53
	6-311++G(df,pd)	-355.46	-357.40	-359.21	-357.92
	6-311++G(2d,2p)	-355.16	-355.54	-357.04	-355.90
	6-311++G(2df,2pd)	-355.87	-356.82	-358.43	-357.27
	6-311++G(3df,3pd)	-355.92	-356.04	-357.62	-356.40
CH_4	6-31G(d,p)	-127.81	-131.85	-132.41	-132.44
	6-311G(d,p)	-129.74	-132.17	-132.75	-132.75
	6-311++G(d,p)	-129.82	-132.23	-132.82	-132.81
	6-311++G(df,pd)	-129.93	-132.94	-133.62	-133.64
	6-311++G(2d,2p)	-130.19	-131.38	-131.81	-131.73
	6-311++G(2df,2pd)	-130.58	-132.37	-132.91	-132.86
NH_3	6-31G(d,p)	-219.54	-219.92	-220.93	-220.82
	6-311G(d,p)	-218.52	-217.31	-218.59	-218.23
	6-311++G(d,p)	-216.14	-213.48	-215.31	-214.54
	6-311++G(df,pd)	-216.03	-213.60	-215.45	-214.70
	6-311++G(2d,2p)	-215.90	-211.46	-213.25	-212.30
	6-311++G(2df,2pd)	-215.90	-211.50	-213.34	-212.39
	6-311++G(3df,3pd)	-215.51	-210.83	-212.71	-211.64
O	6-31G(d,p)	-119.32	-122.12	-123.04	-123.69
	6-311G(d,p)	-119.92	-123.12	-124.21	-124.92
	6-311++G(d,p)	-119.12	-121.47	-122.63	-123.14
	6-311++G(df,pd)	-119.17	-122.30	-123.39	-123.94
	6-311++G(2d,2p)	-119.77	-120.29	-121.09	-121.50
	6-311++G(2df,2pd)	-119.52	-120.16	-120.79	-121.18
	6-311++G(3df,3pd)	-119.91	-120.55	-121.17	-121.45
H_2O	6-31G(d,p)	-179.28	-179.60	-180.56	-180.64
	6-311G(d,p)	-178.21	-178.53	-179.67	-179.41
	6-311++G(d,p)	-174.70	-172.63	-174.80	-173.62
	6-311++G(df,pd)	-175.22	-173.77	-175.96	-174.84
	6-311++G(2d,2p)	-174.35	-170.45	-172.71	-171.33
	6-311++G(2df,2pd)	-174.58	-170.84	-173.07	-171.71
	6-311++G(3df,3pd)	-174.73	-170.58	-172.89	-171.33
HF	6-31G(d,p)	-126.69	-130.03	-130.14	-130.82
	6-311G(d,p)	-122.63	-126.55	-126.98	-127.41
	6-311++G(d,p)	-119.17	-120.51	-122.03	-121.35
	6-311++G(df,pd)	-121.04	-123.66	-125.24	-124.65
	6-311++G(2d,2p)	-120.38	-119.90	-121.36	-120.66
	6-311++G(2df,2pd)	-121.13	-121.09	-122.51	-121.85
	6-311++G(3df,3pd)	-121.68	-120.85	-122.32	-121.38

Base	Basis	HF	MP2	MP3	MP4
OC	6-31G(d,p)	-115.37	-108.25	-113.52	-112.00
	6-311G(d,p)	-112.32	-104.43	-110.15	-107.73
	6-311++G(d,p)	-111.80	-103.16	-109.18	-106.39
	6-311++G(df,pd)	-113.58	-104.90	-110.80	-107.93
	6-311++G(2d,2p)	-110.87	-102.06	-107.74	-105.03
	6-311++G(2df,2pd)	-112.79	-103.88	-109.48	-106.71
	6-311++G(3df,3pd)	-113.04	-103.99	-109.60	-106.82
CO	6-31G(d,p)	-144.17	-152.51	-149.85	-151.63
	6-311G(d,p)	-144.04	-151.64	-149.17	-150.79
	6-311++G(d,p)	-143.42	-150.38	-148.11	-149.45
	6-311++G(df,pd)	-143.81	-150.66	-148.47	-149.75
	6-311++G(2d,2p)	-143.49	-148.90	-146.48	-147.85
	6-311++G(2df,2pd)	-144.29	-150.13	-147.85	-149.20
	6-311++G(3df,3pd)	-144.38	-149.74	-147.46	-148.78
HCN	6-31G(d,p)	-180.95	-177.42	-180.05	-178.77
	6-311G(d,p)	-179.78	-175.86	-178.76	-177.28
	6-311++G(d,p)	-179.05	-174.54	-177.75	-176.00
	6-311++G(df,pd)	-180.32	-175.56	-178.76	-176.90
	6-311++G(2d,2p)	-179.09	-173.72	-176.57	-174.69
	6-311++G(2df,2pd)	-180.08	-174.90	-177.83	-175.89
	6-311++G(3df,3pd)	-180.03	-174.69	-177.58	-175.62
N_2	6-31G(d,p)	-120.51	-124.02	-125.23	-125.84
	6-311G(d,p)	-121.01	-124.22	-125.79	-126.18
	6-311++G(d,p)	-120.37	-122.49	-124.51	-124.43
	6-311++G(df,pd)	-121.53	-123.27	-125.17	-125.08
	6-311++G(2d,2p)	-119.81	-120.96	-122.53	-122.46
	6-311++G(2df,2pd)	-121.04	-122.27	-123.87	-123.74
	6-311++G(3df,3pd)	-120.83	-121.98	-123.47	-123.40
O_2	6-31G(d,p)	-113.15	-100.80	-107.27	-107.24
	6-311G(d,p)	-113.47	-101.34	-108.57	-107.36
	6-311++G(d,p)	-112.38	-99.52	-106.96	-105.23
	6-311++G(df,pd)	-113.09	-101.06	-108.26	-106.59
	6-311++G(2d,2p)	-113.89	-99.48	-106.72	-104.84
	6-311++G(2df,2pd)	-113.96	-99.50	-106.46	-104.59

Note added in proof: The vibrational frequency of OH^- has been determined[34] to be 3556 cm^{-1}, in very good accord with the scaled HF/6-31+G(d) value of 3532. The scaled HF/6-31G(d) value, by comparison, is 3328 cm^{-1}. While only one result, this value supports the use of a scale factor of 0.89 with the HF/6-31+G(d) theoretical model to predict vibrational frequencies for negative ions.

We have computed the proton affinities of CH_4 and O_2 with the MP4/6-311++G(3df, 3pd) theoretical model. The resulting values, 129.4 and 100.0 kcal mol^{-1} respectively, are little different from those reported in Table V. There is thus a discrepancy of greater than 2 kcal mol^{-1} between the theoretical and experimental PA's of methane.

The proton affinity of carbon monoxide at oxygen has been estimated to be 109±6 kcal mol^{-1} from the observed correlation of O_{1s} binding energies with measured PA's, marginally in agreement with the theoretical value of 102.8. It should be noted that the PA's of MK were used in the correlation of the core binding energies with proton affinities; use of the BMS values would lead to a somewhat lower estimate for the PA of carbon monoxide at oxygen.

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