# Assessment of Gaussian-2 and density functional theories for the computation of enthalpies of formation

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A set of 148 molecules having well-established enthalpies of formation at 298 K is presented. This set, referred to as the G2 neutral test set, includes the 55 molecules whose atomization energies were used to test Gaussian-2 (G2) theory [J. Chem. Phys. **94**, 7221 (1991)] and 93 new molecules. The G2 test set includes 29 radicals, 35 nonhydrogen systems, 22 hydrocarbons, 47 substituted hydrocarbons, and 15 inorganic hydrides. It is hoped that this new test set will provide a means for assessing and improving new theoretical models. From an assessment of G2 and density functional theories (DFT) on this test set it is found that G2 theory is the most reliable method both in terms of average absolute deviation (1.58 kcal/mol) and maximum deviation (8.2 kcal/mol). The largest deviations between experiment and G2 theory occur for molecules having multiple halogens. Inclusion of spin–orbit effects reduces the average absolute deviation to 1.47 kcal/mol and significantly improves the results for the chlorine substituted molecules, but little overall improvement is seen for the fluorine substituted molecules. Of the two modified versions of G2 theory examined in this study, G2(MP2,SVP) theory (average absolute deviation=1.93 kcal/mol) performs better than G2(MP2) theory (2.04 kcal/mol). The G2(MP2,SVP) theory is found to perform very well for hydrocarbons, radicals, and inorganic hydrides. Of the seven DFT methods investigated, the B3LYP method has the smallest average absolute deviation (3.11 kcal/mol). It also has a significantly larger distribution of error than the G2 methods with a maximum deviation of 20.1 kcal/mol. © *1997 American Institute of Physics.* [S0021-9606(97)02202-2]

## I. INTRODUCTION

Critical documentation and evaluation of theoretical models of electronic structure is essential. If such methods are to become proper tools for chemical investigation, their predictions must be presented together with convincing evidence of reliability. In recent years, we have approached this problem by assembling a large set of good, credible experimental data and systematically comparing them with corresponding results from theoretical models. The mean differences between the two sets of numbers are then measures of their combined error. If the experimental data set is limited to measurements of very high accuracy, these mean differences document the overall accuracy of the theory. In this manner, reasonable error bars can be placed on theoretical predictions in situations where experimental results are either unavailable or suspect.

We followed this route in the development of Gaussian-2 (G2) theory,[1] a model for calculation of total energies of molecules which targets an accuracy of 2 kcal/mol. It has been tested on a total of 125 energies (atomization energies, ionization energies, electron affinities, and proton affinities), chosen because they have well-established experimental values. The molecules in this test set contained elements from the first- and second-rows of the periodic chart. They were all small, all except $SO_2$ and $CO_2$ containing one or two non-hydrogen atoms. G2 theory met the target, the mean absolute deviation being 1.21 kcal/mol for these reaction energies. This set of energies has since been used by others to test new quantum chemical methods and is often referred to as the ''G2 test set.''

The G2 theory[1,2] is a composite one, based on the 6-311G($d$,$p$) basis set and several basis extensions. Treatment of electron correlation is by Moller–Plesset (MP) perturbation theory and quadratic configuration interaction (QCI). The final energies are effectively at the QCISD(T)/6-311+G($3df$,$2p$) level, making certain assumptions about additivity and appending a small higher-level empirical correction (HLC) to accommodate remaining deficiencies. Since publication of the original G2 method, several modifications have been proposed in which one or more of the steps have been changed. G2(COMPLETE) theory[3,4] is a variation in which the additivity assumptions are eliminated. It has an average absolute deviation of 1.17 kcal/mol on the G2 test set, a small improvement over G2 theory. G2(MP2) and G2(MP3) theories[5] are based on reduced orders of Moller–Plesset perturbation theory and have larger deviations (1.58 and 1.52 kcal/mol, respectively), but save computational

time and disk space. G2(MP2, SVP) theory[6] is similar to G2(MP2) theory except that the time consuming QCISD(T)/6-311G($d,p$) calculation is replaced by a QCISD(T) calculation using the smaller basis set 6-31G($d$). This modification saves considerable time and is nearly as accurate as G2(MP2) theory (deviation: 1.63 kcal/mol). Several variations of G2 theory using other methods for evaluating correlation energy [CCSD(T) and BD(T)], geometries (QCISD), and vibrational frequencies (MP2) were tested and found to give little or no improvement in the accuracy of the method.[4] Bauschlicher and Partridge[7] have proposed a modification of G2(MP2) theory which uses geometries and vibrational frequencies from density functional theory (DFT) methods. Also Mebel, Morokuma, and Lin[8] have proposed G2 modifications using spin-projected Moller–Plesset theory for radicals and triplets.

There have been other approaches based on *ab initio* molecular orbital theory for the calculation of molecular energies. Among these are the CBS and PCI methods. The CBS (complete basis set) method of Petersson *et al.*[9–11] uses a basis extrapolation to estimate residual energy errors. The PCI (parameterized configuration interaction) method of Siegbahn *et al.*[12] uses multiplicative empirical corrections, rather than the additive HLC type of G2 theory. In addition, there has recently been considerable interest among quantum chemists in the development of DFT methods. Their capability to calculate atomization energies accurately has been the subject of several papers. Bauschlicher *et al.*[13,14] have reported testing of various DFT methods on the G2 test set. Becke[15] has also used the G2 test set to evaluate new energy functionals.

It has become apparent that there is a need for a test set of reaction energies which includes molecules that are larger than those contained in the original G2 set. In addition, further testing may detect types of systems for which G2 may fail; improvements in the method can then be sought. While the G2 test set has provided a useful set of reaction energies on which new methods can be tested and compared with the performance of other methods, it has certain deficiencies. First, most of the molecules have at most two non-hydrogen atoms. Second, it lacks any aromatic ring compounds such as benzene. Third, there are few molecules containing halogens. Fourth, the original set used only data available for zero temperature, ignoring the significant amount of accurate data on larger compounds at 298 K. The purpose of the work reported in this paper is to examine the performance of G2 theory on a well-defined set of molecules without the above deficiencies. Included in this new set, referred to as the ''G2-2 test set'' (the original G2 test set will be referred to as the ''G2-1 test set'') are 93 molecules which have up to six non-hydrogen atoms, aromatic ring compounds, and halogen-containing molecules. In this paper we also examine the performance of several other G2 based methods [G2(MP2), G2(MP2,SVP)] and several DFT methods. In Sec. II we describe the theoretical methods. In Sec. III the molecules choosen for the test set and the sources of the experimental data are described. In Sec. IV the results are presented and discussed.

TABLE I. Enthalpies of formation at 0 K for gaseous atoms and ($H^{298}-H^0$) values for elements in their standard states from experiment.[a]

| Atoms | $\Delta_f H^0$ (0 K) | $H^{298}-H^0$ |
|---|---|---|
| H | 51.63±0.001 | 1.01 |
| Li | 37.69±0.2 | 1.10 |
| Be | 76.48±1.2 | 0.46 |
| B | 136.2 ±0.2[b] | 0.29 |
| C | 169.98±0.1 | 0.25 |
| N | 112.53±0.02 | 1.04 |
| O | 58.99±0.02 | 1.04 |
| F | 18.47±0.07 | 1.05 |
| Na | 25.69±0.17 | 1.54 |
| Mg | 34.87±0.2 | 1.19 |
| Al | 78.23±1.0 | 1.08 |
| Si | 106.6 ±1.9 | 0.76 |
| P | 75.42±0.2 | 1.28 |
| S | 65.66±0.06 | 1.05 |
| Cl | 28.59±0.001 | 1.10 |

[a]Reference 25.
[b]Reference 26 and 27.

## II. THEORETICAL METHODS

Gaussian-2 theory and its modifications have been described in detail elsewhere.[1,2,5,6] Seven density functional methods are tested in this study: BLYP, B3LYP, BP86, B3P86, BPW91, B3PW91, and SVWN. The basis set used is the 6-311+G($3df,2p$) basis and GAUSSIAN94[16] is used for all of the DFT calculations.

The density functional models considered may be broadly divided into nonempirical and empirical types. The simplest is the local spin density functional, which treats the environment of a given position in a molecule as if it were a uniform gas of the density at that point. Our implementation is denoted SVWN, using the Slater functional[17] for exchange and the uniform gas approximate correlation functional of Vosko, Wilk, and Nusair.[18] This model is without any parameterization. Next we have examined the more sophisticated functional BPW91, which combines the 1988 exchange functional of Becke[19] with the correlation functional of Perdew and Wang.[20] Both components involve local density gradients as well as densities. The Becke part involves a single parameter which fits the exchange functional to accurate computed atomic data. The BP86 is similar, but uses an older correlation functional of Perdew.[21] BLYP[22] also uses the Becke 1988 for exchange, together with the correlation part of Lee, Yang, and Parr.[23] This LYP functional is based on a treatment of the helium atom and really only treats correlation between electrons of opposite spin. BLYP is empirical only in the sense that various other combinations of exchange and correlation pieces gave inferior results.

The other three functionals considered use parameters which are fitted to the data in the previous G2 set. There are three such, giving a functional which is a linear combination of Hartree–Fock exchange, 1988 Becke exchange, and various correlation parts. This idea was introduced by Becke.[15] He gave good reasons why correct functionals should be intermediate between Hartree–Fock and normal DFT forms, but actual parameters were obtained by fitting to the molecu-

lar data. This is the basis of the B3PW91 functional. The others (B3P86 and B3LYP) are constructed in a similar manner, although the parameters are the same as in B3PW91.

As in previous work,[24] theoretical enthalpies of formation at 0 K are calculated by subtracting calculated nonrelativistic atomization energies $\Sigma D_0$ from known enthalpies of formation of the isolated atoms. For any molecule, such as $A_x B_y H_z$, the enthalpy of formation at 0 K is given by

$$\Delta_f H^0(A_x B_y H_z, 0 \text{ K}) = x\Delta_f H^0(A, 0 \text{ K})$$
$$+ y\Delta_f H^0(B, 0 \text{ K})$$
$$+ z\Delta_f H^0(H, 0 \text{ K}) - \Sigma D_0. \quad (1)$$

The JANAF[25] values for the atomic $\Delta_f H^0$ are used with the exception of boron, for which we have used a revised value recommended by Ruscic *et al.*[26] based on new experimental results of Storms and Mueller.[27] These numerical values are listed in Table I. Petersson and co-workers[11] and Grev and Schaefer[12] have recommended new atomic enthalpy of formation values for several elements (Be, B, and Si) based on a comparison of experimental enthalpies of formation and theoretical atomization energies of several small molecules containing these elements. We have decided to use the experimental atomic enthalpies throughout rather than combining theory and experiment to obtain new values. The enthalpies of formation of Si, Be, and Al have large uncertainties (2.0, 1.2, and 1.0 kcal/mol, respectively). This means that the calculated enthalpies of formation containing these atoms will have uncertainties due to the use of the atomic enthalpies in Eq. (1) as well as the theoretical methods. The other atomic enthalpies are quite accurate ($\pm 0.2$ kcal/mol).

Theoretical enthalpies of formation at 298 K are calculated by correction to $\Delta_f H^0$ (0 K) as follows:

$$\Delta_f H^0(A_x B_y H_z, 298 \text{ K}) = \Delta_f H^0(A_x B_y H_z, 0 \text{ K}) + [H^0(A_x B_y H_z, 298 \text{ K}) - H^0(A_x B_y H_z, 0 \text{ K})] - x[H^0(A, 298 \text{ K}) - H^0(A, 0 \text{ K})]_{st}$$
$$- y[H^0(B, 298 \text{ K}) - H^0(B, 0 \text{ K})]_{st} - z[H^0(H, 298 \text{ K}) - H^0(H, 0 \text{ K})]_{st}. \quad (2)$$

The heat capacity corrections (in square brackets) are treated differently for compounds and elements. The correction for the $A_x B_y H_z$ molecule is made using scaled HF/6-31G($d$) frequencies for the vibrations in the harmonic approximation for vibrational energy,[29] the classical approximation for translation ($\frac{3}{2}RT$) and rotation ($\frac{3}{2}RT$ for nonlinear molecules, $RT$ for linear molecules) and the $PV$ term. The harmonic approximation may not be appropriate for some low frequency torsional modes, although the error should be small in most cases; we have used the harmonic treatment for all frequencies. The elemental corrections are for the standard states of the elements [denoted as ''st'' in Eq. (2)] and are taken directly from the JANAF tables. These are listed in the last column of Table I. The resulting values of $\Delta_f H^0$ (298 K) are discussed as theoretical numbers, although they are based on some experimental data for monatomic and standard species.

The same set of geometries [MP2(FULL)/6-31G($d$)] and zero-point energies [scaled HF/6-31G($d$)] are used for all the G2-based and DFT methods used in this study. The geometries and zero-point energies are available via anonymous ftp.[30]

## III. THE G2-2 TEST SET

The 93 molecules chosen for the new G2-2 test set were obtained from several sources including the JANAF thermochemical tables,[25] a compilation of thermochemical data of organic compounds by Pedley *et al.*,[31] and a recent review of Berkowitz, Ellison, and Gutman.[32] The criterion for choosing the molecules is that their experimental enthalpies of forma-

tion at 298 K have a quoted uncertainty of $\pm 1$ kcal or less. This is not necessarily a guarantee of the accuracy of the experimental data; however, it is the best that we can do. Most of the molecules contain three or more non-hydrogen atoms, although there are some containing one or two that were not included in the original G2 test set. They have been added for completeness. The $H_2$ molecule, which was not included in the original set, has also been included.

The original G2 test set (G2-1) consisted of 55 molecules which were used for comparison of theoretical and experimental atomization energies. Most of these molecules are smaller than the ones in the G2-2 test set as they contain only one or two nonhydrogen atoms with the exceptions of $CO_2$ and $SO_2$. They contain at most one halogen atom with the exception of $F_2$, $Cl_2$, FCl. In this paper we include the experimental and theoretical enthalpies of formation (298 K) for these 55 molecules, which were not reported in the original paper on G2 theory. Thus experimental values for $\Delta_f H^0$(298 K) were sought for this study. In most cases the same experimental source that was used for the $\Sigma D_0$ in the original G2 paper[1,33] was used for the 298 K values in this study. In some cases, such as the diatomics from Huber and Herzberg,[34] the $D_0$ values had to be corrected to $\Delta_f H^0$(298 K) values. This was done using experimental vibrational frequencies. In addition, in a number of cases more accurate values have come to our attention and we have used these new values in the comparison between theory and experiment. The molecules for which new experimental data is used are $CH_3$, $NH_2$, OH, $SiH_3$, $PH_2$, $PH_3$, LiF, $C_2H_2$, $C_2H_6$, CN, HCN, HCO, $H_2CO$, $H_3COH$, $CH_3Cl$, $CH_3SH$.

The combined G2-1 and G2-2 sets provide enthalpies of formation of 148 molecules that can be used for testing of new quantum chemical methods for energy calculations. The combined set will be subsequently referred to as the ''G2 neutral test set.'' We note that the criterion used for selecting the molecules in the G2-1 set in some cases was not as stringent as that for G2-2. It is useful to break the full set into chemical categories. Somewhat arbitrarily, we have separated out the radicals and then further separated the closed shell species into (1) non-hydrogen systems, (2) hydrocarbons, (3) substituted hydrocarbons, and (4) inorganic hydrides. In the full G2 test set there are 29 radicals, 35 non-hydrogen systems, 22 hydrocarbons, 47 substituted hydrocarbons, and 15 inorganic hydrides.

## IV. RESULTS AND DISCUSSION

The G2 total energies ($E_e$, $E_0$, $H_{298}$) and enthalpies of formation at 0 and 298 K [from Eqs. (1) and (2)] for the 148 molecules in the G2 test set are listed in Table II. The $H_{298}$ values include the correction to 298 K for the molecules (vibration, translation, rotation, and PV terms). The deviations with experiment of the enthalpies calculated at 298 K from the G2, G2(MP2), and G2(MP2,SVP) methods are listed in Table III. Also listed in Table III are the experimental enthalpies of formation at 0 and 298 K for the molecules, including uncertainties if available. The deviations of the seven DFT methods with experiment are given in Table IV. A summary of the average absolute deviations and maximum deviations for the various G2 and DFT methods are given in Table V. The average absolute deviations for the different types of molecules are summarized in Table VI.

### A. G2 theory

The average absolute deviation of G2 theory for the enthalpies at 298 K of the G2-1 test set is 1.23 kcal/mol. The average deviation for the comparison between the G2 and experimental atomization energies (at 0 K) reported in Ref. 1 for the G2-1 test set was 1.19 kcal/mol.[35] This is slightly smaller than the average absolute deviation for the enthalpies. Most of the difference is due to the use of revised experimental values for several of the molecules. The use of enthalpies of formation at 298 K instead of atomization energies to compare with experiment introduces only small differences of either sign (at most 0.3 kcal/mol) in the deviations.

The average absolute deviation of G2 theory for the enthalpies of formation of the 93 molecules in the G2-2 test set is 1.80 kcal/mol. The maximum deviation is that of $C_2F_4$ which is off by 8.2 kcal/mol. The results for the G2-2 test set are broken down into different types of molecules in Table VI. The results show that of the five general types of molecules in the G2-2 test set, four (hydrocarbons, substituted hydrocarbons, inorganic hydrides, and radicals) have average absolute deviations of less than 2 kcal/mol. The deviation is 1.14 kcal/mol for radicals, 1.41 kcal/mol for hydrocarbons, 0.67 kcal/mol for inorganic hydrides, and 1.54 kcal/mol for substituted hydrocarbons. G2 theory has the largest devia-

tions with experiment for the non-hydrogen systems (absolute deviation of 3.06 kcal/mol). The large average absolute deviation for the non-hydrogen systems in the G2-2 test set is mainly due to the errors in the enthalpies of formation of the molecules with two or more fluorines. These 11 molecules along with $CH_2F_2$ and $CHF_3$ in the substituted hydrocarbon group have an average absolute deviation of 3.73 kcal/mol. The seven molecules in the G2-2 test set that have multiple chlorines have an average absolute deviation of 2.47 kcal/mol, much less than the deviation for the fluorine substituted molecules. This is reduced to 0.67 kcal/mol when spin–orbit effects are included (see next section). No overall improvement is found for the molecules with multiple fluorines when spin–orbit effects are included.

The eight cyclic hydrocarbons in the G2-2 test set have an average absolute deviation of 1.94 kcal/mol compared to 0.92 kcal/mol for the 14 noncyclic hydrocarbons. The increased deviation is largely due to the three hydrocarbons with unsaturated carbon rings. Benzene, cyclobutene, and cyclopropene have deviations with experiment of $-3.9$, $-2.9$, $-2.9$ kcal/mol, respectively. The four substituted hydrocarbons with unsaturated rings (furan, thiophen, pyrole, and pyridine) also have larger deviations (average absolute deviation of 1.94 kcal/mol) than for the 43 other substituted hydrocarbons (1.44 kcal/mol). All seven of the unsaturated ring compounds have negative deviations suggesting a systematic error. All of the radicals in the G2-2 set are hydrocarbons, except $NO_2$. This group has an average absolute deviation of 1.14 kcal/mol which is consistent with the performance of G2 theory for the noncyclic hydrocarbons. It has been noted previously[1] that G2 theory does poorly for some triplet states such as $O_2$. The G2-2 test set does not include any triplet states.

The average absolute deviation for the combined G2 test set of 148 enthalpies is 1.58 kcal/mol. The increase of 0.35 kcal/mol compared to the G2-1 subset is due primarily to the larger deviations from experiment for the unsaturated cyclic systems and for non-hydrogen systems, especially those containing two or more fluorines. The distribution of deviations for G2 theory is given in Fig. 1. Over 70% of the G2 enthalpies fall within $\pm 2$ kcal/mol of the experimental values and 87% fall within $\pm 3$ kcal/mol.

We have investigated whether the higher level correction (HLC) that was derived on the basis of the original G2 test set is still appropriate for this new test set. The HLC for G2 theory was derived to give a zero mean deviation for the 55 atomization energies in the G2-1 test set. It also gives the smallest average absolute deviation for the 125 energies (atomization energies, ionization energies, electron affinities, and proton affinities) used to test G2 theory. When the HLC is optimized to give the smallest average absolute deviation for the 148 enthalpies in the new G2 test set the optimal HLC is 4.94 mh per electron pair, only slightly lower than the value of 5.00 mh originally derived for G2 theory. The resulting average absolute deviation is 1.57 kcal/mol, only a slight improvement of over 1.58 kcal/mol obtained using the

TABLE II. G2 total energies and enthalpies of formation.[a]

| Molecule | $E_e$ | $E_0$ | $H_{298}$[b] | $\Delta H_f^0$ (0 K)[c] | $\Delta H_f^0$ (298 K)[d] |
|---|---|---|---|---|---|
| *G2-1 test set* | | | | | |
| LiH | −8.025 36 | −8.022 48 | −8.019 16 | 32.7 | 32.7 |
| BeH | −15.199 28 | −15.194 91 | −15.191 60 | 82.6 | 83.2 |
| CH | −38.418 80 | −38.412 58 | −38.409 27 | 141.1 | 141.9 |
| $CH_2(^3B_1)$ | −39.085 45 | −39.069 00 | −39.065 20 | 94.6 | 94.7 |
| $CH_2(^1A_1)$ | −39.074 44 | −39.058 40 | −39.054 62 | 101.3 | 101.4 |
| $CH_3$ | −39.772 74 | −39.745 09 | −39.740 84 | 35.7 | 35.1 |
| $CH_4$ | −40.453 54 | −40.410 88 | −40.407 07 | −16.7 | −18.6 |
| NH | −55.149 35 | −55.142 17 | −55.138 86 | 86.2 | 86.3 |
| $NH_2$ | −55.807 38 | −55.789 02 | −55.785 24 | 45.7 | 45.0 |
| $NH_3$ | −56.491 69 | −56.458 65 | −56.454 84 | −9.1 | −10.8 |
| OH | −75.652 04 | −75.643 91 | −75.640 60 | 9.0 | 9.1 |
| $OH_2$ | −76.352 56 | −76.332 05 | −76.328 26 | −57.4 | −58.1 |
| FH | −100.358 87 | −100.350 01 | −100.346 70 | −66.2 | −66.2 |
| $SiH_2(^1A_1)$ | −290.179 02 | −290.167 71 | −290.163 90 | 62.7 | 62.3 |
| $SiH_2(^3B_1)$ | −290.142 17 | −290.130 49 | −290.126 65 | 86.1 | 85.7 |
| $SiH_3$ | −290.793 92 | −290.773 51 | −290.769 54 | 48.0 | 46.7 |
| $SiH_4$ | −291.448 94 | −291.419 04 | −291.415 01 | 8.3 | 6.0 |
| $PH_2$ | −342.062 18 | −342.049 13 | −342.045 33 | 33.8 | 32.9 |
| $PH_3$ | −342.702 41 | −342.679 04 | −342.675 18 | 3.9 | 2.0 |
| $SH_2$ | −398.945 41 | −398.930 73 | −398.926 93 | −4.1 | −4.8 |
| ClH | −460.346 65 | −460.340 17 | −460.336 86 | −22.4 | −22.4 |
| $Li_2$ | −14.906 45 | −14.905 76 | −14.902 04 | 49.5 | 49.6 |
| LiF | −107.286 31 | −107.284 21 | −107.280 86 | −81.4 | −81.4 |
| $C_2H_2$ | −77.212 03 | −77.185 74 | −77.182 05 | 56.0 | 55.8 |
| $C_2H_4$ | −78.464 83 | −78.415 93 | −78.411 92 | 14.8 | 12.8 |
| $C_2H_6$ | −79.702 11 | −79.630 90 | −79.626 41 | −16.8 | −20.6 |
| CN | −92.586 79 | −92.582 76 | −92.579 45 | 106.5 | 107.3 |
| HCN | −93.300 95 | −93.284 89 | −93.281 42 | 31.3 | 31.2 |
| CO | −113.182 45 | −113.177 49 | −113.174 18 | −29.0 | −28.2 |
| HCO | −113.711 67 | −113.698 83 | −113.695 03 | 9.2 | 9.3 |
| $H_2CO$ | −114.364 95 | −114.338 88 | −114.335 06 | −27.0 | −27.9 |
| $H_3COH$ | −115.584 30 | −115.534 89 | −115.530 60 | −46.8 | −49.4 |
| $N_2$ | −109.398 22 | −109.392 61 | −109.389 31 | 1.3 | 1.3 |
| $H_2NNH_2$ | −111.732 29 | −111.680 45 | −111.676 22 | 27.2 | 23.7 |
| NO | −129.744 47 | −129.739 95 | −129.736 65 | 21.0 | 21.0 |
| $O_2$ | −150.152 28 | −150.148 22 | −150.144 91 | 2.4 | 2.4 |
| HOOH | −151.391 94 | −151.365 78 | −151.361 60 | −30.8 | −32.3 |
| $F_2$ | −199.326 50 | −199.323 97 | −199.320 64 | 0.3 | 0.3 |
| $CO_2$ | −188.372 69 | −188.361 31 | −188.357 74 | −96.7 | −96.7 |
| $Na_2$ | −323.723 32 | −323.723 00 | −323.719 03 | 32.2 | 31.6 |
| $Si_2$ | −577.984 91 | −577.983 76 | −577.980 23 | 139.6 | 140.3 |
| $P_2$ | −681.821 15 | −681.819 30 | −681.815 92 | 36.1 | 35.7 |
| $S_2$ | −795.466 78 | −795.465 12 | −795.461 72 | 33.9 | 33.9 |
| $Cl_2$ | −919.443 42 | −919.442 20 | −919.438 69 | 1.4 | 1.4 |
| NaCl | −621.680 95 | −621.680 22 | −621.676 52 | −44.5 | −44.8 |
| SiO | −364.219 04 | −364.216 18 | −364.212 86 | −23.2 | −22.9 |
| SC | −435.713 90 | −435.711 00 | −435.707 68 | 65.1 | 65.9 |
| SO | −472.832 17 | −472.829 49 | −472.826 17 | 3.8 | 3.8 |
| ClO | −534.757 86 | −534.756 17 | −534.752 77 | 26.4 | 26.4 |
| FCl | −559.408 53 | −559.406 67 | −559.403 29 | −13.9 | −14.0 |
| $Si_2H_6$ | −581.715 15 | −581.668 08 | −581.662 03 | 20.0 | 16.2 |
| $CH_3Cl$ | −499.590 17 | −499.553 83 | −499.549 85 | −18.6 | −20.5 |
| $H_3CSH$ | −438.192 78 | −438.148 47 | −438.143 89 | −2.9 | −5.3 |
| HOCl | −535.421 51 | −535.408 58 | −535.404 70 | −17.6 | −18.3 |
| $SO_2$ | −548.022 88 | −548.015 72 | −548.011 72 | −65.3 | −65.9 |
| *G2-2 test set* | | | | | |
| Non-hydrogen systems | | | | | |
| $BF_3$ | −324.249 33 | −324.237 44 | −324.232 93 | −270.8 | −271.4 |
| $BCl_3$ | −1404.149 37 | −1404.142 14 | −1404.136 72 | −98.2 | −98.3 |
| $AlF_3$ | −541.506 92 | −541.499 45 | −541.494 01 | −286.8 | −287.6 |
| $AlCl_3$ | −1621.453 24 | −1621.448 74 | −1621.442 36 | −142.1 | −142.5 |
| $CF_4$ | −437.083 43 | −437.066 31 | −437.061 40 | −227.2 | −228.6 |
| $CCl_4$ | −1876.993 83 | −1876.984 19 | −1876.977 62 | −25.2 | −25.7 |
| COS | −510.956 80 | −510.948 00 | −510.944 17 | −35.9 | −35.8 |
| $CS_2$ | −833.540 06 | −833.533 55 | −833.529 48 | 25.6 | 25.8 |

TABLE II. (*Continued.*)

| Molecule | $E_e$ | $E_0$ | $H_{298}$[b] | $\Delta H_f^0$ (0 K)[c] | $\Delta H_f^0$ (298 K)[d] |
|---|---|---|---|---|---|
| CF$_2$O | −312.705 44 | −312.691 34 | −312.687 09 | −147.8 | −148.6 |
| SiF$_4$ | −688.366 06 | −688.353 98 | −688.347 97 | −377.7 | −378.8 |
| SiCl$_4$ | −2128.256 77 | −2128.249 76 | −2128.242 23 | −161.8 | −162.2 |
| N$_2$O | −184.448 11 | −184.437 12 | −184.433 49 | 21.0 | 20.2 |
| ClNO | −589.482 70 | −589.476 38 | −589.472 01 | 12.0 | 11.6 |
| NF$_3$ | −353.749 41 | −353.738 02 | −353.733 62 | −33.8 | −35.3 |
| PF$_3$ | −640.288 04 | −640.279 64 | −640.274 64 | −222.4 | −223.7 |
| O$_3$ | −225.182 30 | −225.174 49 | −225.170 60 | 33.7 | 33.0 |
| F$_2$O | −274.397 12 | −274.391 09 | −274.387 04 | 5.9 | 5.3 |
| ClF$_3$ | −758.775 96 | −758.768 51 | −758.763 39 | −37.4 | −38.4 |
| C$_2$F$_4$ | −475.043 46 | −475.022 05 | −475.015 84 | −164.8 | −165.6 |
| C$_2$Cl$_4$ | −1915.026 24 | −1915.010 88 | −1915.003 42 | −7.3 | −7.5 |
| CF$_3$CN | −430.012 23 | −429.989 45 | −429.983 39 | −122.3 | −123.2 |
| Hydrocarbons | | | | | |
| CH$_3$CCH (propyne) | −116.472 83 | −116.419 17 | −116.414 31 | 47.4 | 45.7 |
| CH$_2$=C=CH$_2$ (allene) | −116.470 92 | −116.417 84 | −116.413 08 | 48.2 | 46.4 |
| C$_3$H$_4$ (cyclopropene) | −116.435 32 | −116.381 29 | −116.377 01 | 71.2 | 69.1 |
| CH$_3$CH=CH$_2$ (propylene) | −117.721 39 | −117.645 09 | −117.639 98 | 8.9 | 5.3 |
| C$_3$H$_6$ (cyclopropane) | −117.709 07 | −117.631 15 | −117.626 79 | 17.7 | 13.6 |
| C$_3$H$_8$ (propane) | −118.954 53 | −118.855 80 | −118.850 22 | −20.0 | −25.4 |
| CH$_2$CHCHCH$_2$ (butadiene) | −155.746 00 | −155.664 27 | −155.658 55 | 31.5 | 28.0 |
| C$_4$H$_6$ (2-butyne) | −155.732 04 | −155.651 15 | −155.644 44 | 39.7 | 36.9 |
| C$_4$H$_6$ (methylene cyclopropane) | −155.714 59 | −155.632 67 | −155.627 41 | 51.3 | 47.6 |
| C$_4$H$_6$ (bicyclobutane) | −155.703 59 | −155.620 45 | −155.615 73 | 59.0 | 54.9 |
| C$_4$H$_6$ (cyclobutene) | −155.727 12 | −155.643 88 | −155.639 05 | 44.3 | 40.3 |
| C$_4$H$_8$ (cyclobutane) | −156.964 67 | −156.858 60 | −156.853 40 | 12.8 | 7.0 |
| C$_4$H$_8$ (isobutene) | −156.979 62 | −156.876 35 | −156.869 95 | 1.7 | −3.4 |
| C$_4$H$_{10}$ (*trans* butane) | −158.207 22 | −158.081 18 | −158.074 30 | −23.6 | −30.4 |
| C$_4$H$_{10}$ (isobutane) | −158.210 00 | −158.084 31 | −158.077 51 | −25.5 | −32.4 |
| C$_5$H$_8$ (spiropentane) | −194.963 00 | −194.852 53 | −194.846 58 | 51.3 | 45.7 |
| C$_6$H$_6$ (benzene) | −231.876 67 | −231.780 53 | −231.775 08 | 27.8 | 23.7 |
| Substituted hydrocarbons | | | | | |
| CH$_2$F$_2$ | −238.750 10 | −238.717 97 | −238.713 89 | −109.0 | −110.8 |
| CHF$_3$ | −337.919 05 | −337.893 93 | −337.889 50 | −169.2 | −170.9 |
| CH$_2$Cl$_2$ | −958.727 53 | −958.698 92 | −958.694 39 | −21.8 | −23.4 |
| CHCl$_3$ | −1417.862 87 | −1417.843 21 | −1417.837 80 | −24.5 | −25.7 |
| CH$_3$NH$_2$ (methylamine) | −95.728 44 | −95.666 91 | −95.662 52 | −1.9 | −5.5 |
| CH$_3$CN (methyl cyanide) | −132.566 71 | −132.523 05 | −132.518 47 | 19.8 | 18.1 |
| CH$_3$NO$_2$ (nitromethane) | −244.727 86 | −244.679 14 | −244.673 81 | −17.4 | −20.5 |
| CH$_3$ONO (methyl nitrite) | −244.724 07 | −244.676 13 | −244.670 87 | −15.5 | −18.6 |
| CH$_3$SiH$_3$ (methyl silane) | −330.716 03 | −330.657 82 | −330.652 57 | −3.6 | −7.4 |
| HCOOH (formic acid) | −189.549 56 | −189.516 48 | −189.512 34 | −90.8 | −92.5 |
| HCOOCH$_3$ (methyl formate) | −228.788 43 | −228.728 09 | −228.722 59 | −85.6 | −88.8 |
| CH$_3$CONH$_2$ (acetamide) | −208.950 88 | −208.880 38 | −208.874 09 | −53.5 | −57.2 |
| C$_2$H$_4$NH (aziridine) | −133.731 95 | −133.664 13 | −133.659 93 | 34.5 | 30.5 |
| NCCN (cyanogen) | −185.402 73 | −185.386 48 | −185.381 74 | 74.4 | 74.8 |
| (CH$_3$)$_2$NH (dimethylamine) | −134.971 60 | −134.882 80 | −134.877 37 | 0.5 | −4.7 |
| CH$_3$CH$_2$NH$_2$ (*trans* ethylamine) | −134.983 48 | −134.894 57 | −134.889 15 | −6.8 | −12.1 |
| CH$_2$CO (ketene) | −152.399 66 | −152.369 12 | −152.364 68 | −11.4 | −12.1 |
| C$_2$H$_4$O (oxirane) | −153.588 50 | −153.532 88 | −153.528 77 | −10.9 | −13.9 |
| CH$_3$CHO (acetaldehyde) | −153.630 35 | −153.576 84 | −153.571 93 | −38.5 | −41.0 |
| HCOCOH (glyoxal) | −227.546 71 | −227.510 24 | −227.505 07 | −52.2 | −53.6 |
| CH$_3$CH$_2$OH (ethanol) | −154.841 26 | −154.764 45 | −154.759 15 | −52.9 | −57.2 |
| CH$_3$OCH$_3$ (dimethylether) | −154.823 59 | −154.746 68 | −154.741 33 | −41.8 | −46.0 |
| C$_2$H$_4$S (thiooxirane) | −476.217 52 | −476.164 47 | −476.160 12 | 21.7 | 18.9 |
| (CH$_3$)$_2$SO (dimethyl sulfoxide) | −552.564 55 | −552.487 90 | −552.481 31 | −30.2 | −34.8 |
| C$_5$H$_2$SH (ethanethiol) | −477.446 27 | −477.374 38 | −477.368 64 | −6.7 | −10.7 |
| CH$_3$SCH$_3$ (dimethyl sulphide) | −477.444 68 | −477.371 87 | −477.365 99 | −5.1 | −9.1 |
| CH$_2$=CHF | −177.614 68 | −177.572 13 | −177.567 81 | −33.0 | −34.9 |
| C$_2$H$_5$Cl (ethyl chloride) | −538.846 25 | −538.782 37 | −538.777 32 | −24.1 | −27.6 |
| CH$_2$=CHCl (vinyl chloride) | −537.609 49 | −537.568 28 | −537.563 78 | 7.0 | 5.2 |
| CH$_2$=CHCN (acrylonitrile) | −170.583 04 | −170.533 98 | −170.528 84 | 47.6 | 45.9 |
| CH$_3$COCH$_3$ (acetone) | −192.893 96 | −192.813 68 | −192.807 24 | −49.2 | −53.0 |
| CH$_3$COOH (acetic acid) | −228.813 51 | −228.753 81 | −228.748 27 | −101.8 | −104.9 |
| CH$_3$COF (acetyl fluoride) | −252.810 79 | −252.763 43 | −252.758 14 | −105.4 | −107.7 |

TABLE II. (*Continued.*)

| Molecule | $E_e$ | $E_0$ | $H_{298}$[b] | $\Delta H_f^0$ (0 K)[c] | $\Delta H_f^0$ (298 K)[d] |
|---|---|---|---|---|---|
| CH$_3$COCl (acetyl chloride) | −612.793 02 | −612.747 40 | −612.741 80 | −57.7 | −59.8 |
| CH$_3$CH$_2$CH$_2$Cl (propyl chloride) | −578.099 19 | −578.007 99 | −578.001 59 | −27.7 | −32.7 |
| (CH$_3$)$_2$CHOH (isopropanol) | −194.100 02 | −193.996 46 | −193.989 94 | −60.6 | −66.4 |
| C$_2$H$_5$OCH$_3$ (methyl ethyl ether) | −194.080 90 | −193.976 84 | −193.970 23 | −48.3 | −54.0 |
| (CH$_3$)$_3$N (trimethylamine) | −174.219 57 | −174.103 94 | −174.097 40 | −0.3 | −7.1 |
| C$_4$H$_4$O (furan) | −229.700 23 | −229.632 61 | −229.627 92 | −4.2 | −7.3 |
| C$_4$H$_4$S (thiophene) | −552.321 59 | −552.257 27 | −552.252 18 | 32.8 | 29.9 |
| C$_4$H$_5$N (pyrrole) | −209.857 64 | −209.778 38 | −209.773 38 | 32.1 | 28.1 |
| C$_5$H$_5$N (pyridine) | −247.906 51 | −247.821 29 | −247.815 98 | 39.8 | 35.8 |
| Inorganic hydrides | | | | | |
| H$_2$ | −1.175 81 | −1.166 36 | −1.163 05 | −1.1 | −1.1 |
| HS | −398.292 88 | −398.286 98 | −398.283 67 | 34.4 | 34.4 |
| Radicals | | | | | |
| CCH | −76.486 44 | −76.473 04 | −76.469 28 | 137.8 | 138.7 |
| C$_2$H$_3$($^2A'$) | −77.774 40 | −77.739 84 | −77.735 77 | 73.7 | 72.7 |
| CH$_3$CO($^2A'$) | −152.976 99 | −152.935 43 | −152.930 46 | −1.3 | −2.8 |
| H$_2$COH($^2A$) | −114.917 48 | −114.881 56 | −114.877 29 | −2.2 | −3.8 |
| CH$_3$O($^2A'$) | −114.903 50 | −114.867 53 | −114.863 57 | 6.6 | 4.8 |
| CH$_3$CH$_2$O($^2A''$) | −154.159 39 | −154.096 13 | −154.091 00 | 1.1 | −2.3 |
| CH$_3$S($^2A'$) | −437.545 68 | −437.511 27 | −437.507 11 | 31.6 | 29.9 |
| C$_2$H$_5$($^2A'$) | −79.026 73 | −78.970 17 | −78.965 23 | 32.4 | 29.9 |
| (CH$_3$)$_2$CH($^2A'$) | −118.283 29 | −118.198 88 | −118.192 77 | 26.8 | 22.8 |
| (CH$_3$)$_3$C (*t*-butyl radical) | −157.541 66 | −157.429 86 | −157.422 44 | 19.7 | 14.3 |
| NO$_2$ | −204.845 66 | −204.836 86 | −204.832 98 | 7.9 | 7.2 |

[a]Total energies ($E_e$, $E_0$, $H_{298}$) in hartrees, enthalpies in kcal/mol. The $E_e$ energies (in hartrees) of the atoms are H (−0.500 00), Li (−7.432 22), Be (−14.622 34), B (−24.602 05), C (−37.784 32), N (−54.517 98), O (−74.982 03), F (−99.632 82), Na (−161.846 18), Mg (−199.645 14), Al (−241.930 97), Si (−288.933 25), P (−340.818 22), S (−397.654 95), Cl (−459.676 64).
[b]$H_{298}$ is the calculated enthalpy of the molecule at 298 K.
[c]From Eq. (1).
[d]From Eq. (2).

original HLC. Hence, the original HLC derived for G2 theory is close to optimal and will not be changed.

## B. Spin−orbit corrections

It has previously been noted that spin−orbit effects are important in calculating the ionization potential of sulfur atom[36] and also in some molecules containing third-row non-transition metal elements Ga−Kr.[37] We have investigated the importance of including spin−orbit effects in the calculated enthalpies of formation for the G2 test set by adding a spin−orbit correction $\Delta E(\text{SO})$ to the total G2 energies that are used to calculate the atomization energies in Eq. (1)

$$E_0[\text{G2}_{\text{SO}}] = E_0[\text{G2}] + \Delta E(\text{SO}). \qquad (3)$$

The spin−orbit correction has been included in the G2 energies for $^2P$ and $^3P$ atoms and $^2\Pi$ molecules.[38] These are cases for which it is a first-order effect and should be most important. We neglect it for the other atoms and molecules. Also we neglect the temperature effects from the electronic states due to the spin−orbit effect. The $\Delta E(\text{SO})$ values are listed in a footnote in Table VII and were derived from experimental data in Moore's tables[39] for the atoms and Huber and Herzberg's[34] compilation for the molecules. The atomic spin−orbit corrections are significant for atoms such as Cl (−1.34 mh per atom), S (−0.89 mh per atom), and F (−0.61 mh per atom).

The effect of the inclusion of spin−orbit corrections in the G2 energies via Eq. (3) on the enthalpies is summarized in Table VII. The overall average absolute deviation for the full G2 test set decreases from 1.58 to 1.47 kcal/mol when spin-orbit corrections are included as described above. The decrease is largely due to the improvement in the non-hydrogen systems. The average absolute deviation for the 22 non-hydrogen enthalpies in the G2-2 test set is reduced by 0.71 to 2.36 kcal/mol when the spin−orbit correction is included. This is due to the better agreement between theory and experiment for chlorine-containing compounds. The average absolute deviation of the seven chlorine-substituted molecules in the G2-2 test set is reduced from 2.47 to 0.67 kcal/mol when spin−orbit effects are included. For example, the atomization energy of CCl$_4$ is reduced by 3.5 kcal/mol when the atomic spin−orbit corrections are included. The spin−orbit correction does not improve the results for the molecules containing two or more fluorine atoms in the G2-2 test set as the average absolute deviation for these 13 molecules is 3.74 kcal/mol compared to 3.73 kcal/mol without the spin−orbit correction. Apparently there is some inherent problem in G2 theory with some of the fluorine molecules other than the neglect of the spin−orbit effect.

The inclusion of the spin−orbit correction increases the average absolute deviations of the hydrocarbons and radicals slightly, while the deviation for the substituted hydrocarbons decreases slightly. Application of the spin−orbit correction

TABLE III. Deviation of enthalpies calculated by G2 theory with experiment.[a]

| Molecule | Expt. | | Deviation (Expt. Theory)[b] | | | Ref.[c] |
|---|---|---|---|---|---|---|
| | $\Delta H_f^0$ (0 K) | $\Delta H_f^0$ (298 K) | G2 | G2(MP2) | G2(MP2,SVP) | |
| *G2-1 test set* | | | | | | |
| LiH | 33.3 | 33.3 | 0.6 | 0.2 | −0.2 | d |
| BeH | 81.3 | 81.7 | −1.5 | −2.4 | −4.3 | d |
| CH | 141.7 | 142.5 | 0.6 | 0.3 | 0.4 | d |
| $CH_2(^3B_1)$ | 93.6 | 93.7±0.6 | −1.0 | −1.5 | −1.5 | e |
| $CH_2(^1A_1)$ | 102.6 | 102.8 | 1.4 | 1.1 | 1.4 | f |
| $CH_3$ | 35.8 | 35.0±0.1 | −0.1 | −0.6 | −0.7 | g,h |
| $CH_4$ | −16.0 | −17.9±0.1 | 0.7 | 0.2 | −0.1 | i |
| NH | 85.2 | 85.2±0.4 | −1.1 | −1.3 | −1.7 | j |
| $NH_2$ | 45.8 | 45.1±0.3 | 0.1 | −0.1 | −0.7 | g,h |
| $NH_3$ | −9.3 | −11.0±0.1 | −0.2 | −0.1 | −0.8 | i |
| OH | 9.3 | 9.4±0.1 | 0.3 | 0.6 | 0.1 | g,h |
| $OH_2$ | −57.1 | −57.8±0.0 | 0.3 | 1.1 | 0.2 | i |
| FH | −65.1 | −65.1±0.2 | 1.0 | 1.6 | 1.5 | i |
| $SiH_2(^1A_1)$ | 65.6 | 65.2±0.7 | 2.9 | 2.7 | 1.9 | k |
| $SiH_2(^3B_1)$ | 86.6 | 86.2±1.0 | 0.5 | 0.3 | −0.4 | k |
| $SiH_3$ | 49.4 | 47.9±0.6 | 1.2 | 1.1 | −0.3 | g,h |
| $SiH_4$ | 10.5 | 8.2±0.5 | 2.2 | 2.0 | −0.1 | i |
| $PH_2$ | 34.0 | 33.1±0.6 | 0.2 | −0.2 | −0.5 | g,h |
| $PH_3$ | 3.2 | 1.3±0.4 | −0.7 | −1.0 | −1.5 | g,h |
| $SH_2$ | −4.2 | −4.9±0.2 | −0.1 | 0.7 | 0.8 | i |
| ClH | −22.0 | −22.1±0.0 | 0.4 | 1.2 | 1.4 | i |
| $Li_2$ | 51.5 | 51.6±0.8 | 2.0 | 2.4 | 2.6 | i |
| LiF | −80.1 | −80.1 | 1.3 | 1.7 | 1.6 | d,h |
| $C_2H_2$ | 54.5 | 54.2±0.1 | −1.6 | −2.1 | 0.1 | h,i,l |
| $C_2H_4$ | 14.6 | 12.5±0.1 | −0.2 | −0.7 | 0.7 | i |
| $C_2H_6$ | −16.3 | −20.1±0.1 | 0.5 | −0.2 | 0.0 | g,h,l |
| CN | 104.1 | 104.9±0.5 | −2.4 | −2.6 | −1.7 | m,h |
| HCN | 31.6 | 31.5±1.0 | 0.3 | 0.1 | 1.1 | h,l |
| CO | −27.2 | −26.4±0.0 | 1.8 | 2.9 | 3.2 | i |
| HCO | 9.9 | 10.0±0.2 | 0.7 | 1.3 | 1.1 | g,h |
| $H_2CO$ | −25.1 | −26.0±0.1 | 2.0 | 2.6 | 2.3 | h,l |
| $H_3COH$ | −45.4 | −48.0±0.1 | 1.4 | 1.8 | 0.9 | g,h,l |
| $N_2$ | 0.0 | 0.0 | −1.3 | −1.1 | −1.0 | i |
| $H_2NNH_2$ | 26.2 | 22.8±0.2 | −0.9 | −0.5 | −1.9 | i |
| NO | 21.5 | 21.6±0.0 | 0.6 | 1.4 | 0.1 | i |
| $O_2$ | 0.0 | 0.0 | −2.4 | −2.1 | −3.6 | i |
| HOOH | −31.0 | −32.5 | −0.2 | 1.2 | −0.8 | i |
| $F_2$ | 0.0 | 0.0 | −0.3 | 0.7 | −0.4 | i |
| $CO_2$ | −94.0 | −94.1±0.0 | 2.7 | 4.2 | 4.2 | i |
| $Na_2$ | 34.6 | 34.0±0.3 | 2.4 | 2.8 | 3.0 | i |
| $Si_2$ | 139.2 | 139.9 | −0.4 | 0.0 | 0.3 | d |
| $P_2$ | 34.7 | 34.3 | −1.3 | −1.1 | −0.3 | d |
| $S_2$ | 30.7 | 30.7±0.1 | −3.2 | −1.3 | −1.2 | d |
| $Cl_2$ | 0.0 | 0.0 | −1.4 | 0.7 | 1.0 | i |
| NaCl | −43.2 | −43.6 | 1.2 | 1.7 | 2.0 | d |
| SiO | −24.9 | −24.6 | −1.7 | 1.1 | 0.2 | d |
| SC | 66.1 | 66.9 | 1.0 | 2.8 | 4.1 | d |
| SO | 1.2 | 1.2±0.3 | −2.6 | −1.9 | −3.1 | i |
| ClO | 24.2 | 24.2±0.5 | −2.2 | −1.4 | −1.8 | i |
| FCl | −13.2 | −13.2 | 0.7 | 1.5 | 1.4 | d |
| $Si_2H_6$ | | 19.1 | 2.9 | 2.5 | −0.4 | n |
| $CH_3Cl$ | −17.7 | −19.6±0.2 | 0.9 | 1.5 | 1.7 | h,l |
| $H_3CSH$ | −3.0 | −5.5±0.1 | −0.2 | 0.6 | 0.8 | g,h |
| HOCl | −17.1 | −17.8±0.5 | 0.5 | 2.0 | 1.1 | i |
| $SO_2$ | −70.3 | −71.0±0.1 | −5.0 | −1.2 | −2.3 | i |
| *G2-2 test set* | | | | | | |
|   Nonhydrogen systems | | | | | | |
| $BF_3$ | | −271.4±0.4 | 0.0 | 0.4 | 1.2 | i |
| $BCl_3$ | | −96.3±0.2 | 2.0 | 4.2 | 5.6 | i |
| $AlF_3$ | | −289.0±0.6 | −1.4 | −0.5 | −0.5 | i |
| $AlCl_3$ | | −139.7±0.7 | 2.8 | 5.3 | 5.8 | i |
| $CF_4$ | | −223.0±0.3 | 5.5 | 7.0 | 7.7 | i |
| $CCl_4$ | | −22.9±0.5 | 2.8 | 6.5 | 9.0 | i |

TABLE III. (*Continued.*)

| Molecule | Expt. | | Deviation (Expt. Theory)[b] | | | Ref.[c] |
| | $\Delta H_f^0$ (0 K) | $\Delta H_f^0$ (298 K) | G2 | G2(MP2) | G2(MP2,SVP) | |
|---|---|---|---|---|---|---|
| COS | | $-33.1\pm0.2$ | 2.7 | 4.8 | 5.6 | i |
| $CS_2$ | | $28.0\pm0.2$ | 2.1 | 4.9 | 6.9 | i |
| $CF_2O$ | | $-152.7\pm0.4$ | $-4.1$ | $-2.8$ | $-2.5$ | i |
| $SiF_4$ | | $-386.0\pm0.2$ | $-7.1$ | $-5.3$ | $-5.2$ | i |
| $SiCl_4$ | | $-158.4\pm0.3$ | 3.8 | 3.3 | 4.2 | i |
| $N_2O$ | | $19.6\pm0.1$ | $-0.6$ | 0.7 | $-0.2$ | i |
| ClNO | | $12.4\pm0.1$ | 0.8 | 2.8 | 2.1 | i |
| $NF_3$ | | $-31.6\pm0.3$ | 3.7 | 5.4 | 4.1 | i |
| $PF_3$ | | $-229.1\pm0.9$ | $-5.4$ | $-3.7$ | $-3.6$ | i |
| $O_3$ | | $34.1\pm0.5$ | 1.1 | 2.8 | 0.3 | i |
| $F_2O$ | | $5.9\pm0.5$ | 0.5 | 2.1 | 0.1 | i |
| $ClF_3$ | | $-38.0\pm0.7$ | 0.4 | 2.7 | 1.7 | i |
| $C_2F_4$ | | $-157.4\pm0.7$ | 8.2 | 10.1 | 11.2 | i |
| $C_2Cl_4$ | | $-3.0\pm0.7$ | 4.5 | 8.5 | 12.5 | i |
| $CF_3CN$ | | $-118.4\pm0.7$ | 4.8 | 5.8 | 7.6 | i |
| Hydrocarbons | | | | | | |
| $CH_3CCH$ (propyne) | | $44.2\pm0.2$ | $-1.5$ | $-2.2$ | 0.5 | o |
| $CH_2=C=CH_2$ (allene) | | $45.5\pm0.3$ | $-0.9$ | $-1.5$ | 1.6 | o |
| $C_3H_4$ (cyclopropene) | | $66.2\pm0.6$ | $-2.9$ | $-3.5$ | $-0.8$ | o |
| $CH_3CH=CH_2$ (propylene) | | $4.8\pm0.2$ | $-0.5$ | $-1.3$ | 0.7 | o |
| $C_3H_6$ (cyclopropane) | | $12.7\pm0.1$ | $-0.9$ | $-1.5$ | 0.1 | o |
| $C_3H_8$ (propane) | | $-25.0\pm0.1$ | 0.4 | $-0.5$ | 0.2 | o |
| $CH_2CHCHCH_2$ (butadiene) | | $26.3\pm0.2$ | $-1.7$ | $-2.6$ | 1.2 | o |
| $C_4H_6$ (2-butyne) | | $34.8\pm0.3$ | $-2.1$ | $-3.1$ | 0.2 | o |
| $C_4H_6$ (methylene cyclopropane) | | $47.9\pm0.4$ | 0.3 | $-0.5$ | 2.9 | o |
| $C_4H_6$ (bicyclobutane) | | $51.9\pm0.2$ | $-3.0$ | $-3.7$ | $-0.5$ | o |
| $C_4H_6$ (cyclobutene) | | $37.4\pm0.4$ | $-2.9$ | $-3.8$ | $-0.4$ | o |
| $C_4H_8$ (cyclobutane) | | $6.8\pm0.1$ | $-0.2$ | $-1.1$ | 0.9 | o |
| $C_4H_8$ (isobutene) | | $-4.0\pm0.2$ | $-0.6$ | $-1.6$ | 0.9 | o |
| $C_4H_{10}$ (*trans* butane) | | $-30.0\pm0.2$ | 0.4 | $-0.8$ | 0.5 | o |
| $C_4H_{10}$ (isobutane) | | $-32.1\pm0.2$ | 0.3 | $-0.8$ | 0.5 | o |
| $C_5H_8$ (spiropentane) | | $44.3\pm0.2$ | $-1.4$ | $-2.4$ | 1.1 | o |
| $C_6H_6$ (benzene) | | $19.7\pm0.2$ | $-3.9$ | $-5.1$ | 1.8 | o |
| Substituted hydrocarbons | | | | | | |
| $CH_2F_2$ | | $-107.7\pm0.4$ | 3.1 | 3.9 | 3.8 | i |
| $CHF_3$ | | $-166.6\pm0.8$ | 4.3 | 5.2 | 5.5 | i |
| $CH_2Cl_2$ | | $-22.8\pm0.3$ | 0.6 | 2.3 | 3.1 | i |
| $CHCl_3$ | | $-24.7\pm0.3$ | 1.0 | 3.8 | 5.4 | i |
| $CH_3NH_2$ (methyl amine) | | $-5.5\pm0.1$ | 0.0 | $-0.2$ | $-0.8$ | o |
| $CH_3CN$ (methyl cyanide) | | $18.0\pm0.2$ | $-0.1$ | $-0.5$ | 0.9 | n |
| $CH_3NO_2$ (nitromethane) | | $-17.8\pm0.2$ | 2.7 | 3.7 | 1.9 | o |
| $CH_3ONO$ (methyl nitrite) | | $-15.9\pm0.2$ | 2.7 | 4.1 | 2.3 | o |
| $CH_3SiH_3$ (methyl silane) | | $-7.0\pm1.0$ | 0.4 | 0.1 | $-1.4$ | n |
| HCOOH (formic acid) | | $-90.5\pm0.1$ | 2.0 | 3.2 | 2.5 | o |
| $HCOOCH_3$ (methyl formate) | | $-85.0\pm0.2$ | 3.8 | 4.8 | 4.1 | o |
| $CH_3CONH_2$ (acetamide) | | $-57.0\pm0.2$ | 0.2 | 0.4 | 0.3 | o |
| $C_2H_4NH$ (aziridine) | | $30.2\pm0.2$ | $-0.3$ | $-0.5$ | 0.1 | o |
| NCCN (cyanogen) | | $73.3\pm0.2$ | $-1.5$ | $-1.7$ | 0.8 | o |
| $(CH_3)_2NH$ (dimethylamine) | | $-4.4\pm0.2$ | 0.3 | $-0.2$ | $-0.4$ | o |
| $C_2H_5NH_2$ (ethylamine) | | $-11.3\pm0.2$ | 0.8 | 0.3 | 0.3 | o |
| $CH_2CO$ (ketene) | | $-11.4\pm0.4$ | 0.8 | 1.2 | 2.4 | o |
| $C_2H_4O$ (oxirane) | | $-12.6\pm0.1$ | 1.3 | 1.7 | 1.7 | o |
| $CH_3CHO$ (acetaldehyde) | | $-39.7\pm0.1$ | 1.3 | 1.5 | 1.6 | o |
| HCOCOH (glyoxal) | | $-50.7\pm0.2$ | 2.9 | 3.9 | 4.1 | o |
| $CH_3CH_2OH$ (ethanol) | | $-56.2\pm0.1$ | 1.0 | 1.1 | 0.8 | o |
| $CH_3OCH_3$ (dimethylether) | | $-44.0\pm0.1$ | 2.0 | 2.2 | 1.4 | o |
| $C_2H_4S$ (thiooxirane) | | $19.6\pm0.3$ | 0.7 | 1.6 | 2.9 | o |
| $(CH_3)_2SO$ (dimethyl sulfoxide) | | $-36.2\pm0.2$ | $-1.4$ | 0.5 | 0.0 | o |
| $C_2H_5SH$ (ethanethiol) | | $-11.1\pm0.1$ | $-0.4$ | 0.1 | 0.9 | o |
| $CH_3SCH_3$ (dimethylsufide) | | $-8.9\pm0.2$ | 0.2 | 0.7 | 1.3 | o |
| $CH_2=CHF$ (vinyl fluoride) | | $-33.2\pm0.4$ | 1.7 | 1.8 | 3.1 | o |
| $C_2H_5Cl$ (ethyl chloride) | | $-26.8\pm0.3$ | 0.8 | 1.2 | 1.8 | o |
| $CH_2=CHCl$ (vinyl chloride) | | $8.9\pm0.3$ | 3.7 | 4.3 | 6.3 | o |
| $CH_2=CHCN$ (acrylonitrile) | | $43.2\pm0.4$ | $-2.7$ | $-3.3$ | $-0.3$ | o |

TABLE III. (*Continued.*)

| Molecule | Expt. | | Deviation (Expt. Theory)[b] | | | Ref.[c] |
|---|---|---|---|---|---|---|
| | $\Delta H_f^0$ (0 K) | $\Delta H_f^0$ (298 K) | G2 | G2(MP2) | G2(MP2,SVP) | |
| $CH_3COCH_3$ (acetone) | | −51.9±0.2 | 1.1 | 1.0 | 1.6 | o |
| $CH_3COOH$ (acetic acid) | | −103.4±0.4 | 1.5 | 2.4 | 2.1 | o |
| $CH_3COF$ (acetyl fluoride) | | −105.7±0.8 | 2.0 | 2.6 | 2.9 | o |
| $CH_3COCl$ (acetyl chloride) | | −58.0±0.2 | 1.8 | 3.0 | 3.7 | o |
| $CH_3CH_2CH_2Cl$ (propyl chloride) | | −31.5±0.3 | 1.1 | 1.3 | 2.5 | o |
| $(CH_3)_2CHOH$ (isopropanol) | | −65.2±0.1 | 1.2 | 1.1 | 1.3 | o |
| $C_2H_5OCH_3$ (methyl ethylether) | | −51.7±0.2 | 2.3 | 2.3 | 2.0 | o |
| $(CH_3)_3N$ (trimethylamine) | | −5.7±0.2 | 1.4 | 0.8 | 0.9 | o |
| $C_4H_4O$ (furan) | | −8.3±0.2 | −1.0 | −0.8 | 2.4 | o |
| $C_4H_4S$ (thiophene) | | 27.5±0.2 | −2.4 | −1.3 | 3.5 | o |
| $C_4H_5N$ (pyrrole) | | 25.9±0.1 | −2.2 | −2.7 | 1.4 | o |
| $C_5H_5N$ (pyridine) | | 33.6±0.2 | −2.2 | −2.9 | 2.4 | o |
| Inorganics hydrides | | | | | | |
| $H_2$ | | 0.0±0.0 | 1.1 | 1.1 | 0.9 | i |
| HS | | 34.2±0.7 | −0.3 | 0.0 | 0.0 | g |
| Radicals | | | | | | |
| CCH | | 135.1±0.7 | −3.6 | −4.3 | −1.8 | g |
| $C_2H_3(^2A')$ | | 71.6±0.8 | −1.1 | −1.8 | 0.0 | g |
| $CH_3CO(^2A')$ | | −2.4±0.3 | 0.4 | 0.6 | 0.8 | g |
| $H_2COH(^2A)$ | | −4.1±0.8 | −0.3 | 0.1 | −0.6 | g |
| $CH_3O(^2A')$ | | 4.1±0.9 | −0.7 | −0.8 | −1.2 | g |
| $CH_3CH_2O(^2A'')$ | | −3.7±0.8 | −1.4 | −1.8 | −1.7 | g |
| $CH_3S(^2A')$ | | 29.8±0.4 | −0.1 | 0.1 | 0.3 | g |
| $C_2H_5(^2A')$ | | 28.9±0.4 | −1.0 | −1.8 | −1.4 | g |
| $(CH_3)_2CH(^2A')$ | | 21.5±0.4 | −1.3 | −2.3 | −1.4 | g |
| $(CH_3)_3C$ | | 12.3±0.4 | −2.0 | −3.3 | −1.8 | g |
| $NO_2$ | | 7.9±0.2 | 0.7 | 2.0 | 0.3 | i |

[a]Enthalpies and deviations in kcal/mol.
[b]Deviation between experiment and theory for $\Delta H_f^0$ (298 K).
[c]References for the experimental values. For the G2-1 test set these references are the same as used in the original G2 paper (Refs. 1, 33) for dissociation energies with some exceptions where revised values, as noted, are used.
[d]$\Delta H_f^0$ (0 K) calculated from $D_0$ recommended by Huber and Herzberg (Ref. 34). Vibrational frequency from Huber and Herzberg used to obtain temperature correction to 298 K. This reference does not give uncertainties. All values chosen for this study are listed to an accuracy of 0.01 eV (0.2 kcal/mol) or better.
[e]Based on enthalpy of formation at 0 K recommended by R. K. Lengel and R. N. Zare, J. Am. Chem. Soc. **100**, 7495 (1978). The correction to 298 K is from the JANAF tables (Ref. 25).
[f]Based on the singlet–triplet splitting determined by A. R. W. McKellar, P. R. Bunker, T. J. Sears, K. M. Evenson, R. J. Saykally, and S. R. Langhoff, J. Chem. Phys. **79**, 5251 (1983). The correction to 298 K for the triplet state is used.
[g]Gutman, Berkowitz, and Ellison review article (Ref. 32).
[h]The source for the experimental enthalpy is different than that used to obtain the $D_0$ in the original paper on G2 theory (Ref. 1, 33).
[i]JANAF tables (Ref. 25).
[j]S. T. Gibson, J. P. Greene, and J. Berkowitz, J. Chem. Phys. **83**, 4319 (1985). The correction to 298 K is from the JANAF tables (Ref. 25).
[k]J. Berkowitz, J. P. Greene, H. Cho, and b. Ruscic, J. Chem. Phys. **86**, 1235 (1987).
[l]Gurvich *et al.* compilation (Ref. 41).
[m]Based on $D_0$ reported by Y. Huang S. A. Barts, and J. B. Halpern, J. Phys. Chem. **96**, 425 (1992) and correction to 298 K using vibrational frequency of Ref. 34.
[n]Lias *et al.*, J. Phys. Chem. Ref. Data **17** Suppl. No. 1 (1988).
[o]Pedley compilation (Ref. 31).

to the G2-1 test set energies increases the deviation slightly to 1.26 kcal/mol. The increase in the deviation for the G2-1 test set of smaller molecules is due to the fact that the corrections are largest for the Cl and F containing molecules which tend to have atomization energies that are low compared to experiment.

The deviations between experiment and theory for the atomization energies of some of the $AX_n$ and $A_2X_n$ molecules (A=B,C,N,Al,Si,P; X=F,Cl) from the G2-2 test set are shown in Fig. 2. The figure illustrates the large deviations of G2 theory for the fluorine-containing molecules. It is interesting to note that when A is a first-row atom (B,C,N) the G2 atomization energy is too large, while when A is a second-row atom (Al,Si,P) it is too low. The large deviations for $CF_4$ and $SiF_4$ have been noted previously by Michels and Hobbs.[40] In contrast, for the chlorine-containing molecules *all* of the atomization energies are too large. Inclusion of the spin–orbit correction lowers the atomization energies of the chlorine substituted molecules improving agreement with experiment in all cases. However, inclusion of the spin–orbit correction improves agreement between experiment and theory for the first-row fluorides, but *not* the second-row fluorides. As far as we are aware there is little reason to question the reliability of the experimental data for the fluorine molecules. Thus we conclude that G2 theory may be suspect for molecules containing two or more fluorines and

TABLE IV. Deviation of enthalpies calculated by DFT methods with experiment.[a]

| | Deviation (Expt.-Theory) | | | | | | |
|---|---|---|---|---|---|---|---|
| Molecule | SVWN | BLYP | BP86 | BPW91 | B3LYP | B3P86 | B3PW91 |
| *G2-1 test set* | | | | | | | |
| LiH | 3.3 | 0.1 | 0.5 | −4.6 | 0.4 | 1.2 | −3.3 |
| BeH | 11.2 | 7.3 | 8.5 | 6.5 | 8.2 | 10.0 | 7.4 |
| CH | 9.9 | 1.8 | 4.1 | −0.1 | 1.7 | 3.9 | 0.0 |
| $CH_2(^3B_1)$ | 24.1 | 0.0 | 8.5 | 2.8 | 2.1 | 10.3 | 4.2 |
| $CH_2(^1A_1)$ | 20.7 | −0.6 | 4.2 | −3.7 | 0.2 | 4.9 | −2.7 |
| $CH_3$ | 35.2 | 0.4 | 10.4 | 0.3 | 3.3 | 13.1 | 2.9 |
| $CH_4$ | 46.8 | −2.3 | 10.4 | −3.4 | 1.6 | 14.1 | 0.2 |
| NH | 13.7 | 6.0 | 8.6 | 3.8 | 4.6 | 7.1 | 2.5 |
| $NH_2$ | 29.7 | 8.0 | 13.5 | 4.3 | 6.5 | 11.9 | 3.0 |
| $NH_3$ | 44.3 | 4.3 | 13.3 | 0.3 | 3.5 | 12.4 | −0.4 |
| OH | 19.5 | 3.4 | 6.6 | 2.0 | 1.8 | 5.1 | 0.4 |
| $OH_2$ | 37.3 | 0.6 | 7.8 | −0.9 | −1.3 | 5.8 | −3.1 |
| FH | 22.9 | 0.4 | 4.1 | −0.2 | −1.6 | 2.2 | −2.3 |
| $SiH_2(^1A_1)$ | 16.3 | 0.3 | 3.6 | −4.3 | 2.1 | 5.1 | −2.0 |
| $SiH_2(^3B_1)$ | 17.3 | −0.3 | 6.6 | 0.5 | 2.3 | 8.7 | 2.9 |
| $SiH_3$ | 23.3 | −0.9 | 6.6 | −3.7 | 3.2 | 10.2 | −0.6 |
| $SiH_4$ | 28.1 | −4.0 | 4.6 | −9.5 | 1.9 | 10.0 | −3.1 |
| $PH_2$ | 23.2 | 4.9 | 9.4 | 0.9 | 6.0 | 10.0 | 2.5 |
| $PH_3$ | 31.3 | 1.0 | 8.2 | −4.0 | 3.3 | 9.7 | −1.2 |
| $SH_2$ | 26.1 | −1.6 | 5.6 | −2.1 | −0.3 | 6.2 | −1.0 |
| ClH | 15.4 | −1.6 | 3.0 | −0.8 | −1.0 | 3.1 | −0.5 |
| $Li_2$ | −0.4 | −3.6 | −3.6 | −6.4 | −3.5 | −3.6 | −5.7 |
| LiF | 21.6 | 2.9 | 2.2 | −0.8 | −0.5 | −0.8 | −3.8 |
| $C_2H_2$ | 60.4 | −0.2 | 11.7 | 2.2 | −2.5 | 9.5 | −1.5 |
| $C_2H_4$ | 76.6 | −1.8 | 16.2 | 0.4 | 0.6 | 18.4 | −2.5 |
| $C_2H_6$ | 90.7 | −6.4 | 18.1 | −3.9 | 0.6 | 24.6 | 1.5 |
| CN | 43.2 | 8.5 | 13.4 | 8.9 | −2.2 | 3.3 | −2.5 |
| HCN | 54.4 | 7.7 | 15.1 | 6.8 | 0.0 | 7.8 | −1.8 |
| CO | 44.8 | 3.2 | 9.0 | 4.8 | −3.9 | 2.1 | −3.5 |
| HCO | 59.7 | 9.2 | 17.9 | 11.1 | 2.2 | 11.1 | 2.9 |
| $H_2CO$ | 66.5 | 4.9 | 16.5 | 6.2 | 0.4 | 12.1 | 0.4 |
| $H_3COH$ | 81.8 | −0.5 | 17.4 | 0.4 | 0.1 | 17.8 | −0.3 |
| $N_2$ | 44.2 | 10.6 | 14.4 | 7.2 | −1.4 | 2.7 | −5.3 |
| $H_2NNH_2$ | 86.9 | 9.7 | 26.1 | 5.6 | 6.3 | 22.4 | 1.5 |
| NO | 52.3 | 13.9 | 19.3 | 13.7 | 3.0 | 8.4 | 1.8 |
| $O_2$ | 56.7 | 15.3 | 21.3 | 17.2 | 2.0 | 7.8 | 2.9 |
| HOOH | 71.8 | 7.5 | 18.6 | 6.6 | −1.8 | 9.2 | −3.5 |
| $F_2$ | 40.4 | 9.7 | 12.9 | 9.6 | −2.6 | 0.6 | −3.1 |
| $CO_2$ | 93.8 | 12.6 | 25.5 | 19.1 | −0.2 | 13.0 | 3.5 |
| $Na_2$ | 3.7 | 1.0 | −0.2 | −2.9 | 0.2 | −0.8 | −2.8 |
| $Si_2$ | 20.6 | 1.4 | 6.4 | 4.2 | −5.4 | 4.4 | 1.8 |
| $P_2$ | 30.9 | 4.9 | 7.6 | 1.7 | −1.4 | 0.7 | −4.6 |
| $S_2$ | 36.1 | 5.7 | 12.2 | 9.7 | 1.2 | 7.2 | 4.0 |
| $Cl_2$ | 26.4 | −0.3 | 5.8 | 4.0 | −2.9 | 2.6 | 0.1 |
| NaCl | 8.7 | −5.7 | −2.2 | −4.3 | −4.6 | −0.3 | −3.6 |
| SiO | 35.0 | 2.5 | 4.6 | −0.2 | −5.5 | −2.8 | −8.6 |
| SC | 34.9 | 1.2 | 7.4 | 4.0 | −4.9 | 1.0 | −3.3 |
| SO | 45.0 | 9.7 | 14.9 | 11.3 | 0.7 | 5.8 | 1.3 |
| ClO | 41.5 | 10.5 | 15.8 | 12.7 | 1.6 | 6.7 | 2.8 |
| FCl | 35.3 | 5.6 | 9.7 | 7.2 | −1.1 | 2.9 | −0.3 |
| $Si_2H_6$ | 54.7 | −10.2 | 7.5 | −14.5 | 0.2 | 16.8 | −4.3 |
| $CH_3Cl$ | 58.4 | −3.8 | 11.8 | 0.0 | −0.8 | 14.3 | 1.5 |
| $H_3CSH$ | 69.3 | −5.2 | 13.6 | −2.2 | −1.2 | 16.6 | 0.2 |
| HOCl | 50.2 | 4.5 | 12.9 | 6.0 | −1.5 | 6.7 | −1.0 |
| $SO_2$ | 82.3 | 7.1 | 18.8 | 11.6 | −10.0 | 1.7 | −7.9 |
| *G2-2 test set* | | | | | | | |
| Non-hydrogen sytems | | | | | | | |
| $BF_3$ | 87.1 | 0.2 | 9.4 | 3.3 | −3.9 | 7.2 | −2.8 |
| $BCl_3$ | 68.0 | −8.6 | 9.1 | 5.8 | −6.3 | 10.8 | 4.1 |
| $AlF_3$ | 60.6 | −7.3 | −2.6 | −8.3 | −11.9 | −4.3 | −14.0 |
| $AlCl_3$ | 44.9 | −15.4 | −1.5 | −4.9 | −10.2 | 3.8 | −2.9 |
| $CF_4$ | 135.1 | 3.6 | 24.1 | 14.4 | −4.5 | 16.1 | 2.3 |
| $CCl_4$ | 99.4 | −12.2 | 15.1 | 8.2 | −14.0 | 11.3 | 1.0 |

TABLE IV. (*Continued.*)

| Molecule | Deviation (Expt.-Theory) | | | | | | |
|---|---|---|---|---|---|---|---|
| | SVWN | BLYP | BP86 | BPW91 | B3LYP | B3P86 | B3PW91 |
| COS | 84.1 | 11.1 | 24.0 | 18.4 | 0.5 | 13.3 | 5.1 |
| CS$_2$ | 73.5 | 7.9 | 21.3 | 16.4 | −0.2 | 12.5 | 5.5 |
| CF$_2$O | 108.0 | 2.5 | 19.0 | 11.0 | −9.1 | 7.7 | −3.9 |
| SiF$_4$ | 87.8 | −16.2 | −6.3 | −15.7 | −20.1 | −7.8 | −21.8 |
| SiCl$_4$ | 69.3 | −24.8 | −1.8 | −7.4 | −18.8 | 3.0 | −6.5 |
| N$_2$O | 100.0 | 25.9 | 37.9 | 28.2 | 2.9 | 14.8 | 3.0 |
| ClNO | 81.8 | 22.9 | 32.5 | 24.7 | 2.0 | 11.1 | 2.2 |
| NF$_3$ | 116.4 | 25.2 | 38.8 | 28.7 | 4.0 | 17.3 | 5.3 |
| PF$_3$ | 85.4 | 1.4 | 10.0 | 0.8 | −7.1 | 2.3 | −9.4 |
| O$_3$ | 100.2 | 23.6 | 35.3 | 26.9 | −8.6 | 2.6 | −7.3 |
| F$_2$O | 81.6 | 20.9 | 28.6 | 21.9 | −0.4 | 7.1 | −0.6 |
| ClF$_3$ | 108.6 | 23.8 | 36.1 | 28.7 | 1.9 | 13.9 | 4.5 |
| C$_2$F$_4$ | 176.6 | 16.4 | 41.6 | 30.4 | 3.2 | 28.8 | 12.0 |
| C$_2$Cl$_4$ | 137.4 | −7.8 | 26.0 | 17.6 | −11.3 | 20.8 | 7.1 |
| CF$_3$CN | 167.3 | 12.0 | 36.5 | 23.0 | −3.7 | 21.2 | 2.5 |
| Hydrocarbons | | | | | | | |
| CH$_3$CCH (propyne) | 107.4 | −2.6 | 21.4 | 3.8 | −1.9 | 22.0 | 1.7 |
| CH$_2$=C=CH$_2$ (allene) | 112.5 | 2.2 | 26.2 | 8.5 | 1.9 | 25.9 | 5.5 |
| C$_3$H$_4$ (cyclopropene) | 113.1 | −4.9 | 23.0 | 6.0 | −3.2 | 24.2 | 4.0 |
| CH$_3$CH=CH$_2$ (propylene) | 122.0 | −6.0 | 24.1 | 0.0 | −0.6 | 29.0 | 2.5 |
| C$_3$H$_6$ (cyclopropane) | 127.8 | −9.5 | 24.7 | 1.3 | −2.2 | 31.3 | 4.9 |
| C$_3$H$_8$ (propane) | 134.8 | −11.7 | 24.7 | −5.7 | −1.5 | 34.2 | 1.6 |
| CH$_2$CHCHCH$_2$ (butadiene) | 153.5 | −4.8 | 30.7 | 4.5 | −1.5 | 33.6 | 3.7 |
| C$_4$H$_6$ (2-butyne) | 153.1 | −6.1 | 30.1 | 4.4 | −2.4 | 33.4 | 3.4 |
| C$_4$H$_6$ (methylene cyclopropane) | 163.1 | −4.9 | 35.0 | 9.6 | 0.0 | 39.2 | 9.5 |
| C$_4$H$_6$ (bicyclobutane) | 163.7 | −14.0 | 30.3 | 5.3 | −7.1 | 36.1 | 6.4 |
| C$_4$H$_6$ (cyclobutene) | 158.8 | −11.7 | 29.3 | 3.7 | −6.1 | 34.2 | 4.3 |
| C$_4$H$_8$ (cyclobutane) | 172.5 | −16.2 | 31.0 | −1.0 | −5.2 | 40.8 | 4.7 |
| C$_4$H$_8$ (isobutene) | 166.9 | −11.7 | 30.7 | −1.9 | −3.1 | 38.6 | 2.5 |
| C$_4$H$_{10}$ (*trans* butane) | 178.8 | −17.2 | 31.3 | −7.5 | −3.7 | 43.7 | 1.6 |
| C$_4$H$_{10}$ (isobutane) | 178.9 | −18.5 | 30.2 | −8.8 | −4.8 | 42.8 | 0.6 |
| C$_5$H$_8$ (spiropentane) | 210.9 | −15.7 | 40.2 | 7.1 | −5.4 | 49.2 | 10.2 |
| C$_6$H$_6$ (benzene) | 228.7 | −8.9 | 44.3 | 14.2 | −4.5 | 48.2 | 10.7 |
| Substituted hydrocarbons | | | | | | | |
| CH$_2$F$_2$ | 88.8 | 3.1 | 18.3 | 6.7 | 0.0 | 15.3 | 1.6 |
| CHF$_3$ | 111.8 | 3.7 | 21.3 | 10.7 | −2.2 | 15.6 | 1.8 |
| CH$_2$Cl$_2$ | 75.1 | −6.1 | 12.9 | 2.8 | −4.6 | 13.5 | 1.6 |
| CHCl$_3$ | 84.8 | −8.9 | 14.0 | 5.5 | −9.0 | 12.4 | 1.4 |
| CH$_3$NH$_2$ (methylamine) | 88.3 | 1.1 | 21.4 | 0.2 | 3.2 | 23.2 | 1.1 |
| CH$_3$CN (methyl cyanide) | 101.1 | 5.1 | 24.7 | 8.3 | 0.6 | 20.2 | 1.4 |
| CH$_3$NO$_2$ (nitromethane) | 157.1 | 18.7 | 45.6 | 24.8 | 2.4 | 28.8 | 5.0 |
| CH$_3$ONO (methyl nitrite) | 152.1 | 18.2 | 43.8 | 22.4 | 1.3 | 26.4 | 2.4 |
| CH$_3$SiH$_3$ (methyl silane) | 70.4 | −9.9 | 10.6 | −11.6 | −1.0 | 18.9 | −3.5 |
| HCOOH (formic acid) | 107.3 | 7.2 | 25.2 | 11.6 | −0.9 | 17.2 | 1.1 |
| HCOOCH$_3$ (methyl formate) | 152.3 | 5.1 | 34.0 | 11.8 | −0.2 | 28.6 | 2.9 |
| CH$_3$CONH$_3$ (acetamide) | 159.6 | 4.6 | 36.7 | 10.5 | 1.6 | 33.6 | 4.0 |
| C$_2$H$_4$NH (aziridine) | 124.7 | −0.6 | 29.3 | 6.6 | 1.0 | 30.2 | 5.0 |
| NCCN (cyanogen) | 111.1 | 18.7 | 32.6 | 21.8 | −0.4 | 14.2 | −0.1 |
| (CH$_3$)$_2$NH (dimethylamine) | 133.2 | −3.0 | 28.9 | −0.8 | 2.0 | 33.4 | 1.8 |
| CH$_3$CH$_2$NH$_2$ (*trans* ethylamine) | 133.6 | −3.0 | 29.3 | −0.4 | 2.2 | 33.8 | 2.3 |
| CH$_2$CO (ketene) | 105.4 | 9.4 | 27.8 | 15.7 | 2.4 | 20.9 | 6.0 |
| C$_2$H$_4$O (oxirane) | 117.8 | −0.7 | 26.1 | 7.7 | −1.4 | 25.0 | 3.8 |
| CH$_3$CHO (acetaldehyde) | 112.8 | 1.3 | 24.9 | 6.2 | −0.3 | 23.1 | 2.0 |
| HCOCOH (glyoxal) | 132.5 | 9.0 | 31.1 | 16.0 | −1.6 | 20.8 | 1.9 |
| CH$_3$CH$_2$OH (ethanol) | 126.0 | −5.7 | 24.0 | −1.4 | −1.9 | 27.3 | −0.2 |
| CH$_3$OCH$_3$ (dimethylether) | 126.5 | −3.3 | 25.5 | 0.0 | 0.0 | 28.4 | 0.8 |
| C$_2$H$_4$S (thiooxirane) | 106.4 | −6.7 | 21.7 | 4.5 | −3.1 | 24.1 | 4.4 |
| (CH$_3$)$_2$SO (dimethyl sulfoxide) | 150.9 | −7.3 | 28.9 | 1.6 | −6.5 | 28.7 | −1.6 |
| C$_2$H$_5$SH (ethanethiol) | 113.3 | −10.7 | 20.1 | −4.1 | −3.6 | 26.0 | 0.2 |
| CH$_3$SCH$_3$ (dimethyl sulphide) | 113.3 | −9.4 | 21.2 | −2.8 | −2.8 | 26.7 | 1.0 |
| CH$_2$=CHF | 101.4 | 3.2 | 22.7 | 8.1 | 1.5 | 21.0 | 3.9 |
| C$_2$H$_5$Cl (ethyl chloride) | 102.8 | −8.9 | 18.8 | −1.5 | −2.7 | 24.1 | 1.8 |
| CH$_2$=CHCl (vinyl chloride) | 94.7 | 0.7 | 22.3 | 8.4 | 1.6 | 22.6 | 6.5 |

TABLE IV. (*Continued.*)

| Molecule | SVWN | BLYP | BP86 | BPW91 | B3LYP | B3P86 | B3PW91 |
|---|---|---|---|---|---|---|---|
| | | | | Deviation (Expt.-Theory) | | | |
| $CH_2$=CHCN (acrylonitrile) | 130.3 | 4.9 | 29.6 | 11.2 | −2.0 | 22.9 | 0.8 |
| $CH_3COCH_3$ (acetone) | 158.2 | −3.7 | 32.0 | 5.0 | −2.0 | 33.3 | 2.7 |
| $CH_3COOH$ (acetic acid) | 152.0 | 1.9 | 31.9 | 10.0 | −2.6 | 27.3 | 1.7 |
| $CH_3COF$ (acetyl fluoride) | 136.7 | 3.7 | 29.4 | 11.9 | −1.5 | 24.1 | 3.0 |
| $CH_3COCl$ (acetyl chloride) | 129.0 | 1.3 | 28.6 | 11.8 | −2.5 | 24.2 | 4.1 |
| $CH_3CH_2CH_2Cl$ (propyl chloride) | 147.1 | −14.0 | 25.7 | −3.0 | −4.6 | 33.9 | 2.2 |
| $(CH_3)_2CHOH$ (isopropanol) | 170.8 | −11.6 | 30.2 | −3.7 | −4.5 | 36.6 | −0.5 |
| $C_2H_5OCH_3$ (methyl ethyl ether) | 171.2 | −8.0 | 32.7 | −1.3 | −1.5 | 38.5 | 1.5 |
| $(CH_3)_3N$ (trimethylamine) | 179.1 | −7.9 | 36.0 | −2.5 | 0.2 | 43.2 | 1.9 |
| $C_4H_4O$ (furan) | 190.1 | −2.1 | 39.0 | 16.1 | −4.2 | 36.5 | 7.7 |
| $C_4H_4S$ (thiophene) | 175.8 | −9.6 | 33.6 | 12.1 | −7.9 | 33.9 | 6.8 |
| $C_4H_5N$ (pyrrole) | 198.8 | −1.1 | 43.2 | 16.1 | −0.8 | 42.9 | 10.1 |
| $C_5H_5N$ (pyridine) | 226.6 | 1.0 | 49.7 | 20.5 | −0.2 | 48.2 | 11.9 |
| Inorganic hydrides | | | | | | | |
| $H_2$ | 3.7 | 0.2 | 2.3 | −3.5 | 1.0 | 2.8 | −2.0 |
| HS | 12.3 | 0.9 | 4.4 | 0.3 | 1.4 | 4.4 | 0.7 |
| Radicals | | | | | | | |
| CCH | 47.8 | −0.4 | 9.4 | 4.2 | −3.4 | 6.8 | −0.3 |
| $C_2H_3(^2A')$ | 69.1 | 2.6 | 18.1 | 6.0 | 3.3 | 18.8 | 5.2 |
| $CH_3CO(^2A')$ | 105.7 | 6.3 | 26.9 | 11.7 | 2.1 | 22.6 | 5.1 |
| $H_2COH(^2A)$ | 74.6 | 3.8 | 19.1 | 5.6 | 2.4 | 17.6 | 3.0 |
| $CH_3O(^2A')$ | 69.8 | 4.6 | 18.7 | 5.6 | 3.7 | 17.7 | 3.6 |
| $CH_3CH_2O(^2A'')$ | 113.2 | −0.7 | 25.2 | 3.7 | 1.4 | 26.9 | 3.4 |
| $CH_3S(^2A')$ | 54.7 | −0.8 | 14.4 | 2.2 | 1.7 | 16.3 | 3.3 |
| $C_2H_5(^2A')$ | 81.4 | −2.7 | 19.3 | 0.8 | 2.8 | 24.3 | 4.7 |
| $(CH_3)_2CH(^2A')$ | 127.5 | −6.5 | 27.4 | 0.6 | 1.8 | 35.0 | 5.9 |
| $(CH_3)_3C$ (*t*-butyl radical) | 172.3 | −12.4 | 33.7 | −1.6 | −1.1 | 44.0 | 5.5 |
| $NO_2$ | 104.7 | 28.4 | 40.8 | 32.2 | 5.2 | 17.4 | 6.9 |

[a]Using 6-311+G($3df$,2p) basis. Deviations (in kcal/mol) are with respect to the experimental enthalpies of formation at 298 K (in kcal/mol).

that a spin–orbit correction is needed for the molecules containing two or more chlorines.

## C. G2(MP2) and G2(MP2,SVP) theory

The two modified versions of G2 theory, G2(MP2) and G2(MP2,SVP), have average absolute deviations of 2.45 and 2.30 kcal/mol with maximum deviations of 10.1 and 12.5 kcal/mol, respectively, for the G2-2 test set. These two modifications do better on the G2-1 test set (deviations are 1.35 and 1.32 kcal/mol, respectively) than on the G2-2 test set. The overall deviations for the G2(MP2) and G2(MP2,SVP) methods are 2.04 and 1.93 kcal/mol, respectively, about 0.4

TABLE V. Summary of average deviations and maximum deviations in kcal/mol).

| Method | G2-1 (55) | | | G2-2 (93) | | | G2 (148) |
|---|---|---|---|---|---|---|---|
| | Avg. abs. dev. | Maximum. deviation[b] | | Avg. abs. dev. | Maximum deviation[b] | | Avg. abs. dev. |
| G2 | 1.23 | 2.9 | −5.0 | 1.80 | 8.2 | −7.1 | 1.58 |
| G2(MP2) | 1.35 | 4.2 | −2.6 | 2.45 | 10.1 | −5.3 | 2.04 |
| G2(MP2,SVP) | 1.32 | 4.2 | −4.3 | 2.30 | 12.5 | −5.2 | 1.93 |
| SVWN | 39.60 | 93.8 | −0.4 | 121.21 | 228.7 | c | 90.88 |
| BLYP | 4.69 | 15.3 | −10.2 | 8.50 | 28.4 | −24.8 | 7.09 |
| BPW91 | 5.20 | 19.1 | −14.4 | 9.42 | 32.2 | −15.7 | 7.85 |
| BP86 | 10.53 | 26.1 | −3.6 | 25.91 | 49.7 | −6.3 | 20.19 |
| B3LYP | 2.43 | 8.2 | −10.0 | 3.52 | 5.2 | −20.1 | 3.11 |
| B3PW91 | 2.59 | 7.4 | −8.6 | 4.06 | 12.0 | −21.8 | 3.51 |
| B3P86 | 7.84 | 24.6 | −3.6 | 23.95 | 49.2 | −7.8 | 17.97 |

[a]Number of molecules in each test set given in parentheses. The G2 test set is a combination of the G2-1 and G2-2 test sets.
[b]Largest negative and positive deviations in each test set.
[c]No negative deviations.

TABLE VI. Average absolute deviations (in kcal/mol) for different types of molecules.

| Method | Test set | Type of molecule[a] | | | | |
|---|---|---|---|---|---|---|
| | | Non-hydrogen | Hydrocarbons | Substituted hydrocarbons | Radicals | Inorganic hydrides |
| G2 | G2-1 | 1.73 (14) | 0.88 (5) | 0.95 (5) | 1.18 (18) | 0.99(13) |
| | G2-2 | 3.06 (21) | 1.41(17) | 1.54(42) | 1.14 (11) | 0.67 (2) |
| | G2 | 2.53 (35) | 1.29(22) | 1.48(47) | 1.16 (29) | 0.95(15) |
| G2(MP2) | G2 | 3.30 | 1.83 | 1.89 | 1.36 | 1.20 |
| G2(MP2,SVP) | G2 | 3.57 | 0.77 | 2.04 | 1.20 | 0.91 |
| SVWN | G2 | 73.58 | 133.71 | 124.41 | 54.56 | 33.65 |
| BLYP | G2 | 10.30 | 8.09 | 6.10 | 6.09 | 3.13 |
| BPW91 | G2 | 12.25 | 4.85 | 7.99 | 6.48 | 4.21 |
| BP86 | G2 | 16.61 | 25.82 | 26.80 | 15.76 | 8.16 |
| B3LYP | G2 | 5.35 | 2.76 | 2.10 | 2.98 | 1.84 |
| B3PW91 | G2 | 5.14 | 3.96 | 2.77 | 3.21 | 1.99 |
| B3P86 | G2 | 7.80 | 30.81 | 25.49 | 13.53 | 7.86 |

[a]Number of molecules in each type is listed in parentheses.

kcal/mol larger than G2 theory.

The faster G2(MP2,SVP) method does slightly better than the G2(MP2) method in terms of average absolute deviation. This is largely because G2(MP2,SVP) theory does better for the hydrocarbons than G2(MP2) theory. G2(MP2,SVP) has an average absolute deviation of 0.77 kcal/mol for the 22 hydrocarbons, while G2(MP2) theory has a deviation of 1.83 kcal/mol for the same set. Surprisingly, G2(MP2,SVP) theory also does significantly better than G2 theory which has an average absolute deviation of 1.29 kcal/mol for the hydrocarbons. The eight cyclic hydrocarbons have an average absolute deviation of 1.06 kcal/mol in G2(MP2,SVP) theory, much smaller than the 1.94 kcal/mol

for G2 theory and 2.70 kcal/mol for G2(MP2) theory. The reason for the very good performance of G2(MP2,SVP) theory on cyclic systems compared to the other methods is not obvious. Only one of the cyclic systems (methylene cyclopropane) differs by more than 2 kcal/mol with experiment. G2(MP2,SVP) theory also does well for the set of radicals, which are all hydrocarbons except $NO_2$, and the inorganic hydrides.

## D. Density functional methods

The DFT methods give a wide range of average absolute deviations (3.11 to 91.2 kcal/mol) for the G2 test set. As
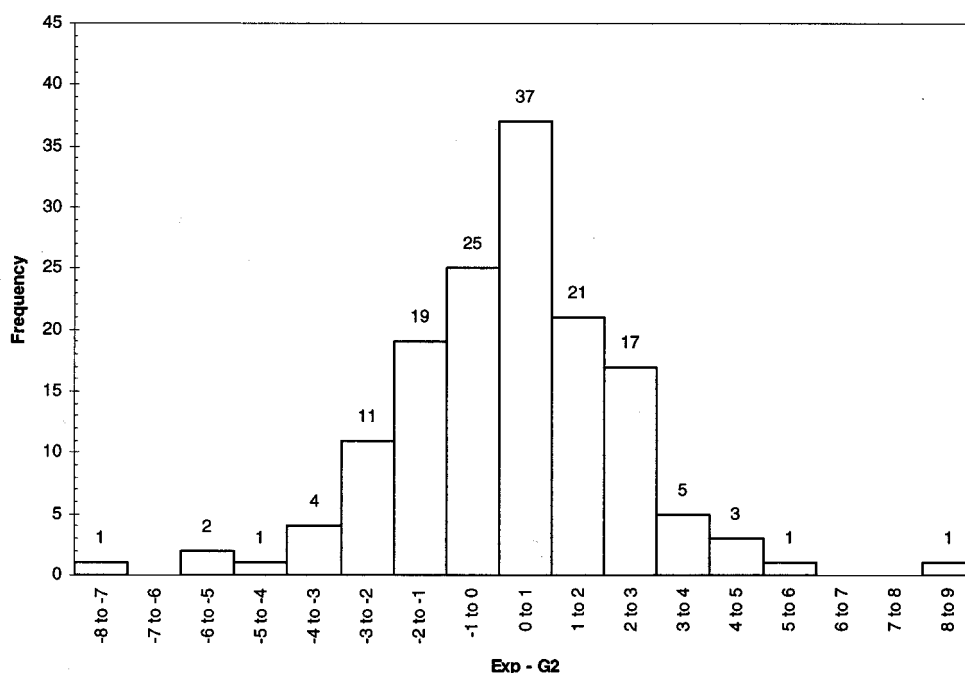


FIG. 1. Effect of inclusion of spin–orbit effect on the deviation between G2 and experimental atomization energies for selected fluorides and chlorides. The experimental atomization energies are derived from experimental enthalpies of formation at 0 K (Ref. 25) via Eq. (1).

TABLE VII. Average absolute deviations (in kcal/mol) for G2 theory when spin–orbit corrections are included.[a,b]

|  | G2-1 | G2-2 | G2 |
|---|---|---|---|
| Overall | 1.26 (0.03) | 1.59 (−0.21) | 1.47 (−0.11) |
| Non-hydrogen | 1.81 (0.08) | 2.36 (−0.71) | 2.14 (−0.39) |
| Hydrocarbon | 0.88 (0.00) | 1.59 (0.19) | 1.43 (0.14) |
| Substituted hydrocarbon | 0.77 (−0.18) | 1.32 (−0.23) | 1.26 (−0.22) |
| Radicals | 1.33 (0.15) | 1.32 (0.18) | 1.32 (0.17) |
| Inorganics hydrides | 0.90 (−0.09) | 0.64 (−0.10) | 0.86 (−0.08) |

[a]Spin–orbit corrections are included for $^2P$ and $^3P$ atoms and $^2\Pi$ molecules as described in text. Corrections (in mh) for atoms are derived from Moore's Tables (Ref. 38, 39): B (−0.05), C (−0.14), O (−0.36), F (−0.61), Al (−0.34), Si (−0.68), S (−0.89), Cl (−1.34). Corrections (in mh) for molecules are derived from Huber and Herzberg (Ref. 34): CH (−0.06), OH (−0.32), SH (0.86), NO (−0.27), ClO (−0.73).

[b]Change from average absolute deviation for G2 theory from Table VI listed in parentheses.

expected, the local density method (SVWN) performs poorly with a deviation of 90.9 kcal/mol and overbinds all systems except $Li_2$. However, it should be noted that this model contains no parameterization, and application of empirical corrections as in other methods can significantly improve its performance. For the remaining gradient corrected functionals, the average absolute deviation ranges from 3.11 to 20.19
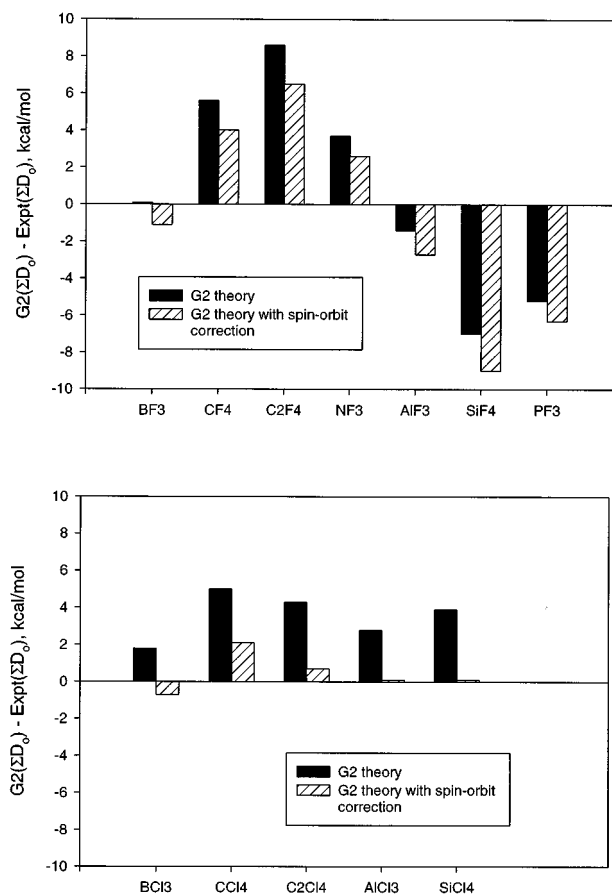




FIG. 2. Histogram of G2 deviations for the G2 neutral test set. Each vertical bar represents deviations in a 1 kcal/mol range.

kcal/mol. The Becke three parameter functional performs better than the Becke exchange functional with all three correlation functionals. Bauschlicher[14] has examined the five DFT methods [BLYP, B3LYP, BP86, B3LYP, BP] for the 55 molecule G2-1 test set using the same $6-311+G(3df,2p)$ basis set. He also finds that B3LYP gives the best agreement with experiment (average absolute deviation of 2.20 kcal/mol). The slightly lower deviation than what we find for the G2-1 test set (2.43 kcal/mol) may be due to his use of B3LYP/$6-31G(d)^*$ geometries and zero-point energies instead of MP2/$6-31G(d)^*$ geometries and scaled HF/$6-31G(d)^*$ zero-point energies. The B3PW91 average absolute deviation is 2.59 kcal/mol for the G2-1 test set. This is consistent with Becke's[15] results (2.4 kcal/mol) on the original G2 test set using a numerical basis set. Becke used the PW91 correlation functional in combination with his three parameter exchange functional.

The maximum deviations of the DFT methods are significantly larger than those of the G2 methods. For example, B3LYP has a maximum deviation of 20.1 kcal/mol compared to 8.2 kcal/mol for G2 theory. The B3LYP method has the largest deviation for non-hydrogen systems (5.35 kcal/mol) while hydrocarbons, substituted hydrocarbons, and radicals have smaller average deviations (2 to 3 kcal/mol). The distribution of deviations for B3LYP is given in Fig. 3. About 50% of the B3LYP enthalpies fall within ±2 kcal/mol of the experimental values and 63% fall within ±3 kcal/mol. While the deviations for G2 theory are quite equally distributed (Fig. 1), the B3LYP method has more negative deviations (underbinding). The B3LYP distribution covers a much larger range (−20 to 8 kcal/mol) than G2 theory (−8 to 7 kcal/mol). The distribution for the BLYP method is also given in Fig. 3. The distribution for this non-hybrid DFT method is over a larger range (−25 to 28) than the B3LYP method, but is more equally distributed. The performance measures discussed above have important consequences. The best performing B3LYP functional has an average absolute deviation (3.11 kcal/mol) almost twice that of G2 theory. Among the 148 molecules studied, only 5 have deviations of 5 kcal/mol or more with G2 theory, whereas 25 molecules have deviations of more than 5 kcal/mol with the B3LYP functional. These considerations may be important for assessing the thermochemistry of systems where there is disagreement between theory and experiment or for making predictions for systems where there are no experimental measurements.

We have calculated B3LYP/$6-31G(d)$ geometries and zero-point energies for the G2 test set and recalculated the B3LYP enthalpies [$6-311+G(3df,2p)$ basis]. The use of unscaled B3LYP/$6-31G(d)$ zero-point energies gives an average absolute deviation with experiment that is significantly larger than obtained with scaled HF/$6-31G(d)$ zero-point energies. The use of B3LYP/$6-31G(d)$ geometries has little effect on the average absolute deviation. Scale factors for B3LYP zero-point energies are being investigated and the results of this study will be published elsewhere.[42]
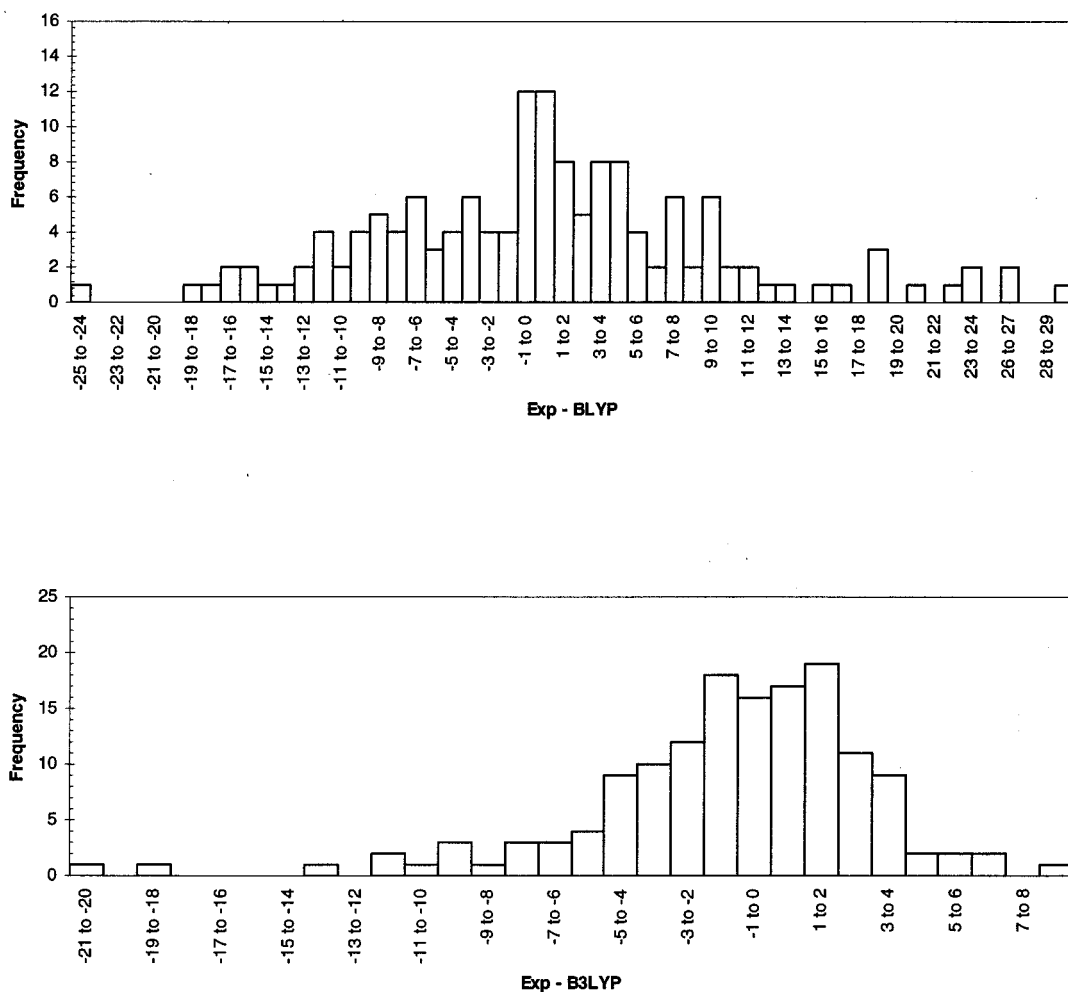
FIG. 3. Histogram of B3LYP and BLYP deviations for the G2 neutral test set. Each vertical bar represents deviations in a 1 kcal/mol range.

## V. CONCLUSIONS

A set of 148 molecules having well-established enthalpies of formation at 298 K has been presented. This set, referred to as the G2 neutral test set, includes the 55 molecules whose atomization energies were used to test G2 theory[1] and 93 new molecules. The G2 test set has 29 radicals, 35 non-hydrogen systems, 22 hydrocarbons, 47 substituted hydrocarbons, and 15 inorganic hydrides. The critical documentation and evaluation of theoretical models is essential to their becoming proper tools for chemical investigation. It is hoped that this new test set will provide a means for assessing and improving new theoretical models. We have used the new G2 test set to assess the performance of G2 and DFT theories in the calculation of enthalpies of formation. The following conclusions can be drawn from this study:

(1) G2 theory is the most reliable of the methods examined. The average absolute deviation for the 148 enthalpies is 1.58 kcal/mol. This is larger than for the original G2 test set of 55 molecules (1.23 kcal/mol), mainly due to the new molecules containing multiple halogens and molecules with unsaturated rings. Inclusion of spin–orbit effects reduces the average absolute deviation to 1.47 kcal/mol.

(2) The largest deviations between experiment and G2 theory (up to 8 kcal/mol) occur for molecules having multiple halogens. Inclusion of spin–orbit effects significantly improves the results for the chlorine substituted molecules, but little overall improvement is seen for the fluorine substituted molecules.

(3) The G2 enthalpies of formation for cyclic hydrocarbons with unsaturated rings deviate with experiment by 2–4 kcal/mol. The other hydrocarbons are generally in good agreement with experiment.

(4) The two modified versions of G2 theory, G2(MP2) G2(MP2,SVP), have average absolute deviations of 2.04 and 1.93 kcal/mol, respectively. G2(MP2,SVP) theory appears to be very good for hydrocarbons, radicals, and inorganic hydrides. Surprisingly, this approximation does better for hydrocarbons than G2 theory, especially cyclic systems for which it has an average absolute deviation of 1.06 kcal/mol. Since G2(MP2,SVP) theory uses considerably less cpu time and disk storage than G2 theory it may be a useful alternative for large hydrocarbons.

(5) The B3LYP method performs the best of the seven DFT methods investigated. This is consistent with the find-

ings of Bauschlicher[14] who examined five DFT methods on the G2-1 test set. B3LYP has an average absolute deviation of 3.11 kcal/mol for the full G2 test set. The BLYP method performs the best of the nonhybrid DFT methods, although it has a much larger average absolute deviation (7.09 kcal/mol). The maximum deviations of the DFT methods are much larger than those of the G2 methods.

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