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Simultaneous Adjustment of Experimentally Based Enthalpies of Formation of CF_3X, X = nil, H, Cl, Br, I, CF_3, CN, and a Probe of G3 Theory

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The enthalpies of formation of the title compounds have been determined by simultaneous least-squares solution of a thermochemical network containing 28 experimental measurements extracted from the literature. The new enthalpies differ considerably from the older tabulated values and now show a high degree of internal consistency achieved through excellent agreement with newer experiments, as well as older calorimetric determinations. The fitted values are: $\Delta H_{f298}°(CF_3) = -111.3 \pm 0.5$ kcal/mol (-110.6 ± 0.5 kcal/mol at 0 K), $\Delta H_{f298}°(CF_3H) = -165.6 \pm 0.5$ kcal/mol (-163.9 ± 0.5 kcal/mol at 0 K), $\Delta H_{f298}°(CF_3Cl) = -169.5 \pm 0.7$ kcal/mol (-168.3 ± 0.7 kcal/mol at 0 K), $\Delta H_{f298}°(CF_3Br) = -155.3 \pm 0.5$ kcal/mol (-152.4 ± 0.5 kcal/mol at 0 K), $\Delta H_{f298}°(CF_3I) = -140.1 \pm 0.5$ kcal/mol (-138.7 ± 0.5 kcal/mol at 0 K), $\Delta H_{f298}°(C_2F_6) = -321.3 \pm 0.8$ kcal/mol (-319.3 ± 0.8 kcal/mol at 0 K), and $\Delta H_{f298}°(CF_3CN) = -118.4 \pm 0.4$ kcal/mol (-117.5 ± 0.4 kcal/mol at 0 K). Theoretical calculations at the Gaussian-3 (G3) level of theory have been performed for a subgroup of these molecules, which were problematic at the Gaussian-2 (G2) level of theory. In comparison to G2 theory, the G3 results show a remarkable improvement in accuracy and agree with experiment within <2 kcal/mol. An isodesmic bond-separation scheme brings the calculated values even closer to the experiment. In addition, the G3 value for the ionization energy of CF_3, 9.08 eV, was found to be in good agreement with the recent experimental value of $9.05_5 \pm 0.01_1$ eV. Further indications that the experimental value for $\Delta H_f°(C_2F_4)$ is probably too high are also presented.

1. Introduction

The implication that the generally accepted enthalpies of formation[1,2] of trifluoromethanes, CF_3X (X = H, Cl, Br, and I), are probably not entirely consistent has been resurfacing periodically over the years. For example, Berman et al.[3] pointed out that $\Delta H_f°(CF_3Cl)$ and $\Delta H_f°(CF_3Br)$ were determined relative to $\Delta H_f°(CF_3I)$ while the latter had been determined relative to $\Delta H_f°(CF_3H)$ and, hence, tended to favor the value of $\Delta H_f°(CF_3^+)$ established relative to $\Delta H_f°(CF_3I)$. Similarly, Tsang[4] preferred $\Delta H_{f298}°(CF_3) = -110.0 \pm 1.0$ kcal/mol derived from tabulated kinetic data relating to CF_3H over the lower value of -111.3 ± 1.7 kcal/mol implied by his measurement of the CF_3-Br bond dissociation energy. Another example is the recent analysis of kinetic measurements on several halocarbon species in which Kumaran et al.[5] stated that various experimental, theoretical, and tabulated values can be reconciled only if error bars are increased beyond their original magnitudes.

Very recently, Asher and Ruscic,[6] while determining the CF_3-I and CF_3-Br bond dissociation energies and an upper limit to the CF_3-Cl bond energy using the photoionization mass spectrometric method, furnished additional and more direct indications that the tabulated enthalpies of formation of trifluorohalomethanes may be inconsistent on a level of ~1 kcal/mol. The value $D_{298}(CF_3-I) = 53.9 \pm 1.3$ kcal/mol, implied by the enthalpies of formation tabulated in JANAF,[1] $\Delta H_{f298}°(CF_3I) = -140.8 \pm 0.8$ kcal/mol and $\Delta H_{f298}°(CF_3) = -112.4 \pm 1.0$ kcal/mol, is in relatively good agreement with the value $D_{298}(CF_3-I) = 54.3 \pm 0.3$ kcal/mol obtained by Asher and Ruscic,[6] which is in turn in excellent agreement with recent kinetic determinations by Skorobogatov et al.[7−9] ($54.4_4 \pm 0.4$ kcal/mol at 298 K) and in reasonable agreement with Kumaran et al.[10] (55.6 ± 1.5 kcal/mol at 298 K). On the other hand, $D_{298}(CF_3-Br) = 70.8 \pm 0.3$ kcal/mol, which was obtained by Asher and Ruscic[6] in a completely analogous fashion, is ~1.4 kcal/mol higher than the value of 69.4 ± 1.2 kcal/mol derived using JANAF's[1] $\Delta H_{f298}°(CF_3Br) = -155.1 \pm 0.7$ kcal/mol while at the same time it is in exceedingly good agreement with the kinetic determinations by Tsang[4] and Skorobogatov et al.[11,12] (70.5 ± 1.0 and 70.8 ± 0.2 kcal/mol, respectively) and has been additionally corroborated by the most recent measurements of Hranisavljevic et al.[13] Hence, while it appears that these newer experiments achieve a consensus on the CF_3-Br and CF_3-I bond dissociation energies, they are at least partly at variance with JANAF's values.

Since one can generally assume that enthalpies of formation of radicals are less firmly established than those of stable substances, it appears quite reasonable to try to use the measured bond energies to redetermine the value for $\Delta H_f°(CF_3)$. One of the consequences of the discrepancy noted above is that the two values of $\Delta H_f°(CF_3)$ that can be obtained by combining the newer measurements of bond dissociation energies with the tabulated enthalpies of formation of CF_3I and CF_3Br differ by 1.0 ± 1.1 kcal/mol. Asher and Ruscic[6] pointed out the inconsistency and side-stepped the problem by proposing a weighted average of the two possibilities, $\Delta H_{f298}°(CF_3) = -111.4 \pm 0.9$ kcal/mol, which is ~1.0 kcal/mol higher than JANAF.[1] Al-

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though this approach is not an unreasonable compromise, the situation is potentially hazardous since it does not really address a possible underlying discrepancy between $\Delta H_f°(CF_3Br)$ and $\Delta H_f°(CF_3I)$. In addition, Asher and Ruscic[6] have shown that the inconsistencies may also involve CF_3Cl since an analysis based on their upper limit to $D(CF_3-Cl)$, their new value for $\Delta H_f°(CF_3)$, and the kinetic results by Kumaran et al.[5] led them to an estimate that the tabulated[1,2] $\Delta H_f°(CF_3Cl)$ is probably too high by 0.5−1.0 kcal/mol.

Very recently Hranisavljevic and Michael[14] have examined the forward and reverse rate constants for the reaction $CF_3 + H_2 \rightarrow CF_3H + H$ and found that their data agrees very well with $\Delta H_{r0}°$ of $-1.5_6 \pm 0.6_0$ kcal/mol. This implies $D_{298}(CF_3-H) = 106.3_0 \pm 0.6_0$ kcal/mol, which is virtually identical to JANAF's[1] value. In other words, accepting JANAF's $\Delta H_{f298}°(CF_3H) = -166.6 \pm 0.8$ kcal/mol, which appears more "fundamental" than the enthalpies of formation of either CF_3Br or CF_3I, tends to favor the older tabulated value $\Delta H_{f298}°(CF_3) = -112.4 \pm 1.0$ kcal/mol, in contrast to the studies discussed above.

Although superficially it may appear as if all the discrepancies can be resolved by a judicious selection of the proper value for $\Delta H_f°(CF_3)$, further analysis shows that this is not the case. One can easily derive a relation such as $\Delta H_f°(CF_3X) - \Delta H_f°(CF_3Y) = D(CF_3-Y) - D(CF_3-X) + \Delta H_f°(X) - \Delta H_f°(Y)$, which does not explicitly involve $\Delta H_f°(CF_3)$. Together with well-established[15] enthalpies of formation of the halogen atoms, the measurements discussed above produce $\Delta H_{f298}°(CF_3I) - \Delta H_{f298}°(CF_3Br) = 15.3 \pm 0.4$ kcal/mol, to be compared to JANAF's[1] 14.3 ± 1.0 kcal/mol. Similarly, $\Delta H_{f298}°(CF_3-Br) - \Delta H_{f298}°(CF_3-H) = 10.1 \pm 0.7$ kcal/mol, while JANAF gives 11.5 ± 1.0 kcal/mol. On the other hand, $\Delta H_{f298}°(CF_3-I) - \Delta H_{f298}°(CF_3-H) = 25.4 \pm 0.7$ kcal/mol is in much more reasonable agreement with JANAF's 25.8 ± 1.1 kcal/mol. This may suggest that the enthalpies of formation of CF_3H and CF_3I are mutually consistent and all that may be necessary is to lower $\Delta H_f°(CF_3Br)$ by ∼1.0−1.4 kcal/mol.

However, such an approach would be blatantly simplistic since the enthalpies of formation of these compounds, as they appear in the JANAF tables,[1] were derived by Syverud[16] via a least-squares fit of a thermochemical network defined by 20 links representing the experimental enthalpies of reaction available at the time. The network involves C_2F_4, C_2F_6, CF_3CN, CF_3H, CF_3Cl, CF_3Br, CF_3I, and CF_3, although the latter appears to be more loosely coupled to the others, and hence, there may be some basis for adjusting it independently. Here we note parenthetically that the compilation by Gurvich et al.,[2] which lists values that are practically the same as those given by JANAF for the compounds of interest, refers to a somewhat similar simultaneous determination that included CF_3H, CF_3Cl, CF_3Br, CF_3I, and C_2F_6 (but not CF_3, CF_3CN, and C_2F_4), albeit without giving the level of details provided by Syverud.[16] Clearly, the tabulated enthalpies are related in a nontrivial way, and a change in value of one of the trifluorohalomethanes affects the others. In particular, the error bar quoted for $\Delta H_f°(CF_3Br)$, ±0.7 kcal/mol, is slightly lower than the error bars associated with CF_3H or CF_3I (both ±0.8 kcal/mol), making it appear that, if anything, the former is slightly more "fundamental" than the latter two. Hence, any attempt to adjust $\Delta H_f°(CF_3Br)$ from the outside is likely to immediately produce even larger incompatibilities, since both $\Delta H_f°(CF_3H)$ and $\Delta H_f°(CF_3I)$ are related to it through obscure relationships. The only possible approach that can alleviate the inconsistencies discussed above is to redetermine simultaneously all the enthalpies of formation involved in the thermochemical network while including the newer data.

The group of halogenated compounds examined here has an environmental relevance, and knowledge of reasonably accurate thermochemical values is desirable for predicting the outcome of various chemical reactions, hence helping the design of potential routes of clean disposal of stockpiles of various industrial halocarbons that have been phased out.

Reliable experimental thermochemical values are also highly desirable to efficiently develop and test state of the art ab initio calculations, which now appear to approach experimental accuracies. When a variance between an experimental and a theoretical enthalpy of formation arises, it is not always immediately obvious whether the calculated value or the individual experimental determination is in error or, perhaps, whether there are inaccuracies in both. On the other hand, when systematic variances between experimental values and calculated results at a particular level of theory are discovered for a class of compounds, one tends to implicitly assume that inaccuracies in the individual experimental results have been largely eliminated by virtue of statistical averaging over the large number of comparisons and, hence, tends to conclude that theory is at fault. However, such a conclusion is not as unambiguous as it may seem at first sight. Thermodynamical tables are essentially collections of evaluated experimental cross-links between enthalpies of formation of various compounds. In particular, experimental enthalpies of formation within a class of related compounds tend to be pegged to each other. In such situations, if there are hidden errors in some of the key values, the inaccuracies will tend to propagate through the thermochemical table and cause a systematic distortion of the enthalpies of formation for a larger group of compounds. Several of the molecules reexamined here are to some degree in the class of such "key" compounds.

For small molecules containing elements H−Cl, Gaussian-2 (G2) theory[17,18] has by now established a very good track record of routinely delivering enthalpies of formation that are on the average accurate within 2 kcal/mol.[19,20] However, recently it became apparent that a variety of ab initio approaches may have a problem in correctly reproducing the thermochemical properties of molecules containing multiple fluorine atoms.[21] This observation includes the G2 theory, where a recent reassessment[19] using a set of 148 apparently well-established experimental enthalpies of formation has shown that some of the largest deviations between experiment and calculations tend to occur for these types of molecules. To correct this problem, as well as other known deficiencies of the G2 theory, Curtiss et al.[22] have set forth Gaussian-3 (G3) theory. The new features of G3 theory give a significant improvement in the heats of formation of non-hydrogen compounds and substituted hydrocarbons, as well as in ionization potentials and electron affinities. The initial report[22] shows that the average absolute deviation for enthalpies of formation for non-hydrogen molecules in the test set decreases from 2.5 (G2) to 1.7 kcal/mol (G3), for hydrocarbons from 1.3 to 0.7 kcal/mol, and for substituted hydrocarbons from 1.5 to 0.6 kcal/mol, while for ionization energies and electron affinities, the average absolute error reduces from 1.4 to 1.1 kcal/mol.

This paper has two parts. The first part addresses the primary goal of this investigation, which is the determination of adjusted experimentally based enthalpies of formation for CF_3X, X = nil, H, Cl, Br, I, CF_3, and CN, that will have a significantly higher degree of internal consistency than the older values found in JANAF[1] and Gurvich et al.[2] Since the level of inconsistency in the old values appears to be of the order of ~1 kcal/mol, one can anticipate that the adjusted values will differ from the tabulations by similar amounts. The second part of this paper uses these adjusted values to probe the newly developed G3 level of theory. Since the expected deviations between calculated and experimental enthalpies of formation even at the G3 level of theory are larger than 1 kcal/mol, one should not expect that theory will be particularly helpful in validating the new adjusted values versus the old tabulated values (or vice versa). However, the availability of adjusted (and hence authenticated) experimental values provides a very attractive opportunity to candidly test the performance of the new G3 theory. These molecules fall within the group of cases that appeared problematic at the G2 level of theory but were not included in the G2197 test set, since they did not necessarily appear sufficiently well-established experimentally.

2. Computational Details

A. Simultaneous Adjustment of Experimental Enthalpies of Formation. The basic procedure applied here follows the standard guidelines for solving overdetermined thermochemical networks.[23,24] A thermochemical network is a collection of experimentally derived links interrelating the elements of a block of thermodynamic properties, such as enthalpies of formation of a group of molecules.

The creation of links that define the network is best illustrated by an example. Let us consider an experimental determination of the enthalpy of some chemical reaction $AB + C \rightarrow AC + D$, $\Delta H_{r298}{}^\circ(i) = A_i \pm \Delta_i$, which provides link i in the thermochemical network. Here, $\Delta H_{f298}{}^\circ(AB)$ and $\Delta H_{f298}{}^\circ(AC)$ are treated as unknowns, since AB and AC belong to the group of molecules whose enthalpies of formation are to be determined, while $\Delta H_{f298}{}^\circ(C)$ and $\Delta H_{f298}{}^\circ(D)$ are treated as constants, since they are assumed to be well-known from other, independent measurements. $A_i \pm \Delta_i$ is the experimental determination of $\Delta H_{r298}{}^\circ(i)$ together with the associated uncertainty. At least initially, the uncertainty Δ_i is customarily chosen simply to correspond to the value assigned by the authors of the original measurements, although, if necessary, this can be changed by the evaluator. From $\Delta H_{r298}{}^\circ(i) = \Delta H_{f298}{}^\circ(AC) + \Delta H_{f298}{}^\circ(D) - \Delta H_{f298}{}^\circ(AB) - \Delta H_{f298}{}^\circ(C)$, one obtains $\Delta H_{f298}{}^\circ(AC) - \Delta H_{f298}{}^\circ(AB) = (A_i \pm \Delta_i) + \Delta H_{f298}{}^\circ(C) - \Delta H_{f298}{}^\circ(D)$ or, after substituting the known values for $\Delta H_{f298}{}^\circ(C)$ and $\Delta H_{f298}{}^\circ(D)$, $\Delta H_{f298}{}^\circ(AC) - \Delta H_{f298}{}^\circ(AB) = a_i \pm \delta_i$. The error bar δ_i combines the original experimental uncertainty Δ_i of the measurement and the uncertainties associated with $\Delta H_{f298}{}^\circ(C)$ and $\Delta H_{f298}{}^\circ(D)$ via standard error propagation methods. Hence, a thermochemical network of m links defining n enthalpies of formation reduces to a set of m linear algebraic equations $\sum_j c_{ij} x_j = a_i \pm \delta_i$, $j = 1,2,...n$, $i = 1,2,...m$. The coefficients c_{ij} reflect the stoichiometry of the chemical reaction i, while x_j are the enthalpies of formation to be solved for. In general, the network is overdetermined if $m > n$. As a rule, the coefficient matrix of the network is very sparse, since in every row i there are typically only one or two (and very rarely three) $c_{ij} \neq 0$ coefficients.

The optimal solution for the system is then achieved by a least-squares fit using linearly weighted residuals r_i/δ_i, where $r_i = a_i - \sum_j c_{ji} x_j$. The weighting of residuals ensures that the uncertainties of the experimental determinations are taken into account by the fit. Under these conditions, the standard deviations (and/or various confidence limits) normally obtained from the least-squares analysis reflect both the experimental uncertainties of the individual links and the overall uncertainty of the fit. Inverse linear weighting (as opposed to inverse square) has been advocated[24] to avoid overemphasizing measurements which may have unrealistically tight error bars.

According to the CODATA recommendation, the final error-weighted least-squares fit is to be preceded by a least absolute sum analysis performed on an equally weighted set.[24] This approach is used to assess the overall consistency of the data and as a diagnostic tool to identify measurements that may require reexamination. During this step, various possible subsets of equations are selected and solved exactly. The differences between the experimental values a_i and values obtained by these linear solutions are compared with the associated nominal uncertainties δ_i to give an overall measure of goodness. If for any link such residuals are systematically larger than the experimental uncertainty δ_i, then one has to consider revising the latter accordingly before the final fit.

B. Ab Initio Calculations. Ab initio calculations at the G3[22] level of theory have been performed using the Gaussian 94 package.[25] G3 theory, the latest in the series of Gaussian-*n* theories, uses a sequence of calculations similar to those performed at the G2 level[17] but achieves higher accuracy than its predecessor on the G2/97 test set.[19,20] Full details of the G3 theory are given elsewhere.[22] Here we highlight only the main differences in this new approach. One major change is the use of a larger basis set, G3Large,[22] instead of the 6-311+G(3df,2p) basis set in the last step, which is now carried out at the MP2(full) level rather than MP2(fc). At the same time, the smaller 6-31G(d) basis set is used instead of 6-311G(d) at the MP4 and QCISD(T) levels. Other changes involve the introduction of separate higher level corrections for atoms and molecules and a spin−orbit correction for atoms. If different additivity approximations work well, the G3 sequence should produce a result that is effectively at the QCISD(T,full)/G3Large level, compared to an effective QCISD(T)/6-311+G(3df,2p) level for the G2 calculation. The use of a smaller basis set at the higher levels of calculation substantially decreases the overall amount of needed computational resources.

3. Results and Discussion

A. Simultaneous Determination of the Enthalpies of Formation. *I. Outline of the Thermochemical Network.* The 20 original links used by Syverud[16] are listed in Table 1. These reflect a substantial body of various calorimetric, equilibrium, and kinetic measurements.[26−43] The individual links were already very thoroughly analyzed and discussed by Syverud.[16] In several instances, Syverud's analysis led to values and/or associated uncertainties that are slightly different than those proposed by the original authors. In particular, the equilibrium data involved in links 6−12 have been reduced by second- and third-law analysis and the adopted value A_i was taken as the mean of the third-law values derived from the individual equilibrium constants while the uncertainty Δ_i was estimated as the larger of the precision index of the individual values or the uncertainty of the product $T\Delta S_{rT}{}^\circ$.[16] In several other cases Syverud's analysis led to the adoption of a slightly increased uncertainty. During the initial setup of the thermochemical network, we completely accept the $\Delta H_{r298}{}^\circ$ values (and associated uncertainties) as selected and adopted by Syverud, including all of his amendments and departures from original values. The only exception is a very slight change in links 19 and 20, which correspond to the equilibrium measurements on C_2F_6/CF_3CN and the calorimetric measurement on CF_3CN. At the time of ref 16, $\Delta H_{r298}{}^\circ(19)$ and $\Delta H_{r298}{}^\circ(20)$ were at a level of private communication by Perettie and Walker to Syverud. Since then,

TABLE 1: Twenty Original Reactions Used in the Simultaneous Adjustment of JANAF Enthalpies of Formation for CF_3X, X = nil, H, Cl, Br, I, CF_3, CN, as Well as C_2F_4[a]

i^b	reaction[c]	$\Delta H_{r298}^{\circ d}$ (kcal/mol)	$a_i \pm \delta_i^e$ (kcal/mol)	ref
1	$\mathbf{C_2F_4}(g) \rightarrow CF_4(g) + C(\text{graphite})$	-65.4 ± 0.5	$-157.6_4 \pm 0.5_3$	26
2	$\mathbf{C_2F_4}(g) + 2H_2(g) \rightarrow 2C(\text{graphite}) + 4HF(50H_2O)$	-150.9 ± 1.2	$-156.2_2 \pm 1.2_6$	26
3	$\mathbf{C_2F_4}(g) + 4Na(c) \rightarrow 2C(\text{graphite}) + 4NaF(c)$	-392.9 ± 1.3	$-157.1_8 \pm 1.4_3$	27
4	$1.5\mathbf{C_2F_6}(g) + NF_3(g) \rightarrow 3CF_4(g) + 0.5N_2(g)$	-155.8 ± 1.5	$-481.8_4 \pm 1.6_1$	28
5	$\mathbf{CF_3H}(g) + 0.5O_2(g) + H_2O(l) \rightarrow CO_2(g) + 3HF(50H_2O)$	$-90.4_3 \pm 1.0$	$-165.6_5 \pm 1.0_4$	29
6	$\mathbf{C_2F_6}(g) + Br_2(g) \rightarrow 2\mathbf{CF_3Br}(g)$	$3.3_0 \pm 0.7$	$-10.6_9 \pm 0.7_0$	30
7	$\mathbf{CF_3H}(g) + Br_2(g) \rightarrow \mathbf{CF_3Br}(g) + HBr(g)$	$-4.5_5 \pm 0.3$	$-11.5_1 \pm 0.3_0$ $[\pm 1.7_0]$	31, 32
8	$\mathbf{CF_3H}(g) + I_2(g) \rightarrow \mathbf{CF_3I}(g) + HI(g)$	$17.1_1 \pm 0.5_5$	$-25.7_0 \pm 0.5_5$	33
9	$\mathbf{CF_3Br}(g) + I_2(g) \rightarrow \mathbf{CF_3I}(g) + IBr(g)$	$9.6_0 \pm 0.4$	$-14.7_7 \pm 0.4_0$ $[\pm 0.6_0]$	34
10	$\mathbf{CF_3Cl}(g) + I_2(g) \rightarrow \mathbf{CF_3I}(g) + ICl(g)$	$17.2_8 \pm 0.4$	$-28.0_4 \pm 0.4_0$ $[\pm 1.8_0]$	34
11	$\mathbf{CF_3Br}(g) + Cl_2(g) \rightarrow \mathbf{CF_3Cl}(g) + BrCl(g)$	$-10.7_7 \pm 0.4$	$14.3_0 \pm 0.4_0[\pm 0.6_0]$	35
12	$\mathbf{CF_3Cl}(g) + Br_2(g) \rightarrow \mathbf{CF_3Br}(g) + BrCl(g)$	$10.5_8 \pm 0.4$	$-14.4_3 \pm 0.4_0[\pm 0.6_0]$	35
13	$\mathbf{CF_3H}(g) + Cl(g) \rightarrow \mathbf{CF_3}(g) + HCl(g)$	$2.9_3 \pm 0.7$	$-53.9_8 \pm 0.7_0$	36−38
14	$\mathbf{CF_3H}(g) + Br(g) \rightarrow \mathbf{CF_3}(g) + HBr(g)$	$18.8_9 \pm 0.5$	$-54.3_0 \pm 0.5_0$	37, 39
15	$\mathbf{CF_3H}(g) + I(g) \rightarrow \mathbf{CF_3}(g) + HI(g)$	35.5 ± 3.0	$-54.6_8 \pm 3.0_0$	33
16	$\mathbf{CF_3I}(g) + I(g) \rightarrow \mathbf{CF_3}(g) + I_2(g)$	17.1 ± 2.0	$-27.7_0 \pm 2.0_0$	33, 40, 41
17	$\mathbf{CF_3H}(g) + CH_3(g) \rightarrow \mathbf{CF_3}(g) + CH_4(g)$	0.6 ± 2.0	$-53.4_6 \pm 2.0_0$	36
18	$\mathbf{C_2F_6}(g) \rightarrow 2\mathbf{CF_3}(g)$	97.6 ± 6.0	$-96.6_0 \pm 6.0_0$	30, 42, 43
19	$\mathbf{C_2F_6}(g) + C_2N_2(g) \rightarrow 2\mathbf{CF_3CN}(g)$	$10.5_4 \pm 0.1_4{}^f$	$-84.4_2 \pm 0.2_4$	44
20	$\mathbf{CF_3CN}(g) + {}^5/_3NF_3(g) \rightarrow 2CF_4(g) + {}^4/_3N_2(g)$	$-275.1_9 \pm 0.2_2{}^f$	$-118.4_3 \pm 0.5_8$	44

[a] These links were evaluated by Syverud.[16] [b] Running index of the link. [c] The species with enthalpies of formation that are treated as unknowns in the thermochemical network are bold. [d] Except where noted, this column reports the values adopted by Syverud, ref 16. [e] The error bar in brackets has been increased after the initial analysis and used in the final fit. [f] Links 19 and 20 were at the time of the original fit (ref 16) at the level of a private communication by Perettie and Walker to Syverud; the numbers in the third and forth column are slightly different than those used in ref 16 and correspond to those appearing in the completed report (ref 44) that was subsequently published.

TABLE 2: Additional Reactions Included in the Current Simultaneous Adjustment of Enthalpies of Formation for CF_3X, X = nil, H, Cl, Br, I, CF_3, and CN

i^a	reaction[b]	ΔH_{r298}° (kcal/mol)	$a_i \pm \delta_i^c$ (kcal/mol)	ref
21	$\mathbf{CF_3I}(g) + Br(g) \rightarrow \mathbf{CF_3}(g) + IBr(g)$	9.8 ± 1.1	$-26.7_8 \pm 1.1_0[\pm 1.9_0]$	45
22	$\mathbf{CF_3Br}(g) + Br(g) \rightarrow \mathbf{CF_3}(g) + Br_2(g)$	24.9 ± 0.6	$-44.2_5 \pm 0.6_0$	46, 47, 38
23	$\mathbf{CF_3Br}(g) \rightarrow \mathbf{CF_3}(g) + Br(g)$	70.5 ± 1.0	$-43.7_6 \pm 1.0_0$	4
24	$\mathbf{CF_3Br}(g) \rightarrow \mathbf{CF_3}(g) + Br(g)$	70.8 ± 0.2	$-44.0_6 \pm 0.2_0$	11, 12
25	$\mathbf{CF_3I}(g) \rightarrow \mathbf{CF_3}(g) + I(g)$	$54.4_4 \pm 0.4$	$-28.9_2 \pm 0.4_0$	7, 8, 9
26	$\mathbf{CF_3Br}(g) \rightarrow \mathbf{CF_3}(g) + Br(g)$	$70.8 \pm 0.3_0$	$-44.0_6 \pm 0.3_0$	6, 13
27	$\mathbf{CF_3I}(g) \rightarrow \mathbf{CF_3}(g) + I(g)$	54.3 ± 0.3	$-28.7_8 \pm 0.3_0$	6
28	$\mathbf{CF_3H}(g) + H(g) \rightarrow \mathbf{CF_3}(g) + H_2(g)$	$2.0_9 \pm 0.6$	$-54.1_9 \pm 0.6_0$	14

[a] Running index of the link. [b] The species with enthalpies of formation that are treated as unknowns in the thermochemical network are bold. [c] The error bar in brackets has been increased after the initial analysis and used in the final fit.

the completed report has been published[44] with slightly different values and somewhat improved error bars.

Measurements reported in recent literature offer a number of possible additional links. Here we have selected eight determinations that appeared to be reliable and independent. These are listed in Table 2. Link 21 is based on kinetic measurements of thermal bromination of CF_3I by Okafo and Whittle,[45] who combined their determination of the forward activation energy of 10.8 ± 0.5 kcal/mol with an assumed reverse activation barrier of 1 ± 1 kcal/mol. Link 22 reflects the measurements by Ferguson and Whittle[46] on the reaction of HBr with CF_3Br; they combine their forward activation barrier with a small reverse barrier obtained by Tucker and Whittle[47] and also previously by Amphlett and Whittle.[38] The measurements underpinning links 23−28 were already partly discussed in the Introduction. Link 23 is due to the determination of the CF_3−Br bond energy by Tsang.[4] Links 24 and 25 reflect a series of kinetic measurements by Skorobotagov and colaborators,[7−9,11,12] yielding values for $D_{298}(CF_3-Br)$ and $D_{298}(CF_3-I)$. Links 26 and 27 are based on photoionization determinations of the CF_3−Br and CF_3−I bond dissociation energies by Asher and Ruscic,[6] while link 28 reflects the recent determination of forward and reverse rates for the reaction of atomic hydrogen with CF_3H by Hranisavljevic and Michael.[14] The initial selections of $A_i \pm \Delta_i$ for links 21−28 basically conform to those proposed by the original authors, since we found no convincing, *a priori*, reasons either to change any of the values or to modify the original error bars.

Auxiliary enthalpies of formation, which are needed to convert $\Delta H_{r298}^{\circ}(i)$ to $a_i \pm \delta_i$ are listed in Table 3. A fair number of these belong to the set of key values given by CODATA,[15] while most others are very well-known and have been evaluated both by Gurvich et al.[2] and JANAF.[1] Although in general the differences between the latter two tabulations are minute, here we adopt the values given by the Russian compilation,[2] which in many cases reports somewhat higher accuracy than JANAF,[1] partly because it often includes slightly more recent data. For $\Delta H_f^{\circ}(CH_3)$, we use the most recent refinement by Litorja and Ruscic.[48] Several of the enthalpies of formation in Table 3 necessitate further discussion. One rather crucial quantity is the enthalpy of formation of tetrafluoromethane, $\Delta H_f^{\circ}(CF_4)$, since it enters in calorimetric measurements 1, 4, and 20. The value for $\Delta H_f^{\circ}(CF_4)$ reported by JANAF[1] is in itself a result of a (different) least-squares fit of a thermochemical network of 23 links connecting seven related enthalpies of formation, from which those of CF_4, $HF(50H_2O)$, NaF(cr), and $NF_3(g)$ are of interest here. However, except for the infamous enthalpy of formation of HF(g), which is off by 0.18 kcal/mol, the fitted values have very strong support in individual measurements. In fact, the final values reported in JANAF for NaF(cr) and

TABLE 3: Auxiliary Enthalpies of Formation

species	$\Delta H_{r298}°$ (kcal/mol)	ref
Br(g)	26.738 ± 0.029	15
Br_2(g)	7.388 ± 0.026	15
BrCl(g)	3.535 ± 0.038	2
C(graphite)	0	std
C_2N_2(g)	73.88 ± 0.19	2
CF_4(g)	−223.04 ± 0.18	2, 49, 50
CH_3(g)	35.03 ± 0.09	48
CH_4(g)	−17.83 ± 0.07	2
Cl(g)	28.992 ± 0.002	15
Cl_2(g)	0	std
CO_2(g)	−94.051 ± 0.031	15
H(g)	52.1028 ± 0.0014	15
H_2(g)	0	std
H_2O(l)	−68.315 ± 0.010	15
HBr(g)	−8.674 ± 0.038	15
HCl(g)	−22.063 ± 0.024	15
HF(g)	−65.32 ± 0.17	15
HF(50 H_2O)	−76.78 ± 0.10	1, 16, 49, 50
HI(g)	6.334 ± 0.024	15
I(g)	25.516 ± 0.010	15
I_2(g)	14.919 ± 0.019	15
IBr	9.75 ± 0.03	2
ICl	4.157 ± 0.010	2
N_2	0	std
Na(cr)	0	std
NaF(cr)	−137.52 ± 0.15	1, 16
NF_3(g)	−31.48 ± 0.24	2
O_2(g)	0	std

NF_3(g), although identical to those obtained during the simultaneous determination, appear to have been derived from independent considerations. Gurvich et al.,[2] who have not performed such a simultaneous determination but instead performed a series of individual evaluations, list very similar values for most of these compounds. Whenever possible, those were adopted in Table 3. For example, the enthalpy of formation of CF_4 reported by JANAF is almost identical to that reported by Gurvich et al.[2] who simply considered all relevant measurements available at the time and adopted the very accurate calorimetric measurement by Greenberg and Hubbard,[49] which we also adopt here. The selected value is also very close to that obtained in a similar calorimetric study by Domalski and Armstrong.[50] Both studies can be used to more directly corroborate the enthalpy of formation of HF(xH_2O) as given in JANAF[51] and is relevant to links 2 and 4. One should also note that the values listed in Table 3 have stood largely unchanged during the last three decades and are, hence, quite similar (mostly identical within less than 0.1 kcal/mol) to those used by Syverud.[16]

The overall topology of the thermochemical network considered here is conveniently depicted in Figure 1, showing both original and added links. The square boxes denote the enthalpies of formation which are to be determined. The numbers in circles or ovals connecting two boxes refer to links interrelating two compounds, while those at the bottom of Figure 1 refer to calorimetric links determining only one unknown enthalpy of formation. The direction of the arrows has the following arithmetic meaning: [AB]→[CD] means that the link represents the equation $\Delta H_{f298}°(AB) - \Delta H_{f298}°(CD) = a_i \pm \delta_i$, where i corresponds to the number in the circle or oval and follows the numbering scheme outlined in Tables 1 and 2. The network in Figure 1 has a quasi-pyramidal shape, where the enthalpies toward the bottom are, very roughly speaking, more "fundamental" (or independent) than those higher up in the scheme. In particular, four compounds at the base, C_2F_4, CF_3H, CF_3CN, and C_2F_6, have associated calorimetric measurements and are anchoring the whole network on an absolute scale.

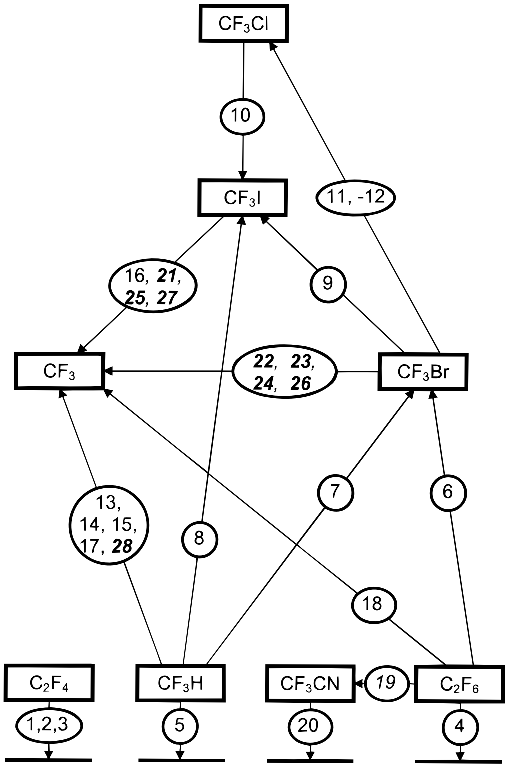

Figure 1. Schematic representation of the topology of the thermodynamic network considered in the present paper. The square boxes denote the enthalpies of formation which are to be determined. The numbers in circles or ovals connecting two boxes refer to links obtained from kinetic, equilibrium, and photoionization measurements interrelating two compounds, while those at the bottom of Figure 1 refer to calorimetric links determining only one unknown enthalpy of formation. The direction of the arrows has the following arithmetic meaning: [AB]→[CD] means that the link represents the equation $\Delta H_{f298}°(AB) - \Delta H_{f298}°(CD) = a_i \pm \delta_i$, where i corresponds to the number in the circle or oval. The links are listed in Tables 1 and 2.

II. Initial Analysis of the Thermochemical Network. As outlined in section 2, the initial analysis mainly consists of the application of linear (or absolute sum) methods to an equally weighted set of links. The primary purpose of this step is to check the network for overall consistency and to help identify links that may be problematic or that may have unrealistically tight error bars, since they may influence the final solution in an undesired manner.[24] It should be noted that the JANAF values did not get the benefit of such analysis, since the absolute sum approach was skipped by Syverud.[16]

A brief inspection of the topology immediately discloses that C_2F_4 and its three associated calorimetric links, 1−3 are not connected to the remainder of the network. Hence, it is not quite clear why this compound was included in the original[16] simultaneous determination since one can (and should) treat it as a separate problem. Indeed, a separate least-squares fit of links 1, 2, and 3 produces $\Delta H_{f298}°(C_2F_4) = -157.40 \pm 0.72$ kcal/mol, which is exactly the JANAF[1] value. The only difference is the subtly different meaning of the error bar, since here we chose to report 95% confidence limits of the fit rather than twice the standard error reported by Syverud.[16] The fact that the determination of the enthalpy of formation of C_2F_4 is not coupled to the rest of the network allows us to omit it from further analysis. However, we shall discuss the value of $\Delta H_f°(C_2F_4)$ later on. Here it should be parenthetically added that as an additional check we have performed a least-squares fit of links 4−20 as well as 1−20. It does not come as a surprise that the fitted values are identical in both cases, with an average absolute deviation from Syverud's[16] solutions of 0.07 kcal/mol. The small differences are traceable to slight changes we have introduced in the last two links and the auxiliary values (Table 3) as well as round-off errors (since Syverud's solutions were reported to the nearest 0.1 kcal/mol).

Links 4−28, which are not related to C_2F_4, create an intertwined overdetermined network. The connections with multiple definitions (such as those relating CF_3H and CF_3) can be easily checked for consistency by comparing the reported error bars of the individual links to their deviation from the simple and weighted averages of the whole set. Links are considered consistent if the deviation from the average(s) is smaller than or comparable to the quoted error bar.

The test shows that the links (and their error bars) connecting CF_3H to CF_3 and CF_3Br to CF_3 appear essentially mutually consistent. The situation is slightly more complicated with respect to the links connecting CF_3I to CF_3. When compared to the weighted average, links 16, 25, and 27 pass the consistency test while link 21 deviates by ∼1.6 times its error bar. Since the set is not entirely consistent, the simple average is skewed in such a way that only link 16, which has the highest error bar, passes the linear test. While there is no easy way to change the unweighted average, other than by eliminating one or more links, the weighted average test can be easily satisfied by simply increasing the error bar of link 21 to ±1.9 kcal/mol. Alternative approaches, which leave 21 pristine but change the error bars of the other three links by up to a factor of 5, even simultaneously, do not lead to a successful resolution of the inconsistency.

The initial inspection of various possible paths using the absolute sum approach shows several interesting features. Overall, the paths in the lower section of the network seem to be more self-consistent than those in the upper portion. It is particularly pleasing and reassuring to see several almost completely closed (i.e., entirely consistent) paths interconnecting the enthalpies of formation that define the base of the pyramid. For example, links 4, 19, and 20 appear to be quite consistent, since this path is completely closed within 0.05 kcal/mol. Similarly, the path starting at the bottom of Figure 1 and following through CF_3H, CF_3, CF_3Br, C_2F_6, and CF_3CN back to the bottom, which involves at least six links, is on the average closed within a cumulative deviation of only 0.45 kcal/mol (equivalent to an average deviation of 0.18 kcal/mol per link). Despite the quite large nominal error bar associated with link 18, the slightly shorter path starting at the bottom through CF_3H and following through CF_3, C_2F_6, and CF_3CN back to the bottom has a surprisingly small average cumulative deviation of 0.26 kcal/mol. These paths substantially boost the confidence in the underlying calorimetric measurements, 4, 5, and 20. Hence, it appears that the pyramid rests on a relatively sound foundation.

In contrast to this, the path starting at the bottom of Figure 1 and following through CF_3H, CF_3Br, and C_2F_6 through CF_3CN back to the base shows a somewhat larger cumulative deviation of 1.60 kcal/mol. This tends to make link 7, which is the only new link tested by this path, somewhat suspect. Similarly, the quite short path involving link 7 that proceeds from CF_3H through CF_3, CF_3Br, and back to CF_3H has, again, an average deviation of 1.60 kcal/mol. Hence, one finds that link 7 should probably have an error bar larger than the stated ±0.3 kcal/mol.

With a few exceptions, one tends to generally find larger cumulative discrepancies along various closed paths in the upper portion of the network. For example, the path from CF_3 through CF_3I, CF_3Br, and back to CF_3 has a cumulative deviation of 1.22 kcal/mol, while the path from CF_3I through CF_3Cl, CF_3Br, and back to CF_3I has a cumulative deviation of 1.10 kcal/mol. This would tend to make link 9, which is in common, somewhat suspect. However, the more circuitous path which completely avoids this link, starting at CF_3, proceeding through CF_3I, CF_3Cl, CF_3Br, and back to CF_3 has an even larger average cumulative deviation of 2.31 kcal/mol. Further analysis along similar lines shows that except for noting the overall inconsistency in the links along the CF_3I, CF_3Cl, CF_3Br triangle, it is not easy to uniquely single out any of them, and it appears that all four may have rather optimistic error bars. On the other hand, the path starting at CF_3H, through CF_3, CF_3I, and back to CF_3H has an average cumulative deviation of only 0.20 kcal/mol. This tends to indicate that the multiple link between CF_3I and CF_3 is on average consistent with link 8, which relates CF_3H to CF_3I.

The preliminary analysis of the data can be completed by performing an initial least-squares fit of all links while retaining the original error bars. When comparing these preliminary solutions to JANAF[1] values, one immediately notices that the enthalpy of formation of CF_3 has become higher by 1.0 kcal/mol, CF_3H higher by 0.5 kcal/mol, and CF_3I higher by 0.4 kcal/mol, with very small changes in other values (under 0.1 kcal/mol). All error bars (95% confidence limits) are rather high at this stage, ranging from ± 0.8 to ± 1.2 kcal/mol. The main purpose of this step is to perform yet another check of the consistency of individual links by comparing them to the solutions. This tends to corroborate the linear analysis outlined above, since links 10 and 7 appear to deviate from the overall solution by almost twice their error bars while link 21 deviates by an amount that is slightly larger than twice its original error bar. The next largest deviation is found for link 24, which deviates by ∼1.3 times its error bar, but this may not be particularly significant since the initial solution is certainly skewed by the presence of at least three inconsistent links. The deviations of all other links are within 1.1 times their stated error bar or less.

III. Simultaneous Least-Squares Solution of the Network. The preliminary analysis provides strong grounds for modifying the error bars associated with links 7, 10, and 21. Manipulation of error bars is always somewhat arbitrary and requires judgment. However, the preliminary analysis rather clearly suggests that the error bar of link 21 should be increased from the original ±1.1 kcal/mol to at least ±1.9 kcal/mol. For links 7 and 10, one should consider the magnitude of discrepancies along various paths that include those links. Since link 7 appears to be involved in inconsistencies of the order of ∼1.6 kcal/mol, we set its error bar to ±1.7 kcal/mol. Similarly, link 10 (although together with other links) is involved in possible discrepancies of the order of 1.1−2.3 kcal/mol. Hence, we set its error bar to ±1.8 kcal/mol. In addition, we double the error bars of links 9, 11, and 12 to ±0.8 kcal/mol. The intervention on these three links, which together with link 10 define the $CF_3Cl-CF_3I-CF_3Br$ triangle, attempts to reflect the fact that the linear analysis does not necessarily single out link 10 as a culprit for inconsistencies. A test fit shows that by itself the additional simultaneous amplification of error bars on links 9, 11, and 12 has an almost insignificant impact on the final values (changes range between 0.005 and 0.093 kcal/mol, with an average absolute change of 0.039 kcal/mol) but it produces error bars which significantly better reflect the inherent uncertainty in $\Delta H_f°(CF_3Cl)$. The final values produced by the fit are presented in Table 4. The listed error bars correspond to the 95% confidence level as obtained from the least-squares procedure and reflect the uncertainty of the fit as well as the uncertainties

TABLE 4: Currently Recommended Values for Gas-Phase Enthalpies of Formation (all values in kcal/mol)

species	$\Delta H_{f298}°$	$\Delta H_{f0}°^{a}$
$CF_3(g)$	$-111.2_8 \pm 0.4_9$	$-110.6_1 \pm 0.4_9$
$CF_3H(g)$	$-165.5_8 \pm 0.5_3$	$-163.9_2 \pm 0.5_3$
$CF_3Cl(g)$	$-169.5_3 \pm 0.7_1$	$-168.3_2 \pm 0.7_1$
$CF_3Br(g)$	$-155.3_0 \pm 0.4_7$	$-152.4_1 \pm 0.4_7$
$CF_3I(g)$	$-140.0_9 \pm 0.5_2$	$-138.6_9 \pm 0.5_2$
$C_2F_6(g)$	$-321.2_7 \pm 0.7_6$	$-319.2_8 \pm 0.7_6$
$CF_3CN(g)$	$-118.4_3 \pm 0.3_9$	$-117.5_2 \pm 0.3_9$

[a] The implied enthalpies of formation at 0 K are listed here only for convenience. The thermochemical values needed for the corrections from 298 and 0 K have been adopted from the compilation by Gurvich et al.,[2] except the correction for CF_3CN, which has been taken from the JANAF tables.[1]

TABLE 5: Comparison of the Values Given by the JANAF Tables with Currently Recommended Values for the Enthalpies of Formation and Resulting Bond Dissociation Energies (all values in kcal/mol)

enthalpy of formation or bond dissociation energy	current result	JANAF[a]	JANAF − current
$\Delta H_{f298}°(CF_3)$	−111.3 ± 0.5	−112.4 ± 1.0	−1.1
$\Delta H_{f298}°(CF_3H)$	−165.6 ± 0.5	−166.6 ± 0.8	−1.0
$\Delta H_{f298}°(CF_3Cl)$	−169.5 ± 0.7	−169.2 ± 0.8	0.3
$\Delta H_{f298}°(CF_3Br)$	−155.3 ± 0.5	−155.1 ± 0.7	0.2
$\Delta H_{f298}°(CF_3I)$	−140.1 ± 0.5	−140.8 ± 0.8	−0.7
$\Delta H_{f298}°(C_2F_6)$	−321.3 ± 0.8	−321.2 ± 1.2	0.1
$\Delta H_{f298}°(CF_3CN)$	−118.4 ± 0.4	−118.4 ± 0.7	0.0
$D_{298}(CF_3{-}H)$	106.4 ± 0.7	106.3 ± 1.3	−0.1
$D_{298}(CF_3{-}F)$	130.7 ± 0.5[b]	129.6 ± 1.0	−1.1
$D_{298}(CF_3{-}Cl)$	87.3 ± 0.9	85.8 ± 1.3	−1.5
$D_{298}(CF_3{-}Br)$	70.8 ± 0.7	69.4 ± 1.2	−1.3
$D_{298}(CF_3{-}I)$	54.3 ± 0.7	53.9 ± 1.3	−0.4
$D_{298}(CF_3{-}CF_3)$	98.7 ± 1.2	96.4 ± 2.3	−2.3

[a] Reference 1. [b] Using $\Delta H_f°(CF_3)$ above, $\Delta H_f°(CF_4)$ from Table 3, and $\Delta H_f°(F)$ from ref 15.

of the various links. As an alternative to 95% confidence limits, the table could have listed two standard deviations. The difference between the two is minute, and the selected approach leads to error bars that are slightly larger (by 0.03 kcal/mol on the average) than the alternate choice.

At this point, it may be instructive to reexamine the network defined by the first 20 links. One immediately notices that this reduced network lacks the links interconnecting CF_3Br and CF_3, which are crucial in demonstrating that link 7 and possibly also 9 may be not as accurate as one would expect. That may have been the primary origin of the internal inconsistencies in the JANAF values.

IV. Analysis of the Adjusted Enthalpies of Formation. The values presented in Table 4 are substantially different from those given in JANAF.[1] A detailed comparison is given in Table 5. Major changes involve significant increases in the enthalpies of formation of CF_3, CF_3H, and CF_3I of 1.1, 1.0, and 0.7 kcal/mol and simultaneous decreases in those of CF_3Cl and CF_3Br by 0.3 and 0.2 kcal/mol while the corrections for CF_3CN and C_2F_6 are quite small. In addition to these changes, there is an overall moderate decrease in the associated error bars. The largest error bar (±0.8 kcal/mol) appears on C_2F_6, but that is simply a consequence of the fact that this molecule has two CF_3 moieties, which effectively doubles the uncertainty. Disregarding C_2F_6, the largest uncertainty (±0.7 kcal/mol) is associated with CF_3Cl, the smallest (±0.4 kcal/mol) with CF_3CN, while all others are in the neighborhood of ±0.5 kcal/mol.

The new enthalpies of formation appear to be quite consistent with available experimental data. For example, the shift of 1.0 kcal/mol (compared to JANAF) in the new enthalpy of formation of CF_3H to −165.6 ± 0.5 kcal/mol brings it significantly closer to the original measurement by Neugebauer and Margrave,[29] so that now all three anchor compounds (CF_3H, CF_3CN, and C_2F_6) are in excellent agreement with their calorimetric determinations. Table 5 also lists several bond dissociation energies that can be derived from the simultaneous solutions. Quite pleasingly, they are in extremely good agreement with newer experimental evidence. For example, the $CF_3{-}H$ bond energy of 106.4 ± 0.7 kcal/mol is in excellent agreement with the measurement of Hranisavljevic and Michael[14] of 106.3 ± 0.6 kcal/mol as well as with several older measurements.[33,36−39] The $CF_3{-}Br$ bond dissociation energy of 70.8 ± 0.7 kcal/mol is exactly the same as the value obtained by Skorobogatov et al.,[11,12] Asher and Ruscic,[6] and Hranisavljevic et al.[13] and in excellent agreement with the values of 70.5 ± 1.0 kcal/mol by Tsang[4] and 71.0 ± 0.6 kcal/mol by Ferguson and Whittle.[46] The $CF_3{-}I$ bond dissociation energy of 54.3 ± 0.7 kcal/mol is identical to the determination by Asher and Ruscic[6] and in excellent agreement with the value of 54.4 ± 0.4 by Skorobogatov et al.[7−9] The implied $CF_3{-}Cl$ bond energy of 87.3 ± 0.9 kcal/mol is in agreement, within the error bar, with the result of Kumaran et al.[5] who obtained 88.4 ± 1.5 kcal/mol (87.5 ± 1.5 kcal/mol at 0 K) from Troe/Lennard−Jones and RRKM/Gorin fits of their kinetic data and who early on suggested that the $CF_3{-}Cl$ bond energy implied by JANAF is too low. The present value for this bond energy is also significantly closer to the upper limit[6] of <88.8 ± 0.3 kcal/mol, originally estimated to be perhaps ∼1.8 kcal/mol higher than the true value but not as much as 3.0 kcal/mol, as would have been suggested by the original JANAF values.

Finally, one should also note that the enthalpy of formation of CF_3, −111.3 ± 0.5 kcal/mol, is in extremely good agreement with the value of −111.4 ± 0.9 kcal/mol proposed by Asher and Ruscic,[6] albeit with a significantly smaller error bar. The agreement is partly fortuitous because, as it will be recalled, the value of Asher and Ruscic[6] was based on averaging over the original discrepancy between the tabulated[1,2] values of $\Delta H_f°(CF_3Br)$ and $\Delta H_f°(CF_3I)$. However, the agreement is very important since the value of $\Delta H_f°(CF_3)$ was recently used to derive other thermochemical quantities, such as[21] $\Delta H_{f298}°(CF_3OH)$.

B. Comparison of G3 and G2 ab Initio Calculations to Experimental Values. *I. Enthalpies of Formation.* Table 6 juxtaposes enthalpies of formation for CF_3, CF_3Cl, and C_2F_6, calculated at the G3 level of theory with the currently recommended experimental values. To allow for a more thorough comparison, the table includes G3 results for CF_3H, CF_4, CF_3CN, and C_2F_4 published elsewhere.[22] It also lists a G3 result for CF_3Br, which is only tentative, since this procedure is not yet fully defined for elements beyond second row. In addition, Table 6 lists available enthalpies of formation at the G2 level, accumulated from a variety of sources.[19,20,52]

In all cases where comparison is possible, the G3 result appears to be appreciably closer to the experimental value than G2. Examining the table in more detail, one notes that all G2 enthalpies of formation in this group are systematically lower (more negative) than the experimental values, with deviations ranging between 3.4 and 8.2 kcal/mol. All G3 enthalpies of formation are higher than their G2 counterparts, with upward shifts ranging from 1.2 to 4.6 kcal/mol (with a mean of 3.1 kcal/mol). Although closer to experiment than the G2 results, all G3 results in this group still appear to be systematically lower than the experimental values. Disregarding the very large

TABLE 6: Comparison of G2 and G3 ab Initio Calculations with Current and Other Related Experimental Enthalpies of Formation and Resulting Bond Energies (all values in kcal/mol)

species	current results	G2[a]	G2 − current	G3[a]	G3 − current
$\Delta H_{f298}^\circ(CF_3)$	−111.3 ± 0.5	−114.7[b]	−3.4	−112.2	−0.9
$\Delta H_{f298}^\circ(CF_3H)$	−165.6 ± 0.5	−170.9[c] (−166.5)[d]	−5.3 (−0.9)[d]	−167.1[e] (−166.4)[d]	−1.5 (−0.8)[d]
$\Delta H_{f298}^\circ(CF_4)$	−223.0 ± 0.2[f,g]	−228.6[c]	−5.5	−223.9	−0.9
$\Delta H_{f298}^\circ(CF_3Cl)$	−169.5 ± 0.7	−174.9[b] (−170.4)[d]	−5.6 (−0.9)[d]	−170.7 (−170.4)[d]	−1.2 (−0.9)[d]
$\Delta H_{f298}^\circ(CF_3Br)$	−155.3 ± 0.5	−159.2 (−156.1)[d]	−3.9 (−0.8)[d]	[−158.0][h] [(−156.3)][d,h]	[−2.7][h] [(−1.0)][d,h]
$\Delta H_{f298}^\circ(C_2F_6)$	−321.3 ± 0.8			−324.1 (−322.9)[d]	−2.8 (−1.6)[d]
$\Delta H_{f298}^\circ(CF_3CN)$	−118.4 ± 0.4	−123.2[c] (−119.5)[d]	−4.8 (−1.1)[d]	−120.2[e] (−119.5)[d]	−1.8 (−1.1)[d]
$\Delta H_{f298}^\circ(C_2F_4)$	−157.4 ± 0.7[f]	−165.6[c] (−161.0)[d]	−8.2 (−3.6)[d]	−162.3[e] (−161.6)[d]	−4.9 (−4.2)[d]
$D_{298}(CF_3{-}H)$	106.4 ± 0.7	108.3 (103.9)[d]	1.9 (−2.5)[d]	107.0 (106.3)[d]	0.6 (−0.1)[d]
$D_{298}(CF_3{-}F)$	130.7 ± 0.5[g,h]	132.8	2.1	130.7	0.0
$D_{298}(CF_3{-}Cl)$	87.3 ± 0.9	89.2 (84.7)[d]	1.9 (−2.6)[d]	87.5 (87.2)[d]	0.2 (−0.1)[d]
$D_{298}(CF_3{-}Br)$	70.8 ± 0.7	71.2 (68.1)[d]	0.4 (−2.7)[d]	[72.5][h] [(70.8)][d,h]	[1.7][h] [(0.0)][d,h]
$D_{298}(CF_3{-}CF_3)$	98.7 ± 1.2			99.7 (98.5)[d]	1.0 (−0.2)[d]
$D_{298}(CF_3{-}CN)$	112.6 ± 1.3[i]	115.8 (112.1)[d]	3.2 (−0.5)[d]	114.7 (114.0)[d]	2.1 (1.4)[d]

[a] Present results, unless stated otherwise. [b] Reference 52. [c] From Curtiss et al., ref 19. [d] After additional isodesmic correction. [e] From Curtiss et al., ref 20. [f] JANAF value (ref 1), since no new experimental value is proposed here. [g] From Table 3, refs 49 and 50. [h] Tentative result, since the G3 procedure is not yet fully formulated for elements beyond second row. [i] Using $\Delta H_{f298}^\circ(CN) = 105.5 \pm 1.1$ kcal/mol from Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744.

discrepancy for C_2F_4 of 4.9 kcal/mol (to which we shall return later), the G3 results deviate from the experiment between 0.9 and 2.8 kcal/mol. Perhaps not surprisingly, the two largest discrepancies occur for CF_3Br and C_2F_6 (2.7 and 2.8 kcal/mol). All other enthalpies of formation appear to be lower by a surprisingly uniform amount, between 0.9 and 1.8 kcal/mol (averaging at ∼1.3 kcal/mol).

For all cases amenable to such corrections, improved G2 and G3 enthalpies of formation have been produced by applying the isodesmic bond separation scheme of Raghavachari et al.[53,54] In this scheme, a unique bond separation reaction is set up, which has all formal bonds between non-hydrogen atoms of the subject molecule separated into the simplest parent molecules containing these same linkages. The bond separation reaction energy is then evaluated at a certain level of theory and combined with the experimental enthalpies of formation for the reference molecules in the reaction to derive an enthalpy of formation for the molecule in question. The guiding criterion for the choice of parent or reference molecules in the set of Raghavachari et al.[53] was the availability of experimental enthalpies of formation within a ±0.1 kcal/mol accuracy. Unfortunately, the enthalpy of formation of CH_3F, which would be needed to extend the scheme to fluorides, has a very significant experimental uncertainty.[1,2] Therefore, we have used the enthalpy of formation of CF_4, which has an experimental uncertainty[2,49,50] of ±0.18 kcal/mol (see also Table 3). For example, with this choice the bond separation reaction for hexafluoroethane becomes $2C_2F_6 + 3CH_4 \rightarrow 3CF_4 + 2C_2H_6$. The other two new reference molecules used in the bond separation reactions in this study are CH_3Cl and CH_3Br, since their enthalpies of formation, $\Delta H_{f298}^\circ(CH_3Cl) = -19.57 \pm 0.14$ kcal/mol and $\Delta H_{f298}^\circ(CH_3Br) = -8.70 \pm 0.12$ kcal/mol, are rather well-known.[1,2] Hence, the bond separation reaction for trifluorochloromethane is $4CF_3Cl + 3CH_4 \rightarrow 3CF_4 + 4CH_3Cl$. The values for all other reference molecules used here were from Raghavachari et al.[53]

The isodesmic approach generally increases the accuracy of the calculated values through cancellation of systematic errors that occurs in the reactions. The improved values are given in Table 6 in parentheses, beneath the regular values. It is immediately noticeable that all corrected values are closer to the experiment than their uncorrected counterparts. While the isodesmic correction imparts a dramatic improvement on the G2 values (averaging ∼4 kcal/mol), the improvement of the G3 values is much more moderate (in most cases only a fraction of kcal/mol). In fact, regardless of whether one starts with the G2 or the G3 value, the isodesmic correction appears to yield a very similar value.

With corrections using the isodesmic bond separation scheme, the overall agreement of G3 theory with experiment appears to be quite good. For C_2F_6, the discrepancy is 1.6 kcal/mol. Disregarding this molecule as well as C_2F_4, which persists in displaying a substantial variance, one can summarize by saying that all other theoretical values are quite uniformly lower by 0.8−1.1 kcal/mol, mildly suggestive of a systematic shift.

II. Bond Dissociation Energies. The lower section of Table 6 compares various bond energies implied by the enthalpies of formation presented in the upper section. Here the agreement between theory and experiment appears to be even better. In fact, at the G3 level, and including the isodesmic correction, the agreement for all bond dissociation energies appears quite impressive, since, with the exception of $CF_3{-}CN$, the experimental values are reproduced within 0.2 kcal/mol or less. This, of course, is a direct result of a fortuitous cancellation of the deviation of −0.9 kcal/mol of the calculated enthalpy of formation of CF_3 with very similar deviations in the CF_3X parents. While such a high level of agreement between calculated and experimental bond dissociation energies is rather unexpected and one should not hope that it can be reproducibly obtained in a general case, it is undeniable that the results at the G3 level of calculation show a significant improvement compared to the G2 level of theory. Furthermore, it is quite clear that the calculated enthalpies of formation can be even further improved by applying the empirical corrections according to the isodesmic bond separation scheme.

Here it should be parenthetically mentioned that if one insists on comparing the G3 results to the original JANAF[1] values, the apparent agreement improves for CF_3 and CF_3H but worsens for CF_3Cl and CF_3Br and becomes significantly worse for most of the bond dissociation energies. As tempting as it may be to ignore all cases of worsened agreement and attach importance to the better agreement between G3 and JANAF's values for CF_3 and CF_3H, the latter has to be regarded as purely accidental and with no statistical significance, especially in view of the fact that the average deviation of G3 values[22] is comparable to or larger than the individual differences between the adjusted and JANAF's enthalpies. In fact, if anything, the displayed overall behavior in which all calculated values are uniformly lower by very similar amounts (which may be marginally statistically significant) from the adjusted experimental values becomes largely lost when JANAF values are considered.

Although the differences between currently recommended values and JANAF are too small to be clearly distinguishable by the calculations, the generally better agreement of theory and experiment can help in other areas of immediate concern. One is the experimental value of $\Delta H_f°(C_2F_4)$ and another the adiabatic ionization energy of CF_3, IE(CF_3).

III. The Adiabatic Ionization Energy of CF_3. First, we would like to focus on the experimental adiabatic ionization energy of CF_3. Its value has been recently accurately determined by Asher and Ruscic[6] who considered two fragmentation processes that are very close in energy: $C_2F_4 \rightarrow CF_3^+ + CF$ and $C_2F_4 \rightarrow CF_3 + CF^+$. They remeasured the related fragment appearance energies as $EA_0(CF_3^+/C_2F_4) = 13.721 \pm 0.005$ eV and $EA_0(CF^+/C_2F_4) = 13.777 \pm 0.005$ eV as well as their difference, $EA_0(CF_3^+/C_2F_4) - EA_0(CF^+/C_2F_4) = 0.055 \pm 0.003$ eV. One should take notice of the fact that the difference can be fully corroborated by simple superposition of suitably scaled spectra, thus avoiding any possible influences arising from the interpretation of the threshold shapes and their individual fitting with model functions. The results of Asher and Ruscic[6] are in very good agreement with the slightly coarser measurements by Walter et al.[55] who give 13.70 ± 0.02 and 13.76 ± 0.01 eV for the two appearance energies and 0.06 eV for the difference. Since the two fragmentation processes differ only by the final location of the positive charge, the difference between the two appearance energies simply corresponds to the difference in the adiabatic ionization potentials of CF_3 and CF, EI(CF_3) − EI(CF). With the well-known ionization energy of CF determined by Dyke et al.[56] as 9.11 ± 0.01 eV, Asher and Ruscic[6] obtain $EI(CF_3) = 9.05_5 \pm 0.01_1$ eV. A very similar result of 9.05 ± 0.02 eV was derived by Berkowitz[57] using the fragment appearance energies given by Walter et al.[55] One should also note that this path to IP(CF_3) does not involve any additional thermochemical values, such as $\Delta H_f°(C_2F_4)$, $\Delta H_f°(CF_3)$, or $\Delta H_f°(CF)$ nor does it depend on direct measurement of the adiabatic threshold for direct ionization, which suffers from very unfavorable Franck−Condon factors[58,59] and is, hence, prone to produce only an upper limit. In fact, at least technically, this approach produces a lower limit to the ionization energy of CF_3. While the value for EI(CF_3) that is obtained in this manner is in reasonably good agreement with several previous measurements[60−63] which imply an ionization energy of 9.0−9.1 eV, it is in sharp contrast with a number of previous[64−67] (and even subsequent[68]) studies that either explicitly propose or imply substantially lower values. These range from suggestions of an upper limit of <8.9 eV to values as low as 8.6 eV. As criticized by Asher and Ruscic,[6] such values are generally a result of incorrect interpretations of the fragmentation threshold shapes.

At the G2 level of theory, the calculated adiabatic ionization energy of CF_3 is[52] 9.00 eV. While this is much closer to 9.05_5 eV than to any of the "low" values and, hence, it tends to provide direct support to this determination, the possibility of a significant error bar that may arise from problems with multiple fluorinated compounds prevented the G2 result from ruling out the upper end of the "low" values with a satisfactory degree of certainty. However, it now appears that the G3 theory has largely removed the problems associated with non-hydrogen compounds.[22] At the least, the thermochemical properties of the fluorinated species considered in this paper are reproduced with very good accuracy. In addition, the overall accuracy with which this level of theory reproduces the ionization energies has also significantly improved.[22] The gap between the value of Asher and Ruscic[6] and even the highest of the "low" values, 0.15 eV, is 3 times larger than the average absolute deviation of G3 theory for ionization potentials[22] of 0.05 eV. It is thus very interesting to see how the G3 approach compares to the experiments.

Indeed, at the G3 level of theory, we calculate $EI(CF_3) = 9.08$ eV. This is in excellent agreement with (and hence fully corroborates) the experimental value of $9.05_5 \pm 0.01_1$ eV. Furthermore, even when pessimistic error bars are contemplated, the G3 calculated value makes the entire range of proposed "low" values highly unlikely.

IV. The Relationship between the Enthalpies of Formation of C_2F_4, CF_3, and CF. The only truly outstanding variance between theory and experiment in Table 6 is displayed by the enthalpy of formation of C_2F_4. The quite significant discrepancy persists at the G3 level, even after the isodesmic correction is applied, and begins to question the experimental value.

Asher and Ruscic[6] have already provided some ground for doubting the accuracy of the experimental enthalpy of formation of C_2F_4. Namely, the appearance threshold of CF^+ from C_2F_4, already discussed above in conjunction with EI(CF_3), together with[56] EI(CF) determines the enthalpy of reaction for $C_2F_4 \rightarrow CF_3 + CF$ as 107.6 ± 0.3 kcal/mol at 0 K, which corresponds to 108.6 ± 0.3 kcal/mol at 298 K. Pointing out that this inference is valid only if one takes the JANAF[1] value for $\Delta H°_{f\,0}(C_2F_4) = -156.6 \pm 0.7$ kcal/mol for granted, Asher and Ruscic[6] use their $\Delta H°_{f\,0}(CF_3) = -110.7 \pm 0.9$ kcal/mol to infer $\Delta H°_{f\,0}(CF) = 61.7 \pm 1.1$ kcal/mol or $\Delta H_{f298}°(CF) = 62.5 \pm 1.1$ kcal/mol.

Unfortunately, the enthalpy of formation of CF is not experimentally known with sufficient precision to pass definitive judgment on this matter. Asher and Ruscic[6] conclude that their derived value is perhaps not entirely incongruent with the tabulated values of 61 ± 2 (JANAF[1]) or 58.3 ± 2.5 kcal/mol (Gurvich et al.[2]). In retrospect, the derived value for CF may be too high, perhaps by as much as 1.5−2.5 kcal/mol, indicating that the tabulated value for the enthalpy of formation of C_2F_4 is too high by a comparable amount. At the G3 level, we calculate $\Delta H_{f298}°(CF) = 58.0$ kcal/mol, very similar to the selection of Gurvich et al.[2] Although it is not quite clear what level of accuracy to expect from the calculated enthalpy of formation of CF, additional support may come from the fact that at the G3 level the error for the isoelectronic NO is only 0.2 kcal/mol.[22] Based entirely on G3 values, the 298 K enthalpy of reaction for $C_2F_4 \rightarrow CF_3 + CF$ is predicted to be 108.1 or 107.4 kcal/mol when the isodesmic correction for C_2F_4 is incorporated. Both values are in very good agreement with the experimental determination.[6]

If one assumes that at 298 K the enthalpy of formation of CF is close to ~58 kcal/mol at 298 K, as indicated by Gurvich et al.[2] and also suggested by G3 theory, then the neutral possible conclusion is that the experimental value for $\Delta H_f°(C_2F_4)$ is too high by as much as 2.5 kcal/mol. If this is indeed the case, then the G3 value, after applying the isodesmic corrections, is only 1.7 kcal/mol lower, which is in the range of acceptable inaccuracies for the theoretical values. However, to pass definite judgment on this matter, one would need experimental values for CF and C_2F_4 that are significantly more accurate than those presently available.

4. Conclusion

The enthalpies of formation of CF_3X, X = nil, H, Cl, Br, I, CF_3, and CN, have been determined by simultaneous least-squares solution of a thermochemical network containing 28 experimental measurements extracted from the literature. The new enthalpies differ considerably from the older tabulated values[1,2] and now show a significantly greater degree of internal consistency, demonstrated by excellent agreement with newer experiments as well as with older calorimetric determinations. The fitted values are $\Delta H_{f298}°(CF_3) = -111.3 \pm 0.5$ kcal/mol (-110.6 ± 0.5 kcal/mol at 0 K), $\Delta H_{f298}°(CF_3H) = -165.6 \pm 0.5$ kcal/mol (-163.9 ± 0.5 kcal/mol at 0 K), $\Delta H_{f298}°(CF_3Cl) = -169.5 \pm 0.7$ kcal/mol (-168.3 ± 0.7 kcal/mol at 0 K), $\Delta H_{f298}°(CF_3Br) = -155.3 \pm 0.5$ kcal/mol (-152.4 ± 0.5 kcal/mol at 0 K), $\Delta H_{f298}°(CF_3I) = -140.1 \pm 0.5$ kcal/mol (-138.7 ± 0.5 kcal/mol at 0 K), $\Delta H_{f298}°(C_2F_6) = -321.3 \pm 0.8$ kcal/mol (-319.3 ± 0.8 kcal/mol at 0 K), and $\Delta H_{f298}°(CF_3CN) = -118.4 \pm 0.4$ kcal/mol (-117.5 ± 0.4 kcal/mol at 0 K).

Theoretical calculations at the G3 level of theory have been performed for several molecules from this set, which appeared problematic at the G2 level of theory. Compared to G2 theory, the G3 results show a remarkable improvement in accuracy. The agreement can be further improved by applying, where applicable, corrections according to the isodesmic bond separation scheme. Interestingly, all theoretical enthalpies of formations that were scrutinized here have values lower (more negative) than the experiment at all levels of theory. Since the deviations for the computed enthalpies of formation of CF_3X have the same sign as that for CF_3, the inherent cancellation of errors leads to bond dissociation energies $D_{298}(CF_3-X)$ that show better agreement with experiment. At the G2 level, the deviations of theoretical enthalpies of formation from experiment are in the range of 3.4−5.6 kcal/mol, with the enthalpy of formation of C_2F_4 differing by as much as 8.2 kcal/mol. With the exception of C_2F_4, the variances between theory and experiment diminish to <2.8 kcal/mol at the G3 level of theory and become <1.6 kcal/mol after isodesmic corrections. The calculated value for C_2F_4 persists in being lower by 4.9 kcal/mol at the G3 level and by 4.2 kcal/mol even after isodesmic corrections are applied. However, an analysis of previous measurements, together with an assumed enthalpy of formation of CF of ~58 kcal/mol, as suggested both by one of the tabulations[2] and by theory at the G3 level, produces indications that the experimental enthalpy of formation of C_2F_4 may be too high by as much as 2.5 kcal/mol. Hence, the actual discrepancy of the theoretical value for C_2F_4 may in reality be much less than that shown by direct comparison. In addition, at the G3 level of theory, the ionization energy of CF_3 was calculated to be 9.08 eV, which agrees extremely well with the recent experimental value of $9.05_5 \pm 0.01_1$ eV.

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