Pitfalls for the Frozen-Core Approximation: Gaussian-2 Calculations on the Sodium Cation Affinities of Diatomic Fluorides

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The Gaussian-2 (G2) total energies for species having the formula $Na(FX)^+$ [X = H, Li → F, or Na → Cl], calculated using conventional and widely used ab initio computational program suites, show serious deficiencies which are attributable to two different effects. Firstly, for the sodium-ion adducts of almost all of the covalent fluorides—namely HF, BF, CF, NF, OF, F_2, SF, and ClF—the orbital corresponding most closely to the fluorine 2s orbital possesses a more negative eigenvalue than the set of three orbitals corresponding most closely to the sodium $2p_x$, $2p_y$, and $2p_z$ orbitals, so that routine selection of the "frozen-core" option (in the single-point calculations involved in determining the G2 total energy) leads to an inappropriate correlation space. Secondly, for the sodium-ion adducts of several fluorides—most notably, but not solely, the ionic fluorides LiF, NaF, MgF, and AlF—there is very significant mixing of the fluorine 2s and sodium $2p_z$ orbitals, with the result that the G2 frozen-core calculations yield an incorrect correlation energy. This latter problem cannot be properly compensated for in standard G2 theory. The magnitude of either effect can be quite large, with the result that "blind" implementation of G2 theory produces apparent G2 SCA values ranging from −100 to −200 kJ mol^{-1} for most of the covalent fluorides. Here we investigate this phenomenon and assess three different strategies for obtaining corrected G2-like results: namely, inclusion of all Na 2s and 2p orbitals among those correlated (the G2(thaw) technique); exclusion of all Na 2p and F 2s orbitals from the correlation space (the G2(F-2s) approach); and correlation of F 2s, but not Na $2p_x$, $2p_y$, or $2p_z$, in a noncontiguous correlation space (which we term G2(NCCS)). Of the three possible approaches, the G2(thaw) procedure appears the most intrinsically reliable, but is nevertheless significantly more computationally intensive than standard G2. To this end, we assess also several methods that seek to emulate G2(thaw) at reduced cost: the best such "budget" method, G2(MP2(thaw/MP2)), is the least demanding of CPU time and is generally less computationally expensive than G2 itself.

I. Introduction

In recent years, several sophisticated "model" quantum chemical methods have been developed with the aim of yielding benchmark-quality ab initio results for molecular geometries and energies, at comparatively minor computational expense. Probably the most widely used such "models" are those based around the Gaussian-2 (G2) procedure,[1] of which many variants have now been devised[2−9] depending upon the user's requirements in terms of expected accuracy, computing facilities, etc. The G2 technique is designed to emulate, at a fraction of the cost in CPU time, a single-point total energy calculation at the QCISD(T)(fc)/6-311+G(3df,2p)//MP2(full)/6-31G* level of theory. This is done by a combination of several less expensive single-point calculations using a variety of basis sets: the results of these single-point calculations are then combined and adjusted empirically with an additional "higher level correction" which depends upon the number of paired and unpaired valence electrons. Results obtained with G2 theory are generally impressive: a recent study[10] has found that the average absolute deviation of G2 from experiment is 6.61 kJ mol^{-1} for a set of 148 well-characterized experimental enthalpies of formation for small molecules and radicals.

While G2 theory performs very well overall for most molecules, radicals, and ions composed of first- and second-row atoms, certain classes of species are not particularly well treated by G2 theory: these include triplet states,[1] polyfluorinated species,[10] and molecular dications.[11] We have recently reported.[12] that G2 also appears to underestimate the sodium cation affinity (SCA) of HF by a staggering 186 kJ mol^{-1}. While G2 does not perform particularly well for sodium cation affinity values in general, due to its underestimation of the ionization energy of Na by 0.19 eV,[1] the reported G2 value of SCA(HF) = −119.1 kJ mol^{-1} [12] is in much stronger disagreement with the expected (positive) value than are the calculated G2 SCAs of NH_3, H_2O, PH_3, H_2S and HCl.[12] Finally, Duke and Radom[13] have also identified a number of problem cases in the G2 treatment of species containing the third-row, main-group elements Ga−Kr: for example, G2 systematically underestimates the ionization energies of the sequence Ga, Ge, As, Se, Br, and Kr. The performance of G2 theory for third-row-containing species is generally enhanced if the filled 3d orbitals are included among those correlated in the "frozen-core" single-point calculations, and in some instances correlation of these 3d orbitals is essential if the calculated thermochemical properties of these species are to be even qualitatively correct. In the light of this recent study[13] on correlation in third-row compounds, we can comprehend the importance of an appropriate

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definition (and not necessarily the G2 definition) of the correlation space for species such as $NaFH^+$, in which some "valence" orbitals are found to be lower in potential energy than some "core" orbitals. The present work explores this phenomenon and assesses methods by which accurate G2-like total energies can be obtained for species in which the distinction between core and valence orbitals is questionable.

II. Theoretical Methods

The total energy of a species is obtained using the G2 procedure according to the following sequence of calculations:

$$E_0(\text{G2}) = E_e(\text{MP4/6-311+G**}) + E_e(\text{MP4/6-311G(2df,p)}) - 2E_e(\text{MP4/6-311G**}) + E_e(\text{QCISD(T)/6-311G**}) + E_e(\text{MP2/6-311+G(3df,2p)}) + E_e(\text{MP2/6-311G**}) - E_e(\text{MP2/6-311+G**}) - E_e(\text{MP2/6-311G(2df,p)} + \text{HLC} + \text{ZPE} \quad (1)$$

where the single-point total energy calculations are all implemented (using the frozen-core assumption) on molecular geometries obtained at the MP2(full)/6-31G* level and where the higher level correction, HLC, and the corrected ZPE are as described previously.[1]

This study is concerned with the performance of several variants of standard G2 theory, and it is important to distinguish clearly between all of these variants, which are enumerated below.

(i) G2(COL). We use this term to denote values obtained using eq 1, in which the simplifying assumption has been made that all the (frozen) core orbitals are lower in energy than any of the (correlated) valence orbitals. This assumption, which is not necessarily correct (as we shall discuss), is equivalent to selecting the FC option in a calculation performed using the GAUSSIAN94 programming suite,[14] for example. G2(COL) therefore amounts to the default implementation of G2 theory using most computational programming packages and, to the best of our knowledge, almost always yields true G2 values for molecules, radicals, and ions. Nevertheless, the G2(COL) total energies for species of the form $NaFX^+$ are often inappropriate.

(ii) G2(NCCS). This denotes a calculation performed using the G2 method (i.e., eq 1) in which each of the MP2, MP4, and QCISD(T) single-point total energy calculations is executed with a noncontiguous correlation space, to allow for the situation that one or more valence orbitals [in the present work, F 2s or Ne 2s] possess more negative eigenvalues than some of the core orbitals [in this case, Na $2p_x$, $2p_y$, and $2p_z$].

(iii) G2(thaw). In this method, the correlation space is expanded to include all of the core orbitals that possess eigenvalues close to, or above, those of the lowest lying valence orbitals. In a previous work,[12] we have defined the G2(thaw: Na-*n*) method as

$$E_0[\text{G2(thaw: Na-}n\text{)}] = E_0[\text{G2(raw: Na-}n\text{)}] + m\Delta_{\text{Na}(n)} \quad (2)$$

and this definition is essentially retained in the expression for the more general G2(thaw) method:

$$E_0[\text{G2(thaw)}] = E_0[\text{G2(raw)}] + \Sigma(\Delta_M) \quad (3)$$

The two parameters in eq 3 require clarification. The value E_0[G2(raw)] is a raw total energy that is obtained in accordance with expression (1) but that (in contrast to G2) includes in the correlation space, for all single-point calculations, the following orbitals: 1s for Li and Be, and 2s, $2p_x$, $2p_y$, and $2p_z$ for Na, Mg, and Al. There is also a calibration constant, Δ_M, required for each Li, Be, Na, Mg, or Al atom included in the molecule of interest: this quantity is designed to normalize G2(thaw) values so that they may be directly compared with, or used in conjunction with, standard G2 values. The value of Δ_M for each element is different and is defined as $E_0[\text{G2}] - E_0[\text{G2(raw)}]$ for the gas-phase atom *M*. Values of Δ_M for G2(thaw) and for related methods (see below) are listed in Table 1. Please note that the higher level correction, HLC, for this method is identical to that employed in G2 theory and is calculated from the number of valence electrons rather than the number of electrons occupying correlated orbitals.

TABLE 1: Correction Factors, Δ_M (M = Li, Be, Na, Mg, Al), for Calibration of "Thawed" G2 (or G2(MP2)) Values to the Standard G2 (or G2(MP2)) Energy Scale

	Δ_M/mHartree		
M	G2(thaw)	G2(MP2(thaw))	G2(thaw/MP2)[a]
Li	15.60	15.61	13.26
Be	16.48	16.48	15.21
Na	139.46	138.87	137.53
Mg	129.45	129.11	128.44
Al	140.22	140.03	139.64

[a] The values in this column apply also to G2(MP2(thaw/MP2)) calculations.

(iv) G2(thaw/MP2). This technique involves adjustment of the G2 total energy via an additional calculation at the MP2/6-311+G(3df,2p) level of theory, in which the same extra orbitals as in G2(thaw) (namely 1s for Li and Be, and 2s, $2p_x$, $2p_y$, and $2p_z$ for Na, Mg, and Al) are correlated. The total energy for this technique is defined as

$$E_0[\text{G2(thaw/MP2)}] = E_0[\text{G2}] + E[\text{MP2(raw)/6-311+G(3df,2p)}] - E[\text{MP2(fc)/6-311+G(3df,2p)}] + \Sigma(\Delta_M) \quad (4)$$

where the MP2(raw) calculation is performed with correlation of the additional orbitals noted above and where the calibration constants Δ_M for metallic elements are defined in the same manner as for G2(thaw). See Table 1 for values of Δ_M for this method.

(v). G2(MP2(thaw)). This technique bears the same relation to the G2(MP2) procedure[4] as does G2(thaw) to G2. The G2(MP2(thaw)) total energy is, therefore,

$$E_0 = E[\text{QCISD(T)(raw)/6-311G**}] + E[\text{MP2(raw)/6-311+G(3df,2p)}] - E[\text{MP2(raw)/6-311G**}] + \text{HLC} + \text{ZPE} + \Sigma(\Delta_M) \quad (5)$$

where the "raw" notation indicates that the additional orbitals (1s for Li and Be, and 2s, $2p_x$, $2p_y$, and $2p_z$ for Na, Mg, and Al) are included among those correlated. For convenience, we assume that the higher level correction (HLC) takes the same value as in standard G2(MP2) theory: appropriate values of the parameter Δ_M, which is the calibration constant necessary to reproduce the G2(MP2) total energy for the indicated metal atom, are in Table 1.

(vi) G2(MP2(thaw/MP2)). This method bears the same relation to G2(MP2) as does G2(thaw/MP2) to G2. The total energy is defined as

$$E_0[\text{G2(MP2(thaw/MP2))}] = E_0[\text{G2(MP2)}] + E[\text{MP2(raw)/6-311+G(3df,2p)}] - E[\text{MP2(fc)/6-311+G(3df,2p)}] + \Sigma(\Delta_M) \quad (6)$$

where the MP2(raw) calculation is the same as defined above for the G2(thaw/MP2) procedure. The values of the respective calibration constants Δ_M are also identical to those used in G2-(thaw/MP2).

(vii) G2(F-2s). In this method, the correlation space is defined to exclude the 2s orbitals of any fluorine atoms in the molecule of interest, with the total energy given as

$$E_0[\mathrm{G2(F\text{-}2s)}] = E_0[\mathrm{G2(raw)}] + n\Delta_{\mathrm{F(2s)}} \qquad (7)$$

Here E_0[G2(raw)] denotes a total energy, obtained in accordance with expression 1, for which all single-point calculations exclude the fluorine 2s orbital(s) from among those correlated; n is the number of fluorine atoms within the molecule; and $\Delta_{\mathrm{F(2s)}}$ is a calibration constant, defined as E_0[G2] − E_0[G2(raw)] for gas-phase atomic F, having the value −83.33 mHartrees. A related procedure, G2(Ne-2s), has been used for one calculation in the present study and is defined in an entirely analogous manner, substituting the Ne 2s orbital for F 2s in the above formula and requiring a calibration factor $\Delta_{\mathrm{Ne(2s)}} = -76.12$ mHartrees. As with G2(thaw), the higher level correction, HLC, used here is identical to the G2 value, despite the smaller number of correlated orbitals.

In addition to the methods described above, we have also performed standard G2(ZPE=MP2)[7] calculations when qualitative differences in the HF/6-31G* and MP2(full)/6-31G* potential energy surfaces necessitated such an approach.

The geometry optimizations, frequency calculations, and all single-point calculations involving a continuous correlation space were obtained using the GAUSSIAN92[15] and GAUSSIAN94[14] programming packages. For G2(NCCS) calculations, in which a noncontiguous correlation space was required, the ACES II package[16] was employed.

III. Results and Discussion

A. G2(COL) Calculations on Ions Containing Na and F. We have located stationary points for the species $NaFX^+$, where X includes all first- and second-row elements except the noble gases, at the HF/6-31G* and MP2(full)/6-31G* levels of theory. Optimized geometries at the MP2(full)/6-31G* level are reported in Table 2. These geometries define the structures for which total energies have been determined in the present work.

The G2(COL) results for cations containing both sodium and fluorine are indicated in Table 3. A large majority of the sodium cation affinity values listed here are negative, with the most extreme examples approaching −200 kJ mol^{-1}. The calculation of negative SCA values is symptomatic of some computational problem, since the electrostatic factors associated with the interaction of Na^+ and a polar or polarizable neutral X indicate that the species X should invariably possess a *positive* (if perhaps only small) sodium cation affinity. The calculated SCA values for fluorides may be compared with G2 values for the SCAs of non-fluorine-containing species,[12] which are routinely positive. Furthermore if the G2(COL) sodium cation affinity values are contrasted with the MP2(full)/6-3lG* values for the same parameters, as listed in Table 4, it can be seen that the MP2/6-31G* values are almost always positive and almost invariably exceed the apparent G2 SCAs, often by as much as 200 kJ mol^{-1}.

TABLE 2: Optimized Geometries for $NaFX^+$ Stationary Points, Obtained at the MP2(full)/6-31G* Level of Theory

species	r(Na−F) (Å)	r(F−X) (Å)	r(X−Na) (Å)	∠(NaFX)[a] (deg)
$^2NaF^+$	2.620			
$NaFH^+$	2.138	0.945		
$NaFLi^+$	2.025	1.647		
$^2NaFBe^+$	2.148	1.430		
$NaBF^+$		1.253	2.681	
T-Na(BF)$^+$	2.712	1.290	2.982	88.95
$NaFB^+$	2.305	1.325		
$^2NaCF^+$		1.254	2.527	
$^2NaFC^+$	2.292	1.339		
$^3NaNF^+$		1.292	2.507	
$^3NaFN^+$	2.249	1.374		
$^2NaOF^+$		1.321	2.471	
^{2}Na(FO)$^+$ bent	2.341	1.368	3.387	130.02
$^2NaFO^+$	2.280	1.369		
$NaFF^+$	2.368	1.414		
T-Na(F_2)$^+$	2.480	1.436	2.480	73.17
$NaFNa^+$	1.993	1.993		
$^2NaFMg^+$	2.059	1.834		
$NaFAl^+$	2.099	1.757		
$^2NaSiF^+$		1.598	3.042	
$^2NaFSi^+$	2.132	1.711		
$^3NaPF^+$		1.589	3.073	
$^3NaFP^+$	2.141	1.697		
^{2}Na(FS)$^+$ bent	2.180	1.681	3.750	152.27
$^2NaFS^+$	2.162	1.681		
Na(FCl)$^+$ bent	2.231	1.684	3.643	136.62
$NaFCl^+$	2.188	1.680		

[a] All species for which a bond angle is not shown are linear.

The problem with the apparent G2 SCA values for fluorides can be traced to an assumption that all valence molecular orbitals have relative energies above all core orbitals: we shall henceforth refer to this concept as the COL (core orbitals lowest) assumption. The COL assumption is implicit when performing frozen-core single-point calculations using virtually any of the existing widely used ab initio programming packages. The COL assumption is problematic when we compare Na (in which the 2s and 2p are, formally, core orbitals) with F or Ne (for which 2s and 2p are the valence orbitals): as shown in Table 5, the eigenvalues for the three Na 2p orbitals are above the 2s orbitals of both F and Ne. We might, therefore, expect that application of the COL assumption in G2 calculations on NaF would yield an incorrect total energy, since comparison of the orbital eigenvalues for isolated Na and F suggests the COL assumption is invalid for this combination. In fact, NaF is a largely ionic compound: it is thus more meaningful to compare orbital eigenvalues of Na^+ and F^- as a predictor of potential problems for this compound. The values in Table 5 show that the orbital eigenvalues of Na are sufficiently reduced on ionization, while those of F are sufficiently increased on electron attachment, to imply that the COL assumption for the combination Na^+F^- is valid; the G2 total energy for NaF yields an enthalpy of formation satisfactorily close to that determined experimentally. By extension, we expect that the COL assumption should also be correct for other more-or-less purely ionic Na- and F-containing compounds, but will not necessarily be correct for compounds in which Na is combined with covalently bonded fluorine-containing moieties. This hypothesis is supported by the problems evident in the G2(COL) SCA values reported in Table 3.

We can, of course, test this notion more directly. In Table 6 we provide some illustrative examples of molecular orbital parameters, in the vicinity of the core/valence boundary, for FX and $NaFX^+$ species. Several points can be noted in connection with these orbital parameters. Firstly, for each of the F-containing neutrals (HF, BF, AlF, SiF, and FCl) included here, the eigenvalue for the molecular orbital most closely related to F 2s is quite close to that seen in the isolated F atom, even though a species such as AlF is expected to possess a substantial quantity of ionic character; as noted above, this

TABLE 3: G2 Total Energies, Enthalpies of Formation, and Ion−Ligand Binding Energies for NaFX$^+$ Stationary Points

species[a]	ZPE[b] (mHartrees)	$n(i)$[c]	E_0(G2)[d] (Hartrees)	$\Delta H°_{f,0}$[e] (kJ mol^{-1})	D_0(Na$^+$−X)[f] (kJ mol^{-1})
^{1}BF	2.99	0	−124.523 02	−121.5	
^{3}BF	2.80	0	−124.386 02	237.7	
^{2}OF	2.39	0	−174.696 27	110.4	
^{2}NaF$^+$	0.04	0	−261.257 88	765.6	−103.0
NaFH$^+$	9.92	0	−261.968 93[g]	427.5[g]	−119.1[g]
NaFLi$^+$	3.13	0	−269.021 00	54.6	190.3 (324.4)[h]
^{2}NaFBe$^+$	3.33	0	−276.104 00	498.0	−67.3
NaBF$^+$	4.52	0	−286.140 64	586.1	−122.5
T-Na(BF)$^+$	3.17[i]	1[j]	−286.117 06[k]	648.0[k]	− 184.4[k]
NaFB$^+$	3.16	0	−286.123 03	632.4	−168.7
^{2}NaCF$^+$	4.02	1	−299.229 91	983.9	− 161.2
^{2}NaFC$^+$	2.98	0[l]	−299.222 47	1003.5	−180.7
^{3}NaNF$^+$	3.38	0	−315.863 88	1005.3	−190.2
^{3}NaFN$^+$	2.83	0[m]	−315.869 93	989.4	−174.3
^{2}NaOF$^+$	2.84	1	−336.287 23	888.1	−192.5
^{2}Na(FO)$^+$ bent	2.80	0	−336.289 18	883.0	−187.4
^{2}NaFO$^+$	2.65	2	−336.288 98	883.5	− 187.9
NaFF$^+$	2.77	2	−360.912 57	785.5	−198.7
T-Na(F$_2$)$^+$	2.79	0	−360.920 17	765.6	−178.8
NaFNa$^+$	2.26	0	−423.415 75	54.8	235.9
^{2}NaFMg$^+$	2.42	0	−461.162 15	231.7	137.8 (358.2)[n]
NaFAl$^+$	2.32	0	−503.493 39	295.8	20.6 (311.7)[o]
^{2}NaSiF$^+$	2.42	1	−550.455 04	518.7	9.8
^{2}NaFSi$^+$	2.31	0	−550.419 82	611.1	−82.6
^{3}NaPF$^+$	2.14	2	−602.281 77	541.2	−3.0
^{3}NaFP$^+$	2.32	0	−602.241 05	648.1	−109.9
^{2}Na(FS)$^+$ bent	2.23[i]	0[j]	−659.031 75[k]	728.1[k]	−133.2[k]
^{2}NaFS$^+$	2.34	0[l]	−659.031 89	727.7	−132.8
Na(FCl)$^+$ bent	2.27[i]	0[j]	−721.015 62[k]	672.3[k]	−144.6[k]
NaFCl$^+$	2.28	0[m]	−721.015 73	671.9	−145.0

[a] Unless otherwise indicated, all species are of singlet multiplicity. [b] Zero-point vibrational energy, obtained at the HF/6-31G* level of theory (corrected by a factor of 0.8929) unless otherwise indicated. [c] Number of imaginary frequencies obtained in the frequency calculation used to determine ZPE. [d] Calculated G2 total energy, including ZPE. [e] Calculated G2 (0 K) enthalpy of formation, in kJ mol^{-1}. [f] Na$^+$/ligand bond strength, obtained at the G2 level of theory. [g] Previously reported in ref 12. [h] For dissociation to Li$^+$ + NaF. [i] ZPE obtained for the MP2(full)/6-31G* optimized geometry (and scaled by a factor of 0.9427).[17] [j] From the MP2(full)/6-31G* frequency calculation. [k] G2(ZPE=MP2) value. [l] The linear structure corresponds to a transition state at the MP2(fu11)/6-31G* level of theory. [m] The linear structure corresponds to a second-order saddle point at the MP2(full)/6-31G* level of theory. [n] For dissociation to Mg$^+$ + NaF. [o] For dissociation to Al$^+$ + NaF.

suggests that the COL assumption is hazardous when these F-containing neutrals are combined with sodium. Secondly, there are indeed instances for NaFX$^+$, among these examples, where the COL assumption is clearly wrong: namely, NaFH$^+$, Na(BF)$^+$ (both isomers), and NaFCl$^+$ (at the equilibrium geometry). Thirdly, there are also instances (NaFAl$^+$, NaFSi$^+$) where the mixing between F 2s and Na 2p$_z$ orbitals is too great to satisfactorily identify any molecular orbital as either F 2s or Na 2p$_z$; in such cases it is clearly inappropriate to place the sodium 2p orbitals within the core, since at least one of these orbitals is behaving as a valence orbital. Fourthly, there are instances in which either the orientation (Na(FSi)$^+$) or the Na/ligand bond length (NaFCl$^+$) is crucial in assigning the molecular orbitals: the eigenvalues for orbitals 9−12 change very little between NaFSi$^+$ and NaSiF$^+$ (in both species, all four of these orbitals have eigenvalues in the range −1.78 to −1.73), yet in NaFSi$^+$ it is orbital 9 that has the greatest F 2s character, while in NaSiF$^+$ the F 2s character resides predominantly in orbital 12. Under the COL assumption, orbital 9 is core while 12 is valence, so the COL assumption is correct for NaSiF$^+$ but not for NaFSi$^+$; thus, the apparent G2 total energy, given in Table 3, for NaSiF$^+$ (but not NaFSi$^+$) can be assumed to be intrinsically reliable. The influence of bond length for NaFCl$^+$, mentioned above, can also be seen graphically. In Figure 1, we compare the calculated potential energy profile for (linear) NaFCl$^+$ as a function of bond length, for the MP2/6-31G* and G2(MP2(COL)) levels of theory. It should be clear from this figure, in conjunction with the values listed in Table 6, that the problems with G2(MP2(COL)) values at Na−F bond lengthsless than about 3 Å are connected with the inadequacy of the COL assumption for such geometries of this species. It is also instructive to compare the MP2(full) and MP2(FC,COL) potential energy curves, obtained using a 6-31G* basis, on this figure: good agreement (COL assumption valid) is seen between the frozen-core and full-correlation calculations at larger Na/ligand separations, while the divergence at shorter separations is consistent with orbital mixing and with the inversion of the F 2s and Na 2p orbitals' relative energies. Presumably, also, the failure of the COL assumption for G2(MP2) at larger separations than is seen for MP2/6-31G* is connected with the more extensive basis set (effectively 6-311+G(3df,2p)) employed in G2(MP2).

In summary, we can see that the COL assumption is generally not valid for species of the formula NaFX$^+$; from Table 3, it is apparent that the magnitude of the discrepancy introduced by using the COL assumption in calculating a G2 total energy must be, in some of the examples given, at least 200 kJ mol^{-1}. Such a result is highly undesirable, and it is important to seek methods for obtaining more reliable calculated values for NaFX$^+$ and for other species for which standard G2 theory has similar difficulties.

B. G2(NCCS) Calculations on Selected Na(FX)$^+$ Species. While several strategies can be advanced to attempt to rectify the problems outlined in the above section, perhaps the most obvious solution is to specify the correct correlation space for the G2 calculation in question, that is, for NaFX$^+$, ensuring that all of the valence orbitals for F and for X are included in the correlation space, with all filled orbitals corresponding to Na 2s or 2p placed in the frozen core. This method will produce G2(NCCS) values for many of the NaFX$^+$ species included in

TABLE 4: MP2(full)/6-31G* Total Energies and Ion−Ligand Binding Energies for NaFX$^+$ Stationary Points

species^a	ZPE^b (mHartrees)	$n(i)^c$	$E_0{}^d$ (Hartrees)	SCA(FX)^e (kJ mol^{-1})	ΔSCA[MP2-COL]^f (kJ mol^{-1})
^{2}NaF$^+$	0.201	0	−261.150 58	1.9	105
NaFH$^+$	9.487	0	−261.872 32	95.2	214
NaFLi$^+$	3.183	0	−268.878 18	236.4	46
^{2}NaFBe$^+$	3.373	0	−276.009 74	96.0	163
NaBF$^+$	4.597	0	−286.033 22	87.8	210
T-Na(BF)$^+$	3.164	1	−286.007 57	20.4	205
NaFB$^+$	3.132	0	−286.011 78	31.5	200
^{2}NaCF$^+$	4.091	1	−299.111 81	60.6	222
^{2}NaFC$^+$	2.701	1	−299.100 01	29.7	210
^{3}NaNF$^+$	3.336	0	−315.726 78	26.7	217
^{3}NaFN$^+$	2.678	2	−315.731 27	38.6	213
^{2}NaOF$^+$	3.481	1	−336.105 25	14.1	206
^{2}Na(FO)$^+$ bent	3.785	0	−336.112 11	32.0	219
^{2}NaFO$^+$	3.347	2	−336.111 36	30.1	218
NaFF$^+$	2.519	2	−360.702 62	13.8	213
T-Na(F$_2$)$^+$	2.699	0	−360.712 69	40.2	219
NaFNa$^+$	2.284	0	−423.267 86	293.7	58
^{2}NaFMg$^+$	2.437	0	−461.011 44	175.1	37
NaFAl$^+$	2.357	0	−503.344 62	123.4	103
^{2}NaSiF$^+$	2.480	1	−550.249 29	13.8	4
^{2}NaFSi$^+$	2.342	0	−550.281 08	97.2	180
^{3}NaPF$^+$	2.208	2	−602.057 88	-5.1	−2
^{3}NaFP$^+$	2.320	0	−602.093 74	89.0	199
^{2}Na(FS)$^+$ bent	2.232	0	−658.858 92	74.7	208
^{2}NaFS$^+$	2.252	1	−658.858 84	74.5	207
Na(FCl)$^+$ bent	2.267	0	−720.824 14	67.8	212
NaFCl$^+$	2.161	2	−720.821 34	60.4	205

[a] Unless otherwise indicated, all species are of singlet multiplicity. [b] Zero-point vibrational energy, obtained at the MP2(full)/6-31G* level of theory (corrected by a factor of 0.9427).[17] [c] Number of imaginary frequencies. [d] Calculated MP2(full)/6-31G* total energy, including ZPE. [e] Sodium cation affinity of ligand FX at the MP2(full)/6-31G* level of theory. [f] Difference between the MP2(full)/6-31G* and G2(COL) SCA values.

TABLE 5: Calculated Parameters for Orbitals in Atomic and Ionized Na, F, and Ne

species	orbital no.^{a}	eigenvalue^b	ID^c	correlation status^d
Na	2	−2.9743	Na 2s	N−Y−
	3, 4, 5	−1.5182	Na 2p	N−Y−
Na$^+$	2	−3.0684	Na 2s	N−Y−
	3, 4, 5	−1.7968	Na 2p	N−Y−
F	2	−1.6626	F 2s	Y− −N
	3	−0.8342	F 2p$_z$	Y− −Y
F$^-$	2	−0.9924	F 2s	Y− −N
	3	−0.1064	F 2p	Y− −Y
Ne	2	−1.9194	Ne 2s	Y− −N
	3, 4	−0.8415	Ne 2p	Y− −Y

[a] Orbitals are numbered in order of increasing eigenvalue. [b] Orbital (alpha) eigenvalues, obtained from MP4(FC)/6-311G** population calculations. [c] Identification of the atomic orbital. [d] The four-character string listed for each orbital summarizes its treatment by, respectively, the following four techniques: (i) G2(COL), (ii) G2(NCCS), (iii) G2(thaw), and (iv) G2(X-2s) [X = F or Ne]. The status for each method is identified as Y (orbital is included in correlation space); N (orbital is excluded from correlation); and − (indicated method is identical to G2(COL) for this species).

the present study, but there are two principal objections to such an approach. The first objection, which has been raised elsewhere by Duke and Radom,[13] is that there is no clear theoretical justification for excluding, from correlation, orbitals that lie above the lowest lying orbital to be correlated; if the eigenvalue of the lowest lying occupied valence orbital is sufficiently close to the datum to require its correlation, then it would appear reasonable also that all occupied orbitals with higher eigenvalues should also be correlated. A second objection, which has also been raised by Duke and Radom,[13] is more pragmatic: in some instances (some of which are identified in Table 6) the mixing of the F 2s and Na 2p$_z$ orbitals is sufficiently strong to preclude satisfactory identification of any molecular orbital as F 2s, and so a G2(NCCS) calculation cannot be performed for such species. Notwithstanding these objections, it remains a useful exercise to test the reliability of G2(NCCS) calculations, on Na(FX)$^+$, by computation. The results of such calculations, using the ACES II[16] program suite, are given in Table 7. We have not performed G2(NCCS) calculations for any NaFX$^+$ species featuring X = Na−Cl: most such species exhibit strong Na 2p/F 2s orbital mixing, and so G2(NCCS) is not appropriate. Similarly, we have not calculated a total energy for NaFLi$^+$, for which the COL assumption holds.

In those instances where the mixing of Na 2p with F 2s orbitals is not too severe—that is, for most of the compounds included in Table 7—the use of a noncontiguous correlation space does indeed yield a substantially improved G2 total energy than does blind implementation of G2 using the COL assumption. For example, the G2(NCCS) SCA values for HF, BF, CF, NF, OF, and F$_2$ are all positive quantities, in sharp contrast to the large negative values obtained with G2(COL).

Assessment of the appropriateness (or otherwise) of segmenting the correlation space in these calculations is difficult. Of all the species exhibiting difficult relative orbital energies for F 2s and Na 2p, only one—NaFNa$^+$—has been subjected to experimental study, and the experimental thermochemistry of this species is not known to high precision. Furthermore, this is a species in which the problem is one of F 2s/Na 2p$_z$ orbital mixing, with most of the F 2s character residing in an orbital that is outside the frozen core using the COL assumption; this is not, therefore, a case for which a noncontiguous correlation space is appropriate. The only species that can serve as a test set for G2(NCCS) is NaNe$^+$, for which there is very little core/valence orbital mixing and for which the COL assumption fails spectacularly (with a G2(COL) SCA(Ne) value of −160.9 kJ mol^{-1}). Here the G2(NCCS) technique yields an excellent sodium cation affinity of 7.1 kJ mol^{-1}—agreement with experimental values is within ±1 kJ mol^{-1}—but the calculated enthalpy of formation would appear to be incorrect by a similar

TABLE 6: Calculated Parameters for Orbitals at the Core/Valence Boundary in Selected FX and NaFX$^+$ Species

species	orbital no.[a]	eigenvalue[b]	assumed status[c]	f_{Na} (max)[d]	f_X (max)[e]	true ID[f]	correlation status[g]
HF	2	−1.5812	valence		0.605	F 2s	Y− −N
NaFH$^+$	4	−1.8162	core	0.130	0.593	F 2s	NYYN
	5, 6	−1.7543	core	0.651	0.001	Na $2p_{x,y}$	NNYN
	7	−1.7517	valence	0.637	0.128	Na $2p_z$	YNYN
BF	3	−1.6913	valence		0.607	F 2s	Y− −N
NaBF$^+$	5	−1.8699	core	0.027	0.605	F 2s	NYYN
	6, 7	−1.7500	core	0.651	0.000	Na $2p_{x,y}$	NNYN
	8	−1.7495	valence	0.651	0.001	Na $2p_z$	YNYN
NaFB$^+$	5	−1.8709	core	0.049	0.607	F 2s	NYYN .
	6, 7	−1.7755	core	0.651	0.001	Na $2p_{x,y}$	NNYN
	8	−1.7749	valence	0.649	0.050	Na $2p_z$	YNYN
AlF	7	−1.5224	valence		0.605	F 2s	Y− −N
NaFAl$^+$	9	−1.7376	core	0.532	0.339	?	N*YN
	10, 11	−1.7273	core	0.651	0.001	Na $2p_{x,y}$	NNYN
	12	− 1.7033	valence	0.375	0.503	?	Y*YN
SiF	7	−1.5808	valence		0.605	F 2s	Y− −N
NaFSi$^+$	9	− 1.7647	core	0.292	0.537	?	N*YN
	10, 11	−1.7381	core	0.651	0.001	Na $2p_{xy}$	NNYN
	12	−1.7304	valence	0.581	0.282	?	Y*YN
NaSiF$^+$	9, 10	−1.7788	core	0.651	0.000	Na $2p_{xy}$	N−YN
	11	−1.7787	core	0.651	0.001	Na $2p_z$	N−YN
	12	−1.7437	valence	0.010	0.606	F 2s	Y−YN
FCl	7	−1.6271	valence		0.598	F 2s	Y− −N
NaFCl$^+$	9	−1.8151	core	0.120	0.587	F 2s	NYYN
(2.188 Å)[h]	10, 11	-1.7577	core	0.651	0.001	Na $2p_{x,y}$	NNYN
	12	−1.7556	valence	0.639	0.094	Na $2p_z$	YNYN
NaFCl$^+$	9	− 1.7768	core	0.488	0.395	?	N*YN
(2.88 Å)[i]	10, 11	-1.7761	core	0.651	0.000	Na $2p_{x,y}$	NNYN
	12	− 1.7741	valence	0.431	0.449	?	Y*YN
NaFCl$^+$	9, 10	−1.7781	core	0.651	0.000	Na $2p_{x,y}$	N−YN
(3.00 Å)[i]	11	− 1.7778	core	0.646	0.071	Na $2p_z$	N−YN
	12	−1.7699	valence	0.078	0.594	F 2s	Y−YN
NaNe$^+$	4	−2.1517	core	0.009	0.662	Ne 2s	NYYN
	5	−1.7920	core	0.651	0.014	Na $2p_z$	NNYN
	6	−1.7918	core	0.651	0.001	Na $2p_x$	NNYN
	7	−1.7918	valence	0.651	0.001	Na $2p_y$	YNYN

[a] Orbitals are numbered in order of increasing eigenvalue. [b] Orbital (alpha) eigenvalues, obtained from MP4(FC)/6-311G** population calculations. [c] Assignment of orbital to the (frozen) core or to the correlation space (valence), on selection of the FC option in a routine GAUSSIAN94 single-point calculation. [d] Maximum alpha orbital coefficient for the sodium atom. [e] Maximum alpha orbital coefficient for the fluorine or neon atom. [f] Identification, where possible, of the atomic orbital which this molecular orbital most closely resembles. [g] The four-character string listed for each orbital summarizes its treatment by, respectively, the following four techniques: (i) G2(COL), (ii) G2(NCCS), (iii) G2(thaw), and (iv) G2(X-2s) [X = F or Ne]. The status for each method is identified as Y (orbital is included in correlation space); N (orbital is excluded from correlation); − (indicated method is identical to G2(COL) for this species); and * (this molecular orbital cannot be appropriately identified with any atomic orbital: indicated method is not defined for this species). [h] MP2(full)/6-31G* optimized (linear) geometry. [i] MP2(full)/6-31G* partially-optimized linear geometry. See text for discussion.

amount to the G2 error in $\Delta H^\circ_f(\mathrm{Na}^+)$,[1,12,20] namely by about 18 kJ mol^{-1}.

Of several species for which we cannot determine meaningful G2(NCCS) total energies (mostly due to Na/F orbital mixing), NaF$^+$ requires special comment. For this species, which is a doublet with 10 α and 9 β electrons, there is little mixing of Na/F orbitals, but the ordering of the F 2s and Na 2p orbitals is different for the α and β electrons. An appropriate noncontiguous correlation space for this species would therefore include, for the α electrons, the filled orbitals numbered 4, 8, 9, and 10 (and all virtual orbitals), and for the β electrons, orbitals 7, 8, and 9 (plus all virtual orbitals). ACES II does not currently permit the definition of such a correlation space, and we are not aware of any widely available packages that can perform such a calculation.

We conclude that segmentation of the correlation space can yield plausible total energies for systems in which the problem is one of core/valence orbital energy reversal (rather than core/valence mixing). Nevertheless, it is not a valid strategy when core/valence mixing does occur, and in such cases other methods must be used. Furthermore, since the G2(NCCS) total energy for Na$^+$ is identical to the G2 value which is substantially in error, it follows that G2(NCCS) will not be able to provide both a highly accurate $\Delta H^\circ_f(\mathrm{NaFX}^+)$ value and a highly accurate SCA(FX) value for the same species FX.

C. Assessment of the G2(thaw) Procedure for Na-Containing Cations. The G2(thaw) procedure has been described previously,[12] albeit in a limited and somewhat incomplete fashion. In the present work, and as described in the Theoretical Methods section above, we have defined the G2(thaw) method more explicitly in order to minimize problems with relative energies of correlated and frozen orbitals in cases (such as NaFM$^+$, M = Li, Be, Mg, Al) where Na and another metal atom are both present.

The central notion behind the G2(thaw) method is this. In most of its compounds, and especially within cations, the sodium atom can be treated largely as Na$^+$. Since Na$^+$ is isoelectronic with F$^-$ and Ne, and since the 2s and 2p orbital energies for these three entities are not greatly disparate, it seems appropriate to accord a similar electron correlation treatment to all three; thus, if the 2s and 2p orbitals define the valence shell of F$^-$ and of Ne, these same orbitals can also be considered as the valence shell for Na$^+$. Our previous introductory study on G2(thaw)[12] claimed two notable successes over standard G2 theory: a significant improvement in the agreement between calculated and experimental ionization energies of Na and a

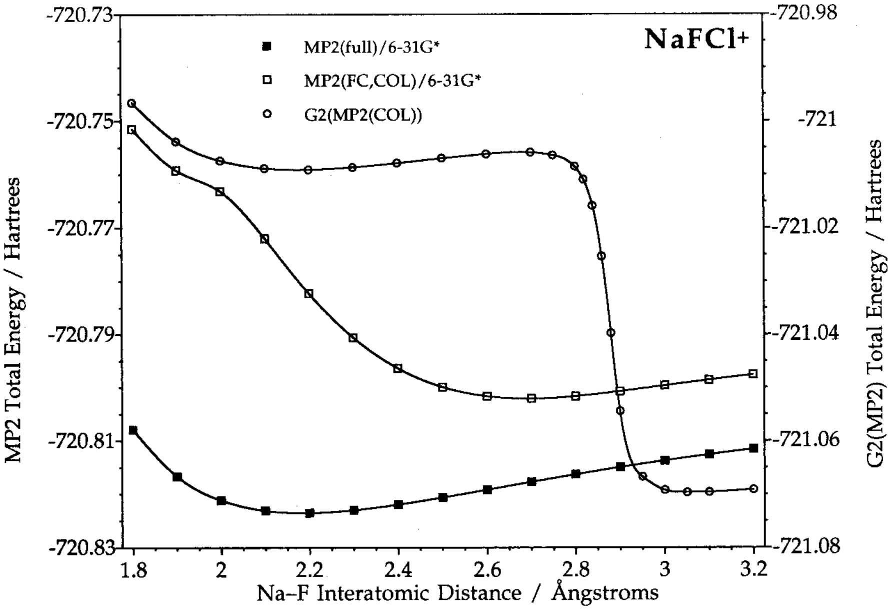

Figure 1. Dependence of total energy E_e for NaFCl$^+$ upon the Na−F bond length, at various levels of theory. All calculations are for the linear NaFCl$^+$ configuration (with optimization of the F−Cl distance in the MP2 calculations for each point). At MP2(full)/6-31G*, the global minimum is a bent NaFCl$^+$ structure as detailed in Table 2: however, at all levels of theory employed here, the energy difference between linear and bent geometries is slight and does not greatly influence the observed dependence of E_e upon the sodium−fluorine distance. The partially optimized MP2(full)/6-31G* results were used to obtain the G2(MP2(COL)) values depicted.

TABLE 7: G2(NCCS) Total Energies, Enthalpies of Formation, and Ion−Ligand Binding Energies for NaFX$^+$ Stationary Points

species	E_0[a] (Hartrees)	ΔE_0(NCCS)[b] (mHartrees)	$\Delta H^\circ_{f,0}$[c] (kJ mol^{-1})	SCA[d] (kJ mol^{-1})
NaFH$^+$	−262.033 56	−64.63	257.8	50.6
^{2}NaFBe$^+$	−276.132 75	−28.75	422.5	8.2
NaBF$^+$	−286.211 45	−70.81	400.2	63.4
T-Na(BF)$^+$	−286.187 73	−70.67	462.5	1.1
NaFB$^+$	−286.192 08	−69.05	451.1	12.6
^{2}NaCF$^+$	−299.290 74	−60.83	824.2	−1.5
^{2}NaFC$^+$	−299.294 05	−71.58	815.5	7.2
^{3}NaNF$^+$	−315.939 65	−75.77	806.3	8.7
^{3}NaFN$^+$	−315.941 87	−71.94	800.5	14.6
^{2}NaOF$^+$	−336.362 73	−75.50	689.9	5.7
^{2}Na(FO)$^+$ bent	−336.366 54	−77.36	679.9	15.7
^{2}NaFO$^+$	−336.363 95	−74.97	686.7	8.9
NaFF$^+$	−360.988 38	−75.81	586.5	0.3
T-Na(F$_2$)$^+$	−360.995 05	−74.88	569.0	17.8
NaNe$^+$	−290.486 01	−63.97	578.1	7.1

[a] Total energy, including ZPE, at the G2(NCCS) level of theory. [b] E_0[G2(NCCS)] − E_0[G2(COL)]. [c] Calculated enthalpy of formation, at 0 K. [d] Sodium cation affinity at 0 K.

dramatic improvement in the (as yet not experimentally characterized) sodium cation affinity of HF. In fact, as is now seen from an examination of the orbital energies (see Table 6), the reported G2 value for SCA(HF) = −119 kJ mol^{-1} [12] is really a G2(COL) value, because the COL assumption is violated for this species. Correlation of the same total number of orbitals, in a G2(NCCS) calculation, is seen to deliver a substantially improved value for SCA(HF). Nevertheless, in view of our finding (see above) that G2(NCCS) values cannot be obtained for some of the Na(FX)$^+$ species, a method such as G2(thaw) would appear to be required in several instances.

We have not previously reported a rigorous assessment of the relative performance of G2 and G2(thaw). Here we perform such an assessment, with reference to several experimentally determined energetic parameters for sodium-containing ions. Unfortunately, few of the experimental measurements are of sufficient accuracy (i.e., with an uncertainty not greater than ±2 kJ mol^{-1}) to provide truly useful benchmarks for our purposes of comparing the thawed and unthawed Gaussian-2 procedures; however, several useful conclusions can still be drawn from the existing data. In Table 8, we present G2-based total energies for the sodium-containing species selected for this comparison, while in Table 9 we compare the experimental and calculated energetic parameters for these species. Note that, for almost all members of this test set, G2(COL) appears to give meaningful thermochemical values. Failure of the COL assumption is, after all, a rather rare occurrence among first- and second-row compounds!

The results reported in Table 8 show, firstly, that there is very close accord between the standard G2 and G2(MP2) total energies for all species: note that the differences between G2 and G2(MP2) E_0 values for chlorine- or argon-containing species reflect differences in the E_0 values of the Cl and Ar atoms themselves. Secondly, the various thawed methods are seen to have very similar effects; in all the examples chosen for calculation, E_0 for molecular ions is increased upon thawing by slightly less than ΔE_0(thaw) for Na$^+$ itself. There are too few sodium-containing neutrals in Table 8 for any trends to be particularly clear, but it appears that ΔE_0(thaw) for such species is generally slightly negative. Therefore, G2(thaw) should yield generally higher ionization energies than G2 for sodium-containing neutrals.

The relative quality of the various calculated values displayed in Table 8 is best judged by reference to the experimental values, and this is done in Table 9.[24] It is apparent that both the "standard" methods (G2 and G2(MP2)) and the various "thawed" methods tend to underestimate the experimental sodium cation affinities and ionization energies. However, for most systems in Table 9 (including the experimentally-well-characterized species Na$^+$, NaHe$^+$, NaAr$^+$, and Na$_2$$^+$), the thawed techniques perform rather better than standard G2 or G2(MP2), particularly for the calculation of sodium cation affinities. As with G2(NCCS), NaNe$^+$ is arguably the crucial case, since this is the sole species in Table 9 for which the COL assumption is not

TABLE 8: Total Energies, E_0, Calculated for Experimentally Characterized Sodium-Containing Cations and Related Species

	G2				G2(MP2)			
species[a]	E_0[a]	(thaw)[a]	ΔE_0(thaw)[b]	(thaw/MP2)[a]	E_0[a]	(thaw)[a]	ΔE_0(thaw)[b]	(thaw/MP2)[a]
Na^+	−161.664 29[c]	−161.659 08[d]	+5.21[d]	−161.659 76	−161.664 29[e]	−161.659 43	+4.86	−161.659 76
$NaHe^+$	−164.565 64	−164.560 80	+4.84	−164.561 45	−164.565 64	−164.561 14	+4.50	−164.561 45
$NaNe^+$	−290.422 04[f]	−290.481 82	−59.78	−290.479 70	−290.422 19[g]	−290.478 80	−56.62	−290.479 85
$NaAr^+$	−688.725 49	−688.721 49	+4.00	−688.722 10	−688.714 78	−688.711 10	+3.68	−688.711 39
$^2NaLi^+$	−169.129 96	−169.127 50	+2.46	−169.129 99	−169.129 96	−169.127 64	+2.32	−169.129 99
$^2NaNa^+$	−323.545 68	−323.541 41	+4.27	−323.541 95	−323.545 68	−323.541 68	+4.00	−323.541 95
$NaCH_4^+$	−202.084 44	−202.081 54	+2.90	−202.082 04	−202.083 17	−202.080 54	+2.63	−202.080 78
$NaNH_3^+$	−218.161 85[d]	−218.159 42[d]	+2.43	−218.159 85	−218.159 99	−218.157 79	+2.20	−218.157 99
$NaOH_2^+$	−238.030 16[d]	−238.027 65[d]	+2.51	−238.028 05	−238.027 89	−238.025 59	+2.29	−238.025 78
$NaClH^+$	−622.019 41[d]	−622.015 97[d]	+3.44	−622.016 53	−622.010 70	−622.007 55	+3.15	−622.007 82
$NaNN^+$	−271.068 03	−271.064 73	+3.30	−271.065 26	−271.065 05	−271.062 03	+3.02	−271.062 29
$NaCO^+$	−274.856 11	−274.852 97	+3.14	−274.853 49	−274.853 97	−274.851 07	+2.90	−274.851 31
$NaCO_2^+$	−350.043 56	−350.041 47	+2.09	−350.041 81	−350.038 93	−350.037 04	+1.89	−350.037 18
$NaClNa^+$	−783.419 96	−783.415 84	+4.12	−783.416 78	−783.410 59	−783.406 96	+3.63	−783.407 40
NaLi	−169.313 78	−169.314 91	−1.13	−169.317 34	−169.314 40	−169.315 62	−1.22	−169.317 96
Na_2	−323.723 00[c]	−323.724 75	− 1.75	−323.725 28	−323.723 58	−323.725 52	− 1.94	−323.725 86
NaCl	−621.680 22[c]	−621.679 01	+ 1.21	−621.679 37	−621.671 01[e]	−621.670 01	+1.00	−621.670 16
$^2Na_2Cl$	−783.557 53	−783.557 69	−0.16	−783.558 00	−783.548 20	−783.548 56	−0.36	−783.548 67

[a] Total energy, including ZPE, at the indicated level of theory. [b] Change in E_0(G2) or E_0(G2(MP2)), in mHartrees, due to sodium inner-electron correlation. [c] Previously reported in ref 1. [d] Previously reported in ref 12. [e] Previously reported in ref 4. [f] G2(COL) value. See Table 7 for the corresponding G2(NCCS) value. [g] G2(MP2)(COL) value. Corresponding G2(MP2)(NCCS) value is −290.478 55 Hartrees.

TABLE 9: Comparison of Experimental and Calculated Parameters for Sodium-Containing Cations

			G2			G2(MP2)		
species	parameter	expt[a]	G2	(thaw)	(thaw/MP2)	G2(MP2)	(thaw)	(thaw/MP2)
Na^+	IE	495.8[b]	477.6	491.2	489.4	477.5	490.3	489.4
$NaHe^+$	SCA	3.3; 3.9; 5.0; 5.8	2.9	3.8	3.8	2.9	3.8	3.8
$NaNe^+$	SCA	6.1; 6.4; 7.4	−160.9[c]	9.7	2.4	−152.8[d]	8.6	10.5
$NaAr^+$	SCA	15.5; 18.4; 20.4	14.4	17.6	17.4	14.4	17.5	17.4
$^2NaLi^+$	SCA	93 ± 5[b,e]	87.8	95.0	99.8	87.8	94.5	99.8
	IE	487 ± 4[b,e]	482.6	492.0	491.9	484.3	493.5	493.5
$^2NaNa^+$	SCA	95[b]	92.4	94.9	94.5	92.5	94.7	94.6
	IE	471.72 ± 0.02[b]	465.6	481.4	481.3	467.1	482.7	482.9
$NaCH_4^+$	SCA	34	24.3	30.4	29.9	24.2	30.1	29.8
$NaNH_3^+$	SCA	124	102.2	109.5	108.8	100.8	108.1	107.8
$NaOH_2^+$	SCA	103; 113	88.8	95.9	95.2	88.2	94.9	94.5
$NaClH^+$	SCA	54	39.3	43.9	43.6	38.8	43.3	43.2
$NaNN^+$	SCA	38	29.2	34.2	33.8	29.6	34.4	34.3
$NaCO^+$	SCA	57	37.6	43.1	42.6	37.5	42.6	42.4
$NaCO_2^+$	SCA	62; 71	47.2	55.3	54.5	47.3	55.1	54.6
$NaClNa^+$	SCA	178 ± 23;[b,f] 176 ± 17[g]	198.1	201.0	201.6	197.7	200.9	201.2
	IE	400 ± 21;[b,f] 396 ± 10[b,h]	361.2	372.4	370.8	361.3	371.8	370.9
NaLi	D_0(Na−Li)	84 ± 1[b,c]	92.9	95.9	102.2	94.5	97.7	103.9
NaNa	D_0(Na−Na)	71[b]	80.4	85.0	86.4	82.0	87.1	87.9
NaCl	D_0(Na−Cl)	407[b]	413.3	410.1	411.0	415.1	412.5	412.9
NaClNa	D_0(NaCl−Na)	82;[b,f] 72[b,h]	81.7	85.3	85.2	81.4	85.0	84.9
	ΔH°_f	−155;[b,f] −144[b,h]	−160.2	−160.6	−161.4	−161.8	−162.7	−163.0

[a] Literature value of indicated parameter (adjusted to 0 K), taken from the compilation of Keesee and Castleman[21] unless otherwise indicated. [b] Reference 20. [c] G2(COL) value. The G2(NCCS) value for this parameter is +7.1 kJ mol^{-1}. [d] G2(MP2)(COL) value. The G2(MP2)(NCCS) value for this parameter is −4.8 kJ mol^{-1}. [e] See text for discussion. [f] Reference 22. This is one of two independently listed values for this parameter in ref 20. [g] Reference 23. [h] Please note that the tabulation of gas-phase ion and neutral thermochemistry[20] incorrectly cites $\Delta H^\circ_f(Na_2Cl) = -244 \pm 17$ kJ mol^{-1} as the value from the study of Kappes et al.;[23] in fact, the data tabulated by Kappes et al.[23] yield alternatively $\Delta H^\circ_f(Na_2Cl) = -147 \pm 25$ and -142 kJ mol^{-1} from two different thermochemical cycles.

valid. All four thawed methods yield positive SCA(Ne) values within ±5 kJ mol^{-1} of the experimental values; while this is not so impressive as the ±1 kJ mol^{-1} agreement with experiment afforded by G2(NCCS), it is likely that the excellent value yielded by G2(NCCS) is somewhat fortuitous, since the analogous G2(MP2(NCCS)) method, based on G2(MP2) theory, yields a small negative value for SCA(Ne).

D. G2(thaw) calculations on $Na(FX)^+$. In Table 10, we present the results of our G2(thaw) calculations upon sodium- and fluorine-containing ions. It is very readily apparent that the calculated SCAs for the relevant fluorides are substantially improved from their respective G2(COL) values; of the SCA(FX) values listed in Table 10, only one species (NaF^+) is calculated to possess a (marginally) negative Na^+−(FX) bond strength, and even in this instance the SCA value has been improved from G2(COL) by almost 100 kJ mol^{-1}.

Comparison with experiment is possible only in the instance of Na_2F^+, for which Kappes et al.[23] have obtained SCA(NaF) = 255 + 13 kJ mol^{-1}. This result is in excellent agreement with our G2(thaw) value of SCA(NaF) = 259 kJ mol^{-}, and may be contrasted with the standard G2 value (see Table 3) of SCA(NaF) = 236 kJ mol^{-1}. Of several theoretical studies on Na_2F^+,[26−29] the most recent[29] reports a value of SCA(NaF) = 244 kJ mol^{-1} at the MP4SDTQ(fc)/6-311+G*//MP2(full)/6-31+G* level of theory. While the best agreement with the experimental value is obtained by G2(thaw), it should be noted

TABLE 10: G2(thaw) Total Energies, Enthalpies of Formation, and Ion−Ligand Binding Energies for NaFX$^+$ Stationary Points

species	E_0[a] (Hartrees)	ΔE_0(thaw)[b] (mHartrees)	$\Delta H°_{f,0}$[c] (kJ mol^{-1})	SCA[d] (kJ mol)
^{2}NaF$^+$	−261.290 25	−32.37	680.6	−4.3
NaFH$^+$	−262.034 53[e]	−65.60[e]	255.2[e]	66.8[e]
NaFLi$^+$	−269.025 66	−4.66	42.3	216.3
^{2}NaFBe$^+$	−276.158 08	−54.08	356.0	88.4
NaBF$^+$	−286.208 69	−68.05	407.5	69.8
T-Na(BF)$^+$	−286.183 99	−67.00	472.3	5.0
NaFB$^+$	−286.189 58	−66.55	457.7	19.6
^{2}NaCF$^+$	−299.306 35	−76.44	783.2	53.2
^{2}NaFC$^+$	−299.291 39	−68.92	822.5	13.9
^{3}NaNF$^+$	−315.945 12	−81.24	792.0	36.8
^{3}NaFN$^+$	−315.939 73	−69.80	806.1	22.7
^{2}NaOF$^+$	−336.360 76	−73.53	695.1	14.2
^{2}Na(FO)$^+$ bent	−336.361 69	−72.51	692.6	16.6
^{2}NaFO$^+$	−336.361 04	−72.06	694.3	14.9
NaFF$^+$	−360.985 20	−72.63	594.8	5.7
T-Na(F$_2$)$^+$	−360.991 96	−71.79	577.1	23.4
NaFNa$^+$	−423.419 39	−36.4	45.3	259.1
^{2}NaFMg$^+$	−461.162 57	−0.42	230.6	152.6
NaFAl$^+$	−503.522 84	−29.45	218.4	111.6
^{2}NaSiF$^+$	−550.451 55	+3.49	527.8	14.4
^{2}NaFSi$^+$	−550.475 16	−55.34	465.8	76.3
^{3}NaPF$^+$	−602.277 81	+3.96	551.6	0.3
^{3}NaFP$^+$	−602.301 99	−60.94	488.1	63.8
^{2}Na(FS)$^+$ bent	−659.096 99	−65.29	556.7	51.8
^{2}NaFS$^+$	−659.097 02	−65.13	556.7	51.9
Na(FCl)$^+$ bent	−721.082 78	−67.21	495.9	31.1
NaFCl$^+$	−721.082 71	−66.98	496.1	30.9

[a] Total energy, including ZPE, at the G2(thaw) level of theory. [b] Change in E_0(G2) due to sodium inner electron correlation. [c] Calculated enthalpy of formation, at 0 K. [d] Sodium cation affinity at 0 K. This parameter has been calculated using the G2(thaw) value for Na$^+$ and G2 total energies for the ligands. [e] Previously reported in ref 12.

that the experimental uncertainty is fairly large compared to the difference between G2 and G2(thaw) values of SCA(NaF), and so this is not a particularly useful test of the relative reliability of the thawed and standard G2 approaches. Nevertheless, NaFNa$^+$ is a species for which our calculations show significant core/valence mixing, and so a procedure such as G2(thaw), which effectively expands the valence shell, might well be expected to produce superior results. We contend that the ability of G2(thaw) to return positive SCA values for all of the diatomic fluorides surveyed here is also a very good affirmation of the merits of this technique.

While a comparison with the other new variants of G2 will be explored in somewhat more detail in a subsequent section, a brief comment on the G2(thaw) and G2(NCCS) values is appropriate at this juncture. In most instances, the two techniques deliver reasonably similar total energies, enthalpies of formation, and SCAs, but the values for NaFBe$^+$ and NaCF$^+$ are in serious disagreement: G2(NCCS) delivers total energies for these two species that are significantly higher than the G2(thaw) total energies. This discrepancy appears to arise from a high degree of F 2s/Na 2p$_z$ mixing in NaFBe$^+$ and NaCF$^+$, and we expect the G2(thaw) results to be the more accurate for these species.

E. Less Computationally Intensive Variants of G2(thaw). The inclusion of sodium inner-electron correlation is not without some additional cost in CPU time; for example, the constituent single-point calculations for the G2(thaw) calculation on NaFH$^+$ consume almost 4 times as much CPU time as do the analogous G2 calculations. While the relative increase in CPU time for a larger sodium-containing ion is not, in most instances, as great as that of NaFH$^+$—since the sodium inner-core orbitals to be thawed comprise a smaller proportion of the total set of orbitals for the larger ion—the absolute increase is often still considerable, and the computational cost of such G2(thaw) calculations for larger sodium-containing ions may be judged to be prohibitive. In this context, we note that very similar numerical values are obtained with the less computationally expensive G2(MP2(thaw)), G2(thaw/MP2), or G2(MP2(thaw/MP2)) techniques, and we display the G2(MP2(thaw)) and G2(MP2(thaw/MP2)) values in Table 11.[30] In the absence of reliable experimental values for the relevant sodium cation affinity values, it is not possible to judge precisely which technique is the most accurate; however, G2(thaw) includes a consideration of core−valence electron correlation at a higher level (fourth-order Møller−Plesset) than do the other thawing techniques, and we would therefore expect G2(thaw) to be the most reliable of these procedures. Of the other three methods, G2(thaw/MP2)[30] displays the greatest systematic variation from the G2(thaw) results; we therefore suggest that the G2(thaw/MP2) method is probably the least reliable of the thawing techniques surveyed here. We recommend instead the use of G2(MP2(thaw/MP2))—which is less computationally intensive than G2(thaw/MP2) and appears more reliable—if an economical treatment of sodium inner-shell electron correlation is desired.

F. Assessment of the G2(F-2s) Procedure. The final strategy that we have explored as a route to improved G2 values for the NaFX$^+$ species is perhaps counterintuitive: the G2(F-2s) approach involves a reduction in the number of molecular orbitals to be correlated. There are two potential advatages to such an approach: firstly, it is relatively inexpensive in CPU time; and secondly, because both the orbital energy conflict and the core/valence mixing for NaFX$^+$ and NaNe$^+$ involve only the Na 2p and (F or Ne) 2s orbitals, we might expect that removal of all of them offending orbitals from the correlation space may obviate the deficiencies evident in the G2(COL) total energies for these species.

Nevertheless, the F 2s orbital is normally considered as part of fluorine's valence shell, and its removal from the correlation space may give rise to other problems. As an assessment of the reliability of G2(F-2s), we have determined the total energies and enthalpies of formation of the diatomic fluorides HF, LiF → F$_2$, and NaF → FCl. These values are displayed in Table 12. The agreement between G2 and G2(F-2s) for these 15 fluorides is (perhaps surprisingly) generally quite good: only five species (CF, NF, OF, F$_2$, and FCl) show discrepancies of more than 2 mHartrees between G2 and G2(F-2s) total energies. Moreover, there is a strong connection between this discrepancy, ΔE_0[G2(F-2s) − G2], and the degree of covalent character expected in the various F−X bonds; for the most purely ionic fluoride NaF, exclusion of the F 2s orbitals from the correlation space actually reduces the total energy by a small amount, while in all other cases (and most notably where X is C, N, O, F, or Cl) the G2(F-2s) total energies are somewhat higher than G2, with by far the greatest difference being seen for the only purely covalent species (F$_2$). It seems very reasonable that neglect of F 2s orbital correlation will be more important in species in which this orbital is involved to some extent in covalent bond formation, and this is indeed borne out by our calculated values.

In terms of assessment versus experimental values (which is not, in this instance, the primary objective), G2(F-2s) is obviously rather poor for CF, NF, OF, and especially F$_2$; G2(F-2s) is (fortuitously?) better than G2 for FCl; and there are also a few species, notably BeF, MgF, and SiF, for which G2, G2(MP2), and G2(F-2s) all predict enthalpies of formation in good mutual agreement, but disagree significantly with the

TABLE 11: G2(MP2), G2(MP2(thaw)), and G2(MP2(thaw/MP2) Total Energies, Enthalpies of Formation, and Sodium Cation Affinities for NaFX$^+$ Stationary Points

	G2(MP2)		G2(MP2(thaw))				G2(MP2(thaw/MP2))		
species	E_0[a]	SCA[b]	E_0[a]	ΔE_0(thaw)[c]	$\Delta H°_{f,0}$[d]	SCA[b]	E_0[a]	$\Delta H°_{f,0}$[d]	SCA[b]
^{2}NaF$^+$	−261.255 59	−98.8	−261.286 78	−31.19	679.5	−4.2	−261.284 98	684.2	−9.8
NaFH$^+$	−261.968 98	−111.2	−262.031 78	−62.80	252.3	66.5	−262.031 04	254.2	63.6
NaFLi$^+$	−269.017 92	190.9	−269.022 28	−4.36	41.0	215.1	−269.022 12	41.4	213.8
^{2}NaFBe$^+$	−276.103 02	−60.9	−276.154 63	−51.61	357.9	87.4	−276.153 06	362.1	82.4
NaBF$^+$	−286.141 56	−114.1	−286.206 67	−65.11	404.3	69.7	−286.206 84	403.9	69.2
T-Na(BF)$^+$	−286.118 14	−175.6	−286.182 10	−63.96	468.8	5.1	−286.182 46	467.9	5.2
NaFB$^+$	−286.124 15	−159.8	−286.187 63	−63.48	454.3	19.7	−286.187 84	453.8	19.4
^{2}NaCF$^+$	−299.229 65	−152.9	−299.303 28	−73.63	780.0	53.2	−299.302 19	782.8	49.5
^{2}NaFC$^+$	−299.222 42	−171.9	−299.288 41	−65.99	819.0	14.2	−299.287 98	820.1	12.2
^{3}NaNF$^+$	−315.862 11	−182.0	−315.940 58	−78.47	789.3	36.8	−315.938 61	794.4	30.8
^{3}NaFN$^+$	−315.868 45	−165.3	−315.935 30	−66.85	803.1	22.9	−315.934 27	805.8	19.4
^{2}NaOF$^+$	−336.284 54	−183.9	−336.355 17	−70.63	690.7	14.3	−336.352 99	696.4	7.7
^{2}Na(FO)$^+$ bent	−336.287 56	−176.0	−336.356 05	−68.49	688.4	16.6	−336.354 38	692.8	11.3
^{2}NaFO$^+$	−336.286 89	177.8	−336.355 42	−68.53	690.1	14.9	−336.353 76	694.4	9.7
NaFF$^+$	−360.910 04	−189.2	−360.979 29	−69.26	589.9	5.4	−360.977 86	593.7	0.8
T-Na(F$_2$)$^+$	−360.917 83	−168.7	−360.986 23	−68.39	571.7	23.6	−360.985 01	574.9	19.6
NaFNa$^+$	−423.412 75	236.4	−423.416 13	−3.38	43.6	258.0	−423.416 02	43.9	256.9
^{2}NaFMg$^+$	−461.154 59	140.0	−461.162 57	−7.98	220.4	160.9	−461.158 13	232.0	148.4
NaFAl$^+$	−503.492 01	26.6	−503.519 76	−27.75	213.6	112.2	−503.518 54	216.8	108.1
^{2}NaSiF$^+$	−550.449 19	10.7	−550.445 98	+3.21	523.8	15.0	−550.446 25	523.0	14.9
^{2}NaFSi$^+$	−550.416 77	−74.4	−550.469 62	−52.86	331.3	77.1	−550.468 76	333.5	74.0
^{3}NaPF$^+$	−602.273 87	−2.5	−602.270 20	+3.66	549.9	0.6	−602.270 49	549.2	0.5
^{3}NaFP$^+$	−602.236 58	−100.4	−602.294 62	−58.04	444.9	64.7	−602.294 11	446.2	62.5
^{2}Na(FS)$^+$ bent	−659.024 37	−123.7	−659.086 46	−62.08	553.3	52.0	−659.086 24	553.8	50.6
^{2}NaFS$^+$	−659.024 63	−123.1	−659.086 57	−61.94	553.0	52.3	−659.086 32	553.6	50.8
Na(FCl)$^+$ bent	−721.006 65	−136.0	−721.070 07	−63.42	493.0	43.2	−721.070 42	492.1	43.3
NaFCl$^+$	−721.006 82	−135.6	−721.070 44	−63.63	492.0	44.2	−721.070 28	492.5	42.9

[a] Total energy (in Hartrees), including ZPE, calculated at the indicated level of theory. [b] Sodium cation affinity of ligand FX, in kJ mol^{-1}, obtained at the indicated level of theory. [c] Change in E_0(G2(MP2)) due to sodium inner-electron correlation. [d] Enthalpy of formation, in kJ mol^{-1}, at 0 K, at the indicated level of theory.

TABLE 12: Comparison of G2, G2(MP2), and G2(F-2s) Total Energies and Enthalpies of Formation for Diatomic Fluorides

		G2		G2(MP2)		G2(F-2s)			lit.
species	ZPE (mHartrees)	E_0[a] (Hartrees)	$\Delta H°_{f,0}$[c] (kJ mol^{-1})	E_0[a] (Hartrees)	$\Delta H°_{f,0}$[c] (kJ mol^{-1})	E_0[a] (Hartrees)	ΔE_0(G2−F)[b] (mHartrees)	$\Delta H°_{f,0}$[c] (kJ mol^{-1})	$\Delta H°_{f,0}$[d] (kJ mol^{-1})
HF	8.86	−100.350 01	−276.8	−100.347 04[e]	−279.2	100.348 87	+1.14	−273.8	−272.5 ± 0.8[f]
LiF	2.10	−107.284 21	−340.2	−107.280 92[e]	−341.8	−107.282 62	+1.59	−336.1	−340.6 ± 8.4[f]
^{2}BeF	2.68	−114.465 35	−154.5	−114.461 93	−152.6	−114.464 56	+0.79	−152.4	−172.2 ± 8
BF	2.99	−124.523 02	−121.5	−124.520 71	−123.9	−124.522 60	+0.42	−120.4	−118.8
^{2}CF	2.87	−137.627 00	237.6	−137.623 59	235.3	−137.623 89	+3.11	245.8	231.6 ± 8
^{3}NF	2.59	−154.272 02	229.9	−154.267 13	228.2	−154.267 57	+4.45	241.6	232.2 ± 2.1
^{2}OF	2.39	−174.696 27	110.4	−174.690 31	107.1	174.690 52	+5.75	125.5	109 ± 8
F$_2$	2.53	−199.323 97	1.7	−199.317 80[e]	−2.5	−199.310 71	+13.26	36.5	0
NaF	1.20	−261.661 62	−294.5	−261.658 42	−296.3	−261.662 24	−0.62	−296.1	−288.8 ± 2.1[f]
^{2}MgF	1.58	−299.445 38	−215.7	−299.441 85	−213.8	−299.444 31	+1.07	−212.9	−236.4 ± 8.4[f]
AlF	1.76	−341.821 27	−268.9	−341.817 59	−272.1	−341.821 03	+0.24	−268.3	−265.6 ± 3.4
^{2}SiF	1.87	−388.787 00	−56.7	−388.780 83	−59.1	−388.786 72	+0.28	−55.9	−22 ± 25
^{3}PF	1.86	−440.618 62	−47.0	−440.610 54	−47.4	−440.617 68	+0.94	−44.5	−52 ± 21
^{2}SF	1.88	−497.418 18	9.7	−497.407 21	7.4	−497.416 31	+1.87	14.6	12 ± 6
FCl	1.86	−559.406 67	−58.2	−559.394 17[e]	−61.6	−559.404 34	+2.33	−52.1	−50.2 ± 4

[a] Total energy, including ZPE, at the G2(F-2s) level of theory. [b] Change in E_0(G2) due to removal of F 2*s* orbital from correlation space, expressed as E_o[G2(F-2s)] − E_o(G2). [c] Comparison of G2(thaw) and G2(F-2s) methods, expressed as E_0[G2(F-2s)] − E_0[G2(thaw)]−E_0[G2(F-2s)]. [d] Calculated enthalpy of formation, at 0 K. [e] Previously quoted in ref 4. [f] Ref 31.

rather uncertain experimental values. We recommend an experimental reevaluation of the thermochemistry of the latter three species.

G. G2(F-2s) Calculations on Na(FX)$^+$. We have performed G2(F-2s) calculations upon all of the Na(FX)$^+$ stationary points and have also calculated the G2(Ne-2s) total energy for NaNe$^+$. All of these values are detailed in Table 13. If, in the absence of benchmarks for almost all of these species, we regard an ability to determine positive SCA values as an initial indication of reliability, then G2(F-2s) performs fairly well: negative values are obtained only for SCA(F) and SCA($\underline{P}$F). The determination of SCA(Ne) = 5.4 kJ mol^{-1}, within 2 kJ mol^{-1} of the experimental values,[18,19] is also encouraging.

Some interesting points of comparison are possible between individual G2(thaw) and G2(F-2s) values. Curiously, the two techniques show somewhat better agreement for SCA values of the covalent fluorides OF, F$_2$, and FCl than for the ionic fluorides LiF, NaF, BeF, and AlF, even though the G2(F-2s) treatment of the isolated covalent fluorides is quite poor. The good values for covalent fluoride SCAs in G2(F-2s) arise via a fortuitous cancellation of errors, since the G2 (and G2(F-2s)) total energy for Na$^+$ is also poor.

A more detailed relative assessment of these methods is the subject of our next section.

H. Comparison of the G2(NCCS), G2(thaw), and G2-(F-2s) Approaches. Can we decide which of G2(NCCS), G2-

TABLE 13: G2(X−2s) [X = F, Ne] Total Energies, Enthalpies of Formation, and Ion−Ligand Binding Energies for $NaFX^+$ and $NaNe^+$

species	E_0[a] (Hartrees)	ΔE_0(X-2s)[b] (mHartrees)	$\Delta H°_{f,0}$[c] (kJ mol^{-1})	SCA[d] (kJ mol^{-1})
$^2NaF^+$	−261.294 47	−36.59	669.5	−6.9
$NaFH^+$	−262.036 76	−67.83	249.4	62.0
$NaFLi^+$	−269.025 59	−4.59	42.5	206.6
$^2NaFBe^+$	−276.158 57	−54.57	354.7	78.0
$NaBF^+$	−286.210 58	−69.94	402.5	62.2
T−Na(BF)$^+$	−286.187 47	−70.41	463.2	1.5
$NaFB^+$	−286.192 73	−69.70	449.4	15.3
$^2NaCF^+$	−299.305 55	−75.64	785.3	45.6
$^2NaFC^+$	−299.292 17	−69.70	820.4	10.5
$^3NaNF^+$	−315.939 66	−75.78	806.3	20.5
$^3NaFN^+$	−315.939 35	−69.42	807.1	19.7
$^2NaOF^+$	−336.357 72	−70.49	703.0	7.6
$^2Na(FO)^+$ bent	−336.360 20	−71.02	696.5	14.2
$^2NaFO^+$	−336.359 31	−70.33	698.9	11.8
$NaFF^+$	−360.975 12	−62.55	621.3	0.3
T-Na$(F_2)^+$	−360.982 10	−61.93	603.0	18.6
$NaFNa^+$	−423.422 08	−6.33	38.2	250.9
$^2NaFMg^+$	−461.166 15	−4.00	221.2	151.1
$NaFAl^+$	−503.524 25	−30.86	214.7	102.2
$^2NaSiF^+$	550.454 57	+0.47	519.9	9.3
$^2NaFSi^+$	550.477 48	−57.66	459.7	69.5
$^3NaPF^+$	−602.273 60	+8.17	562.6	−22.0
$^3NaFP^+$	−602.303 80	−62.75	483.3	57.3
$^2Na(FS)^+$ bent	−659.098 16	−66.41	553.7	46.1
$^2NaFS^+$	−659.098 11	−66.22	553.8	46.0
$Na(FCl)^+$ bent	−721.083 61	−67.99	493.7	39.3
$NaFCl^+$	−721.083 30	−67.57	494.5	38.5
$NaNe^+$	−290.485 38	−63.34	579.7	5.4

[a] Total energy, including ZPE, at the G2(X−2s) level of theory. [b] Change in E_0(G2) due to removal of F or Ne 2*s* orbital from correlation space, expressed as E_0[G2(X−2s)] − E_0(G2). [c] Calculated enthalpy of formation, at 0 K. [d] Sodium cation affinity at 0 K. This parameter has been calculated using the G2 value for Na^+ and G2(X−2s) total energies for the ligands.

(thaw), and G2(F-2s) offers the best performance in cases where the COL assumption fails? Such an assessment is made more complicated since, of the species for which all three methods are applicable, an accurate experimental value is known only for $NaNe^+$. It is not reasonable to make judgment on the basis of one point, and so an internal comparison of all three methods against each other must be attempted. We can preface such a comparison with some pertinent observations.

(i) The inadequacy of G2(NCCS), for species exhibiting strong mixing between F 2s and Na 2p orbitals such as $NaFBe^+$, indicates that this method is not as widely applicable as the other methods.

(ii) The results of any comparison will depend upon the parameters being compared. For $NaFX^+$, we can examine the calculated enthalpies of formation or the sodium cation affinities of the corresponding fluoride FX. The enthalpies of formation obtained using G2(NCCS), G2(thaw), and G2(F-2s) are all standardized in the sense that they are calculated from atomization energies at these respective levels of theory, and the total energies of all atoms, at each of G2(NCCS), G2(thaw), and G2-(F-2s), are defined to be equal to their standard G2 values. This is not the case with sodium cation affinities. The total energies of Na^+ and of FX are, at G2(NCCS), equal to their G2 values, but the G2(thaw) total energy of Na^+ differs from G2, as does the G2(F-2s) total energy of FX. These distinctions need to be remembered in analyzing the data.

(iii) We must also decide (within reason) whether the main criterion is accuracy or speed of calculation. G2(thaw) is substantially the most CPU-intensive method explored here, with G2(MP2(thaw/MP2)) and G2(F-2s) being the cheapest methods. (It would, indeed, be possible to concoct even less expensive variants of G2(NCCS) and G2(F-2s), by analogy with the G2-(MP2) technique, but this is an issue that we do not explore further here.)

In our discussion connected with Table 9, we have observed that G2(thaw) is significantly superior to G2 theory for calculating sodium cation affinities, when the core and valence orbitals are sufficiently separated that mixing or core/valence confusion is not a problem. There is thus an expectation that G2(thaw) should also treat difficult $NaFX^+$ species reasonably well, since all of the contentious orbitals are included in the correlation space.[32] In contrast, our expectations of G2(F-2s) theory are not so high, since there are several diatomic fluorides within Table 12 for which G2(F-2s) does not perform as well as G2.

A more detailed assessment is made possible by the calculated differences in enthalpies of formation and sodium cation affinity, which we have presented in Table 14. We have calculated mean deviations (MD) and mean absolute deviations (MAD) for each pair of techniques and have also calculated adjusted values of these parameters (when difficult species are excluded from the comparison). If we examine the unadjusted MAD values for enthalpies of formation, we find that the lowest MAD (7.1 kJ mol^{-1}) is seen between the (G2(thaw) and G2(X-2s) techniques. This value is not drastically improved by exclusion of the Na^+/F_2 stationary points (which are not well treated by G2(F-2s) theory), while the MAD values for comparisons involving G2-(NCCS) are much improved by exclusion of the strongly mixed species $NaBeF^+$ and $NaFC^+$. Nevertheless, even when all difficult species are excluded, the lowest MAD is still that seen between G2(thaw) and G2(X-2s).

If we make a comparison on the basis of sodium cation affinity, we find that the lowest unadjusted MAD value is again that seen between G2(thaw) and G2(X-2s). In this case, however, exclusion of $NaFF^+$ and $Na(F_2)^+$ actually increases the MAD slightly (because of a cancellation of errors arising from the bad G2(F-2s) total energies for F_2 and for NaF_2^+), while the lowest adjusted MAD for SCA is that seen between G2(NCCS) and G2(X-2s).

Finally, if we compare mean deviations and mean absolute deviations, we find that G2(thaw) almost always yields the highest sodium cation affinities, while G2(NCCS) usually yields the lowest SCA values. How can these observations be interpreted?

In the absence of accurate literature values for the $NaFX^+$ species, the best assessment we can make is that the G2 variants between which there is the closest agreement are probably the more accurate methods. However, while such a consensus argument may be reasonable for enthalpies of formation, it may not be valid in the case of sodium cation affinities, since the G2(thaw) total energy for Na^+ is significantly different from the standard G2 value employed by both G2-(NCCS) and G2(X-2s). Thus we may infer that a survey of MAD values for the enthalpies of formation tentatively supports our expectation that G2(NCCS) is, inherently, a less reliable technique than G2(thaw) or G2(X-2s); we cannot make such a statement concerning the sodium cation affinity values, but presumably if the G2(NCCS) $\Delta H°_{f,0}$ values are regarded as being of inferior quality, the same will apply to the G2(NCCS) SCA values.

As a result of the three-way comparison embodied in Table 14, as well as the comparison between G2(thaw) and G2 sodium cation affinities in Table 9 and the G2 and G2(F-2s) enthalpies

TABLE 14: Deviations between G2(NCCS), G2(thaw), and G2(X−2s) [X = F, Ne] Values for $\Delta H^\circ_{f,0}$ and SCA

	G2(NCCS) − G2(thaw)		G2(NCCS) − G2(X−2s)		G2(thaw) − G2(X−2s)	
NaFX$^+$	Δ[ΔH°_f] (kJ mol^{-1})	ΔSCA (kJ mol^{-1})	Δ[ΔH°_f] (kJ mol^{-1})	ΔSCA (kJ mol^{-1})	Δ[ΔH°_f] (kJ mol^{-1})	ΔSCA (kJ mol^{-1})
^{2}NaF$^+$					+11.1	+2.6
NaFH$^+$	+2.6	−16.2	+8.4	−11.4	+5.8	+4.8
NaFLi$^+$					−0.2	+9.7
^{2}NaFBe$^+$	+66.5	−80.2	+67.8	−69.8	+1.3	+10.4
NaBF+	−7.3	−6.4	−2.3	+1.2	+5.0	+7.6
T-Na(BF)$^+$	−9.8	−3.9	−0.7	−0.4	+9.1	+3.5
NaFB$^+$	−6.6	−7.0	+1.7	−2.7	+8.3	+4.3
^{2}NaCF$^+$	+41.0	−54.7	+38.9	−47.1	−2.1	+7.6
^{2}NaFC$^+$	−7.0	−6.7	−4.9	−3.3	+2.1	+3.4
^{3}NaNF$^+$	+14.3	−28.1	0.0	−11.8	−14.3	+16.3
^{3}NaFN$^+$	−5.6	−8.1	−6.6	−5.1	−1.1	+3.0
^{2}NaOF$^+$	−5.2	−8.5	−13.1	−1.9	−7.9	+6.6
^{2}Na(FO)$^+$ bent	−12.7	−0.9	−16.6	+1.5	−3.9	+2.4
^{2}NaFO$^+$	−7.6	−6.0	−12.2	−2.9	−4.6	+3.1
NaFF$^+$	−8.3	−5.4	−34.8	0.0	−26.5	+5.4
T-Na(F$_2$)$^+$	−8.1	−5.6	−34.0	−0.8	−25.9	+4.8
NaFNa$^+$					+7.1	+8.2
^{2}NaFMg$^+$					+9.4	+1.5
NaFAl$^+$					+3.7	+9.4
^{2}NaSiF$^+$					+7.9	+5.1
^{2}NaFSi$^+$					+6.1	+6.8
^{3}NaPF$^+$					−11.0	+22.3
^{3}NaFP$^+$					+4.8	+6.5
^{2}Na(FS)$^+$ bent					+3.0	+5.7
^{2}NaFS$^+$					+2.9	+5.9
Na(FCl)$^+$ bent					+2.2	−8.2
NaFCl$^+$					+1.6	−7.6
NaNe$^+$	−11.0	−2.6	−1.6	+1.7	+9.4	+4.3
MD[a]	+2.3	−16.0	−0.7	−10.2	+0.1	+5.6
MAD[b]	14.2	16.0	16.2	10.8	7.1	6.7
MD (adj)[a,c]	−5.6	−8.1	−4.4	−3.2	+2.1	+5.6
MAD (adj)[b,c]	8.2	8.1	6.2	4.0	5.6	6.8

[a] Mean deviation of the specified parameter for the two computational procedures indicated. [b] Mean absolute deviation of the specified parameter for the two computational procedures indicated. [c] Adjusted deviation. For comparisons involving G2(NCCS), the adjusted value excludes NaFBe$^+$ and NaCF$^+$. For comparisons involving G2(X-2s), NaFF$^+$ and T-Na(F$_2$)$^+$ have been excluded.

of formation of diatomic fluorides in Table 12, we can conclude that G2(thaw) is probably the most accurate technique to employ in cases where problems of core/valence orbital overlap or mixing prevent the satisfactory execution of standard G2 calculations. The G2(thaw) method is certainly the most robust of the three different correlation strategies investigated here (by which we mean that shortcomings are evident in G2(NCCS), if Na/F orbital mixing is severe; or in G2(F-2s), if the NaFX$^+$ ion contains an essentially purely covalent F−X bond, as does F$_2$). It is rather unfortunate that G2(thaw) is also the most computationally intensive method. However, as a result of our comparisons between different thawed methods, we can also suggest that G2(MP2(thaw/MP2)) is a good substitute for G2-(thaw) when an inexpensive method is especially desired.

I. Structural and Bonding Trends Evident in Na(FX)$^+$. Having assessed the various computational techniques, we are now finally in a position to discuss the chemical aspects of NaFX$^+$ structure, bonding, and isomerism revealed by these calculations. We will base this discussion upon the G2(thaw) values contained in Table 10.

There are several trends visible in the fluoride SCA values. Firstly, it is apparent that the SCA(FX) value is uniformly higher, by at least 20 kJ mol^{-1}, for second-row fluorides than for the corresponding first-row fluorides. This is in direct contrast to the observation[12,33,34] that the calculated sodium cation affinities of simple hydrides are uniformly higher for the first-row hydrides (NH$_3$, H$_2$O, HF) than for their second-row counterparts (PH$_3$, H$_2$S, HCl); the trend in hydride SCAs is matched by a similar trend in lithium cation affinities of hydrides.[33−38] The qualitative difference in bonding trends for first- and second-row hydrides and fluorides is nevertheless consistent with the expectation that the Na$^+$/ligand bond is largely electrostatic in all of these species. The electrostatic interaction between Na$^+$ and a ligand involves both an ion/dipole component (dependent upon the dipole moment, μ, of the ligand) and an ion/induced dipole component (which depends upon the ligand's polarizability, α). For the hydrides, the first-row compounds NH$_3$, H$_2$O, and HF possess substantially greater dipole moments (1.47, 1.85, and 1.82 D, respectively) than do their second-row counterparts (0.58, 0 97, and 1.08 D for PH$_3$, H$_2$S, and HCl), ensuring that the ion/dipole component of the electrostatic attraction with Na$^+$ is larger for the first-row species than for the second-row counterparts. Comparison with calculated dipole moments for the diatomic fluorides reveals that the second-row fluorides possess significantly larger dipole moments than the first-row fluorides (for example, at the MP2(full)/6-31G* level of theory, PF, SF, and ClF have μ = 1.449, 1.507, and 1.328 D, respectively; the corresponding values for NF, OF, and F$_2$ are μ = 0.340, 0.345, and 0.0 D). This argument is somewhat simplistic, neglecting as it does the effect of ligand polarizability upon the electrostatic interaction; however, it does seem to satisfactorily account for the observation that, in contrast to the hydrides, the second-row fluorides are seen to have larger sodium cation affinities than are the first-row fluorides.

A second trend is that there is a consistent decrease in SCA for FX in a progression of the atom X from group I to group VII; this trend is broken only for OF → F$_2$ (perhaps reflecting the existence of a bridged structure for Na(FF)$^+$, but not for Na(FO)$^+$). Again, this appears to be largely a result of the trend in ligand dipole moments; the greatest degree of charge separation is apparent in the metallic fluorides LiF, NaF, and MgF, and it is reasonable to expect that the SCA(FX) values for these species will be appreciably higher than the SCAs of covalent fluorides such as OF, F_2, and ClF.

Thirdly, the results in Table 10 verify that the only diatomic fluorides FX possessing a higher SCA at the X atom than at fluorine are BF, CF, and NF. A preference for Na^+ attachment at any atom other than fluorine is somewhat counterintuitive, since F is the most electronegative atom and might therefore be expected to exhibit the strongest electrostatic interaction with Na^+. We surmise that the bonding in $NaXF^+$ (X = B, C, N) is partially covalent; these X atoms are clearly not valence-satisfied in neutral FX, and association with Na^+ may assist toward satisfaction of their valence requirements.

With further reference to the preferred orientation of FX relative to Na^+, it is notable that bent forms are virtually absent from the second-row fluoride adducts $Na(FX)^+$, and that for these species also the $NaXF^+$ structure is uniformly disfavored relative to the $NaFX^+$ geometry. This can be accounted for on the basis of the much larger atomic radius of second-row atoms than of their first-row analogues. For example, the optimum $Na^+{-}SiF$ distance (in the transition state for SiF rotation relative to Na^+) is about 0.9 Å greater than the optimum $Na^+{-}FSi$ distance, whereas the difference between $r(Na^+{-}CF)$ and $r(Na^+{-}FC)$ is only 0.24 A; the large $Na^+{-}SiF$ separation ensures that the electrostatic interaction between the metal ion and the ligand is comparatively weak. Furthermore, the comparatively high dipole moment of the second-row fluorides reflects the greater tendency for negative charge localization upon F in these species, ensuring that linear $NaFX^+$ (or a slightly bent form thereof) is the preferred geometry for all second-row fluorides.

J. General Comments. We should finally stress that the species $NaFX^+$ are not poorly treated by G2 theory alone. The problems evident here are a consequence of the implementation of the frozen-core approximation in quantum chemical computational suites, and the various strategies that we have employed to obviate these problems are equally applicable to complete-basis-set calculations such as CBS-Q[39] or to any high-level, single-point frozen-core calculation. Indeed, it is worth noting that Sannigrahi, Nandi, and Schleyer[40] have previously reported a negative sodium cation affinity for HF on the basis of a frozen-core calculation, although in their study the discrepancy was attributed to differences in the intramonomer and intermonomer correlation energy and not to problems of core/valence orbital assignment.

The assignment of orbitals is problematic for ions containing sodium and either F or Ne. These represent only a minute subset of species comprising only first- or second-row atoms, and at present we are not aware of any other classes of first- and second-row compounds that may also exhibit a similar problem. The scope for such difficulties is very much enhanced, however, if we begin to consider compounds containing third-row main-group elements also, and several studies concerning the extension of G2 to K, Ca, and Ga−Kr[13,41,42] have touched upon the necessity for caution in describing an appropriate correlation space in instances where significantly electropositive and electronegative elements are combined. The present work appears to support the view[13,41,42] that the most appropriate course of action for such compounds is to expand the correlation space to include all possible contentious atomic orbitals.

IV. Conclusion

Perhaps alone among species constructed from the elements H to Ar, molecular cations containing Na and either F or Ne can feature a reversal of the energies of some core and valence orbitals, such that the molecular orbitals most closely related to the atomic sodium 2p orbitals lie higher in energy than the orbitals featuring the greatest amount of F or Ne 2s character. This phenomenon effectively prevents the calculation of meaningful enthalpies of formation using a frozen-core technique such as the G2 procedure, and alternative strategies must be implemented to treat such compounds appropriately. Of several strategies employed in the present work to obtain corrected G2-like total energies, enthalpies of formation, and sodium cation affinities, we have found that the most successful approach is to expand the correlation space to include all sodium 2s and 2p orbitals as well as the normal valence orbitals of other elements (and some core orbitals of the other electropositive atoms Li, Be, Mg, and Al) in a G2(thaw) calculation. While such an approach can be computationally intensive, other, less expensive techniques such as G2(MP2(thaw/MP2)) also appear to yield good results, while (somewhat surprisingly) excluding the F or Ne 2s orbital from the correlation space is also often quite successful. Difficulties in defining an appropriate correlation space are expected to be much more commonplace in compounds containing third-row or larger atoms than in compounds comprising only first- and second-row atoms.

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