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A Comparison of Methods To Predict Solid Phase Heats of Formation of Molecular Energetic Salts

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In this study a variety of methods were used to compute the energies for lattice enthalpies and gas phase heats of formation of the ionic constituents used in Born−Fajans−Haber cycles to produce solid phase heats of formation of molecular ionic energetic crystals. Several quantum mechanically based or empirical approaches to calculate either the heat of formation of the ionic constituents in the gas phase ($\Delta H^\circ_{f(g)}$) or the lattice enthalpy ($\Delta H^\circ_{Lattice}$) were evaluated. Solid phase heats of formation calculated from combinations of $\Delta H^\circ_{f(g)}$ and $\Delta H^\circ_{Lattice}$ determined through various approaches are compared with experimental values for a series of molecular energetic salts with 1:1, 2:1 and 2:2 charge ratios. Recommendations for combinations of $\Delta H^\circ_{f(g)}$ and $\Delta H^\circ_{Lattice}$ to produce best agreement with experiment are given, along with suggestions for improvements of the methods.

1. Introduction

For decades, special attention has been given to the prediction of properties that are used to provide an initial assessment of the potential performance of an energetic material in a gun or warhead. Quantum mechanically based approaches to predict the heat of formation, a key property, have been developed for weakly bound neutral CHNO energetic crystals.[1] One of these approaches combines quantum mechanical predictions of the gas phase heats of formation with quantum mechanically based estimates of the heats of sublimation to produce the solid phase heat of formation.[2] This particular method, however, is completely unsuited for ionic materials since the intermolecular binding interactions of ionic crystals differ substantially from those of a neutral molecular crystal. The dominant binding forces in an ionic system are typically substantially larger than the main binding forces in molecular crystals (van der Waals). Therefore, a different procedure based on the Born−Fajans−Haber cycle[3] is appropriate to determine the solid state heat of formation for ionic crystals.

The Born−Fajans−Haber cycle allows the use of information which can be calculated (i.e., the gas phase heats of formation of the ions and lattice enthalpies) to predict that which cannot be calculated directly (the solid phase heat of formation, [$\Delta H^\circ_{f(s)}$]). Any series of reactions that will lead to the formation of the ionic crystal from its constituent ions (in the gas phase) can be used to create a Born−Fajans−Haber cycle. A simple Born−Fajans−Haber cycle is

$$M_{(g)} + X_{(g)} \xrightarrow{\text{IE, EA}} M^+_{(g)} + X^-_{(g)} \xrightarrow{\Delta H^\circ_{\text{Lattice}}} M^+X^-_{\text{solid}} \qquad (1)$$

where IE and EA denote the ionization energy and electron affinity of the cation and anion, respectively, and $\Delta H^\circ_{Lattice}$ denotes the lattice enthalpy. While the two components used to determine the $\Delta H^\circ_{f(s)}$ (i.e., the heat of formation of the ionic constituents in the gas phase [$\Delta H^\circ_{f(g)}$] and the lattice enthalpy) can be calculated, in most instances the individual components cannot be measured directly. Rather, the only experimental information usually available is the solid phase heat of formation. In such cases, any error in the predicted solid phase heat of formation cannot be unequivocally attributed to the $\Delta H^\circ_{Lattice}$ and/or $\Delta H^\circ_{f(g)}$.

The Born−Fajans−Haber cycle approach has been utilized extensively in estimating solid phase heats of formation for energetic molecular salts, using information generated through numerous theoretical approaches.[4−9] Two of the more recent studies[8,9] utilized computational approaches in which the components of the thermochemical cycle were ascertained in a similar fashion: the gas phase heats of formation of the ions were determined from isodesmic reactions schemes and the lattice enthalpies were calculated using lattice potential energies derived from a widely used quantitative structure property relationship (QSPR) approach. In the latter approach, the lattice potential energy $U_{pot}(M_p^+X_q^-)$ is a parametrized function of the inverse cube root of the formula unit volume of an $M_p^+X_q^-$ ionic crystal as proposed by Jenkins et al. (hereafter referred to as the Jenkins model).[10−12] As noted by Gutowski et al.,[9] predictions of lattice energies for 1:1 salts for a range of nitrogen- and carbon-containing cations using the Jenkins model[10−12] had significant errors when compared to experimental values. Gutowski et al.[9] subsequently reparametrized the function used by Jenkins to predict lattice energies for 1:1 salts and substantially reduced the error. The new model was then used to estimate lattice enthalpies for subsequent calculation of solid phase heats of formation of imidazolium, 1,2,4-triazolium-, and tetrazolium-based energetic salts. Unfortunately, the predicted heats of formation were in substantial disagreement with the experimental values for most of the salts. It is not clear how much of the errors are due to (1) the lattice energy estimates; (2) the calculated energies resulting from the isodesmic reaction schemes or (3) experimental error.

Such disparities between predictions and experiment call for an evaluation of the methodologies used to predict heats of formation of energetic molecular salts. Toward this end, we present a quantum mechanically based procedure using Born−Fajans−Haber cycles to predict the heats of formation of ionic energetic materials in the solid phase. Because the only available experimental thermodynamic information is the solid phase heats of formation for the systems studied here, we cannot determine the error in the individual contributions to the solid phase of formation. We will, however, first predict both $\Delta H^\circ_{Lattice}$ and $\Delta H^\circ_{f(g)}$ using a variety of different theoretical approaches, and then compare solid phase heats of formation generated

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through the various combinations of predicted $\Delta H^{\circ}_{\mathrm{Lattice}}$ and $\Delta H^{\circ}_{\mathrm{f(g)}}$ with experimental values. It is hoped that this will reveal an acceptably accurate approach for prediction of the solid phase heats of formation of energetic molecular salts.

2. Theoretical Approaches

2a. Calculation of $\Delta H^{\circ}_{\mathrm{f(g)}}$. There are a multitude of different options for computing the gas phase heats of formation of the ions, ranging from isodesmic reaction schemes[13] to atom/group additivity methods[14,15] to Gaussian-X procedures.[16] Atom/group additivity methods are empirical and often accurately predict $\Delta H^{\circ}_{\mathrm{f(g)}}$ for compounds that are outside of their training sets but within the same chemical family. Unfortunately, accuracy cannot be guaranteed in predicting heats of formation for compound types not included in the parametrization. $\Delta H^{\circ}_{\mathrm{f(g)}}$ calculated using isodesmic reactions can be in excellent agreement with experiment,[13] but error can be introduced for each required quantum mechanical evaluation in the reaction scheme. For example, the error will depend on which reaction scheme is chosen, to the extent that different possible reactions will yield different results.[17] Also, a multiple-step reaction scheme may be required to generate the ΔH°f(g) for the constituent ions, with each step possibly introducing further error. Error using reaction schemes can be reduced by the use of reliable experimental information. Unfortunately, such information is often not available (as in the systems studied here). In order to avoid the issues associated with reaction schemes and to allow for a purely predictive methodology without reliance on experiment, we have chosen to forego the use of isodesmic reactions. Instead, we will compute the gas phase heats of formation solely from the molecular ionic information through two different approaches: group additivity, using group equivalents parametrized to neutral CHNO systems,[2] and G3 methods.

In a previous work,[7] the gas phase heats of formation for the ions required for the Born−Fajans−Haber cycle were determined using

$$\Delta H^{\circ}_{\mathrm{f(g)M^+}} = \Delta H^{\circ}_{\mathrm{f(g)M}} + \mathrm{IE_M} \tag{2}$$

$$\Delta H^{\circ}_{\mathrm{f(g)X^-}} = \Delta H^{\circ}_{\mathrm{f(g)X}} + \mathrm{EA_X} \tag{3}$$

where we computed the $\Delta H^{\circ}_{\mathrm{f(g)M}}$, $\Delta H^{\circ}_{\mathrm{f(g)X}}$, IE and EA using a modified form of G3(MP2)//B3LYP (G3MP2B3) theory[18,19] (denoted here as modG3). The modified form of G3 uses a B3LYP/6-31+G** optimized structure rather than a B3LYP/6-31G* structure. This was necessary because the optimized B3LYP/6-31G* structure of the neutral form of the ion was either a constitutional isomer of the parent ions or the neutral form did not exist: it dissociated into fragments upon optimization, indicating that the neutral form of the ion is not a minimum on the B3LYP/6-31G* potential energy surface. In an attempt to overcome this issue, we increased the basis set to the 6-31+G** basis set, and in most (but not all) cases were able to converge to neutral molecules which had the same connectivity as the ionic moieties for most of the systems. The remainder of the G3MP2B3 method was unchanged. We did not reparametrize the higher-level correction terms used in G3 theory, assuming that this would have a minor effect on the final results. The structures of the neutral forms of the ions often significantly differed from those of the ionic forms; for example, several exhibited puckered configurations whereas the corresponding ion was planar. The use of vertical ionization energies in such cases is erroneous; structural relaxation must be considered. Since all of these complications potentially introduce error, we decided to use G3MP2B3 theory[18,19] on the ions without involving computations on the neutral moieties in order to eliminate possible errors in the ionization energies, electron affinities, strain energies, and convergence issues. The validity of the direct application of G3MP2B3 theory to the ions for calculating their gas phase heats of formation will be examined by comparing with the modG3 results [eqs 2 and 3]. Also, inspired by the work of Beaucamp et al.,[15] we applied a previously developed group additivity method (denoted hereafter as Byrd−Rice) to predict gas phase heats of formation for CHNO neutral molecules[2] on the ions, and have compared those results with those generated using G3 methods. Additionally, the G3MP2B3 and Byrd−Rice theories are directly applied to another set of ions for which gas phase heats of formation of the ions were determined from isodesmic reactions schemes.[9]

2b. Calculation of $\Delta H^{\circ}_{\mathrm{Lattice}}$. The lattice enthalpy can be determined from the lattice potential energy (U_{pot}), the measure of the cohesive energy of the ionic crystal:[20]

$$\Delta H^{\circ}_{\mathrm{Lattice}} = U_{\mathrm{pot}}(\mathrm{M}_p^+\mathrm{X}_q^-) + [p(n_{\mathrm{M}^+}/2 - 2) + q(n_{\mathrm{X}^-}/2 - 2)]RT \tag{4}$$

where the values of n_{M^+} and n_{X^-} are dependent on whether the ions are monatomic, linear polyatomic, or nonlinear polyatomic species. For the calculations in this paper, T is taken to be 298 K. There are also several options available for the calculation of the lattice potential energy U_{pot}. The most direct approach is the summation of all interactions between atoms within the crystal, i.e. through an extended lattice summation. This requires a reasonable description of the interatomic interactions and knowledge of all positions of the atoms within the crystal. For an ionic system, the most common form of the interactions is a function composed of van der Waals plus Coulombic terms, with the latter approximated by partial point charges centered on the atomic nuclei interacting through a Coulomb potential. These point charges can be approximated from quantum mechanically derived charges of the atoms in the isolated molecules.

However, the lattice positions of the atoms are not always known, thus rendering such an approach to calculating lattice energies impossible. In lieu of experimental information, however, theoretical methods can be used for *a priori* prediction of crystal structures, but only recently have these become viable tools for accurate determination of crystal structures.[21] Therefore, for cases in which experimental or theoretically generated crystal structures are not available, QSPR approaches have been developed to determine U_{pot}.[10−12,15,22] As indicated earlier, the Jenkins model[10−12] is a widely used QSPR model for evaluating lattice energies of molecular ionic energetic materials (many of which contain large molecular cations).[4−9] This model assumes that the lattice potential energy of the ionic system has an inverse cube root dependence on the formula unit volume. However, it is not established whether the Jenkins model[10−12] is accurate for the systems under study here, and even has been suggested to be "insufficiently accurate to be used for all 1:1 salts...."[9] The ionic crystals used in the original parametrization of the Jenkins model[10−12] for salts with charge ratios of 1:1, 2:1 and 1:2 were composed of alkali metal and alkaline earth cations (Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba) coupled with larger anions. The information used in the parametrization of the model for salts with charge ratios of 2:2 were oxides, sulfates and carbonates of the divalent metallic elements. The data used in the fitting were derived either from thermochemical cycles using experimental information or from lattice summation calculations using the known crystal structures.[23] The remaining QSPR models we shall examine have only been parametrized for a limited set of salts (e.g., ammonium or nitrate salts).[15,22] The QSPR for the ammonium salts, developed by Politzer and Murray,[22] established a correlation between lattice energies with features of quantum mechanically calculated electrostatic potentials on isosurfaces of electron densities of isolated molecules. Beaucamp et al. established a correlation between self-consistent charge density functional tight-binding (SCC-DFTB)[24] derived Mulliken charges to generate lattice energies for nitrate salts.[15] While we cannot directly compare the predicted lattice energies with experimental values, we hope to determine which of these methods, when combined with the gas phase heats of formation, yields accurate solid phase heats of formation of molecular ionic energetic materials.

2c. Calculation of $\Delta H^{\circ}_{f(s)}$. In our earlier study,[7] we calculated the components required to predict the solid phase heats of formation of three tetrazolium salts using the Jenkins method[10−12] and modG3 as described heretofore. Also, other theoretical predictions of $\Delta H^{\circ}_{f(s)}$ were available for comparison;[25] in these, isodesmic reaction schemes and G2 theory were used to calculate the gas phase heats of formation of the ions. The lattice enthalpies for both sets of predictions were calculated using the Jenkins model[10−12] and the experimentally determined formula unit volume. The two theoretical predictions[7,25] were within 6 kcal/mol of one another, while the differences with experiment were between 30−50 kcal/mol.

This limited comparison, in which the two theoretical methods produce results that are in agreement but have the same differences from experimental values suggested that error might be due to the predicted lattice enthalpy. It further suggested that the modG3 approach is reasonable for prediction of gas phase heats of formation of ions. However, conclusions cannot be reached using only three data points. Thus, the purpose of this paper is to expand the data set and test various approaches for evaluating the solid phase heats of formation for molecular ionic energetic materials by comparison with available experimental data.

In this paper, we will compare predicted gas phase heats of formation of ions using modG3 (as described heretofore) and both group additivity and G3MP2B3 applied to the ions without neutral precursors. We will also calculate lattice potential energies using extended lattice summations (assuming van der Waals and Coulombic terms) for molecular ionic crystals for which crystallographic information is available and compare these with results generated from QSPR methods.[10−12,15,22] The extended lattice summations will use a pair-additive interatomic interaction potential composed of van der Waals and Coulomb potentials. Three different charge models (CHELPG,[26] RESP,[27] and Mulliken[28]) will be used in the Coulomb potential, and the van der Waals model is one developed for CHNO molecular crystals.[29]

Organization of the remainder of the paper is as follows: Section 3 describes the details of the calculations used in this study. Results and Discussion will be presented in section 4, and concluding remarks will be given in section 5.

3. Details of the Calculations

A set of 63 crystalline ionic energetic materials for which crystallographic and/or heats of formation are available were studied; experimental information is given in Figure 1S in the Supporting Information.

The group additivity method to calculate gas phase heats of formation was used as described in ref 2, although the method was originally developed for and applied to neutral CHNO energetic molecules. No reparametrization or modification of the method was done in order to adapt it to ionic systems.

The popular G3 method, specifically the G3MP2B3 approach, was applied directly to the ionic species to predict their gas phase heats of formation. The overall procedure involves multiple calculations at the B3LYP, MP2, and QCISD(T) levels. The G3MP2B3 method also attempts to correct for basis set size effects, zero point energy and includes a general empirical correction. We compared those results with results calculated using a modified version of the G3MP2B3 method, denoted modG3 as described heretofore.

We calculated formula unit volumes required by the Jenkins method[10−12] to predict lattice enthalpies. This choice is predicated on our goal of developing a purely predictive capability for generating solid phase heats of formation. The formula unit volume is the sum of the volumes of the individual ions contained in the formula unit and correspond to the volume within the 0.001 electron/bohr^3 isosurface of electron density of an isolated molecule calculated at the B3LYP/6-31G** level.[30] We have also scaled the computed formula unit volumes to correct for number of hydrogens, as determined in ref 30, where the corrected volumes are

$$V_{\text{corrected,Opt}} = V_{\text{uncorrected,Opt}} - \left[0.6763 + 0.9418\left(\sum_{\text{formula unit}} H\right)\right] \quad (5)$$

When applying the Beaucamp et al. QSPR method,[15] we did not employ the SCC-DFTB[24] model in order to generate the Mulliken charges. Rather, we used the Mulliken charges determined for the optimized structure of an isolated ion at the B3LYP/6-31G** level. The Politzer and Murray QSPR for generating lattice energies for NH_4^+ compounds was applied exactly as prescribed in ref 22.

Partial atomic charges were required for the Coulombic potential used in the extended lattice summation calculations; these were derived through quantum mechanical calculations for the individual ions at their experimental structure using three different charge models (CHELPG,[26] RESP,[27] and Mulliken[28]) and the B3LYP/6-31G** level of theory. The interatomic interactions for CHNO molecular crystals were used to describe the van der Waals interactions.[29]

All quantum mechanical calculations were performed using the Gaussian 03 suite of quantum mechanical software;[31] default settings were used in all calculations. The extended lattice summations were calculated using the DL_POLY Version 2 suite of molecular dynamics simulation software.[32] The lattice potential energies were calculated using supercells composed of blocks of unit cells, with the contents arranged in the experimental configuration. The sizes of the supercells were selected to ensure that the widths between crystal faces were at least twice the interaction potential cutoff distance (12.0 Å). Coulombic interactions were handled using Ewald summations.

4. Results and Discussion

We begin with a comparison of the methods to calculate gas phase heats of formation of the ions with G3MP2B3 applied directly to the ions and modG3 to the neutral forms of the ions plus either the ionization energy or electron affinity, as appropriate. Comparison of the two methods of calculating the gas phase heats of formation for twenty-five (25) ions is illustrated in Figure 1, and chemical structures and identities of the ions are given in Figure 2S in the Supporting Information. The heats of formation calculated applying G3MP2B3 directly on the ions are on average 0.17% higher in energy (0.07 kcal/mol) than those of the neutral moieties and their IEs or EAs determined using modG3. The corresponding root-mean-square

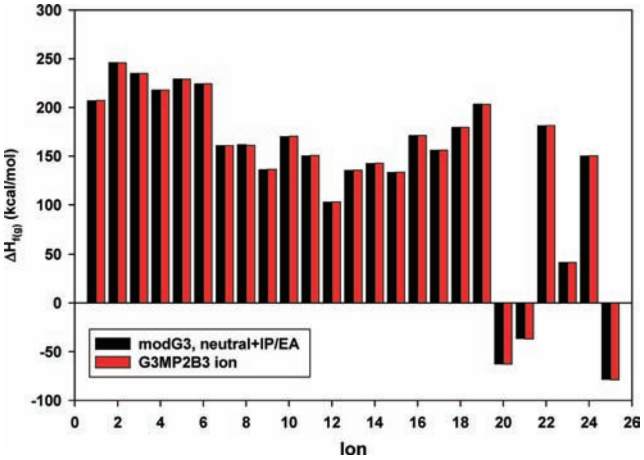

Figure 1. Comparison of gas phase heats of formation of molecular ions calculated using modG3 applied to neutral forms of the ions plus corresponding IA or EA with G3MP2B3 applied directly to the ions. Ordering of the molecular ions in this figure is the same as that in Figure 2S in the Supporting Information.

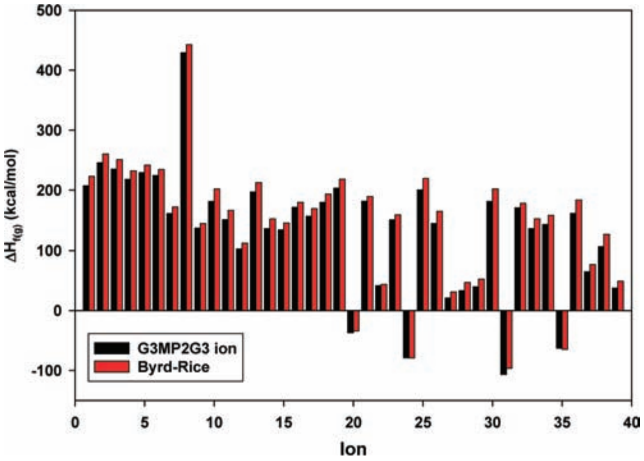

Figure 2. Comparison of gas phase heats of formation of molecular ions calculated using G3MP2G3 with the group equivalent method of Byrd−Rice (ref 2) applied directly to the ions. Ordering of the molecular ions in this figure is the same as that in Figure 3S in the Supporting Information.

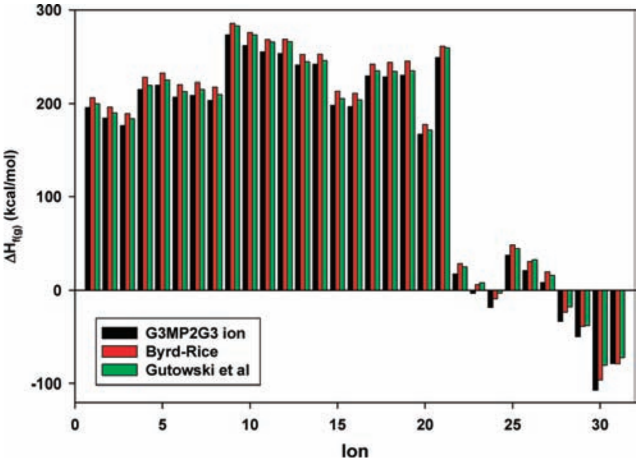

Figure 3. Comparison of gas phase heats of formation of thirty-one molecular ions given in ref 9 calculated using G3MP2G3 or the group equivalent method of Byrd−Rice (ref 2) applied directly to the ions and values calculated by Gutowski et al. (ref 9) using isodesmic reaction schemes.

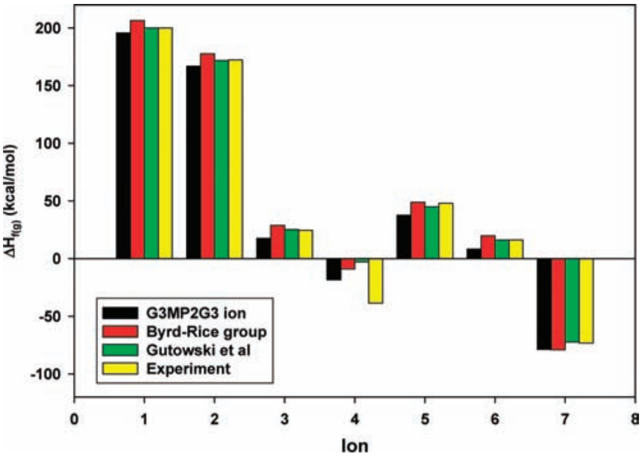

Figure 4. Comparison with experiment of gas phase heats of formation of seven molecular ions given in ref 9 calculated using G3MP2G3 or the group equivalent method of Byrd−Rice (ref. [2]) applied directly to the ions and values calculated by Gutowski et al. (ref 9) using isodesmic reaction schemes.

(rms) difference is 0.31 kcal/mol, and the maximum difference is −0.71 kcal/mol. Since results using the two methods are in excellent agreement, and the direct evaluation method always yields a converged solution (as opposed to modG3) and requires less user and computational time, we will eliminate the use of modG3 in determining gas phase heats of formation of ions. We next predicted gas phase heats of formation of a larger set of ions by direct application of a quantum mechanically based group-additivity procedure[2] previously developed for CHNO neutral molecules; the results are provided for comparison with the G3MP2B3 results in Figure 2. With one exception, the results from the group additivity method are higher in energy than those of the G3MP2B3 results; rms deviation of the Byrd−Rice results from G3MP2B3 results is 13.6 kcal/mol. Finally, we compare the G3MP2B3 and Byrd−Rice methods with results predicted using isodesmic reaction schemes and the MP2/CBS level for thirty-one ions given in ref 9 (Figure 3); experimental values for seven of these ions are also available for comparison (Figure 4). As evident in Figure 3, the G3MP2B3 heats of formation are consistently lower than the Gutowski et al. predictions by an average 8.5 kcal/mol; rms deviation from Gutowski predictions is 9.7 kcal/mol. The Byrd−Rice values are, on average, higher than the Gutowski et al. predictions with an unsigned average of 5.9 kcal/mol; the rms error is 6.7 kcal/mol. Figure 4 shows that with one exception (compound XXIV), the Gutowski et al. predictions are in closer agreement with experiment than the other methods for this small set of ions. A statistical analysis of the results (excluding compound XXIV), the unsigned average and rms deviation of the Gutowski predictions from experiment are 0.9 and 1.4 kcal/mol respectively. G3MP2B3 unsigned and rms deviations are 6.7 and 7.0 kcal/mol respectively. Byrd−Rice bridges the error between the two methods with an unsigned average and rms errors of 4.3 and 4.7 kcal/mol. However, it is unreasonable to make conclusions using a statistical analysis for such a small sample set.

Turning to the determination of the $\Delta H^{\circ}_{\text{Lattice}}$ we begin by examining the differences in methods to calculate the lattice potential energy U_{pot}. Lattice potential energies for sixty-three (63) systems for which crystallographic information is available were calculated with the Jenkins model[11,12] and theoretical formula unit volumes[30] or extended lattice sums using three different Coulombic interactions (CHELPG, RESP, and Mulliken). Identities of the crystals, theoretical unit volumes, and corresponding lattice energies are given in Table 1S in the Supporting Information.

TABLE 1: Mean, Unsigned Mean and rms Differences of Predicted Lattice Energies from CHELPG Values (kcal/mol)

	model					
	RESP	Mulliken	Jenkins	Gutowski[a]	Beaucamp[a]	Politzer[b]
mean	−1.02	11.31	19.31	−5.36	11.06	5.91
unsigned mean	1.07	11.62	22.25	8.34	12.73	8.44
rms	1.65	14.78	27.06	10.64	16.70	10.76

[a] Applied only to 1:1 salts. [b] Applied only to ammonium salts.

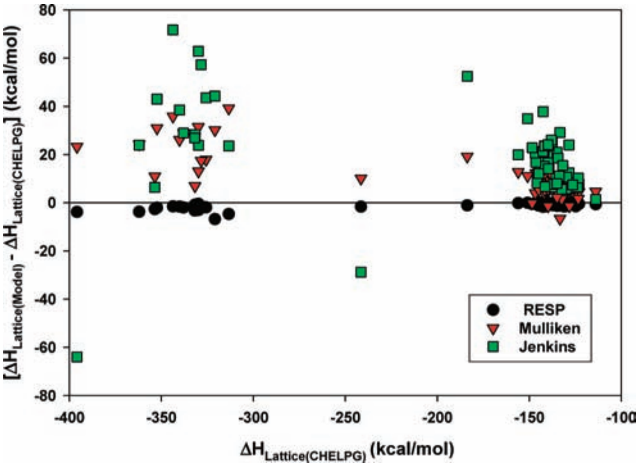

Figure 5. Comparison of differences in lattice potential energies calculated using extended lattice summations and different charge models relative to the CHELPG charge model results.

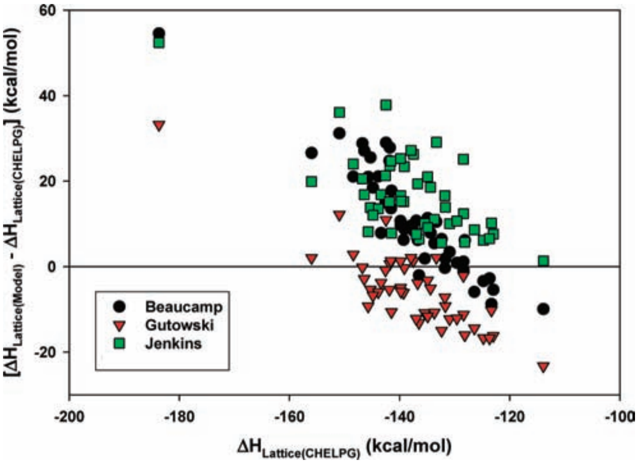

Figure 6. Comparison of differences in lattice potential energies calculated using the Jenkins, Gutowski and Beaucamp QSPR models relative to the CHELP charge model results.

The lattice energies determined from lattice summations using the CHELPG charges are used as the point of comparison among the methods that were applied to all 63 systems. The mean, unsigned mean and rms error of RESP, Mulliken, and Jenkins lattice energies relative to CHELPG are given in Table 1, while the energy differences are shown in Figure 5. As readily observed in Figure 5, the lattice energies fall into two distinct groups, with the more negative lattice energies corresponding to salts with 2:1/2:2 charge ratios; the remainder have 1:1 charge ratios. The value at −240 kcal/mol corresponds to a salt with a 2:1 charge ratio. As evident in Figure 5, RESP derived lattice energies are almost identical to CHELPG values, with a rms of less than 2 kcal/mol and a maximum deviation of ∼−7 kcal/mol. The Jenkins values differ significantly from the CHELPG lattice energies with an unsigned mean of 22 kcal/mol, a rms of 27 kcal/mol and a maximum deviation of 72 kcal/mol. For all but two systems, the Jenkins values are higher in energy than the CHELPG values. Also, for all but four systems, the Mulliken predicted lattice energies are also higher than the CHELPG values; with a rms error of 15 kcal/mol and a maximum deviation of 39 kcal/mol.

We have also applied a reparametrized version of the Jenkins model, developed by Gutowski et al., to the set of 1:1 salts within the set of 63 systems. [9] The Gutowski application recommends use of experimental formula unit volumes where available; however, as we desire a completely predictive tool for generating solid phase heats of formation, this assumes that an *a priori* knowledge of the crystal structure (i.e., volumes) is unknown. Therefore, we have applied the Gutowski model to the 1:1 salts within the 63 systems using theoretical formula unit volumes as defined in eq 5. The Beaucamp et al. QSPR model[15] was also applied to all 1:1 salts within the 63 systems. Although this model had been parametrized to nitrate salts, it can be easily generalized due to its dependence on atom-centered partial charges. The assumptions inherent in this model preclude its use for 2:1 or 2:2 salts. Differences in the Jenkins, Gutowski and Beaucamp models to calculate the lattice potential energies U_{pot} relative to CHELPG values are shown in Figure 6 for 1:1 salts. Beaucamp has unsigned and rms errors of 12.7 and 16.7 kcal/mol; Gutowski has unsigned and rms errors of 8.3 and 10.7; and Jenkins has unsigned and rms errors of 16.7 and 19.3, clearly showing that the refitted Gutowski model more closely agrees with the CHELP model. Maximum deviations for the Jenkins, Gutowski and Beaucamp predictions from CHELPG values are 52.4, 33.2, 54.6 kcal/mol, respectively.

We caution the reader not to attribute too much significance to the loosely linear dependence of the lattice energy differences of the three methods relative to CHELPG values that are apparent in Figure 6, since this is a difference plot with an arbitrarily chosen reference (the CHELPG results). Insight into these apparent correlations can be gained upon examining the dependencies of the lattice energies on formula unit volumes as illustrated in Figure 7. Examination of the CHELPG lattice energies with increasing formula unit volume show a weakly positive correlation. The Jenkins and Gutowski models have an inverse cube root volume dependence, thus they also have a positive correlation. Due to the dearth of experimental lattice potential energies, the inherent assumption of size dependencies with lattice energies for these two QSPR models cannot be accurately assessed. However, the Gutowski model dependence on size is not as strong as that of the original Jenkins model. Additionally, direct comparison of the Gutowski lattice potential energies with the CHELPG values show better agreement at larger formula unit sizes, clearly indicating that the Jenkins model, originally parametrized using salts with alkali metal and alkaline earth (atomic) cations, is not an adequate description for ions containing large, diffuse molecular units such as those considered here and in Gutowski et al.[9] The results for the 1:1 salts indicate that a reparametrization of the Jenkins model for salts with 1:2, 2:1 and 2:2 charge ratios should be considered. We note that such a reparametrization would require reliable experimental or theoretically generated information. The Beau-

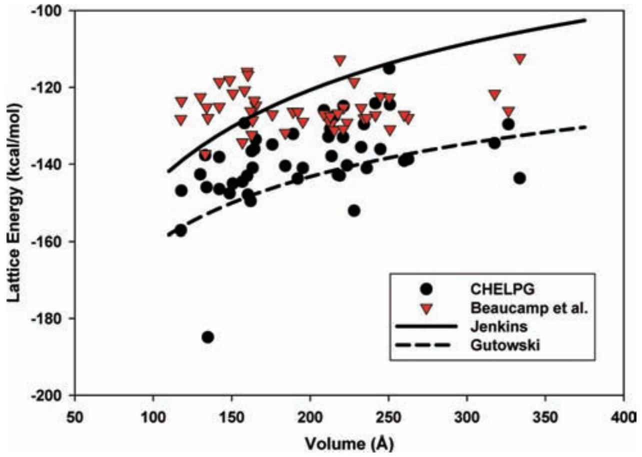

Figure 7. Comparison of lattice energies of 1:1 salts as a function of formula unit volume using the CHELP charge model/extended lattice summation approach, and Beaucamp, Jenkins and Gutowski models. The CHELPG and Beaucamp results correspond to the 1:1 molecular systems identified in Table 5S in the Supporting Information; the lines denoting the Jenkins and Gutowski results were generated using the functional forms for the 1:1 salts, with specific values given in Table 5S in the Supporting Information.

TABLE 2: Solid Phase Heats of Formation Predicted Using Various Methods To Calculate Component $\Delta H^\circ_{f(g)}$ and $\Delta H^\circ_{Lattice}$

theoretical method			
$\Delta H^\circ_{f(g)}$	$\Delta H^\circ_{Lattice}$	unsigned mean error (kcal/mol)	rms error (kcal/mol)
1:1, 2:1, 2:2 Salts			
G3MP2B3	CHELPG	22.8	31.2
G3MP2B3	Mulliken	26.6	32.7
G3MP2B3	Jenkins	29.7	36.6
Byrd−Rice	CHELPG	32.6	40.3
Byrd−Rice	Mulliken	39.4	50.7
Byrd−Rice	Jenkins	49.7	61.4
1:1 Salts			
G3MP2B3	Gutowski	19.1	24.0
G3MP2B3	CHELPG	19.9	25.0
G3MP2B3	Beaucamp	21.0	25.6
G3MP2B3	Mulliken	21.6	25.6
G3MP2B3	Jenkins	24.4	28.0
Byrd−Rice	Gutowski	23.9	27.6
Byrd−Rice	CHELPG	26.9	31.2
Byrd−Rice	Mulliken	31.0	36.3
Byrd−Rice	Beaucamp	33.4	38.2
Byrd−Rice	Jenkins	39.4	45.0

camp results do not seem to have a dependence on formula unit size, but clearly better agree with CHELPG values for larger volumes than for the smaller volumes. The reasonable performance of the Beaucamp model for these compounds is notable, since it was parametrized solely to nitrate salts. The Politzer and Murray QSPR method[22] assumes the cation to be NH_4^+; thus, it was applied only to ammonium salts. Only seven of the 63 molecules fall within this category. Out of the seven, two predictions are lower by −0.2 to −8.7 and the remaining range from 3.8−23 kcal/mol higher in energy (Table 2S in the Supporting Information). The maximum error in this set is for a salt with a 2:1 charge ratio; the fitting set used in this parametrization included only two salts with 2:1 charge ratios; thus, it is not unreasonable that the Politzer model does not describe these salts well.

There are numerous possible sources of error for prediction of the lattice potential energies. One possible source of error in the extended lattice summation calculations could be due to the description of the van der Waals interactions. We have assumed these are properly described using an interaction potential that reasonably describes a large series of CHNO neutral molecular crystals.[21] It is possible that this is an inadequate description of the van der Waals forces for the systems in this study (high-nitrogen salts). An estimate of the magnitude of the van der Waals interactions relative to the total lattice energy can be made from the results of the extended lattice summations using the CHELPG charges. For the series of systems studied, the van der Waals contribution to the lattice energy is ∼−7 kcal/mol on average, whereas the Coulombic contributions range from −105 to −410 kcal/mol. The contributions of the van der Waals interactions for all but two of the 63 systems are significantly smaller than those of the Coulombic contributions. However, those two systems have van der Waals contributions that are a factor of 5 less than the Coulombic contributions. Possible error in the Coulombic description could be due to the quantum-mechanically derived partial charges, leading us to explore different charge models. An additional possible source of error in lattice potential energies generated with the Jenkins-type models is our use of theoretical formula unit volumes. We compared lattice potential energies calculated using the original Jenkins model and experimental formula unit volumes with those reported above; these results differed by 2 kcal/mol, with only ten of the systems differing by more than 2 kcal/mol, and the largest deviation being 13.8 kcal/mol.

Having calculated the required components, we are now able to compare predictions of the solid phase heats of formation calculated from various combinations of gas phase ionic heats of formation and lattice enthalpies with each other and experiment. The theoretical $\Delta H^\circ_{f(s)}$ are determined by adding either the G3MP2B3 or Byrd−Rice heats of formation of the ions in the gas phase with lattice enthalpies determined in one of six ways (i.e., Jenkins model, Politzer, Gutowski and Beaucamp (with the Politzer method limited to ammonium salts and the latter two only for the 1:1 salts) or CHELPG and Mulliken lattice summations). Because the lattice enthalpies derived from the RESP charge model are statistically equivalent to the values generated using the CHELPG model, we will exclude these values from comparison with experiment. The $\Delta H^\circ_{f(s)}$ will be denoted by the method in which the lattice potential energy is calculated.

Experimental solid phase heats of formation for twenty-five (25) compounds were available for comparison with the predictions. Of these, 21 are 1:1 salts to which the Beaucamp and Gutowski models are applicable. Of the six ways in which lattice potential energies are calculated, the Politzer method is the most limited in applicability to the systems here, since it can only address ammonium salts. Within this set of 25 compounds, there were only four compounds; comparison of these predictions (using the G3MP2B3 $\Delta H^\circ_{f(g)}$) with experiments are given in Table 2S in the Supporting Information. As there are only four compounds for which comparison is possible, we will not discuss this method further; however, the error using this method for its target compounds is reasonable and comparable to other methods within this work.

The unsigned and rms errors of the theoretical predictions compared to experiment for each combination of gas phase $\Delta H^\circ_{f(g)}$ and lattice enthalpies are given in Table 2, with information used to generate these errors given in Tables 3S and 4S in the Supporting Information. For the entire set of 25 salts, solid phase heats of formation using G3MP2B3 $\Delta H^\circ_{f(g)}$ values yield better agreement with experiment than those

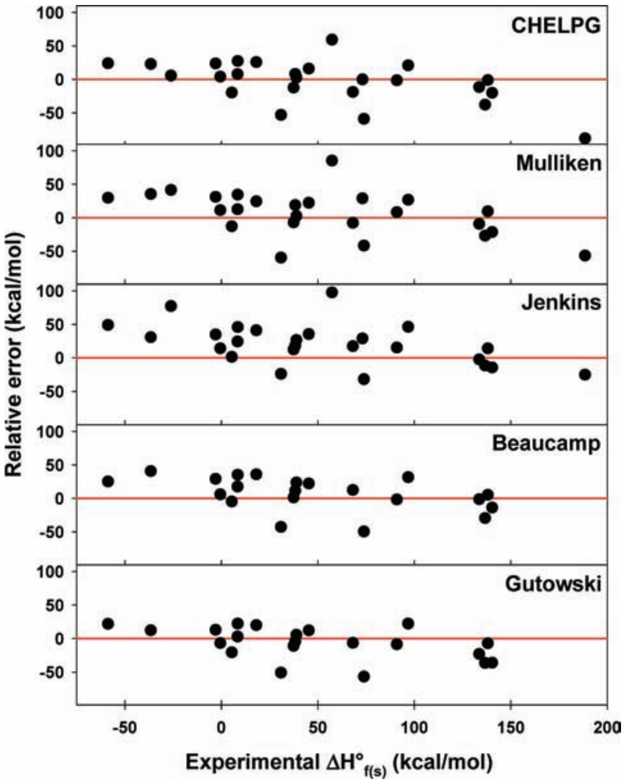

Figure 8. Error in solid phase heats of formation relative to experimental values for the various approaches to predict lattice enthalpy. The gas phase heat of formation is determined using G3MP2B3LYP applied directly to the ions.

generated using the Byrd−Rice method. Additionally, the $\Delta H^\circ_{f(s)}$ follow a CHELPG−Mulliken−Jenkins order of increasing error when used with $\Delta H^\circ_{f(g)}$ calculated with either the G3MP2B3 or Byrd−Rice method. When limiting the comparison to 1:1 salts, the $\Delta H^\circ_{f(s)}$ calculated using the Gutowski model have the best agreement with experiment for the sets of calculations corresponding to $\Delta H^\circ_{f(g)}$ calculated with either the G3MP2B3 or Byrd−Rice method. As seen above, G3MP2B3 $\Delta H^\circ_{f(s)}$ for 1:1 salts are in better agreement with experiment than the series of Byrd−Rice $\Delta H^\circ_{f(s)}$ with the sole exception being the Byrd−Rice/Gutowski combination performing marginally better than the G3MP2B3/Jenkins (the worst of the G3MP2B3 combinations). It is not surprising that the approaches that utilize the Byrd−Rice $\Delta H^\circ_{f(g)}$ do not perform as well as those that use the G3MP2B3 $\Delta H^\circ_{f(g)}$, as the Byrd−Rice method was parametrized to only neutral systems. Since we have established that the Byrd−Rice methods are inferior to the G3MP2B3 approaches, we will limit the remainder of our remarks to $\Delta H^\circ_{f(s)}$ heats of formation calculated using G3MP2B3 $\Delta H^\circ_{f(g)}$.

A comparison of the errors of the predicted values using the various G3MP2B3 combinations relative to experimental $\Delta H^\circ_{f(s)}$ is given in Figure 8. This figure shows significant scatter for all of the methods, and it is not apparent that one method significantly outperforms the other. While the predictions using extended lattice sums are better than the Jenkins predictions, one must temper that conclusion by the knowledge that the extended lattice summation method is more computationally demanding, and requires knowledge of the crystal structure, information that is not always available. However, for the 1:1 salts, the Gutowski and Beaucamp models are on par with the extended lattice sums, and superior to the Jenkins model. The similar agreement in unsigned mean and rms deviation from experiment for all methods (except Jenkins) indicates that no true benefit is gained by using the extended lattice summation method. Also, these results strengthen the argument that a reparametrization of the Jenkins model for molecular salts with 1:2, 2:1 and 2:2 charge ratios should be performed.

5. Summary and Conclusions

We performed a comparison among a variety of methods to calculate solid phase heats of formation of ionic molecular crystals using predicted gas phase heats of formations of the ionic components and predicted lattice enthalpies. The gas phase heats of formation of the ionic components were determined in two ways: through direct application to the ions of either the G3MP2B3 method or an atom-equivalent method originally derived to predict $\Delta H^\circ_{f(g)}$ for CHNO neutrals. Six methods were used to predict the lattice energies of the salts. Of the six methods tested, three used extended lattice summations assuming the experimental crystal structures and an interaction potential composed of van der Waals and Coulombic contributions. The Coulombic terms used quantum mechanically derived partial atomic charges; three different charge models were examined (CHELPG, Mulliken and RESP). The results using RESP and CHELPG models were nearly identical to one another. The remaining methods utilize QSPR-type relationships, two of which are functions of the inverse cube root of formula unit volume (the Jenkins model and the Gutowski model, a reparametrized version of the Jenkins model). The remaining QSPR model (Beaucamp) is dependent on quantum mechanically generated atom-centered Mulliken charges. Solid phase heats of formation for 25 energetic molecular ionic salts with charge ratios of 1:1, 2:1 and 2:2 were predicted using the various methods and compared with experimental values. $\Delta H^\circ_{f(s)}$ generated using G3MP2B3 $\Delta H^\circ_{f(g)}$ were in better agreement with experimental values than those using the atom-equivalent method, and for the entire set of compounds, $\Delta H^\circ_{f(s)}$ calculated using extended lattice summations to generate the lattice enthalpies were in better agreement with experiment than those generated from the QSPR-type models. However, solid phase heats of formation calculated using the Gutowski $\Delta H^\circ_{\mathrm{Lattice}}$ and the G3MP2B3 $\Delta H^\circ_{f(g)}$ values for the subset of salts with a 1:1 charge ratio (the only salts for which the Gutowski model is applicable) were in better agreement with experiment than values generated using the other methods. Since our goal is to obtain a completely predictive methodology for determination of solid phase heats of formation of molecular energetic salts, it is encouraging that the Jenkins/Gutowski models, which require information that can be readily predicted using theoretical methods, produce results that are on par with methods that require knowledge of the crystal structure. The latter requirement is met through either obtaining experimental information (thus defeating our goal) or generating theoretical crystal structures, which is computationally intensive and has only recently emerged as a viable methodology.[21] The Jenkins/Gutowski models, on the other hand, require no experimental information, require very modest computational resources (and can be obtained quickly) and produce results that are approximately as accurate as those obtained using methods that explicitly calculate interatomic interactions in an ionic crystal (extended lattice summations). The success of the Gutowski model, which is a reparametrization of the Jenkins model for 1:1 salts, indicates that further reparametrization of the Jenkins model is required to reduce the error when applied to 2:1 and 2:2 salts such as those studied here. However, this cannot be accomplished until a larger and more robust set of experimental solid and gas phase heats of formation is available. Until then, we can reasonably assume that the potential errors in the Gutowski and Jenkins models for predicting lattice potential energies when applied to 1:1 molecular ionic crystals such as those presented here are on the order of 24 to 28 kcal/mol, respectively.

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Supporting Information Available: Additional tables and figures as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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