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Relationships between Lattice Energies and Surface Electrostatic Potentials and Areas of Anions

Peter Politzer* and Jane S. Murray

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148

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We show that the lattice energies of ammonium, sodium, and potassium salts can be expressed analytically in terms of the total charges of the anions and their computed surface electrostatic potentials and areas. The calculations have been carried out at the HF/6-31+G* level for 17 singly and doubly charged anions. Predicted lattice energies are presented for 10 compounds.

Introduction

In recent years, we have shown that a variety of liquid, solid, and solution properties that depend on noncovalent interactions can be represented analytically in terms of the electrostatic potentials on the molecular surfaces.[1−10] This approach has been used to correlate and predict enthalpies of vaporization, sublimation, and fusion, boiling points and critical constants, solubilities, partition coefficients, liquid and solid densities, diffusion constants, viscosities, surface tensions, pK_a values, and impact sensitivities.

We now proceed to a property that involves stronger interactions than do those listed above: the lattice energy of an ionic crystal. This reflects the electrostatic forces within the three-dimensional array of positive and negative ions. An effective method for determining lattice energies computationally is of course useful in its own right, and it also permits the calculation of other thermochemical properties of ionic solids, such as heats of formation.

Procedure and Results

In Table 1 are listed 17 monatomic and polyatomic singly and doubly charged anions. For each of these, we have used the Gaussian 92 code[11] at the HF/6-31+G* level to optimize the geometry and to compute the electrostatic potential on the surface of the ion; we take this to be the 0.001 au contour of the electronic density, as suggested by Bader et al for neutral molecules.[12]

The electrostatic potential that is created at any point **r** by a system of nuclei and electrons is given by eq 1

$$V(\mathbf{r}) = \sum_{\mathrm{A}} \frac{Z_{\mathrm{A}}}{|\mathbf{R}_{\mathrm{A}} - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}')\,\mathrm{d}\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|} \qquad (1)$$

in which Z_A is the charge on nucleus A, located at $\mathbf{R}_A$, and $\rho(\mathbf{r})$ is the electronic density. For present purposes, our interest will be specifically in two properties of the electrostatic potential calculated on the ionic surface: (a) the most negative value, $V_{S,min}$, and (b) the average negative value, $\bar{V}_S^-$, defined as $V_S^- = (1/n)\sum_{j=1}^{n} V^-(\mathbf{r}_j)$, the summation being over the surface points $\mathbf{r}_j$ at which the potential is negative; for these anions, this is the entire surface.

$V_{S,min}$ and V_S^- have been computed for each anion and are given in Table 1 along with the total area of the ionic surface. Also included, when available, are the experimental lattice energies of the corresponding NH_4^+, Na^+, and K^+ salts.[13]

We used a statistical analysis procedure[14] to develop relationships between the lattice energies for a given positive ion and the computed surface quantities of the negative ions. The results are presented as eqs 2−4, and are shown graphically in Figures 1−3. (In these equations, Q is the charge on the ion in atomic units, either −1 or −2. The energies and electrostatic potentials are in kcal/mol, and the areas in Å^2.)

NH_4^+ Compounds:

$$\text{Lattice energy} = -287.8Q - 0.6246V_{S,min} - 1.72 \times 10^{-7}[(\text{area})(\bar{V}_S^-)]^2 - 199.4 \qquad (2)$$

Standard deviation = 7 kcal/mol

Na^+ Compounds:

$$\text{Lattice energy} = -464.7Q - 0.5636V_{S,min} - 4.65 \times 10^{-7}[(\text{area})(\bar{V}_S^-)]^2 - 317.9 \qquad (3)$$

Standard deviation = 8 kcal/mol

K^+ Compounds:

$$\text{Lattice energy} = -381.2Q - 0.4785V_{S,min} - 3.42 \times 10^{-7}[(\text{area})(\bar{V}_S-)]^2 - 252.2 \qquad (4)$$

Standard deviation = 6 kcal/mol

The standard deviations, in conjunction with Figures 1−3, indicate the effectiveness of eqs 2−4 in reproducing the experimental lattice energies. It is interesting that the same form of functional relationship can be used for both singly and doubly charged anions and for the polyatomic NH_4^+ cation as well as the monatomic Na^+ and K^+. Less general approaches can of course be investigated using the data in Table 1; however, those that we tested have led to relatively little improvement. For example, keeping the same functional form but including only singly charged anions affects the standard deviation only for the K^+ compounds, lowering it by 1 kcal/mol. Going one step further and allowing the functional form to depend upon the

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TABLE 1: Computed (HF/6-31+G*) and Experimental Properties of Anions[a]

				experimental lattice energy[b]		
anion	$V_{S,min}$	$\bar{V}_S^-$	area	NH_4^+	Na^+	K^+
ClO_4^-	−125.6	−118.9	97.8	139	155	144
SCN^-	−124.8	−116.9	95.1	146	163	147
CH_3COO^-	−163.1	−117.7	98.8	157	182	163
HS^-	−137.9	−130.3	75.0	159	179	158
CN^-	−143.4	−138.4	67.7	160	177	160
NO_3^-	−144.3	−129.6	82.0	162	181	164
HF_2^-	−148.8	−147.4	62.4	168	188	167
HCO_3^-	−156.0	−125.9	85.7	177	196	176
N_3^-	−136.1	−129.8	77.8		175	157
NO_2^-	−157.9	−136.9	71.7		179	159
Cl^-	−141.1	−141.1	65.9		188	171
HCO_2^-	−99.3	−42.9	77.3		194	174
OH^-	−181.9	−159.9	52.2		215	192
F^-	−178.2	−178.2	42.4		221	196
S^{-2}	−230.8	−230.8	95.6		526.5	
SiF_6^{2-}	−241.5	−223.0	116.9	412.8		389.1
SO_4^{2-}	−245.6	−230.3	105.6	424.7	463.2	429.3

[a] $V_{S,min}$, $\bar{V}_S^-$ and lattice energies are given in kcal/mol. The area is in Å.^{2} [b] Reference 13.

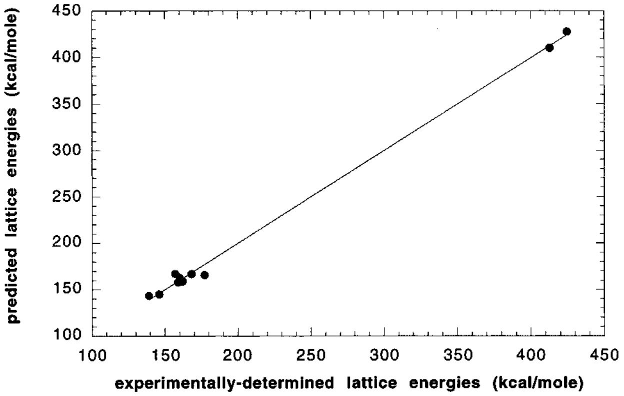

Figure 1. Comparison of predicted (eq 2) and experimental lattice energies for ammonium compounds.

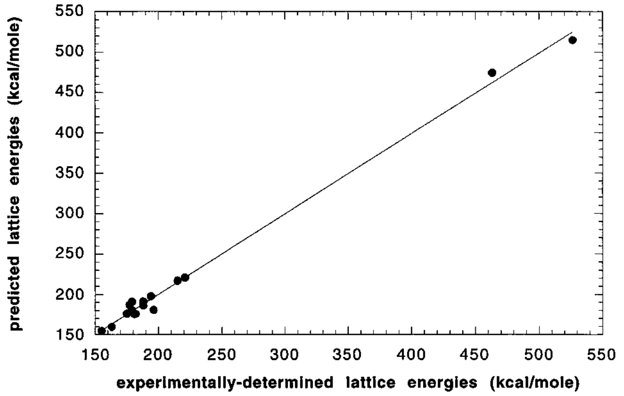

Figure 2. Comparison of predicted (eq 3) and experimental lattice energies for sodium compounds.

cation helps primarily the NH_4^+ correlation, improving the standard deviation by 2 kcal/mol.

Discussion

The dominant contributor to the lattice energies in Table 1 is the overall anionic charge Q; this can be seen in eqs 2−4 as well as by simply noting that the magnitudes for the doubly charged anions are 2−3 times as large as those for the singly charged anions. The effects of $V_{S,min}$ and the product (area)($\bar{V}_S^-$) are evident in the ranges of values covered by the lattice energies for the singly- and doubly charged anions taken separately, as much as 66 and 101 kcal/mol, respectively. The roles of $V_{S,min}$ and (area)($\bar{V}_S^-$) in eqs 2−4 can be interpreted in terms of the directional nature of the interactions in a crystal lattice. Localized surface sites with highly negative potentials ($V_{S,min}$) promote lattice cohesiveness since they can presumably be oriented so as to interact strongly with cations, which are usually relatively small. Thus the terms involving $V_{S,min}$ increase the lattice energy. On the other hand, the product (area)($\bar{V}_S^-$), which can be viewed as the total negative potential on the entire surface, is a global property rather than a site-specific one. It can be regarded, to some extent, as a measure of negative charge that is not effective in directional interactions. Accordingly, large values for surface area and/or (area)($\bar{V}_S^-$) tend to decrease the lattice energy.

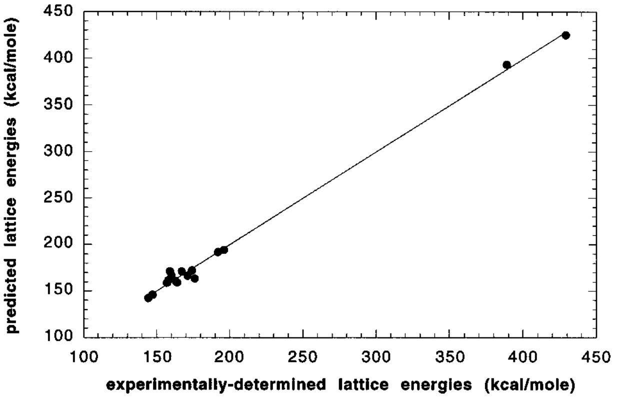

Figure 3. Comparison of predicted (eq 4) and experimental lattice energies for potassium compounds.

TABLE 2: Computed (HF/STO-5G*) Properties of Cations[a]

cation	$V_{S,max}$	$\bar{V}_S^+$	area
N_4^+	172.3	171.0	48.5
Na^+	245.3	245.3	23.4
K^+	189.8	189.8	39.7

[a] $V_{S,max}$ and $\bar{V}_S^+$ are given in kcal/mol. The area is in Å.^{2}

Thus the largest lattice energies among the singly charged anions are for OH^- and F^-, which combine a strongly negative $V_{S,min}$ with a low surface area. HCO_2^- also has relatively high lattice energies, despite having the weakest $V_{S,min}$, because of its low average potential, $\bar{V}_S^-$. In contrast, the smallest lattice energies among these anions are those for ClO_4^-, SCN^-, and CH_3COO^-, which have the largest areas. Among the doubly charged anions, $V_{S,min}$ and ($\bar{V}_S^-$) are quite similar; accordingly the ordering of their lattice energies is determined by their areas.

The same sort of reasoning can be used to explain the fact that, for any particular anion, the Na^+ salt invariably has the highest lattice energy while those of the NH_4^+ and K^+ compounds are remarkably similar. Table 2 presents computed surface properties for NH_4^+, Na^+, and K^+ analogous to those given in Table 1 for the anions; $V_{S,max}$ and $\bar{V}_S^+$ are, respectively, the most positive and the average positive electrostatic potentials on the ionic surface. (These calculations were at the HF/STO-5G* level because the 6-31+G* basis set is not available for K^+ in Gaussian 92.) Na^+ has a much more positive $V_{S,max}$ and smaller area than either NH_4^+ or K^+, which accounts for its always having the highest lattice energy. K^+ has a more positive $V_{S,max}$ than NH_4^+, but its (area)($\bar{V}_S^+$) product is smaller; the net contribution of these factors is apparently nearly the same.

As an additional test of eq 2, we used it to estimate the lattice energy of ammonium dinitramide, $NH_4N(NO_2)_2$, an ionic

TABLE 3: Lattice Energies Predicted Using Eqs 2−4

compound	predicted lattice energy, kcal/mol
NH_4N_3	156
NH_4NO_2	170
NH_4Cl	162
NH_4HCO_2	149
NH_4OH	190
NH_4F	190
$NH_4N(NO_2)_2$	139
$(NH_4)_2S$	437
$NaSiF_6$	431
K_2S	454

compound that is a potential replacement for ammonium perchlorate in propellant formulations.[15−17] Our computed HF/6-31+G* surface properties for the $N(NO_2)_2^-$ ion are: $V_{S,min} = -126.1$ kcal/mol, $\bar{V}_S^- = -107.5$ kcal/mol, and area = 118.2 Å^2. Equation 2 yields a lattice energy of 139 kcal/mol, in good agreement with a value of 143 kcal/mol that we have obtained earlier by an independent density functional computational approach.[18]

We have used eqs 2−4 to predict the lattice energies of those compounds in Table 1 for which the experimental data are not available. The results are in Table 3, along with the value for ammonium dinitramide.

Another possible application of eqs 2−4 is in estimating the heats of formation of ammonium, sodium and potassium salts. The lattice energy of an ionic compound M_aX_b can readily[13] be converted to ΔH for the process

$$M_aX_b(s) \rightarrow aM^{n+}(g) + bX^{m-}(g) \tag{5}$$

from which, in conjunction with experimental[13,19] or computed[20,21] heats of formation of the gas-phase ions, can be obtained the heat of formation of solid M_aX_b.

Summary

We have shown that the lattice energies of ammonium, sodium, and potassium salts can be related quantitatively to the total charges of the anions and to their calculated surface electrostatic potentials and areas. This procedure can be used to predict lattice energies and related thermochemical properties such as solid-phase heats of formation, even for proposed ionic compounds that have not yet been prepared.

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