

**Figure 2.** Percent difference between calculated and literature vibrational frequencies for  $\text{SiH}_4$  and  $\text{Si}_2\text{H}_6$ , i.e., (calculated value - literature value)  $\times 100\%$ /literature value.

to account for known deficiencies in such calculations. We have previously shown<sup>5</sup> that this method is valid for the  $\text{SiH}_n$ ,  $\text{SiCl}_n$ , and  $\text{SiH}_n\text{Cl}_m$  systems. For  $\text{Si}_2\text{H}$ ,  $\text{Si}(\text{H}_2)\text{Si}$ , and  $\text{HSiSiH}_2$ , no other heat of formation data are available in the literature. We have also calculated several transition-state energies, which are summarized in Table VI.

Consistent with previous workers, we find that disilane decomposition to  $\text{SiH}_4$  and  $\text{SiH}_2$  is the lowest energy pathway and that formation of  $\text{Si}_2\text{H}_4$  and  $\text{H}_2$  should also occur. However, our mechanism for the formation and reaction of  $\text{Si}_2\text{H}_4$  differs significantly from previous studies. We find that 1,1- $\text{H}_2$  elimination from disilane leading to  $\text{H}_3\text{SiSiH}$  is only a few kilocalories per mol more endothermic than the  $\text{SiH}_2 + \text{SiH}_4$  channel. The  $\text{H}_3\text{SiSiH}$  species can subsequently rearrange to disilene ( $\text{H}_2\text{Si}=\text{SiH}_2$ ) with a very low activation barrier ( $\sim 3 \text{ kcal mol}^{-1}$ ). Direct production of disilene from disilane via 1,2- $\text{H}_2$  elimination is virtually ruled out by a high reaction barrier which arises from a sterically unfavorable four-center transition state. Decomposition of  $\text{Si}_2\text{H}_6$  to radical products ( $\text{Si}_2\text{H}_5$  or  $\text{SiH}_3$ ) is significantly more endothermic than either silylene or  $\text{H}_2$  elimination.

In agreement with previous studies, our results indicate that  $\text{H}_2\text{Si}=\text{SiH}_2$  is the most stable isomer of  $\text{Si}_2\text{H}_4$ . However, our value of  $23 \text{ kcal mol}^{-1}$  for the separation between  $\text{H}_3\text{SiSiH}$  and  $\text{H}_2\text{Si}=\text{SiH}_2$  is larger than those obtained in previous studies ( $6\text{--}10 \text{ kcal mol}^{-1}$ ). The difference results primarily from our corrections for basis set limitations. We also propose that disilene decomposes through 1,1- $\text{H}_2$  elimination to form  $\text{H}_2\text{Si}=\text{Si}$ , which should rearrange easily to the bridged species  $\text{Si}(\text{H}_2)\text{Si}$  (the most stable isomer of  $\text{Si}_2\text{H}_2$ ). Due to its high endothermicity, the reaction

$\text{H}_2\text{Si}=\text{SiH}_2 \rightarrow 2\text{SiH}_2$  should not be important under most conditions.

In agreement with other theoretical and experimental work, a general conclusion of this work is that decomposition reactions of silicon-hydrogen compounds occur by elimination of silylenes or molecular hydrogen rather than free-radical formation. This situation is noticeably different from the corresponding hydrocarbon reactions. Our calculations also indicate that 1,1- $\text{H}_2$  eliminations are favored over 1,2- $\text{H}_2$  eliminations.

The results presented in this paper indicate that the method of empirically correcting ab initio calculations provides useful thermochemical information. In several cases, estimates of heats of formation have been obtained for species for which no experimental data are available. From these calculations, new insight has been obtained regarding the mechanism of disilane decomposition.

**Note Added in Proof.** After preparation of this manuscript, several experimental papers have appeared<sup>56-59</sup> that support a higher value for the  $\text{SiH}_2$  heat of formation.

**Acknowledgment.** We thank Mark S. Gordon for providing us with transition-state geometries for the  $\text{Si}_2\text{H}_6 \rightarrow \text{H}_2\text{Si}=\text{SiH}_2 + \text{H}_2$  and  $\text{H}_3\text{SiSiH} \rightarrow \text{H}_2\text{Si}=\text{SiH}_2$  reactions. We also thank Morey Ring and Ed O'Neal for preprints of their most recent work. This work was performed at Sandia National Laboratories and supported by the U.S. Department of Energy under Contract No. DE-A0476DP00789 for the Office of Basic Energy Sciences.

## Appendix

The procedure used to correct calculated harmonic frequencies for systematic errors has been described previously.<sup>5</sup> Experimental data for reference species are compared to calculated frequencies to derive a scaling factor. As shown in Figure 2, the percentage difference between experimental and calculated frequencies averages 10% for the compounds for which experimental data are available ( $\text{SiH}_4$  and  $\text{Si}_2\text{H}_6$ ). We have therefore corrected vibrational frequencies in  $\text{Si}_2\text{H}_n$  species by dividing the calculated frequencies by 1.1. Table VII lists calculated, literature, and corrected vibrational frequencies for these species.

**Registry No.**  $\text{Si}_3\text{H}_8$ , 7783-26-8;  $\text{H}_3\text{SiSiH}$ , 50420-90-1;  $\text{H}_2\text{SiSiH}_2$ , 15435-77-5;  $\text{HSiSiH}_2$ , 102437-77-4;  $\text{H}_2\text{Si}=\text{Si}$ , 87970-40-9;  $\text{Si}_2\text{H}_5$ , 73151-72-1;  $\text{Si}_2\text{H}_6$ , 1590-87-0;  $\text{Si}_2\text{H}$ , 102437-78-5.

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## Analysis of the Born Model for Hydration of Ions

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The use of the macroscopic permittivity and the interpretation of the hydration radius are critical points of the Born model which have been investigated in this study. We conclude that the Born model cannot provide significant information about the configuration or structure of molecules near hydrated ions. It can, however, give good insight into intermolecular forces. To this end we have extended the simple Born model by a distance-dependent permittivity to an expression for the electrostatic energy between an ion and the surrounding water molecules. Comparison with experimental hydration energies shows the contribution from short-range interactions. We found that for alkali-metal, alkaline-earth, and halide ions repulsive and attractive short-range forces largely cancel. Ions with an outermost d shell, on the other hand, show a dominance of short-range attraction.

## Introduction

The electrostatic Born model<sup>1</sup> for hydration of ions yields free (Gibbs) energies of hydration

$$\Delta G = -\frac{1}{2} \frac{Z^2 e^2}{r_B} \left( 1 - \frac{1}{\epsilon_0} \right) \quad (1)$$

in terms of the permittivity  $\epsilon_0$  of the solvent, a characteristic "ionic radius"  $r_B$ , and the ionic charge  $Ze$ . Here  $e$  is the elementary

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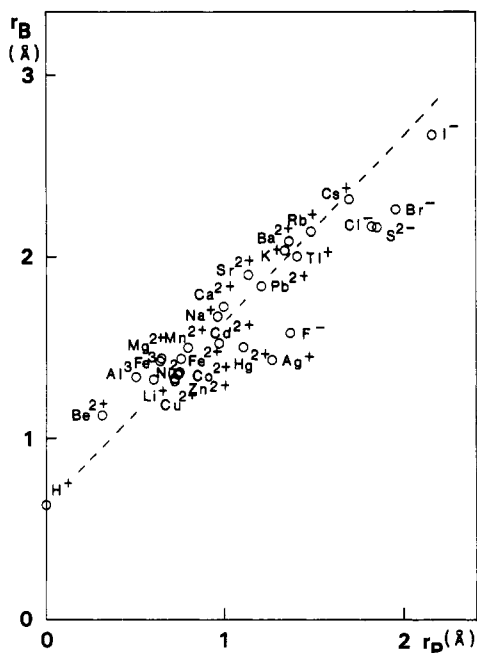


Figure 1. Born radius  $r_B$  vs. Pauling radius  $r_P$  of ions.

charge and  $Z$  is an integer. The striking simplicity of the model and its promising results have led to its wide application and have stimulated a great many investigations.<sup>2-14</sup> Two objections, however, are frequently raised. One objection concerns the use of the macroscopic quantity  $\epsilon_0$ . This treatment becomes particularly crucial in describing the immediate vicinity of an ion in solution where strongly inhomogeneous electric fields up to  $10^8$  V/m exist. The other point of controversy concerns the interpretation of the Born radius  $r_B$ . When Born radii obtained from eq 1 and experimental data for  $\Delta G$  and  $\epsilon_0$  are compared with actual (e.g., Pauling<sup>15</sup>) ionic radii  $r_P$ , approximately linear relations for several ionic families are found (see Figure 1). Various explanations for such relations have been proposed including voids around hydrated ions, integer hydration numbers, and the asymmetric location of the dipole center in water molecules.

In this paper we want to focus on both objections to the Born model. To this end we used Debye's classical theory for static permittivity<sup>16,17</sup> to calculate the electric field  $E(r)$  and permittivity  $\epsilon(r)$  depending on the distance  $r$  from the center of a simple hydrated ion. Debye's theory has been considered inappropriate for polar liquids<sup>18-20</sup> because of the assumption of the Lorentz

expression for the local field. We argue that this criticism is not justified and that Debye's theory does indeed hold for strong polar liquids.

Knowledge of the distance-dependent permittivity  $\epsilon(r)$  allows us to calculate an improved electrostatic interaction energy between a hydrated ion and its surrounding polarized medium. A comparison of this quantity with observed hydration energies of ions  $\Delta G$  reveals the contributions from short-range interactions which are not accounted for by the Born model.

### Electric Field Near Hydrated Ions

**Debye Theory for Static Permittivity.** The electrostatic energy  $w$  of a permanent dipole moment  $p$  in a (local) electric field  $E_{loc}$  is

$$w = -pE_{loc} \cos \theta \quad (2)$$

where  $\theta$  is the angle between the orientation of the dipole and the direction of the field. The polarization  $P$  of a medium consisting of polar molecules is the sum of the electronic and the orientational parts

$$P = \frac{\alpha}{v} E_{loc} + \frac{p}{v} \langle \cos \theta \rangle \quad (3)$$

Here  $\alpha$  is the isotropic polarizability and  $v$  is the volume of a molecule. Assuming a Boltzmann distribution of dipole orientations in a static electric field gives the average orientation

$$\langle \cos \theta \rangle = \frac{\int_0^\pi \cos \theta \exp\left(-\frac{w}{kT}\right) \sin \theta d\theta}{\int_0^\pi \exp\left(-\frac{w}{kT}\right) \sin \theta d\theta} \quad (4)$$

with Boltzmann's constant  $k$  and temperature  $T$ . Evaluation of the integrals yields Langevin's equation<sup>17</sup>

$$\langle \cos \theta \rangle = -\frac{1}{x} + \coth(x) \quad (5)$$

with  $x = (pE_{loc})/(kT)$ . Expansion of eq 5 for  $x \ll 1$  gives  $\langle \cos \theta \rangle = x/3$ , neglecting third- and higher-order terms. Inserting into eq 3, we obtain

$$P = \left( \frac{\alpha}{v} + \frac{p^2}{3vkT} \right) E_{loc} \quad (6)$$

The Lorentz expression for the local field

$$E_{loc} = E + \frac{4\pi}{3} P = \frac{\tilde{\epsilon}(\omega) + 2}{3} E \quad (7)$$

establishes the connection with the macroscopic electric field  $E$ . The right-hand side of eq 7 follows from eliminating  $P$  through the frequency-dependent permittivity  $\tilde{\epsilon}(\omega) = 1 + 4\pi P(\omega)/E(\omega)$ . For fields with very high frequency, only electronic dipoles contribute to  $P$ . This relates the polarizability  $\alpha$  to the macroscopic high-frequency permittivity  $\epsilon_\infty$  (Clausius-Mossotti relation)

$$\frac{\alpha}{v} = \frac{3}{4\pi} \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \quad (8)$$

For static or low-frequency fields the local field, eq 7, can be expressed through the static permittivity  $\epsilon_0$  as

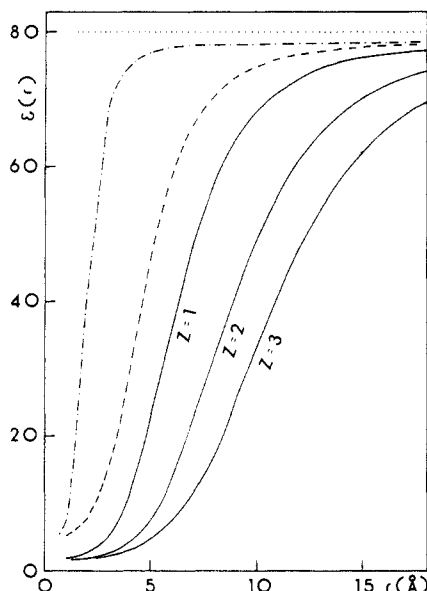
$$E_{loc} = \frac{\epsilon_0 + 2}{3} E \quad (9)$$

Inserting into eq 6 gives the permanent dipole moment

$$p^2 = \frac{27}{4\pi} kTv \frac{\epsilon_0 - \epsilon_\infty}{(\epsilon_0 + 2)(\epsilon_\infty + 2)} \quad (10)$$

in terms of macroscopic quantities. Notice that the underlying approximation  $x \ll 1$  is well-fulfilled for the small electric fields used in measurements of  $\epsilon_0$ . For large electric fields the approximation  $x \ll 1$  no longer holds. Therefore, the exact expression of eq 3 must be used for the polarization. We assume, however, that large fields affect only the dipole orientation but

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**Figure 2.** Distance-dependent permittivity  $\epsilon(r)$  vs. distance  $r$  from hydrated ions with charge  $Ze$  (full lines); modified versions  $\epsilon^H(r)$  and  $\epsilon^G(r)$  due to Hill and Grahame, respectively, for  $Z = 1$  (dashed and dash-dotted lines); macroscopic permittivity  $\epsilon_0$  (dotted line).

not the dipole moment  $p$  given by eq 10.

In a polar medium the macroscopic field

$$E(r) = \frac{1}{\epsilon(r)} \frac{Ze}{r^2} \quad (11)$$

at a distance  $r$  from a point charge  $Ze$  is screened with the distance-dependent static permittivity  $\epsilon(r)$ . With eq 9 we get the distance-dependent local field

$$E_{\text{loc}}(r) = \frac{\epsilon(r) + 2}{3\epsilon(r)} \frac{Ze}{r^2} \quad (12)$$

Inserting into eq 3 gives, after some algebra, an implicit equation for  $\epsilon = \epsilon(r)$

$$\epsilon = 1 + \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2}(\epsilon + 2) + \frac{4\pi e p r^2}{Z e v} \left[ -\frac{1}{y} + \coth(y) \right] \quad (13)$$

with the abbreviation  $y = (\epsilon + 2)Zep/(3kTr^2\epsilon)$ .

**Results.** We solved the transcendental eq 13 numerically using experimental data at  $T = 25^\circ\text{C}$ . The volume  $v = 29.82 \text{ \AA}^3$  for the water molecule was obtained from the density of water<sup>21</sup> of  $999.045 \text{ kg/m}^3$ . For the static permittivity we used a value<sup>22</sup> of  $\epsilon_0 = 78.39$ . The high-frequency permittivity  $\epsilon_\infty = n^2 = 1.78$  was obtained from the index of refraction<sup>23</sup>  $n = 1.33252$  for the sodium D line. Figure 2 shows<sup>24</sup> that with  $Z = 1$  the permittivity  $\epsilon(r)$  comes close to its asymptotic value  $\epsilon_0$  (dotted line) for distances larger than  $\sim 15 \text{ \AA}$ . The dramatic decrease to values near  $n^2$  occurs in the range between 3 and 10  $\text{\AA}$ . Figure 2 also shows that for ions with  $Z = 2$  and  $Z = 3$  the steep-slope and off-leveled regions of  $\epsilon(r)$  are more spread out and shifted further away from the ion.

The use of  $\epsilon_\infty = n^2$  was criticized by Hill et al.<sup>25</sup> on grounds that strong dispersion in the infrared spectrum was not accounted for. In order to see the influence of this dispersion on  $\epsilon(r)$ , we did a separate calculation with Hill's suggested value  $\epsilon_\infty^H = 4.55$ .

The dashed line in Figure 2 shows that, for  $Z = 1$ , the corresponding permittivity  $\epsilon^H(r)$  drops within a closer and narrower region than the former  $\epsilon(r)$ .

**Discussion.** A crucial point in Debye's theory of static permittivity is the use of the Lorentz expression for the local field in eq 7. The Lorentz field is commonly accepted for gases and for cubic crystals, but it is controversial for polar liquids. In particular, Onsager's critique<sup>18</sup> is based on the observation that Debye's theory gives considerably smaller permanent dipole moments for the same molecules when they are in liquid than in gaseous states. An example for this discrepancy is Debye's value of 1.85 and 0.82 D for water molecules in gaseous and liquid states, respectively. Onsager attributes this finding to an inappropriate description of the local field through the Lorentz expression of eq 7. Onsager's underlying assumption is that the permanent dipole moment is a fixed quantity of a molecule regardless of its environment. This point of view is closely related to the hard-sphere model which attributes invariable sizes to atoms, ions, or molecules. In the meantime many indications have been found which demonstrate the dependence of molecular quantities on the actual environment, particularly between a molecule in a free and a condensed state. Among those quantities are the size,<sup>26</sup> polarizability,<sup>27,28</sup> permanent dipole moment,<sup>29</sup> and deformation dipoles<sup>30</sup> of molecules. Deformation dipoles actually present an obvious example for environment-dependent quantities since they are completely absent for free molecules. On the other hand, when molecules are in a condensed state, overlap and short-range forces give rise to deformation dipoles. For ideal crystal configurations with inversion symmetry, these dipoles are apparently hidden since their net contribution vanishes. However, in asymmetric configurations such as displacements of optical phonons, the effect of such dipoles can be observed in terms of "effective charges" (ref 30).

We can expect that similar dipole mechanisms related to short-range repulsion are also present in condensed states of water and, perhaps together with mechanisms related to the hydrogen bond,<sup>31</sup> give rise to changes of dipole moments. Of course, a detailed investigation of the dependence of permanent dipole moments of molecules on their microscopic environment is subject to a quantum-mechanical treatment which is beyond the scope of this paper. Nevertheless, from today's perspective it is very likely that the observed differences between permanent dipole moments of water in gaseous or liquid states are caused by molecular mechanisms rather than by modified local fields acting on rigid molecular entities. In fact, our investigation of the local field for molecules in general surroundings<sup>32</sup> shows that for liquid water the Lorentz field presents a very good approximation. These findings weaken considerably Onsager's original motivation for introducing local field modifications.<sup>33</sup> In view of this situation we consider a reinvestigation of the electric field near hydrated ions justified in terms of Debye's classical theory.

In our derivation of  $\epsilon(r)$  we assumed that all water molecules had the same time-average volume  $v = v_0$  for the liquid state in absence of an electric field. In reality, the polarized molecules, oriented by a field  $E$ , occupy smaller time-average volumes than  $v_0$ . It is known from measurements that the shrinkage contributions from all polarized molecules around a hydrated ion amount to a shrinkage volume which is comparable to the volume  $v_0$  of a complete water molecule.<sup>34</sup> With incorporation of model assumptions for distance-dependent molecular volumes  $v(r)$  into the Debye formalism, we found qualitatively that the region of strong

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(24) The solid curve in Figure 2 for  $Z = 1$  is in close agreement with the so-called tangential permittivity in Debye's original graph (ref 17).

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decrease in  $\epsilon(r)$  shifts closer to the hydrated ion.

In Grahame's<sup>35</sup> analysis of the Born model for ion hydration the problem of the local field was circumvented. Grahame proposes an expression for the permittivity  $\epsilon(E)$  depending on the electric field  $E$ . Parameters of this expression are fitted to data from experiments by Malsch<sup>36</sup> with field strengths up to  $10^7$  V/m. Grahame transforms  $\epsilon(E)$  to a distance-dependent  $\epsilon^G(r)$  with extrapolations for small distances  $r$  from a hydrated ion. Since  $\epsilon^G(r)$  does not involve data of  $\epsilon_\infty$  or assumptions on permanent dipole moments and the local field, we have an independent source for comparison with our own  $\epsilon(r)$ .

The dash-dotted curve in Figure 2 shows that Grahame's  $\epsilon^G(r)$  for  $Z = 1$  remains close to the macroscopic value  $\epsilon_0$  for distances larger than 3.5 Å. According to Graham's theory, the dramatic drop in  $\epsilon^G(r)$  occurs essentially within the closest shell of water molecules around a hydrated ion.<sup>37</sup>

All curves of distance-dependent permittivities for  $Z = 1$  in Figure 2 are also close to those obtained by Ritson and Hasted<sup>38</sup> based on two sets of model assumptions.

### Hydration Energy

**Model.** The dielectric energy density  $u(r)$  at a distance  $r$  from the center of a hydrated ion is

$$u(r) = \frac{1}{8\pi} \epsilon(r) E^2(r) \quad (14)$$

We insert  $E$  from eq 11 and integrate over shells of concentric spheres to obtain the total dielectric energy between a hydrated ion and its surrounding medium

$$U = \frac{1}{2} Z^2 e^2 \int_{r_c}^{\infty} [\epsilon(r)r^2]^{-1} dr \quad (15)$$

Subtracting from  $U$  the electric self-energy of a sphere of charge  $Ze$  and radius  $r_c$  under vacuum gives an improved expression for the electrostatic contribution to the hydration energy

$$\Delta G_{el} = -\frac{1}{2} Z^2 e^2 \left\{ r_c^{-1} - \int_{r_c}^{\infty} [\epsilon(r)r^2]^{-1} dr \right\} \quad (16)$$

The total hydration energy  $\Delta G$  is the sum of contributions from electrostatic and short-range interactions between the hydrated ion and all surrounding water molecules

$$\Delta G = \Delta G_{el} + \Delta G_{sr} \quad (17)$$

The critical quantity in eq 16 is the lower limit of integration,  $r_c$ , representing the inner boundary of the dielectric medium. The simplest choice for  $r_c$  consists of using traditional ionic radii, e.g., Pauling radii.<sup>15</sup> This choice is based on the assumption of a hard-sphere type of contact between the hydrated ion and the surrounding water molecules. A more sophisticated choice may assign  $r_c$  to the distance between the center of the ion and the time-averaged centers of dipoles in the closest shell of surrounding water molecules. With the second choice the radius  $r_c$  could be interpreted as the "dielectric beginning" of the polarizable medium. Because of the asymmetric shape of the water molecule, the center of the permanent dipole moment is closer to the H side than to the O side of the molecule.<sup>39</sup> Assuming again hard-sphere contact,  $r_c$  could be expressed as the sum of traditional ionic radii  $r_p$  and the distance  $\Delta r$  of the center of the permanent dipole from the O and H side of the water molecule for cation and anion hydration, respectively. Accordingly,  $r_c$  would be larger for cations than for anions of the same size. This mechanism was suggested by Latimer et al.<sup>5</sup> for an interpretation of the Born radii in their em-

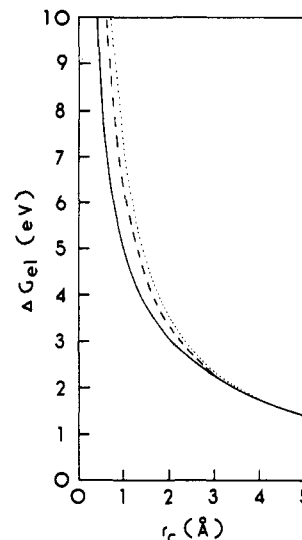


Figure 3. Electrostatic contribution to the hydration energy of ions  $\Delta G_{el}$  vs. lower integration limit  $r_c$  (see eq 16) for  $Z = 1$  using  $\epsilon(r)$  (solid line),  $\epsilon^H(r)$  (dashed line), and the macroscopic permittivity  $\epsilon_0$  (dotted line).

TABLE I: Experimental Hydration Energies (in eV) of Ions  $\Delta G$ , Electrostatic Contributions  $\Delta G_{el}$ , and Differences  $\Delta G_{sr}$

ion	$-\Delta G^a$	$-\Delta G_{el}$	$\Delta G_{sr}$
H <sup>+</sup>	11.30	11.30	0.00
Li <sup>+</sup>	5.36	5.22	-0.14
Na <sup>+</sup>	4.26	4.20	-0.06
K <sup>+</sup>	3.50	3.52	0.02
Rb <sup>+</sup>	3.32	3.32	0.00
Cs <sup>+</sup>	3.08	3.07	-0.01
Ag <sup>+</sup>	4.97	3.63	-1.34
Tl <sup>+</sup>	3.56	3.42	-0.14
F <sup>-</sup>	4.50	3.48	-1.02
Cl <sup>-</sup>	3.29	2.94	-0.35
Br <sup>-</sup>	3.14	2.80	-0.34
I <sup>-</sup>	2.66	2.62	-0.04
Be <sup>2+</sup>	25.25	32.25	7.00
Mg <sup>2+</sup>	19.75	21.15	1.40
Ca <sup>2+</sup>	16.51	16.39	-0.12
Sr <sup>2+</sup>	15.00	15.12	0.12
Ba <sup>2+</sup>	13.66	13.56	-0.10
Mn <sup>2+</sup>	18.98	18.66	-0.32
Fe <sup>2+</sup>	19.79	19.30	-0.49
Co <sup>2+</sup>	20.79	19.56	-1.23
Ni <sup>2+</sup>	21.43	19.89	-1.54
Cu <sup>2+</sup>	21.63	19.89	-1.74
Zn <sup>2+</sup>	21.01	19.56	-1.45
Cd <sup>2+</sup>	18.67	16.60	-2.07
Hg <sup>2+</sup>	18.92	15.37	-3.55
Pb <sup>2+</sup>	15.52	14.57	-0.95
S <sup>2-</sup>	13.17	11.25	-1.92

<sup>a</sup> Reference 2, p 55.

pirical relation  $r_B = r_p + \Delta r$  with  $\Delta r = 0.85$  Å for alkali-metal ions and  $\Delta r = 0.25$  Å for halide ions.

Our choice of  $r_c$  for univalent cations is based on the assumption that the hydration energy of H<sup>+</sup> originates solely from electrostatic interaction of a proton in the center of a time-averaged spherical dipole distribution represented by  $\epsilon(r)$  for  $r > r_c(\text{H}^+)$ . For other univalent cations we then assume

$$r_c = r_p + \Delta r \quad (18)$$

with  $\Delta r = r_c(\text{H}^+)$ . We do not have a similar criterion for anions and divalent cations. Thus, we must rely on further assumptions for these ions introduced below.

**Results and Discussion.** Figure 3 shows  $\Delta G_{el}$  for  $Z = 1$  as a function of the lower integration limit  $r_c$  by using  $\epsilon(r)$  as well as the modification  $\epsilon^H(r)$  and the macroscopic  $\epsilon_0$  (dashed and dotted curves). The different versions for  $\epsilon(r)$  lead for  $Z = 1$  ions to differences in  $\Delta G_{el}$  values around 30%, 15%, and 5% for  $r_c = 1, 2$ , and 3 Å, respectively. Since the diameter of a water molecule<sup>39</sup>

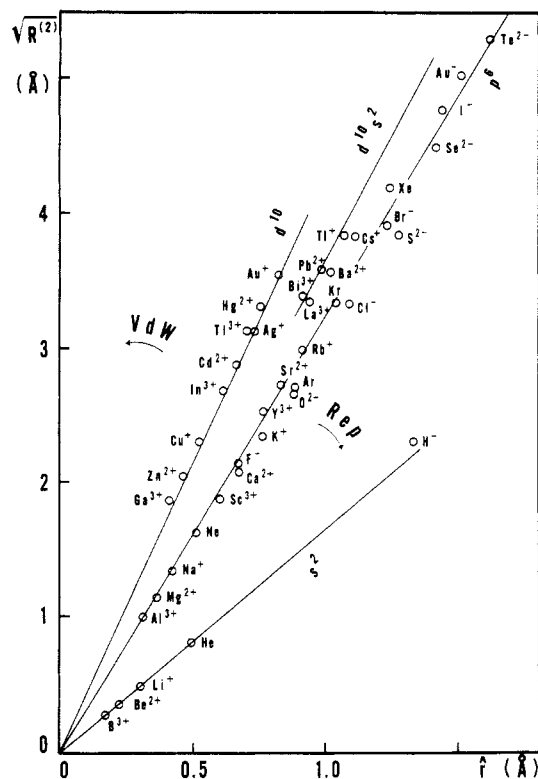
(35) D. C. Grahame, *J. Chem. Phys.*, **18**, 903 (1950).

(36) J. Malsch, *Phys. Z.*, **29**, 770 (1928); **30**, 837 (1929).

(37) We note that  $\epsilon^G(r)$  in Figure 2 represents Grahame's "integral" permittivity used in the Born model. This is in contrast to the "differential" permittivity displayed in Grahame's figure (ref 35).

(38) D. M. Ritson and J. B. Hasted, *J. Chem. Phys.*, **16**, 11 (1948).

(39) C. W. Kern and M. Karplus in *Water*, Vol. 1, F. Franks, Ed., Plenum, New York, 1972, Chapter 2, pp 21-91.



**Figure 4.** Root total second orbital moment,  $[R^{(2)}]^{1/2}$ , vs. first orbital moment of the outermost orbital,  $p$ , of closed-shell ions and atoms. (For ions with outermost  $d^{10}s^2$  shells  $\bar{p}$  denotes the average of the first moments of an outermost  $d$  and  $s$  orbital.) The slope of a line from the origin to an ion's position in the chart indicates a dominance of van der Waals attraction (VdW) or short-range repulsion (Rep). All moments are calculated from first principles in local density approximation (see ref 26).

is  $\sim 2.8$  Å, this means that only the electrostatic contribution from the closest shell of surrounding water molecules depends sensitively on the actual version of the permittivity  $\epsilon(r)$ .

Fitting  $\Delta G_{el}$  to the experimental hydration energy of  $H^+$  gives  $r_c(H^+) = 0.35$  Å. With  $\Delta r = 0.35$  Å in eq 18 for univalent cations we obtained electrostatic hydration energies  $\Delta G_{el}$  for  $Li^+$  through  $Cs^+$  listed in Table I. According to eq 17, we regard the differences between  $\Delta G_{el}$  and the experimental  $\Delta G$  as the net contribution from short-range interaction to hydration energies  $\Delta G_{sr}$ . A division of Gibbs free energy into electrostatic and short-range contributions has been previously considered by Haugen and Friedman<sup>40</sup> for transfer of alkali metal perchlorates and perchlorates between water and nitromethane. However, no interpretation of their finding of more negative short-range energies for larger ions was offered. The  $\Delta G_{sr}$  values for alkali-metal ions in Table I are found to be very small. This can be interpreted as an almost complete cancellation of repulsive and attractive short-range interaction between hydrated alkali-metal ions and surrounding water molecules.

The large negative  $\Delta G_{sr}$  of  $Ag^+$  represents a dominance of short-range attraction. It is likely that this results from strong van der Waals interaction between  $Ag^+$  and surrounding water molecules. This point of view is supported by the finding of very strong van der Waals interaction in silver halides<sup>41</sup> and by an analysis<sup>26</sup> of the ionic radius and orbital moments of  $Ag^+$ . In the latter study we found that a dominance of either van der Waals attraction or short-range repulsion in the bonding of closed-shell ions is indicated by the ratio  $q$  between the root total second orbital moment,  $[R^{(2)}]^{1/2}$ , and the first moment of the outermost orbital,  $\bar{p}$ . This ratio  $q$  is shown by the slope of a line from the origin to an ion's position in Figure 4. According to this figure, we can expect a dominance of van der Waals attraction not only for  $Ag^+$

but also for other ions with outermost  $d^{10}$  shells. In contrast to  $Ag^+$ , we find in Table I the short-range energy  $\Delta G_{sr}$  of  $Tl^+$  only slightly attractive. This finding agrees qualitatively with smaller  $q$  values (flatter slope) in Figure 4 for ions with outermost  $d^{10}s^2$  shells.

Lacking a criterion to determine  $r_c$  for halogen ions, we used the same  $\Delta r = 0.35$  Å as for univalent cations. This gives in Table I strong short-range attraction  $\Delta G_{sr}$  for  $F^-$ . We have no explanation for this behavior of  $F^-$ . Moderate attractive terms are found for  $Cl^-$  and  $Br^-$  while for the large  $I^-$  ion short-range repulsions and attractions cancel almost completely. This trend agrees with the behavior of the alkali-metal ions for increasing ionic radii.

We assumed the same trend for alkaline-earth ions ( $Z = 2$ ) and determined  $\Delta r$  such that  $\Delta G_{sr}$  became smaller for large ions. We found that this was best satisfied with  $\Delta r = 0.17$  Å which is about half of  $\Delta r$  for univalent ions. This gives very strong and fairly strong repulsive  $\Delta G_{sr}$  for the small cations  $Be^{2+}$  and  $Mg^{2+}$ , respectively, but only small short-range terms for the larger alkaline-earth ions.

Using the same  $\Delta r = 0.17$  Å for divalent cations with partly filled 3d shells yields increasing attractive  $\Delta G_{sr}$  contributions for  $Mn^{2+}$  through  $Cu^{2+}$  (see Table I). Because of the open d shells, covalent bonding may contribute to these values. The sequence  $Zn^{2+}$ ,  $Cd^{2+}$ , and  $Hg^{2+}$  shows a dramatic increase of short-range attraction which is likely to result from strong van der Waals interaction due to the ions' outermost closed d shells. The attractive  $\Delta G_{sr}$  term for  $Pb^{2+}$ , on the other hand, is comparatively moderate and may originate, as in the case of  $Tl^+$ , from the ion's outermost  $d^{10}s^2$  shell.

Considerable short-range attraction was finally obtained (using again  $\Delta r = 0.17$  Å) for  $S^{2-}$ . This is not too surprising considering a larger van der Waals contribution than for the isoelectronic  $Cl^-$  ion and the amplified effect of short-range interactions among divalent ions. The significance of this value, however, requires further investigation.

## Conclusion

The simple Born model for ion hydration, eq 1, accounts only for the electrostatic interaction between a hydrated ion and all surrounding water molecules. Any contributions from short-range interactions are neglected. The use of the macroscopic permittivity  $\epsilon_0$  in the Born model must be regarded as an approximation for the actual distance-dependent permittivity  $\epsilon(r)$ . As we see in Figure 2, the quantity  $\epsilon(r)$  remains close to  $\epsilon_0$  as we approach a hydrated ion up to surprisingly small distances in the range of 10–20 Å. With closer approach,  $\epsilon(r)$  drops drastically to the high-frequency value  $\epsilon_\infty$  according to dielectric saturation. From Figure 3 we see that the effect of this saturation on the electrostatic contribution to the hydration energy  $\Delta G_{el}$  concerns significantly only the region from 1 to 3 Å. However, this small region which corresponds to the innermost shell of surrounding water molecules accounts for up to half of the total electrostatic energy contribution  $\Delta G_{el}$ .

The linear relations between Born radii, obtained from eq 1 and experimental values of  $\Delta G$ ,  $\epsilon_0$ , and actual crystal radii of alkali-metal and halide ions, which were discovered by Voet<sup>4</sup> and Latimer et al.<sup>5</sup> have been considered by several authors as a means for deriving molecular properties. Latimer et al. interpreted their findings through the asymmetric location of the center of the permanent dipole moment within the water molecule. Other investigators<sup>10–14</sup> used this relation for insight into the structural configuration of the water molecules. Their conclusions were based on the assumption of integer hydration numbers or molecular voids around hydrated cations.

We think that Born radii cannot provide reliable information about length-related molecular quantities because of the neglect of the short-range interaction and the use of the macroscopic permittivity  $\epsilon_0$  in the simple Born model. If, however,  $\epsilon_0$  is replaced by a distance-dependent permittivity  $\epsilon(r)$ , we can formulate an improved expression for the electrostatic contribution  $\Delta G_{el}$  given by eq 16. This term still contains a microscopic quantity  $r_c$  which is beyond the electrostatic-statistical framework. Only if we can

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(41) M. Bucher, *Phys. Rev. B: Condens. Matter*, **30**, 947 (1984).

make reasonable assumptions for  $r_c$  are we able to obtain useful information about the short-range contribution  $\Delta G_{sr}$  due to eq 17.

With our special assumptions for  $r_c$  of univalent cations based on the hydration energy of  $H^+$ , we find that, for cations with closed p shell, repulsive and attractive short-range contributions actually cancel almost completely (see Table I). The fact that for these ions the hydration energy is essentially electrostatic in nature,  $\Delta G \cong \Delta G_{el}$ , may explain the approximately linear relation between Born and Pauling radii of alkali-metal, alkaline-earth, and halide ions discovered by several authors.<sup>4-9</sup>

The remaining ions which were avoided in most former investigations deviate from this linear relation. From the  $r_B$  vs.  $r_P$  plot in Figure 1 we get a qualitative measure for the dominance of short-range attraction if cations fall below the straight-line region associated with closed p-shell ions. The quantitative es-

timates of the net short-range interaction  $\Delta G_{sr}$  between these ions and surrounding water molecules show three features. First, overall short-range attraction increases with increasing numbers of electrons in the open d shells of transition element ions. Second, the ions with outermost closed d shells,  $Ag^+$ ,  $Zn^{2+}$ ,  $Cd^{2+}$ , and  $Hg^{2+}$ , show very large short-range attraction. This behavior is interpreted as a dominance of van der Waals interaction. Finally, moderate short-range attraction is found for  $Tl^+$  and  $Pb^{2+}$  which have outermost closed s shells and lower lying closed d shells. We interpret this finding as a reduction of large van der Waals attraction by considerable short-range repulsion as indicated by the trend of orbital moments in Figure 4.

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## Core Electron Spectroscopy of Hydrated Ions

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We have calculated hydration energies of core-ionized and Auger-state ions with an electrostatic model using the distance-dependent permittivity  $\epsilon(r)$  of the surrounding dielectric medium before photoionization. Overall agreement between theory and recent experiments is good. The same electrostatic formalism is used to calculate differences in the extraionic part of electron promotion energies between free and hydrated ions. The deviation of these quantities from experimental data on core ionization is about 4 eV for several ion families. We interpret this finding as an increase of core electron binding caused by expanded outer electron shells in hydrated ions.

### Introduction

The large significance of ion hydration in physical chemistry has challenged a great many studies, both experimental and theoretical, with particular emphasis on monatomic ions.<sup>1</sup> A central quantity is the ionic hydration energy  $\Delta G$ , which is commonly measured by thermochemical methods. Theoretical interpretations of measured  $\Delta G$  values and deduced hydration mechanisms are mostly based on modifications of the electrostatic Born model<sup>2</sup>

$$\Delta G = -\frac{1}{2} \frac{Z^2 e^2}{r_B} \left( 1 - \frac{1}{\epsilon_0} \right) \quad (1)$$

which uses the permittivity  $\epsilon_0$  of the solvent, a characteristic "ionic radius"  $r_B$ , and the ionic charge  $Ze$ . Here  $e$  is the elementary charge and  $Z$  is an integer.

Recently, Siegbahn and co-workers<sup>3-7</sup> have applied core electron spectroscopy to ions in solution. With this new technique the authors obtained data for temporary higher ionized states. Experimental conditions required organic solvents like glycol or

ethanol. The authors point out, however, that very similar results can be expected for hydrated ions. In such experiments ions are irradiated with X-rays of photon energy  $h\nu$ , and the kinetic energy  $E_{kin}$  of ejected core electrons is measured. The binding energy  $E_b$  of those core electrons is then determined with the photoelectric law

$$E_b = h\nu - E_{kin} \quad (2)$$

For later reference let us denote the difference between the binding energy of a core electron to an ion with charge  $Ze$  in solution and in a free (gaseous) state by

$$\Delta E_b = E_b^{liq} - E_b^{gas} \quad (3)$$

A core-ionized ion of charge  $(Z+1)e$  exists for only about  $10^{-15}$  s. The hypothetical hydration energy  $\Delta G^*$  for such an ion can be derived via a Born-Haber cycle (Figure 1) as

$$\Delta G^* = \Delta G + \Delta E_b \quad (4)$$

In this paper we present calculated  $\Delta G^*$  values and the extraionic contribution to  $\Delta E_b$  for monatomic ions in comparison with experimental data from Siegbahn et al.<sup>3-7</sup> Our approach is electrostatic using a distance-dependent permittivity  $\epsilon = \epsilon(r)$  derived from Debye's theory.<sup>8</sup>

The first quantity,  $\Delta G^*$ , can be divided into electrostatic and short-range contributions

$$\Delta G^* = \Delta G_{el}^* + \Delta G_{sr}^* \quad (5)$$

The electrostatic part,  $\Delta G_{el}^*$ , may be regarded as a generalization

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