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INVESTIGATIONS OF THE STRUCTURE, ENERGETICS, AND SPECTRA OF WATER CLUSTERS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

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*****

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"If it can not be expressed in figures, it is not science; it is an opinion."

- Robert Heinlein
ABSTRACT

The nature of water in combination with itself and solvated ions has been investigated in terms of structure and energetics. A PM3 investigation of neutral water clusters from the well known linear hydrogen-bonded dimer structure towards bulk has found several structural families that contribute to the global minimum energy clusters. At the trimer \((n=3)\), structures consisting of a single nearly planar ring form the most stable family. At \(n=6\), PM3 finds the "cage" structure determined by \textit{ab initio} methods and spectroscopic experiments. Structures consisting of stacked 4-, 5-, and 6-membered rings become the most stable from \(n=7\) to an undetermined size less than \(n\approx145\), where ice-like crystal structures overtake the stacked ring families. Use of the extrapolation of the ice-I\(h\) structures to bulk on an excess molecular binding energy per molecule basis has given a good calibration of PM3 total atomic binding energy values over the entire cluster range. PM3 finds energies that are 75\% of the experimental excess molecular binding energy across the entire cluster size regime on a per molecule basis.

A new value for the bulk single-ion solvation enthalpy and free energy for the proton in water from a method forced to yield maximum consistency with bulk has been determined from cluster data, \(-1148.7(2.1)\) kJ/mol and \(-1101(0.3)\) kJ/mol (e.s.d) respectively. A comparison with other reported values is included.
The emission of infrared light from collisionally activated H$_3$O$^+$($\text{H}_2\text{O}$)$_n$ clusters in a fast ion beam has been detected and a low resolution spectrum obtained. The spectrum through the O–H stretching region is in good agreement with spectroscopic data. The application of an electrostatic particle guide (EPG) to a fast ion beam is explored with the ultimate goal of achieving greater photon collection efficiency and longer times in front of the detector. A total undispersed emission of $\sim$1pW has been found with an EPG apparatus.
For Joanie
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TABLE OF CONTENTS

Dedication ..................................................................................................................................iv
Acknowledgments ......................................................................................................................v
Vita ..............................................................................................................................................viii
List of Figures ...........................................................................................................................xi
List of Tables ...........................................................................................................................xix

Chapter 1. Water Cluster Families and Their Trends Toward Bulk Structures ...............................................................1
  1.01 PM3 Calculations ...............................................................................................................3
  1.02 Plots of Excess Cluster Binding Energy vs. \(n^{1/3}\) ........................................................4
  1.03 General Fit Expression ...................................................................................................6
  1.04 Water Dimer .....................................................................................................................7
  1.05 Chain Structures ................................................................................................................8
  1.06 Ring Structures ..................................................................................................................9
  1.07 The Hexamer Case .........................................................................................................10
  1.08 Stacked Cube Structures ...............................................................................................12
  1.09 Other Stacked Structures .............................................................................................14
  1.10 Hexagonal Ice Structures ............................................................................................15
  1.11 Cubic Ice Structures .......................................................................................................18
  1.12 Empty Clathrate Cages .................................................................................................22
  1.13 Ab Initio Results ...........................................................................................................23
  1.14 Discussion .....................................................................................................................25
  1.15 Conclusions ..................................................................................................................31
  1.16 References ....................................................................................................................32

Chapter 2. Single Ion Bulk Solvation Enthalpies and Free Energies of Selected Halide Ions, Hydroxide, and Alkali Metal Ions from Cluster Studies ...............................................................61
  2.01 Thermodynamic Conventions for the Electron ............................................................63
  2.02 Cluster Viewpoint of Bulk Solvation Enthalpies ..........................................................66
  2.03 Previous Bulk Single-Ion Solvation Methods ...............................................................72
  2.04 Coe's Difference-Over-Sum Cluster Method ...............................................................74
  2.05 Linear \(\Delta H_{\text{sol,0}}\) vs. \(\Delta H_{\text{sol,5}}\) Method ...........................................................76
  2.06 The Y' Method .............................................................................................................80
  2.07 Discussion ....................................................................................................................84
# Chapter 3. Studies of Intense Ion Beams in an Electrostatic Particle Guide

- **3.01 Current System** ................................................................. 100
- **3.02 Simion Results** ................................................................. 103
- **3.03 Acceptance Angle** ............................................................ 105
- **3.04 Energy and Mass Dependence** ........................................ 106
- **3.05 Experimental Results** ...................................................... 108
- **3.06 Discussion** ........................................................................ 109
- **3.07 Conclusions** .................................................................... 110
- **3.08 References** ...................................................................... 111

# Chapter 4. Infrared Emission Spectra of H₂O⁺(H₂O)ₙ Clusters in Fast Ion Beams

- **4.01 Multiple Collision Analysis** .............................................. 125
- **4.02 Previous Results** .............................................................. 128
- **4.03 Circular Variable Filter** .................................................... 129
- **4.04 Discussion** ....................................................................... 133
- **4.05 Conclusions** ................................................................... 134
- **4.06 References** ..................................................................... 136

# Appendices

- **Appendix A - MathCAD Templates** ........................................ 143
- **Appendix B - Fortran Programs** ............................................. 161
- **Appendix C - Periodic Box Values in Hyperchem** ................ 176
- **Appendix D - Calculation of Cartesian Coordinates for Ordered Ice-Ih and Ice-Ic Crystal Unit Cells** ..................................... 179
- **Appendix E - Selected Hyperchem Files** ................................. 186
- **Appendix F - PM3 Calculated Binding Energies and Excess Binding Energies per Water Molecule for Selected Clusters** .......... 192

# List of References

- **List of References** ................................................................. 200
List of Figures

1.1 The minima for the water dimer, \((H_2O)_2\). The linear hydrogen bonded structure is the experimentally determined global minimum. ...........................................38

1.2 The alternating chain structure. Two orientations are shown for the hydrogen atoms not involved in hydrogen-bonding. The second structure was used by Suhai as his model, projected to infinite length, for ice-Ih. .............................................................................................................................................39

1.3 The bridging chain structure. Both the alternating and bridging chains are present in the ice structures, but in differing degrees. ..........................................................39

1.4 Excess binding energy plot for the chain families. The convergence of the curves at \(n=4\) is due to distortion of both families towards a similar structure. ...........................................................................................................................................40

1.5 The ring family structures. These are the minimum energy structures for the rings found by PM3. In each case, the individual water molecules donate one hydrogen bond and accept one hydrogen bond to form the “backbone” of the ring. ...........................................................................................................................................41

1.6 Several structural isomers of the tetramer. The cluster marked with the star is the minimum energy structure. .................................................................................................................42

1.7 Excess binding energy plot for the ring structures. Ring structures for \(n=3\ldots9\) have been calculated and plotted on the same scale as the chain structures presented previously. The upward bend to the plot at \(n>6\) is due to the “collapse” of the ring towards three-dimensional structures. .........................43

1.8 Comparison of four low energy hexamer water clusters. Four of the low energy configurations for \((H_2O)_6\) are shown with the PM3 calculated binding energy. Structure a, the “ring,” was originally predicted to be the global minimum, but recent calculations have shown the other three structures to be more stable. It is generally believed that the “cage” structure is the global minimum, but all three remaining structures are nearly equivalent in energy and the ordering becomes dependent on the calculation method. ....................................................................................................................44
1.9 Electron attachment mass spectrum of water clusters by Bowen, et al. For an electron to attach to a cluster, the electron must either be solvated or the cluster have a large dipole moment. The continuum of peaks at n≥11 is due to solvation of the electron. The isolated peaks at 2, 6, and 7 indicate the structures for the corresponding clusters must have a large dipole moment. The cyclic (H₂O)₆ structure has a small dipole moment, while the other, more three-dimensional, structures have PM3 calculated dipoles >1.7 debye.

1.10 Example stacked cube structures. The highly strained hydrogen bond angles are consistent throughout the structure which allows the fitting routine to be employed.

1.11 Excess binding energy plot for the stacked cube structures with the fitted curve. The stacked cube structures for n=8,12,...36, and 92 have been calculated and added to the previous plot of chains and stacked cubes. The extrapolation to bulk (n=0) is found to be -7.51 kcal/mol.

1.12 Excess binding energy plot for the stacked hexagons and pentagons. The clusters and fitted expressions for the stacked hexagons and pentagons has been placed on a plot with the stacked cubes shown previously. The pentagons become most stable at n≈28 and the hexagons become the minimum at n≈70. The extrapolated bulk values for the pentagons and hexagons is -7.56 and -7.60 kcal/mol respectively.

1.13 Comparison of the stacked pentagon and stacked cube decamers. The stacked pentagon decamer is more stable at n=10 despite the fact that the stacked cube family is more stable at that cluster size. The global minimum for water clusters overall does not follow one family in particular as the value of n is incremented, but in general follows the trends shown previously.

1.14 The crystal structure of ice-Ih. Normal hexagonal ice is comprised of sheets of fused hexagonal rings (top). The stacking of the layers form puckered hexagons in the conformational equivalent of the cyclohexane “boat” configuration (bottom). The c-crystal axis is unique in normal ice.

1.15 The minimum ice-Ih structure. The cluster shown is the minimum structure with the ice-Ih bonding pattern that does not contain waters with only one hydrogen bond. Note that all the hexagonal rings present are in the “boat” configuration.

1.16 Several ice-Ih structures. The shown structures of normal ice were used to determine the values of E₄, E₃, and E₂ for the family. These clusters also represent the smallest of the structures with values of n₄, n₃, and n₂ predicted by Eqs. (13), (14), and (15).
1.17 Excess binding energy plot for hexagonal ice structures. The ice-Ih structures and the fitted extrapolation to bulk is added to the previous plot for comparison. The PM3 predicted 0K bulk value for ice-Ih is -8.36 kcal/mol (compared to the experimental -11.3 kcal/mol). ........................................53

1.18 The minimum ice-Ic structure. The cluster shown is the minimum size structure for ice-Ic that does not contain molecules with only one hydrogen bond. Note that, unlike the normal ice structure, which contained all “boat” configuration hexagonal rings, all those present in this cluster are in the “chair” configuration ........................................................................54

1.19 The fitted ice-Ic structures. These clusters follow the general shape, that of the octahedron, of materials with the cubic-crystal type at bulk, cubic ice, diamond, and silicon. These were used for the determination of the values of $E_4$, $E_3$, and $E_2$ and were used to determine Eqs. (16), (17), and (18). .............................................................................................................55

1.20 Excess binding energy plot for cubic ice. The values and extrapolated curve for cubic ice has been plotted with the previous families. Note that the ice-Ic clusters are everywhere more stable than the hexagonal ice structures. The curve determines a bulk value of -9.09 kcal/mol. ...............................56

1.21 The minimum energy $(\text{H}_2\text{O})_{25}$ clathrate structure. This structure is a representative of the empty clathrate cages that form another family for analysis. ........................................................................................................................................57

1.22 Excess binding energy plot with the $(\text{H}_2\text{O})_{25}$ clathrate structure. ........................................58

1.23 Excess binding energy plot for several levels of ab initio calculation. The ring and early stacked cube structures were calculated and plotted at several levels of theory. The lower levels are shown to severely overestimate the value of the hydrogen bond as many of the clusters have calculated binding energies per molecule greater than bulk. The MP2/aug-cc-pVDZ curve from the data of Xantheas$^5$ is the closest to the predicted values from the scaled PM3 and could become better if BSSE counterpoise techniques are employed. ........................................................................59

1.24 Scaled excess binding energy plot. The values for the clusters and fitted curves were scaled globally by the value of $\alpha_{\text{PM3}}=1.35$. The hexagonal ice curve is forced to extrapolate to the experimental value of -11.3 kcal/mol. Cubic ice is predicted to be 0.97 kcal/mol more stable at 0K. ...............................60
2.1 Plot of the bulk single-ion solvation enthalpies determined with Morris' absolute value for the proton (-1103 kJ/mol) vs. the cluster solvation enthalpies for clusters with 5 water molecules. The positive and negative ions are grouped separately and display a different slope illustrating the two problems that must be overcome to achieve consistency of a particular absolute value of the proton with the cluster data set.

2.2 Plot of the bulk single-ion solvation enthalpies for clusters with Klots' absolute value for the proton (-1136.4 kJ/mol) vs. the cluster solvation enthalpies for clusters with 5 water molecules. Klots' chosen set of ions gives a fitted line successfully grouping the positive ions and selected negative ions onto a common line (albeit with a slightly increased slope over that of the positive ions alone). The strategy of eliminating OH$^-$ and F$^-$ from the process has not dealt successfully with the problem of a different slope for the negative ions, leaving the OH$^-$ and F$^-$ species as deviant without explanation.

2.3 Plot of the bulk single-ion solvation enthalpies determined with the Coe method's absolute value for the proton (-1152.5 kJ/mol) vs. the cluster solvation enthalpies for clusters with 5 water molecules. The large halides were left out of the fit because they are surface states at n=5 and will not exhibit the same functional dependence of stepwise hydration energetics as do the internalized ions. The included ions all fit very well to a common line with a slope very close (less than a 0.5% difference) to that exhibited by the positive ions alone.

2.4 The correlation of the Y' approximation and the bulk difference in ion volume for various pairs of alkali and halide ions. The value of Y' (-1152.1±1.8 kJ/mol) when the difference in bulk ion volumes is zero represents the best value of the proton’s hydration enthalpy upon invoking the Born concept that ions of the same volume have the same bulk solvation enthalpies.

2.5 The correlation of the Y' approximation and the bulk difference in ion solvation enthalpy. This correlation is very similar to that shown in Figure 2.4 regarding the position of ion pairs. The intercept value of (-1151.0±1.6 kJ/mol) is consistent with that determined by invoking the Born concept showing that, in general, ions of the same volume have the same cluster solvation enthalpies as well as bulk solvation enthalpies. The problem of the proton's bulk hydration enthalpy can be equivalently approached with the difference in bulk ion volumes or cluster solvation enthalpies.
2.6 The correlation of the Y' approximation and the difference in cluster ion solvation enthalpy vs. cluster size. This plot contains the same data as in Figure 2.5 except that the cluster size has been specified. If the Y' approximation is good at only one particular pair of ions, then each data set at a particular cluster size can be expected to share the good value in common. At each cluster size the data have been fit to a line by the method of least squares. The spread in these fitted lines vs. the difference in cluster ion solvation enthalpy was used to determine a most common value of \(-1148.7\pm2.1\) kJ/mol which represents our best determination of the absolute proton hydration value without invoking the Born concept. This value is consistent with the values determined previously that had invoked the Born concept. 

2.7 The correlation of the free energy or X' approximation with the difference in cluster ion solvation free energy vs. cluster size. These data show an even more commonly shared point of \(-1101.8\pm0.3\) kJ/mol which represents our best determination of the proton's free energy of hydration without invoking the Born concept. This value compares favorably to the center-of-weight of previous determinations providing confidence in the enthalpic results of Figure 2.6.

2.8 The dependence of the bulk constants, \(-\frac{1}{2}[k(A^+)+k(B^-)]\), on the difference in cluster solvation enthalpy vs. cluster size. The cluster approximation employed in the Y' approximation involves only the first term of Eq. (48) which is essentially zero at the common point, so that the proton's absolute value is determined almost entirely by the behavior of the bulk constants from Table 2.3 vs. the difference in cluster ion solvation enthalpy. Notice the linearity of the data sets at particular cluster sizes and the shared common point of \(-1149.1\pm2.0\) kJ/mol which is consistent with the previous determinations for the proton's absolute hydration enthalpy.

3.1 Diagram of the Kingdon Trap. Ions were generated internally and trapped into orbits about the central wire. The end caps restricted the ions axially.

3.2 Diagram of the current EPG system. Note the angle of the ion beam relative to the EPG.

3.3 Diagram of the vacuum chamber. Two 1500 L/s diffusion pumps, one water baffled, one l-N\(_2\), provided a base pressure of \(~5x10^{-5}\) Torr.

3.4 Gas rack plumbing diagram.

3.5 Kimble Physics pattern of holes for the elements of the ion beam. The lightly shaded holes were used for the primary support. Each hole is 0.3" center-to-center.
3.6 Typical Mass Spectrum obtained from the glow discharge source. The x-axis is measured in volts as the spectrum is from a Wein velocity filter. This also accounts for the non-linearity in mass.

3.7 Diagram of the source circuit. The voltage applied by the beam power supply determines the beam voltage and the discharge voltage determines the source brightness. The ballast resistance improves the steadiness of the beam output. The back plate is kept more negative than the front for maximum cluster products. Reversing this polarity will give electron bombardment ions.

3.8 Diagram of the ion optical element circuit. The series of resistors acts as a voltage divider for the beam voltage \( V_b \), adjustable by varying the position of the potentiometer inputs. This arrangement maintains a constant ratio between the voltage applied on the ion optical element and the beam voltage, despite any changes in \( V_b \).

3.9 Simion grid coordinates. The upper portion of the figure shows the potential surface of a cross-section of the EPG. The coordinate system and general layout of the Simion grid is shown in the lower portion. Note the exaggerated size of the central wire (2mm diameter in the simulation vs. ~0.04 mm for the actual device). This constraint was imposed for ion trajectory purposes as an ion is considered to have struck a surface and been neutralized only if the grid points immediately surrounding the ion all are contained by an electrode. The 2 mm diameter was the smallest available that would guarantee the correct ion behavior near the central electrode.

3.10 Potential plot inside the guide tube. The points are samples taken from the Simion simulation and were plotted as a function of radius. The solid curve is the predicted potential from Eq. (2).

3.11 Spot picture. The initial trajectories for the ions in the simulation were arranged to imitate the real size of the ion source. Each of the 5 points contained 10 rays varying in both the xy- and xz-plane.

3.12 Example trajectories from the simulation. The upper portion of the figure shows the typical spiral nature of the ion spot trajectories for the initial portion of the EPG. The lower plots are single ion trajectories viewed along the x-axis. The notation on each plot refers to the azimuth angle of each initial ion condition. Note that as the angle increases, the eccentricity of the ion “orbit” decreases.

3.13 Azimuth and elevation angle plot. A surface involving flight times as a function of azimuth and elevation angles for the initial ion trajectory for a given starting position. Note the narrow range where the ions are successfully transmitted down the length of the guide tube. The symmetry of the plot confirms that the direction of the spiral is unimportant.
3.14 Time of flight plot. Several single ion trajectories involving ions of different masses are shown. The linearity shows that the EPG is functioning in the same manner as a time-of-flight mass spectrometer, despite its inherent curved trajectories. The ions followed the same path and struck the Faraday tube in the same spot regardless of the mass. ..........................................................121

3.15 Transmission window. Single ion trajectories were performed as a function of radial position and ion energy for a given set of input angles. The upper surface plot shows the flight time throughout the range studied. Note that the flight time dramatically increases as the wire is approached. The lower plot shows the same plot as a single-line contour around the base of the surface. Three failure modes have been identified for ion transmission. The “Wire Shadow” is caused by the ions coming into contact with the central wire. This is exaggerated by the unphysical size of the simulation wire. The “Low V_y” failure involves the ions not possessing sufficient energy to overcome the fringe field of the guide tube and being repelled. “High V_y” refers to the ion energy being too great for the tube voltage to bend the ions into an orbit before striking the outer wall .............................................................................................................................122

3.16 Oscilloscope plot of the modulated ion current. A trace of the experimental modulated ion current at the Faraday tube of the EPG. The modulation square wave was set to 100 Hz and a 1kΩ input impedance was used resulting in the y-axis being 1 mV equal to 1 mA of ion current. The arrows denote the points where the modulation voltage changed. The delay was measured as ~25 μs. ..........................................................123

4.1 Multiple collision analysis of H_3O^+(H_2O). The data points and the fit that produced the value for r, the fraction of the original ion beam that underwent one glancing collision, did not dissociate, and reached the end of the beam path. The solid P* curve is the total fraction of the ion beam, at a given attenuation, that has underwent a collision and absorbed excess energy. The dash-dot curve labeled 1 is the contribution from ions that underwent a single collision, and the dash-dot curve labeled 2 is the result of 2 collisions and similarly for the CID curves (dashed). This analysis can be read as, on average, one collision does not dissociate the ion while 2 will cause dissociation. As the experimental dissociation energy for H_3O^+(H_2O) is 1.37 eV, a collision energy of ~1 eV can be concluded......................................................................................137

4.2 Original apparatus for finding total emission of infrared light. The ion beam was directed at through a set of 4 grounded rods towards a CaF_2 lens. After a short time (< 1 second), the lens charges and repels the beam as it exits the region bounded by the rods. The fact that the beam is “pointed” at the detector gives long times (~5μs) in the detector field of view. .........................................................................................................................................138
4.3 The undispersed infrared light detected from the emission of water clusters. When the ion source was turned off (labeled "beam off"), little light was observed on the detector. Turning the source on without adding collision gas ("gas off"), a light level of ~3 pW was detected. Addition of collision gas ("gas on"), although decreasing the total ion current in the photon collection area, raised the detected light to ~13 pW. Note that a large time constant, as evidenced by the long tail between "gas on" and "gas off," was applied to reduce the noise.

4.4 Diagram of the spectrometer. Ion clusters are extracted from the ion source and undergo glancing collisions with the argon introduced by a tube. The beam is amplitude modulated by a square wave sufficient to prevent ions from entering the photon collection region during the "high" portion of the wave. The emission from the ions, also modulated with respect to the photon collection region, passes through the circular variable filter and is focused on the InSb detector. The signal is then demodulated through a lock-in amplifier and the signal averaged over long periods of time.

4.5 Low resolution infrared emission spectrum of $H_2O'(H_2O)_n$. The background scan was produced using Ar as the source gas. The downward feature at 3000 cm$^{-1}$ common to both scans is an artifact of the circular variable filter. The excess light above 3300 cm$^{-1}$ is consistent with absorption measurements by Lee et al. Peak power is ~33 fW.

4.6 Typical mass spectrum from the ion source. The dispersive element is a Wein filter.

D.1 MathCAD generated positions of atoms in the unit cell. Note that the atoms marked H14 and H16 must be translated -1 unit cell lengths along the x-dimension to achieve a real bond distance.

D.2 Hyperchem graphic of the Ice-Ih unit cell.
List of Tables

1.1 Low lying local minima of water dimer. The molecular binding energy for three minima was calculated with three semi-empirical and one \textit{ab initio} method and compared to the experimental global minima, the linear hydrogen bonded structure. .................................................................8

1.2 The PM3 calculated excess molecular binding energy per water molecule \((E_{\text{ab}})\) for the alternating and bridging chain structures. .................................................................9

1.3 The PM3 calculated excess molecular binding energy per water molecule \((E_{\text{ab}})\) for the ring structures. ...................................................................................10

1.4 The numerical comparison of the PM3 calculated excess molecular binding energy per water molecule \((E_{\text{ab}})\) and the predicted value from the fit of the stacked cube structures. .......................................12

1.5 The numerical comparison of the PM3 calculated excess molecular binding energy per water molecule \((E_{\text{ab}})\) and the predicted value from the fit of the stacked pentagon structures. ...............................................13

1.6 The numerical comparison of the PM3 calculated excess molecular binding energy per water molecule \((E_{\text{ab}})\) and the predicted value from the fit of the stacked hexagon structures. .......................................15

1.7 The progression of water molecule types in ice-Ih. The fitting expression requires a mathematical expression for the number of water molecules in a particular structure that have 2, 3, or 4 hydrogen bonds \((n_2, n_3, \text{ and } n_4\) respectively) as the clusters grow towards bulk. The clusters used were constructed and the numbers in each category tabulated as a function of the “growth index,” or number of shells, \(S\) ................................................................................................16

1.8 The numerical comparison of the PM3 calculated excess molecular binding energy per water molecule \((E_{\text{ab}})\) and the predicted value from the fit of the hexagonal ice structures. .................................................................18

1.9 The progression of water molecule types in ice-Ic. The fitting expression requires a mathematical expression for the number of water molecules in a particular structure that have 2, 3, or 4 hydrogen bonds \((n_2, n_3, \text{ and } n_4\) respectively) as the clusters grow towards bulk. The clusters used were constructed and the numbers in each category tabulated as a function of the “growth index,” or number of shells, \(S\) ................................................................................................21
1.10 The numerical comparison of the PM3 calculated excess molecular binding energy per water molecule \( (E_{ab}) \) and the predicted value from the fit of the cubic ice structures. .................................................................22

1.11 Numerical results from PM3 and two STO-KG \((K=3,4)\) ab initio levels with MP2 corrections. ..................................................................................................................23

1.12 Numerical results from PM3 and several Gaussian-type orbital ab initio levels with MP2 corrections ...........................................................................................................................................24

1.13 Numerical results from PM3 and two basis sets of Dunning with MP2 corrections.........................................................25

2.1 Solvation free energy, \( \Delta G^\circ_{,water} \) (kJ/mol), and solvation enthalpy, \( \Delta H^\circ_{,water} \) (kJ/mol), to place a pair of oppositely charged, gas phase ions into water at 25 °C from tabulated free energies and enthalpies of formation (ref. 4). The values in parenthesis were not directly available from data in ref. 4. There were determined from the differences (Table 2-2) of values that were available........................................................................................................64

2.2 Bulk average differences (first ion-second ion) in the single ion bulk solvation free energies of similarly charged ions, \( \Delta G_{so}(\text{ion 1}) - \Delta G_{so}(\text{ion 2}) \), and enthalpies, \( \Delta H_{so}(\text{ion 1}) - \Delta H_{so}(\text{ion 2}) \), Uncertainties are not available for the values based on free energies and heats of formation (ref. 4) because this data has apparently been made internally consistent. Alternative cycles (ref. 21) can be employed for the enthalpies (values are given in the second row of each enthalpy set with 1\(^{st}\) standard deviations in parenthesis) suggesting that a range of uncertainties of 3-10 kJ/mol is reasonable for all of these values. ..................................................................................67

2.3 The bulk solvation free energy and enthalpy of various ions relative to \( \text{H}^+ \). ........................................................................................................68

2.4 Cluster ion solvation free energy and enthalpy partial sums of various ions vs. cluster size. Ion values have been averaged from the shown references. Entries in parenthesis are estimated from the expected trend to the known bulk value. ..................................................................................71

2.5 Ion radii as reported by Gourary and Adrian. .........................................................................................................................83

2.6 Slopes and intercepts of \( Y^\circ \) (or \( X^\circ \)) vs. the difference in cluster solvation enthalpy (or free energy) for different cluster sizes, n. Estimated standard deviations are given in parenthesis. ..................................................................................84

2.7 Single ion bulk solvation free energies and enthalpies from several different sources. Each data set has been used to generate data as in Table 2.1. The standard deviation of the comparison with the bulk experimental data in Table 2-1 is given as \( \sigma \) at the bottom. ........................................................................................................86

xx
C.1 Edge length to achieve a specified neutral water cluster size, \( n \) .........................................177
C.2 Edge length to achieve a specified \( X(\text{H}_2\text{O})_n \) cluster size where \( X \)
is a halide ion, alkali ion, \( \text{OH}^- \), or \( \text{H}_2\text{O}^- \) .................................................................178

D.1 Positions of unique atoms within the unit cell of ordered Ice-I\( h \)as reported by Leadbetter et al. Units are fractions of unit cell
ege length in each respective dimension. .................................................................181
D.2 Symmetry operations for the space group, \( Cm\bar{2} \). ..............................................................181
D.3 Generated positions of atoms in the unit cell. Shaded atoms are
in redundant positions. .................................................................................................182
D.4 Final generated atomic positions in Angstroms. .................................................................183
D.5 Crystallographic properties of ice polymorphs. Note the
difference in space group for Ice-I\( h \). This is the result of the
hydrogen positions determined in ref. (1). .................................................................183

F.1 PM3 values for the monomer, alternating chains, and bridging
chain structures studied in Chapter 1. .................................................................193
F.2 Rings and stacked cube structures. ...............................................................................194
F.3 Stacked pentagon and hexagon structures. ................................................................195
F.4 Partial stacked cube structures. ....................................................................................196
F.5 Hexagonal ice structures. .............................................................................................197
F.6 Cubic ice structures. .....................................................................................................198
F.7 Other structures. ..........................................................................................................199
CHAPTER 1

WATER CLUSTER FAMILIES AND THEIR TRENDS TOWARD BULK STRUCTURES

The nature of bulk water is difficult to describe. This has resulted in a large body of work in the realm of clusters. A simple electronic search of periodicals from 1968-1996 found 473 references to water clusters, 421 of which are in English. The goal of this work is to perform calculations on the neutral water clusters which are valid for the whole cluster size range from dimer to bulk. This “global view” of the effect of size is important as technology extends into the nanoparticle-sized region.

Early models of liquid water were divided into two broad categories. The continuum model was first expressed by Pople in 1951 and followed by the related “random network model” of Bernal in 1964. In both of these models, a continuous network of molecules with tetrahedral coordination occurring to the first neighbor is present. Beyond that neighbor, flexible hydrogen bonds deform to create a continuous distribution of O⋯O distances. Orentlicher used a similar approach, but allowed the hydrogen bonds to break rather than bend. Weres also used this basic idea to develop a thermodynamic lattice gas
model in 1972. Ohmine used networks of hydrogen bonds to describe collective motions in both liquid water and clusters.

Early versions of the mixture, or cluster, model, proposed by Frank and Wen, and Frank and Quist, dealt with “flickering clusters,” where an amorphous globular sample of water at any instant contained water monomers and short-lived hydrogen-bonded clusters at room temperature. Nemethy and Scheraga provided a variation of this in 1962. They proposed a mixture of species with two-, three- and four-coordination. Giguère and Dannenberg have also suggested that there is a significant fraction of species, possibly intermediates, where three-centered “bridging” hydrogen bonds are present as a defect, similar to the defect proposed by Dunitz to account for electrical conductivity in ice, in order to explain some molecular diffusion and rotation observations.

Symons has proposed interpretation of the properties of water in terms of concentrations of broken and unbroken hydrogen bonds. A statistical treatment by Hagler et al. is based on a distribution of water clusters centered at n=11. In a more recent development, Benson and Siebert have put forward the idea that the heat capacity data for water can only be modeled with discrete water clusters, in their theory, hydrogen-bound octamers. Support for this theory can be found in the infrared data of Libnau.

Water clusters are also becoming more prominent in several more recent problems. The unexpected absorption of sunlight by clouds, the “seeding” for water droplet growth, and some formation pathways for acid rain formation have also been
attributed to the contribution of small clusters of water. Naturally occurring airborne ice crystals are believed to be the cause of “haloes” seen around the sun at $22^\circ$, $46^\circ$ (hexagonal ice),$^{26}$ and $28^\circ$ (cubic ice).$^{27}$ These are examples of cases where knowledge of water clusters over a broad size range is of direct importance.

**PM3 Calculations**

An approach similar to this line of research, using PM3 for calculation of small water clusters, was undertaken by Vasilyev,$^{28}$ although this fact was unknown at the start of this work. The present results correspond to the reported global minimum except at $n=6$. The $n=1-16$ results presented here that matched the earlier work of Vasilyev were originally calculated by Muhammed$^{29}$ although vibrational frequencies were included in the later work.

The advent of affordable, high speed personal computers and commercial software packages has opened an avenue of research to scientists interested in comparing their results with those obtained by theoretical/computational chemistry. For clusters of even moderate size, however, *ab initio* methods become very time consuming and give artificially large molecular binding energies at even modest levels of theory, i.e. MP2/6-31G**, if more than one molecule is involved.$^{30}$ It has been shown that, in order to get a reasonable answer for water clusters, large basis sets are required, greatly multiplying the computational time required.$^{31}$ Semi-empirical methods, such as AM1$^{32}$, SAM1$^{33}$, and PM3$^{34-36}$, are better able to handle large cluster sizes, but some questions have been raised about their ability to calculate accurately the molecular binding energy of clusters.$^{37,38}$ A comparison of these
and several \textit{ab initio} methods for strong and moderate hydrogen bonds, albeit hydrocarbon-water and molecular ion-water interactions, is reported by Zheng and Merz.\textsuperscript{39}

The PM3 calculations in this work were performed on several P166 computers with the Hyperchem\textsuperscript{40} molecular modeling program. This program provides a graphical interface and a convenient method for manipulation of the positions of the constituent atoms or molecules in a cluster.

\textbf{Plots of Excess Cluster Binding Energy vs. }n^{-1/3}

The PM3 calculation of all the clusters in this study, being semi-empirical and only dealing with valence electrons, does not calculate a total electronic energy. The value reported by the calculation is the atomic binding energy. This number is not in and of itself useful for comparison to other methods, but calculation of the excess molecular binding energy per water molecule, $E_{\text{ab}}$, via the expression

$$E_{\text{ab}} = \frac{E_{\text{ab}} - nE_w}{n},$$

where $E_{\text{ab}}$ is the total atomic binding energy determined by the calculation, $E_w$ is the binding energy of a single water molecule from the same calculation method (-217.22 kcal/mol for PM3), and $n$ is the number of waters in the cluster, allows any \textit{ab initio} or semi-empirical calculation to be directly compared to these results.\textsuperscript{41}

The choice of $n^{-1/3}$ as the ordinate is from the relation of the radius of a sphere to the volume. Consider a property of a spherical cluster with $n$ molecules that varies with the
radius, $R$, such as the Laplace equation for the additional pressure inside a spherical cluster or drop,$^{42}$

$$P^{(d)} - P^w = \frac{1}{R} 2\gamma$$  

(2)

where $\gamma$ is the bulk surface tension, and each constituent of the cluster occupies a given, constant, volume, $V_s$. Note that the interstitial volume is counted as part of the occupied volume of the constituents. The volume of the cluster can be approximated as

$$V_{\text{Cluster}} = n V_s$$  

(3)

Substitution of the volume expression for a sphere yields,

$$\frac{4}{3} \pi R^3 = n \frac{4}{3} \pi r_s^3$$  

(4)

where $r_s$ is the effective radius of the molecule.$^{43}$ Simplification of Eq.(4) gives the expression,

$$R = r_s n^{\frac{1}{3}}$$  

(5)

Rearrangement gives,

$$n^{\frac{1}{3}} = \frac{r_s}{R}$$  

(6)
If the radius of the cluster, $R$, is equal to $r$, one molecule is present and $n^{1/3}$ is unity. If the cluster gets very large, i.e. $R \gg r$, and bulk is approached, $n^{1/3}$ approaches zero. Clusters do not necessarily have a spherical shape, especially at small $n$, and, as such, will not always resemble uniform spheres. This approach is an approximation only, but represents a convenient method for extrapolation of a property, such as internal pressure, to bulk.

**General Fit Expression**

If the total atomic binding energy of a cluster is considered to be the result of contributions of the water molecules with one, two, three, and four hydrogen bonds and all the molecules in each category are considered equivalent throughout the family, the general equation to which all the clusters are fit is given by

$$E_{ab,Family} = \sum_{i=1}^{4} n_i E_{i,Family}$$  \hspace{1cm} (7)

where $E_{ab,Family}$ is the calculated PM3 energy of a cluster in the designated family with $n_i$ ($i=1-4$) water molecules, each with $i$ hydrogen bonds, and $E_{i,Family}$ is the fitted value for the energy of one water molecule in the cluster with $i$ hydrogen bonds in that family. The quality of the fit is given by calculating the predicted $E_{ab}$ for each cluster in the fit and calculating the estimated standard deviation

$$\sigma = \sqrt{\frac{\sum_{j=1}^{N_{points}} (E_{ab,j} - E_{fit,j})^2}{N_{points} - N_{parameters}}}$$  \hspace{1cm} (8)
where $\sigma$ is the error in the fit, $N_{\text{points}}$ is the number of clusters used in the fit, $N_{\text{parameters}}$ is the number of parameters being fit (in this instance, it is numerically equal to the number of categories of water molecules present, i.e. 1-4), $E_{\text{ab}}$ is the PM3 energy of the $j$-th cluster, and $E_{\text{fit}}$ is the predicted energy of the $j$-th cluster.

**Water Dimer**

The water dimer is one of the most studied clusters. The existence of associated water molecules in the gas phase was first put forward by Pimentel\textsuperscript{45} from PVT observations of vapor. Many theoretical studies\textsuperscript{15, 32, 46-66} and experiments\textsuperscript{67-71} have been performed to determine the structure and binding energy of this species. The dimer has been found to have three distinct minima, shown in Figure 1.1, of which experimental evidence\textsuperscript{69, 72} has shown the linear hydrogen bonded structure to be the global minimum. Table 1.1 shows the minimized molecular binding energy relative to the global minimum for three semi-empirical methods (MNDO, AM1 and PM3) and a moderate level \textit{ab initio} calculation (MP2/6-31G**). One of the primary reasons for the choice of PM3 as the method for this work is the fact that it predicts the linear hydrogen bonded structure to be most stable, in agreement with \textit{ab initio} and experimental results. Zheng and Merz\textsuperscript{39} found good correlation between PM3 and \textit{ab initio} to be the case over a wide range of compounds and ions with a single water molecule.
Table 1.1. Low lying local minima of water dimer. The molecular binding energy for three minima of the dimer was calculated with three semi-empirical and one *ab initio* method and compared to the experimental global minima, the linear hydrogen bonded structure.

### Chain Structures

Chains of hydrogen-bound water molecules represent the lowest stability, or highest energy, family of small clusters that contain a global minimum structure at a given cluster size, n, the water dimer, (H\(\text{2}\text{O})\(_2\)). Some chain structures have been explored by *ab initio* methods as they grow by Ojamäe and Hermansson.\(^{73}\)

Two distinct repeating structures exist for the chains. The first, more stable, system, denoted as the "alternating chain," is one where each water molecule in the chain contributes one hydrogen to the chain structure (Figure 1.2). Each water in this family (excepting the terminal molecules) donates one hydrogen and accepts one hydrogen to the "backbone" of the chain. The second structure, the "bridging chain," involves 50% of the waters contributing one hydrogen to the chain, 25%, two hydrogen atoms, and 25%, zero, in the following pattern: ...1,2,1,0,1,2,1,0... (Figure 1.3). A mixture of these two extremes is possible, but these chains can be broken down into segments of these base structures in much the same way a vector can be given by the sum of orthogonal vectors along the axes of a coordinate system.
<table>
<thead>
<tr>
<th>n</th>
<th>PM3 Excess Molecular Binding Energy</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Alternating Chain</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>-2.72</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>-2.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>-3.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>-3.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>-3.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>-3.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bridging Chain</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-2.62</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-2.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-2.92</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-2.83</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-3.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-2.92</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1.2. The PM3 calculated excess molecular binding energy per water molecule ($E_{wb}$) for the alternating and bridging chain structures.

The PM3 results for these structures are given in Figure 1.4 and Table 1.2. The "convergence" of the 2 families at n=4 is due to similar distortions of both chains toward a ring-like configuration.

**Ring Structures**

Cyclic water structures, being easily accessible due to their small size, are among the most computationally studied clusters. The infrared spectroscopy experiments of Saykally et al. have confirmed the theoretical prediction that the ring system of structures becomes the global minimum at n=3. These minimum energy structures (Figure 1.5 and Table 1.3) consist of a ring where each water contributes one covalently bound hydrogen to the backbone. The orientation of the hydrogen atoms not hydrogen-bonded is the determinant between several energetically near-equivalent structures (Figure 1.6).

The general fitting routine breaks down in this case. While each water molecule present is "2-bonded," the hydrogen bonds are not consistent from one structure to another.
Table 1.3. The PM3 calculated excess molecular binding energy per water molecule (E_{ab}) for the ring structures.

<table>
<thead>
<tr>
<th>n</th>
<th>PM3 E_{ab}</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>-3.36</td>
</tr>
<tr>
<td>4</td>
<td>-4.59</td>
</tr>
<tr>
<td>5</td>
<td>-4.77</td>
</tr>
<tr>
<td>6</td>
<td>-4.91</td>
</tr>
<tr>
<td>7</td>
<td>-4.87</td>
</tr>
<tr>
<td>8</td>
<td>-4.86</td>
</tr>
<tr>
<td>9</td>
<td>-4.77</td>
</tr>
</tbody>
</table>

There exists in these structures (up to n = 6) varying O⋯O⋯O angles and, as a result, varying degrees of strain in the hydrogen bonds, introducing an angular dependence in the energy not covered by the general expression.

The ring excess binding energy curve, shown in Figure 1.7, also bends towards lower stability, higher energy, beyond n = 6. Closer examination of the PM3-minimized structures reveal that these large rings tend to “buckle” towards more three-dimensional shapes.

The Hexamer Case

It has been shown \(^{38, 46, 81, 82, 91, 92}\) that the global minimum structure for n = 3-5 is a ring and n ≥ 7 form more three-dimensional structures. One of the issues in the cluster community is the structure of the hexamer, (H\(_2\)O)_6. Theoretical studies, separately by Kim\(^{92}\) and Campbell\(^{81}\), have predicted the cyclic S\(_6\) symmetry structure (Figure 1.8a) to be the global minimum. Others\(^{82-84, 93, 94}\) have predicted more three-dimensional, non-cyclic, structures to be most stable. Jordan\(^{38}\), in his work utilizing TIP4P potentials, identified 137 distinct minimum energy structures, which were further grouped into 10
classes determined by the numbers of three-, four-, five-, and six-membered rings (based on the oxygen atoms) present in the structure. The calculations of this work, though not as exhaustive for this one case, generally agree with the relative ordering determined by Jordan.

Both methods identify the "cage" structure (Figure 1.8b) as the most stable, in agreement with experimental results by Saykally. The slightly less stable structures differ between the two methods. Jordan reported a "prism" structure (Figure 1.8c) while PM3 finds the "book" structure (Figure 1.8d) to be the next more stable structure. The differences between all 3 of these structures is small (<1 kcal/mol in total atomic binding energy) and slight variations in the basis sets makes an absolute computational prediction difficult. In this case, it is known that TIP4P overestimates the strength of a hydrogen bond (6.4 kcal/mol compared to an experimental 5.4 ± 0.7 and 5.4 ± 0.2 for the dimer binding energy) and the greater number of such interactions in the "prism" structure could lead to an over-estimation of the binding energy despite the greater "strain" of the hydrogen bonds (average O−H⋯O angle is ~148° for the "prism" versus ~154° for the "cage") in the structure. While none of these structures are either "ring"- or "stacked cube"-like, the "book" is a member of the stacked cube family (a cube of 8 water molecules with an edge removed). The experimental evidence that the ring structures are not the global minimum at n=6 is the dipole moment and infrared spectroscopy. Bowen, in electron attachment experiments, found strong mass spectrometric peaks of (H₂O)ⁿ at n=2, 6, and 7, and the complete series at n≥11 as shown in Figure 1.9. For a cluster to bind an excess electron, a large dipole must be present, or the electron must be internalized, as is the case for the larger clusters. The exact dipole value required is an open question and is
probably a function of cluster size. For the hexamer, the cyclic structure has a PM3 dipole moment of only 0.21 debye, compared to values of 1.92, 2.61, and 1.71 debye for the “book”, “prism”, and “cage” structures respectively. This would seem to preclude the ring as the dominant form experimentally, but the large dipole of the remaining structures makes a conclusion about the actual structure difficult to make from this data alone. In recent vibration-rotation-tunneling work, Saykally\textsuperscript{95} has found the spectrum for the hexamer to be most consistent with the “cage” form.

**Stacked Cube Structures**

Stacked cube structures, rings of 4 water molecules aligned with each other (with related structures having less than 4 waters in the last ring), become the global minimum structure at \( n = 7 \). The complete cube at \( n = 8 \), in particular, as been the subject of extensive studies.\textsuperscript{98-103} Examples of the calculated family of structures are shown in Figure 1.10.

<table>
<thead>
<tr>
<th>( n )</th>
<th>PM3</th>
<th>Prediction</th>
<th>( \Delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>-6.074</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>-6.503</td>
<td>-6.498</td>
<td>-0.005</td>
</tr>
<tr>
<td>16</td>
<td>-6.765</td>
<td>-6.768</td>
<td>0.003</td>
</tr>
<tr>
<td>20</td>
<td>-6.928</td>
<td>-6.929</td>
<td>0.001</td>
</tr>
<tr>
<td>24</td>
<td>-7.036</td>
<td>-7.036</td>
<td>0</td>
</tr>
<tr>
<td>28</td>
<td>-7.113</td>
<td>-7.113</td>
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</tr>
<tr>
<td>32</td>
<td>-7.171</td>
<td>-7.171</td>
<td>0</td>
</tr>
<tr>
<td>36</td>
<td>-7.216</td>
<td>-7.216</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 1.4. The numerical comparison of the PM3 calculated excess molecular binding energy per water molecule (\( E_{ab} \)) and the predicted value from the fit of the stacked cube structures. The octamer is not included in the fit because it lacks the highly "strained" internal rings and is more stable on a per molecule basis than the rest of the family.
Table 1.5. The numerical comparison of the PM3 calculated excess binding energy per water molecule ($E_{ab}$) and the predicted value from the fit of the stacked pentagon structures. The decamer was excluded from the fit because it lacks the higher “strain” of internal rings and is more stable on a per molecule basis than the rest of the family.

<table>
<thead>
<tr>
<th>n</th>
<th>PM3</th>
<th>Prediction</th>
<th>Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>-6.227</td>
<td>-6.599</td>
<td>-0.004</td>
</tr>
<tr>
<td>15</td>
<td>-6.603</td>
<td>-6.862</td>
<td>-0.004</td>
</tr>
<tr>
<td>20</td>
<td>-6.866</td>
<td>-7.031</td>
<td>0.001</td>
</tr>
<tr>
<td>25</td>
<td>-7.030</td>
<td>-7.139</td>
<td>-0.003</td>
</tr>
<tr>
<td>30</td>
<td>-7.141</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The progression of the number of water molecules with 3 or 4 hydrogen bonds is a simple expression. The terminal rings each contain 4 molecules participating in 3 hydrogen bonds (8 water molecules total). The remaining, “internal,” molecules in the cluster (n-8 molecules) all have 4 “strained” hydrogen bonds. This gives the expression for the growth of stacked cubes as

$$E_{ab,SC} = 8E_{3,SC} + (n-8)E_{4,SC}$$

(9),

where $E_{4,SC}$ (the energy contribution of water molecules with four hydrogen bonds) and $E_{3,SC}$ (3 hydrogen bonds present) are -224.794(0.003) kcal/mol and -223.180 (0.002) kcal/mol respectively. These values contain the single water total atomic binding energy value of -217.22 kcal/mol as well as the fraction of the molecular binding energy that can be attributed to that type (n$_4$ vs. n$_3$) of water molecule in the cluster. The overall estimated standard deviation (c.e.d.) for the stacked cube fit, $\sigma_{SC}$, is 0.033 kcal/mol. The PM3 values for the family and the results of this fit are shown graphically in Figure 1.11 and in numerical format in Table 1.4.
Other Stacked Structures

The stacked cube structures represent the global minimum structures from $n \approx 7$ to an undetermined cluster size less than $\sim 145$, where the cubic ice becomes more stable. Four-member rings are not the only possible stacked structure in this range. Five- and six-membered rings also form families of similar binding energy on a per water molecule basis. These structures are shown on an excess binding energy plot with the stacked cube structures presented previously (Figure 1.12).

The fitting expressions for the stacked pentagons and hexagons are similar to those for the stacked cubes. For the pentagons, the equation becomes,

$$E_{ab,SP} = 10E_{3,SP} + (n-10)E_{4,SP}$$

with $E_{4,SP} = -224.899 (0.009) \text{kcal/mol}$ and $E_{3,SP} = -223.279 (0.006) \text{kcal/mol}$ respectively, and a bulk value of $-7.68 \text{kcal/mol}$. The overall error in the fit, $\sigma_{SP} = 0.072 \text{kcal/mol (e.s.d.)}$. These results are presented in Table 1.5. Similarly, the stacked hexagons are,

$$E_{ab,SH} = 12E_{3,SH} + (n-12)E_{4,SH}$$

with $E_{4,SH} = -224.883 (0.002) \text{kcal/mol}$, $E_{3,SH} = -223.479 (0.002) \text{kcal/mol}$ (see Table 1.6) and a value of $-7.67 \text{kcal/mol}$ at bulk. The error in this fit, $\sigma_{SH} = 0.016 \text{kcal/mol (e.s.d.)}$. 

14
Table 1.6. The numerical comparison of the PM3 calculated excess binding energy per water molecule ($E_{ew}$) and the predicted value from the fit of the stacked hexagon structures. The dodecamer was omitted because it lacked the highly “strained” internal rings of the rest of the family.

<table>
<thead>
<tr>
<th>$n$</th>
<th>PM3</th>
<th>Prediction</th>
<th>$\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>-6.406</td>
<td>-6.728</td>
<td>-0.003</td>
</tr>
<tr>
<td>18</td>
<td>-6.728</td>
<td>-6.727</td>
<td>0</td>
</tr>
<tr>
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</tr>
<tr>
<td>30</td>
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<td>0</td>
</tr>
</tbody>
</table>

The stacked pentagons do not, as a family, overtake the stacked cubes in binding energy per water molecule until $n \approx 28$ (according to their fit expressions), but at $n = 10$, the pentagonal structure is more stable (Figure 1.13). The stacked hexagons also overtake the stacked cube family in stability at $n \approx 45$, although it does not become more stable than the pentagon structures. This is due to the fact that the internal angle of a planar pentagon is closer to the tetrahedral 109.5° angle. It is interesting to note that a stack of the other “ring-like” hexamer structure, the “book” form (see the hexamer case section) is 5-6 kcal/mol less stable at $n = 12$.

**Hexagonal Ice Structures**

Normal, or hexagonal ice (sometimes denoted ice-I or, in this work, ice-Ih), is the dominant form of bulk, solid water from $-120^\circ$C to $0^\circ$C. This is the most common form of solid water found in nature and is final form of ice prior to melting (at atmospheric pressure). Small atmospheric ice crystals account for the observance of haloes about the
sun at 22° and 46° and may be responsible for larger than expected atmospheric absorption of sunlight.\textsuperscript{22}

Most of its properties have been interpreted in terms of its crystal structure and the forces present in the crystal lattice.\textsuperscript{104} The basic structure, first proposed by Bragg,\textsuperscript{105} is well established for ice-Ih just below the melting point,\textsuperscript{104} and recently, with a low temperature annealed crystal from neutron scattering experiments\textsuperscript{106}. Table D-6 (see Appendix D) lists the properties of ice-Ih and several other polymorphs.

In the bulk ice-Ih structure, each water molecule is hydrogen-bonded to the four nearest neighbors. The O–H bonds directed towards the lone pairs of two neighbors (forming O–H⋯O' hydrogen bonds) and the remaining neighbors reciprocate by directing an O–H bond towards the lone pairs of the oxygen under scrutiny (O⋯H–O' hydrogen bonds). The arrangement allows for 2 orientations, the hexagonal and cubic forms. The hexagonal arrangement, shown graphically in Figure 1.14, is an open lattice where the layers perpendicular to the z-axis (or c-crystal axis) consist of fused hexagonal rings in a conformation similar to the chair form of cyclohexane. The combined layers also result in hexagonal rings perpendicular to the z-axis, but these have the "boat" conformation. The structures utilized in this study were created from a large crystal based on the unit cell (See Appendix D). Excess molecules were then removed until a likely structure candidate was present. One boundary condition was used, however. A water molecule with only 1 hydrogen bond is very easily distorted from its "crystal" position and, as a result, none of the structures in this study contained such a water molecule. The smallest structure possible for this arrangement and boundary condition is a local minimum octamer, (H\textsubscript{2}O)	extsubscript{8}, shown in
Figure 1.15. At one point, this structure was purported\textsuperscript{107} to be the global minimum, although later work has since shown this not to be the case.

The sub-family of structures for determination of the constants $E_4$, $E_3$, and $E_2$ are shown in Figure 1.16. The structures are indexed by $S$, the number of "shells" of water present around a central water pair and the energy was fit to the expression,

$$E_{\text{Total, ice-Ih}} = n_4 E_{4, \text{ice-Ih}} + n_3 E_{3, \text{ice-Ih}} + n_2 E_{2, \text{ice-Ih}}$$

$$\hspace{2cm} (12).$$

The progression of $n_2$, $n_3$, and $n_4$ to bulk was determined from the smallest clusters in the sub-family. Table 1.7 shows the total $n$, and the number of waters in each cluster which participated in either 2, 3, or 4 hydrogen bonds respectively. These values were then used to obtain mathematical expressions, as a function of size (indexed by the number of "shells" in the cluster), for this subfamily:

<table>
<thead>
<tr>
<th>S</th>
<th>Total</th>
<th>$n_2$</th>
<th>$n_3$</th>
<th>$n_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8</td>
<td>6</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>34</td>
<td>12</td>
<td>14</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>152</td>
<td>30</td>
<td>50</td>
<td>72</td>
</tr>
<tr>
<td>3</td>
<td>402</td>
<td>60</td>
<td>98</td>
<td>244</td>
</tr>
<tr>
<td>4</td>
<td>832</td>
<td>102</td>
<td>158</td>
<td>572</td>
</tr>
<tr>
<td>5</td>
<td>1490</td>
<td>156</td>
<td>230</td>
<td>1104</td>
</tr>
<tr>
<td>6</td>
<td>2424</td>
<td>222</td>
<td>314</td>
<td>1888</td>
</tr>
</tbody>
</table>

Table 1.7. The progression of water molecule types in ice-Ih. The fitting expression requires a mathematical expression for the number of water molecules in a particular structure that have 2, 3, or 4 hydrogen bonds ($n_2$, $n_3$, and $n_4$ respectively) as the clusters grow towards bulk. The clusters used were constructed and the numbers in each category tabulated as a function of the “growth index,” or number of shells, $S$
Table 1.8. The numerical comparison of the PM3 calculated excess binding energy per water molecule ($E_{\text{th}}$) and the predicted value from the fit of the hexagonal ice structures.

<table>
<thead>
<tr>
<th>$n$</th>
<th>PM3</th>
<th>Prediction</th>
<th>$\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>-5.903</td>
<td>-5.943</td>
<td>0.040</td>
</tr>
<tr>
<td>34</td>
<td>-6.032</td>
<td>-6.070</td>
<td>0.038</td>
</tr>
<tr>
<td>48</td>
<td>-6.350</td>
<td>-6.290</td>
<td>-0.060</td>
</tr>
<tr>
<td>70</td>
<td>-6.565</td>
<td>-6.574</td>
<td>0.009</td>
</tr>
</tbody>
</table>

The results of this fit are shown in Table 1.8 and Figure 1.17. The values for $E_{4, \text{ice-ih}}$ and $E_{2, \text{ice-ih}}$ were found to be -225.578 (0.13), -223.468 (0.09), and -221.390 (0.19) kcal/mol respectively (recall the single water value is -217.22 kcal/mol). The error in this fit, $\sigma_{\text{ice-ih}}$, was found to be 1.4 kcal/mol (e.s.d.) and an extrapolated bulk value, $E_{\text{bulk,ice-ih}}$, of -8.36 kcal/mol. The slope in $n^{-1/3}$ space was found to be 11.7 kcal/mol, which can be considered a PM3 estimate of the surface tension for the sub-family.

**Cubic Ice Structures**

Cubic ice, often designated ice-Ic, is a low temperature, standard pressure, polymorph of solid water. It can be formed by warming amorphous ice (believed to be a glassy form
of water at low temperature, \(<133 \text{ K}\), from the deposition of water vapor). This
crystallization has been reported to occur at \(\sim 144 \text{ K}\)\(^{108}\) with an accompanying energy
release of 0.2-0.3 kcal/mol\(^{109, 110}\) but this transition has recently been reported to occur
anywhere from 143 K\(^{110}\) to 203 K\(^{111}\) dependent on the thermal history of the sample. It
can also be formed by condensation of water vapor onto a surface held between 133K and
153 K\(^{112}\) or by warming any of the quenched high-pressure ices\(^{113, 114}\). In any case,
further heating causes the ice-Ic sample to transform irreversibly to ice-Ih.\(^{104}\)

There is some speculation about the presence of cubic ice in nature. One of the earliest
observations, in 1629, that has been attributed to natural occurrence of this ice polymorph
is the rare “Scheiner’s halo” at an angle of \(\sim 28^\circ\) from the sun or moon.\(^{27}\) Halos due to ice
crystals in the upper atmosphere are not uncommon, but the hexagonal prism structure of
Ice-Ih gives the common halo angles\(^{26, 115}\) of \(\sim 22^\circ\) on the hexagon sides and \(\sim 46^\circ\) if the
ray passes through the 90° terminal face of the crystal (see Figures. 1-3 of reference 27).
The index of refraction of cubic ice has not been ascertained, but if it is similar to that of
ice-Ih, an angle near 28° is expected if the light passes through two sides of the crystal
sharing an apex.\(^{27}\) The rarity of Scheiner’s halo can be attributed to the relatively narrow
temperature range where laboratory experiments have found cubic ice to form on a
surface,\(^{112}\) but the fact that it is present for a very short time, on the order of a minute,
could also contribute to the lack of observations. The other tangible evidence comes from
the structure of some dendritic snowflakes, where the c-crystal axes of the arms are often at
70° to one another.\(^{116}\) While the physical properties of this crystal are that of ice-Ih, the
angle is atypical. One speculation\textsuperscript{117} is that the core of the flake is an octahedral crystal of cubic ice with the hexagonal ice growing from the surface of that internal structure.

Theoretical calculations have confirmed that this is a low energy interface.\textsuperscript{117}

The structure of cubic ice has been studied with X-ray\textsuperscript{118} and electron\textsuperscript{119, 120} diffraction techniques. The distribution of oxygen atoms is similar to that of ice-I\textsubscript{h} discussed previously. Each water molecule is tetrahedrally hydrogen bonded to its four nearest neighbors. Like the hexagonal structure, the molecules are arranged in layers. Also like the previous structure, the layers form hexagons perpendicular to the layers. These rings, however, are in the "chair" form in a lattice where the oxygen atoms are isostructural with the diamond lattice, unlike the ice-I\textsubscript{h} structure. The smallest structure possible, with the same boundary condition of eliminating structures with water molecules participating in a single hydrogen bond, is a local minimum decamer, (H\textsubscript{2}O)\textsubscript{10}, shown in Figure 1.18.

The minimized atomic binding energies for a sub-family of cubic ice were calculated and fit to the general expression given previously in Eq. (12) whereby the constants can be compared to the value for a single water (-217.22 kcal/mol). The structures used in this fit, shown in Figure 1.19, are the typical octagonal structure observed for a cubic crystal.\textsuperscript{27} The series of structures were generated by adding a shell to one of the "pyramid-like" sides and presented in Table 1.9. The number of molecules in each of the bonding categories is a function of the shell index, S and the number of molecules in each category (the number of waters with 2, 3, or 4 hydrogen bonds) was found to progress mathematically to bulk by the following equations:
Table 1.9. The progression of water molecule types in ice-Ic. The fitting expression requires a mathematical expression for the number of water molecules in a particular structure that have 2, 3, or 4 hydrogen bonds \((n_2, n_3,\) and \(n_4\) respectively) as the clusters grow towards bulk. The clusters used were constructed and the numbers in each category tabulated as a function of the “growth index,” or number of shells, \(S\).

\[
n_{4,\text{Ice-ic}}(S) = S + \left[ \sum_{j=1}^{S} 4(j - 1) + \left[ \sum_{i=1}^{j} 4(2i - 1) \right] \right]
\]

\[
n_{3,\text{Ice-ic}}(S) = 4(S + 1) + \sum_{i=1}^{S} 8(i + 1)
\]

\[
n_{2,\text{Ice-ic}}(S) = 6
\]

The constant value for \(n_2\) as a function of size is due to the fact that doubly hydrogen-bonded waters are only present at the corners of the octahedron.

The parameters, \(E_{4,\text{Ice-ic}}\), \(E_{3,\text{Ice-ic}}\), and \(E_{2,\text{Ice-ic}}\) were fit to Eq.(7) and yielded values of -226.31 (0.13) kcal/mol, -223.64 (0.07) kcal/mol, and -221.22 (0.12) kcal/mol respectively \((n_i=0)\). The overall error in the fit, \(\sigma_{\text{Ice-ic}}\), is 0.65 kcal/mol (e.s.d.) and the extrapolated bulk value, \(E_{\text{bulk,Ice-ic}}\), is -9.09 kcal/mol. The tabulated results are shown in Table 1.10 and displayed in Figure 1.20.
<table>
<thead>
<tr>
<th>n</th>
<th>PM3</th>
<th>Prediction</th>
<th>Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>-4.916</td>
<td>-4.970</td>
<td>0.054</td>
</tr>
<tr>
<td>18</td>
<td>-5.658</td>
<td>-5.627</td>
<td>-0.031</td>
</tr>
<tr>
<td>35</td>
<td>-6.374</td>
<td>-6.385</td>
<td>0.011</td>
</tr>
<tr>
<td>53</td>
<td>-6.709</td>
<td>-6.704</td>
<td>-0.005</td>
</tr>
<tr>
<td>84</td>
<td>-7.071</td>
<td>-7.072</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Table 1.10. The numerical comparison of the PM3 calculated excess binding energy per water molecule ($E_{\text{wb}}$) and the predicted value from the fit of the cubic ice structures.

**Empty Clathrate Cages**

Clathrates structures, particularly the $X$(H$_2$O)$_{20}$ species ($X$ is an associated atom, molecule, or ion) is of interest in a number of fields. The discovery of the extraordinary stability$^{121}$ of $\text{H}^+$(H$_2$O)$_{20}$ has been explained$^{122-126}$ as an H$_3$O$^+$ ion inside a clathrate cage with 20 water molecules. The empty cage structures have become increasingly of interest and have begun to receive attention from the theoretical community.$^{101-103, 127, 128}$

Graph theoretical work by Singer et al. has found 30,026 unique structures for the (H$_2$O)$_{20}$ cage (Figure 1.21) based solely on hydrogen bonding topologies which satisfy the Bernal-Fowler "ice rules." To date, the energy of 193 of the structures have been calculated and they span an estimated 53 kcal/mol range (total atomic binding energy) from least to most stable.$^{101}$ A similar analysis would yield a family of empty cages that could be analyzed in much the same way as the earlier families. While the empty cages are not necessarily of interest in and of themselves, knowledge of the cage can help sort out the factors contributing to the excess binding energy of a species associated with the cage. The addition of this clathrate cage to the excess binding energy plot is shown in Figure 1.22.
**Ab Initio Results**

Calculation of the excess binding energy per water molecule was performed with several levels of theory using *ab initio* methods. This is described in detail elsewhere.\textsuperscript{129} Gaussian94\textsuperscript{130} was utilized for all the calculations on three Pentium 166MHz personal computers and a RISC workstation.

Slater-type orbitals, STO-KG (K=3-4) basis sets,\textsuperscript{131-134} at the Möller-Plesset (MP2) level give values shown in Table 1.11. It has been shown that the larger expansion (K=4) is more suitable\textsuperscript{46} when long range interactions become important, specifically the case of hydrogen-bonded complexes, such as neutral water clusters.

<table>
<thead>
<tr>
<th>n</th>
<th>PM3</th>
<th>scaled PM3</th>
<th>STO-3G</th>
<th>STO-4G</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>-3.36</td>
<td>-4.47</td>
<td>-8.02</td>
<td>-8.57</td>
</tr>
<tr>
<td>4</td>
<td>-4.59</td>
<td>-6.10</td>
<td>-14.53</td>
<td>-15.64</td>
</tr>
<tr>
<td>5</td>
<td>-4.77</td>
<td>-6.34</td>
<td>-15.62</td>
<td>-16.73</td>
</tr>
<tr>
<td>6</td>
<td>-4.91</td>
<td>-6.53</td>
<td>-15.82</td>
<td>-16.94</td>
</tr>
<tr>
<td>7</td>
<td>-4.87</td>
<td>-6.48</td>
<td>-16.83</td>
<td></td>
</tr>
</tbody>
</table>

|          |       |            |         |         |
| Stacked Cube Structures |       |            |         |         |
| 6   | -5.04| -6.70      | -16.20  | -17.13  |
| 7   | -5.27| -7.01      | -16.97  | -17.98  |
| 8   | -6.04| -8.03      | -18.84  | -20.32  |

Table 1.11. Numerical results from PM3 and 2 STO-KG (K=3,4) *ab initio* levels with MP2 corrections.
Table 1.12. Numerical results from PM3 and several Gaussian-type orbital *ab initio* levels with MP2 corrections.

Gaussian-type orbital basis sets, 3-21G\(^{135-139}\) and 6-31G\(^{140-142}\) were also used to calculate the excess binding energy per water molecule at the MP2 level (Table 1.12).

Polarization functions for the higher level, both 6-31G* and 6-31G**,\(^{141, 143}\) were included in the study. These results are also tabulated in Table 1.6. Each succeeding level gives results that are higher energy (less stable) than the previous, approaching the PM3 and experimental values.

Finally, two basis sets of Dunning were used (for comparison to the results of Xantheas and Dunning). The cc-pVDZ and aug-cc-pVDZ sets,\(^{144-148}\) were utilized at the MP2 level to calculate the excess binding energy per water molecule (Table 1.13) and compared with the values derived from the binding energies reported by Xantheas.\(^{149}\) Table 1.6 lists the literature results reported as well as the point from this study that coincides with Xantheas.
Table 1.13. Numerical results from PM3 and two of basis sets of Dunning with MP2 corrections.

The $E_{ab}$ values determined by these calculations are presented graphically in Figure 1.23. The curve labeled "Scaled PM3" is discussed below.

Discussion

The intermediate region of the cluster regime is difficult to access with computational methods. The large size and number of conformers and structural isomers make \textit{ab initio} calculations, even with minimal basis sets, time- and computationally-intensive. While early versions of semi-empirical methods gave unacceptably large errors in bulk determinations of certain thermochemical properties, namely heats of formation and heat capacity, more recent methods, such as PM3, AM1, and some of the specialized water-water potentials give useful results and are able to extend the practical cluster size range available to computational analysis.

The PM3 results for $n \leq 8$ of this study yielded no surprising results. Vasilyev\textsuperscript{28} reported many of the same results in 1993. The inclusion of the chain structures may at first seem superfluous as only the dimer is a global minimum. However, Suhaï\textsuperscript{150} used an alternating
structure has been used, when projected to infinite length, as a model for ice. The dimer “chain” gave way to cyclic structures at n=3. The extensive studies of the dimer structure and energetics and the ready accessibility of the trimer to semi-empirical and \textit{ab initio} studies means this transition is well defined. When the cluster size reached n=6, the rings no longer represent the most stable, lowest energy, structural family. The stacked cubes, pentagons, and hexagons (all nearly equivalent in stability) become the global minimum at n=7, with a curve that slowly flattens as the effect of the three-bonded water molecules of the terminal rings becomes diluted in an ever-increasing number of four-bonded waters, extrapolating to bulk values of -7.57, -7.68, and -7.66 kcal/mol respectively.

At n≈145 and 1000, the ice structures, cubic and hexagonal respectively, overtake the stacked ring series in overall stability on a per water molecule basis. There exist a large number of structural sub-families that fit in each class of ice, making determination of the most stable sub-family difficult at best. The fitted sub-families represent one possible solution.

A problem arises if the transition to ice structures is from the stacked ring series. At such a large n, the stacked ring structures are not very compact, resembling in many ways a two-dimensional chain structure more than a bulk-like three-dimensional entity. The probability that another cluster family exists between the size region where stacked rings are the global minimum and the ice structures dominate and is more stable is an open question. The determination of this family, if it exists, is beyond the scope of this work, but the assignment of energies for two-three- and four-hydrogen bonded waters provides an avenue
of research. A topological mapping routine is possible, with appropriate boundary
conditions and based on these fitted energies, and can explore the number of each category
of water molecules to give clues to the structure of such a family.

The fact that ice-Ih is extrapolated to bulk is important. A bulk value for the binding
energy of hexagonal ice at 0 K is available. The ratio of the bulk value, -11.3 kcal/mol,
and the extrapolated value is found from the curve fit. Substitution of the expansion of
Eq. (7) for $E_{xb}$ in Eq. (1) yields

$$E_{xb} = \frac{n_1E_1 + n_2E_2 + n_3E_3}{n}$$

In the limit as $n \to \infty$, $n_1 \approx n_{Total}$, $n_2$, and $n_3$ become negligible and Eq. (19) becomes

$$E_{Ext,Ice-Ih} = E_{xb}(bulk) \equiv E_{4,Ice-Ih} - E_1$$

and provides a way of calibrating the results of PM3 calculations. This ratio,

$$\alpha_{PM3} = \frac{E_{bulk}}{E_{Ext,Ice-Ih}}$$

applies to the entire range of cluster size and was determined to be 1.35. To some degree,
"absolute" values for the excess binding energy per water molecule for any optimized water
cluster structure found by PM3 are possible via,

$$E_{xb,Scaled} = \alpha_{PM3} E_{xb,Calc}$$
though the result is more credible at large \( n \), near where the ratio was determined. The
scaled plot of the families determined in this study are shown in Figure 1.24.

Application of this calibration factor to the ring structures, early stacked cube structures
\((n \leq 8)\), and the “book” form of the hexamer determined values for these structures for
comparison to \textit{ab initio} \( E_{ab} \) values calculated at several levels of theory. The plots shown in
Figure 1.23 clearly show the level of theory required to approach the answer given by the
scaled PM3 curve. Slater-type orbitals, even if the empty orbitals at \( K = 4 \) are included,
clearly overestimate the value of the hydrogen bond and is worse as the cluster gets larger.
It is clearly an unphysical result to have a value of \( E_{ab} \) for \( 3 \leq n \leq 8 \) be greater than that of the
bulk hexagonal ice values. The other Gaussian-type orbitals fare little better until the
polarization functions are included, as represented by the MP2/6-31G* and MP2/6-31G**
curves. While neither plot actually exceeds the bulk \( E_{ab} \) at \( n \leq 8 \), both are sufficiently close to
the value that larger structures would be approximately the same energy on a per molecule
basis, resulting in little energetic reason for larger clusters to form.

The results from the HF/aug-cc-pVDZ and MP2/aug-cc-pVDZ basis sets, as reported
by Xantheas,\textsuperscript{149} actually bracket the predicted values for the cyclic structures from the
scaled PM3. It is possible that small corrections to these basis sets, such as basis set
superposition error (BSSE) counterpoise techniques,\textsuperscript{153-156} may come closer to the
predicted values.

The comparison of the two ice polymorphs leads to several interesting conclusions.
The PM3 calculated structures and energies are all 0 K values. This method predicts the
cubic form of ice to be more stable over the entire size range, and the difference predicted at bulk is 0.9 kcal/mol. It is not surprising that the cubic form is more stable at low temperature as it is formed in the range discussed earlier. It would probably form lower than the specified range except for the severely slowed molecular motions that contribute to rearrangement, resulting in the amorphous form.

Since the hexagonal form is the dominant one atmosphere polymorph from ~-120°C to the melting point of 0°C, the difference must either lie in the temperature response of the crystal structure or the method of calculation. The latter explanation is a possibility if an incorrect sub-family were used for either of the polymorphs. The ice-Ic form is the expected macroscopic octahedral structure and is a reasonable choice. The sub-family of hexagonal ice was chosen due to the resemblance to the cubic structure and could represent a problem. As was discussed in the cubic ice section, the macroscopic crystal of ice-Ih is a hexagonal prism shape, but the structure grows quickly as a function of “shells,” and is not as easily calculated or, as a result, extrapolated to bulk.

If the temperature effects are the reason for the difference, several lines of reasoning found in the literature have a bearing. The cubic form will spontaneously undergo a phase transition to the hexagonal form upon heating. The energy change was found experimentally to be ~0.037 kcal/mol. Much of this energy, however, has been attributed to the release of surface energy when small ice-Ic crystals transform into larger ice-Ih crystals and the actual energy difference in the crystal lattice may be <0.005 kcal/mol, further complicating predictions.
One possible explanation for the change in global minimum from 0 K to room temperature is hydrogen ordering in the structure. Bjerrum, using a point-charge model for the water molecule, predicted that at room temperatures, the hydrogen atoms in hexagonal ice are more ordered than in ice-Ic, up to the melting point. He attributed this to electrostatic interactions of the molecules along the unique c-crystal axis. This is not consistent with later work by Pitzer who showed that, if more interactions are included, the Bjerrum model breaks down. However, Pitzer did show that if a small amount of ordering is present, hexagonal ice is the more stable form.

All the ice structures presented in this work were derived from unit cells, and the hydrogen atom positions were ordered to prevent an additional variable from entering the progression of the family structures. One structure was selected to test the effect of this ordering and the hydrogen positions were randomized. Optimization of this cluster gave a total PM3 energy <0.3 kcal/mol different from the ordered structure. This work does not prove nor disprove the notion that hydrogen ordering is responsible for the room temperature bulk dominance of the hexagonal form, but it does lend credence to the idea that there are discernible differences in the large cluster regime. In this vein, Beaumont explored the different reported unit cells for cubic ice. The one reported by Leadbetter used KOH as a dopant to help order the cubic structure, and the resulting crystal, referred to as the “C-structure,” had a definite dipole moment. Beaumont used the expansion of high-pressure ices instead of KOH and found the “P-Structure” which did not have a large dipole, but turned out to be energetically equal rather than more stable. In a recent paper, Dunning and Payne used a “supercell,” where 2 unit cells were combined and disordered.
in their interior, to perform some ab initio studies on ice at a large (aug-cc-pVDZ) basis set with periodic boundary conditions to avoid this problem.

The general fit expression proved to be quite sensitive to the family of structures used. In a separate series of hexagonal ice structures, the error in the fit was quite small, 0.5 kcal/mol. Addition of an ice-Ih cluster from a different, but similar, sub-family, however, increased the error to 5 kcal/mol. It has been suggested\cite{44} that the fit values for $E_i$ ($i=1-4$) can be used to determine a general continuum fit from dimer to bulk for global minimum structures, although the details are not clear at this time.

**Conclusions**

The series of water clusters in several families has been optimized with PM3, a semi-empirical method. These families have been fit to a general expression to give bulk values and crossing points. The calculated PM3 bulk value of hexagonal ice was found to be -8.36 kcal/mol. This value, when compared to the experimental bulk value of -11.3 kcal/mol, gave a global scaling factor, $\alpha_{PM3}$, of 1.35. This value was applied to the $n<8$ clusters and compared to several levels of *ab initio* calculations. It has been determined that the MP2/aug-cc-pVDZ basis set is the minimum level of theory required to approach the predicted value of these clusters derived from the scaled PM3, but at a much greater cost in computational capacity and time.
References

41. The claim has been made that an accurate comparison requires the ab initio results include corrections for zero point energy since the semi-empirical parameterization occurred at a finite temperature. (Zheng, J. & Merz, K. M., Jr. *J Comput Chem* **13**, 1151 (1992))
43. The relations found for the temperature dependence of r, for liquid water can be found in the appendix of Coe, J.V. *J Phys. Chem. A* **101**, 2055-2063 (1997)
Figure 1.1 The minima for the water dimer, \((H_2O)_2\). The linear hydrogen bonded structure is the experimentally determined global minimum.
Figure 1.2. The alternating chain structure. A similar structure was used by Suhai as his model, projected to infinite length, for ice-Ih.

Figure 1.3. The bridging chain structure. Both the alternating and bridging chains are present in the ice structures, but in differing degrees.
Figure 1.4. Excess binding energy plot for the chain families. The convergence of the curves at $n=4$ is due to distortion of both families towards a similar structure.
Figure 1.5. The ring family structures. These are the minimum energy structures for the rings found by PM3. In each case, the individual water molecules donate one hydrogen bond and accept one hydrogen bond to form the "backbone" of the ring.
Figure 1.6. The four unique isomers of the tetramer with each water as a single-donor/single acceptor.
Figure 1.7. Excess binding energy plot for the ring structures. Ring structures for \( n = 3 \ldots 9 \) have been calculated and plotted on the same scale as the chain structures presented previously. The upward bend to the plot at \( n > 6 \) is due to the "collapse" of the ring towards three-dimensional structures.
Figure 1.8. Comparison of four low energy hexamer water clusters. Four of the low energy configurations for \((\text{H}_2\text{O})_6\) are shown with the PM3 calculated binding energy. Structure a, the "ring," was originally predicted to be the global minimum, but recent calculations have shown the other three structures to be more stable. It is generally believed that the "cage" structure is the global minimum, but all three remaining structures are nearly equivalent in energy and the ordering becomes dependent on the calculation method.
Figure 1.9. Electron attachment mass spectrum of water clusters by Bowen, et al.\textsuperscript{97} For an electron to attach to a cluster, the electron must either be solvated or the cluster have a large dipole moment. The continuum of peaks at n≥11 is due to solvation of the electron. The isolated peaks at 2, 6, and 7 indicate the structures for the corresponding clusters must have a large dipole moment. The cyclic (H\textsubscript{2}O)\textsubscript{6} structure has a small dipole moment, while the other, more condensed, structures have PM3 calculated dipole moments >1.7 debye.
Figure 1.10. Example stacked cube structures. The highly strained hydrogen bond angles are consistent throughout the structure which allows the fitting routine to be employed.
Figure 1.11. Excess binding energy plot for the stacked cube structures with the fitted curve. The stacked cube structures for $n=8,12,...,36$ have been calculated and added to the previous plot of chains and stacked cubes. The extrapolation to bulk ($n^{1/3}=0$) is found to be $-7.56$ kcal/mol.
Figure 1.12. Excess binding energy plot for the stacked hexagons and pentagons. The clusters and fitted expressions for the stacked hexagons and pentagons has been placed on a plot with the stacked cubes shown previously.
Figure 1.13. Comparison of the stacked pentagon and stacked cube decamers. The stacked pentagon decamer is more stable at \(n=10\). This is despite the fact that the stacked cube family is more stable in this range. The global minimum for water clusters overall does not follow one family in particular as the value of \(n\) is incremented, but in general follows the trends shown previously.
Figure 1.14. The crystal structure of ice-Ih. Normal hexagonal ice is comprised of sheets of fused hexagonal rings (top). The stacking of the layers form puckered hexagons in the conformational equivalent of the cyclohexane "boat" configuration (bottom). The c-crystal axis is unique in normal ice.
Figure 1.15. The minimum ice-Ih structure. The cluster shown is the minimum structure with the ice-Ih bonding pattern that does not contain waters with only one hydrogen bond. Note that all the hexagonal rings present are in the “boat” configuration.
Figure 1.16. Several ice-Ih structures. The shown structures of normal ice were used to determine the values of $E_{1}$, $E_{2}$, and $E_{3}$ for the family. These clusters also represent the smallest of the structures with values of $n_{1}$, $n_{2}$, and $n_{3}$ predicted by Eqs. (13), (14), and (15).
Figure 1.17. Excess binding energy plot for hexagonal ice structures. The ice-Ih structures and the fitted extrapolation to bulk is added to the previous plot for comparison. The PM3 predicted 0K bulk value for ice-Ih is -8.36 kcal/mol (compared to the experimental -11.3 kcal/mol).
Figure 1.18. The minimum ice-Ic structure. The cluster shown is the minimum size structure for ice-Ic that does not contain molecules with only one hydrogen bond. Note that, unlike the normal ice structure, which contained all “boat” configuration hexagonal rings, all those present in this cluster are in the “chair” configuration.
Figure 1.19. The fitted ice-Ic structures. These clusters follow the general shape, that of the octahedron, of materials with the cubic-crystal type at bulk, cubic ice, diamond, and silicon. These were used for the determination of the values of $E_0$, $E_1$, and $E_2$ and were used to determine Eqs. (16), (17), and (18).
Figure 1.20. Excess binding energy plot for cubic ice. The values and extrapolated curve for cubic ice has been plotted with the previous families. Note that the ice-Ic clusters are everywhere more stable than the hexagonal ice structures. The curve determines a bulk value of -9.09 kcal/mol.
Figure 1.21. The minimum energy (H₂O)₂₀ clathrate structure. This structure is a representative of the empty clathrate cages that form another family for analysis.
Figure 1.22. Excess binding energy plot with the clathrate structure \((H_2O)_{20}\).
Figure 1.23. Excess binding energy plot for several levels of \textit{ab initio} calculation. The ring and early stacked cube structures were calculated and plotted at several levels of theory. The lower levels are shown to severely over-estimate the value of the hydrogen bond as many of the clusters have calculated binding energies per molecule greater than bulk. The MP2/aug-cc-pVDZ curve from the data of Xantheas\textsuperscript{149} is the closest to the predicted values from the scaled PM3 and could become better if BSSE counterpoise techniques are employed.
Figure 1.24. Scaled excess binding energy plot. The values for the clusters and fitted curves were scaled globally by the value of \( \alpha_{PM} = 1.35 \). The hexagonal ice curve is forced to extrapolate to the experimental value of -11.3 kcal/mol. Cubic ice is predicted to be 0.97 kcal/mol more stable at 0K. The included \textit{ab initio} results are for comparison at small values of \( n \).
CHAPTER 2

SINGLE ION BULK SOLVATION ENTHALPIES AND FREE ENERGIES OF SELECTED HALIDE IONS, HYDROXIDE AND ALKALI METAL IONS FROM CLUSTER STUDIES

With the advent of large cluster experiments and nanosynthetic methods,\textsuperscript{1, 2} it is currently technologically and scientifically important to characterize the evolution of chemical and physical properties of clusters from small gas phase monomers to bulk. It is important to establish in what ways cluster properties are both similar and different from their bulk counterparts. The first step, in connecting the properties of small clusters to bulk, is to obtain the best bulk parameters available. The issue of absolute values for single ion solvation properties is a long standing problem in electrochemistry.\textsuperscript{3} Traditional bulk measurements are performed on inherently neutral, dilute, electrolytic solutions and basically characterize the thermochemistry of a pair of oppositely charged ions. Cluster ion experiments circumvent the bulk limitation by examining the properties of isolated single ions.
For the uninitiated, the problem of absolute, single ion solvation thermochemistry can be illustrated by considering the enthalpy to place a gas phase chloride ion into water. The solvation enthalpy is just the difference between the heats of formation of \( \text{Cl}^-(\text{aq}) \) and \( \text{Cl}^-(\text{g}) \):

\[
\text{Cl}^-(\text{g}) \rightarrow \text{Cl}^-(\text{aq}); \quad \Delta H_{\text{solv},\infty}^{\circ}[\text{Cl}^-] \\
\Delta H_{\text{solv},\infty}^{\circ}[\text{Cl}^-] = \Delta H_f^{\circ}[\text{Cl}^-(\text{aq})] - \Delta H_f^{\circ}[\text{Cl}^-(\text{g})]
\]

(1)

(2)

Using values of \( \Delta H_f^{\circ}[\text{Cl}^-(\text{g})] = -246 \, \text{kJ/mol} \) and \( \Delta H_f^{\circ}[\text{Cl}^-(\text{aq})] = -167 \, \text{kJ/mol} \) from the CRC's NBS tables, one gets \( \Delta H_{\text{solv},\infty}^{\circ}[\text{Cl}^-] = +79 \, \text{kJ/mol} \) which has the wrong sign and magnitude for this obviously favorable process (the value determined in this work is \( \Delta H_{\text{solv},\infty}^{\circ}[\text{Cl}^-] = -308.4 \, \text{kJ/mol} \)). This contrived example simultaneously employs both the \( \Delta H_f^{\circ}[\text{H}^+(\text{aq})] = 0 \) and \( \Delta H_f^{\circ}[\text{H}_2(\text{g})] = 0 \) conventions producing erroneous results. This problem is generally avoided by constructing thermochemical cycles with pairs of oppositely charged ions (as it is pairs that exist in the neutral bulk solutions on which conventional experiments are employed) effectively canceling the unknown calibration offsets for the conversion of heats of formation of the aqueous ions to an absolute scale. Although electrochemists may employ reference electrodes, this problem can no longer be avoided by those experimenting on large size cluster ions.

In this and other cluster-ion-based work, the adopted value for the absolute solvation free energy or enthalpy of the proton is required to be consistent with both the body of cluster ion data and bulk thermochemistry. There have been a number of observations regarding the connection of stepwise cluster ion thermochemistry to single-ion bulk
solvation thermochemistry.\textsuperscript{5-9} This work builds on these observations, but avoids some of the more drastic assumptions which may have prevented general acceptance of the cluster ion constrained results. In the following section, the consequences are examined with regard to the cluster ion solvation data of three different literature values for the absolute solvation enthalpy of the proton.

**Thermodynamic Conventions for the Electron**

Good values of bulk solvation free energies and enthalpies are available for pairs of oppositely charged ions as given in Table 2.1 using heats and free energies of formation.\textsuperscript{4} A thermochemical cycle can be constructed with the following reactions:

\[ \text{A}(s) + \frac{1}{2}\text{B}_2(g) \rightarrow \text{AB}(aq) \equiv \text{A}^+(aq) + \text{B}^-(aq); \ \Delta H^\circ_r[\text{AB(aq)}] \]  
\[ \text{A}^+(g) \rightarrow \text{A}(s); \ - \Delta H^\circ_r[\text{A}^+(g)] \]  
\[ \text{B}^-(g) \rightarrow \frac{1}{2}\text{B}_2; \ - \Delta H^\circ_r[\text{B}^-(g)] \]

such that

\[ \Delta H_{\text{solv}}(\text{AB}) = \Delta H^\circ_r[\text{AB(aq)}] - \Delta H^\circ_r[\text{A}^+(g)] - \Delta H^\circ_r[\text{B}^-(g)] \] \hspace{1cm} (6)

Care must be taken when considering the gas phase ion formation enthalpies. Two conventions are present when a cycle includes gas phase ions. Consider the ionization reaction,

\[ \text{A} \rightarrow \text{A}^+ + e^-; \ \Delta H^\circ_{\text{izn}} \] \hspace{1cm} (7)
\( \Delta G^\circ_{\text{water}} \) (kJ/mol)

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<th>Cl(^+)</th>
<th>Br(^+)</th>
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\( \Delta H^\circ_{\text{water}} \) (kJ/mol)

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<td>-601.9</td>
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Table 2.1. Solvation free energy and enthalpy to place a pair of oppositely-charged gas-phase ions into water at 25°C from the free energies and enthalpies of formation of the gas phase neutral atoms and the corresponding salt. The values in parenthesis were not directly available from data in ref 4. They were determined from the differences (Table 2.2) that were available.

at 0K and 298K. In the 0K case, \( \Delta H_{\text{on}} \) is the adiabatic ionization energy, \( \text{IE}_A \), of \( A \). At 298K, \( \Delta H_{\text{on}} \) is the enthalpy of the reaction for the ionization, \( \Delta H_{\text{ion}} \), and is related to Eq. (7) by,

\[
A_{0K} \rightarrow A_{298K} ; \text{IHC}(A) \tag{8}
\]
\[
A_{0K}^\ast \rightarrow A_{298K}^\ast ; \text{IHC}(A^\ast) \tag{9}
\]
\[
e_{0K} \rightarrow e_{298K} ; \text{IHC}(e^\ast) \tag{10}
\]
where \( IHC \) is the integrated heat capacities of the species. In both conventions, \( \Delta H^\circ_r(e^-) \) is zero at 0K. As a result,

\[
\Delta H^\circ_r(A^+)_{0K} = \Delta H^\circ_r(A)_{0K} + IE_a
\]

(11),

the energy difference between the molecule and the ion is simply the adiabatic ionization potential.

When the temperature is raised to 298K, Eq. (11) becomes,

\[
\Delta H^\circ_r(A^+)_{298K} = \Delta H^\circ_r(A)_{298K} - \Delta H^\circ_r(e^-)_{298K} + \Delta H_{izn}
\]

(12),

where

\[
\Delta H_{izn} = IE_a + IHC(e^-) + IHC(A^+) - IHC(A)
\]

(13).

A typical assumption is that the integrated heat capacities for a molecule and its ion are approximately equal, i.e. \( IHC(A) \approx IHC(A^+) \), and Eq. (12) becomes,

\[
\Delta H^\circ_r(A^+)_{298K} = \Delta H^\circ_r(A)_{298K} - \Delta H^\circ_r(e^-)_{298K} + IE_a + IHC(e^-)
\]

(14).

In the "Electron Convention," or EC, the electron is treated as a chemical element in its standard state, i.e. \( \Delta H^\circ_r(e^-) \) is zero at all temperatures. In this convention, Eq. (14) reduces to

\[
\Delta H^\circ_r(A^+)_{298K} = \Delta H^\circ_r(A)_{298K} + IE_a + IHC(e^-)
\]

(15).
The "Ion Convention," or IC, used in most of the body of literature on the thermochemistry of ions, has been stated several ways, but essentially assumes the integrated heat capacity of the electron is equal to enthalpy of formation of the electron at any temperature. This reduces Eq. (14) to

\[ \Delta H_f^\circ(A^+)_{298K} = \Delta H_f^\circ(A)_{298K} + IE_a \quad (16). \]

Usually, when the "Electron Convention" is used, the integrated heat capacity for the electron is estimated to be an ideal gas following Boltzmann statistics, \( \frac{5}{2}RT \). At 298K, this gives the relation between the two conventions as

\[ \Delta H_f^\circ(A^+)_{298K}^{(IC)} = \Delta H_f^\circ(A^+)_{298K}^{(EC)} - 6.197 \text{ kJ/mol} \quad (17). \]

A similar series of arguments exist for negative ions and electron affinities, resulting in the relation

\[ \Delta H_f^\circ(B^-)_{298K}^{(IC)} = \Delta H_f^\circ(B^-)_{298K}^{(EC)} + 6.197 \text{ kJ/mol} \quad (18). \]

Note the change in sign for the Boltzmann factor.

**Cluster Viewpoint of Bulk Solvation Enthalpies**

The merits and difficulties associated with a particular value for the absolute solvation enthalpy of the proton can be illustrated with regard to cluster work by plotting the absolute bulk solvation enthalpies of a variety of ions (that correspond to the absolute proton value of interest) vs. the cluster ion solvation enthalpy at a certain cluster size (n=5 in this case). In the following paragraph the procedure to obtain absolute bulk single-ion solvation...
Table 2.2. Bulk average differences (first ion - second ion) in the single ion bulk solvation free energies and enthalpies. Uncertainties are not available for the thermochemical cycle used to find these differences because the original data (ref. 4) has apparently been made internally consistent. Alternative cycles can be employed for the enthalpies (ref. 21) suggesting that a range of uncertainties of 3-10 kJ/mol is reasonable for all of these values.

enthalpies given an absolute value for the proton is described. Following that is the procedure for obtaining the corresponding cluster ion solvation enthalpy.

It is unclear how each entry in Table 2.1 is distributed between the two contributing ions of opposite charge. The entries in Table 2.1 reveal accurate differences between ions of similar charge as summarized in Table 2.2 with positive ions relative to Na⁺ and negative ions relative to OH⁻; but there is no bulk constraints which fix the positive ions relative to the negative ions. The bulk situation is such that a determination of the absolute value for one ion effectively determines all the rest. Table 2.3 makes use of the data in Tables 2.1 and

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<td>I⁻, OH⁻</td>
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Table 2.3. The bulk solvation free energy and enthalpy of various ions relative to \( H^+ \).

In order to compare bulk solvation values to cluster data, the extensive literature of stepwise ion solvation thermochemistry must be converted from stepwise values to solvation. Throughout this paper, we employ enthalpies to illustrate the concepts, however it should be understood that for each enthalpic equation or relation, there is a similar equation or relation for free energies. The stepwise enthalpy for addition of water to an aqueous cluster ion is given by

\[
Z(H_2O)_{i-1} + H_2O \rightarrow Z(H_2O)_i ; \quad \Delta H_{i-1,i}(Z)
\]  

(19).

A set of equations like Eq. (19) from \( i=1 \) to \( n \), will build up a cluster ion of size \( n \),

\[
Z + H_2O \rightarrow Z(H_2O) ; \quad \Delta H_{0,1}(Z)
\]  

(20)

\[
Z(H_2O) + H_2O \rightarrow Z(H_2O)_2 ; \quad \Delta H_{1,2}(Z)
\]  

(21)
\[ Z(H_2O)_2 + H_2O \rightarrow Z(H_2O)_3 ; \ \Delta H_{2-3}(Z) \]  
(22)

\[ \vdots \]

\[ Z(H_2O)_{n-1} + H_2O \rightarrow Z(H_2O)_n ; \ \Delta H_{n-1,n}(Z) \]  
(23)

\[ Z + nH_2O \rightarrow Z(H_2O)_n ; \ \sum_{i=1}^{n} \Delta H_{i-1,i}(Z) \]  
(24).

This is only one part of solvating an ion in a cluster of size, \( n \). A set of equations for the production of a neutral water cluster must also be considered,

\[ (H_2O)_{n-1} + H_2O \rightarrow (H_2O)_n ; \ \Delta H_{n-1,n}(H_2O) \]  
(25).

Note that in this index, \( \Delta H_{n,1}(H_2O) = 0 \), or, stated in terms of a chemical expression,

\[ H_2O \rightarrow H_2O ; \ \Delta H_{0,1}(H_2O) \]  
(26).

Subtraction of the equations for the stepwise construction of the neutral water cluster, Eq. (25), from the set of equations for the ion-molecule cluster, Eq. (19), gives the solvation relation:

\[ Z + (H_2O)_n \rightarrow Z(H_2O)_n ; \ \Delta H_{\text{sol},n}(Z) \]  
(27),

where,

\[ \Delta H_{\text{sol},n}(Z) = \sum_{i=1}^{n} \Delta H_{i-1,i}(Z) - \sum_{i=1}^{n} \Delta H_{i-1,i}(H_2O) \]  
(28).

The bulk single ion solvation enthalpy appears in the limit as \( n \) goes to infinity. The determination of the solvation enthalpy of an ion, \( Z \), requires knowledge of the stepwise
enthalpies of neutral water clusters in addition to the stepwise enthalpies of the aqueous cluster ion. The summations of stepwise enthalpies for solute and solvent that appear in Eq. (28) are called partial sums and are accumulated from literature values\textsuperscript{10-15} in Table 2.4. The solvation enthalpy for each ion is simply the value entered in Table 2.4 for the ion of interest minus the value in Table 2.4 for water. The water value has been determined\textsuperscript{16} from PM3 water cluster calculations that have been corrected for zero point energy and calibrated for the excess energy of hydrogen bonding by comparison to high level \textit{ab initio} (HF/aug-cc-pVDZ and MP2/aug-cc-pVDZ) calculations\textsuperscript{17, 18} on small water clusters.
\[ \sum_{i=1}^{n} \Delta G_{i-1,i} \,(kJ/mol) \]

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Table 2.4. Cluster ion solvation free energy and enthalpy partial sums of various ions vs. cluster size. Ion values have been averaged from the shown references. Entries in parenthesis are estimated from the expected trend to the known bulk value.
Previous Bulk Single-Ion Solvation Methods

Two sets of single-ion solvation values often quoted are those of Morris\textsuperscript{19} ($Y=-1103$ kJ/mol) and Klots\textsuperscript{20} ($Y=-1136.4$ kJ/mol). The bulk solvation enthalpies for various ions of both Morris and Klots are plotted against the cluster solvation enthalpies at $n=5$ in Figures 2.1 and 2.2 respectively. The ions have been separately fit to lines by the method of least squares.

Examination of Figure 2.1 shows two disturbing features: 1) the positive ions are grouped separately from the negative ions and 2) the negative ions display a different slope (1.399) than the positive ions (1.109). The observations are disturbing because it is not expected that there should be any generalized differences between the negative ions and positive ions on such a plot.\textsuperscript{21} It hardly needs to be mentioned that there would be a large standard deviation in $\Delta H_{\text{vol,me}}$ (or a low correlation coefficient) if the positive and negative ions were fit to a common line. Both of these problems cannot be fixed simply by changing the absolute proton value.

Klots presented a set of absolute single-ion solvation enthalpies and free energies based on cluster data. The approach assumes that all of the stepwise additions of a water molecule to the cluster ions of $A^+$ and $B^-$ are equivalent after $n=5$, i.e.

$$\sum_{i=6}^{\infty} \Delta H_{i-1,i}(A^+) = \sum_{i=6}^{\infty} \Delta H_{i-1,i}(B^-)$$ (29).
Inspection of a plot of cluster solvation enthalpy vs. $n^{1/3}$ shows that strongly solvated ions (like Li$^+$) and weakly solvated ions (like Cl$^-$) have different stepwise solvation energies at $n=6$. It is not necessary to make such a drastic assumption, since the difference in the cluster ion partial sums could be taken as a relative or proportional indication of the difference that will develop at bulk.

Figure 2.2 shows the plot of the bulk single-ion solvation enthalpies based on the proton value reported by Klots of $-1136.4$ kJ/mol against the cluster solvation enthalpies at $n=5$. Klots chose to work with a set of ions, Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cl$^-$, and Br$^-$ (but not OH$^-$ and F$^-$). This set exhibits a common linear relation for the positive ions and chosen negative ions with a slope increased a bit (6%) over that of the positive ions alone and a standard deviation in $\Delta H_{\text{sol}}$ of 13 kJ/mol which has doubled from that of the positive ions alone. By eliminating OH$^-$ and F$^-$ and adjusting the absolute solvation enthalpy of the proton, the method of Klots succeeds in finding a common fitting line for the positive and selected negative ions addressing the first problem with Figure 2.1, i.e. the issue of why the negative ions, as a group, exhibit a different slope than the positive ions. It is now reasonably well established that large halide ions prefer to reside on the surface of small water clusters, gradually working their way into the interior of clusters upon addition of 60 or so solvating water molecules. The stepwise energetics associated with the hydration of a surface state can be expected to be different than the stepwise energetics of the corresponding internalized ion at a given $n$. Klots noted that OH$^-$ fails to conform to the pattern, but in retrospect it would seem that the large halides (he used only chloride and bromide) are the deviant species.
Coe's Difference Over Sum Cluster Method

The cluster ion method of Coe solves both of the above-mentioned problems of Figure 2.1 and avoids the drastic assumptions inherent in the method of Klots. The method of Coe assumes only that both the positive and negative internalized cluster ions have a common functional dependence in stepwise hydration, i.e. there is a common linear relation for internally solvated positive and negative cluster ions (that gets better as n gets larger) between the cluster solvation enthalpy and the bulk solvation enthalpy. There is no generalized energetic difference in the way negative and positive cluster ions progress to bulk; all differences result from the differences in the most immediate interactions between the ion and its nearby solvating water molecules. The cluster data indicate bulk differences between ions of opposite charge in a relative way (the differences are not fully developed by n=5); so the cluster relative differences were normalized to corresponding sums and projected to bulk with the parameter 1/s as follows:

\[
\frac{1}{s} \frac{\Delta H_{\text{sol},n}(A^+) - \Delta H_{\text{sol},n}(B^-)}{\Delta H_{\text{sol},n}(A^+) + \Delta H_{\text{sol},n}(B^-)} = \frac{\Delta H_{\text{sol,e}}(A^+) - \Delta H_{\text{sol,e}}(B^-)}{\Delta H_{\text{sol,e}}(A^+) + \Delta H_{\text{sol,e}}(B^-)}
\]

(30)

The normalized differences (difference over sum ratios) are projected to bulk without the assumption of equivalency for \(A^+\) and \(B^-\) an n>5 by using a scaling parameter, s, which is common to all pairs of ions. The normalization of differences by sums makes this method equivalent to minimizing the deviations from a common line for positive and negative ions on the \(\Delta H_{\text{sol,e}}\) vs. \(\Delta H_{\text{sol,5}}\) plots. The value of s for any particular set of bulk single ion values does not need to be fitted and can be determined by dividing the sum of the
magnitudes of the cluster difference-over-sum ration for all pairs of oppositely charged ions by the same type of sum for the magnitudes of the bulk difference-over-sum ratios as follows

\[
S = \sum_{A^-} \sum_{B^-} \sqrt{\frac{\left(\sum_n \Delta H_{\text{sol}.n}(A^-) - \sum_n \Delta H_{\text{sol}.n}(B^-)\right)^2}{\sum_n \Delta H_{\text{sol}.n}(A^-) + \sum_n \Delta H_{\text{sol}.n}(B^-)}} \]

\[
S = \sum_{A^-} \sum_{B^-} \sqrt{\frac{\left(\sum_n \Delta H_{\text{sol},\infty}(A^-) - \sum_n \Delta H_{\text{sol},\infty}(B^-)\right)^2}{\sum_n \Delta H_{\text{sol},\infty}(A^-) + \sum_n \Delta H_{\text{sol},\infty}(B^-)}} \]

(31).

The optimal set of absolute single-ion values is the set that minimizes the differences between the left and right sides of Eq. (30) over all pairs of oppositely charged internalized ions. In recalculating the results from ref. 21, two minor errors were discovered: 1) the partial sum for water at n=6 was used instead of n=5 giving a high s value but not affecting the absolute proton value, and 2) there was a small data entry error (the numbers in the table are correct). The final results should have been reported as \( \Delta H_{\text{sol},\infty}[H^+] = -1147.7\pm6.0 \) kJ/mol and \( s=1.573 \). This value is 4.8 kJ/mol smaller in magnitude than that reported in ref. 21, but is still within the error bars (±1σ).

The same type of \( \Delta H_{\text{sol},\infty} \) vs. \( \Delta H_{\text{sol},5} \) plot as presented in Figures 2.1 and 2.2 is now presented in Figure 2.3 using the absolute proton solvation enthalpy determined by the Coe difference-over-sum method (-1152.5 kJ/mol, i.e. as given in ref. 21). Only internalized cluster ions at n=5 were desired, so \( \text{OH}^- \) and \( F^- \) were used and the large halides were left out. The subset of internalized ions, \( \text{Li}^+ \), \( \text{Na}^+ \), \( \text{K}^+ \), \( \text{Rb}^+ \), \( \text{OH}^- \), and \( F^- \), all fit very well to a common line \( \Delta H_{\text{sol},\infty}(\text{kJ/mol}) = 1.103 \Delta H_{\text{sol},5} - 162.9 \). The standard deviation (5.8 kJ/mol)
and the slope (1.103) are quite close to the values exhibited by the positive ions themselves (as in Figure 2.2). This observation supports the fundamental assertion that the stabilization of sufficiently-sized, internalized cluster ions by further clustering is energetically insensitive to the sign of the charge being solvated. The halides do not fall on the common internalized $\Delta H_{\text{sol, in}}$ vs. $\Delta H_{\text{sol,5}}$ line because they are surface states at $n=5$ and progress to bulk with a different stepwise functional dependence. So the difference-over-sum ratio method also succeeds in grouping the positive ions together (without doubling the standard deviation of the positive ions alone as with the Klots method), although the group now consists only of internalized ions. The difference-over-sum ratio method further identifies the physical reason for the difference in the negative ion group slope, the surface vs. internal ion issue. In practice, the most important difference of this method from the Klots method is the use of the OH and F internalized cluster ions (excluded as deviant by Klots) in place of the surface state cluster ions (at $n=5$) of Cl and Br which have a different stepwise solvation functional dependence.

The Linear $\Delta H_{\text{sol, in}}$ vs. $\Delta H_{\text{sol,5}}$ Method

The basic assumptions and contrasts of the Coe difference-over-sum and Klots methods are much more apparent when presented in terms of $\Delta H_{\text{sol, in}}$ vs. $\Delta H_{\text{sol,5}}$ plots. In fact, the Coe difference-over-sum method criteria (choosing an absolute proton solvation enthalpy which minimizes the comparison of the left and right sides of Eq. (30) over all the pairs of oppositely charged ions) is mathematically equivalent to the plot with minimum
deviations. This latter approach is less complicated mathematically, easier to explain, and easier to visualize; so we present the following alternative to the Coe method.

The method starts by choosing a value of $Y$, the absolute bulk solvation enthalpy of the proton. Once a value of $Y$ is chosen, absolute, single-ion, bulk values are determined for all of the ions by virtue of the data in Table 2.3. This set of bulk values is used with the corresponding cluster solvation enthalpies at $n=5$ to fit to the following linear equation

$$[\Delta H_{\text{sol},5,i}] = m[\Delta H_{\text{sol},5,i}] + b$$  \hspace{1cm} (32),

where $i$ is an index for the $N$ internally solvated ions (both positive and negative) at cluster size $n=5$. The slope ($m$) and intercept ($b$) are given by the standard least squares expressions

$$m = \frac{-\left(\sum_{i} [\Delta H_{\text{sol},5,i}]\right)\left(\sum_{i} [\Delta H_{\text{sol},\infty,i}]\right) + N\left(\sum_{i} [\Delta H_{\text{sol},5,i}][\Delta H_{\text{sol},\infty,i}]\right)}{N\sum_{i} [\Delta H_{\text{sol},5,i}]^2 - \left(\sum_{i} [\Delta H_{\text{sol},5,i}]\right)^2}$$  \hspace{1cm} (33)

$$b = \frac{\left(\sum_{i} [\Delta H_{\text{sol},5,i}]\right)\left(\sum_{i} [\Delta H_{\text{sol},\infty,i}]\right) + \left(\sum_{i} [\Delta H_{\text{sol},5,i}][\Delta H_{\text{sol},\infty,i}]\right)}{N\sum_{i} [\Delta H_{\text{sol},5,i}]^2 - \left(\sum_{i} [\Delta H_{\text{sol},5,i}]\right)^2}$$  \hspace{1cm} (34).

Note that $m$ and $b$ are functions of $Y$. For any particular choice of $Y$, the standard deviation ($\sigma$) of the fit is evaluated using
The method proceeds by varying the proton solvation (Y) until $\sigma$ is minimized.

This $\Delta H_{\text{sol,vs.}}$ vs. $\Delta H_{\text{sol,5}}$ method is simpler but essentially equivalent to the Coe difference-over-sum method. To demonstrate this, the scaling parameter $s$ of Eq. (30) can be related to the slope ($m$) and intercept ($b$) of the $\Delta H_{\text{sol,vs.}}$ vs. $\Delta H_{\text{sol,5}}$ plot as

$$s = 1 + \frac{2b}{m} \left( \frac{1}{\Delta H_{\text{sol,5}}(A^+) + \Delta H_{\text{sol,5}}(B^-)} \right)$$

or expanded as

$$s = 1 + \frac{2b}{m} \frac{1}{n_{\text{pairs}}} \sum_{A^-.B^- \text{ pairs}} \frac{1}{\Delta H_{\text{sol,5}}(A^+) + \Delta H_{\text{sol,5}}(B^-)}$$

where $n_{\text{pairs}}$ is the number of pairs of oppositely charged ions and the summation is over the pairs. Use of the values of $m$ and $b$ determined from both the bulk data and absolute proton solvation enthalpy from ref. 21 gives $s=1.578$ which is essentially the same value determined by the difference-over-sum method as given above ($s=1.573$). The optimized absolute proton solvation enthalpy using the $\Delta H_{\text{sol,vs.}}$ vs. $\Delta H_{\text{sol,5}}$ method with the ref. 21 data set is $-1151.3 \pm 6.5$ kJ/mol which can be compared to the difference-over-sum value of $-1152.5 \pm 6$ kJ/mol. The two methods have the same result within the random errors of the
procedures, although there may be some subtle differences in the contribution of errors to each method.

Both the difference-over-sum and the $\Delta H_{\text{sol,$\infty$}}$ vs. $\Delta H_{\text{sol,}5}$ methods differ from the Klots method in the use of stepwise clustering energetics of neutral water clusters. The difference-over-sum and $\Delta H_{\text{sol,$\infty$}}$ vs. $\Delta H_{\text{sol,}5}$ methods are not very sensitive to the value of the water partial sum (Table 2.4). This value can be changed by a factor of more than two without any change in the optimal absolute value for the proton (although this does effect the value of $s$). Therefore, it is not essential for these methods to have the best value for the water partial sum. Most importantly, the use of the neutral water cluster data allows the comparison of similar bulk and cluster properties providing the key to the simplicity of this new alternative method.

As mentioned previously, that the water partial sum for enthalpies was obtained using semi-empirical PM3 calculations corrected for zero point energy with calibration of the excess energy of hydrogen bonding by comparison to high level \textit{ab initio} methods.\textsuperscript{16-18} The free energy partial sum was obtained using the equilibrium concentration measurements of Kell and McLaurin\textsuperscript{26} on small water clusters in steam at temperatures from 425-725K. These data (see Fig. 2 of ref. 25) have been graphically extrapolated back to 300K in order to provide room temperature values for $\Delta G_{n,n}[\text{H}_2\text{O}]$ of 6.7, 4.6, and 3.8 kJ/mol for $n=2, 3$, and 4 respectively. We only require a value for $n=5$ which is obtained by estimating the general trend. The stepwise free energies of water will extend to a value\textsuperscript{4} of -8.59 kJ/mol at bulk (i.e. $-\Delta G_{\text{vap}}[^{\circ}\text{H}_2\text{O}]$, the negative of the vaporization free energy of water at room
temperature). The same functional form that was previously found to connect the calculated stepwise enthalpies of Buffey and Brown\textsuperscript{27} (in an averaged way) to bulk was used for the free energies. The following relations were obtained by fitting this functional form to the cluster data of Kell and McLaurin\textsuperscript{26} with the constant term fixed at its bulk value to obtain (for \( n \geq 1 \)):

\[
\Delta G_{n-1,n}^\circ[H_2O](kJ/mol) = -8.59 + (26.6 \pm 0.5)[n^{2/3} - (n-1)^{2/3}] \tag{38}
\]

\[
\Delta H_{n-1,n}^\circ[H_2O](kJ/mol) = -44.0 + (57.6 \pm 8.1)[n^{2/3} - (n-1)^{2/3}] \tag{39}
\]

It is interesting that the stepwise free energies for adding a water cross over from unfavorable to favorable at some intermediate cluster size (~\( n=10 \)). Over the cluster size range presently being used, the neutral stepwise solvation free energies and enthalpies are much smaller than the ion stepwise solvation energies, so again some lack of exact knowledge of the neutral values can be tolerated by the method. Partial sums of the stepwise free energy and enthalpy of neutral water clusters have been accumulated in Table 2.4.

**Y' Method**

A correlation has been observed\textsuperscript{28} that provides further evidence for a value for the proton enthalpy greater than previously reported and achieves a greater consistency with bulk. The data in Table 2.3 can be written as

\[
\Delta H_{sol,\infty}[A^+] = Y + k(A^+) \tag{40}
\]
\[ \Delta H_{\text{sol,\infty}}[B^-] = -(Y + k(B^-)) \]  (41),

where \( k(A^+) \) and \( k(B^-) \) are the constants representing the bulk differences of the proton and the positive and negative ion respectively. Solving Eq. (41) for \( Y \) gives

\[ Y = \frac{1}{2} \left[ \Delta H_{\text{sol,\infty}}[A^+] - \Delta H_{\text{sol,\infty}}[B^-] - k(A^+) - k(B^-) \right] \]  (42).

The difference between the bulk positive and negative ions in any pair is not known. The solvation enthalpy for a cluster of size \( n \), however, can be related to the bulk single-ion solvation enthalpy by

\[ c_n(A^+) = \frac{\Delta H_{\text{sol,n}}(A^+)}{\Delta H_{\text{sol,\infty}}(A^+)} \]  (43),

\[ c_m(B^-) = \frac{\Delta H_{\text{sol,m}}(B^-)}{\Delta H_{\text{sol,\infty}}(B^-)} \]  (44),

where \( c_n(A^+) \) and \( c_m(B^-) \) are the fraction of the bulk solvation enthalpy of \( A^+ \) and \( B^- \) respectively that a cluster of size \( n \) or \( m \) has achieved. This remains an unknown quantity, but introduces the cluster data into Eq. (42) giving

\[ Y = \frac{1}{2} \left[ \frac{\Delta H_{\text{sol,n}}(A^+)}{c_n(A^+)} - \frac{\Delta H_{\text{sol,m}}(B^-)}{c_m(B^-)} - k(A^+) - k(B^-) \right] \]  (45).

The values of the cluster sizes \( n \) and \( m \) are not rigorously required to be equal.

As mentioned previously, the difference at bulk between the solvation enthalpies of \( A^+ \) and \( B^- \) are not known. The sums are known and are the bulk solvation enthalpies of Table 81.
2.1. A new constant, $c_{n,m}(A^+,B^-)$ can be defined from the sums of both the cluster and bulk solvation enthalpies, which are known,

$$c_{n,m}(A^+,B^-) = \frac{\Delta H_{\text{solv,n}}(A^+) + \Delta H_{\text{solv,m}}(B^-)}{\Delta H_{\text{solv,n}}(A^+) + \Delta H_{\text{solv,m}}(B^-)}$$

(46)

When the two ions in question are similar in single-ion solvation enthalpy at both cluster size $n$ and bulk, then

$$c_{n,m}(A^+,B^-) \equiv c_n(A^+) \equiv c_n(B^-)$$

(47)

This allows an approximation for $Y$, the proton single-ion solvation enthalpy, in Eq. (45) as

$$Y' = \frac{1}{2} \left[ \frac{\Delta H_{\text{solv,n}}(A^+) - \Delta H_{\text{solv,n}}(B^-)}{c_{n,n}(A^+,B^-)} - k(A^+) - k(B^-) \right]$$

(48)

where $Y'$ is the value of the proton single ion solvation enthalpy based on the cluster data, $\Delta H_{\text{solv,n}}(A^+)$ and $\Delta H_{\text{solv,n}}(B^-)$, which are known. $Y'$ is rigorously equal to $Y$ when the fraction of the bulk single-ion solvation enthalpy for the positive ion, $c_n(A^+)$ is equal to the fraction for the negative ion, $c_n(B^-)$.

According to the Born concept for ionic solvation,\textsuperscript{29} this will be true when the volume of the ions being solvated is similar. Figure 2.4 shows the calculated value for $Y'$ with respect to the difference in ion volumes (Table 2.5) at different cluster sizes, as reported by Gourary and Adrian.\textsuperscript{30} The cluster volumes were estimated by adding a constant value for
Table 2.5. Ion radii as reported by Gourary and Adrian

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each water molecule in the cluster to the ion volume. The best fit line shows an intercept (when Bornian ions would have equal solvation bulk solvation energies) of -1152.1±1.8 kJ/mol.

A more informative plot would involve the differences in cluster ion solvation enthalpies instead of volumes (Figure 2.5). Once again, a good correlation is seen, with an intercept of -1151.0±1.6 kJ/mol. The observation of a similar intercept in both Figures 2.4 and 2.5 gives credence to the Bornian concept applying to cluster solvation enthalpies. With this in mind, the cluster-based difference-over-sum method is given some justification as the cluster ordering is indicative of the bulk values.

Figure 2.6 shows the same information at Figure 2.5 except each cluster size is individually fit. Table 2.6 gives the slopes and intercepts for these fitted lines. The common point in the cluster enthalpy differences in Figure 2-6 is near the intercept, i.e. the cluster calculated value for Y' exhibits the least standard deviation (2.1 kJ/mol) at the Bornian expectation value. The corresponding free energy difference plot by cluster size (Figure 2-7) shows an even greater consistency (X'=-1101.8±0.3 kJ/mol).
The correlation shown by Eq. (48) can also be expressed by plotting its components against one another. A plot of $1/c_{n,\alpha}(A',B)$ vs. $\Delta H_{solv}(A')-\Delta H_{solv}(B')$ is nearly constant (although the constant differs for each $n$). As a result, the first term of Eq. (48) is linear in $\Delta H_{solv}(A')-\Delta H_{solv}(B')$ and will not contribute to $Y'$ at the intercept; the latter terms, $k'(A')$ and $k(B)$, determine the best value for $Y'$. These constants are known bulk values and are not derived from cluster data. Figure 2.8 shows the plot of the latter terms ($k'(A')$ and $k(B)$) vs $\Delta H_{solv}(A')-\Delta H_{solv}(B')$. The relations are linear and share a common point near the intercept at a value of $-1148.7\pm2.0$ kJ/mol.

Discussion

The results of the $Y'$ method are compared to other selected results in Table 2.7. The presently obtained value of $\Delta H_{solv}[\text{H}^+] = -1148.7\pm2.1$ kJ/mol is somewhat higher than many literature values (see Table 2.7) and constitutes an important reassessment of this value. The presently obtained value of $\Delta G_{solv}[\text{H}^+] = -1101\pm0.3$ kJ/mol compares favorably
to the center of weight of determinations in the chronological survey of Friedman and
Krishnan (see Fig. 5 in Ref. 35, Chapter 1, p.25).

When the three different proton solvation enthalpies were examined in the early
sections of this paper, they were compared using a common set of bulk constraints (from
Table 2.3) in order to highlight the consequences of these values relative to the cluster data.
One can also evaluate any set of absolute single ion values for consistency to bulk. Since
bulk measurements on inherently neutral, dilute, electrolytic solutions basically characterize
the thermochemistry of a pair of oppositely charged ions, any set of single ion
thermochemical properties can be compared to bulk by adding the values of oppositely
charged pairs in the set. The standard deviation of comparison, between the bulk values
available in the NBS tables† as provided in Table 2.1 using all but the top row (avoiding the
issue of H⁺ vs H₂O⁻) and each of the selected data sets, is presented at the bottom of the
free energy and enthalpy sections in Table 2.7. For instance, Friedman and Krishnan’s[^31]
set of single ion solvation free energies exhibits a first standard deviation of 28.1 kJ/mol with
respect to bulk, while the set of Gomez and Tryson[^32] shows a value of 40.6 kJ/mol. If
there is confidence in the bulk data, then this comparison can be used to evaluate the quality
of single ion thermochemical data sets. Consistency does not in itself guarantee quality (the
examples in Figures 2.1 to 2.2 are equally consistent with bulk, but not with the cluster data),
but lack of consistency is indicative of problems.
<table>
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Comparison to bulk

| $\sigma$ (kJ/mol) | 0.04 | 8.2 | 8.0 | 28.1 | 40.6 |

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<th>Friedman\textsuperscript{31}</th>
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</table>

Comparison to bulk

| $\sigma$ (kJ/mol) | 0.6  | 9.9\textsuperscript{b} | 15.5 | 15.4 | 35.9 |

Table 2.7. Single ion bulk solvation free energies and enthalpies from several sources. Each data set has been used to generate data as in Table 2.1. The standard deviation of the comparison with the bulk experimental data in Table 2.1 is given as $\sigma$ at the bottom. a) calculated using the current web page value of 691 kJ/mol for the room temperature proton affinity of water. b) this value was 2.4 kJ/mol with the bulk set used in ref. 21.
The single ion sets of Conway,\textsuperscript{33} Klots\textsuperscript{20} and Coe\textsuperscript{22} were all forced to be consistent with their bulk data sets (Rosseinsky\textsuperscript{35} for the Conway\textsuperscript{20, 33} and Klots sets), but there is considerable difference between that older set and the CRC's NBS tables (17 kJ/mol for enthalpies and 8.4 kJ/mol for free energies). The enthalpic single ion set of Coe exhibited a standard deviation of 2.4 kJ/mol from its alternative bulk data (based on heats of dilution, gas phase bond energies, and lattice energies), but shows a standard deviation of 9.9 kJ/mol relative to the presently employed bulk constraints. However the differences in the bulk data have had little (if any) effect on the absolute proton solvation enthalpies determined with the present method and from ref. 21.

The overly consistent differences between similarly charged ions in Table 2.1 shows that the NBS database\textsuperscript{4} contains bulk values which have been optimized for internal consistency. In order to evaluate the presently determined set of single ion solvation properties, we compare it to the set determined with more rigorous error analysis (2\textsuperscript{nd} column, bottom section of Table V. Ref. 21.). These two sets exhibit a standard deviation of 6.3 kJ/mol which falls comfortably within the range of individual errors reported by Coe, providing confidence in the extension of the method to free energies (where data for such checks are not available).

The enthalpic data set of Randles\textsuperscript{34} represents an experimental determination of the absolute single ion enthalpies. It exhibits a first standard deviation of 15.4 kJ/mol relative to the present bulk set which could be taken as an indication of the random error of the experimental method. Each of Randles single ion enthalpy values has been used to determine absolute solvation enthalpy using the data in Table 2.3. The average and standard
deviation of this exercise (-1131±9 kJ/mol) is exhibited in brackets in Table 2.7 under H⁺.
Notice that the uncertainty of this procedure is in reasonable agreement with the comparison to bulk. Comparison of the present single ion values to those of Randles shows a standard deviation of 21 kJ/mol. Consequently, roughly half of the difference may be attributed to systematic differences between the cluster approach and the Randles separation method which does not account for the surface potential of water (~13 kJ/mol). The presently determined set of single ion values is: 1) consistent with experiment when surface potentials are considered, 2) completely consistent with bulk as only NBS heats and free energies of formation have been employed, and 3) maximally consistent with the cluster. It is hoped that these values will find utility in the increasingly important activity of connecting cluster ion data to bulk.
References


Figure 2.1. Plot of the bulk single-ion solvation enthalpies determined with Morris’ absolute value for the proton (-1103 kJ/mol) vs. the cluster solvation enthalpies for clusters with 5 water molecules. The positive and negative ions are grouped separately and display a different slope illustrating the two problems that must be overcome to achieve consistency of a particular absolute value of the proton with the cluster data set.
Figure 2.2. Plot of the bulk single-ion solvation enthalpies determined with Klots’ absolute value for the proton (-1136.4 kJ/mol) vs. the cluster solvation enthalpies for clusters with 5 water molecules. Klots’ chosen set of ions gives a fitted line successfully grouping the positive ions and selected negative ions onto a common line (albeit with a slightly increased slope over that of the positive ions alone). The strategy of eliminating OH$^-$ and F$^-$ from the process has not dealt with the problem of a different slope for the negative ions, leaving the OH$^-$ and F$^-$ species as deviant without explanation.
Figure 2.3. Plot of the bulk single-ion solvation enthalpies determined with the Coe method's absolute value for the proton (−1152.5 kJ/mol) vs. the cluster solvation enthalpies for clusters with 5 water molecules. The large halides were left out of the fit because they are surface states at n=5 and will not exhibit the same functional dependence of stepwise hydration energetics as do the internalized ions. The included ions fit very well to a common line with a slope very close (less than 0.5% difference) to that exhibited by the positive ions alone.
Figure 2.4. The correlation of the $Y'$ approximation and the bulk difference in ion volume for various pairs of alkali and halide ions. The value of $Y'$ (-1152.1 ± 1.8 kJ/mol) when the difference in bulk ion volumes is zero represents the best value of the proton's hydration enthalpy upon invoking the Born concept that ions of the same volume have the same bulk solvation enthalpies.
Figure 2.5. The correlation of the Y’ approximation and the difference in cluster ion solvation enthalpy. This correlation is very similar to that shown in Figure 2.4 regarding the position of ion pairs. The intercept value of -1151.0 ± 1.6 kJ/mol is consistent with that determined by invoking the Born concept showing that, in general, ions of the same volume have the same cluster solvation enthalpies as well as bulk solvation enthalpies. The problem of the proton’s bulk hydration enthalpy can be equivalently approached with the difference in bulk ion volumes or cluster solvation enthalpies.
Figure 2.6. The correlation of the $Y'$ approximation and the difference in cluster ion solvation enthalpy vs. cluster size. This plot contains the same data as in Figure 2.5 except that the cluster size has been specified. If the $Y'$ approximation is good at only one particular pair of ions, then each data set at a particular cluster size can be expected to share the good value in common. At each cluster size the data have been fit to a line by the method of least squares. The spread in these fitted lines vs. the difference in cluster ion solvation enthalpy was used to determine a most common value of $-1148.7 \pm 2.1 \text{ kJ/mol}$ which represents our best determination of the absolute proton hydration value without invoking the Born concept. This value is consistent with the values determined previously that had invoked the Born concept.
Figure 2.7. The correlation of the free energy or $X'$ approximation with the difference in cluster ion solvation free energy vs. cluster size. These data show an even more commonly shared point of $-1101.8(0.3)$ kJ/mol which represents our best determination of the proton's free energy of hydration without invoking the Born concept. This value compares favorably to the center-of-weight of previous determinations providing confidence in the enthalpic results of Figure 2.6.
Experimental Solvation Enthalpy Differences

Figure 2.8. The dependence of the bulk constants, $-\frac{1}{2}[k(A^+)+k(B^-)]$, on the difference in cluster solvation enthalpy vs. cluster size. The cluster approximation employed in the $Y'$ approximation involves only the first term of Eq. (48) which is essentially zero at the common point, so that the proton's absolute value is determined almost entirely by the behavior of the bulk constants from Table 2.3 vs. the difference in cluster solvation enthalpy. Notice the linearity of the data sets at particular cluster sizes and the shared common point at $-1149.1\pm2.0$ kJ/mol which is consistent with the previous determinations for the proton's absolute hydration enthalpy.
Transmission of ion beams over long distances or through the fringe field of a magnet has been extensively studied. Quadrupole, hexapole, and octopole guide rods, elaborate lens configurations, and stacked ring setups have been used to maintain ion beam density or overcome the magnetic "mirror." The simplest of these methods is the Electrostatic Particle Guide (EPG) based on the work of H. H. Kingdon.

Kingdon introduced an ion trap to minimize space charge effects in 1923. His design consisted of a tube with electrically connected end caps (Figure 3.1). A thin filament wire was mounted concentrically and a negative voltage was applied. Positive ions generated by a discharge were confined by the field directed inward towards the wire. The work was based on the investigation by Hull into the motion of an ion between concentric cylinders in electric and magnetic fields and expanded upon by Page. The specific case of motion in the Kingdon trap was studied much later by Lewis.
In 1964, Herb introduced the EPG as an avenue to better ion gauges. Terms the "Orbitron," Herb produced electrons from a filament inside the outer tube and used the extended path provided by the radial force to achieve the same level of accuracy as other contemporary gauges with ten times less emission current. He later extended this idea to ion pumps. Motion in the "Orbitron" was described numerically by Hooverman.

More recently, the EPG has been applied to studies of radioactive recoil ions and other secondary particles by time of flight mass spectrometry (TOF-MS). The primary concern to these experiments is the collection efficiency, or entry angle, and distortion, if any, of the TOF-MS peaks. Low energy and high-resolution TOF-MS have also been conducted with some success.

**Current System**

A version of the EPG was applied to a glow discharge source with the ultimate goal of detecting an infrared emission spectrum from the cluster ions of the beam (See Chapter 4). The goal of this line of investigation was to increase the transmitted current over a longer path, in turn increasing the average time each cluster was in a photon detection region.

A diagram of the EPG as it is applied to our system is given in Figure 3.2. The entry into the EPG consisted of a grounded stainless steel tube (2.5 cm ID and 1.2 cm in length). Mounted on this by means of Kimble Physics plates, and electrically isolated by Teflon spacers, is a stainless steel rod (1 mm diameter). This rod provides support for the central nichrome electrode (20 μm diameter). The repulsive drift tube was also constructed of stainless steel (2.5 cm ID and ~35 cm in length). The drift tube extended through the
Plexiglas flange and was sealed with a Cajon o-ring fitting (2.5 cm ID). A third stainless steel tube (2.5 cm ID and 4.5 cm in length) acted as the Faraday cup separated by a Plexiglas spacer (2.3 cm ID) and sealed with epoxy. A stainless steel rod mounted in the Plexiglas supported the nichrome wire at the exit of the drift tube. The spiral path predicted by theoretical models precluded the need to “cap” this tube with a conducting material as all ion trajectories left the drift tube with sufficient radial velocities to reach the outer tube without exiting the end. The end of the Faraday “tube” was sealed for vacuum use by a second Plexiglas spacer (2.3 cm ID) on which was mounted a NaCl window sealed with epoxy.

The experiments were performed inside a stainless steel vacuum chamber diagrammed in Figure 3.3. The pumping system consisted of 2 5000 L/s oil diffusion pumps (Balzers Diff 5000 with Dow Corning DP704 diffusion pump oil). The backing pumps are a Welch 1375 and a Welch 1398 mechanical pump, rated at 35.4 and 53.1 cfm respectively. An ion gauge (Kurt J. Lesker G075N Ion Gauge Tube, MKS Type 290 Ion Gauge Controller) monitored the chamber pressure throughout the experiment. Typical base pressure in the chamber was ~2 x 10⁻⁶ Torr. Source gas routinely raised this value to ~5 x 10⁻⁵ Torr. Addition of collision gas further raised the pressure from 7 x 10⁻⁵ up to a maximum of 2 x 10⁻⁴ Torr. Beyond this point, the chamber pressure is high enough that discharges occur at other points in the apparatus. The foreline pressure, monitored by thermocouple gauges (Varian Type 0531 Gauge, Varian Type 801 Controller) generally ranged from 5 mTorr to 15 mTorr.

Source and collision gases were introduced and regulated through use of a gas regulation system. A diagram of the gas line arrangement is shown in Figure 3.4. A mechanical pump
(Welch 1397, 17.7 cfm) was used to evacuate the gas lines before the valves to the chamber are opened. This pressure is monitored by a thermocouple gauge mounted on the roughing line. Needle valves (Nupro) are used for precise control of the gas flow to the apparatus. All lines are polyethylene tubing (6 mm ID).

The ion beam used in these experiments utilized a glow discharge source reported in earlier documentation\(^1\). The source consisted of 2 plates of mild steel separated by a Pyrex glass tube \(\approx 4\) cm in length. Viton O-rings in protective grooves on the plates provide a vacuum seal between the plates and the glass. The anodic front plate was a hexagon 3.5 cm across and 6 mm thick with a tapered 2.5 mm aperture. Holes were drilled into the plate to allow easy connection of ion optical components with a Kimble Physics hole pattern (Figure 3.5). The back plate was also a hexagon 18 mm thick. This plate had a port to allow introduction of the source gas to the discharge. A potential of \(~2500\) V placed across the plates with a 500 k\(\Omega\) ballast resistance in series will typically produce \(H_3O^+\) predominately with small amounts of \(H_3O^+(H_2O)_n\) clusters where \(n=1-4\) (Figure 3.6). This relative cluster ratio could be adjusted by changing the source conditions.

The ion beam voltage was established by an isolation scheme which floated the ion source to the requested voltage. A diagram of the circuit is shown in Figure 3.7. The discharge power supply determines the potential difference between the source plates and is isolated from ground. Initially, this power supply consisted of a bank of 510 V batteries (Eveready \#497) connected in series. This provided a steady voltage, but the cost of replacement batteries soon became prohibitive. In later experiments, the batteries were replaced with a Fluke 410B power supply and an isolation transformer. The beam power
supply (Fluke 410B) was used to establish the beam voltage, \( V_b \). This supply provides the float voltage for the front plate of the source. It is important to note that the polarity of the power supplies is arranged in such a way that the back plate is at a more negative voltage than the front plate as given by

\[ V_{\text{backplate}} = V_b - V_{\text{discharge}} = V_{\text{frontplate}} - V_{\text{discharge}}. \]  

A source with the back plate positive relative to the front will give electron bombardment ions. Ion currents between 5 and 20 \( \mu \)A were routinely obtained throughout these experiments.

The voltage to the other elements was provided through the use of a voltage divider circuit as shown in Figure 3.8. The beam voltage is divided by multiple 2W 160k\( \Omega \) resistors in series. The position of the potentiometer is selected by a banana-plug arrangement.

Connection to a Plexiglas disk electrically isolates the potentiometer. The wiper of the potentiometer is connected to the element being controlled.

**Simion Results**

The potential of a radial electric field, \( E(r) \), i.e. that generated by two coaxial cylinders is given by

\[ E(r) = -\frac{\text{d}\Phi}{\text{d}r} = \frac{V_o - V_i}{\ln(r_o/r_i)} \frac{1}{r}. \]  

(2)
where $V_o$ and $V_i$ are the voltages at the outer and inner cylinders respectively, $r_o$ is the inner diameter of the outer cylinder, and $r_i$ is the outer diameter of the inner cylinder. Placing a positive potential on the outer cylinder (or a negative potential on the inner cylinder) yields a net force inward for positive ions. From a safety point of view, the potential should be applied to the inner cylinder, but the present physical arrangement of the ion optics made this problematic.

The EPG tube assembly dimensions were entered into an ion optical simulation program, Simion. This program sets up a grid with cylindrical symmetry for calculating potentials. The grid used in this investigation and coordinate system are shown in Figure 3.9. A potential was placed on the drift tube and the potential array refined. As a check, the potential at several points was obtained and plotted in Figure 3.10 against the theoretical curve obtained from Eq. (2) with $V_o=1000$ and $V_i=0$.

The injection of the ions presents 3 variables with respect to the EPG. The first is the position of the ion beam where it crosses the $y$-$z$ plane at $x=0$. This represents the point of entry into the grounded end-cap of the EPG. The other parameters are the angles that the ions enter the tube relative to the coordinate system shown in Figure 3.9. The azimuth angle is defined at the angle from the $x$-$y$ plane towards positive $z$ and the elevation angle is from the $x$-$z$ plane towards positive $y$. Other items to be controlled are the ion mass and energy. For the purposes of this investigation, the ion is assumed to be $H_2O^+(H_2O)_n$ where $n=0-3$.

As the studies were intended for real world applications, single ion trajectories would be insufficient for comparison. Glow discharges sources are not point sources and space...
charge effects lead to beam spreading. As a result, a “spot” was simulated for the input of
the EPG (Figure 3.11). A 3 mm diameter circle was divided into 5 points, the center and 4
ordinate positions relative to the simulation coordinate system. From each of these points,
a pencil of rays was initiated with a 5° spread in both the y- and z-axis. The program took
space charge effects into account by assigning a portion of the arbitrary 10 μA ion current
to each trajectory and integrating the ions as line charges.

Some example ion trajectories are shown in Figure 3.12. The different trajectories
shown are the result of varying the injection angle from a fixed point.

Acceptance Angle

Angle of injection is the single most important element in transmission through the
EPG. For a given ion mass, ion energy and drift tube voltage, only a narrow range of
azimuth-elevation angle combinations permit passage through the EPG. Figure 3.13 shows
the results of simulations on H$_2$O$^+$ at 1000V and a drift tube voltage of 700V. The x- and y-
axes are the elevation and azimuth angles respectively. The elevation, z, on the plots is the
average flight time of all ions entering the grounded entrance tube. Of those trajectories
that successfully reached the end of the EPG, the average flight time ranged from ~5 to 14
μs. The straight line flight time for this device under those conditions, i.e. $V_{\text{drift tube}}=0$, and
zero elevation angle was 3.2 μs, an increase of only ~30% on the low end, although
experimentally some advantage is gained (see discussion). The closer the ion trajectory
passed the central wire during the initial entry into the high field region, the longer the
observed flight time. This effect reached an upper limit when the attraction of the ion to
the center electrode increased to the point that the ion collides with the wire and is neutralized.

As expected by symmetry, the direction of the spiral is unimportant. This is shown by the fact that the transmission band is "mirrored" about the center point of the plot in Figure 3.13.

**Energy and Mass Dependence**

The behavior of the ion transmission through the EPG was explored in terms of energy and mass dependence. The change in mass from one simulation to the next changed only in the time-of-flight of the cluster yielding no change in the actual ion path, and the effect was equivalent to a field free linear time-of-flight experiment where the time can be anticipated merely by the velocity, whether initially determined or derived from starting conditions, as evidenced by the linear time-vs. mass $^{1/2}$ plot of $\text{H}_2\text{O}^+(\text{H}_2\text{O})_{n=1,3}$ in Figure 3.14. For the conditions used for the figure, the expression,

$$L = vt$$

where $L$ is the ion path length in meters, $v$ is the ion velocity and $t$ is the time in seconds, can be expanded by substitution for $v$,

$$v = \sqrt{\frac{2qV_b}{m}}$$

(4),

to give,
Rearrangement to a linear expression yields,

$$L = \sqrt{\frac{2qV_b}{m}}$$  \hspace{1cm} (5),

where $t$ is the flight time, $m$ is the ion mass, $q$ is the fundamental charge, and $V_b$ is the beam voltage.

The energy dependence is more complex. The ratio of the energy of the ion to the potential difference of the cylinder-wire combination,

$$\alpha = \frac{V_{ion}}{V_o - V_i}$$  \hspace{1cm} (7),

determines the curvature of the ion path. As $\alpha$ approaches 0, the ion passes a critical threshold where it no longer possesses the energy to overcome the fringe fields of the EPG and is repulsed (for a given angle and starting position). A large $\alpha$ results in the internal field of the EPG being too small to bend the ion into a spiral path and the ion colliding into the outer cylinder and being neutralized.

The "energy transmission window" that is produced is dependent on the initial position and angle of the ion beam. Figure 3.15 shows the typical window produced at a given beam angle as a function of radial position. The "wire shadow" portion of the curve is exaggerated by the unrealistic size of the central wire in the simulation. The failure mode
shown as "Low $V_b$" is the result of reflection out of the tube by the large repulsive field of the apparatus. The slant of the "High $V_b$" area, a smaller window at large radius than at smaller, is counterintuitive without a closer examination of the injection region. When the radial initial position is large, the fringe field of the electrodes reduces the elevation angle of the trajectory, towards the straight line path. As the radius is reduced, the fringe field encountered changes, causing the elevation angle to increase beyond the transmission angle shown previously.

**Experimental Results**

The apparatus previously described (Figure 3.2) was intended to be used in experiments dealing with infrared emission (see Chapter 4). The behavior of the ion current was found to coincide with the behavior expected from the simulations. Experimentally it is difficult to decouple the position and angle dependence. A deflector mounted on the ion beam can change the angle, but also changes the position where the ion beam crosses the y-z plane and enters the first grounded tube of the EPG.

A deflector modulation of ~250V was applied and the current on the "Faraday tube" was recorded on a digitizing oscilloscope (LeCroy Model 9350AM). An example of these traces is shown in Figure 3.16. The broadcast from the modulation square wave is visible as a artifact prior to the rise or fall of the ion current. This allowed a direct measurement of the flight time between the modulation voltage going to zero and the arrival of the first ions. Small changes in the entry angle/position (via deflector or lens voltage changes earlier in the beam path) had profound effects on the profile observed. For maximum response
from the lock-in amplifier, the square wave shape was optimized, even at the expense of longer flight times.

**Discussion**

Throughout its history, the EPG has been used to increase the path length or the collection angle for charged species. The behavior of the ion inside the field tube with no perturbation by the ends has been dealt with in detail by Lewis, but starting in a field free region and entering the EPG, through the fringe fields, is a more difficult proposition. While the increase in time over the “straight-line” flight time is not necessarily large enough to warrant the added work, the real gain is in terms of current. The current of a similar source as a function of the beam path distance was investigated and the details are reported elsewhere. At times, the EPG system transmitted ~20μA over its length (~40 cm), far in excess of the “open path” current of ref. 21.

Use of the EPG with an ion beam requires careful alignment of the beam angle to the entrance tube and the point the beam crosses the entry plane. Some small corrections are possible with electrostatic deflectors, but gross changes usually result in very low currents, indicative of most of the ions being lost.

Often, the modulated current is adjusted to give the cleanest square wave possible for use with a lock-in amplifier. This particular combination of deflector and lens voltages also typically corresponds to the maximum transmitted current, although at the expense of flight time. An examination of Figure 3-15 demonstrates the reason for this phenomena. A “clean” square wave will occur when the range of flight times is small from a spot that
contains a range of both position and angle. This corresponds to the “flat” regions of the transmission windows, well away from the maximum flight times near the wire. If flight time is increased (i.e. the spot is moved closer to the wire), the range of flight times increases, distorting the square wave, and often loss of current as these longer times are near the edge of the window.

One enormous advantage to the stringent conditions necessary for ion transmission is in modulation. Since the transmission is very angle dependent, very little voltage (~200 V) is required to completely eliminate the transmission, providing a clean modulation, despite beam energies in excess of 1 keV.

Conclusions

The application of an electrostatic particle guide to the ion beams utilized in this research group is demonstrated theoretically and experimentally. The transmission for a representative \( V_{\text{w}}/V_{\text{tube}} \) ratio was explored in terms of entry angle, position, mass, and energy as a guide for coupling an ion beam to an EPG to be used in other experiments.
References

Figure 3.1. Diagram of the Kingdon Trap. Ions were generated internally and trapped into orbits about the central wire. The end caps restricted the ions axially.

Figure 3.2. Diagram of the current EPG system. Note the angle of the ion beam relative to the EPG.
Figure 3.3. Diagram of the vacuum chamber. Two 1500 L/s diffusion pumps, one water baffled, one l-N₂, provided a base pressure of ~5x10⁻⁷.
To Vacuum Chamber

Gas A  
Gas B  
Gas C  
Gas D

Source Gas Cut-off Valve

Needle Valve

Pumpout Valve

Vacuum Cutoff Valve

Mechanical Pump

Figure 3.4. Gas rack plumbing diagram.

Figure 3.5. Kimble Physics pattern of holes for the elements of the ion beam. The lightly shaded holes were used for the primary support. Each hole is 0.3” center-to-center.
Positive Ion Mass Spectrum
-1 Torr neat water vapor

Figure 3.6. Typical mass spectrum obtained from the glow discharge source. The x-axis is measured in volts as the spectrum is from a Wein velocity filter. This also accounts for the non-linearity in mass.
Figure 3.7. Diagram of the source circuit. The voltage applied by the beam power supply determines the beam voltage and the discharge voltage determines the source brightness. The ballast resistance improves the steadiness of the beam output. The back plate is kept more negative than the front for maximum cluster products. Reversing this polarity will give electron bombardment ions.

Figure 3.8. Diagram of the ion optical element circuit. The series of resistors acts as a voltage divider for the beam voltage ($V_b$), adjustable by varying the position of the potentiometer inputs. This arrangement maintains a constant ratio between the voltage applied on the ion optical element and the beam voltage, despite any changes in $V_b$. 
Figure 3.9. Simion grid and coordinates. The upper portion of the figure shows the potential surface of a cross-section of the EPG. The coordinate system and general layout of the Simion grid is shown in the lower portion. Note the exaggerated size of the central wire (2 mm diameter in the simulation vs. ~0.04 mm for the actual device). This constraint was imposed for ion trajectory purposes as an ion is considered to have struck a surface and been neutralized only if the grid points immediately surrounding the ion all are contained by an electrode. The 2 mm diameter was the smallest available that would guarantee the correct ion behavior near the central electrode.
Figure 3.10. Potential plot inside the guide tube. The points are samples taken from the Simion simulation and were plotted as a function of radius. The solid curve is the predicted potential from Eq. (2).

Figure 3.11. Spot picture. The initial trajectories for the ions in the simulation were arranged to imitate the real size of the ion source. Each of the 5 points contained 10 rays varying both in the xy- and xz-plane.
Figure 3.12. Example trajectories from the simulation. The upper portion of the figure shows the typical spiral nature of the ion spot trajectories for the initial portion of the EPG. The lower plots are single ion trajectories viewed along the x-axis. The notation on each plot refers to the azimuth angle of each initial ion condition. Note that as the angle increases, the eccentricity of the ion "orbit" decreases.
Figure 3.13. Azimuth and elevation angle plot. A surface involving flight time as a function of azimuth and elevation angles for the initial ion trajectory for a given starting position. Note the narrow range where the ions are successfully transmitted down the length of the guide tube. The symmetry of the plot confirms that the direction of the spiral is unimportant.
Figure 3.14. Time of flight plot. Several single ion trajectories involving ions of different masses are shown. The linearity shows that the EPG is functioning in the same manner as a time-of-flight mass spectrometer, despite its inherently curved trajectories. The ions followed the same path and struck the Faraday tube in the same spot regardless of mass.
Figure 3.15. Transmission window. Single ion trajectories were performed as a function of radial position and ion energy for a given set of input angles. The upper surface plot shows the flight time throughout the range studied. Note that the flight time dramatically increases as the wire is approached. The lower plot shows the same plot as a single-line contour around the base of the surface. Three failure modes have been identified for ion transmission. The "Wire Shadow" is caused by the ions coming into contact with the central wire. This is exaggerated by the unphysical size of the simulation wire. The "Low $V_e$" failure involves the ions not possessing sufficient energy to overcome the fringe field of the guide tube and being repelled. "High $V_e$" refers to the ion energy being too great for the tube voltage to bend the ions into an orbit before striking the outer wall.
Figure 3.16. Oscilloscope plot of the modulated ion current. A trace of the experimental modulated ion current at the Faraday tube of the EPG. The modulation square wave was set to 100 Hz and a 1kΩ input impedance was used resulting in the y-axis being 1 mV equal to 1 μA of ion current. The arrows denote the points where the modulation voltage changed. The delay was measured as ~25 µs.
Numerous methods exist to record vibrational spectra of molecular ions such as direct absorption in ion beams, photodissociation, photoinduced charge transfer cross-section change, and absorption/emission from discharges. A general technique for obtaining variable resolution spectra over a wide range of cluster ions and larger polyatomic ions is not presently available. Application of ion beams to this problem offers two clear advantages. The emitting ion species can be identified and isolated with standard mass spectrometric methods such as a Wein filter, and spatial separation of the photon collection region from the ion generation region where excited neutrals and radicals can interfere, complicating the resultant spectrum.

Infrared emission techniques require a high density of vibrationally excited ions to obtain suitable spectra. The spectroscopic method of choice is often cool ions "pumped" by a laser, but direct absorption in fast ion beams resulted in only $10^6$ excited ions.
Discharge techniques, however, often expend great amounts of effort\textsuperscript{14, 15} to minimize the "hotbands" often observed.\textsuperscript{16-18}

Ion beams do present some challenges, however. Sufficient densities of like-charged emitting ions is limited by space charge effects and ion lifetimes in fast ion beams are considerably shorter (\approx 5 \mu s) than the vibrational lifetimes of the cluster ions (> 1 ms). Unfortunately, optimization of one of these effects is at the expense of the other. Each apparatus presented here represents a different compromise.

**Multiple Collision Analysis**

The application of M.S. Kim's glancing collision definitions to the ion beam experiments performed in this research group has been previously discussed in detail.\textsuperscript{19} Attenuation measurements revealed that, even under multiple collision conditions, some fraction of the original ion beam current reached the end of the beam path. Kim's definition for total collision cross-section, $\sigma_T$, is given by

$$\sigma_T = \sigma_L + \sigma_{CA}$$  \hspace{1cm} (1)

where $\sigma_L$ is the cross-section resulting in ion loss and $\sigma_{CA}$ is the collisional activation cross-section, where ion current is still detected at the end of the beam path, either as the original parent ion, or as a fragment ion as a result of collision induced dissociation (CID).
The value of $\sigma_{CA}$ can be thought of as occurring in one of 2 pathways. The first is the case where the energy transferred in the collision is greater than the weakest bond in the cluster. This is the CID path and can be shown as

$$A^+(B)_n \rightarrow A^+(B)_{n-1} + B \rightarrow \ldots \rightarrow A^+ + nB. \quad (2)$$

The second case is one where the energy imparted to the ion cluster is less than the weakest bond, internal excitation. Multiple collisions of this type could be considered equivalent to the spectroscopic method of multi-photon dissociation and can be written as

$$A^+(B)_n \rightarrow A^+(B)_{n-1} \rightarrow A^+(B)_{n-2} \rightarrow \ldots \rightarrow A^+(B)_{n-1} + B \quad (3)$$

where energy is added until the total accumulated energy overcomes the weakest bond. The difference between the spectroscopic method and collisional activation is due to the nature of the excitation event. Photons with a narrow range of energies provide the excitation in spectroscopy, whereas the energy transfer due to collisions is a wider distribution.

These definitions, while useful for theoretical purposes, are not the parameters measured in the laboratory. Typical measurements include parent attenuation cross-section, $\sigma_p$, and the collision induced dissociation cross-section, $\sigma_{CID}$. The relation of these 2 parameters to Kim's definitions is easily seen. The ion loss cross-section, $\sigma_L$, is the loss of total ion current and does not include the fragment ions that reach the end of the beam path. The parameter $\sigma_p$, however, does include CID products as parent loss, and $\sigma_L$ can be written as
\[ \sigma_L = \sigma_p - \sigma_{\text{CID}}. \]  

(4)

The relationship between \( \sigma_{\text{CA}} \) and the measurable parameters is also a simple one,

\[ \sigma_{\text{CA}} = \frac{\sigma_{\text{CID}}}{1 - r_1}. \]  

(5)

The parameter \( r_1 \) is the key to the technique. It represents the fraction of the original ion beam that underwent a single collision, did not dissociate, and reached the end of the beam path. The expression in Eq. 5 yields the cross-section for ions that underwent one collision and reached the end of the beam path, regardless of dissociation.

All of these parameters were determined by fitting attenuation data with derived equations from Kim using \( r_1 \). The values of \( r_1 \) for \( \text{H}_3\text{O}^+(\text{H}_2\text{O}) \) and \( \text{H}_3\text{O}^+(\text{H}_2\text{O})_2 \) were determined to be 0.90 and 0.60, respectively. Once the value of \( r_1 \) is known for a species, the values of for the fraction that underwent \( n \) collisions, did not dissociate and remained in the ion beam, \( r_n \), are known. An inherent assumption in this method is that \( r_n = 0 \), i.e. no unimolecular processes account for ion loss. This assumption is valid for the experiments that determined these values for reasons given elsewhere.\(^1\)

The fact that the values of \( r_1 \) for these clusters are non-zero means a fraction of the collisions result in internal excitation of the ion cluster without loss from the ion beam. The cross-section that results in parent excitation, written as \( \sigma_{p^+} \), is expressed as

\[ \sigma_{p^+} = \sigma_{\text{CA}} - \sigma_{\text{CID}}. \]  

(6)
The results of this determination are shown in Figure 4.1 along with the data points for the fit of $r_\nu$. In the case of $H_2O^+(H_2O)$, a single collision most often results in internal excitation of up to 6% of the original beam (solid line) while 2 collisions cause dissociation in the majority of the cases (dashed line). This can be interpreted as transferring, on average, less than the bond energy of the cluster, 1.37 eV, with 1 collision and greater than this amount with 2 collisions, $\sim$1 eV.

The determination that a fraction of the ion beam can undergo a collision, acquire energy, and remain in the ion beam lends itself to a number of possibilities. One of the more attractive possibilities is detecting infrared photons emitted as the ion clusters relax.

**Previous Results**

Experiments performed earlier on a simple test apparatus (Figure 4.2) investigated total infrared emission from an ion beam of water clusters through the use of a collision gas to internally excite water clusters via glancing collisions. The water ion clusters were extracted and passed through a collision cell containing a higher pressure of argon. Next, parallel plate deflectors used for the modulation scheme and beam steering in one dimension were employed. The photon collection region consisted of a large (6") diameter cylinder containing 4 grounded rods. The end of the cylinder was sealed with an aluminum flange. Centered on this flange was a biconvex CaF$_2$ lens (f=2.5 cm). The outer cylinder was allowed to “float” at the potential placed upon it by the charging of the ion beam. The ions entered the tube and were kept nominally at a ground potential by the rods. When the ions left the “shielding” rods, they experienced a repulsive potential due to the “charged”
tube/lens flange and deflected away from the ion beam axis. The net effect of this arrangement was a “long” time (≈5 μs) spent by the ions in front of the collecting lens.

The fact that the emission from the ion clusters is several orders of magnitude lower than the blackbody background required the use of a modulation scheme in all the experiments performed. A 700-1000V square wave was applied to a set of parallel plate deflectors. The deflection was sufficient to move the ion beam out of the photon collection region. The net effect of this was an amplitude modulation of the transmitted ion current. All light measurements were taken with a liquid nitrogen cooled InSb detector (Cincinnati Electronics Model SDD-1963-S1) which has a maximum response in the O-H stretching region and very little response in the visible. The output of the detector was sent to a lock-in amplifier (Stanford Research SR510) and the signal was recorded.

Figure 4.3 shows the results of this preliminary investigation. The discharge turned off represents the background signal level. The discharge on, with the collision gas, in this case Ar, off, the light level increased slightly. Addition of the collision gas, despite the fact that the total ion current is reduced by 33%, increased the detected light by a factor of 4. The low response of the detector in the visible region lends credence to the identification of this response as infrared radiation.

Circular Variable Filter

Initial attempts at dispersion of the emission were accomplished by use of a Circular Variable Filter (CVF) with a transmission range of 2.5-4.5 μm (Optical Coating Laboratory, Inc.). The experimental apparatus is shown in Figure 4.4. Water ion clusters extracted at 1
keV from the glow discharge source and undergo glancing collisions with Ar introduced into the beam path via a 1/8” teflon tube, gaining on average 1 eV of internal energy. This ion beam is then modulated by a 700-1000 V square wave applied to the deflector at 160 Hz, experimentally determined to be a quiet area in the noise spectrum. The excited clusters then enter the photon collection cell where they “dwell” for approximately 0.1 μs. A Faraday cup to monitor the ion current terminated the beam path. This short time is offset by obtaining the highest possible ion density, limited only by space charge. This constraint required the ion beam path from the source to the photon collection cell to be as short as possible.

A fraction of the light emitted from the clusters while in the photon collection cell passes through the CVF and is focused on the InSb detector with a fast CaF₂ (f=2.5cm) lens. The CVF was controlled by a stepping motor directed by a FORTRAN program, Step6.for (see Appendix C), which divided the filter into 50 steps (10 of these steps at the 2.5 μm end were lost due to a crack that developed in the filter, which was subsequently covered by a small piece of stainless steel shim stock to prevent unfiltered light from reaching the detector).

The advantage of this arrangement, the ion beam orthogonal to the detector, as opposed to in line as in the previous experiment, is one of background. The presence of the ion source itself in the field of view of the detector greatly increased the background light level present in the original experiment. While the source light is not directly modulated, some experiments revealed that the modulation applied to the deflectors did result in the plasma of the source also being modulated. Under certain conditions, with a
sufficiently low frequency and high pressure, the discharge could be seen with the naked eye coming out of the source and modulated by the deflectors.

Detection of the emission perpendicular to the ion beam meant a fundamental tradeoff was present. To increase the time in front of the detector, the beam voltage should be lowered. The velocity of ions in an ion beam is found from,

\[ \frac{1}{2}mv^2 = qV_{acc} \]  \hspace{1cm} (7),

or, rearrangement gives,

\[ v_{ion} = \sqrt{\frac{2qV_{acc}}{m}} \]  \hspace{1cm} (8).

Inside the photon collection cell, the electric potential is at ground, and \( V_{acc} \) is equal to \( V_b \), the real voltage applied to the beam. It is obvious that the velocity is decreased with the beam voltage and the time to pass a given distance, or field of view, is increased. As the voltage is decreased, however, space charge effects have an increased influence on the ion current (see Chapter 3). The general space charge equation for ions is given\textsuperscript{20} as

\[ I_{max} = 0.90 \left[ \frac{q}{m} \right]^{1/2} V_{acc}^{3/2} \left( \frac{D}{L} \right)^2 \]  \hspace{1cm} (9)

where \( I_{max} \) is the maximum current in \( \mu A \), \( q \) is the ion charge, \( m \) is the mass in a.m.u., \( V_{acc} \) is the accelerating voltage, \( D \) is the tube diameter, and \( L \) is the tube length. This equation
clearly shows the decrease in maximum ion current (for a transport tube of given diameter) as $V_{acc}$ or $V_b$ at ground, is decreased.

The optimum condition for light detection is where both the number of ions and the time in front of the detector is a maximum. This can be written as

$$\text{IRF}_{\text{optimum}} = I_{FC} \frac{t}{\tau}$$

where $I_{FC}$ is the ion current in the Faraday cup, $t$ is the time in front of the detector and $\tau$ is the fluorescence lifetime. Use of the velocity relation,

$$v = \frac{L}{t}$$

and substitution of Eq. (7) into Eq. (10) yields,

$$\text{IRF}_{\text{optimum}} = I_{FC} \frac{L}{\tau} \sqrt{\frac{m}{2qV_b}}.$$  \hspace{1cm} (12)

Collection of the constants for a given species and apparatus gives

$$\text{IRF}_{\text{optimum}} = k \frac{I_{FC}}{\sqrt{V_b}}.$$\hspace{1cm} \hspace{1cm} (13)

where $k$ contains the instrumental and system factors and is expressed as.
Each system could be optimized by careful choice of $V_b$ such that Eq. 13 is a maximum.

The low resolution IR spectrum obtained and a background scan are shown in Figure 4.5. The blackbody background was produced with a discharge of Ar in place of the neat water vapor. The feature centered at 3700 cm$^{-1}$ shows good correlation with various experiments on $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ clusters$^{21, 22}$ if the low resolution nature of the experiment is taken into account. A typical mass spectrum from a similar source is nominally 40% $\text{H}_3\text{O}^+$, 25% $\text{H}_3\text{O}^+(\text{H}_2\text{O})$, 20% $\text{H}_3\text{O}^+(\text{H}_2\text{O})_2$, 10% $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$, and 5% other species (Figure 4.6). The central downward feature is an artifact of the CVF.

Discussion

The low resolution IR emission spectrum presented above demonstrates the feasibility of application of fast ion beam techniques to the general problem. The "peak" nature of the feature argues against the light being bremsstrahlung in origin. Such a source would be expected to emit over a much larger range of wavelengths, although it could be present in the background curve. The good correlation to the absorption spectra reported by Yeh$^{21}$ and Begemann$^{22}$ is also indicative of emissions from a molecular source.

Some fundamental problems are also shown, however. The peak power from the spectrum is $\sim 40$ fW. Each data point on the spectrum required 20 minutes of run time and a large time constant (10 sec typically) to acquire. This low power and long observation
time required means careful consideration is needed before attempting the experiment with a higher resolution spectrometer.

The use of a monochromator or other spatially dispersive method is difficult in the extreme. Loss of signal through the instrument makes alignment and subsequent scanning very time consuming. A Fourier transform approach, where the multiplex advantage could result in a greater “scan time” per point (for a fixed experiment time) and could conceivably give better results, but the interferometer would require a stepping action rather than a continuous sweep because of the large time constant required.

Cursory examination of the system used for the CVF shows that it was not optimized for resolution of the infrared peaks. Light that passes through a broad section of the filter can reach the detector, spreading a peak over a wide range. This was a concession to the physical dimensions of the vacuum system utilized. A two lens system where the photon collection region is imaged with a magnification of ~0.2 would greatly improve the resolution of the spectrum. This technique was not employed for this “proof of concept” study.

Initial work with undispersed emission from the EPG device has found ~1 pW of infrared light present from the unattenuated ion beam. Examination of Fig. 4-3 reveals that the corresponding light level (unattenuated ion beam, i.e. no collision gas) in the orthogonal setup was ~3 pW. The greater level observed was due to modulated background signal from ion-surface collisions in the modulation region. The EPG system does not have the modulation region in the field of view of the detector, eliminating this source of background
and lowering the amount of undispersed light recorded. This is encouraging as the \( \sim 1 \) pW of power observed is wholly due to vibrational relaxation.

**Conclusions**

An infrared emission spectrum from a fast ion beam of unresolved \( \text{H}_3\text{O}^+(\text{H}_2\text{O})_n \) clusters has been obtained through the crudest of spectrometers, a circular variable filter. The spectrum shows good agreement with published high resolution spectra.\(^{21, 22}\) Despite the low power of the signal, this method shows promise for general, low resolution spectra of cluster ions once optimization of the system (i.e. the physical layout of the photon collection region, improved optical setup for spectrum resolution).
References

Figure 4.1. Multiple collision analysis of $\text{H}_3\text{O}^+(\text{H}_2\text{O})$. The data points and the fit that produced the value for $r_1$, the fraction of the original ion beam that underwent one glancing collision, did not dissociate, and reached the end of the beam path. The solid $P^*$ curve is the total fraction of the ion beam, at a given attenuation, that has undergone a collision and absorbed excess energy. The lower solid curve and the dashed curve are the fraction of the original beam that dissociated. The dash-dot curve labeled 1 is the contribution from ions that underwent a single collision, and the dash-dot curve labeled 2 is the result of 2 collisions and similarly for the CID curves (dashed). This analysis can be read as, on average, one collision does not dissociate the ion while 2 will cause dissociation. As the experimental dissociation energy for $\text{H}_3\text{O}^+(\text{H}_2\text{O})$ is 1.37 eV, a collision energy of $\sim$1 eV can be concluded.
Figure 4.2. Original apparatus for finding total emission of infrared light.

The ion beam was directed at through a set of 4 grounded rods towards a CaF$_2$ lens. After a short time (< 1 second), the lens charges and repels the beam as it exits the region bounded by the rods. The fact that the beam is "pointed" at the detector gives long times (~5μs) in the detector field of view.
Figure 4.3. The undispersed infrared light detected from the emission of water clusters. When the ion source was turned off (labeled "beam off"), little light was observed on the detector. Turning the source on without adding collision gas ("gas off"), a light level of ~3 pW was detected. Addition of collision gas ("gas on"), although decreasing the total ion current in the photon collection area, raised the detected light to ~13 pW. Note that a large time constant, as evidenced by the long tail between "gas on" and "gas off," was applied to reduce the noise.
Figure 4.4. Diagram of the spectrometer. Ion clusters are extracted from the ion source and undergo glancing collisions with the argon introduced by a tube. The beam is amplitude modulated by a square wave sufficient to prevent ions from entering the photon collection region during the "high" portion of the wave. The emission from the ions, also modulated with respect to the photon collection region, passes through the circular variable filter and is focused on the InSb detector. The signal is then demodulated through a lock-in amplifier and the signal averaged over long periods of time.
Figure 4.5. Low resolution infrared emission spectrum of H$_3$O$^+$($\text{H}_2\text{O}$)$_n$. The background scan was produced using Ar as the source gas. The downward feature at 3000 cm$^{-1}$ common to both scans is an artifact of the circular variable filter. The excess light above 3300 cm$^{-1}$ is consistent with absorption measurements by Lee et al. Peak power is $\sim$33 fW.
Figure 4.6. Typical mass spectrum from the ion source. The dispersive element is a Wein filter.
APPENDIX A

MATHCAD TEMPLATES

Family Energetics II.mcd

This is the original calculation and plotting worksheet for the neutral water cluster calculations studied in Chapter 1. Each data set is converted to the excess binding energy per water molecule and plotted against $n^{-1/3}$. 
Family Energetics II.mcd

Read energetics data for chains and set up counter, i

Chains = READPRN. energetics.dat  \[i = 0..\text{rows(Chains)} - 1\]

Display values for chain data

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<th>Alternating Chain</th>
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</thead>
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<td>Chains_{i,2}</td>
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</tr>
<tr>
<td>12</td>
<td>3.16</td>
<td>4.09</td>
</tr>
</tbody>
</table>

Enter values for ring data and set up counter, ii

\(ii = 3..9\)

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<th>Convert counter to (n^{1.3}) plot</th>
</tr>
</thead>
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<td>(661.74)</td>
</tr>
<tr>
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<td>(1109.96)</td>
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<tr>
<td>5</td>
<td>1332.79</td>
<td>(1554.61)</td>
</tr>
<tr>
<td>6</td>
<td>1776.66</td>
<td>(1997.90)</td>
</tr>
</tbody>
</table>

Convert to binding energy per particle

\(\text{Ring}_{ii} = \frac{\text{Ring}_{ii}}{217.22}\)
Enter stacked cube data and set up counter, $j$

$$n_{sc,j} = \text{Stacked Cube Energy (Total)}$$

<table>
<thead>
<tr>
<th>$j$</th>
<th>$n_{sc,j}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>1786.12</td>
</tr>
<tr>
<td>12</td>
<td>2684.24</td>
</tr>
<tr>
<td>16</td>
<td>3583.12</td>
</tr>
<tr>
<td>20</td>
<td>4482.01</td>
</tr>
<tr>
<td>24</td>
<td>5380.96</td>
</tr>
<tr>
<td>28</td>
<td>6279.87</td>
</tr>
<tr>
<td>32</td>
<td>7178.81</td>
</tr>
<tr>
<td>36</td>
<td>8077.69</td>
</tr>
<tr>
<td>60</td>
<td>13471.29</td>
</tr>
<tr>
<td>92</td>
<td>20662.91</td>
</tr>
</tbody>
</table>

Convert counter to $n^{1.3}$ plot

$$n_j = \frac{1}{n_{sc,j}}$$

Convert to binding energy per particle

$$\text{SCube}_j = \frac{\text{SCube}_j}{n_{sc,j}} (217.22)$$

Enter hexagonal ice data and set up counter, $m$

$$m_{p} = \text{Ice Energy (Total)}$$

<table>
<thead>
<tr>
<th>$p$</th>
<th>$m_{p}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>1770.41</td>
</tr>
<tr>
<td>30</td>
<td>6683.35</td>
</tr>
<tr>
<td>39</td>
<td>8697.53</td>
</tr>
<tr>
<td>57</td>
<td>12736.72</td>
</tr>
<tr>
<td>72</td>
<td>16101.54</td>
</tr>
<tr>
<td>90</td>
<td>20140</td>
</tr>
</tbody>
</table>

Convert counter to $n^{1.3}$ plot

$$n_{m,p} = \frac{1}{m_{p}}$$

Convert to binding energy per particle

$$\text{Ice}_p = \frac{\text{Ice}_p - m_{p} (217.22)}{m_{p}}$$

Place point at bulk

$$n_{bulk} = 0 \quad \text{Bulk} = 11.3$$
Enter clathrate data and set up counter, mc

\[ \text{mc}_q \]

\[ \text{Clath}_q \]

\[
\begin{array}{c|c}
\text{n} & \text{Clath}_q \\
\hline
10 & 2232.54 \\
12 & 2674.81 \\
14 & 3123.45 \\
15 & 3346.93 \\
16 & 3571.90 \\
18 & 4013.83 \\
20 & 4459.63 \\
22 & 4897.48 \\
24 & 5358.69 \\
26 & 5804.17 \\
28 & 6248.77 \\
30 & 6692.72 \\
32 & 7146.30 \\
36 & 8038.68 \\
40 & 8923.62 \\
50 & 11154.58 \\
60 & 13388.22 \\
\end{array}
\]

Enter Stacked cube-1 data and set up counter, mm1

\[ \text{mm1}_{pp} \]

\[ \text{SCm1}_{pp} \]

\[
\begin{array}{c|c}
\text{n} & \text{SCm1}_{pp} \\
\hline
7 & 1557.45 \\
11 & 2455.59 \\
15 & 3354.12 \\
19 & 4252.94 \\
\end{array}
\]

Enter Stacked cube-2 data and set up counter, mm2

\[ \text{mm2}_{pp} \]

\[ \text{SCm2}_{pp} \]

\[
\begin{array}{c|c}
\text{n} & \text{SCm2}_{pp} \\
\hline
6 & 1333.57 \\
10 & 2233.54 \\
14 & 3131.79 \\
18 & 4030.37 \\
\end{array}
\]
Enter Stacked cube-3 data and set up counter, mm2

<table>
<thead>
<tr>
<th>pq</th>
<th>n</th>
<th>Cube Energy (Total)</th>
<th>Convert counter to n$^{1/3}$ plot</th>
</tr>
</thead>
<tbody>
<tr>
<td>mm3</td>
<td>SCm3</td>
<td>mm3</td>
<td>mm3</td>
</tr>
<tr>
<td>9</td>
<td>2008.03</td>
<td>2008.03</td>
<td>2008.03</td>
</tr>
<tr>
<td>13</td>
<td>2907.50</td>
<td>2907.50</td>
<td>2907.50</td>
</tr>
<tr>
<td>17</td>
<td>3804.76</td>
<td>3804.76</td>
<td>3804.76</td>
</tr>
</tbody>
</table>

Enter cubic ice data and set up counter, m

<table>
<thead>
<tr>
<th>pc</th>
<th>n</th>
<th>Ice Energy (Total)</th>
<th>Convert counter to n$^{1/3}$ plot</th>
</tr>
</thead>
<tbody>
<tr>
<td>mc1</td>
<td>IceC</td>
<td>mc1</td>
<td>mc1</td>
</tr>
<tr>
<td>10</td>
<td>2221.35</td>
<td>2221.35</td>
<td>2221.35</td>
</tr>
<tr>
<td>18</td>
<td>4011.93</td>
<td>4011.93</td>
<td>4011.93</td>
</tr>
<tr>
<td>26</td>
<td>5804</td>
<td>5804</td>
<td>5804</td>
</tr>
<tr>
<td>32</td>
<td>7154.6</td>
<td>7154.6</td>
<td>7154.6</td>
</tr>
<tr>
<td>34</td>
<td>7605.58</td>
<td>7605.58</td>
<td>7605.58</td>
</tr>
<tr>
<td>38</td>
<td>8499.63</td>
<td>8499.63</td>
<td>8499.63</td>
</tr>
<tr>
<td>42</td>
<td>9397.27</td>
<td>9397.27</td>
<td>9397.27</td>
</tr>
<tr>
<td>43</td>
<td>9614</td>
<td>9614</td>
<td>9614</td>
</tr>
<tr>
<td>45</td>
<td>10066.01</td>
<td>10066.01</td>
<td>10066.01</td>
</tr>
<tr>
<td>48</td>
<td>10742.43</td>
<td>10742.43</td>
<td>10742.43</td>
</tr>
<tr>
<td>57</td>
<td>12762</td>
<td>12762</td>
<td>12762</td>
</tr>
<tr>
<td>52</td>
<td>11638</td>
<td>11638</td>
<td>11638</td>
</tr>
<tr>
<td>68</td>
<td>15240</td>
<td>15240</td>
<td>15240</td>
</tr>
<tr>
<td>90</td>
<td>20180</td>
<td>20180</td>
<td>20180</td>
</tr>
<tr>
<td>92</td>
<td>20635.77</td>
<td>20635.77</td>
<td>20635.77</td>
</tr>
<tr>
<td>113</td>
<td>25343.25</td>
<td>25343.25</td>
<td>25343.25</td>
</tr>
<tr>
<td>120</td>
<td>26921.46</td>
<td>26921.46</td>
<td>26921.46</td>
</tr>
<tr>
<td>136</td>
<td>30500.63</td>
<td>30500.63</td>
<td>30500.63</td>
</tr>
</tbody>
</table>

Enter Stacked cubes of 5 data and set up counter, pq5

<table>
<thead>
<tr>
<th>pq5</th>
<th>n</th>
<th>Cube Energy (Total)</th>
<th>Convert counter to n$^{1/3}$ plot</th>
</tr>
</thead>
<tbody>
<tr>
<td>nsc5</td>
<td>SC5</td>
<td>nsc5</td>
<td>SC5</td>
</tr>
<tr>
<td>10</td>
<td>2234.35</td>
<td>2234.35</td>
<td>2234.35</td>
</tr>
<tr>
<td>15</td>
<td>3357.15</td>
<td>3357.15</td>
<td>3357.15</td>
</tr>
<tr>
<td>20</td>
<td>4481.27</td>
<td>4481.27</td>
<td>4481.27</td>
</tr>
</tbody>
</table>

mm3$^{1/3}$ $\frac{SCm3}{mm3}$

mc1$^{1/3}$ $\frac{IceC}{mc1}$

nsc5$^{1/3}$ $\frac{SC5}{nsc5}$
Cubic Ice Octa Multifit.mcd

Once the equations for "growing" a crystal of octahedral cubic ice to bulk are determined (see Chapter 1), the equations are used along with the calculated energies and the resulting fits for $E_4$, $E_3$, and $E_2$ to place the large $n$ curve on the excess binding energy plot. A similar template is created for the hexagonal ice structures.
**Cubic Ice Multifit - Octahedral Structures**

Input number of parameters to be fit ($E_4$, $E_3$, and $E_2$)

```
npar = 3
```

Input number of structures in fit

```
npts = 5
```

Set up counters

```
i = 0..npts - 1  j = 0..npar - 1  k = 0..npar - 1
```

Enter Structures by number of waters, $n$, and total atomic binding energy, $E$

```
<table>
<thead>
<tr>
<th>$N_i$</th>
<th>$E_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>2221.36</td>
</tr>
<tr>
<td>18</td>
<td>4011.81</td>
</tr>
<tr>
<td>35</td>
<td>7825.80</td>
</tr>
<tr>
<td>53</td>
<td>11868.25</td>
</tr>
<tr>
<td>84</td>
<td>18840.44</td>
</tr>
</tbody>
</table>
```

Input an array with the number of waters with 2, 3, and 4 hydrogen bonds for each structure

```
<table>
<thead>
<tr>
<th>$n$</th>
<th>$N_2$</th>
<th>$N_3$</th>
<th>$N_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>4</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>10</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>24</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>34</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>52</td>
<td>26</td>
<td></td>
</tr>
</tbody>
</table>
```

Convert the total atomic binding energy to excess binding energy per water molecule

```
$E_{b_i} = \frac{E_i - N_i \cdot 217.22}{N_i}$
```

Set up A and H matrices for fit

```
A_{j,k} = \sum_{i} n_{i,j} \cdot n_{i,k}  \quad  H_j = \sum_{i} n_{i,j} \cdot E_{i}  \quad  A_{inv} = A^{-1}
```

Output $A$ values

```
| 206 | 788 | 277 |
| 788 | 4552 | 1890 |
| 277 | 1890 | 846 |
```
Calculate $\alpha$ for each parameter

$$\alpha = \text{Ainv-H}$$

$$\alpha = -223.637$$

Calculate the fitted total atomic binding energy for each structure and output values

$$\text{Ecal}_i = \sum_j a_{i,j} n_{i,j}$$

<table>
<thead>
<tr>
<th>$\text{Ecal}_i$</th>
<th>$E_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>221.895</td>
<td>2221.36</td>
</tr>
<tr>
<td>4011.251</td>
<td>4011.81</td>
</tr>
<tr>
<td>7826.183</td>
<td>7825.8</td>
</tr>
<tr>
<td>11867.947</td>
<td>11868.25</td>
</tr>
<tr>
<td>18840.528</td>
<td>18840.44</td>
</tr>
</tbody>
</table>

Calculate the error in $y$

$$\sigma_y = \left( \frac{\sum_i (\text{Ecal}_i - E_i)^2}{\text{npts} - \text{npar}} \right)^{1/2}$$

$$\sigma_y = 0.65$$

Calculate the individual errors

$$\sigma_{\alpha_j} = \text{Ainv}_{i,j} \cdot \sigma_y$$

$$\sigma_{\alpha} = 0.072$$

Setup the counter for the cluster "shells"

$$S = 1..100$$

Input the equations for cluster growth

$$n_{4g} = S - \sum_{j=1}^{S} 4 \cdot (j - 1) - \sum_{i=1}^{j} (4 \cdot (2 \cdot i - 1))$$

$$n_{3g} = 4 \cdot (S - 1) - \sum_{i=1}^{S} (8 \cdot (i - 1))$$

$$n_{2g} = 6$$
Get total number of waters

\[ N_{\text{c}\text{s}} = n_4^s - n_3^s - n_2^s \]

Calculate the total atomic binding energy from the fitting expression

\[ E_s = n_4^s \cdot \alpha_2 - n_3^s \cdot \alpha_1 - n_2^s \cdot \alpha_0 \]

Convert to excess binding energy per water molecule

\[ \text{Exb}_s = \frac{E_s - N_{\text{c}\text{s}} \cdot 217.22}{N_{\text{c}\text{s}}} \]
This is the template that calculated the various values for the proton solvation enthalpy from the $Y'$ approximation method.
<table>
<thead>
<tr>
<th>bulk sums</th>
<th>1047.2</th>
<th>1020.0</th>
<th>879.2</th>
<th>845.7</th>
<th>816.6</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>938.2</td>
<td>911.0</td>
<td>770.2</td>
<td>736.8</td>
<td>707.4</td>
</tr>
<tr>
<td></td>
<td>855.8</td>
<td>828.6</td>
<td>687.8</td>
<td>654.3</td>
<td>625.0</td>
</tr>
<tr>
<td></td>
<td>830.4</td>
<td>803.2</td>
<td>662.4</td>
<td>628.9</td>
<td>599.8</td>
</tr>
</tbody>
</table>

We don't know the radius to use for OH-, so we pick one that fits the trend. 1.40 is Goldschmidt value, 1.1 fits well.

<table>
<thead>
<tr>
<th>cluster index</th>
<th>pos ion index</th>
<th>neg ion index</th>
</tr>
</thead>
<tbody>
<tr>
<td>n 0.. 5</td>
<td>m 0.. 5</td>
<td>w_n</td>
</tr>
<tr>
<td></td>
<td>r_p_i</td>
<td>r_n_j</td>
</tr>
<tr>
<td>0.0</td>
<td>0.0</td>
<td>.94</td>
</tr>
<tr>
<td>18.9</td>
<td>1.17</td>
<td>1.11</td>
</tr>
<tr>
<td>41.9</td>
<td>1.49</td>
<td>1.64</td>
</tr>
<tr>
<td>67.1</td>
<td>1.63</td>
<td>1.80</td>
</tr>
<tr>
<td>93.9</td>
<td></td>
<td>2.05</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Hp</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0 142.3</td>
<td>250.2</td>
<td>336.8</td>
</tr>
<tr>
<td>0 104.6</td>
<td>187.4</td>
<td>251.8</td>
</tr>
<tr>
<td>0 109.6</td>
<td>188.3</td>
<td>257.7</td>
</tr>
<tr>
<td>0 66.9</td>
<td>123.8</td>
<td>174.8</td>
</tr>
<tr>
<td>0 97.5</td>
<td>172.4</td>
<td>233.1</td>
</tr>
<tr>
<td>Hn</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 60.2</td>
<td>113.8</td>
<td>162.8</td>
</tr>
<tr>
<td>0 54.4</td>
<td>104.6</td>
<td>152.3</td>
</tr>
<tr>
<td>0 43.9</td>
<td>84.6</td>
<td>123.5</td>
</tr>
</tbody>
</table>

These are the constants relative to absolute proton value:

<table>
<thead>
<tr>
<th>constants</th>
<th>k_p_i</th>
<th>k_n_j</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>578.0</td>
<td>1624.5</td>
</tr>
<tr>
<td></td>
<td>687.0</td>
<td>1597.5</td>
</tr>
<tr>
<td></td>
<td>769.4</td>
<td>1456.7</td>
</tr>
<tr>
<td></td>
<td>794.8</td>
<td>1423.2</td>
</tr>
</tbody>
</table>

replaced Br- value of 1423.2 with a Rosseinsky scaled value of 1444, i.e.
the relative spacing between Cl-, Br-, and I- in Ross. was scaled to the Cl-, I- gap in the NBS data. the best fit value is 1464.0. this would give Bromine a bigger bulk value than Chlorine by 6.3 kJ/mol, i.e. they are the same! since internalized fit better, maybe this procedure should only be done with the halides. with all cluster ions, optimal Br- constant was found to be 1449.9.
this is the fraction of bulk obtained at n = 5
\[ c(i,j,n,m) = \frac{Hsp_{i,n} - Hsn_{j,m}}{Hbsum_{i,j}} \]
\[ c(0,0,nx,mx) = 0.6225 \]

absolute proton value is Ytry
\[ Ytry = 1146.2 \]
Coe results
\[ Hpb_i - kp_j - Ytry \quad Hnb_j - kn_j - Ytry \]
\[ cp(i,n) = \frac{Hsp_{i,n}}{Hnb_j} \cdot \frac{Hsn_{j,n}}{cp(i,n)} \]
\[ cn(j,nx) = \frac{Hnb_j}{cn(j,nx)} \]

\[ c(0,0,nx,mx) = 0.6225 \]

define the difference from the approximating constant, \( \delta p \) and \( \delta n \)
\[ \delta p(i,j,n,m) = cp(i,n) - c(i,j,n,m) \quad \delta n(i,j,n,m) = cn(j,n) - c(i,j,n,m) \]

constraints on \( cp \) and \( cn \) values using only sign of cluster differences
\[ cdiff(i,j,nn,mm) = \frac{Hsp_{i,nn} - Hsn_{j,mm}}{Hsp_{i,nn} Hsn_{j,mm}} \]
\[ cdiff(1,1,nx,nx) = 1 \]
\[ cdiff(1,1,nx,nx) = -1 \]

All of the calculated proton values are either upper or lower limits as indicated by \( cdiff \), this includes only cluster data because the \( c \) are undefined for the monomers
\[ Ycalc(i,j,nn,mm) = \frac{1}{2} \frac{Hsp_{i,nn} - Hsn_{j,mm}}{c(i,j,nn,mm)} - kp_i - kn_j \]
\[ Ycalc(3,0,nx,mx) = 1.1086 \times 10^3 \]
\[ r_{pi} = r_{pi} - 0.0 - 1.0 \quad r_{pbc_{i,n}} = r_{pi} \cdot n(1.928 - 0.885)^3 \cdot 3 \]
\[ r_{pi} = r_{pi} - 0.15 - 1.19 \]
\[ m_{j} = m_{j} - 0.0 - 1.0 \quad r_{mbc_{j,n}} = m_{j} \cdot n(1.928 - 0.885)^3 \cdot 3 \]
\[ r_{mbc_{i,n}} = r_{mbc_{i,n}} \cdot 3 - n(1.928 - 0.885)^3 \cdot 3 \]
\[ r_{mbc_{i,n}} = r_{mbc_{i,n}} - 0.0 - 1.33 \]
\[ r_{mbc_{i,n}} = r_{mbc_{i,n}} \cdot 1.8 \]
\[ r_{mbc_{i,n}} = r_{mbc_{i,n}} \cdot 3 \]

<table>
<thead>
<tr>
<th>( r_{pbc_{i,n}} )</th>
<th>( r_{mbc_{i,n}} )</th>
<th>( m_{j} )</th>
<th>( m_{j} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.9499</td>
<td>2.9689</td>
<td>0.94</td>
<td>1.1</td>
</tr>
<tr>
<td>2.9791</td>
<td>2.9776</td>
<td>1.17</td>
<td>1.16</td>
</tr>
<tr>
<td>3.0419</td>
<td>3.0811</td>
<td>1.49</td>
<td>1.64</td>
</tr>
<tr>
<td>3.0783</td>
<td>3.1302</td>
<td>1.63</td>
<td>1.8</td>
</tr>
<tr>
<td>3.2222</td>
<td>3.2222</td>
<td>2.05</td>
<td>2.05</td>
</tr>
</tbody>
</table>
$$\Delta V(i,j,n3,m3) = \frac{4}{3} \pi r_{pbc,i,n3}^3 \Delta V(i,j,n1,m1) = \frac{4}{3} \pi r_{pbc,i,n1}^3$$

$$k_l = 0.499 \quad y_l = Y_{calc}(i,j,n3,m3)$$

$$x_{1,25i-25j-5(n3-1)-(m3-1)} = \Delta V(i,j,n3,m3) \quad \text{intercept}(x_1,y_1) = -1.1714 \times 10^3$$

$$y_{calc_k1} = \text{slope}(x_1,y_1) \cdot x_{kl} - \text{intercept}(x_1,y_1)$$

$$i_l = 0 \quad j_l = 4 \quad n_l = 5 \quad m_l = n_l$$

Check for consistency of both monomer ions and clusters with Born theory

$$H_v = 44.01 \quad H_{pbc,i,n} = H_{p,i,n} - H_{pb,i} - n \cdot H_v \quad H_{nbc,j,n} = H_{n,j,n} - H_{nb,j} - n \cdot H_v$$
\[ \begin{align*}
\text{Hpcl}_{i,5} & \quad \text{Hnbc}_{j,5} \\
324.65 & \quad 322.25 \\
324.15 & \quad 327.35 \\
304.35 & \quad 282.45 \\
305.85 & \quad 253.65 \\
& \quad 268.05
\end{align*} \]

Born slope \( ib = 0 \ldots 1 \quad b_0 = 0 \quad b_1 = -685.8 \quad rm1_0 = 0 \quad rm1_1 = 1 \)

\[ \begin{align*}
\text{Hpcl}_{i,n} & \quad \text{Hnbc}_{j,n} \\
\text{Hpcl}_{i,n} & \quad \text{Hnbc}_{j,n} \\
\text{Hpcl}_{i,n} & \quad \text{Hnbc}_{j,n} \\
\text{Hpcl}_{i,n} & \quad \text{Hnbc}_{j,n} \\
\text{Hpcl}_{i,n} & \quad \text{Hnbc}_{j,n} \\
\text{Hpcl}_{i,n} & \quad \text{Hnbc}_{j,n}
\end{align*} \]

\[ \begin{align*}
kn = 0 \ldots 19 \\
yn1_{-i-j} = \text{Ycalc}(i,j,1,1) \quad xn1_{-i-j} = \text{Hsp}_{i,1} - \text{Hsn}_{j,1}
\end{align*} \]

\[ \begin{align*}
yn1_{\text{calc}}_{kn} &= \text{slope}(xn1,yn1) \cdot xn1_{kn} + \text{intercept}(xn1,yn1) \\
\text{slope}(xn1,yn1) &= 0.6379 \quad \text{intercept}(xn1,yn1) = -1.1427 \cdot 10^3
\end{align*} \]
\[ y_{n2}^{i-j} = Y_{\text{calc}(i,j,2,2)} \quad x_{n2}^{i-j} = H_{s_i} - H_{s_j} \]

\[ y_{n2}^{i-j} = \text{slope}(x_{n2}, y_{n2}) \cdot x_{n2}^{i-j} - \text{intercept}(x_{n2}, y_{n2}) \]
\[ \text{slope}(x_{n2}, y_{n2}) = 0.4144 \quad \text{intercept}(x_{n2}, y_{n2}) = -1.1467 \times 10^3 \]

\[ y_{n3}^{i-j} = Y_{\text{calc}(i,j,3,3)} \quad x_{n3}^{i-j} = H_{s_i} - H_{s_j} \]

\[ y_{n3}^{i-j} = \text{slope}(x_{n3}, y_{n3}) \cdot x_{n3}^{i-j} - \text{intercept}(x_{n3}, y_{n3}) \]
\[ \text{slope}(x_{n3}, y_{n3}) = 0.3312 \quad \text{intercept}(x_{n3}, y_{n3}) = -1.1462 \times 10^3 \]

\[ y_{n4}^{i-j} = Y_{\text{calc}(i,j,4,4)} \quad x_{n4}^{i-j} = H_{s_i} - H_{s_j} \]

\[ y_{n4}^{i-j} = \text{slope}(x_{n4}, y_{n4}) \cdot x_{n4}^{i-j} - \text{intercept}(x_{n4}, y_{n4}) \]
\[ \text{slope}(x_{n4}, y_{n4}) = 0.2799 \quad \text{intercept}(x_{n4}, y_{n4}) = -1.1447 \times 10^3 \]

\[ y_{n5}^{i-j} = Y_{\text{calc}(i,j,5,5)} \quad x_{n5}^{i-j} = H_{s_i} - H_{s_j} \]

\[ y_{n5}^{i-j} = \text{slope}(x_{n5}, y_{n5}) \cdot x_{n5}^{i-j} - \text{intercept}(x_{n5}, y_{n5}) \]
\[ \text{slope}(x_{n5}, y_{n5}) = 0.254 \quad \text{intercept}(x_{n5}, y_{n5}) = -1.1422 \times 10^3 \]

\[ n2 = 1..5 \]
\[ k2 = 0..99 \quad y_{2}^{i,j} = Y_{\text{calc}(i,j,n2, n2)} \quad x_{2}^{i,j} = \Delta V_{i,j, n2, n2} \]

\[ y_{2}^{i,j} = \text{slope}(x_{2}, y_{2}) \cdot x_{2}^{i,j} - \text{intercept}(x_{2}, y_{2}) \]
\[ \text{slope}(x_{2}, y_{2}) = 1.7387 \quad \text{intercept}(x_{2}, y_{2}) = -1.148 \times 10^3 \]

\[ n6 = 1..5 \]
\[ x_{6}^{i,j} = H_{s_i} - H_{s_j} \]

\[ y_{6}^{i,j} = \text{slope}(x_{6}, y_{2}) \cdot x_{6}^{i,j} - \text{intercept}(x_{6}, y_{2}) \]
\[ \text{slope}(x_{6}, y_{2}) = 0.3088 \quad \text{intercept}(x_{6}, y_{2}) = -1.1462 \times 10^3 \]

\[ ii = 3 \quad jj = 2 \quad nn = 2 \quad mm = nn \]
fits with error in both x and y, k2 is index of points, y2 vs x2 and y2 vs x6 for bulk electron
density volumes and cluster solvation enthalpies respectively

\[
\begin{align*}
\alpha x_2 &= 3 & \alpha x_6 &= 8 & \alpha y_2 &= 10 \\
ib &= 0.20 & bx_{2ib} &= 1.9 - ib \cdot 0.1 & bx_{6ib} &= 2.5 - ib \cdot 0.05 \\
\end{align*}
\]

\[
\begin{align*}
wx_{2ib} &= \frac{1}{(\alpha y_2)^2 - bx_{2ib}^2 - (\alpha x_2)^2} \\
\sum_{k2} wx_{2ib} \cdot y_2 \cdot k2 \\
ax_{2ib} &= \sum_{k2} wx_{2ib} \\
\chi^2_{2ib} &= \frac{y_2 \cdot ax_{2ib} \cdot k2}{(\alpha y_2)^2 - bx_{2ib}^2 - (\alpha x_2)^2} \\
\end{align*}
\]

\[
\begin{align*}
wx_{6ib} &= \frac{1}{(\alpha y_2)^2 - bx_{6ib}^2 - (\alpha x_2)^2} \\
\sum_{k2} wx_{6ib} \cdot y_2 \cdot k2 \\
ax_{6ib} &= \sum_{k2} wx_{6ib} \\
\chi^2_{6ib} &= \frac{y_2 \cdot ax_{6ib} \cdot k2}{(\alpha y_2)^2 - bx_{6ib}^2 - (\alpha x_2)^2} \\
\end{align*}
\]

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160
APPENDIX B

FORTRAN PROGRAMS

Step6.for

This program was designed to control the step motor circuit for the circular variable filter (CVF) and display the output of the lock-in amplifier as read by a analog-digital converter (ADC) board during the later infrared emission experiments (Chapter 4).

```
c routine for controlling the step motor and dispersing IR
   emission. STEP version 6.0
   --Michael D Tissandier
   Alan Earhart
   8/19/95

   Variable List
   ydata Array to hold averaged values from all scans
   ysing Array to hold values from single scan
   xy Needed for graphics display-moveto
   dummy Needed for graphics display-lineto, setpixel
   fln Filename for saving data
   nread Number of readings per point
   nwait Delay time before recording detector output
   navg Number of scans to average
   xyz Dummy variable to slow loop
   posit Record of CVF step number
   inpos Integer form of posit
   key Holder for proceed/stop inputs from keyboard
   kkey Placeholder for stopping a scan
   npos New position for CVF movement
   steps Counter for movement by position number
   basel Baseline for non-CVF scan
   zlevel Array for summation of light levels
```
zleveltot Final value for summation
i,j,k,kk,t,tt,z Loop counters
This list is now incomplete....
End Variable List

INCLUDE 'FGRAPH.FI'
INCLUDE 'FGRAPH.FD'
dimension ydata(50)
dimension ysing(50)
dimension yy(700)
dimension zlevel(7201)
dimension zlevavg(2000)
dimension zlevsd(2000)
RECORD /xycoord/ xy
INTEGER*2 dummy
integer*2 iiiter
character*15 fln
logical*1 kkey
data ioadl,ioadh,ibyte/768,769,0/
c set gain
call oup(0,779,ibyte)
c set mux input channel to 0 (use 17 in first parameter to read
c from channel 1)
call oup(0,770,ibyte)
c be sure CVF is in start position
5
call cls
posl=0
write(5,*)'Set CVF into starting (0) position'
write(5,*)' press <space> when ready'
call inkey(key)
if(key.eq.32)goto 100
goto 5

*****************************************************************
c display main menu
c*****************************************************************
100
call cls
write(5,*)'Step Program Main Menu'
write(5,*)'1-Scan CVF'
write(5,*)'2-Reset CVF to starting point'
write(5,*)'3-Change position of CVF'
write(5,*)'4-Move CVF to "open" position'
write(5,*)'5-Move CVF to "blocked" position'
write(5,*)'6-Manual reset of CVF to 0'
write(5,*)'7-Scan without CVF'
write(5,*)'8-Integrate light level'
write(5,*)'Q-Quit'
write(5,*)'
write(5,*)'Enter Number of Choice: '
call inkey(key)

C Goto section specified
if(key.eq.49)goto 10
if(key.eq.50)goto 20
if(key.eq.51)goto 30
if(key.eq.52)goto 40
if(key.eq.53)goto 50
if(key.eq.54)goto 60
if(key.eq.55)goto 70
if(key.eq.56)goto 80
if(key.eq.113)goto 999
goto 100

C ************************************************************
C Scan CVF Section
C ************************************************************

10 call cls
C set number of readings per point
    write(5,*)'enter number of readings per point'
    read(5,*)nread

C set scan wait time
    write(5,*)'enter scan wait time'
    read(5,*)nwait

C set number of scans to average
    write(5,*)'enter number of scans'
    read(5,*)navg

C wait to begin scanning
110 write(5,*)'press <space> to begin scan'
call inkey(key)
if(key.eq.32)goto 120
goto 110

120 continue

C initialize ydata
    do 130 i=1,50
130 ydata(i)=0

C record scan loop
    dummy= setvideomode ( $vres16COLOR)
dummy= setcolor(1)
    do 140 k=1,navg
call moveto (2,230,xy)
call oup(2,771,0)

c point gathering loop

c take single spectrum

do 150 i=1,50
dummy= setpixel(2,479)

c take multiple readings and average for data point

   y=0.
do 160 kk=1,nread
call oup(iword,ioadl,ibyte)
call inp(iadl,ioadl,ibyte)
call inp(iadh,ioadh,ibyte)
   160 y=y+16.*iadh+int(iadl/16.)
y=y/(nread*1.)
ydata(i)=y+ydata(i)
ysing(i)=y

c take step for next reading

call oup(10,771,0)
call oup(2,771,0)
posit=posit+1

c wait loop

   do 170 tt=1,nwait
   xyz=1
   170 continue

c plot on screen - single scan

   iy=int((ysing(i)*460.)/4096.)
dummy=setpixel(2,479)
   ix=i*10
   150 dummy=lineto(ix,iy)

c changing directions for reset

call oup(0,771,0)
do 180 i=1,50
do 190 j=1,1000
   190 xx=1
call oup(8,771,0)
call oup(0,771,0)
posit=posit-1
   180 continue
   140 continue

c normalize signal average

   do 200 i=1,50
   ydata(i)=ydata(i)/(navg*1.)
c display total average

dummy=setcolor(15)
call moveto(2,230,xy)
do 210 t=1,50
  ty=int((ydata(t)*460.)/4096.)
dummy=setpixel(2,479)
tx=t*10
210  dummy=lineto(tx,ty)
c ready for next scan?
220  write(5,*),'press <space> to stop viewing'
call inkey(key)
if(key.eq.32)go to 230
goto 220
call cls
230  continue
dummy=setvideomode ($DEFAULTMODE)
c Save spectrum
240  write(5,*),'Would you like to save spectrum? (y/n)'
call inkey(key)
if(key.eq.110)go to 250
if(key.eq.121)go to 260
goto 240
260  write(*,'(a\')','enter filename '
  read(*,'(a)')fln
  open(3,file=fln)
do 270 i=1,50
270  write(3,*)i,ydata(i)
close(3)
250  continue
c Scan again?
280  write(5,*),'Would you like to scan with the same settings? (y/n)'
call inkey(key)
call cls
if(key.eq.121)go to 110
if(key.eq.110)go to 290
goto 280
290  write(5,*),'Scan with different settings? (y/n)'
call inkey(key)
if(key.eq.121)go to 10
if(key.eq.110)go to 100
goto 290

c *****************************************************
c Reset CVF Section

c *****************************************************
c Determine current position of CVF and set direction
20  if(posit.gt.0)go to 300
  if(posit.lt.0)go to 310
  if(posit.eq.0)go to 320

c Greater than 0 case

300    call oup(0,771,0)
cnt=posit
    do 330 z=1,cnt
call oup(8,771,0)
call oup(0,771,0)
    do 340 j=1,1000
340    xyz=1
    posit=posit-1
    continue

330    write(5,'*')'Position reset to start'
350    write(5,'*')'press <space> to proceed'
call inkey(key)
    if(key.eq.32)goto 100
goto 350

c Less than 0 case

310    call oup(2,771,0)
cnt=posit*(-1)
    do 360 z=1,cnt
call oup(10,771,0)
call oup(2,771,0)
    do 370 j=1,1000
370    xyz=1
    posit=posit+1
    continue

360    write(5,'*')'Position reset to start'
380    write(5,'*')'press <space> to proceed'
call inkey(key)
    if(key.eq.32)goto 100
goto 380

c Equal to 0 case

320    write(5,'*')'CVF already appears to be at the starting position'
330    write(5,'*')'Please make sure that this is the case.'
340    write(5,'*')'If not, manually set the filter to 0'
350    write(5,'*')'press <space> to continue'
call inkey(key)
    if(key.eq.32)goto 100
goto 390


c Change Position Section

30    call cls

    Manually or by position number?

31    write(5,'*')'Change position menu'
32    write(5,'*')' 1-Manual change using arrow keys'
33    write(5,'*')' 2-By position number'
34    write(5,'*')' 3-Return to Main Menu'
write(5,*)' '  
write(5,*)'Enter choice'  
call inkey(key)

c Goto section specified
   if(key.eq.49)goto 400
   if(key.eq.50)goto 410
   if(key.eq.51)goto 100
   goto 30
   goto 400

c Manual change section
   call cls
   write(5,*)'Right arrow moves clockwise'
   write(5,*)'Left arrow moves counterclockwise'
   write(5,*)'<space> returns to Position menu'
   call inkey(key)

c Determine filter direction
   if(key.eq.54)goto 420
   if(key.eq.52)goto 430
   if(key.eq.32)goto 30

c Go clockwise (right arrow)
   call oup(2,771,0)
   call oup(10,771,0)
   call oup(2,771,0)
   do 440 z=1,500
   440 xyz=1
    posit=posit+1
    goto 400

c Go counterclockwise (left arrow)
   call oup(0,771,0)
   call oup(8,771,0)
   call oup(0,771,0)
   do 450 z=1,500
   450 xyz=1
    posit=posit-1
    goto 400

c Change by position number
   call cls
   inpos=int(posit)
   write(5,*)'Present position number is ',inpos
   write(5,*)''
   write(5,*)'Enter new position number'
   read(5,*)npos

c Determine direction for movement
if(npos.lt.posit)goto 460
if(npos.gt.posit)goto 470
if(npos.eq.posit)goto 480

c Less than case (move counterclockwise)

460 call cls
call oup(0,771,0)
steps=posit-npos
do 490 z=1,steps
call oup(8,771,0)
call oup(0,771,0)
posit=posit-1
do 500 i=1,1000
500 xyz=1
490 continue
goto 30

c Greater than case (move counterclockwise)

470 call cls
call oup(2,771,0)
steps=npos-posit
do 510 z=1,steps
call oup(10,771,0)
call oup(2,771,0)
posit=posit+1
do 520 i=1,1000
520 xyz=1
510 continue
goto 30

c Equal to case (no movement)

480 call cls
write(5,*)'It appears that the CVF is already in that position.'
write(5,*)'If you do not believe that to be the case, you will'
write(5,*)'probably want to run the "Manual reset" portion of'
write(5,*)'the program.'
write(5,*)''
530 write(5,*)'press <space> to continue'
call inkey(key)
if(key.eq.32)goto 30
goto 530

c Move to open position Section

c Move to open position Section

40 call cls
write(5,*)'Press <space> to move CVF to the'
write(5,*)"open" (-50) position.'
call inkey(key)
if(key.eq.32)goto 600
goto 40

c move CVF to position
c determine direction for movement

600     if(posit.gt.-50)goto 610
       if(posit.lt.-50)goto 620
       if(posit.eq.-50)goto 630

c Greater than case

610     steps=posit+50
       call oup(0,771,0)
       do 640 z=1,steps
       call oup(8,771,0)
       call oup(0,771,0)
       do 650 i=1,1000
650     xyz=1
640     continue
       posit=-50
       write(5,*)'CVF is in "open" position.'
660     write(5,*)'press <space> to return to Main Menu'
       call inkey(key)
       if(key.eq.32)goto 100
       goto 660

c Lesser than case

620     steps=posit-50
       call oup(2,771,0)
       do 670 z=1,steps
       call oup(10,771,0)
       call oup(2,771,0)
       do 680 i=1,1000
680     xyz=1
670     continue
       posit=-50
       write(5,*)'CVF is in "open" position.'
690     write(5,*)'press <space> to return to Main Menu'
       call inkey(key)
       if(key.eq.32)goto 100
       goto 690

c Equal to case

630     call cls
       write(5,*)'It appears that the CVF is already in that position.'
       write(5,*)'If you do not believe that to be the case, you will'
       write(5,*)'probably want to run the "Manual Reset" portion of'
       write(5,*)'the program.'
       write(5,*)''
       write(5,*)'press <space> to return to Main Menu'
       call inkey(key)
       if(key.eq.32)goto 100
       goto 690

C *****************************************************************
C Move to blocked position Section
C *****************************************************************

169
50    call cls
    write(5,*),'Press <space> to move CVF to the'
    write(5,*),'"blocked" (-20) position.'
    call inkey(key)
    if(key.eq.32)goto 700
    goto 50

c    move CVF to position

c    determine direction for movement

700   if(posit.gt.-20)goto 710
    if(posit.lt.-20)goto 720
    if(posit.eq.-20)goto 730

c    Greater than case

710   steps=posit+20
    call oup(0,771,0)
    do 740 z=1,steps
    call oup(8,771,0)
    call oup(0,771,0)
    do 750 i=1,1000
    750  xyz=1
    740  continue
    posit=-20
    write(5,*),'CVF in "blocked" position.'

760   write(5,*),'press <space> to return to Main Menu'
    call inkey(key)
    if(key.eq.32)goto 100
    goto 760

c    Lesser than case

720   steps=((posit+20)*(-1))
    write(5,*),'steps = ',steps
    call oup(2,771,0)
    do 770 z=1,steps
    call oup(10,771,0)
    call oup(2,771,0)
    do 780 i=1,1000
    780  xyz=1
    770  continue
    posit=-20
    write(5,*),'CVF in "blocked" position.'

790   write(5,*),'press <space> to return to Main Menu'
    call inkey(key)
    if(key.eq.32)goto 100
    goto 790

c    Equal to case

730   call cls
    write(5,*),'It appears that the CVF is already in that position.'
    write(5,*),'If you do not believe that to be the case, you will'
    write(5,*),'probably want to run the "Manual Reset" portion of'
    write(5,*),'the program.'
write(5,*)' '  
write(5,*)'press <space> to return to Main Menu'  
call inkey(key)  
if(key.eq.32)goto 100  
goto 790

c ***********************************************************
c Manual reset Section  
c ***********************************************************

60   call cls
write(5,*)'This is to reset the position counter. Do this'
write(5,*)'ONLY if you believe that the CVF has lost track of'
write(5,*)'its position.'
write(5,*)' '  
write(5,*)'Make sure the CVF is in the "start" position before'
write(5,*)'continuing.'
write(5,*)' '
800   write(5,*)'Do you wish to reset counter? (y/n)'  
call inkey(key)  
if(key.eq.121)goto 810  
if(key.eq.110)goto 820  
goto 800

c Reset counter

810   posit=0  
write(5,*)'Counter reset.'  
830   write(5,*)'Press <space> to return to Main Menu.'  
call inkey(key)  
if(key.eq.32)goto 100  
goto 830

c Do NOT reset

820   write(5,*)'Counter NOT reset.'  
840   write(5,*)'Press <space> to return to Main Menu'  
call inkey(key)  
if(key.eq.32)goto 100  
goto 840

c ***********************************************************
c Scan Without CVF Section  
c ***********************************************************

70   call cls
write(5,*)'Enter number of readings per point '  
read(5,*)nread  
900   write(5,*)'press any key to begin'  
call inkey(key)  
if(key.eq.32)goto 905  
goto 905

905   dummy=setvideomode($vres16COLOR)  
dummy=setcolor(1)  
basel=240  
call moveto(2,479,xy)  
do 910 i=1,638
y = 0.
do 920 k k = l,n read
dummy=setpixel(2,479)
call oup(iword,iadl,ibyte)
call inp(iadl,ioadl,ibyte)
call inp(iadh,ioadh,ibyte)
y = y + 16.*iadh+int(iadl/16.)
continue
y = y/(1.*nread)
yy(i) = y
iy = int((y-2048.)*460./2048.)
iy = base1-iy
dummy=setpixel(2,479)
dummy=lineto(i,iy)
910 continue

C Check keyboard
930 if(key.eq.114)go to 940
call chkr(kkey)
if(kkey)go to 940
goto 40

C Output to disk
940 call inkey(key)
dummy=setvideomode($DEFAULTMODE)
950 write(5,*)'Would you like to save this scan? (y/n)'
call inkey(key)
if(key.eq.110)go to 960
if(key.eq.121)go to 970
goto 950
970 write(*,'(a\')')'Enter filename '
read(*,'(a')')fln
open(2, file = fln)
do 980 i = 1,638
980 write(3,*)i,yy(i)
close(3)
960 write(5,*)'would you like to scan again? (y/n)'
call inkey(key)
if(key.eq.110)go to 100
if(key.eq.121)go to 990
goto 960
990 write(5,*)'Use same number of readings per point? (y/n)'
call inkey(key)
if(key.eq.110)go to 70
if(key.eq.121)go to 900
990 goto 990

C ******************************************************
C Integration Section
C ******************************************************
80 call cls
c initialize variables

ziteravg=0.
sdsum=0.
zleve=0.
zlevtot=0.
elapsed=0.
isecs=0.
do 85 jj=1,7201
  zlevel(jj)=0.
do 86 ll=1,2000
  zleve(ll)=0.
do 86 zlevsd(ll)=0.
write(5,*),'Enter time for Integration in seconds'
write(5,*),'Present maximum: 7200s (2 hours)'
read(5,*),itime
write(5,*),'Enter number of iterations'
write(5,*),'Present maximum: 2000'
read(5,*),ii
write(5,*),'Press <space> to begin'
call inkey(key)
if (key.ne.32) goto 88

number of iterations loop

call cls
  irow=7
  icol=4

  call locate(irow-6,icol,ier)
  ztime=itime/60.
  write(5,*),'Time for each iteration (in sec) : ',itime
  call locate(irow-5,icol,ier)
  write(5,*),'Time for each iteration (in min) : ',ztime
  call locate(irow-4,icol,ier)
  write(5,*),'Total number of iteration(s) : ',ii

do 9999 i=1,ii
  zlevtot=0
  elapsed=0
  isecs=0

number of seconds loop

  inelapse=int(elapsed)
  call locate(irow-2,icol,ier)
  write(5,*),'Current iteration number : ',i
  call locate(irow-1,icol,ier)
  write(5,*),'Time elapsed (in min) : ',inelapse
  do 1000 kk=1,itime
c 1 second of scanning loop

    do 1010 jj=1,10000
       call oup(iword,ioidl,iobyte)
       call inp(iadl,ioidl,iobyte)
       call inp(iadh,ioidh,iobyte)
    1010
       y=y+16.*iadh+int(iadl/16.)
       y=y/10000.
       zlevel(kk)=y
       isecs=isecs+1
       if(isecs.ne.60) goto 1000
       isecs=0
       elapsed=elapsed+1
       inelapsed=int(elapsed)

    c
       call cls
       call locate(irow,icol,ier)
       write(5,'(A)')
       call locate(irow,icol,ier)
       write(5,'(A)') ' Time Elapsed (in min) : ',inelapsed
    1000
       continue

c total averaging loop

    do 1020 jj=1,itime
       zlevtot=(zlevtot*1.)+(zlevel(jj)*1.)
    1020
       continue
       zlevavg(i)=(zlevtot*1.)/(itime*1.)

c Display integration result

    call locate(irow+i,icol,ier)
    write(5,'(A)') 'Iteration : ',i,' :
    &write(5,'(A)') ' Ave Light Value (in DAC units) = ',zlevavg(i)

    c
    write(5,'(A)') 'Average Light Value (in DAC units) = ',zlevavg(i)
    write(5,'(A)')

9999
    continue

c Display average and standard deviation

    do 1099 zz=1,iiter
       ziteravg=ziteravg+zlevavg(zz)
    1099
       continue
       ziteravg=ziteravg/(iiter*1.)

    do 1098 zy=1,iiter
       zlevsd(zy)=zlevavg(zy)-ziteravg
    1098
       continue

       zlevsd(zy)=zlevsd(zy)*zlevsd(zy)
       sdsum=sdsum+zlevsd(zy)

    do 1098 zy=1,iiter
       zlevsd(zy)=zlevavg(zy)-ziteravg
       zlevsd(zy)=zlevsd(zy)*zlevsd(zy)
    1098
       continue

    sdsum=sdsum/(iiter*1.-1.)
sd=sqrt(sdsum)
zleveerr=sd/sqrt(iiter)
    write(5,'(A)') 'Average Light Value = ',ziteravg,' +/- ',zleveerr
1025  write(5,*) 'Would you like to save this data to a file? (y/n)'
call inkey(key)
if(key.eq.110) goto 1030
if(key.eq.121) goto 1027
goto 1025

1027  write(*,'(a\)') ' Enter filename: '
read(*,'(a)') fln
open(3, file=fln)
do 1028 i=l, i iter
1028  write(3,*) i, zlevavg(i)
write(3,*) ziteravg, zleveerr
close(3)

1030  write(5,*) 'Would you like to integrate again? (y/n)'
call inkey(key)
if(key.eq.110) goto 100
if(key.eq.121) goto 80
goto 1030

999   end
APPENDIX C

PERIODIC BOX VALUES IN HYPERCHEM

One of the features of Hyperchem is the ability to create a box of specified size around a solute and fill it with randomly oriented water molecules. Use of this feature required a knowledge of the appropriate edge length of the box to obtain the desired cluster size. Listed below are the sizes required for a cube (a=b=c) to achieve a specified number of solvating waters, n, for both neutral water (Table C-1) and with a solute, X, where X is a halide ion, alkali ion, OH⁻, or H₂O⁺ (Table C-2).
Table C-1. Edge length to achieve a specified neutral water cluster size, $n$. 

<table>
<thead>
<tr>
<th>$n$</th>
<th>Box Size</th>
<th>$n$</th>
<th>Box Size</th>
<th>$n$</th>
<th>Box Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>26</td>
<td>8.98</td>
<td>51</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>27</td>
<td>9</td>
<td>52</td>
<td>12.1</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>28</td>
<td>9.3</td>
<td>53</td>
<td>12.165</td>
</tr>
<tr>
<td>4</td>
<td>5.5</td>
<td>29</td>
<td>9.4</td>
<td>54</td>
<td>12.2</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>30</td>
<td>9.462</td>
<td>55</td>
<td>12.25</td>
</tr>
<tr>
<td>6</td>
<td>6.2</td>
<td>31</td>
<td>9.5</td>
<td>56</td>
<td>12.3</td>
</tr>
<tr>
<td>7</td>
<td>6.5</td>
<td>32</td>
<td>9.7</td>
<td>57</td>
<td>12.5</td>
</tr>
<tr>
<td>8</td>
<td>6.7</td>
<td>33</td>
<td>10</td>
<td>58</td>
<td>12.55</td>
</tr>
<tr>
<td>9</td>
<td>7</td>
<td>34</td>
<td>10.3</td>
<td>59</td>
<td>12.6</td>
</tr>
<tr>
<td>10</td>
<td>7.3</td>
<td>35</td>
<td>10.35</td>
<td>60</td>
<td>12.7</td>
</tr>
<tr>
<td>11</td>
<td>7.4</td>
<td>36</td>
<td>10.4</td>
<td>61</td>
<td>12.77</td>
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<tr>
<td>12</td>
<td>7.5</td>
<td>37</td>
<td>10.425</td>
<td>62</td>
<td>13</td>
</tr>
<tr>
<td>13</td>
<td>7.6</td>
<td>38</td>
<td>10.5</td>
<td>63</td>
<td>13.05</td>
</tr>
<tr>
<td>14</td>
<td>7.9</td>
<td>39</td>
<td>10.56</td>
<td>64</td>
<td>13.07</td>
</tr>
<tr>
<td>15</td>
<td>7.997</td>
<td>40</td>
<td>10.57</td>
<td>65</td>
<td>13.2</td>
</tr>
<tr>
<td>16</td>
<td>8</td>
<td>41</td>
<td>10.59</td>
<td>66</td>
<td>13.25</td>
</tr>
<tr>
<td>17</td>
<td>8.1</td>
<td>42</td>
<td>10.7</td>
<td>67</td>
<td>13.3</td>
</tr>
<tr>
<td>18</td>
<td>8.2</td>
<td>43</td>
<td>11</td>
<td>68</td>
<td>13.35</td>
</tr>
<tr>
<td>19</td>
<td>8.22</td>
<td>44</td>
<td>11.1</td>
<td>69</td>
<td>13.4</td>
</tr>
<tr>
<td>20</td>
<td>8.3</td>
<td>45</td>
<td>11.3</td>
<td>70</td>
<td>13.45</td>
</tr>
<tr>
<td>21</td>
<td>8.5</td>
<td>46</td>
<td>11.35</td>
<td>71</td>
<td>13.5</td>
</tr>
<tr>
<td>22</td>
<td>8.51</td>
<td>47</td>
<td>11.5</td>
<td>72</td>
<td>13.51</td>
</tr>
<tr>
<td>23</td>
<td>8.6</td>
<td>48</td>
<td>11.8</td>
<td>73</td>
<td>13.6</td>
</tr>
<tr>
<td>24</td>
<td>8.9</td>
<td>49</td>
<td>11.9</td>
<td>74</td>
<td>13.65</td>
</tr>
<tr>
<td>25</td>
<td>8.96</td>
<td>50</td>
<td>11.95</td>
<td>75</td>
<td>13.7</td>
</tr>
</tbody>
</table>

$(\text{H}_2\text{O})_n$
Table C-1. Edge length to achieve a specified $X(H_2O)_n$ cluster size where $X$ is a halide ion, alkali ion, OH', or H$_2$O'.
APPENDIX D

CALCULATION OF CARTESIAN COORDINATES FOR THE ORDERED ICE-Ih CRYSTAL UNIT CELL

Leadbetter et al. obtained a neutron scattering pattern of annealed D₂O at 5 K. The annealing process and low temperature obtained a highly ordered crystal for the subsequent experiment. The crystal was found to belong to the $Cmc2_1$ space group with the following dimensions for the unit cell: $a=4.5019 \text{ Å}$, $b=7.7978 \text{ Å}$, and $c=7.3280 \text{ Å}$. The five unique positions for atoms in the unit cell are given in Table D-1.

The $Cmc2_1$ space group has 4 symmetry operations as well as 2 positions for each operation. These are given in Table D-2.

Each of the 5 atoms given in Table D-1 are used to generate 7 additional atomic positions, in fractional coordinates, through use of the operations given in Table D-2. The generated results are given in Table D-3. Note that the ratio of oxygen to hydrogen is greater than 1:2. This is the result of the fact that not all of the generated coordinates are unique. Elimination of the shaded equivalent positions in Table D-3 yields the coordinates given in Table D-4. These coordinates are in Angstroms, obtained by multiplying the fractional coordinates by the appropriate unit cell dimension. Negative values for positions have been translated 1 unit cell length. The hydrogen atoms were paired with their
corresponding oxygen atoms by the distance between positions in the unit cell. Note that two hydrogen atoms, labeled H14 and H16, are on the opposite side of the unit cell from their corresponding oxygen (Figure D-1). The position of these atoms has been translated 1 unit cell to allow a reasonable bond distance. The structure of the unit cell was then entered into a Hyperchem input file (.hin) format (Figure D-2). The graphical output is shown in Figure D-3. The remaining structures in the ice studies were generated by addition of one or more unit cells in the 3 dimensions.

References

Table D-1. Positions of unique atoms within the unit cell of ordered Ice-Ih as reported by Leadbetter et al. Units are fractions of unit cell edge length in each respective dimension.

<table>
<thead>
<tr>
<th></th>
<th>O1</th>
<th>O2</th>
<th>D1</th>
<th>D2</th>
<th>D3</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>0.0000</td>
<td>0.5000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.6766</td>
</tr>
<tr>
<td>y</td>
<td>0.6648</td>
<td>0.8255</td>
<td>0.6636</td>
<td>0.5363</td>
<td>-0.2252</td>
</tr>
<tr>
<td>z</td>
<td>0.0631</td>
<td>-0.0631</td>
<td>0.1963</td>
<td>0.0183</td>
<td>-0.0183</td>
</tr>
</tbody>
</table>

Table D-2. Symmetry operations for the space group, $Cm\overline{2}$.

<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(0, 0, 0)</td>
<td>(+$\frac{1}{2}$, +$\frac{1}{2}$, 0)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(x, y, z)</td>
<td>(-x, -y, $\frac{1}{2}$ + z)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(x, -y, $\frac{1}{2}$ + z)</td>
<td>(-x, y, z)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table D-3. Generated positions of atoms in the unit cell. Shaded atoms are in redundant positions.
### Table D-4. Final generated atomic positions in Angstroms.

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>0.000</td>
<td>5.184</td>
<td>0.4624</td>
<td>H</td>
<td>0.000</td>
<td>5.175</td>
<td>1.438</td>
</tr>
<tr>
<td></td>
<td>0.000</td>
<td>2.614</td>
<td>4.126</td>
<td></td>
<td>0.000</td>
<td>2.623</td>
<td>5.102</td>
</tr>
<tr>
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<td>2.251</td>
<td>1.285</td>
<td>0.4624</td>
<td></td>
<td>2.251</td>
<td>1.276</td>
<td>1.438</td>
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<td>2.251</td>
<td>6.513</td>
<td>4.126</td>
<td></td>
<td>2.251</td>
<td>6.522</td>
<td>5.102</td>
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<td>2.251</td>
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<td>0.000</td>
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<td>0.000</td>
<td>3.616</td>
<td>3.798</td>
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<td>2.538</td>
<td>6.866</td>
<td></td>
<td>2.251</td>
<td>0.283</td>
<td>0.134</td>
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<td>0.000</td>
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<td>2.251</td>
<td>7.515</td>
<td>3.798</td>
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<td></td>
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<td>3.046</td>
<td>6.042</td>
<td>7.194</td>
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<td></td>
<td></td>
<td></td>
<td>1.456</td>
<td>1.756</td>
<td>3.530</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>3.046</td>
<td>1.756</td>
<td>3.530</td>
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<td></td>
<td>1.456</td>
<td>6.042</td>
<td>7.194</td>
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<td></td>
<td>0.795</td>
<td>2.143</td>
<td>7.194</td>
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<td></td>
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<td>3.707</td>
<td>5.655</td>
<td>3.530</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>0.795</td>
<td>5.655</td>
<td>3.530</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.707</td>
<td>2.143</td>
<td>7.194</td>
</tr>
</tbody>
</table>

### Table D-5. Crystallographic properties of ice polymorphs. Note the difference in space group for Ice-Ih. This is the result of the hydrogen positions determined in ref. (1).

<table>
<thead>
<tr>
<th>Ice</th>
<th>Ih</th>
<th>Ic</th>
<th>II</th>
<th>III</th>
<th>V</th>
<th>VI</th>
<th>VII</th>
<th>VIII</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal System</td>
<td>Hexagonal</td>
<td>Cubic</td>
<td>Rhombohedral</td>
<td>Tetragonal</td>
<td>Monoclinic</td>
<td>Tetragonal</td>
<td>Cubic</td>
<td>Cubic</td>
</tr>
<tr>
<td>Space Group</td>
<td>P63/mmc</td>
<td>F43m</td>
<td>R̅3</td>
<td>P41212</td>
<td>A2/a</td>
<td>P41/nmc</td>
<td>Im3m</td>
<td>Im3m</td>
</tr>
<tr>
<td>Cell Dimensions</td>
<td>a 4.48</td>
<td>a 6.35</td>
<td>a 7.78</td>
<td>a 113.1°</td>
<td>a 6.73</td>
<td>c 6.83</td>
<td>a 9.22</td>
<td>b 7.54</td>
</tr>
<tr>
<td>No molecules / unit cell</td>
<td>4</td>
<td>8</td>
<td>12</td>
<td>12</td>
<td>28</td>
<td>10</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Density at 1 atm and -175°C</td>
<td>0.94</td>
<td>...</td>
<td>1.17</td>
<td>1.14</td>
<td>1.23</td>
<td>1.31</td>
<td>...</td>
<td>1.50</td>
</tr>
</tbody>
</table>
Figure D-1. MathCAD generated positions of atoms in the unit cell. Note that the atoms marked H14 and H16 must be translated -1 unit cell lengths along the x-dimension to achieve a real bond distance.
Figure D-2. Hyperchem graphic of the Ice-Ih unit cell.
APPENDIX E

SELECTED HYPERCHEM FILES

Ice-Ih Unit Cell

This is the unit cell derived from the calculations of Appendix D. As a first step for creation of larger clusters, this set of 8 molecules is combined with additional unit cells where combinations of the x-, y-, and z-values have been added to an integer number of cell lengths to provide molecules in a different unit cell position in the same crystal. The values for the unit cell lengths are: a (or x): 4.5019, b (y): 7.7978, and c (z): 7.3280 Å. This file is i1huc.hin.

forcefield opls
sys 0
view 40 0.16869551510001 10001 -1.1255 -3.899 -58.664
seed -1111
mol 1
atom 1 - O ** - -0.3586454 0 5.184 0.4624 2 2 s 3 s
atom 2 - H ** - 0.1793224 0 5.175 1.438 1 1 s
atom 3 - H ** - 0.1793228 0 4.182 0.1341 1 1 s
endmol 1
mol 2
atom 1 - O ** - -0.3586454 0 2.614 4.126 2 2 s 3 s
atom 2 - H ** - 0.1793224 0 2.623 5.102 1 1 s
atom 3 - H ** - 0.1793228 0 3.616 3.798 1 1 s
endmol 2
mol 3
atom 1  - O ** - -0.3586454 2.251 1.285 0.4624 2 2 s 3 s
atom 2 - H ** - 0.1793224 2.251 1.276 1.438 1 1 s
atom 3 - H ** - 0.1793228 2.251 0.2831 0.1341 1 1 s
endmol 3

mol 4
atom 1  - O ** - -0.3586454 2.251 6.513 4.126 2 2 s 3 s
atom 2 - H ** - 0.1793224 2.251 7.515 3.798 1 1 s
atom 3 - H ** - 0.1793228 2.251 6.522 5.102 1 1 s
endmol 4

mol 5
atom 1  - O ** - -0.3586454 2.251 6.437 6.866 2 2 s 3 s
atom 2 - H ** - 0.1793224 3.046 6.042 7.194 1 1 s
atom 3 - H ** - 0.1793228 1.456 6.042 7.194 1 1 s
endmol 5

mol 6
atom 1  - O ** - -0.3586454 2.251 1.361 3.202 2 2 s 3 s
atom 2 - H ** - 0.1793224 1.456 1.756 3.53 1 1 s
atom 3 - H ** - 0.1793228 3.046 1.756 3.53 1 1 s
endmol 6

mol 7
atom 1  - O ** - -0.3586454 0 2.538 6.866 2 2 s 3 s
atom 2 - H ** - 0.1793224 0.795 2.143 7.194 1 1 s
atom 3 - H ** - 0.1793228 -0.795 2.143 7.194 1 1 s
endmol 7

mol 8
atom 1  - O ** - -0.3586454 0 5.26 3.202 2 2 s 3 s
atom 2 - H ** - 0.1793224 0.795 5.655 3.53 1 1 s
atom 3 - H ** - 0.1793228 -0.795 5.655 3.53 1 1 s
endmol 8
Ice-Ic Unit Cell

This unit cell is also derived from the calculations of Appendix D. This file is named icuc.hin.

forcefield opls
sys 0
view 40 0.16056 55 15 -0.5683673 -0.6634484 0.4866156 0.04593136 -0.6160949 -0.7863316
0.8214919 -0.4245742 0.3806414 -0.53265 3.5352 -55.27
seed -1111
mol 1
atom 1 - O ** - -0.3586454 0 0 0 2 2 s 3 s
atom 2 - H ** - 0.1793224 -0.57 -0.57 0.57 1 1 s
atom 3 - H ** - 0.1793228 0.57 -0.57 -0.57 1 1 s
endmol 1
mol 2
atom 1 - O ** - -0.3586454 0 3 3 2 2 s 3 s
atom 2 - H ** - 0.1793224 2.43 0.57 2.43 1 1 s
atom 3 - H ** - 0.1793228 3.57 3.57 3.57 1 1 s
endmol 2
mol 3
atom 1 - O ** - -0.3586454 3 0 3 2 2 s 3 s
atom 2 - H ** - 0.1793224 2.43 2.43 0.57 1 1 s
atom 3 - H ** - 0.1793228 3.57 3.57 3.57 1 1 s
endmol 3
mol 4
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atom 3 - H ** - 0.1793228 3.57 2.43 -0.57 1 1 s
endmol 4
mol 5
atom 1 - O ** - -0.3586454 1.5 1.5 1.5 2 2 s 3 s
atom 2 - H ** - 0.1793224 0.93 0.93 0.93 1 1 s
atom 3 - H ** - 0.1793228 0.93 2.07 2.07 1 1 s
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atom 3 - H ** - 0.1793228 5.07 2.07 3.93 1 1 s
atom 1 - O ** - -0.3586454 4.5 4.5 1.5 2 2 s 3 s
atom 2 - H ** - 0.1793224 3.93 3.93 0.93 1 1 s
atom 3 - H ** - 0.1793228 3.93 5.07 2.07 1 1 s
Hexamer “Cage” Structure

This is the predicted global minimum for the (H₂O)₆ cluster. The file is named w6cage.hin.

forcefield opls
sys 0
view 40 0.25252 55 15 -0.6417714 0.03414106 -0.7661357 0.672842 0.5044283 -0.541143
0.3679853 -0.8627783 -0.3466992 -0.24365 -3.6632 -51.523
seed -1111
mol 1
atom 1 - O ** - -0.4493923 2.126599 2.323017 -1.497497 2 2 s 3 s
atom 2 - H ** - 0.218823 2.525375 2.981963 -0.9197923 1 1 s
atom 3 - H ** - 0.2217103 1.528313 2.785526 -0.6417714 0.03414106 -0.7661357 0.672842 0.5044283 -0.541143
0.3679853 -0.8627783 -0.3466992 -0.24365 -3.6632 -51.523
seed -1111
endmol 1
mol 2
atom 1 - O ** - -0.4573765 1.128879 4.16688 -3.200283 2 2 s 3 s
atom 2 - H ** - 0.2031428 0.7029992 4.005824 -4.034363 1 1 s
atom 3 - H ** - 0.2575462 2.03613 4.475164 -3.363219 1 1 s
endmol 2
mol 3
atom 1 - O ** - -0.4133043 0.4083072 5.518684 -0.9975004 2 2 s 3 s
atom 2 - H ** - 0.2324671 0.4652861 5.219837 -1.912589 1 1 s
atom 3 - H ** - 0.1909525 -0.2147924 4.959805 -0.5452226 1 1 s
endmol 3
mol 4
atom 1 - O ** - -0.4390173 2.94619 4.703122 -0.5362201 2 2 s 3 s
atom 2 - H ** - 0.1999322 3.407141 4.984723 0.2456926 1 1 s
atom 3 - H ** - 0.2454461 2.101593 5.173109 -0.5885701 1 1 s
endmol 4
mol 5
atom 1 - O ** - -0.4307775 4.163649 2.056881 -3.2327 2 2 s 3 s
atom 2 - H ** - 0.1871048 4.92021 1.621016 -2.858141 1 1 s
atom 3 - H ** - 0.2352961 3.400439 1.884941 -2.6651 1 1 s
endmol 5
mol 6
atom 1 - O ** - -0.4522634 3.759859 4.712348 -3.129035 2 2 s 3 s
atom 2 - H ** - 0.2181992 3.72924 4.807296 -2.171691 1 1 s
atom 3 - H ** - 0.2315114 4.137646 3.84959 -3.333793 1 1 s
endmol 6
Hexamer “Book” Structure

This is the \( \text{(H}_2\text{O)}_6 \) structure related to the stacked cube family. The file is named \text{w6book.hin}.

\begin{verbatim}
forcefield opls
sys 0
view 40 0.27429 55 15 -0.4983553 -0.03145489 -0.8664022 0.6402284 0.6604965 -0.3922396
0.5845936 -0.75017 -0.3090237 0.31213 4.4924 -35.684
seed -1111
mol 1
atom 1 - O ** -0.419446 16.85972 2.18321 7.683013 2 2 s 3 s
atom 2 - H ** -0.1889791 17.19156 1.300119 7.564598 1 1 s
atom 3 - H ** -0.228382 17.53305 2.800068 7.374084 1 1 s
endmol 1
mol 2
atom 1 - O ** -0.4120512 18.88703 3.968249 7.349269 2 2 s 3 s
atom 2 - H ** -0.2287725 18.99966 4.226315 8.270097 1 1 s
atom 3 - H ** -0.1891757 18.67931 4.749976 6.848832 1 1 s
endmol 2
mol 3
atom 1 - O ** -0.4309664 16.9319 6.900735 10.31988 2 2 s 3 s
atom 2 - H ** -0.2413985 16.19659 6.382643 10.67272 1 1 s
atom 3 - H ** -0.1925387 16.61993 7.361262 9.548277 1 1 s
endmol 3
mol 4
atom 1 - O ** -0.4366894 14.97405 5.104637 10.80846 2 2 s 3 s
atom 2 - H ** -0.1914896 14.66856 4.940009 11.69374 1 1 s
atom 3 - H ** -0.242732 15.41553 4.304416 10.49283 1 1 s
endmol 4
mol 5
atom 1 - O ** -0.4631286 16.64746 3.060616 10.23047 2 2 s 3 s
atom 2 - H ** -0.2319939 16.50785 2.610924 9.389964 1 1 s
atom 3 - H ** -0.2167262 17.47842 3.542399 10.17341 1 1 s
endmol 5
mol 6
atom 1 - O ** -0.4410105 18.68808 4.865365 9.911213 2 2 s 3 s
atom 2 - H ** -0.2033096 19.38601 4.898227 10.55652 1 1 s
atom 3 - H ** -0.2477954 18.15038 5.664542 9.997121 1 1 s
endmol 6
\end{verbatim}
APPENDIX F

PM3 CALCULATED BINDING ENERGIES AND EXCESS BINDING ENERGIES PER WATER MOLECULE FOR SELECTED CLUSTERS

The following tables, organized by family, contain the results of the calculations on numerous water clusters using PM3. This is intended as a reference guide of structures for future work.
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**Bridging Chain Structures**

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**Alternating Chain Structures**

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Table F.1. PM3 values for the monomer, alternating chains, and bridging chain structures studied in Chapter 1.
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Table F.2 Rings and stacked cube structures
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Table F.3 Stacked pentagon and hexagon structures
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Table F.4 Partial stacked cube structures
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**Hexagonal Ice**

"Double Cone" Structures

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"Partial Prism" Structures

Table F.5  Hexagonal ice structures
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Table F.6 Cubic ice structures
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Table F.7 Other structures
LIST OF REFERENCES


