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FEATURE ARTICLE

Ab Initio Studies of the Microsolvation of Ions

Szczepan Roszak[†,‡] **and Jerzy Leszczynski***[,†]

The Computational Center for Molecular Structure and Interactions, Department of Chemistry,
Jackson State University, P.O. Box 17910 J. R. Lynch Street, 39217 Jackson, Mississippi, and
Institute of Physical and Theoretical Chemistry, Wroclaw University of Technology, Wyb. Wyspianskiego 27,
50-370 Wroclaw, Poland

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The building of ionic complexes by consecutive reactions of ligand coordination to the charged ion offers an attractive way to study complex systems. Modern experimental techniques allow the properties of complexes to be measured, successively from the bare ion to the condensed phase, or to restrain large molecular aggregates. Experiments provide direct or indirect information on structure, thermodynamics, reactivity, electron detachment properties, and molecular vibrations. The complementary, high-level ab initio studies supplement experimental findings, enhancing the interpretation and helping to remove the often-present ambiguities. The most distinguishing property of charged complexes is the formation of ligand shells around the ion. Such an organization determines properties of both the core ion and its ligand environment. Theoretical studies of nature of interactions lead to a simplified description of bonding and provides the base for developing the chemical intuition.

Introduction

A possible road leading to the understanding of complex systems are studies of increasing sizes “building blocks”, small fragments of the system of interest.[1] Such an approach is especially attractive when complexes are formed from weekly interacting fragments. Molecular crystals, liquids, and restrained large molecular aggregates are good examples of such moieties. In the case of microsolvated ions, modern experiments allow to detect cations or anions coordinating consecutive molecules or atoms. The evolution of properties may be followed from the bare ion to the final complex aggregate or to bulk properties of the condensed phase by such techniques.[2,3]

In most cases, ionic clusters are detected were matter is exposed to the ionizing radiation. Nuclear reactors, fusion, and magnetodynamic devices are examples of industrial appliances were such species are observed.[4] The upper atmosphere,[5] outer space,[6] and flames[7] are areas were charged clusters are being identified. The cluster structures in a small volume around the charged core often resemble the local order in condensed phases. The hopes associated with cluster studies reach far beyond a basic scientific interest and have also practical impacts. Chemical reactions are often controlled by the catalytic impact of an external medium.[8] Despite the fact, that cluster science has a long history with its root in the early studies of colloids,[9] recent development in experimental techniques of cluster production and selection have led to the fast advances in the field. The pioneering works performed in Sixties have produced enough data to create a separate field known as a cluster physics.[3] Significant progress was made when sophisticated tools such as lasers, modern flow reactors, molecular beam sources, and improved mass spectrometers become available. One of the first and still widely used technique, is the high-pressure mass spectrometry technique, a tool for deriving chemical equilibrium

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[†] The Computational Center for Molecular Structure and Interactions.
[‡] Institute of Physical and Theoretical Chemistry.

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constants for solvated ionic species.[10−14] Thermodynamical data for consecutive cluster ions have revealed the presence of solvation shells. The discontinuities in the otherwise smoothly changing characteristics are known today as “magic numbers”. The photodetachment experiment has been used to study anionic aggregates since the late Seventies.[15] With the development of negative ion photoelectron spectroscopy and its variations, this technique produces valuable information concerning the electronic properties and energetics of cluster sequences.[16] In recent years, great progress has also been made due to the high-resolution spectroscopic studies of ionic complexes.[17,18] High-resolution electronic, mid-infrared, and microwave spectra are now available for a large number of systems.

The experimental results provide direct information concerning the structures, thermodynamics, reactivity, electronic detachment properties, and molecular vibrations of charged clusters. However, the measured data are often too complex and ambiguous to be properly understood. This is especially true for larger clusters composed of more then two interacting components. The development of new theoretical methods together with increasing computational power allows advanced computations to supplement the experimental findings. Quantum-chemical investigations and Monte Carlo/molecular dynamics simulations are two complementary theoretical approaches. The quantum-mechanics-based Car-Parrinello molecular dynamics represents fast developing theoretical tools utilizing ideas of both above-mentioned approaches. Ab initio calculations are especially useful for studies of clusters were ions interact with solvent molecules within the close range. The convergence of the evolution of properties from those characterizing the bare ion to those representing the medium of interest (e.g., a solution) is dependent on many factors concerning ions and the surrounding environment. The order of basicities of H^- and NH_2^- ions is reversed when comparing bare ions and ions solvated in ammonia. It was shown experimentally[19,20] and confirmed theoretically[21] that only two NH_3 molecules are needed in the cluster to qualitatively reproduce the situation in the solution. The hydration of Cl^- anion, however, requires more then a dozen water molecules to form the stable cluster with chlorine nested inside the complex.[22] The reliable ab initio reproduction of such process through the consecutive complex building is not feasible at present.[23] Despite certain obvious restrictions of the ab initio approach, imposed by the necessity to use techniques and atomic basis sets able to account for most of the correlation energy, such studies provide valuable information for small clusters. High-level ab initio calculations are available for structures consisting of up to 12 components. The details of technical requirements for quantum-chemical methods depend on the particular case and may be found in works reporting calculations. Ab initio data are also valuable input for other theoretical techniques such as molecular dynamics.

At present theoretical studies are mostly used to supplement experimental findings, help to enhance their interpretation, and clarify ambiguities. The results of recent ab initio studies on charged clusters are presented in this paper. Structures, energetics, thermodynamics, vibrational spectra, and electron detachment properties are discussed with its relevance to experimental observations. The elucidation and rationalization of features of complexes difficult to explain basing on experimental data is discussed in view of theoretical studies. Electron population analysis and interaction energy decomposition schemes are presented as methods for exploring the nature of bonding and rationalizing unexpected observations such as an unusual bonding patterns in proton bound clusters. The most promising properties of clusters are those not found in their corresponding bulk states, and the future research will need to explore these properties in the light of potential applications. The clustering process acting as a precise control tool over gas-phase reactions is an example of such promising development.

Charged Clusters: Structures and Properties

A. Core Ions. In most cases characteristics of a core ion are a driving force for the formation of complexes. The neutralization of its charge dramatically changes properties of the complex, and in same cases, the system can undergo total destruction.[2] The properties of core ions, such as molecular structure, electronic charge, and internal vibrations, are largely preserved in complexes and their modifications due to the clustering process may be considered as perturbations to those of bare ions.

Let’s analyze NO^- ion. The photoelectron spectra of the $NO^-(H_2O)_n$ closely resemble that of a single NO^- anion. The spectra of clusters are shifted to higher electron binding energy, but largely preserve structural features of the parent anion.[24] An experimental study indicated that the excess negative charge is largely conserved in the NO^- subion. Such a conclusion was confirmed by a theoretical study in which a population analysis indicated that the electron is mostly localized on NO.[25] Following the above pioneering experimental work, similar behavior was found for a number of systems charged both negatively and positively. The small dispersion of the ionic charge over the coordinated ligands was found as a general feature of ionic clusters.[2]

The distinct localization of an electron is also quite visible as small and systematic changes in the electron detachment energies in O^-Ar_n and $X^-(H_2O)_n$ ($X = Cl$, Br, and I) complexes.[26,27] Theoretical electron population analysis confirms the charge conservation on core ions in these complexes. [28−30] The positive charge is more delocalized compared to anionic clusters even through the central ion is still the distinctly charged center.[31] The ionization potential of CH_3Ar_n clusters is little changed as an effect of the consecutive argon coordination. Molecular beam photoionization of $(H_2S)_n$ also indicates the little change of the ionization potentials due to the cluster formation.[32] The localization of the charge on the single fragment is not as obvious, however, as in the case of clusters composed of fragments of the different nature. Theoretical studies are needed to provide a definitive answer.

The interaction of an ion with ligands influences its properties and leads to valuable information, which may not be available otherwise. Boo and Lee have studied the microsolvation of the CH_5^+ cation[33] as a possible approach for resolving the structure and dynamics of protonated methane. Schreiner et al. have shown[34] that the energetical differences between possible isomeric structures of CH_5^+ are very small, and have concluded that the CH_5^+ ion does not possess a definitive structure. The cation is likely to scramble constantly through low-lying transition states. Experimental studies indicate that coordination of H_2 stabilizes the CH_5^+ ion and that the scrambling decreases as a function of the number of ligands. Theoretical studies support above experimental findings.[35]

The conditions under which an experiment is performed often determine the properties of the formed cluster. Photoelectron studies for $NO^-(N_2O)_2$ give evidence for a complex were an excess electron is located on NO, despite its higher electronic affinity comparing to that found for N_2O.[36] The controversy was solved as a result of mass spectroscopy measurements detecting the N_2O^-NO isomer of the lower energy.[37] Such

TABLE 1: Consecutive Dissociation Energies (in kcal/mol),[a] Enthalpies (in kcal/mol),[b] Vibrational Frequencies for Stretching Modes of H_2 (in cm^{-1}),[a] and Molecular Charges on H_2 for the External Shell (in electron)[a] for the $SiH_3^+(H_2)_n$ Cluster

n	shell occupation	D_o	ΔH	ν_{H-H}	charge on H_2
1	A(1)	−13.70	−14.2	4092	0.226
2	A(2)	−5.23	−1.8	4283	0.156
3	A(2)B(1)	−0.82	<1.5	4506	0.015
4	A(2)B(2)	−0.81		4507	0.014
5	A(2)B(3)	−0.73		4509	0.012
6	A(2)B(4)	−0.74		4510	0.013
7	A(2)B(5)	−0.69		4513	0.012
8	A(2)B(6)	−0.69		4513	0.012
9	A(2)B(6)C(1)	−0.49		4518	0.010
10	A(2)B(6)C(1)	−0.49			0.010
11	A(2)B(6)C(1)	−0.47			0.010

[a] Theoretical, ref 44. [b] Experimental, ref 45.

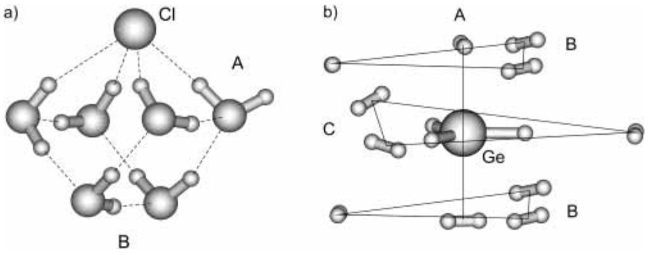

Figure 1. Molecular structures for (a) $Cl^-(H_2O)_6$ and (b) GeH_3^+(H2)$_{11}$. Different shells are denoted by capitol letters.

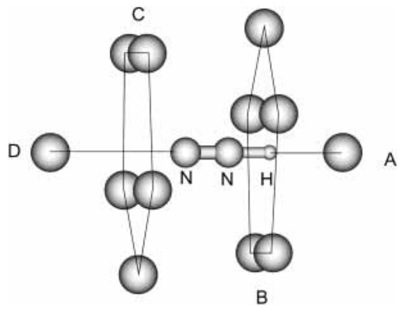

Figure 2. The structure of the $N_2H^+Ar_{12}$ complex. Consecutive shells are denoted as A, B, C, and D.

experimental findings were rationalized by theoretical studies of both isomers.[37,38]

The practical definition of the core ion does not necessarily involve the simplest possible ion, which may be observed. Assuming that the interaction energy between the ion and the closest solvent molecule is smaller than 100 kJ/mol, the formation of the clusters fall into the category classified in chemistry as interactions.[39] More importantly, values of interaction energy in this range lead to limited changes in the properties of monomers involved in interactions and complex systems are easily divided into subunits. The same simple ion may be conveniently considered as a core in one environment but not in the other. The reactive cations H^+ and CH_3^+ form the more complex chemical species H_3^+, N_2H^+, CH_5^+, and $CH_3N_2^+$ in H_2 and N_2 solutions[17,40] but are well-defined centers in the noble atom environment.[17] It was also postulated that the solvated electron in liquid oxygen exists as a O_4^- ion.[9] For simple molecules, the cores of cluster ions are better represented by dimer cations such as $(CO)_2^+$ and $(CO_2)_2^+$.[14]

B. Clusters. The smallest interacting building blocks of clusters are charged ion−ligand and neutral ligand−ligand dimers. Vast experimental and theoretical data exist concerning such moieties.[17,39] For these relatively simple complexes experimental results can be better interpreted in the comparison to large clusters and resolved data often yield very detailed information. These relatively small systems can also be well-characterized by applying high-level ab initio methods. The theoretical potential energy surfaces for dimers, with the tested reliability against the available experimental data, allow for the development of simplified analytical functions representing potential energy surfaces. Such functions are being later used to study systems where ab initio calculations are not feasible.[41] Monte Carlo methods and classical molecular dynamics benefit from the progress made in this field and these approaches are often used for studies of larger clusters.[9] A large variety of possible potentials has been used in the past with the most popular pairwise[42] and three-body functions.[43]

The main feature observed in data sets collected for consecutive complexes is the distinct organization of ligands into groups according to properties (Table 1).[44,45] It was previously realized that the cluster properties are a function of their structural organization, and the adopted name "shell" seemed appropriate (Figure 1).[14] The shell-like skeleton of charged clusters, deduced from previous thermodynamical measurements, was recently confirmed by theoretical predictions. Hiraoka and Yamabe made large contributions to such studies by performing both experimental and theoretical investigations.[14] The interaction energies responsible for the formation of clusters are small, therby permitting rotational and vibrational freedom within the shells for coordinated molecules. Clusters may be divided into two categories regarding their main structural organization. The first group is characterized by ligand−ligand interactions of a magnitude comparable in value to the interaction of the ion−ligand. The hydration process of halogen anions in water leads to clusters representing such moieties (Figure 1a). The second category includes clusters formed mainly due to the central ion−ligand interactions with negligible ligand−ligand forces. The ionic complexes formed in the noble gas environment fall into this category. Despite the differences the clusters representing both groups form shell structures which are quite visible.[23,46,47] The word "solvation" was originally adopted for describing processes in liquid solutions and is an apt name for clusters of the first category. The term "solvation" is commonly used for all clustering processes based on charged species. Because of qualitative differences between both families of charged complexes the separate name "shellvation" has been proposed for the second category.[44] The clusters discussed in this paper represent mostly moieties which belong to the "shellvated" class.

Structures of clusters, formed due to forces dominated by ion−ligand interactions, reflect the symmetry of the central ion to a large extent. The symmetry is even more apparent when rotational averaging is taken into account. The closing of the shell is often seen as the recovery of the full symmetry of the ion (Figure 1b). The symmetry of the linear core ions cannot be preserved when the ligands are coordinated outside the axial position (Figure 2); however, the formed complexes significantly reflect the symmetry of the core, and the infinite rotation axes C_∞ become the highly symmetrical C_4 or C_5 elements. The shells are located on planes perpendicular to the core axes (Figure 2). The centro-symmetric ions offer a number of possible ways to reduce the symmetry in the cluster formation process. The H^+-Ar_4 cluster assumes the C_{2v} symmetry due to the $H^+(Ar)_2(Ar)_2$ shell structure with the linear Ar−H^+−Ar fragment.[48] However, its close analogue Na^+Ar_4 possesses the tetrahedral symmetry (T_d).[49] The capacity of the shell restricted by the symmetry conditions may be extended if such an overcrowding of the shell is energetically preffered.[50] The $H_3^+Ar_4$ isomer with C_{2v}

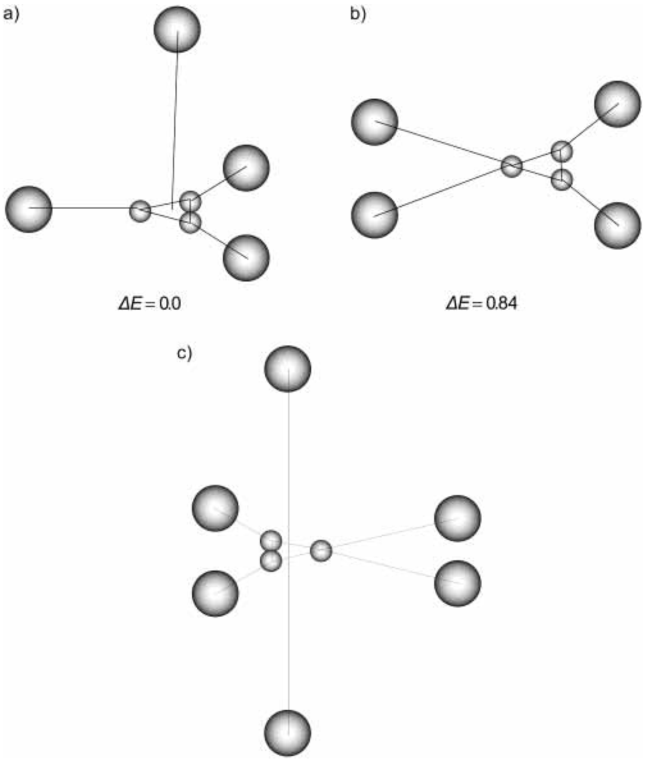

Figure 3. The $H_3^+Ar_4$ isomers (a and b) and $H_3^+Ar_6$ cations (c). ΔE in kcal/mol.

TABLE 2: The Experimental and Theoretical Enthalpies (in kcal/mol) and Entropies (in cal/molK) for the ($H_3^+Ar_{n-1}$)−Ar Bond Dissociation

n	shell ocupation	ΔH^a	ΔH^b	ΔS^a	ΔS^b
2	A(1)	6.69	6.97	13.4	16.2
3	A(2)	4.56	5.12	16.0	15.9
4	A(3)	4.28	4.40	17.3	17.9
5	A(3)B(1)	2.45	2.37	16.1	11.7
6	A(3)B(2)	2.27	2.25	16.7	13.8
7	A(3)B(3)	2.18	2.27	18.7	12.7
8	A(3)B(4)	1.56	1.57	23.0	23.0
9	A(3)B(5)		1.39		13.2

[a] Experimental, ref 71. [b] Theoretical, ref 50.

TABLE 3: The Consecutive Dissociation Energies (in kcal/mol) for Different Isomers of $CH_5^+(H_2)_n$ Complexes[a]

n	shell occupation	D_e
1	A(1)B(1)	2.80
2	A(1)B(2)	2.38
3	A(1)B(2)C(1)	1.17
	A(1)B(2)D(1)	0.99
4	A(1)B(2)C(1)D(1)	1.00
	A(1)B(2)C(2)	0.94
	A(1)B(2)D(2)	0.68
5	A(1)B(2)C(2)D(1)	0.99
	A(1)B(2)C(1)D(2)	0.88
	A(1)B(2)C(3)	0.86

[a] Theoretical, ref 35.

symmetry is less stable than its more symmetrical partner of the higher (C_{3v}) symmetry; however, the lower symmetry fragment is found as a part of the larger cluster $H_3^+Ar_6$ (Figure 3). The available theoretical studies failed to reproduce, with the precision available to present ab initio methods, the experimental trend of consecutive enthalpies for the $H_3^+(H_2)_{n-1} + H_2 = H_3^+(H_2)_n$ reaction.[51] A possible explanation of this feature may be the existence (currently unexplored) the energetically preferred isomer of the $H_3^+(H_2)_6$ with four H_2 molecules residing on the first shell, in analogy to the $H_3^+Ar_6$ structure (Figure 3c).

The shells are especially well-preserved when larger binding energies are involved. Weaker bonds allow for potential energy surfaces which are more shallow and which in effect, undergo long deflections from equilibrium positions. With an increasing number of shellvents−molecules (atoms) coordinated, the binding energy decreases. However, the motions of the ligands become more restricted due to the spacial hindrance from neighbors. Often the decreasing values of $\Delta H_{n,n-1}$ is concurrent with higher negative values of $\Delta S_{n,n-1}$ for the successive attachment of molecules (Table 2). Theoretical studies have supplied a large amount of structural and energetical data providing insight into the shell building. Theoretically determined structures indicate that the shells are mostly well-separated in space (Figures 1 and 2). More important positions of ligands are also well-established within each shell, and the molecules trapped in the shell are only slightly affected by other ligands. Ligands possess significant rotational and vibrational freedom within their positions in the shell. However, the transfer from one position to another within the same shell may be difficult due to the height of the energetical barriers. The reorganization of the shells would sometimes require the prior dissociation of the clusters.[35,44] Various possibilities for the arrangements of shells leads to a number of isomers. Although the occupation of shells is govern by energetical criteria, computational studies have indicated the simultaneous existence of partially filled stable shells characterized by different binding energies (Table 3).[35] The molecules trapped in the shell possess similar properties including geometrical parameters, dissociation energies, vibrational frequencies, and charge (Table 2). Their impact on the central ion is also similar as has been shown for electronic affinity,[27] ionization potential,[31] and the ion's vibrational motions.[35]

The heterogeneous environment facilitates for formation of clusters with mixed ligands and such species were observed experimentally.[52,53] The results of theoretical study are available for $H_3^+Ar_n(H_2)_m$ clusters.[54] Pure $H_3^+Ar_n$ and $H_3^+(H_2)_n$ complexes follow different geometrical patterns.[50,51] The mixed species form isomers following both patterns characteristic for homogeneous complexes. The energetical differences between the isomers are small; thus, all of them may be observed. The ligands interact with each other through the modification of the core ion. Such interactions lead to different properties of coordinated ligands in comparison to that found in homogeneous clusters.[54]

Unusual Properties of Proton Bound Clusters AH^+-L_n

The proton-bound AH^+−L dimers are the foundation for further extension toward more complex structures. The studies performed for a number of dimers (e.g., N_2H^+−He, Ne, Ar, H_2, N_2: OCH^+−He, Ne, Ar, and H_2) indicate the formation of conventional, linear hydrogen bonds.[17] The A−H stretching vibration in A−H^+−L is red shifted in comparison to the simple AH^+ cation. The further enlargement of the complex leads to the formation of the shell located on the ring perpendicular to the A−H^+−L axes (Figure 2). The plane of the ring divides the A−H^+ bond into two almost equal parts. It was first observed in OCH^+−Ar_n and later in N_2H^+−Ar_n complexes[55,56] that the consecutive attachment of ligands to the AH^+−Ar complex leads to the distinct blue shift of the C−H and N−H stretching vibrations. With little perturbation, the effect continues also when subsequent shells are being filled. Detailed theoretical studies complementing the experiment confirm the original findings.[57,58] The blue shift of the A−H vibrations is ac-

TABLE 4: Dissociation Energy (in kcal/mol), Consecutive Dissociation Entropy (in cal/mol K), Stretching Vibrations of N−H (cm^{-1}), and N−H Bond Distances (in angstroms) for $N_2H^+Ar_n$ Complexes[a]

n	D_e	$-\Delta S_{n,n-1}$	ν_{N-H}	r_{N-H}
0			3109	1.036
1	7.61	17.52	2636	1.088
2	1.43	17.46	2658	1.086
3	1.98	17.70	2686	1.084
4	2.02	17.89	2707	1.081
5	2.19	18.38	2731	1.080
6	2.40	21.42	2747	1.078

[a] Ref.[58]

companied by the shortening of the $A-H^+$ bond. The relationship between the $\Delta\nu_{AH}$ and $\Delta r_e(AH)$ shifts was found to satisfy the Badger's rule.[59] The initial large red-shift followed by small incremental blue-shifts as a cluster grows was interpreted in terms of subsequent Ar atoms pushing the first Ar further from the proton and thus diminishing the $Ar-H^+$ interaction.[55] Calculations confirmed these suggestions,[57] even though the mechanism is probably more complex. The explanations proposed in a somewhat similar phenomenon, in an improper blue-shifting H bonding,[60] suggest the important role of the dispersion energy in bonding as a counter balance for electrostatic interactions. Applying the interaction energy decomposition the studies of the nature of interactions could shed more light on the above phenomenon.

The binding energies of ligands forming the second shell systematically increase showing anomalous behavior when compared with most of the thermodynamic data available for ionic clusters.[14] The energy of coordination of the second ligand to the proton bound complex is, as expected, much lower compared to the $AH^+\cdots Ar$ interaction energy. A further filling of the shell, however, continues with an increase in binding energy until the shell is completed. A similar effect was also discovered in the $N_2H^+-(H_2)_n$ cluster applying high-temperature mass spectrometry.[61] Complementary ab initio calculations fully reproduce the experimental pattern. The explanations of the above feature was proposed through the balancing of binding components coming from ligand−ligand and core−ligand interactions.[57] The role of the favorable distribution of charge was also considered as a reason for observed behavior.[61]

The sequential decrease of the $A-H^+$ distances for $n = 2-5$ (Table 4) indicates the stabilization of the A−H bond for larger clusters and is observed experimentally as the ν_{A-H} vibrations shift to the blue. Additionally, with the anomalous stabilization of the Ar bonding energy, it seems reasonable to assume that both of the observed phenomena possess common ground. Additional studies of the electronic charge distribution and the nature of physical components of interaction energy decomposition could help to rationalize the observed complex phenomenon.

Nature of Interactions

The methods leading to a simplified description of bonding have a long history as useful tools for attaining chemical intuition. The popular concepts take into consideration the ionic and covalent natures of chemical bonds and interactions. The modern authors often consider the exchange repulsion interactions as a third component.[62] The conversion of intuitive concepts into well-defined mathematical models is not always simple. One successful accomplishment is an electronic population analysis, a useful and widely used tool for describing electronic charge distributions.[63] Of the many practical realizations, the most commonly used are the Muliken[64] and natural orbital analyses.[65] Population analysis provide the rough measure of the charge transfer between the interacting fragments. It was found, similarly to other properties, that the charge distribution also displays regularities regarding the shell structures of clusters. The amount of charge, which is transferred to the central ion, can be considered as a measure of its ability to coordinate ligands (Table 5). The population analysis approaches are not unique and have to be treated with caution. However, this tool is especially useful to study the ralative changes in electrostatic distribution for systematically build clusters.

More detailed information concerning the nature of interactions may be deduced from the physical components of the interaction energy. The probably most successful partitioning scheme for the decomposition of the Hartree−Fock (HF) interaction energy was proposed by Kitaura and Morokuma.[66] The above scheme was later extended to include the basis set superposition error correction.[67] The HF interaction components are additionally supplemented by the correlation energy part that can be calculated at MP2 or higher levels of theory.[68] The above approach has been shown to be the reasonable approximation for the rigorous spin adapted perturbation theory.[68] In the aforementioned scheme the interaction energy is partitioned into physical terms: electrostatic ($\epsilon_{el}^{(10)}$), Heitler−London exchange (ϵ_{ex}^{HL}), delocalization (ΔE_{del}^{HF}), and correlation components ($\Delta E_{MP2}^{(2)}$). The delocalization term accounts mostly for the charge transfer and induction energies. For longer distances, $\Delta E_{MP2}^{(2)}$ represents mostly dispersion interactions ($\epsilon_{disp}^{(20)}$).

The atomic charges and components of the interaction energy for consecutive clusters of H^+Ar_n (Table 5) indicate the dramatic difference in the character of binding for Ar atoms in the two A and B shells (Figure 4).[48] The binding in the shell A mimics the real chemical bond with the main stabilizing effect arriving

TABLE 5: Atomic Charges from Mulliken and Natural Orbital (in Parentheses) Population Analysis and Interaction Energy Components for Consecutive Clusters of H^+Ar_n ($n = 2-6$)[a]

	atomic charge			ΔE decomposition components					
N	H	Ar A-shell	Ar B-shell	$\epsilon_{el}^{(10)}$	ϵ_{ex}^{HL}	ΔE_{del}^{HF}	ΔE_{SCF}	$\epsilon_{MP}^{(2)}$	ΔE_{TOT}
2	0.417 (0.359)	0.291 (0.324)		3.09	36.13	−58.58	−19.35	−5.18	−24.82
3	0.488 (0.351)	0.251 (0.323)	0.009 (0.002)	−0.34	1.69	−1.62	−0.32	−1.34	−1.68
4	0.487 (0.351)	0.248 (0.322)	0.009 (0.002)	−0.50	2.03	−1.55	−0.02	−1.75	−1.77
5	0.488 (0.350)	0.244 (0.321)	0.008 (0.002)	−0.60	2.38	−1.49	0.29	−2.17	−1.88
6	0.488 (0.349)	0.240 (0.320)	0.008 (0.002)	−0.63	2.45	−1.49	0.33	−2.24	−1.91

[a] Reference 48.

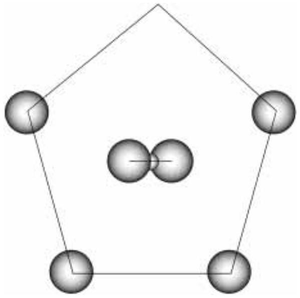

Figure 4. The optimal geometry structure the of H^+Ar_6 complex.

from the HF delocalization term. The electrostatic ArH^+-Ar interaction is repulsive despite the large electronic density transfer from the Ar ligand to the ArH^+ core. The nature of interactions is changed drastically for atoms from the second shell. The bonding is stabilized mainly by the dispersion energy, but attractive electrostatic forces are also important. The atomic charge distributions representing different schemes exhibit large differences indicating the qualitative character of these theoretical tools.

The D_{4h}-like structure of the $H^+(CO)_2(CO)_3$ complex was believed to be stabilized mostly by charge transfer (covalent) interactions.[69] Unfortunately, the same simple concept fails to predict the geometry of $H^+(N_2)_2(N_2)_3$, where the population analysis is indicative of the electrostatic nature of interactions. As a consequence, the expected structure would possess D_{3v} symmetry. The calculated geometry, however, is an analogue of that found in $H^+(CO)_n$ cluster (D_{4h}). Applying a more rigorous formalism, such as the interaction energy decomposition scheme presented above, one may solve the noted discrepancy.

Summary

The micro-solvated cluster ions are moieties, which due to their unique properties are considered as the intermediate state of matter.[2] They are also model species for understanding of the condensed phase and restrain large aggregates. Modern laboratories are able to produce clusters and measure their properties as a function of the number of coordinated ligands. The evolution of thermodynamics, reactivity, electronic properties, and molecular vibrations has been observed in such systems. Quantum-chemical studies provide information concerning clusters formed within the close range of the core ion. Theoretical studies supplement experimental findings, help to enhance their interpretation, and clarify often-present ambiguities. Ab initio calculations provide useful data for developing and testing simplified potentials reproducing potential energy surfaces. Monte Carlo/molecular dynamics studies may benefit from the aforementioned developments and also directly from ab initio calculations in situations where direct comparisons are possible. The improvement and further development of general theoretical methods, such as the Born relationship used to predict solvation energies in the condensed state,[70] are also possible due to ab initio investigations.

The most striking property of charged clusters is the occurrence of shells. The shells are visible through the structure of complexes, but are also apparent as small and systematic changes in the properties of ligands within the shells and as perturbations of the central ion due to the presence of ligands. Theoretical studies allowed for elucidation, and rationalization of features of complexes difficult to detect experimentally.

Detailed information concerning the nature of interactions may be deduced from physical components of the interaction energies in energy partitioning schemes. These methods lead to a simplified description of bonding in clusters and support chemical intuitions on the bases of popular concepts concerning the ionic and covalent natures of the interaction forces. The theoretical interpretation of the nature of bonding in clusters sheds more light on the formation of complexes and may lead to the understanding of unexpected observations, such as the unusual bonding patterns in proton bound clusters.

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References and Notes

(1) Gora, R. W.; Bartkowiak, W.; Roszak, S.; Leszczynski, J. *J. Chem. Phys.* **2002**, *117*, 1031.

(2) Roszak, S,; Leszczynski, J. In *Computational Chemistry: Reviews of Current Trends*; Leszczynski, J., Ed.; World Scientific: Singapore, 2001; p 179.

(3) Castleman, A. W., Jr.; Bowen, K. H. Jr. *J. Phys. Chem*. **1996**, *100*, 12911.

(4) Henks, W. *Phys. Lett*. **1964**, *12*, 322.

(5) Smith, D.; Adams, N. G. *Top. Curr. Chem*. **1980**, *89*, 1.

(6) Smith, D.; Adams, N. G. *Int. Rev. Phys. Chem.* **1981**, *1*, 271.

(7) Goodings, J. M.; Tanner, S. D., Bohme, D. K. *Can. J. Chem*. **1982**, *60*, 2766.

(8) Castleman, A. W., Jr.; Wei, S. *Annu. Rev. Phys. Chem*. **1994**, *45*, 685.

(9) Thomas, J. M. *Michael Faraday and The Royal Institution;* Adam Hilger; Bristol, 1991.

(10) Castleman, A. W., Jr.; Holland, P. M.; Lindsay, D. M.; Peterson, K. I. *J. Am. Chem. Soc.* **1978**, *100*, 6039.

(11) Kaberle, P. In *Interaction Between Ions and Molecules*; Ausloos, P., Ed.; Plenum: New York, 1974; p 459.

(12) Kaberle, P. In *Ion−Molecule Reactions*; Franklin, J. L., Ed.; Plenum: New York, 1972; p 315.

(13) Castleman, A. W., Jr.; Keesee, R. G. *Chem. Rev*. **1986**, *86*, 589.

(14) Hiraoka, K.; Yamabe, S. In *Dynamics of Excited Molecules*, Kuchitsu, K., Ed.; Studies in Physical and Theoretical Chemistry 82; Elsevier Science: Amsterdam, 1994; p 399.

(15) Golub, S.; Stainer, B. *J. Chem. Phys*. **1968**, *49*, 5191.

(16) Bowen, K. H.; Eaton, J. G. In *The Structure of Small Molecules and Ions*; Naaman, R., Vager, Z., Eds.; Plenum: New York, 1988.

(17) Bieske, E. J.; Dopfer, O. *Chem. Rev*. **2000**, *100*, 3963.

(18) Neusser, H. J.; Siglow, K. *Chem. Rev*. **2000**, *100*, 3921.

(19) Snodgrass, J. T.; Coe, J. V.; Freidhoff, C. B.; McHugh, K. M.; Bowen, K. H. *Faraday Discuss. Chem. Soc*. **1988**, *86*, 241.

(20) Snodgrass, J. T.; Coe, J. V.; Freidhoff, C. B.; McHugh, K. M.; Bowen, K. H. *J. Phys. Chem*. **1995**, *99*, 9675.

(21) Roszak, S. *J. Chem. Phys*. **1996**, *105*, 7569.

(22) Perera, L.; Berkowitz, M. L. *J. Chem. Phys*. **1993**, *99*, 4236.

(23) Gora, R. W.; Roszak, S.; Leszczynski, J. *Chem. Phys. Lett.* **2000**, *325*, 7.

(24) Eaton, J. G.; Arnold, S. T., Bowen, K. H. *Intern. J. Mass Spectrosc. Ion Processes* **1990**, *102*, 303.

(25) Roszak, S. *Chem. Phys. Lett*. **1994**, *221*, 255.

(26) Arnold, S. T.; Hendricks, J. H.; Bowen, K. H. *J. Chem. Phys*. **1995**, *102*, 39.

(27) Markovich, G.; Pollack, S.; Giniger, R.; Chesnowsky, O. *J. Chem. Phys*. **1994**, *101*, 9344.

(28) Roszak, S.; Gora, R. W.; Leszczynski, J. *Chem. Phys. Lett*. **1999**, *313*, 198.

(29) Roszak, S.; Kowal, M.; Gora, R. W.; Leszczynski, J. *J. Chem. Phys*. **2001**, *115*, 3469.

(30) Kowal, M.; Roszak, S.; Gora, R. W.; Leszczynski, J. *J. Chem. Phys*. **2001**, *115*, 9260.

(31) Gora, R. W.; Roszak, S.; Leszczynski, J. *J. Chem. Phys*. **2001**, *115*, 771.

(32) Walters, W. A.; Blais, N. C. *J. Chem. Phys*. **1981**, *75*, 4208.

(33) Boo, D. W.; Lee, Y. Y. *J. Chem. Phys*. **1995**, *103*, 520.

(34) Schreiner, P. R.; Kim, S.-J.; Schaefer H. F., III; Schleyer, P. v. R. *J. Chem. Phys*. **1993**, *99*, 3716.

(35) Roszak, S.; Leszczynski, J. *Chem. Phys. Lett*. **2000**, *323*, 268.

(36) Coe, J. V.; Snodgrass, J. T.; Freidhoff, C. B.; McHugh, K. M.; Bowen, K. H. *J. Chem. Phys*. **1987**, *87*, 4302.

(37) Hiraoka, K,; Fujimaki, S.; Aruga, K.; Yamabe, S. *J. Phys. Chem*. **1994**, *98*, 8295.

(38) Gora, R. W.; Roszak, S.; Leszczynski, J. *Asian J. Spectrom*. **2000**, *4*, 1.

(39) Chalasinski, G.; Szczesniak, M. M. *Chem. Rev*. **1994**, *94*, 1723.

(40) Gora, R. W.; Roszak, S.; Leszczynski, J. *J. Phys. Chem. A* **1999**, *103*, 9138.

(41) Meuwly, M. *J. Chem. Phys*. **1999**, *111*, 2633.

(42) Sokalski, W. A.; Lowrey, A. H.; Roszak, S.; Lewchenko, V.; Blaisdell, J.; Hariharan, P. C.; Kaufman, J. J. *J. Comput. Chem*. **1986**, *7*, 693.

(43) Kaplan, I. G.; Murrell, J. N.; Roszak, S.; Leszczynski, J. *Mol. Phys*. **2002**, *100*, 843.

(44) Roszak, S.; Leszczynski, J. *Chem. Phys. Lett*. **1999**, *314*, 333.

(45) Hiraoka,.K.; Katsuragawa, J.; Minamitsu, A. *Chem. Phys. Lett*. **1997**, *267*, 580.

(46) Urban, J.; Roszak, S.; Leszczynski, J *Chem. Phys. Lett*.. **2001**, *346*, 512.

(47) Roszak, S.; Babinec, P.; Leszczynski, J.*Chem. Phys*. **2000**, *256*, 177.

(48) Giju, K.; Roszak, S.; Leszczynski, J. *J. Chem. Phys*. **2002**, *117*, 000.

(49) Giju, K.; Gora, R. W.; Roszak, S.; Leszczynski, J. In preparation.

(50) Kaczorowska, M.; Roszak, S.; Leszczynski, J. *J. Chem. Phys*. **2000**, *113*, 3615.

(51) Ignacio, E. W.; Yamabe, S. *Chem. Phys. Lett*. **1998**, *287*, 563.

(52) Boo, D. W.; Lee, Y. T. *Int. J. Mass Spectrosc. Ion Processes* **1996**, *159*, 209.

(53) Hiraoka, K,; Fujimaki, S.; Nasu. M.; Minamitsu, A. *J. Chem. Phys*.. **1997**, *107*, 2550.

(54) Kaczorowska, M.; Roszak, S.; Leszczynski, J. *J. Phys. Chem. A* **2000**, *105*, 7938.

(55) Nizkorodov, S. A.; Dopfer, O.; Ruchti, T.; Meuwly, M.; Maier, J. P.; Bieske, E. J. *J. Phys. Chem*. **1995**, *99*, 17118.

(56) Dopfer, O.; Olkhov, R. V.; Maier, J. P. *J. Phys. Chem. A* **1999**, *103*, 2982.

(57) Sullivan, K. O.; Gellene, G. I. *Int. J. Mass Spectrom*. **2000**, *201*, 121.

(58) Sheng, Y.; Gora, R. W.; Roszak, S.; Kaczorowska, M.; Leszczynski, J. *J. Phys. Chem. A* **2002**, *106*, 11162.

(59) Badger, R. M. *J. Chem. Phys*. **1935**, *2*, 710.

(60) Hobza, P.; Havlas, Z. *Chem. Rev*. **2000**, *100*, 4253.

(61) Hiraoka, K.; Katsuragawa, J.; Minamitsu, A.; Ignacio, E. W.; Yamabe, S. *J. Phys. Chem. A* **1998**, *102*, 1214.

(62) Uddin, J.; Frenking, G. *J. Am. Chem. Soc*. **2001**, *123*, 1683.

(63) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular orbital Theory*; Wiley-Interscience: New York, 1986.

(64) Mulliken, R. S. *J. Chem. Phys*. **1955**, *23*, 1833.

(65) Weinhold, F.; Carpenter, J. E. *The Structure of Small Molecules and Ions*; Plenum: New York, 1988.

(66) Kitaura, K. Morokuma, K. *Int. J. Quantum Chem*. **1976**, *10*, 325.

(67) Sokalski, W. A.; Roszak, S.; Pecul, K. *Chem. Phys. Lett*. **1998**, *153*, 153.

(68) Chalasinski, G.; Szczesniak, M. M. *Mol. Phys.* **1988**, *63*, 205.

(69) Hiraoka, K.; Mori, T. *Chem. Phys*. **1989**, *137*, 345.

(70) Thomson, J. J. *Application of Dynamics in Physics and Chemistry*; Cambridge University Press: Cambridge, 1988.

(71) Hiraoka, K.; Mori, T. *J. Chem. Phys*.. **1989**, *91*, 4821.