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Study of interactions of various ionic species with solvents toward the design of receptors

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Abstract In earlier studies, the interactions of isolated ionic species with various solvents were investigated using ab initio calculations. The ionic species investigated included cations (proton, hydronium, ammonium, and metal cations) and anions (single electron, hydroxide, and halide anions). However in the present study, we investigate the interactions of these ionic species with the solvent in the presence of other competing ionic species. We also elaborate on how the information obtained from these extensive studies have been employed in designing and synthesizing various kinds of novel ionophores and receptors.

1 Introduction

Interest in the interactions involving ionic species stems from their importance in understanding ion solvation phenomena, molecular recognition, ionophore and receptor design, ion mediated self-assembly, and more recently nanomaterial design [1–29]. Most of the existing theoretical investigations have been devoted to the interactions of isolated ionic species with various solvents and ligands [30–113]. While these investigations have yielded valuable information on the interaction energies, thermodynamic and vibrational properties, and location of ligand or solvent molecules around the ionic species, little is known about the modulation of these properties in the presence of other counterions. Knowledge of this modulation is an essential and important component in the design of novel receptors and ionophores [114–123].

Apart from the interaction energies, one of the fundamental issues pertaining to receptor design and ion solvation is the location of the ligand or solvent molecules around the ionic species [3,4]. The position of the ligand or solvent molecule is governed by three important factors (1) size/shape of the ion, (2) charge on the ion (cation or anion), and (3) nature of the ion (metallic or organic). In the course of several studies carried out by our group on cationic and anionic water clusters, it emerges that cations are generally more symmetrically hydrated and hence form internally solvated structures [30–45]. On the other hand, the structure of anion–water cluster seems to be dependent on the number of water molecules hydrating it [34–45]. Surface solvated structures generally seem to prevail for smaller sized anionic clusters, while internally solvated structures emerge only when the size of the water cluster is very large [30–33].

The significant differences noted in the solvation of cationic and anionic species can be attributed to the fact that these intermolecular interactions binding the ions to the solvent are dominated by electrostatic and inductive energies [3,4]. Electrostatic interactions involving anions are less effective because they have a lower ratio of charge to radius than isoelectronic cations, while the polarization effect in anions becomes significant. In particular, the non-valence type excess electron around the anion (except for F^- which has partially valence-like excess electron) needs a large empty space to be stabilized due simply to the uncertainty principle. Thus, the anion needs an empty space on one side, while it interacts with ligands on the other side. Furthermore, while cations prefer to interact with heavy non-hydrogen atoms (such as oxygen and nitrogen), anions interact with the smaller-sized hydrogen atoms. As a consequence, the electron clouds of the anion are anisotopically and directionally polarized toward the electron acceptor sites (in most cases, hydrogen atoms). Full coordination is therefore difficult to achieve in the case of anion solvation, as the coulombic repulsion between hydrogen atoms of solvents or ligands prevents them to come to close to each other.

It is therefore apparent that different strategies have to be adopted to design tailor-made cation- or anion- specific ionophores. Indeed, the large body of our work on cation-specific (K^+, NH_4^+, acetylcholine, etc.) and anion- specific

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(F^-, Cl^-, $H_2PO_4^-$, acetate, ADP, ATP, GTP, etc.) receptors which were initially designed and subsequently synthesized and tested attests to the success of this strategy [114–123]. The strategy could be phrased as the optimization of the interaction between the ion and the receptor in the presence of solvent molecules.

Hitherto, most of our work neglected the role of counterions in modulating the interaction of ion with solvent or receptor molecules. However, most chemical or biological systems are charge-neutral [11–16]. Therefore, it is of importance to examine the solvation of ions in the presence of other competing ions. In particular, it would be interesting to delineate the effect of a cation on the solvation of an anion or vice-versa. In particular, it is important to study how ion dissociation would be facilitated by the solvent molecules. It can readily be noted that this work is relevant to the hydration of acids, bases, and salts.

Therefore in the course of this paper, we examine the characteristics of water clusters containing both cations and anions. To facilitate the discussion, we briefly highlight our earlier results obtained on water clusters of isolated cations and anions. Since the ultimate aim of the present work is to design novel ionophores and receptors, we also examine the relevance of the current results in the context of new strategies for ionophore and receptor design.

2 Computational methods

Given the fact that we have to take care of both compact cations and the diffuse nature of the anions, most of the calculations in the study were carried out at the second-order Möller–Plesset (MP2) level of theory using the augmented correlation consistent (aug-cc-pVDZ) basis set for water [124,125]. In the case of metal ions, we employed the correlation consistent (cc-pVDZ) basis sets. In the case of larger cations, we used the energy-adjusted Stuttgart ECPs, and added the appropriate *d* exponents to the valence bases [126–130]. In calculations involving anions (F^-, Cl^-, OH^-), the heavy atoms were represented using an aug-cc-pVDZ basis set augmented with a diffuse (2*s*2*p*/2*s*) shell [34–38]. In the case of calculations involving ionic clusters, the interaction energies were corrected for basis set superposition error (BSSE), using the median value of the fully corrected and uncorrected interaction energies [131]. Since for mid-size basis sets, full BSSE correction often underestimates the binding energies due to the underestimation of dispersion energy, the 50% BSSE correction has often been quite successful in predicting binding energies of various molecular systems. In calculations involving dissociation phenomena of acids, bases, and salts, the BSSE correction could be somewhat ambiguous because the corrections for the dissociated and undissociated cases would not be equivalently taken into account. Thus, here the BSSE-uncorrected energies were used to compare the energies of various conformers. For more details on the BSSE and its use in various kinds of clusters, the reader is directed to some of our earlier references. The calculations involved full geometry optimizations and the evaluation of vibrational frequencies on the optimized geometries. The zero-point vibrational energy (ZPE) and thermodynamic corrections were carried out using the evaluated frequencies. Some of the starting structures were obtained from density functional calculations carried out at the B3LYP (Becke's three-parameter hybrid method using the Lee–Yang–Parr correlation functional) level [132,133].

3 Results and discussion

The optimized structures of the $M^+ \cdot (H_2O)_{1–6}$ complexes (M = Li, Na, K, Rb, Cs, NH_4, H_3O) in Fig. 1 indicate that the smaller cations tend to be spherically and symmetrically coordinated by the water molecules [30], and so these ions favor the internal state in structure. Thus, in the case of the larger cations like Rb^+ and Cs^+, the clusters exhibit asymmetrical structures because the water–water interactions are energetically more important than water–cation interactions [30–33,134].

Though electrostatic interactions are also responsible for the binding of mono-cations of noble metals like Cu, Ag, and Au, to water clusters, we do not discuss it here, because the presence of *d* orbitals and relativistic effects markedly modulate the nature of interaction [46–48].

In sharp contrast to the cation–water complexes, surface states are the norm in the anion water cluster complexes shown in Fig. 2 [34–45]. The water cluster complexes of F^- (to which the excess electron is strongly bound as if it were a partially valence-like electron) are partly internal state as in Cs^+ . However, the surface state is still favored unless the water cluster size is very large. All other anions (e^-, Cl^-, Br^-, I^-, OH^-) favor surface structures [34–45]. The excess electron, which is not strongly bound to the anion, tends to be stabilized in a large vacant space around the anion. In particular, the oxygen atom in OH^- is four-coordinated while the hydrogen atom behaves almost like a hydrophobic site [45].

With this information, it is of interest to examine the hydration of acids and bases. HF, a weak acid, does not dissociate even when it is hydrated by up to six water molecules (Fig. 3). On the other hand, only four water molecules initiate the dissociation of strong acids like HCl, HBr, and HI [49, 50]. In the case of bases, six water molecules are needed to observe the full dissociation of bases like NaOH (while dissociated and undissociated structures are energetically competing in the presence of four and five water molecules), but only four water molecules are needed for the full dissociation of CsOH (Fig. 4) [51,52]. Though structures containing only four/five or three water molecules can induce dissociation of NaOH and CsOH, they are either isoenergetic or energetically less favored than the corresponding undissociated structures (Table 1).

The replacement of the proton with Na^+ in the acid leads to very interesting consequences (Fig. 5). In sharp contrast to what is observed in the case of HF, one observes the

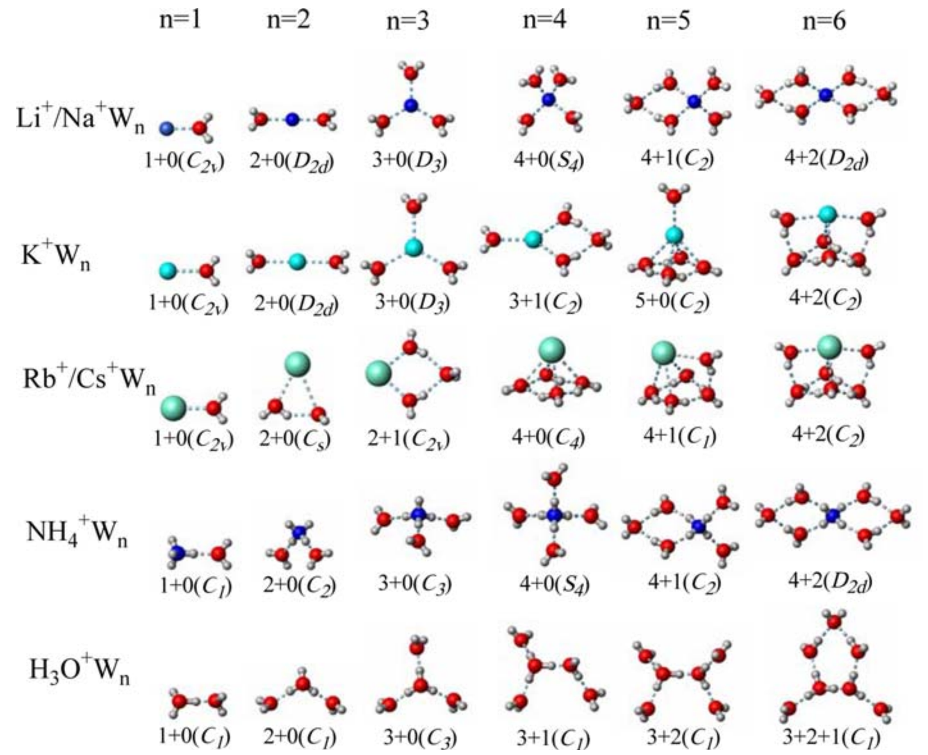

Fig. 1 Structures of the $M^{+} \cdot (H_2O)_{1-6}$ complexes ($M = \mathrm{Li, Na, Rb, Cs, NH_4, H_3O}$)

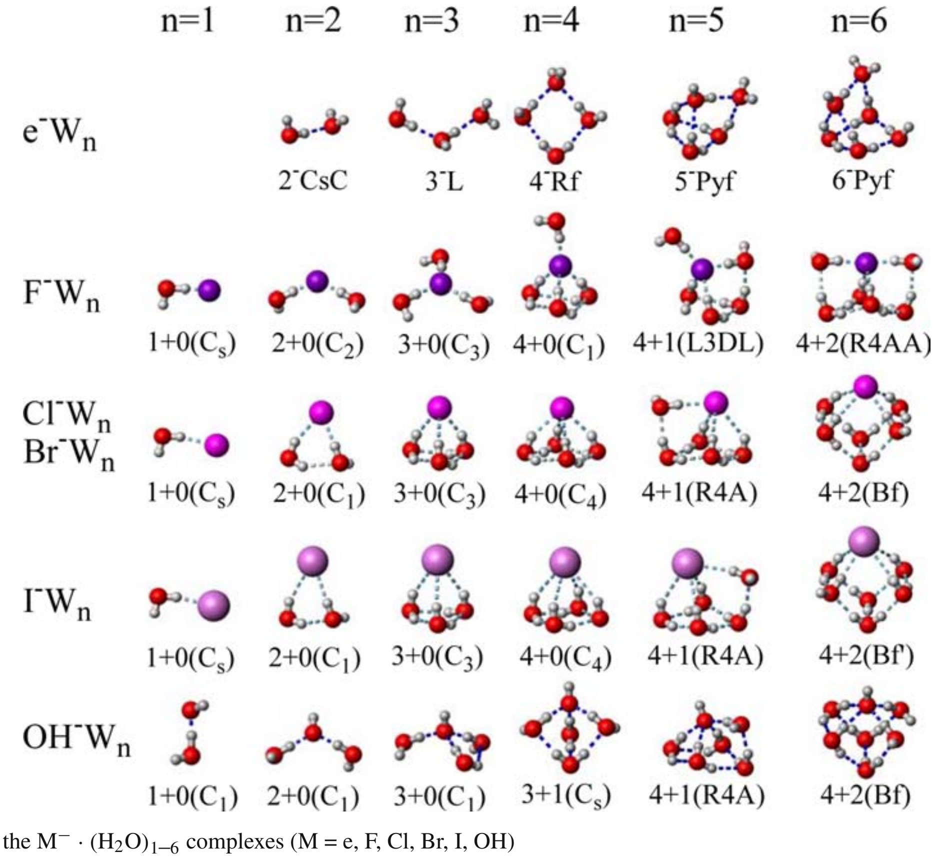

Fig. 2 Structures of the $M^{-} \cdot (H_2O)_{1-6}$ complexes (M = e, F, Cl, Br, I, OH)

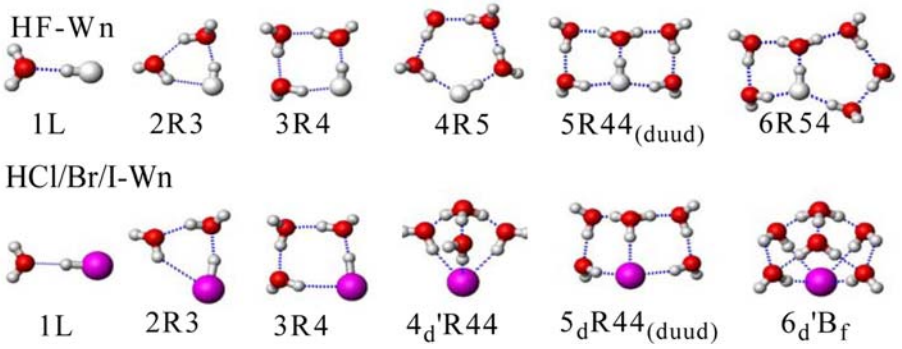

Fig. 3 Lowest-energy structures of hydrated hydrogen halides

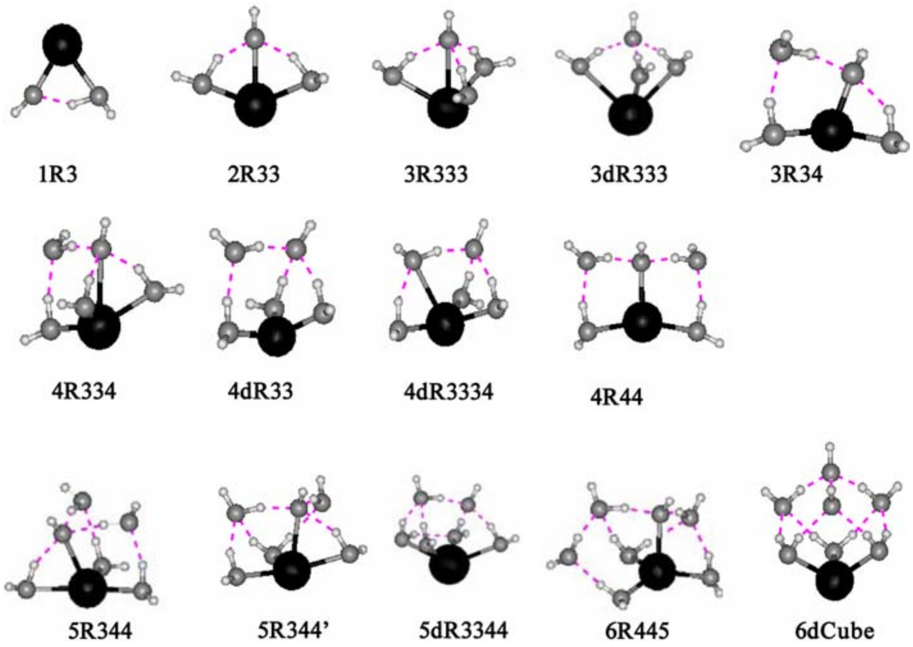

Fig. 4 Structures of hydrated alkali metal hydroxides (NaOH, CsOH)

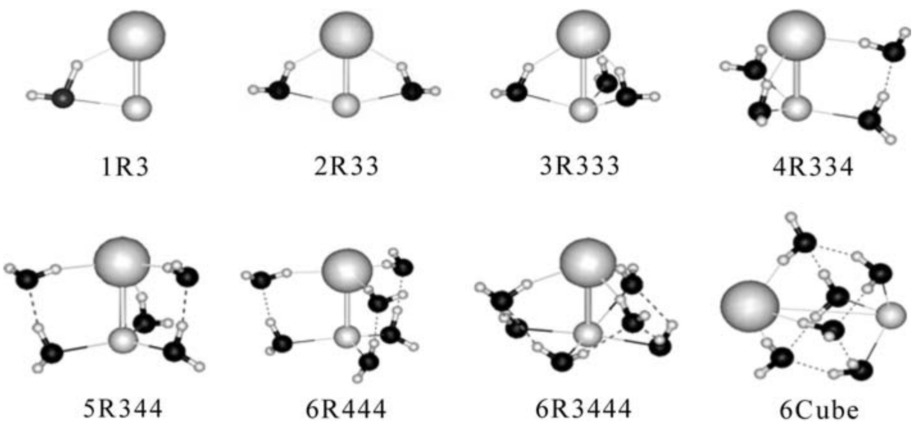

Fig. 5 Structures of the NaF $(H_2O)_{1-6}$ and NaCl $(H_2O)_{1-6}$ clusters

Table 1 MP2/aug-cc-pVDZ+(2s2p/2s) interaction energies (kcal/mol) of hydrated alkali hydroxides $-\Delta E_e$ and $-\Delta E_0$ are the binding energies without and with zero-point vibrational energy correction, respectively

	$NaOH\,(H_2O)_n$		
n	Conf	$-\Delta E_e$	$-\Delta E_0$
1	1R3	23.24	21.25
2	2R33	43.56	39.27
3	3R333	62.05	55.08
4	4R334	75.47	66.35
	4dR3334	75.39	66.51
5	5R344	88.81	76.96
	5R344′	88.84	76.55
	5dR3344	88.50	76.86
6	6R445	101.85	88.01
	6dCube	104.48	88.75
	$CsOH\,(H_2O)_n$		
n	Conf	$-\Delta E_e$	$-\Delta E_0$
1	1R3	20.73	19.33
2	2R33	39.98	36.39
3	3dR333	56.79	51.50
	3R34	53.69	48.18
4	4dR334	69.17	61.39
	4R44	66.29	58.36

Table 2 MP2/aug-cc-pVDZ+$[2s2p/2s]$ interaction energies (kcal/mol) of $NaF\,(H_2O)_{1-6}$and $NaCl\,(H_2O)_{1-6}$ clusters

	$NaF\,(H_2O)_{1-6}$		
n	Conf	$-\Delta E_e$	$-\Delta E_0$
1	1R3	21.92	19.98
2	2R33	41.54	37.44
3	3R333	59.53	52.74
4	4R334	73.59	64.57
5	5R344	87.22	75.86
6	6R444	100.47	86.56
	6Cube	102.28	86.46
	$NaCl\,(H_2O)_{1-6}$		
n	Conf	$-\Delta E_e$	$-\Delta E_0$
1	1R3	17.52	15.67
2	2R3	34.38	30.72
3	3R3	50.30	44.48
4	4R334	63.72	55.74
5	5R344	76.69	66.48
6	6R3444	90.59	77.34
	6Cube	89.97	75.05

dissociation of NaF in the presence of six water molecules (though the dissociated and undissociated conformers are nearly isoenergetic). Again, in sharp contrast to the case of HCl, the dissociation of NaCl is not favorable even when it is hydrated by six water molecules (since the dissociated *Cube* structure is less stable than the undissociated *6R3444* structure). Clearly, the nature of the cation bound to an anion seems to have a considerable role in modulating the hydration characteristics of the anion. It can be seen from the ZPE-corrected interaction energies listed in Table 2 that the *6R3444* structure is energetically more favored than the corresponding cube structure. The major difference in the *6R3444* and *6Cube* structures is that the former harbors a strong ionic bond between the cation and the anion. Though the presence of the ionic bond can be attributed to the strong electrostatic interaction between the ions, the observation has important implications in the design of ionophores and receptors. Thus in the absence of destabilizing steric interactions, structures which have a cation or anion in close proximity would be energetically favored. The predominance of electrostatic interactions implies that the dielectric of the solvent molecules would play a major role in determining the local structure and efficacy of the receptor or ionophore toward the ion.

While a detailed description of all the conformers of these hydrated NaX (X=F/Cl/Br/I) clusters would be presented elsewhere, it is useful to compare their structures and vibrational frequencies to the corresponding cationic (Na^+) and anionic (F^-, Cl^-) water clusters.

It can be seen from the lowest energy structures of both the hydrated NaF and NaCl clusters, that the local structure of the water cluster around the cation or anion has a strong semblance to the lowest energy structure of the corresponding cation or anion. Thus in case of the *6R3444* structure of $NaCl\,(H_2O)_6$, the Na^+ cation is hydrated by four water molecules. The anion, which is hydrated by three water molecules, exhibits a structure similar to that observed in case of the hydration of a bare anion by three water molecules. On the other hand, the energetically higher but dissociated *6Cube* structure of $NaCl\,(H_2O)_6$ is hydrated by three water molecules for the cation and three water molecules for the anion.

While the structures and energies are nearly similar, the –OH vibrational spectra of these hydrated NaF and NaCl exhibit marked differences from the corresponding clusters of Na^+, F^-, and Cl^-, as well as distinctive differences between the dissociated and undissociated structures of the hexa-hydrated systems (Fig. 6). While the magnitudes of the frequency shifts are much larger than those of the corresponding Na^+-water clusters, they are smaller but much closer to the shifts observed in the case of the corresponding F^--and Cl^--water clusters.

Based on the above findings, it can be expected that smaller cations and the F^- anion can be ensconced in an anionic specific ionophore/receptor, while larger cations and most anions would prefer surface-bound states. This has been demonstrated in our recent theoretical and experimental studies [114–123].

Our endeavors in ionophore and receptor design had its origins in developing novel ionophores/receptors having potential utilities in environmental and biological systems [135–142]. The theoretical challenge is to describe the affinity and selectivity of the synthetic ionophore/receptors toward ions. The situation is complicated because the affinity and selectivity have to be displayed in the presence of a number of competing factors like counterions, solvents, etc. However, in order to design receptors with high affinity for a specific ion, we need to consider the enthalpy-driven interactions. In this case, the binding enthalpy is highly correlated with the binding internal energy, and so the ab initio characterized interaction energies for an ion interacting with diverse receptors are very useful. Since we have discussed the interaction of various ions with water molecules, it is possible to

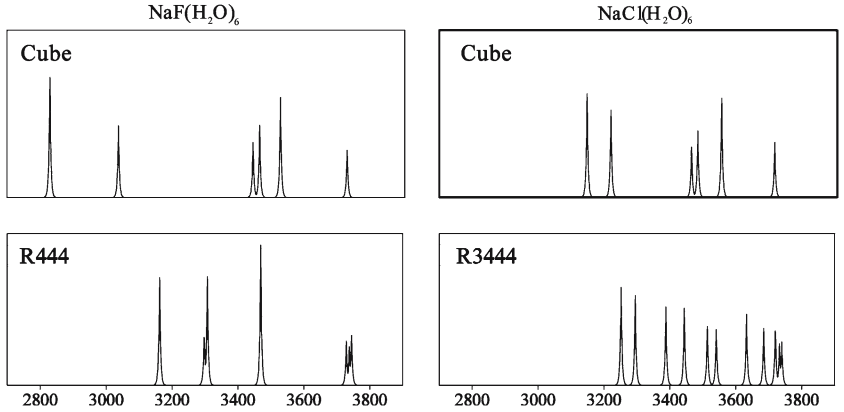

Fig. 6 Calculated MP2/aug-cc-pVDZ+($2s2p/2s$) frequencies of the –OH stretching modes of NaF $(H_2O)_6$ and NaCl $(H_2O)_6$

replace the water molecules of the hydrated ion clusters by energetically most favorable organic moieities as the binding arms of the receptor. Indeed, we have investigated the interaction energies of various ions with diverse synthetic organic receptors.

One of our initial endeavors in ionophore/receptor design was to tackle one of the seemingly intractable problems of contemporary biochemistry: the selective recognition of the ammonium cation (NH_4^+). Much of the problem is due to the nearly equivalent sizes of $NH_4^+$and the potassium cation (K^+). The first step in the receptor design was that high selectivity for NH_4^+could be achieved with cation–π interactions [143–148], if the receptors have an optimal space to capture $NH_4^+$and exhibit strong interactions toward NH_4^+. However, the ionic radius of K^+ is nearly similar to that of NH_4^+, so spatial differentiation is not useful. On the other hand, the difference in coordination numbers can be utilized. K^+ favors coordination number of six, while NH_4^+ favors only four. Furthermore, one has also to take into account the directional H-bonds involving NH_4^+ cations, to describe the higher selectivity for NH_4^+ over K^+ . Our initial calculations indicated that a benzene-based tripodal system with dihydro-imidazole moieties (Fig. 7a) possessed vacant sites for the interaction with only one solvent molecule, while the K^+ ion has three vacant sites for three solvent molecules. In order to maximize the affinity and selectivity of these receptors for NH_4^+, it becomes important to maximize the π-electron density of the receptor. Indeed, receptors with enhanced π-electron density by trimethylated phenyl ring with the strong proton-withdrawing subunits exhibit much higher affinities and selectivities [114].

Given this background, an extended concept has been applied to the receptor design for a biologically important molecule, acetylcholine [115]. The receptor should have higher affinity and selectivity for acetylcholine over NH_4^+. This requires enhanced dispersion interactions and diminished ionic interactions, which is met by replacing the imidazole arms of the NH_4^+ receptors with pyrrole (Fig. 7b). These theoretical inferences were confirmed by experiments.

Interactions involving anions are very different from those of cations. Since anions are more polarizable and hence more susceptible to polar solvents than cations, it becomes important to take into account solvent effects. Based on molecular dynamics simulations combined with ab initio calculations, highly selective anion ionophores have been designed [116, 117]. Enhanced dipole moments (Fig. 7c) were employed by attaching an electron-withdrawing group. This approach would also aid design of novel functional molecular systems and biologically important chemosensors. Utilizing the $(C\text{-}H)^+ \ldots X^-$ ionic H-bonds, fluorescent photoinduced electron transfer chemosensors for the recognition of $H_2PO_4^-$ have also been designed and synthesized (Fig. 7d) [118,119]. Recently, we have extended this concept to design receptors (R1: Trimethyl-[4-(3-methyl-imidazol-1-ium)-butyl]-ammonium substituted at 1,8 Anthracene position) specific for the biologically important phosphates (GTP and ATP) (Fig. 7e, f) [121] and calix-[4]-imidazolium compounds (Fig. 7g, h) [122,123] for selectively sensing flouride anion. In addition, we have also been successful in designing various amphi-ionophores with cyclopeptides [149,150].

4 Concluding remarks

In this paper, we have detailed the interactions of diverse systems like ions, acids, bases, or salts with water clusters. In particular, we have focused our attention on the local structure around the ion and its relevance to hydration and dissociation phenomena. We have elaborated on how the local hydration structure is modulated in the presence of counterions. In the course of this study, we have demonstrated that these investigations are useful in the de novo design of functional ionophores and receptors by the experimental realization of some of the designed ionophores/receptors. Of course, subtle differences in competing and cooperative interactions could also modulate the efficacy of these ionophores and receptors. However, it can be seen from this work that a systematic investigation of these interactions could be a useful tool in the quest for computer-aided ionophore and receptor design. An example of this is our recent work on calix[4]hydroquinone nanotubes, wherein quantum chemical investigations heralded the design of novel nanomaterials

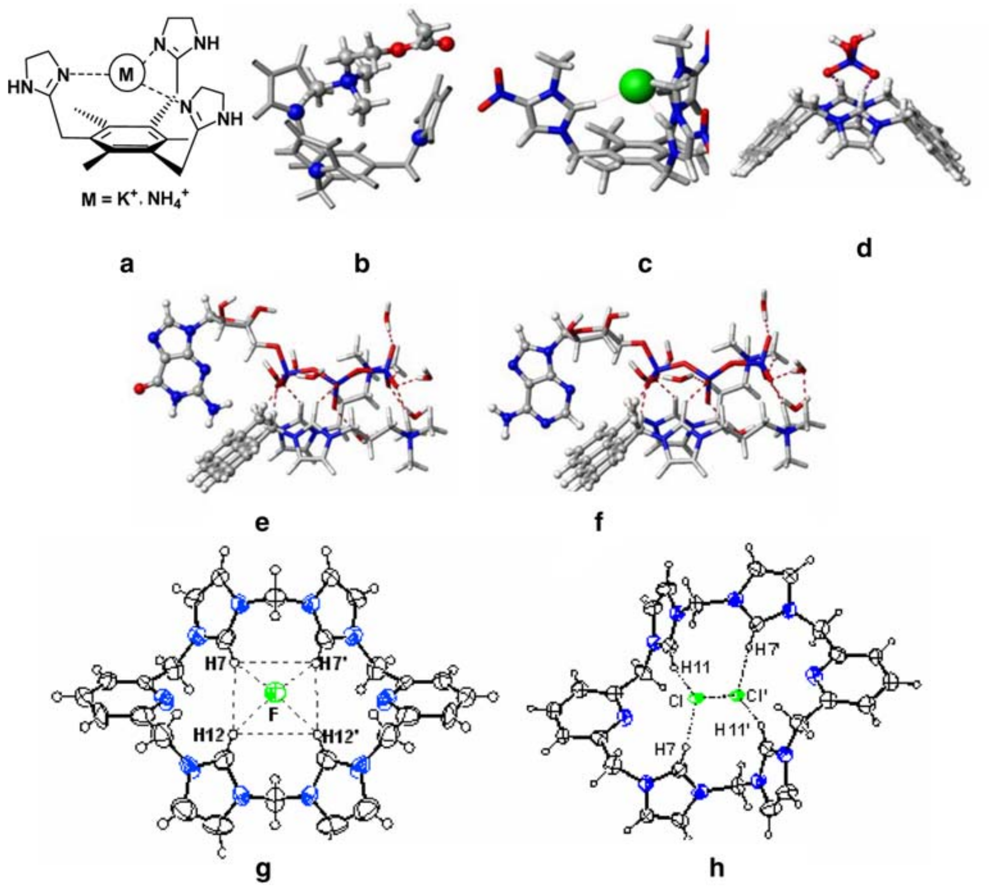

Fig. 7 Receptors for NH_4^+ (**a**), acetylcholine (**b**), Cl^- (**c**), $H_2PO_4^-$ (**d**) R1-GTP (**e**), and R1-ATP (**f**) complexes (R1 as defined in the text), Crystal structure of F^--Calix[4]imidazolium[2]pyridine (**g**), and Cl^--Calix[4]imidazolium[2]pyridine (**h**)

[151,154]. Though the field is still in its infancy, the advent of fast computers and extremely powerful programs could dramatically increase its pace in the near future. Finally, we believe that the present work on molecular level interactions could also help obtain an enhanced understanding of important chemical and biological processes in the macroscopic world.

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