Ab initio molecular orbital calculations on ion pair–water complexes of metal halides and oxides

P MOHANDAS[a], SURJIT SINGH[*a] and J CHANDRASEKHAR[b]

[a]Department of Chemistry, Indian Institute of Technology, Madras 600036, India
[b]Department of Organic Chemistry, Indian Institute of Science, Bangalore 560012, India

Abstract. *Ab initio* MO calculations are performed on a series of ion–molecular and ion pair–molecular complexes of $H_2O + MX$ (MX = LiF, LiCl, NaCl, BeO and MgO) systems. BSSE-corrected stabilization energies, optimized geometrical parameters, internal force constants and harmonic vibrational frequencies have been evaluated for all the structures of interest. The trends observed in the geometrical parameters and other properties calculated for the mono-hydrated contact ion pair complexes parallel those computed for the complexes of the individual ions. The bifurcated structures are found to be saddle points with an imaginary frequency corresponding to the rocking mode of water molecules. The solvent-shared ion pair complexes have high interaction energies. Trends in the internal force constant and harmonic frequency values are discussed in terms of ion-molecular and ion-pair molecular interactions.

Keywords. *Ab initio* MO calculations; hydrogen bonding; force constants; water; metal halides and oxides.

1. Introduction

A major part of research in chemistry and biology pertains to and is conducted in liquid solutions involving ionic species. In many of these systems the ions interact with one another as well as with the solvent. Usually these interactions are of prime interest to chemists and biochemists alike. Moreover, the association of oppositely charged ions is an important step in chemical reactions which in many cases have very small barriers and are diffusion controlled. In the field of solvation chemistry, quantum mechanical calculations on solvated ions and ion pairs have proved to be valuable tools for providing complementary data to those obtained in experiments and computer simulations. Besides being a means of deriving force fields, such calculations can provide valuable insight into the energetics and structural details of microscopic subsystems which cannot be experimentally separated.

Because of the importance of water as a solvent a large number of studies on hydrogen bonding and hydration of ions and ion pairs have been reported in the literature (Kress *et al* 1975; Mulliken and Ermler 1981; Kecki *et al* 1982; Kleeberg and Luck 1983; Larson and McMahon 1983; Hermansson *et al* 1984; Marcus 1985; Falk *et al* 1986; Gao *et al* 1986, 1991; Latajka and Scheiner 1987; Friedman 1988; Yates *et al* 1988; Cammi *et al* 1989; Hashimoto and Iwata 1989; Probst *et al* 1989; Luu *et al* 1990; Arbman *et al* 1992; Benson and Siebert 1992; Caldwell and Kollman

* For correspondence

1992; Hermansson 1992; Latajka 1992; Probst 1992; Sola *et al* 1992). Computer simulation studies (Berkowitz *et al* 1984; Belch et al 1986; Pettitt and Rossky 1986; Dang and Pettitt 1990; Fukushima *et al* 1991; Ohtaki and Fukushima 1991) as well as X-ray diffraction (Ohtaki and Fukushima 1992) and neutron scattering (Enderby 1985) experiments showed the existence and significance of different types of ion pairs in aqueous solutions. Although there have been several *ab initio* results at various degrees of sophistication with respect to basis sets and electron correlation on ion hydration (Mulliken and Ermler 1981; Kecki *et al* 1982; Hermansson *et al* 1984; Marcus 1985; Falk *et al* 1986; Gao *et al* 1986; Latajka and Scheiner 1987; Yates *et al* 1988; Cammi *et al* 1989; Hashimoto and Iwata 1989; Probst *et al* 1989; Arbman *et al* 1992; Caldwell and Kollman 1992; Latajka 1992; Probst 1992; Sola *et al* 1992), *ab initio* studies on ion-pair hydration are rather limited in the literature (Kress *et al* 1975; Mulliken and Ermler 1981; Marcus 1985; Gao *et al* 1991). Moreover, in most of the cases reported earlier, the studies have been confined to the geometries and energetics of the complexes whereas it is known that the nature and strength of the hydration is reflected more precisely in the force constants and vibrational frequencies than any other property.

As an extension of our work on molecular interactions (Brakaspathy and Singh 1986; Shivaglal *et al* 1988; Shivaglal and Singh 1989, 1992; Singh and Knoezinger 1992; Mohandas *et al* 1993) we report here *ab initio* MO results on structure, energetics, internal force constants and harmonic vibrational frequencies for a number of complexes of $H_2O + MX$ (MX = LiF, LiCl, NaCl, BeO and MgO) systems. In the case of LiF, LiCl and NaCl several possible geometries corresponding to the mono-hydrated contact ion pair and solvent-shared ion pair structures have been considered whereas calculations for BeO and MgO were confined to the mono-hydrated structures only. Similar calculations have also been carried out for the corresponding hydrated cations and anions in a number of orientations in order to provide a common basis for comparison. Such hydrated ions and ion-pair structures considered are of importance since they are tailored microscopic subsystems of the actual solvation structure of ion pairs in water and also of water adsorbed on the corresponding crystal surfaces (Heidberg and Haser 1990). The calculations also provide interesting insights into the structural and energetic effects resulting from the presence of a counterion on ion molecular interactions.

2. Computational details

Ab initio molecular orbital calculations were carried out using the Gaussian-86 package (Frisch *et al* 1984) of computer codes at 3–21G and 6–31G levels. Since the trends in the values of various parameters calculated at these two levels are similar, only the latter qualitatively superior set of values are considered for the discussion. The geometry optimization in each case was carried out using a super-molecular approach where all the geometrical parameters of the complex were allowed to vary within the symmetry point group. The gradient algorithms contained within the program were used for the calculation of internal force constants and vibrational frequencies. Interaction energies were corrected using the Boys–Bernardi (1970) counterpoise scheme. The calculations were performed on VAX/VMS version V5.1 and Siemens 7580-E computer systems.

3. Results and discussion

3.1 *Energetics and geometrical parameters*

The various structures examined are shown in figure 1, along with definitions of the geometrical parameters of interest. The optimized geometrical parameters and BSSE-corrected interaction energies are given in table 1. The interaction energies of the solvent shared ion pair complexes correspond to the stabilization relative to M^+, X^- and one H_2O unit whereas that for the hydrated contact ion pair is relative to MX and one H_2O unit.

3.1a *Complexes of water with LiF, LiCl and NaCl*: The results for the complexes of water with the free ions M^+ and X^- (III, IV and V) are in general accord with
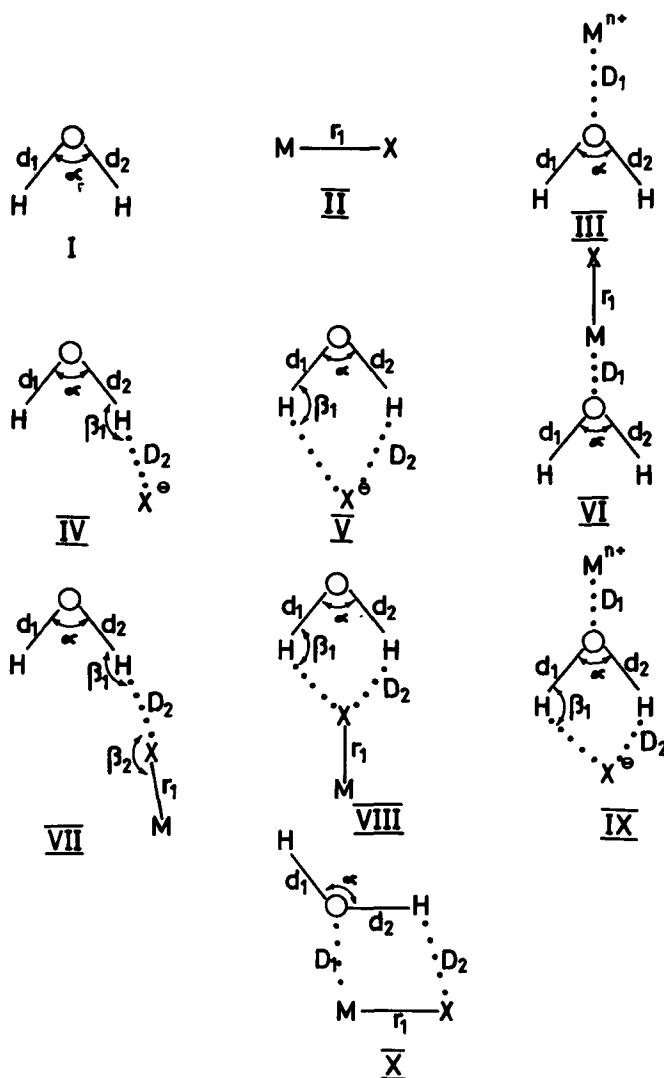

Figure 1. Structural parameters for various complexes of water with M^{n+}, X^- and MX.

Table 1. Geometrical parameters and stabilisation energies of H_2O, MX, $(H_2O)M^{n+}$, $(H_2O)X^-$, $(H_2O)(MX)$ and $M^+(H_2O)X^-$ complexes obtained by *ab initio* 6–31G MO calculations.

Structure (symmetry)	Species	Bond length (Å)					Bond angles (degrees)			$-\Delta E$ (kcal/mole)
		d_1	d_2	r_1	D_1	D_2	α	β_1	β_2	
I (C_{2v})	H_2O	0.9502	0.9502				111.54			
II ($C_{\infty v}$)	LiF			1.5701						
	LiCl			2.0678						
	NaCl			2.3882						
	BeO			1.3289						
	MgO			1.7381						
III (C_{2v})	H_2O...Li$^+$	0.9550	0.9550		1.8273		110.44			44.72
	H_2O...Na$^+$	0.9535	0.9535		2.1731		110.20			31.98
	H_2O...Be^{2+}	0.9809	0.9809		1.5426		109.10			147.81
	H_2O...Mg^{2+}	0.9673	0.9673		1.9197		107.52			90.91
IV (C_s)	HOH..F$^-$	0.9517	1.0371			1.4106	107.60	171.54		34.95
	HOH..Cl$^-$	0.9494	0.9721			2.2049	108.20	164.60		16.54
V (C_{2v})	OH$_2$...F$^-$	0.9603	0.9603			1.9573	94.26	111.70		25.87
	OH$_2$...Cl$^-$	0.9545	0.9545			2.6297	102.10	112.50		15.27
VI (C_{2v})	H_2O...LiF	0.9502	0.9502	1.5902	1.8780		112.52			25.16
	H_2O...LiCl	0.9509	0.9509	2.0961	1.8649		112.60			28.18
	H_2O...NaCl	0.9509	0.9509	2.4111	2.2153		111.84			20.26
	H_2O...BeO	0.9527	0.9527	1.3333	1.6087		114.34			56.16
	H_2O...MgO	0.9521	0.9521	1.7424	2.0153		111.92			30.95
VII (C_s)	HOH..FLi	0.9486	0.9652	1.5837		1.6914	110.51	171.27	171.00	11.26
	HOH..ClLi	0.9488	0.9543	2.0818		2.4953	111.37	172.73	176.30	5.18
	HOH..ClNa	0.9498	0.9552	2.4015		2.4746	111.70	175.50	178.70	6.29
	HOH..OBe	0.9490	0.9622	1.3306		1.8383	110.81	171.89	173.10	10.25
	HOH..OMg	0.9513	0.9732	1.7503		1.7011	110.05	170.80	173.10	11.49

(Continued)

Table 1. *(Continued)*

Structure (symmetry)	Species	Bond length (Å)					Bond angles (degrees)			$-\Delta E$ (kcal/mole)
		d_1	d_2	r_1	D_1	D_2	α	β_1	β_2	
VIII (C_{2v})	OH_2...FLi	0·9505	0·9505	1·5806		2·2240	104·18	108·10		8·39
	OH_2...ClLi	0·9505	0·9505	2·0815		2·8612	108·20	110·20		4·73
	OH_2...ClNa	0·9509	0·9509	2·4024		2·8244	107·80	110·40		5·82
	OH_2...OBe	0·9506	0·9506	1·3313		2·3417	104·70	108·90		8·03
	OH_2...OMg	0·9522	0·9522	1·7771		2·2272	104·20	108·10		8·49
IX (C_{2v})	Li^+...OH_2...F^-	0·9921	0·9921		1·6984	1·6463	84·33	113·90		176·01
	Li^+...OH_2...Cl^-	0·9717	0·9717		1·7252	2·2501	95·43	113·60		144·34
	Na^+...OH_2...Cl^-	0·9663	0·9663		2·0543	2·3170	96·64	113·53		123·48
X (C_s)	H_2O–LiF (SB)	0·9439	0·9746	1·6512	1·8669	1·7275	117·25			30·12
	H_2O–LiCl (SB)	0·9479	0·9549	2·1574	1·8482	2·9184	113·49			37·58
	H_2O–NaCl (SB)	0·9499	0·9627	2·4621	2·1846	2·8489	114·60			21·96

previously established patterns (Kecki *et al* 1982; Hermansson *et al* 1984; Falk *et al* 1986; Gao *et al* 1986; Latajka and Scheiner 1987; Yates *et al* 1988; Cammi *et al* 1989; Latajka 1992). The oxygen lone pair interacts strongly with the cations leading to a C_{2v} structure, III. Correspondingly, the computed M...O distances are shorter than the values obtained at higher theoretical levels (Hermansson *et al* 1984; Probst *et al* 1989; Probst 1992). Interaction of anions with a water molecule leads to minima (IV) where one of the O–H units is involved in hydrogen bonding with a slightly nonlinear configuration. The bifurcated structures (V) with two symmetrical hydrogen bonds are higher in energies than the corresponding nonlinear hydrogen-bonded structures (IV). The computed stabilization energies are in accord with previous theoretical and experimental values (Latajka 1992), after allowance is made for the differences in internal energy and enthalpy values.

The trends in the results obtained for the mono-hydrated contact ion pairs are parallel to those of the complexes of the individual ions. The interaction energies for these complexes are however lower than those of the respective hydrated ions because the presence of the counter ion markedly reduces the acidic and basic characters, respectively, of M^+ and X^- ions. Thus, coordination through the oxygen of water molecule with the metal end of the ion pair leads to a stable structure (VI) with C_{2v} symmetry. Hydrogen-bonded structures VII and VIII have lower interaction energies. The bifurcated structures (VIII) are calculated to be less stable than the corresponding mono-hydrogen-bonded strutures (VII). The interaction energy of the $H_2O...Li^+$ complex reduces from 44·72 kcal/mol to 28·18 and 25·16 kcal/mol for $H_2O...LiCl$ and $H_2O...LiF$ complexes, respectively, which shows the effect of the relative basicities of the counter ions on stabilization energies. Similarly, for the hydrogen-bonded structures of water with ion pairs (VII and VIII) the interaction energies are much lower than the corresponding water–anion ccomplexes. The interaction energy for $HOH...F^-$ is reduced from 34·95 kcal/mol to 11·26 kcal/mol for $HOH...FLi$ complex. The corresponding reduction in the case of $HOH...Cl^-$ is from 16·54 kcal/mol to 6·29 and 5·18 kcal/mol, respectively, for NaCl and LiCl complexes. A similar trend is observed in the case of the bifurcated complexes (VIII) also.

For the solvent-shared ion pairs two possible structures were considered for the optimization. In the C_{2v} from IX, the M^+ ions interact with the oxygen atom whereas the X^- ion makes a bifurcated hydrogen bond with the H_2O molecule. The extra source of stabilization in these complexes is provided by the long range electrostatic interaction between the ions. However, these structures are computed to have a Hessian index of 1, corresponding to saddle points. Another form of solvent-shared ion pair complex can be visualised with a directional hydrogen bond of the X^- ion with one of the O–H bonds of H_2O. Optimization of such unsymmetrical forms $(M^+...H-O-H...X^-)$ resulted in the formation of another interesting type of structure X, called a solvent bound (SB) structure, in which water interacts with the ion pairs in a cyclic arrangement. Incidentally, these structures are found to have the highest stabilization energies among all the mono-hydrated contact ion pairs, even higher than the corresponding $H_2O...MX$ complexes (VI).

The geometrical changes associated with the complexation of water with the contact ion pairs and individual ions follows the pattern of the interaction energies. Consistently, hydrogen bonding lengthens the corresponding O–H bond and the elongation depends upon the site of interaction. The increase in the hydrogen bonded O–H distance for the water-ion pair complexes follows the order $OH_2...XM$ (VIII) <

$H_2O...MX$ (VI) < $HOH...XM$ (VII) < $H_2O–MX$ (SB) (X) < $M^+...OH_2...X^-$ (IX). Thus, the maximum change is observed for solvent-shared complexes, IX, which may be attributed to the cooperativity effect due to the presence of the counter ion in a favourable orientation. The non-hydrogen-bonded O–H distances (d_1) for the complexes with structures VII and X show a small decrease, the effect being larger in the latter case. The O...M distances (D_1) are greater in the contact ion pair complexes VI, compared to those in the corresponding ion-water complexes III. Similarly, the interaction distances (D_2) in the hydrogen-bonded forms VII and VIII are also higher than those in the structures IV and V. For the solvent-shared ion pair complexes, IX, both the distances D_1 and D_2 are found to be shorter than the corresponding values in the ion-water complexes III and V. In all the cases the ion pair distances (r_1) show an increase on complexation with water. All these changes follow the trends in the corresponding interaction energies.

3.1b *Complexes of water with BeO and MgO*:

Restuls obtained for mono-hydrated structures of BeO and MgO follow the pattern of the corresponding halide structures. Of the three structures considered, two structures, VI and VII, represent minima and the other one (VIII) corresponds to a saddle point as in the case of the halide complexes. Within these three structures the stabilization energies are highest for the structures (VI) and lowest for the bifurcated forms (VIII). Further, the stabilization energies for the complexes, VI, are found to be substantially lower than the corresponding ion-water complexes (III). The geometrical changes associated with the complexation are in accordance with the trends observed in the interaction energies. The elongation of the hydrogen bonded O–H distances are in the order $OH_2...OM$ (VIII) < $H_2O...$ MO (VI) < $HOH...OM$ (VII) < $H_2O...M^{2+}$ (III). Geometry optimization was also attempted for a solvent-bound type structure which resulted in the breaking of one of the O–H bonds of water and the formation of the corresponding hydroxide structures.

3.2 *Internal force constants*

The internal force constants of various complexes considered are provided in table 2. For the unsymmetrically hydrogen-bonded O–H bonds of water molecules, the force constant, f_{11}, refers to the force constant of the non-hydrogen bonded and f_{22} for the hydrogen bonded O–H bonds.

3.2a *Complexes of water with LiF, LiCl and NaCl*:

Hydrogen bonding reduces the force constant f_{22} of the O–H bond, the extent of reduction being a measure of the strength of the hydrogen bond. For the unsymmetrically hydrogen-bonded complexes the O–H stretching force constant f_{11} does not show any significant change in its value on complexation except for the solvent-bound complexes where the values are found to increase. In general, the value of the interaction force constant f_{12} becomes less negative on complexation, and even attains positive values in some bifurcated structures as well as in cases where the lone pair of electrons on oxygen atom also interact. The f_{12} values are highest in structures where both the effects are present. The HOH bonding force constant, f_{33} for the water molecule is found to increase on complexation with cations, anions and ion pairs except for the nonlinear cases (structures IV and VII) where the value is found to decrease slightly. The force

Table 2. Internal force constants of H_2O, MX, $(H_2O)M^{n+}$, $(H_2O)X^-$,($H_2O)(MX)$ and $M^+(H_2O)X^-$ complexes obtained by *ab initio* 6-31G MO calculations.

Structure (symmetry)	Species	Force constants (mdyne/Å)						
		f_{11}	f_{22}	f_{12}	f_{33}	f_{MX}	$f_{O...M}$	$f_{H...X}$
I (C_{2v})	H_2O	9.21	9.21	−0.14	0.76			
II ($C_{\infty v}$)	LiF					3.08		
	LiCl					1.47		
	NaCl					1.14		
	BeO					9.03		
	MgO					3.60		
III (C_{2v})	$H_2O...Li^+$	8.99	8.99	−0.04	0.95		1.19	
	$H_2O...Na^+$	9.07	9.07	−0.06	0.92		0.75	
	$H_2O...Be^{2+}$	7.32	7.32	0.08	1.15		3.60	
	$H_2O...Mg^{2+}$	8.20	8.20	0.04	1.10		2.08	
IV (C_s)	$HOH...F^-$	8.96	5.07	−0.13	0.56			0.97
	$HOH...Cl^-$	9.22	7.87	−0.12	0.72			0.33
V (C_{2v})	$OH_2...F^-$	8.59	8.59	0.12	0.82			0.68
	$OH_2...Cl^-$	8.98	8.98	−0.02	0.88			0.30
VI (C_{2v})	$H_2O...LiF$	9.29	9.29	−0.09	0.85	2.75	0.90	
	$H_2O...LiCl$	9.25	9.25	−0.08	0.86	1.29	0.96	
	$H_2O...NaCl$	9.23	9.23	−0.09	0.85	1.04	0.62	
	$H_2O...BeO$	9.13	9.13	−0.04	0.94	8.63	2.39	
	$H_2O...MgO$	9.16	9.16	−0.06	0.92	3.27	1.22	
VII (C_s)	$HOH...FLi$	9.26	8.39	−0.12	0.70	2.80		0.32
	$HOH...ClLi$	9.28	8.99	−0.14	0.74	1.37		0.16
	$HOH...ClNa$	9.21	8.94	−0.14	0.73	1.10		0.17
	$HOH...OBe$	9.24	8.54	−0.13	0.70	8.70		0.28
	$HOH...OMg$	9.09	7.83	−0.13	0.68	3.40		0.35
VIII (C_{2v})	$OH_2...FLi$	9.29	9.29	−0.06	0.80	2.85		0.27
	$OH_2...ClLi$	9.24	9.24	−0.11	0.81	1.38		0.13
	$OH_2...ClNa$	9.22	9.22	−0.10	0.82	1.05		0.14
	$OH_2...OBe$	9.27	9.27	−0.07	0.81	8.64		0.24
	$OH_2...OMg$	9.13	9.13	−0.06	0.79	2.79		0.27
IX (C_{2v})	$Li^+...OH_2...F^-$	6.31	6.31	0.60	0.93		2.14	1.70
	$Li^+...OH_2...Cl^-$	7.67	7.67	0.24	1.01		1.93	0.87
	$Na^+...OH_2...Cl^-$	8.09	8.09	0.16	0.99		1.31	0.72
X (C_s)	H_2O-LiF (SB)	9.78	7.31	−0.10	0.68	2.23		
	$H_2O-LiCl$ (SB)	9.43	8.99	−0.09	0.82	1.07		
	$H_2O-NaCl$ (SB)	9.29	8.26	−0.10	0.74	0.97		

constant values for the M–X bond, f_{MX} are found to decrease in all the mono-hydrated contact ion pair complexes. The nature and strength of interaction is also reflected in the values of interspecies stretching force constants $f_{O...M}$ and $f_{H...X}$.

The trends in the force constant values obtained for the complexes of water with the free ions are in general accord with the previously established patterns (Kecki et al 1982; Falk et al 1986; Probst et al 1989; Hermansson 1992; Probst 1992). For all the mono-hydrated cation complexes (structure III) the O–H stretching force constant value decreases in accordance with the interaction energies. The variation

in the values of f_{12}, f_{33} and $f_{O...M}$ also follows the same trend. For the mono-hydrated contact ion pair complexes in which the oxygen is coordinated to the metal end of the ion pair (structure VI) the O–H stretching force constants show a slight increase. Variation in the values of the force constants f_{12}, f_{33} and $f_{O...M}$ are parallel to those for the $H_2O...M^+$ complexes (structure III), the extent of variation being smaller due to the lower acidities of the ion pairs compared to those of the corresponding cations. For the hydrogen-bonded contact ion pair complexes (structure VII) f_{22} values show a decrease compared to the water monomer value as in the case of the $HOH...X^-$ complexes (structure IV). Nevertheless, the variation is due only to a smaller extent to the presence of counter ions. The O–H stretching force constant values for the bifurcated hydrogen-bonded complexes (structure VIII) do not show any significant change on complexation. For the solvent-shared ion pair complexes (structure IX) the reduction in the value of the O–H stretching force constant is highest among all the structures considered. This may be attributed to the cooperativity effect due to the presence of the counter ion in a favorable orientation. The force constant value is reduced from 9·21 mdyne/Å for the monomer water molecule to 6·31, 7·67 and 8·09 mdyne/Å, respectively, for LiF, LiCl and NaCl ion pair complexes. The interaction force constant values (f_{12}) are increased considerably to 0·60, 0·24 and 0·16 mdyne/Å respectively from $-0·14$ mdyne/Å for the free water molecule. Variation in the interspecies stretching force constants, $f_{O...M}$ and $f_{H...X}$ clearly shows the relative acidities and basicities of the corresponding cations and anions. The trends observed in all these force constant values are similar to those observed in the case of interaction energies and geometrical parameters. The case of solvent-bound ion pair complexes (structure X) is more interesting. The hydrogen-bonded O–H stretching force constant value, f_{22}, is decreased in all the three cases, whereas the non-hydrogen-bonded O–H stretching force constant value, f_{11}, shows a significant increase. The values of f_{11} are 9·78, 9·43 and 9·29 mdyne/Å, respectively, for the complexes of LiF, LiCl and NaCl compared to the water monomer value of 9·21 mdyne/Å.

3.2b *Complexes of water with BeO and MgO*: The results obtained for the mono-hydrated complexes of BeO and MgO follow more or less the pattern of the corresponding halide counterparts. For all the three types of complexes considered the hydrogen-bonded O–H stretching force constant value decreases compared to the monomer water value. The non-hydrogen-bonded O–H stretching force constant for the complexes (structure VII) does not show much variation. For the most stable hydrated complexes of BeO and MgO (structure VI) the changes in the values of the force constants, f_{12}, f_{33} and $f_{O...M}$ parallel those for the $H_2O...M^{2+}$ complexes (structure III), the variation being smaller as in the case of the halide complexes.

3.3 *Harmonic vibrational frequencies*

The harmonic vibrational frequencies of various complexes considered are given in table 3. The calculated uncorrected harmonic frequencies for monomer water molecule are found to be 4137 (ω_3), 3981 (ω_1) and 1739 (ω_2) cm^{-1}.

3.3a *Complexes of water with LiF, LiCl and NaCl*: The asymmetric stretching frequency of water molecule (ω_3) suffers a red shift in all the complexes except for the solvent-bound structures of LiF and LiCl, whereas the symmetric stretching

Table 3. Harmonic vibrational frequencies of H_2O, MX, $(H_2O)M^{n+}$, $(H_2O)X^-$, $(H_2O)(MX)$ and $M^+(H_2O)X^-$ complexes obtained by *ab initio* 6-31G MO calculations.

Structure (symmetry)	Species	Frequency (cm^{-1})							
		ω_3	ω_1	ω_2	HOH$_{(rock)}$	H$_{oop}$	ω_{MX}	$\omega_{O...M}$	$\omega_{H...X}$
I (C_{2v})	H_2O	4137	3981	1739					
II $(C_{\infty v})$	LiF						1012		
	LiCl						654		
	NaCl						372		
	BeO						1632		
	MgO						799		
III (C_{2v})	$H_2O...Li^+$	4061	3953	1840	645	697		632	
	$H_2O...Na^+$	4084	3968	1827	543	625		355	
	$H_2O...Be^{2+}$	3635	3594	1864	988	983		1008	
	$H_2O...Mg^{2+}$	3856	3796	1890	825	935		585	
IV (C_s)	$HOH...F^-$	4005	2473	1865	564	1245			408
	$HOH...Cl^-$	4070	3680	1831	402	818			216
V (C_{2v})	$OH_2...F^-$	3911	3943	1810	581i	1040			346
	$OH_2...Cl^-$	4042	3975	1845	173i	769			204
VI (C_{2v})	$H_2O...LiF$	4132	4007	1782	537	487	1035	350	
	$H_2O...LiCl$	4131	3998	1787	562	515	778	283	
	$H_2O...NaCl$	4129	3994	1785	464	470	414	238	
	$H_2O...BeO$	4098	3978	1818	814	606	1700	583	
	$H_2O...MgO$	4108	3984	1811	609	602	827	396	
VII (C_s)	$HOH...FLi$	4086	3763	1822	440	820	965		246
	$HOH...ClLi$	4122	3957	1763	264	473	632		115
	$HOH...ClNa$	4106	3937	1763	306	509	363		119
	$HOH...OBe$	4086	3813	1808	421	755	1602		207
	$HOH...OMg$	4042	3564	1805	459	805	807		213
VIII (C_{2v})	$OH_2...FLi$	4121	4029	1802	364i	681	972		202
	$OH_2...ClLi$	4129	4001	1790	61i	479	633		129
	$OH_2...ClNa$	4121	3999	1797	100i	526	363		131
	$OH_2...OBe$	4119	4022	1804	316i	656	1594		178
	$OH_2...OMg$	4087	3995	1778	331i	670	709		193
IX (C_{2v})	$Li^+...OH_2...F^-$	3256	3583	1724	833i	1320		899	482
	$Li^+...OH_2...Cl^-$	3669	3755	1854	200i	1095		826	309
	$Na^+...OH_2...Cl^-$	3788	3832	1866	144i	1042		526	227
X (C_s)	$H_2O–LiF$ (SB)	4172	3614	1696	674	860	856		
	$H_2O–LiCl$ (SB)	4141	3970	1772	432	546	603		
	$H_2O–NaCl$ (SB)	4096	3821	1760	348	630	307		

frequency (ω_1) suffers a blue shift in two cases (structures VI and VIII) and is red-shifted in the rest of the cases. The red shift in the stretching frequency is attributed to the elongation of the O–H bond due to the interactions. The blue shift observed in the two cases may be due to an increase in the absolute value of the interaction force constant f_{12}. The HOH bending frequency (ω_2) is blue-shifted in almost all the cases as expected for hydrogen-bonded systems. The symmetric stretching frequency of water (ω_1) for the solvent-shared ion pair complexes (structure IX) are found to be higher than the asymmetric stretching frequencies (ω_3). This is because of the

change in sign as well as increase in value of the interaction force constant (f_{12}). The asymmetric stretching frequency of water (ω_3) for the solvent-bound ion pair complexes of LiF and LiCl show a blue shift which is not observed in any other case. This increase in the frequency value is in accordance with the values of the internal force constants (f_{11}) and O–H bond distances (d_1) for these complexes.

The calculated frequency values of the interspecies vibrational modes of all the complexes are within the general range normally expected for hydrogen-bonded complexes (Knoezinger and Schrems 1987). All the frequencies for intermolecular vibrational modes, except for the rocking mode of the water molecule in three cases (structures V, VIII and IX), are found to be real. The observation of imaginary frequency for the rocking mode in these cases shows the transition state nature of these complexes and these represent the reaction coordinates which take these states back to either of the two local minimum configurations involved in such cases. The observation of the imaginary frequency in these systems is similar to the earlier reports (Latajka 1992; Mohandas *et al* 1993) in the case of water interacting with F⁻, Cl⁻ and CN⁻ ions as well as the LiCN ion pair in the bifurcated configuration. The values of hydrogen out-of-plane bending frequencies (ω_{oop}) and the interspecies stretching frequencies $(\omega_{O\cdots M}$ and $\omega_{H\cdots X})$ are direct measures of the strength of the interaction. The out-of-plane bending frequencies are found to be the maximum for solvent-shared ion pair complexes (structure IX), whereas for mono-hydrated contact ion pair complexes (structures VI, VII, VIII and X) ω_{oop} values are found to be lower than those for the corresponding ion–water complexes. This clearly shows that in hydrated contact ion pairs the interaction is less pronounced, thus confirming the less acidic or basic nature of the ion pairs compared to those of the individual ions. The comparison of the interspecies stretching frequencies for the two types of complexes also substantiates this fact. The interspecies stretching frequencies are found to be maximum for the solvent shared ion pair complexes (structure IX) in which both $\omega_{O\cdots M}$ and $\omega_{H\cdots X}$ values are higher than those in the corresponding ion–water complexes. This again shows the cooperativity effect due to the presence of a counter ion in a favorable orientation.

3.3b *Complexes of water with BeO and MgO*: The results obtained for the mono-hydrated complexes of BeO and MgO follow the pattern of their $H_2O + MX$ counterparts. The symmetric stretching frequency of water (ω_1) suffers a blue shift in the bifurcated complexes (structure VIII) and is red-shifted in the other two cases (structures VI and VIII), whereas the asymmetric stretching frequency (ω_3) is red-shifted in all the three cases. The HOH bending frequency (ω_2) also suffers a blue shift in all the complexes. The observation of an imaginary frequency for the rocking mode of water for the bifurcated complexes (VIII) shows their transition state nature. The magnitude in the frequencies of the interspecies stretching modes show the relative strengths of interaction in these complexes.

4. Conclusions

The results obtained for the complexes of water with the individual ions are in general agreement with previously established patterns. The structures and energetics of the mono-hydrated contact ion pairs parallel those for the corresponding ion–water

complexes. However, the presence of a counter ion reduces the effects to a considerable extent. In the case of the halides, in addition to the three mono-hydrated complexes, solvent-shared and solvent-bound ion pair structures were also considered. The solvent-shared ion pair complexes show high interaction energies and the variation in other properties computed for these complexes are also higher than in any other case. In general, the variations in the values of internal force constants and harmonic vibrational frequencies are consistent with the trends observed in the energetics and structural parameters of the various structures considered. Solvent-bound ion pair complexes are found to have the highest stabilization energies among all the hydrated contact ion pair còmplexes. These structures are also found to have higher values for the O–H internal force constants and frequencies compared to those of the free water molecule. The stabilization of such structures supports the adsorption of water on alkali halide crystal surfaces as well as the possibility of their involvement in the hydration of contact ion pairs. Furthur work in this direction is in progress.

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