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Ab Initio Study of Cation–Dipole Interactions. Proton, Lithium, and Sodium Affinities of Hydrogen and Alkali Halides and Natural Orbital Study of Bonding

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Abstract: The H$^+$, Li$^+$, and Na$^+$ affinities of hydrogen and alkali halides have been calculated at 6-31+G*//6-31+G*, MP2(FULL)/6-31+G*//MP2(FULL)/6-31+G*, HF/6-311+G*//MP2(FULL)/6-31+G*, MP2(FC)/6-311+G*//MP2(FULL)/6-31+G*, and MP4SDTQ(FC)/6-311+G*//MP2(FULL)/6-31+G* levels. In the case of protonated species 6-31+G** and 6-311+G** basis sets have been used. All the complexes except H$_2$F$^+$, H$_2$Cl$^+$, LiHCl$^+$, and NaHCl$^+$ are predicted to have linear structure. The calculated structural parameters and cation affinities are in very good agreement with available experimental data. The nature of bonding has been studied on the basis of NPA (natural population analysis) atomic charges and bond indices calculated at the HF level at the MP2(FULL) geometries using 6-31+G* and 6-311+G* basis sets. In all cases the bond index of the donor–acceptor bond varies linearly as the amount of charge transfer. The bonding in M1XM2$^+$ (M1, M2 = Li, Na) complexes has been found to be essentially electrostatic in nature. Making use of this observation K$^+$, Rb$^+$, and Cs$^+$ affinities of hydrogen and alkali halides have been predicted. An appreciable degree of valence interaction is found to be operative in the protonated species which accounts for their very high interaction energies and bent structure in most cases. The trends in the electronic structure and stability of the complexes have been rationalized on the basis of charge transfer, bond indices, and other considerations.

I. Introduction

The interaction between a cation and a dipolar molecule is a particular type of acid–base interactions where the cation acts as an acid and the dipolar molecule as a base. The study of cation–dipole interactions has been found to be useful in a wide variety of fields.[1-5] Gas-phase studies of ion–molecule interactions provide information about the structure and bonding of complexes which in turn are useful in the study of strong electrolytes and ionic solids.[2] Ion–molecule complexes are often the reaction products[3] of the scattering of high-energy neutral and ionic particles from surfaces. Cation–dipole interactions find extensive applications[4] also in plasma chemistry, atmospheric chemistry, molecular biology, zeolite chemistry, in the field of molecular catalysis, mass spectrometry, etc. In view of their importance in various fields of chemistry cation–dipole interactions have received considerable attention from both experimentalists[1,6-27] and theoreticians.[28-69] Still sufficient experimental information is not available about the structure and interaction energies of cation–dipole complexes. The nature of bonding in these species especially the role of valence interaction has also not been carefully analyzed.

Ab initio MO calculations when carried out at a sufficiently high level of theory provide a reliable source of information about the electronic structure and interaction energies of small binary complexes. The pertinent wave function also can be meaningfully used for bonding analysis. Recently, Sannigrahi et al.[68,69a] studied the electronic structure, stability, and bonding of complexes of hydrogen and alkali halides with halide ions. A similar albeit preliminary studies have been reported by us[69b] on complexes of

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alkali halides with alkali cations. In the former interactions alkali halides act as acids, while in the reactions with alkali cations they act as bases. In the present investigation we have carried out a comparative study of the proton, lithium, and sodium affinities of HF, HCl, LiF, LiCl, NaF, and NaCl laying special emphasis on the nature of bonding in the resulting complexes. Since the chosen bases represent dipoles with varying magnitude and the acids represent cations with varying size, a knowledge of their interaction will be useful in understanding the nature of cation–dipole interactions, in general.

Among the protonated species considered here, H_2F^+ and H_2Cl^+ were studied extensively, both experimentally[1,6–9] and theoretically.[35–43] A number of theoretical calculations[44–52] have also been reported on the remaining protonated species. All possible symmetric dialkali halide cations, formed in the chemiionization reactions of alkali dimers with halogen molecules, were characterized by Reck et al.[14] by means of a crossed-beam apparatus. Lin et al.[34a] and Reck et al.[14] studied the potential energy surface for all 20 M_2X^+ ions using the classical ionic model based on the Rittner model[34b] and its extensions.[34c] They predicted bent structures for Li_2F^+, Li_2Cl^+, and Na_2Cl^+ with binding energies ranging from 35 to 52 kcal mol^{-1}. A number of quantum chemical calculations[53–67] dealing mainly with the structure and stability of the neutral as well as ionic microclusters of alkali halides of a broad size range have been carried out. These were, however, mostly performed at the ab initio SCF level and confined to the symmetric species. Experimental information about the structure and energetics is available only for H_2F^+,[1a,9] H_2Cl^+,[1c] and the symmetric dialkali halide cations.[17,21] Thus the present study is also aimed at supplementing the available experimental data with accurate theoretical estimates which may provide guidance to the future experimental studies on alkali hydrogen or mixed dialkali halide cations.

Smith et al.[33] calculated the interaction energies and geometries of the complexes of H^+, Li^+, and Na^+ with several first- and second-row bases at the 6-31G**//3-21G level. Deviations of the calculated values from experiment were attributed by them to zero-point energy (ZPE) corrections. We have considered here a series of halide bases and employed a level of theory which represents an almost state of the art procedure[70] in computational quantum chemistry. The ZPE correction has been taken into account while calculating the interaction energies, and the nature of bonding has been analyzed on the basis of local quantities like atomic charges and bond indices. The MPA (Mulliken population analysis)[71] and LPA (Löwdin population analysis)[72] schemes, which are widely employed in the calculation of these quantities, fail[69,73] conspicously in the case of ionic systems as have been considered here. We have, therefore, employed NPA (natural population analysis)[73a] scheme for the calculation of atomic charges[73a] and bond indices.[74] The earlier studies[69,73,74] indicate that these methods are rather insensitive to basis sets and quite adequate for ionic molecules.

II. Method of Calculation

The geometry of the complexes has been optimized at the Hartree–Fock (HF) and MP2(FULL) levels using the 6-31+G* basis set and the analytical gradient technique. Additional single point calculations have been performed using the 6-311+G* basis at HF, MP2(FC), and MP4SDTQ(FC) levels at the MP2(FULL)/6-31+G* optimized geometries in order to calculate the cation affinities (CA). For the protonated species we have always used 6-31+G** and 6-311+G** basis sets. However, it has not been explicitly mentioned hereafter. The ZPE corrections have been estimated at the HF/6-31+G*//HF/6-31+G* level by scaling[70] the calculated values by a factor of 0.89. All calculations have been performed using GAUSSIAN 90 program.[75] The bonding analysis has been carried out at the HF level on the basis of NPA atomic charges (q_A)[73a] and bond indices (I_{AB})[74] obtained at the MP2(FULL) geometries using 6-31+G* and 6-311+G* basis sets. In the original work[74] the term bond

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Table 1. Calculated and Experimental Bond Lengths (r, in Å) and Ion-Pairing Energies (ΔE_{IP}, in kcal mol^{-1}) of Hydrogen and Alkali Halides

	r				
MX	HF/ 6-31+G*	MP2(FULL)/ 6-31+G*	MP2(FC)/ 6-311+G*	MP2(FC)/ 6-311+G (2df)	expt[a]
HF	0.902	0.926	0.917	0.918	0.917
HCl	1.266	1.269	1.274	1.272	1.275
LiF	1.576	1.588	1.595	1.583	1.564
LiCl	2.068	2.056	2.016	2.025	2.021
NaF	1.932	1.945	1.972	1.952	1.926
NaCl	2.406	2.400	2.376	2.376	2.361

	ΔE_{IP}		
MX	6-31+G*// 6-31+G	MP4SDTQ(FC)/ 6-311+G*// MP2(FULL)/ 6-31+G*	expt
HF	374.5	372.0	376.0[b]
HCl	327.0	338.2	337.0[b]
LiF	181.9	181.0	183.5 ± 2.2[c]
LiCl	147.3	155.9	154.0 ± 0.1[c]
NaF	152.1	149.2	153.3 ± 0.9[c]
NaCl	126.9	131.1	132.4 ± 0.8[c]

[a] Reference 18. [b] Reference 19. [c] Reference 20.

order instead of bond index has been used. We have, however, preferred to use the latter term in the spirit of current practice.[76]

Table 2. Optimized Geometrical Parameters of MIXM2$^+$ (M1, M2 = H, Li, Na; X = F, Cl) Complexes[c]

(M1XM2)$^+$ [a]	no. of imaginary freq	structural[b] parameters	HF/6-31+G*	MP2(FULL)/ 6-31+G*
$H_2F^+(C_{2v})$	0	H–F	0.948 (0.046)	0.969 (0.043)
		∠HFH	116.4	113.4
$H_2F(D_{\infty h})$	2	H–F	0.948 (0.046)	0.967 (0.041)
$H_2Cl^+(C_{2v})$	0	H–Cl	1.291 (0.025)	1.294 (0.025)
		∠HClH	97.1	95.8
$H_2Cl^+(D_{\infty h})$	2	H–Cl	1.320 (0.054)	1.311 (0.042)
$Li_2F^+(D_{\infty h})$	0	Li–F	1.658 (0.082)	1.671 (0.083)
$Li_2Cl^+(D_{\infty h})$	0	Li–Cl	2.187 (0.119)	2.159 (0.103)
$Na_2F^+(D_{\infty h})$	0	Na–F	2.013 (0.081)	2.034 (0.089)
$Na_2Cl^+(D_{\infty h})$	0	Na–Cl	2.515(0.109)	2.481 (0.081)
$LiHF^+(C_{\infty v})$	0	H–F	0.914 (0.012)	0.937 (0.011)
		Li–F	1.814 (0.238)	1.789 (0.201)
$LiHCl^+(C_s)$	0	H–Cl	1.274 (0.008)	1.278 (0.009)
		Li–Cl	2.415 (0.347)	2.372 (0.316)
		∠HClLi	108.9	106.3
$LiHCl^+(C_{\infty v})$	2	H–Cl	1.274 (0.008)	1.275 (0.006)
		Li–Cl	2.505 (0.437)	2.406 (0.350)
$NaHF^+(C_{\infty v})$	0	H–F	0.911 (0.009)	0.934 (0.008)
		Na–F	2.184 (0.252)	2.148 (0.203)
$NaHCl^+(C_s)$	0	H–Cl	1.272 (0.006)	1.275 (0.006)
		Na–Cl	2.812 (0.406)	2.746 (0.346)
		∠HClNa	114.7	112.5
$NaHCl^+(C_{\infty v})$	2	H–Cl	1.272 (0.006)	1.274 (0.005)
		Na–Cl	2.881 (0.475)	2.789 (0.389)
$LiNaF^+(C_{\infty v})$	0	Li–F	1.648 (0.072)	1.654 (0.066)
		Na–F	2.025 (0.093)	2.049 (0.104)
$LiNaCl^+(C_{\infty v})$	0	Li–Cl	2.163 (0.095)	2.129 (0.073)
		Na–Cl	2.553 (0.147)	2.512 (0.112)

[a] The molecular point groups of each species are included in parentheses. [b] The bond lengths are given in Å, and the angles are in deg. [c] The values in parentheses stand for the changes in bond length upon complex formation.

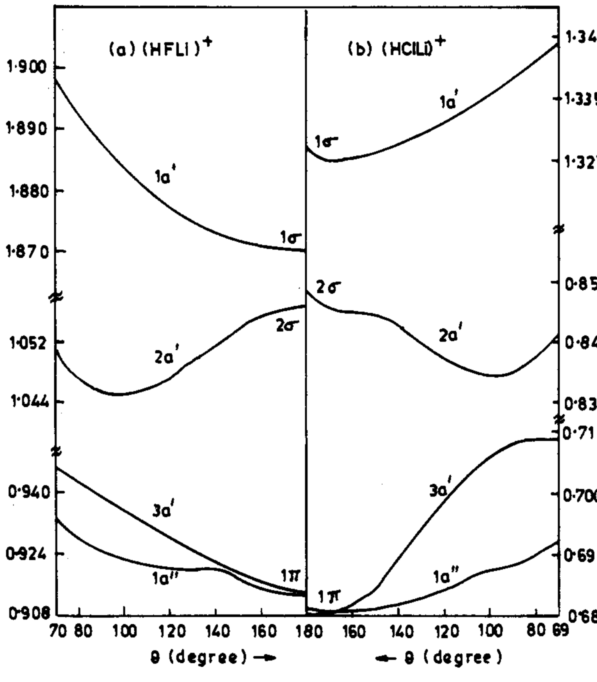

Figure 1. Angular correlation diagrams of the valence MOs of HFLi$^+$ (a) and HClLi$^+$ (b). The bond lengths have been fixed at the HF/6-31+G* optimized geometry, and MO energies have been calculated using the same basis set.

III. Results and Discussion

Since the experimental data on the complexes considered here are rather scantly, we have first calculated the bond lengths and ion-pairing energies of the bases at various levels of theory in order to assess the accuracy of the present calculations. These calculated quantities are compared with experiment[18-20] in Table 1. At the highest level of theory the bond lengths of all but LiF and NaF are in excellent agreement with experiment. Surprisingly these bond lengths are most accurately reproduced at the lowest level of theory employed here. This is certainly fortuitous. Comparing the results of columns 4 and 5 in Table 1 it is found that a closer agreement between theory and experiment can be obtained for the bond lengths of LiF and NaF if still higher basis sets are used. This may be practically feasible for the diatomics but not for the complexes. Therefore, in order to strike a compromise between accuracy and computational costs we have optimized the geometry of the complexes at the MP2(FULL)/6-31+G* level. At this level of theory the maximum deviation of the monomer bond lengths from experiment is 0.04 Å. At the highest level of theory the ion-pairing energies are obtained in excellent agreement with experiment, the maximum discrepancy being about 3% in the case of NaF. These results indicate that the level of theory employed in the present calculations is adequate for the description of the complexes.

A. Equilibrium Geometries of the Complexes. The optimized ground state geometries of the complexes are listed in Table 2, where the quantities in parentheses are the changes in monomer (base) bond lengths upon complex formation. The protonated species, H_2F^+, H_2Cl^+, $LiHCl^+$, and $NaHCl^+$ are found to have bent structure, while the remaining complexes are linear. The optimized bond lengths corresponding to the linear conformations of the bent species are also included in Table 2.

According to the Walsh rules[77] H_2A and HAB molecules with eight valence electrons (as in the present cases) should be bent. Since exception is provided by $LiHF^+$ and $NaHF^+$ we have compared the angular correlation diagrams of $LiHF^+$ and $LiHCl^+$ in Figure 1. These are qualitatively similar and predict bent structure for both the species in disagreement with the present finding.

An explanation of the structural difference between MHF^+ and $MHCl^+$ (M = Li, Na) can be given on the basis of ES potentials[78] of HF and HCl. At larger distances as preferred by Li^+ and Na^+, the minimum in the ES potential of HF occurs along the internuclear axis and that in HCl occurs away from the

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Table 3. Calculated Proton (PA), Lithium (LA), and Sodium (SA) Ion Affinity (in kcal mol^{-1})[a] of the Hydrogen and Alkali Halides (MX)

MX	HF/6-31+G*// HF/6-31+G*	MP2(FULL)/6-31+G*// MP2(FULL)/6-31+G*	/6-311+G*MP2(FULL)/6-31+G* HF	MP2(FC)	MP4SDTQ(FC)	ΔE_{ZPE} HF/6-31G*// HF/6-31G*
			PA			
HF	114.7	113.9	114.3	115.1	116.0	−5.60
HCl	128.1	133.1	129.8	135.0	137.3	−5.30
LiF	215.5	209.7	216.0	212.5	213.4	−4.62
LiCl	193.0	203.8	192.5	196.6	199.0	−4.13
NaF	238.8	232.8	240.6	205.8	205.8	−5.19
NaCl	208.7	220.6	209.7	214.4	216.8	−4.18
			LA			
HF	22.8	24.0	23.8	22.6	22.4	−0.44
HCl	13.0	15.9	14.1	16.5	16.6	−0.88
LiF	68.8	68.6	69.9	67.1	66.8	−1.11
LiCl	50.2	59.8	50.8	51.4	51.6	−0.55
NaF	81.8	81.1	83.4	79.8	79.4	−1.20
NaCl	59.6	70.4	61.4	62.9	63.0	−0.67
			SA			
HF	16.6	17.2	17.0	−15.4	−17.0	−0.45
HCl	8.4	10.6	8.4	9.7	9.7	−0.59
LiF	51.4	51.4	52.2	48.0	47.6	−0.66
LiCl	39.1	48.2	38.6	38.4	38.3	−0.32
NaF	62.2	61.5	63.0	59.4	58.9	−0.66
NaCl	47.1	57.1	47.4	47.6	47.6	−0.36

[a] These values include ZPE corrections which are also shown separately.

internuclear axis. Thus MHF^+ complexes should be linear and $MHCl^+$ should be bent in agreement with the present observation. We will later show that the CT interaction in the bent conformation of $MHCl^+$ is appreciably stronger than that in the linear conformation. At short distances from the base as preferred by H^+ the minimum in the ES potential of HF and HCl occurs away from the dipole axis suggesting that both H_2F^+ and H_2Cl^+ should be bent.

Very few experimental data are available to check the accuracy of the calculated structural parameters. In the case of H_2F^+ and H_2Cl^+ an excellent agreement is obtained with experiment[9] (r_{HF} = 0.958 Å, < HFH = 114.6° and r_{HCl} = 1.304 Å, < HClH = 94.2°). The results of some earlier calculations[33,57,60] although carried out at a lower level of theory are in reasonable agreement with the present values in the case of H_2F^+, H_2Cl^+, Li_2F^+, Li_2Cl^+, Na_2F^+, Na_2Cl^+, $LiHCl^+$, and $NaHCl^+$. Earlier theoretical studies[14,34a] based on classical ionic model predicted bent structures for Li_2F^+, Li_2Cl^+, and Na_2Cl^+. A bent structure for $LiHF^+$ was also predicted by Huber and Latajka.[45]

The calculated HF and MP2 bond lengths of the symmetric species obtained using the 6-31+G* basis differ at most by 0.03 Å. The corresponding difference in the heteronuclear species is some time as large as 0.06 Å. In general, electron correlation increases the M–F and H–X bond lengths and decreases the M–Cl (M = Li, Na) bond lengths and bond angles in the bent species.

It can be seen from Table 2 that in the protonated species MHX^+ (M = Li, Na) the H–X distance is almost the same as in free HX molecule and the M–X bond is considerably elongated. In all the complexes the M–Cl (M = Li, Na) bond length increases to a greater extent than the corresponding M–F bonds, while a reverse trend is observed in the case of H–F and H–Cl bonds. The donor–acceptor distances in the Li^+ and Na^+ complexes bear a linear relationship (see also section IIIC) indicating a strong similarity between the nature of these interactions.

B. Proton, Lithium, and Sodium Affinity of Hydrogen and Alkali Halides. The calculated proton affinity (PA), lithium affinity (LA), and sodium affinity (SA) (including zero point energy corrections) of hydrogen and alkali halides are given in Table 3. The CA values are expressed in kcal mol^{-1}. In order to avoid repetitions the unit for CA has not henceforth been mentioned. The ZPE corrections are rather marginal (0.3–1.2) in the case of alkali halide complexes but quite appreciable (4.0–6.0) for the protonated species due to higher force constant of H–X bonds than M–X bonds. Inclusion of electron correlation (MP2(FULL)/6-31+G*//MP2(FULL)/6-31+G*) was found to cause only a marginal change in the ZPE corrections (not tabulated). It was also observed in this context that the BSSE corrections[79] to the CAs at the 6-31+G*//6-31+G* level are rather negligible (0.1–0.6) which indicates that similar corrections are not warranted for the 6-311+G* basis.

The CAs obtained at 6-31+G*//6-31+G* and HF/6-311+G*//MP2(FULL)/6-31+G* levels differ only marginally (the maximum difference is 1.8) indicating that these quantities are not quite sensitive to variations in geometrical parameters within a small range. The magnitude of correlation corrections to the PAs of the chloride bases increases with the increasingly high level of correlation treatments employed. However, the effect of electron correlation on the LAs and SAs are rather small and almost independent of the order of corrections.

The Li^+ and Na^+ affinities of alkali fluorides obtained at 6-31+G*//6-31+G* and MP2(FULL)/6-31+G*//MP2(FULL)/6-31+G* levels differ by a very narrow margin (~1.0). In the protonation of LiF and NaF, however, the corresponding interaction energies decrease by about 6.0. Electron correlation increases the CAs of the chloride complexes by about 3.0–5.0 for HCl and 9.0–12.0 for LiCl and NaCl. A comparison of the results of MP4SDTQ(FC)/6-311+G* and HF/6-311+G* calculations confirms the above general trend barring a few cases. The PA of NaF and the SA of HF are drastically lowered (by ≃35.0) in the MPn treatments. This lowering exceeds even the binding energy of $NaHF^+$ leading to an energetically unfavorable interaction between HF and Na^+. Intramonomer correlation probably outweighs the intermonomer correlation in the fluoride complexes leading to an overall lowering in their stability.

At the highest level of theory employed here, the PA values of HF and HCl show a remarkable agreement with the available experimental[1a,c] estimates, 116.0 and 140.0, respectively. The calculated LA of LiCl and SA of NaF and NaCl are also in good accord with the corresponding experimental[17,21] values (47 ± 3, 61 ± 6, and 42 ± 4). The classical ionic model[14,34] considerably underestimates (by about 6.0–20.0) the LA of LiF and LiCl and SA of NaF and NaCl compared to our best calculated values.

For the bent species (H_2F^+, H_2Cl^+, $LiHCl^+$, and $NaHCl^+$) the MP4SDTQ/6-311+G*//MP2(FULL)/6-31+G* values (including ZPE correction) of the barrier to linearity are 15.8, 58.4, 7.6, and 3.9, respectively. Interestingly, the deviation from linearity in these species (H_2F^+ is an exception) increases in the

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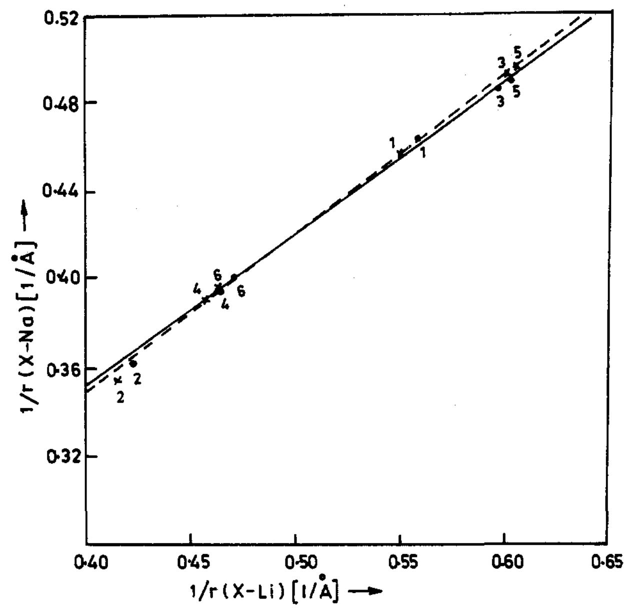

Figure 2. Plots of the inverse of the distance between Na^+ and the donor atom of the base ($1/r_{X\text{-}Na}$) vs inverse of the distance between Li^+ and the donor atom of the base ($1/r_{X\text{-}Li}$). The dashed (points represented by ×) and the solid (points represented by •) lines are obtained using HF/6–31+G* and MP2(FULL)/6–31+G* calculated distances (Å), respectively. Points 1, 2, 3, 4, 5, and 6 correspond, respectively, to HF, HCl, LiF, LiCl, NaF, and NaCl.

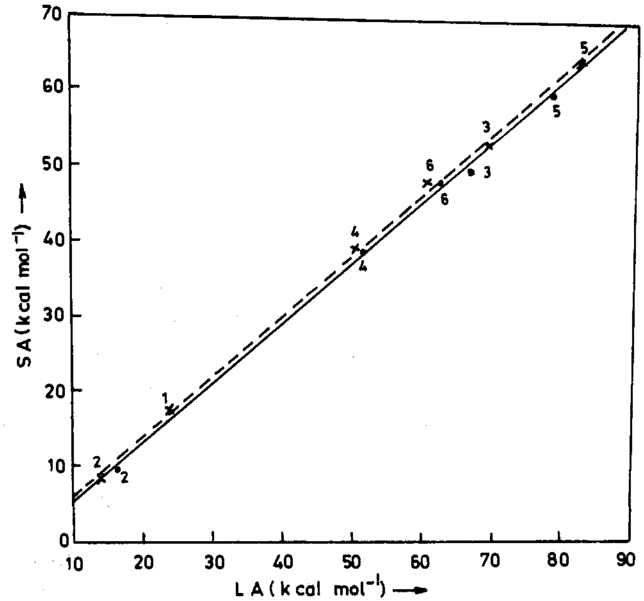

Figure 3. Plots of SAs vs LAs. The dashed (points represented by ×) and the solid (points represented by •) lines are obtained using HF/6–311+G*//MP2(FULL)/6–31+G* and MP4SDTQ(FC)/6–311+G*//MP2(FULL)/6–31+G* values, respectively. Points 1, 2, 3, 4, 5, and 6 correspond, respectively, to HF, HCl, LiF, LiCl, NaF, and NaCl.

Table 4. Calculated Ion–Molecule Distances (in Å)[a] and the Constants X_B and Y_B[b]

base	r(X–Li)	r(X–Na)	X_B		Y_B	
HF	1.789	2.148	72.8		–16.9	
HCl	2.372	2.746	99.3	120.2	–27.8	–34.1
LiF	1.671	2.049	160.3	173.9	–26.0	–37.3
LiCl	2.159	2.512	187.4	204.3	–36.0	–43.0
NaF	1.654	2.034	180.6	181.5	–25.8	–30.0
NaCl	2.129	2.481	210.1	231.1	–37.3	–45.5

[a] MP2(FULL)/6-31+G* values have been taken. [b] The two sets of values for X_B and Y_B are obtained using HF/6-311+G*//MP2(FULL)/6-31+G* and MP4SDTQ(FC)/6-311+G*//MP2(FULL)/6-31+G* LA and SA values including ZPE corrections.

same order. As can be seen from Table 3 the LA and SA values are of the same order of magnitude and smaller by almost an order than the corresponding PA values. This suggests that there may be a correlation between the former quantities. We shall show in the following subsection that a linear relationship indeed exists between LA and SA.

The Li^+ and Na^+ affinities of hydrogen and alkali halides vary in the order HCl < HF < LiCl < NaCl < LiF < NaF at both HF and all correlated levels except MP2(FULL)/6-31+G*//MP2(FULL)/6-31+G* for which the order is HCl < HF < LiCl < LiF < NaCl < NaF. The PA of the bases follows the above trends (with a reversal of the order for HF and HCl) at the HF and MP2(FULL)/6-31+G*//MP2(FULL)/6-31+G* levels, respectively. The drastic reduction of the PA of NaF at the other correlated levels leads to a slightly different trend, viz., HF < HCl < LiCl < NaF < LiF < NaCl. For a given cation, the interaction energies vary in the order HX < LiX < NAX.

C. Prediction of the K^+, Rb^+, and Cs^+ Affinity of Hydrogen and Alkali Halides. Smith et al.[33] exploited the importance of electrostatic interaction in the complexes of Li^+ and Na^+ to predict the K^+, Rb^+, and Cs^+ affinities of the bases considered by them. Their method of estimation was based on the following observations.

(a) The inverse of the distance of Li^+ to the donor atom ($1/r_{D\text{-}Li}$) of the base varies linearly with the inverse of the corresponding distance to Na^+ ($1/r_{D\text{-}Na}$).

(b) Calculated LA and SA values also bear a linear relationship, and the slope of this straight line is almost the same as in (a).

(c) The difference between the calculated $r_{D\text{-}Na}$ and $r_{D\text{-}Li}$ is nearly constant for all bases and corresponds to the difference in the ionic radii of Na^+ and Li^+. Using these facts they derived the following empirical relation

$$E_{D\text{-}M} = \frac{X_B}{r_{D\text{-}M}} + Y_B \qquad (1)$$

where $E_{D\text{-}M}$ is the ion–molecule interaction energy, $r_{D\text{-}M}$ is the distance between the alkali atom and the donor atom of the base, and X_B and Y_B are constants characteristic of the base.

In the present investigation the donor atom is represented by X which refers to the halogen atom. The variation of $1/r_{X\text{-}Na}$ with $1/r_{X\text{-}Li}$ is shown in Figure 2. The slope of the two straight lines corresponding to HF/6-31+G* and MP2/6-31+G* values are 0.713 and 0.691, respectively. The SAs are plotted against LAs in Figure 3. The straight lines corresponding to the HF/6-311+G* and MP4SDTQ/6-311+G* values have the slopes of 0.785 and 0.779, respectively. The relation, $r_{X\text{-}Na} - r_{X\text{-}Li} = r_{Na^+} - r_{Li^+}$, also holds good within a reasonable degree of accuracy for the chosen complexes. Thus eq 1 should hold for the present systems. We have now employed this relation to make a rough estimate of interaction energies and ion–molecule distances for heavier alkali cations. The calculated values of X_B and Y_B are given in Table 4, and the predicted values of $r_{X\text{-}M}$ (M = K, Rb,- and Cs) and K^+, Rb^+, and Cs^+ affinities are listed in Table 5. The estimated CAs of HF and HCl are found to be somewhat smaller than those predicted by Smith et al.[33] who did not include electron correlation and ZPE corrections.

D. Nature of Bonding. The results presented in the preceding sections indicate that the electronic structure and stability of the MIXM2+ systems exhibit the following trends.

(a) The structural and energetic changes associated with the formation of the MIXM2+ complex depend on the nature of the interacting species. It may be formed either by the interaction of MIX with M2+ or M2X with M1+. However, the process where the interacting cation is more electronegative or has higher ionic potential (charge to radius ratio) is more exogeric. In this type of interaction the bond length of the base increases, and the cation–donor distance decreases in the order $H^+ > Li^+ > Na^+$.

(b) For a given base the CAs vary in the order $H^+ > Li^+ > Na^+$ and for a given cation the corresponding variation is HX <

Table 5. Predicted Ion–Molecule Distances (in Å)[a] and Interaction Energies, CA (in kcal mol^{-1}) for K^+, Rb^+, and Cs^+ Complexes

	K^+			Rb^+			Cs^+		
base	r(X–K)	CA		r(X–Rb)	CA		r(X–Cs)	CA	
HF	2.519	12.0		2.669	10.4		2.879	8.4	
	2.528			2.678			2.888		
HCl	3.102	4.2	4.6	3.252	2.7	2.9	3.462	0.9	0.6
	3.126			3.276			3.486		
LiF	2.388	41.1	35.5	2.538	37.2	31.2	2.748	32.3	26.0
	2.405			2.555			2.765		
LiCl	2.917	28.2	27.0	3.067	25.1	23.6	3.277	21.2	19.3
	2.933			3.083			3.293		
NaF	2.378	50.1	46.0	2.528	45.6	41.5	2.738	40.2	36.0
	2.392			2.543			2.753		
NaCl	2.893	35.3	34.4	3.043	31.7	30.4	3.253	27.3	25.5
	2.895			3.045			3.255		

[a] The two sets of r(X–M) values are estimated from r(Li–X) and r(Na–X), respectively.

LiX < NaX. With the exception of the PA of HF and HCl the CAs of fluorides are greater than that of chlorides.

In this subsection we will try to rationalize the above trends in the light of our bonding analysis. The interaction energy of a cation–dipole complex (in fact, any binary complex) can be conveniently decomposed[29a,b] into contributions from electrostatic (ES), charge transfer (CT), polarization (PL), exchange repulsion (EX), and dispersion interactions. Of these all but the dispersion interaction can be reasonably accounted for at the HF level. The ES, CT, and PL interactions are attractive. However, the dominant contributions to the binding energy are generally from the first two interactions.

In an excellent review article Reed et al.[32] have highlighted the importance of CT interaction in several H-bonded complexes. Using numerical values they have shown that CT not only results in an increase in binding energies but also allows a significant amount of exchange repulsion to be overcome. In this way the monomers can come closer than would be possible if the interaction between the molecules were purely electrostatic in nature. This CT-driven closer approach will facilitate the ES interaction as well.

The fact that eq 1 is applicable to the Li^+ and Na^+ complexes indicates that their stability stems mainly from the ES interaction. In this equation, X_B may be regarded as the effective charge at the donor atom which also includes contributions from the molecular dipole moment as well as from polarization effects. The Y_B term contains all of the remaining interactions and is net repulsive. Since a similar relation does not hold for the protonated species their stability cannot be accounted for solely in term of ES interaction. In these cases the valence interaction possibly plays an equally important role. Although ES is the most dominant term in Li^+ and Na^+ complexes the role of valence interaction in these cases cannot be ignored.

The main component of the valence interaction is CT, and the bond index is a direct measure of covalency of a bond. We have used these quantities to assess the degree of valence or charge-overlapping interaction in the present cation–dipole complexes. Using a similar approach and MPA charge and bond index Nandi and Sannigrahi[80] have rationalized the trends in interaction energies of several metal cations with CO and N_2. Although the net CT takes place from the base to the cation the pertinent contribution to the interaction energy (ΔE_{CT}) is usually estimated[32] by considering the transfer of charge density from the donor to the acceptor and vice versa. However, the former predominates over the latter, and it has been observed[32] in a series of cation–dipole complexes that ΔE_{CT} varies roughly as CT. We have, therefore, taken net CT as a qualitative measure of ΔE_{CT}.

The calculated atomic charges of the complexes and the net amount of CT from the base to the cation are presented in Table 6. The charge distribution in all cases follows the classically expected pattern; the hydrogen and alkali atoms bear a net positive charge with a greater magnitude on the more electropositive atom, while the halogens are negatively charged. It can be seen from Table 6 that the extension of basis set from 6–31+G* to 6–311+G* generally (Na_2F^+ and Na_2Cl^+ are exceptions) reduces the magnitude of atomic charges and enhances CT.

Table 6. Calculated[a] Natural Atomic Charge (q_A)[b] in the Complexes, $(M1XM2)^+$ and the Amount of Charge Transfer (CT)[c] Resulting from the Reaction, $M1^+ + M2X \rightarrow (M1XM2)^+$

	M2X					
$M1^+$	HF	HCl	LiF	LiCl	NaF	NaCl
H^+						
q_H	+0.729	+0.395	+0.672	+0.345	+0.653	+0.338
	+0.696	+0.352	+0.642	+0.302	+0.621	+0.295
	+0.787	+0.597		+0.397		+0.374
	+0.763	+0.584		+0.362		+0.336
q_X	–0.457	+0.211	–0.669	–0.323	–0.653	–0.328
	–0.391	+0.296	–0.638	–0.278	–0.620	–0.284
	–0.575	–0.195		–0.391		–0.371
	–0.527	–0.168		–0.355		–0.334
q_{M2}	+0.729	+0.395	+0.997	+0.978	+1.000	+0.990
	+0.696	+0.352	+0.997	+0.976	+0.999	+0.989
	+0.787	+0.597		+0.994		+0.999
	+0.763	+0.584		+0.993		+0.998
q_{CT}	0.272	0.606	0.328/0.003	0.655/0.022	0.347/0.000	0.662/0.010
	0.305	0.648	0.359/0.004	0.698/0.024	0.379/0.001	0.705/0.011
	0.212	0.403		0.603/0.006		0.626/0.001
	0.237	0.416		0.638/0.007		0.664/0.002

M_1^+	LiF	LiCl	NaF	NaCl
Li^+				
q_{Li}	+0.994	+0.984	+0.993	+0.979
	+0.993	+0.980	+0.991	+0.976
q_X	–0.988	–0.968	–0.991	–0.971
	–0.987	–0.961	–0.989	–0.968
q_{M2}	+0.994	+0.984	+0.998	+0.992
	+0.993	+0.980	+0.998	+0.992
q_{CT}	0.006	0.016	0.007/0.002	0.021/0.008
	0.007	0.020	0.009/0.002	0.024/0.008

	M2X					
	NAF			NaCl		
$M1^+$	q_{NA}	q_F	q_{CT}	q_{Na}	q_{Cl}	q_{CT}
Na	+0.997	–0.995	0.003	+0.981	–0.962	0.019
	+0.998	–0.995	0.002	+0.989	–0.979	0.011

[a] The two successive values for each base (M2X) refer to HF/6-31+G*//MP2(FULL)/HF/6-31+G* and HF/6-311+G*//MP2(FULL)/6-31+G* calculations. The second set of two values under HF, HCl, LiCl, and NaCl corresponds to those for the linear structures of the complexes. [b] The atomic charges (q_{M2}) of the bases (M2X) calculated at HF/6-31+G*//MP2(FULL)/6-31+G* and HF/6-311+G*//MP2(FULL)/6-31+G* levels are +0.594/+0.559 (HF), +0.287/+0.247 (HCl), +0.982/+0.977 (LiF), +0.944/+0.942 (LiCl), +0.989/+0.988 (NaF), and +0.961/+0.960 (NaCl), respectively. [c] The values after slash correspond to CT associated with the reactions $M2^+ + M1X \rightarrow (M1XM2)^+$.

Due to the greater size and lower electronegativity the CT interaction is more prominent in the chloride than in the fluoride complexes. For the 6–311+G* basis the amount of CT varies in the order HF < LiF < NaF < HCl < LiCl < NaCl in the case of H^+ and HF < LiF < NaF < LiCl < HCl < NaCl in the case of Li^+ and Na^+. For a given base the corresponding variation follows the order $H^+ \gg Li^+ > Na^+$ which is also the order of their interaction energies. Thus the maximum CT is found to take place in the protonation of NaCl.

The cation affinities of alkali halides are plotted against the atomic charge (q_X) on the donor atom of the free bases in Figure 4. These plots are linear with a correlation coefficient of about 0.99 for both LA and SA reaffirming that the ES interaction is the dominating factor in the stability of the corresponding complexes. However, the PA curve deviates strongly form linearity.

It is interesting to note that for the fluoride bases CT, dipole moment, and their affinity for a given cation varies in the same

Table 7. Calculated NPA Bond Indices (I_{MX}) and the Corresponding Changes (ΔI_{MX})[a] upon Complex Formation

	$I_{M1X}(\Delta I_{M1X})$[b]		$I_{M2X}(\Delta I_{M2X})$[b]	
species (M1XM2)	I	II	I	II
HFH^+ (C_{2v})	0.271 (0.135)	0.303 (0.137)		
HFH^+ ($D_{\infty h}$)	0.212 (0.194)	0.228 (0.212)		
$HClH^+$ (C_{2v})	0.604 (0.109)	0.645 (0.108)		
$HClH^+$ ($D_{\infty h}$)	0.403 (0.310)	0.399 (0.354)		
$LiFLi^+$ ($D_{\infty h}$)	0.006 (0.008)	0.007 (0.017)		
$LiClLi^+$ ($D_{\infty h}$)	0.016 (0.038)	0.020 (0.034)		
$NaFNa^+$ ($D_{\infty h}$)	0.003 (0.008)	0.002 (0.010)		
$NaClNa^+$ ($D_{\infty h}$)	0.007 (0.032)	0.011 (0.029)		
$HFLi^+$ ($C_{\infty v}$)	0.328 (0.078)	0.357 (0.083)	0.003 (0.011)	0.002 (0.022)
$HClLi^+$ (C_s)	0.655 (0.058)	0.704 (0.049)	0.022 (0.032)	0.011 (0.043)
$HClLi^+$ ($C_{\infty v}$)	0.602 (0.111)	0.635 (0.117)	0.007 (0.047)	0.008 (0.046)
$HFNa^+$ ($C_{\infty v}$)	0.346 (0.060)	0.378 (0.062)	0.001 (0.010)	0.001 (0.011)
$HClNa^+$ (C_s)	0.662 (0.051)	0.704 (0.049)	0.009 (0.030)	0.011 (0.029)
$HClNa^+$ ($C_{\infty v}$)	0.626 (0.087)	0.662 (0.091)	0.003 (0.036)	0.003 (0.037)
$LiFNa^+$ ($C_{\infty v}$)	0.004 (0.010)	0.009 (0.015)	0.002 (0.009)	0.002 (0.010)
$LiClNa^+$ ($C_{\infty v}$)	0.020 (0.034)	0.023 (0.031)	0.007 (0.032)	0.008 (0.032)

[a] $\Delta I_{MX} = I_{MX}$ (monomer) − I_{MX} (complex). [b] The values under I and II refer to HF/6-31+G*//MP2(FULL)/6-31+G* and HF/6-311+G*//MP2(FULL)/6-31+G* calculations, respectively. At these levels (I/II) the bond indices of the monomers are 0.406/0.440 (HF), 0.713/0.753 (HCl), 0.014/0.024 (LiF), 0.054/0.054 (LiCl), 0.011/0.012 (NaF), and 0.039/0.040 (NaCl), respectively.

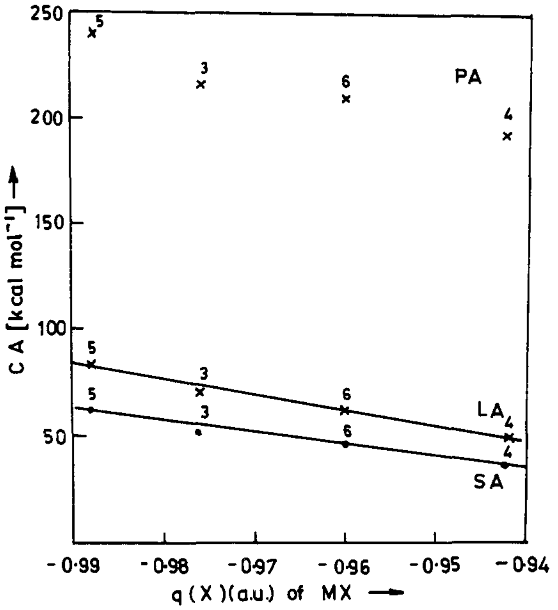

Figure 4. Plots of HF/6–311+G*//MP2(FULL)/6–31+G* cation affinities vs the net atomic charges on the halogen atom of the bases. Points 3, 4, 5, and 6 correspond, respectively, to LiF, LiCl, NaF, and NaCl.

order, namely, HF < LiF < NaF indicating that CT and ES interactions cooperate with each other. In the series of chloride bases LiCl seems to be an exception. Of the two alternative reactions $M1^+ + M2X \rightarrow M1XM2^+$ and $M2^+ + M1X \rightarrow M1XM2^+$, the former is more exoergic if M1 is more electronegative (smaller size) than M2. Under this situation both CT and ES (note that M2X has higher dipole moment than M1X) cause an increase in the interaction energy. The greater proton affinity of HCl than HF is mainly due to greater CT.

So far no mention has been made of the EX and PL interactions. The former is the main repulsive component of binding energies. It should roughly vary (compare Y_B values of Table 4) in the order $H^+ < Li^+ < Na^+$ for a given base and in the order F < Cl for a given cation. Thus the contribution of EX to CAs should follow a reverse trend. The polarizability of the bases varies in the order HF < HCl < LiF < LiCl < NaF < NaCl, and the polarizing power of the cations varies in the order $Na^+ < Li^+ < H^+$. The polarization or charge-induced dipole interaction between the cations and bases should augment the charge dipole interaction to some extent. It is interesting to note that the extent of elongation of the monomer bond upon complexation follows qualitatively the order of polarizabilities of the bases.

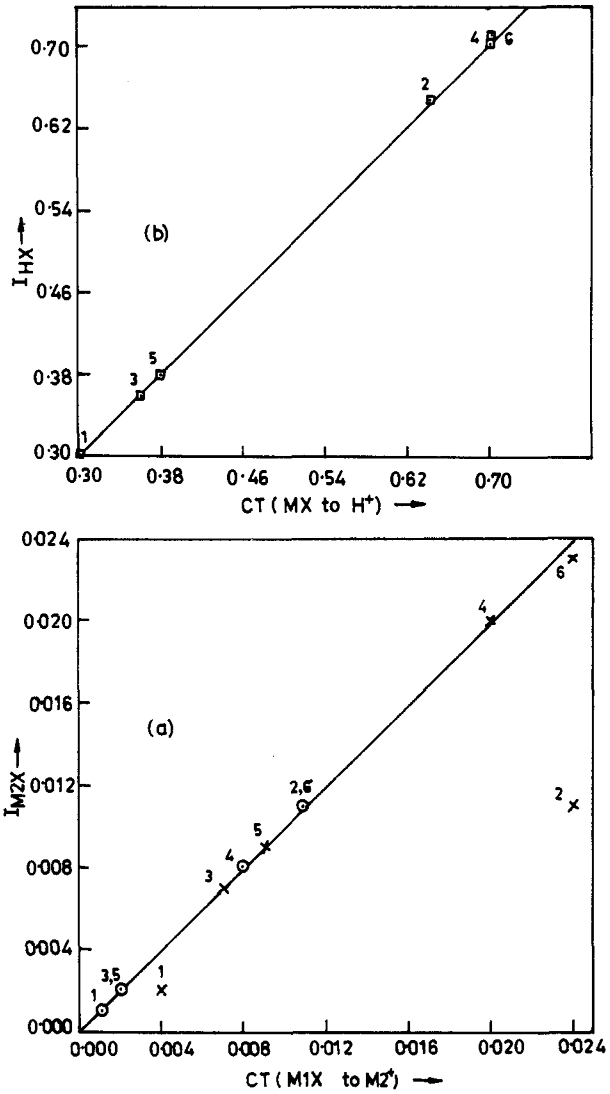

Figure 5. Plots of donor-cation bond index (I_{HX} and I_{M2X}) vs CT. In (a) points × and ⊙ correspond to M2 = Li and Na, respectively. Points 1, 2, 3, 4, 5, and 6 correspond, respectively, to HF, HCl, LiF, LiCl, NaF, and NaCl.

The NPA bond indices and the corresponding changes (with respect to the monomer value) upon complex formation are given in Table 7. Extension of the basis set from 6–31+G* to 6–311+G* generally increases (except LiF, LiCl, and NaF in the MHX^+ species) bond indices. In the mixed halides the I_{M1X} values are appreciably greater than I_{M2X} where M1 is lighter than M2. This is consistent with the corresponding deviations from the respective monomer bond length.

For the bent species, the bond indices in the bent structures are higher than the corresponding values in the linear conformations indicating stronger charge overlapping interaction in the former owing to favorable (angular) orientation. The higher proton affinity of HCl than HF can be rationalized in terms of bond indices and CT. Since bond index is a measure of covalency of a bond a correlation is expected to exist between CT and the bond index of the donor–cation bond. Comparing the results of Tables 6 and 7 it is seen that bond indices generally increase with CT. This is further illustrated in Figure 5 where the bond indices of the cation–donor bond are plotted against CT. As can be seen, both bond indices and CT vary in the order HF < LiF < NaF < HCl < LiCl < NaCl. In general the bond index of the base decreases on complex formation which is in qualitative agreement with the increase in bond lengths.

IV. Concluding Remarks

The ground state electronic structure and stability of the complexes of H^+, Li^+, and Na^+ and hydrogen and alkali halides have been calculated using high-level ab initio MO methods. In the analysis of their bonding attention has been focussed mainly on the CT and the bond index of the cation–donor bond calculated at the HF level using the NPA scheme. These quantities show a linear correlation and can be used as a qualitative measure of the valence or charge-overlapping interaction operative in the formation of the cation–dipole complexes. In most cases CT and ES interactions cooperate with each other. The protonated species are generally bent, and the Li^+ and Na^+ complexes are linear. In the latter complexes ES is the most dominant interaction. Making use of this fact the K^+, Rb^+, and Cs^+ affinities of hydrogen and alkali halides have been estimated. For the protonated species the valence interaction plays an equally important role. The trends in both geometries and interaction energies of the complexes have been rationalized in the light of NPA bonding analysis.

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