

Polarization effects and charge separation in AgCl-water clusters

S. S. M. C. Godinho

Grupo de Física Matemática da Universidade de Lisboa, Avenida Professor Gama Pinto 2, 1649-003 Lisboa, Portugal

P. Cabral do Couto and B. J. Costa Cabral^{a)}

Grupo de Física Matemática da Universidade de Lisboa, Avenida Professor Gama Pinto 2, 1649-003 Lisboa, Portugal and Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade de Lisboa, 1749-016 Lisboa, Portugal

(Received 20 July 2004; accepted 6 October 2004; published online 11 January 2005)

Structural, energetic, vibrational, and electronic properties of salt ion pairs (AgCl and NaCl) in water (W) clusters were investigated by density functional theory. In agreement with recent theoretical studies of NaCl-water clusters, structures where the salt ion pair is separated by solvent molecules or solvent separated ion pair (SSIP) were found in AgCl-W₆ and AgCl-W₈ aggregates. Our results indicate that for small AgCl-water clusters, contact ion pair (CIP) structures are energetically more stable than SSIP, whereas an opposite tendency was observed for NaCl-water clusters. In comparison with CIP, SSIP are characterized by extensive electronic density reorganization, reflecting enhanced polarization effects. A major difference between AgCl-water and NaCl-water CIP aggregates concerns charge transfer. In AgCl-water CIP clusters, charge is transferred from the solvent (water) to the ion pair. However, in NaCl-water CIP clusters charge is transferred from the ion pair to the water molecules. The electronic density reorganization in the aggregates was also discussed through the analysis of electronic density difference isosurfaces. Time dependent density functional theory calculations show that upon complexation of AgCl and NaCl with water molecules, excitation energies are significantly blueshifted relative to the isolated ion pairs (~2 eV for AgCl-W₈ SSIP). In keeping with results for NaI-water clusters [Peslherbe *et al.*, *J. Phys. Chem. A* **104**, 4533 (2000)], electronic oscillator strengths of transitions to excited states are weaker for SSIP than for CIP structures. However, our results also suggest that the difference between excitation energies and oscillator strengths of CIP and SSIP structures may decrease with increasing cluster size. © 2005 American Institute of Physics. [DOI: 10.1063/1.1826032]

I. INTRODUCTION

Charge separation of salt ion pairs in solution is one of the most important processes in chemistry.¹⁻⁷ The understanding at a molecular level of the electronic reorganization leading to charge separation is of wide interest. One fundamental process driven by charge polarization and separation is the dissolution of salts in polar solvents.⁸⁻¹⁴ The classical example is the NaCl dissolution in water. Although this process is empirically well known, theoretical investigations of the NaCl ionic separation in small water clusters are quite recent.¹⁵⁻¹⁸ These works were based on quantum mechanical calculations and provided relevant information on the energetics and structure of NaCl-water clusters. In general, these previous studies on small NaCl-water clusters indicated that they can be characterized as contact ion pair (CIP) structures. This means that the Na-Cl distance is only slightly increased in comparison with the isolated ion pair.^{16,18} CIP aggregates are, at least from the structural point of view, quite different from solvent-separated ion pair (SSIP), where the insertion of some solvent molecules between the two ions may induce additional polarization and charge separation.

The energetics and structure of SSIP clusters were the subject of several computer simulation studies based on interaction potential models.^{6,7,13,14,19} On the other hand, quantum mechanical studies of SSIP in small salt-water clusters are relatively scarce. One exception is an *ab initio* study by Jungwirth¹⁷ that predicted the separation of the NaCl ion pair when it is microsolvated in a cluster with six water molecules. However, several aspects concerning the microsolvation of salt ion pairs deserve further investigation. Two of them are polarization effects and charge transfer,²⁰⁻²² which are often analyzed through the calculation of atomic charges, although a direct approach based on the reorganization of the electronic density $\rho(r)$ induced by the interactions of the ion pair with the solvent can also be carried out. Moreover, it is of interest to know how electronic properties such as excitation energies depend on the cluster size for both CIP and SSIP structures. This is motivated by relevant experimental works on reaction dynamics in gas phase clusters,^{23,24} which involve transitions from the ground state to dissociative excited states.

Another issue concerns the dependence of the charge polarization and separation on the specific nature of the ion-pair and ion-pair-solvent interactions. This is the case for systems such as silver chloride (AgCl) and silver iodide (AgI), where induction effects including quadrupolar

^{a)}Author to whom correspondence should be addressed. Electronic mail: ben@adonis.cii.fc.ul.pt

induction²⁵ are expected to play a significant role in the solvation process. These systems are of great interest for atmospheric chemistry. They were detected in condensates collected from volcanoes,²⁶ and there is experimental evidence that the presence of water vapor increases the concentration of AgCl in the condensates by up to two orders of magnitude, strongly suggesting the formation of hydrated AgCl agglomerates.²⁶ The study of the formation of these agglomerates is important in the chemistry of aerosols and may also contribute to understand how rain precipitation is induced by cloud saturation with silver salts.^{27,28}

In this work we are reporting an investigation on the structural, energetic, vibrational, and electronic properties of small AgCl-water clusters. The results are compared with those for NaCl-water aggregates, which were the subject of some theoretical studies.^{15–18} This paper is organized as follows. Section II presents the computational methods used to study AgCl-water and NaCl-water clusters. Results for the structural, vibrational, and energetic properties are presented in Sec. III. Charge polarization and electronic density reorganization are discussed in Sec. IV. Kohn–Sham orbitals and excitation energies are analyzed in Sec. V. We conclude by pointing out some fundamental differences between NaCl-water and AgCl-water clusters and placing emphasis on the importance of carrying out a theoretical analysis of charge polarization based on the electronic density reorganization.

II. COMPUTATIONAL DETAILS

The properties of AgCl-water ($\text{AgCl}-W_N$) and NaCl-water ($\text{NaCl}-W_N$) clusters, where $N=1-6$ and $N=8$ is the number of water molecules (W), were investigated by density functional theory.²⁹ The well known B3LYP hybrid functional, which provides an adequate description of ionic systems was adopted. In this method, the exchange functional is represented by the Becke's three parameter functional (B3),³⁰ which is combined with the Lee, Yang, and Parr (LYP)³¹ correlation functional.

Ag was described by the Stuttgart/Dresden (SDD) effective core potential.^{32–36} In this approach 19 valence electrons ($4s^2 4p^6 4d^{10} 5s^1$) are included.³³ Full geometry optimizations and frequency calculations were carried out with the 6-31+G(d,p) basis set^{37,38} for the hydrogen, oxygen, sodium, and chlorine atoms. Additional single-point energy results with the 6-311++G($2df,p$) basis set^{39,40} for these atoms are also reported. Although no extensive energy search has been carried out, the optimized aggregates were characterized as local minima on the potential energy surface, i.e., all vibrational frequencies are real. Transition state structures connecting CIP and SSIP were not investigated.

The energetics of the $\text{AgCl}-W_N$ and $\text{NaCl}-W_N$ aggregates was investigated through the analysis of the formation and binding energies. The formation energy of the aggregate with the salt ion pair $X=(\text{AgCl},\text{NaCl})$ and N water molecules is given by

$$\Delta E_{f,N} = E[X - W_N] - E[X] - NE[W_1]. \quad (1)$$

The binding energy of X to a cluster with N water molecules is defined as

$$\Delta E_{b,N} = E[X - W_N] - E[X] - E[W_N]. \quad (2)$$

The above quantities, which are identical for $N=1$, include unscaled zero-point vibrational energy corrections. By adding thermal corrections at $T=298.15$ K we define the enthalpies $\Delta H_{f,N}$ and $\Delta H_{b,N}$. Binding energies calculated at the B3LYP/6-311++G($2df,p$)/B3LYP/6-31+G(d,p) level were corrected for BSSE by using the counterpoise method.⁴¹ These corrections amount to 5%–10% of the total energy depending on the cluster size. For estimating binding energies, the structure of the water clusters (W_N) for $N=1-6, 8$ were also optimized. These structures correspond to the most stable conformer for each N .^{42–44}

The analysis of polarization effects and charge transfer was carried out with charges fitted to the electrostatic potential (ESP charges) and with charges derived from natural atomic orbitals (NAO).^{20,21} ESP charges were calculated by the Breneman method.⁴⁵ All the atomic radii for the charges correspond to ESP default values with the exception of Ag for which the value of 1.4 Å was used. We also provide a discussion on the electronic density reorganization in the clusters by representing electronic density difference isosurfaces.⁴⁶

Excitation energies were calculated by time dependent density functional theory (TDDFT).^{47–50} A detailed comparison between theoretical excitation energies based on TDDFT and experimental results for a series of molecules was recently reported by Furche and Ahlrichs.⁴⁸ It was concluded that TDDFT is a reliable procedure for predicting vertical excitation energies. All the calculations were carried out with the GAUSSIAN 98 program.⁵¹ Molecular orbitals and electronic densities were analyzed by using the Molekel visualization program.⁵²

III. STRUCTURE, VIBRATIONAL, AND ENERGETIC PROPERTIES

A. Structure and vibrational properties

B3LYP/6-31+G(d,p) optimized structures of AgCl-water and NaCl-water clusters are presented in Figs. 1 and 2, and AgCl-water structural parameters are reported in Table I. For the isolated ion pair, the Ag–Cl distance $R(\text{Ag}-\text{Cl})$ is 2.33 Å, in good agreement with experimental^{53,54} and theoretical results.^{55,56} The dependence of $R(\text{Ag}-\text{Cl})$ on the cluster size N is illustrated in Fig. 3. $R(\text{Ag}-\text{Cl})$ increases from 2.31 Å ($\text{AgCl}-W_1$) to 2.65 Å ($\text{AgCl}-W_5$). In these structures the ion pair is in contact.

For $\text{AgCl}-W_6$ and $\text{AgCl}-W_8$ clusters, CIP and SSIP structures were found. Two SSIP structures of $\text{AgCl}-W_6$ were found and are represented in Fig. 1. In the first cluster [$\text{AgCl}-W_6$ (a)], a few water molecules separate the ion pair. The chlorine atom is on the cluster “surface,” but the Ag atom is surrounded by four water molecules. This result is in keeping with experimental information for Ag^+ in water.⁵⁷ X-ray and neutron diffraction studies predict that the coordination number of Ag^+ in water is 4 in a tetrahedral arrangement.⁵⁷ In the second cluster [$\text{AgCl}-W_6$ (b)] the ions are at the cluster surface and the ion pair is separated by six water molecules. A similar SSIP structure for $\text{NaCl}-W_6$ was reported by Jungwirth.¹⁷ For $\text{AgCl}-W_6$ CIP, $R(\text{Ag}-\text{Cl})$ is

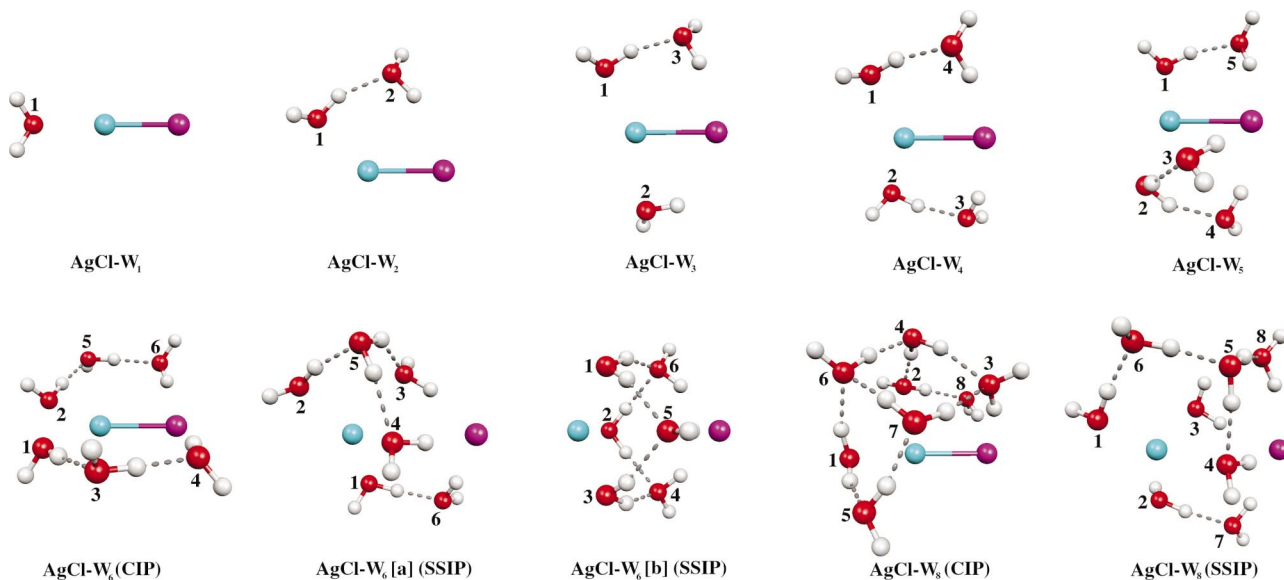


FIG. 1. (Color) Optimized structures of AgCl-W_{1-6} and AgCl-W_8 clusters. $\text{O}\cdots\text{H}$ hydrogen bonds are represented by dashed lines.

2.43 Å. In comparison with the CIP aggregate, AgCl-W_6 SSIP clusters are characterized by larger $R(\text{Ag-Cl})$ distances of 3.89 and 4.45 Å for the conformers (a) and (b), respectively. Smaller $R(\text{O}_x\text{-Ag})$ and $R(\text{H}\cdots\text{Cl})$ hydrogen bond distances are also observed in SSIP structures. For example, the average $R(\text{O-Ag})$ distance is 2.87 Å in AgCl-W_6 (a) SSIP and 3.41 Å in AgCl-W_6 CIP. The same tendency is observed when AgCl-W_8 CIP and SSIP clusters are compared. Ag-Cl distances for AgCl-W_8 (2.41 Å) and AgCl-W_6 (2.43 Å) CIP structures are quite similar.

Vibrational frequencies related to the Ag-Cl stretching ($\nu_{\text{Ag-Cl}}$) are also reported in Table I. With the exception of the AgCl-W_1 cluster, $\nu_{\text{Ag-Cl}}$ is redshifted by 189 cm^{-1} when we move from AgCl to AgCl-W_6 CIP.

The optimized structures of NaCl -water clusters are reported in Fig. 2 and some geometrical parameters are reported in Table II. Several quantum mechanics studies on NaCl -water clusters were reported.^{15–18} A good agreement is

observed between the present results for the structural properties and data from the literature (see Table II). In keeping with the results reported by Yamabe *et al.*¹⁸ we also find two NaCl-W_1 conformers. This is in contrast with the results for AgCl-W_1 for which only one conformer was found. We note, however, that Ag -water interactions are strongly anisotropic due to the presence of $\text{Ag } d$ orbitals. NaCl-W_1 (a) is stabilized by a $\text{H}\cdots\text{Cl}$ hydrogen bond. NaCl-W_1 (b) involves the head-to-tail alignment of the dipoles of the ion pair and water. The dependence of the structural properties on the cluster size N (Fig. 3) shows similarities with AgCl -water. The $R(\text{Na-Cl})$ distance increases from 2.39 in NaCl to 2.76 Å in NaCl-W_5 . The present results for NaCl with six and eight water molecules confirm that both CIP and SSIP structures can be found in these aggregates. For NaCl-W_6 SSIP two conformers were found. In the first one [NaCl-W_6 (a)], the ion pair is separated by a few water molecules and it is characterized by the three $\text{H}\cdots\text{Cl}$ hydrogen bonds. The Na

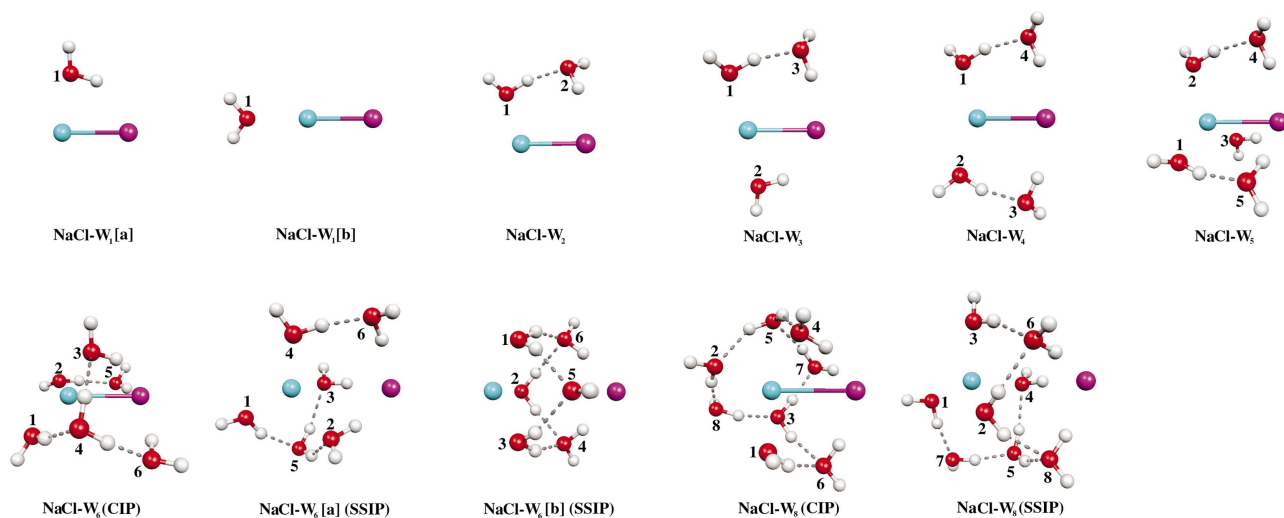


FIG. 2. (Color) Optimized structures of NaCl-W_{1-6} and NaCl-W_8 clusters. $\text{O}\cdots\text{H}$ hydrogen bonds are represented by dashed lines.

TABLE I. Structural properties of AgCl-water clusters from B3LYP/6-31+G(*d,p*) optimizations. Distances in Å. $\nu_{\text{Ag-Cl}}$ stretching frequency in cm^{-1} . Different oxygen atoms are represented by *x* (see Fig. 1).

	$R(\text{Ag-Cl})$	$\nu_{\text{Ag-Cl}}$	<i>x</i>	$R(\text{O}_x-\text{Ag})$	$R(\text{H}\cdots\text{Cl})$
AgCl	2.33	316
	2.31; ^{a,c} 2.28; ^b	
	2.33 ^d				
AgCl-W ₁	2.31	349	1	2.25	...
AgCl-W ₂	2.37	307	1	2.29	...
			2	3.14	2.52
AgCl-W ₃	2.51	249	1	2.29	...
			2	2.44	...
			3	3.38	2.25
AgCl-W ₄	2.53	202	1	2.34	...
			2	2.34	...
			3	3.57	2.23
			4	3.57	2.23
AgCl-W ₅	2.65	170	1	2.29	...
			2	2.29	...
			3	3.47	2.31
			4	3.55	...
			5	3.61	2.22
AgCl-W ₆ CIP	2.43	127	1	2.34	...
			2	2.38	...
			3	3.91	...
			4	3.94	...
			5	3.91	2.23
			6	3.98	2.21
AgCl-W ₆ (a) SSIP	3.89	...	1	2.26	...
			2	2.31	...
			3	2.54	2.06
			4	2.66	2.07
			5	3.47	...
			6	3.95	2.07
AgCl-W ₆ (b) SSIP	4.45	...	1	3.05	2.07
			2	3.05	2.07
			3	3.05	2.07
			4	4.16	...
			5	4.16	...
			6	4.16	...
AgCl-W ₈ CIP	2.41	...	1	2.20	...
			2	2.84	...
			3	3.56	2.22
			4	3.68	...
			5	3.71	...
			6	3.80	...
			7	3.92	...
			8	3.96	...
AgCl-W ₈ SSIP	4.16	...	1	2.30	...
			2	2.37	...
			3	2.44	2.26
			4	2.55	2.09
			5	3.90	...
			6	3.96	...
			7	4.00	2.15
			8	4.44	2.21

^aExperimental (Ref. 53).

^bExperimental (Ref. 54).

^cMP2/6-311+G(2*df,p*) and SDD for Ag (Ref. 55).

^dCASSCF (Ref. 56).

atom of NaCl-W₆ (a) interacts with four water molecules and the average $R(\text{O}-\text{Na})$ distance is 2.72 Å. NaCl-W₆ (b) is a symmetrical structure where the separated ions are at the cluster surface. In this case, the average $R(\text{O}-\text{Na})$ distance is 3.06 Å. The $R(\text{Na}-\text{Cl})$ distances are 3.72 and 4.59 Å for

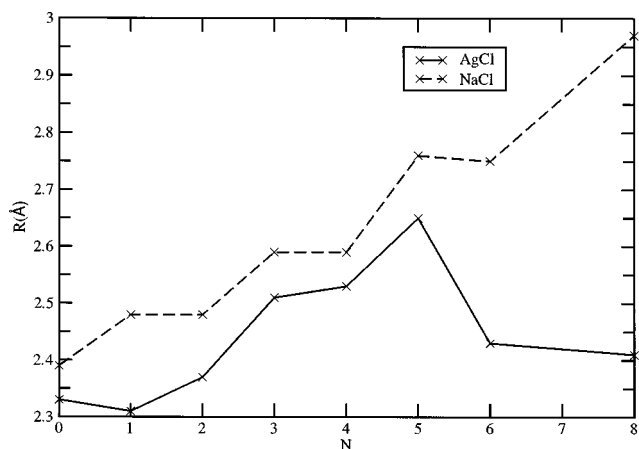


FIG. 3. Distance between the ion pair in AgCl-water and NaCl-water CIP clusters as a function of the number of water molecules (*N*).

NaCl-W₆ SSIP (a) and (b), respectively. This last distance is in good agreement with the MP2/6-31+G(*d*) result reported by Jungwirth¹⁷ (4.43 Å). $R(\text{Na}-\text{Cl})$ distances of 2.97 and 4.24 Å are found in NaCl-W₈ CIP and SSIP respectively. In both structures, four oxygen atoms are close to Na at average distances of 2.39 Å (CIP) and 2.30 Å (SSIP). The average $R(\text{H}\cdots\text{Cl})$ distances are 2.29 and 2.06 Å for CIP and SSIP, respectively.

Na-Cl stretching frequencies ($\nu_{\text{Na-Cl}}$) are also reported in Table II. For NaCl-W₁₋₂ they are in excellent agreement with the MP2/cc-pVDZ results reported by Woon and Dunning.¹⁵

B. Energetic properties

Formation and binding enthalpies for the AgCl-water and NaCl-water clusters are reported in Tables III (AgCl) and IV (NaCl). The discussion will be based on B3LYP/6-311+G(2*df,p*) results. For completeness, B3LYP/6-31+G(*d,p*) results are also reported. For CIP structures, the dependence of the formation ($\Delta H_{f,N}$) and binding ($\Delta H_{b,N}$) enthalpies on the number of water molecules (*N*) is illustrated in Fig. 4. $\Delta H_{f,1}$, the formation enthalpy of the AgCl-W₁ cluster is -0.82 eV (-18.9 kcal/mol). $\Delta H_{f,N}$ changes from -1.26 eV (*N*=2) to -4.51 eV for the CIP complex with eight water molecules.

AgCl-W₆ CIP is more stable than the AgCl-W₆ SSIP (a) and (b) conformers by -0.42 and -0.23 eV, respectively. The difference between $\Delta H_{f,N}$'s of conformers (a) and (b) (0.2 eV) reflects the stabilization of conformer (b) by O \cdots H hydrogen bonding (see Fig. 1). AgCl-W₈ CIP is -0.49 eV more stable than the SSIP structure. Binding enthalpies ($\Delta H_{b,N}$) for AgCl-water clusters from AgCl-W₁ to AgCl-W₆ follow a very simple pattern, which reflects the energetical stabilization of the clusters with an even number of water molecules (see Fig. 4). This is basically related to the formation of hydrogen bonds involving water molecules. $\Delta H_{b,N}$ for AgCl-W₆ CIP is -1.05 eV, which is -0.2 eV lower than $\Delta H_{b,N}$ for AgCl-W₆ (b) SSIP (-0.86 eV). $\Delta H_{b,N}$ for AgCl-W₈ CIP and SSIP are -1.2 and -0.8 eV,

TABLE II. Structural properties of NaCl-water clusters from B3LYP/6-31+G(*d,p*) optimizations. Distances in Å. ν_{NaCl} stretching frequency in cm^{-1} . Different oxygen atoms are represented by *x* (see Fig. 2).

	$R(\text{Na}-\text{Cl})$	$\nu_{\text{Na-Cl}}$	<i>x</i>	$R(\text{O}_x-\text{Na})$	$R(\text{H}\cdots\text{Cl})$
NaCl	2.39	348
	2.36 ^a 2.43 ^b	
NaCl-W ₁ (a)	2.48	318	1	2.22	2.25
	2.51 ^b	311 ^b		2.32 ^b	2.23 ^b
NaCl-W ₁ (b)	2.41	317	1	2.28	...
	2.41 ^c			2.25 ^c	...
NaCl-W ₂	2.48	278	1	2.21	...
	2.63 ^b	275 ^b		2.33 ^b	...
			2	3.39	2.13
NaCl-W ₃	2.59	244	1	2.23	...
			2	2.25	2.29
			3	3.50	2.15
NaCl-W ₄	2.59	216	1	2.25	...
	2.54 ^d			2.42 ^d	...
			2	2.25	...
				2.42 ^d	...
			3	3.59	2.17
				1.90 ^d	1.90 ^d
			4	3.59	2.17
				1.90 ^d	1.90 ^d
NaCl-W ₅	2.76	183	1	2.28	...
			2	2.28	...
			3	2.31	2.28
			4	3.68	2.18
			5	3.69	2.17
NaCl-W ₆ CIP	2.75 (2.66) ^e	127	1	2.24	...
			2	2.27	...
			3	2.43	2.17
			4	3.49	...
			5	3.75	2.19
			6	4.17	2.22
NaCl-W ₆ (a) SSIP	3.72		1	2.25	...
			2	2.27	...
			3	2.36	2.06
			4	2.37	2.07
			5	3.17	...
			6	3.92	2.12
NaCl-W ₆ (b) SSIP	4.59 (4.43) ^e		1	3.06	2.08
			2	3.06	2.08
			3	3.06	2.08
			4	4.15	...
			5	4.15	...
			6	4.15	...
NaCl-W ₈ CIP	2.97	...	1	2.32	...
			2	2.39	...
			3	2.41	...
			4	2.43	2.11
			5	2.98	...
			6	3.43	2.09
			7	3.48	2.42
			8	3.71	...
NaCl-W ₈ SSIP	4.24	...	1	2.27	...
			2	2.29	...
			3	2.30	...
			4	2.35	2.05
			5	3.61	...
			6	3.65	2.05
			7	3.89	...
			8	4.12	2.10

^aReference 70.^bMP2/cc-pVDZ (Ref. 15).^cB3LYP/6-31+G(*d*) (Ref. 18).^dRHF/6-31G(*d*) for NaCl and EFP for water (Ref. 16).^eMP2/6-31+G(*d*) (Ref. 17).TABLE III. Energetic properties of AgCl-water clusters. $\Delta E_{f,N}$ and $\Delta E_{b,N}$ are the formation and binding energies, respectively. The formation ($\Delta H_{f,N}$) and binding ($\Delta H_{b,N}$) enthalpies include thermal corrections at $T = 298.15$ K. Data in eV. Values in square brackets include counterpoise correction for BSSE.

	$\Delta E_{f,N}$	$\Delta H_{f,N}$	$\Delta E_{b,N}$	$\Delta H_{b,N}$
B3LYP/6-31+G(<i>d,p</i>)				
AgCl-W ₁	-0.72	-0.74	-0.72	-0.74
AgCl-W ₂	-1.02	-1.07	-0.86	-0.89
AgCl-W ₃	-1.31	-1.39	-0.79	-0.78
AgCl-W ₄	-1.85	-1.97	-0.84	-0.83
AgCl-W ₅	-2.12	-2.26	-0.76	-0.74
AgCl-W ₆ CIP	-2.69	-2.85	-1.04	-1.03
AgCl-W ₆ (a) SSIP	-2.26	-2.45	-0.60	-0.63
AgCl-W ₆ (b) SSIP	-2.33	-2.55	-0.67	-0.72
AgCl-W ₈ CIP	-3.45	-3.71	-1.11	-1.10
AgCl-W ₈ SSIP	-3.04	-3.28	-0.71	-0.68
B3PLYP/6-311++G(2 <i>df,p</i>)				
AgCl-W ₁	-0.80	-0.82	-0.80 [-0.75]	-0.82 [-0.77]
AgCl-W ₂	-1.20	-1.26	-0.97 [-0.93]	-1.00 [-0.96]
AgCl-W ₃	-1.56	-1.64	-0.85 [-0.77]	-0.85 [-0.77]
AgCl-W ₄	-2.21	-2.33	-0.94 [-0.83]	-0.93 [-0.82]
AgCl-W ₅	-2.58	-2.71	-0.90 [-0.79]	-0.89 [-0.78]
AgCl-W ₆ CIP	-3.23	-3.39	-1.21 [-1.06]	-1.20 [-1.05]
AgCl-W ₆ (a) SSIP	-2.70	-2.97	-0.76 [-0.67]	-0.79 [-0.70]
AgCl-W ₆ (b) SSIP	-2.94	-3.16	-0.92 [-0.80]	-0.98 [-0.86]
AgCl-W ₈ CIP	-4.25	-4.51	-1.36 [-1.20]	-1.35 [-1.19]
AgCl-W ₈ SSIP	-3.78	-4.02	-0.88 [-0.79]	-0.85 [-0.76]

respectively. Therefore, the present results for small AgCl-water clusters indicate that CIP are more stable than SSIP structures.

Formation enthalpies ($\Delta H_{f,N}$) of NaCl-W_N clusters change from -0.77 [NaCl-W₁ (a)] to -5.0 eV (NaCl-W₈ SSIP). Our B3LYP/6-311++G(2*df,p*) prediction for the formation (or binding) energy NaCl-W₁ (a) is -0.76 eV, which is in very good agreement with the MP2/cc-pVDZ result reported by Woon and Dunning (-0.75 eV).¹⁵ The hydrogen bonded NaCl-W₁ (a) conformer is -0.14 eV more stable than NaCl-W₁ (b), illustrating the role played by hydrogen bond for the energetical stabilization of the aggregates. Formation enthalpies for NaCl-W₆ CIP and SSIP are nearly identical (-3.9 eV). Therefore, in agreement with the *ab initio* results by Jungwirth,¹⁷ SSIP and CIP clusters of NaCl with six water molecules are practically isoenergetic. $\Delta H_{f,N}$ for NaCl-W₈ CIP and SSIP are -5.0 and -4.9 eV, respectively, indicating that these structures are nearly isoenergetic.

Binding enthalpies ($\Delta H_{b,N}$) in NaCl-water clusters change slowly from -1.21 (NaCl-W₂) to -1.59 eV (NaCl-W₈ SSIP). The SSIP and CIP NaCl-W₆ clusters have very similar binding enthalpies. However, for NaCl-W₈ SSIP the binding enthalpy of the ion pair to the water molecules is ~0.1 eV stronger than in the CIP cluster. Therefore, in contrast with the present results for AgCl-water we are providing evidence that for *small* NaCl-water clusters, SSIP can be more stable than CIP structures. This tendency seems to increase for larger aggregates, in keeping with previous studies on NaI-water clusters.⁶ Once again, this is a consequence of the specific interactions between the NaCl ion pair

TABLE IV. Energetic properties of NaCl-water clusters. $\Delta E_{f,N}$ and $\Delta E_{b,N}$ are the formation and binding energies, respectively. The formation ($\Delta H_{f,N}$) and binding ($\Delta H_{b,N}$) enthalpies include thermal corrections at $T = 298.15$ K. Data in eV. Values in square brackets include counterpoise correction for BSSE.

	$\Delta E_{f,N}$	$\Delta H_{f,N}$	$\Delta E_{b,N}$	$\Delta H_{b,N}$
B3LYP/6-31+G(d,p)				
NaCl-W ₁ (a)	-0.73	-0.76	-0.73	-0.76
NaCl-W ₁ (b)	-0.61	-0.61	-0.61	-0.61
NaCl-W ₂	-1.35	-1.41	-1.19	-1.23
NaCl-W ₃	-1.99	-2.06	-1.46	-1.45
NaCl-W ₄	-2.52	-2.63	-1.51	-1.49
NaCl-W ₅	-2.99	-3.12	-1.63	-1.60
NaCl-W ₆ CIP	-3.36	-3.52	-1.69	-1.70
NaCl-W ₆ (a) SSIP	-3.35	-3.53	-1.66	-1.71
NaCl-W ₆ (b) SSIP	-3.31	-3.54	-1.70	-1.71
NaCl-W ₈ CIP	-4.07	-4.33	-1.74	-1.73
NaCl-W ₈ SSIP	-4.23	-4.49	-1.90	-1.88
B3LYP/6-311++G(2df,p)				
NaCl-W ₁ (a)	-0.76	-0.77	-0.76[-0.71]	-0.77[-0.72]
	-0.75; ^a	-0.67 ^c		
	-0.68 ^b			
NaCl-W ₁ (b)	-0.63	-0.63	-0.63[-0.57]	-0.63[-0.57]
	-0.55 ^b			
NaCl-W ₂	-1.45	-1.52	-1.22[-1.17]	-1.26[-1.21]
NaCl-W ₃	-2.14	-2.21	-1.43[-1.31]	-1.42[-1.30]
NaCl-W ₄	-2.74	-2.85	-1.48[-1.36]	-1.46[-1.34]
NaCl-W ₅	-3.28	-3.41	-1.61[-1.42]	-1.58[-1.39]
NaCl-W ₆ CIP	-3.73	-3.90	-1.72[-1.55]	-1.71[-1.54]
NaCl-W ₆ (a) SSIP	-3.73	-3.90	-1.72[-1.49]	-1.72[-1.49]
NaCl-W ₆ (b) SSIP	-3.73	-3.96	-1.71[-1.55]	-1.77[-1.61]
NaCl-W ₈ CIP	-4.63	-4.89	-1.74[-1.54]	-1.73[-1.53]
NaCl-W ₈ SSIP	-4.75	-5.00	-1.85[-1.60]	-1.84[-1.59]

^aMP2/cc-pVDZ (Ref. 15).

^bB3LYP/6-31+G(d) (Ref. 18).

^cRHF/6-31G(d) for NaCl and EFP for water (Ref. 16).

and water, and seems to illustrate basic energetical features of small clusters that can be related to the well known solubility and ionic dissociation of NaCl in bulk water.¹⁹

The presence of energetically stable SSIP aggregates in small salt-water clusters may be eventually related to the structure of alkali halide solutions.⁵⁸⁻⁶¹ Based on a recent IR spectroscopy study, Max and Chapados⁶¹ suggested that each pair of ions are close bound and form a complex in a cluster organization with a fixed number of water molecules (5 for NaCl). It was proposed that strongly bound aggregates, where the cation and anion are *inseparable* are present in alkali halide solutions.⁶¹ However, we stress that comparison between the present results with solution data is difficult.

IV. POLARIZATION EFFECTS, CHARGE TRANSFER, AND ELECTRONIC DENSITY DIFFERENCE

A. Polarization effects and charge transfer

Atomic charges fitted to the ESP and derived from NAO are shown in Table V, where we also report the total dipole moments of the AgCl-water and NaCl-water clusters. These results are from B3LYP/6-311++G(2df,p)//B3LYP/6-31+G(d,p) calculations. It may be instructive to analyze separately polarization effects and charge transfer (CT).²² For our purposes the discussion can be focused on the ion pair. Po-

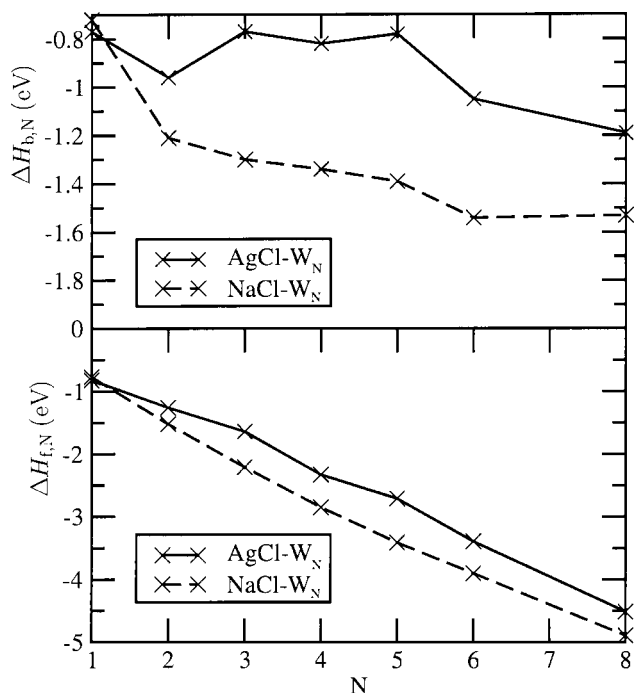


FIG. 4. Formation ($\Delta H_{f,N}$) and binding ($\Delta H_{b,N}$) enthalpies (eV) vs the cluster size N for AgCl-water and NaCl-water CIP clusters.

larization effects are induced by the interaction of the ion pair with the water molecules and are related to the electronic density reorganization induced by the electrostatic field of the water molecules. It should be stressed that the atomic charges of the water clusters are in fact associated with polarization effects as well as with charge transfer. CT can be discussed by estimating the total charge of the ion pair. If it is not zero, then the value can be associated with the global charge transferred between the ion pair and the water molecules. The total charge of the ion pair is represented as δq_{CT} (see Table V). To discuss specifically polarization effects, the following iterative procedure was adopted. Initially, ESP or NAO atomic charges of the isolated ion pair in the geometry of the cluster were calculated. By using these charges, the charges of the water molecules were estimated. In the following step new charges on the ion pair induced by the charges of the water molecules were calculated. The process was then repeated until convergence, which was attained after four to five steps. These charges are essentially related to polarization effects because CT between the ion pair and the water molecules is not allowed. They are represented as q_{pol} and are also reported in Table V. The iterative self-consistent procedure was carried out at the B3LYP/6-311++G(2df,p)//B3LYP/6-31+G(d) level. Convergence was assumed when the difference between the charges of successive cycles was less than $10^{-4}e$.

First, ESP atomic charges will be discussed. Upon complexation with one water molecule the Ag charge is reduced from $0.57e$ to $0.45e$ and the Cl charge is not significantly changed, indicating electronic density migration from the water molecule to the Ag atom. Charge transfer from water to Ag^+ was previously pointed out by Lee *et al.*,⁶² who attributed the effect to electronic density migration from the

TABLE V. Atomic charges and total dipole moments (D) in AgCl–water and NaCl–water clusters [B3LYP/6-311++G(2df,p)]. δq_{CT} (e) is total charge of the ion pair. q_{pol} (e) is the charge associated with polarization effects.

AgCl	ESP				NAO				μ
	Ag	Cl	δq_{CT}	q_{pol}	Ag	Cl	δq_{CT}	q_{pol}	
AgCl	0.570	−0.570			0.705	−0.705			5.7(6.07±0.06) ^a
AgCl–W ₁	0.452	−0.573	−0.121	0.629	0.661	−0.713	−0.052	0.732	9.1
AgCl–W ₂	0.553	−0.588	−0.035	0.669	0.734	−0.771	−0.037	0.787	5.5
AgCl–W ₃	0.592	−0.621	−0.029	0.750	0.797	−0.842	−0.045	0.871	4.1
AgCl–W ₄	0.604	−0.634	−0.030	0.794	0.808	−0.834	−0.026	0.896	3.2
AgCl–W ₅	0.621	−0.565	0.056	0.828	0.808	−0.851	−0.043	0.925	2.0
AgCl–W ₆ CIP	0.559	−0.619	−0.060	0.806	0.774	−0.794	−0.020	0.869	2.5
AgCl–W ₆ (a) SSIP	0.687	−0.621	0.066	0.948	0.855	−0.785	0.070	0.988	5.7
AgCl–W ₆ (b) SSIP	0.725	−0.604	0.121	0.964	0.869	−0.789	0.080	0.996	1.4
AgCl–W ₈ CIP	0.519	−0.575	−0.056	0.791	0.769	−0.806	−0.037	0.859	2.3
AgCl–W ₈ SSIP	0.741	−0.621	0.120	0.962	0.869	−0.819	0.050	0.995	2.9
NaCl	ESP				NAO				
	Na	Cl	δq_{CT}	q_{pol}	Na	Cl	δq_{CT}	q_{pol}	μ
NaCl	0.763	−0.763			0.933	−0.933			8.8(8.97) ^b
NaCl–W ₁ (a)	0.799	−0.726	0.073	0.807	0.945	−0.906	0.039	0.959	7.5
NaCl–W ₁ (b)	0.677	−0.761	−0.084	0.796	0.929	−0.938	−0.009	0.951	11.8
NaCl–W ₂	0.780	−0.719	0.061	0.831	0.942	−0.893	0.049	0.967	6.9
NaCl–W ₃	0.826	−0.687	0.139	0.866	0.942	−0.886	0.056	0.980	5.6
NaCl–W ₄	0.803	−0.710	0.093	0.887	0.936	−0.882	0.054	0.984	4.9
NaCl–W ₅	0.927	−0.633	0.294	0.888	0.927	−0.863	0.064	0.989	3.7
NaCl–W ₆ CIP	0.827	−0.629	0.198	0.913	0.928	−0.863	0.065	0.991	3.3
NaCl–W ₆ (a) SSIP	0.905	−0.622	0.283	0.923	0.931	−0.792	0.139	0.996	6.0
NaCl–W ₆ (b) SSIP	0.916	−0.611	0.305	0.948	0.949	−0.794	0.155	0.998	3.8
NaCl–W ₈ CIP	0.804	−0.654	0.150	0.906	0.903	−0.844	0.059	0.992	5.4
NaCl–W ₈ SSIP	0.987	−0.604	0.383	0.943	0.929	−0.784	0.145	0.998	3.9

^aExperimental (Ref. 63).^bExperimental (Ref. 64).

water lone-pair to hybridized orbitals comprised of occupied $4d$ and empty $5s$ orbitals of Ag^+ . With the exception of AgCl-W_5 , CIP clusters exhibit a negative δq_{CT} , indicating charge transfer from the water molecules to the ion pair. Quite interestingly, δq_{CT} is positive in SSIP. This can be explained by observing that SSIP structures involve the preferential interaction of each ionic species with, at least, a few solvent molecules. In these cases, the final charges depend mainly on the interaction of the polarized ionic species with the water molecules. Polarization effects can be estimated by comparing q_{pol} in the clusters with the charges of isolated AgCl. Our results clearly show that these effects are enhanced in SSIP structures (see Table V). In addition, significant charge transfer from chlorine to water is observed in SSIP. For example, if only polarization effects are taken into account, the Cl charge in AgCl-W_6 (a) SSIP would be $-0.95e$ instead of $-0.62e$. This means that $0.33e$ are transferred from Cl to water, whereas only $0.26e$ are transferred from water to Ag. Therefore, our results indicate that positive δq_{CT} 's for AgCl–water SSIP structures are basically related to charge transfer from Cl to water.

In comparison with ESP charges, NAO charges lead to quite similar conclusions about polarization effects and charge transfer. From NAO results, the Ag charge in AgCl-W_1 is reduced by $0.04e$ relative to the isolated ion

pair and the Cl charge is not significantly modified. For CIP clusters, small variations of the Ag charge relative to AgCl are observed from AgCl-W_2 to AgCl-W_6 . In agreement with ESP charges, NAO charges indicate that δq_{CT} is negative for CIP and positive for SSIP clusters. NAO atomic charges also show that AgCl–water SSIP are characterized by stronger polarization effects than CIP. For example, q_{pol} of Ag in AgCl-W_8 are $0.86e$ and $0.99e$ for CIP and SSIP, respectively. The dipole moment of AgCl (5.7 D) is in good agreement with experiment (6.07 ± 0.06 D).⁶³ In AgCl–water clusters, dipole moments decrease from 9.1 (AgCl-W_1) to 2.5 D (AgCl-W_6 CIP). The AgCl-W_6 (a) SSIP has a strong dipole (μ) of 5.7 D. However, $\mu = 1.4$ D for the AgCl-W_6 (b) SSIP aggregate. Although polarization effects are enhanced in SSIP clusters, the total dipole of AgCl-W_6 (b) is small due to obvious cancellation effects. The dipole moments of AgCl-W_8 CIP (2.3 D) and SSIP (2.9 D) are quite similar.

Atomic charges of NaCl water clusters are also reported in Table V. From ESP values, the Na charge shows some weak dependence on the cluster size. It is $0.76e$ in NaCl and increases up to $0.99e$ in NaCl-W_8 SSIP. In contrast, NAO results indicate that the Na charge is not very dependent on the cluster size and almost identical values are found for NaCl ($0.933e$) and for NaCl-W_8 SSIP ($0.929e$). With the

exception of NaCl–W₁ (b), $\delta q_{CT} > 0$ for NaCl-water clusters, although NAO charges lead to a δq_{CT} close to zero. Moreover, it should be observed that in the case of NaCl–W₁ (b), the Cl atom is not directly involved in the interaction with the water molecule (see Fig. 2). Both approaches (ESP and NAO) indicate a reduction of the chlorine charge from the isolated ion pair to the larger aggregates. These trends, together with positive δq_{CT} 's indicate charge migration from the chlorine atom to the water molecules. Small differences between q_{pol} and atomic charges of Na are observed in NaCl-water clusters. This seems to confirm negligible charge transfer between the Na atom and the water molecules. Consequently, our results suggest that NaCl-water clusters are characterized by charge transfer from the ion pair (essentially from the Cl atom) to the water molecules for both CIP and SSIP structures.

The size dependence of the dipole moments in NaCl-water clusters follows a pattern quite similar to the AgCl-water clusters. Our prediction for the NaCl dipole moment is 8.8 D, which is in very good agreement with the experimental value (8.97 D).⁶⁴ NaCl–W₁ (b) has a strong dipole of 11.8 D, reflecting polarization effects and the head-to-tail orientation of the water and ion pair dipoles. For the others NaCl-water clusters μ decreases from 7.5 D in the most stable NaCl–W₁ (a) conformer to 3.7 D in NaCl–W₅. We find a significant difference between the dipole moments for the NaCl–W₆ CIP (3.3 D) and NaCl–W₆ (a) SSIP (6.0 D) structures. The dipole moments of AgCl–W₈ CIP and SSIP are 5.4 and 3.9 D, respectively.

B. Electronic density difference

Although the analysis of polarization effects and charge transfer in the aggregates based on the ESP and NAO charges leads to similar conclusions, atomic charges are not observable quantities. Different population analysis and atomic charge partitions can be defined.⁶⁵ Therefore, to further discuss polarization effects in the aggregates, the electronic density difference for a X–W_N cluster was defined as

$$\Delta^N \rho(r) = \rho_{X-W_N}(r) - \rho_X(r) - \rho_{W_N}(r), \quad (3)$$

where $\rho_{X-W_N}(r)$ is the total electronic density in the aggregate with the salt ion pair X and N water molecules. $\rho_X(r)$ and $\rho_{W_N}(r)$, which were calculated in the geometry of the X–W_N cluster, are the total electronic densities of the isolated X ion pair and W_N, respectively. $\Delta^N \rho(r)$ isosurfaces for AgCl-water and NaCl-water clusters are reported in Figs. 5 and 6 for a few clusters of different size including CIP and SSIP structures. $\Delta^N \rho(r)$ isosurfaces for complexes of one and two water molecules with Ag⁺ are also represented in Fig. 5. We find that they are useful to understand the nature of the interactions involved in the AgCl-water clusters. For these clusters, $\Delta^N \rho(r)$ isosurfaces indicate some electronic density rearrangement involving the ion pair. In particular, electronic density difference isosurfaces around the Ag atom suggest an anisotropic reorganization of $\rho(r)$. This is well illustrated for Ag⁺–W₁ (Fig. 5), where $\Delta^N \rho(r)$ shows migration of the electronic density from the lobes of the Ag⁺ d_{z²} orbital to the ring⁶⁶ and the significant polarization

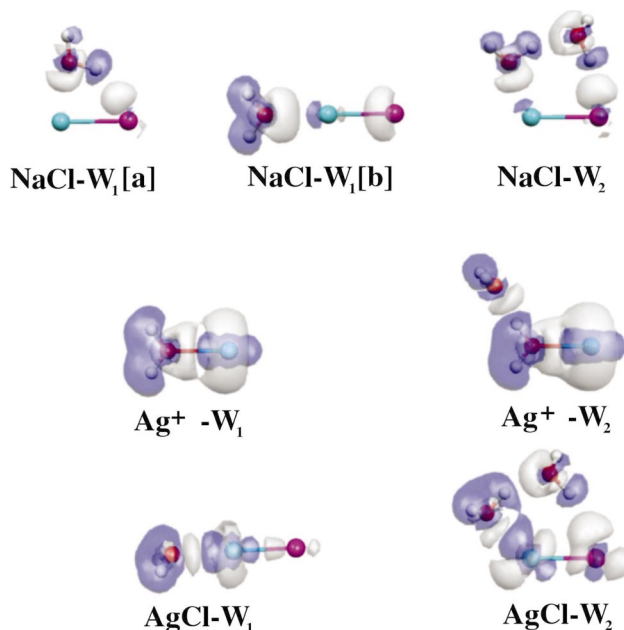


FIG. 5. (Color) Electronic density difference $\Delta^N \rho(r)$ for AgCl–W_{1–2} and NaCl–W_{1–2}, and for complexes of Ag⁺ with one and two water molecules. For NaCl–W₁, two conformers [(a) and (b)] are shown. The isosurfaces correspond to electronic density differences of $-0.02e \text{ \AA}^{-3}$ (dark) and $+0.02e \text{ \AA}^{-3}$ (white).

of the water molecule. A rather similar electronic density reorganization is observed in AgCl–W₁ and reflects specific Ag-water interactions, where the Ag d orbitals play an important role. Increased polarization effects are present in AgCl–W₂. The anisotropic reorganization of $\rho(r)$ around Ag is clearly visible. In addition, H···Cl hydrogen bond induces some reorganization of $\rho(r)$ around Cl. In comparison with Ag⁺, $\Delta^N \rho(r)$ for Ag⁺–W₂ reflects increased polarization effects induced by hydrogen bonding. The isosurfaces also suggest an increase of the electronic density close to the Cl atom. The electronic density around the water oxygen atoms is almost not changed in these clusters. Comparison between $\Delta^N \rho(r)$ of AgCl–W₆ CIP and SSIP structures (Fig. 6) supports our conclusion concerning the importance of polarization effects and electronic density reorganization in SSIP clusters.

$\Delta^N \rho(r)$ isosurfaces for NaCl–W₁ (a) and NaCl–W₁ (b) (Fig. 5) indicate a negligible reorganization of $\rho(r)$ around the Na atom. They also illustrate the changes on $\rho(r)$ induced by hydrogen bonding [NaCl–W₁ (a)] and charge-dipole [NaCl–W₁ (b)] interactions. In agreement with the NAO results, $\Delta^N \rho(r)$ isosurfaces for the NaCl-water clusters indicate that the atomic charge of Na is not strongly dependent on the cluster size (see Fig. 6). The electronic density reorganization around the water oxygen atoms suggests an increase of the electronic density, which can be possibly associated with charge transfer from the ion pair to the water molecules as it was previously indicated by the analysis based on atomic charges.

The relevance of charge transfer in halides (X[−])-water clusters (X[−]···W, X = F, Cl, Br, I) was discussed by Thompson and Hynes.²² By examining Löwdin charges on different fragments within the clusters, these authors provided evi-

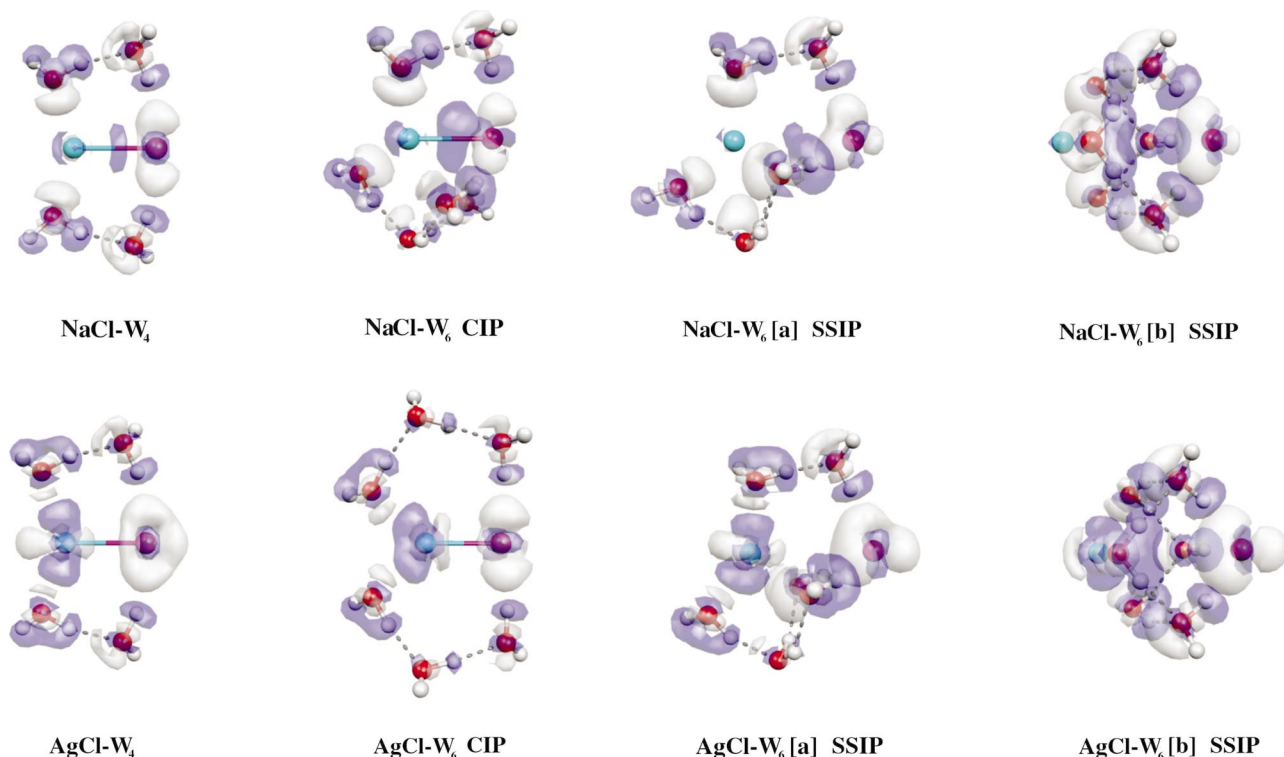


FIG. 6. (Color) Electronic density difference $\Delta^N \rho(r)$ for AgCl-water and NaCl-water clusters. The isosurfaces correspond to electronic density differences of $-0.025 e \text{ \AA}^{-3}$ (dark) and $+0.025 e \text{ \AA}^{-3}$ (white).

dence on charge migration from X^- to water. Not surprisingly, the present results indicate that charge transfer from Cl to water is also observed in AgCl-water and NaCl-water clusters. Moreover, our results strongly suggest that specific Ag-water interactions involving the Ag d orbitals may induce charge transfer from water molecules to the ion pair in AgCl-water CIP structures.

V. KOHN–SHAM ORBITALS AND EXCITATION ENERGIES

A. Kohn–Sham orbitals

The great interest in excitation energies of salt ion pairs microsolvated in clusters of polar molecules is motivated by the fact that these energies and their dependence on the cluster size can be useful to investigate routes to photodissociation reactions.² A detailed discussion on this subject can be found in some recent works.^{2–5} We only stress that photodissociation and charge separation involve the adiabatic coupling of the ionic and covalent electronic states, which is observed for systems such as NaCl and AgCl.⁶⁷ The electronic states (Σ^+ , Σ^- , Π , ...) of the isolated AgCl and NaCl species are defined by the symmetry species of $C_{\infty v}$. The interaction of the ion pair with the water molecules will break this symmetry and it can be of interest to investigate how Kohn–Sham (KS) orbitals are modified upon complexation with the water molecules. KS frontier orbitals and the corresponding eigenvalues are represented in Fig. 7 (AgCl– W_1) and Fig. 8 (NaCl– W_1), where they are compared with the orbitals and eigenvalues of the isolated water molecule and the salt ion pair. Upon complexation with one

water molecule, the σ^* orbital (LUMO, lowest unoccupied molecular orbital) of AgCl is raised by 1.4 eV. The LUMO of AgCl– W_1 delocalizes over the whole complex. The twofold degenerate π orbitals (HOMO, highest occupied molecular orbital and HOMO-1) and the σ (HOMO-2) orbital of AgCl are destabilized by ~ 0.6 eV. There is no significant contribution from the water molecule to these orbitals and they keep in the complex the same character they have in the isolated ion pair, although the degeneracy of the AgCl π orbitals is slightly lifted. The next five lower AgCl orbitals (two δ 's, two π 's, and one σ) apparently do not play any role in the energetical stabilization of the aggregate and their shapes are not modified upon complexation. They are, however, shifted to higher energies, and the twofold degeneracy of the δ 's and π orbitals is also lifted. The next lower orbital reflects the interaction between the water $1b_1$ orbital with one π orbital from AgCl. The following orbital involves the water $3a_1$ and the AgCl σ . The lowest represented orbital corresponds essentially to the water $1b_2$ orbital stabilized by the electrostatic interaction with the ion pair.

KS orbitals for NaCl– W_1 (a) and (b) are reported in Fig. 8. In the most stable hydrogen bonded isomer [NaCl– W_1 (a)] the two π 's and σ orbitals of NaCl are slightly stabilized. Moreover, the degeneracy of the π orbitals is significantly lifted, reflecting different interactions of the two π 's with the water molecule. In comparison with the isolated ion pair, the LUMO energy is raised by 0.6 eV. The next three lower orbitals of the complex correspond essentially to the water molecule valence orbitals, which are lowered by the interaction with the ion pair. When KS orbitals of NaCl– W_1 (b) and AgCl– W_1 are compared to those of the isolated ion pairs,

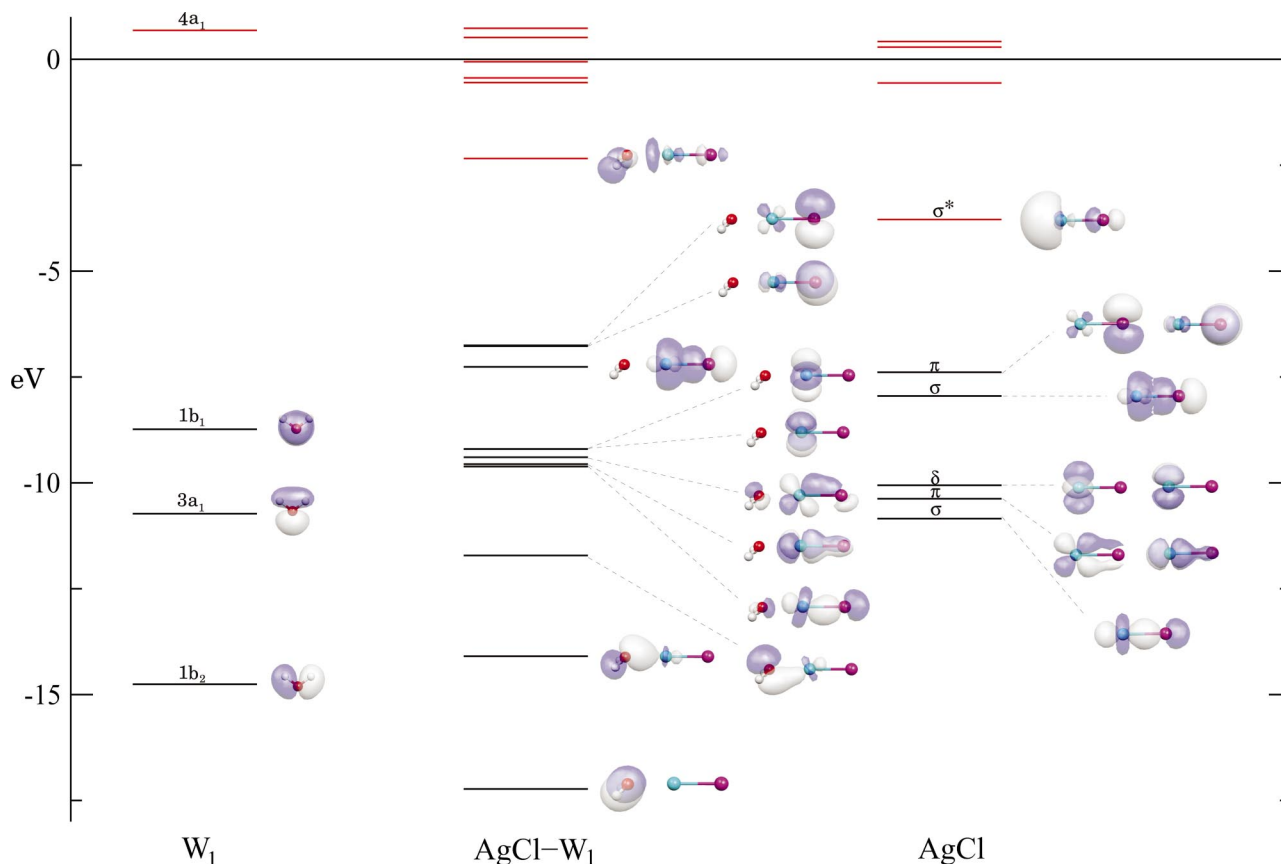


FIG. 7. (Color) Kohn-Sham eigenvalues and frontier orbitals for AgCl-water clusters.

similar changes induced by complexation can be observed. Now, the LUMO of NaCl- W_1 (b) is mainly localized on the water molecule and its energy is nearly the same of the NaCl LUMO. Upon complexation, the π and σ orbitals are destabilized by ~ 0.4 eV. The different structures of KS orbitals for NaCl- W_1 (a) and NaCl- W_1 (b) reflect the role played by hydrogen bond and ion-dipole interactions, respectively, in the energetical stabilization of the complexes.

B. Excitation energies

The excitation energies related to the transitions between the three highest occupied molecular orbitals (HOMO-2, HOMO-1, and HOMO) and the LUMO were calculated. Only transitions from the ground state to singlets were considered. Excitation energies and electronic oscillator strengths are reported in Tables VI (AgCl) and VII (NaCl). No significant basis set dependence of these properties was observed and the discussion will be based on B3LYP/6-311++G(2df,p) results. For AgCl the first two energies (2.6 eV) correspond to the ${}^1\Pi \leftarrow X {}^1\Sigma^+$ transition involving the degenerate π orbitals. The third energy (3.46 eV) corresponds to the ${}^1\Sigma \leftarrow X {}^1\Sigma^+$ transition, which has an oscillator strength of 0.066, much greater than those for the ${}^1\Pi \leftarrow X {}^1\Sigma$ transitions (0.007). The TDDFT result for the ${}^1\Sigma \leftarrow X {}^1\Sigma^+$ transition (3.46 eV) is in fair agreement with experimental data (3.92 eV)⁶⁸ and the theoretical result re-

ported by Ramírez-Solís (3.89 eV).⁵⁶ Inclusion of spin-orbit coupling effects^{56,69} may still increase the deviation from experiment.

Upon complexation with one water molecule, excitation energies corresponding to the transitions from the HOMO and HOMO-1 to the LUMO are blueshifted by 1 eV. The LUMO \leftarrow HOMO-2 transition is blueshifted by ~ 0.8 eV relative to the isolated NaCl. From AgCl- W_2 to AgCl- W_6 (CIP), excitation energies increase by ~ 0.7 eV for the LUMO \leftarrow HOMO-2 transitions, indicating a weak dependence on the cluster size. The LUMO \leftarrow HOMO-2 excitation energy of AgCl- W_6 (b) SSIP is redshifted by ~ 0.5 eV relative to that of AgCl- W_6 CIP. In comparison with CIP, oscillator strengths are smaller for AgCl- W_6 SSIP structures, particularly for AgCl- W_6 (b) SSIP. For AgCl- W_8 , CIP and SSIP excitation energies and oscillator strengths corresponding to the LUMO \leftarrow HOMO-2 transition are rather similar.

For NaCl, the $\sigma^* \leftarrow \sigma$ excitation energy (4.06 eV) is in good agreement with the experimental result (~ 4.2 eV).⁷⁰ Upon complexation with one water molecule, LUMO \leftarrow HOMO-2 excitation energies are blueshifted by 0.6 eV in NaCl- W_1 (a) and redshifted by 0.4 eV in NaCl- W_1 (b). This can be explained by the different structure of the KS orbitals for the two conformers (see Fig. 7). With the exception of NaCl- W_1 (b), from NaCl to NaCl- W_6 CIP, LUMO \leftarrow HOMO-2 transition energies are blueshifted by ~ 1.8 eV and their size dependence seems to reflect the energetical stabilization of the aggregates. For CIP structures,

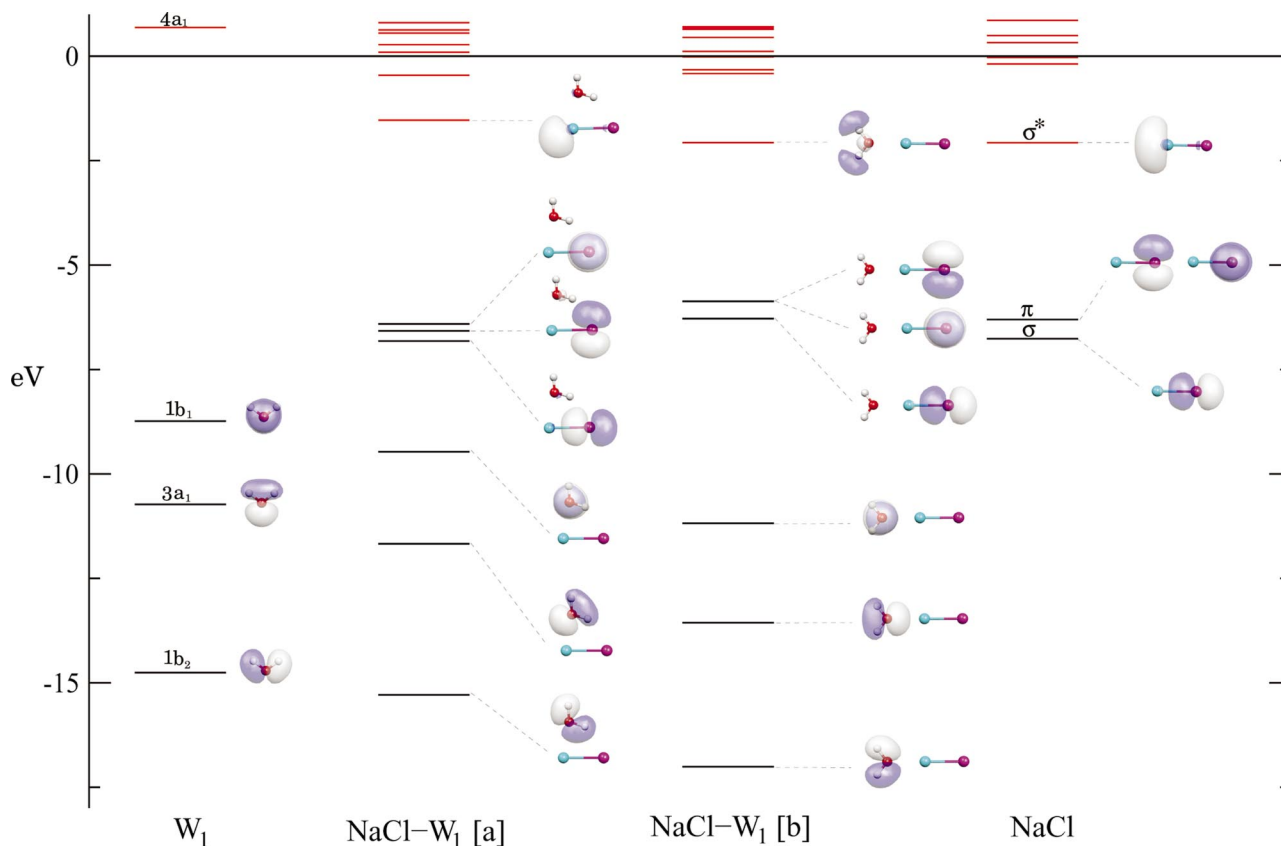


FIG. 8. (Color) Kohn–Sham eigenvalues and frontier orbitals for NaCl-water clusters.

TABLE VI. Excitation energies (eV) from the valence orbitals (π =HOMO, π_{-1} =HOMO-1, σ =HOMO-2) to the σ^* =LUMO in AgCl-water clusters. Oscillator strengths in parentheses (X =AgCl).

	$\sigma^* \leftarrow \pi$	$\sigma^* \leftarrow \pi_{-1}$	$\sigma^* \leftarrow \sigma$
B3LYP/6-31+G(<i>d,p</i>)			
<i>X</i>	2.60 (0.007)	2.60 (0.007)	3.49 (0.068)
	LUMO←HOMO	LUMO←HOMO-1	LUMO←HOMO-2
<i>X</i> - <i>W</i> ₁	3.62 (0.006)	3.64 (0.007)	4.29 (0.058)
<i>X</i> - <i>W</i> ₂	3.82 (0.010)	3.91 (0.017)	4.41 (0.070)
<i>X</i> - <i>W</i> ₃	4.08 (0.015)	4.13 (0.011)	4.42 (0.036)
<i>X</i> - <i>W</i> ₄	4.38 (0.022)	4.51 (0.011)	4.72 (0.041)
<i>X</i> - <i>W</i> ₅	4.39 (0.012)	4.96 (0.014)	5.05 (0.035)
<i>X</i> - <i>W</i> ₆ (CIP)	4.74 (0.040)	4.94 (0.011)	5.08 (0.056)
<i>X</i> - <i>W</i> ₆ (a) (SSIP)	4.62 (0.011)	4.67 (0.009)	4.77 (0.017)
<i>X</i> - <i>W</i> ₆ (b) (SSIP)	4.55 (0.008)	4.62 (0.003)	4.62 (0.003)
<i>X</i> - <i>W</i> ₈ (CIP)	5.05 (0.021)	5.25 (0.016)	5.27 (0.023)
<i>X</i> - <i>W</i> ₈ (SSIP)	4.77 (0.006)	5.15 (0.018)	5.21 (0.025)
B3LYP/6-311++G(2 <i>df,p</i>)			
<i>X</i>	2.61 (0.007) < 3.13 ^a	2.61 (0.007)	3.46 (0.066) 3.89 ^a 3.92 ^b
	LUMO←HOMO	LUMO←HOMO-1	LUMO←HOMO-2
<i>X</i> - <i>W</i> ₁	3.60 (0.006)	3.62 (0.007)	4.23 (0.056)
<i>X</i> - <i>W</i> ₂	3.82 (0.010)	3.89 (0.017)	4.38 (0.069)
<i>X</i> - <i>W</i> ₃	4.05 (0.014)	4.12 (0.011)	4.39 (0.035)
<i>X</i> - <i>W</i> ₄	4.35 (0.021)	4.50 (0.010)	4.69 (0.041)
<i>X</i> - <i>W</i> ₅	4.36 (0.012)	4.93 (0.013)	5.01 (0.035)
<i>X</i> - <i>W</i> ₆ (CIP)	4.72 (0.042)	4.93 (0.011)	5.04 (0.055)
<i>X</i> - <i>W</i> ₆ (a) (SSIP)	4.61 (0.009)	4.65 (0.009)	4.75 (0.017)
<i>X</i> - <i>W</i> ₆ (b) (SSIP)	4.51 (0.008)	4.57 (0.002)	4.57 (0.002)
<i>X</i> - <i>W</i> ₈ (CIP)	5.04 (0.022)	5.25 (0.023)	5.25 (0.023)
<i>X</i> - <i>W</i> ₈ (SSIP)	4.77 (0.006)	5.02 (0.005)	5.20 (0.026)

^aTheoretical (Ref. 56).^bExperimental (Ref. 68).

TABLE VII. Excitation energies (eV) from the valence orbitals (π =HOMO, π_{-1} =HOMO-1, σ =HOMO-2) to the σ^* =LUMO in NaCl-water clusters. Oscillator strengths in parentheses (X =NaCl).

	$\sigma^* \leftarrow \pi$	$\sigma^* \leftarrow \pi_{-1}$	$\sigma^* \leftarrow \sigma$
B3LYP/6-31+G(<i>d,p</i>)			
X	3.35 (0.013)	3.35 (0.013)	4.03 (0.103)
	LUMO←HOMO	LUMO←HOMO-1	LUMO←HOMO-2
X - W_1 (a)	4.06 (0.013)	4.25 (0.021)	4.61 (0.070)
X - W_1 (b)	3.25 (0.005)	3.25 (0.005)	3.75 (0.041)
X - W_2	4.49 (0.017)	4.72 (0.024)	4.99 (0.061)
X - W_3	4.98 (0.016)	5.32 (0.039)	5.42 (0.048)
X - W_4	5.24 (0.018)	5.59 (0.030)	5.65 (0.053)
X - W_5	5.69 (0.033)	5.76 (0.043)	5.81 (0.045)
X - W_6 CIP	5.77 (0.030)	5.90 (0.037)	5.97 (0.066)
X - W_6 (a) SSIP	5.42 (0.027)	5.48 (0.026)	5.59 (0.042)
X - W_6 (b) SSIP	5.57 (0.036)	5.62 (0.029)	5.62 (0.029)
X - W_8 CIP	5.41 (0.021)	5.51 (0.026)	5.74 (0.053)
X - W_8 SSIP	5.58 (0.028)	5.63 (0.035)	5.68 (0.037)
B3LYP/6-311++G(2 <i>df,p</i>)			
X	3.41 (0.011)	3.41 (0.011)	4.06 (0.101)~[4.2] ^a
	LUMO←HOMO	LUMO←HOMO-1	LUMO←HOMO-2
X - W_1 (a)	4.09 (0.011)	4.27 (0.021)	4.61 (0.068)
X - W_1 (b)	3.22 (0.004)	3.22 (0.004)	3.68 (0.038)
X - W_2	4.52 (0.014)	4.73 (0.024)	4.99 (0.058)
X - W_3	4.96 (0.012)	5.28 (0.039)	5.36 (0.048)
X - W_4	5.20 (0.014)	5.53 (0.027)	5.57 (0.055)
X - W_5	5.65 (0.030)	5.69 (0.039)	5.74 (0.041)
X - W_6 CIP	5.72 (0.025)	5.84 (0.034)	5.89 (0.063)
X - W_6 (a) SSIP	5.39 (0.020)	5.44 (0.023)	5.55 (0.031)
X - W_6 (b) SSIP	5.53 (0.034)	5.57 (0.027)	5.57 (0.027)
X - W_8 CIP	5.37 (0.017)	5.47 (0.023)	5.67 (0.051)
X - W_8 SSIP	5.53 (0.023)	5.57 (0.031)	5.61 (0.034)

^aExperimental (Ref. 70).

as the excitation energies increase from NaCl to NaCl- W_6 the total dipole moment decrease from 8.8 D for NaCl to 3.3 D for NaCl- W_6 CIP. LUMO←HOMO-2 excitation energies of the NaCl- W_6 SSIP clusters are redshifted by ~ 0.3 eV relative to CIP. In comparison with CIP structures, electronic oscillator strengths are reduced in NaCl- W_6 SSIP. For NaCl- W_8 , small differences between transition energies and oscillator strengths of CIP and SSIP structures are observed.

In general, the present results concerning the size dependence of excitation energies for AgCl-water and NaCl-water clusters are consistent with experimental² and theoretical⁷ studies on NaI-water clusters. For example, the ~ 0.8 eV blueshift induced by complexation with one water molecule and the relatively weak size dependence with increasing number of water molecules are in qualitative agreement with experimental information for NaI-water clusters.² Another issue concerns electronic oscillator strengths. Dedonder-Lardeux *et al.*² observed that the transition dipole moments (or electronic oscillator strengths) can be strongly dependent on the distance between the ion pair. More important, as long as the ion pair is in contact (CIP structures), small changes on the transition probabilities are expected. However, electronic oscillator strengths may be reduced by the insertion of some solvent molecules between the ion pair or by the increase of the distance between the ions. Therefore, vanishing or very small electronic oscillator strengths could be interpreted as an indication of charge separation.² From the theoretical point of view, Peslherbe *et al.*⁷ pointed out that in

comparison with ions in contact, electronic oscillator strengths are reduced for NaI and NaI- W_1 when the distance between the ion pair was stretched up to 6.0 Å. On the other hand, it was presently found that upon complexation with one water molecule, NaCl- W_1 excitation energies can be blueshifted [NaCl- W_1 (a)] or redshifted [NaCl- W_1 (b)]. In addition, it was also found that excitation energies and electronic oscillator strengths of CIP and SSIP structures are not very different for X - W_8 clusters (X =Ag,Na). One possible explanation for these results is that the size dependence of the excitation energies and oscillator strengths is determined by a complex orbital energy distribution of the aggregates for both ground and excited states. This would make difficult a simple relationship between vanishing oscillator strengths and charge separation.

VI. CONCLUSIONS

The structural, energetic, and electronic properties of AgCl-water clusters were investigated by density functional theory.

In agreement with recent investigations on NaCl-water clusters¹⁷ we are providing further evidence about the presence of SSIP structures in *small* AgCl-water clusters. For NaCl-water clusters, SSIP can be energetically more stable than CIP structures. The opposite tendency was observed for AgCl-water clusters. In comparison with CIP, SSIP structures are characterized by stronger polarization effects. This con-

clusion was based on the analysis of atomic charges associated with polarization, which were estimated through an iterative self-consistent procedure.

In keeping with previous theoretical works on halide-water clusters^{21,22} we find that charge transfer is very important in salt-water clusters. It was found that for both AgCl-water and NaCl-water SSIP clusters, charge migrates from the Cl atom to the water molecules. This effect is basically driven by polarization induced by hydrogen bonding involving the water molecules. However, as a consequence of specific Ag-water interactions, AgCl-water clusters are also characterized by charge transfer from the water molecules to the Ag atom. The above conclusions concerning polarization effects and charge transfer were supported by a detailed investigation on the electronic density reorganization.

The size dependence of the excitation energies was discussed and exhibits a pattern quite similar to what is observed in NaI-water clusters, although some differences related to the specific structure of the orbital energies were pointed out. Our results suggest that the difference between CIP and SSIP excitation energies may decrease with increasing cluster size. Extrapolation of the present results to larger clusters or to bulk situation is difficult. However, it seems reasonable to assume that the polarization effects and charge separation that were analyzed in small clusters also play an important role in larger aggregates.

ACKNOWLEDGMENTS

P.C.C. (Ph.D. Grant No. SFRH/BD/6503/2001) and S.S.M.C.G. (Post-Doc Grant No. SFRH/BPD/6457/2001) gratefully acknowledge the support of the Fundação para a Ciência e a Tecnologia (FCT). This work was partially supported by the Sapiens program of the FCT, Portugal (Project No. POCTI/43315/QUI/2001).

- ¹G. H. Peslherbe, R. Bianco, J. T. Hynes, and B. M. Ladanyi, *J. Chem. Soc., Faraday Trans.* **93**, 977 (1997).
- ²C. Dedonder-Lardeux, G. Grégoire, C. Jouvet, S. Martrenchard, and D. Solgadi, *Chem. Rev. (Washington, D.C.)* **100**, 4023 (2000).
- ³G. Grégoire, M. Mons, C. Dedonder-Lardeux, and C. Jouvet, *Eur. Phys. J. D* **1**, 5 (1998).
- ⁴G. Grégoire, M. Mons, and I. Dimicoli, *J. Chem. Phys.* **110**, 1521 (1999).
- ⁵G. H. Peslherbe, B. M. Ladanyi, and J. T. Hynes, *J. Phys. Chem. A* **102**, 4100 (1998).
- ⁶G. H. Peslherbe, B. M. Ladanyi, and J. T. Hynes, *Chem. Phys.* **258**, 201 (2000).
- ⁷G. H. Peslherbe, B. M. Ladanyi, and J. T. Hynes, *J. Phys. Chem. A* **104**, 4533 (2000).
- ⁸D. E. Smith and L. X. Dang, *J. Chem. Phys.* **100**, 3757 (1994).
- ⁹T. Morita, B. M. Ladanyi, and J. T. Hynes, *J. Phys. Chem.* **93**, 1386 (1989).
- ¹⁰G. Ciccotti, M. Ferrario, J. T. Hynes, and R. Kapral, *J. Chem. Phys.* **93**, 7137 (1990).
- ¹¹G. Makov and A. Nitzan, *J. Phys. Chem.* **96**, 2965 (1992).
- ¹²R. Rey, E. Guàrdia, and J. A. Padró, *J. Chem. Phys.* **97**, 1343 (1992).
- ¹³D. Laria and R. F. Fernandez-Prini, *Chem. Phys. Lett.* **205**, 260 (1993).
- ¹⁴D. Laria and R. F. Fernandez-Prini, *J. Chem. Phys.* **102**, 7664 (1995).
- ¹⁵D. E. Woon and T. H. Dunning, Jr., *J. Am. Chem. Soc.* **117**, 1090 (1995).
- ¹⁶C. P. Petersen and M. S. Gordon, *J. Phys. Chem. A* **103**, 4162 (1999).
- ¹⁷P. Jungwirth, *J. Phys. Chem. A* **104**, 145 (2000).
- ¹⁸S. Yamabe, H. Kouno, and K. Matsumara, *J. Phys. Chem. B* **104**, 10242 (2000).
- ¹⁹L. X. Dang, *J. Chem. Phys.* **97**, 1919 (1992).
- ²⁰A. E. Reed and F. Weinhold, *J. Chem. Phys.* **78**, 4066 (1983).

- ²¹A. E. Reed, L. A. Curtiss, and F. Weinhold, *Chem. Rev. (Washington, D.C.)* **88**, 899 (1988).
- ²²W. H. Thompson and J. T. Hynes, *J. Am. Chem. Soc.* **122**, 6278 (2000).
- ²³V. Engel, H. Metiu, R. Almeida, R. A. Marcus, and A. H. Zewail, *Chem. Phys. Lett.* **152**, 1 (1988).
- ²⁴A. H. Zewail, in *Femtosecond Chemistry*, edited by J. Manz and L. Woste (VCH, Weinheim, 1994).
- ²⁵M. Wilson, P. A. Madden, and B. J. Costa Cabral, *J. Phys. Chem.* **100**, 1227 (1996).
- ²⁶A. A. Migdisov, A. E. Williams-Jones, and O. M. Suleimenov, *Geochim. Cosmochim. Acta* **63**, 3817 (1999).
- ²⁷B. J. Mason, *The Physics of Clouds* (Oxford University Press, London, 1971).
- ²⁸H. R. Pruppacher and J. D. Klett, *Microphysics of Clouds and Precipitation* (Kluwer Academic, London, 1996).
- ²⁹R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, Oxford, 1989).
- ³⁰A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
- ³¹C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988).
- ³²P. Fuentealba, H. Preuss, H. Stoll, and L. v. Szentpaly, *Chem. Phys. Lett.* **89**, 418 (1989).
- ³³D. Andrae, U. Haussermann, M. Dolg, H. Stoll, and H. Preuss, *Theor. Chim. Acta* **77**, 123 (1990).
- ³⁴M. Dolg, H. Stoll, and H. Preuss, *Theor. Chim. Acta* **85**, 441 (1993).
- ³⁵A. Nicklass, M. Dolg, H. Stoll, and H. Preuss, *J. Chem. Phys.* **102**, 8942 (1995).
- ³⁶T. Leininger, A. Nicklass, H. Stoll, M. Dolg, and P. Schwerdtfeger, *J. Chem. Phys.* **105**, 1052 (1996).
- ³⁷R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.* **54**, 724 (1971).
- ³⁸R. C. Binning, Jr. and L. A. Curtiss, *J. Comput. Chem.* **11**, 1206 (1990).
- ³⁹A. D. McLean and G. S. Chandler, *J. Chem. Phys.* **72**, 5639 (1980).
- ⁴⁰M. J. Frisch, J. A. Pople, and J. S. Binkley, *J. Chem. Phys.* **80**, 3265 (1984).
- ⁴¹S. F. Boys and F. Bernardi, *Mol. Phys.* **19**, 553 (1970).
- ⁴²P. Cabral do Couto, R. C. Guedes, B. J. Costa Cabral, and J. A. Martinho Simões, *J. Chem. Phys.* **119**, 7344 (2003).
- ⁴³J. Kim, D. Majumdar, H. M. Lee, and K. S. Kim, *J. Chem. Phys.* **110**, 9128 (1999).
- ⁴⁴H. M. Lee, S. B. Suh, J. Y. Lee, P. Tarakeshwar, and K. S. Kim, *J. Chem. Phys.* **112**, 9759 (2000).
- ⁴⁵C. M. Breneman and K. B. Wiberg, *J. Comput. Chem.* **11**, 361 (1990).
- ⁴⁶W. H. E. Schwarz, K. Ruedenberg, and L. Mensching, *J. Am. Chem. Soc.* **111**, 6926 (1989).
- ⁴⁷R. Bauernschmitt and R. Ahlrichs, *Chem. Phys. Lett.* **256**, 454 (1996).
- ⁴⁸F. Furche and R. Ahlrichs, *J. Chem. Phys.* **117**, 7433 (2002).
- ⁴⁹R. E. Stratman, G. E. Scuseria, and M. J. Frisch, *J. Chem. Phys.* **109**, 8218 (1998).
- ⁵⁰M. A. L. Marques and E. K. U. Gross, in *A Primer in Density Functional Theory*, edited by C. Fiolhais, F. Nogueira, and M. Marques (Springer, Berlin, 2002), Chap. 4.
- ⁵¹M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 98, Gaussian Inc., Pittsburgh, PA, 1998.
- ⁵²P. F. Flüeliger, Thèse 2561, Département de Chimie Physique, Université de Genève, Genève, 1992; S. Portmann and H. P. Lüthi, *Chimia* **54**, 766 (2000).
- ⁵³F. A. Jenkins and G. D. Rochester, *Phys. Rev.* **52**, 1141 (1937).
- ⁵⁴J. D. Graybeal, *Molecular Spectroscopy* (McGraw-Hill, Singapore, 1988).
- ⁵⁵C. K. Kim, J. Won, H. S. Kim, Y. S. Kang, H. G. Li, and C. H. Kim, *J. Comput. Chem.* **22**, 827 (2001).
- ⁵⁶A. Ramírez-Solís, *J. Chem. Phys.* **117**, 1047 (2002).
- ⁵⁷N. T. Skipper and G. W. Neilson, *J. Phys.: Condens. Matter* **1**, 4141 (1989).
- ⁵⁸S. Cummings, J. E. Enderby, G. W. Neilson, J. R. Newsome, R. A. Howe, W. S. Howells, and A. K. Soper, *Nature (London)* **287**, 714 (1980).
- ⁵⁹D. H. Powell, G. W. Neilson, and J. E. Enderby, *J. Phys.: Condens. Matter* **5**, 5723 (1993).
- ⁶⁰J.-J. Max and C. Chapados, *J. Chem. Phys.* **113**, 6803 (2000).
- ⁶¹J.-J. Max and C. Chapados, *J. Chem. Phys.* **115**, 2664 (2001).
- ⁶²E. C. Lee, H. M. Lee, P. Tarakeshwar, and K. S. Kim, *J. Chem. Phys.* **119**, 7725 (2003).
- ⁶³K. P. R. Nair and J. Hoelt, *J. Phys. B* **17**, 735 (1984).
- ⁶⁴A. J. Hebert, F. J. Lovas, C. A. Melendres, C. D. Hollowell, T. L. Story, Jr., and K. Street, Jr., *J. Chem. Phys.* **48**, 2824 (1968).

- ⁶⁵C. J. Cramer, *Essentials of Computational Chemistry* (Wiley, England, 2003); F. Jensen, *Introduction to Computational Chemistry* (Wiley, England, 1999).
- ⁶⁶B. S. Fox, M. K. Beyer, and V. E. Bondybey, *J. Am. Chem. Soc.* **124**, 13613 (2002).
- ⁶⁷M. B. Faist and R. D. Levine, *J. Chem. Phys.* **64**, 2953 (1976).
- ⁶⁸G. J. Stueber, M. Foltin, and E. R. Bernstein, *J. Chem. Phys.* **109**, 9831 (1998).
- ⁶⁹A. Ramírez-Solís, V. Vallet, Ch. Teichteil, T. Leininger, and J. P. Daudey, *J. Chem. Phys.* **115**, 3201 (2001).
- ⁷⁰K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).