

# Photochemistry of AgCl–water clusters: Comparison with Cl<sup>−</sup>–water clusters

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## Abstract

The electronic structure of AgCl– $w_n$  ( $w \equiv \text{H}_2\text{O}$  and  $n = 1–6, 8$ ) clusters is investigated by ab initio and time dependent density functional theory calculations with emphasis on the electronic density  $[\rho(r)]$  reorganization of the aggregates upon photoexcitation that is characterized by charge migration from the Ag d orbitals and delocalization of  $\rho(r)$  around the cation. This is in contrast with NaCl– $w_n$  aggregates, where charge migration from Cl<sup>−</sup> to the water molecules takes place when  $n \geq 5$ . The results for AgCl–water clusters are also compared with those for photoexcited Cl<sup>−</sup>–water clusters, which provide a classical illustration of CTTS precursor states.

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## 1. Introduction

The electronic density reorganization associated with the interaction of ion pairs with solvent molecules is of crucial interest for understanding charge separation and chemical reactivity in solution [1–5]. One fundamental process driven by charge polarization and separation is the dissolution of salts in polar solvents [6–9]. Although a full quantum mechanical description of the electronic structure of ionic solutions is not a trivial task, several experimental and theoretical studies pointed out the interest of investigating the electronic properties of aggregates, where a salt ion pair is ‘solvated’ by a few polar molecules. One relevant issue concerns the minimum number of solvent molecules that are necessary to induce charge separation or the formation of solvent-separated ion pair (SSIP) clusters, which are in contrast with structures, where the ion pair is in contact or CIP aggregates [10]. Another aspect of interest concerns the electronic properties of

the aggregates upon photoexcitation. Several experimental works on photodissociation of salt ion pairs in clusters of polar molecules pointed out that the formation of SSIP structures can be investigated through an excitation scheme involving, initially, the transition from the ionic ground state (GS) to a covalent dissociative state [1,2]. The excitation scheme assumes a relationship between the formation of SSIP aggregates (charge separation) and the decrease of the excitation efficiency (or oscillator strengths) associated with the transition from the GS to excited states. By adopting such a scheme it is also assumed that upon photoexcitation the dissociation route of the ion pair in the clusters should be akin to that of the isolated ion pair. Recently [11], we have shown that the electronic density reorganization induced by photoexcitation of small NaCl–water clusters was strongly dependent on the cluster size. More important, when  $n \geq 5$  (formation of SSIP structures is observed when  $n \geq 6$  [10,12]), excited NaCl–water clusters are characterized by charge migration from the Cl<sup>−</sup> anion to hydrogen bonded water molecules, which is typical of charge transfer to solvent (CTTS) precursor states. However, the dependence of

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CTTS formation on the specific nature of the ion pair interaction and also on the interaction of the ionic species with the solvent deserves further attention.

In this Letter, we are reporting a theoretical investigation on the electronic structure of photoexcited  $\text{AgCl-w}_n$  ( $w \equiv \text{H}_2\text{O}$  and  $n = 1-6, 8$ ) clusters. In contrast with  $\text{NaCl-w}_n$  clusters, we are providing data indicating that no CTTS states related to charge migration from  $\text{Cl}^-$  to the solvent are observed upon photoexcitation of small  $\text{AgCl-w}_n$  clusters. For comparison, we are also reporting results for excited  $\text{Cl}^-$ -water clusters, which were the subject of some recent theoretical studies [13,14].

## 2. Computational details

The structures of  $\text{AgCl-w}_n$  [12] and  $\text{Cl}^-$ - $w_n$  ( $n = 1-6, 8$ ) clusters were determined by density functional theory (DFT) optimizations. The calculations were carried out with the B3LYP hybrid functional. In this method, the exchange functional is represented by the Becke's three parameter functional (B3) [15], which is combined with the Lee, Yang, and Parr (LYP) [16] correlation functional. Full geometry optimizations and frequency calculations were carried out with the 6-31+G(d,p) basis set [17] for the hydrogen, oxygen, and chlorine atoms. The calculation of excitation energies and charge distribution was performed with the 6-31++G(d,p) basis set, which includes diffuse functions on all of the atoms. Ag was described by the Stuttgart/Dresden (SDD) effective core potential (ECP) [18–22]. In this approach, 19 valence electrons ( $4s^2 4p^6 4d^{10} 5s^1$ ) are included [19].

Configuration interaction with single excitations (CIS) [23] and time dependent density functional theory (TDDFT) [24] calculations were carried out to predict excitation energies from the ground state to excited states. The discussion on polarization effects and charge transfer was based on charges fitted to the electrostatic potential (ESP charges) calculated by the Breneman method [25]. We also report a discussion on the electronic density reorganization in the clusters upon photoexcitation by calculating the electronic density difference between ground and excited states. The calculations were carried out with the GAUSSIAN 98 program [26]. Electronic density difference isosurfaces were represented by using the Molekel visualization program [27].

## 3. Results and discussion

### 3.1. Vertical excitation energies

The structures of  $\text{AgCl-w}_n$  clusters are presented in Fig. 1 ( $n = 1-5$ ) and Fig. 2 ( $n = 6, 8$ ). A detailed analysis of the energetic and structural properties of these aggregates has been recently reported [12]. For completeness interionic distances are reported in the captions of Figs. 1 and 2. When  $n = 6$ , two SSIP conformers ( $\text{AgCl-w}_6[\text{a}]$  and  $\text{AgCl-w}_6[\text{b}]$ ) were found.

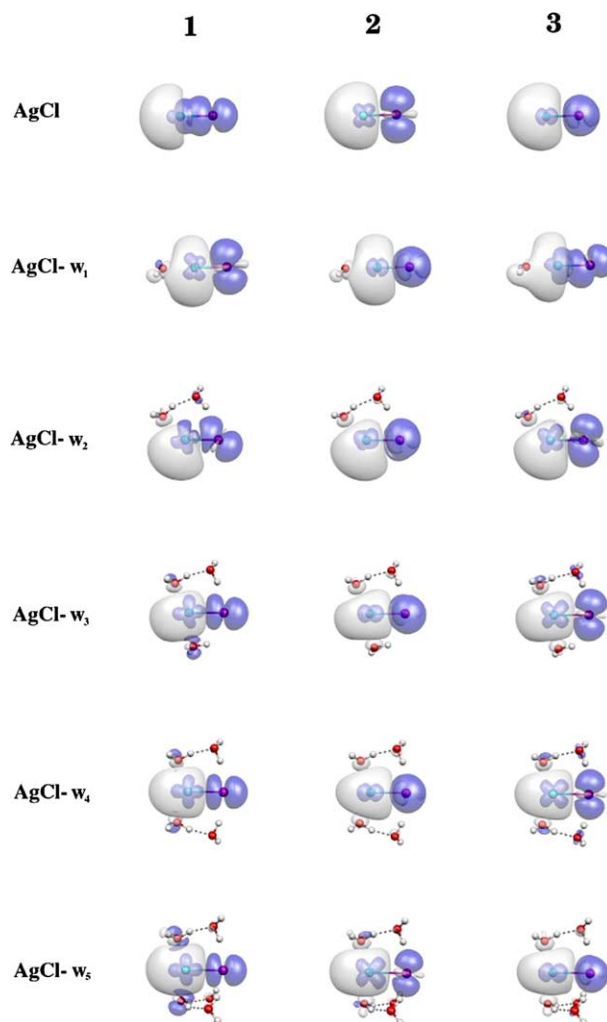


Fig. 1. Optimized structures of  $\text{AgCl-w}_{1-5}$  clusters. The interionic distances (in Å) are the following.  $\text{AgCl}$ , 2.33;  $n = 1$ , 2.31;  $n = 2$ , 2.37;  $n = 3$ , 2.51;  $n = 4$ , 2.53;  $n = 5$ , 2.65. The electronic density difference between excited and ground states is also represented. The isosurfaces correspond to electronic density difference of  $-0.0006 \text{ \AA}^{-3}$  (dark) and  $+0.0006 \text{ \AA}^{-3}$  (white).

Excitation energies related to the transitions between the three highest occupied molecular orbitals (HOMO, HOMO – 1, and HOMO – 2) and the lowest unoccupied molecular orbital (LUMO) were calculated. The  $\text{LUMO} \leftarrow \text{HOMO}$ ,  $\text{LUMO} \leftarrow \text{HOMO} - 1$ , and  $\text{LUMO} \leftarrow \text{HOMO} - 2$  transitions were named as (1), (2), and (3), respectively. Excitation energies and electronic oscillator strengths for  $\text{AgCl-w}_n$  clusters from CIS and TDDFT calculations are reported in Table 1. For isolated  $\text{AgCl}$  the first two energies correspond to the  ${}^1\Pi \leftarrow X^1\Sigma^+$  transition from the  $\pi$  orbitals to the LUMO. The third energy corresponds to the  $A^1\Sigma^+ \leftarrow X^1\Sigma^+$  transition. CIS excitation energies are significantly higher than TDDFT, a feature that has been usually associated with lack of correlation in CIS calculations. In addition, for isolated  $\text{AgCl}$ , CIS calculations lead to a 3-low lying quasi-degenerate state, whereas B3LYP calculations predict the energetical stabilization of the  $\sigma$

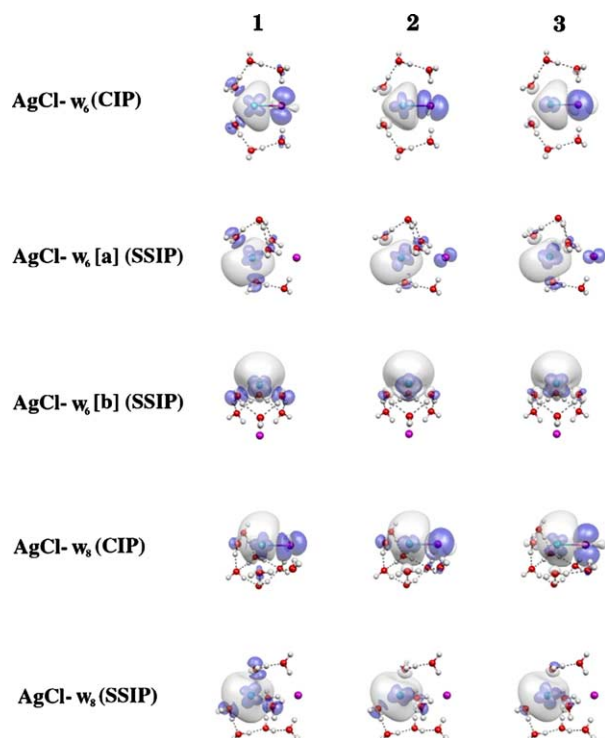


Fig. 2. Optimized structures of  $\text{AgCl-w}_{6,8}$  clusters. The interionic distances (in Å) are the following.  $n=6$  (CIP), 2.43;  $n=6$  [a] (SSIP), 3.89;  $n=6$  [b] (SSIP), 4.45;  $n=8$  (CIP), 2.41;  $n=8$  [a] (SSIP), 4.16. The electronic density difference between excited and ground states is also represented. The isosurfaces correspond to electronic density difference of  $-0.0006 \text{ \AA}^{-3}$  (dark) and  $+0.0006 \text{ \AA}^{-3}$  (white).

orbital by mixing of a Cl p orbital with an s–d hybridized Ag orbital [12]. Considering that a fair agreement is observed when we compare TDDFT (3.49 eV) and experimental data for the  $\text{AgCl } A^1\Sigma^+ \leftarrow X^1\Sigma^+$  transition (3.92 eV) [28], the present results indicate that the effect leading to the AgCl  $\sigma$  orbital stabilization may be underestimated by CIS calculations.

Upon complexation with one water molecule, excitation energies for transition (3) are blue shifted by 0.8 eV (TDDFT) and 1.14 eV (CIS). From AgCl to  $\text{AgCl-w}_8$  CIP, TDDFT and CIS predict that excitation energies corresponding to transition (3) are blue shifted by  $\sim 1.8$  and  $\sim 2.5$  eV, respectively. The size dependence of the excitation energies seems to reflect basically the energetic stability of the aggregates [12]. We note that both CIS and TDDFT approaches predict a similar dependence of excitation energies on the cluster size  $n$ , although it is known that CIS excitation energies are overestimated. In agreement with results for NaCl–water clusters [12] TDDFT calculations indicate that excitation energies of SSIP clusters are slightly lower than in CIP clusters. However, with the exception of the results for  $\text{AgCl-w}_6$ [b] SSIP, CIS excitation energies are higher for SSIP aggregates, which are characterized by promotion of Ag d electrons upon photoexcitation. As illustrated in Figs. 1 and 2, no charge migration from the Cl p orbitals is observed in SSIP clusters upon photoexcitation. Therefore, we believe that the behavior of CIS excitation energies for SSIP clusters can be related to the overestimation of the Ag atom excitation energies.

The optimized structures of  $\text{Cl}^-$ –water clusters are shown in Fig. 3. Excitation energies are reported in Table 2. TDDFT excitation energies corresponding to the HOMO–LUMO transition (1) are slightly blue-shifted (0.28 eV) when we move from  $\text{Cl}^-$ – $w_1$  to  $\text{Cl}^-$ – $w_2$ . Although CIS energies are significantly higher than TDDFT, a similar shift is also predicted by CIS calculations (0.3 eV). TDDFT HOMO–LUMO excitation energies are blue shifted by 1.28 eV when we move from  $\text{Cl}^-$ – $w_1$  to  $\text{Cl}^-$ – $w_8$  clusters. A quite similar value (1.26 eV) is predicted by CIS calculations. Although experimental values are apparently not available for  $\text{Cl}^-$ –water clusters, our results are in good agreement with theoretical predictions by Majumdar et al. [13] (see Table 2). The experimental excitation energy (1)

Table 1  
Excitation energies (eV) of AgCl–water clusters

	(1)		(2)		(3)	
	CIS	B3LYP	CIS	B3LYP	CIS	B3LYP
AgCl	4.75 (0.050)	2.60 (0.007)	4.79 (0.027)	2.60 (0.007)	4.79 (0.027)	3.49 <sup>a</sup> (0.068)
AgCl– $w_1$	5.84 (0.030)	3.62 (0.006)	5.87 (0.035)	3.61 (0.007)	5.93 (0.075)	4.29 (0.058)
AgCl– $w_2$	5.85 (0.027)	3.82 (0.010)	5.98 (0.039)	3.90 (0.017)	6.03 (0.089)	4.41 (0.070)
AgCl– $w_3$	6.07 (0.012)	4.07 (0.015)	6.62 (0.048)	4.12 (0.011)	6.73 (0.069)	4.40 (0.036)
AgCl– $w_4$	6.43 (0.024)	4.36 (0.022)	6.94 (0.046)	4.50 (0.011)	6.96 (0.064)	4.71 (0.041)
AgCl– $w_5$	6.46 (0.009)	4.37 (0.012)	7.23 (0.042)	4.95 (0.014)	7.35 (0.039)	5.04 (0.035)
AgCl– $w_6$ CIP	6.84 (0.050)	4.73 (0.040)	6.94 (0.079)	4.93 (0.011)	7.07 (0.042)	5.03 (0.056)
AgCl– $w_6$ [a] SSIP	6.93 (0.000)	4.61 (0.011)	7.33 (0.014)	4.67 (0.009)	7.38 (0.062)	4.76 (0.017)
AgCl– $w_6$ [b] SSIP	6.44 (0.000)	4.45 (0.008)	6.45 (0.000)	4.46 (0.003)	7.03 (0.042)	4.54 (0.003)
AgCl– $w_8$ CIP	6.78 (0.043)	5.05 (0.021)	7.20 (0.034)	5.24 (0.016)	7.25 (0.048)	5.27 (0.023)
AgCl– $w_8$ [a] SSIP	7.06 (0.004)	4.76 (0.006)	7.29 (0.008)	5.01 (0.018)	7.43 (0.007)	5.13 (0.025)

Oscillator strengths in parentheses. LUMO  $\leftarrow$  HOMO, LUMO  $\leftarrow$  HOMO – 1, and LUMO  $\leftarrow$  HOMO – 2 transitions were named as (1), (2), and (3), respectively.

<sup>a</sup> The experimental value is 3.92 eV [28].

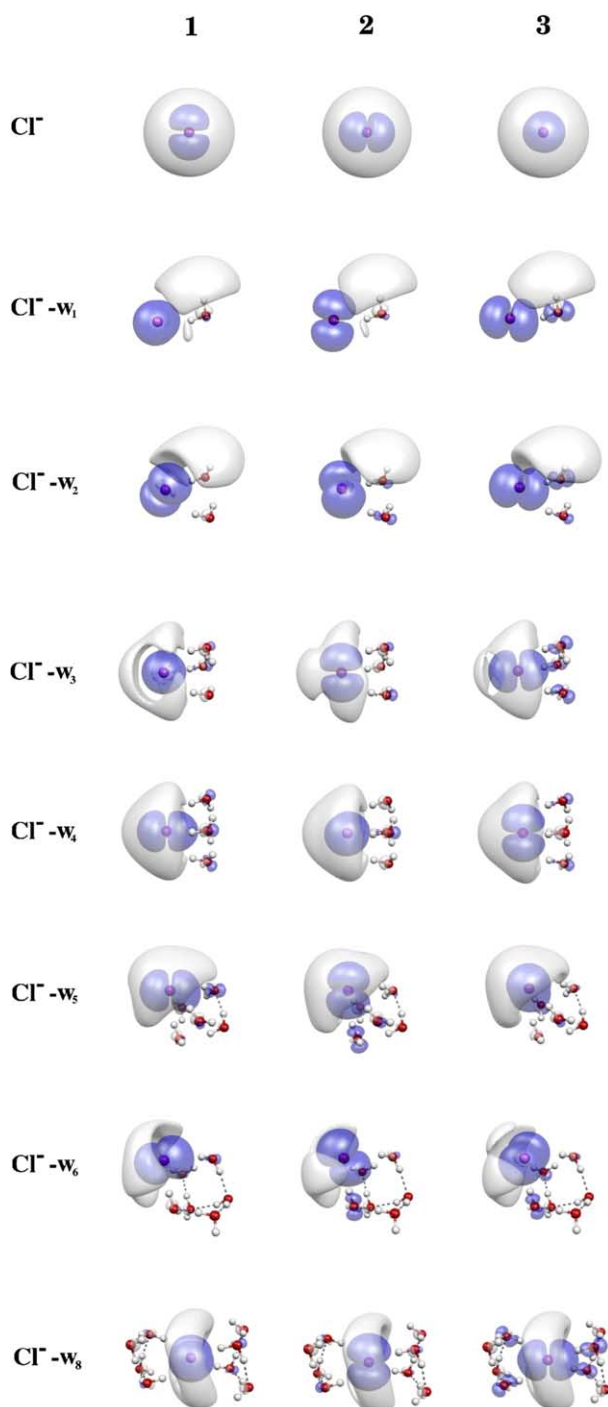


Fig. 3. Optimized structures of  $\text{Cl}^-$ - $w_{1-6,8}$  clusters. The electronic density difference between excited and ground states is also represented. The isosurfaces correspond to electronic density difference of  $-0.0006 \text{ \AA}^{-3}$  (dark) and  $+0.0006 \text{ \AA}^{-3}$  (white).

for  $\text{Cl}^-$  in bulk water is 7.10 eV [29], which is apparently in keeping with CIS results for the larger aggregates. However, the comparison is not direct. Excitation energies are very dependent on the cluster size and the small number of water molecules makes difficult to assess the convergence of the results with  $n$ .

### 3.2. Charge distribution and electronic density difference

For AgCl–water clusters Ag and Cl ESP charges, calculated at the CIS/6-31++G(d,p)//B3LYP/6-31+G(d,p) level, are reported in Table 3. For the ground state (GS), the Cl charge shows a weak dependence on the cluster size. The charge distribution of excited states reflects an important reorganization of the electronic density upon photoexcitation. This effect can be assessed by evaluating the difference between the atomic charges of excited and ground states, which is represented as  $\delta q$ . Here, we will focus on the ion pair.  $\delta q$  is strongly dependent on the cluster size ( $n$ ). This is illustrated in Fig. 4, where  $\delta q$  is represented as a function of  $n$ . CIS calculations predict that upon excitation (1),  $\delta q$  for the Ag atom changes from  $\sim -0.178 \text{ e}$  ( $\text{AgCl}-w_1$ ) to  $-0.130 \text{ e}$  ( $\text{AgCl}-w_6$  CIP) and for Cl  $\delta q$  changes from 0.425 to 0.254 e. The results for  $\delta q$  also suggest some stabilization of the electronic density reorganization when  $n \geq 5$  (see Fig. 4). It is worth remarking that ESP charges indicate that there is almost no change of the Cl charge upon photoexcitation in SSIP clusters. This is in contrast with NaCl–water clusters, where a significant charge transfer from Cl to water molecules was observed in SSIP as well as in CIP aggregates [11].

The reorganization of  $\rho(r)$  in AgCl–water clusters upon excitation is illustrated in Figs. 1 ( $n = 1-5$ ) and 2 ( $n = 6, 8$ ). In CIP clusters charge migration from both Cl p and Ag d orbitals can be clearly discerned. The excess electron density delocalizes around the Ag ion and some changes of  $\rho(r)$  associated with the water oxygen atoms is also visible. In contrast with NaCl–water clusters [11] for which CTTS states are observed when  $n \geq 5$ , there is no migration of  $\rho(r)$  from Cl to the nearby water molecules. In addition, for AgCl– $w_6$  (SSIP) and AgCl– $w_8$  (SSIP), the electronic density associated with Cl is not significantly changed and the excess electronic density is mainly related to charge migration from the Ag d orbitals combined with delocalization of the Ag s orbital. The results for the electronic density difference in excited AgCl–water clusters indicate that the  $\rho(r)$  associated with the Ag atom is similar to the s–d hybridized electronic density observed for the GS of  $\text{Ag}^+$ –water aggregates [30]. Some recent studies discussed the interaction between the Ag atom and water [31,32]. It was suggested that the Ag–water interaction can be described by that of an  $\text{Ag}^+$  core plus a negative charge distribution delocalized around the Ag atom [32]. We believe that our results support this description of the Ag–water interactions in excited AgCl–water clusters.

Charges for the GS state and three excited states of  $\text{Cl}^-$ –water clusters are reported in Table 4 and the dependence of  $\delta q$  on the number of water molecules ( $n$ ) is illustrated in Fig. 5. For excitation (1)  $\delta q$  is 0.438 e for  $n = 1$  and 0.160 e for  $n = 5$ . For the  $\text{Cl}^-$ - $w_3$  cluster, the amount of charge transfer from Cl to water (0.171 e) is smaller than  $\delta q = 0.715 \text{ e}$  reported by Majumdar et al. [13], which was

Table 2  
Excitation energies (eV) of Cl<sup>-</sup>-water clusters

	(1) <sup>a</sup>		(2)		(3)	
	CIS	B3LYP	CIS	B3LYP	CIS	B3LYP
Cl <sup>-</sup>	6.63 (0.198)	5.66 (0.190)	6.63 (0.198)	5.66 (0.190)	6.63 (0.198)	5.66 (0.190)
Cl <sup>-</sup> -w <sub>1</sub>	6.19 (0.052) [6.27]	4.14 (0.009) [4.28]	6.20 (0.074)	4.17 (0.019)	6.28 (0.108)	4.36 (0.076)
Cl <sup>-</sup> -w <sub>2</sub>	6.49 (0.071) [6.55]	4.42 (0.0153) [4.52]	6.57 (0.091)	4.52 (0.017)	6.62 (0.107)	4.66 (0.070)
Cl <sup>-</sup> -w <sub>3</sub>	6.93 (0.011) [6.99]	5.12 (0.042) [5.21]	6.93 (0.011)	5.12 (0.042)	6.99 (0.012)	5.19 (0.076)
Cl <sup>-</sup> -w <sub>4</sub>	7.12 (0.109) [7.42]	5.29 (0.065) [5.45]	7.13 (0.127)	5.34 (0.059)	7.13 (0.127)	5.34 (0.059)
Cl <sup>-</sup> -w <sub>5</sub>	7.41 (0.105)	5.38 (0.033)	7.46 (0.118)	5.44 (0.042)	7.50 (0.142)	5.53 (0.069)
Cl <sup>-</sup> -w <sub>6</sub>	7.09 (0.094)	4.55 (0.004)	7.14 (0.101)	4.59 (0.015)	7.16 (0.109)	4.63 (0.009)
Cl <sup>-</sup> -w <sub>8</sub>	7.45 (0.099)	5.42 (0.038)	7.45 (0.101)	5.42 (0.038)	7.58 (0.109)	5.51 (0.074)
Bulk water	7.10 <sup>b</sup>					

Oscillator strengths in parentheses. LUMO ← HOMO, LUMO ← HOMO - 1, and LUMO ← HOMO - 2 transitions were named as (1), (2), and (3), respectively.

<sup>a</sup> Bracketed values are theoretical calculations from Majumdar et al. [13] based on first-order configuration interaction (FOCI) and first-order DFT random phase approximation (DFT-RPA).

<sup>b</sup> Experimental value from Takahashi et al. [29].

Table 3  
ESP charges in AgCl-water clusters for the ground state (GS) and for the excitations (1), (2), and (3)

	GS		(1)		(2)		(3)	
	Ag	Cl	Ag	Cl	Ag	Cl	Ag	Cl
AgCl	0.728	-0.728	0.154	-0.154	0.154	-0.154	0.345	-0.345
AgCl-w <sub>1</sub>	0.608	-0.706	0.430	-0.281	0.431	-0.294	0.704	-0.479
AgCl-w <sub>2</sub>	0.678	-0.719	0.278	-0.377	0.383	-0.439	0.384	-0.484
AgCl-w <sub>3</sub>	0.742	-0.738	0.628	-0.506	0.628	-0.506	0.599	-0.345
AgCl-w <sub>4</sub>	0.750	-0.746	0.669	-0.519	0.664	-0.576	0.664	-0.576
AgCl-w <sub>5</sub>	0.762	-0.682	0.715	-0.494	0.750	-0.437	0.742	-0.558
AgCl-w <sub>6</sub> CIP	0.708	-0.738	0.578	-0.484	0.643	-0.689	0.716	-0.659
AgCl-w <sub>6</sub> [a] SSIP	0.813	-0.726	0.850	-0.713	0.643	-0.689	0.842	-0.714
AgCl-w <sub>6</sub> [b] SSIP	0.836	-0.715	0.684	-0.764	0.623	-0.765	0.622	-0.765
AgCl-w <sub>8</sub> CIP	0.663	-0.699	0.664	-0.684	0.523	-0.625	0.515	-0.552
AgCl-w <sub>8</sub> [a] SSIP	0.858	-0.725	0.941	-0.741	1.006	-0.738	1.006	-0.738

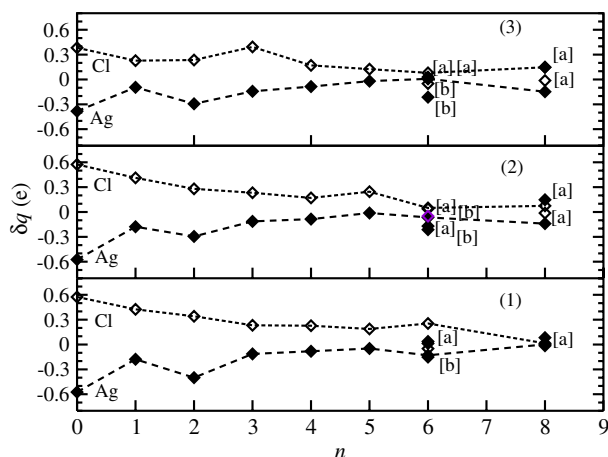


Fig. 4. Difference between the ESP charges of excited and ground states ( $\delta q$ ) versus the number of water molecules ( $n$ ) in AgCl-water clusters for the transitions (1), (2), and (3).

based on Mulliken charges and effective core potential (ECP) for chlorine but it is close to  $\delta q = 0.23$  e for a cluster of I<sup>-</sup> with three water molecules [33] which was based on AIM charges. The differences on the magnitude of the

Table 4  
ESP charges in Cl<sup>-</sup>-water clusters for the ground state (GS) and for the excitations (1), (2), and (3)

	GS	(1)	(2)	(3)
Cl <sup>-</sup> -w <sub>1</sub>	-0.954	-0.516	-0.514	-0.533
Cl <sup>-</sup> -w <sub>2</sub>	-0.908	-0.560	-0.577	-0.540
Cl <sup>-</sup> -w <sub>3</sub>	-0.883	-0.712	-0.712	-0.660
Cl <sup>-</sup> -w <sub>4</sub>	-0.874	-0.650	-0.718	-0.718
Cl <sup>-</sup> -w <sub>5</sub>	-0.828	-0.668	-0.674	-0.701
Cl <sup>-</sup> -w <sub>6</sub>	-0.859	-0.642	-0.566	-0.652
Cl <sup>-</sup> -w <sub>8</sub>	-0.825	-0.099	-0.098	-0.317

charge transfer upon photoexcitation between the present results and those of [13] for Cl<sup>-</sup>-water clusters are related to the fact that Mulliken charges were used by Majumdar et al. [13]. Interestingly, our results indicate a significant charge transfer from Cl to water when  $n = 8$ . The electronic density reorganization in Cl<sup>-</sup>-water clusters induced by photoexcitation is illustrated in Fig. 3. Electronic density migrates from the Cl p orbitals to a diffuse electronic distribution that is stabilized by the interaction with the water hydrogen atoms indicating the formation of CTTS precursor states.

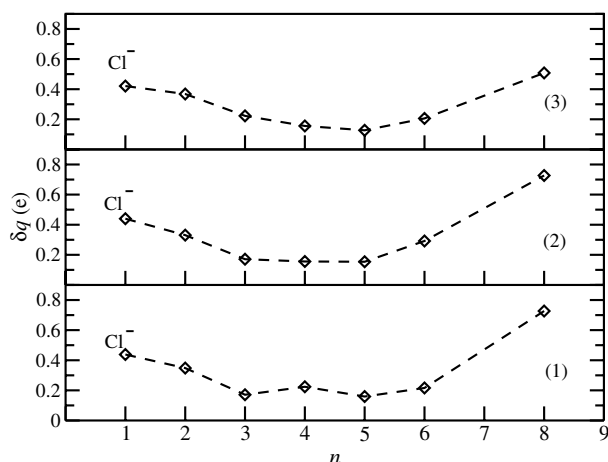


Fig. 5. Difference between the ESP charges of excited and ground states ( $\delta q$ ) versus the number of water molecules ( $n$ ) in  $\text{Cl}^-$ -water clusters for the transitions (1), (2), and (3).

#### 4. Summary and conclusions

Electronic properties of  $\text{AgCl}$ -water clusters were investigated by CIS and TDDFT calculations. Our results strongly indicate that in contrast with  $\text{NaCl}$ -clusters [11], there is no formation of CTTS structures associated with charge migration from  $\text{Cl}^-$  to the water molecules in photoexcited  $\text{AgCl}$ -water clusters. The analysis of the electronic density flow between ground and excited states suggests that this can be explained by the nature of interionic interaction as well as the interaction between the ionic species and the water molecules. The specific role of the Ag d orbitals should be stressed. Upon photoexcitation of SSIP clusters, charge migrates from Ag d to s orbitals. The diffuse electronic density of the photoexcited aggregates is localized around the cation and interacts with the surrounding water molecules. This feature seems to be similar to excitonic states characterizing the hydration of the Ag atom [32].

In  $\text{NaCl}$ -water clusters, CTTS precursor states related to charge migration from  $\text{Cl}^-$  to water are observed for a minimum number of five water molecules [11]. This means that when  $n \geq 5$  the electrostatic field associated with the hydrogen bond network (which is polarized by the ion pair) is strong enough to stabilize the diffuse electronic distribution associated with the excitation of the Cl p electron. CTTS formation in solvated ion pairs reflects the competition between the electrostatic potential field created by the ion pair and by the water molecules. This is different from CTTS states of solvated anionic species, which was illustrated by photoexcited  $\text{Cl}^-$ -water clusters. However, the conceptual core explaining the formation of CTTS is apparently the same for both situations. The excited delocalized state is formed when an electron is bound in the potential field created by the solvent molecules, which are also polarized by the ionic species [34,35].

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