



Charge separation and charge transfer to solvent in NaCl–water clusters

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Abstract

The electronic structure of NaCl– w_n ($w \equiv \text{H}_2\text{O}$ and $n = 1–6, 8$) clusters was investigated by ab initio and time dependent density functional theory calculations. Upon photoexcitation, when $n < 5$ the electronic density migrates from one of the Cl valence p orbitals to the Na atom. When $n \geq 5$, the electronic density associated with one of these orbitals delocalizes over the nearby water molecules indicating the formation of CTTS states in the clusters. When $n \geq 6$, contact ion-pair (CIP) and solvent separated ion-pair (SSIP) structures are found. The onset of charge separation in the ground state of small NaCl–water clusters seems to coincide with the formation of CTTS states upon photoexcitation.

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1. Introduction

Charge separation of salt ion pairs in solution is one of the most important processes in chemistry [1–6]. The classical example is the dissolution of NaCl in water. Although this process is empirically well known, it is not very well understood at the microscopic level. Several studies of NaCl in water clusters were reported [7–10]. One relevant issue concerns the minimum number of solvent molecules that are necessary to characterize charge separation of the ion pair in the aggregates [8–10]. Charge separation is characterized by the presence of solvent molecules between the ions and by a large interionic distance in comparison with the isolated ion pair. These aggregates are named as solvent-separated ion pair (SSIP). Clusters where the interionic distance is similar to that of the isolated ion pair are contact ion pair (CIP) structures. Most of the quantum mechanical studies of small NaCl–water clusters pointed

out the presence of CIP structures [8,10]. However, one ab initio study of Jungwirth [9] concluded that NaCl– w_6 is the first cluster size where a SSIP structure can be found. The presence of several SSIP structures in small AgCl–water and NaCl–water clusters was recently confirmed [11].

On the other hand, experimental works on photodissociation of salt ion pairs in clusters of polar molecules show that charge separation, or 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. The excitation scheme for the prototype NaI system was described in detail elsewhere [1,2]. For this particular case, the electronic oscillator strength associated with the transition from the GS $X^1\Sigma^+$ to the excited $A^1\Sigma^+$ state is proportional to the overlap of the electronic wave function of I^- and Na ($3s^1S_{1/2}$), which is dependent on the interionic distance. For CIP, this dependence should be weak. Only small variations of the interionic distance with the cluster size are observed in CIP structures. For SSIP structures, the increase of the interionic distance

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and the insertion of solvent molecules between the ion pair may induce a significant decrease of oscillator strengths. Therefore, reduced excitation efficiency can be taken as an indication of charge separation in the aggregates [1,2]. By adopting such a procedure it is assumed that the photodissociation route of the salt-ion pair in the clusters is akin to that of the isolated ion pair. However, the possibility that photoexcitation of salt-water aggregates leads to the formation of charge transfer to solvent (CTTS) states, with totally different dynamics from that of the excited ion pair, remains open to discussion [5,6]. CTTS states are characterized by the redistribution of the electronic density initially localized on the solvated anion over the nearby solvent molecules. The excited state is formed when the electron is bound in the electrostatic potential field created by the solvent, which is also polarized by the solute [12]. Although CTTS of inorganic ions in solution have been extensively discussed [12–17] we are not aware of studies about their presence in small salt-water aggregates.

In this Letter we are reporting a theoretical investigation on the electronic properties of NaCl–water clusters. We have the following objectives. First, to investigate the presence and nature of CTTS states in excited NaCl–water aggregates. Second, to analyse the difference between excitations of CIP and SSIP structures. Finally, emphasis will be placed on the eventual relationship between the formation of CTTS states and the onset of charge separation in small NaCl–water clusters.

2. Computational details

The structures of NaCl– w_n ($w \equiv (\text{H}_2\text{O})$ and $n = 1–6, 8$) clusters were determined by a previous density functional theory study (DFT) [11]. These calculations were carried out with the B3LYP functional, where the exchange-correlation functional is the Becke's three parameter functional (B3) [18] combined with the Lee, Yang, and Parr correlation functional [19]. The 6-31+G(d,p) basis set [20] was used in the DFT optimizations.

Configuration interaction with single excitations (CIS) [21] and time dependent density functional theory (TDDFT) [22–25] calculations were carried out to predict excitation energies from the ground state to excited states. The calculation of excitation energies were performed with the 6-31++G(d,p) basis set, which includes diffuse functions on all of the atoms. 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 [23]. It was concluded that, in general, TDDFT predicts vertical excitation energies in better agreement with experiment than CIS calculations.

The analysis of polarization effects and charge transfer was carried out with charges fitted to the electrostatic potential (ESP charges). ESP charges were calculated by the Breneman method [26]. We also report a discussion on the electronic density reorganization in the clusters upon photoexcitation by representing the electronic density difference between ground and excited states. All the calculations were carried out with the GAUSSIAN-98 program [27]. Electronic densities were analysed by using the Molekel visualization program [28].

3. Results and discussion

3.1. Vertical excitation energies

The structure of NaCl–water clusters are represented in Fig. 1 ($n = 1–4$) and Fig. 2 ($n = 5, 6, 8$). A detailed analysis of the structural properties of these aggregates has been reported elsewhere [11]. For completeness interionic distances are reported in the captions of

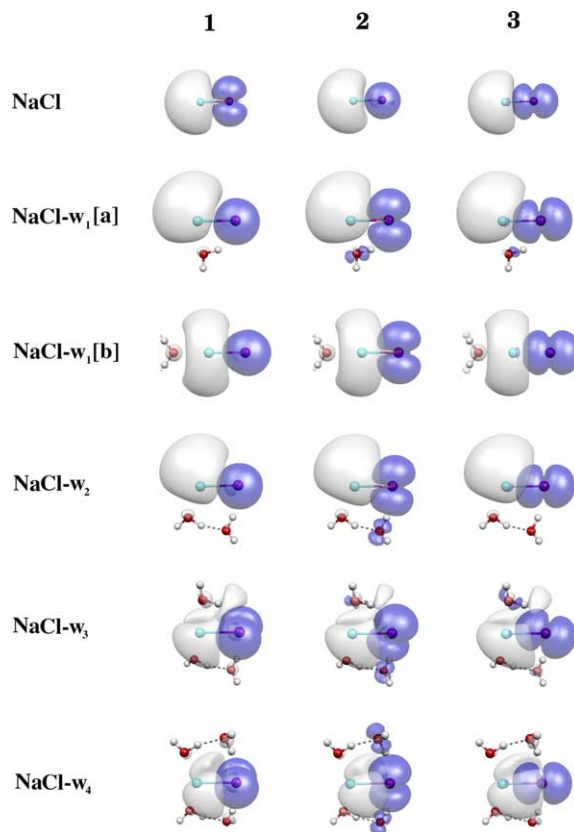


Fig. 1. Structure of NaCl– w_n ($n = 1–4$) clusters. For NaCl– w_1 , two conformers ([a] and [b]) are shown. The interionic distances (in Å) are the following. NaCl, 2.39; $n = 1$ [a], 2.48; $n = 1$ [b], 2.41; $n = 2$, 2.48; $n = 3$, 2.59; $n = 4$, 2.59. The electronic density difference between excited and ground states is also represented. The isosurfaces correspond to electronic density differences of $-0.02 \text{ e } \text{Å}^{-3}$ (dark) and $+0.02 \text{ e } \text{Å}^{-3}$ (white).

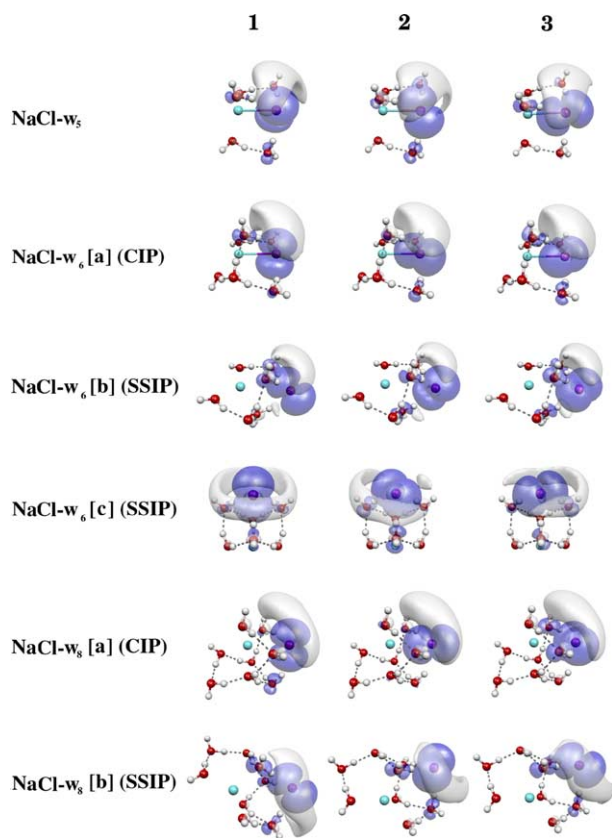


Fig. 2. Structure of NaCl-w_n ($n = 5, 6, 8$) clusters. For NaCl-w_6 , two SSIP conformers [a] and [b] are shown. The interionic distances (in Å) are the following. $n = 5$, 2.76; $n = 6$ [a], 2.75; $n = 6$ [b], 3.72; $n = 6$ [c], 4.59; $n = 8$ [a], 2.97; $n = 8$ [b], 4.24. The electronic density difference between excited and ground states is also represented. The isosurfaces correspond to electronic density differences of -0.02 e \AA^{-3} (dark) and $+0.02 \text{ e \AA}^{-3}$ (white).

Figs. 1 and 2. We note, however, that for $n = 1$, two conformers (NaCl-w_1 [a] and NaCl-w_1 [b]) were found. NaCl-w_1 [a] is stabilized by a $\text{H}\cdots\text{Cl}$ hydrogen bond (see Fig. 1). The conformer [b] involves the head-to-tail dipolar interaction between the ion pair and the water molecule. For $n = 6$ three conformers are shown in Fig. 2. A contact ion pair structure (NaCl-w_6 [a] CIP) and two separated ion pair conformers (NaCl-w_6 [b] SSIP and NaCl-w_6 [c] SSIP). In agreement with Jungwirth [9], we also find that $n = 6$ is the minimum number of water molecules for which SSIP structures can be found in NaCl -water clusters. Two NaCl-w_8 clusters (CIP and SSIP) are shown in Fig. 2. For NaCl-w_8 CIP, the interionic distance is 2.97 Å and the Na atom interacts with five water molecules at distances ranging from 2.32 to 2.98 Å. The Na coordination number (5) is the same reported by experimental studies of alkali halides solutions [29]. The Cl ion forms three $\text{H}\cdots\text{Cl}$ bonds of 2.11, 2.09, and 2.42 Å. NaCl-w_8 SSIP is characterised by a larger interionic distance of 4.24 Å. In this case, the Na atom is in close interaction with four water

molecules and the Cl ion is at the cluster 'surface', where it is stabilised by three $\text{H}\cdots\text{Cl}$ bonds. The 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. Only transitions from the ground state to singlets were considered. 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 from CIS and TDDFT calculations are reported in Table 1. For isolated NaCl the first two energies correspond to the ${}^1\Pi \leftarrow \text{X}^1\Sigma^+$ transition from the degenerated π orbitals to the LUMO. The third energy corresponds to the $\text{A}^1\Sigma^+ \leftarrow \text{X}^1\Sigma^+$ transition. CIS excitation energies are significantly higher than TDDFT. Although experimental results for NaCl -water clusters are apparently not available, the TDDFT prediction for the $\text{A} \leftarrow \text{X}$ transition (4.03 eV) is in good agreement with experiment (~ 4.2 eV) [30]. CIS overestimates the experimental value by 2.3 eV.

Upon complexation with one water molecule, TDDFT excitation energies for transition (3) are blue shifted by 0.6 eV in NaCl-w_1 [a] and red-shifted by 0.4 eV in NaCl-w_1 [b]. CIS calculations predict a blue shift for both conformers, although the shift for NaCl-w_1 [b] (0.46 eV) is 0.24 eV smaller than the value for NaCl-w_1 [a] (0.7 eV). We define δE as the difference between the excitation energy of a cluster with n water molecules and the corresponding excitation energy of the isolated ion pair. The dependence of δE on the cluster size for transition (3) is illustrated in Fig. 3. From NaCl to NaCl-w_6 [a] CIP, TDDFT predicts that excitation energies corresponding to transition (3) are blue shifted by ~ 1.9 eV. A rather similar behaviour of δE as a function of n is observed for transitions (1) and (2). The size dependence of the excitation energies seems to reflect basically the energetical stability of the aggregates [11]. We note that both CIS and DFT approaches predict a similar dependence of excitation energies on the cluster size, although as it was observed, CIS excitation energies are apparently overestimated. Both CIS and TDDFT calculations indicate that excitation energies of SSIP clusters are slightly reduced in comparison with CIP. Another relevant issue concerns the behavior of the oscillator strengths, particularly the difference between oscillator strengths of CIP and SSIP structures. As it has been previously observed (see Section 1), reduced oscillator strengths could be interpreted as an indication of charge separation [1]. Focusing again on the $\text{LUMO} \leftarrow \text{HOMO} - 2$ transition, when $n = 6$, oscillator strengths for the two SSIP structures (0.041 and 0.031) are smaller than that of the CIP structure (0.068). However, when $n = 8$ the difference between the oscillator strengths of CIP and SSIP structures is

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

	(1)		(2)		(3)	
	CIS	B3LYP	CIS	B3LYP	CIS	B3LYP
NaCl	5.27 (0.029)	3.35 (0.013)	5.27 (0.029)	3.35 (0.013)	5.79 (0.097)	4.03 ^a (0.103)
NaCl–w ₁ [a]	6.05 (0.035)	4.06 (0.012)	6.19 (0.047)	4.24 (0.023)	6.49 (0.078)	4.60 (0.069)
NaCl–w ₁ [b]	5.77 (0.048)	3.15 (0.004)	5.77 (0.048)	3.15 (0.004)	6.25 (0.084)	3.65 (0.039)
NaCl–w ₂	6.47 (0.048)	4.48 (0.015)	6.67 (0.055)	4.71 (0.025)	6.89 (0.087)	4.97 (0.060)
NaCl–w ₃	7.16 (0.071)	4.91 (0.013)	7.44 (0.100)	5.26 (0.040)	7.52 (0.085)	5.35 (0.051)
NaCl–w ₄	7.42 (0.086)	5.17 (0.014)	7.76 (0.121)	5.52 (0.028)	7.76 (0.078)	5.57 (0.059)
NaCl–w ₅	7.83 (0.107)	5.64 (0.030)	7.87 (0.097)	5.70 (0.042)	7.92 (0.086)	5.75 (0.045)
NaCl–w ₆ [a] CIP	7.85 (0.098)	5.71 (0.026)	8.00 (0.082)	5.84 (0.035)	8.03 (0.116)	5.91 (0.068)
NaCl–w ₆ [b] SSIP	7.64 (0.078)	5.37 (0.022)	7.68 (0.096)	5.44 (0.025)	7.78 (0.105)	5.55 (0.041)
NaCl–w ₆ [c] SSIP	7.77 (0.090)	5.53 (0.036)	7.80 (0.099)	5.58 (0.031)	7.80 (0.099)	5.58 (0.031)
NaCl–w ₈ [a] CIP	7.68 (0.077)	5.36 (0.018)	7.76 (0.067)	5.46 (0.024)	7.89 (0.121)	5.68 (0.055)
NaCl–w ₈ [b] SSIP	7.74 (0.086)	5.52 (0.026)	7.77 (0.092)	5.57 (0.033)	7.81 (0.100)	5.62 (0.037)

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

^a The experimental value is 4.2 eV [29].

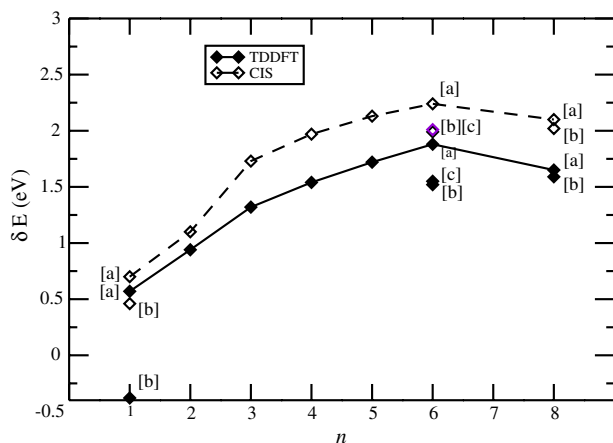


Fig. 3. The shift of the excitation energies relative to isolated NaCl (ΔE) as a function of the number of water molecules (n) in NaCl–water clusters for the LUMO ← HOMO – 2 transition. When $n = 1, 6, 8$ the excitation energies of some conformers are also represented.

only 0.0018 indicating that, although oscillator strengths of SSIP structures are smaller than CIP, the difference between them can decrease as the cluster size increases. CIS oscillator strengths are significantly larger than TDDFT, a tendency already observed in other studies [16].

3.2. Charge distribution and electronic density difference

Atomic charges fitted to the electrostatic potential (ESP) are reported in Table 2. These results are from CIS/6-31++G(d,p)//B3LYP/6-31+G(d,p) calculations. For the ground state (GS), ESP charges show a weak dependence on the cluster size. With the exception of NaCl–w₁[b], the total charge of the ion pair is positive, indicating charge transfer from the ion pair essentially

from the Cl atom) to the water molecules. The importance of charge transfer in halide–water binary complexes was investigated by Thompson and Hynes [31]. In keeping with their results we also find that significant charge transfer from Cl to water can be observed in GS NaCl–water aggregates (0.225e in NaCl–w₆[b] SSIP). Upon excitation (3), the Na charge in the isolated ion pair changes from 0.83e to –0.16e. However, this charge decreases with increasing cluster size. Interestingly, when $n = 8$ and for excitation (3) the Na charge is quite similar to that of the isolated NaCl in its ground state.

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 Δq . Here, we will focus on the ion pair. For NaCl–w₁[a] and for transition (1), Δq is –1.18e and 0.87e for Na and Cl, respectively. A similar effect can be observed with electronic density migration from Cl to Na in NaCl–w₁[a]. Δq is strongly dependent on the cluster size. This is illustrated in Fig. 4, where it is represented as a function of the number of water molecules (n). CIS calculations predict that upon excitation (3), Δq for the Na atom changes from ~–1.16e (NaCl–w₁[a]) to –0.05e (NaCl–w₆[b] SSIP). The size dependence of Δq indicates that upon photoexcitation charge migrates from Cl to Na when $n = 1–4$, whereas migration from Cl to the nearby water molecules is observed in the larger clusters ($n = 5, 6, 8$). For these clusters and for excitation (3), Δq for Cl ranges from 0.38e ($n = 5$) to 0.21e ($n = 8$, SSIP). This amount of charge transfer from Cl to water is smaller than $\Delta q = 0.65e$, predicted by Majumdar et al. [15] for the Cl[–] anion in a cluster with four water molecules, which was based on Mulliken charges. Our values, are

Table 2

ESP atomic charges in NaCl–water clusters for the ground state (GS) and for the excitations (1), (2), and (3)

	GS		(1)		(2)		(3)	
	Na	Cl	Na	Cl	Na	Cl	Na	Cl
NaCl	0.833	−0.833	−0.185	0.185	−0.185	0.185	−0.157	0.157
NaCl–w ₁ [a]	0.859	−0.804	−0.318	0.067	−0.279	0.033	−0.299	0.0058
NaCl–w ₁ [b]	0.764	−0.826	0.167	−0.034	0.173	−0.036	0.204	−0.071
NaCl–w ₂	0.844	−0.797	−0.245	−0.059	−0.215	−0.087	−0.222	−0.079
NaCl–w ₃	0.896	−0.777	0.615	−0.227	0.551	−0.332	0.549	−0.278
NaCl–w ₄	0.873	−0.785	0.723	−0.252	0.662	−0.517	0.649	−0.280
NaCl–w ₅	0.987	−0.733	1.248	−0.391	1.214	−0.450	1.172	−0.351
NaCl–w ₆ [a] CIP	0.893	−0.720	1.128	−0.304	1.051	−0.334	1.025	−0.428
NaCl–w ₆ [b] SSIP	0.960	−0.735	1.015	−0.334	0.947	−0.389	0.906	−0.373
NaCl–w ₆ [c] SSIP	0.959	−0.717	0.950	−0.345	0.907	−0.484	0.907	−0.483
NaCl–w ₈ [a] CIP	0.872	−0.747	1.058	−0.446	0.946	−0.296	0.835	−0.524
NaCl–w ₈ [b] SSIP	0.873	−0.747	0.999	−0.492	0.883	−0.366	0.816	−0.539

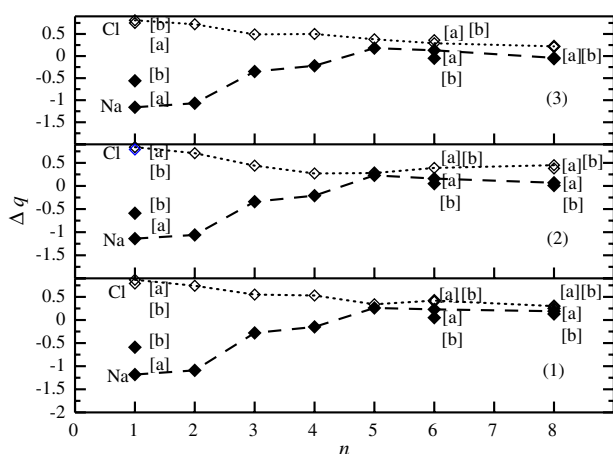


Fig. 4. Difference between the atomic charges of excited and ground states (Δq) versus the number of water molecules (n) in NaCl–water clusters for the transitions (1), (2), and (3). When $n = 1, 6, 8$ results for different conformers are also reported.

however, similar to $\Delta q = 0.23e$ for a cluster of I^- with three water molecules [16], which was based on AIM charges. We note that our results for the size dependence of Δq suggest some stabilization of the electronic density reorganization when $n \geq 5$ (see Fig. 4).

The reorganization of $\rho(r)$ upon excitation is illustrated in Fig. 1 ($n = 1-4$) and Fig. 2 ($n = 5, 6, 8$). From Fig. 1 it is clear that upon photoexcitation $\rho(r)$ migrates from the Cl p orbitals to the Na atom. The only difference between the three excitations concerns the orientation of the Cl p orbitals. When $n \geq 5$, $\rho(r)$ migrates from the Cl atom to the water molecules. Two factors can be associated with this interesting change. First, the coordination of the Na atom by at least three water molecules. Second, the stabilization of the delocalized electronic density distribution by the electrostatic field of the water molecules in close interaction with the Cl anion.

The migration of $\rho(r)$ from the Cl atom to the water molecules is a strong indication of CTTS precursor states in excited NaCl–water clusters when $n \geq 5$.

Although SSIP structures are characterized by enhanced polarization effects in comparison with CIP [11], no significant difference between the nature of CTTS states of CIP and SSIP structures were observed. However, we stress that the appearance of CTTS states in the excited aggregates practically coincides with the formation of ground state SSIP structures ($n = 6$).

4. Summary and conclusions

Electronic properties of NaCl–water clusters were investigated by CIS and TDDFT calculations. As it should be expected, electronic properties of excited NaCl–water clusters are significantly modified in comparison with the ground state. The size dependence of the excitation energies follows a simple pattern, which reflects the energetical stability of the aggregates [11]. One major conclusion concerns the electronic density rearrangement induced by excitations. For very small clusters ($n = 1-4$), it was found that $\rho(r)$ migrates from the Cl p orbitals to the Na s orbital. However, when $n \geq 5$, an interesting transition to a CTTS excited states occurs, where the electronic density associated with one of the Cl p orbitals delocalizes over the water molecules. It is worthwhile to note that only when $n = 6$, SSIP structures are observed in NaCl–water clusters and that, in addition, for this number of water molecules, photoexcitation of CIP and SSIP structures lead to CTTS states.

The present results may have important implications for photodissociation experiments. It may be difficult to characterize charge separation in NaCl–water clusters by assuming that upon photoexcitation the dissociation route of the ion pair in the clusters is akin to that of isolated NaCl. Further studies on this issue should be carried out and could be of interest for a better understanding of solvent-selective charge separation

behaviour as observed in clusters of NaI with different polar molecules [2].

Finally, we observe that the stabilization of the delocalized electronic density in excited NaCl- w_n clusters involves the hydrogen bond network as well as the electrostatic field of the Na cation. This is a major difference in comparison with CTTS states of solvated anionic species, for which several studies were carried out.

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