

Charge transfer to solvent (CTTS) energies of small $X - (H_2O)_n$ ($n=1-4$) ($X=F, Cl, Br, I$) clusters: Ab initio study

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Charge transfer to solvent (CTTS) energies of small $X^-(H_2O)_{n=1-4}$ ($X=F, Cl, Br, I$) clusters: *Ab initio* study

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Charge transfer to solvent (CTTS) energies of small halide–water clusters, $X^-(H_2O)_{n=1-4}$ ($X=F, Cl, Br, I$) have been studied using first-order configuration interaction as well as time dependent discrete Fourier transform density functional methods. The only available experimental data are the recently reported CTTS energies for $I^-(H_2O)_{n=1-4}$ clusters by Johnson and co-workers [D. Serxner, C. E. H. Dessent, and M. A. Johnson, *J. Chem. Phys.* **105**, 7231 (1996)]. These results are in good agreement with our predicted values. The calculated CTTS energies indicate that there is regularity in the change of CTTS energies with respect to the change of halide anion as well as the cluster size. Our investigations have shown that this observed trend of CTTS energies of $X^-(H_2O)_n$ clusters could be quantitatively explained by the ionization potential of the halide anions and the binding energies of the respective clusters. © 2000 American Institute of Physics. [S0021-9606(00)30101-5]

INTRODUCTION

The ultraviolet (UV) absorption spectra of halide ions in water constitute a unique class of electronic spectra.¹ The electronic transitions in solvated halides involve bound excited states, which are not property of the ion itself, but exist due to stabilizing potential created by the surrounding solvent molecules. The aqueous solution of iodine, e.g., exhibits broad electronic bands in the UV region corresponding to the electron ejection from iodide to the solvent,² known as charge transfer to solvent (CTTS) states. The spectrum consists of two bands around 2100 Å, separated by the characteristic spin–orbit splitting ($A_{so}=0.94$ eV) of neutral iodine.³

The CTTS phenomenon finds importance as a device to trap electrons in polar solvents, which in turn plays an important role in radiation chemistry, electron transfer, and charge induced chemistry. A microscopic understanding of the factors that govern such electron solvation is of particular importance. CTTS bands of various inorganic ions have been extensively catalogued and discussed earlier by Rabinowitch⁴ and Blandamer and Fox.⁵ All these investigations were restricted to the ion solvated in bulk solvent medium. The dynamics of the states were later experimentally investigated by Eisenthal,⁶ Gaudeul,⁷ and Bradforth⁸ and their co-workers, while theoretical simulations were made by Sheu and Rosky⁹ and Staib and Borgis.¹⁰ Recent availability of the techniques to generate halide water clusters of desired size has prompted scientists to study this phenomenon from a real microscopic point of view. Johnson and co-workers¹¹ have measured the photodetachment spectra of $I^-(H_2O)_{n=1-4}$ clusters to identify the CTTS bands, while in a recent article, Neumark and co-workers¹² have studied the dynamics of the electron solvation in the photoexcited anion

clusters of $I^-(D_2O)_{n=4-6}$ and $I^-(H_2O)_{n=2-4}$. The CTTS spectra of Cl^- and Br^- are available experimentally in bulk water but there is no available data for their small water clusters.

In our earlier studies on the $F^-(H_2O)_{n=1-6}$ clusters,¹³ we have calculated the possible CTTS excitation energies of F^- ion due to stepwise increase in the water cluster size. This has prompted us to explore the CTTS transition energies of the other halide ions also. The present report is thus based on the calculation and plausible interpretation of the CTTS bands of $X^-(H_2O)_{n=1-4}$ ($X=F, Cl, Br, I$) clusters. The precise definition of the CTTS energy indicates that it is an electronic transition related to transfer of charges from halide to the water, and the energy would be less than the ionization potential (IP) of the corresponding anion–water system.^{11,14} Keeping this definition in mind we have explored the vertically excited states of the minimum energy clusters of $X^-(H_2O)_n$ through configuration interaction (CI) calculations. Results on $I^-(H_2O)_n$ CTTS energies have been found to be in good agreement with experiment.¹¹ Our investigations have further revealed that the IP of the halide anion and the binding energy of the $X^-(H_2O)_n$ cluster have the dominant role to interpret the nature and energy ordering of their CTTS bands. To the best of our knowledge, such theoretical studies on the small halide–water clusters have not been reported earlier.

METHODS OF COMPUTATION

The central theme of our calculation is to get more or less accurate energy of the vertically excited first singlet state (S_1) of $X^-(H_2O)_n$ clusters. The vertical transition energy (E_{VT}) with respect to the ground state (S_0) would be the measure of the CTTS energy (E_{CTTS}) of these clusters. To achieve our goal we have initially used restricted Hartree–Fock (RHF) wave functions to generate the S_1 states of these

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TABLE I. S_0 to S_1 vertical excitation energies ($\Delta E_{VT}/\text{eV}$) and the amount of charge transfer ($\Delta q/\text{a.u.}$) from halide to water in the S_1 states of the $X^-(\text{H}_2\text{O})_{n=1-4}$ ($X=\text{F}, \text{Cl}, \text{Br}, \text{I}$) clusters. Experimental E_{CTTS} of $\text{I}^-(\text{H}_2\text{O})_n$ ($n=1-4$)^a and the E_{CTTS} of halides in bulk water are also included for comparison.

Cluster size (n)	ΔE_{VT}^b				$E_{\text{CTTS}}(\text{I}^-)$ (Expt) ^c	Δq			
	F^-	Cl^-	Br^-	I^-		F^-	Cl^-	Br^-	I^-
1	4.61 (6.94)	4.28 (6.27)	4.00 (5.58)	3.74 (4.98)	3.60	0.036	0.857	0.496	0.395
2	5.34 (7.58)	4.52 (6.55)	4.19 (5.83)	4.08 (5.17)	3.95	0.013	0.828	0.561	0.487
3	5.77 (7.94)	5.21 (6.99)	4.78 (6.22)	4.29 (5.49)	4.25	0.010	0.715	0.493	0.439
4	6.02 (8.00)	5.45 (7.42)	5.01 (6.45)	4.44 (5.65)	4.50	0.010	0.654	0.495	0.466
Bulk water ^a	...	[7.10]	[6.29]	[5.47]					

^aExperimental values as obtained from Ref. 14.

^bThe ΔE_{VT} values are calculated at the time dependent DFT-B3LYP and FOCI levels of calculation. The $\Delta E_{VT}/\text{FOCI}$ values are presented within parentheses.

^cReference 11.

clusters through first-order configuration interaction (FOCI) calculations. The Mulliken charges calculated for the S_0 and the S_1 states were used to monitor the amount of charge transfer to the water from the halide anion in the CTTS state. The restricted space FOCI generated S_1 states usually overestimate the E_{VT} values, and to get more reliable results we have further calculated the energy of the S_1 states using time dependent discrete Fourier transform density functional (DFT) technique.¹⁵ The Becke-3 exchange correlation¹⁶ together with the nonlocal functional provided by Lee, Yang, and Parr¹⁷ (B3LYP) was employed. The method is basically a first-order random phase approximation (RPA) calculation within the framework of DFT, and throughout the article we term this method as DFT-RPA. The accuracy of the calculation in DFT-RPA technique was checked against the experimental values of $\text{I}^-(\text{H}_2\text{O})_n$ clusters¹¹ and it was quite satisfactory. The minimum energy ground state geometries of the clusters were available through second-order Møller–Plesset (MP2) optimizations.¹⁸

In case of $\text{F}^-(\text{H}_2\text{O})_n$ clusters, Pople's 6-311++G** basis sets¹⁹ were used both for F and water. For other halide–water clusters the effective core potential (ECP) of Christiansen *et al.*²⁰ were used for the halogen (Cl, Br, and I) atoms, while the same 6-311++G** basis set was used for water. Following the suggestion of Combariza *et al.*,²¹ the Cl basis set was further augmented with one diffuse and three sets of d orbitals. The d orbital exponents were optimized for the use in ECP basis sets (exponents: 2.53, 0.76, and 0.2598). The Br ECP basis set was augmented with a set of one diffuse and five d orbitals, while the I basis set was augmented with two sets of diffuse and an extra d orbital. The choice of exponents was similar to the suggestion of Combariza and co-workers.²¹ All the calculations were carried out using GAMESS²² and GAUSSIAN98²³ program suites.

RESULTS AND DISCUSSION

The vertical transition energies of $X^-(\text{H}_2\text{O})_n$ clusters for the $S_0 \rightarrow S_1$ transition are presented in Table I. The calculations have been carried out using the minimum energy geometry of each halide cluster optimized at the MP2 level. For $\text{F}^-(\text{H}_2\text{O})_{n=1-4}$ clusters the chosen mono-, di-, tri-, and tetra-hydrated structures are of $1(C_1)$, $2(C_2)$, $3(C_3)$, and $4(C_1)$

geometry, and they were obtained from our previous calculation on the $\text{F}^-(\text{H}_2\text{O})_n$ clusters.¹³ The notation of each structure is represented by coordination number (n_1+n_2), with symmetries presented within parentheses. Here n_1 and n_2 , respectively, denote the number of water molecules in primary and secondary hydration shells, and consequently when $n_2=0$, the structure is simply represented as n_1 . The $\text{Cl}^-(\text{H}_2\text{O})_n$, $\text{Br}^-(\text{H}_2\text{O})_n$, and $\text{I}^-(\text{H}_2\text{O})_n$ clusters are of similar symmetry. Their mono-, di-, tri-, and tetra-hydrated cluster structures are of $1(C_s)$, $2(C_1)$, $3(C_3)$, and $4(C_4)$ type, respectively. These minimum energy structures are of the same type as obtained by Combariza *et al.*²¹ and have been found to explain their vibrational spectra.²⁴ A stereo view of the optimized structures for $\text{I}^-(\text{H}_2\text{O})_n$ clusters are presented in Fig. 1 as representative for the structures of $X^-(\text{H}_2\text{O})_n$ ($X=\text{Cl}, \text{Br}, \text{I}$) clusters. Regarding the position of the halide and the water molecules, the $\text{F}^-(\text{H}_2\text{O})_n$ clusters are similar in structure with respect to the other halide–water clusters up to $n=3$. In the case of tetra-coordinated cluster, the $\text{F}^-(\text{H}_2\text{O})_4$ cluster structure differs from the other halide–water clusters regarding the arrangement of water molecules around it. While in Cl^- , Br^- , and I^- cases the water molecules are on the same side of the halide ion (Fig. 1), in the $\text{F}^-(\text{H}_2\text{O})_4$ cluster the F^- ion is situated in the center of a pyramid with three water molecules on one side of F^- and the last water molecule on the opposite vertex, making it a strongly bound internal structure.¹³

The ΔE_{VT} values presented in Table I indicate that the values calculated at the RHF-FOCI level grossly overestimate the E_{CTTS} values when compared with the corresponding DFT-RPA values. A comparison of the ΔE_{VT} values of $\text{I}^-(\text{H}_2\text{O})_{n=1-4}$ clusters calculated at the DFT-RPA level with the experimental values of Johnson *et al.*¹¹ indicates that

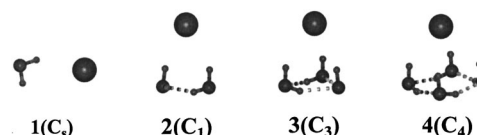


FIG. 1. Stereo view of the optimized minimum energy geometries of $\text{I}^-(\text{H}_2\text{O})_{n=1-4}$ clusters. The Cl^- and Br^- clusters have similar geometrical arrangements. For $\text{F}^-(\text{H}_2\text{O})_{n=1-4}$ cluster geometries, see Ref. 13.

TABLE II. Dissociation energies (ΔE_0), vertical binding energies (ΔE_0^v), electrostatic interaction energies between halides and water clusters (ΔE_{es}), the empirical CTTS energies (E_{CTTS}) for the $X^-(H_2O)_n$ ($X=F, Cl, Br, \text{ and } I; n=1-4$) clusters, and the dipole moments (μ/D) of the water clusters in the geometry of $X^-(H_2O)_n$.^a

X	n	Structure	$-\Delta E_0$	$-\Delta E_0^v$	μ of $(H_2O)_n$	$-\Delta E_{es}$	Empirical E_{CTTS}		
							$-\Delta E_0 + IP^b$	$-\Delta E_0 + IP^b + E_C^c$	$-\Delta E_0^v + IP^b + E_C^c$
F	1	1(C_s)	1.09	1.18	2.35	0.83	4.49	4.59	4.68
	2	2(C_2)	1.88	2.05	0.14	0.81	5.28	5.38	5.37
	3	3(C_3)	2.53	2.73	1.35	1.15	5.93	6.03	6.29
	4	4(C_1)	3.04	3.12	1.29	2.34	6.44	6.54	6.62
Cl	1	1(C_s)	0.57	0.57	2.33	0.54	4.18	4.28	4.28
	2	2(C_1)	1.07	0.99	3.85	0.93	4.68	4.78	4.70
	3	3(C_3)	1.57	1.28	3.33	1.25	5.18	5.28	4.99
	4	4(C_4)	2.03	1.54	3.91	1.64	5.64	5.74	5.25
Br	1	1(C_s)	0.50	0.52	2.32	0.23	3.86	3.96	3.99
	2	2(C_1)	0.96	0.89	3.93	0.30	4.32	4.42	4.36
	3	3(C_3)	1.43	1.16	3.98	0.63	4.79	4.89	4.63
	4	4(C_4)	1.86	1.38	4.19	0.93	5.24	5.34	4.85
I	1	1(C_s)	0.41	0.43	2.32	0.22	3.47	3.57	3.59
	2	2(C_1)	0.81	0.71	4.13	0.27	3.87	3.97	3.89
	3	3(C_3)	1.24	0.88	3.98	0.52	4.30	4.40	4.04
	4	4(C_4)	1.67	1.00	4.89	0.75	4.73	4.83	4.16

^aAll the energy values are in eV. ΔE_0 and ΔE_0^v are corrected with ZPE and $\frac{1}{2}$ (BSSE) at the MP2 level. The structures of Cl^- , Br^- , and I^- water clusters are available in Fig. 1, while the $F^-(H_2O)_n$ cluster structures are in Ref. 13.

^bThe IPs of F^- , Cl^- , Br^- , and I^- are taken to be 3.40, 3.61, 3.37, and 3.06 eV, respectively (Ref. 30).

^cThe E_C values are the energies for process C in Fig. 2. For 1, 2, 3, and 4 water clusters the values are uniformly taken to be 0.1 eV. See the text for more details.

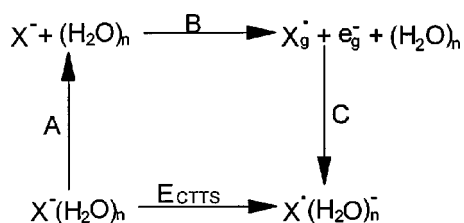
they are quite satisfactory. Henceforth, for further analysis, these DFT-RPA values would be used as representatives of the theoretically calculated E_{CTTS} energies. An examination of the calculated charge transfer from halide to water (Δq) in the S_1 state indicates that for Cl^- , Br^- , and I^- clusters, the charge transfer to water is appreciable, while for F^- clusters this charge transfer is marginal. This observation develops a feeling that the CTTS phenomena could be less probable in fluoride clusters. However, for the sake of completeness of our study for halide series we will consider the ΔE_{VT} values of fluorides also for further analyses.

The ΔE_{VT} ($\equiv E_{CTTS}$) values of $X^-(H_2O)_n$ clusters as presented in Table I indicate that there is a regularity in the change of these values with respect to the halide ion and the cluster size. For a particular cluster size, the E_{CTTS} values decrease from F^- to I^- , while keeping the halide ion fixed, the E_{CTTS} values increase with increase of cluster size. Let us first try to visualize the increase of E_{CTTS} values with the increase of cluster size for a particular halide ion. Johnson and co-workers,¹¹ while explaining the observed trend of E_{CTTS} values on $I^-(H_2O)_{n=1-4}$ clusters, suggested that since in their optimized minimum energy structures the water molecules are on the same side of the I^- ion, the electron is increasingly getting stabilized by interaction with the increasing dipole moment of the water cluster. This increasing dipole moment of the water cluster arises due to the presence of halide ion, as the isolated neutral $n=3$ and 4 water clusters display very small or zero ($n=4$) dipole moment.^{25,26} This explanation is qualitatively reasonable but needs quantitative explanation of the increasing E_{CTTS} values. Table II lists the extracted dipole moment of the water clusters in the equilibrium geometry of $X^-(H_2O)_n$. The results are more or less consistent with the observation of Johnson and

co-workers.¹¹ However, in $F^-(H_2O)_n$ clusters the dipole moment trend is not consistent with the increasing E_{CTTS} values. For other halide clusters also there are deviations in $n=2$ and 3 cases. The dipole moment of the $n=2$ water cluster is slightly larger or almost similar to the $n=3$ clusters. Thus for electrostatic stabilization the charge on the halide is also important. The calculated electrostatic interaction energies between the halide and the water clusters as presented in Table II indicate that for a particular halide the electrostatic stabilization increases with cluster size. It could also be seen that for a particular cluster size the electrostatic stabilization decreases from F^- to I^- . Thus this decreasing stabilization could also be taken as a factor to account for their decreasing E_{CTTS} values. The variation of the E_{CTTS} values as observed in Table I, of course, still needs to be explained in a more quantitative way.

It has been observed both experimentally¹¹ and in the present theoretical calculation, that the CTTS bands of iodide-water clusters show blue shift with stepwise increment of water cluster size. The calculated CTTS bands of other halide-water clusters show a similar trend. In case of $I^-(H_2O)_{n=1-4}$ clusters it has been argued that presumably the cluster analogs to the CTTS band correspond to excitation of the electron from an orbital localized on I^- into a delocalized state supported by the network of water molecules in the cluster. The neutral molecules with dipole moments larger than ~ 2.5 D can bind an electron in a dipole state due to exchange repulsion between the excess electron and the electrons in the molecules.^{26,27} In view of the dipole moments of the water molecules induced by the halides (Table II), it could be reasonable to assign the upper state of the $I^-(H_2O)_{n=1-4}$ cluster, initially generated by the pump

pulse, to a short-lived state of the form $I(^3P_2) \cdot (H_2O)_n^-$ in which the electron is transferred from the iodide to a dipole-bound state of solvent network.¹¹ This argument could be generalized for other halide–water cluster CTTS spectra also. In the earlier attempts to explain the CTTS spectra theoretically,⁵ the formation of $X \cdot (H_2O)_n^-$ species was assumed to involve several energy steps. It is obvious from the present discussion that the transfer of an electron from X^- to the water network needs preliminary dissociation of the $X^-(H_2O)_n$ to X^- and $(H_2O)_n$ to facilitate the detachment of an electron from the halide anion. The electron would then be finally recaptured by the water network with the resolution of the halogen atom to form the $X \cdot (H_2O)_n^-$ species. These, of course, are the well-known energy steps to explain the CTTS process⁵ and the energy cycle as presented in Scheme I



could be considered to be operative. The success of such an energy cycle to explain the CTTS spectra obviously lies in the proper interpretation of the energy steps involved. Process A in Scheme I involves separation of the halide anion and water cluster in the gas phase. The energy associated for the process would be the dissociation energy of the halide cluster. Process B involves the transition of the electron from the halide to the solvent and the energy factor would be the IP of the halide anion. Process C is usually approximated to be associated with two energy terms. The first one is the binding energy (i.e., electron affinity, EA) of the water clusters and the second term is the enthalpy of solvation $\Delta H(X^*)$, as process C also involves the resolution process of X^* . These two terms are not usually easy to calculate satisfactorily. However, both the calculated²⁶ and experimental²⁸ EA values for small water clusters are known to be very small. For the anionic water cluster geometries, analogous to our $X^-(H_2O)_{n=1-4}$ cluster structures, they were predicted to be 0.0, 0.01, 0.04, and 0.03 eV, respectively for $n=1-4$ at very high levels of calculation, and these values do not change significantly unless the geometries are drastically changed.²⁶ The $\Delta H(X^*)$ term is also very small and in most of the previous calculations they were considered to be the half of the heat of solution of the corresponding halogen molecule and uniformly taken to be 4.6 kcal mol⁻¹ for all the halogens in aqueous solution.⁵ The estimation of $\Delta H(X^*)$ is, however, very gross here. In small clusters this value could be expected to be much less than 4.6 kcal mol⁻¹ and the value could only be between 0.05 and 0.1 eV for $n=1-4$ clusters. Thus, in view of the very small contribution of EA and $\Delta H(X^*)$ values, we approximate the E_C term uniformly to be 0.1 eV for all the clusters. The contribution of this E_C term to the total CTTS energy is obviously very small, and thus the main factors to account

for the E_{CTTS} values of the $X^-(H_2O)_n$ clusters would be the IP of the halide anion and the dissociation energy of the halide–water cluster. The electrostatic interaction energy could be responsible for the cluster stability but its inclusion with IP values of the respective halides could explain only 20% of the observed/calculated trend of the E_{CTTS} values. Table II lists the calculated dissociation energy (ΔE_0) of the halide clusters. These dissociation energies are corrected with the zero-point energy (ZPE) and the basis set superposition error (BSSE) corrections. Since the full BSSE correction usually does not accurately explain the observed thermodynamic properties, we have used 50% BSSE correction here from our previous experiences of the medium-size basis results.²⁹ The empirical E_{CTTS} values calculated as the sum of $IP(X^-)$ and $\Delta E_0[X^-(H_2O)_n]$ are presented in Table II and they are in good agreement with the magnitude as well as the variation of ΔE_{VT} ($\equiv E_{CTTS}$) values presented in Table I. In view of the small contribution of the E_C values, this term was not included in this approximation. The inclusion of this term ($E_{CTTS} = -\Delta E_0 + IP + E_C$) generally improves the E_{CTTS} values when compared to our theoretically estimated energies, but in case of $I^-(H_2O)_n$ this approximation could be seen to slightly overestimate the CTTS energy for higher n (Table II). In view of the vertical nature of the CTTS energy, one may consider the ΔE_0 values to be an empirical representative of the energy step A, as its estimation involves solvent relaxation. The vertical binding energy (ΔE_0^V), where the water molecules have their dipoles oriented towards the anion, could be viewed as the more logical definition of step A. These values are given in Table II and it could be seen from the table that the combination of ΔE_0^V with IP and E_C gives almost equivalent answer to the E_{CTTS} values with respect to the two previous approximations. It is to be noted further that the dissociation energy of the halide clusters in bulk water is higher than its small water clusters, and it is thus quite obvious why the E_{CTTS} values of the halides in bulk water as represented in Table I are much higher than their small clusters.

CONCLUSIONS

DFT-RPA calculations have been carried out on the minimum energy halide–water clusters, $X^-(H_2O)_{n=1-4}$ ($X=F, Cl, Br, I$) in order to calculate their CTTS energies. The calculations have been verified against the known observed CTTS spectra of $I^-(H_2O)_{n=1-4}$ clusters¹¹ and the results are found to be quite satisfactory. The calculated CTTS values of $X^-(H_2O)_n$ clusters indicated that they have a regular change of CTTS energy with the change of the halide anion and with the variation of the cluster size. For a particular cluster size the CTTS energy decreases from F^- to I^- clusters, while for a fixed halide cluster the CTTS energy increases with the increase in cluster size. Our present analyses have indicated that although the electrostatic stabilization is an important factor to explain the observed trend, the ground state stabilization energy of the clusters together with the halide IPs are the deciding factors to quantitatively explain the observed CTTS energy variations. The decreasing IPs from F^- to I^- together with the decreasing binding en-

ergies for a fixed cluster size clearly account for their decreasing CTTS energy trend. Similarly the increasing binding energy in a particular $X^-(H_2O)_n$ series accounts for their increasing CTTS energy. Furthermore, the dependence of CTTS energy on the ground state binding energy of the halide cluster accounts for the higher CTTS energy value of the halide ions in bulk water with respect to the small clusters.

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