Intersystem Electron-Transfer in Di-hydrated Iodide Anion

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The hydrated electrons of small size have been experimentally and theoretically investigated.[1-9] The electron-water clusters can be prepared from neutral water vapor using low-energy electron beam and from charge transfer from anions.[1-5] The hydrated anions with small numbers of waters have been studied through the experimental and theoretical tools for their structures, interaction energies, and spectra, especially for iodide among halide anions.[10-17] These two categories are very close in view of chemical insight.

Many chemists reported the charge-transfer phenomena in hydrated halide anions using laser excitation.[18-28] The excitation energies of hydrated anions were reported as the charge-transfer-to-solvent (CTTS) energies. The hydration of electron from iodide-water clusters was studied by using the photo-excitation and the ultrafast dynamics using femtosecond time-resolved spectra.[22] Molecular dynamics and simulation studies were performed for the hydration of electron from halide anions.[23-25] The charge-transfer phenomena can be figured out in various chemical processes.[26,27] Already we studied the CTTS and CTTS precursor states, iodine relaxation at excited state, rearrangement pathway to the lowest-energy electron-water pentamer and hexamer from the lowest-energy iodide-water pentamer and hexamer using high level *ab initio* calculations.[28]

Here the CTTS process of iodide-water dimer and the hydration of excited excess electron [$I^-W_2(^1P_1) \rightarrow I^0(^2P_{3/2}) + e^-W_2(^2S_{1/2})$] are studied by using *ab initio* methods. This study is interesting and important in order to understand the formation mechanism and stabilization of electron-water dimer, the relationships between anion-water and electron-water dimer, and the electronic properties and phenomena of solvated or hydrated anions and electrons.

The structures of di-hydrated iodide[17] and electron[6] previously studied at B3LYP/6-311++G**, B3LYP/6-311++G** [sp] and MP2/aug-cc-pVDZ+(2s2p/2s) levels were adapted in this study. The extra diffuse functions in brackets and parentheses have the exponent values scaled by 1/8 from those of the outermost basis functions in conventional basis sets. The CTTS energies of halide-water clusters were

predicted at the RPA-B3LYP/6-311++G**, CIS/6-311++G**(sp) and CIS/aug-cc-pVDZ+(2s2p/2s) levels of theory. The IR spectra were calculated at B3LYP/6-311++G**(sp), MP2/6-311++G**(sp), CIS/6-311++G**(sp), MP2/aug-cc-pVDZ+(2s2p/2s), and CIS/aug-cc-pVDZ+(2s2p/2s) levels of theory. All calculations were performed by using a Gaussian 03 suite of programs.[29] Some important figures were plotted using the Pohang-Tech Molecular Modeling (POSMOL) package.[30]

Iodide-water dimer: The iodide-water clusters have been investigated and compared to the experimental results.[14-17] The lowest-energy iodide-water dimer has C_1 symmetry and one water-water H-bond interaction and two ion-water interactions as shown in Figure 1. The iodide anion is surface-bound state with two water molecules. Its structure, energetics, spectroscopic data and electronic properties have already been discussed.[14-17] Here we use its structure in order to understand the electron transfer and the formation of electron-water dimer.

CTTS of iodide-water dimer: The iodide-water dimer shows the iodine-released excited state from the vertical third singlet excited state at MP2/6-311++G**(sp) level (Figure 1). The B3LYP, MP2 and CIS calculations using 6-311++G**(sp) basis set provide the transformation from CsT to CsC conformer, in which the latter conformer is known to be more stable than the former. However, the MP2 and CIS calculations using aug-cc-pVDZ+(2s2p/2s) basis set give slightly high-energy barrier between CsT and CsC conformers, due to the augmented and diffuse basis functions. The CIS/6-311++G**(sp) calculation can also provide the iodine-released structure with $^2P_{1/2}$. And then here, we report the CIS/6-311++G**(sp) calculation results. Table 1

Rearrangement and rehybridization
of cluster orbitals and configuration interactions
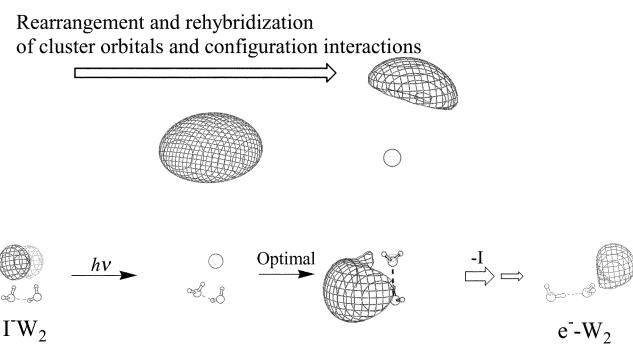
Figure 1. Prediction of CTTS process from iodide-water dimer.

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Table 1. The B3LYP/6-311++G**[sp] HOMO-LUMO and HOMO-LUMO2 energy gaps (δE_{H-L} and δE_{H-L2}) of I^-W_6, the vertical excitation energies (CTTS) from the ground state, and the VDE of the CTTS precursor state[a]

B3LYP		CTTS			CIS		MP2	
δE_{H-L}	δE_{H-L2}	RPA	CIS	MP2	$\delta q^I(S_0^{1;3})$	$r^{O-I}(S^{1;3})$	μ_{neut}	VDE
3.77	3.85	4.08	4.37;4.53[b] (3.93;4.07)	3.98 (3.86)	0.00;0.01 0.33;0.20	10.2;8.3	4.14	0.007

[a]All energies are in eV. The 6-311++G**[sp] was used at B3LYP calculations, 6-311++G**(sp) at CIS, and aug-cc-pVDZ+(2s2p/2s) at MP2. For realistic values, the shifted values by 0.90 are in parentheses at CIS/6-311++G**(sp) level and 0.97 at MP2/aug-cc-pVDZ+(2s2p/2s) level. The δq^I values in the first row are transferred charges at vertical excited states and those in the second row at optimized excited states. [b]The second values for iodide-water dimer at CIS are of the third CIS/6-311++G**(sp) excitation which has a virtual orbital for the charge transfer. $r^{O-I}(S^{1;3})$ indicates minimal oxygen-iodine distance (Å) of optimized excited state at CIS/6-311++G**(sp). The CIS/aug-cc-pVDZ+(2s2p/2s) calculation of iodide-water dimer results in the excitation energies for S_1; 4.32, S_2; 4.35, S_3; 4.35, S_4; 4.35 and S_5; 4.35 eV.
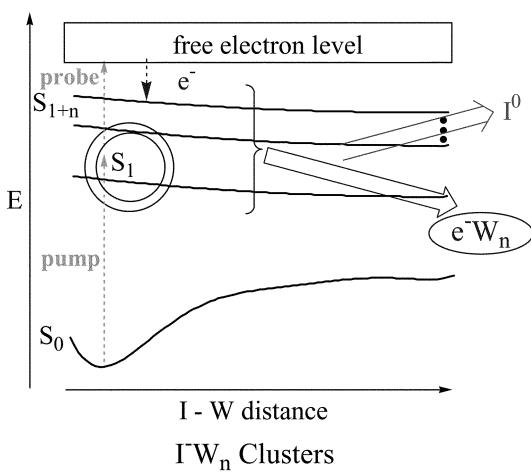
Figure 2. Potential-energy-surfaces (PESs) for the release process of iodine atom at excited states of iodide-water clusters.

lists the excitation energies and interesting electronic properties of iodide-water dimer.

The brief CTTS processes are drawn in Figure 2. Some excited states can easily decay due to the unfavorable electron-water binding states (Figure 2), which depend on the corresponding virtual orbitals and water structures for the excited electron. Experimentally, iodide-water pentamer and hexamer showed the kinetic energy changes from the excited states (CTTS states) due to the VDE variations, while iodide-water tetramer did not provide any kinetic energy change.[22] In iodide-water dimer case, the VDEs of vertical and optimal excited states (^1D or $^2P_{3/2}+^2P_{1/2}$) as the CTTS states are very low and similar to that of electron-water dimer. Then, the experimental and computational CTTS processes could give weak variations in the electron kinetic energy spectra, but the photo-induced charge transfer to water dimer complex could appear in iodide-water dimer due to the low-energy dihydrated electron. The excitation energies are close to the experimental data (~3.9 eV) as listed in Table 1.[11]

The optimal distances between iodine atom and water dimer at the first and second singlet excited states at the CIS/6-311++G**(sp) level are similar to that of ground state of iodide-water dimer within about 1~2 Å of the difference, while the iodine-water distance at the third singlet excited state is released upto about 8.3 Å. The rehybridization and

rearrangement of cluster orbitals and configuration interactions were performed through the iodine release process. The optimized structures at excited states have nearly degenerate low-energy excited states for the singlet excitation, due to the nearly degenerate three p orbitals of iodide anion. The first excited state releases the iodine at about 10 Å, and the second excited state, at about 8.4 Å. The ^1P ($^2P+^2S$) state is higher excited state than the ^1D states at vertical excited states, due to the hydration effect. The transferred charges are about 0.2-0.3 a.u. Through the intersystem crossing (ISC) process, the singlet excited state can be transformed into the triplet excited state with a hole and an electron of the opposite spin states, inducing more released structure.

Electron-water dimer: For the iodide-water hexamer, some rearrangement pathways to the lowest energy electron-water hexamer from the CTTS state are essential, as noted in Neumark's experiments,[22] while the electron water dimer (with s-like singly occupied cluster orbital; $^2S_{1/2}$) can be easily formed with iodine-detaching from the iodide-water dimer *via* a CTTS process, without any rearrangement pathway of water structure. The electron-water dimer is one of the magic numbers of excess electron-water clusters in mass spectra.[1-5] The VDE observed was about 0.05 eV. In theoretical calculations, two possible isomers (CsC and CsT conformers) have been observed. The CsC conformer is more stable, with larger dipole moment and higher VDE, which is estimated to be close to the experimental value at MP2/aug-cc-pVDZ+(2s2p/2s), CCSD//MP2/aug-cc-pVDZ+(2s2p/2s) levels and higher levels of theory.[6]

IR spectra of di-hydrated iodide and electron: Figure 3 reports the IR spectra of the ground and excited states for iodide-water dimer, the electron-water dimer, and neutral water dimer at B3LYP/6-311++G**[sp], MP2/6-311++G**(sp), and MP2/aug-cc-pVDZ+(2s2p/2s) levels of theory. These spectra were drawn using the shift values for the OH stretching modes of component water molecules with respect to the average value of asymmetric and symmetric OH stretching frequencies of pure water monomer, and the zero-shift value is compatible to the experimental average value (~3700 cm^{-1}) for two stretching data ($\nu_3 = 3756$ and $\nu_1 = 3657$ cm^{-1}) of pure water monomer.[31] The complexes provide the characteristic spectral changes for OH stretching modes through the photo-induced charge-transfer process.
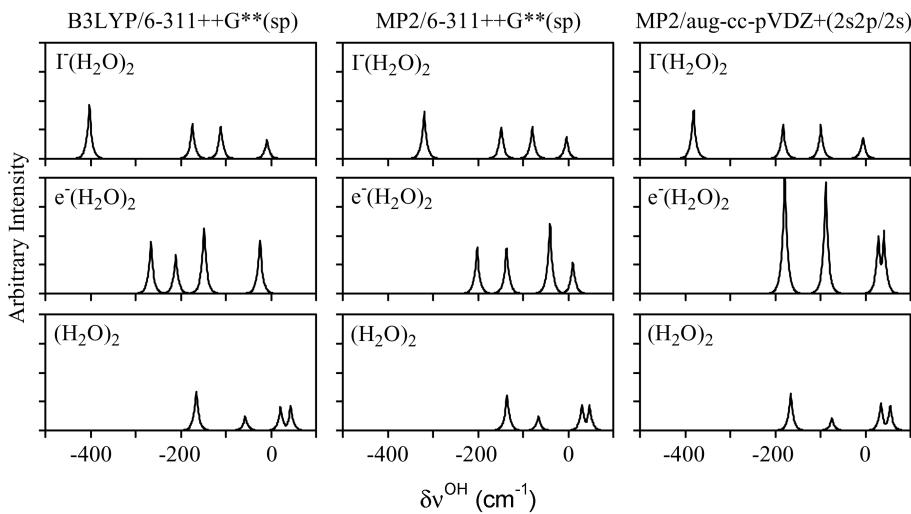
Figure 3. B3LYP/6-311++G**(sp) (in the first column), MP2(CIS)/6-311++G**(sp) (in the second column), and MP2/aug-cc-pVDZ+(2s2p/2s) (in the third column) IR spectra of the ground and excited states of iodide-water dimer, electron-water dimer, and neutral water dimer.

The excited iodide-water dimer and electron-water dimer show the intensive IR peaks due to flexible electron density. The red shifts depend on the strengths of ion-water, water-water and electron-water interactions. The shifts of iodide-water dimer are higher due to strong ion-water interactions than those of electron-water dimer and neutral water dimer. The neutral water dimer has the smaller shifted spectra. The B3LYP/6-311++G**(sp) IR spectra show higher shifted OH stretching frequencies with respect to the MP2 ones. The estimated IR spectra of iodide-water dimer are very close to the experimental results.[14]

In summary, using these quantum chemical calculations, the photo-induced electron-transfer of iodide-water dimer was investigated, and the spectroscopic characteristics from iodide-water dimer to electron-water dimer were understood through the CTTS process. The water dimer clusters can be easily detected probabilistically. At the CTTS state, the neutral iodine atom was released, and excited electron was transferred to dipolarized water dimer. The water structure of excited iodide-water dimer is very similar to di-hydrated electron. The release of iodine atom at the excited state of iodide-water dimer from the ground state of iodide-water dimer could be expected to be exothermal process. This study could be useful to understand other photo-induced charge-transfer phenomena.

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