Proton and charge transfers in water solvent have been an issue in the quantum dynamics and energetics of (H$_2$O)$_n$ clusters. Although the structure and solvent effect of hydrated and neutral water clusters in chemical and biological processes have been extensively investigated with the theoretical and experimental methods, the Rydberg (H$_2$O)$^+(e^-)_n$ radical has not been studied until now. The Rydberg (H$_2$O)$^+(e^-)_n$ radical can be formed in water clusters like the Rydberg (NH$_3$)$^+(e^-)_n$ radical. In the Rydberg (NH$_3$)$^+(e^-)_n$ radical, the stability and electronic structure of NH$_3$ depend greatly on the avoided curve crossing between the dissociative state of (NH$_3$)$^+(e^-)_n$ and the repulsive state emerging from (NH$_3$)$_n$. In ammonia clusters, NH$_3$ has been known to be stabilized by the complexation with ammonia species. The lifetime of the NH$_4$ radical in cluster was measured to be 13 picosecond.

In this work, we studied state-to-state transfer curves of the ground and excited states for H$_2$O dissociating into (H$_2$O + H). For the dissociation reaction, the molecular orbitals and geometric structures at each internuclear distance were optimized using the restricted open-shell Hartree-Fock method (ROHF), keeping $C_2v$ symmetry. And the molecular orbitals and optimized structures were used as input for subsequent the singly and doubly excited configuration interaction (SDCI) calculations. That is, the molecular orbitals for a configuration interaction (CI) are determined with the ROHF's results. The singly and doubly excited configuration interaction (SDCI) calculation is used with the GAMESS package. By changing the internuclear distance, the entire procedure was repeated from H$_2$O to (H$_2$O + H). The internuclear distances [R$_{	ext{H..O}}$] range from 0.80 to 10.0 Å. The SDCIs for H$_2$O, H$_2$O$^+$, and H$_2$O$_2$ are also performed separately. The geometric structures of the ground states of H$_2$O, H$_2$O$^+$, and H$_2$O$_2$ are also optimized with the second-order Muker-Plesset (MP2) and coupled cluster with both single and double substitution [CCSD(T)] levels using GAUSSIAN 94. The basis sets chosen are the triple-zeta basis on O (311111/32211) and H(511). Two extra $d$ type polarization functions are added to oxygen ($\alpha_{o}=2.22, 0.874$) and one extra $p$ type function is added to hydrogen ($\alpha_{p}=0.0990495$). The diffuse Rydberg basis functions ($\alpha_{o}=0.08$, 0.032; $\alpha_{p}=0.051, 0.02$; $\alpha_{o}=0.345, 0.145$) are further augmented on oxygen to describe the Rydberg states of H$_2$O and H$_2$O.

The geometric parameters and the relative energies of H$_2$O dissociating into (H$_2$O + H) are listed in Table 1 together with the ionization and excitation energies of H$_2$O and H$_2$O. There are no previous experimental and theoretical results on H$_2$O to compare with our results. Since the ground state of H$_2$O has an electron in a Rydberg 3$s$ orbital, H$_2$O itself is often called the Rydberg radical and H$_2$O is a semi-ionic structure described as (H$_2$O$^+$)(e$^-$)$_n$. Therefore, in the ground geometric structure of H$_2$O, the equilibrium internuclear distance of R$_{\text{H..O}}=1.02$ Å is longer than that of R$_{\text{H..O}}=0.962$ Å of H$_2$O. The bond length [R$_{\text{H..O}}$] at the transition state is $\approx$ 1.21 Å, that is, the bond breaking takes place near the equilibrium geometry of H$_2$O. The energy barrier heights from the transition state to H$_2$O and (H$_2$O + H) are $\approx$ 0.11 and 0.93 eV, respectively. The energy gap between H$_2$O and (H$_2$O + H) is $\approx$ 0.82 eV. Because the ground potential of H$_2$O has an energy barrier of $\approx$ 0.11 eV along the OH bond rupture, H$_2$O is very unstable. Because of the weak interaction between the nucleus and a Rydberg electron, the ionization and excitation energies of H$_2$O are relatively low.

Potential energy curves for the ground and low lying excited states of H$_2$O dissociating into (H$_2$O + H) are drawn in Figure 1. They are labeled as 1$A_g$, 2$A_g$, 3$A_g$, 1$B_g$, and 2$B_g$, respectively. The potential energy of (H$_2$O + H) is set equal to zero. To represent the avoided curve crossing clearly, the broken lines indicate estimated diabatic potential energy curves and these were drawn by hands. The ground 3$A_g$ state of H$_2$O correlates with an antibonding orbital emerging from the [H$_2$O(2$A_g$) + H(c$S$)] asymptote. This

### Table 1. Geometric parameters and relative energies (eV) for the ground 3$A_g$ state along the H$_2$O radical dissociating into (H$_2$O + H).

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>SDCI</th>
<th>MP2$^{ab}$</th>
<th>CCSD(T)$^{ab}$</th>
<th>MP2$^{ab}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E_{\text{3$A_g$}}$</td>
<td>0.984</td>
<td>0.984</td>
<td>1.018</td>
<td>1.021</td>
<td>1.020</td>
</tr>
<tr>
<td>$\Delta E_{\text{3$A_g$}}$</td>
<td>107.6</td>
<td>106.3</td>
<td>105.0</td>
<td>105.7</td>
<td>105.9</td>
</tr>
<tr>
<td>$\Delta E_{\text{3$A_g$}}$</td>
<td>1.741</td>
<td>1.222</td>
<td>1.201</td>
<td>1.210</td>
<td>1.210</td>
</tr>
<tr>
<td>$\Delta E_{\text{3$A_g$}}$</td>
<td>0.099</td>
<td>0.132</td>
<td>0.112</td>
<td>0.11</td>
<td>0.11</td>
</tr>
<tr>
<td>$\Delta E_{\text{3$A_g$}}$</td>
<td>1.45</td>
<td>1.047</td>
<td>0.970</td>
<td>0.91</td>
<td>0.93</td>
</tr>
<tr>
<td>$\Delta E_{\text{3$A_g$}}$</td>
<td>-1.99</td>
<td>-1.84</td>
<td>-0.90</td>
<td>0.82</td>
<td>1.09</td>
</tr>
</tbody>
</table>

$^{ab}$MP2 energies were obtained with GAUSSIAN 94. 
$^{9}$Ref. 10. 
$^{10}$Ref. 15. 
$^{11}$Unit of internuclear distance is angstrom. 
$^{12}$Unit of angle is degree. 
$^{13}$Ionization energy of H$_2$O. 
$^{14}$Optical ionization energy of H$_2$O. 
$^{15}$Proton affinity of H$_2$O. 
$^{16}$Ref. 13. 
$^{17}$Ref. 9. 
$^{18}$Ref. 11.
communications to the editor

b. the Rydberg H$_2$O radical dissociating into (H$_2$O + H)

curve is quasibound, which means that its equilibrium energy is higher than that of the dissociation asymptote of (H$_2$O + H). The potential curve has an energy barrier near the equilibrium geometry of H$_2$O. It is made by an avoided curve crossing between the diabatic diabatic state of the Rydberg [H$_2$O($^1A_g$)] radical and the repulsive diabatic state emerging from an antibonding orbital of the [H$_2$O ($^1A'_g$) + H($^1S$)] asymptote. The barrier height and potential well are very low and shallow, respectively. The maximum position $R_{\text{min}}$ = 1.21 Å of the transition state of the ground potential curve is located out of line of those $R_{\text{min}} \approx 1.95$ Å of the first and higher excited states. In H$_2$O dissociating into (H + O), the ground Rydberg H$_2$O radical diabatically dissociates into two kinds of asymptotes, that is, H$_2$O diabatically dissociates into the [H$_2$O($^1A'$)] + H($^1S$) and [H$_2$O ($^1A'_g$) + H($^1S$)] asymptotes. In the second dissociation pathway, one electron jumps from the 1b$_1$ orbital of H$_2$O to the 1s orbital of H. The ion pair has strongly attractive ionic character as the ions approach each other. Therefore, by avoided curve crossing between two diabatic diabatic states of [(H$_2$O)$^2e^-$($^1A_g$)] and the repulsive diabatic state emerging from [H$_2$O($^1A'$)] + H($^1S$)], the potential well and barrier height should be very deep and high, respectively. But, since the energy gap between the [H$_2$O($^1A'_g$) + H($^1S$)] and [H$_2$O($^1A'_g$) + H($^1S$)] asymptotes is large, the potential energy barrier of the ground $^2A_g$ state is shifted to the equilibrium geometry of H$_2$O. The barrier height of the curve is found to be very low.

The dominant configuration for the ground $^2A_g$ state is [core]2$a^2_1$ 1$b^2_1$ 3$a^2_1$ 1$b^2_1$ 4$a^4_1$ at the H$_2$O structure and [core]2$a^2_1$ 1$b^2_1$ 3$a^2_1$ 1$b^2_1$ 4$a^4_1$ at large distance $R_{\text{OH}}$ = 10.0 Å. 2$a^2_1$ 1$b^2_1$ 3$a^2_1$ 1$b^2_1$ is an electronic configuration of H$_2$O$^-$ and 4$a^4_1$ indicates an electron of the Rydberg 3s orbital having a H$_2$O$^-$ structure as a core. Therefore, the electronic structure of H$_2$O appears to be [H$_2$O$^-$($^1e^-$)] and as a semionic state. Along OH bond rupture, the 4a$_1$ orbital is nonbonding, i.e., a character of 1s of H. 4a$_1$ indicates one electron in the 1s orbital of H.

Generally, the ground-to-Rydberg transition energies are found to be higher than 5 eV> eV. But, in H$_2$O the Rydberg excitation energy is found to be low, that is, the excitation energy (3s $\rightarrow$ 3p)$_{Rydberg}$ is 2.05 eV. While, in H$_2$O the excitation energy (1b$_1$ $\rightarrow$ 3p$_{\text{core}}$) is $\approx$ 10.21 eV. In the correlation curve, if the potential energy barriers of the ground and excited states are determined by the avoided curve crossings, the barrier height should be high and the maximum position should be located at the middle place between H$_2$O and (H$_2$O + H). But, in our ground potential curve of the dissociation, the potential energy barrier of $\approx 0.11$ eV is located near the equilibrium geometry of H$_2$O. In the avoided curve crossing between the attractive diabatic states emerging from [H$_2$O($^1A'_g$) + H($^1S$)] and [H$_2$O ($^1A'_g$) + H($^1S$)] and the repulsive state from an antibonding interaction of [H$_2$O($^1A'_g$) + H($^1S$)], the energy gap between two asymptotes plays an important role in the ground correlation curve. As a result, the position of the potential barrier is shifted to the equilibrium geometry of H$_2$O. That is, the maximum position of potential barrier of the ground state formed by the avoided curve crossing is located out of line of those of the excited potential energy curves. And the barrier height is found to be very low. Because of the low barrier, the existence of the Rydberg H$_2$O radical has not been observed experimentally.

In the excited $^2A_g$ state, the curve crossing between the diabatic diabatic excited states of (H$_2$O)($^1e^-$) and the repulsive diabatic states from the antibonding interaction of [H$_2$O($^1A'_g$) + H($^1S$)] are found around $R_{\text{min}}$ = 1.5 Å and 4.0 Å. In the excited $^2B_1$ (3s $\rightarrow$ 3p$_{\text{core}}$) state of H$_2$O, the state correlates with a bonding interaction of the [H$_2$O($^1B_1$) + H($^1S$)] asymptote. An antibonding interaction emerging from [H$_2$O($^1B_1$) + H($^1S$)] is found to be repulsive. By the avoided curve crossings between the attractive diabatic state emerging from the electrostatic interaction of [H$_2$O ($^1e^-$)] and the other states with the same symmetry, the potential energy curves of the ground and excited states for the dissociation of H$_2$O into (H + O) show an irregular shape. Our state-to-state correlation diagram gives detailed information of the crossing positions and barrier heights for H$_2$O dissociating into (H + O).

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