

**Protonation-Modulated Localization of Excess Electron in Histidine Aqueous
Solutions Revealed by Ab Initio Molecular Dynamics Simulations:
Anion-Centered versus Cation-Centered Localization**

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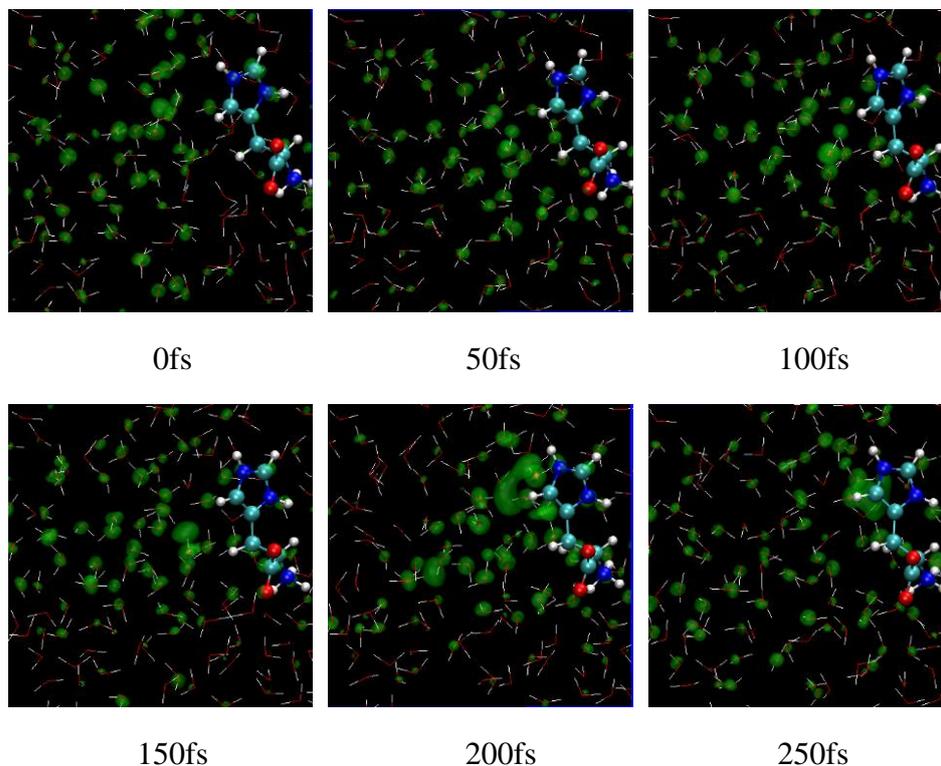
Supporting Information

Contents

- 1. The Excess Electron Localization in $\text{H}_3\text{His}^+_{\text{aq}}$.**
- 2. The Excess Electron Localization in $\text{H}_2\text{His}^0_{\text{aq}}$.**
- 3. The Excess Electron Localization in $(\text{H}_3\text{His}^+ + \text{Cl}^-)_{\text{aq}}$.**
- 4. The Excess Electron Localization simulated by PBE method**
 - 4.1 The Excess Electron Localization in $\text{H}_2\text{His}^0_{\text{aq}}$ simulated by PBE method.**
 - 4.2 The Excess Electron Localization in $(\text{H}_3\text{His}^+ + \text{Cl}^-)_{\text{aq}}$ simulated by PBE method.**
- 5. The Excess Electron Localization in relatively low concentrations.**
 - 5.1 The Excess Electron Localization in $\text{H}_3\text{His}^+_{\text{aq}}$ with a relatively low concentration.**
 - 5.2 The Excess Electron Localization in $\text{H}_2\text{His}^0_{\text{aq}}$ with a relatively low and realistic concentration.**
- 6. Comparison between Spin Density and Differential Electronic Density.**
- 7. Exchange Process of Solvating Water Molecules during Excess Electron Localization.**

1. The Excess Electron Localization in $\text{H}_3\text{His}^+_{\text{aq}}$

To obtain some representative configurations of slightly acidic histidine solution ($\text{H}_3\text{His}^+_{\text{aq}}$), 3 ns classical molecular dynamics (MD) simulations are performed on the $(\text{H}_3\text{His}^+) + (\text{H}_2\text{O})_{120}$ system in a cubic cell ($15.67 \text{ \AA} \times 15.67 \text{ \AA} \times 15.67 \text{ \AA}$) which corresponds to H_3His^+ with a density of 1.0 g/cm^3 . Periodic boundary conditions are applied in all three directions to reproduce the matrix. MD simulations are accomplished using Discover package implemented in the CERIUSt² 4.6 suite of program from Accelrys, Inc. Then AIMD simulations are carried out on different snapshot configurations extracted from the aforementioned equilibrated system. The periodically repeated box is equilibrated in the canonical ensemble (NVT) using the CP2K/Quickstep package. After equilibrating the system for 5 ps, one EE was added and another 1.0 ps simulation was carried out.



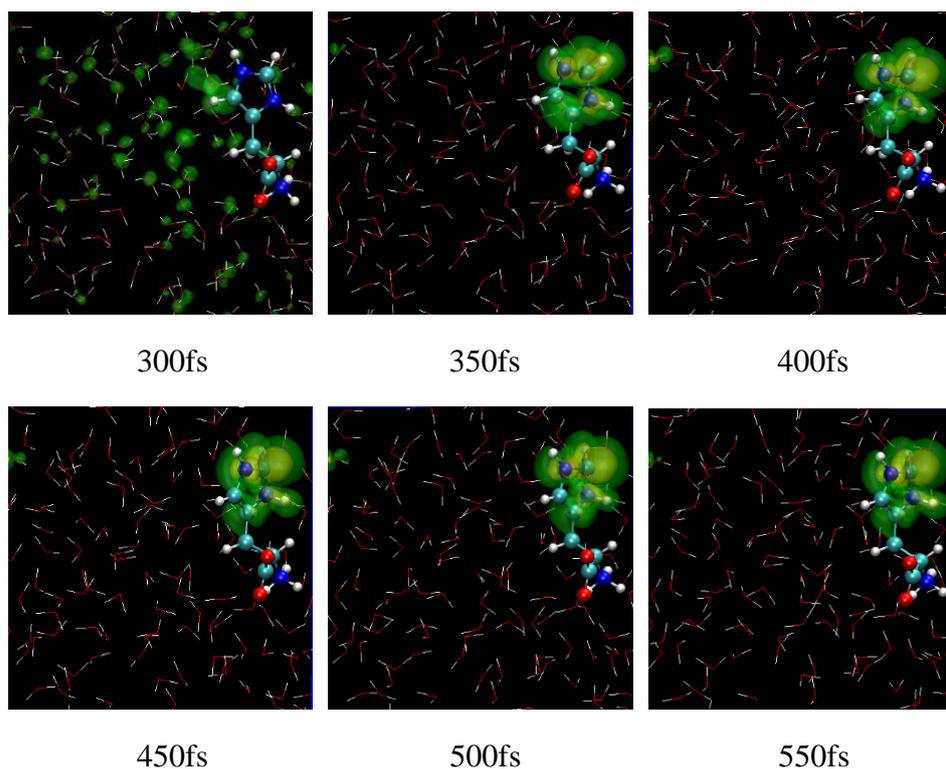


Figure S1. Visualized spin density distributions (isoval=0.0004) of representative snapshot configurations at different times in EE localization towards the ImH_2^+ group in $\text{H}_3\text{His}^+_{\text{aq}}$.

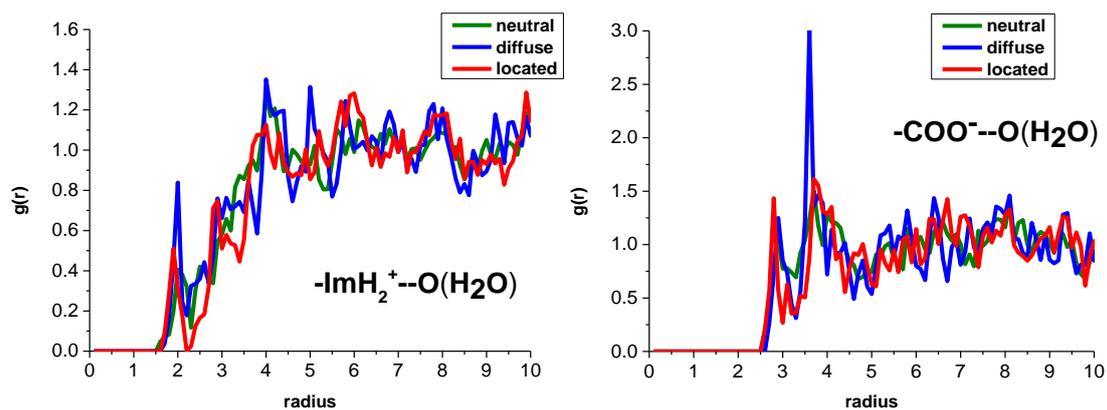
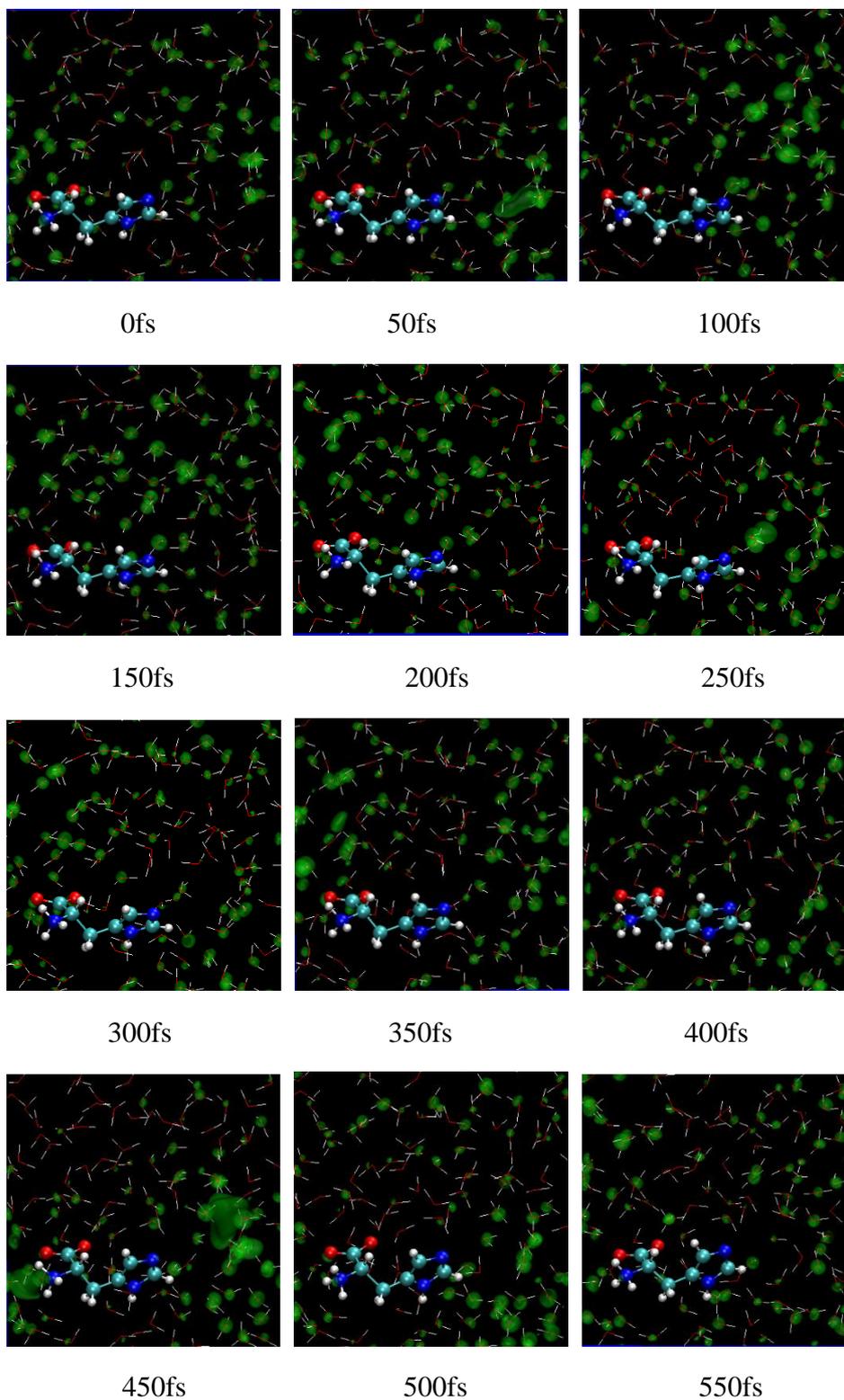
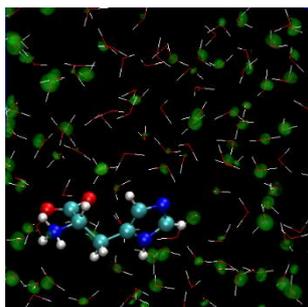


Figure S2. Radical distribution function (RDF) of ImH_2^+ group (left) and -COO^- group (right) with O in H_2O (Green: in neutral solution; Blue: in diffuse state; Red: in localized state).

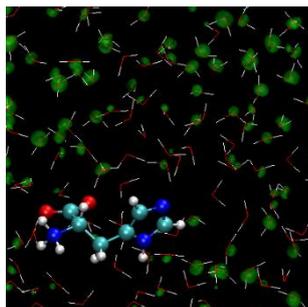
2. The Excess Electron Localization in $\text{H}_2\text{His}^0_{\text{aq}}$

The neutral histidine solution is simulated by a $(\text{H}_3\text{His}^+)+(\text{H}_2\text{O})_{120}$ system in a cubic cell ($15.67 \text{ \AA} \times 15.67 \text{ \AA} \times 15.67 \text{ \AA}$), which is treated in the same method as mentioned above..

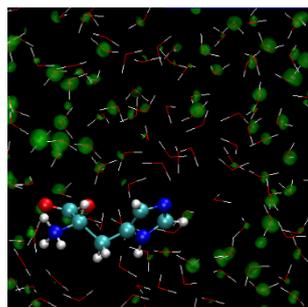




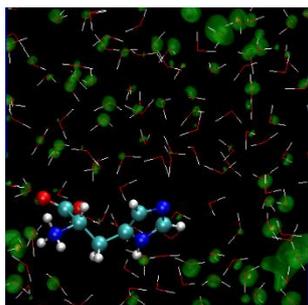
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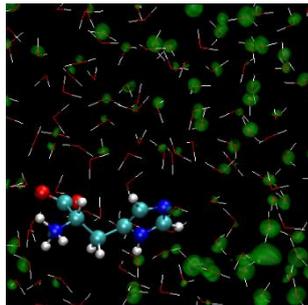
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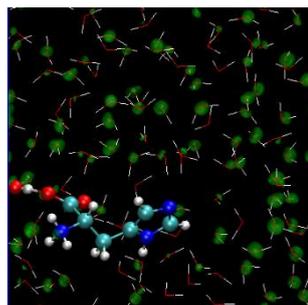
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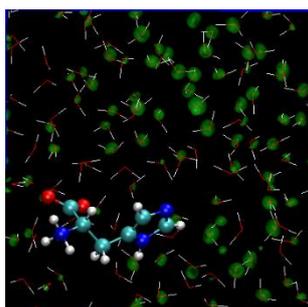
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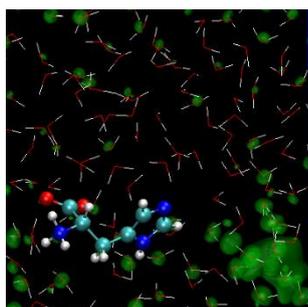
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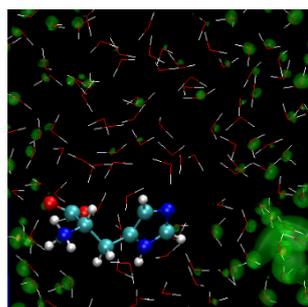
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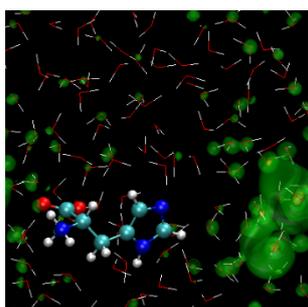
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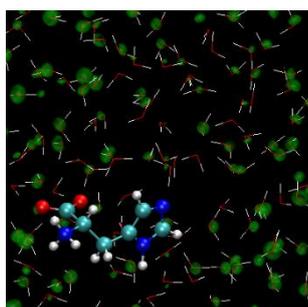
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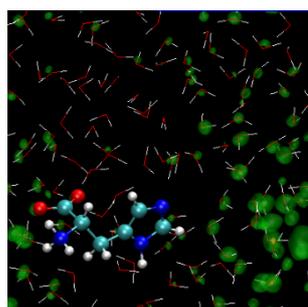
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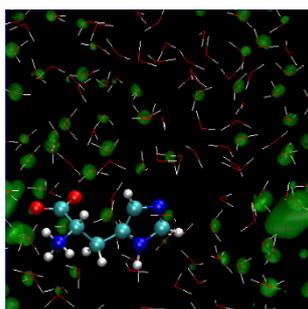
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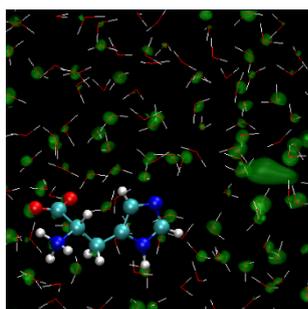
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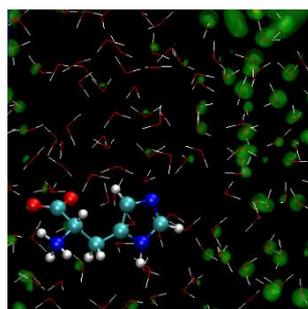
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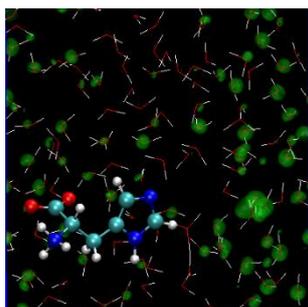
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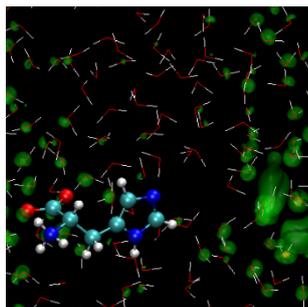
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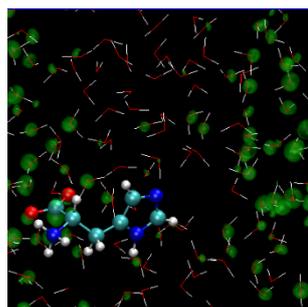
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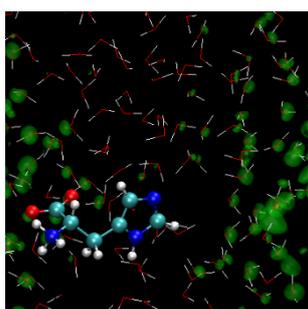
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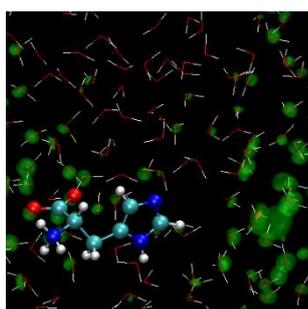
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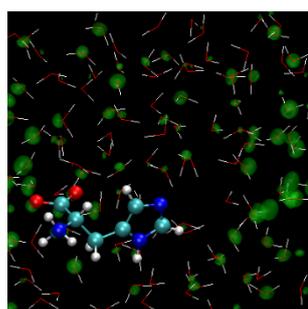
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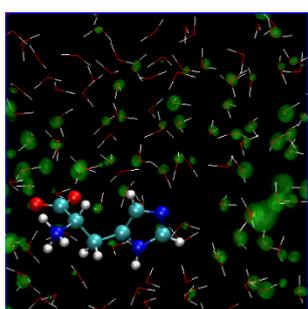
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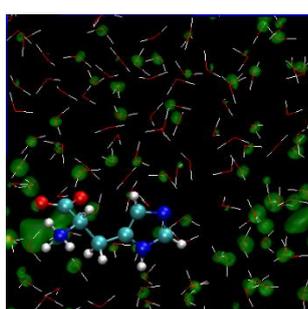
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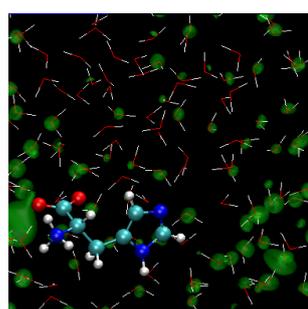
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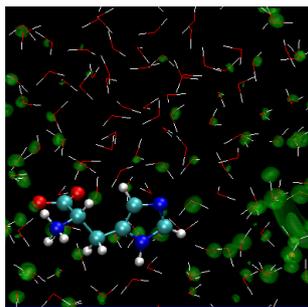
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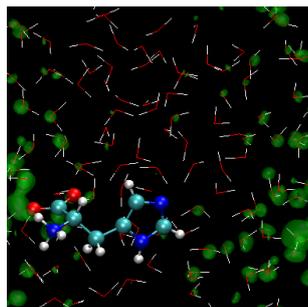
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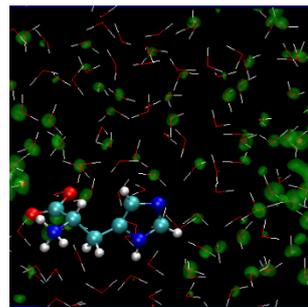
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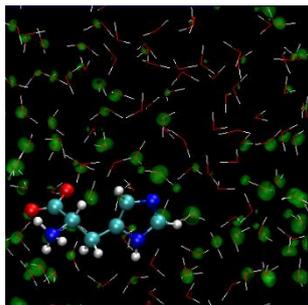
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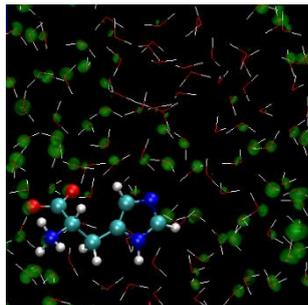
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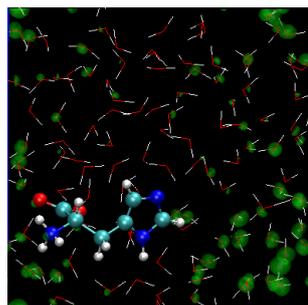
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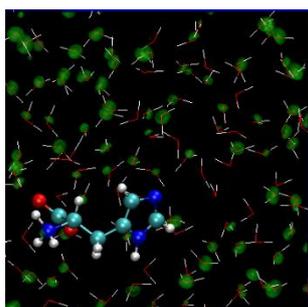
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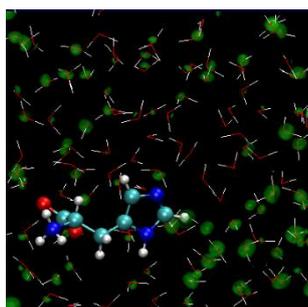
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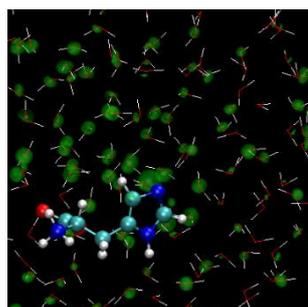
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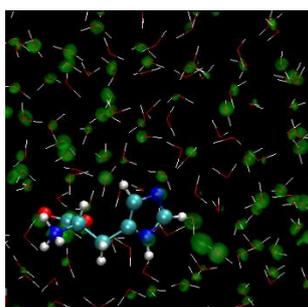
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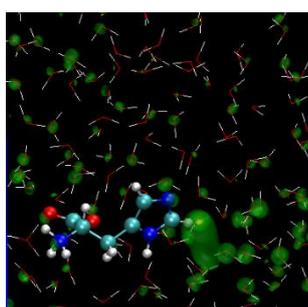
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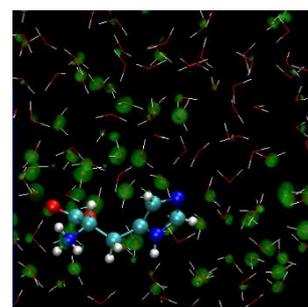
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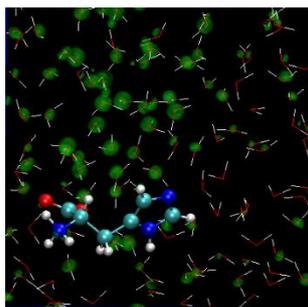
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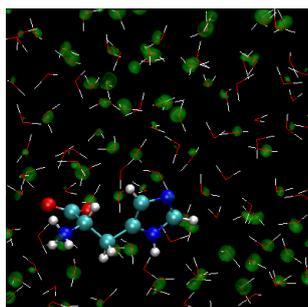
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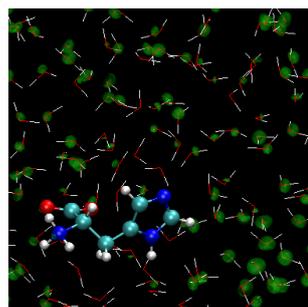
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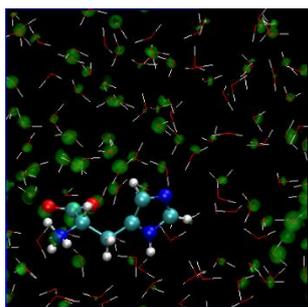
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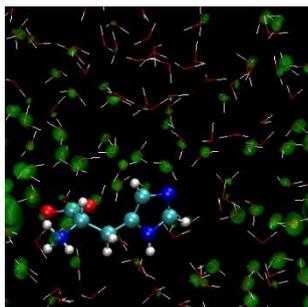
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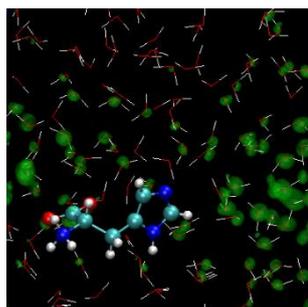
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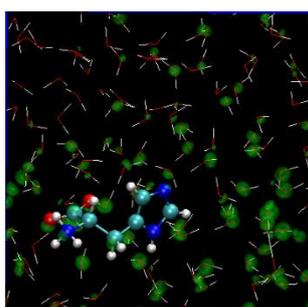
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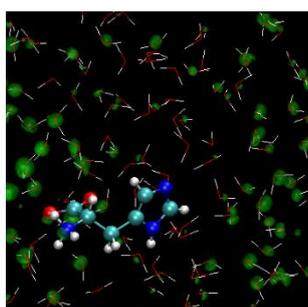
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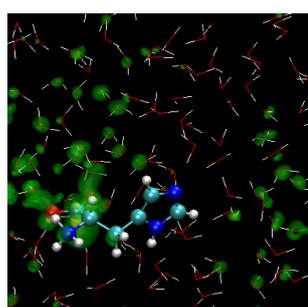
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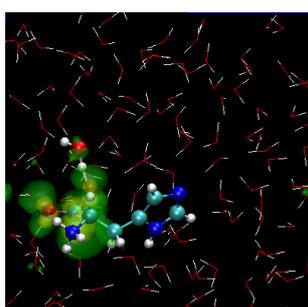
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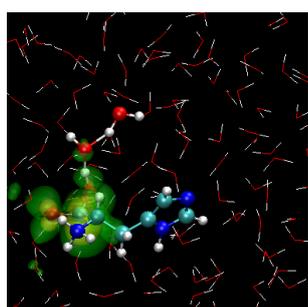
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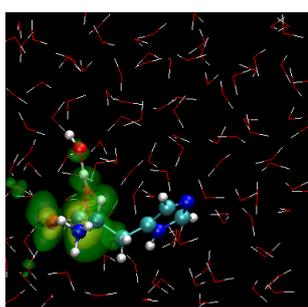
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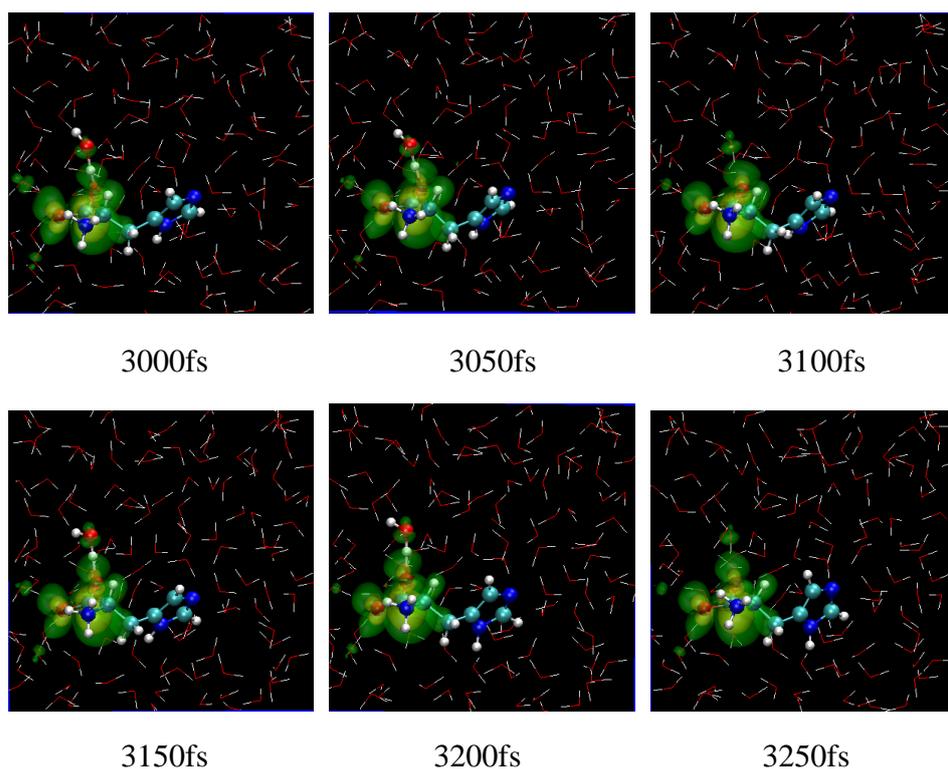


Figure S3. Visualized spin density distributions (isovalue=0.0004) of representative snapshot configurations at different times in EE localization towards the $-\text{COO}^-$ anion group in $\text{H}_2\text{His}^0_{\text{aq}}$.

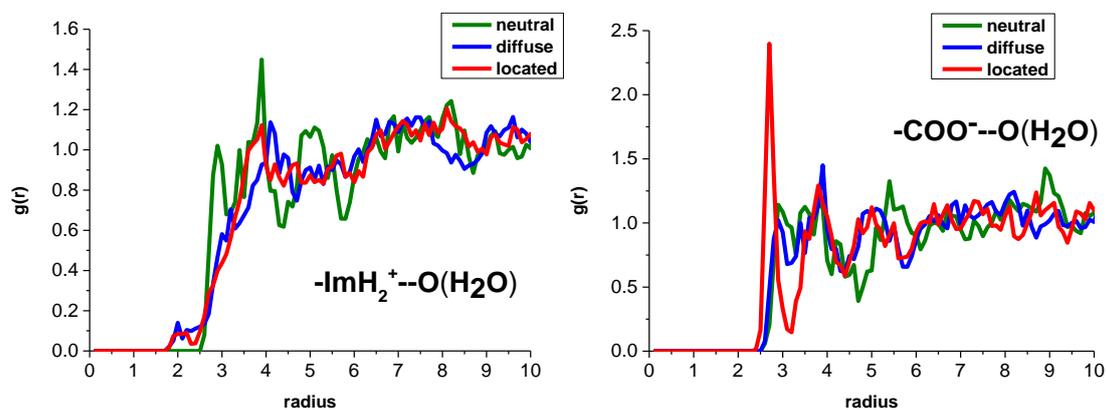


Figure S4. Radical distribution function (RDF) of ImH_2^+ group (left) and $-\text{COO}^-$ group (right) with O in H_2O (Green: in neutral solution; Blue: in diffuse state; Red: in localized state).

3. The Excess Electron Localization in $(\text{H}_3\text{His}^+\text{+Cl}^-)_{\text{aq}}$

We investigate the $(\text{H}_3\text{His}^+) + \text{Cl}^- + (\text{H}_2\text{O})_{120}$ system in a cubic cell ($15.75 \text{ \AA} \times 15.75 \text{ \AA} \times 15.75 \text{ \AA}$), to examine possible influence of the positive charge of the whole system due to protonation of the ImH group. The systems are dealt with the same method as mentioned above.

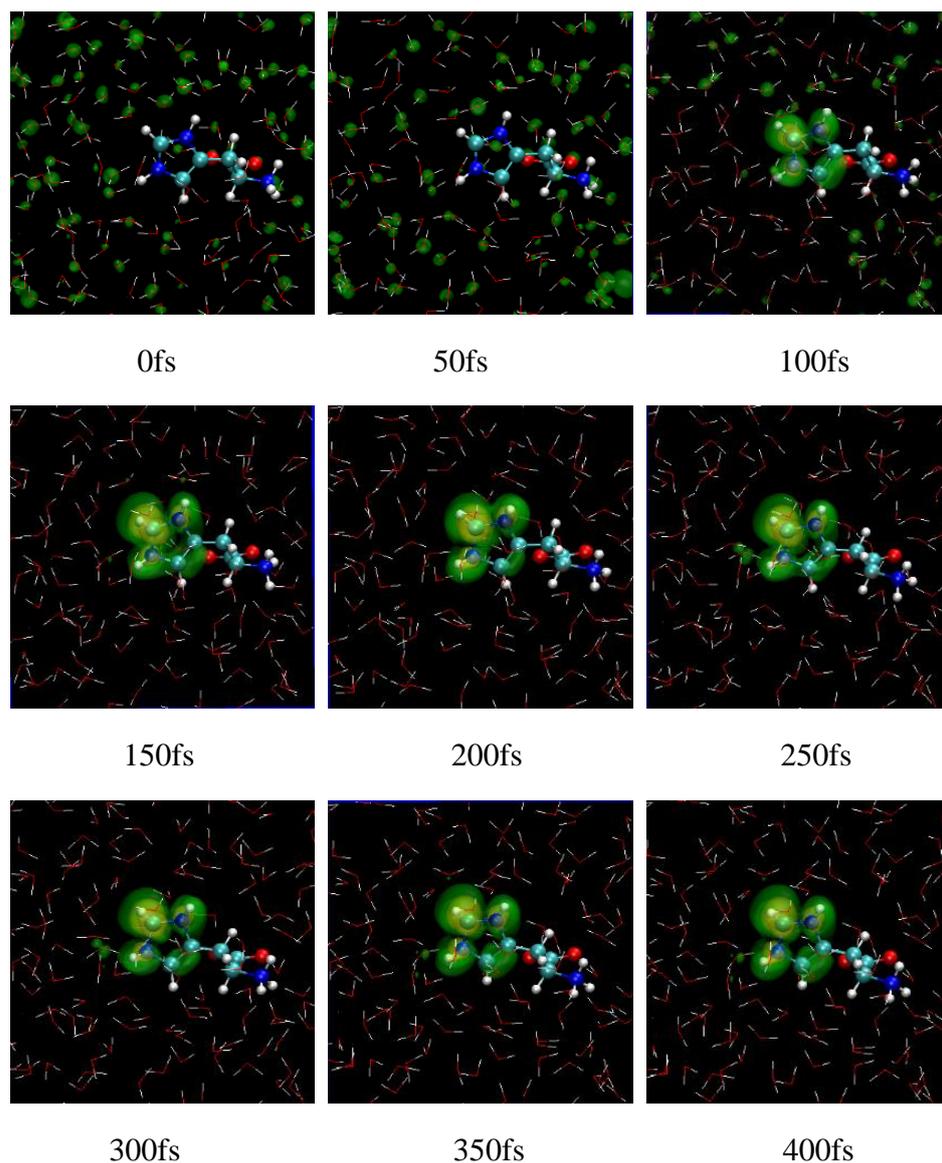


Figure S5. Visualized spin density distributions (isovalue=0.0004) of representative snapshot configurations at different times in EE localization towards the ImH_2^+ group in $(\text{H}_3\text{His}^+\text{+Cl}^-)_{\text{aq}}$.

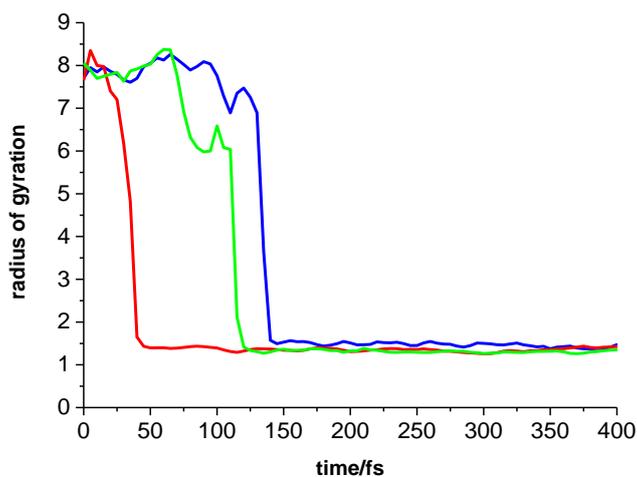


Figure S6. Time evolutions of the radius of gyration of the excess electron in $(\text{H}_3\text{His}^+ + \text{Cl}^-)_{\text{aq}}$.

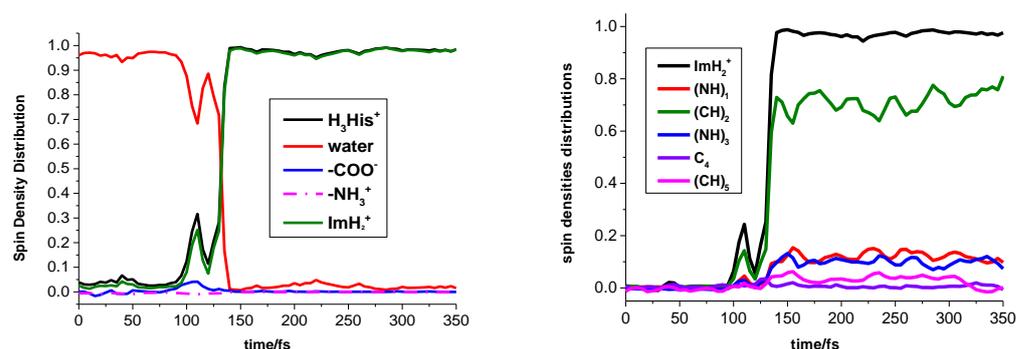


Figure S7. Time evolutions of spin densities in $(\text{H}_3\text{His}^+ + \text{Cl}^-)_{\text{aq}}$.

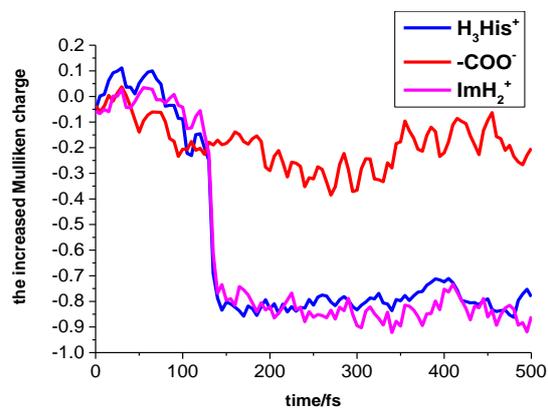


Figure S8. Time evolutions of the increased Mulliken charge of the histidine molecule (Blue) and functional groups (Red for carboxyl group and Pink for imidazole group), in $(\text{H}_3\text{His}^+ + \text{Cl}^-)_{\text{aq}}$.

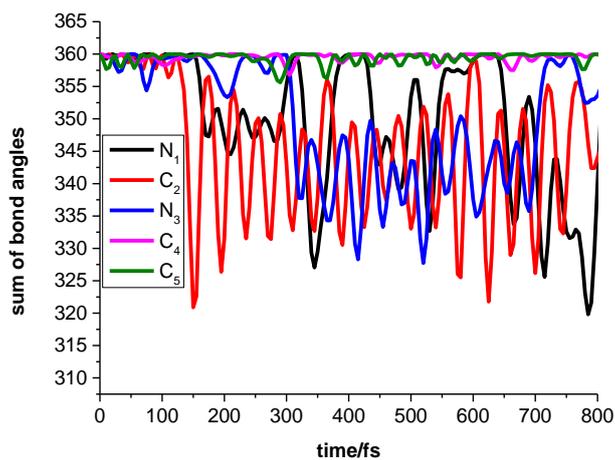
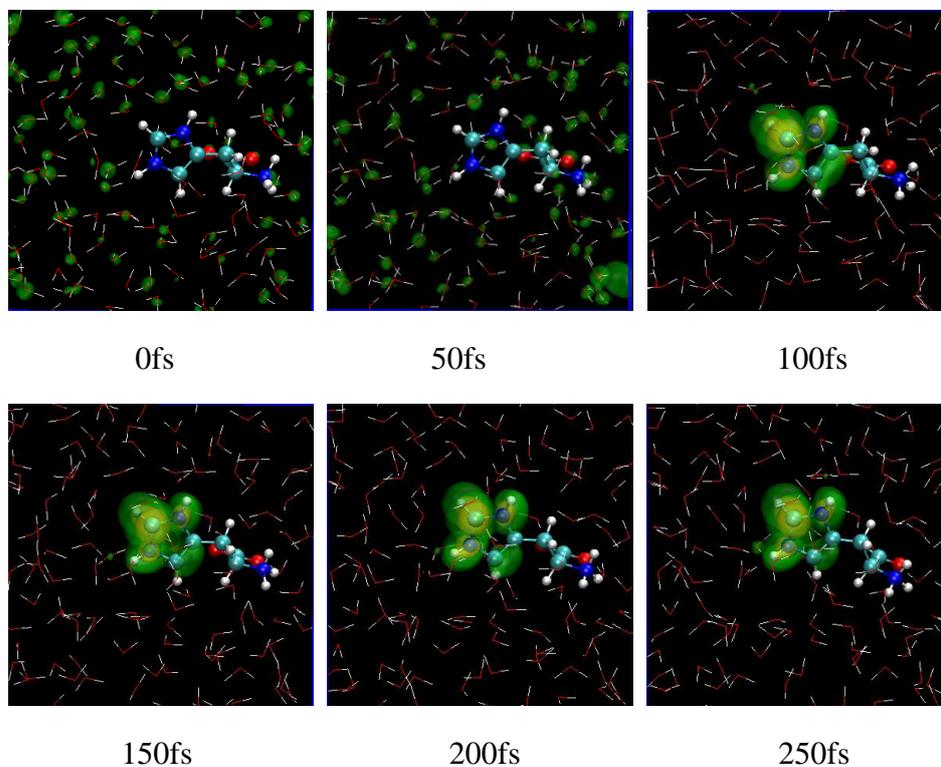


Figure S9. The sums of three bond angles at different positions of imidazole in $(\text{H}_3\text{His}^+ + \text{Cl}^-)_{\text{aq}}$.

4. The Excess Electron Localization simulated by PBE method.

To address the reasonableness and generality of our results, we perform additional AIMD simulation at PBE/TZV2P level, using the same initial equilibrium configuration as mentioned above.

4.1 The Excess Electron Localization in $(\text{H}_3\text{His}^+ + \text{Cl}^-)_{\text{aq}}$ simulated by PBE method



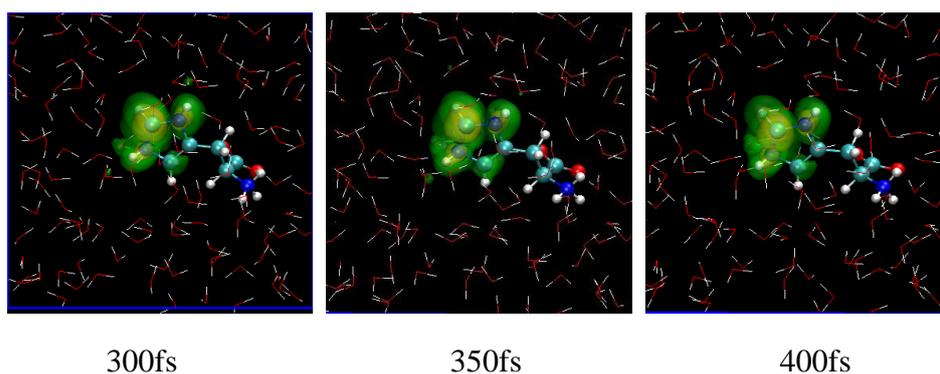


Figure S10. Visualized spin density distributions (isovalue=0.0004) of representative snapshot configurations at different times in EE localization towards the ImH_2^+ group.

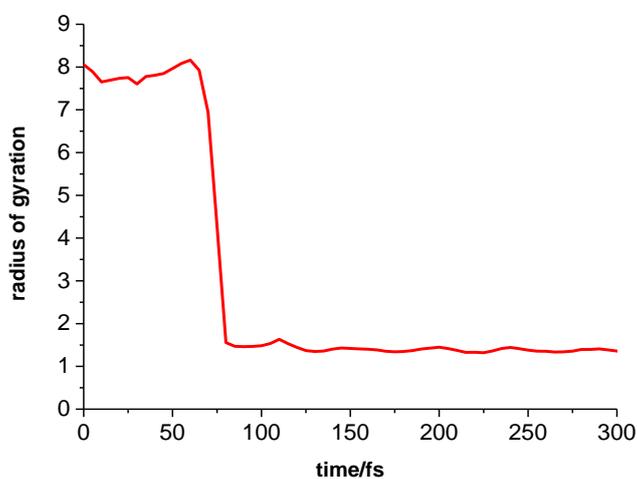


Figure S11. Time evolutions of the radius of gyration of the electron.

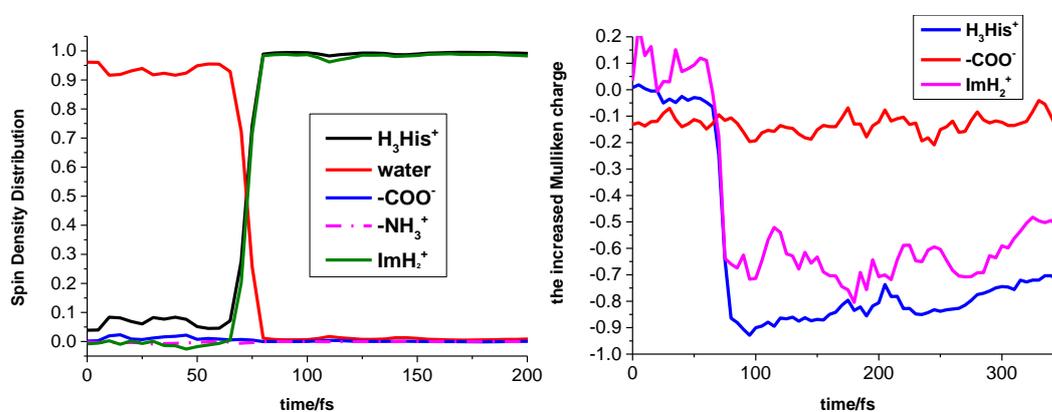
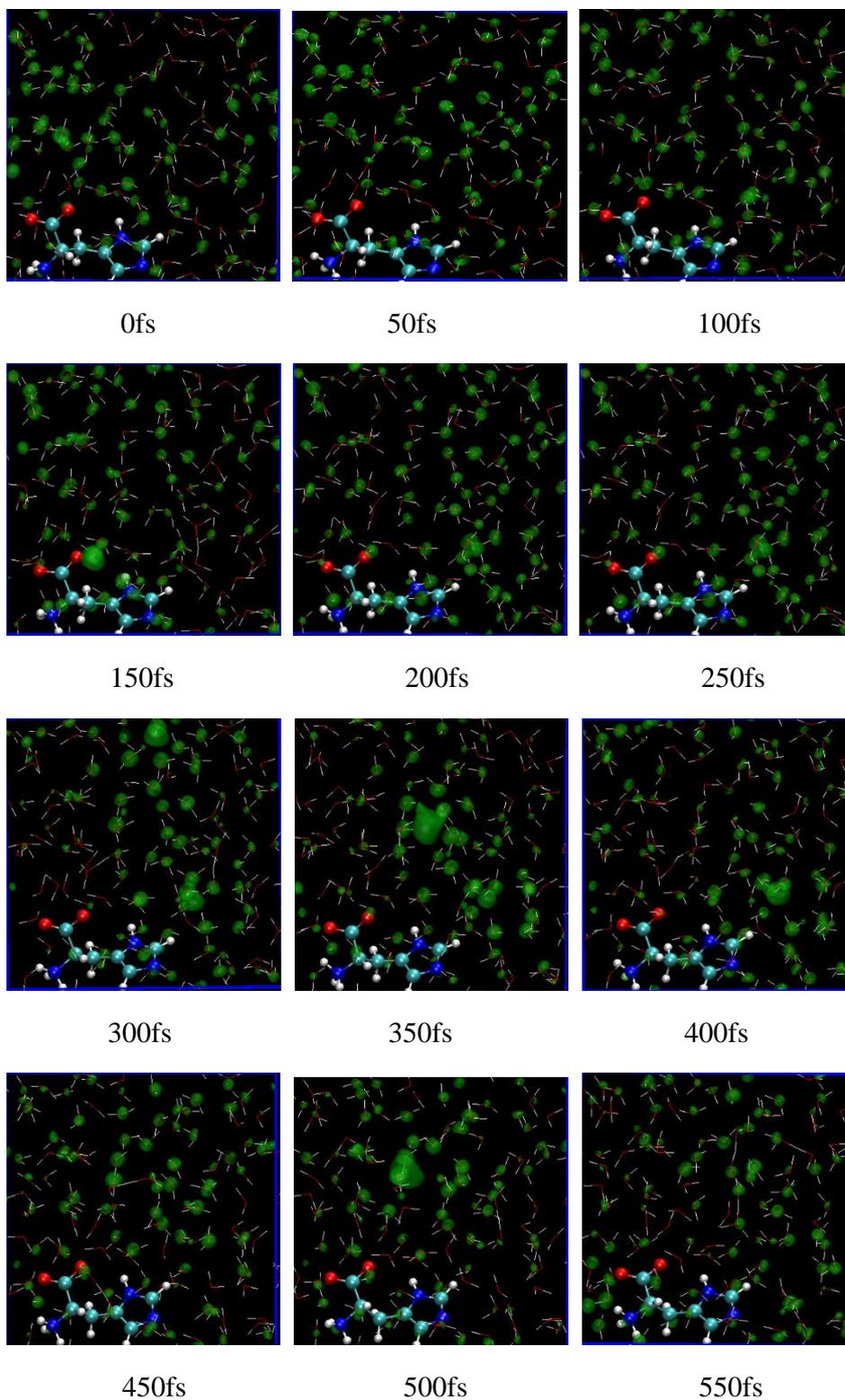


Figure S12. Time evolutions of spin densities (left) and the increased Mulliken charge (right).

4.2 The Excess Electron Localization in $\text{H}_2\text{His}^0_{\text{aq}}$ simulated by PBE method



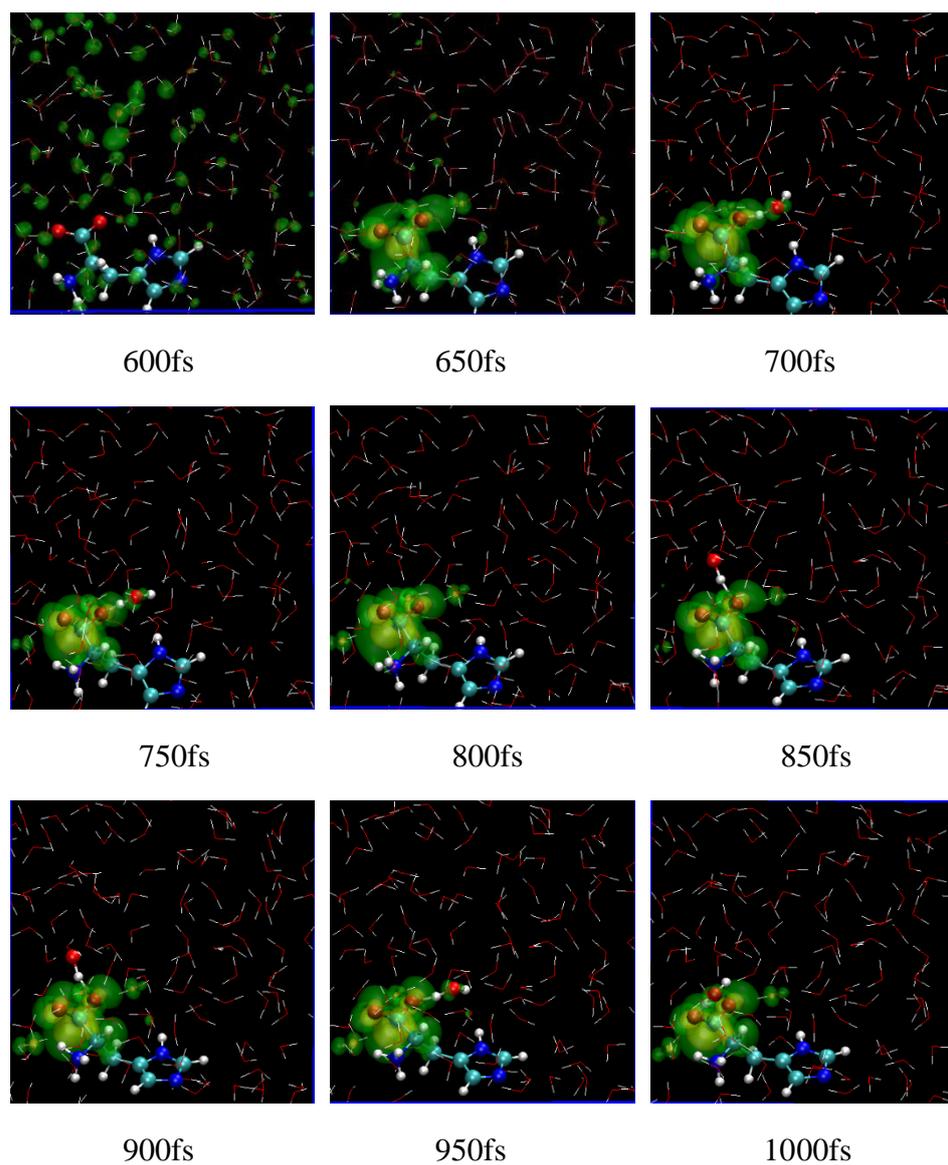


Figure S13. Visualized spin density distributions (isovalue=0.0004) of representative snapshot configurations at different times in EE localization towards the $-\text{COO}^-$ anion group in $\text{H}_2\text{His}^0_{\text{aq}}$.

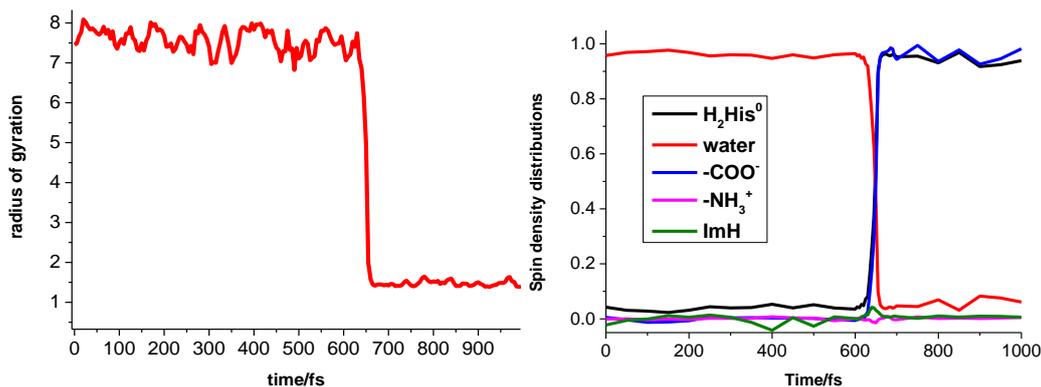
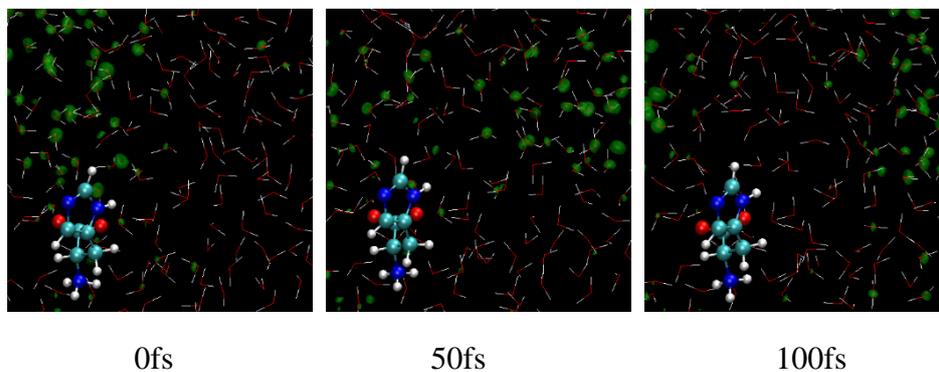


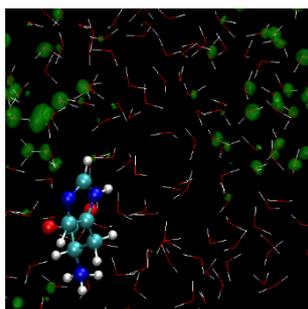
Figure S14. Time evolutions of the radius of gyration (left) and spin densities (right) of the excess electron.

5. The Excess Electron Localization in relatively low concentrations.

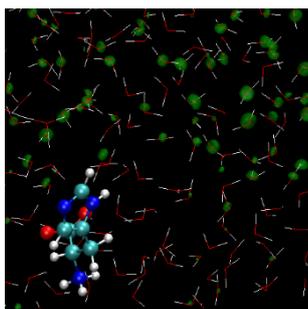
The systems we examined above may represent the interaction part for EE and histidine in an aqueous solution, rather than the whole solution. Their concentrations may be bigger than that in real conditions, especially in the neutral situation. So we rebuild the simulation boxes with 1 histidine and 200 water molecules under a density of 1.0 g/cm^3 , whose concentrations can reach the saturated solution of neutral histidine aqueous solution. Their results show the same qualitative trend as the tight boxes, implying the conclusions we proposed in this work are hardly affected by the concentration condition.

5.1 The Excess Electron Localization in $\text{H}_2\text{His}^0_{\text{aq}}$ with a relatively low and realistic concentration.

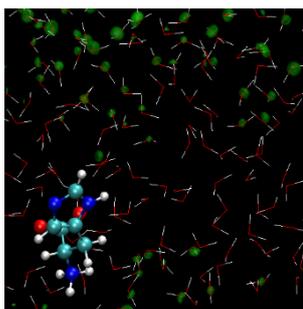




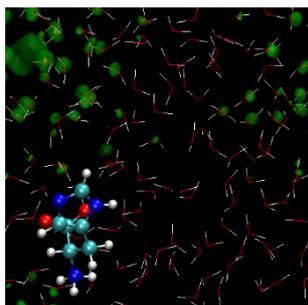
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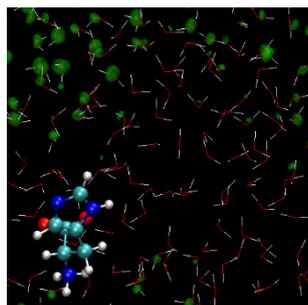
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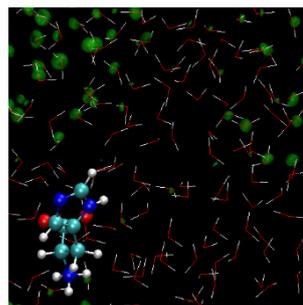
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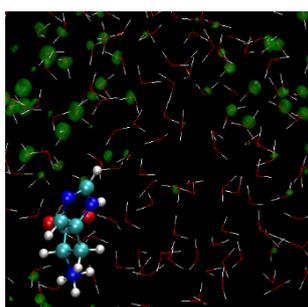
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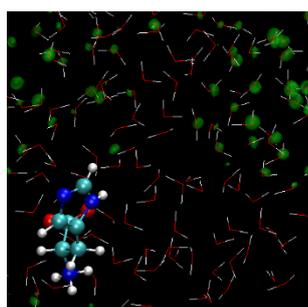
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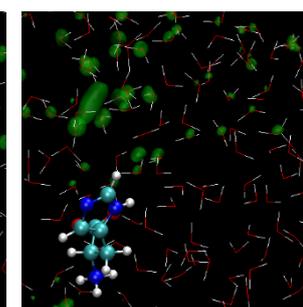
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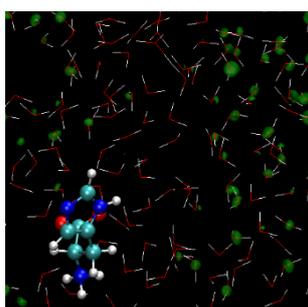
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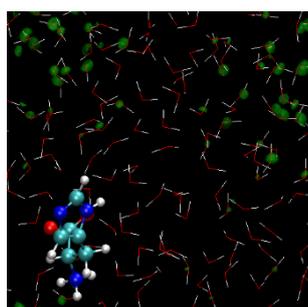
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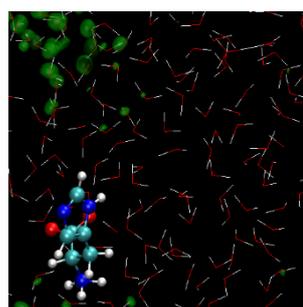
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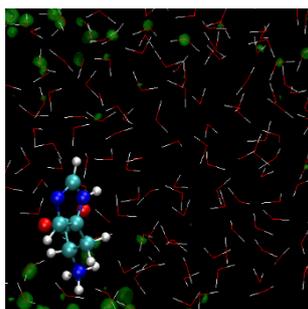
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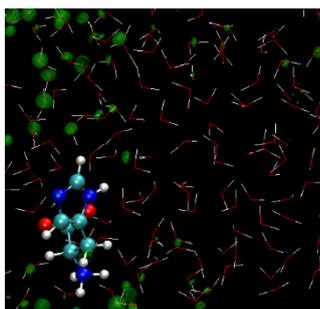
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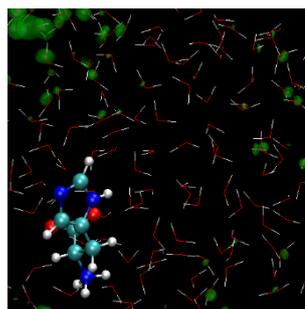
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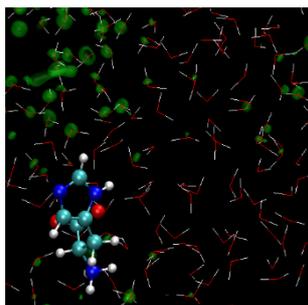
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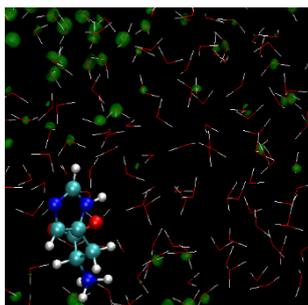
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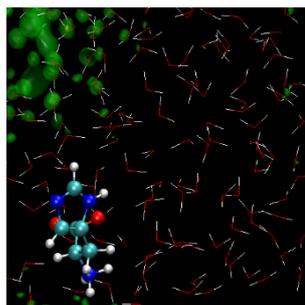
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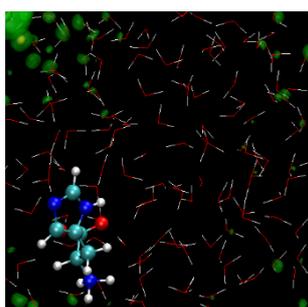
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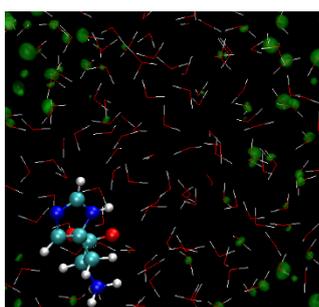
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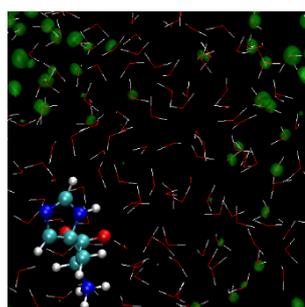
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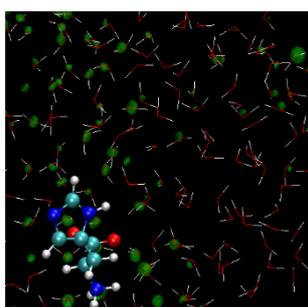
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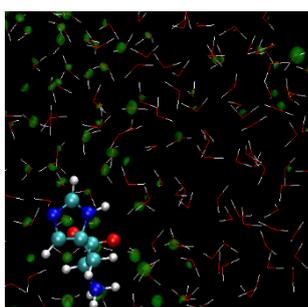
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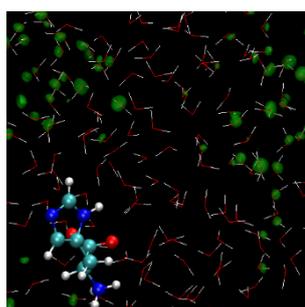
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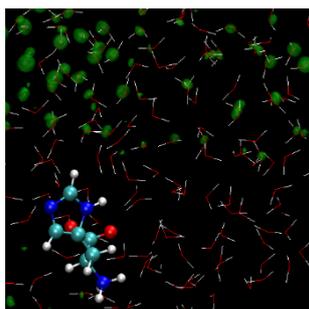
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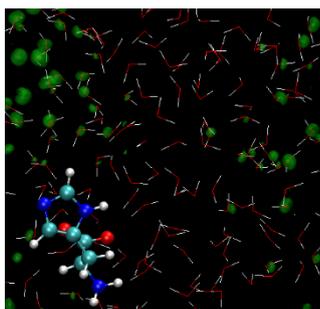
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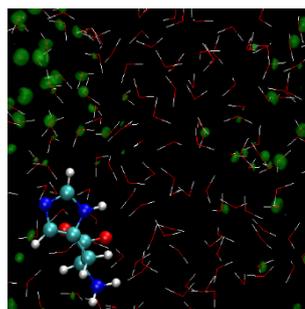
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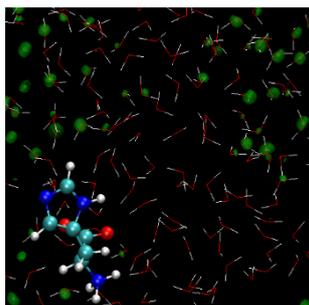
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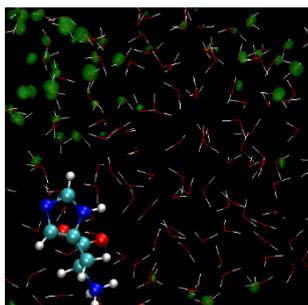
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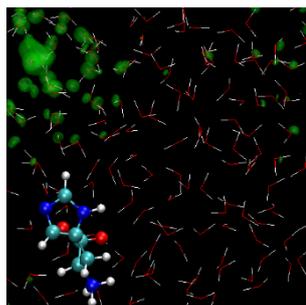
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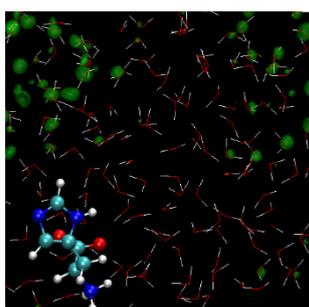
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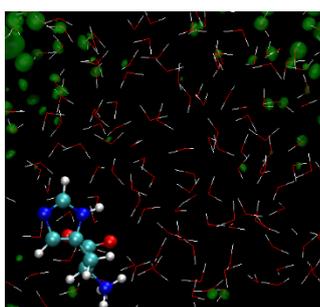
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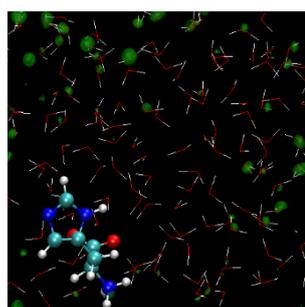
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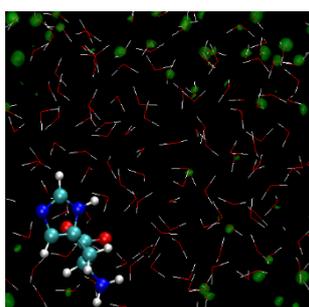
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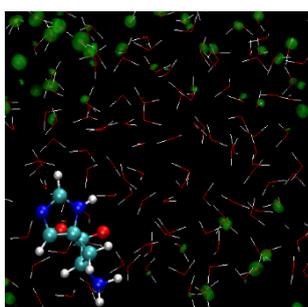
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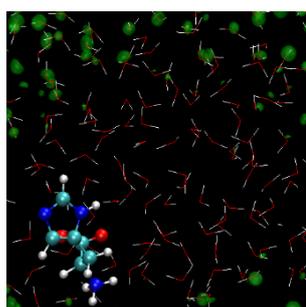
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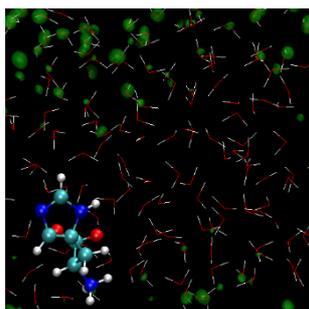
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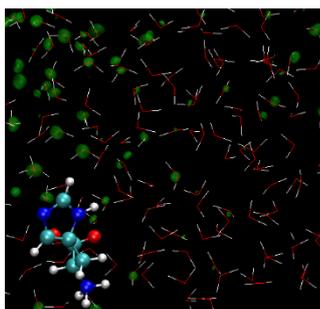
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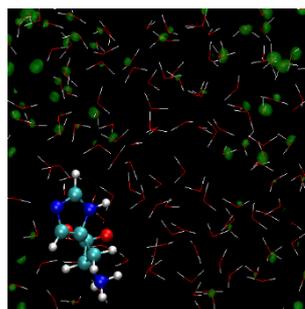
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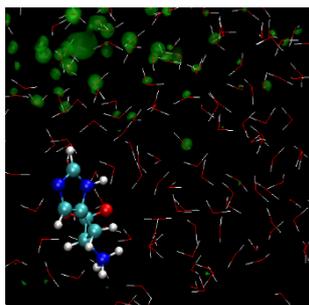
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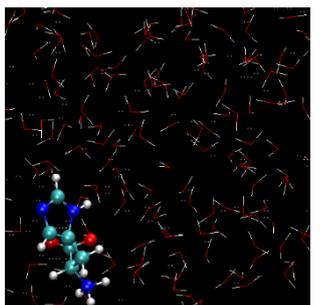
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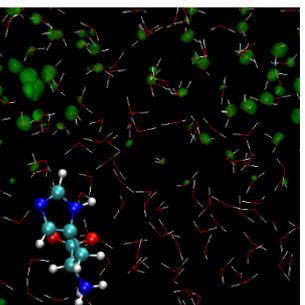
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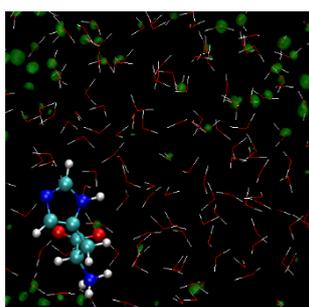
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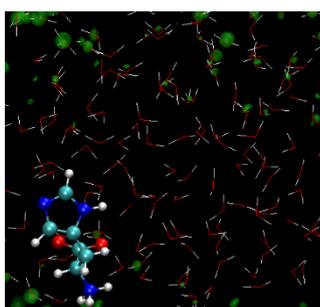
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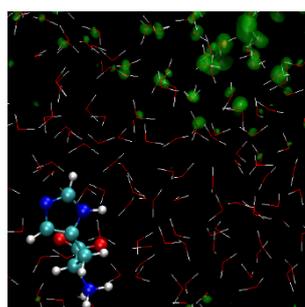
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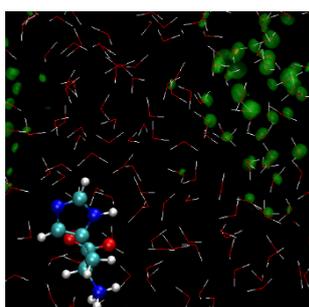
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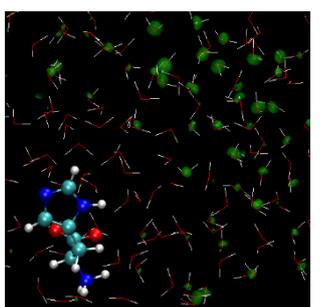
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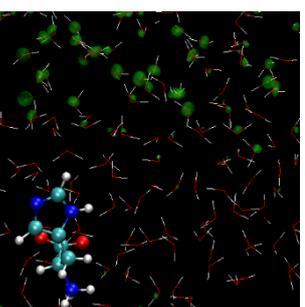
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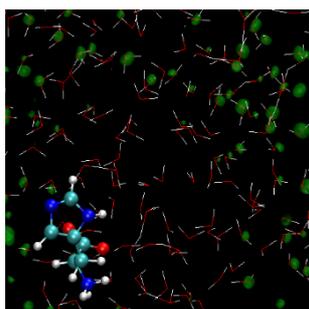
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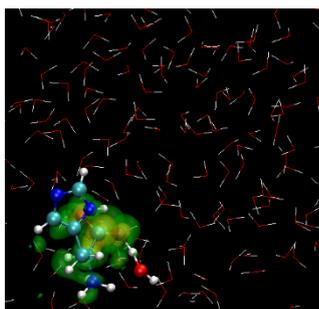
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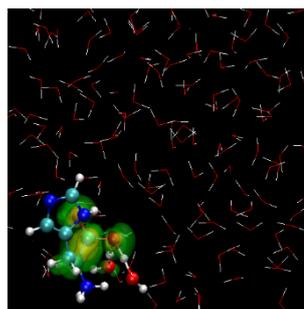
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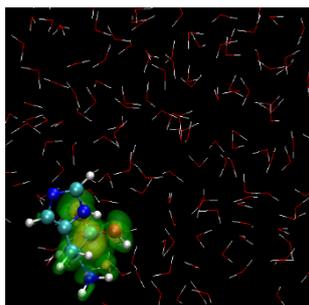
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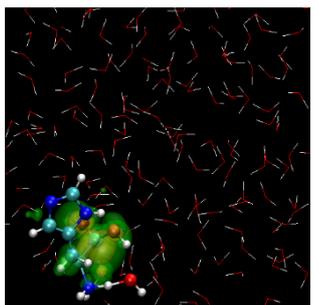
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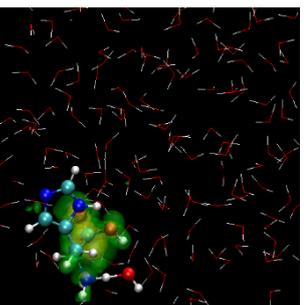
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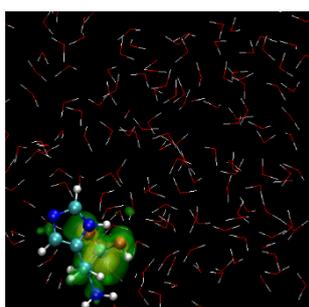
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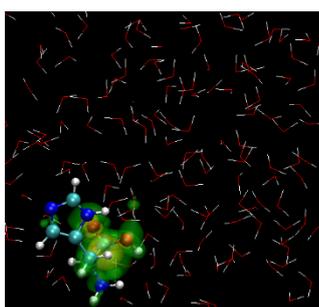
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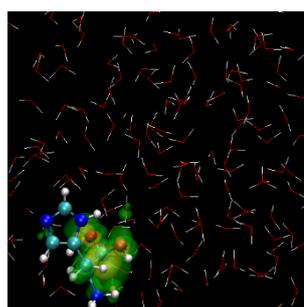
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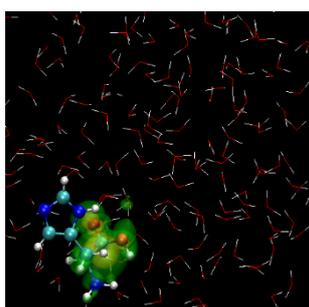
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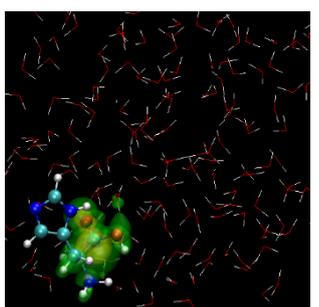
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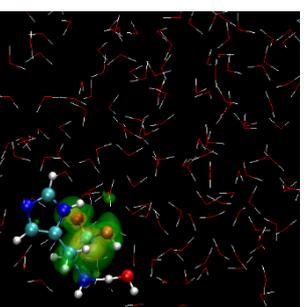
2950fs



3000fs



3050fs



3100fs

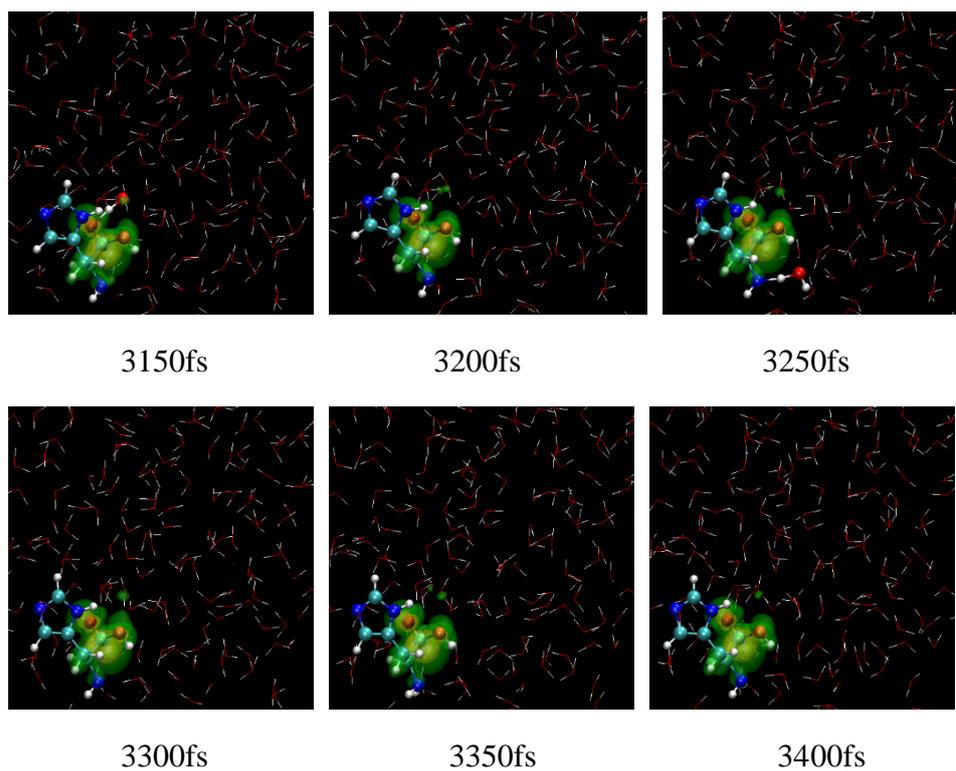


Figure S15. Visualized spin density distributions (isovalue=0.0004) of representative snapshot configurations at different times in EE localization towards the $-\text{COO}^-$ anion group in $\text{H}_2\text{His}^0_{\text{aq}}$.

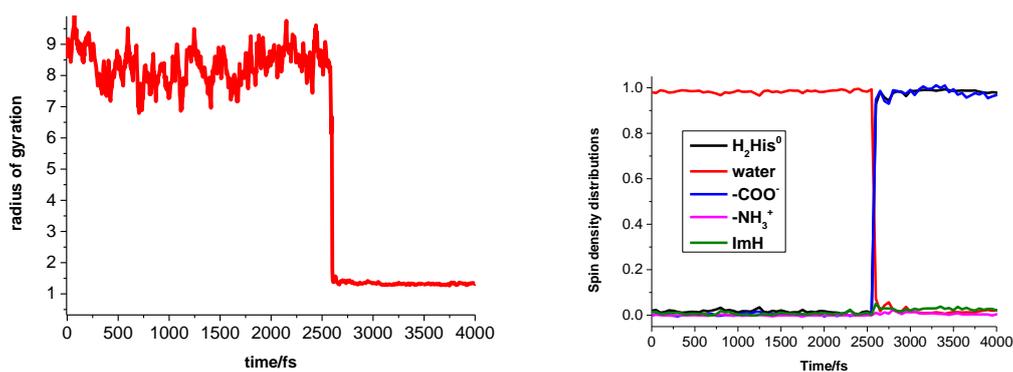
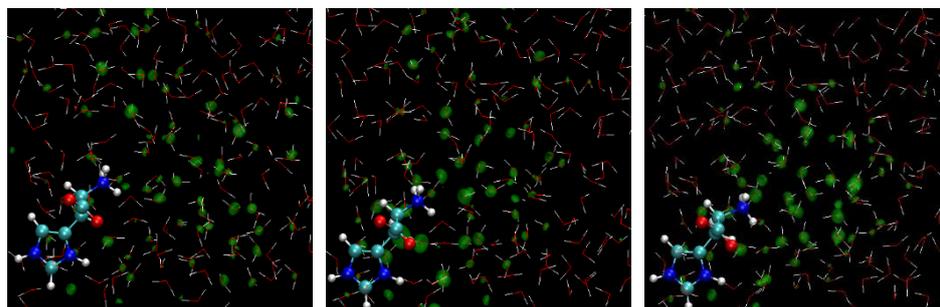


Figure S16. Time evolutions of the radius of gyration (left) and spin densities (right) of the excess electron.

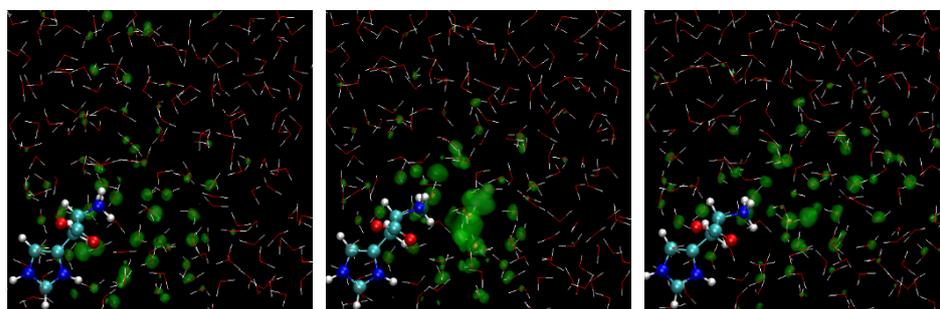
5.2 The Excess Electron Localization in $\text{H}_3\text{His}^+_{\text{aq}}$ with a relatively low concentration.



0fs

50fs

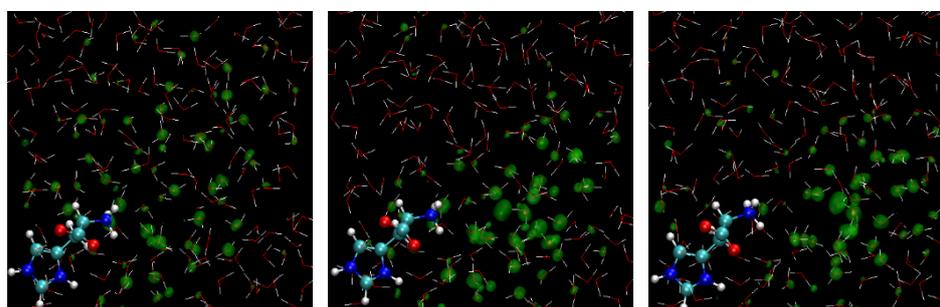
100fs



150fs

200fs

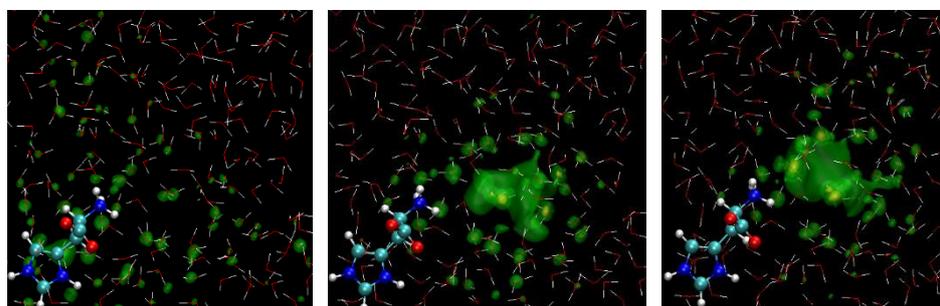
250fs



300fs

350fs

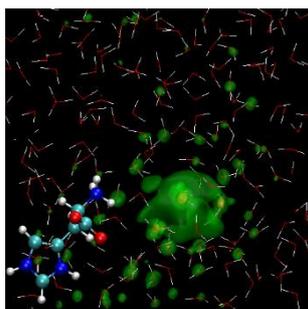
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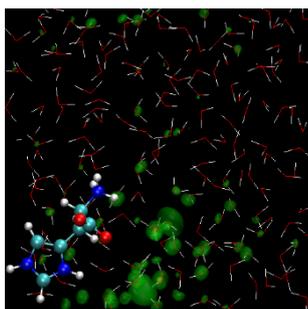
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500fs

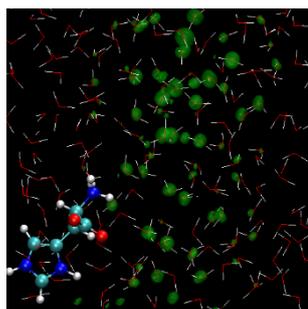
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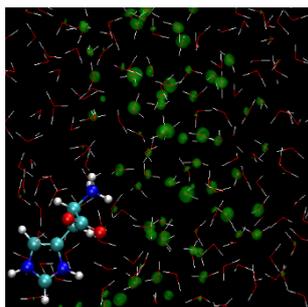
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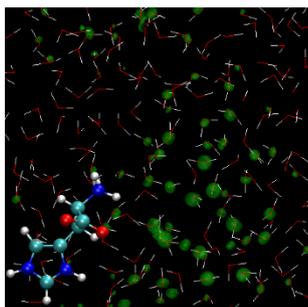
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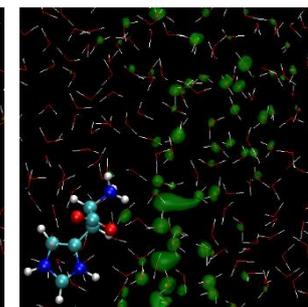
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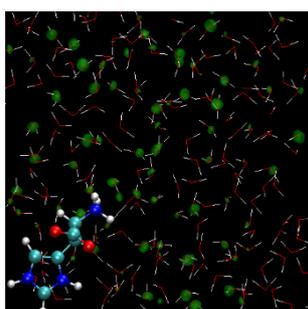
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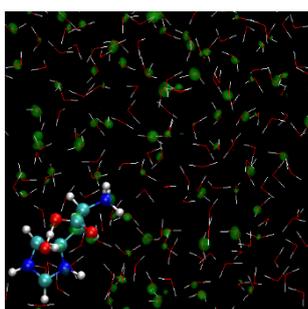
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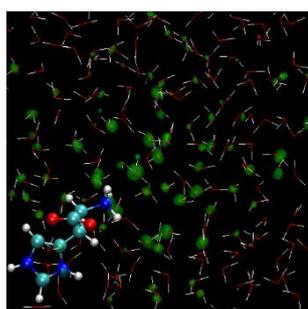
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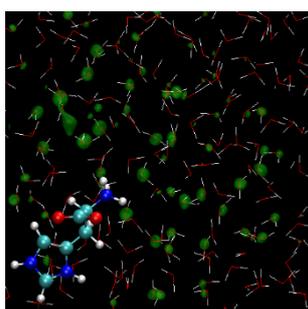
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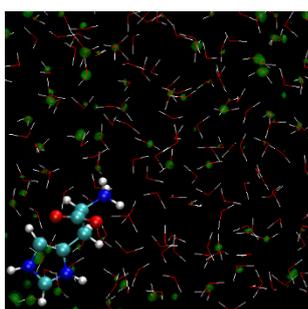
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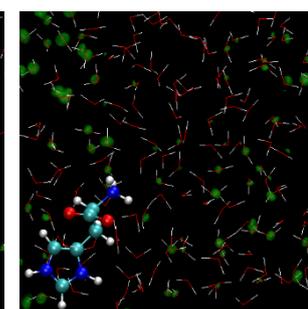
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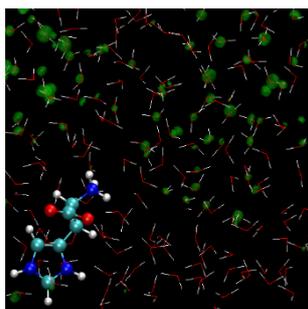
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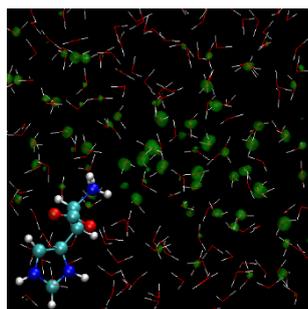
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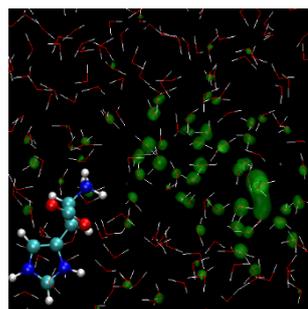
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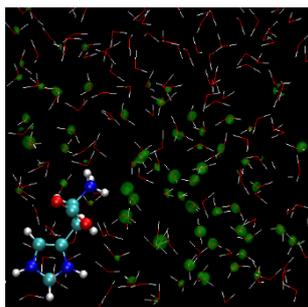
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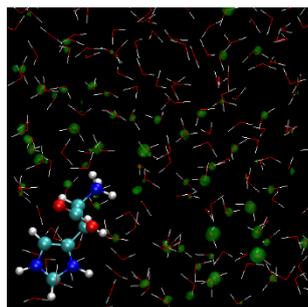
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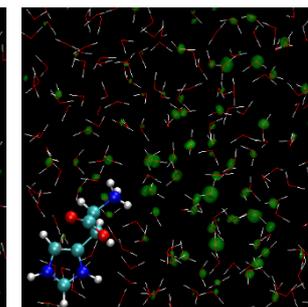
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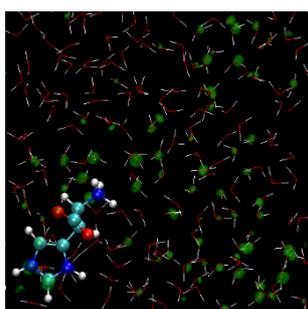
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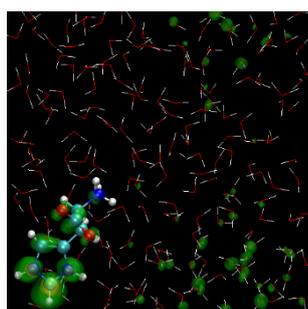
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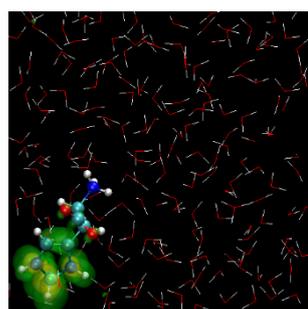
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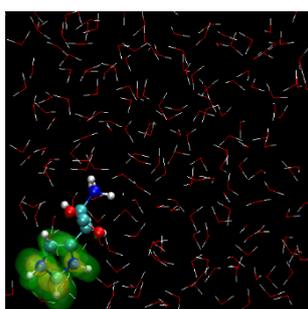
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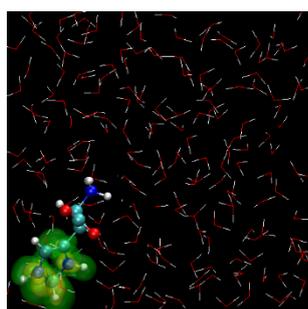
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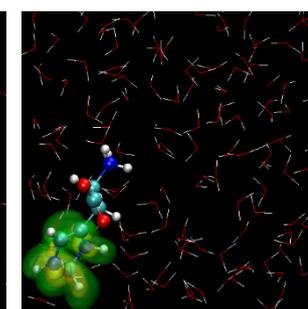
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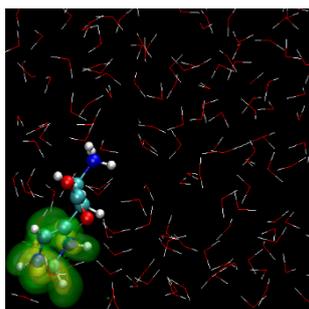
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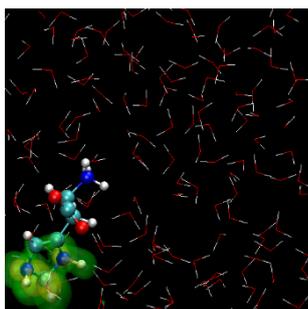
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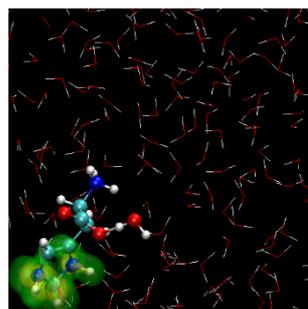
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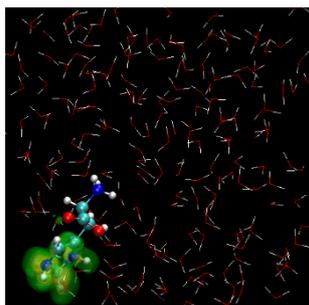
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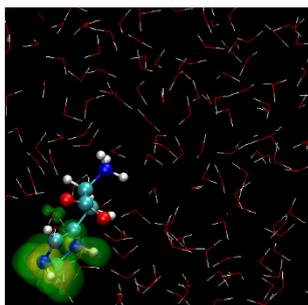
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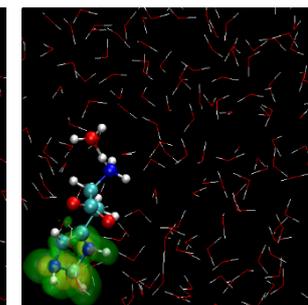
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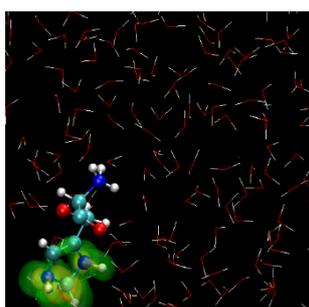
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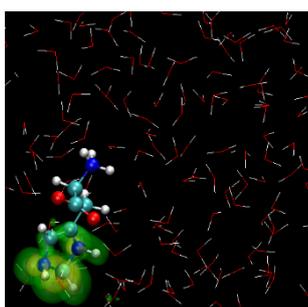
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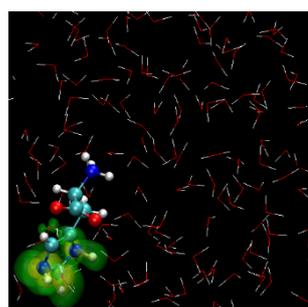
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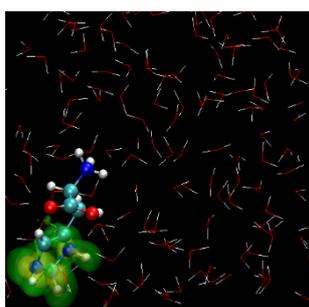
2100fs



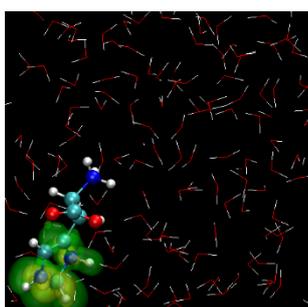
2150fs



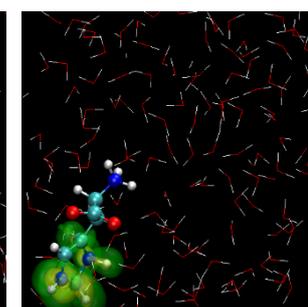
2200fs



2250fs



2300fs



2350fs

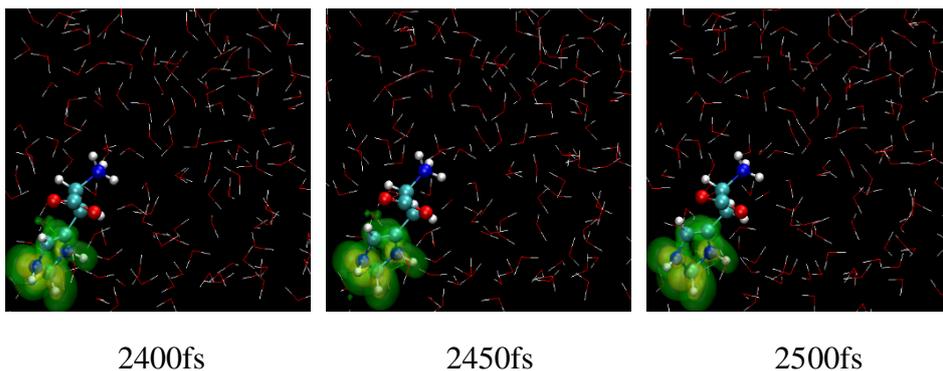


Figure S17. Visualized spin density distributions (isovalue=0.0004) of representative snapshot configurations at different times in EE localization towards the ImH_2^+ group.

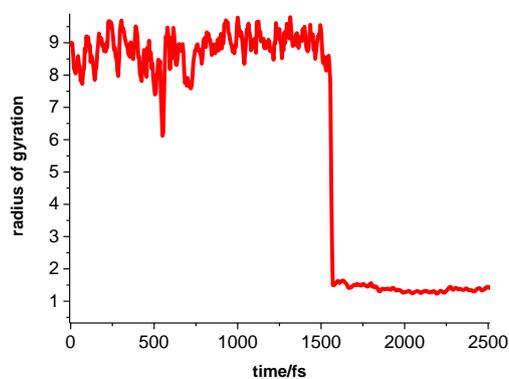


Figure S18. Time evolutions of the radius of gyration of the electron.

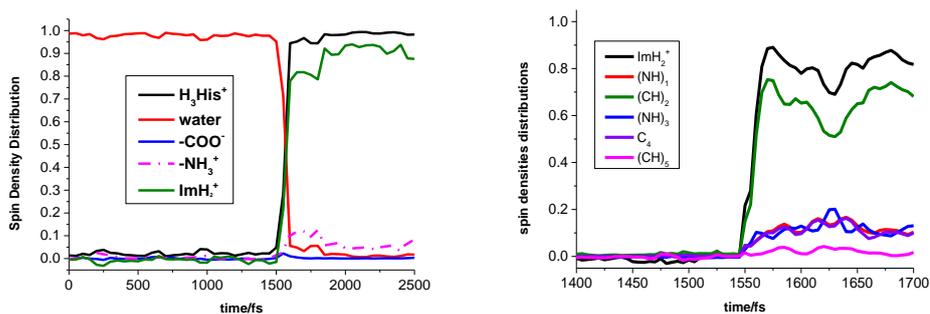


Figure S19. Time evolutions of spin densities in $\text{H}_3\text{His}^+_{\text{aq}}$.

6. Comparison between Spin Density and Differential Electron Density

Firstly, due to the restricted open shell Kohn–Sham scheme we employed, the total spin density of the system coincides with the density of the singly occupied molecular orbital (SOMO) (see Marsalek, O.; Uhlig, F.; Jungwirth, P. Electrons in Cold Water Clusters: An ab Initio Molecular Dynamics Study of Localization and Metastable States. *J. Phys. Chem. C*, **2010**, *114*, 20489):

$$\mathbf{s}(\vec{r}) = \Phi_{SOMO}(\vec{r}) \cdot \Phi_{SOMO}^*(\vec{r}) \quad (1)$$

$$\int \mathbf{s}(\vec{r}) \cdot d^3r = 1 \quad (2)$$

So the spin density is easy to be obtained. Secondly, the spin density is a useful and measurable quantity. Its first and second moments can reflect where and how the excess electron localizes.

$$\vec{r}_c = \int \vec{r} \cdot \mathbf{s}(\vec{r}) \cdot d^3r \quad (3)$$

$$r_g = \int (\vec{r} - \vec{r}_c)^2 \cdot \mathbf{s}(\vec{r}) \cdot d^3r \quad (4)$$

Finally, it has been verified “spin density in the electron-water cluster overlapped very well with the differential electronic density (i.e., the difference between electron densities of the anionic and neutral systems in the anionic geometry), although the latter was somewhat more diffuse.” (Frigato, T.; Vandevondele, J.; Schmidt, B. et al. Ab Initio Molecular Dynamics Simulation of a Medium-Sized Water Cluster Anion: From an Interior to a Surface-Located Excess Electron via a Delocalized State. *J. Phys. Chem. A*, **2008**, *112*, 6125). Here we compare their distributions (please see the following three figures) and get a similar conclusion.

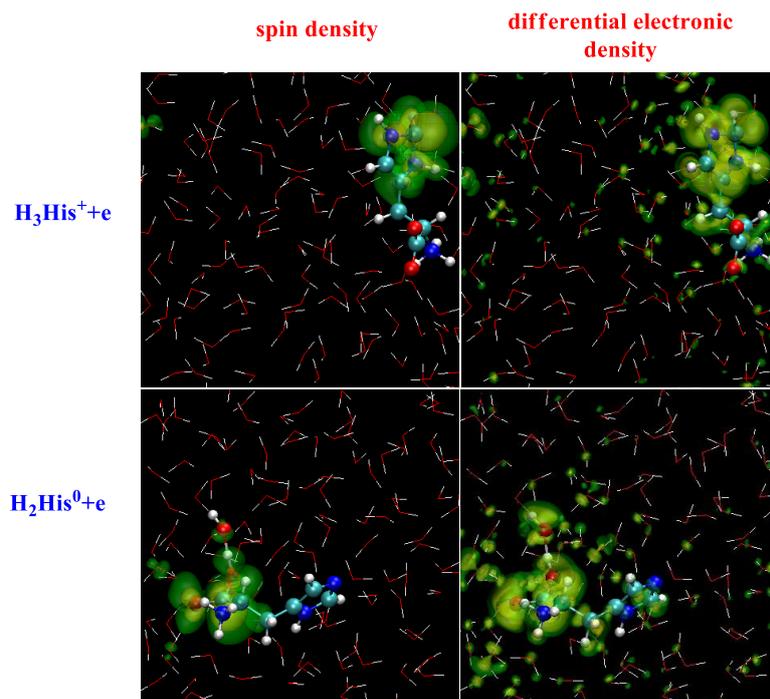


Figure S20. Visualized spin density and differential electronic density distributions of excess electron localized systems. The green isosurface encapsulates more than 90% density. Its isovalue is 0.0004 for spin density and 0.001 for differential electronic density. The yellow one encapsulates more than 70% density with the isovalue of 0.004 for spin density and 0.002 for differential electronic density.

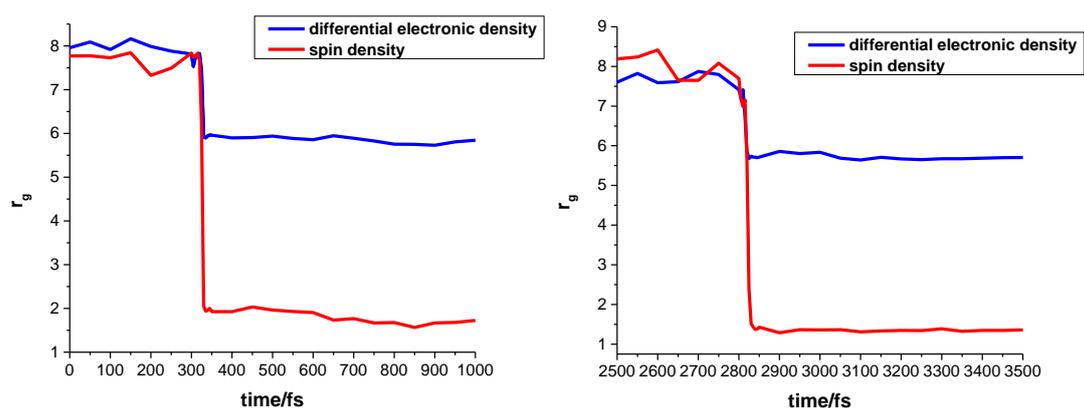


Figure S21. Time evolutions of the radii of gyration of excess electrons (r_g) calculated by equation (4) using spin density (red curve) and differential electronic density (blue curve), in slightly acidic $\text{H}_3\text{His}^+_{\text{aq}}$ solution (Left) and neutral $\text{H}_2\text{His}^0_{\text{aq}}$ solution (Right).

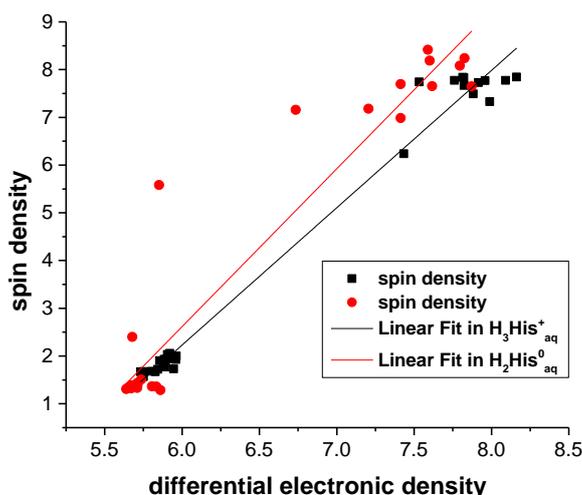


Figure S22. Linear correlations of r_g calculated by spin density and differential electronic density in slightly acidic $\text{H}_3\text{His}^+_{\text{aq}}$ solution (black) and neutral $\text{H}_2\text{His}^0_{\text{aq}}$ solution (red).

7. Exchange Process of Solvating Water Molecules during Excess Electron Localization

We examine the hydrogen bond distances between histidine and neighboring water molecules and their variations in the excess electron localization process as below (Figures S23 and S24).

As we can see in Figure S23, before excess electron localization, there is a hydrogen bond formed by H3 of the ImH_2^+ group and oxygen of a neighboring water molecule, with the orientation parallel to the imidazole ring plane. As the excess electron localizes, this hydrogen bond is elongated with fluctuation. At the same time, a water molecule with a slightly long distance from histidine gets close and rotates one of its O-H bond towards N3 of the ImH_2^+ group. A new hydrogen bond is finally formed between them perpendicular to the imidazole ring plane. That is, an already existing hydrogen bond is gradually weakened while a new hydrogen bond is gradually formed in this process. Clearly, as an overall role, the changes of the two hydrogen bonds enhance the ability of the ImH_2^+ group to accept the excess electron.

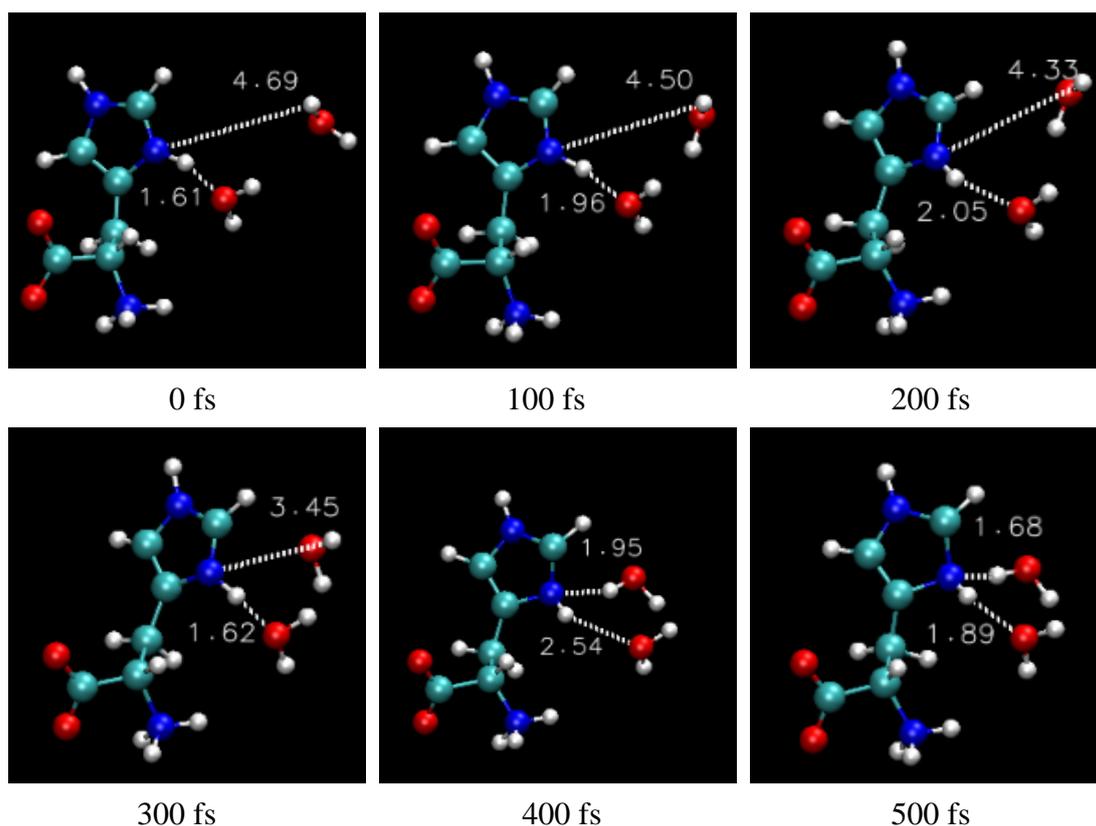


Figure S23. The exchange process of the solvating water molecules along with EE localization towards the ImH_2^+ group in $\text{H}_3\text{His}^+_{\text{aq}}$, which takes place at 350 fs.

In addition, as shown in Figure S24 (below), before excess electron localization, there always a hydrogen bond formed by one of oxygen atoms in $-\text{COO}^-$ group and a hydrogen of a neighboring water molecule with a distance of $\sim 1.8 \text{ \AA}$. The water molecule can be replaced by its neighborhoods in thermodynamic solution structure fluctuation. This ligand exchange process happens to occur along with the excess electron localization here. As we see above, another water gets instead of the already existing one forms a new hydrogen bond and donates its proton to the $-\text{COO}^-$ group at the end. On the other hand, hydrogen bonds of the other oxygen atom in the $-\text{COO}^-$ group is also enhanced due to the increased excess negative charge in the $-\text{COO}^-$ group after excess electron localization.

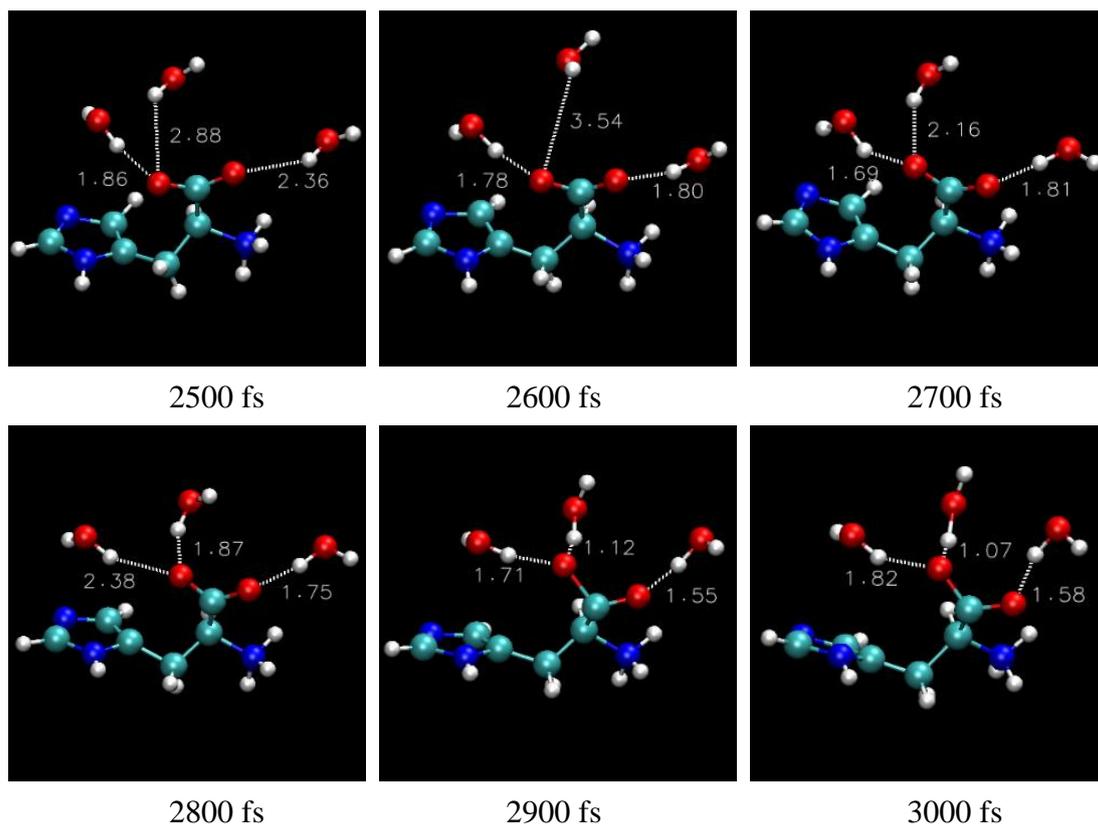


Figure S24. The exchange process of the solvating water molecules along with EE localization towards the -COO^- group in $\text{H}_2\text{His}^0_{\text{aq}}$, which takes place at 2800 fs.