

**Bifurcate Localization Modes of Excess Electron in Aqueous Ca^{2+} ...Amide Solution
Revealed by Ab Initio Molecular Dynamics Simulation: Towards Hydrated Electron
versus Hydrated Amide Anion**

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Supporting Information

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0. Energy Levels and Distributions of the Lowest Unoccupied Molecular Orbital (LUMO) of Hydrated Acetamide Clusters and Structure of Hydrated Electron

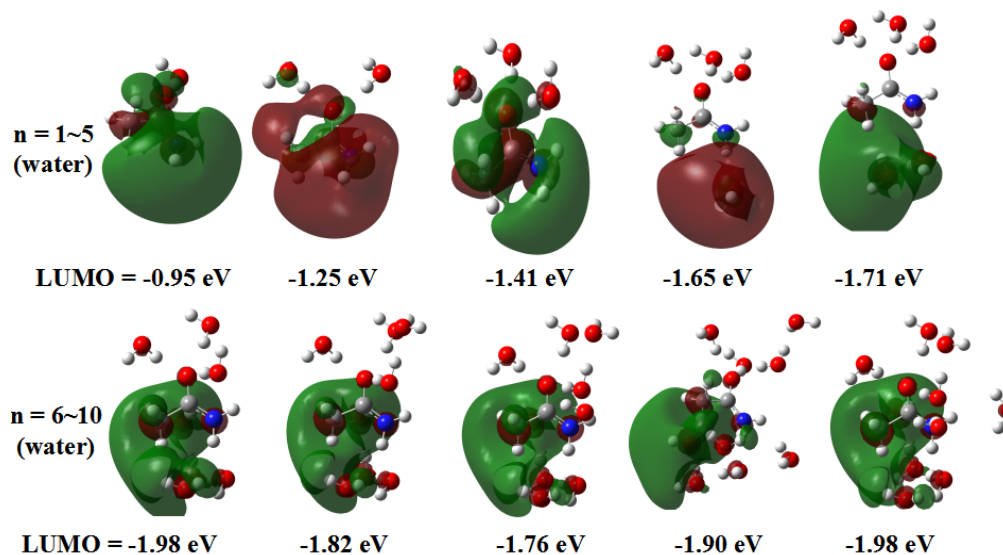


Figure S1. Energy levels and distribution of LUMO (the lowest unoccupied molecule orbital) in acetamide with 1~10 water molecules calculated at the B3LYP/6-31++G(d,p) level. These results indicate that hydration can effectively lower the LUMO orbital level and thus enhance the electron-binding ability of acetamide molecule. The corresponding vertical electron affinities are -1.08, -0.54, 0.01, 0.27, 0.27, 0.54, 0.86, 0.54, and 1.08 eV for the above mentioned clusters, respectively.

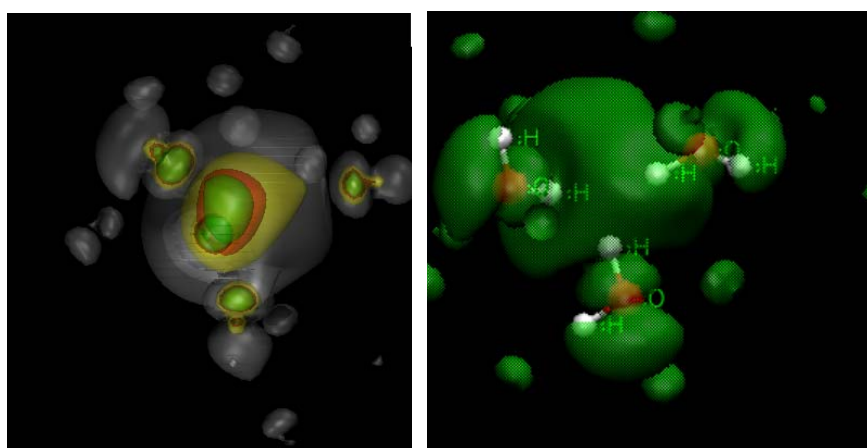


Figure S2. Left) Structure of a hydrated electron presented by spin density in which different colors denote different isovalues: isovalue = 0.0004 (grey), 0.008 (yellow), 0.004 (orange), 0.01 (green), respectively. Right) Positional relation of the hydrated electron and the closely associated three water molecules.

1. Excess Electron Localization Dynamics in Aqueous Acetamide Solution

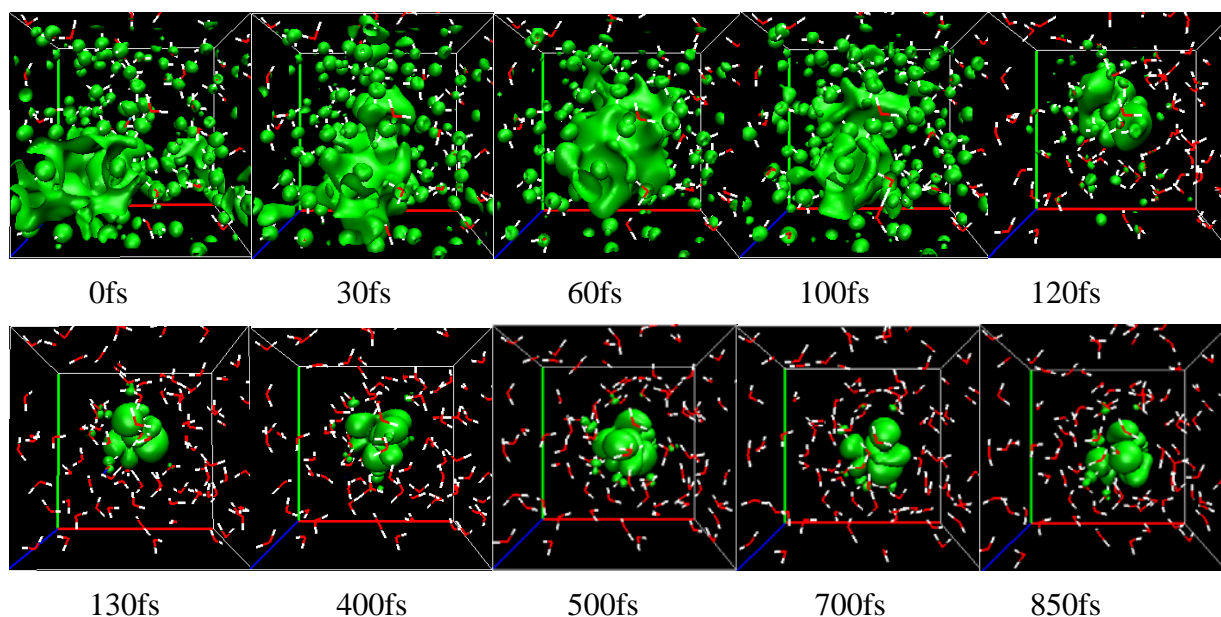


Figure S3. Spin density distributions (isovalue=0.0001) of representative snapshot configurations at different times. In this aqueous solution, an excess electron (EE) localizes in acetamide eventually, forming hydrated amide anion.

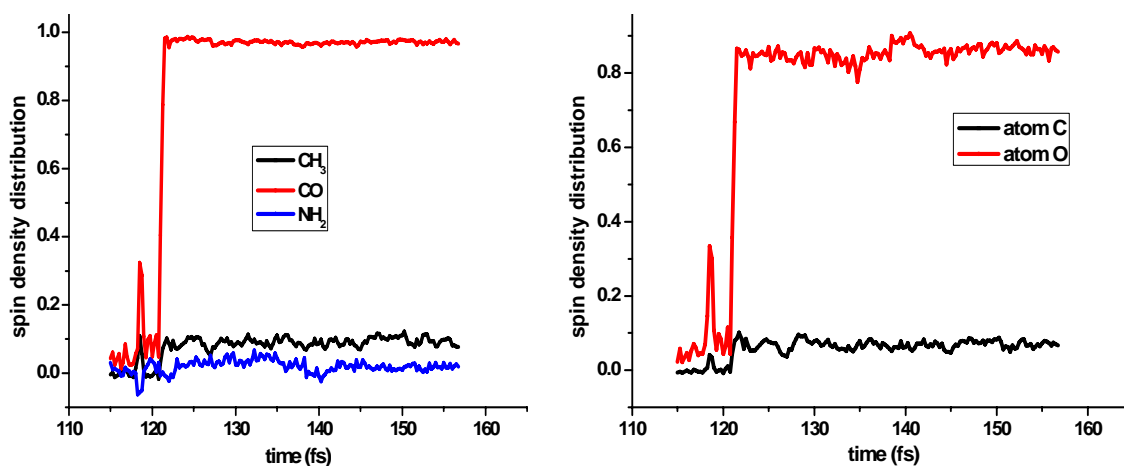


Figure S4. Spin density distributions at different groups in whole acetamide molecule (**left**) and at different atoms in whole carbonyl group (**right**) in time evolution.

2. Excess Electron Localization Dynamics in Aqueous Ca^{2+} -Acetamide Solutions

2.1. Localization of Excess Electron in Aqueous Solution with the Tightest $\text{C}=\text{O}\dots\text{Ca}^{2+}$

Contact

Forming Hydrated Electron

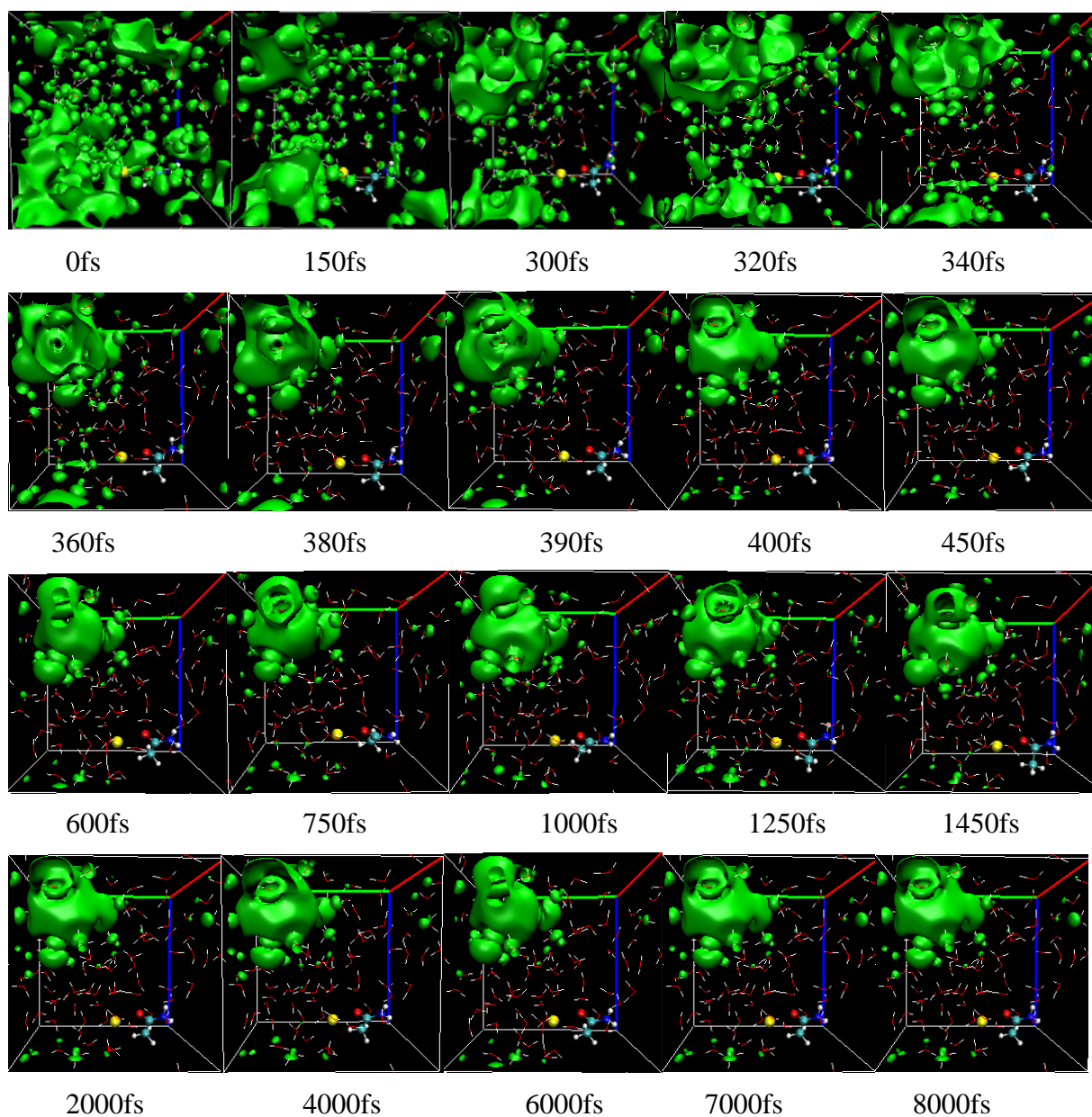


Figure S5. Spin density distributions (isovalue=0.0001) of some representative snapshot configurations at different times. In this situation, an excess electron localizes in a hydration cavity constructed by 3-4 water molecules (yellow atom represents Ca) eventually, forming a hydrated electron.

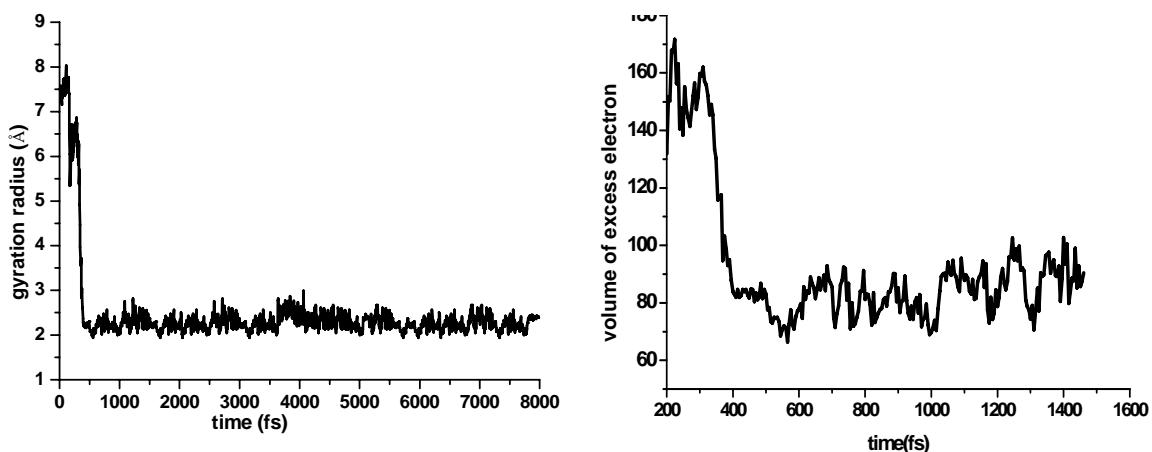


Figure S6. Time evolutions of radius of gyration (**left**) and volume of an EE (**right**).

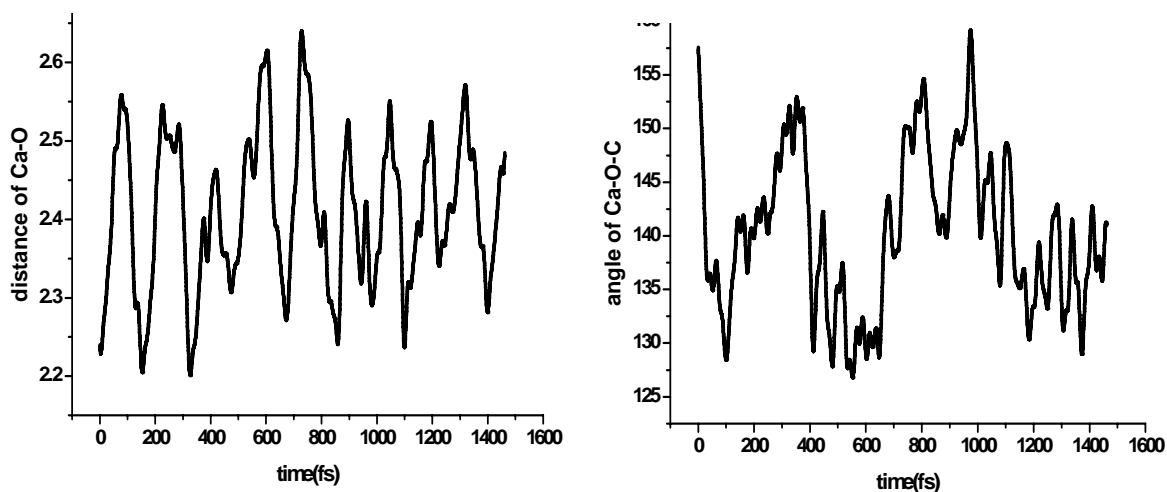


Figure S7. Time evolutions of the distance between Ca^{2+} and carbonyl oxygen (**left**) and angle of $\angle\text{Ca-O-C}$ (**right**). The two quantities both fluctuate around their average values and have no obvious tendency to shorten or elongate.

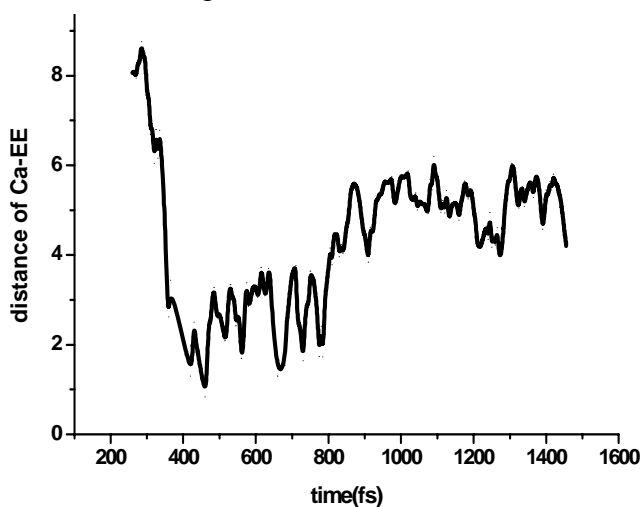


Figure S8. The distances between Ca^{2+} and the center of excess electron in time evolution.

Forming Hydrated Amide Anion

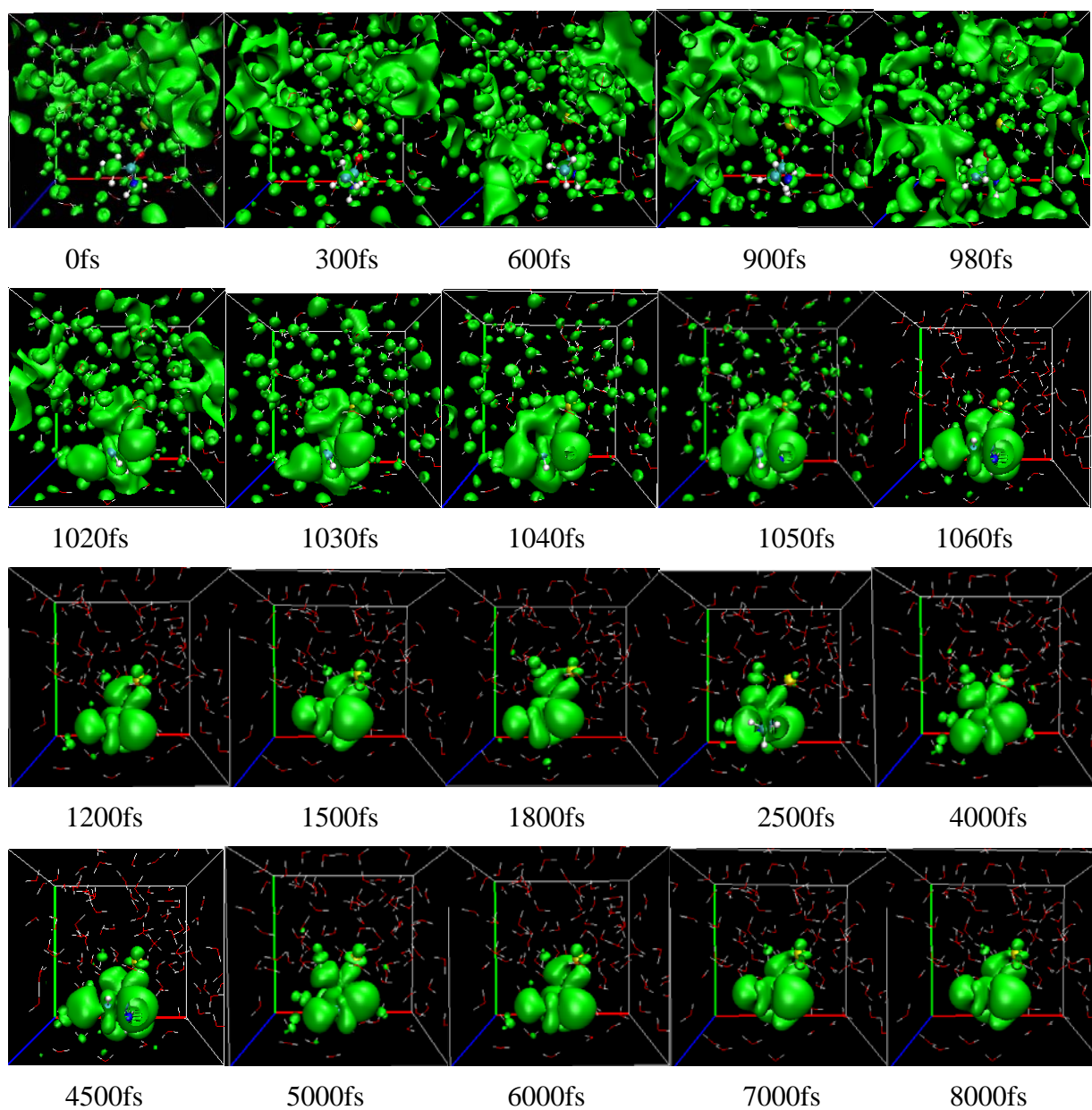


Figure S9. Spin density distributions (isovalue=0.0001) of representative snapshot configurations at different times. An excess electron localizes in acetamide eventually, forming hydrated amide anion.

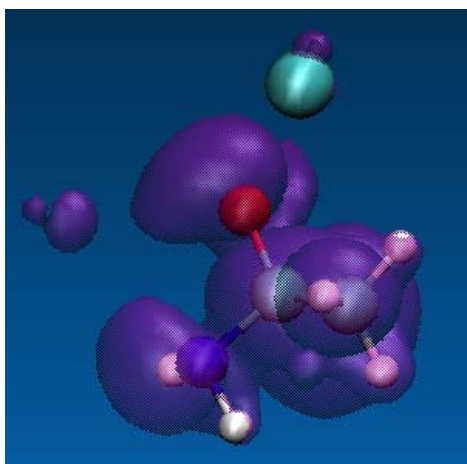


Figure S10. A representative snapshot of the formed hydrated anionic acetamide (isovalue = 0.0004).

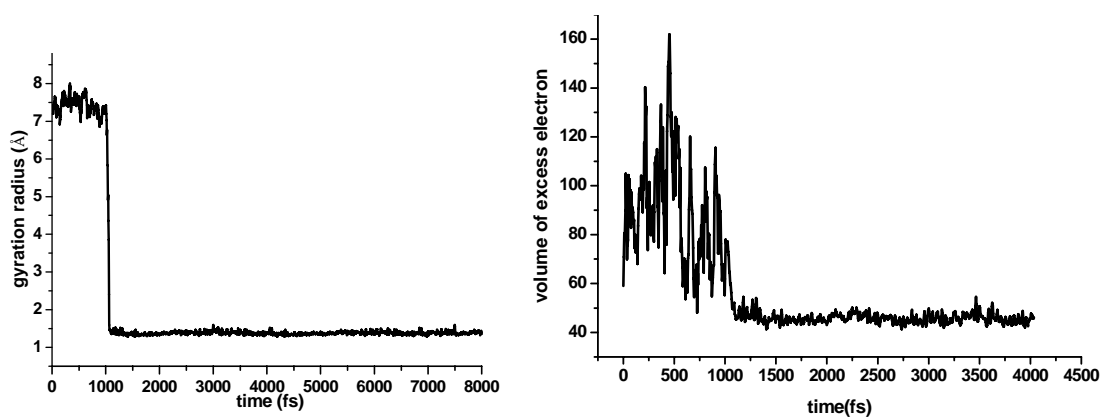


Figure S11. Radius of gyration (**left**) and volume of an EE (**right**) in time evolution.

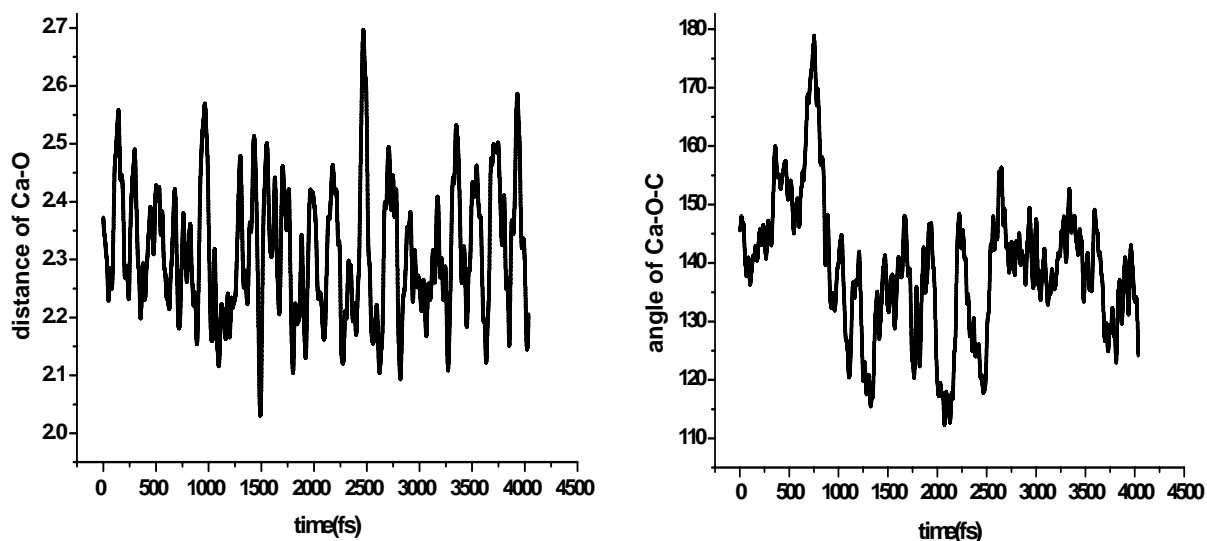


Figure S12. The distance between Ca^{2+} and carbonyl oxygen (**left**) and angle of $\angle\text{Ca-O-C}$ (**right**) in time evolution. The two quantities also have no obvious variation tendency to shorten or to elongate.

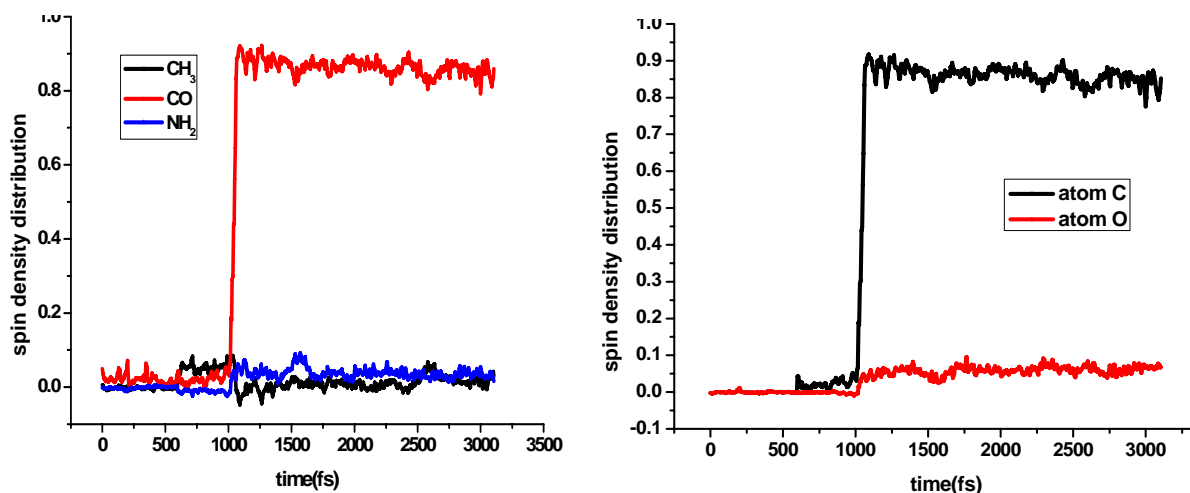


Figure S13. Spin density distributions at different groups in whole acetamide molecule (**left**) and those at different atoms in whole carbonyl (**right**) in time evolution.

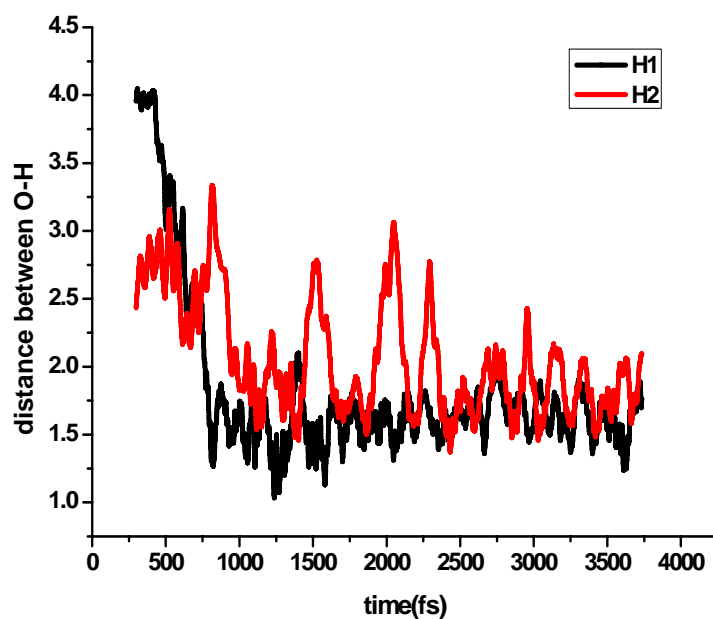


Figure S14. Variations of distance between carbonyl O and two H atoms of the two nearest H₂O molecules. The distance decreases rapidly to a stable value after EE localization, indicating that two hydrogen bonds form between the carbonyl O and its two surrounding water molecules.

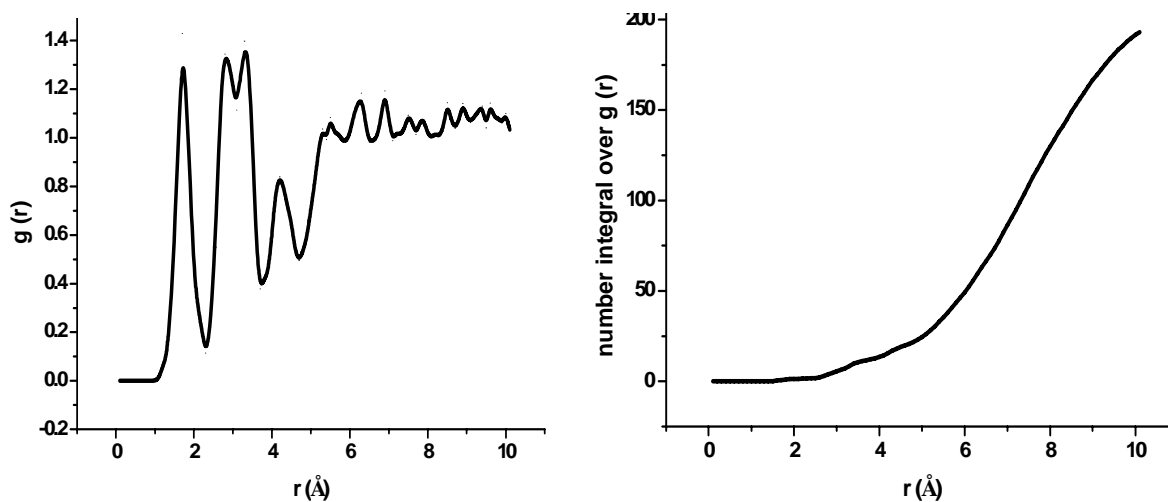


Figure S15. Radical distribution function with respect to r (the radius of a carbonyl oxygen-centered spherical shell). The left picture reflects variation of intensity and the right reflects the number of H atoms.

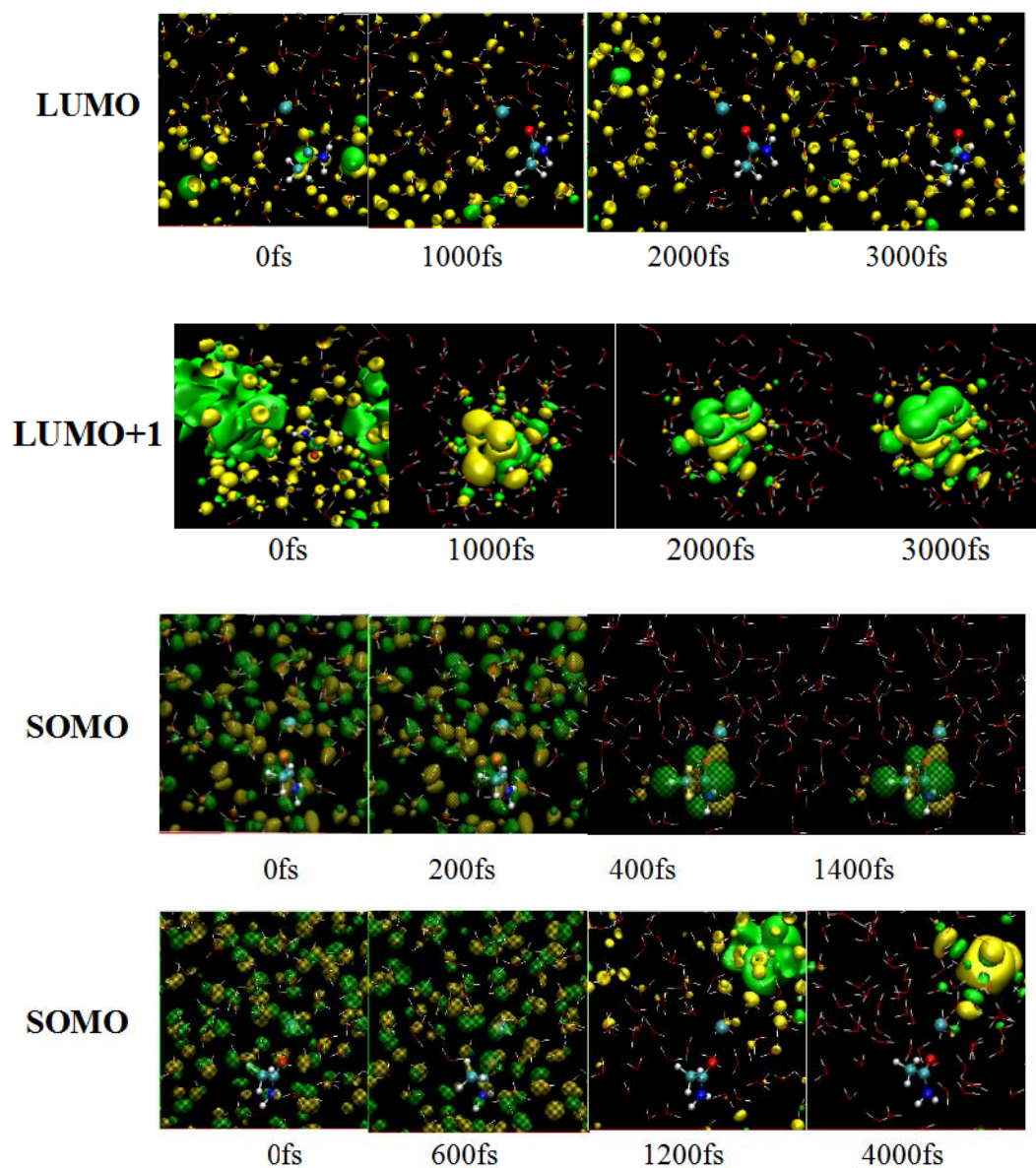


Figure S16. Time evolution of diffuse LUMO distribution before EE injection (**upper**) and two different SOMO distributions after EE injection which correspond to the formations of hydrated amide anion (**middle**) and hydrated electron (**lower**), respectively.

2.2. Localization of EE in Aqueous Solution with Weak C=O...Ca²⁺ Interaction

Forming Hydrated Electron.

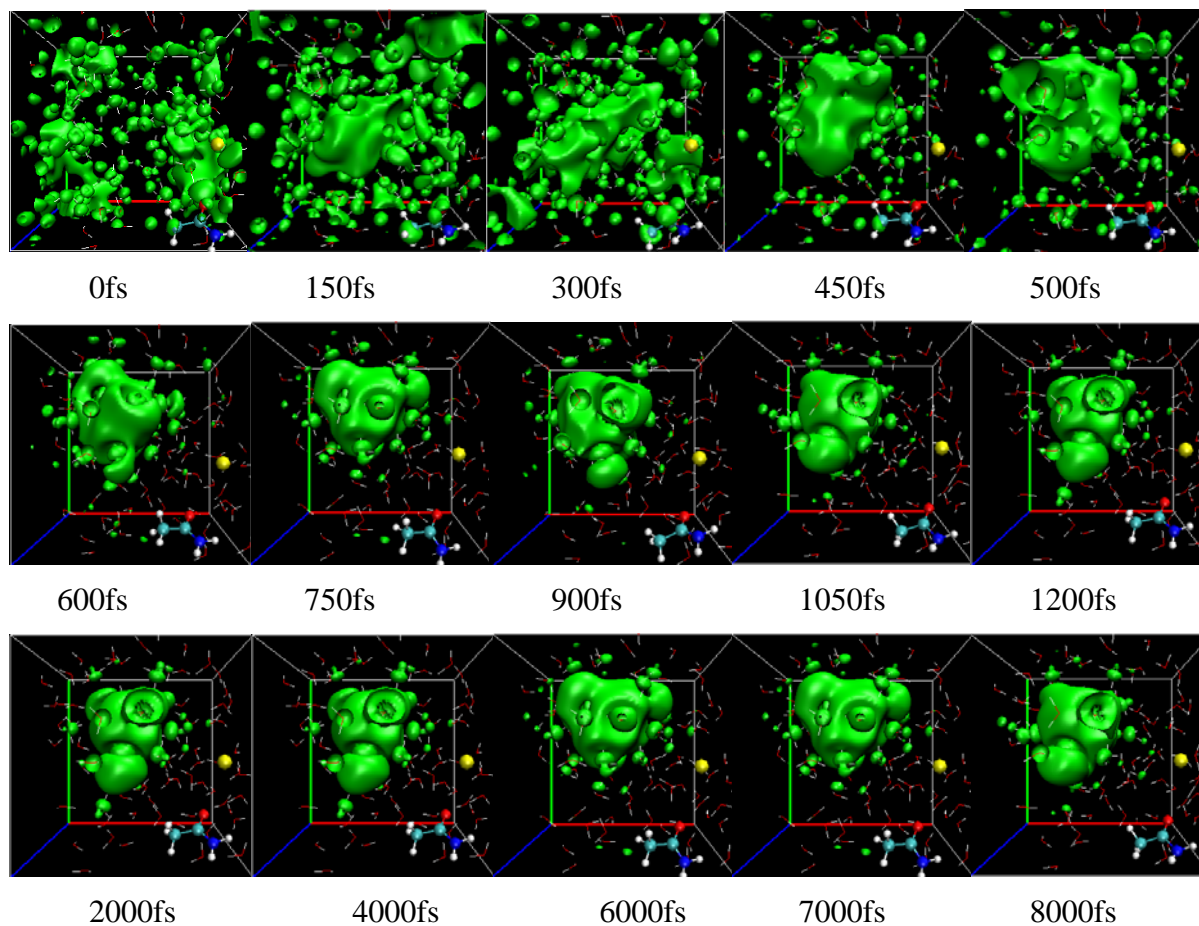


Figure S17. Visualized spin density distributions (isovalue=0.0001) of representative snapshot configurations at different times. An excess electron localizes at a hydration cavity constructed by 3-4 water molecules eventually (the yellow represents Ca).

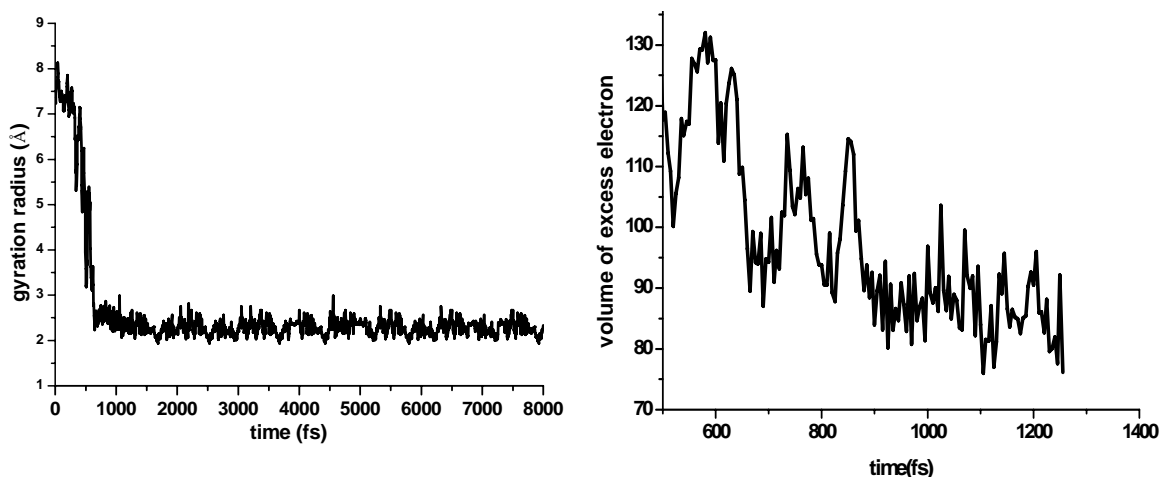


Figure S18. Variation of radius of gyration (**left**) and volume of an EE (**right**) in time evolution.

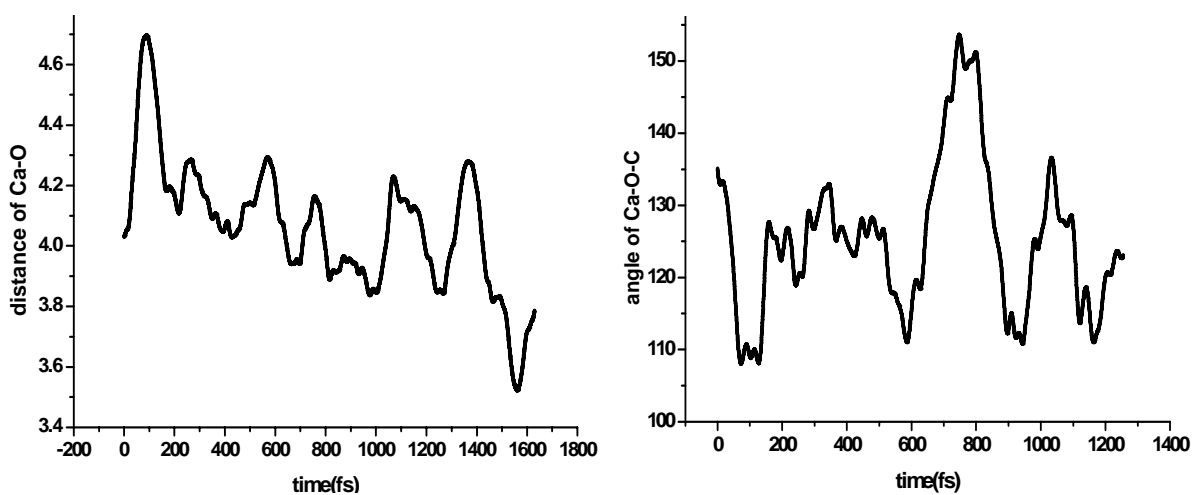


Figure S19. The distance between Ca^{2+} and carbonyl oxygen (**left**) and angle of $\angle\text{Ca-O-C}$ (**right**) in time evolution.

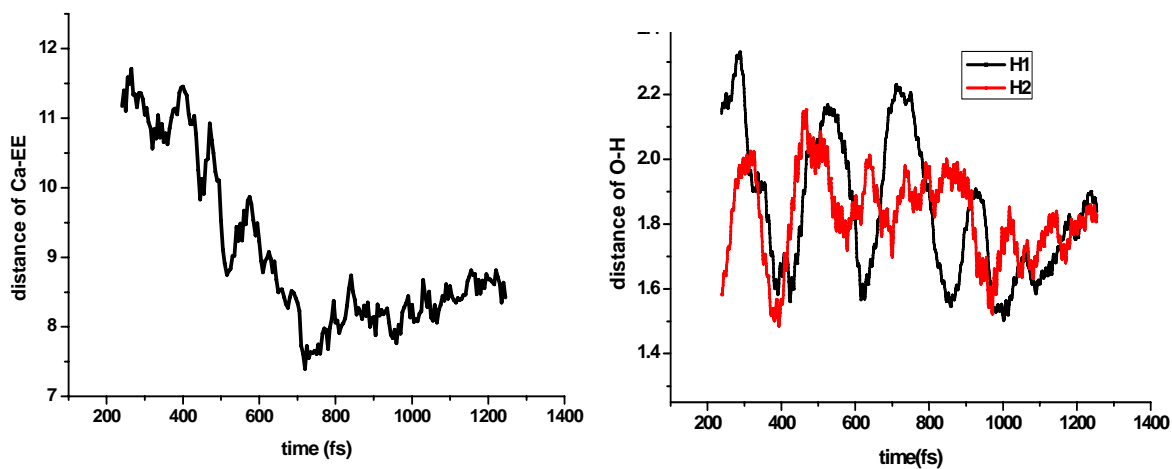


Figure S20. **Left**) The distance between Ca^{2+} and the center of excess electron in time evolution. **Right**) The distances between carbonyl O and two H atoms coming from two

nearest H₂O molecules in time evolution.

Forming Hydrated Amide Anion.

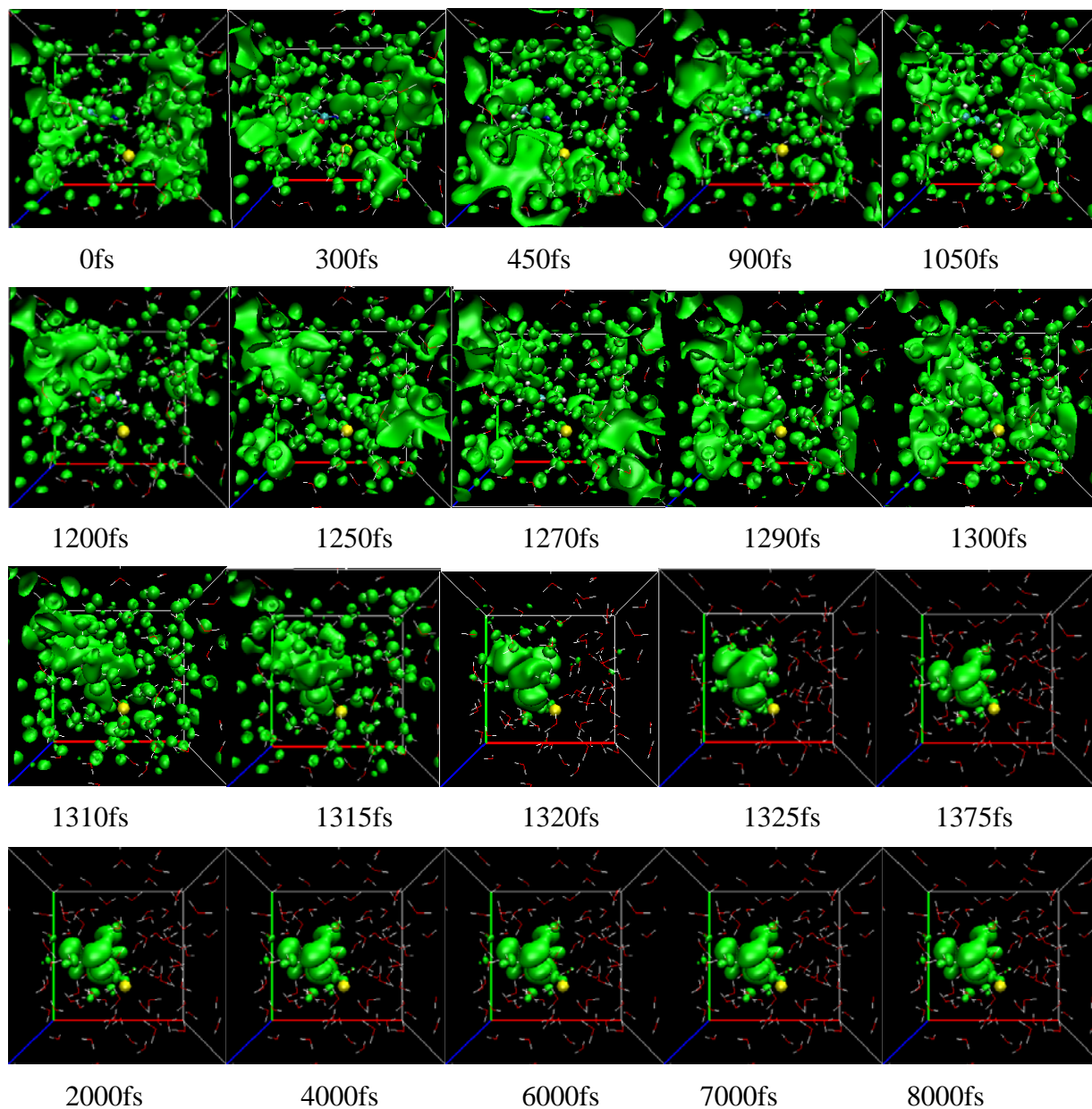


Figure S21. Spin density distributions (isovalue=0.0001) of representative snapshot configurations at different times. An excess electron localizes at acetamide eventually, forming a hydrated acetamide anion.

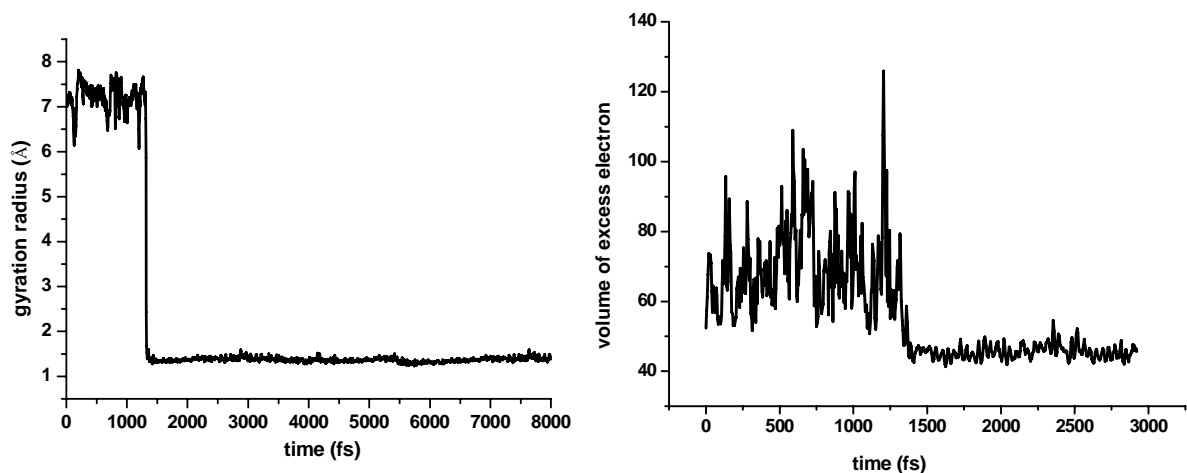


Figure S22. Radius of gyration (**left**) and volume of an EE (**right**) in time evolution.

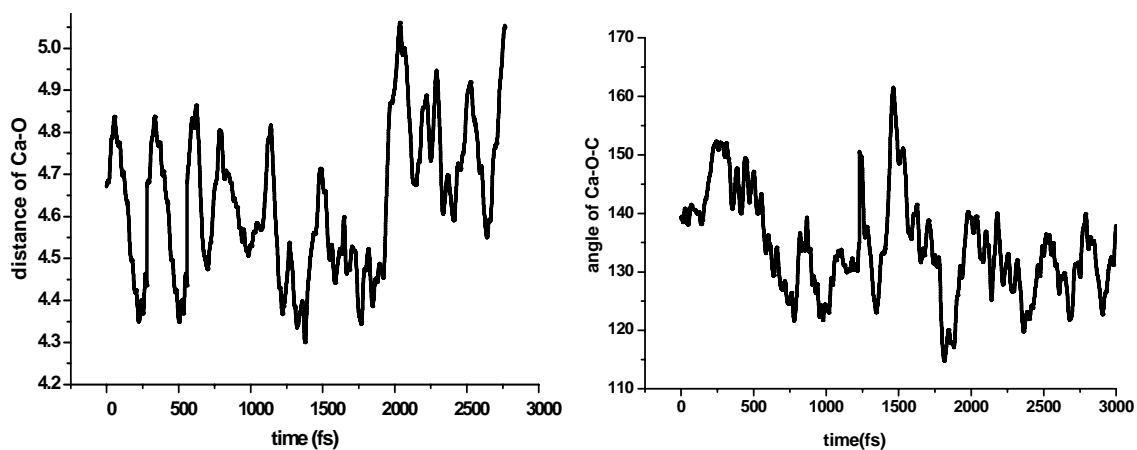


Figure S23. The distance between Ca^{2+} and carbonyl oxygen (**left**) and angle of $\angle\text{Ca-O-C}$ (**right**) in time evolution.

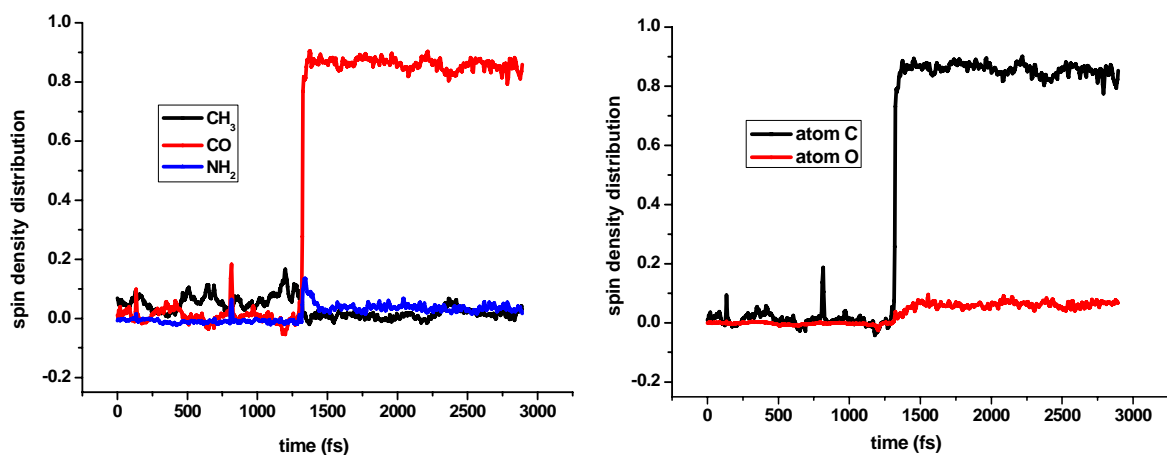


Figure S24. Spin density distribution at different groups (**left**) and different atoms (**right**) in time evolution.

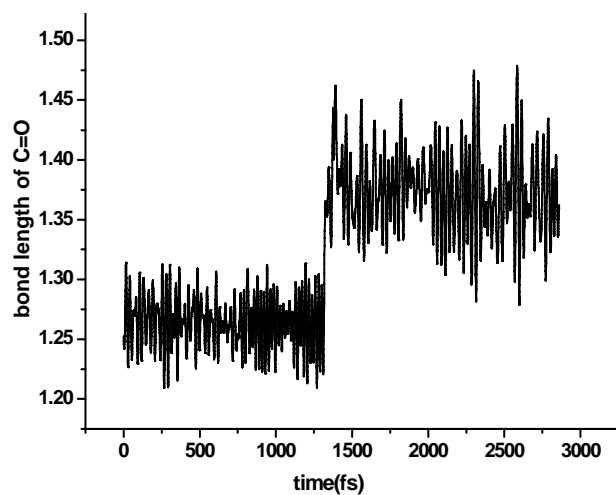


Figure S25. Variation of bond length of C=O in carbonyl in time variation.

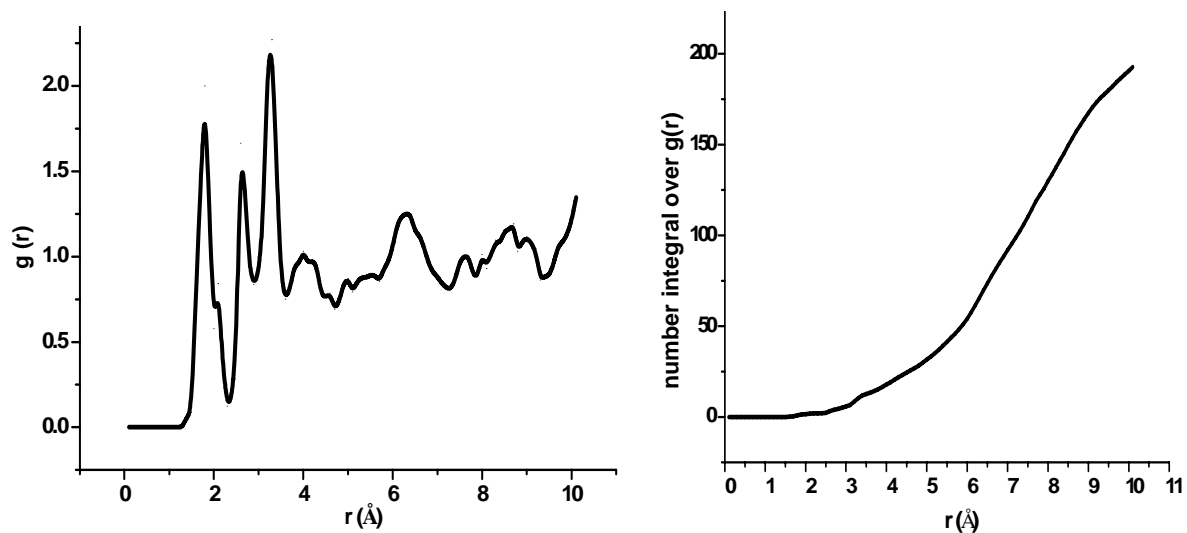


Figure S26. Radical distribution function with respect to r (radius of the carbonyl oxygen-centered spherical shell). The left curve reflects the intensity at r and the right reflects the number of H atoms at r .

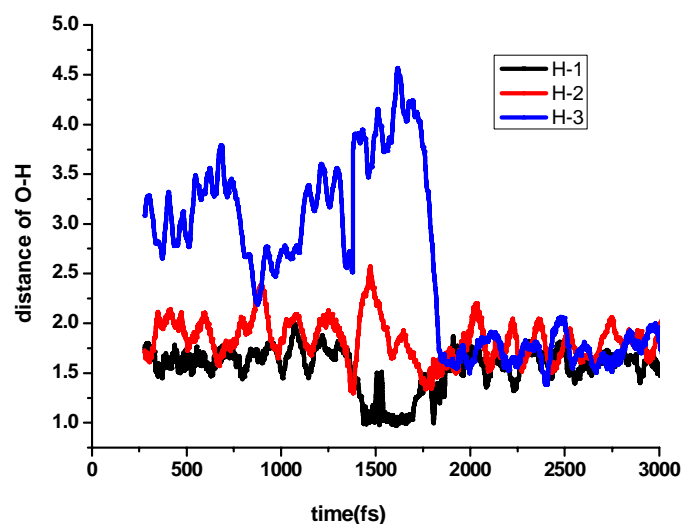


Figure S27. Time evolution of the distance between carbonyl O and three H atoms that come from three nearest H₂O molecules and form hydrogen bonds with carbonyl O, respectively.

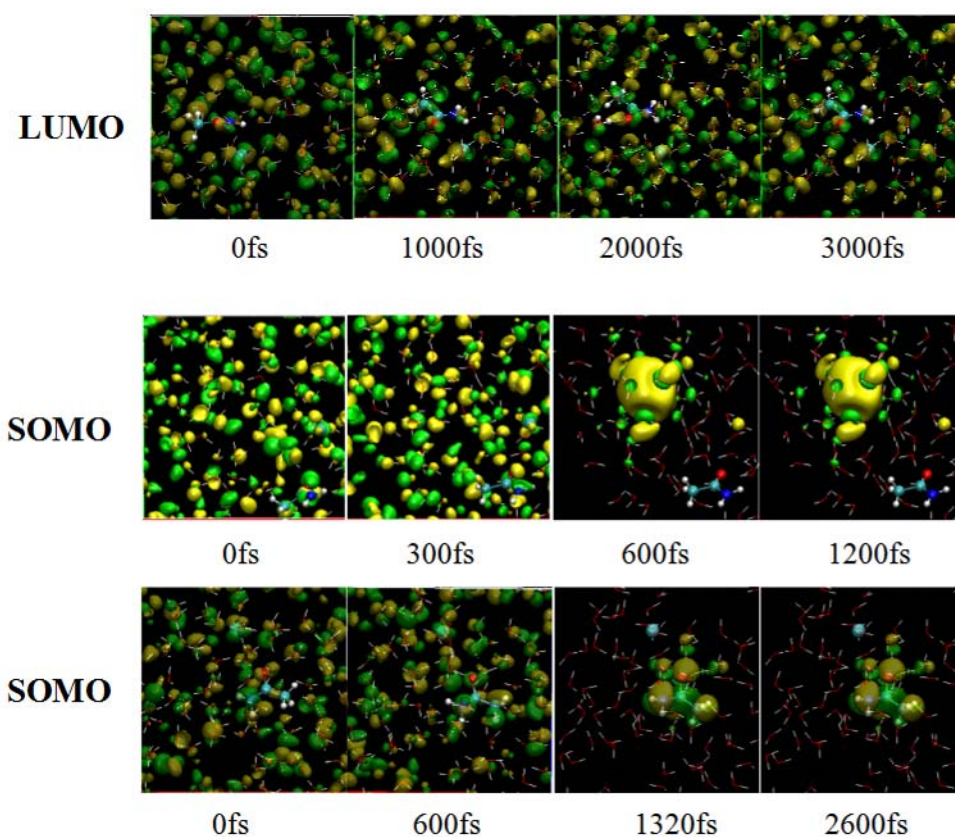


Figure 28. Time evolution of diffuse LUMO distribution before EE injection (**upper**) and two different SOMO distributions after EE injection which correspond to the formation of hydrated electron (**middle**) and hydrated amide anion (**lower**), respectively.

2.3. Localization of EE in Aqueous Solution with Separated Amide and Ca^{2+} Cation.

Forming Hydrated Amide Anion.

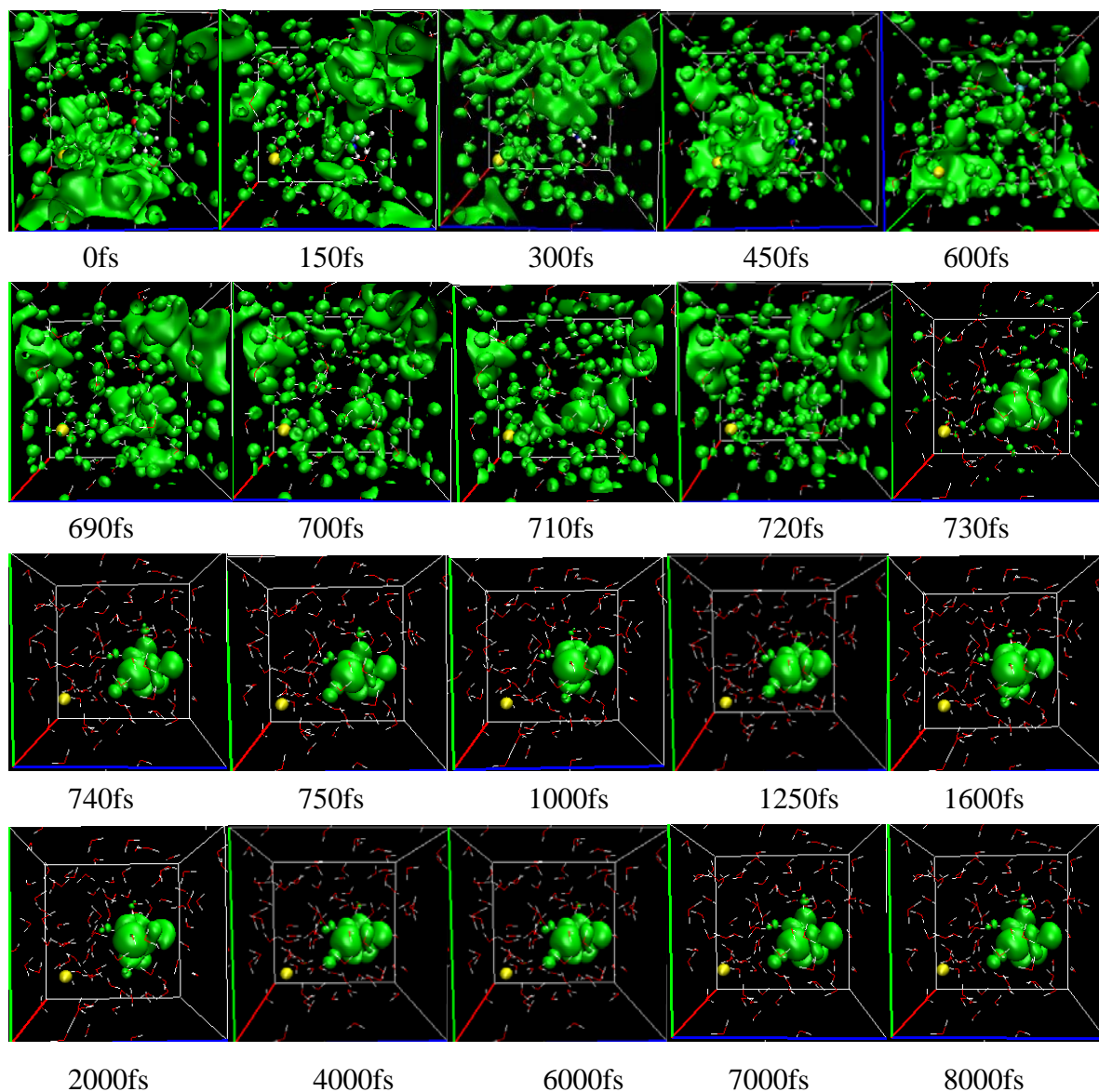


Figure S29. Visualized spin density distributions (isovalue=0.0001) of representative snapshot configurations at different times in time evolution. An excess electron localizes at acetamide eventually, forming hydrated amide anion.

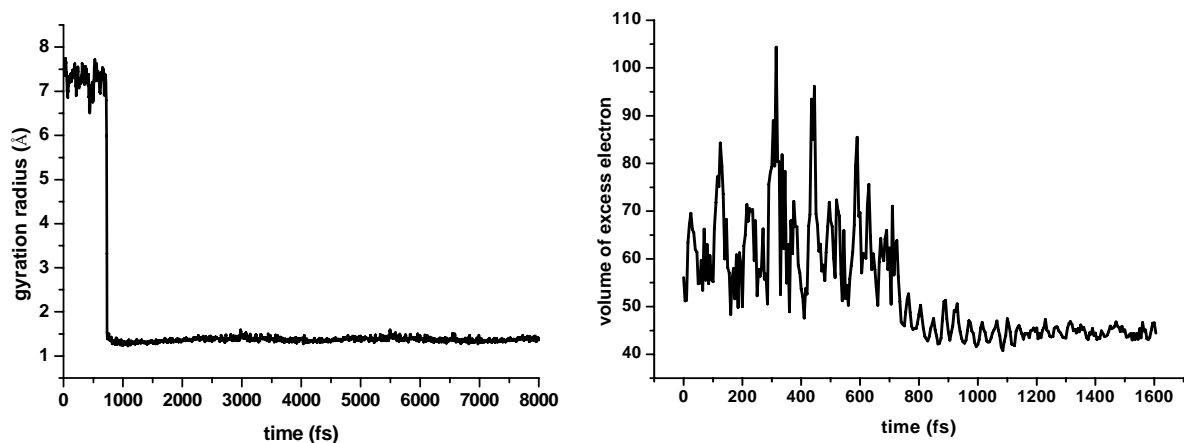


Figure S30. Variation of radius of gyration (**left**) and volume of an EE (**right**) in time variation.

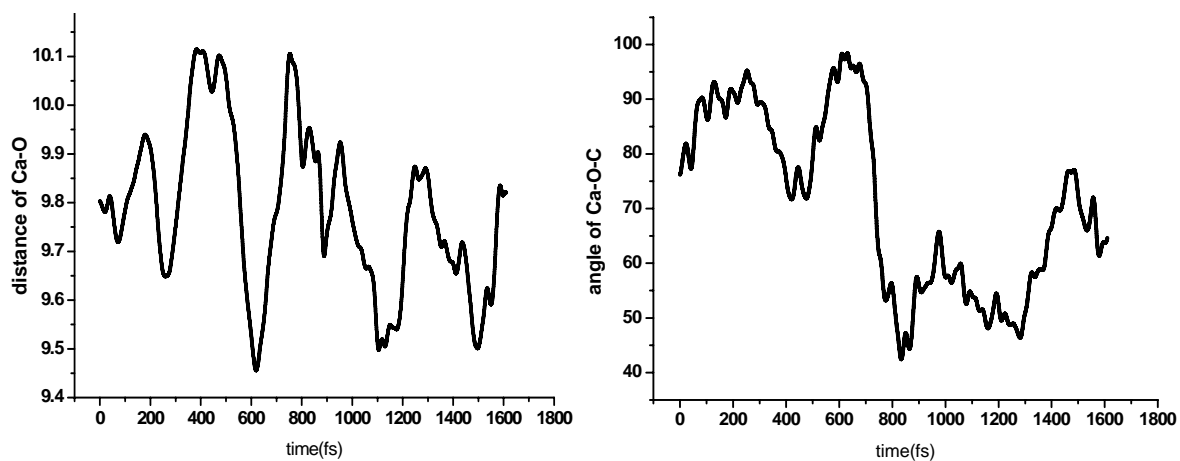


Figure S31. Distance between Ca^{2+} and carbonyl oxygen (**left**) and angle of $\angle\text{Ca-O-C}$ (**right**) in time evolution.

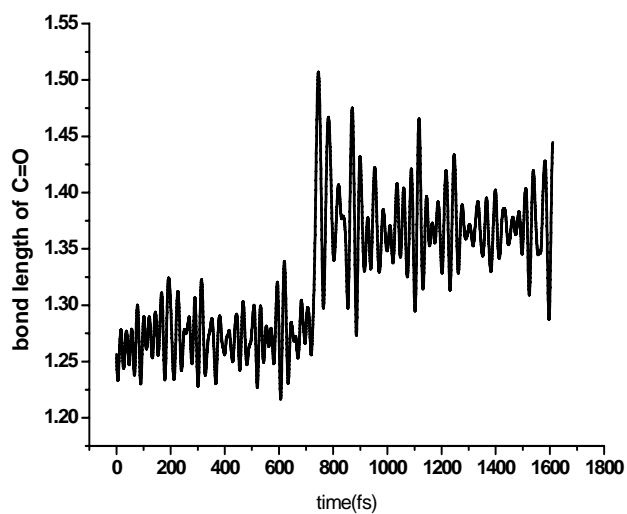


Figure S32. Bond length variation of C=O in carbonyl in time evolution.

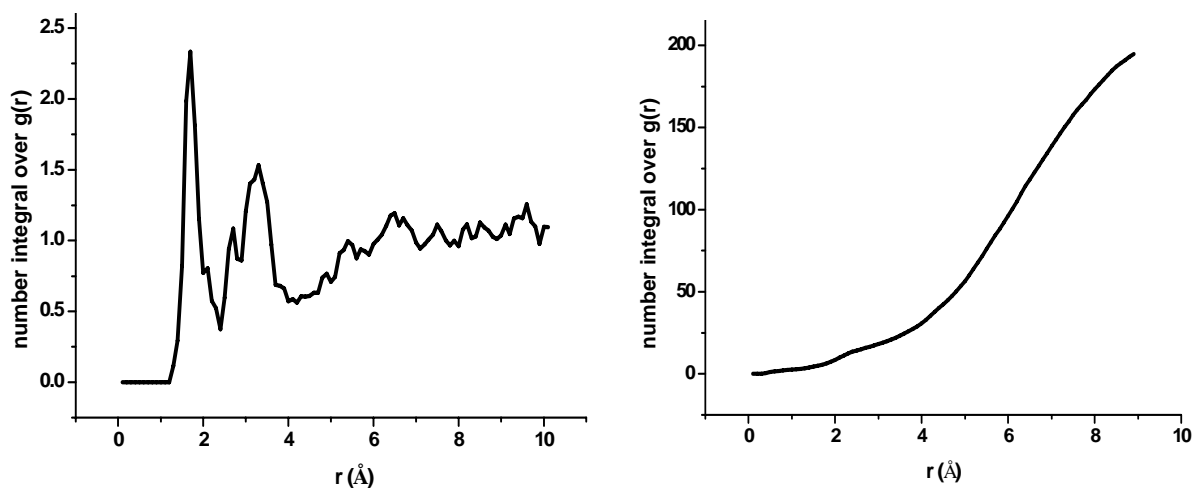


Figure S33. Radical distribution function with respect to r (radius of the carbonyl oxygen-centered spherical shell). The left curve reflects the intensity at r and the right reflects the number of H atoms at r .

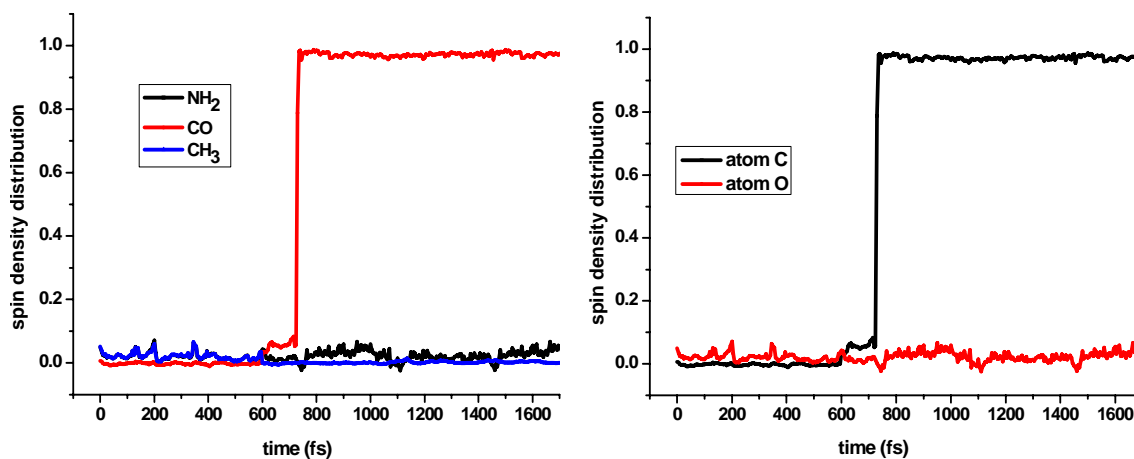


Figure S34. Spin density distributions of various groups in whole acetamide molecule (**left**) and those of different atoms in whole carbonyl (**right**) in time evolution, respectively.

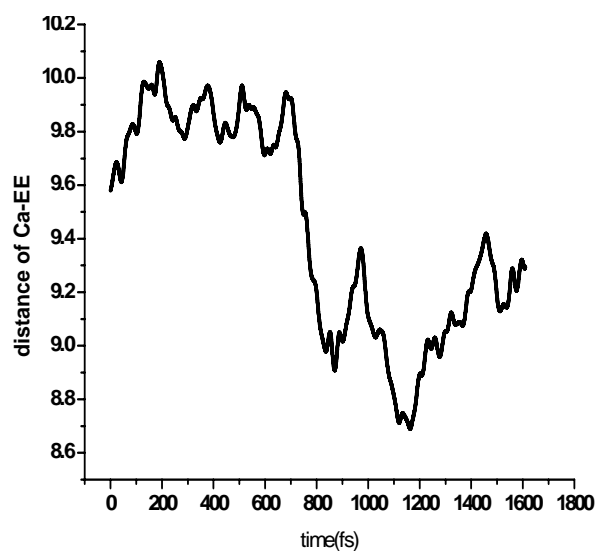


Figure S35. Distance between Ca^{2+} and carbonyl C in time evolution.

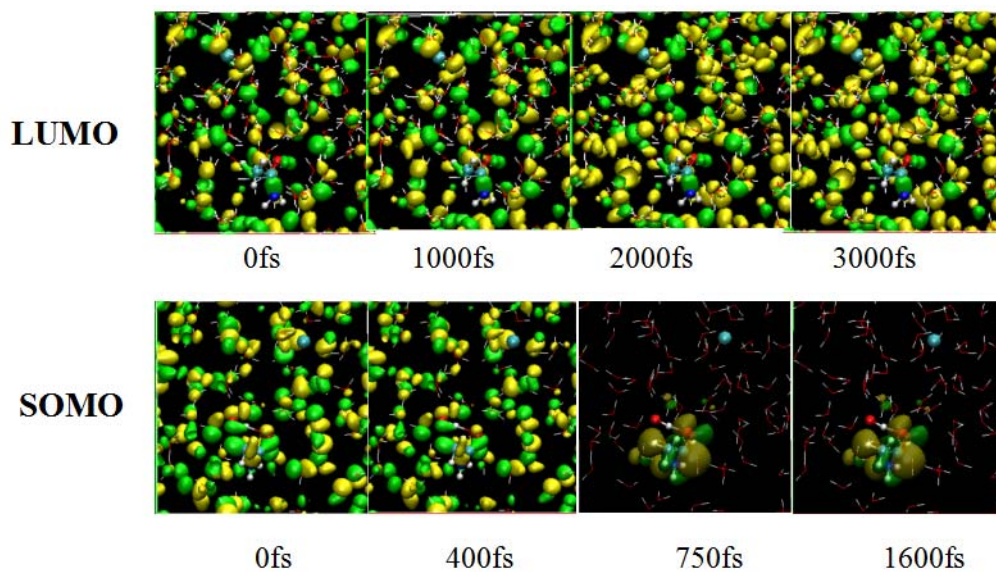


Figure S36. Time evolutions of diffuse LUMO distribution before EE injection (**upper**) and SOMO distribution after EE injection (**lower**).

Amide-Ca ²⁺ interaction	Localization mode	BLYP	PBE
Tight contact	Hydrated electron	380fs	600fs
	Amide anion	1050fs	1520fs
Solvent-shared contact	Hydrated electron	600fs	980fs
	Amide anion	1320fs	2050fs
Separated state	Amide anion	740fs	1050fs

Figure S37. The PBE functional is used to further verify these results about time scales in our simulations. The results obtained using the two different functionals (BLYP versus PBE) exhibit slight differences, but their excess electron localizing patterns and varying trends of localization times are consistent.

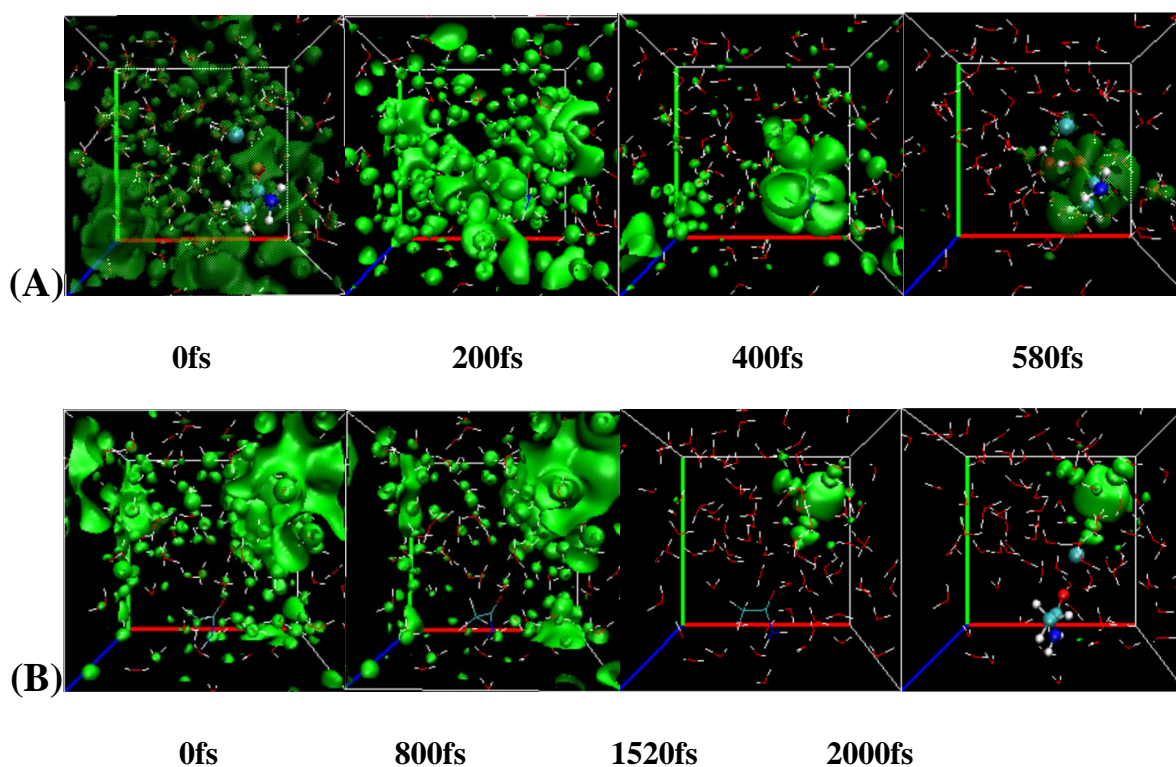


Figure S38. Spin density distributions of two types of excess electron dynamics in tight acetamide-Ca²⁺ contact solutions, simulated using the PBE functional.

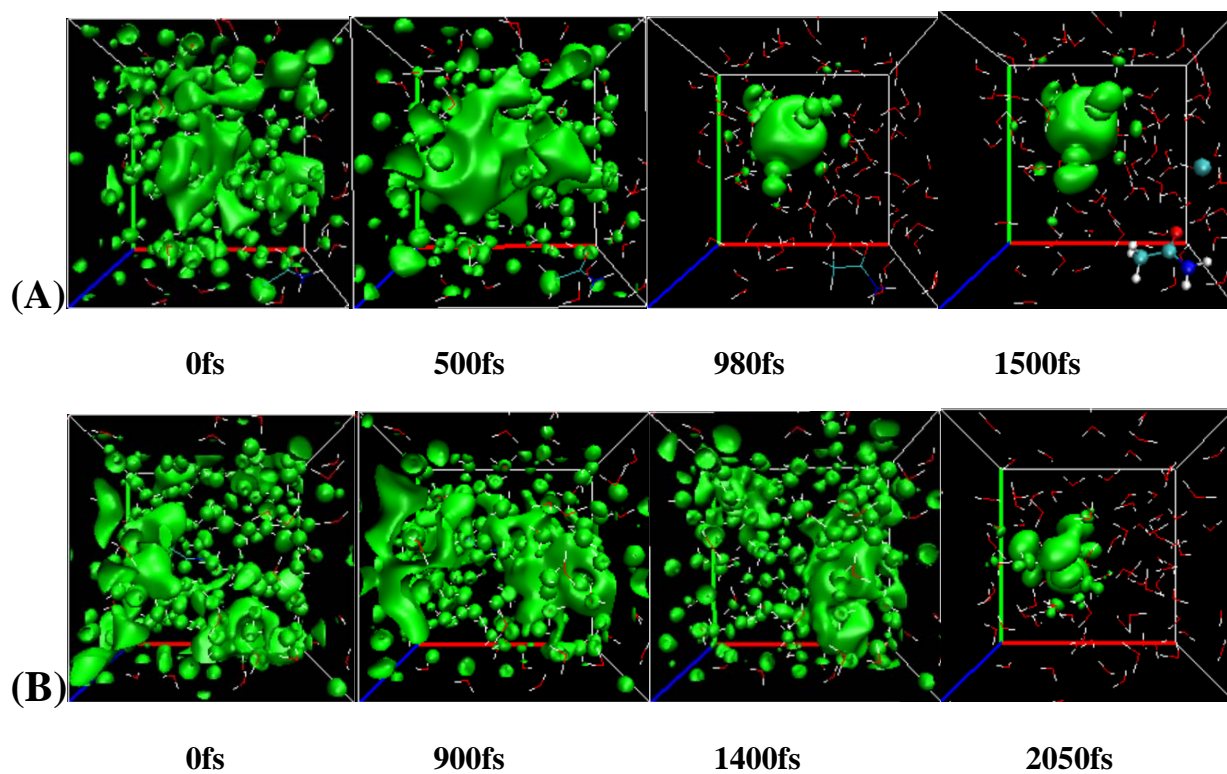


Figure S39. Spin density distributions of two types of excess electron dynamics in solvent-shared acetamide- Ca^{2+} contact solutions, simulated using the PBE functional.

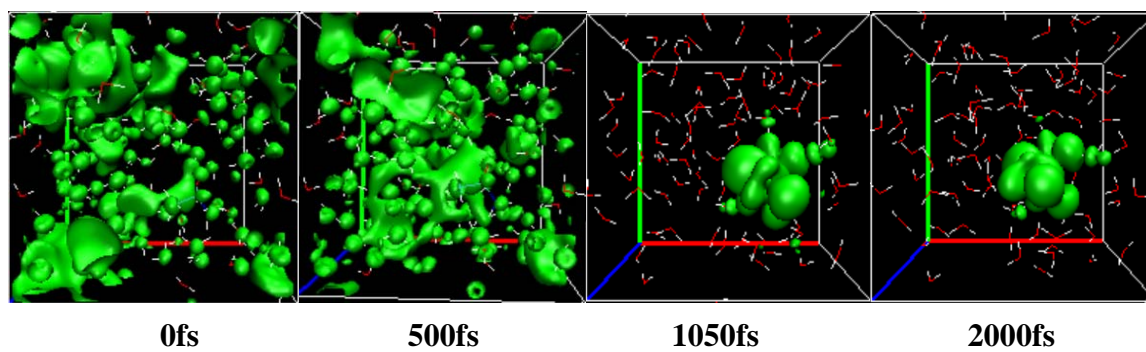


Figure S40. Spin density distributions of excess electron dynamics in separated acetamide- Ca^{2+} solutions, simulated using the PBE functional.

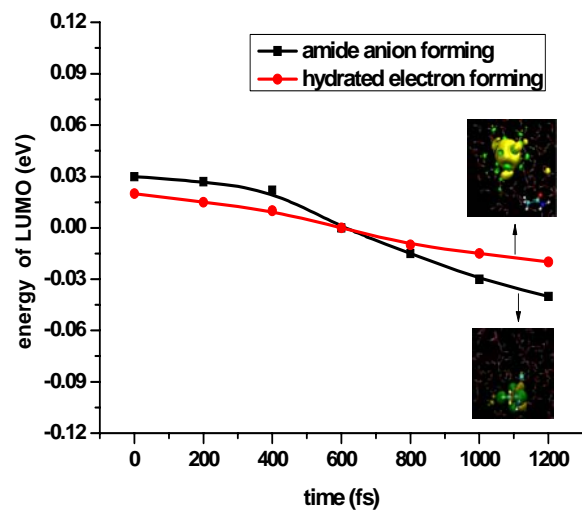


Figure S41. Time evolutions of the LUMO energy levels for the two electron localization modes in tight contact Ca^{2+} -acetamide solutions, simulated using the PBE functional.