

Ordered Solvents and Ionic Liquids Can Be Harnessed for Electrostatic Catalysis

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Introduction and Main Conclusion

1. Tuning electrostatic environment for catalysis has been an important field for a long time.
2. Recently, several strategies have been used for electrostatic catalysis in the Coote group.
3. It has been found that the external electric field can form ordered solvent and ionic liquids.
4. **Main conclusion:** The internal electric field of the ordered solvent and ionic liquids can be used for electrostatic catalysis.

Computational Details

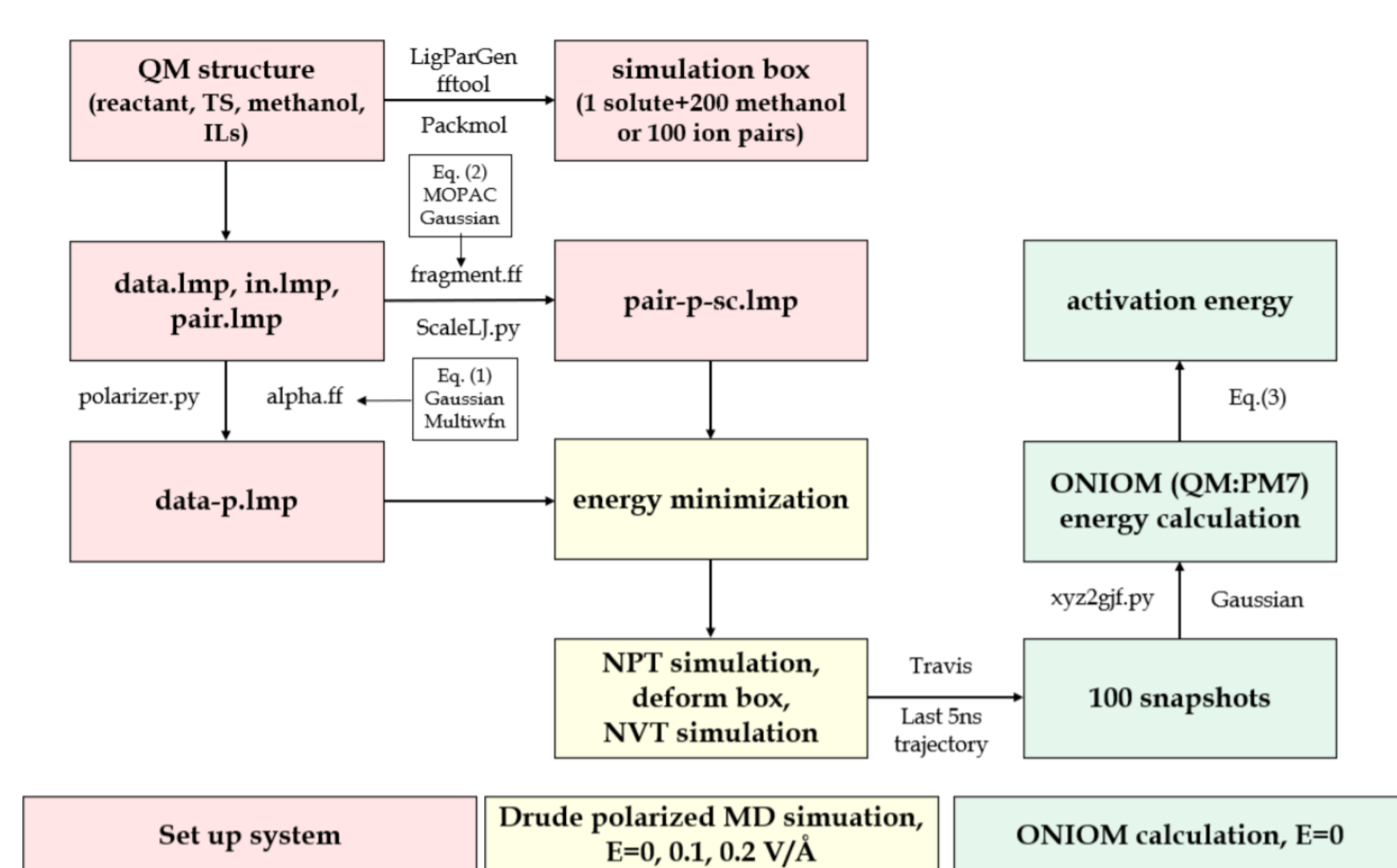


Figure 1:Workflow

- The hydrogen-transfer reaction of oalkylphenyl ketones is the test system.
- CL&Pol Drude polarizable force field and OPLS-AA force field are used for classical MD simulation of the solvent environment under external electric field.
- Activation energy of the reaction is obtained using the average energy of a set of snapshots taken from the MD simulation of reactant and transition state.
- Energy in each snapshot is calculated by ONIOM(DFT:semi-empirical) multiscale method.
- More details can be found in SI of our paper **J. Am. Chem. Soc. 2020, 142, 29, 12826–12833.**

Results (My personal website: <https://longkunxuluke.github.io/>)

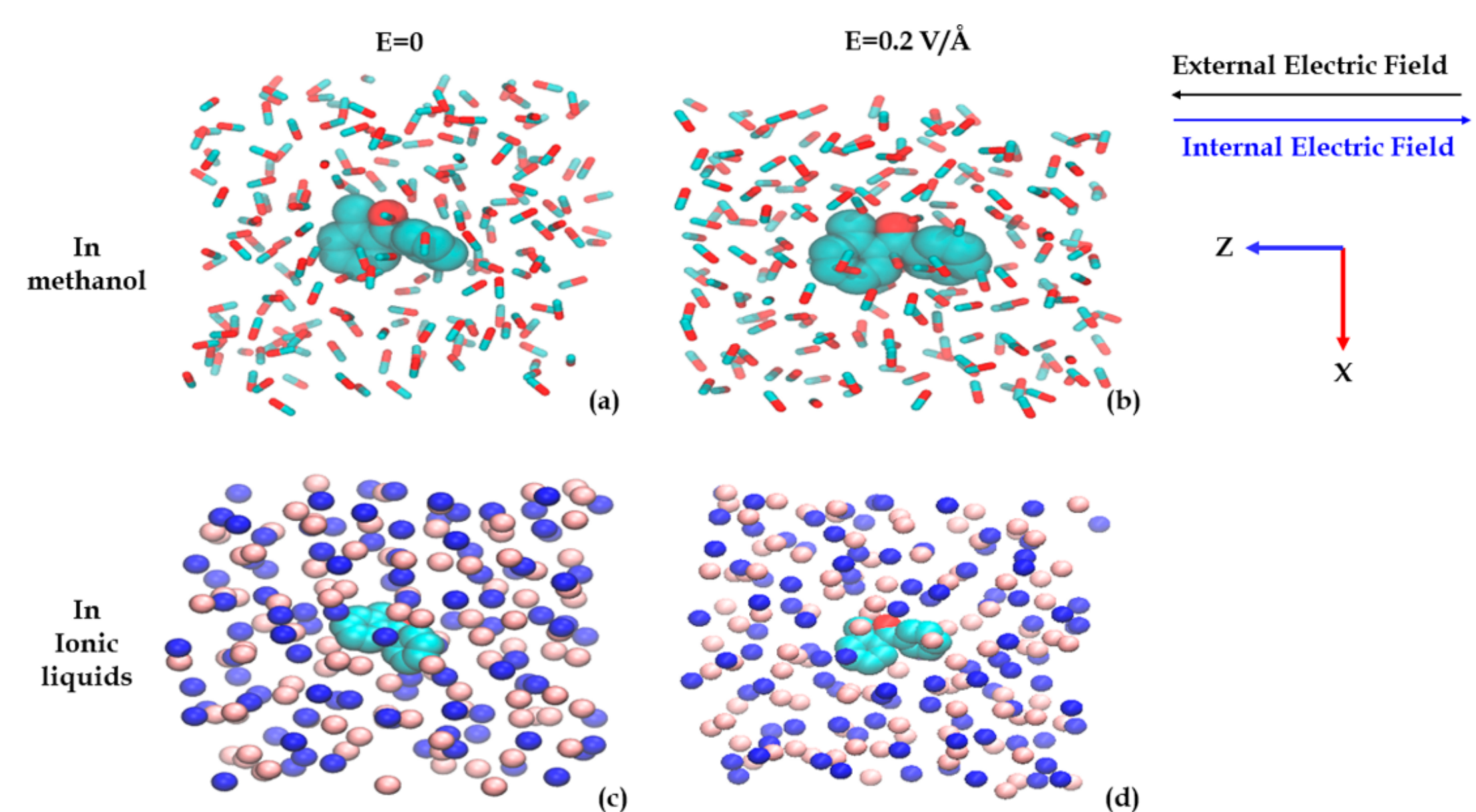


Figure 2: Snapshots obtained without and with a 0.2 V/Å external electric field of the TS solute molecule in methanol (a and b) and in [EMIM][BF₄] ionic liquids (c and d). For clarity, only non-hydrogen atoms of the solute molecule are shown in the VDW drawing method. Only C (in green) and O (in red) atoms of the methanol molecules (a and b) are shown. Only N (in blue, atom N3 in Figure 4d) and B (in pink) atoms representing the mass centers of the cations and anions, respectively, of [EMIM][BF₄] ionic liquids (c and d) are shown. All pictures are rendered using the VMD program.⁷⁶ External electric field is applied along the z direction.

Figure 2: The external electric field forms ordered solvent

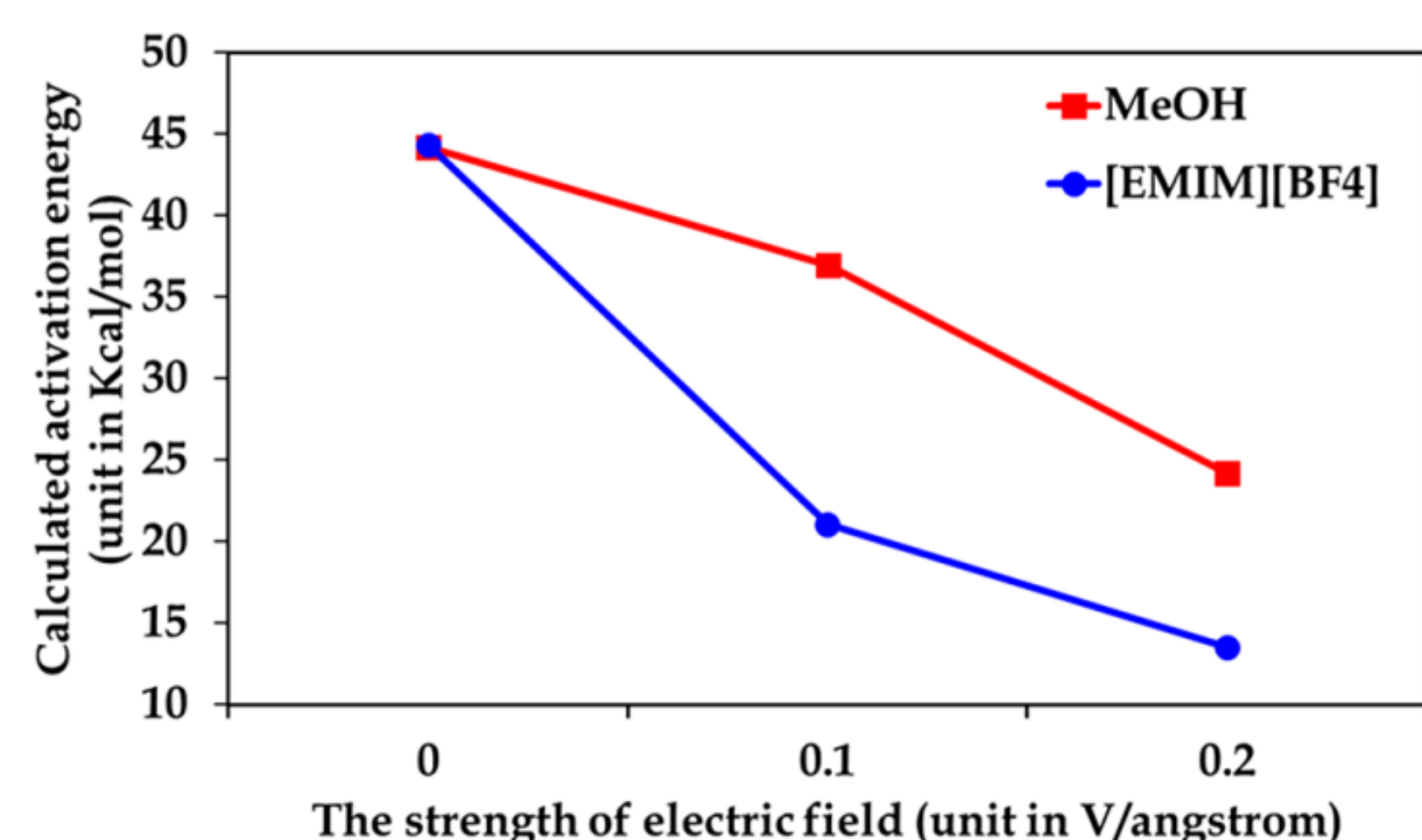


Figure 5. Calculated activation energy obtained in methanol solvent and the ionic liquid [EMIM][BF₄] without an external electric field as a function of the field strength used to order the surrounding solvent environment.

Figure 4: Activation energy of the reaction is decreased in ordered solvent

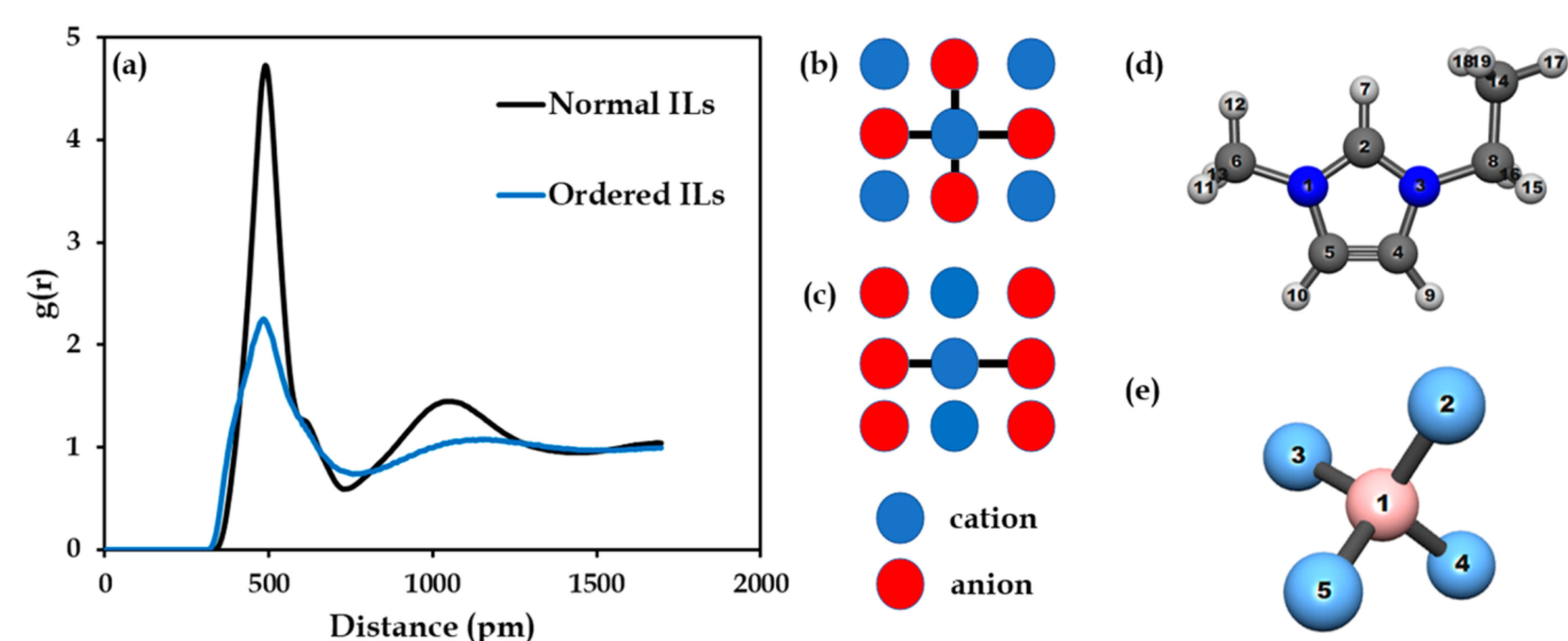


Figure 4. (a) Radial distribution function (RDF) between [EMIM] C2 atoms and [BF₄] B1 atoms in normal and ordered ionic liquids. (b and c) Simplified model of normal ionic liquids and ordered ionic liquids, respectively, where the interactions between the center cation and the nearest anion are labeled. (d and e) Structure of the cation and anion and their atomic index, respectively; pictures are rendered using the IQmol program.⁸²

Figure 3: Ordered ionic liquids can be characterized by RDF

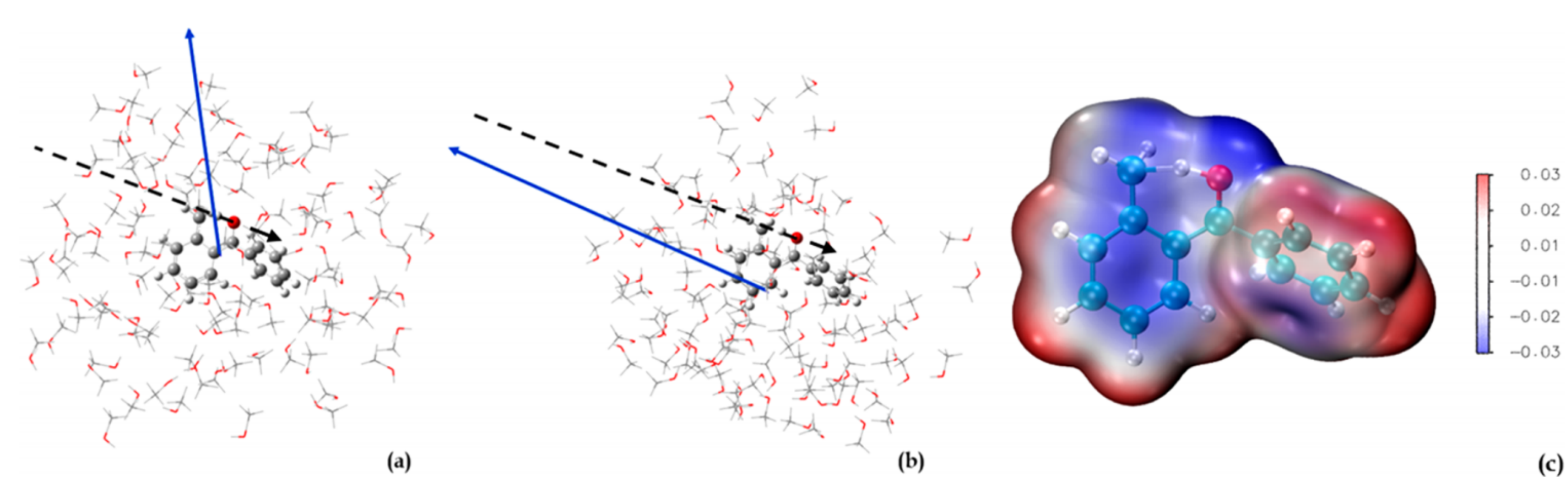


Figure 5: The relationship between the dipole moment and the reaction axis

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