Theoretical study of the photodissociation reaction of sulfate ion in water solution

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Photolysis of SO_4^{2-} in water after excitation to the second and fourth excited states (S_2 and S_4) was studied by an on-the-fly *ab initio* molecular reaction dynamics (MRD) simulation based on Particle Mesh Ewald summation [1] with ONIOM model (PME-ONIOM [2]). SA-CASSCF /MIDI4* basis set [3] was employed to describe the electronic structure of SO_4^{2-} (QM part); the water solution was treated at MM level. At the photoexcitation to S_2, the two different dissociation channels, $O(^1D)$ + $SO_3^{2-}(1^1A_1)$ and $O^-(^2P)$ + $SO_3^-(1^2A_1)$, were found. But the vertical excitation energy was 9.96 eV, which means that the photolysis might not happen by solar-flux. On the other hand, we found dispersion function for basis set plays an important role to reduce the excitation energy by 5.30 eV. Therefore, on-the-fly *ab initio* MD are going to be executed at aug-cc-pVDZ basis set. We will discuss the result at that level.

Table 1. Vertical excitation energy that calculated by CASSCF method / eV

State	Basis function			
	MIDI4*	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ
S_1	9.76	9.56	9.13	5.14
S_2	9.96	9.76	9.26	5.30
S_3	10.5	10.4	9.73	5.37
S_4	11.1	10.8	10.3	6.67

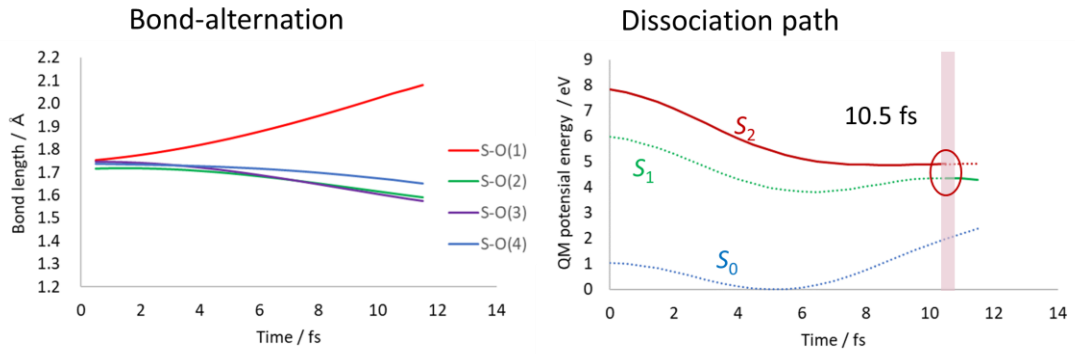

Figure 1: Result from photoexcitation to S_2 by aug-cc-pVDZ

References

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