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溶液中での1,3-シクロヘキサジエン/1,3,5-ヘキサトリエン間 光異性化反応に対する理論的研究

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Theoretical study of photoisomerization reaction between 1,3-cyclohexadiene and 1,3,5-*cis*-hexatriene in liquid phase

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[Introduction]

Photoisomerization between 1,3-cyclohexadiene (CHD) and 1,3,5-*cis*-hexatriene (HT) has attracted great interest as the representative model-system of photochromic molecules like diarylethenes. It is well known that the reaction mechanism is governed by the nonadiabatic transition between the electronic ground state (S_0) and the excited states. The product-branch occurs at conical intersection (CoIn), and the branching ratio is about 50:50. Simple photoisomerization has been experimentally investigated both in gas phase [1,2] and in liquid phase [3,4]. Quantum chemical dynamics have been carried out with two-dimensional reaction model in Jacobi coordinates by Tamura et al [5]. However, the used two-dimensional model is still open to question about whether or not this simple model is reasonable to describe the photochromic process. Additionally quantum chemical dynamics in liquid phase have not been investigated.

[Methods]

The photoisomerization reaction in liquid phase was composed of quantum mechanics (QM) and molecular mechanics (MM) models; the CHD molecule was treated as a centered QM part in a whole system and also solvent molecules as a surrounding MM part. Hexane and ethanol were employed as solvent. The *ab initio* method for the QM part was at complete active space 2nd perturbation (CASPT2) levels with cc-pVDZ basis set. Trajectory Surface Hopping (TSH) method [6] with Zhu-Nakamura formula [7] was employed to treat the nonadiabatic transition. Semiclassical dynamics of the photoisomerization was carried out based on the full-dimensional model which consists of 42 degrees of freedom.

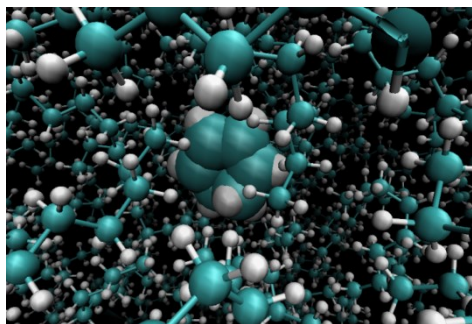


Fig.1 CHD in hexane solvent

[Result]

Photoexcitation in liquid phase was explored for the cases of S_1/S_2 excitations. Fig.2 shows the typical trajectory decaying from S_2 in hexane. The solid line means the state that molecule is staying in at the moment and the dotted line are nearby states. The blue, red and green lines represent that the potential energies of S_0 , S_1 and S_2 states. The black circle describe when nonadiabatic transition

happens. In the case of hexane solution, the decay times from S_1 and S_2 state were respectively found to be 111 and 93 fs. The nonadiabatic transition from excited states took a longer lifetime than our result in gas phase and weaker energy-fluctuation than gas phase was observed. On the other hand, nonadiabatic coupling vectors when the trajectory passed through each CoIn were revealed as same vectors in gas phase: the

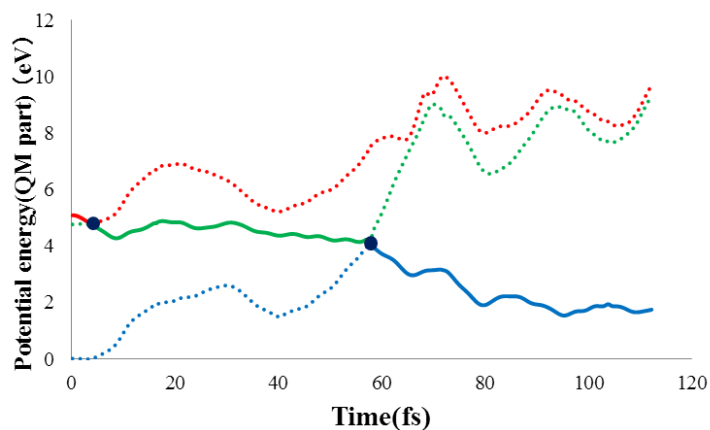


Fig.2 The result of the typical trajectory in hexane

the C2-C3-C4 bending motion at S_2 - S_1 CoIn and the Kekulé type vibrational mode at S_1 - S_0 CoIn.

The solvent effect on the nonadiabatic dynamics was found by comparing results in hexane solvent with in ethanol solvent. S_2 became a more adjacent state to S_1 in ethanol solvent than in hexane solvent, and then the feature of excited state lifetime that is different from hexane solvent was observed.

[Reference]

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