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シクロヘキサジエン/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 hexatriene in both of vapor and liquid phase

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【Introduction】

Photoisomerization between 1,3-cyclohexadiene (CHD) and 1,3,5-*cis*-hexatriene (HT) has been attracting great interest as the model system of large-size photochromic molecules like diarylethenes.

Figure.1   1,3-cyclohexadiene(left)
1,3,5-*cis*-hexatriene(right)

This isomerization has been experimentally investigated in vapor phase [1,2] and in liquid phase [3]. In 2009, Kosma et al. has measured the energy-relaxation time after photoexcitation to the first excited state (S_1) in vapor phase, and they have found that the relaxation time is 136 fs, which is an only experimental data for the energy-relaxation time from CHD.

On the other hand, several groups have performed *ab initio* calculations and discussed the reaction mechanism and the product branching ratio of CHD to HT so far. [4,5]   The first quantum dynamics using the two-dimensional reaction model based on Jacobi coordinates has been executed by Tamura et al. in 2006.   They have suggested that the branching ratio of CHD to HT is approximately 50 : 50, and also they have found that the S_1-lifetime approximates 130 fs, which has been proven by Kosma et al. 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.

In this study, firstly semiclassical dynamics of the photoisomerization of CHD in vapor phase was carried out based on the full-dimensional model which consists of 42 degrees of freedom. the photoexcitation process from CHD was assumed to go along with Franck-Condon (FC) principle. Specifically, the energy-relaxation processes after the photoexcitation to not only S_1 but also S_2 were explored by *ab initio* molecular dynamics (MD) simulation. Tully's Surface Hopping (TSH) method [6] with Zhu-Nakamura formula [7] was employed to treat the non-adiabatic transition.   The used *ab initio* method was at multi-reference configuration interaction (MRCI) and complete active space 2nd perturbation (CASPT2) levels with cc-pVDZ basis set. For the excitation to S_1 and S_2, 15 and 17 trajectory-computations were executed by our Intel XEON (Westmere, Nehalem, and Sandybridge cores) computers.
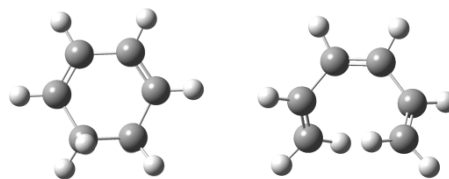
Table 1 analysis for transition dipole moments

	MRCI	CASPT2
$d_{S_1-S_0}$/Bohr	0.063999151	0.016761036
$d_{S_2-S_0}$/Bohr	1.080936402	1.196021555

【Result】

First, the transition dipole moments were explored by MRCI and CASPT2 methods around the equilibrium geometry of S_0. Table 1 shows the dependence analysis for transition dipole moments on these methods. Since the transition dipole moments for the excitation to the S_2 state have a certain amount, the excitation to S_2 should be explored to understand the photoisomerization.
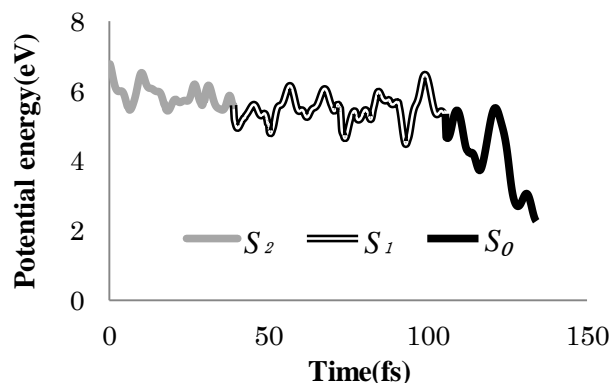
Figure.2 is the typical trajectory decaying from S_2 in vapor phase. The product branching

Figure.2 result of the typical trajectory in vapor phase

ratio of CHD to HT after photoexcitation to S_1 is found to be 50 : 50, equivalence. Contrary to our expectation, the S_1-lifetime is 78.5 fs on an average, which is shorter than previous studies. However, since the number of our trajectories is not enough to get the converged result, we still need more trajectories.

The ratio of CHD to HT after excitation to S_2 is 70 : 30; the photoisomerization prefers CHD product. Figure.3 shows that the points where the non-adiabatic transitions occurred at conical intersection between S_2 and S_1 states (CoIn-S_2/S_1) and CoIn-S_1/S_0. The decay time to reach S_0 is 57.8 fs on an average. This shorter lifetime than S_1 would be reasonable if we consider the excess energy comparing with the case of the transition to S_1, and moreover S_1 and S_2 states are lying close to each other.

On the other hand, the conformational feature when the non-adiabatic transition occurs is found to be quite similar in every case even for CoIn-S_2/S_1 and CoIn-S_1/S_0. The actual changing structure seemed to be a stretching motion for each of C-C bonds, because the corresponding non-adiabatic vectors also show such a stretching motion.

Ab initio MD simulation in liquid phase was performed with QM/MM method. The fluctuation of potential energy was smaller than that in vapor phase, but the non-adiabatic transition has happened at the shorter lifetime in the excited states than the vapor phase.

【Reference】

[1] K. Kosma, S. A. Trushin, W. Fuß, W. E. Schmid, *Phys. Chem. Chem. Phys.***11**, 172 (2009). [2] J. L. White, J. Kim, V. S. Petrović, P. H. Bucksbaum, *J. Chem. Phys.***136**, 054303 (2012). [3] E. C. Carroll, B. J. Pearson, A. C. Florean, P. H. Bucksbaum ,R. J. Sension, *J. Chem. Phys.*, **124**, 114506 (2006). [4] H. Tamura, S. Nanbu, T. Ishida, H. Nakamura, *J. Chem. Phys.* **124**, 084313 (2006). [5] J. B. Schönborn, J. Sielk, B. Hartke, *J. Phys. Chem. A*, **114**, 4036 (2010). [6] J. C. Tully, R. K. Preston, *J. Chem. Phys*, **55**, 562 (1971). [7] H. Nakamura, *Nonadiabatic Transition: Concept, Basic Theories and Applications ,2nd Edition*(World Scientific, Singapore, 2012)