Theoretical study on the photodissociation of methanol in the interstellar medium

Megumi Kayanuma[1], Mitsuo Shoji[1,2], Yuri Aikawa[1,2], Masayuki Umemura[1,2], Yasuteru Shigeta[1,2]

[1] *University of Tsukuba, Center for Computational Sciences, Tennodai 1-1-1, Tsukuba 305-8577, Japan*

[2] *University of Tsukuba, Graduate School of Pure and Applied Sciences, Tennodai 1-1-1, Tsukuba 305-8571, Japan*

E-mail: kayanuma@ccs.tsukuba.ac.jp

In the interstellar medium, the formation of complex organic molecules is considered to proceed via radical reactions on icy grain. One of the major sources of radical production in astrophysical environments is UV photolysis. Thus, understanding the photochemistry in space is important to reveal the rich and diverse chemistry in space. Many laboratory experiments of photochemistry on interstellar ice analogs have been carried out to elucidate the mechanisms, and previous experimental studies of vacuum ultraviolet light irradiation of methanol showed that the photodissociation branching ratios were different between in gas phase[1] and in solid phase[2], i.e., the branching ratio in gas phase was reported as $(CH_2O+H+H):(CH_3O+H):(CH_2OH+H) \approx 1:0.25:0.15$, on the other hand, the effective branching ratio of $CH_2OH + H$ was about 5 times larger than that of $OCH_3 + H$ in methanol ice. However, the reason for such difference in the dissociation branching ratio of methanol depending on a kind of matrix was not yet clarified.[3] The detailed mechanism of photodissociation of methanol is not yet elucidated, though the potential energy curves along the O-H and C-O bond dissociations in gas phase were examined at the time-dependent density functional theory (TDDFT) level [4] in a previous study.

In the present study, we investigate the photodissociation mechanisms of a methanol molecule by state-averaged complete active space self-consistent field (SA-CASSCF) and the second-order multireference perturbation theory (CASPT2) methods with aug-cc-pVTZ basis sets. At first, potential energy curves along the C-H, O-H, and C-O bond dissociations were analyzed. The initial geometry was optimized on the electronic ground state at B3LYP/6-311++G(d,p) level of theory, and only bond distances related to the dissociation were elongated while other parameters were kept as those of the initial structure. For the calculations of electronic excited states, 12 states were considered, and 4 electrons and 12 orbitals were included in the active space. Next, we perform *ab initio* molecular dynamics simulations on the electronic excited states to reveal the more details of the dissociation mechanisms.

Fig. 1 shows the potential energy curves along C-H, O-H, and C-O bond dissociations calculated at the CASPT2 level. The first excited state ($1^1A''$ at the ground state equilibrium structure which corresponds to the excitation from $2a''$ to $3s$ orbital) became monotonically lower during O-H bond dissociation, while this state became lowered when the bond distances were longer than about 1.7 Å during C-H and C-O bond dissociations. Among the higher excited states, $4^1A'$ at the ground state equilibrium structure, which correspond to the

excitation from 7a' to 3s orbital, became lower along the C-H and C-O bond dissociations, while this state remained high in energy during O-H bond dissociation. The results of dynamics will be shown in the presentation.
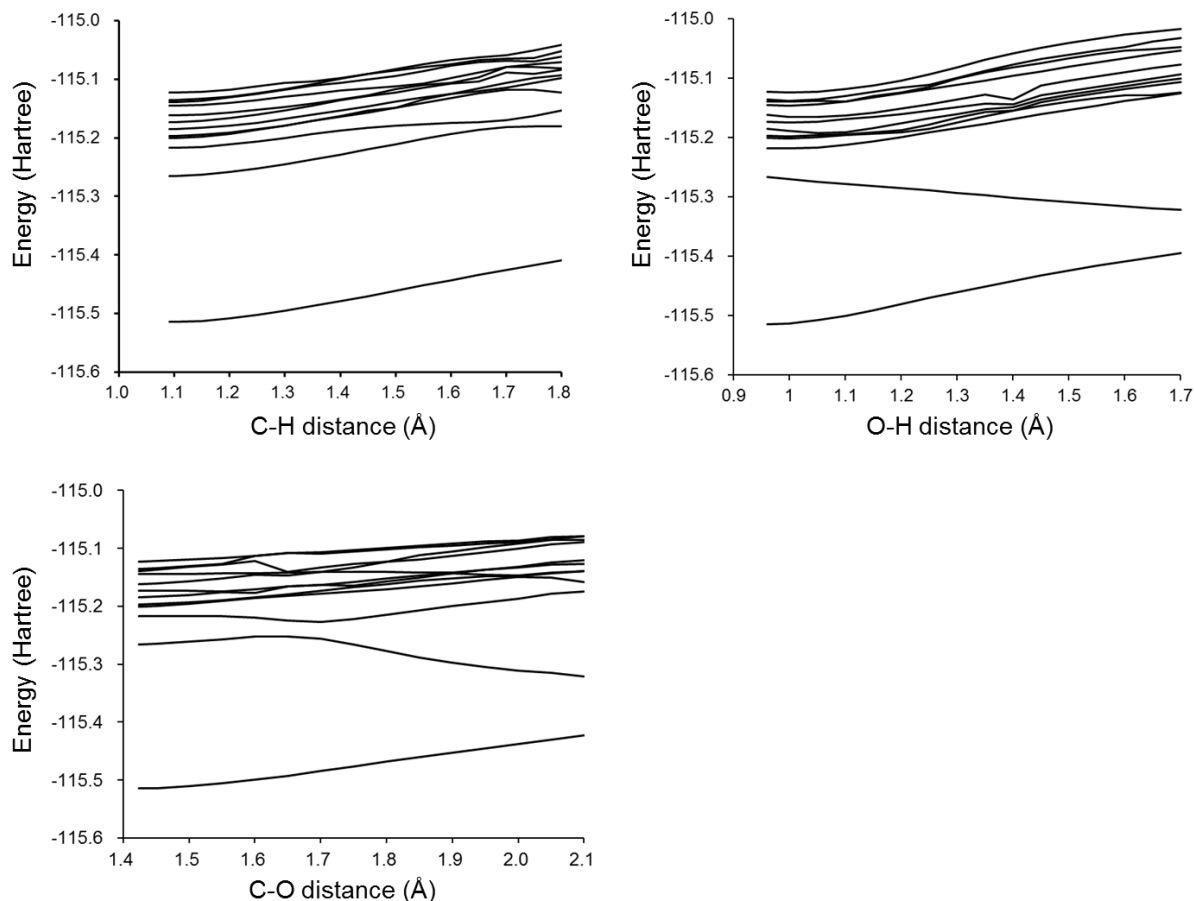
Figure 1. Potential energy curves along with the C-H, O-H, and C-O bond dissociations.

References:

[1] M. Lucas, Y. Liu, R. Bryant, J. Minor, J. Zhang, *Chem. Phys. Lett,* **2015**, 619, 18.

[2] K. I. Öberg, R. T. Garrod, E. F. van Dishoeck, H. Linnartz, *Astron. Astrophys.*, **2009**, 504, 891.

[3] K. I. Öberg, *Chem. Rev.*, **2016**, 116, 9631.

[4] B.-M. Cheng, M. Bahou, W.-C. Chen, C.-h. Yui, Y.-P. Lee, L. C. Lee, *J. Chem. Phys.*, **2002**, 117, 1633.