A path integral molecular dynamics study of muoniated acetone radicals

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Muonium (Mu) atom is formed by a positive muon (μ^+) and an electron, where the mass of μ^+ is much smaller than that of a proton and Mu atom has larger nuclear quantum effect than hydrogen. Muoniated radicals are used to muon spin resonance (μSR) by using large magnetic moment of μ^+. μSR technique provides the determination of hyperfine structures of muoniated radicals, which is characterized by the reduced muon hyperfine coupling constant (A_μ') on a radical. The experimental measured A_μ' value of muoniated acetone radical (Mu-ACE, Figure 1) is found to be 8.56 MHz at 300 K [1], and to be smaller as the temperature decreases [2]. However, theoretical A_μ' value for Mu-ACE is calculated to be -5.8 MHz by static optimization calculation [2] and it does not reproduce experimental A_μ' values because it does not include the nuclear quantum and thermal effects. We therefore performed *ab initio* path integral molecular dynamics (PIMD) simulation, which can include these effects, to reproduce A_μ' value of Mu-ACE and explain the temperature dependence of A_μ'.

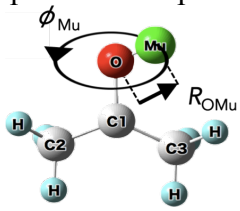

Figure 1: The molecular structure of Mu-ACE.

We performed on-the-fly *ab initio* PIMD simulation with O3LYP/6-31+G level. We used the massive Nosé-Hoover chain thermostat to control the system temperature. We also calculated hydrogenated acetone radical (H-ACE) to compare with Mu-ACE. The numbers of beads for Mu-ACE and H-ACE were 64 and 16, respectively. Imaginary-time step sizes for these simulations were 40 asec/step and 0.1 fsec/step, respectively. The number of total time steps was 95,000 steps for both simulations.

Table 1 shows the experimental and theoretical A_μ' values. Our A_μ' values at 300 K are computed as 32.1 MHz and 3.97 MHz for Mu-ACE and H-ACE, respectively, and our results qualitatively reproduced the relationship between A_μ' of Mu-ACE and H-ACE for corresponding experimental values. This is caused by increase of spin density on Mu atom due to both "neutral dissociation of Mu atom from acetone molecule" and "rotation of Mu atom around C1-O bond" using large nuclear quantum and thermal effects [3]. Temperature dependence and structural discussion will be reported in poster presentation.

Table 1: Summarized A_μ' values for Mu-ACE.

Hyperfine Coupling Constant A_μ' [MHz]		
Molecule^{Method}	300 K	150 K
Mu-ACE^{PIMD}	32.12	28.76
H-ACE^{PIMD}	3.97	-1.40
Mu-ACE$^{Exptl.}$	8.56 (300 K)[1]	3.64 (180 K)[1]

References

1. D. Buttar *et al.*, *Hyperfine Interact.* **65**, 927 (1990). [2] R.M. Macrae *et al.*, *Physica B*, **326**, 81 (2003). [3] Y. Oba *et al.*, *J. Chem. Phys.*, **145**, 064301 (2016).