Path integral molecular dynamics simulations for muoniated and hydrogenated thioacetone radicals

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Synopsis Theoretical understanding of hyperfine coupling constant (HFCC) is important to analyze muon spin rotation/relaxation/resonance (μSR) spectrum. We performed *ab initio* path integral molecular dynamics simulations to predict and analyze the reduced HFCCs of muoniated thioacetone radical (Mu-TACE) and hydrogenated thioacetone radical (H-TACE). Our predicted HFCC value of Mu in Mu-TACE was larger than that of H in H-TACE, because of the larger nuclear quantum effect of positive muon.

Muonium (Mu) is consisted of a positive muon (μ^+) and an electron (e^-) [1]. The mass of μ^+ is about 1/9 times smaller than proton. Accordingly, Mu atom can be regarded as an ultralight isotope of hydrogen atom and is highly responsive to magnetic field. Such features have led Mu to the application for magnetic measurement technique such as muon spin resonance (μSR). This provides the informations of hyperfine structures of muoniated radicals, characterized by hyperfine coupling constant (HFCC): magnitude of the interaction between radical electron and nuclear spins. Although the HFCC values for various muoniated radicals have been measured by μSR, theoretical understanding of HFCC is needed to assign μSR spectra to their molecular structures. However, in some cases, it is difficult to estimate HFCCs precisely by using conventional *ab initio* molecular orbital method [2]. Systematic analysis for small molecules is essential to understand μSR spectra, even though they have no experimental data, e.g. muoniated thioacetone radical (Mu-TACE) as shown in **Figure 1**(a) [3]. Therefore, in this study, we calculated reduced HFCC values of Mu-TACE and hydrogenated thioacetone radical (H-TACE). To discuss the nuclear quantum effect of μ^+, we applied path integral molecular dynamics (PIMD) simulation for these species.

Table 1 shows our predicted HFCC values of Mu-TACE and H-TACE. For Mu-TACE, predicted HFCC value was 52.6 MHz, which is larger than that of H-TACE, 43.5 MHz. We have found that the C-Mu bond length and the electron density on Mu have positive correlations, as shown in **Figure 1**(b), since electron density on each Mu increases according to the dissociation from thioacetone molecule. We can conclude that the large nuclear quantum effect of μ^+ made the large HFCC of Mu-TACE.

Table 1. Predicted HFCC values [MHz] of Mu-TACE and H-TACE.

	Mu-TACE	H-TACE
HFCC	52.6	43.5

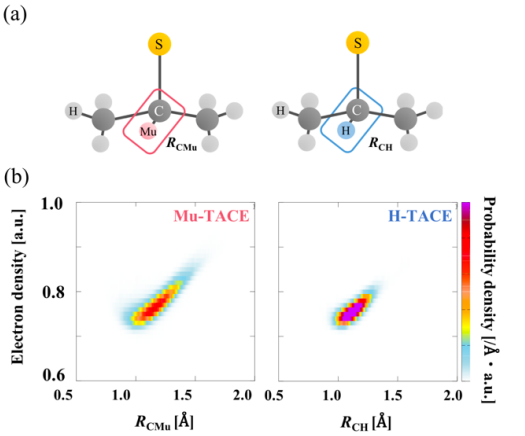

Figure 1. (a) Molecular structures of Mu-TACE and H-TACE, (b) two dimentional distributions for the bond length and electron density in Mu-TACE and H-TACE

References

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