μSR Study of thioaldehyde/thioketones

In insulators (= most of organic compounds), the positive muon captures an electron to generate a muonium (Mu = [μ^+e^-]), an equivalent to light hydrogen atom. The muoniums add to unsaturated molecular units, and the corresponding radicals via muonium addition can be observed by μSR.

The carbonyl (>C=O) group is one of the most important functional groups in organic chemistry. Also, thiocarbonyl group (>C=S) has been useful for recent organic synthesis. Recently, we conducted μSR experiments by using a sterically encumbered thioaldehyde developed by Okazaki and Ishii in 1982. The predominant addition of Mu to the sulfur atom was characterized. The experimentally determined muon hyperfine coupling constant indicated considerable isotope effect due to the light mass of muon ($0.1126m_p$).

In addition, the sulfur analog of xanthene-9-thione and thioxanthene-9-thione are promising thioketones as functional radical precursors. S TF-μSR disclosed decisive effects of the bridging chalcogen atoms (O, S) on muon hyperfine constants.

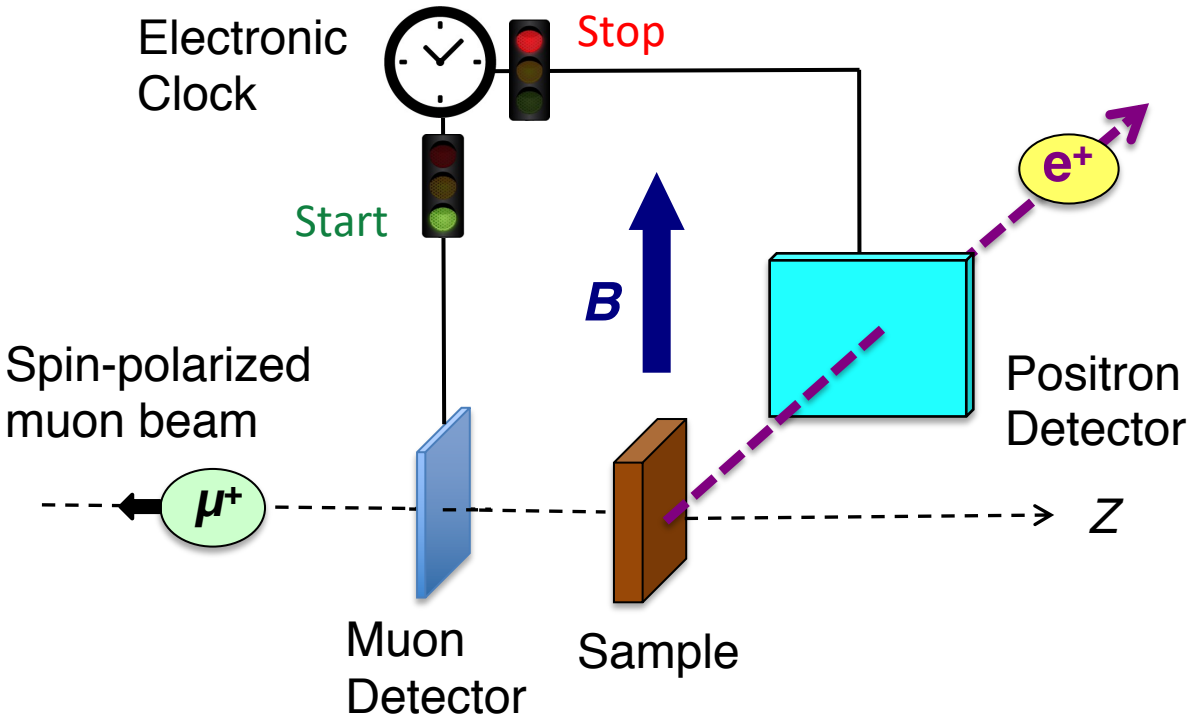
Phosphorus, Sulfur, Silicon, and the Related Elements **2019**, *194*, 735.
Bull. Chem. Soc. Jpn. **2023**, *96*, 461.

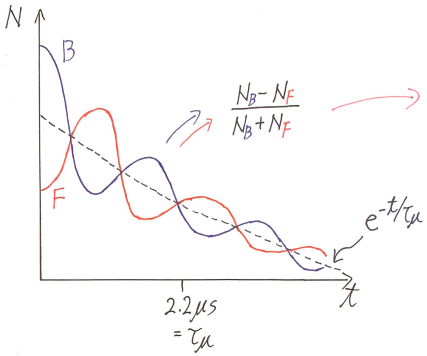
TF-μSR Measurement

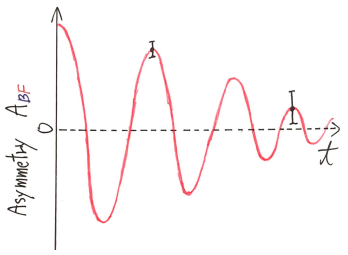
Illustration of Experiment

(Transverse-Field Muon Spin Rotation)

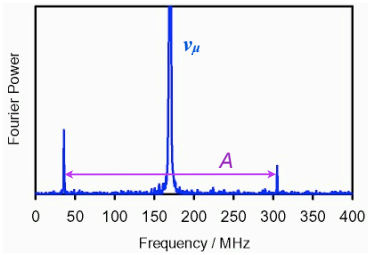
横磁場ミュオンスピン回転





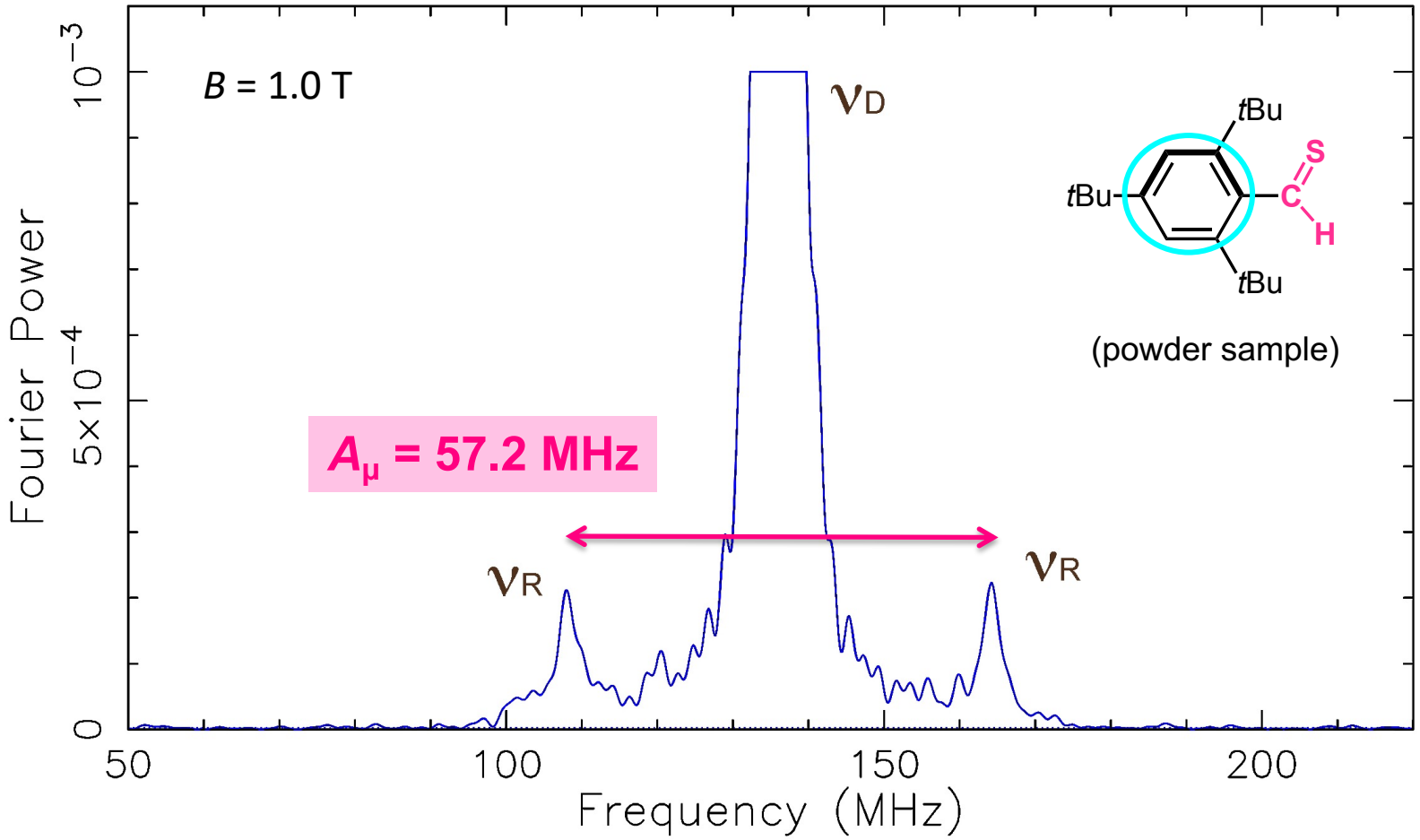


FT



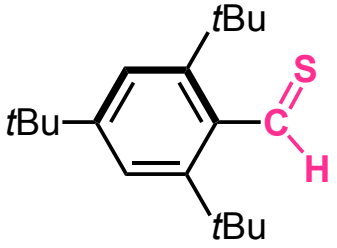
Ref) http://cmms.triumf.ca/intro/musr/cap/musr0097.htm

TF-μSR of Mes*CH=S



Muonium does not add to the benzene ring.

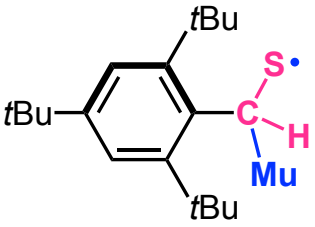
Muonium Addition to Mes*CH=S



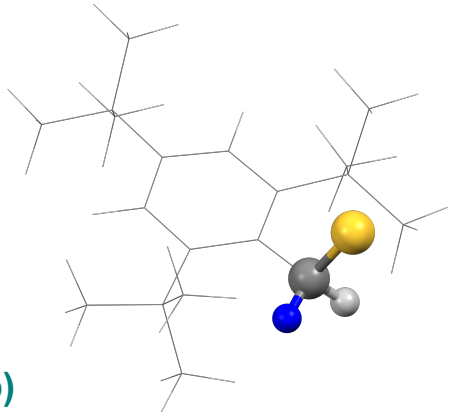
Mu

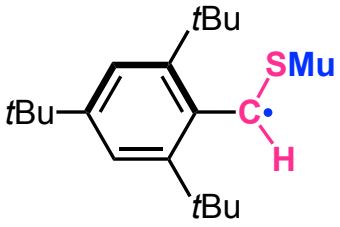
Mes*CHSMu•

A_μ = 57.2 MHz

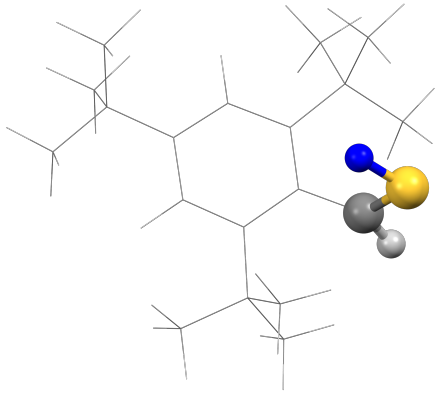


A_μ = 193.2 MHz





A_μ = 6.43 MHz

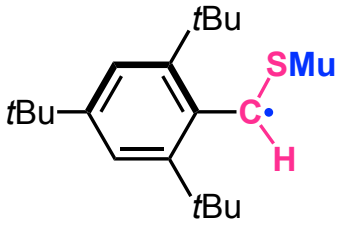


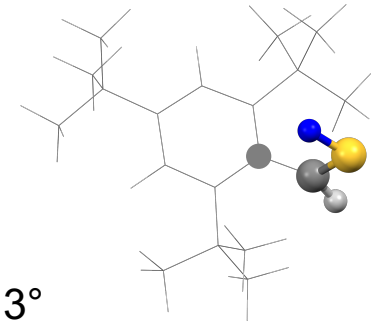
UCAM-B3LYP/6-31G(d,p)

The DFT-optimized structure can determine addition of Mu to the sulfur atom.
However, the calculated hfc parameter considerably deviates from the experimental result.

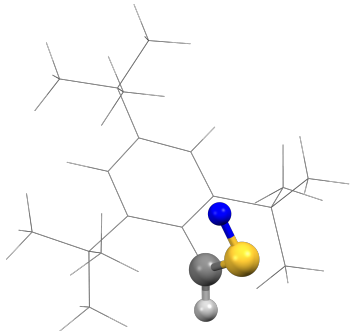
Muonium Addition to Mes*CH=S

Manual Scanning of the Torsion Angle for Characterization of the Isotope Effect

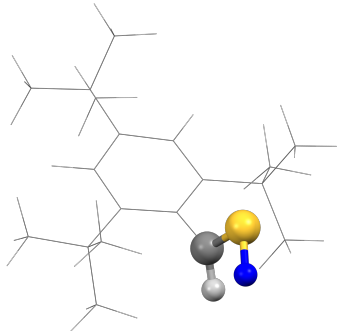




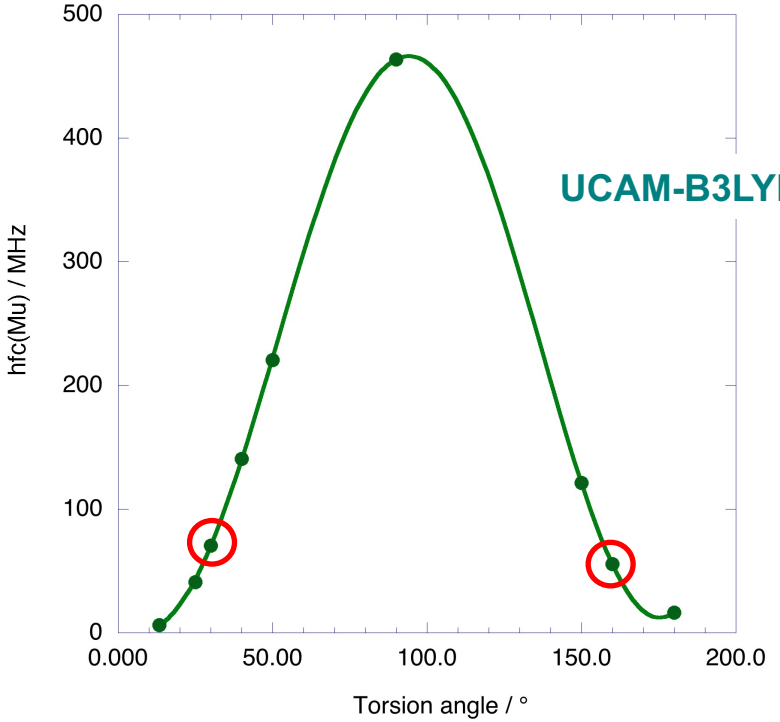
τ_{CCSMu}(opt) = 13.3°



τ_{CCSMu} = 27°
A_μ = 52.3 MHz
E_a = 0 kJ mol^{-1}

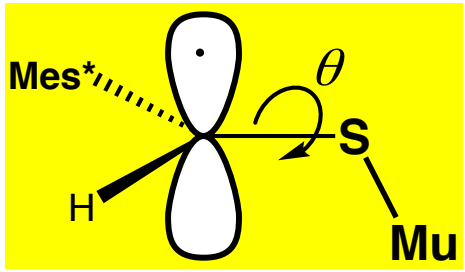


τ_{CCSMu} = 160°
A_μ = 55.6 MHz
E_a = 0 kJ mol^{-1}



UCAM-B3LYP/6-31G(d,p)

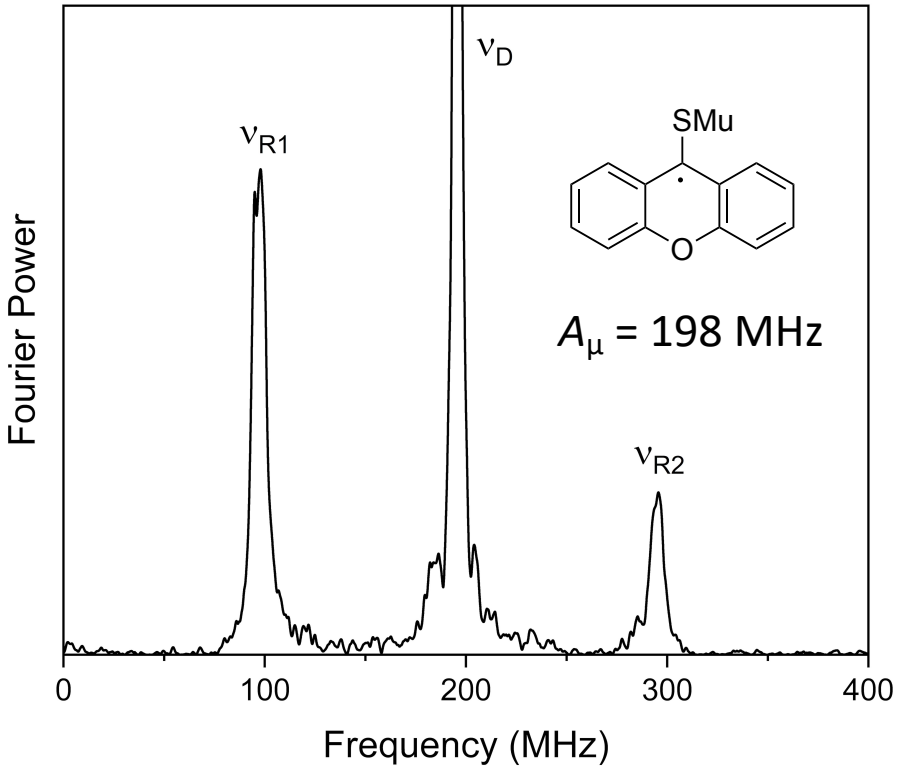
A_μ = 57.2 MHz (exp)

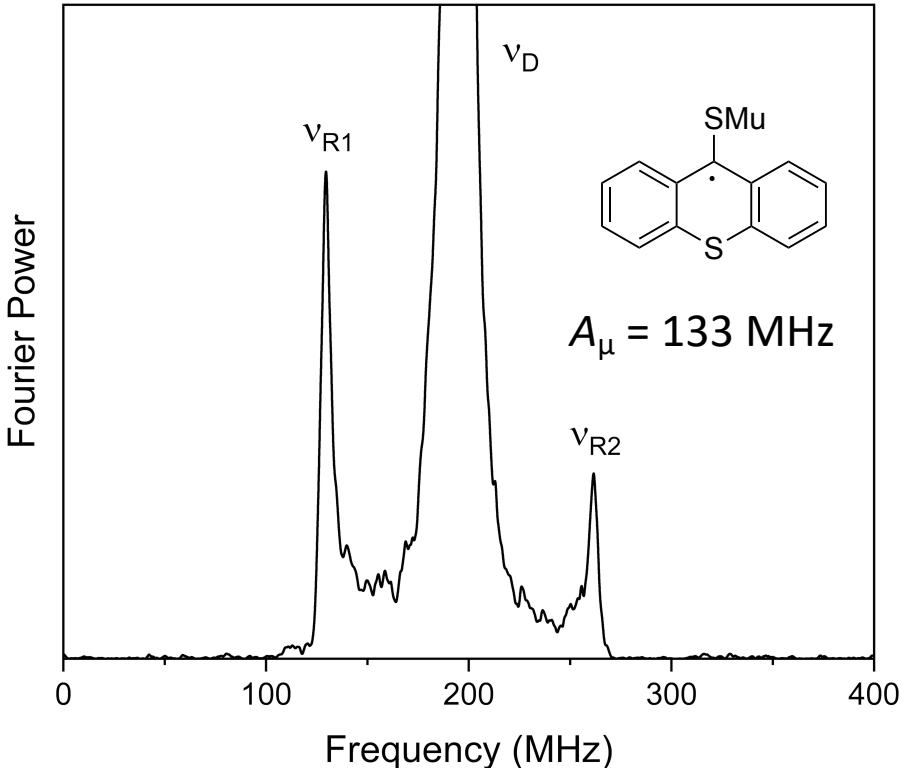


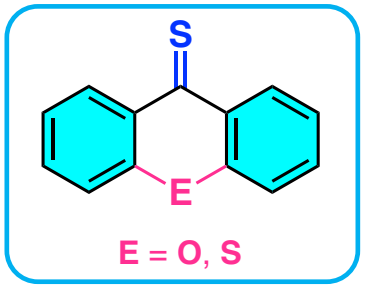
The S–Mu bondmight promote slight overlap with the p orbital.

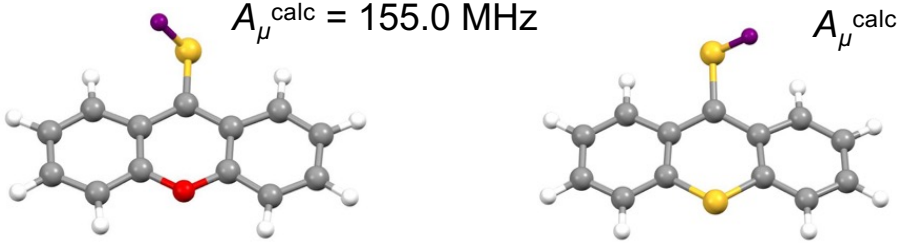
Muonium Addition to Thioketones

TF-μSR (B_{TF} = 1.44 T, ν_D = 196 MHz)









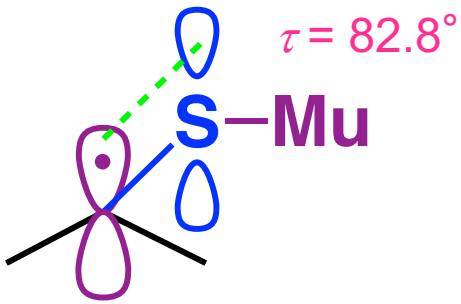
UωB97XD/6-311G(d,p)

The larger experimental muon hfcs correlate with increase of zero-point energy (muon isotope effect).

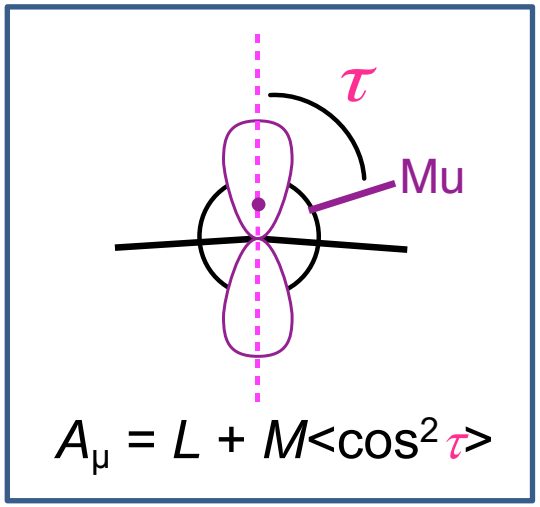
Thiocarbonyl-Muonium Chemistry: *Old But New*

Muonium Radical from Thioacetone

π_{rad}-$\pi_{lonepair}$ overlap

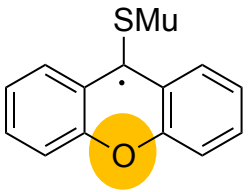


A_μ^{calc} = 20.6 MHz

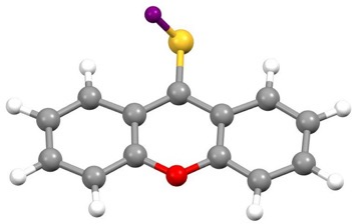


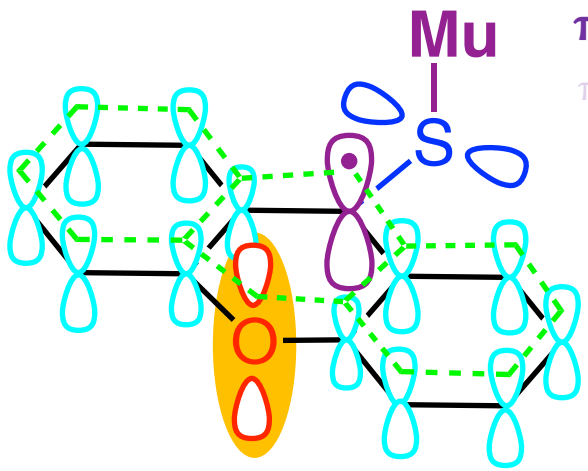
C. Heller, H. M. McConnel, *J. Chem. Phys.* **1960**,*32*, 1535.

Muonium Radical from 9*H*-Xanthenethione



τ = 54.0°





π_{rad}-σ_{SMu} overlap

π_{rad}-$\pi_{lonepair}$ overlap

A_μ^{calc} = 155.0 MHz