The pulsed-jet, Fourier Transform microwave spectrum of methyl thiolformate (HCOSCH$_3$) has been observed in the 5-20 GHz region. An earlier study observed no internal rotation doublets. Those authors noted that either the internal rotation splitting was too small to be observed or much larger than exists in methyl formate. They chose the former interpretation, an unlucky choice, which implies a methyl barrier greater than 2.5 kcal/mol. The compound exists in a conformation with the methyl group eclipsing the carbonyl oxygen. Spectra of the parent isotopomer and the $^{33}$S (with assigned quadrupole splittings), $^{34}$S, and both $^{13}$C isotopomers have been assigned including both A- and E-state transitions arising from methyl internal rotation. The 3-fold barrier is 147-8 cm$^{-1}$ (420 cal/mol) in the various isotopomers.

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