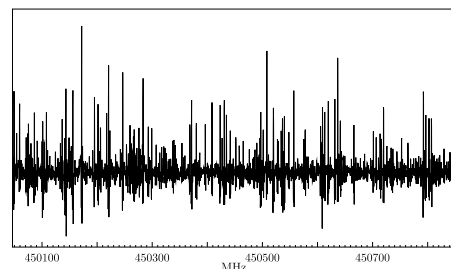


ON THE CHOICE OF HAMILTONIAN REDUCTION AND REPRESENTATION FOR THE ROTATIONAL SPECTRUM OF 1,1-DIFLUOROACETONE RECORDED UP TO 640 GHz

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While recording the cm-wave spectrum of the title compound^a we discovered that the Watson A reduction in the I^r representation resulted in a poorly fitting Hamiltonian to the observed ground state transitions. However, the Watson S reduction in the I^r representation gave satisfactory results as did both reductions in the III^r representation. The prior work used only measurements between 6 GHz and 16 GHz and only quartic centrifugal distortion (CD) constants were needed in the fits. In order to further explore the reduction/representation-dependence of the spectroscopic fits quartic and sextic CD constants have been obtained from quantum chemical calculations. Furthermore higher frequency measurements have been recorded which i) provide greater certainty in the experimental CD constants, and ii) now require up to decadic CD constants in the Hamiltonian. Further insights into the failure of the A- I^r approach will be presented. In the course of performing this work the methyl group barrier to internal rotation has been improved and will also be discussed.



^aG.S. Grubbs, P. Groner, Stewart E. Novick, S.A. Cooke, "Methyl group internal rotation and the choice of Hamiltonian for the rotational spectrum of 1,1-difluoroacetone", *Journal of Molecular Spectroscopy*, Volume 280, 2012, Pages 21-26