BROADBAND MICROWAVE SPECTROSCOPY AND AUTOMATED ANALYSIS OF 12 CONFORMERS OF 1-HEXANAL

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The rotational spectrum of 1-hexanal is used as a test case for developing automated assignment algorithms in molecular rotational spectroscopy, for the purpose of lowering the barrier to new users of rotational spectroscopy. There are two ways that the automated fitting algorithm, implemented in the AUTOFIT program, is used: 1) Assignment of the rotational spectrum of a molecule expected to be in the sample mixture (in this case, a conformer of 1-hexanal), using quantum chemistry estimates of the spectroscopic parameters to efficiently guide the search for the experimental spectrum. 2) Once a new spectrum is assigned, the algorithm is used to automatically assign isotopologue spectra (sensitivity permitting) to provide verification of the molecular structure.

Using a combination of quantum chemical calculations and automated spectral assignment, 12 conformations of 1-hexanal have been identified using chirped-pulse Fourier transform (CP-FTMW) spectroscopy in the 6.5-18, 18-26 and 26-40 GHz bands. Of these 12 conformers, the four lowest energy conformers were intense enough to resolve each of the six ^{13}C isotopologues for each conformer, and sufficient intensity was achieved to assign the ^{18}O isotopologues of the two lowest energy conformers. The full set of assignments were made using the AUTOFIT program, and a summary of results for all 38 observed species via automated assignment will be presented.

Additionally, by using all 12 conformers of 1-hexanal as a benchmark set, a discussion of dispersion-corrected density functional theory for the purpose of automated broadband spectroscopic searches will be presented, with specific results regarding rotational constant prediction. Results will also be presented on the correlation between the predicted conformational energetics predicted by multiple levels of theory and the sensitivity limits of the 1-hexanal CP-FTMW spectrum.