THE 2,4-CHALLENGE IN THE MICROWAVE SPECTRA OF 2,4-DIMETHYLTHIAZOLE AND 2,4-DIMETHYLFLUOROBENZENE: STRATEGY TO ASSIGN VERY LOW BARRIER METHYL INTERNAL ROTATION

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The analysis and modeling of internal rotations with extremely low barriers is a challenging task in microwave spectroscopy. An almost free internal rotation hindered by a barrier less than 20 cm^{-1} causes large torsional splittings in the spectrum. For molecules with two inequivalent methyl groups, the methyl rotations couple with each other, especially in aromatic molecules through π conjugation, and all rotational lines split into quintets, making spectral assignment and modeling very difficult. The spectral analysis becomes even more complicated if additional effects are present such as the ^{14}N nuclear quadrupole coupling, which causes quadrupole hyperfine splittings in addition to the torsional splittings.[1] Probably for these reasons, a very limited number of studies on aromatic systems undergoing nearly barrier-free internal rotations have been reported.[2]

We will present here the challenges for two such molecules, 2,4-dimethylthiazole (24DMTA) and 2,4-dimethylfluorobenzene (24DMFB). The microwave spectra were recorded using a pulsed molecular jet Fourier transform microwave spectrometer operating in the frequency range from 2.0 to 26.5 GHz.[3] The experimental work was supported by quantum chemical calculations. For both molecules, the $XIAM_{mod}$ program[4,5] was used at the beginning to fit the first assigned lines, but it fails to predict new lines at higher J and K values, as well as to achieve the measurement accuracy of 2 kHz for the final data set.[6] To assign more lines, fitting each torsional species separately using odd power order parameters to get reliable predictions using the *WS18* code[7] and the *SFLAMS* code,[4] as well as checking the assigned frequencies by

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combination difference loops (Ritz cycles)[8] is the key to success. Finally, the *BELGI-C_s-2Tops-hyperfine*[9] and *BELGI-C_s-2Tops*[10] programs were used for 24DMTA and 24DMFB, respectively, to decrease the standard deviation to measurement accuracy in a global fit. For 24DMTA, the barriers to internal rotation of the 2- and 4-methyl groups were determined to be 19.070(58) cm^{-1} and 396.707(25) cm^{-1}, respectively. They are 3.23(40) cm^{-1} and 227.039(51) cm^{-1} for 24DMFB.

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