Coupled Large Amplitude Motions: a Case Study of the Dimethylbenzaldehyde Isomers

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The microwave spectra of the *3,4*- (*syn* and *anti*), *2,5*- (*syn*) and *3,5*-dimethylbenzaldehyde (DMBA) molecules have been recorded for the first time, using the high resolution COBRA-Fourier transform microwave (FTMW) spectrometer in Hannover [1]. The experimental assignments in the 2-26.5 GHz frequency range and fits are supplemented by *ab initio* quantum chemical calculations of the conformational energy landscape and dipole moment components. The analysis of the spectra of the four observed isomers, including spectroscopic constants and large amplitude motion parameters, are presented here.

We also made far-IR measurements (50-650 cm^{-1}) at the AILES beamline of the synchrotron radiation facility SOLEIL. The high resolution Fourier transform infrared (FTIR) spectrometer coupled to a long absorption path cell [2] permitted the observation of very weak bands whose positions represented an additional validation of our *ab initio* calculations.

The DMBA isomers belong to a series of similar molecules obtained formally by adding a second methyl group at the aromatic ring of m-tolualdehyde. These molecules serve as prototype systems for the development of the theoretical model of asymmetric top molecules having C_s symmetry while containing in addition two nonequivalent methyl tops (C_{3v}), exhibiting different barrier heights and other coupling terms. Thus, the DMBA isomers represent benchmark species for testing the recently developed two-top internal rotors BELGI program [3, 4].

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