LOCAL AND GLOBAL APPROACHES TO TREAT THE TORSIONAL BARRIERS OF 4-METHYL-ACETOPHENONE USING MICROWAVE SPECTROSCOPY

SVEN HERBERS, SEAN FRITZ, PIYUSH MISHRA, *Department of Chemistry, Purdue University, West Lafayette, IN, USA*; HA VINH LAM NGUYEN, *CNRS UMR 7583, Université Paris-Est Créteil, Université de Paris, Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), Créteil, France*; TIMOTHY S. ZWIER[a], *Department of Chemistry, Purdue University, West Lafayette, IN, USA*.

The Fourier transform microwave spectrum of 4-methylacetophenone recorded from 8 GHz to 18 GHz under jet-cooled conditions has revealed large tunneling splittings arising from a low barrier to internal rotation of the ring methyl group and small splittings from a high torsional barrier of the acetyl methyl group. The large splittings are especially challenging to model, while the small splittings are difficult to analyze due to the resolution limit of 120 kHz. The combination of two methyl groups undergoing internal rotations caused each rotational transition to split into five torsional species, which were resolved and fitted using a modified version of the *XIAM* code and the newly developed *ntop* code to a root-mean-square deviation close to measurement accuracy, providing an estimate of the V_3 potential barriers of about 22 $\mathrm{cm}^{-1}$and 584–588 $\mathrm{cm}^{-1}$for the ring and the acetyl methyl groups, respectively. The assignment was aided by separately fitting the five torsional species using odd-power order operators. Only one conformer in which all heavy atoms are located on a symmetry plane could be identified in the spectrum, in agreement with results from conformation analysis using quantum chemical calculations.

[a]Current address: Combustion Research Facility, Sandia National Laboratories, Livermore, CA 94551-0969, USA.