

## INTERNAL ROTATION AND CHLORINE NUCLEAR QUADRUPOLE COUPLING IN 2-CHLORO-4-FLUOROTOLUENE EXPLORED BY MICROWAVE SPECTROSCOPY AND QUANTUM CHEMISTRY

K.P. RAJAPPAN NAIR, SVEN HERBERS, DANIEL A. OBENCHAIN, JENS-UWE GRABOW, *Institut für Physikalische Chemie und Elektrochemie, Gottfried-Wilhelm-Leibniz-Universität, Hannover, Germany*; WILLIAM C. BAILEY, *Department of Chemistry-Physics, Kean University (Retired), Union, NJ, USA*; ALBERTO LESARRI, *Departamento de Química Física y Química Inorgánica, Universidad de Valladolid, Valladolid, Spain*; HA VINH LAM NGUYEN, *CNRS UMR 7583, Université Paris-Est Créteil, Université de Paris, Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), Créteil, France*.

2-Chloro-4-fluorotoluene was investigated using a combination of molecular jet Fourier transform microwave spectroscopy in the frequency range from 5 to 21 GHz and quantum chemistry. The molecule experiences an internal rotation of the methyl group, which causes a fine splitting of all rotational transitions into doublets with separation on the order of a few tens of kHz. In addition, hyperfine effects originating from the chlorine nuclear quadrupole moment coupling its spin to the end-over-end rotation of the molecule are observed. The torsional barrier was derived using both the rho<sup>a</sup> and the combined-axis-method,<sup>b</sup> giving a value of 462.5(41) cm<sup>-1</sup>. Accurate rotational constants and quadrupole coupling constants were determined for two <sup>35</sup>Cl and <sup>37</sup>Cl isotopologues and compared with Bailey's semi-experimental quantum chemical predictions.<sup>c</sup> The gas phase molecular structure was deduced from the experimental rotational constants supplemented with those calculated by quantum chemistry at various levels of theory. The values of the methyl torsional barrier and chlorine nuclear quadrupole coupling constants were compared with the theoretical predictions and with those of other chlorotoluene derivatives.

---

<sup>a</sup>A. Belloche, A.A. Mescheheryakov, R.T. Garrod, V.V. Ilyushin, E.A. Alekseev, R.A. Motiyenko, I. Margules, H.S.P. Müller, K.M. Menten, *Astron. Astrophys.* **601**, A49 (2017).

<sup>b</sup>H. Hartwig, H. Dreizler, *Z. Naturforsch.* **51a** 923 (1996).

<sup>c</sup>W.C. Bailey, *J. Mol. Spectrosc.* **209** 57 (2001).