INFRARED ION-GAIN SPECTROSCOPY AND FRACTIONAL ABUNDANCE MEASUREMENTS OF CONFORMER POPULATIONS

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Studies of the single-conformation spectroscopy of large, flexible molecules has as one of its goals providing incisive tests of the predictions of calculations on the isolated molecules, whether ab initio or semi-empirical in nature. An important aspect of this comparison that is often lacking is quantitative data on the fractional abundances of the conformations. Previous studies from our group have provided such data using mass-resolved infrared population transfer (IRPT) spectroscopy.[a] In this talk, we present an alternative method that in certain circumstances has advantages over IRPT, especially in ease of implementation. The method, infrared ion-gain (IRIG) spectroscopy, was first introduced by Fujii and co-workers on molecules without conformational isomers.[b] Here we extend the method to conformationally flexible molecules, and test whether it can be used to provide fractional abundances by comparing with IRPT results[a] on jet-cooled Ac-γ^2-hPhe-NHMe, using thermal methods for vaporization of the molecule. The comparison provides some confidence that IRIG can be used for this purpose, but also points out conditions where it must be used with care. Analogous fractional abundance measurements on a prototypical lignin monomer will also be described, this time brought into the gas phase by laser desorption. Details of the laser desorption scheme used will also be provided.

[a] W. H. James III, C. W. Muller, E. G. Buchanan, M. G. D. Nix, L. Guo, L. Roskop, M. S. Gordon, L. V. Slipchenko, S. H. Gellman and T. S. Zwier *J. Am. Chem. Soc.* **131** (14243-14245), 2009.

[b] S. Ishiuchi, H. Shitomi, K. Takazawa and M. Fujii *Chem. Phys. Lett.* **283** (243-250), 1998.