AUTOMATIC ASSIGNMENT AND INTERNAL ROTATION WITH PGOPHER

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This talk describes recent updates to the PGOPHER program[a] (http://pgopher.chm.bris.ac.uk), including new tools for computer assisted assignment of spectra and simulate spectra involving internal rotation. The new tools for assignment are described in a recent paper[b] and include (I) a method of trying multiple assignments automatically based on the AUTOFIT algorithm of the group of Brooks Pate[c], and (II) a new form of presenting assignments, a nearest lines plot. These latter plots allow possible sets of assignments to be accepted (or rejected) quickly, and also allow the rapid extension of initial assignments to an entire branch or band. Both these tools have been applied to the analysis of high resolution IR spectra, allowing the rapid assignment of 10,000 lines for a band, even in the presence of strong overlapping transitions. These tools are now being supplemented with tools for handling internal rotation in PGOPHER, including a general way of handling the special permutation inversion symmetry that is typically required for such molecules, and calculating levels affected by internal rotation, either by adding empirical terms to a standard asymmetric top Hamiltonian, or a more elaborate approach based on including multiple torsional states. Progress on the development of these tools will be presented, with applications to spectra taken on the far IR beamline of the Canadian light source[d].

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[a] C. M. Western, J Quant. Spec. Radiat Trans., 186 221 (2017)

[b] C. M. Western and B. E. Billinghurst, Phys. Chem. Chem. Phys., 21 13986 (2019)

[c] N. A. Seifert, I. A. Finneran, C. Perez, D. P. Zaleski, J. L. Neill, A. L. Steber, R. D. Suenram, A. Lesarri, S. T. Shipman, B. H. Pate, J Mol. Spectrosc. 312, 13, (2015)

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