PGOPHER 8.0 – force field analysis and other recent additions.

C. M. Western[a]

[a] School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK

PGOPHER [1] is a general purpose program for simulating and fitting rotational, vibrational and electronic spectra. It will simulate the rotational structure for linear molecules and symmetric and asymmetric tops, including effects due to unpaired electrons and nuclear spin, with a separate mode for vibrational structure. The program can handle many sorts of transitions, including Raman, multiphoton and forbidden transitions. It can simulate multiple species and states simultaneously, including special effects such as perturbations and state dependent predissociation. Fitting can be to line positions, intensities or band contours.

This poster presents the most recent version of PGOPHER, 8.0, released summer 2013, for which the most significant addition is a set of tools for performing a force field analysis. Calculation of the vibrational frequencies, *l* matrix and quantities derived from it, including vibrational dependence of rotational constants, centrifugal distortion and Coriolis coupling constants from a force field expressed in terms of internal or symmetry co-ordinates is now fully supported. The force field can be derived by fitting to any combination of the derived values from one or more isotopologues. Alternatively the vibrational frequencies and *l* matrix can be imported from an *ab initio* program and the force field in terms of internal or symmetry co-ordinates back calculated from this. A typical workflow might involve scaling *ab initio* force constants to improve agreement with experiment; a single scaling factor or a set of scaling factors can be used as appropriate for the available data. If done for two electronic states the Franck-Condon factors for the transition can then be calculated. The method of calculation is similar to the ASYM40 program by Hedberg and Mills [2][3], though implemented in a more flexible way.

The new release also includes many smaller improvements and bug fixes. These include custom population functions, allowing an essentially arbitrary function to be used as an alternative to the Boltzmann distribution, calculation of axis switching effects and custom transition moment functions to allow for Herman-Wallis factors. A wider range of matrix elements can be displayed symbolically, and the simplified line list format for line position fitting has been extended. Current users are encouraged to upgrade; the main changes to the user interface is where required for new features and old data files can be used as is.

The program is freely downloadable from http://pgopher.chm.bris.ac.uk, for Microsoft Windows and Linux, with a beta version available for the Apple Mac. The program is released as open source, and can be compiled with open source tools.

[1] PGOPHER, C. M. Western, University of Bristol, http://pgopher.chm.bris.ac.uk
[2] L. Hedberg, I. M. Mills, *J. Molec. Spectrosc.* **1993**, *160*, 117.
[3] L. Hedberg, I. M. Mills, *J. Molec. Spectrosc.* **2000**, *203*, 82.