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PGOPHER: A program for simulating rotational, vibrational and electronic spectra

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ABSTRACT

The PGOPHER program is a general purpose program for simulating and fitting molecular spectra, particularly the rotational structure. The current version can handle linear molecules, symmetric tops and asymmetric tops and many possible transitions, both allowed and forbidden, including multiphoton and Raman spectra in addition to the common electric dipole absorptions. Many different interactions can be included in the calculation, including those arising from electron and nuclear spin, and external electric and magnetic fields. Multiple states and interactions between them can also be accounted for, limited only by available memory. Fitting of experimental data can be to line positions (in many common formats), intensities or band contours and the parameters determined can be level populations as well as rotational constants. PGOPHER is provided with a powerful and flexible graphical user interface to simplify many of the tasks required in simulating, understanding and fitting molecular spectra, including Fortrat diagrams and energy level plots in addition to overlaying experimental and simulated spectra. The program is open source, and can be compiled with open source tools. This paper provides a formal description of the operation of version 9.1.

1. Introduction

Perhaps the key feature of rotationally resolved molecular spectra is the immense amount of information on the molecule and its environment that can be extracted from spectroscopic measurements. The necessary downside is that such informative spectra are necessarily complicated, and extracting the information can be a daunting task. The program described here, PGOPHER, has been developed as a general purpose tool to assist in this task by simulating and fitting rotational, vibrational and electronic molecular spectra. The focus is on an interactive graphical user interface to make simulation and assignment of spectra as easy as the underlying spectroscopy permits, but it is also available in a command line version for use in combination with other programs. Its current form has come about as the result of applying it to many different spectroscopic problems and it has thus become useful in a wide range of applications. This ranges from simple undergraduate spectroscopy practicals where the rotational constant of CO is determined from a traditional infrared spectrum to complex cases involving multiple interacting rovibronic states [1], including open shell systems and nuclear hyperfine structure. It is not the first molecular spectroscopy program to be published – Pickett's CALPGM suite [2] has become something of a standard and there are several others available including ASYTOP [3], ASYROTWIN [4], SPECVIEW [5] and JB95 [6]. PGOPHER aims to cover similar ground, but in a much more general and easy-to-use way.

For many spectroscopic problems much of the required logic used in the handling of basis sets, energy levels and transitions is independent of the molecular type, and the program structure reflects this. An object-oriented approach is used, which allows the molecule-specific part to be restricted to a relatively small part of the

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program, with much of the program, including the user interface, written in a general way. There are thus separate units of the program for linear molecules, symmetric tops and asymmetric tops which are each outlined below, and these are all concerned with the rotational structure of a particular vibronic state. A fourth unit, which calculates vibrational structure of electronic states ignoring rotation, is also available and is covered in the on-line documentation but not described here as it is a relatively recent addition and has a significantly different structure.

The PGOPHER program has been developed as an open source application, and the source and executables can be freely downloaded from the website [7]; see also [8,9] for permanently deposited versions of the program with a doi. This paper formally describes the internal structure of the program and the algorithms used; as far as possible the program tries to use standard spectroscopic notation and conventions, but there are necessary details that must be specified. Detailed instructions for running the program, and example files are distributed with the program. The paper is specifically based on version 9.1 of the program [9]; earlier versions are broadly similar, though some features may not be available or are slightly different, as described in the release notes. Most results are quoted without derivation; see standard spectroscopic texts [10–17] for the cases where details are not given.

2. Overall operation

The underlying structural assumption is that the Hamiltonian is expressed in terms of a series of rotational constants given explicitly for each vibrational state of each electronic state included in the calculation. The generic term vibronic state is used here, as the calculation makes no distinction between the electronic and vibrational parts of the wavefunction. At a minimum the information required for each vibronic state, η, will include the symmetry, an origin for the state (the energy in the absence of rotational terms) and one or more rotational constants. The rotational part of the Hamiltonian is taken to include some small terms that are notionally part of the electronic Hamiltonian, including spin–orbit and spin–spin coupling and any lifting of vibronic degeneracies, such as lambda-doubling. These are conventionally included in the rotational Hamiltonian, and indeed accurate energy level calculations require this.

To allow multiple states to be included, the calculation is set up using a series of objects laid out in a tree structure, as shown in Fig. 1. The key object is a “state” object, which specifies the symmetry and constants of a single vibronic state. One or more of these are grouped under “manifold” objects which are in turn grouped under “molecule” objects which are grouped under “species” objects. The intent is that isotopically substituted variants of a molecule are grouped under a species object so that, for example, the intensity of a particular transition involves the product of a relative concentration (specified at the species level) and an abundance (specified at the molecule level). “Transition moment” objects specify the possible transitions between states which are grouped under “Transition moments” objects which specify the connected manifolds. At the top level is a “mixture” object, implying a mixture of several different compounds, each of which has a species object. The “mixture” object also contains a “simulation” object that contains global parameters such as the temperature and line width which govern the overall appearance of the simulation. A minimal set of objects to produce a simulation is shown in Fig. 1; any level other than the top level can have multiple objects if required.

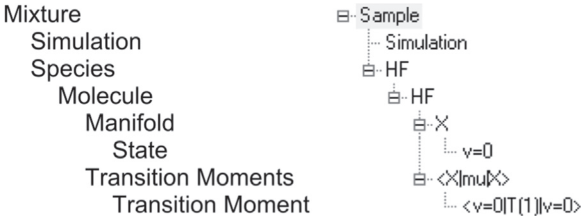

Fig. 1. Minimum sample set of objects for a simulation. The left side shows the generic object types, and the right shows a screenshot from the program set up to simulate the pure rotational spectrum of HF. The “$\nu=0$” object contains the rotational constants, and $<\nu=0|T(1)|\nu=0>$ the (transition) dipole moment.

An important optional possibility is a “perturbation” object, which specifies interactions between vibronic states, and can also be used to add non-standard terms to the Hamiltonian for a vibronic state. The perturbation objects are placed under the manifold containing the states involved and interacting states must therefore be in the same manifold. The concept of a manifold of states in fact arises out of the requirement to handle perturbations, and is used to group interacting states together. In the absence of perturbations the grouping into manifolds is arbitrary, though the calculation is slightly more efficient if the number of states in any given manifold is minimized and states with no interactions with other states are in their own manifold. To give a specific example, in simulating the B–X transition in S_2 [18], the ground electronic state shows no perturbations so the calculation can be structured so that each vibrational level of the ground state is in its own manifold. In contrast, the excited B state shows significant interaction with the B" state, and one vibrational level of the B electronic state can interact with more than one vibrational level of the B" state, so calculation of the excited states must be set up as a single manifold containing several vibrational levels from both the B and B" states. A fragment of the object tree required in this case is shown in Fig. 2.

Other objects are also available for more specialised types of calculation, such as “nucleus” objects under each state which allow hyperfine structure to be simulated. There are no hard limits on the number of any type of object, though the calculation will be slower and take more memory as the number of objects is increased. The limiting step for larger calculations is typically the matrix diagonalization step; to give an indication a model involving ~20 interacting asymmetric top states [19,20] takes a few seconds on a current desktop machine. PGOPHER makes use of parallel processing where possible; many of the calculations split naturally into independent parts, making