Supplementary Material for PCCP

Documentation for Matlab/Fortran program "runRaman"

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runRaman is a function written in Matlab for optimizing the molecular parameters in simultaneous modeling of optical absorption spectra and resonance Raman excitation profiles. runRaman interfaces ramfunc, a Fortran function that calculates the absorption spectra and Raman excitation profiles for a given set of model parameters, to the Matlab curve fitting function lsqcurvefit.
Within lsqcurvefit, it uses the "largescale" algorithm, which is the Trust Region Reflective Newton Algorithm.

Requirements

Matlab 7.3.0 with Optimization Toolbox

Compaq Visual Fortran 6 or equivalent (for compiling the external functions that are written in Fortran)

Installing runRaman

1. Place runRaman.m, inram.for, ramfunc.for, and the input files (see description below) into the folder accessed by Matlab.
(e.g. C:\Program Files\MATLAB\foldername)

(Note: ">>" is the command line in Matlab to which the user must type).

2. >> mex -setup
Please choose your compiler for building external interface (MEX) files:

Would you like mex to locate installed compilers [y]/n? y

Select a compiler:
[1] Compaq Visual Fortran version 6.6 in c:\program files\microsoft visual *studio (or other path to your Fortran compiler)*

other compilers may also be listed

Compiler: 1

Please verify your choices:

Compiler: Compaq Visual Fortran 6.6
Location: c:\program files\microsoft visual studio

Are these correct?([y]/n): y

3. >> mex ramfunc.for
4. >> mex inram.for

runRaman is now ready to use.

Meaning of variables:

nstep = number of points in calculated absorption spectrum and excitation profiles
nmode = total # vibrational modes (30 max)
nline = # Raman lines to calculate (40 max)
ntime = # time steps in Fourier transform (5000 max)
*e0 = electronic zero-zero energy (cm^{-1})
*gamma = electronic homogeneous linewidth from solvent broadening (FWHM in cm^{-1})
rkappa = lineshape parameter in stochastic model, usually 0.1
*sig = electronic inhomogeneous width (Gaussian standard dev. in cm^{-1})
*u = electronic transition length (Å)
alow,ahigh = minimum and maximum values of x-axis (cm^{-1})
delt = time step in Fourier transform (fs), typically around 0.5
refrac = solvent refractive index
wg(n) = vibrational frequency (cm^{-1}) of mode "n"
*delta(n) = dimensionless displacement of mode "n"
temp = temperature (Kelvin)
nquanta(n,m) = # of quanta excited in mode "m" in Raman line "n"
*alife = electronic homogeneous linewidth from lifetime broadening (FWHM in cm^{-1})
lb_e0,lb_gamma,lb_u,lb_sig,lb_alife,lb_delta = lower bounds on these parameters
ub_e0,ub_gamma,ub_u,ub_sig,ub_alife,ub_delta = upper bounds on these parameters
abs_weights = weighting factor for absorption spectrum, usually = 1
raman_weights = weighting factor for all Raman profiles, may be different from 1

*Variables that are to be refined by the program

Using runRaman

Start MATLAB
Invoke the optimization routine (runRaman) by typing:
[e0,gamma,u,sig,delta,alife,error] =
runRaman(1,'ramabs.in',absorp_file,raman_profile,output_file)
To have it merely run the ramabs function once, type:
[e0,gamma,u,sig,delta,alife,error] =
runRaman(0,'ramabs.in',absorp_file,raman_profile,output_file)

ramabs.in is the file that contains the information about the molecular model. It includes all of the parameters needed for calculation of the absorption spectrum and Raman excitation profiles, of which some are to be refined to give the best fits while others are fixed. It also

contains information about which Raman transitions are to be calculated for comparison with experimental data.

The format for ramabs.in is as follows:

```
nmode,nline,ntime,nstep
sig,temp
e0,gamma,rkappa,u,alife
alow,ahigh,delt,refrac
abs_weights,raman_weights
lb_e0,lb_gamma,lb_u,lb_sig,lb_alife,lb_delta
ub_e0,ub_gamma,ub_u,ub_sig,ub_alife,ub_delta
wg(1),delta(1)
wg(2),delta(2)
  .
  .
wg(nmode),delta(nmode)
nquanta(1,1)     .... nquanta(nmode,1)
  .                  .
  .                  .
nquanta(1,nline) .... nquanta(nmode,nline)
```

A sample ramabs.in file:

```
5,5,5000,800
391.,298.
13270.,1898.,0.1,0.82,0.
9000.,24000.,0.5,1.40
1.,1.
13000.,200.,0.5,0.,0.1
30000.,2000.,2.5,2000.,2.0
242.,0.45
551.,0.43
1392.,0.39
1553.,0.97
2227.,0.4
1 0 0 0 0
0 1 0 0 0
0 0 1 0 0
0 0 0 1 0
0 0 0 0 1
```

The format for the experimental absorption spectrum (absorp_file) is as follows:

Frequencies (cm^{-1}) in left column, absorption cross sections ($Å^2$/molecule) in right column

sample absorp_file:

11000	3.153E-6
11014	3.409E-6
11028	3.683E-6
11041	3.978E-6
11055	4.294E-6
11069	4.634E-6
11083	4.998E-6
11096	5.389E-6
11110	5.809E-6
11124	6.259E-6
.	.
.	.
last frequency	last cross-section

Because of the algorithm used to incorporate inhomogeneous broadening, it is recommended to set "alow" to 2000 lower than the first experimental frequency and to set "ahigh" to 2000 higher than than the last experimental frequency.

The format for the experimental Raman profiles (Raman_file) is as follows:

12900	0.028	0.079	0.172	1.258	0.226
13437	0.076	0.271	0.551	3.614	0.650
14180	0.211	0.808	1.770	12.151	2.080
15598	0.162	0.850	4.183	28.541	6.149
16424	0.106	0.502	3.104	24.674	7.619
17774	0.071	0.363	2.130	15.614	5.831
19205	0.034	0.170	0.969	7.837	3.131
19687	0.023	0.123	0.742	6.570	2.527
20431	0.014	0.072	0.480	3.898	1.497
21987	0.003	0.016	0.125	0.884	0.352

The first column contains the laser frequencies (cm^{-1}) and the rest of the columns contain the Raman differential cross sections (10^{-8} $Å^2$/molecule-sr). Each column corresponds to a different Raman transition, which must be listed in the same order in which they are listed in ramabs.in. If there are missing data for any of the profiles, put in NaN for each value missing.

Supplementary Material for PCCP

Understanding ramfunc and inram

ramfunc is the function that calculates the absorption spectrum and Raman profiles for a given set of parameters. Its syntax (in case it is desired to use the function outside of runRaman) is:

[spectrum,xs,xfreq] = ramfunc(int32(nmode), int32(nline),...int32(ntime), int32(nstep), sig, temp, e0,gamma, rkappa, u,...alow, ahigh, delt, refrac,wg, delta,int32(nquanta));

spectrum contains the calculated Raman profiles, xs the calculated absorption spectrum

inram is the function that handles the input file, ramabs.in. It is used in the following way:

[nmode, nline, ntime, nstep, sig, temp, e0,gamma, rkappa,...u, alow, ahigh, delt, refrac,wg, delta,nquanta, lb, ub, ...abs_weight, raman_weight, alife] = inram('ramabs.in');

Note that all variables in Matlab are automatically double precision (64 bit) real numbers. All values "int32" around them have to be single precision (32 bit) integers.