LIPFR

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LIPFR was created by IHW (University of Bath). Its function is to calculate isotopic partition function ratios (hereafter referred to as IPFRs) from a Hessian obtained by means of an electronic-structure calculation for a full molecular system comprising N atoms and corresponding to a stationary point on a potential energy surface.

LIPFR is written in Fortran90, with some elements of earlier versions, but compiles fluidly under standard GNU compilers (gfortran…). In the event of compiler errors, g77 generally overcomes these appropriately. The present version is dimensioned by using the external CAM_SIZE file which can be edited to change the number of atoms and valence coordinates (MAXNAT=1000).

```
! Header file for CAMVIB, CAMISO, LIPFR and UJISO to set array
! sizes as functions of the maximum number of atoms.
!
! 31 April 1997 - AJT
! 16 October 2016 - IHW

      parameter(MAXNAT =1000)

! These should not be touched:
      parameter(MAXNC  = MAXNAT * 3)
      parameter(MAXNI  = MAXNAT * 3 + MAXNAT / 2)
      parameter(MAXNINT= MAXNC  - 6)
      parameter(MAXDIAG= MAXNC  * (MAXNC + 1) / 2)
      parameter(MAXAPO = MAXNAT + 1)

! For CAMISO:
      parameter(MAXFCMS = MAXDIAG * 3)
      parameter(MAXXYZ =  MAXNAT * 10)
```

Figure 1. The CAM_SIZE file, used to dimension the arrays in CAMVIB, LIPFR, and UJISO. Parameter MAXNAT (currently set at 1000) determines the maximum number of atoms. For most purposes a much smaller number may be chosen.

The aim of this user guide is to gently introduce the individual to the functionalities of LIPFR and provide explicit descriptions of the input and output one can expect from standard LIPFR runs. We will begin by discussing the format of the input, suggesting possible edits to the source code, which is available from the SULISO_source repository on Github: https://github.com/pbw20/SULISO_source

```
IPFR 3
 1      298.15
 1 1 0 METHYL CATION
 16O    0.0000000   0.0000000   0.0000000
 12C    0.0000000   0.0000000   1.5648200
  1H    1.0603810   0.0000000   1.8385000
  1H   -0.5301910   0.9183170   1.8385000
  1H   -0.5301910  -0.9183170   1.8385000
  1H    0.0000000  -0.7867260  -0.5582910
  1H    0.0000000   0.7867260  -0.5582910
 16O    0.0000000   0.0000000   6.0000000
  1H    0.0000000   0.7867260   6.5582910
  1H    0.0000000  -0.7867260   6.5582910
 16O    3.0000000   0.0000000   3.0000000
  1H    3.5910170   0.7640530   3.0000000
  1H    3.5910170  -0.7640530   3.0000000
 16O   -1.5000000   2.5980760   3.0000000
  1H   -2.4571980   2.7278860   3.0000000
  1H   -1.1338190   3.4919390   3.0000000
 16O   -1.5000000  -2.5980760   3.0000000
  1H   -1.1338190  -3.4919390   3.0000000
  1H   -2.4571980  -2.7278860   3.0000000
 *
  -0.127348296105E-01 -0.232972102681E-09  0.831095148728E+00
   0.589045734617E-02 -0.465768156891E-09  0.602083496451E+00
  -0.242695453744E-01  0.581165553997E-09 -0.759234872116E-02
   0.609969745858E+00 -0.201651988530E-09 -0.897634034220E-01
  -0.289719867144E-09 -0.134976915168E-09  0.644848606873E+00
  -0.440325443001E-02  0.465180054522E-09 -0.779132962097E-01
   0.483746068416E-02 -0.316021893179E-09  0.238532159709E+00
   0.831652137074E-02 -0.163426252751E-09  0.948900751414E-02
  -0.326806342628E+00  0.267687307576E-09 -0.688459198195E-01
  ------ SUBSEQUENT LINES OF HESSIAN ------
   0   6   6   7   8   9  10  11
 1 1 0 14C
 16O  14C   1H   1H   1H   1H   1H  16O   1H   1H  16O   1H   1H  16O
1H   1H
 16O   1H   1H
   0   6   6   7   8   9  10  11
 1 1 0 2H
 16O  12C   2H   2H   2H   1H   1H  16O   1H   1H  16O   1H   1H  16O
1H   1H
 16O   1H   1H
   0   6   6   7   8   9  10  11
STOP
```

Header section

Atom specification

Hessian

Tail section, containing isotopologue data and program termination.

Figure 2. Sample input file for LIPFR. In the interest of space, only the first few lines of the Hessian are included, with the "------ SUBSEQUENT LINES OF HESSIAN ------" line indicating their original position.

Overview of LIPFR input

1. Header section, line 1: (FORMAT A4, I2, 1X, A4)

   `PROG,NISO,IFLIB`

   PROG takes the value 'IPFR' (A4) to start the program (or 'STOP' to finish).
   NISO is the integer number (I2) of isotopologues **including** the parent.
   IFLIB takes the value 'LIBR' (A4) if the 6 external degrees of freedom of the molecular species are to be treated as vibrations (or 'librations') instead of translations and rotations.

2. Header section, line 2: (FORMAT I2, 3X, 5F10.4)

   `NT,(T(I),I=1,NT)`

NT is the number of temperatures (I2) and the values of
T are the absolute temperatures in Kelvin (5F10.4) to be used in the IPFR evaluations.

3. Header section, line 3: (FORMAT 3I3,74A)

    `IS,IG,IFFREQ,TITLE`

    IS in a symmetry number (as appropriate, or set equal to 1 if symmetry is not required),
    IG is the electronic degeneracy (usually = 1),
    IFFREQ is the number of frequencies to be input (= 0 if a Hessian is supplied, but otherwise as appropriate).
    TITLE is text string used as a description for the file or calculation.

4. Coordinate input, one line per atom, from line 4 to line $4 + N$, where N is the number of atoms: (FORMAT A4, 1X, 3F12.7).

    `IA,(X(J,N),J=1,3)`

    IA is the element symbol (right-justified in the A4 field) for an atom, and is followed by a space; X are the $x, y,$ and z Cartesian coordinates in Ångström (3F12.7).

    The following element symbols are currently accepted, although the UJISO source code may be edited to make additions or changes:

    1H, 2H, 3H, 12C, 13C, 14C, 14N, 15N, 16O, 17O, 18O, F, 32S, 34S, 35CL, 37CL, 6LI, 7LI, 9BE, 10B, 11B, SI, P, 79BR, 81BR, NA, SP, MG, AL, CL, K, CA, ZN, BR, RB, I, CS, B, H, C, N, O, S, HE, NE, AR, KR, 33S, 36S, 11C

    An element symbol preceded by an atomic mass specify a particular isotope (e.g. ^{1}H) whereas an element symbol without a mass specifies the chemical atomic weight (e.g. H = 1.00797). The special symbol 'SP' specifies a mass of 999.

5. Data separation line, line $5 + N$: (FORMAT A4)

    Consists of an asterisk '*' (left-justified in the A4 field) to separate the coordinate input from the Hessian. (This character is a special value for 'IA' in item 4.)

6. *Either* (if IFFREQ = 0):

    Hessian input lines, from line $6 + N$ to line $6 + N + m$: (FORMAT: 3E20.10)

    `(F(I),I=1,NNC)`

    This is the lower triangle of a square symmetric Hessian matrix, stored as a linear array. The number of unique elements is NNC = $N \times (N + 1)/2$. The number of three-column lines of data in this section is therefore given by:

    $$\text{Number of lines of Hessian,} \, m = \frac{3N}{2} \times \frac{3N + 1}{3}$$

    The number of lines of Hessian output from a calculation can be used to verify the reasonableness of the input, by comparing this with the number of atoms using the formula above.

    Or (if IFFREQ = NFREQ)):

    Frequency input lines, line $6 + N$ to line $6 + N + m$: (FORMAT(6F12.4))

    `(FREQ(I),I=1,NFREQ)`

FREQ are a selection vibrational frequencies (as wavenumbers / cm^{-1}) from a prior calculation on this molecular species. NFREQ does not need to be equal to either $3N$ or $3N - 6$ but may have any integer value.

Number of lines of frequencies, $m = \text{ROUNDUP(NFREQ/6, 0)}$

[The total number of lines of data up to this point is q.]

7. Frequency control line for parent species, line $q + 1$: (FORMAT 20I4)

    `ITS,NX,(IX(L),L=1,NX)`

    ITS = 0 if the species is **not** to be treated as a transition structure. Normally this is because the species is an equilibrium structure corresponding to a minimum on the potential energy surface.

    ITS = n (a positive integer) specifies the ordinal number of the reaction coordinate frequency (RCF) in the list of all $3N$ vibrational frequencies for a species which **is** to be treated as a transition structure. Usually a transition structure corresponds to a first-order saddle point and possesses a single imaginary frequency which appears first in the ordered list of vibrational frequencies; in this case ITS = 1. Sometimes a species may correspond to a higher-order saddle point, but it may be desired to treat other imaginary frequencies as if they were real; for example, if the RCF appears as third in the list, then ITS = 3, and this frequency alone will be excluded from the partition function but used instead to determine the tunnelling correction.

    NX quantifies the number of frequencies to be excluded from the IPFR evaluation.

    If the species corresponds to a genuine zero-gradient stationary point, then 6 eigenvalues of the full $3N$-dimensional Hessian should be zero. In practice, these values may not be exactly equal to zero for a number of reasons, including numerical rounding errors, and it is helpful to identify them explicitly. Usually, NX = 6, and the corresponding degrees of freedom are considered as translations and rotations which are excluded from evaluations of vibrational IPFRs and zero-point energies.

    The third and subsequent integers IX (format I4) on this line refer to the ordinal numbers of the frequencies to be excluded from the calculations. If the molecular species is an equilibrium structure with $3N - 6$ real vibrational frequencies, this line would read as:

    ___0___6___1___2___3___4___5___6

8. Isotopologue 1 title specification, line $q + 2$: (FORMAT 3I3,74A)

    `IS,IG,IFFREQ,TITLE`

    This is the same as for item 3, but with appropriate data to describe the first isotopically substituted species.

9. Isotopologue 1 atom specification lines, from line $q + 2$ to line (N/16) where N/16 refers to the 16 slots of atoms on one line of the specification, and is therefore equal to the nearest integer, rounded up. For example, an 18-atom species would be specified by one line of 16 atoms and another of 2 atoms, i.e. 2 lines (FORMAT (16(A4,1X))).

    `(IAT(I),I=1,NAT)`

    Each of the n atoms specified in the coordinate input lines (from line 5 to line $5 + n$) is included in the format of 16 slots of format A4, separated by one space between each atom (1X). This is where the isotopic substitution can take place. Therefore, for the following atoms in the coordinate input:

    12C, 1H, 1H, 1H

The isotopologue 1 atom specification line for a triply deuterated isotopologue would be:

_12C___2H___2H___2H

where again the underscores are used to represent the formatting.

(if IFFREQ = NF)):

This line is followed by *m* lines of frequencies for this isotopologue (also applies to subsequent isotopologues). Sample input files for a frequency-based IPFR calculation, as well as traditional Hessian-based calculations are included in the following GitHub repository: https://github.com/pbw20/SULISO_sample_files

10. Frequency control line for isotopologue 1: (FORMAT 20I4)

   As for item 7 for the parent structure, this line specifies whether or not the species is to be treated as a transition structure, and whether any frequencies are to be excluded from the IPFR calculation. The guidelines for item 7 can be followed here.

11. Subsequent isotopologue lines.

   A repeat of items 8, 9 and 10 for subsequent isotopologues, therefore a minimum of 3 new lines per additional isotopologue. Remember that the number of isotopologues for IPFRs to be calculated here, including the parent structure, must match that specified in the Header section line 1.

12. Final line: (FORMAT A4)

   The final line of the program consists of the word STOP, followed by a line break, in order to inform the program that no more input remains to be read.
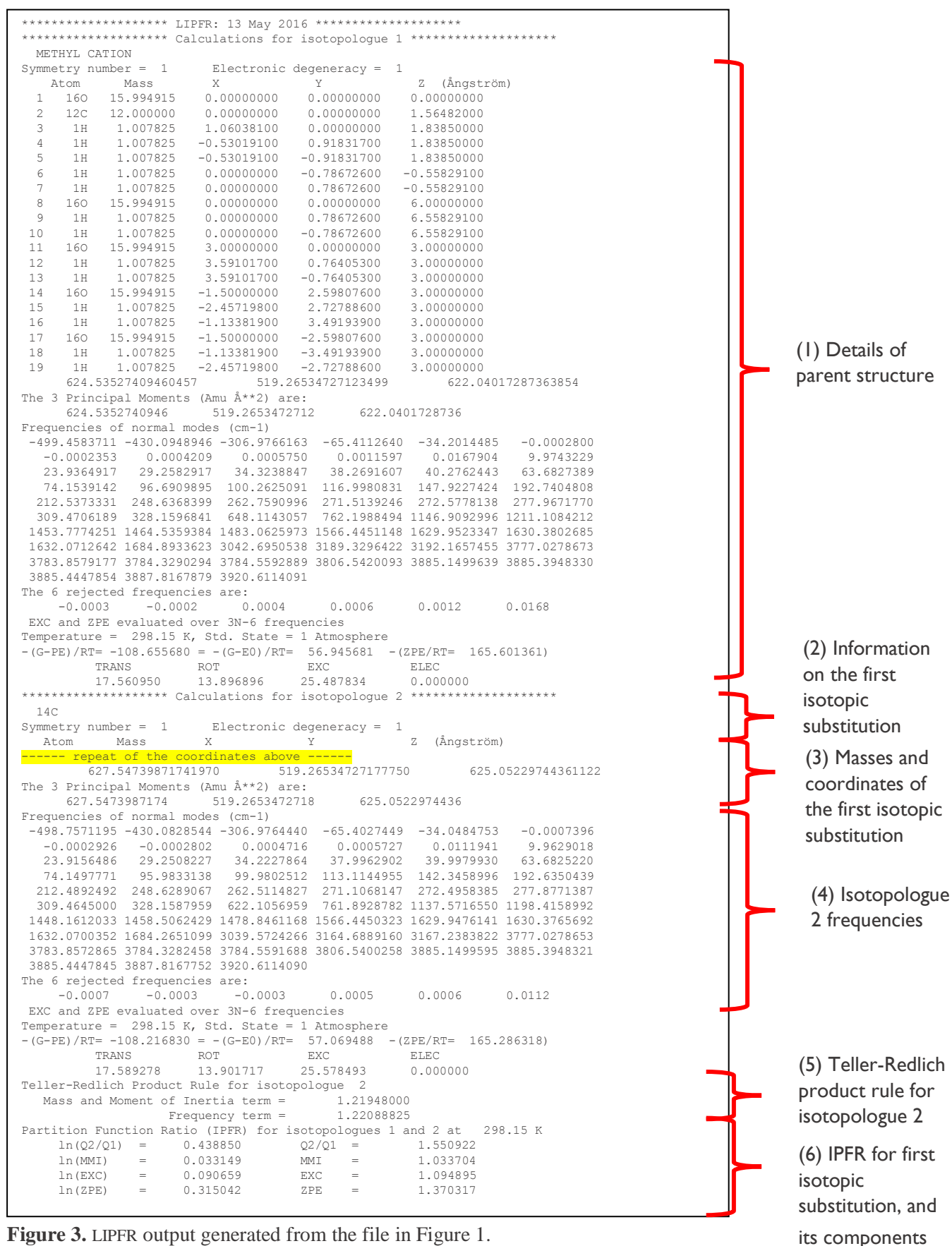
Overview of LIPFR output

```
******************** LIPFR: 13 May 2016 ********************
******************** Calculations for isotopologue 1 ********************
   METHYL CATION
Symmetry number = 1      Electronic degeneracy = 1
   Atom      Mass          X              Y              Z    (Ångström)
  1    16O   15.994915   0.00000000    0.00000000    0.00000000
  2    12C   12.000000   0.00000000    0.00000000    1.56482000
  3    1H    1.007825    1.06038100    0.00000000    1.83850000
  4    1H    1.007825   -0.53019100    0.91831700    1.83850000
  5    1H    1.007825   -0.53019100   -0.91831700    1.83850000
  6    1H    1.007825    0.00000000   -0.78672600   -0.55829100
  7    1H    1.007825    0.00000000    0.78672600   -0.55829100
  8    16O   15.994915   0.00000000    0.00000000    6.00000000
  9    1H    1.007825    0.00000000    0.78672600    6.55829100
 10    1H    1.007825    0.00000000   -0.78672600    6.55829100
 11    16O   15.994915   3.00000000    0.00000000    3.00000000
 12    1H    1.007825    3.59101700    0.76405300    3.00000000
 13    1H    1.007825    3.59101700   -0.76405300    3.00000000
 14    16O   15.994915  -1.50000000    2.59807600    3.00000000
 15    1H    1.007825   -2.45719800    2.72788600    3.00000000
 16    1H    1.007825   -1.13381900    3.49193900    3.00000000
 17    16O   15.994915  -1.50000000   -2.59807600    3.00000000
 18    1H    1.007825   -1.13381900   -3.49193900    3.00000000
 19    1H    1.007825   -2.45719800   -2.72788600    3.00000000
       624.53527409460457       519.26534727123499       622.04017287363854
The 3 Principal Moments (Amu Å**2) are:
       624.5352740946       519.2653472712       622.0401728736
Frequencies of normal modes (cm-1)
 -499.4583711 -430.0948946 -306.9766163  -65.4112640  -34.2014485   -0.0002800
   -0.0002353    0.0004209    0.0005750    0.0011597    0.0167904    9.9743229
   23.9364917   29.2582917   34.3238847   38.2691607   40.2762443   63.6827389
   74.1539142   96.6909895  100.2625091  116.9980831  147.9227424  192.7404808
  212.5373331  248.6368399  262.7590996  271.5139246  272.5778138  277.9671770
  309.4706189  328.1596841  648.1143057  762.1988494 1146.9092996 1211.1084212
 1453.7774251 1464.5359384 1483.0625973 1566.4451148 1629.9523347 1630.3802685
 1632.0712642 1684.8933623 3042.6950538 3189.3296422 3192.1657455 3777.0278673
 3783.8579177 3784.3290294 3784.5592889 3806.5420093 3885.1499639 3885.3948330
 3885.4447854 3887.8167879 3920.6114091
The 6 rejected frequencies are:
    -0.0003     -0.0002     0.0004      0.0006     0.0012      0.0168
 EXC and ZPE evaluated over 3N-6 frequencies
Temperature = 298.15 K, Std. State = 1 Atmosphere
-(G-PE)/RT= -108.655680 = -(G-E0)/RT= 56.945681 -(ZPE/RT= 165.601361)
          TRANS        ROT         EXC          ELEC
        17.560950   13.896896   25.487834    0.000000
******************** Calculations for isotopologue 2 ********************
   14C
Symmetry number = 1      Electronic degeneracy = 1
   Atom      Mass          X              Y              Z    (Ångström)
------ repeat of the coordinates above ------
       627.54739871741970       519.26534727177750       625.05229744361122
The 3 Principal Moments (Amu Å**2) are:
       627.5473987174       519.2653472718       625.0522974436
Frequencies of normal modes (cm-1)
 -498.7571195 -430.0828544 -306.9764440  -65.4027449  -34.0484753   -0.0007396
   -0.0002926   -0.0002802    0.0004716    0.0005727    0.0111941    9.9629018
   23.9156486   29.2508227   34.2227864   37.9962902   39.9979930   63.6825220
   74.1497771   95.9833138   99.9802512  113.1144955  142.3458996  192.6350439
  212.4892492  248.6289067  262.5114827  271.1068147  272.4958385  277.8771387
  309.4645000  328.1587959  622.1056959  761.8928782 1137.5716550 1198.4158992
 1448.1612033 1458.5062429 1478.8461168 1566.4450323 1629.9476141 1630.3765692
 1632.0700352 1684.2651099 3039.5724266 3164.6889160 3167.2383822 3777.0278653
 3783.8572865 3784.3282458 3784.5591688 3806.5400258 3885.1499595 3885.3948321
 3885.4447845 3887.8167752 3920.6114090
The 6 rejected frequencies are:
    -0.0007     -0.0003     0.0005      0.0006     0.0112
 EXC and ZPE evaluated over 3N-6 frequencies
Temperature = 298.15 K, Std. State = 1 Atmosphere
-(G-PE)/RT= -108.216830 = -(G-E0)/RT= 57.069488 -(ZPE/RT= 165.286318)
          TRANS        ROT         EXC          ELEC
        17.589278   13.901717   25.578493    0.000000
Teller-Redlich Product Rule for isotopologue 2
   Mass and Moment of Inertia term =       1.21948000
                   Frequency term =        1.22088825
Partition Function Ratio (IPFR) for isotopologues 1 and 2 at   298.15 K
       ln(Q2/Q1) =     0.438850       Q2/Q1  =        1.550922
       ln(MMI)   =     0.033149       MMI    =        1.033704
       ln(EXC)   =     0.090659       EXC    =        1.094895
       ln(ZPE)   =     0.315042       ZPE    =        1.370317
```

(1) Details of parent structure

(2) Information on the first isotopic substitution

(3) Masses and coordinates of the first isotopic substitution

(4) Isotopologue 2 frequencies

(5) Teller-Redlich product rule for isotopologue 2

(6) IPFR for first isotopic substitution, and its components

Figure 3. LIPFR output generated from the file in Figure 1.

1. LIPFR output begins by printing the version of the code currently being executed, in this case, the 13th May 2016 release. Then follows the data for the parent structure, in this case a methyl cation structure within a cage of water molecules.

2. Information on the first isotopic substitution (isotopologue 2) is output, including the 'Title' line, which was read from the input, as well as the electronic degeneracy and symmetry of the molecule.

3. The masses, atoms, and coordinates are then printed out for isotopologue 2, the coordinates should be the same as for the parent structure (isotopologue 1). In the interest of space, these have been omitted in this output in order to show more of the calculation results.

4. Frequencies calculated from the input un-mass-weighted Hessian and the specified isotopic substitutions are calculated. For heavier isotopologues the frequencies should be lower, and *vice versa*. This is another option to check the reasonableness of the calculations.

5. The product rule is printed out to test the frequency/ mass term equality which should be present in all calculations. If the two terms are equal, then there is little error in the calculated IPFR and input structures, however the holding of the Teller-Redlich product rule is a good measure of the quality of input structures and it is always a good idea to inspect it in order to check that both components are equal to all or the majority of decimal places. For more information on the Teller-Redlich product rule, see:

    E. Teller, cf. Angus, W. R.; Bailey, C. R.; Hale, J. B.; Ingold, C. K.; Leckie, A. H.; Raisin, C. G.; Thompson, J. W.; Wilson, C. L. *J. Chem. Soc*. **1936**, 971-987.

    Redlich, O. *Z. Physik. Chem. B* **1935**, *28*, 371-382.

    Williams, I. H., *Journal of Chemical Theory and Computation* **2012,** *8* (2), 542-553.

6. The IPFR calculated as a quotient of partition functions of the heavy isotopologue over the light, is printed out as a component of the different factors: mass (MMI), excitational (EXC), and zero-point (ZPE).

Kinetic isotope effects may be obtained from IPFRs evaluated for light (L) and heavy (H) isotopologues of RS and TS species as follows:

$$\text{KIE} = \frac{k_{\text{light}}}{k_{\text{heavy}}} = \frac{\left(\dfrac{Q_L^{TS}}{Q_L^{RS}}\right)}{\left(\dfrac{Q_H^{TS}}{Q_H^{RS}}\right)} = \left(\frac{Q_H^{RS}}{Q_L^{RS}}\right) \Big/ \left(\frac{Q_H^{TS}}{Q_L^{TS}}\right) = \frac{IPFR^{RS}}{IPFR^{TS}}$$

(where *Q* denotes a molecular partition function). This expression explains the convention of quoting IPFRs as "heavy/light".

Equilibrium isotope effects may be obtained from IPFRs evaluated for light (L) and heavy (H) isotopologues of reactant and product species, by replacing TS by PS in the equation above.

To obtain a KIE averaged over multiple thermally-accessible conformations of a flexible system, within which the atomic subset considered by UJISO is embedded, it is convenient and appropriate to perform independent averaging of IPFRs over individual RS species for the reactant state and individual TS species for the transition state. This may be performed easily by collecting IPFRs from individual UJISO calculations into a spreadsheet.

$$\langle \text{KIE} \rangle = \langle IPFR^{RS} \rangle / \langle IPFR^{TS} \rangle$$

see: Ruiz-Pernía, J. J.; Williams, I. H. *Chem. Eur. J.* **2012**, *18*, 9405-9414.

LIPFR Troubleshooting guide

There are a number of errors that users can come across, which will hopefully decrease in number as they familiarise themselves with the code. The most common of these are input errors. Luckily, the program will inform the user within the UNIX environment of the last read format and line number in the fortran source code, and therefore a likely area linking to the error. Throughout this manual, the formats of input have been specified to allow the user easy identification of the areas which require specific types. This should be the first reference point in the case of incomplete termination.

The advantage of the SULISO suite is that when programs terminate successfully, a line similar to that below will terminate the output:

```
************************ THE END ************************
```

This will ensure that users are certain of normal termination before considering results.

One error that has been noted is the format of certain coordinate/Hessian outputs from electronic structure codes. Some codes simply print out the coordinates, followed directly by the Hessian. However, sometimes the gradient is printed following the coordinates and preceding the Hessian. This consists of *n* lines of a similar format to the Hessian, where *N* is the number of atoms in the structure. This is often noticed upon processing, where erroneous frequencies are printed from the program and the input needs to be re-inspected. The simplest solution is to use the equation in Part 6 of the *Overview of LIPFR input* to deduce the expected number of lines of Hessian, and a program such as Notepad++ with a line count to identify if lines of gradient are present. When located, these can simply be deleted from the input and the programs rerun, which should fix the errors.

Additionally, in order to obtain Hessian matrices from electronic structure programs, frequency calculations must be carried out. For example, in Gaussian09, the keywords *punch=(coord,derivatives)* must be specified, along with *opt* and *freq* for a Hessian to be produced. Single point energy calculations, certainly in Gaussian09, will not yield a meaningful Hessian for isotope effect calculation.

Appendix – Additional examples of input and output

The aim of this section is to provide addition information on different systems which can be treated with the programs of the suite. These can be used on any system based on a Cartesian coordinate array and Hessian matrix.

```
IPFR 2
 1       418.15
 1 1 0 RU 4ts
  RU   -0.9722730  -0.6065750   0.1560350
 16O   -1.8939790  -0.7732900   2.0939040
 12C   -1.0485170  -1.6796020   2.4488440
&&&
 12C    2.0129410   3.7155340   1.3270220
  1H    1.6539620   4.7074760   1.0253450
  1H    2.5608650   3.7809550   2.2802970
*
    0.2508853214E+00    0.1175723034E-01    0.2283493745E+00
    0.5990520998E-01    0.6983872957E-02    0.3947488000E+00
&&&
   -0.3858175958E-02   -0.1752284733E-02   -0.6311020167E-02
    0.1177052557E+00    0.2063465544E-01    0.2544330229E+00
    0   6   1   2   3   4   5   6
 1 1 0 2H
  RU   16O   12C   12C   12C   12C   12C   12C   16O    1H    1H    1H   12C    1H   12C   12C
 12C   12C    2H   12C   12C    2H    2H    2H    2H   12C   12C    1H    1H    1H    1H   12C
  1H    1H    1H   12C    1H    1H    1H   12C    1H    1H    1H   16O   14N   12C   16O   12C
  1H    1H   12C    1H    1H
    0   6   1   2   3   4   5   6
STOP
```

> Atom specification for the first 3 and last 3 of 53 atoms in the structure

> First 2 and last 2 of 4240 lines of Hessian

> Isotopologue specification and program termination

Figure 1A. LIPFR input for a ruthenium-catalysed CH activation intermediate isotope effect calculation. Note the proportionally larger Hessian when compared to the methyl cage systems in the test cases. The majority of the Hessian has been omitted for clarity in the Figure.

```
******************** LIPFR: 13 May 2016 ********************

******************** Calculations for isotopologue 1 ********************

  RU 4ts
Symmetry number =  1    Electronic degeneracy =  1
    Atom      Mass        X            Y            Z  (Ångström)
  1    RU  101.070000   -0.97227300  -0.60657500   0.15603500
  2   16O   15.994915   -1.89397900  -0.77329000   2.09390400
  3   12C   12.000000   -1.04851700  -1.67960200   2.44884400
&&&
 51   12C   12.000000    2.01294100   3.71553400   1.32702200
 52    1H    1.007825    1.65396200   4.70747600   1.02534500
 53    1H    1.007825    2.56086500   3.78095500   2.28029700

The 3 Principal Moments (Amu Å**2) are:
    3672.4089468753    2270.1233143325    3240.9896687397

Frequencies of normal modes (cm-1)
   -0.0089217    -0.0086011    -0.0053639    -0.0048148    -0.0046730     0.0035700
   19.4747794    26.9175719    29.5518333    44.8478110    49.4660068    58.8431581
   66.1448984    67.9118074    74.1458676    81.1583971   105.9571190   120.7041514
  137.5601225   143.3024938   161.2366827   169.6606620   171.5640406   174.1974955
  194.2479040   217.9399135   221.2668046   244.5828926   261.4612802   282.3144697
  285.7729158   293.1509487   299.0516137   313.2492215   325.0842775   341.9109691
  380.4130085   385.8891193   400.7861417   402.4618372   413.8151361   431.5838832
  440.9686477   476.4137306   491.0476906   507.0651183   549.2680654   553.3448951
  589.9470033   606.4353669   623.3742263   636.9380768   651.6264019   666.1937411
  671.1116044   680.3495082   690.4153023   706.9665936   742.8116179   757.3667453
  793.6110794   813.0830830   866.2092835   869.2923474   873.2448826   880.6479667
  886.1183761   910.2250296   920.5406839   933.6126395   936.3691437   939.5978639
  944.1638245   945.4857000   963.9235669   971.3424521   980.9044688   981.6486739
  982.0771926   987.7321121  1007.9328056  1008.9919679  1022.2858535  1032.7948841
 1041.0752795  1072.9056917  1079.9015806  1098.2957592  1101.7065328  1122.9738163
 1128.0255204  1146.8944125  1151.7363579  1174.1797150  1189.7917646  1195.3285272
 1195.9170372  1210.2253632  1222.1380844  1263.1433607  1282.5186572  1297.3842331
 1311.0097214  1314.2492449  1339.0815385  1348.5410764  1352.6744343  1360.2930306
 1364.5828402  1366.0936603  1378.7873367  1398.3243906  1401.1121690  1418.7892304
 1421.6467662  1426.0497737  1440.7554152  1445.7025288  1447.7447267  1449.0642243
 1453.2572304  1455.7734100  1462.1377402  1471.6270155  1474.5842731  1476.7875131
 1482.8318130  1488.7293875  1493.4347428  1514.6607875  1586.8769805  1596.5027834
 1646.6551901  2967.7715946  2973.8730804  2976.7774434  2979.6983454  2992.3427112
 2995.2982457  3024.3278010  3048.7667962  3053.8156323  3054.1479826  3060.6855940
 3064.2869879  3069.9174367  3072.8927017  3087.2117772  3107.0840486  3107.385619+
 3120.4875978  3127.8894605  3129.4972507  3136.9670425  3137.5225913  3141.5871565
 3145.2031936  3147.1835403  3162.3814663

The 6 rejected frequencies are:
    -0.0089     -0.0086     -0.0054     -0.0048     -0.0047      0.0036

 EXC and ZPE evaluated over 3N-6 frequencies

Temperature =  418.15 K, Std. State = 1 Atmosphere

-(G-PE)/RT= -244.759215 = -(G-E0)/RT=  75.850597  -(ZPE/RT=  320.609812)
          TRANS           ROT           EXC           ELEC
          20.612394      16.852961     38.385242      0.000000
The 6 rejected frequencies are:
    -0.0089     -0.0086     -0.0054     -0.0048     -0.0047      0.0036

******************** Calculations for isotopologue 2 ********************

  2H

Symmetry number =  1    Electronic degeneracy =  1

    Atom      Mass        X            Y            Z  (Ångström)

  1    RU  101.070000   -0.97227300  -0.60657500   0.15603500
  2   16O   15.994915   -1.89397900  -0.77329000   2.09390400
&&&
 52    1H    1.007825    1.65396200   4.70747600   1.02534500
 53    1H    1.007825    2.56086500   3.78095500   2.28029700
```

Output header

Input coordinates for the first 3 and last 3 of 53 atoms in the structure

Moments of inertia and output frequencies for isotopologue 1.

Zero-valued frequencies for translation and rotation

Thermodynamic properties

Coordinates for first 2 and last 2 atoms of isotopologue 2: these are identical to those of isotopologue 1.

```
The 3 Principal Moments (Amu Å**2) are:
    3771.7655272730    2304.5161805509    3336.0983943963
         53
Frequencies of normal modes (cm-1)
  -0.0089748   -0.0085379   -0.0051507   -0.0046751   -0.0045366    0.0032037
  19.0734793   26.5965429   28.7027589   43.9258299   49.2934286   58.8308870
  63.1468052   67.6644943   73.5418236   79.4108921  105.5568273  119.9638830
 136.0000878  141.9825778  159.3830064  168.6611128  171.1998907  172.4773389
 194.1996321  217.6800489  221.1442865  243.9643211  254.7350349  281.3133639
 284.5548683  291.8108012  296.1014792  313.2215207  319.0284821  341.8479730
 350.7587923  369.5619030  384.4388363  402.0235768  413.5521276  431.5830245
 436.0695574  441.1065847  476.4104057  507.0384121  533.5845112  547.0252807
 552.8877323  581.2527611  589.9416198  623.3259310  626.4479943  632.6158532
 634.8659772  636.9635971  666.1911358  671.1276568  686.9990584  706.4393287
 737.3000817  747.3727262  759.9354665  791.8129282  793.6198006  817.8169832
 822.1001521  833.1789887  856.8373168  866.2895034  869.3382094  873.2757608
 880.7158020  910.2300727  920.4962540  933.6162543  936.3288659  938.3123031
 943.6601829  944.2239201  971.4243497  977.9217389  981.5910590  982.1630502
1003.2753337 1008.1864067 1022.3008382 1023.3984053 1041.0685781 1072.9114790
1098.0804798 1101.6911142 1116.7486094 1127.9705810 1146.8901410 1189.7668725
1191.5255440 1195.9097632 1206.4966636 1211.0988539 1263.1072097 1268.9678847
1282.5206646 1311.0233165 1329.5060289 1339.0800246 1351.2846971 1352.6773473
1357.1363792 1364.5946426 1366.0935312 1378.7857544 1382.4160093 1398.3270976
1401.1547697 1418.8294285 1425.9681590 1429.3788427 1440.7899726 1445.7281606
1447.8449237 1453.2151691 1455.7011303 1462.1390300 1471.6291958 1474.5212824
1476.8233704 1482.8727340 1493.2966662 1514.6576935 1555.0341910 1564.8209335
1645.1298618 2299.9771732 2309.3159039 2320.3171044 2330.9386217 2340.3757727
2967.7717565 2973.8733237 2976.7795474 2979.6976850 2992.3530665 2995.3009935
3024.3302753 3048.7752441 3053.8184323 3054.1532434 3060.6926969 3064.2901688
3069.9261207 3072.9139103 3087.2376818 3107.1434560 3107.3979255 3129.4997302
3137.5254304 3141.6224642 3147.1390447
The 6 rejected frequencies are:
    -0.0090     -0.0085     -0.0052     -0.0047     -0.0045      0.0032

 EXC and ZPE evaluated over 3N-6 frequencies
Temperature =  418.15 K, Std. State = 1 Atmosphere
-(G-PE)/RT= -231.731263 = -(G-E0)/RT=  76.754880  -(ZPE/RT=  308.486143)
         TRANS          ROT           EXC           ELEC
        20.628809     16.888289     39.237782      0.000000


Teller-Redlich Product Rule for isotopologue  2
  Mass and Moment of Inertia term =     170.90350750
                  Frequency term =     170.90391362


Partition Function Ratio (IPFR) for isotopologues 1 and 2 at   418.15 K
    ln(Q2/Q1) =    13.027952      Q2/Q1 =    454954.206218

    ln(MMI)   =     0.051743      MMI   =         1.053105
    ln(EXC)   =     0.852540      EXC   =         2.345598
    ln(ZPE)   =    12.123669      ZPE   =    184180.080017

***************************** The End *****************************
```

Moments of inertia and output frequencies for isotopologue 2.

Teller-Redlich product rule: equality of both terms indicates internal consistency of calculations

Partition functions ratios and their natural logarithms for the isotopic substitution

Figure 2A. Output for LIPFR calculation of deuterium substitution on an oxazolidinone intermediate in a Ru-catalysed CH activation.