UJISO

UJISO was created by IHW while on sabbatical at the Universitat Jaume I in Castellon de la Plana, Spain. Its function is to calculate isotopic partition function ratios (referred to as IPFRs from hereon in) from subset Hessians which had been subjected to the cutoff procedure (the manual for program CUTOFF is included in the elsewhere at the following Github repository: https://github.com/pbw20/SULISO_manuals).

UJISO is written in Fortran90, with some elements of earlier versions, but compiles fluidly under standard GNU compilers (gfortran…).

The aim of this user guide is to gently introduce the individual to the functionalities of UJISO and provide explicit descriptions of the input and output one can expect from standard UJISO 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

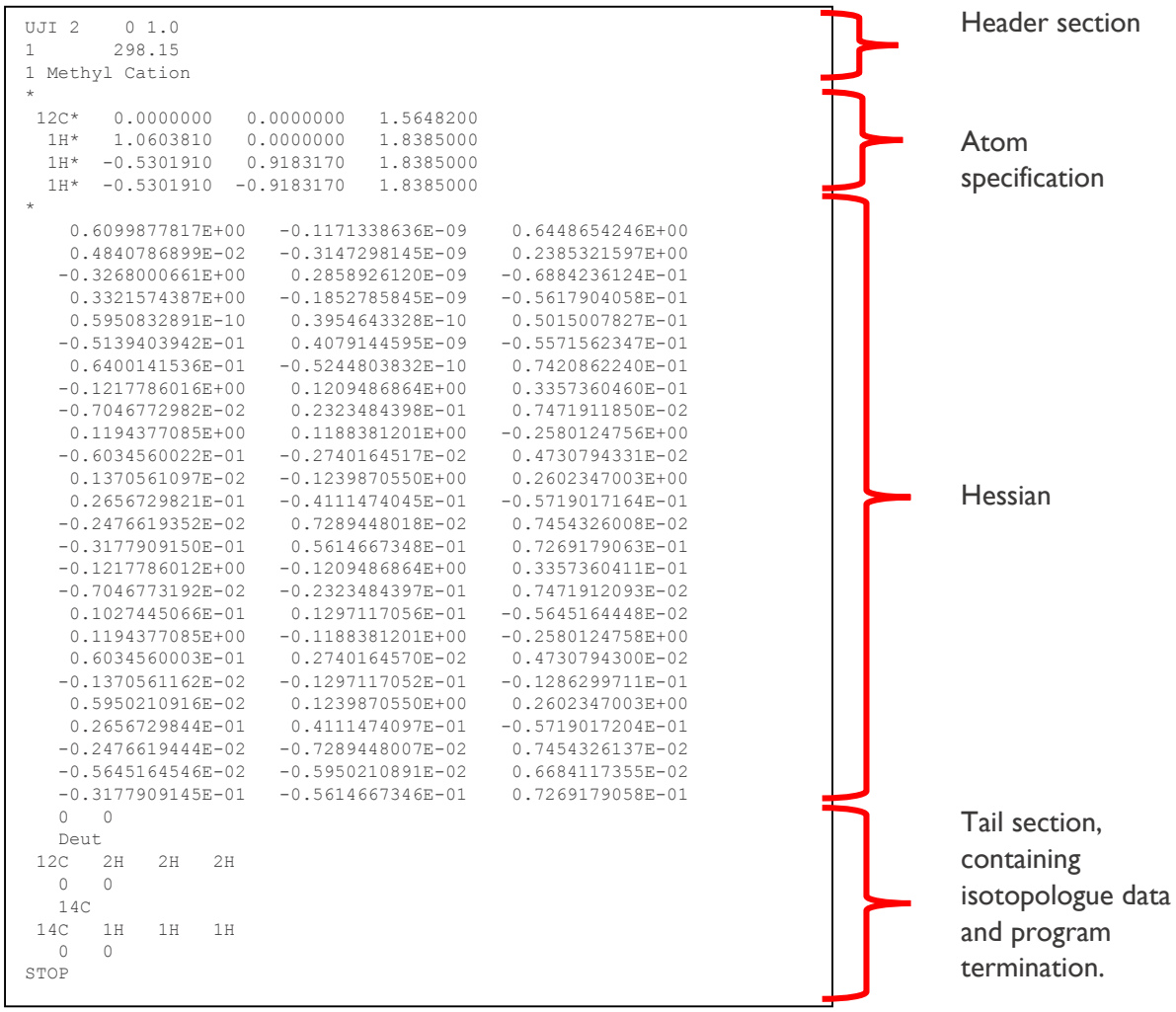

Figure 1. Sample input file for UJISO.

Overview of UJISO input

1. Header section, line 1: (FORMAT A4, I1, I5, F6.3)

   UJISO reads in the UJI specification to start the program (A4), followed by the integer number of isotopologues excluding the parent (I1), the number of frequencies to be read in (I5) and the vibrational scaling factor to be applied (F6.3), which is equal to 1.0 if none required.

2. Header section, line 2: (FORMAT I2, 3X, 7F10.2)

   the temperature section is read in, with the number of temperatures entered in format I2, followed by 3 spaces, and the individual values for the desired temperatures in format 7F10.2.

3. Header section, line 3: (FORMAT 64A)

   The title line: this line can be anything at all and does not enter into the calculation routines of the program. Most often used as an additional descriptor for the file or calculation.

4. Header separation line: (FORMAT A1)

   This line constitutes of a single asterisk (*) which separated the coordinate input from the header and PROG section of the input.

5. Coordinate input, line 5 – line 5 + *n*, where *n* is the number of atoms: (FORMAT A4, A1, 3F12.7)

   n atoms and their Cartesian coordinates are input as the isotopologues, followed by a space, followed by the *x*, *y*, and *z* coordinates in the format 3F12.7. The following isotopologues are currently accepted, although the nature of UJISO allows editing and inclusion of any entity by editing the source code:

   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

6. Coordinate-Hessian separation line, line 6 + *n* : (FORMAT A5)

   Consists of an asterisk (*) followed by four spaces, to separate the coordinate input from the Hessian.

7. Hessian input lines, line 7 + *n* – line *q*, where q = number of lines before Hessian section (7) + number of atoms (*n*), + number of lines of Hessian (*m)*: (FORMAT: 1X, 3E20.15)

   The number of lines of Hessian can be calculated based on the three column input being specified. Where:

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

Therefore 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.

8. Parent structure transition state and frequency omission line, line q + 1: (FORMAT 20I4)

   This line specifies first whether the structure is a transition state (number larger than 0), or a minimum on the PES (number = 0). If a transition structure, the number to be specified in the first I4 slot should correspond to the ordinal number of the reaction coordinate frequency (RCF). Therefore, if the RCF appears as third on the list of frequencies, this first I4 slot would be exactly:

   ___3

   where the underscores represent spaces in this explanation.

   The following entries of format I4 refer to the number of frequencies to be excluded from the calculations (as external degrees of freedom, or other reasons). This next slot of I4 includes the total number of frequencies to be ignored, with each of the following slots corresponding to the ordinal numbers of the frequencies to be excluded. So for example, if the first 6 frequencies of a reactant structure (minimum on PES) calculation were translations and rotations with magnitudes of 0.00 and they were to be ignored, the line would approximate as:

   ___0___6___1___2___3___4___5___6

   where again, the first 0 corresponds to the fact that the structure considered is a minimum on the PES, and the following slots of format I4 refer to the total number of excluded frequencies (6), and their placings in the order they appear from the calculation.

9. Isotopologue 1 title specification, line q + 2: (FORMAT 64A)

   Again this can reflect the isotopologue being specified below, and is a general character input which does not factor into the calculations.

10. Isotopologue 1 atom specification lines, line q + 2 – 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. Therefore, for 18 atoms, there would be one line of 16 atoms, and another of 2 atoms, which = 2 lines (FORMAT (16(A4,1X)))

    Each of the n atoms specified in the coordinate input lines (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.

11. Isotopologue 1 transition state and frequency omission line, [q + 2 – line (n/16)] +1 : (FORMAT 20I4)

    Exactly like Part 8 for the parent structure, this line specifies if the investigated structure is a transition state or PES minimum, and whether any frequencies are to be excluded from the IPFR calculation. The guidelines in Part 8 can be followed here.

12. Subsequent isotopologue lines

    A repeat of Parts 9, 10 and 11 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, excluding the parent structure, must match that specified in the Header section line 1.

13. 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 UJISO output

```
******************** UJISO: May 2016 ********************

******************** Calculations for isotopologue 1 ********************
Frequencies scaled by 1.000
Structure 1 Methyl Cation
    Atom      Mass        X             Y             Z(Angstrom)
  1   12C   12.000000     0.0000000     0.0000000     0.0000000
  2    1H    1.007825     0.0000000     1.0603810     0.0000000
  3    1H    1.007825     0.0000000    -0.5301910     0.9183170
  4    1H    1.007825     0.0000000    -0.5301910    -0.9183170
Frequencies of normal modes (cm-1)
    113.0411    211.3297    299.6085    488.1557   1128.7665   1142.6678
   1447.1914   1458.9378   1480.4228   3042.6484   3189.3085   3191.9987
EX and ZP evaluated over 3N frequencies
******************** Calculations for isotopologue 2 ********************
Frequencies scaled by 1.000
Structure    Deut

    Atom      Mass        X             Y             Z(Angstrom)
  1   12C   12.000000     0.0000000     0.0000000     0.0000000
  2    2H    2.014102     0.0000000     1.0603810     0.0000000
  3    2H    2.014102     0.0000000    -0.5301910     0.9183170
  4    2H    2.014102     0.0000000    -0.5301910    -0.9183170

Frequencies of normal modes (cm-1)
    100.5770    185.3978    212.4500    463.5179    833.1060    851.1020
   1052.6690   1072.2237   1072.2940   2168.5079   2377.5907   2381.5630

EX and ZP evaluated over 3N frequencies

Product Rule for isotopologue  2
   Isotopic mass term (IM) =         0.0443472301
       Frequency term (VP) =         0.0443472301

Partition Function Ratio for isotopologues 1 and 2 at     298.15 K

Q(heavy)/Q(light) =        IM       *        EX       *        ZP
  0.2850878498E+04  0.4434723010E-01  0.1488633644E+01  0.4318415032E+05

******************** Calculations for isotopologue 3 ********************
Frequencies scaled by 1.000
Structure    14C

    Atom      Mass        X             Y             Z(Angstrom)
  1   14C   14.003242     0.0000000     0.0000000     0.0000000
  2    1H    1.007825     0.0000000     1.0603810     0.0000000
  3    1H    1.007825     0.0000000    -0.5301910     0.9183170
  4    1H    1.007825     0.0000000    -0.5301910    -0.9183170

Frequencies of normal modes (cm-1)
    106.6660    199.8500    299.5484    455.0891   1119.5056   1131.2400
   1439.2525   1453.5897   1475.6042   3039.5310   3164.6710   3167.1144

EX and ZP evaluated over 3N frequencies

Product Rule for isotopologue  3
   Isotopic mass term (IM) =         0.7932845165
       Frequency term (VP) =         0.7932845165

Partition Function Ratio for isotopologues 1 and 3 at     298.15 K

Q(heavy)/Q(light) =        IM       *        EX       *        ZP
  0.1230776298E+01  0.7932845165E+00  0.1100274036E+01  0.1410097951E+01

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

(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

(7) Same order of data for isotopologue 3

Figure 2. UJISO output generated from the file in Figure 1.

1. UJISO output begins by printing the version of the code currently being executed, in this case, the May 2016 release. Then follows the data for the parent structure, in this case a methyl cation structure as a minimum on the PES.

2. Information on the first isotopic substitution (isotopologue 2) is output, including the 'Title' line, which was read from the input, as well as any scaling which is taking place.

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).

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 viability of the calculations.

5. The product rule is printed out to test the vibrational product (VP) 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:

   Redlich, M. G., *Proceedings of the National Academy of Sciences of the United States of America* **1953,** *39* (6), 560-563.

   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 (MI), excitational (EX), and zero-point (ZP).

The output IPFRs can then be used to calculate isotope effects based on the following relationships:

$$\mathrm{KIE} = \frac{k_{\mathrm{light}}}{k_{\mathrm{heavy}}} = \frac{\left(\frac{{Q_L}^{TS}}{{Q_L}^{RS}}\right)}{\left(\frac{{Q_H}^{TS}}{{Q_H}^{RS}}\right)} = \frac{{Q_L}^{TS}{Q_H}^{RS}}{{Q_L}^{RS}{Q_H}^{TS}} \equiv \frac{{Q_L}^{TS}}{{Q_L}^{RS}} \times \frac{{Q_H}^{RS}}{{Q_H}^{TS}} = \left(\frac{\left(\frac{{Q_H}^{RS}}{{Q_H}^{TS}}\right)}{\left(\frac{{Q_L}^{RS}}{{Q_L}^{TS}}\right)}\right)$$

which explains the convention of quoting IPFRs as Heavy/Light.

UJISO 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 7 of the *Overview of UJISO 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.