SoftwareX 6 (2017) 1–6

Contents lists available at ScienceDirect

SoftwareX

journal homepage: www.elsevier.com/locate/softx

SULISO: The Bath suite of vibrational characterization and isotope effect calculation software

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ARTICLE INFO

Article history:
Received 31 August 2016
Received in revised form
22 October 2016
Accepted 8 November 2016

Keywords:
Isotope effects
Vibrational frequencies
Computational chemistry
Fortran

ABSTRACT

Isotope effects are subtle but powerful probes of chemical reaction mechanisms and environmental conditions, with applications across chemical, biological and earth sciences. Their meaningful interpretation often relies on calculations based upon fundamental theories for their origin. The SULISO suite consists of four programs for the calculation of vibrational frequencies and isotope effects. CAMVIB is a broad vibrational characterization code developed for analysis of calculated harmonic frequencies and of normal modes in terms of internal coordinates. LIPFR calculates isotopic partition function ratios for pairs of isotopically substituted whole molecules, corresponding to conventional methodology, whereas UJISO is designed to perform similar calculations on subsets of atoms from very large systems. CUTOFF is a utility which truncates a force-constant matrix for a large system to obtain a smaller matrix appropriate for a specified subset of atoms.

Code metadata

Current Code version	*v 2.0*
Permanent link to code/repository used of this code version	https://github.com/ElsevierSoftwareX/SOFTX-D-16-00074
Legal Code License	*MIT*
Code Versioning system used	*none*
Software Code Language used	*fortran*
Compilation requirements, Operating environments & dependencies	*UNIX*
If available Link to developer documentation / manual	https://github.com/pbw20/SULISO_manuals
Support email for questions	Philippe.B.Wilson@bath.edu

Software metadata

Current software version	*2.0*
Permanent link to executables of this version	https://github.com/pbw20/SULISO/
Legal Software License	*MIT*
Computing platform / Operating System	*UNIX*
Installation requirements & dependencies	*None.*
If available Link to user manual — if formally published include a reference to the publication in the reference list	https://github.com/pbw20/SULISO_manuals
Support email for questions	Philippe.B.Wilson@bath.edu

1. Introduction

Isotope effects (IEs) on rate or equilibrium constants are exquisitely subtle but yet extraordinarily powerful experimental probes of reaction mechanisms, environmental conditions and structural changes throughout chemistry geochemistry and biochemistry [1]. IEs are employed in studies of chemical reactions and equilibria in a wide range of contexts in both gaseous and condensed-phases including enzyme-catalyzed processes. Substitution of one isotope of an element with another isotope (of the same element but with different mass) in general causes small but significant variations in the properties of a molecule or a material which are manifest in ratios of rate constants or equilibrium constants that differ from unity for reactions or equilibria involving the isotopic variants.

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http://dx.doi.org/10.1016/j.softx.2016.11.001
2352-7110/

It is vital to have robust computational protocols in place for their reliable calculation and interpretation. Existing programs for IE calculations were designed for isolated molecules and are inappropriate for subsets of atoms embedded in large supramolecular systems, such as commonly arise in quantum-mechanical/molecular-mechanical (QM/MM) simulations of condensed matter, including enzyme-catalyzed reactions and chemical reactions in solution [2]. The SULISO suite[1] comprises four programs to facilitate IE calculations based upon Cartesian force-constant (Hessian) matrices computed externally by means of electronic-structure (e.g. Gaussian09 [3]) or molecular-simulation (e.g. fDynamo [4]) codes. CAMVIB is an extensive vibrational calculation program, with numerous features for characterization and correlation of frequencies and normal modes. LIPFR calculates isotopic partition function ratios for pairs of isotopically substituted whole molecules, corresponding to conventional methodology, whereas UJISO is designed to perform similar calculations on subsets of atoms from very large systems. CUTOFF is a utility which truncates a force-constant matrix for a large system to obtain a smaller matrix appropriate for a specified subset of atoms; this is helpful in the determination of the minimal but sufficient size of Hessian for subsets of supramolecular systems. UJISO and LIPFR both act as end-of-line codes, taking input from CAMVIB and/or CUTOFF to calculate isotope effects from the vibrational frequency data.

2. Problems and background

The traditional theory of IEs based on molecular partition functions and the Bigeleisen equation [1] assume that each molecular system corresponds to a zero-gradient stationary point on a potential energy surface. Reliable optimized geometries and Hessians are readily available from modern quantum-chemical packages employing second-derivative methods, provided that convergence thresholds are set suitably tightly. However, since the turn of the millennium, it has become common to perform simulations for very large molecular systems (either molecules in solution or within enzyme active sites) but to compute explicit Hessians for only a subset of the total number of atoms in the system. For example, relaxation of a specified subset of atoms to a local minimum (or saddle point) may be performed within a frozen environment of the remaining atoms. In the context of QM/MM methods, the mobile subset and the frozen environment may be the same as the QM and MM regions, although different selections may also be made. In these circumstances the N_s subset atoms do not in themselves constitute a stationary structure in which vibrational degrees of freedom are separable from translations and rotation. The constraining influence of the environment means that diagonalization of the mass-weighted $3N_s \times 3N_s$ Hessian in Cartesian coordinates generally yields $3N_s$ non-zero eigenvalues which include six corresponding to libration of the whole subset with respect to its environment: "translation" and "rotation" of the subset as a whole are not free or separable motions but are coupled with the internal vibrational degrees of freedom.

It appears that other programs for IE calculations (e.g. QUIVER [5] and ISOEFF98 [6]) employ the Bigeleisen equation for $3N_s - 6$ internal degrees of freedom even for atomic subsets embedded within a supramolecular environment, and this has been achieved in published work either by projecting out the six external degrees of freedom or by simply ignoring the six lowest frequencies. In principle these procedures are both invalid and unnecessary, and should be replaced by methodology that uses all $3N_s$ frequencies of the embedded subset, as described elsewhere [7]. Moreover, other programs tend to be organized in order to provide an equilibrium IE or a kinetic IE for a particular reaction involving single structures for each of the initial and final states of the system. This approach is valid for gas-phase processes but arguably is not very suitable for reactions in condensed phases. We have argued elsewhere that it is essential to determine the isotopic sensitivity of a large flexible supramolecular system by averaging over thermally accessible conformations [8]. This may be done by consideration of the ("reduced") isotopic partition function ratio [1] (IPFR), f, for each conformation of each system. The average IE is obtained as the quotient of average IPFRs for the initial state (IS) and final state (FS).

$$\langle \mathrm{IE} \rangle = \langle f_{\mathrm{IS}} \rangle / \langle f_{\mathrm{FS}} \rangle \tag{1}$$

where each individual value of f involves a product of partition functions for $3N_s$ degrees of freedom (or $3N_s - 1$ for a first-order saddle point together with a one-dimensional tunneling factor along the direction of the transition vector, within the range of validity of the harmonic approximation with respect to the de Broglie wavelength). Our programs LIPFR and UJISO are designed to compute IPFR values for a simple structure but for as many different isotopic substitutions as are desired; the results for many different conformations are collated and averaged by means of a spreadsheet.

3. Software framework

3.1. Software architecture

The four programs are written in FORTRAN and output from CAMVIB and CUTOFF is used as input for LIPFR and UJISO, respectively. Each code is split into individual subroutines which carry out individual part of the calculation explicitly, the different functionalities being called by a series of keywords. (See Fig. 1.)

3.2. Software functionalities

CAMVIB functions with three main aims. Firstly, normal coordinates and vibrational frequencies can be calculated for any number of atoms up to a limit set by a parameter MAXNAT in the included file CAM_SIZE. Secondly, the code allows for transformation of Cartesian force constants to internal or symmetry force constants, which can all individually be scaled and manipulated. CAMVIB can also compute compliance constants and relaxed force constants. All of these options are requested by a series of keywords within the program.

CUTOFF performs the function of truncating a $3N \times 3N$ Hessian to a smaller matrix representing the atomic positions specified in the input file. This outputs a new coordinate system and Hessian for input to UJISO.

UJISO and LIPFR calculate isotope effects with input originating from either program CUTOFF or CAMVIB, respectively. UJISO is particularly tailored to post-CUTOFF use to calculated IEs from subset Hessians, while LIPFR acts upon full systems. Multiple isotopes can be substituted and IPFRs calculated for each structure and Hessian The calculations can also be carried out at a number of temperatures. In order to confirm the integrity of the IPFR calculations, the Teller–Redlich product rule [1] is employed: the independently calculated "masses and moments of inertia" and "vibrational product" terms should be exactly equal.

[1] In the Roman era the city of Bath was known as Aquae Sulis.