VARIFLEX MANUAL

(Revised 9/2/98 by SJK)

Overview

VariFlex is a program package for estimating rate constants of several types of gas phase reactions. Its focus is the application of transition state theory with an accurate treatment of the flexibility of the interfragment modes for variable definitions of the reaction coordinate. Although aimed at calculating rates at this high level of sophistication, the package also allows convenient preliminary estimates of the rates using various lower precision approaches which are less computationally demanding [such as phase space theory (PST) calculations, tight transition state, i.e., rigid rotor harmonic oscillator estimates (RRHO), and generic standard hydrocarbon estimates].

The following reaction types may be considered:

I. **Bimolecular association** reactions A + B => C.

II. **Unimolecular dissociation** reactions A => B + C.

III. **Bimolecular** reactions A + B => C + D.

IV. Competitive **multichannel** versions of each of the above, where more than one set of products is available, but involving only one complex or in the low pressure limit.

For each of these reaction types one may consider either **ionic** or **neutral** species.

The program focuses on the description of the temperature and/or pressure dependence of thermal reactions, where the reactants have a Boltzmann distribution of energies and angular momenta. However, microcanonical and *E/J* resolved dissociation rates are also generally available as a subset of the thermal calculations (that is, rates for reactants of specified energy, or specified energy and total angular momentum).

Methods are described for calculating

I. **High-pressure** limiting thermal rates evaluated at the ***T***, ***E***, and/or ***E/J*** resolved levels.

II. **Pressure-dependence** of thermal rates using the **RRKM** or **master equation** or Troe's **modified strong collision** formalism.

III. Zero-pressure and **low-pressure** limit thermal rates.

More detailed description

This is a general program to calculate variable reaction coordinate/flexible transition state theory kinetic and dynamic estimates for barrierless reactions. It implements the most recent algorithms for evaluating individual *T*, *E*, or *E/J* resolved rate constants. These algorithms are coupled with master equation or Troe strong coupling analyses to provide kinetic estimates for a complete range of pressures. Procedures appropriate for both radical-radical and ion-molecule reactions are explicitly built in.

The basic **variable reaction coordinate-transition state theory** (VRC-TST**)** formalism is described in:

[S. J. Klippenstein, *Chem. Phys. Letts*. 170, 71 (1990); *J. Chem. Phys*. 94, 6469 (1991*); J. Chem. Phys*. 96, 367 (1992); S. H. Robertson, A. F. Wagner, and D. M. Wardlaw, *Faraday Disc. Chem. Soc.* 102, 65 (1995).]

This formalism is in turn based on the **flexible transition state theory** (FTST) formalism:

[D. M. Wardlaw and R. A. Marcus, *Chem. Phys. Letts*. 110, 230 (1984); *J. Chem. Phys*. 83, 3462 (1985); *J. Phys. Chem*. 90, 5383 (1986); *Adv. Chem. Phys*. 70, 231 (1988).]

The VRC-TST formalism has been implemented in this program at three different levels of resolution for evaluating the TS partition functions:

(i) The **T** resolved level [S. H. Robertson, A. F. Wagner, and D. M. Wardlaw, *Faraday Disc. Chem. Soc*. 102, 65 (1995); S. J. Klippenstein, *J. Chem. Phys*. 98, 6994 (1991)].

(ii) The **E** resolved level [S. J. Klippenstein, *Chem. Phys. Letts.* 214, 418 (1993)] – *in this first version this level is simply implemented as the integral over J of the E/J resolved results*.

(iii) The **E/J** resolved level [S. J. Klippenstein, *J. Phys. Chem*. 98, 11459 (1994)].

The following alternative procedures for estimating the TS partition functions are also available:

(a) **Quantum phase space theory** (PST) [P. Pechukas and J. C. Light, *J. Chem. Phys.* 42, 3281 (1965); P. Pechukas, R. Rankin, and J. C. Light, *J. Chem. Phys.* 44, 794 (1966)].

(b) **Tight transition state theory**, i.e., rigid rotor harmonic oscillator (**RRHO**) based estimates.

(c) **Inverse Laplace transformation** [S. H. Robertson, M. J. Pilling, D. L. Baulch, and N. J. B. Green, *J. Phys. Chem.* 99, 13452 (1995)].

(d) **Classical phase space theory** is not explicitly built in. However, a close analogue may be obtained by simply incorporating the appropriate long range isotropic potential within the VRC-TST formalism and then considering the appropriate range of center-of-mass separation distances. Alternatively, efficient PST estimates may be obtained by simply using large angular momentum step sizes in the quantum PST algorithm.

1-dimensional hindered and free rotor treatments of any particular mode are available for the separated fragments, the complex and the transition state. Eckart and Wigner type tunneling corrections may be include for the transition state analyses.

The high pressure limiting thermal rate constants may be evaluated at any of the three levels of resolution and using any of the algorithms for evaluating the TS partition functions. When evaluated, the individual dissociation rate constants obtained at the *E* and *E/J* resolved levels are also printed out in secondary output files.

Treatments for the **pressure dependence** require evaluations at the *E* and/or *E/J* resolved level and implement either:

(i) The master equation formalism [R. G. Gilbert and S. C. Smith, *Theory of Unimolecular Reactions*, Blackwell, 1990; K. A. Holbrook, M. J. Pilling, and S. H. Robertson, *Unimolecular Reactions*, Wiley, 1996] or

(ii) Troe's modified strong collision format: [J. Troe, *J. Chem. Phys*. 66, 4745, 4758 (1977)].

The various implementations of the master equation incorporated here are based on work described in:

[M. A. Hanning-Lee, N. J. B. Green, M. J. Pilling, and S. H. Robertson, *J. Phys. Chem.* 97, 860 (1993); N. J. B. Green, S. H. Robertson, M. J. Pilling, *J. Chem. Phys*. 100, 5259 (1994); S. H. Robertson, M. J. Pilling, D. L. Baulch, N. J. B. Green, *J. Phys. Chem*. 99, 13452 (1995); N. J. B. Green, Z. A. Bhatti, *Chem. Phys. Lett*. 254, 358 (1996).]

For **ionic** reactions we have also built in various components of the **standard hydrocarbon** analysis [R. C. Dunbar , *Int. J. Mass Spec. Ion* Proc. 160, 1 (1997); 100, 423 (1990)]. This procedure provides generic estimates for the zero-pressure radiative association rate constant.

Also available as subcomponents of the calculations are *E* or *E/J* resolved estimates for

(i) Dissociation rate constants.

(ii) Rovibronic densities of states for the complex.

(iii) Transition states numbers of states.

(iv) Radiative rate constants.

and *T* resolved estimates for the

(v) Partition functions for the complex and for the primary fragments.

(vi) The equilibrium constant.

Input

We try to provide a complete description of the data below, and this description should be at least perused prior to usage. However, the best way to prepare the data, at least initially, will be to make modifications to that sample data file which most closely matches your own desired calculation. We encourage you to follow this approach. However, you must consider the convergence of your results with respect to *E* and/or *J* in any *E* or *E/J* resolved calculations. A detailed description of such convergence procedures is provided in Appendix 3. It is absolutely essential that one study this Appendix prior to running any *E* or *E/J* resolved calculations.

Rules for keyword input format

The input is keyword-based. It is case insensitive, that is, uppercase and lowercase letters are not distinguished. Different types of lines: (i) Blank lines are permitted (except as noted below) and are ignored. (ii) Comment lines beginning with ! are also ignored, but cannot immediately follow a keyword line with a data keyword. (iii) Lines beginning with * denote the beginning of sections, and the program reads these to keep track of and ensure proper input flow. (iv) Lines beginning with & can follow immediately after any section header line; these are read as title information, and are printed verbatim in the primary output. (v) All lines not of these four types are read as keywords or data, depending on the context. On a given keyword line (but not a data line), everything after a ! is comment, and is ignored.

Keyword lines contain first a single primary keyword followed on occasion by one or more qualifier keywords on the same line. The primary keywords are of three types:

1. *Program keywords* (all end with P) give program instructions, and have no argument.
2. *Data keywords* (all end with D) are followed by an argument consisting of a specific set of data read in free format (i.e., separated by spaces, or commas, or on separate lines). This argument must be given on a separate line from the data keyword.
3. *List keywords* (all end with L) are followed by an argument consisting of multiple lines of data, where the number of items of data expected will usually be set by the keyword preceding the list keyword. Unless noted otherwise, data items are again read in free format and may appear separated by commas or spaces on one line, or may be on separate lines. Again this argument must begin on a separate line from the data keyword.

The qualifier keywords are of the same three types and end in PQ, DQ, or LQ, with the P, D, and L components of these suffixes having the same meaning as for the primary keywords. These qualifier keywords give instructions relevant to the primary program keyword, which appears on the same line.

Comments on input error messages

Error messages have been incorporated throughout suggesting which mandatory keyword was expected. In some cases you may instead have been trying to input an optional keyword. Thus, one should really read the error messages as an indication that something was wrong prior to the expected keyword point. Furthermore, these messages may in some instances be incorrect since it is difficult to test all possible circumstances for erroneous input information.

Debugging options:

Any of the debugging keywords may be inserted at any point in the input file, and the corresponding debugging output will be printed starting with that point in the program execution. Currently there are two debugging keywords:

> **KeyDebugP** is useful for debugging input files. It causes the program to print out each keyword as it is read by the program. This output is printed in the main output file variflex.out (if you are using the vrfx_run shell this file will instead be named 'job'.out).
>
> **TSPFDebugP** prints out information about the Transition State Partition Function. It is useful for debugging the actual VTST calculation. It also provides additional information about the transition state that may be of interest to the user. The output is in the file tspf.out (or 'job'_tspf.out). See the output section of the manual for more details.

Input Sections

The sections must appear in the order given below, but (except as noted for Mandatory sections) sections may be omitted. The end of each section is detected by the appearance of a new * line, and the input file **must end** with the line ***END** (*and should include the carriage return or end of line command*).

***** 1. Title *****

(Mandatory section).

This section begins with the line

***Title**

which is the first line expected in the input file. The only input expected in this section (other than comment lines and debugging keywords) are **title lines** beginning with &, which will be read and echoed in the output files.

***** 2. Calculation Type *****

(Mandatory section)

Begins with the line

***CalculationType**

The basic choices here fall into the following categories. Choose one keyword from each group. But some groups may be omitted, depending on other choices. See the general discussion above for guidance regarding which combinations of choices are currently implemented. The order of keyword entry in this section is unimportant, aside from the qualifier keywords which must be on the same line as their corresponding keyword.

A. *Ionic or neutral reactants*

IonP

NeutralP

B. *Reaction type*.

AssociationP Treat only the association direction.

DissociationP Treat only the dissociation direction.

ReversibleP Treat both association and dissociation simultaneously.

C. *Channels*.

If more than one reaction channel is to be considered, use the keyword

ChannelsD Allows more than one product channel. Requires the number of product channels as argument. (Default is one channel).

D. *Level of Resolution in the Transition State Evaluations*

TResP Evaluate the TS partition function at the *T* resolved level

EResP Evaluate the TS partition function at the *E* resolved level

EJResP Evaluate the TS partition function at the *E/J* resolved level

StHydroP generic standard hydrocarbon estimate -- only appropriate for ionic association reactions. If this keyword is given, no other Section 2 keywords will be used. The input should include the temperature and binding energy parts of Section 3, and then should proceed to the special format specified in the Standard Hydrocarbon Radiative Association input section given below.

E. *Treatment of Collisional and Radiative Relaxation*.

HighPresP or equivalently **HighEffP** Consider only the high pressure/high efficiency limit for the reaction.

LowEffP or equivalently **LowPresP** Consider only the low pressure/low efficiency limit for the reaction.

LimitJPQ Qualifier for **LowEffP** and **LowPresP** calculations which limits the range of J for certain integrals. (Default is no limit which can also be specified with **NoLimitJPQ**.)

StrongCollisionP Perform a strong collision (collision efficiency = 1) RRKM analysis.

TroeP Perform a Troe style analysis incorporating both the Strong Collision and Weak Collision broadening factors as described in [J. Troe, *Ber. Bunsenges. Phys. Chem.* 87, 161 (1983); R. G. Gilbert, K. Luther, and J. Troe, *Ber. Bunsenges. Phys. Chem.* 87, 169 (1983)]

ModifiedStrongP Perform a modified strong collision RRKM analysis evaluating the collisional efficiency in terms of the Troe formalism described in [J. Troe, *Ber. Bunsenges.* Phys. Chem. 87, 161 (1983)]; but with no weak collision correction.

1DMasterP Employ 1-D Master equation in treating the pressure dependence. In all cases a simple exponential down model is employed for the energy transfer coefficients. The radiative relaxation rates are evaluated from the individual populations in each of the *E,J* levels and the Einstein coefficients for absorption and emission as obtained from the IR intensities.

PCompPQ, PReacPQ: Qualifiers for **1DMasterP** which specify the particular form of J averaging employed in deriving the 1D master equation from E/J resolved rate constants. (Default is **PCompPQ**.)

PCompPQ implies the use of the Boltzman probability for the J distribution in the master equation

k(E) = ∫ dJ k(E,J) P_comp (E,J;T) / ∫ dJ P_comp (E,J; T);

P_comp(E,J) = rho_comp(E,J)*exp(-E/k_B T) / Q_comp(T)

PReacPQ implies the use of the product of the Boltzman probability for the complex with the stabilization probability for the J distribution in the master equation as described in [S. C. Smith and R. G. Gilbert, *Int. J. Chem. Kinet.* 20, 307,979 (1988)].

k(E) = ∫ dJ k(E,J) P_comp(E,J;T) P_stab(E,J) / ∫ dJ P_comp P_stab;

P_stab(E,J) = ω / [ω + k(E,J)]

The present implementation differs however in the choice of total *E* and total *J* as the separable variables instead of E_{vib} and E_{rot}.

EigenvaluePQ, InversionPQ, DiffusionPQ: Qualifiers for **1DMasterP** which specify the algorithm employed in solving the master equation. For single channel calculations either may be used and the default is **EigenvaluePQ.** For multichannel reactions this parameter is ignored and the program instead forces the use of the eigenvalue based routine for dissociation reactions and the inversion based routine for association reactions.

EigenvaluePQ implies the use of an eigenvalue solver based approach**.**

InversionPQ implies the use of a matrix inversion based approach**.**

DiffusionPQ implies the use of a diffusion equation based approach (this approach is *not currently functioning*)

2DMasterP (*Not currently functioning***)**

F. *State-Counting*.

In the evaluation of vibrational state densities, the default approach is direct state counting by the Beyer-Swinehart algorithm. The steepest-descents approximation may be used instead for either the density of states for the complex (by entering the keyword **RhoCSteeP**) and/or for the conserved mode contribution to the transition state number of states (by entering the keyword **RhoTSSteeP)**. The primary advantage of the steepest descent approach is that it provides a smooth state density even for cases where the direct count vibrational density fluctuates due to a sparsity of the vibrational levels. Sparse vibrational state spacing may be a problem in calculations involving low binding energy, small molecules, or vibrational frequency sets with many degeneracies and few distinct frequencies. Using the steepest descents option will probably never give significant errors for the complex density of states, and if its use gives large changes in results compared with exact counting, one should consider the physical meaning of the sparsity. Quite often the smoothing provided by the steepest descent algorithm will be appropriate. However, some of the algorithms for the conserved mode contribution to the transition state number of states rely on the proper fluctuations in the vibrational density and so **RhoTSSteeP** should only be used with great caution. It may also be important to use the direct count algorithm when performing master equation analyses of the pressure dependence. A secondary advantage of the steepest descent approach is that there are some instances where it will provide a significantly faster calculation, such as when many (e.g., 1000) vibrational modes are considered in a radiative rate calculation.

Note: The steepest descent algorithm will not function properly when some of the modes are treated as free-rotors or as hindered rotors.

G. *Rotational Partition Functions*.

The rotational contributions to the canonical partition functions for the complex and for the fragments are generally evaluated classically. Direct quantum counts may be employed for these partition functions by entering the keywords **QuanPFCompP** (for the complex), **QuanPFFrag1P** (for the first fragment) and/or **QuanPFFrag2P** (for the second fragment). Note, however, that no nuclear spin (e.g., ortho vs. para) will not be considered.

H. *Multiple Wells.*

Low pressure RRKM analyses for bimolecular reactions passing through multiple complexes may be performed by indicating the connectivity of all the different complex wells to each other and to the reactants and products. This requires first the keyword

MultiWellP

Followed by the keyword

NWellD whose argument is the number of complexes to be considered (NWELL) and the number of product channels to consider (NPROD).

Then give the keyword

ReacWellConnectD whose argument is a list of NWELL integers. For each of the integers, a value of 1 implies that the reactants are directly connected to that well and a value of 0 implies that they are not. Explicit entrance channel transition state evaluations will be performed for each of those wells that are connected to the reactants. Typically, all but the first value will be 0.

The next keyword must be

WellProdConnectD whose argument is a list of NWELL x NPROD integers describing the connectivity of each well to each of the products. In this input, the outer loop is over the wells and the inner loop is over the products. I.e., one first inputs the connectivity for the first well to each of the products. Then the connectivity for the second well is given, and so on, until the connectivity for each of the wells has been given. Explicit exit channel transition state evaluations will be performed for each of the wells connected to products.

The next keyword must be

WellWellConnectD whose argument is a list of NWELL x (NWELL – 1) / 2 integers describing the connectivity of each well to each of the other wells. In this input, the lower triangular portion of the matrix is cycled over. I.e., the connectivities are read in the order W_2W_1, W_3W_1, W_3W_2 W_4W_1, …Transition state evaluations will performed for each of the pair of wells which are connected.

The final keyword given is

ReacProdConnectD whose argument is a list of NPROD integers describing the connectivity of the reactants to each of the products. Such connectivities would be appropriate for abstraction reactions for example.

The input of the data for the transition states should follow the order of the abovedescribed input for the connectivities.

Various restrictions: Standard Hydrocarbon calculations (**StHydroP**) are available only for Ionic Associations (**IonicP** and **AssociationP**). Only one channel may be considered in T Resolved calculations (**TResP**) and in High Pressure calculations (**HighPresP** or **HighEffP**). T Resolved (**TResP**) calculations can only consider the High Pressure limit (**HighPresP** or **HighEffP**). 2D Master (**2DMasterP**) equations must employ an E/J Resolved (**EJResP**) determination of the number of states.

***** 3. Calculation Ranges *****

(Mandatory section)

Begins with the line

***CalculationRanges**

This section specifies the temperatures, pressures, radiative rates, binding energies, and downward energy transfer that will be ranged over in the calculations. The parameters may be specified in any order. Also, any number of these specifications may be skipped in which case the defaults will be employed. With two exceptions the basic format is the same for each of the parameters and so we describe in detail only that for the temperature. The radiative rate involves additional possibilities beyond the basic format. The other exception is that the ranges of temperature and pressure may also be input as list of pairs of

Temperatures:

Default is one temperature of 300 K

Keyword **TRangeP**

Followed by one of the following three qualifiers (on the same line):

StepDQ

Specifies a range of equally spaced temperatures. The argument line consists of 3 numbers, which are the minimum temperature, the step interval between temperatures, and the total number of temperatures.

ScaleDQ

Specifies a range of temperatures increasing by a constant factor. The argument line consists of 3 numbers, which are the minimum temperature, the factor by which each temperature is larger than the preceding one, and the total number of temperatures.

ListDQ

Specifies that a series of temperatures will be read in. Its argument (one number) is the number of temperature values to be read. It must be followed by the keyword

ValuesL

after which is given the series of temperatures to be used.

Pressures:

Default is one pressure of 760 torr

Keyword **PRangeP**

Followed by one of the following three qualifiers (on the same line):

StepDQ or

ScaleDQ or

ListDQ followed by

ValuesL

Temperature and Pressure pairs:

If this keyword option is used, the keywords **TRangeP** and **PRangeP** should not be used. Default is one T,P pair of 300 K, 760 torr

Keyword **TPRangeP**

Give the keyword **NTPPairsD** whose argument is the number of sets of T,P pairs of data.

Then give the keyword **TPPairsL** followed by the given number of pairs of T,P values

Radiative rates:

Default is one k_r of zero value

Keyword **KRRangeP**

Followed by one of the following five keywords (on the same line):

CalcPQ

Specifies that the needed radiative rates will be calculated subsequently from the infrared mode intensities.

StepDQ

ScaleDQ

ListDQ followed by

ValuesL

StHydPQ indicates that the radiative emission rate is to be estimated from generic standard hydrocarbon rules

The keyword **MINPROBDQ** may also be added as a third keyword on the radiative keyword lines. This keyword specifies the minimum mode excitation probability considered in the evaluation of the net radiative emission rate (default = 1.0e-05).

Zero-point corrected binding energies D_0.

Energy to go from the vibrational/rotational ground state of the desired electronic state of the complex to the vibrational/rotational ground states of the fragments for channel 1. Default is one D_0 value of 20000 cm^{-1}

Keyword **DZeroRangeP**

Followed by one of the following three keywords (on the same line):

StepDQ

ScaleDQ

ListDQ followed by

ValuesL

Delta E_{down} : the average energy transfer step-down parameter for the collisional process

Default is one *Delta* E_{down} value of -100 cm^{-1} (Note the use of negative values for the input)

Keyword **DeltaEDownRangeP**

Followed by one of the following three keywords (on the same line):

StepDQ

ScaleDQ

ListDQ followed by

ValuesL

***** 4. Experimental Data *****

(Optional Section)

Begins with line

***ExperimentalData**

This section allows for the input of experimental data for the temperatures and/or pressures at which the rate constants are to be calculated. These data are used in evaluating root-mean-square deviations between theory and experiment for each of the parameter ranges.

For comparison with high pressure experimental data give one of the optional keywords **RevHighPExptD** or **BiHighPExptD** or **UniHighPExptD** followed by the corresponding set of experimental data

RevHighPExptD is followed by pairs of data corresponding to the high pressure association and dissociation rate constants for each of the temperatures to be considered.

BiHighPExptD is followed by the bimolecular high pressure association rate constants for each of the temperatures to be considered.

UniHighPExptD is followed by the high pressure unimolecular dissociation rate constants for each of the temperatures to be considered.

For comparison with pressure and temperature dependent experimental data give one of the optional keywords **RevExptD** or **BiExptD** or **UniExptD** followed by the corresponding set of experimental data

RevExptD is followed by sets of data corresponding to the association and dissociation rate constants for each of the channels and each of the temperature/pressure pairs to be considered. For each temperature and pressure combination, pairs of association and dissociation rate constants are given for first channel one and then channel 2, etc.

BiExptD is followed by the bimolecular rate constants for each of the channels and each of the temperature/pressure pairs to be considered. Again the inner loop of this input corresponds to the different channels and the outer loop corresponds to the different temperature and pressure pairs.

UniExptD is followed by the unimolecular dissociation rate constants for each of the temperature/pressure pairs to be considered. Again the inner loop of this input corresponds to the different channels and the outer loop corresponds to the different temperature and pressure pairs.

***** 5. Convolution Ranges *****

(Mandatory for all *E* Resolved and *E/J* Resolved calculations.)

Begins with line

***ConvolutionRanges**

This section specifies the ranges of energy and angular momentum to be used in the convolutions over the thermal distribution of reactants. No defaults are currently included.Thus an **ERangeP** keyword is mandatory for *E* Resolved calculations and both an **ERangeP** and a **JRangeP** keyword are mandatory for *E/J* Resolved calculations. The basic format is the same as in the calculation ranges section.The ordering of the E and J data is immaterial.

Energies:

Keyword **ERangeP**

Followed by one of the following three keywords:

StepDQ

ScaleDQ

ListDQ followed by

ValuesL

Total Angular momenta: must be input as integer values

Keyword **JRangeP**

Followed by one of the following three keywords:

StepDQ

ScaleDQ

ListDQ followed by

ValuesL

One must generally determine the appropriate ranges of *E* and *J* by trial and error. I.e., the calculation must be run for different ranges and then the output should be examined for convergence. The output file intgl.out, which illustrates the contributions to the *E* and *J* integral for high pressure or strong collision or modified strong collision calculations, is often of some use in examining this convergence.

***** 6. Collision *****

[Mandatory except in the High Pressure limit (**HighPresP** or **HighEffP)**]

Begins with line

*__Collision__

Give the mass of the collider (bath gas) with keyword

CollMassD

whose argument is the mass in g mol^{-1}.

Neutrals and ions are different:

A. For ions (keyword **IonP** given in Section 2) give the following:

Collider polarizability, using keyword

PolzD

whose argument is the polarizability in $Å^3$,

and the collider dipole moment (if non-zero), using keyword

DipoleD

whose argument is the dipole moment in Debye.

B. For neutrals, (keyword **NeutralP** given in Section 2) give two sets of Lennard-Jones parameters for the self interactions of the complex and the collider.

SigmaD,

whose argument is the sigma parameters for the complex and the collider in Å.

EpsilonD,

whose argument is the epsilon parameters for the complex and the collider in units of cm-1.

For master equation analysis a pressure for performing the low pressure limit analysis may be specified with the keyword **PlowPD** followed by its argument on the next line. The default pressure for the low pressure limit analysis is 1.0e-10 torr for master equation analyses. For other pressure treatments the low pressure limit is obtained analytically.

***** 7. Complex *****

Mandatory except in the High Pressure limit of an Association calculation ((**HighPresP** or **HighEffP**) + **AssociationP**)

Begin with line

***Complex**

Then

1. Input the structure data for the complex following the standard form in the Structure Data Module instructions (given below).
2. The vibrational step size for the complex density of states calculation may be input here. Give the keyword

   EVCStepD

   followed by the value. (Default is 1.0 cm^{-1})
3. A correction factor for the complex density of states and partition function may be supplied here if desired. Use the keyword

   RhoCorrD

   followed by the value. (Default is 1.0)
4. Either spherical top or symmetric top expressions may be used in evaluating the density of states for the complex by giving either the keyword

   RhoSpherTopP

   or the keyword

   RhoSymmTopP

   The default is to use the symmetric top expressions.

5. Similarly, either spherical top or symmetric top expressions may be used in evaluating the radiative emission rates by giving either the keyword

   KRadSpherTopP

   or the keyword

   KradSymmTopP

   The default is to use the spherical top expression.

In some instances, use of the spherical top expressions for the energies may save a substantial fraction of the CPU, particularly in the radiative emission rate evaluations. Geometric means of the rotational constants are used in the symmetrizations.

***** 8. Channel *****

(Mandatory Section.)

This section begins the input which is specific for each reaction channel. Begin with the keyword for the appropriate section, that is, input one of the section keywords

***Channel1** or

***Channel2** or

***Channel3** etc.

This is followed by the input of the fragment data (as necessary), the transition state data, and the potential data (as necessary) for the given channel.

***** 9. Fragments *****

This section inputs geometries and other properties of the two fragments for the given channel.

For the *first channel* this section is mandatory with the exception of high pressure dissociation calculations which do not involve either PST or VRC. That is, the requirements for omitting Section 8 for channel 1 are (1) **HighPresP** or **HighEffP,** and (2) **DissociationP,** and (3) no **PSTP, VRCP,** or **VRCEffP** transition state treatments (cf. Sec. 10, below). For the *other channels* this section is mandatory *only* for PST (**PSTP**) or VRC (**VRCP** or **VRCEffP**) transition state treatments. This section may always be included and any irrelevant information will simply be ignored.

Begin with the section header

***Fragments**

Then:

1. Input structure data for fragment 1 using the Structure Data module input form. See instructions for keywords and format. (If one fragment is an atom it **must be** fragment 2.) (See notes at the end of this section for special instructions pertaining to fragment structure inputs).

2. Next structure data for fragment 2 is input in exactly the same way, using the Structure Data module again. (See notes at the end of this section for special instructions pertaining to fragment structure inputs).

3. Now the energy of this channel must be input. Use keyword **ChanEnergyD**, followed by the energy relative to the primary channel. (This keyword must be omitted for channel 1, which is defined to be the reference state with an energy of 0.0.)

4. If considering a neutral reaction then the coefficient for an r^{-6} interaction potential between neutral fragments may be input using the following keyword. This value may be used here in any PST calculations. If this property is to be used in a VRC calculation it will need to be input again in the Potential Input Module.

   PotSixD followed by the coefficient (cm^{-1} $Å^6$).

5. If considering an ionic reaction, the default is for fragment 1 to be the neutral fragment. If it is desired to make fragment 2 the neutral, give the keyword **NeutFragD** here followed by the value 2.

6. Again, if considering an ionic reaction, then the polarizability (and dipole if any) of the neutral fragment should be input using the following keywords. These values are used to obtain reference values for the orbiting collision rate and possibly in any PST calculations. If these properties are to be used in a VRC calculation employing, for example, an ion-induced dipole and/or ion-dipole potential, then they will need to be input again in the Potential Input Module.

   PolarizP followed by one of the following three qualifier keywords, which specify the choice for the neutral polarizability assignment:

   EstimatePQ The polarizability is crudely estimated as Mass/10.

   CalculatePQ Approximate calculation based on atom additivity.

ReadDQ Input the neutral polarizability value (Å^3).

Note that both **EstimatePQ** and **CalculatePQ** assume that the first fragment is the neutral fragment unless you specified otherwise in part 4 above.

The dipole moment for the neutral fragment may be input with the keyword

DipoleD

These quantities are using in obtaining reference Langevin and dipole corrected Langevin rate constants. If they are not input then the polarizability for the will be taken to be equal to that for the collider as input in Sec. 5, and the dipole will be set to zero.

7. For the first channel one may input a correction factor for the partition function for the primary fragments using the keyword

FragCorrD

Note 1 on coordinate system orientation: It is required that both fragment structures be input in Cartesian coordinates, using a particular principal axis coordinate frame. If the user does not know the orientation of the "correct" principal axis system (or even any principal axis system), an arbitrary coordinate system should be used to input the atom positions, and the program should be run. The only requirement for this arbitrary coordinate system is that the first atom corresponds to the "bonding" atom. The program will calculate and print out the correct principal axis coordinates of the atoms, and will then stop so that the user can reenter the fragment atom coordinates in the correct orientation before rerunning the program. Note that this will often require repositioning the Pivot Points defined in Section 10C for a VRC calculation, since these will have been input initially using the user's original (arbitrary) coordinate frame.

It may be useful to know the rules the program uses for selecting the axes of its principal coordinate frame, which are as follows:

(a) the first atom read in for each fragment is the "bonding" atom;

(b) the *z* coordinate of the "bonding" atom is always positive;

(c) for linear tops, the *z*-axis coincides with the molecular axis;

(d) for symmetric tops, the *z*-axis coincides with axis of highest symmetry, i.e., the axis whose moment is non-degenerate;

(e) for asymmetric tops, the *z*-axis is chosen as the axis with the smallest moment, and the *x*-axis is then chosen so as to place the "bonding" atom in the first quadrant in the *x*-*y* plane.

Note 2 for use of anisotropic ion-neutral potentials: Three anisotropic ion-neutral potential functions are given as options in the Potential Input Module below, namely anisotropic ion-polarizability, ion-dipole, and ion-quadrupole. The orientation of these terms in the neutral fragment is determined by dummy atoms which must be input in the present Fragments section. If any of these three potentials are used, the user must add the corresponding dummy atom to the end of the atom coordinate list for the neutral fragment. The anisotropic polarizability dummy atom (if any) should be first, followed by the dipole dummy atom (if any), followed by the quadrupole dummy atom (if any). There are thus anywhere from zero to three dummy atoms at the end of the neutral fragment atom list, depending on the potential functions chosen, and it is important to include only those dummy atoms which are required for the potential functions specified. The dummy atoms must have mass 0.0, and may be located anywhere except at the center of mass. Dummy atoms must be included in the total atom count for the fragment.

Note 3 for use of diplaced charge: For ion-neutral calculations, the charge of the ion is located at its center of mass by default. As described in the Potential Input Module, the charge may be displaced to any desired location in the ionic fragment. (If the anisotropic ion-neutral potential terms discussed in the preceding Note are not used, the ion may be either Fragment 1 or Fragment 2). The position of the displaced charge is designated by a dummy atom of mass 0.0 placed at the end of the atom coordinate list for the ionic fragment. This dummy atom should be added only if the **DisplacedChargeP** keyword is used in the Potential Input Module. Dummy atoms must be included in the total atom count for the fragment.

Note 4 for input of linear components of nonlinear fragments: If a nonlinear fragment is input and the general potential is to be used then the first three atoms input must not be linear.

***** 10. Transition State *****

[This section is omitted only for a low-efficiency case designated by the **LowEffP** (or equivalently **LowPresP**) keyword above.]

Begin with the header

***TransState**

Special input format for multiple transition states:

In some cases one may wish to consider the effect of more than one well distinguished TS location for a given channel. In this case, a designation of the form of the effective transition state treatment should be input with one of the following keywords.

MINTSP denotes the minimum of the partition function evaluated for two separate TS locations

EFFTSP denotes the inverse of the sum of the inverses of the partition functions for two separate TS locations

USTTSP denotes the unified statistical theory expression of Miller (W. H. Miller, J. Chem. Phys. **65**, 2216 (1976)) which requires the consideration of three separate TS locations (1/N = 1/N_1 + 1/N_2 – 1/N_3).

SUMTSP denotes the sum of the partition function evaluated for two separate TS locations

RATIOTSP denotes the product N_1*N_2 / N_3 and thus requires three separate TS evaluations. This ratio may be useful, for example, in correcting PST calculations of ortho/para effects for the loss in phase space due to the conversion from free rotors to hindered rotors. I.e., a PST calculation for N_1 could be multiplied by N_2 for a VTST calculation employing classical state counts for the full potential divided by N_3 for the potential which is implicit in PST. For such a correction to be valid the PST potential should be more attractive than the full potential for each orientation.

The default, if none of the above keywords are provided, is to use a single transition state for the channel in question, which will be located at the position of minimum flux over the sampled reaction coordinates. This will generally be the desired approach.

For each of the one, two or three transition states requested for this channel, the type of the TS treatment is specified in turn for the appropriate TS location. For the first TS location you should proceed directly to the next step in TS input. For the second and third TS locations, if any, you must at this point give the mandatory section header ***SecondTS** or ***ThirdTS**, specifying the TS location for which the data is to be entered. Then proceed with the TS input as follows.

You may give one of the optional keywords specifying the form of the conserved mode vibrational convolution: **NoVibConvP**, or **VibAdiabaticP,** or **VibStatisticalP** (Default is **VibStatisticalP**, which will usually be correct for canonical TST calculations. **VibAdiabaticP** will normally be specified for microcanonical TST calculations).

Next you may give the optional keyword **StepSizeD** followed by two numbers, which are the step sizes for evaluation of the vibrational (conserved) and rotational (transitional) mode contributions (default is 1.0, 100.0). In the interest of efficiency, one should generally use a rotational step size which is ≥ the vibrational step size. The convolution integral is carried out using the vibrational step size, with interpolated values of the rotational number of states. The program may revise both the default and input values to larger values if this would result in certain matrix dimensions being exceeded. If desired you can bypass this by increasing the corresponding matrix dimensions in param.f and then recompiling the program. These stepsizes are irrelevant for T resolved calculations (**TResP**).

Next is an optional keyword for the electronic state properties.

Give either keyword **ElecAdiabaticP** or **ElecStatisticalP** to choose the type of folding in of the electronic state contributions (Default is **ElecStatisticalP**).

Give the keyword **NElecStatesD** followed by the number of electronic states of the transition state.

Now the ***cycle over the electronic states*** begins

For the first electronic state give the keyword **ElecStatesL**, followed by the degeneracy and the energy for the first electronic state.

For subsequent electronic states, precede this line with the keyword **NextElecState**

Now specify the algorithm to be employed in evaluating the TS partition function.

RRHOP ==> Rigid Rotor Harmonic Oscillator/tight transition state treatment; employing various simple assumptions for tunneling (i.e., no tunneling, Wigner tunneling or Eckart tunneling).

PSTP ==> phase space theory evaluation of N_{EJ}^{dagger} or N_E^{dagger} or Q_T^{dagger} with a range of possibilities for the conserved-transitional mode convolutions.

VRCP ==> Variable Reaction Coordinate evaluation of N_{EJ}^{dagger} or N_E^{dagger} or Q_T^{dagger} employing various conserved-transitional mode convolution procedures.

LaplaceP ==> read in experimental data for k(T) and use inverse laplace transform techniques to generate N(E)

ReadNP ==> read in N_{EJ}^{dagger} or N_E^{dagger} from nej.dat

ReadKP ==> read in k_{EJ} or k_E from nej.dat

The input stream is different for each of these choices as described in the following subsections.

When the input for the current electronic state is complete, return to the point above designated "***cycle over the electronic states***," and repeat for the next state, if more than one electronic state is available to the fragments.

Special input format for multiple transition states:

After finishing the specification of the first transition state for each of the fragment electronic states, you should return to the beginning of Section 10 if input is needed for a second or third transition state.

Now proceed to Section 11.

***** Section 10, subsection A *****

Input for keyword **RRHOP**

Start by inputing the structure data for the transition state following the standard form in the Structure Data Module instructions.

The treatment of tunneling may be specified by giving one of the following keywords (default is **NoTunnelP**)

NoTunnelP No tunneling correction.

WigTunD Wigner tunneling correction. The argument is first the frequency of the imaginary mode at the barrier top followed by a positive cutoff energy defining how far below the barrier top the consideration of tunneling will extend.

EckTunD Eckart tunneling correction. The argument is first the frequency of the imaginary mode followed by the zero-point corrected energies of the barrier top relative to the reactant and product energies for the tunneling process.

The tunneling corrections are currently only implemented for E/J and E resolved calculations

Next the energy of the transition state relative to the separated fragments is given by

TSEnergyD, whose argument is the energy (cm^{-1}).

Finally, if desired give the correction factor for the transition state partition function with the optional keyword **TSCorrD** (Default is 1.0).

***** Section 10, subsection B *****

Input for keyword **PSTP**

You may give the optional keyword **JStepsD**, followed by five numbers specifying the integration step sizes for the angular momentum variables of the two fragments, j_1, k_1, j_2, and k_2; and l, the orbital angular momentum (default is 1,1,1,1,1).

Now give the rotational symmetry factor for the transition state with keyword **SigRotD.**

A correction factor for the transition state partition function may be supplied here if desired using the optional keyword **TSCorrD** (Default is 1.0).

Finally, either a polarizability (for ion/neutral reactions) or a coefficient for the inverse sixth power potential (for neutral/neutral reactions) may be given.

For ionic reactions the polarizability may be supplied with the **PolarizP** keyword followed by one of the qualifier keywords **EstimatePQ**, **CalculatePQ**, or **ReadDQ**, as specified in Sec. 8 for the fragments. The default value for this parameter is to use that specified in Sec. 8 for the fragments.

For a neutral reaction the coefficient for the r^{-6} potential (C6) may be input here with the keyword:

PotsixD

and the C6 potential parameter entered on the following line in cm^{-1} $Å^6$ (The default is to use the value input for the fragments in Section 9.)

***** Section 10, subsection C *****

Input for keyword **VRCP**

The reaction coordinate for the Variable Reaction Coordinate approach is defined as the distance between a Pivot Point in fragment 1 and a Pivot Point in fragment 2. The Pivot Point locations are defined in each molecule relative to a reference point, which may be either the center of mass or a chosen ("bonding") atom. With respect to the reference point in each fragment, the Pivot Point is located using spherical polar coordinates. The reference frame for these spherical polar coordinates is the principal axis system used for the fragment structure in Section 9 above. The $\theta = 0$ direction is the *z* direction, and the $\phi = 0$ direction is the *x* direction.

Give keyword **BondRefP** or **CMRefP** to choose whether the reference points in the two fragments are the bonding atoms or the centers of mass. If **BondRefP** is used, the bonding atom in each fragment is defined as **the first atom** in the list of atom coordinates given in Section 9.

Next specify the ranges of reaction coordinates to consider. In the most general case this will correspond to specifying R (the separation between the Pivot Points); the position of Pivot Point 1 (specified by Dist1, Theta1 and Phi1, which are the spherical polar coordinates for the vector from the reference point in fragment 1 to the pivot point in fragment 1); and the position of Pivot Point 2, specified by the corresponding quantities Dist2, Theta2, and Phi2 for fragment 2. Note that there are restrictions on the combinations of R, Dist1, and Dist2. In particular, R must be greater than the sum of the magnitudes of the vectors from the center-of-mass to the Pivot Point for each of the fragments. If the reference points are the center-of-mass then this restriction corresponds to R > Dist1 + Dist2. If instead the reference points are the bonding atom the restriction may be written as R > Dist1' + Dist2'; where Dist1' is the distance from the center-of-mass of fragment 1 to the pivot point of fragment 1 which depends on Dist1, Theta1, and Phi1, as well as the vector from the center-of-mass of fragment 1 to its bonding atom.

There are five choices (listed below as A-E) of input systems for specifying the ranges of these quantities. In each instance distances should be given in Å, and angles in degrees.

A. **RRangeP** with the qualifier **NoPPSetsPQ**. The program assumes that the Pivot Points are fixed at the corresponding reference points and only the separation R between the reference points is to be varied. The only input required is a set of R values. The scheme for this case is identical to that for the Ranges input, employing the usual choice of one of the following three qualifiers:

   StepDQ

   ScaleDQ or

   ListDQ (with the number of elements in the list as its argument) and followed by

      ValuesL

   with the list of R values.

B. **RRangeP** with the qualifier **TotalPPSetsPQ**. A range of values for R is given. Separately a series of pairs of Pivot Point positions (Dist1, Theta1, Phi1, Dist2, Theta2, Phi2) is given. A calculation is done for each R value with each given pair of pivot points.

Input the range of R values in the standard format (using **StepDQ**, **ScaleDQ** or **ListDQ** as with option A above). Then give the keyword

NPPSetsD followed by the number of pivot point sets to be read in and then

PPSetsL followed by the specified number of sets of (Dist1, Theta1, Phi1, Dist2, Theta2, Phi2), either six numbers to a line, or in free format.

C. **RRangeP** with the qualifier **TwoPPSetsPQ**. A range of values for R is given. Separately a series of pivot point 1 positions (Dist1, Theta1, Phi1) is given. Finally a series of pivot point 2 positions (Dist2, Theta2, Phi2) is given. A calculation is done for each R value with each possible combination of pivot points.

Input the range of R values in the standard format (using **StepDQ**, **ScaleDQ** or **ListDQ** as with option A above). Then give the keyword

NPP1SetsD followed by the number of pivot point 1 sets to be read in, and then

PP1SetsL followed by the specified number of sets of (Dist1, Theta1, Phi1), either three numbers to a line, or in free format. Then give

NPP2SetsD followed by the number of pivot point 2 sets to be read in, and then

PP2SetsL followed by the specified number of sets of (Dist2, Theta2, Phi2), either three numbers to a line, or in free format.

D. **TotalSetsP**. With this option, a series of seven-number sets (R, Dist1, Theta1, Phi1, Dist2, Theta2, Phi2) is read in. Give the keyword

NSetsD whose argument is the number of sets of values to read, followed by

SetsL which is followed by the given number of sets of values (R, Dist1, Theta1, Phi1, Dist2, Theta2, Phi2), either seven numbers to a line, or free format.

E. **IndividualRangesP**. A range of values for each of the seven parameters is specified separately. A calculation is done for every possible combination of the given values of the seven parameters. The input scheme is again the standard Ranges input, using **StepDQ**, **ScaleDQ** or **ListDQ** for each of the parameters. Cycle through the parameters in the following order using the keywords

RRangeP

Dist1RangeP

Theta1RangeP

Phi1RangeP

Dist2RangeP

Theta2RangeP

Phi2RangeP

Next is the optional keyword for input of R-dependent vibrational frequencies of the conserved modes. (Default is **NoRDepVibP**).

Give **RDepVibP** to select R dependence of the vibrational frequencies, or **NoRDepVibP** to use the same frequencies (those input for the complex) at all R values.

If **RDepVibP** was specified then give the keyword

NRDepModesD followed by the number of reaction coordinate R values at which vibrational frequencies will be input, and a multiplicative scaling factor for those frequencies. The R values must be input in monotonically increasing or decreasing order.

Follow this with the keyword

RDepModesL. Cycle over each of the R points (with R either monontically increasing or decreasing), specifying R and the vibrational frequencies for each of the conserved modes for each of the R's. The definition of R used here to label the sets of mode frequencies should correlate with the definition of the Rmep variable in the potential. The default definition of R as specified in the standard potential is the "bonding" separation defined as the distance between the first atom of fragment 1 and the first atom of fragment 2.

The keyword **MinEPathD** is given next followed by the data for the determination of the minimum energy path. The minimum energy path is determined via a random sampling over the configurations for each of the reaction coordinates which requires an integer seed and a number of sampling points. These two data values are given on the line following this keyword.

Now give keyword **IntegrationParP** followed by <u>one of the following three</u> keywords:

MonteCarloEJD. [only to be used for E or E/J resolved calculations **(EResP or EJResP)**]

It has a one-line set of arguments, consisting of three integers:

1. The starting seed for the Monte Carlo integration
2. Total number of configurational sampling points for the integration
3. Number of momentum samplings per configuration

or

GridIntD [only to be used for T resolved calculations **(TResP)**]

It has a six-line set of arguments:

<u>Line 1</u> consists of three integration parameters specifying features of a grid-based, quadrature evaluation of the transitional mode partition function:

1. The targeted value of overall relative accuracy of the integration. Integration range is subdivided until estimated accuracy is less than this value.
2. Cutoff value of ratio of the minimum to maximum value of integrand in a subsection of the integration range. If exceeded in a given subrange, a finer grid employed in that subrange. Process repeated until this ratio is not exceeded in any subrange.

3. Number of iterations used in extrapolative prediction of integral. An iteration consists of employing twice as fine a grid on all or some of the subranges. The extrapolation relies on the most recent iterations, i.e., those with the finest grids.

Lines 2-6 are identical in form and each pertains to an angular integration involved in evaluation of the transitional mode partition function. Lines 2-6 correspond, respectively to the five angles are required to specify the relative orientation of the two nonlinear fragments: theta1 (T1), phi1 (P1), theta2 (T2), phi2 (P2), and chi (CHI). Each line consists of three integers:

1. The number of symmetrically equivalent integration ranges for the given angle.
2. Spline parameter??
3. Scale factor.....???

If one or both of the fragments is not a nonlinear top, fewer angles are required. However, all five lines must be included for any combination of fragment types. A placeholder line consisting of 1 0 0 must be included for each redundant angle. The chart below shows the lines which are used by the code (i.e., are NOT placeholders) for the various fragment-fragment combinations:

Linear Top + Atom:	Line 2
Nonlinear Top + Atom:	Line 2 & Line 3
Linear Top + Linear Top:	Line 2, Line 4, & Line 6
Nonlinear Top + Linear Top:	Line 2, Line 3, Line 4, & Line 6
Nonlinear Top + Nonlinear Top:	Line 2, Line 3, Line 4, Line 5, & Line 6

or

MonteCarloTD [only to be used for T resolved calculations **(TResP)**]

It has a six-line set of arguments:

Line 1 consists of four integer parameters specifying features of a Monte Carlo integral evaluation of the transitional mode partition function.

1.The type of Monte Carlo integration: .1 for crude; 2 for stratified (selected angles).

2. The number of integration subunits. Cumulative results are printed at end of each subunit.

3. The number of (multidimensional) Monte Carlo points per subunit. The total number of points is the product of this number and number of subunits.

4. Random number seed: must be a negative integer.

Lines 2-6: Same as for GridIntD except that each line consists of only one integer specifying number of symmetrically equivalent integration ranges for the given angle. The second and third entries included under GridIntD are not needed here but, if included, are ignored and will cause no harm.

Now give the rotational symmetry factor for the transition state with keyword **SigRotD.**

Then, if desired, give the correction factor for the transition state with the optional keyword **TSCorrD** (Default is 1.0).

Finally, the potential function must be specified. Begin with the header ***Potential**. Then input the potential parameters using the Potential Input Module given below.

***** 11. Channel 2, 3, etc. *****

If there is more than one channel, you should return to Section 8, input the next channel section keyword, and repeat all the input of sections 8, 9 and 10 for the next channel.

***** End *****

At the end of all input (which will be after the completion of either the Potential Input Module or the TS data for the last channel), give the keyword ***End**.

***** Structure Data Module *****

The following input is given in order each time the structure input module is executed.

Molecule type: Give one of the six molecule type keywords first:

AtomP

LinearP

OblateP (A=B>C, where A,B,C are the rotational constants)

ProlateP (A>B=C)

NearOblateP (A~B>C, where A,B,C are the rotational constants)

NearProlateP (A>B~C)

Electronic states: Next give information for the electronic states:

NElecStatesD followed by the number of electronic states considered. After this must come the following keyword with the list of state degeneracies and energies:

ElecStatesL, with succeeding lines giving the degeneracy and energy (cm^{-1}) of each state relative to that for the ground electronic state of the particular channel or complex. Use 0.0 for each ground electronic state.

If the species is an atom, give the keyword **AtomMassD**, followed by the atomic mass, but omit this keyword if the species is a molecule.

If the species is an atom, this is the end of the **Structure Input** module.

Vibrational modes:

First give the keyword **NModesD**, followed by two parameters, which are the number of vibrational modes of the molecule, and the correction factor which the given mode frequencies are to be multiplied by.

Some or all of the mode frequencies may be estimated automatically by the program according to the Standard Hydrocarbon pattern. To do this, give the optional keyword **StdModesD** here, followed by the number of modes you wish to have the program estimate for you. This number should not be less than 15.

Give the keyword **ModesL**, followed by the list of mode frequencies (cm^{-1}). If some frequencies were estimated according to the preceding paragraph, input only the remaining mode frequencies here. If all were estimated, omit this keyword.

If the data is for the complex and the radiative rate keyword in Section 3 is **CalcPQ**, the radiative intensities must be assigned here using the keyword **ModesIntensL**. There are two choices:

1. The radiative intensities of the modes (km/mol) may be read in from an input list.
2. The qualifier **StdIntensPQ** may be given after **ModesIntensL**, in which case the intensities will be estimated automatically from the standard hydrocarbon model.

If desired, a multiplicative correction factor for the radiative rates may be given with keyword **KRCorrD**.

Free Rotors:

Some of the modes may be treated as classical 1-d free rotors by giving the keyword **FreeRotorD** followed by the number of 1-d free rotors on the next line. Then give the keyword **FreeRotorL** followed by the list of rotational constants (cm-1) for each of the free rotors. The corresponding modes should be removed from the list of vibrational modes.

Hindered Rotors:

Some of the modes may be treated as classical 1-dimensional hindered rotors by giving the **HindRotorD** followed by the number of 1-d hindered rotors on the next line. The corresponding modes should be removed from the list of vibrational modes. Then cycle through each of the hindered rotors providing the following set of data:

Give the keyword **HindTypeD** followd by an integer which specifies the format of the potential for that hindered rotor. Then give the keyword **HindParL** followed by the list of parameters for that format of potential (all in cm^{-1} or cm^{-1}/rad^2). In each case the first parameter specifies the effective rotational constant (cm^{-1}) for the given torsional motion.

HindTypeD = 1. $V = V_0 + V_1 \cos(n\Delta\phi)$. There are three parameters. The second parameter specifies the value of the potential at $\Delta\phi=\pi/n$, and the third parameter specifies the value of n.

HindTypeD = 2. $V = V_0 + V_1 \cos(\Delta\phi) + V_2 \cos(2\Delta\phi)$. There are three parameters. The second parameter specifies $V(\Delta\phi=180)$ and the third parameter specifies the force constant at $\Delta\phi=0$.

HindTypeD = 3. $V = V_0 + V_1 \cos(\Delta\phi) + V_2 \cos(2\Delta\phi)$. There are three parameters. The secondparameter specifies $V(\Delta\phi=180)$ and the third parameter specifies $V(\Delta\phi=90)$.

HindTypeD = 4. $V = V_0 + V_1 \cos(\Delta\phi) + V_2 \cos(2\Delta\phi) + V_3 \cos(3\Delta\phi)$. There are four parameters. The second parameter specifies $V(\Delta\phi=180)$, the third and fourth parameters specify the force constants at $\Delta\phi=0$ and $\Delta\phi=180$, respectively.

HindTypeD = 5. $V = V_0 + V_1 \cos(\Delta\phi) + V_2 \cos(2\Delta\phi) + V_3 \cos(3\Delta\phi)$. There are four parameters. The second parameter specifies $V(\Delta\phi=180)$, the third parameter specifies the force constants at $\Delta\phi=0$ and the fourth parameter specifies $V(\Delta\phi=90)$.respectively.

HindTypeD = 6. $V = V_0 + V_1 \cos(\Delta\phi) + V_2 \cos(2\Delta\phi) + V_3 \cos(3\Delta\phi) + V_4 \cos(4\Delta\phi)$. There are five parameters. The second parameter specifies $V(\Delta\phi=180)$, the third and fourth parameters specify the force constants at $\Delta\phi=0$ and $\Delta\phi=180$, respectively, and the fifth parameter specifies $V(\Delta\phi=90)$.

In each instance $V(\Delta\phi= 0)$ is taken to be the equilibrium point with 0 potential value.

Note that the relation between frequency and rotational constant is $B = \omega^2/(2 * \text{force const.})$ as long as all are in the same energy units (e.g., all in cm-1).

Rotational Symmetry Number:

Next give the rotational symmetry number using the keyword **SigRotD**, followed by the value given as real number.

Note: One may also force the fragment partition function *and* any corresponding PST TS evaluation to include a sum over only the even or odd fragment rotational states by including the keyword **OrthoParaP** followed by either **EvenPQ** or **OddPQ.** For this to work properly one must include the appropriate **QuanPFFrag1P** or **QuanPFFrag2P** keyword in the Calculation Type section.

Geometry:

Now the geometry is input. Give one of the two keywords **RotConstP** or **CartesianP** to specify input of either the rotational constants or of the masses and positions of the individual atoms of the molecule.

A. If the keyword is **RotConstP**, the total mass is first input as the argument to the **MassD** keyword. Then the rotational constant(s) are given as arguments to the **RotConstD** keyword. One value for linear (**LinearP**), three values for nonlinear (**OblateP** or **ProlateP**).

B. If the keyword is **CartesianP**, then the input is as follows:

Use keyword **NAtomsD**, whose argument is the number of atoms in the molecule. If dummy atoms are used in the atom list, they should be included in this count.

Then use keyword **PositionL** followed by the masses and positions of the atoms. On each line, give the mass (g mol^{-1}) and the *x*, *y* and *z* coordinates (Å) of the atom.

Linear species must lie along the *z*-axis.

Nonlinear species should not have the first three atoms as linear if the general potential is to be used.

***** Potential Input Module *****

Each channel for which a VRC (**VRCP**) transition state calculation is to be performed needs potential input, which is done as follows.

Certain standard potential forms are built in, and their parameters are read from the input file. If desired, following input of any standard potential parameters, the user can call a custom potential input, which is read in from a separate input data file "pot.dat". The user must put the necessary potential-reading routine computer code in a subroutine called potdatcust to read his potential parameters. The user must also modify the potential-creation routine mcpot to process his custom potential parameters.

After the ***Potential** header is read in the appropriate "TransState" section, the following standard potential forms are available by specifying the keywords below, any combination of which may be used to construct the total potential. There are some preliminary inputs which may be required:

1. If you are using an ion-neutral potential, the center of charge is located by default at the center of mass of the ion. It may be displaced, if desired, to an arbitrary position in the ionic fragment. Designate this by giving the optional keyword **DisplacedChargeP** here. The position of the center of charge will have been located in the Fragments input section using a dummy atom in the atom coordinate list of the ionic fragment.

2. If you are using one of the anisotropic potentials, and if one (or both) of the fragments is a non-linear polyatomic, first you must inform the program whether the "bonding" atom is terminal or central for fragment 1 (keyword **TerminalAtom1P** or **CentralAtom1P**) and/or fragment 2 (keyword **TerminalAtom2P** or **CentralAtom2P**).

The following standard potential choices may be employed. Note that for choices 2-7 the contributions are added together to form the final potential.

1. **CustomP**. This keyword is set up to execute a separate user-written parameter-input subroutine called potdatcust, located in file potread.f. The parameters for the custom potential terms should be read from a separate input file called pot.dat, unit 15. A sample form for the subroutine potdatcust has been included in the distribution files. The user may use this form with the appropriate data in the file "pot.dat", or substitute his/her own subroutine using the name potdatcust.

   The calculation of the potential from these parameters must be carried out in the subroutine mcpot, located in file potcalc.f. The program actually uses the total potential given by variable vtot located in subroutine mcpot. The user must add code to mcpot to process his custom potential parameters and add the additional potential energy (in atomic units) to the variable vtot. The arrays nipotpar(nchmx), ipotpar(nchmx,nippmx), npotpar(nchmx) and potpar(nchmx,nppmx) are available (included in the common blocks in commonpot.f) for passing data from potdatcust to mcpot.

   A variety of examples of customized potentials are found in the examples section of the manual.

2. **VStretchP**

The stretching potential is defined with respect to the "bonding" separation defined as the distance between the first atom of fragment 1 and the first atom of fragment 2. Specify one of the following three stretching potential forms:

MorseD, whose argument is the three Morse parameters D_e (cm^{-1}), beta ($Å^{-1}$) and R_e (Å). (Positive D_e).

VarshniD, whose argument is the three Varshni potential parameters D_e (cm^{-1}), beta ($Å^{-2}$) and R_e (Å). The Varshni potential is a potential form which may give a more faithful representation of the long-range part of the bond stretching curve than the Morse curve. See S. J. Klippenstein et al., J. Chem. Phys. 89, 4761 (1988); Y. P. Varshni, Rev. Mod. Phys. 29, 664 (1957).

InterpD. This form interpolates between a set of given potential points. The argument is the number of points. This is followed by **PointsL** giving a list of the potential points, given in the form of pairs of numbers consisting of distance (Å) and potential (cm^{-1}) (in ascending order of distances).

3. **VBendP**

This keyword is followed by one of two valence bending potential parameter formats (extrapolation or interpolation). The bending potential is calculated for any given bond length based on the equilibrium bending angles and bending force constants input in this section using either a sinusoidal hindering (**SinHindPQ**) or a quadratic hindering (**QuadraticPQ**). (Angles in degrees, bending force constants in hartree/rad^2, bond lengths in Å.) See Appendix 1 for definitions.

ExtrapP, extrapolation of bending force constants from the values at the equilibrium bonding distance r_e. Give on the same line either the qualifier keyword **SinHindPQ** or **QuadraticPQ**. Then on the next lines provide the following information:

NAnglesD, the number of angular variables (call this n_a).

PeriodD, the period of the potential in fractional multiples of 2π. E.g., 0.5 for a potential which has a period of π. A default value of 1.0 is assumed.

AnglesL, the set of equilibrium values of the angular variables (list of n_a values).

AlphasL, the exponential extrapolation decay constants for each of the angular variables (list of n_a values).

ForcesL, the matrix of bending force constants at $r_{e.}$ (Square matrix of size n_a x n_a).

InterpP, interpolation of bending force constants between the values given for a series of r values. Give on the same line either the qualifier keyword **SinHindPQ** or **QuadraticPQ**. Then on the next lines provide the following information:

NAnglesD, the number of angular variables (n_a).

PeriodD, the period of the potential in fractional multiples of 2π. E.g., 0.5 for a potential

which has a period of π. A default value of 1.0 is assumed.

NPointsD, the number of r values for which the force constant information is going to be given (call this n_r).

PointsL, the list of bond length values for which information is to be given (n_r values).

AnglesL, the equilibrium angle values at each of the given r values (n_r lines having n_a values on each line).

ForcesL, the force constant matrix at each given r value (a series of n_r lower triangular matrices, each of which has dimension n_a).

4. **AtomAtomP** Pairwise atom-atom interactions. Choice of hard-sphere or Lennard-Jones pairwise potentials. Many default values are built in.

HardSphereP

Diameters1L. Diameters of fragment 1 atoms (Å). Enter -1.0 for the default value for a given atom. (Default values are present for H, D, C, N, O, F, Si, P, S, Cl, Ge, As, Se, Br, Sb, I). For dummy atoms, *values must be entered*: use a diameter of -10.0 for these.

Diameters2L. Diameters of fragment 2 atoms (Å). Enter -1.0 for default value.

LennardJonesP

Parameters1L. Epsilon (cm^{-1}) and sigma (Å) values for fragment 1 atoms, entered in pairs. Enter a negative sigma value for each atom you wish to use default parameters for. (Default values are present for H, C, N, O, F, S, Cl, Br). For dummy atoms, *values must be entered*: for these enter 0.0, 0.0.

Parameters2L. Epsilon (cm^{-1}) and sigma (Å) values for fragment 2 atoms, entered in pairs. Enter a negative sigma value for each atom you wish to use default parameters for. For dummy atoms, *values must be entered*: for these enter 0.0, 0.0.

5. **AnisotropicP**, a potential anisotropy form assuming a bonding potential which is cylindrically symmetric with respect to each fragment. It is assumed that the stretching potential form, number 2 above, is used in conjunction with this potential form. See Appendix 1 for definitions. Specify the following keywords:

PowerD, the exponent of the angular dependence function (normally 2).

It must be indicated whether the bonding site in each fragment is one-sided or two-sided. Input one of the two keywords **OneSided1P** or **TwoSided1P**, and one of the two keywords **OneSided2P** or **TwoSided2P** (unless fragment 2 is an atom).

Give the two equilibrium bonding angles:

Theta1eD, the equilibrium value of the fragment 1 bonding angle (degrees)

Theta2eD, the equilibrium value of the fragment 2 angle

6. Ion-neutral interaction potential. The potential may include any or all of three terms, namely ion-induced-dipole, ion-dipole, and ion-quadrupole potentials. The polarizability may be isotropic or anisotropic. The reference axes for the anisotropic potentials are determined by the direction from the center of mass to the appropriate dummy atoms in the neutral fragment input. That is, the "parallel" direction for the anisotropic polarizability (assumed to be cylindrical with parallel and perpendicular components) is in the direction from the center of mass to the polarizability dummy atom; the dipole (positive end) points in the direction from the center of mass to the dipole dummy atom (for positive ions; for negative ions the dummy atom corresponds to the negative end of the dipole); and the quadrupole (assumed to be cylindrical) is oriented in the direction from the center of mass to the quadrupole dummy atom. If the polarizability is isotropic, no dummy atom is used for it. To include any one or more of these terms, give the appropriate keyword group(s) from the following:

i) **IonIndDipP** Ion-induced-dipole potential term. There are four choices for supplying the polarizability of the neutral fragment (give exactly one of these keywords):

EstimateP. The polarizability is crudely estimated as Mass/10.

CalculateP, Approximate calculation based on atom additivity.

PolzD. Input the isotropic neutral polarizability value ($Å^3$).

AniPolzD. Input two numbers which are the parallel and perpendicular components of the anisotropic polarizability ($Å^3$). The parallel component is oriented along the reference axis described by the polarizability dummy atom. The "parallel" direction will normally be assigned along the cylindrical axis, or the highest symmetry rotation axis, of a molecule having symmetry.

ii) **IonDipoleD**. Ion-permanent-dipole potential. The argument is the permanent dipole of the neutral (Debye). The dipole is oriented (positive end) along the reference axis described by the dipole dummy atom.

iii) **IonQuadD.** Ion-permanent-quadrupole potential. The argument is the permanent quadrupole of the neutral (Debye- Å). The quadrupole is oriented (positive field) along the reference axis described by the quadrupole dummy atom.

7. Inverse sixth power potential (for phase space calculation with neutrals). Use the keyword **Inverse6D**, whose argument is the coefficient of the r^{-6} potential term (in units of $cm^{-1}A^6$).

***** Standard Hydrocarbon Radiative Association *****

Giving the keyword **StHydroP** in section 2 invokes a self-contained module which provides a semiquantitative estimate of the radiative association rate constant. No other calculations will be performed when the input file contains this keyword.

The ranges of temperature and binding energy to be considered are input using Section 3. Then the rest of the input takes the special form given below:

After the Section 3 input, give the section header ***StHydro**

Then use the following keywords (any order):

DegreesD, the number of vibrational degrees of freedom of the association complex.

MassesD, the mass of the ion and the mass of the neutral (g/mole).

PolzD, the polarizability of the neutral (A^3). Optional keyword: if it is omitted, an estimated value will be used.

If one of the reactants is an atom, a correction will be applied to the association rate estimation; this is specified by giving the keyword **AtomicP**, which is required if one reactant is monatomic.

After completing the required input, type ***End**.

Appendix 1

Definitions of coordinates for bending potentials in the built-in potential

Read this Appendix if you are using the built-in potential forms designated as Bending (Number 3, **VBendP**) or Anisotropic (Number 5, **AnisotropicP**) in the **Potential Input Module**.

The term General Potential used here refers to the set of built-in potential functions supplied with Variflex. Parameters which specify the General Potential are read in by subroutine **potdat** located in file **Potread.f**.

The potential function generated by the General Potential is calculated as a function of relative orientation of the two fragments by subroutine **mcpot**, located in file **Potcalc_gen.f**.

Note (as described in the Potential Input Module instructions above) that Variflex may be run using solely the potential functions provided by the General Potential; or a user-defined potential function may be used; or the General Potential may be used and supplemented by additional user-supplied potential terms.

The angularly anisotropic potential functions (Potential forms 3 and 5) are calculated based on the deviation of the relative orientation of the two fragments from an equilibrium (or reference) orientation. The input supplied by the user must specify the orientation of the fragments in this reference orientation, using the correct intermolecular coordinates. This appendix describes these coordinates and their relation to the Variflex input.

The angular potentials are defined with reference to a **bonding atom** in each fragment. (These atoms need not actually participate in bonding, but serve as reference positions.) The bonding atom in fragment 1 is designated A_1, and it is the first atom in the atom list for fragment 1. Similarly bonding atom B_1 is the first atom in the atom list of fragment 2. The line **R** joining A_1 and B_1 is a convenient reference axis for keeping track of the relative orientations. The next two atoms in the atom list for fragment 1 are A_2 and A_3, which are used to define angles. Similarly B_2 and B_3 are the second and third atoms in the atom list for fragment 2. The torsions are defined in the form Torsion(ABCD), using the usual Z-matrix convention, viewing from the first atom given, back along the bond to the second atom given, and so forth back along the remaining two atoms.

First define the bonding angles **Theta1** and **Theta2**, which are the angles between **R** and reference axes in the molecules. These are defined by

Theta1 = Angle($B_1A_1A_2$)

Theta2 = Angle($A_1B_1B_2$)

These are the angles used in the **AnisotropicP** potential function input (Potential form 5), and their equilibrium values are to be specified in the input.

The more general potential of Potential form 3 requires the specification of a set of angular coordinates which depends on the specific case. These are described individually below.

1. Fragment 1 linear, Fragment 2 atomic. One coordinate. NAngles = 1. The angle is

Theta1 = Angle($B_1A_1A_2$).

2. Fragment 1 non-linear, Fragment 2 atomic. Two coordinates. NAngles = 2. First angle is Theta1 = Angle($B_1A_1A_2$). Second angle is the torsion Tau1 = Torsion($B_1A_1A_2A_3$).

3. Fragment 1 linear, Fragment 2 linear. Three coordinates. NAngles = 3. First angle is Theta1 = Angle($B_1A_1A_2$). Second angle is Theta2 = Angle($A_1B_1B_2$). Third angle is the torsion Tau1 = Torsion($B_2B_1A_1A_2$).

4. Fragment 1 non-linear, Fragment 2 linear. Four coordinates. Nangles = 4. First angle is Theta1 = Angle($B_1A_1A_2$). Second angle is the torsion Tau2 = Torsion($B_1A_1A_2A_3$). Third angle is Theta2 = Angle($A_1B_1B_2$). Fourth angle is the torsion Tau1 = Torsion($B_2B_1A_1A_2$).

5. Fragment 1 linear, Fragment 2 non-linear. Four coordinates. Nangles = 4. First angle is Theta1 = Angle($B_1A_1A_2$). Second angle is Theta2 = Angle($A_1B_1B_2$).. Third angle is the torsion Tau1 = Torsion($B_2B_1A_1A_2$). Fourth angle is the torsion Tau3 = Torsion($B_3B_1B_2A_1$).

6. Fragment 1 non-linear, Fragment 2 non-linear. Five coordinates. Nangles = 5. First angle is Theta1 = Angle($B_1A_1A_2$). Second angle is the torsion Tau2 = Torsion($B_1A_1A_2A_3$). Third angle is angle is Theta2 = Angle($A_1B_1B_2$). Fourth angle is the torsion Tau1 = Torsion($B_2B_1A_1A_2$). Fifth angle is the torsion Tau3 = Torsion($B_3B_1B_2A_1$).

Appendix 2

Output Contained in the Auxiliary Output Files

In addition to the principal output file **Variflex.out**, several other files contain useful output information. **Flow.out** is always printed, while the other files described here are printed only if the keyword **TspfDebugP** is given in the Title section. (The names given here for these files are the generic names. If the vrfx_run script file is used then these files will be renamed with 'job_' preceding them, except for the Variflex.out file which will be renamed 'job'.out.)

1. **Flow.out**.

This file prints messages at many points during program execution to help track the progress of the calculation. No timing information is provided in the standard distribution version, but the file **numeric.f** contains a subroutine **timer** that includes several timing routines that have been used on various machines. The routine Unixtime works on some UNIX systems to give machine time information. The routine PCtime works on some PC's to give real elapsed time. To activate one of these, remove the initial c character from all lines in the appropriate routine, and recompile. The timing information is printed in **Flow.out**.

2. **Erate.out**.

The first part of this output gives the density-of-states $\rho(E,J)$ and the microcanonical unimolecular dissociation rate (for each channel) for the complex. These values are listed for each value of E and J for which they are calculated.

The second part of the output gives the vibrational photon emission rate from the complex for each value of E and J.

3. **Pf.out**

This file contains the canonical partition functions (at each temperature used) for the complex and for each of the fragments. These are the same values as given in Variflex.out, which are collected together here for convenience.

4. **Tspf.out**.

The first part of this output gives the number of states function $N^{\ddagger}(E,J,\text{transitional})$ for the transitional degrees of freedom in the transition state for each electronic state and each channel. Also given in each case is the reaction coordinate (R) value found for the transition state, and the positions of the two pivot points (either defined, or optimized,

depending on whether a variable reaction coordinate functional form is being used.)

The second part of the output gives the total number-of-states function $N^{\ddagger}(E,J)$ obtained by convoluting $N^{\ddagger}(E,J,\text{transitional})$ with the density-of-states function of the conserved modes.

5. **Intgl.out**.

This file displays the accumulating values of the numerator of the thermal rate constant expression, which are accumulated during the numerical integration of the Boltzmann weighted contributions over all values of J and E.

6. **Trate.out.**

This file gives a summary of the final rate constant values. These are the same values as given in Variflex.out, which are collected together here for convenience.

Appendix 3

Convergence Parameters in E/J and E Resolved Calculations

Obtaining converged results for *E/J* or *E* resolved calculations requires the consideration of a number of different convergence parameters. The following convergence parameters must be considered:

(I) ***For the convergence of the final thermal integrals over E and/or J within the RRKM style analyses (cf Section 5 of this manual, and Eq. (12) of J.Chem.Phys. 104, 4502, 1996). These parameters also play a related role in the master equation analyses.*** The **ERangeP** parameters determine the minimum E, the number of E's and the step size in E for the thermal convolution. Similarly, the **JrangeP** parameters determine the minimum J, the number of J's, and the step size in J for the thermal convolution. Both of these sets of parameters are **key parameters** and one should generally check the convergence of the final results with respect to their variation. For room temperature evaluations an energy step size of about 40 cm^{-1} and a maximum E of 3000 cm^{-1} will be in about the right range. For RRKM analyses the minimum energy should be near 0, while for master equation analyses –1000 cm^{-1} would be a typical minimum energy. The range and step sizes for *J* are system dependent (i.e., due to variations in the rotational constants) but steps of 5 to 20, and maximum values of 100 to 400 are fairly typical. The minimum *J* value should generally be near zero. For convenience the convergence of the thermal integral is printed out in *intgl.out* for the high-pressure limit of the first and last temperatures considered. For RRKM analyses the calculation time will generally be linearly proportional to the total range of energy and to the total number of *J* values considered. For master equation analyses the matrix dimension will be linearly related to the total number of E values and the total number of *J* values. **Even beginning users must adjust these parameters to obtain convergence**

(II) *For the estimate of the transitional mode contribution to the transition state number of states for a given energy (cf.* **MonteCarloEJD** *in Section 10C).* This contribution is evaluated via Monte Carlo integration and there are three integer parameters for this integration. The first integer simply determines the initial seed for the random numbers. Any value for this number is appropriate. The second integer is a **key parameter** which defines the number of configurations sampled in the random sampling. Numbers for this parameter will typically be in the range from 100 to 10000; a value of 1000 will generally provide convergence to about 10-15% which is often satisfactory. A value of 100 is useful for obtaining first estimates of transition state locations and final results, but is not usually satisfactory for final results. Convergence with only 100 points would be limited to about 40%. A value of 10000 is useful for detailed examinations of the transition state, such as the dependence of its location on *E* or *J*. Final estimates can be converged to about 5% or better with a value of 10000. The third parameter defines the number of momentum samplings for each configuration. A value of unity is most common. However, convergence rates for reaction coordinates that are different from the center-of-mass separation can sometimes be improved by choosing values between 2 and 5. **For beginning users we recommend simply choosing these three parameters as 99, 2000, 2.**

(III) *For the convolution of the transitional and conserved modes (cf.* **StepSizeD** *in section 10 of this manual, and Eq. (13) of J.Chem.Phys. 104, 4502, 1996).* The **vibrational** step size determines the step size actually used in the evaluation of the convolution integral. The speed of the calculation seldom depends on the value for this parameter so a small number such as 1.0 cm^{-1} is typically used for this parameter. The code may increase this number above the input value in order to keep certain matrices within the limitations imposed in the program. Such increases are reported in *flow.out*. If necessary, such increases can be shortcircuited via the increase of *mxdme* in *param.f*, and then recompiling the program. The **transitional** mode contribution is first evaluated over a grid of energies whose spacing is determined by the second parameter, which is again a **key parameter**. The total time for the calculation is generally linearly proportional to the number of energies in this grid. Thus, it is generally wise to employ as large as spacing as is feasible. We have found that 100 cm^{-1} often provides an adequate spacing. However, some situations, such as low temperatures, may require much smaller spacings. **For beginning users we recommend simply using the defaults of 1.0, 100.0 cm^{-1} for these two parameters.**

(IV) *For the estimate of the partition functions for the complex (cf.* **EVCStepD** *in Section 7).* This parameter determines the vibrational step size employed in the evaluations of the state density (and when necessary radiative rates) for the complex. Such evaluations are generally not the slow part of the calculation and so a small value of 1.0 cm^{-1} is generally appropriate. Again, the code may internally reset this variable to avoid exceeding certain matrix dimensions and messages to this effect are printed in *flow.out*. To bypass this resetting you will need to increase *mxdmec* in *param.f* and recompile the program.

(V) *For the transition state location (cf. Section 10C).* The location of the variational transition state must lie within the range of reaction coordinate values specified, and the spacing of these values must be close enough to give adequate accuracy for the transition state location. If there is doubt about these questions, the transition state results given in the *tspf.out* output file should be surveyed.

Sample Procedure for Testing Convergence

First analyze the range of E and J that are required to obtain converged results. Use defaults for parts (III) and (IV) above. Using 1000 Monte Carlo configurational points set up a guess for the E and J ranges and step sizes. Run the calculation. Then increase the E range by about 50% and run again. Check for any variation in the final result. Repeat until the results are sufficiently converged. (Note there may be some minor variation from one calculation to the next due to random variations in the Monte Carlo integrations. One way to avoid worrying about these minor variations is to consider the *ingtl.out* file. The variation with E of the terms in this file may be used to determine whether the convergence is complete. Care should be taken to look at the integral for the highest temperature of interest. Note that the range of E required for convergence to be complete in the *intgl.out* file may be larger than necessary if one is only interested in low pressures.) Next do the same thing for the J range. Now increase the number of Monte Carlo points by factors of 2 to 10 until you are satisfied with the variation in this parameter. Then decrease the E step size by about 50% and again check for variation. Similarly, decrease the J step size by about 50% and check for variation. At this point one might test

convergence with respect to the transitional mode step size (paragraph III above) by decreasing it by a factor of two; this would be especially important if one is interested in temperatures below 300 K or in low energies. Finally, one should examine the *tspf.out* file to make sure that the optimized TS locations are never at the limits of the grid of reaction coordinate values considered. If they are then the range should be increased. The variation of the optimized TS results with reaction coordinate step size(s) should also be tested.