

Multiple-Well Isomerization Diffusion Equation Solutions with a Shift and Invert Lanczos Algorithm

Kevin E. Gates*

Department of Mathematics, University of Queensland, Brisbane, Qld 4072, Australia

Struan H. Robertson

Molecular Simulations Inc., 240/250, The Quorum, Barnwell Road, Cambridge CB5 8RE, U.K.

Sean C. Smith

Department of Chemistry, University of Queensland, Brisbane, Qld 4072, Australia

Michael J. Pilling and Martin S. Beasley

School of Chemistry, University of Leeds, Leeds LS2 9JT, U.K.

Kristyn J. Maschhoff

*Department of Computational and Applied Math, Rice University
Houston, Texas 77005*

Received: February 6, 1997; In Final Form: May 7, 1997[⊗]

An RRKM/master equation model is constructed for the isomerization of cyclopropene. It is shown how the dense matrix of the master equation operator can be reduced to a banded form by a combination of diffusion equation approximation and equation rearrangement. The lowest eigenvalues and eigenvectors of the master equation, which are sufficient for simulation purposes, are rapidly found using shift and invert Lanczos based methods.

1. Introduction

Isomerization is important in a number of gas phase processes. For example, soot formation within combustion is thought to proceed via a sequence of isomerization steps. The analysis of gas phase isomerization is complicated by two major considerations. The first is that the relaxation of such systems to equilibrium is, in general, governed by more than one parameter. The second is that these parameters can have a complex dependence on pressure and temperature. Both of these considerations are best tackled within the framework of unimolecular theory using master equation (ME) techniques.^{1–3} In this paper the techniques are extended by introducing a fast method based on the Lanczos algorithm for finding the lowest eigenvalues and associated eigenvectors (eigenpairs) of the diffusion equation (DE) approximation. This truncated model is shown to be a valid approximation to the long term behavior of the isomerization process.

To make the discussion more concrete, a model of the cyclopropene isomerization to allene and propyne will be used. This isomerization is thought to be important in the initiation of soot formation via the production of the propargyl radicals, which can then combine to form unsaturated C₆ species that can go on to form aromatic species. The details of the potential energy surface are shown in Figure 1, where the values of the barrier heights etc. are taken from the calculations of Karni et al.⁴ For the present purposes only the central isomerizing system will be considered in detail, i.e.,



The overall conversion of C₂H₂/CH₂ into C₃H₃/H will be treated in a future publication.⁵

In section 2, the ME description of the system is presented and the methods used to calculate state numbers, $N(E)$, and microcanonical rate coefficients, $k(E)$, are described. Such a ME description requires significant memory and processing power and so an approximate approach, which is less demanding on resources, is important, especially if large sequences of isomerizations are to be investigated. A DE approximation of the full ME and a matrix rearrangement that gives a narrow banded form are described in section 3. Then in section 4 the calculation of the lowest eigenpairs with a shift and invert Lanczos algorithm for the narrow banded DE approximation is described. Results and conclusions are given in section 5.

2. Isomerization Master Equation

The isomerization ME equation has been described previously by a number of workers,^{1,3,6,7} and so only a brief description will be given here. For the simple isomerization reaction



the ME is written as two sets of coupled differential equations, each set describing collisional activation/deactivation process for an isomer, and these sets are also coupled to each other via reactive terms describing the gain/loss of density due to reaction. Representative equations from the two sets of equations have the form

$$\frac{d\rho_i^A}{dt} = \omega \sum_j P_{ij} \rho_j^A - \omega \rho_i^A - k_i^A \rho_i^A + k_i^B \rho_i^B$$

[⊗] Abstract published in *Advance ACS Abstracts*, June 15, 1997.

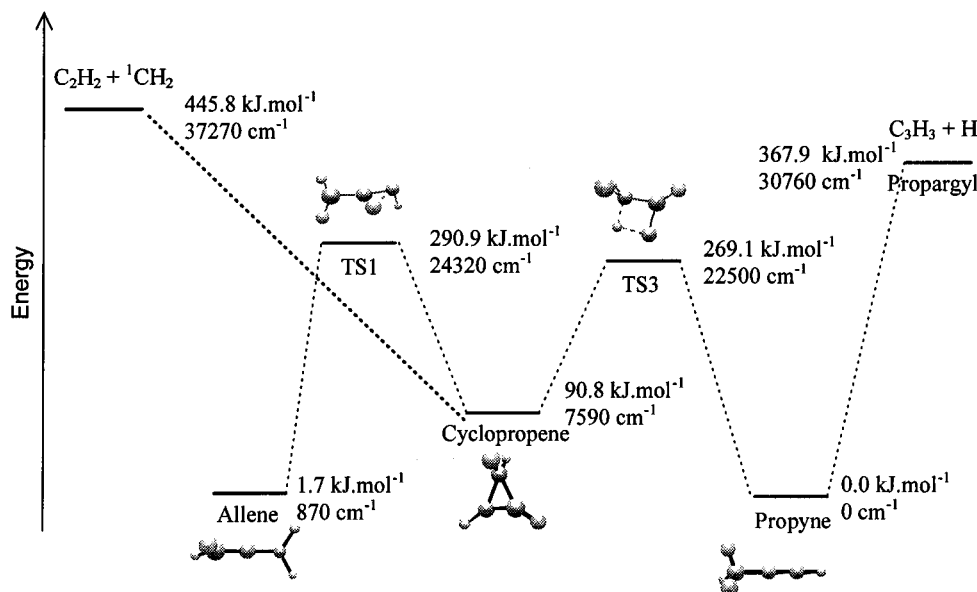


Figure 1. Schematic diagram of the potential energy surface for the isomerization of the cyclopropene system.

$$\frac{d\rho_l^B}{dt} = \omega \sum_m P_{lm} \rho_m^B - \omega \rho_l^B - k_l^B \rho_l^B + k_i^A \rho_i^A \quad (3)$$

where ρ_i^A and ρ_l^B are the time dependent populations of states of i and l of isomers A and B respectively, ω is the collision frequency, P_{ij} is the probability of going from state j to state i , and the k_i^A and k_l^B are the microcanonical rate coefficients describing the reactive exchange between isomers. The states i and l are isoenergetic.

Equations 3 cannot be solved as they stand because the number of states is such that an enormous number of equations would be required to describe the system. Following the standard approach the energy of each isomer is partitioned into grains and assigned a number of states with a mean energy and mean rate coefficient parameters. The structure of the energy grains reflects those of the original equations and are similar in appearance to equations 3. Henceforth the discussion will focus on the energy-grained ME (EGME).

The EGME can be more conveniently written in matrix form

$$\frac{d\rho}{dt} = \mathbf{M}\rho \quad (4)$$

The solution of this matrix differential equation is well-known and can be written as an expansion in terms of the eigenvalues and eigenvectors of the matrix \mathbf{M}

$$\rho = \sum_i c_i \mathbf{u}_i \exp(\lambda_i t) \quad (5)$$

where λ_i and \mathbf{u}_i are the i th eigenpair of \mathbf{M} and c_i is a constant that depends on the initial conditions. There is no overall loss of density from the system, and so one of the eigenvalues must be zero and the corresponding eigenvector must be equivalent to the equilibrium distribution for the system. The remaining eigenvalues are all negative. Provided that the barrier to isomerization is large enough and the temperature of the system low by comparison, it is found that one of the remaining, negative eigenvalues is well separated from the rest in magnitude, and it is this eigenvalue that governs the relaxation of the system to equilibrium.

This analysis can be easily extended to systems where there is more than one isomer and a similar expansion in terms of eigenpairs can be performed. As before there is an eigenvalue

of zero, the corresponding eigenvector of which is the equilibrium eigenvector of the system. The remaining eigenvalues, again, are all negative; however, it is found that more than one eigenvalue, and as many as $n - 1$ eigenvalues where n is the number of isomers, is separated in magnitude from the rest and that the relaxation to equilibrium is dictated by these eigenvalues.

The modeling of the relaxation of the system thus requires the eigenvalues of \mathbf{M} to be determined. The difficulty here is that \mathbf{M} can be a very large matrix, for example, if an energy range of $50\,000\text{ cm}^{-1}$ is required for each isomer and a (relatively coarse) grain size of 200 cm^{-1} is used, then each isomer is described by 250 grains leading to an overall matrix of order 750. Such a matrix is difficult to manipulate on workstations and even when it can be used the determination of eigenvalues can be a very time-consuming process, an important consideration when the focus of these calculations is the fitting of reaction rate parameters, which requires the solution of a series of matrix differential equations. These difficulties are further exacerbated when larger systems of isomers are considered as well as bimolecular source terms.

There is thus a requirement for a fast and efficient method for dealing with such systems. The method described here is extension of earlier work using diffusion models to describe energy transfer discussed by Green et al.⁸ and applied by Robertson et al.⁹ to the problem of two-dimensional ME, work which has recently been extended by applying inverse iteration techniques that could take advantage of the banded matrix form produced by the diffusion approximation.¹⁰ Essentially, the same approach can be applied to isomerizations systems and allow further simplification of the matrix \mathbf{M} that will be described below.

Before this procedure can be applied the state numbers, mean energies, and mean rate coefficients for the grains of each isomer must be calculated. The density of states for each isomer were calculated by executing a standard Beyer–Swinehart procedure upon the classical rotational density of states of each isomer. From this combined density of states, mean grain energies and state numbers for 200 cm^{-1} grains were determined, using standard averaging techniques.³ Mean microcanonical rate coefficients were calculated using RRKM theory. The parameters required to calculate the density of states (vibrational frequencies and geometries) and transition state parameters

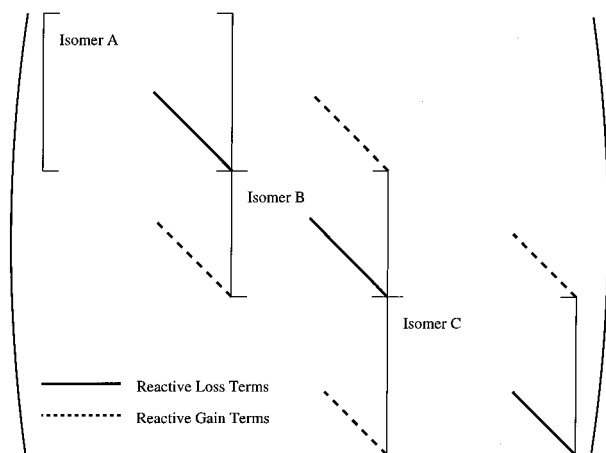


Figure 2. Schematic diagram of the structure of the collision matrix describing the energy transfer and reaction for the isomerization system given in eq 1.

(barrier heights, vibrational frequencies, etc.) were taken from Karni et al.⁴ The high-pressure rate coefficients were calculated and compared with the Arrhenius forms quoted by Karni et al. and found to be in good agreement.

3. Reduction to Narrow Banded Form

The structure of the matrix describing the system of eqs 1 is shown schematically in Figure 2. It consists of three main diagonal blocks that describe the collisional activation/deactivation process for each isomer. These blocks are connected by diagonal and off-diagonal terms describing reactions that are shown as bold diagonal lines in Figure 2. This matrix operates on a vector that is formed by concatenating the vectors of the grain populations of each isomer together. This configuration of the matrix represents the most intuitive form, but as will be shown shortly it is not the most efficient form.

The dense diagonal blocks can be simplified if a diffusion approximation is used to describe energy transfer. The basis of the diffusion approximation is the Kramers–Moyal¹¹ expansion of the ME. Other than at very short times this expansion can be truncated after the second term giving the well-known Fokker–Planck equation. If the linear operator describing energy transfer is denoted L then the Fokker–Planck equation gives

$$L\rho(E, t) = \frac{1}{2} \frac{\partial^2}{\partial E^2} (a_2(E) \rho(E, t)) + \frac{\partial}{\partial E} (a_1(E) \rho(E, t)) \quad (6)$$

The moments $a_i(E)$ are given by

$$a_n(E) = \omega \int_0^\infty (E - E')^n P(E'|E) dE' \quad (7)$$

where $P(E'|E)$ is the kernel describing transfer between the grains of given isomer. In this work the exponential down model¹² (also referred to as the exponential gap model¹³) is used to describe the kernel, though any form could be used. The first moment, $a_1(E)$, determines the drift of the mean of the distribution and is most often denoted by $\mu(E)$. The width of the distribution is determined by $a_2(E)$ and is usually denoted $\sigma^2(E)$ or expressed in terms of the associated diffusion coefficient $D(E) = \sigma^2(E)/2$. The difficulty with such a truncated form for the operator is that at long times the population may not go to a Boltzmann distribution. This situation may be rectified if the diffusion coefficient, $D(E)$, is modified so that a

Boltzmann distribution is produced at long times—this constraint leads to the so-called drift determine model discussed by Green et al.⁸

The principal advantage of using the operator L is the ease with which it can be handled numerically. The numerical representation, based on the same grain structure as used in the ME, is a tridiagonal matrix which requires considerably less storage space. In the isomerization problem the complete DE matrix has a specific form, tridiagonal blocks and diagonal blocks connecting the species. This form motivates a reordering of the matrix by isoenergetic terms, creating a matrix with an extremely narrow bandwidth equal to twice the number of isomers plus one. For the present isomerization system, the 750 by 750 system can be reduced to a banded matrix of 750 by 7 and when symmetry is taken into account the actual storage space required is only 750 by 4. It is important to realize that this rearrangement does not alter either the physical nature of the system or the eigenvalues obtained.

The narrow banded form produced in this way is ideally suited to treatment by inverse iteration techniques such as those applied previously to the problem of the two-dimensional ME. Since a narrow banded matrix can be inverted at a cost related to the bandwidth.

4. Shift and Invert Lanczos

The Lanczos method is an efficient procedure for approximating a subset of the eigensystem of a large sparse matrix \mathbf{M} . After k steps the standard Lanczos method computes a factorization of the form

$$\mathbf{M}\mathbf{V}_k = \mathbf{V}_k\mathbf{T}_k + f_k^T$$

where $\mathbf{V}_k^T\mathbf{V}_k = \mathbf{I}$ and $\mathbf{V}_k^T f_k = 0$. The $k \times k$ tridiagonal matrix \mathbf{T}_k is an orthogonal projection of \mathbf{M} onto a particular *Krylov* subspace, and the eigenvalues of \mathbf{T}_k are referred to as Ritz values or Ritz approximations. The eigenvalues of this small matrix approximate a subset of the eigenvalues of the large matrix \mathbf{M} . It is well-known that Ritz values converge rapidly to well-separated extreme eigenvalues. If the eigenvalues that are desired are interior eigenvalues or if the extreme eigenvalues are tightly clustered, spectral transformations may be necessary to achieve reasonable convergence to these eigenvalues.¹⁴

In the isomerization problem only the lowest eigenvalues are desired. The difficulty here is that the matrix \mathbf{M} is exactly singular. For the isomerization master equation it is the second nonzero eigenvalue that governs the relaxation of the system to equilibrium. In order to achieve fast convergence to the subset of eigenvalues near zero, it is essential to first dampen the influence of the higher eigenvalues.

The shift and invert spectral transformation is used to enhance convergence to a desired portion of the spectrum.¹⁵ Given an original problem

$$\mathbf{M}\rho = \rho\lambda$$

the transformed problem is of the form

$$(\mathbf{M} - \sigma\mathbf{I})^{-1} \rho = \rho\theta \quad \text{where} \quad \theta = \frac{1}{\lambda - \sigma}$$

This transformation is effective for finding eigenvalues near σ since the eigenvalues θ_j of $(\mathbf{M} - \sigma\mathbf{I})^{-1}$ that are largest in magnitude correspond to the eigenvalues λ_j of the original problem that are nearest to the shift σ in absolute value.

Since the transformed eigenvalues of largest magnitude are often large and well separated, these eigenvalues are easy to

TABLE 1: Comparison of Eigenvalues Calculated Using Different Methods and Approximate Execution Times (UltraSparc)

Eispack/dense matrix	Lapack/dense matrix	Lapack/with diffusion operator	Arpack/with diffusion operator, and rearrangement
$-0.277\ 12 \times 10^9$	$-0.277\ 12 \times 10^9$	$-0.268\ 93 \times 10^9$	$-0.268\ 93 \times 10^9$
$-0.228\ 84 \times 10^9$	$-0.228\ 84 \times 10^9$	$-0.221\ 36 \times 10^9$	$-0.221\ 36 \times 10^9$
$-0.199\ 37 \times 10^9$	$-0.199\ 37 \times 10^9$	$-0.192\ 06 \times 10^9$	$-0.192\ 06 \times 10^9$
$-0.183\ 70 \times 10^9$	$-0.183\ 70 \times 10^9$	$-0.176\ 20 \times 10^9$	$-0.176\ 20 \times 10^9$
$-0.156\ 88 \times 10^9$	$-0.156\ 88 \times 10^9$	$-0.154\ 32 \times 10^9$	$-0.154\ 32 \times 10^9$
$-0.117\ 56 \times 10^9$	$-0.117\ 56 \times 10^9$	$-0.113\ 84 \times 10^9$	$-0.113\ 84 \times 10^9$
$-0.116\ 81 \times 10^9$	$-0.116\ 81 \times 10^9$	$-0.113\ 05 \times 10^9$	$-0.113\ 05 \times 10^9$
$-0.129\ 67 \times 10^7$	$-0.129\ 67 \times 10^7$	$-0.126\ 45 \times 10^7$	$-0.126\ 45 \times 10^7$
$-0.848\ 69 \times 10^3$	$-0.848\ 69 \times 10^3$	$-0.839\ 38 \times 10^3$	$-0.839\ 38 \times 10^3$
$0.589\ 91 \times 10^0$	$0.589\ 97 \times 10^0$	$0.589\ 91 \times 10^0$	$0.589\ 97 \times 10^0$
Execution Time/s			
1795.14	89.53	93.36	0.54

compute with a Lanczos method. Once found these eigenvalues can be transformed back to the eigenvalues of the original problem. The eigenvector ρ_j associated with θ_j in the transformed problem is also an eigenvector of the original problem corresponding to λ_j .

To implement this transformation, however, one must provide a means to solve linear systems involving $(\mathbf{M} - \sigma\mathbf{I})$ either with a matrix factorization or with an iterative method. The narrow banded form of the rearranged isomerization matrix can be easily factored without pivoting. Thus we can take advantage of the fast convergence of Lanczos with minimal costs.

The software package ARPACK¹⁶ is used to solve the eigenvalue problem. ARPACK is an implementation of the Implicitly Restarted Arnoldi Method.¹⁷ For symmetric problems a variant of this method, the Implicitly Restarted Lanczos Method, is provided. Implicit restarting allows the problem to be solved with a fixed predetermined amount of storage.

5. Results and Conclusions

As discussed above the time which it takes to calculate eigenvalues is as equally important as the accuracy, as the ultimate goal is to use these methods for the analysis of kinetic data and the extraction of potential energy surface parameters. Such fitting is conducted within the framework of nonlinear least squares where the optimal parameters are found either by gradient following techniques or by a simple grid search. Both approaches can require the evaluation of eigenvalues a number of times. Therefore for this approach to be practical the evaluation must be done rapidly. It is thus far better to use a fast approximate method to obtain initial estimates of the optimal values and then refine them using more exacting methods if the data and the model demand it.

The quality of the above approach was assessed in two ways: through a comparison of the eigenvalues and by comparing the populations of each isomer as a function of time were calculated from a full ME and a DE model. Table 1 shows a comparison of the first 10 eigenvalues and the approximate time take to calculate them for 4 different approaches. The conditions of Karni et al., a temperature of 1400 K and a pressure of 10^4 Torr, were used. The full ME solution represents the benchmark by which the other methods are compared in both time and accuracy. From Table 1 it is seen that eigenvalues decrease in magnitude on going down the column for the full ME solution, the last eigenvalue being the effective zero eigenvalue. The full ME was configured in block diagonal form and diagonalized using routines from the EISPACK¹⁸ and LAPACK¹⁹ program suites. In the third calculation, the ME operators describing energy transfer were replaced by the tridiagonal DE operators but the block configuration was retained. This matrix was diagonalized using LAPACK. This

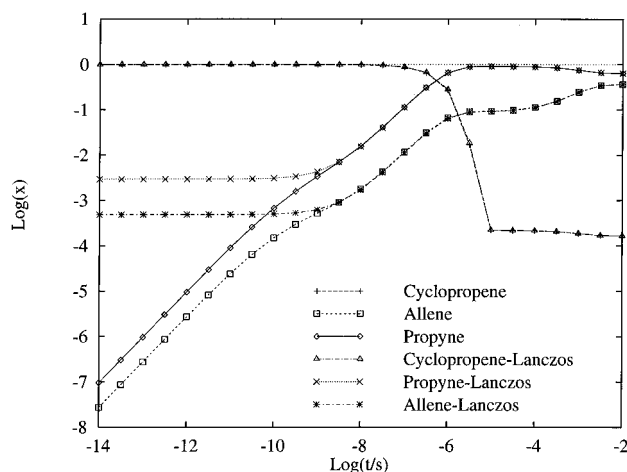


Figure 3. Time dependence of the mole fraction of each isomer at a temperature of 1400 K and a pressure of 10^4 Torr.

alteration produces no enhancement in speed; in fact it is slower, despite the fact that there is a larger number of zero elements. There is clearly a change in the eigenvalues; however, the approximation is within 10% in most cases, though given the span of eigenvalues this is perhaps not surprising. In the final calculation the rearrangement procedure was used to create a narrow banded matrix that could then be solved by the Lanczos approach. The principal difference is in the speed of calculation, which is in excess of a factor of 100 over the full solution.

A significant portion of the speed enhancement of the pivot/Lanczos procedure is that only the lowest 10 eigenpairs are calculated, and it is of interest to know what effect this has on the populations of each isomer. Figure 3 shows a plot for the mole fractions of each isomer (obtained simply by summing the elements of the population vector corresponding to each isomer) as a function of time, for the full ME and the pivot/Lanczos procedure. (The population vector for the system can be obtained at anytime as an expansion in eigenpairs, see Appendix 6 in ref 3.) The initial distribution was chosen so that all the density was in the cyclopropene isomer and within that isomer had a Boltzmann distribution so as to approximately mimic the initial distribution that might be produced from the reaction of $^1\text{CH}_2$ and C_2H_2 . The full ME solution includes contributions from all the eigenpairs of the \mathbf{M} matrix, while that of the pivot/Lanczos solution contains contributions from only the lowest 10 eigenpairs (those whose eigenvalues are smallest in magnitude). For times greater than 10^{-8} s agreement between the two solutions is satisfactory. At shorter times the two solutions diverge because contributions from the higher eigenpairs are missing from the pivot/Lanczos solution. This deficiency can be rectified if more eigenpairs are calculated using the Lanczos procedure, though this will obviously increase

the amount of CPU time that will be required. The number of eigenpairs that are required will depend on the time scale of interest.

The above approach represents a significantly faster algorithm for calculating eigenvalues for these kinetically important systems with only a small reduction in accuracy. It is valid for the range of conditions for which the ME is valid, a range which includes the flame conditions where the reaction modeled here occurs.

The principal aim of this paper has been to report techniques of dealing with multiple isomerization. The details of the cyclopropene system will be the subject of a future publication; however, a few remarks about this isomerization can be made at this point. It is evident from Figure 3 and the eigenvalue spectrum that the relaxation to the equilibrium distribution is nonexponential, confirming the earlier observation of Karni et al. The immediate consequence of nonexponential relaxation is that the system cannot be described by a single relaxation rate coefficient, which has implications for modeling studies. There are three distinct time regimes (10^{-10} and less, 10^{-10} – 10^{-8} , and 10^{-8} – 10^{-3} approximately), and it is interesting to note that the population of propyne goes through a maximum in the last interval, where the initial overpopulation of propyne, due to the larger microcanonical rate coefficients, reverts to its equilibrium value. This over population could potentially give rise to nonthermal features in the formation of the propargyl radical, even in the high-pressure limit, and is currently under investigation.

For isomerization reactions where the pivot/Lanczos is not appropriate, due to a divergence from the eigenpairs of the ME, it is intended that the pivot/Lanczos approach will be used as a starting point for more sophisticated eigenvalue algorithms. This work is currently in progress.

Acknowledgment. K.E.G. and SCS acknowledge the support of the Australian Research Council Small Grant Scheme (Grant No. RCH96/ARCS125G96). K.J.M. acknowledges the support

in part by the U.S. NSF cooperative agreement CCR-9120008, U.S. NSF contract ASC-9408795, and by U.S. ARPA contract DAAL03-91-C-0047 (administered by the U.S. Army Research Office).

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