Experimental and Computational Studies on the Reactions Between Resonance-Stabilised Hydrocarbon Radicals and Oxygen Molecules: A Synergestic Approach

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Academic Dissertation

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List of Publications in the Thesis

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- II Pekkanen, T. T., Joshi, S. P., Lendvay, G., Timonen, R. S., and Eskola, A. J. (2021). Kinetics and thermochemistry of the reaction of 1-methylpropargyl radicals with oxygen molecules: Experiments and computations. *Proceedings of the Combustion Institute*, 38(1), 843–852. https://doi.org/10.1016/j.proci.2020.06.266
- III Pekkanen, T. T., Lendvay, G., Döntgen, M., Timonen, R. S., and Eskola, A. J. (2022). An Experimental and Computational Investigation of the Reaction Between Pent-1-en-3-yl Radicals and Oxygen Molecules Under Autoignition Conditions, *Proceedings of the Combustion Institute*, 39(1), (article in press). https://doi.org/10.1016/j.proci.2022.07.176
- IV Pekkanen, T. T., Timonen, R. S., Robertson, S. H., Lendvay, G., Joshi, S. P., Reijonen, T. T., and Eskola, A. J. (2022). An Experimental and Computational Study of the Reaction Between 2-Methylallyl Radicals and Oxygen Molecules: Optimizing Master Equation Parameters with Trace Fitting. *Physical Chemistry Chemical Physics*, 24(8), 4729–4742. https://doi.org/10.1039/d1cp05591g
- V Pekkanen, T. T., Valkai, L., Joshi, S. P., Lendvay, G., Heinonen, P., Timonen, R. S., and Eskola, A. J. (2022). An experimental and computational study of the reaction between pent-3-en-2-yl radicals and oxygen molecules: switching from pure stabilisation to pure decomposition with increasing temperature. *Faraday Discus*sions. https://doi.org/10.1039/d2fd00031h

I performed the majority of the experiments (> 50 %) and all of the data analysis in these publications. I also performed all of the computations. These publications were written by me. György Lendvay supervised the computations. Eskola, Timonen, Joshi, Reijonen, and Valkai helped with the experiments by either performing some of them or with maintenance. All of the authors helped finalise the manuscripts, György Lendvay in particular.

The publications listed here and on the next page will be referred to by their Roman numeral in the thesis.

Other Related Publications

- VI Joshi, S. P., Seal, P., Pekkanen, T. T., Timonen, R. S., and Eskola, A. J. (2020). Direct Kinetic Measurements and Master Equation Modelling of the Unimolecular Decomposition of Resonantly-Stabilized CH₂CHCHC(O)OCH₃ Radical and an Upper Limit Determination for CH₂CHCHC(O)OCH₃ + O₂ Reaction. Zeitschrift für physikalische Chemie, 234(7–9), 1251–1268. https://doi.org/10.1515/zpch-2020-1612
- VII Joshi, S. P., Pekkanen, T. T., Timonen, R. S., and Eskola, A. J. (2019). Effect of Methyl Group Substitution on the Kinetics of Vinyl Radical + O₂ Reaction. *Journal* of Physical Chemistry A, 123(49), 10514–10519. https://doi.org/10.1021/acs. jpca.9b08028
- VIII Eskola, A. J., Pekkanen, T. T., Joshi, S. P., Timonen, R. S., and Klippenstein, S. J. (2019). Kinetics of 1-butyl and 2-butyl radical reactions with molecular oxygen: Experiment and theory. *Proceedings of the Combustion Institute*, 37(1), 291–298. https://doi.org/10.1016/j.proci.2018.05.069
 - IX Joshi, S. P., Pekkanen, T. T., Timonen, R. S., Lendvay, G., and Eskola, A. J. (2019). Kinetics of the Methyl-Vinyl Radical + O₂ Reactions Associated with Propene Oxidation. Journal of Physical Chemistry A, 123(5), 999–1006. https: //doi.org/10.1021/acs.jpca.8b11017
 - X Döntgen, M., Pekkanen, T. T., Joshi, S. P., Timonen, R. S., and Eskola, A. J. (2019). Oxidation Kinetics and Thermodynamics of Resonance-Stabilized Radicals: The Pent-1-en-3-yl + O₂ Reaction. *Journal of Physical Chemistry A*, 123(37), 7897-7910. https://doi.org/10.1021/acs.jpca.9b03923
 - XI Pekkanen, T. T., Arppe, S. L., Eskola, A. J., Rissanen, M. P., and Timonen, R. S. (2016). An Experimental Study of the Kinetics of the Reactions of Isopropyl, sec-Butyl, and tert-Butyl Radicals with Molecular Chlorine at Low Pressures (0.5-7.0 Torr) in the Temperature Range 190–480 K. International Journal of Chemical Kinetics, 48(12), 796–805. https://doi.org/10.1002/kin.21034
- XII Joshi, S. P., Pekkanen, T. T., Seal, P., Timonen, R. S., and Eskola, A. J. (2021). An experimental and master-equation modeling study of the kinetics of the reaction between resonance-stabilized (CH₃)₂CCHCH₂ radical and molecular oxygen. *Physical Chemistry Chemical Physics*, 23(36), 20419–20433. https: //doi.org/10.1039/d1cp02210e
- XIII Eskola, A. J., Reijonen, T. T., Pekkanen, T. T., Heinonen, P., Joshi, S. P., and Timonen, R. S. (2021). First direct kinetic measurement of *i*-C₄H₅ (CH₂CHCCH₂) + O₂ reaction: Toward quantitative understanding of aromatic ring formation chemistry. *Proceedings of the Combustion Institute*, 38(1), 813–821. https://doi.org/ 10.1016/j.proci.2020.06.031
- XIV Eskola, A. J., Pekkanen, T. T., Lendvay, G, and Timonen (2022). An experimental and theoretical kinetic study of t-butyl radical reaction with molecular oxygen. *Proceedings of the Combustion Institute*, (article in press). https://doi.org/10.1016/j.proci.2022.06.003

Abstract

This thesis is based on laser-photolysis/photoionisation mass spectrometry experiments I have performed in the laboratory of reaction kinetics at the University of Helsinki. Whilst I have measured bimolecular rate coefficients for many different kinds of radical-molecule reactions, this thesis focuses on the reactions between resonance-stabilised hydrocarbon radicals and oxygen molecules. For these reactions, I complemented the experimental work with quantum chemical calculations and master equation simulations. One of the great benefits of the computational work is that it permitted us to, in a way, extrapolate our experimental results to conditions more relevant to practical application. For resonancestabilised hydrocarbon radicals, the obvious application is in modelling the chemistry of unsaturated hydrocarbons in combustion systems. Our experiments are performed at low pressures $(3 \cdot 10^{-4} - 1 \cdot 10^{-2} \text{ bar})$ and relatively low temperatures (190 - 950 K), so there is a real need to extrapolate our rate coefficient data to the high temperatures and pressures encountered in, say, combustion engines. Doing computations in a purely *ab initio* fashion for the studied systems are demanding and costly, which is why experimental input was needed to fix parameters in the models that are either not well-understood or expensive to calculate. This is why I call the approach we have used synergistic. The experiments are used to cover for the shortcomings of the computations and the computations are used to model the reactions under conditions inaccessible to experiment.

I begin the thesis by introducing the experimental technique we employ. This is followed by a description of the theories behind the computational methods we utilise. To limit the scope of the study, I mainly focus on the master equation and unimolecular rate theory. In the results section I summarise the experimental and computational results and discuss the findings.

Tiivistelmä

Väitöskirjatyössäni olen mitannut resonanssistabiloitujen orgaanisten radikaalien ja hapen välisien reaktioiden nopeusvakiota käyttämällä laserfotolyysi-valoionisaatiomassaspektrometriaa. Suoritin nämä mittaukset Helsingin yliopiston reaktiokinetiikan laboratoriossa. Kokeellisen työn lisäksi olen mallintanut tutkittuja reaktioita kvanttikemiallisilla laskuilla ja masteryhtälösimulaatioilla. Laskennallisen työn hyöty oli siinä, että sen avulla kokeelliset tulokset voitiin ikään kuin ekstrapoloida olosuhteisiin, jotka ovat tavallisempia käytännön sovellutuksissa. Tutkimani reaktiot ovat pääasiassa tärkeitä palamisen kemiassa. Kokeet suoritettiin melko matalissa paineissa ($3 \cdot 10^{-4} - 1 \cdot 10^{-2}$ bar) ja lämpötiloissa (190 - 950 K), joten oli aito tarve löytää keino ekstrapoloida mittaukset paineisiin ja lämpötiloihin, joita esiintyy esimerkiksi polttomoottoreissa. Työssäni tutkittujen reaktioiden nopeusvakioita ei pystytä laskemaan tarpeeksi tarkasti molekyylien suuren koon vuoksi, joten kokeita tarvittiin malleissa olevien parametrien kiinnittämiseksi. Tämän vuoksi kutsun käyttämääni lähestymistapaa synergestiseksi. Kokeellisilla tuloksilla korjattiin laskennallisten tuloksien puutteita, ja laskuja puolestaan käytettiin tuloksien ekstrapolointiin olosuhteisiin, joissa kokeita ei ole mahdollista tehdä.

Väitöskirjani alkuosassa esittelen käyttämäni mittaustekniikan historian ja periaatteet, minkä jälkeen esittelen käyttämieni laskennallisten menetelmien teoreettisen taustan. Keskityn lähinnä unimolekulaariseen reaktioteoriaan ja masteryhtälömallinnukseen, koska nämä kaikkein oleellisimmin liittyvät reaktiokinetiikkaan. Väitöskirjani jälkimmäisessä puoliskossa esitän yhteenvedon tekemistäni kokeista ja laskuista ja pohdin niiden merkitystä.

List of Abbreviations

 ${\bf BW:}$ Bartis-Widom

CASPT2: complete active space perturbation theory

CBS: complete basis-set limit

CCSD(T): coupled-cluster singles, doubles, and perturbative triples

CSE: chemically significant eigenvalue

- DLPNO: domain-based local pair natural orbital
 - E: energy
 - $\mathbf{HF:} \ \mathbf{Hartree-Fock}$
 - HW: halocarbon wax
 - **IERE:** internal energy relaxational eigenvalue
 - **ILT:** inverse Laplace transform
 - \boldsymbol{J} : angular momentum
 - **FTST:** flexible transition state theory
 - ME: master equation
 - **1DME:** one-dimensional master equation that only treats energy as a variable
 - **2DME:** two-dimensional master equation that threat both energy and angular momentum as variables.
 - MEP: minimum energy path
 - **PDMS:** polydimethylsiloxane
 - **PES:** potential energy surface
 - \mathbf{R}^{\bullet} : some generic carbon-centred radical, $CH_3CH_2^{\bullet}$ for example
 - \mathbf{RO}_2^{\bullet} : some generic peroxyl adduct, $\mathrm{CH}_3\mathrm{CH}_2\mathrm{O}_2^{\bullet}$ for example
 - rc: reaction coordinate
 - **ROHF:** restricted open-shell Hartree-Fock
- ${\bf RRKM}:$ Rice–Ramsperger–Kassel–Marcus
- **RSHR:** resonance-stabilised hydrocarbon radical
 - SS: staineless steel
 - ${\bf TS:}\xspace$ transition state
 - **TST:** transition state theory
- VRC-TST: variable reaction coordinate transition state theory
 - **ZPE:** zero-point energy

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1 Introduction

1.1 Chemical Kinetics and the Rate Coefficient

Chemical kinetics is the study of reaction rates and mechanisms. In a constant-volume system, the rate law for some arbitrary reaction

$$aA + bB \dots \rightarrow pP + qQ \dots$$
 (1.1)

is given by

$$\frac{1}{\nu_i} \frac{\mathrm{d}[i]}{\mathrm{d}t} = k(p, T) \prod_i [i]^{c_i} .$$
(1.2)

Here k(p,T) is the rate coefficient of the reaction, which is temperature- and pressuredependent in general, ν_i is the stoichiometric number of species *i*, and c_i is some real number which needs to be experimentally determined for non-elementary reactions. For elementary reactions, it can be deduced from the mechanism. The rate laws for the simple uni- and bimolecular reactions

$$A_2 \longrightarrow A + A$$
 and (1.3)

$$A + B \longrightarrow AB , \qquad (1.4)$$

are

$$-\frac{d[A_2]}{dt} = \frac{1}{2} \frac{d[A]}{dt} = k_{dis}(p,T)[A_2] \quad \text{and} \quad (1.5)$$

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[AB]}{dt} = k_{rec}(p,T)[A][B] , \qquad (1.6)$$

respectively. The subscripts "dis" and "rec" stand for dissociation and recombination, respectively. The former example illustrates why one must be careful with stoichiometric numbers; a factor of two mistake is easy to make.

The purpose of this brief reminder about the basics of chemical kinetics was to illustrate what rate coefficients are used for: they are used to relate how the time derivative of a species depends on its own concentration, the concentrations of other species, and on rate coefficients. Thus, if one is to comprehensively model the chemistry of complicated environments, such as those encountered in the atmosphere or combustion engines, one not only needs hundreds (if not thousands) of rate coefficients, but often needs them as a function of temperature and pressure.

1.2 Computational Reaction Kinetics

Increases in computing power and developments in quantum chemistry methods and the chemical master equation (ME) techniques¹ has transformed computational reaction kinetics from an explanatory tool into a predictive one.² This is a welcome development, as kinetic models may contain thousands of pressure- and temperature-dependent rate coefficients, and it is not feasible to determine all of these experimentally. However, this is only part of the solution. The traditional computational approach (one reaction at a time,

a lot of manual input from the chemist) is not suitable for the determination of thousands of rate coefficients either. Recent efforts have focused on automating and streamlining the work that goes into obtaining a rate coefficient.³ By reducing the manual labour of the chemist to an absolute minimum, ideally just to giving the geometries or identifiers of the initial molecules, the hope is that computational methods can mass produce rate coefficients in the near-future.

Despite the advances in computational reaction kinetics, experimental input is still often needed and rate coefficient calculations are rarely performed in a truly *ab initio* fashion. As recently pointed out by Ahren Jasper,⁴ collisional energy transfer is rarely predicted by *ab initio* methods, even in purely computational papers. What is done instead is that crude models with adjustable parameters are used and the values of said parameters are estimated (guessed) based on values known for analogous systems. An additional complication in *ab initio* reaction kinetics is angular momentum conservation. The current standard in ME modelling is to run so-called one-dimensional (1D) simulations that only treat energy as an independent variable. More accurate treatments would also consider angular momentum (2DME). A practical problem in 2DME calculations is finding a way to describe EJ-coupled transition probabilities. Including angular momentum also significantly increases the dimensions of the matrices that need to be diagonalised.^{1,5} However, the latter might not be a problem in practice since the computational bottleneck will most likely be in quantum chemistry calculations (or in trajectory calculations, if they are used to obtain EJ-coupled transition probabilities). The 1D-approach is known to overestimate rate coefficients, and to compensate for this, one can use artificially low collisional energy transfer parameters. Klippenstein has suggested that simply dividing computationally obtained collisional energy transfer parameters by two can be used to approximate angular momentum effects in a 1D-setting.⁶ Going forward, it seems clear that 2DME approaches will need to become the standard in *ab initio* reaction kinetics at some point. Barrierless reactions, such as those studied in this work, are also a challenge. In barrierless reactions the minimum energy path (MEP) of the reaction is never above the energy of the reactants. It is possible nowadays to use statistical methods to compute rate coefficients for such reactions,^{7,8} but these calculations are prohibitively costly for systems with many heavy atoms.

Due to these issues in computational methods, we have chosen to apply a hybrid approach in which accurate experiments are used to correct for computational deficiencies. All of the systems studied in this thesis are so large that we cannot reliably use statistical methods to compute rate coefficients for barrierless reactions and/or to run classical trajectories to obtain energy transfer parameters. Instead, we exploit the inverse Laplace transform (ILT, see section 3.3) approach and our experimental data to obtain microcanonical rate coefficients for barrierless reactions. All of the studied reactions exhibit pressure dependence, and so we can directly fit collisional energy transfer parameters against our pressure-dependent experimental data. The ME models are 1D, but as experimental data is used for parameter optimisation, angular momentum effects are implicitly included. This approach should extrapolate our experimental low-temperature and -pressure data reasonably well to conditions relevant in atmospheric and combustion chemistry.

The experiments are, of course, also valuable in and of themselves. As computational methods are developed, they need to be tested against benchmark-quality experimental data. The results presented in this thesis are suitable for such purposes. Many of the mo-

lecules studied here are quite similar, only differing by the location of a methyl group. The methyl group location does not change the reaction mechanism, but it does have an effect on the observed rate coefficient. It will be interesting to see if high-level computational approaches are able to capture these subtle differences in reactivity.

1.3 Reactions of Resonance-Stabilised Hydrocarbon Radicals with Oxygen Molecules

Resonance-stabilised hydrocarbon radicals (RSHRs) are molecules where the radical orbital is delocalised over multiple carbon atoms. For such molecules, it is usually possible to draw more than one reasonable Lewis structure. These structures can be equivalent, as is the case for allyl (prop-2-en-1-yl) or non-equivalent, like for propargyl (prop-2-yn-1-yl). These Lewis structures are presented in Fig. 1. The triple-bonded structure is dominant in propargyl, with the first carbon having about $\sim 65 \%$ of the spin density.⁹



Figure 1: The Lewis structures for allyl and propargyl.

RSHRs lose their resonance-stabilisation when they recombine with O_2 , which results in them having much shallower $\mathrm{RO}_2{}^{\bullet}$ wells (zero-kelvin binding enthalpies) than similarsized hydrocarbon radicals that lack resonance-stabilisation. For example, the ethyl + O_2 recombination reaction has a well-depth of about 137 kJ mol⁻¹,² whereas for allylic radicals these wells are about 60 kJ mol⁻¹ shallower (**III–V**, **XII**). The shallower wells of RSHRs have at least three important consequences. Firstly, the shallower wells and loss of resonance-stabilisation means that radical $+ O_2$ interaction potentials are less attractive for RSHRs, which results in them exhibiting decreased reactivity. The highpressure rate coefficient at 298 K for the ethyl + O_2 recombination reaction is 8.4 \cdot 10^{-12} cm³ s⁻¹,² whilst the equivalent rate coefficient for allyl + O₂ is much smaller, $5.8 \cdot 10^{-13}$ cm³ s⁻¹.¹⁰ Secondly, the redissociation back to reactants becomes significant for RSHRs at much lower temperatures than for similar-sized hydrocarbon radicals that lack resonance-stabilisation (I-V, XII). Thirdly, because the peroxyl adduct wells are shallow for allylic and propargylic radicals, the barrier for any isomerisation reaction (internal hydrogen abstraction, for example) is likely to lie above the energy of the bimolecular reactants. Reactions over such barriers are expected to be slow.

For the latter two reasons, RSHR + O_2 reactions are often dead-ends in combustion environments, which can lead to RSHR accumulation. As their concentrations increase, selfand cross-reactions start to become important. These reactions are crucial in forming the "first aromatic ring"—a key precursor in soot formation.¹¹ Soot emissions are a symptom of inefficient burning and thus undesirable. To model soot formation (prevention), the competition between RSHR + O_2 and RSHR + RSHR reactions needs to be understood.

An interesting feature of RSHR + O_2 reactions is that a relatively fast reaction (k >

 $10^{-14} \text{ cm}^3 \text{ s}^{-1}$) is observed at room temperature and below, 10,12 but a one or two orders of magnitude slower reaction is observed at higher temperatures (T > 500 K). 13,14 Even more interestingly, the low-temperature rate coefficients exhibit negative temperature dependence and pressure dependence, which is typical for barrierless recombination reactions, but the high-temperature rate coefficient has weak, positive temperature dependence and is pressure-independent. Hahn et al. explained why this behaviour is seen for propargyl + O_2 .¹⁵ Something quite similar is observed for alkyl radical + O_2 reactions, although the effect is less pronounced.¹⁶ The details regarding this are discussed in the results section, but an introductory explanation is given below.

For propargyl, the overall reaction mechanism is

$$HC \equiv C - CH_2^{\bullet} + O_2 \Longrightarrow HC \equiv C - C(OO^{\bullet})H_2$$
(R1)

$$\mathrm{HC} \equiv \mathrm{C} - \mathrm{CH}_{2}^{\bullet} + \mathrm{O}_{2} \rightleftharpoons \mathrm{HC}(\mathrm{OO}^{\bullet}) = \mathrm{C} = \mathrm{CH}_{2} \longrightarrow \mathrm{HCO}^{\bullet} + \mathrm{CH}_{2} = \mathrm{C} = \mathrm{O} \ . \tag{R2}$$

At low temperatures, an irreversible $\mathrm{HC} \equiv \mathrm{C} - \mathrm{CH}_2^{\bullet} + \mathrm{O}_2 \longrightarrow \mathrm{HC} \equiv \mathrm{C} - \mathrm{C}(\mathrm{OO}^{\bullet})\mathrm{H}_2$ reaction is observed. This reaction is barrierless, as demonstrated by the careful experiments and computations by Moradi et al.⁹ As temperature is increased above 300 K, reaction R1 begins to equilibrate and multi-exponential decays are observed. The $\mathrm{HC} \equiv \mathrm{C} - \mathrm{C}(\mathrm{OO}^{\bullet})\mathrm{H}_2$ peroxyl adduct has no low-barrier isomerisation pathways, so this reaction is a dead-end. At even higher temperatures (T > 500 K), the equilibrium begins to overwhelmingly favour the reactants (under typical O_2 concentrations), and there is no net formation of $\mathrm{HC} \equiv \mathrm{C} - \mathrm{C}(\mathrm{OO}^{\bullet})\mathrm{H}_2$. However, a slow radical decay due to R2 is seen. The initial recombination reaction in R2 appears to have a small barrier and thus is unable to compete with R1 at low temperatures. The intermediate product in R2, the peroxyl adduct $\mathrm{HC}(\mathrm{OO}^{\bullet}) = \mathrm{C} = \mathrm{CH}_2$, only ever has a small steady-state concentration, and a direct phenomenological reaction $\mathrm{HC} \equiv \mathrm{C} - \mathrm{CH}_2^{\bullet} + \mathrm{O}_2 \longrightarrow \mathrm{HCO}^{\bullet} + \mathrm{CH}_2 = \mathrm{C} = \mathrm{O}$ is observed. For allylic species, the general principles are the same.

The radicals studied in this work are shown in Fig. 2. In addition, some as of yet unpublished data for propargyl and 3-ethylpropargyl will be presented for comparison purposes.



Figure 2: Radicals studied in this thesis.

2 Methods

2.1 Experimental

2.1.1 History

Using laser/flash-photolysis photoionisation mass spectrometry to study radical-molecule reactions is an experimental technique pioneered by David Gutman and co-workers and Kyle Bayes and co-workers in the 1980s.^{17,18} At the time, the results produced by laserphotolysis techniques were questioned because the activation energies they predicted were not in agreement with existing thermochemical data. Sydney Benson and co-workers argued that the results were contaminated by "hot radicals" and conjectured that radicals formed by laser-photolysis do not have sufficient time to thermalise in the experiments.^{19,20} Moreover, the very low pressure reactor (VLPR) technique employed by Benson and coworkers and the laser-photolysis experiments gave inconsistent rate coefficient predictions. An example of the different predictions given by these two experimental techniques is given in Fig. 3 for the $C_2H_5^{\bullet} + HBr \longrightarrow C_2H_6 + Br^{\bullet}$ reaction. As one can see, not only do the results disagree by more than an order of magnitude, but they also exhibit a different temperature dependence.



Figure 3: Measured $C_2H_5^{\bullet} + HBr \longrightarrow C_2H_6 + Br^{\bullet}$ rate coefficient as a function of temperature. The laser-photolysis experiments are by Nicovich et al., Seetula, and Seakins et al.^{21–23} and the VLPR measurements are from Dobis and Benson.^{19,20}

Krasnoperov and Mehta argued that if the laser-photolysis results are really contaminated by vibrationally excited species, then the laser-photolysis rate coefficients should decrease with pressure due to collisional relaxation.²⁴ Thus, they performed pressuredependent experiments for the $CH_3^{\bullet} + HBr \longrightarrow CH_4 + Br^{\bullet}$ reaction from 1 to 100 bar and compared the results to the low-pressure results of Seakins et al. and Nicovich et al.^{21,23,24} No pressure dependence was observed for the reaction between $2.5 \cdot 10^{-3}$ bar and $1.0 \cdot 10^2$ bar, which clearly demonstrated that "hot radicals" are not a source of error in laser-photolysis measurements. Since then, enough experimental and computational data has accumulated to conclude that the laser-photolysis results are accurate and the VLPR rate coefficient predictions are incorrect. For example, when ethyl radicals are produced by $C_2H_6 + Cl^{\bullet} \longrightarrow C_2H_5^{\bullet} + HCl$ and then the $C_2H_5^{\bullet} + O_2$ rate coefficient is measured,²⁵ the results agree with laser-photolysis experiments. However, it is still unclear why the VLPR technique gives incorrect results.

Raimo Timonen worked in David Gutman's group in the 1980s and 1990s, and when he returned back to Finland, he started building an apparatus very similar to the ones he had used with Gutman. He also managed to secure components from Bayes' laboratory, some of which are still being used by us. He finished constructing the apparatus with Arkke Eskola and they published their first paper in 2003.²⁶ The Helsinki and Gutman apparatuses give very consistent results (as they should), which is shown in Fig. 4 for $\mathbb{R}^{\bullet} + Cl_2 \longrightarrow \mathrm{RCl} + \mathrm{Cl}^{\bullet}$ reactions. Over the years, we have found that the results obtained with the Gutman apparatuses are systematically about 10 - 20 % larger than those obtained in Helsinki. Given the very similar design of the apparatuses, this is somewhat surprising and the reason for it still unknown.



Figure 4: A comparison of $\mathbb{R}^{\bullet} + \mathbb{Cl}_2 \longrightarrow \mathbb{RCl} + \mathbb{Cl}^{\bullet}$ rate coefficient measurements by the Gutman and Helsinki apparatuses.^{27–32}

2.1.2 The Experimental Apparatus

The principles behind the experimental technique are quite simple. Experiments are performed in tubular laminar flow reactors at relatively low pressures (0.2–10 Torr). Although the flow is laminar, the used pressures are low enough to permit rapid radial diffusion. Thus, the molecules spend equal amounts of time, on average, in slow and fast laminars. The pressure range of the experiment is controlled by varying the diameter of the reactors. Reactors with large inner diameters (d = 1.65 - 1.70 cm) are used to perform low-pressure (0.2–3 Torr) measurements and slightly smaller reactors (d = 0.80-0.85 cm) are used to perform high-pressure ones (2–10 Torr). The pressure drop in the reactor is calculated from

$$p = \left(p_0^2 - \frac{16\eta_T RT \dot{n}_{\rm tot}}{\pi R_{\rm rad}^4} L\right)^{\frac{1}{2}} .$$
 (2.1)

Here p_0 is the pressure at the start of the reactor (which is measured), p is the pressure at distance L from the start, η is the viscosity of the gas, T is temperature, \dot{n}_{tot} is the molar flow rate of the gas, and R_{rad} is the radius of the reactor. The pressure drop is usually a few percentage points. The reactant (O₂) concentration is calculated from

$$[O_2] = \frac{\dot{n}_{O_2}}{\dot{n}_{tot}} \frac{p}{RT} \,. \tag{2.2}$$

To control the temperature of the reactor, we circulate methanol (180-300 K) or distilled water (300 - 365 K) through a cooling/heating mantle. To reach higher temperatures (300 - 950 K), resistive heating coils/blocks are used.

The oxygen flow rate is determined by measuring the increase of pressure in a known volume with a stopwatch. The total flow rate is measured with a soap bubble flowmeter and a stopwatch. The concentration of the inert bath gas (usually He, but sometimes N_2) is typically in huge excess over $[O_2]$, although for very slow reactions up to 50 % of the flow can be O_2 . The concentration of O_2 in turn is in huge excess over the radical concentration. That is to say, the measurements are performed under pseudo-first-order conditions ([He] $\gg [O_2] \gg [\mathbb{R}^{\bullet}]$). A schematic of the experimental apparatus is shown in Fig. 5.

2.1.3 Radical Production

We use pulsed exciplex lasers for radical production. The laser pulse is fired along the axis of the reactor to homogeneously produce the radical of interest. Care is taken to ensure that the pulse does not hit the reactor wall. We typically use brominated precursors (RBr) in our experiments, and the radical of interest is photolytically produced by

$$RBr + h\nu \longrightarrow R^{\bullet} + Br^{\bullet}$$
(2.3)

using either 193 nm or 248 nm radiation. Other photolytic precursors can be used, but we have found brominated ones to be quite reliable. However, they have a few drawbacks. One of them is that they start to thermally decompose between 600 K and 750 K, and this often sets the upper temperature limit of our experiments. Another drawback is that they usually have a secondary photolysis channel,

$$RBr + h\nu \longrightarrow R_{-H} + HBr .$$
(2.4)



Figure 5: A schematic of the Helsinki-apparatus

This can complicate the analysis of reaction products as conjugate alkenes (R_{-H}) are important products for many $R^{\bullet} + O_2$ reactions. In general, we try to use more than one photolytic precursor to produce a radical. If consistent results are observed with both precursors, we can be quite confident that the photolysis event only produces the radical of interest. For example, in measuring the kinetics of *t*-butyl radicals, we have to be careful that we are not producing *n*-, *s*- or *i*-butyl radicals. Using different radical precursors to obtain the same result can also be used to show that it is unlikely that the measurements are contaminated by "hot radicals" or any kind of secondary chemistry.

The precursor is introduced into the reactor by bubbling helium or nitrogen through temperature-controlled liquid precursor. The precursor is purified by several freeze-pumpthaw cycles before use.

2.1.4 Radical Detection

Photoionisation mass spectrometry is used for radical detection. We sample a small part of the flowing mixture (3 - 20 %) through a hole on the side of the reactor to a vacuum chamber containing a quadrupole mass spectrometer. The radicals are ionised with resonance-radiation-discharge lamps. We use different kinds of window materials to cut off emission lines higher in energy than the most intensive one (the one we want). Different lamp/window combinations are tested to see which gives the best signal for a given radical. We like to check that we get the same result with different ionisation energies. In these kinds of experiments, one must always be careful of dissociative ionisation. For example, in $\mathbb{R}^{\bullet} + \mathcal{O}_2$ measurements there is always a risk that the adduct dissociates by $\mathbb{RO}_2^{\bullet} + h\nu \longrightarrow \mathbb{R}^+ + \mathcal{O}_2 + e^-$. To avoid this problem, we try to use as low ionisation energies as possible. If dissociative ionisation is a serious problem, it should be detectable by noticing that the radical signal does not return to pre-photolysis baseline. Tables 1 and 2 list ionisation energies and window materials we have used.

Table 1: The UV-wavelengths emitted by some important resonance-radiation-discharge lamp gases.^{33,34}

Atom	UV Emission Line (eV)	Atom	UV Emission Line (eV)
Н	10.20, 12.09	He	21.22, 40.81
Ν	7.11, 8.31, 8.78	Ne	16.67, 16.85, 26.81, 26.91
0	9.49, 9.50, 9.52	Ar	11.62, 11.83, 13.30, 13.48
Cl	8.88, 8.92, 9.09	Kr	10.03, 10.64
Br	7.59-8.33 (7 lines)	Xe	8.44, 9.57

Table 2: Energy thresholds for several window materials. At energies above the threshold, the window absorbs all UV-light. $eV = 1.602677 \cdot 10^{-19}$ J.

Salt Window	Cutoff Energy (eV)
LiF	11.9
MgF_2	11.1
CaF_2	10.2
Al_2O_3 (sapphire)	8.8
SiO_2 (optical quartz)	7.6

The photoionisation mass spectrometry detection technique coupled with a flow reactor permits us to measure the intensity of the radical signal as a function of time. When a laser pulse hits, radicals at the pinhole have not had time to react and the radical signal is at its maximum. This is the zero-time in our measurements. As time passes by, the flow brings to the pinhole a gas mixture that has had more time to react and a decay in the signal intensity is observed. Using a pulsed laser enables us to repeat this measurement thousands of times. The average flow velocity in the reactor is generally about 5 m s⁻¹, and the laser is operated at 5 Hz. Because the reactors are about a metre long, every laser pulse photolyses a fresh gas mixture. An example of a time-dependent

radical trace obtained with the apparatus is shown in Fig. 6. Measuring a trace like this takes 10–60 min, depending on signal quality.



Figure 6: An example of a radical trace.

2.1.5 Wall Reactions

Because radial diffusion is fast in our experiments, the radicals frequently come into contact with the reactor surface. Thus, we need to use suitable reactor material and coating combinations to make the walls as inert as possible. At low temperatures, we have had success with stainless steel reactors coated with halocarbon wax. A limitation of halocarbon wax is that it begins to melt at around 400 K, so other coatings need to be used for high-temperature measurements. At higher temperatures, we utilise quartz and Pyrex (borosilicate glass) reactors. These can be coated with either polydimethylsiloxane (PDMS), which can be used up to about 500 K, or boric oxide, which we have used up to 950 K. To measure a rate coefficient over a wide temperature range, we need to use multiple reactor material/coating combinations. The temperature ranges covered by each combination overlap at some temperatures (at least room temperature), so we can easily check that consistent results are obtained with different combinations. Whenever we make a large change, such as changing a reactor and/or coating, we repeat an old measurement to ensure we still get the same result.

The rate at which radicals react with the walls can be directly measured. We simply measure the radical decay rate in the absence of added reactant (O_2) . Strictly speaking, a decay

rate measured this way also has contributions from radical-radical and radical-precursor reactions, but we can suppress these by using low radical and precursor concentrations. A practical way of checking that these do not contribute to the loss rate is to double/halve the precursor concentration (or pulse power) and see if the loss rate remains unchanged.

A low wall rate (k_w) is a prerequisite for our measurements. The time-window in our experiments is about 50–70 ms, so we try to measure decays that are slower than 250 s⁻¹. If the decays are faster, it becomes increasingly difficult to make a reliable exponential fit. We always try to measure a decay that is at least five times faster than the wall rate, so the maximum wall rate we can tolerate is about 50 s⁻¹. Typically, the wall rates are much lower than this For the radicals studied in this thesis, they were usually under 20 s⁻¹, sometimes even under 10 s⁻¹. In fact, for some resonance-stabilised radicals we have seen wall rates that are essentially zero.

The general trend we have observed is that wall rates tend to increase with radical size and decreasing temperature. Most of the time it is the increase in wall rate that sets the lower temperature limit in our experiments.

2.1.6 Bimolecular Plots

The typical steps of a rate coefficient measurement are the following:

- 1. The desired flow rate, temperature, and pressure it set.
- 2. The wall rate (k_w) is measured. The wall rate is remeasured at the end of a bimolecular rate coefficient determination to ensure that is has remained approximately constant. A single-exponential function

$$[\mathbf{R}^{\bullet}] = A + [\mathbf{R}^{\bullet}]_0 \mathrm{e}^{-k_{\mathrm{w}}t} \tag{2.5}$$

is fitted to these measurements to obtain $k_{\rm w}$. Here A is the signal background, t is time after laser pulse, and $[{\rm R}^{\bullet}]_0$ is some value proportional to the initial radical concentration.

3. After the initial wall rate measurement, a known concentration of O_2 is added into the reactor and the radical trace is measured. Again, a single-exponential function

$$[\mathbf{R}^{\bullet}] = A + [\mathbf{R}^{\bullet}]_0 \mathrm{e}^{-k't} \tag{2.6}$$

is fitted to the obtained trace. Here k' is a pseudo-first-order rate coefficient and is related to the bimolecular rate coefficient k and the wall rate by

$$k' = k[O_2] + k_w . (2.7)$$

The pseudo-first-order rate coefficient is usually determined at 4–5 different oxygen concentrations.

4. After the k' and k_w measurements, the results are plotted as a function of $[O_2]$. When a straight line is fitted to the data, the slope and intercept give k and k_w , respectively. The k_w value obtained from the fit should agree well with the measured values if the experiments have been performed well. We typically report both values. An example of a bimolecular plot for the 2-methylallyl + O_2 reaction is presented in Fig. 7.



Figure 7: A bimolecular plot for the 2-methylallyl + O_2 reaction measured at 203 K and 0.20 Torr. The figure is taken from (IV).

Sometimes radical decays are not purely single-exponential, as is the case when redissociation $(\mathbb{R}^{\bullet} + \mathbb{O}_2 \Longrightarrow \mathbb{RO}_2^{\bullet})$ becomes significant, and more complicated functions need to be fitted to the obtained traces to obtain rate coefficients. For simple $\mathbb{R}^{\bullet} + \mathbb{O}_2 \Longrightarrow \mathbb{RO}_2^{\bullet}$ equilibration, a double-exponential function suffices.³⁵ However, if there are two equilibrating $\mathbb{R}^{\bullet} + \mathbb{O}_2 \Longrightarrow \mathbb{RO}_2^{\bullet}$ reactions, a triple-exponential function is needed. When the reaction mechanisms become more complex, increasingly complicated fitting functions need to be used and the problem easily gets out of hand. Our experience has been that a double-exponential function can still be quite reliably fitted to the obtained traces, but not a triple-exponential function (the fitting uncertainties are as large as the parameters). Fortunately, the recently implemented trace fitting feature in MESMER (a ME code) alleviates some of these problems (this will be discussed in more detail in later sections).^{36,37}

3 Theory

3.1 Transition State Theory

Transition state theory (TST) is the most widely used method to predict uni- and bimolecular rate coefficients in the field of chemical kinetics. The theory itself is fully classical, but typically at least some quantum effects need to be accounted for to obtain quantitative agreement with experiment. For example, classical energy differences can be replaced with zero-point-energy (ZPE) corrected energy differences or classical harmonic oscillator partition functions with their quantum equivalents. The main idea of the theory is that it places a dividing surface (a transition state) between the reactants and the products and then evaluates the flux through this surface in the reactant \rightarrow product direction. The dividing surface can be placed anywhere on a given potential energy surface (PES), but it is most often placed on the first-order saddle-point (if it exists) that connects the reactant and product valleys on the reaction's PES. In its simplest application, only information about the properties of the reactant and the first-order saddle-point is needed to compute a rate coefficient. If one wants to improve on this estimate, typically more information about the PES is needed (hindering potentials for internal rotations, for example). However, in all its variants TST requires no knowledge about the underlying dynamics. In fact, one could say the reason for TST's existence is to predict rate coefficients without having to perform trajectory calculations, which are costly and can only be done accurately for systems with a few heavy atoms and degrees of freedom.

TST can be used to predict thermal rate coefficients (k(T)) in canonical ensembles and E- and J-resolved rate coefficients (k(E, J)) in microcanonical ensembles. The microcanonical version of TST is often called Rice-Ramsperger-Kassel-Marcus (RRKM) theory, named after the people that were instrumental in developing it. Both versions of TST assume there is a dividing surface between the reactant and product that acts as a point of no return. This assumption is often called the "no recrossing assumption" and it has the attractive feature that it necessarily overestimates the reactive flux through the dividing surface on a given PES. Some trajectories will in fact cross the dividing surface but then return back to the reactant valley (trajectory B in Fig. 10, for example). It is also possible that some trajectories will cross the dividing multiple times before finally ending up in the product valley (trajectory D in Fig. 10). Thus, the location of the dividing surface can be variationally selected so as to minimise the overestimation that results from the assumption that all trajectories that cross the dividing surface are reactive. At this point it is worth pointing out that it is somewhat arbitrary how one determines if a trajectory is reactive. After all, a trajectory with a constant (E, J) that enters the product valley from the reactant side will *eventually* return to the reactant side. Therefore, some pragmatic if arbitrary criteria are needed in trajectory calculations to determine if a reaction has taken place. For example, the criterion could be that a certain bond length has reached its equilibrium value on the product side.

The other assumption TST makes is that it assumes the reactants are in an equilibrium. In the canonical case, it is assumed that the energy states of the reactant are always Boltzmann distributed. This assumption is strictly true only in the limit of infinite pressure where collisions are so frequent that thermal equilibrium is always maintained. In practice, the high-pressure limit is reached when the rate coefficient no longer appreciably increases when pressure is increased. For the microcanonical case, the equilibrium assumption is that each region of reactant phase space is always equally populated. Although a reaction will depopulate the reactant phase space, it is assumed that intramolecular energy transfer is sufficiently fast that the reactant phase space will remain homogeneously populated. Implicit in this assumption is that the system is ergodic and mixing, meaning that a trajectory with a given (E, J) is able explore all of the phase space (ergodicity) and that trajectories initiated with slightly different initial conditions will quickly "spread out" to evenly cover the available phase space (mixing). This mixing behaviour is illustrated in Figure 8 for a phase space element in a double-well potential.



Figure 8: An example how a phase space element in a double-well potential spreads to cover the available phase space whilst maintaining its volume.

A consequence of this assumption is that k(E, J) is independent of initial conditions and time (desirable features for a rate coefficient!). The validity of the microcanonical equilibrium assumption has been questioned since the early days of TST,³⁸ but nowadays it is generally accepted that the assumption is accurate for most systems and the systems for which it fails are the exception rather than the rule. The latter systems are often described as being inherently non-RRKM or -statistical. A famous example of such a system was presented by Rynbrandt and Rabinovitch³⁹ when they reacted deuterated singlet methylene with 1,2,2-trifluoro-1-(1,2,2-trifluoroethenyl)-cyclopropane to form excited 1,2,2,1',2',2'-hexafluorobicyclopropane (see Figure 9 below), which subsequently decomposed by ring opening. At pressures below 0.13 bar, they observed that both rings opened with nearly equal probability, indicating that the energy deposited in the one ring had time to be redistributed to the other ring before collision-induced ring-opening occurred. However, as pressure was increased above 0.13 bar, it was increasingly the $-c-C_3F_3D_2$ ring that opened. From this it was concluded that above 0.13 bar the intramolecular energy transfer rate between the two rings and the unimolecular decomposition reaction happen at similar timescales.

The expression for the canonical TST rate coefficient ($\beta = 1/k_{\rm B}T$, $q_{\rm rc}$ = reaction coordin-



Figure 9: A reaction scheme in which chemically excited 1,2,2,1',2',2'-hexafluorobicyclopropane is formed and its subsequent ring-opening reactions.

ate) is

$$k(\beta, q_{\rm rc}) = \frac{\int \delta(f(\boldsymbol{q}) - q_{\rm rc}) (\boldsymbol{\nabla} f(\boldsymbol{q}) \cdot \dot{\boldsymbol{q}}) u(\boldsymbol{\nabla} f(\boldsymbol{q}) \cdot \dot{\boldsymbol{q}}) e^{-\beta \mathcal{H}} \mathrm{d}\boldsymbol{\Gamma}}{\int e^{-\beta \mathcal{H}} \mathrm{d}\boldsymbol{\Gamma}} , \qquad (3.1)$$

which can be expressed in the more conventional form

$$k(\beta, q_{\rm rc}) = \frac{1}{h\beta} \frac{Q^{\ddagger}(\beta)}{Q_{\rm react}(\beta)} e^{-\beta \Delta_{\rm r} E_0^{\ddagger}}$$
(3.2)

if the reaction coordinate is separable and orthogonal to the other coordinates. Here $d\boldsymbol{\Gamma} = d\boldsymbol{q}d\boldsymbol{p}, \ \mathcal{H} = \mathcal{H}(\boldsymbol{q}, \boldsymbol{p})$ is the classical Hamiltonian, $f(\boldsymbol{q})$ is a function that defines the dividing surface, u is the Heaviside step function, $q_{\rm rc}$ is the reaction coordinate, ∇ is the gradient, h is the Planck constant, and Q is the canonical partition function. The equivalent expressions for the microcanonical case are

$$k(E, J, q_{\rm rc}) = \frac{\int \delta(\mathcal{H} - E)\delta(J - J')\delta(f(\boldsymbol{q}) - q_{\rm rc})(\boldsymbol{\nabla}f(\boldsymbol{q}) \cdot \dot{\boldsymbol{q}})u(\boldsymbol{\nabla}f(\boldsymbol{q}) \cdot \dot{\boldsymbol{q}})d\boldsymbol{\Gamma}}{\int \delta(\mathcal{H} - E)\delta(J - J')d\boldsymbol{\Gamma}}$$
(3.3)

and

$$k(E, J, q_{\rm rc}) = \frac{N^{\ddagger}(E, J)}{h\rho_{\rm react}(E, J)} .$$

$$(3.4)$$

Separability and orthogonality was once again assumed to go from the first expression to the second. Here N^{\ddagger} is the number of states of the dividing surface and $\rho_{\text{react}}(E, J)$ is the density of states of the reactant. The latter expression is known as the RRKM-expression. A derivation of the TST rate coefficients is given in Appendix A.

3.2 Flexible Transition State Theory

For barrierless recombination reactions, the TS location is not obvious and it must be variationally sought. A natural choice for the reaction coordinate for such reactions is the centres-of-mass distance of the recombining fragments. It also turns out that this reaction-coordinate definition is in many ways the most convenient as it simplifies much of the mathematics needed to deal with these reactions. However, it was recognised by Klippenstein that other definitions of the reaction coordinate, such as a bond length,⁴⁰

may lead to smaller k(E, J) values and must therefore be a better estimate of the "true" k(E, J) due to the inherent assumptions in TST. So both the value and definition of the reaction coordinate can be variationally chosen in order to minimise the overestimation of the no-recrossing-assumption in TST. This approach is known in the literature as either variable reaction coordinate TST (VRC-TST) or flexible TST (FTST).^{7,8} These theories make one additional assumption to conventional TST; they divide the coordinates of the studied system into "conserved" and "transitional" modes. The conserved modes are those that remain approximately unchanged as the recombining fragments move from large separations to the dividing surface. The transitional modes, in contrast, change significantly as the dividing surface is approached. These modes are typically large-amplitude motions that are often strongly coupled with each other and external rotation.

A short introduction of this approach is given in this thesis for the simplest non-trivial system: an atom-diatom recombination reaction. This system can be used to introduce all the essential features of the theory, but makes the mathematical expressions simpler and, hopefully, easier to follow. A derivation of the TST rate coefficient for this system is given in Appendix B. A derivation for the most general case, the recombination of two asymmetric rotors, has been presented by Robertson, Wardlaw, and Wagner.⁷ A bodyfixed frame is used where the centres of mass of the fragments are placed on the z-axis, with the origin being the centre of mass of the whole system. An angle θ is used to determine the relative orientation of the fragments. A body-fixed frame is used because the interaction potential between the fragments is most naturally expressed in such a frame. A drawback of this choice is that there will be Coriolis-coupling terms in the Hamiltonian. The example system used will be the $H^{\bullet} + O_2 \longrightarrow HO_2^{\bullet}$ reaction, for which an analytical PES has been reported by Harding, Troe, and Ushakov.⁴¹ The PES is shown in Fig. 10. An interesting feature of the surface is the fairly limited anglerange in which the recombination reaction is barrierless. For this system, the transitional modes are the centres-of-mass distance, rotation of the diatom, and the three modes that describe the overall rotation of the system. The conserved mode is the diatom vibration.

The FTST calculations were run with two different reaction-coordinate definitions: centresof-mass distance and O-H bond distance. These results are first compared, after which the performance of FTST is compared to trajectory calculations. To be clear, I made the FTST and trajectory calculations in this thesis only to explore the features of FTST and see how much it overestimates the trajectory result. The results are not found in any of the publications. I wrote the codes myself and they are freely available for inspection and use (https://github.com/ttpekkan/git, folders FTST and TRAJECTORY). The final results are are given below (see Appendix B for details).

$$k(\beta, r) = \frac{Q_{\text{cons}}(\beta)}{Q_{\text{react}}(\beta)} \frac{2^5 \pi^4}{\beta^3 h^5} \int_0^{\pi} |\mathbf{A'}|^{\frac{1}{2}} \mathrm{e}^{-\beta V} \mathrm{d}\theta$$
(3.5)

$$k(E,r) = \frac{2^4 \pi^4}{\nu_{\text{harm}} h^5 \rho_{\text{react}}(E)} \int_0^E \int_0^\pi |\mathbf{A'}|^{\frac{1}{2}} u\left(E - \epsilon - V\right) \left(E - \epsilon - V\right)^2 \mathrm{d}\theta \mathrm{d}\epsilon \qquad (3.6)$$

$$k(E, J, r) = \frac{2^{\frac{9}{2}} J^2 \pi^2}{\nu_{\text{harm}} h^6 \rho_{\text{react}}(E, J)} \int_0^E \int_0^\pi |\mathbf{Z}|^{-\frac{1}{2}} \dots$$
(3.7)

$$\dots \left(\int_0^{2\pi} \int_0^{\pi} u \left(E - \epsilon - E_{\rm rot} - V \right) \left(E - \epsilon - E_{\rm rot} - V \right)^{\frac{1}{2}} \sin(\nu) \mathrm{d}\nu \mathrm{d}\eta \right) \mathrm{d}\theta \mathrm{d}\epsilon$$

Here $k(\beta, r)$ is the canonical (high-pressure) rate coefficient, k(E, r) is the microcanonical rate coefficient, and k(E, J, r) is the *EJ*-resolved microcanonical rate coefficient. The optimal dividing surface is located at the reaction coordinate r value that minimises the rate coefficient expressions. The derivation of $k(\beta, r)$ and k(E, r) follows exactly the one given for k(E, J, r) in the appendix, except that J_x , J_y , J_z are integrated from $-\infty$ to ∞ (one can start from equation B.39). This leads to simpler expressions, but angular momentum conservation is ignored. The expression for the rotational energy is

$$E_{\rm rot} = \frac{J^2}{2} \left(\left[\frac{\sin^2(\eta)}{I_{xx}} + \frac{\cos^2(\eta)}{I_{yy}} \right] \sin^2(\nu) + \frac{\cos^2(\nu)}{I_{zz}} \right) \,. \tag{3.8}$$

The location of the dividing surface can be optimised against any of the three expressions. For the canonical expression, the TS location is optimised at each temperature and this is called canonical optimisation. In microcanonical optimisation, the TS location is optimised at each E to obtain k(E), but angular momentum conservation is not considered. The canonical rate coefficient is then obtained from

$$k(\beta) = \frac{1}{Q_{\text{react}}(\beta)} \int_0^\infty \rho_{\text{react}}(E) k(E) \mathrm{e}^{-\beta E} \mathrm{d}E \;. \tag{3.9}$$

Finally, in EJ-resolved microcanonical optimisation the optimal TS location is sought for each E and J. This is the most expensive of the calculations, but yields the lowest (best) result. After k(E, J) is obtained, the canonical expression is acquired by integrating over E and J,

$$k(\beta) = \frac{1}{Q(\beta)_{\text{react}}} \int_0^\infty \int_0^\infty \rho_{\text{react}}(E, J) k(E, J) \mathrm{e}^{-\beta E} \mathrm{d}J \mathrm{d}E \;. \tag{3.10}$$

The results yielded by the different optimisation schemes are shown in Fig. 11. Sensible ordering is seen. The canonical and EJ-microcanonical give the worst and best result, respectively, as they should. The microcanonical approach gives only slightly worse results than EJ-microcanonical, but is much faster. The figure also shows how the reaction-coordinate choice (centres-of-mass vs. O–H bond distance) affects the calculated rate coefficient. Here the centres-of-mass reaction coordinate performs better, presumably because the system is very small, but this is not true in general.

As is often the case for barrierless reactions, a centrifugal barrier dominates the kinetics at low energies (or temperatures) and the TS is quite far away (see Fig. 12).⁴² At sufficiently far separations the interaction potential is essentially isotropic, and the problem reduces to an atom-atom reaction, for which analytical solutions exist. If the long-range potential is of the form Cr^{-6} , then the temperature dependence of the capture rate will be proportional to $T^{\frac{1}{6}}$ and positive temperature dependence is expected.⁴² The emergence of negative temperature dependence is due to the TS shifting from the outer to the inner one. In a microcanonical setting some k(E, J)-values correspond to the outer and others to the inner TS, and temperature only affects how they are weighted. This is why a smooth canonical rate coefficient is observed in the microcanonical and EJ-microcanonical approaches. In the canonical optimisation the TS location changes "in one go" and causes the kink seen in the curve. The eventual shift back to positive temperature dependence is not very intuitive, but it can be rationalised in terms of conventional TST. At relatively low temperatures, enthalpic effects dominate and the value of the TST expression will be



Figure 10: The analytical potential energy surface reported by Harding, Troe, and Ushakov⁴¹ for the H[•] + O₂ \longrightarrow HO₂[•] reaction. Also shown are example trajectories run at $E = 5.65 \cdot 10^{-22}$ J and $J = 5.04 \cdot 10^{-34}$ Js (see Appendix C). The dividing surface is located at $r = 5.41 \cdot 10^{-10}$ m.



Figure 11: Canonical $H^{\bullet} + O_2 \longrightarrow HO_2^{\bullet}$ rate coefficients. The upper figure shows how the optimisation scheme affects the result. The lower figure shows how much *EJ*-FTST overestimates the trajectory result. Also shown are the trajectory results obtained by Harding, Troe, and Ushakov on the same potential.⁴¹

governed by the exponential term $\exp(-\Delta_r E_0^{\dagger}/RT)$. The reaction is barrierless, so the exponent is positive and increasing temperature makes the exponential term smaller. Thus, negative temperature dependence is expected. At higher temperatures, the exponential term does not matter as much and the TST expression is governed by the pre-factor. The partition function of the tight inner TS is likely to have significantly stronger temperature dependence than that of the reactants. The centres-of-mass motion and relative rotation of the diatom are effectively free at long separations, but become constrained by the potential at short separations. That is to say, over the course of the reaction a translational and a free-rotor partition function become vibrational partition functions.

I also tested how much the *EJ*-FTST-approach overestimates the "true" rate coefficient by performing trajectory calculations (see Appendic C). The calculations were run on the same potential, except that the diatom vibration was included. The Harding-Troe-Ushakov (HTU) potential is two-dimensional, so I used the harmonic frequency of O_2 $(4.74 \cdot 10^{13} \text{ s}^{-1})$ to create a three-dimensional PES

$$V(r, R, \theta) = V_{\rm HTU}(r, \theta) + 2\mu_R \pi^2 \nu_{\rm harm}^2 (R - R_{\rm eq})^2 .$$
(3.11)

There is no potential coupling between the harmonic and the other modes in this potential, but kinetic coupling is included in the calculations. The aim here is to compare FTST to trajectories, so the details of the potential are not important. A fully classical approach was chosen to make the TST-trajectory comparison as straight-forward as possible. This way I did not have worry about zero-point energy effects or if quantum effects were consistently treated in both calculations (the FTST calculations were also fully classical). The trajectories were used to determine a recrossing factor

$$\chi(E,J) = \frac{N_{\text{norecross}}}{N_{\text{norecross}} + N_{\text{recross}}} , \qquad (3.12)$$

where $N_{\text{norecross}}$ and N_{recross} are the number of trajectories that cross the *EJ*-FTST dividing surface only once and more than once, respectively. This correction factor was then used to compute a dynamically corrected canonical rate coefficient from

$$k(\beta) = \frac{1}{hQ(\beta)_{\text{react}}} \int_0^\infty \int_0^\infty \chi(E, J) N_{\text{FTST}}^{\ddagger}(E, J) e^{-\beta E} dJ dE .$$
(3.13)

The results of the trajectory calculations are shown in figures 11 and 13. According to the results, EJ-FTST overestimates the "true" rate coefficient only by 5 – 10 % at temperatures above 50 K. At lower temperatures the agreement is worse because a significant number of trajectories that cross the outer TS get reflected by the inner one (see Fig. 13). However, even here the performance of EJ-FTST is not that bad. Furthermore, poor performance at very low temperatures is of little practical relevance, as the classical assumptions behind both trajectory and TST calculations do not apply there. Figure 11B also shows the trajectory results reported by Harding, Troe, and Ushakov.⁴¹ The results overlap at high temperatures, but begin to diverge at lower temperatures. One obvious explanation for the disagreement is that they treated the diatom as a rigid body in their trajectories, whereas I assumed it was a classical harmonic oscillator. Another possible source of disagreement is inconsistencies in initial-condition sampling.



Figure 12: This figure depicts the optimum transition state location as a function of E and J and shows how the TS state sum $N^{\ddagger}(E, J)$ changes with E and J.



Figure 13: The upper figure shows how the ratio of reactive to total trajectories changes with E and J. The lower figure depicts the recrossing factor ($\chi(E, J) = N_{\text{norecross}}/(N_{\text{norecross}} + N_{\text{recross}})$) as a function of E and J (see main text for details).

3.3 Laplace Transforms

Sometimes a problem is easier to solve in microcanonical/canonical space but the answer is needed in the other. Laplace and inverse Laplace transforms (ILT) provide a convenient way to transform between the spaces. For example, in a canonical ensemble the total partition function of a system where some degrees of freedom are decoupled can simply be expressed as the product of the partition functions of the uncoupled degrees of freedom, whereas in a microcanonical ensemble the total density of states needs to be expressed as a convolution,

$$Q_{A,B}(\beta) = Q_A(\beta)Q_B(\beta) \qquad \qquad \rho_{A,B}(E) = \int_0^E \rho_A(\epsilon)\rho_B(E-\epsilon)d\epsilon . \qquad (3.14)$$

Since

$$Q_{\mathrm{A,B}}(\beta) = \int_0^\infty \rho_{\mathrm{A,B}}(E) \mathrm{e}^{-\beta E} \mathrm{d}E = L[\rho_{\mathrm{A,B}}(E)]$$
(3.15)

(*L* is used to denote the Laplace transform operation) and if $Q_{A,B}(\beta)$ is known, it may be simpler to evaluate $\rho_{A,B}(E)$ as the ILT

$$L^{-1}[Q_{A,B}(\beta)] = \rho_{A,B}(E) . \qquad (3.16)$$

Laplace transforms also provide a way to obtain the canonical TST rate coefficient from its microcanonical equivalent. If the canonical rate coefficient of a bimolecular $A + B \longrightarrow AB$ reaction is expressed in modified Arrhenius form,

$$k_{\rm rec}(\beta) = A \left(\frac{\beta_0}{\beta}\right)^m e^{-\beta E'_{\rm a}} , \qquad (3.17)$$

then applying the ILT technique yields the following J-averaged expression for the state sum of the TS:

$$N^{\ddagger}(E)_{J} = \frac{Ah\beta_{0}^{m}}{\Gamma(m+\frac{3}{2})} \left(\frac{2\pi\mu}{h^{2}}\right)^{\frac{3}{2}} \int_{0}^{E} u(\epsilon + \Delta_{\rm r}E - E'_{\rm a})(\epsilon + \Delta_{\rm r}E - E'_{\rm a})^{m+\frac{1}{2}}\rho_{\rm A,B,rovib}(E-\epsilon)d\epsilon .$$
(3.18)

The RRKM-expression can then be used to obtain $k(E)_J$. Here μ is the reduced mass of the recombining fragments. The expression above has been derived by Davies et al.⁴³ A derivation is also given in Appendix D.

As mentioned before, for barrierless reactions the location of the TS often depends strongly on E and J, and variational approaches are prohibitively costly for larger systems. If the canonical rate coefficient for such a reaction is known approximately from experiments, the ILT technique provides handy way of obtaining $N^{\ddagger}(E)_J$. In the case of barrierless reactions, the Arrhenius expression is typically given for the recombination rather than the dissociation reaction. The reason for this is that unimolecular dissociation reactions have strong temperature dependencies. Therefore, it is difficult to measure $k_{\text{dis}}(\beta)$ over a wide temperature range, and a modified Arrhenius fit performed on experimental data over a narrow temperature range probably does not extrapolate well to temperatures below and above those that were studied. The reliability of the ILT approach to obtain $k(E)_J$ is heavily dependent on how well the modified Arrhenius expression is able to capture the temperature dependence of the canonical rate coefficient. Barrierless recombination reactions typically have much weaker temperature dependencies.⁴³ Thus, one is generally able to perform experiments over a wider temperature range. Furthermore, the Arrhenius expression that is fitted to the experimental data should extrapolate better to temperatures outside the experimental range than in the unimolecular case. The main, perhaps the only, drawback of the ILT approach is that a modified Arrhenius expression is probably not flexible enough to capture the temperature dependence of the canonical rate coefficient of most reactions over very wide temperature ranges.

In our work, we have relied almost entirely on the ILT approach to obtain state sums for loose TSs. The alternative, VRC-TST or FTST,^{7,8} is costly and contains an assumption (recombining fragments are treated as rigid) that becomes worse as the size of the associating fragments increase. We have used the MESMER program³⁶ in our ILT calculations. Whilst our measurements are typically not at the high-pressure limit, there are automated fitting routines in MESMER that can be used to adjust the modified Arrhenius equation parameters to obtain optimal agreement with experiment. Using the ILT approach together with experimental data has the advantage that angular momentum effects are automatically considered. Even recrossing effects are indirectly included. A disadvantage of fitting the modified Arrhenius parameters is that the fit will also try to compensate for intrinsic errors that are in the computational models.

3.4 Symmetry Numbers

One cannot be too careful with symmetry numbers. For example, the symmetry numbers for t-butyl, molecular oxygen, and t-butylperoxyl are 162, 2, and 81, respectively. If one were to ignore symmetry numbers when calculating the t-C₄H₉ $^{\bullet}$ + O₂ \longrightarrow t-C₄H₉O₂ $^{\bullet}$ rate coefficient, one would be making a factor four error in the calculation. The origin of the problem is that identical particles are indistinguishable in quantum mechanics. The total wave function of a molecule needs to remain unchanged or change sign upon exchanging identical bosons or fermions, respectively. For example, in O₂ the nuclei are bosons. This means the total wave function must be symmetric. Since for ground-state O₂ the electronic wave function is antisymmetric and vibrational wave function symmetric, the rotational wave function must be antisymmetric. Thus, only odd rotational states are permitted. For a discrete system, the partition function is defined as

$$Q(\beta) = \sum_{i} e^{-\beta E_i} , \qquad (3.19)$$

so one can see that O_2 is missing half of the terms in the sum. In practice, people compute partition functions without explicitly considering symmetry factors and apply a symmetry number in the end. For O_2 , all terms would be added and the final result then divided with a rotational symmetry number of two.

Although this is a quantum mechanical phenomenon, an expression for the correct symmetry number that needs to be applied for a given reaction can be derived classically.⁴⁴ Classical mechanics overestimates partition functions because identical particles are treated as distinguishable (H1, H2, H3, and so on) and all "distinct" conformations contribute to the configurational integral. However, this overestimation will be the same for both the reactant and the transition state, so it ends up cancelling out in the TST expression. A symmetry number is needed even in classical evaluations of configurational integrals because the evaluations are typically performed in internal coordinates. Integrating over internal coordinates might not cover all the different ways in which equivalent nuclei could be labelled, so a symmetry number is introduced to correct for this *undercounting*. If a molecule has one or more sets of equivalent nuclei, the total number of ways in which the nuclei can be arranged is $\prod_i n_i!$. In general, some of these arrangements can be accessed by internal and external rotations, and integrating over the coordinates that correspond to these rotations will count the contributions from such arrangements. If σ of the total number of possible arrangements can be accessed by internal and/or external rotations, the total number of rotationally distinct conformers that contribute to the configurational integral is

$$\frac{1}{\tau} \prod_{i} n_i! . \tag{3.20}$$

For example, methane would altogether have

$$\frac{1}{12} \cdot 24 = 2 \tag{3.21}$$

(classically) distinct but equivalent conformers.

If the studied molecule is chiral and one deals with racemic mixtures, the contributions from optical isomers to the configurational integral can be included in the symmetry number,

$$\frac{m}{\sigma} \prod_{i} n_i! . \tag{3.22}$$

Here m is the number of optical isomers.

Transition states and reactants will, of course, have the same number of equivalent nuclei, so the overall symmetry number needed in rate coefficient calculations is

$$\sigma_{\rm tot} = \frac{\frac{m^{\ddagger}}{\sigma^{\ddagger}}\prod_{i}n_{i}!}{\frac{m}{\sigma}\prod_{i}n_{i}!} = \frac{m^{\ddagger}\sigma}{m\sigma^{\ddagger}} \,. \tag{3.23}$$

For example, in the *t*-butyl example we have (the TS shares the symmetry of the peroxyl adduct)

$$\sigma_{\rm tot} = \frac{1 \cdot 2 \cdot 162}{1 \cdot 1 \cdot 81} = 4 . \tag{3.24}$$

In the peroxyl adduct, all four internal rotations have a symmetry number of three $(3^4 = 81)$ and there is no external rotational symmetry. For *t*-butyl there are three internal rotations with a symmetry number of three, a three-fold external rotational symmetry, and the umbrella motion has a symmetry number of two $(3^3 \cdot 3 \cdot 2 = 162)$. As mentioned before, O₂ has a rotational symmetry number of two.

Whilst this may seem straight-forward here, it is anything but. Once one moves to consider large and floppy molecules, the situation becomes complicated very quickly. Particular care is needed for multi-dimensional internal rotations.⁴⁵ Automatic determination of symmetry numbers is still an outstanding problem for those looking to automate rate coefficient calculations.

3.5 Torsional Coupling

With increasingly fast computers and better quantum chemistry methods, barrier heights are no longer necessarily the main source of uncertainty in rate coefficient calculations. The quality of partition functions matter too, especially at higher temperatures. One-dimensional (decoupled) torsional treatments are routinely employed, but accurate work may require multi-dimensional treatments. There are many ways to tackle this problem⁴⁶ and here I present the one implemented in MESMER.⁴⁷ The approach is very similar in spirit to FTST and could probably be further developed to include angular momentum effects.

The modes in the molecule are first divided to internal rotors and those for which the harmonic approximation is a good one. It is assumed that these mode groups are not coupled. The internal rotors may couple with each other and external rotation, and the kinetic energy for the coupled system is

$$2\mathcal{T} = \begin{pmatrix} \boldsymbol{\omega} & \dot{\boldsymbol{q}}_{\text{int}} \end{pmatrix} \begin{pmatrix} \boldsymbol{I} & \boldsymbol{C}^{\mathrm{T}} \\ \boldsymbol{C} & \boldsymbol{I}_{\text{int}} \end{pmatrix} \begin{pmatrix} \boldsymbol{\omega} \\ \dot{\boldsymbol{q}}_{\text{int}} \end{pmatrix} = \dot{\boldsymbol{Q}}^{\mathrm{T}} \boldsymbol{A} \dot{\boldsymbol{Q}} .$$
(3.25)

Here $\boldsymbol{\omega} = (\omega_x, \omega_y, \omega_z)$, \boldsymbol{I} is the moment of inertia tensor, \boldsymbol{C} contains the coupling terms between internal and external rotations, and $\boldsymbol{I}_{\text{int}}$ are the inertial moments about a given bond and their coupling terms. The expression can be manipulated similarly to the flux expression in the FTST-derivation (see Appendices B and E) to obtain the partition function for the coupled system,

$$Q(\beta) = 8\pi^2 \left(\frac{2\pi}{\beta h^2}\right)^{\frac{n}{2}} \int |\boldsymbol{A}|^{\frac{1}{2}} \mathrm{e}^{-V(\boldsymbol{q}_{\mathrm{int}})\beta} \mathrm{d}\boldsymbol{q}_{\mathrm{int}} .$$
(3.26)

The ILT technique is then used to obtain the density of states,

$$\rho(E) = 8\pi^2 \left(\frac{2\pi}{h^2}\right)^{\frac{n}{2}} \frac{1}{\Gamma(\frac{n}{2}-1)} \int_0^E \int (E-\epsilon)^{\frac{n}{2}-2} u(\epsilon - V(\boldsymbol{q}_{\rm int}) |\boldsymbol{A}|^{\frac{1}{2}} \mathrm{d}\boldsymbol{q}_{\rm int} \mathrm{d}\epsilon \;. \tag{3.27}$$

The inner integral is solved with Monte-Carlo techniques in MESMER. The real trick in this approach is to obtain the matrix elements for \boldsymbol{A} , which is a daunting task for long-chained alkanes with many internal rotations. An algorithm to systematically obtain the elements has been presented by Gang et al.⁴⁷

The present implementation in MESMER does not take potential coupling into account. The potential is specified as a sum of individual hindered rotor potentials. However, if relaxed scans are used to obtained these, part of the coupling will be included. In addition, the treatment is fully classical and zero-point contributions will effectively be double-counted if care is not taken. When we use this method, we estimate the ZPEs of the hindered rotors with one-dimensional quantum methods and then subtract these from the energy of the species. This gives the wrong result at cold temperatures, but converges to the correct result at higher temperatures.

3.6 The Master Equation

The chemical master equation is a powerful technique that is used to model reactions that occur over multiple interconnected potential energy wells. Here I will follow a recent
introduction given by Struan Robertson.¹ Only the one-dimensional case (no explicit treatment of angular momentum) is considered as generalisation to two dimensions is not complicated. In a chemical ME problem, one specifies sets of rovibrational states for each species and then simulates the population of these states as a function of time (see Fig. 14). Collisions move a species up or down its rovibrational states and chemical reactions from one well to another. The probability to react or be collisionally activated/deactivated depends only on the current state of the system and not on its past (the process is Markovian). Simulations are typically run under dilute conditions to ensure that pressure and temperature remain constant (this is common in experiments too). If a bimolecular reaction is included, it is generally turned into a pseudo-first-order reaction. The time derivative of the probability distribution function of energy for species i is given by

$$\frac{\partial p(E_i,t)}{\partial t} = \int_{E_i,0}^{\infty} \omega(E_j) P(E_i|E_j) p(E_j,t) dE_j - \omega(E_i) p(E_i,t) - \sum_{k\neq i}^{M} k_{ki}(E_i) p(E_i,t)
+ \sum_{k\neq i}^{M} k_{ik}(E_j) p(E_j,t) - k_{\text{dis},i}(E_i) p(E_i,t) - k_{\text{redis},i}(E_i) p(E_i,t)
+ k_{\text{redis},i} K \frac{\rho(E_i) e^{-\beta E_i}}{Q_i(\beta)} n_{\text{R}} n_{\text{O}_2}.$$
(3.28)

The first term on the right-hand side models the probability of gaining population by activating/deactivating collisions, the second term is the loss due to collisions, the third and fourth sums represent the loss and gain by isomerisation reactions, the fifth term is the loss due to irreversible dissociation reactions, and the last two terms are the loss and gain due to recombination and redissociation reactions, respectively. In the expression above it has been assumed that there is only a single bimolecular source and irreversible loss channel. There can, of course, be multiple such channels and modifying the above expression to accommodate these is straight-forward. Here ω is the Lennard-Jones collision frequency

$$\omega = \sigma_{\rm AM}^2 \left(\frac{8\pi}{k_{\rm B}T\mu_{\rm AM}}\right)^{\frac{1}{2}} p\Omega_{\rm AM}^{(2,2)} \tag{3.29}$$

and is assumed to be energy-independent. The collision integral $\Omega_{AM}^{(2,2)}$ is calculated by the method of Neufeld et al.⁴⁸ using knowledge about ϵ_{AM} . Here σ_{AM} and ϵ_{AM} are the arithmetic-mean Lennard-Jones parameters, μ_{AM} is the reduced mass of the colliding pair, and p is pressure. For the recombination reaction, it assumed that the reactants are always Boltzmann-distributed, the idea being that non-reactive collisions are far more numerous then reactive ones for bimolecular reactants under typical conditions. The standard model for the collisional transition probability $P(E_i|E_j)$ is the exponential-down model,

$$P(E_i|E_j) = A(E_j) e^{-\frac{E_j - E_i}{\langle \Delta E \rangle_{\text{down}}}} , \qquad (3.30)$$

where the average energy transferred downward is usually given the temperature-dependent expression

$$\langle \Delta E \rangle_{\text{down}} = \langle \Delta E \rangle_{\text{down,300 K}} \left(\frac{T}{300 \text{ K}} \right)^n$$
 (3.31)

 $A(E_j)$ is a normalisation factor and n is a number that governs the temperature dependence of $\langle \Delta E \rangle_{\text{down}}$. The energy transferred in activating collisions is obtained by applying



Figure 14: A crude sketch of a three-well chemical problem. Taken from Glowacki et al. 36 with permission.

detailed balance

$$P(E_i|E_j)\rho(E_j)e^{-\beta E_j} = P(E_j|E_i)\rho(E_i)e^{-\beta E_i}.$$
(3.32)

Figure 15 shows how average energies transferred in collisions between helium and 1,3dimethylallylperoxyl (**V**) behave as a function of temperature. One can see from the figure that collisions, in general, are weak and multiple collisions are typically needed to excite a molecule that is deep in a well to a reactive state. The single-exponential down model is used due to its simplicity, but trajectory calculations suggest that models with longer "tails" (a double-exponential model, for example) are needed for more accurate work.⁴⁹

In practical work, the nearly-continuous rovibrational energy states are binned into finitesized grains with mean energies ϵ_i . These grains can be represented with delta functions. With this, the probability to go from grain j to i in a deactivating collision becomes

$$P_{ij} = \int \int A(E_j) \mathrm{e}^{-\frac{E_j - E_i}{\langle \Delta E \rangle_{\mathrm{down}}}} \delta(E_j - \epsilon_j) \delta(E_i - \epsilon_i) \mathrm{d}E_j \mathrm{d}E_i$$
(3.33)

$$=A_j e^{-\frac{\epsilon_j - \epsilon_i}{\langle \Delta E \rangle_{\text{down}}}} .$$
(3.34)



Figure 15: Boltzmann populations and average energy transfer quantities for 1,3-dimethyallylperoxyl (Int1E). The figure is taken from (\mathbf{V}) .

Equation 3.28 is now

$$\frac{\mathrm{d}p_i(t)}{\mathrm{d}t} = \omega \sum_{j=1}^m P_{ij}p_j(t) - \omega p_i(t) - \sum_{k\neq i}^M k_{ki}p_i(t)
+ \sum_{k\neq i}^M k_{ik}p_j(t) - k_{\mathrm{dis},i}p_i(t) - k_{\mathrm{redis},i}p_i(t)
+ k_{\mathrm{redis},i}K \frac{\rho(E_i)\mathrm{e}^{-\beta E_i}}{Q_i(\beta)} n_{\mathrm{R}}n_{\mathrm{O}_2} .$$
(3.35)

The microcanonical rate coefficients (k) are typically obtained from microcanonical TST (RRKM). For barrierless reactions, they can be obtained from VRC-TST, FTST, or by exploiting the ILT technique.

This set of coupled-differential equations can be more compactly expressed as

$$\frac{\mathrm{d}\boldsymbol{p}}{\mathrm{d}t} = \boldsymbol{M}\boldsymbol{p} \;, \tag{3.36}$$

where p is the population vector and M is the transition matrix which describes the collisional and reactive loss and gain for each grain. This is a standard matrix diagonalisation problem with a solution

$$\boldsymbol{p}(t) = \boldsymbol{U} \mathrm{e}^{\boldsymbol{\Lambda} t} \boldsymbol{U}^{-1} \boldsymbol{p}_0 , \qquad (3.37)$$

where p_0 are the initial populations, U is the right eigenvector of M and Λ is a diagonal matrix that contains its eigenvalues ($MU = U\Lambda$).

To obtain the time-dependent population of species A, one first sums the grains contributing to A and differentiates the result,

$$x_{\mathcal{A}}(t) = \sum_{i \in \mathcal{A}} p_i(t) \tag{3.38}$$

$$\frac{\mathrm{d}x_{\mathrm{A}}}{\mathrm{d}t} = \sum_{i \in \mathrm{A}} \frac{\mathrm{d}p_i(t)}{\mathrm{d}t} \tag{3.39}$$

$$=\sum_{i\in \mathbf{A}} (\boldsymbol{M}\boldsymbol{p})_i \tag{3.40}$$

$$=\sum_{i\in\mathbf{A}}^{\mathbf{U}} (\boldsymbol{U}\boldsymbol{A}\boldsymbol{U}^{-1}\boldsymbol{p})_i .$$
(3.41)

As $\boldsymbol{\Lambda}$ is diagonal, in component form

$$\frac{\mathrm{d}x_{\mathrm{A}}}{\mathrm{d}t} = \sum_{i \in \mathrm{A}} \sum_{l} \sum_{j} U_{il} \lambda_{l} U_{lj}^{-1} p_{j} .$$
(3.42)

By defining $Z_{Al} = \sum_{i \in A} U_{il}$ we get

$$\frac{\mathrm{d}x_{\mathrm{A}}}{\mathrm{d}t} = \sum_{l} Z_{\mathrm{A}l} \lambda_{l} \sum_{j} U_{lj}^{-1} p_{j} \tag{3.43}$$

$$=\sum_{l} Z_{Al} \lambda_l c_l , \qquad (3.44)$$

from which one can see that $c_l = \sum_j U_{lj}^{-1} p_j$, or

$$\boldsymbol{p} = \boldsymbol{U}\boldsymbol{c} \,. \tag{3.45}$$

By comparing equation 3.44 and 3.38, one can deduce that

$$x_{\rm A}(t) = \sum_{l} Z_{Al} c_l$$
 (3.46)

A more general expression for the mole fractions is given by

$$\boldsymbol{x} = \boldsymbol{Z}\boldsymbol{c} , \qquad (3.47)$$

from which c can be solved if Z is invertible. Z is a matrix in which the elements of all the eigenvectors that correspond to each of the species have been summed.⁵⁰ In general, it is not a square-matrix. To make progress, it is necessary to think about the chemistry of the situation. At very short time-scales, it is obvious that the time-evolution of the system must depend on initial conditions. However, as chemists we know that rate coefficients are transferable, so clearly the long-time behaviour cannot be sensitive to initial conditions. It has been discovered that for a system with n wells, there will, in general, be n eigenvalues that are much smaller in magnitude than the rest. These small eigenvalues have been coined chemically significant eigenvalue (CSEs) and describe the long-time behaviour of the system. The rest are larger in magnitude and have been termed internal energy relaxational eigenvalues (IEREs) as they describe time-dependence of the energy transfer process. Being large in magnitude, their contribution to the time-dependent mole fractions quickly decays to zero. The separation between CSEs and IEREs was exploited early on by Bartis and Widom, 5^{1} and their approach can be used to truncate equation 3.44 to only contain terms associated with the CSEs. After the truncation, many elements in cwill be zero and only the terms in Z which operate on the non-zero elements will matter. This effectively turns Z into a square matrix, which can then be inverted to obtain c. Substituting $Z^{-1}x$ into 3.44 results in the following differential equation system:

$$\frac{\mathrm{d}\boldsymbol{x}}{\mathrm{d}t} = \boldsymbol{Z}\boldsymbol{\Lambda}'\boldsymbol{Z}^{-1}\boldsymbol{x} \tag{3.48}$$

$$= \boldsymbol{K}_r \boldsymbol{x} . \tag{3.49}$$

Here Λ' is a diagonal matrix that only contains the CSEs. The matrix K_r is clearly timeindependent because there is no time-dependence in its elements. Nor is there dependence on initial conditions. The elements of the matrix are rate coefficients that connect each of the wells to each other well. This analysis is called the Bartis-Widom (BW) analysis in the literature. Note that the wells need not be directly connected. Rate coefficients to non-adjacent wells are called called well-skipping and they are not an artefact of the calculations. Contributions from such reactions can be experimentally detected.^{16,52}

A thumb rule has been that if IEREs and CSEs are separated by at least an order of magnitude, then the BW analysis is reliable and the phenomenological time-evolution predicted by the BW rate coefficients should closely match that given by the ME model. When they are not separated by an order of magnitude, one must look carefully at the results. One sign that the BW-analysis fails, at least partly, is that some rate coefficients become negative. Note that the failure of the BW-analysis is not a failure of ME model itself. The traces (species concentration versus time) are still valid and can be compared

with experiment. In fact, one could say the failure of the BW-analysis is evidence of the failure of the rate coefficient approximation itself. When temperature is increased, the potential energy surface matters less and less and distinctions between species become less obvious. If two species re-equilibrate almost instantly after some perturbation (a reaction), one could argue that the two are effectively a single species. From general chemistry courses we are familiar with the pre-equilibrium mechanism, where the

$$A \xrightarrow{\text{fast}} B \xrightarrow{\text{slow}} C \tag{3.50}$$

reaction system yields a single phenomenogical $A \longrightarrow C$ rate coefficient if the $A \rightleftharpoons B$ equilibrium is fast and favours A. One might ask if it would be better to view A and B as a single species. In case of rotamers, master equation modellers intuitively know to combine the different "species" into a single one. One ME code, MESS, has a feature that allows the users to merge wells as needed.⁵³

Our experience with the BW-analysis is that it is quite robust and often works even after IEREs and CSEs begin to converge, at least for the important rate coefficients (those that affect the time-evolution of the system the most). Figure 16 shows that BW-analysis still gives the correct result even at 4500 K for the propargyl + O₂ system (see reactions R1 and R2 or Fig. 27 for details about the reaction mechanism). The high-temperature kinetics of the system is determined by the well-skipping $C_3H_3^{\bullet} + O_2 \longrightarrow HCO^{\bullet} + C_2H_2O$ reaction, and in the figure one can see that the rate coefficient for this reaction is $k = -\lambda_1/[O_2]$. Manual inspection of high-temperature $C_3H_3^{\bullet}$ -traces confirms that they are single-exponential, with λ_1 giving the time constant of decay.

To further investigate the issue, I have compared the phenomenological evolution predicted by the BW rate coefficients to the direct results of a ME simulation. All of the population at time zero was placed on one of the peroxyl adducts, Int1p. These results are plotted in Fig. 17. The results confirm many of the observations made in the previous paragraph. At 400 K and when the initial conditions are Boltzmann, the BW- and ME-time-evolutions are in perfect agreement. This is expected since CSEs and IEREs are well-separated. Even when seriously non-equilibrium initial conditions are set, a Boltzmann distribution that corresponds to T = 1000 K, the long-term behaviour of the system remains unchanged. Note that BW rate coefficients are independent of initial conditions (that is the whole point!) and so cannot capture short-time behaviour caused by non-equilibrium initial conditions. As mentioned in the last paragraph, the BW rate coefficients predict the correct behaviour even at 4500 K, long after two of the three CSEs have converged with IERES. However, one cannot confidently say that this means that *all* the rate coefficients are valid, it may be the case that just a few of kinetically important ones are. In fact, the disagreement at short time-scales perhaps indicates that some of the BW rate coefficients are not valid. The steady-state concentrations are correctly predicted, but this could just be a consequence of the matrices M and K_r obeying detailed balance. That said, these matrices are guaranteed to obey detailed balance only for conservative systems (no sinks); no such guarantee exists for non-conservative systems (like the one studied here).¹

The BW-analysis is useful because it provides a way to compare experimental and ME results. Experimentalists typically report rate coefficients (not kinetic traces). However, sometimes a rate coefficient description of a system is difficult to define (either experimentally or through the ME), and in these cases the only option left is to compare experimental and modelled traces. In many ways, this is actually desirable, as a more dir-

ect comparison with experiments and computations is performed. This also obviates the need for the experimentalist to come up with a kinetic mechanism from which a suitable fitting function can be derived.

Recently, a trace fitting feature has been implemented in MESMER.³⁷ This provides a very convenient way of doing global parameter fitting. It permits the use of experimental data in parameter optimisation under conditions where the BW-analysis has begun to fail. There are also other advantages. In the past, we have had problems in simultaneously fitting well-depths and $\langle \Delta E \rangle_{\rm down}$ parameters since these are very often coupled. Increasing one can be compensated by lowering the other. This can lead to looping behaviour that yields unphysical results. This problem is avoided with trace fitting if the traces contain information about equilibrium concentrations, which are independent of collisional energy transfer parameters, but quite sensitive to well-depths. The error function that is minimised in trace fitting is

$$\chi^{2} = \sum_{i=1}^{n} w_{i} \sum_{j=1}^{m_{i}} \left(\frac{y_{ij,\exp}(t,p,T) - y_{ij,\text{ME}}(t,p,T)}{\sigma_{ij}} \right)^{2} , \qquad (3.51)$$

where $y_{ij}(t, p, T)$ is *j*th point of trace *i* at time *t*, w_i is the weight given to trace *i*, *n* is the number of traces, and m_i is the number of points in trace *i*. The error σ_{ij} associated with each trace point is assumed to be constant if it is not known. The weights w_i that should be given for each traces are usually not known and MESMER can be used to approximate them from

$$w_i = \frac{1/s_i^2}{\frac{1}{n}\sum_{j=1}^{n} 1/s_j^2},$$
(3.52)

where s_i is obtained from an unweighted fit and is defined as

$$s_i^2 = \frac{1}{m_i - 1} \sum_{j=1}^{m_i} \left(y_{ij,\text{exp}}(t, p, T) - y_{ij,\text{ME}}(t, p, T) \right)^2 \,. \tag{3.53}$$

Weights defined this way reduce contributions from noisy and/or outlier data.

The difference between traditional rate coefficient and trace fitting workflows is outlined in Fig. 18.



Figure 16: IEREs, CSEs, and Bartis-Widom rate coefficients plotted as a function of temperature for the propargyl + O_2 system at p = 1 bar and $[O_2] = 1 \cdot 10^{15}$ cm⁻³. The dark yellow line terminates abruptly because the rate coefficient became negative at low temperatures due to numerical problems. Unpublished results

Solid lines: master equation with Boltzmann distribution T = 400 K initial conditions Dashed lines: master equation with Boltzmann distribution T = 1000 K initial conditions Squares: Bartis-Widom phenomenological evolution



Solid lines: master equation with Boltzmann distribution T = 4500 K initial conditions Squares: Bartis-Widom phenomenological evolution



Figure 17: The Bartis-Widom and ME time-evolution compared for the propargyl + O_2 system at p = 1 bar and $[O_2] = 1 \cdot 10^{15}$ cm⁻³. The upper figure also shows how changing the initial distribution affects the results. Unpublished results



Figure 18: Algorithms for rate coefficient (A) and trace (B) fitting. Taken from Medeiros et al. with permission. 37

3.7 Summary of Quantum Chemical Computations

This section outlines how the quantum chemical computations presented in the articles were performed. The focus is on which methods were used and why; the theoretical underpinnings of the methods will not be discussed to limit the scope of the thesis. All the calculations were performed with publicly available codes, Gaussian and ORCA.^{54,55} The aim of the calculations was to obtain chemically accurate ($\sim 4 \text{ kJ mol}^{-1}$) relative energies at a reasonable cost. Typical wall times of the most expensive computations were 2–3 days with around 30 cores.

Nearly all of the studied species are too large to be optimised with high-level wave function methods, so density-functional theory (DFT) was used instead. The functional and basis set we opted to use were MN15 and Def2TZVP, respectively.^{56,57} We felt this was a reasonable compromise between accuracy and cost. The MN15/Def2TZVP method was also used to obtain harmonic frequencies and evaluate one-dimensional hindered rotor potentials. The harmonic frequencies were scaled by 0.979 to approximately account for anharmonic effects.⁵⁸ Single-point energies were mostly calculated with the coupled cluster method with single-, double-, and perturbative triple-excitations using a restricted open-shell Hartee-Fock reference wave function (ROHF-CCSD(T)).⁵⁹ The correlation consistent cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets were used in these calculations.⁶⁰ HF energies were extrapolated to the complete basis set (CBS) limit using a three-parameter exponential function,

$$E_{\rm HF}(X) = E_{\rm HF,\infty} + B_{\rm HF} e^{-\alpha_{\rm HF} X} . \qquad (3.54)$$

Here X = 2, X = 3, or X = 4 are for the cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets, respectively.⁶¹ The CBS limit of the slower converging correlation energy was estimated using a power function⁶²

$$E_{\rm corr}(X) = E_{\rm corr,\infty} + B_{\rm corr} X^{-\alpha_{\rm corr}} .$$
(3.55)

The parameters α , B, and E_{∞} are obtained in both cases by solving a system of three equations. For some of the larger systems (more than six heavy atoms), ROHF-CCSD(T) calculations were prohibitively expensive. In these cases we used the more approximate ROHF-DLPNO-CCSD(T) method that is implemented in ORCA.^{63,64}

For some species there were reasons to suspect that single-reference treatments were not suitable (high T1 diagnostic values, 65 for example), and in these cases we also performed complete active space perturbation theory (CASPT2) calculations. The CBS CASPT2 energy *differences* were estimated using the formula 66

$$\Delta E_{\rm inf} = \Delta E_{\rm cc-pVQZ} - \left(\Delta E_{\rm cc-pVTZ} - \Delta E_{\rm cc-pVQZ}\right) \frac{4^4}{5^4 - 4^4} \,. \tag{3.56}$$

A different extrapolation scheme had to be used in the multi-reference calculations as there are no HF or correlation energies.

ROHF wave functions were used because many of the key transition structures were spin contaminated with unrestricted methods. Examples of this are given in the supplemental material of (IV). For species in which spin contamination was not an issue, UHF- and ROHF-CCSD(T) calculations generally agreed to within two kJ mol⁻¹. In (IV) ROHF-CCSD(T) and ROHF-DLPNO-CCSD(T) energies were also compared. The energies usually agreed to within four kJ mol⁻¹, but only for species that do not exhibit multi-reference character. Thus, we expect the ROHF-DLPNO-CCSD(T) energies to be reliable for the larger species we have studied, provided that they are well-described by single-reference treatments.

4 Results and Discussion

4.1 Trace Fitting

Since trace fitting is a relatively recent feature, we decided to test whether it and the more traditional rate coefficient fitting give equivalent results for a simple system. We did the test for the 2-methylallyl + O_2 reaction (**IV**). The potential energy profile for the reaction is presented in Fig. 19. Although the system looks fairly complex, the



Figure 19: Potential energy profile for the 2-methylallyl + O_2 reaction. The energies are in kJ mol⁻¹ (ROHF-CCSD(T)/CBS//MN15/Def2TZVP or CASPT2/CBS//MN15/Def2TZVP). Figure taken from (**IV**).

barriers are sufficiently high that under our experimental conditions we only observe the initial recombination reaction and its redissociation back to reactants. Thus, the reaction mechanism simplifies to

$$C_{4}H_{7}^{\bullet} + O_{2} \xrightarrow[k_{b}]{k_{b}} C_{4}H_{7}O^{\bullet}$$

$$C_{4}H_{7}^{\bullet} \xrightarrow[k_{w1}]{k_{w1}} \text{ wall}$$

$$C_{4}H_{7}O_{2}^{\bullet} \xrightarrow[k_{w2}]{k_{w2}} \text{ wall} .$$

Here the rate coefficients $k_{\rm f}$, $k_{\rm b}$, and $k_{\rm w2}$ can be obtained from double-exponential fits to traces³⁵ and $k_{\rm w1}$ was measured separately. In the ME-fits, single-exponential down and ILT parameters were fitted simultaneously with the well-depth of C₄H₇O₂[•]. The fitting results with the rate coefficient and trace approaches are reported in Table. 3.

As one can see, very consistent results are obtained. All of the optimised well-depths are close to the computed value of $-81.12 \text{ kJ mol}^{-1}$ and are within computational uncertainties. The only parameter that shows some disagreement is the Arrhenius pre-factor, which in our case is the canonical recombination rate coefficient at 300 K. However, we

are trying to obtain the canonical rate coefficient from low-pressure data, so some uncertainty is expected. That said, when the fall-off curve of the recombination rate coefficient is plotted, the trace values for A appear more reasonable. The fall-off curve is shown in Fig. 21. This figure also shows the experimental equilibrium constant plotted together with those obtained from computations and fitting. Figure 20 gives examples of measured and modelled traces.

Table 3: Optimised master equation model parameters using different fitting approaches. The reported errors are standard errors (1σ) .

Parameter	Rate Coefficient Fit	Unweighted Trace Fit	Weighted Trace Fit
$A (10^{-12} \text{ cm}^3 \text{ s}^{-1})$	1.95 ± 0.06	2.46 ± 0.44	2.42 ± 0.35
m	-0.727 ± 0.086	-0.351 ± 0.387	-0.387 ± 0.318
$\langle \Delta E \rangle_{\rm down, 300 \ K}^{\rm (He)} \ (\rm cm^{-1})$	146 ± 3	139 ± 10	144 ± 11
n	0.0746 ± 0.1131	0.100 ± 0.216	0.0235 ± 0.363
$\Delta_{\rm r} H_0^{\ominus} ~({\rm kJ~mol^{-1}})$	$-79.75^{\rm a} \pm 0.11$	-79.44 ± 0.05	-79.51 ± 0.09
$\langle \Delta E \rangle_{ m down,300~K}^{ m (N_2)}$ (cm ⁻¹)	353 ± 7	339 ± 45	336 ± 57
^a Fixed to the third-law analysi	s value (see V).		



Figure 20: Examples of measured (symbols) and simulated (lines) kinetic traces for the 2-methylallyl + O_2 reaction. Figure taken from (IV).



Figure 21: (a): Fall-off curves for the 2-methylallyl + O_2 reaction calculated using three different sets of optimised parameters obtained from rate coefficient fitting or trace fitting with or without weighting. The results are shown alongside the experimental results. (b): The equilibrium constant of the $CH_2C(CH_3)CH_2^{\bullet} + O_2 \rightleftharpoons CH_2C(CH_3)CH_2OO^{\bullet}$ reaction plotted as a function of temperature with four different $\Delta_r H_0^{\ominus}$ values. The results are shown alongside the experimental results. The bath gas is helium in all experiments and simulations. Figures taken from (IV).

4.2 Reactions of Allylic Radicals with Oxygen Molecules

Allyl is the simplest RSHR encountered in combustion and it reacts very slowly with O_2 at high temperatures $(4.2 \cdot 10^{-19} \text{ cm}^3 \text{ s}^{-1})$.¹³ Four-carbon allylic radicals also appear to react very slowly (**IV**,⁶⁷). Interestingly, Baldwin et al.¹⁴ have observed faster reactivity for five-carbon allylic radicals. This is an important finding because pentenes are often used as surrogate fuels to mimic the behaviour of alkenes present in real fuels. However, they performed their measurements quite long ago, at a single temperature, and there has been no experimental or computational work to corroborate their findings. In fact, our computations in a relatively recent study (**X**) predicted relatively low reactivity for 3-ethylallyl (CH₂=CH=CH-CH₂-CH₃). Since then, we have performed high-temperature experiments for three five-carbon allylic radicals,

$$CH_2 = CH = CH - CH_2 - CH_3 + O_2 \tag{4.1}$$

$$CH_3 - CH = CH = CH - CH_3 + O_2 \tag{4.2}$$

$$CH_2 = CH = C(CH_3)_2 + O_2$$
, (4.3)

(3-ethylallyl, 1,3-dimethylallyl, and 1,1-dimethylallyl, III, V, XII) and measured rate coefficients very similar to those obtained by Baldwin et al.¹⁴ The key to their relatively high reactivity is that the conjugate-alkene-channel $(R^{\bullet} + O_2 \longrightarrow R_{-H} + HO_2^{\bullet})$ does in fact form a conjugated diene! Conjugated dienes are more stable than regular alkenes because of delocalisation between the π -bonds (resonance stabilisation). This additional stabilisation is, to a degree, present in the formally-direct transition state, thus lowering its energy relative to the peroxyl adduct. The $R^{\bullet} + O_2 \longrightarrow R_{-H} + HO_2^{\bullet}$ reaction is called formally-direct because the abstraction of H and dissociation of HO_2^{\bullet} happens simultaneously; there is no $R_{-H}OOH$ intermediate. The five-carbon allylic systems also have slightly deeper RO_2^{\bullet} wells than allyl (~ 10 kJ mol⁻¹ deeper), and the alkyl-substituent effects that make the wells deeper also lowers the energy of the formally-direct TS with respect to the energy of the separated reactants. The formally-direct TSs end up being just 5 - 20 kJ mol⁻¹ above the energy of the reactants. The conjugate-alkene channel is not present in allyl and 2-methylallyl, which likely explains their low reactivity at high temperatures. For 1-methylallyl it is present, so it is a bit perplexing that Knyazev and Slagle did not see any reactivity at high temperatures.⁶⁷ A possible explanation for this is that the formally-direct TS's energy is very sensitive to structural effects and removing a methyl group may substantially increase the barrier height.

The expected high-temperature products, the conjugated dienes, were observed in all of our experiments. Unfortunately, photolysis of the brominated precursors also form the dienes, so it was hard to confirm that the formation rates of these dienes matched the decay rate of the radicals. It also appears that they are formed though some secondary chemistry. When we measured diene signals in the absence of O_2 , we still observed a steadily raising signal. However, the diene signals were quantitatively different in the presence of O_2 , so we are quite confident that the studied reactions produce them.

We had some trouble computing barrier heights for the conjugate-alkene channels that were consistent with experiment. ROFH-CCSD(T) and ROHF-DLPNO-CCSD(T) regularly predicted barriers above 20 kJ mol⁻¹, which are too high. Interestingly, the T1 diagnostic values were quite acceptable for the transition structures, around 0.03, but it is our understanding that the common T1 diagnostic thresholds that are used to assess the multi-reference character of open-shell species cannot always be trusted.⁶⁸ CASPT2(13,11)/CBS// MN15/Def2TZVP calculations gave barrier heights that were more consistent with experiment, though we are fully aware that CASPT2 cannot be relied upon to obtain energies within chemical accuracy ($\sim 4 \text{ kJ mol}^{-1}$). In the end, we optimised the barrier heights with the trace fitting feature in MESMER, and the fitted and CASPT2 values ended up being in pretty close agreement. An example potential energy profile of these allylic systems is shown for 1,3-dimethylallyl in Fig. 22. The essential features of the profile are the same for 3-ethylallyl and 1,1-dimethylallyl. In Table 4 the fitted parameters are tabulated for comparison purposes. Figures 23 and 24 show the low-temperature fall-off curves and high-temperature reactivity, respectively.



Figure 22: Potential energy profile for the 1,3-dimethylallyl + O_2 reaction. The energies are in kJ mol⁻¹. Figure taken from (V).

The canonical recombination rate coefficient is the largest for 1,3-dimethylallyl, slightly smaller for 1,1-dimethylallyl and 3-ethylallyl, still smaller for 2-methylallyl, and much smaller for allyl. This is consistent with what we have seen in our experimental studies. Namely, that alkyl-substitution next to a radical centre tends to increase reactivity, but the effect is subject to diminishing returns. That is to say, the reactivity enhancing effect of substituting a hydrogen of an unsubstituted carbon-centred radical with a methyl is greater than making such a substitution to an already substituted carboncentred radical. This can be seen here with 1,3-dimethylallyl (both radical centres singly substituted) reacting faster than 1,1-dimethyallyl (one centre unsubstituted, the other doubly substituted). At higher temperatures, it is not easy to explain the results in terms of structure-reactivity relationships. What is clear is that the reactivity is governed by the relative energy of the formally-direct TS, but it is harder to say why the relative energy of this TS is the lowest for 1,1-dimethylallyl and highest for 1,3-dimethylallyl. 2-Methylallyl has much lower high-temperature reactivity than the five-carbon species because the conjugate-alkene channel is not present there. Note that the high-temperature rate coefficient for 2-methylally is only a computational prediction. We were experiment-

Parameter	2-methylallyl	3-ethylallyl	1,3-dimethylallyl	1,1-dimethylally	
10 9 1.					
$A_1 \ (10^{-12} \ {\rm cm}^3 \ {\rm s}^{-1})^{\rm a}$	2.42	1.96	3.30	2.34	
m_1	-0.387	-1.15	-1.38	-1.04	
$A_2 \ (10^{-12} \ {\rm cm}^3 \ {\rm s}^{-1})$		0.515	1.59	1.17	
m_2		-0.786	-0.539	-1.06	
$\langle \Delta E \rangle_{\text{derm 200 K}}^{(\text{He})}$ (cm ⁻¹)	144	131	164	166	
	0.0235	0.382	0.362	0.100	
$\Delta_{\rm r} H_0^{\ominus} ~({\rm kJ~mol}^{-1}) ({\rm RO}_2^{\bullet})^{\rm b}$	-79.51 (-81.12)	-80.67 (-79.19)	-83.08 (-79.91)	-81.59 (-84.60)	
$\Delta_{\rm r} H_0^{\ominus} ({\rm kJ \ mol}^{-1}) ({\rm TS})^{\circ}$		11.76 (9.444)	13.42 (10.84)	4.979 (14.18)	
$\langle \Delta E \rangle^{(N_2)}_{\text{down 300 K}} (\text{cm}^{-1})$	336	300	330		

Table 4: Optimised master equation model parameters using trace fitting approaches. The values in brackets for the energies are computed results.

^a Because there are multiple barrierless $\mathbb{R}^{\bullet} + \mathcal{O}_2 \longrightarrow \mathbb{RO}_2^{\bullet}$ channels, multiple ILT expressions had to be used. ^b In case of multiple \mathbb{RO}^{\bullet} adducts, the deepest well was fitted, but so that the energy differences between the \mathbb{RO}^{\bullet} wells were fixed to the computed value.

^c Same as above, but for the formally-direct transition structures.



Figure 23: Fall-off curves for allylic radical + O_2 reactions.^{10,69,70} Figure taken from (V).

ally unable to see any reactivity at 700 K, which means that the high-temperature rate coefficient must be smaller than 10^{-16} cm³ s⁻¹.

We have frequently observed for hydrocarbon radical + O₂ systems that there is eigenvalue "hopping". Klippenstein and co-workers have published articles about this about twenty years ago, ^{15,16} but it has not received much attention since then. What happens is that at low temperatures there is a one-to-one correspondence with the largest (in magnitude) CSE and the observed rate coefficient ($k = -\lambda_{\text{largestCSE}}/[O_2]$), but at high temperatures the correspondence is with the smallest (in magnitude) CSE ($k = -\lambda_{\text{smallestCSE}}/[O_2]$).



Figure 24: High-temperature rate coefficients of allylic radical + O_2 reactions.¹⁴ Figure taken from (**V**).

The rate coefficient, in a sense, hops from one eigencurve to another. This behaviour is shown Fig. 25. However, the rate coefficients describe very different things. At low temperatures, the rate coefficient describes the $R + O_2 \longrightarrow RO_2^{\bullet}$ recombination reaction, whereas at high temperatures it describes the phenomenological $R^{\bullet} + O_2 \longrightarrow R_{-H} + HO_2^{\bullet}$ conjugate-alkene-forming reaction. In between cold and high temperatures, there is region of avoided crossing where multi-exponential behaviour $(R + O_2 \rightleftharpoons RO_2^{\bullet} equilibrium)$ is observed and the rate coefficient cannot be simply assigned to an eigenvalue. The width of this region is pressure dependent; it gets smaller as pressure is decreased and eventually vanishes completely. The location of the region depends on $[O_2]$. This is because the equilibrium fraction of RO_2^{\bullet} is dependent on $[O_2]$ and using larger concentrations pushes the equilibration zone to higher temperatures. We have also observed that in these systems BW rate coefficients, at least the important ones, appear to remain valid even after the order-of-magnitude separation between CSEs and IEREs ceases to exist. We have tested this by assuming pre-equilibrium conditions for RO_2^{\bullet} and then using the BW rate coefficients to compute a phenomenological $\mathbb{R}^{\bullet} + \mathbb{O}_2 \longrightarrow \mathbb{R}_{-H} + \mathbb{HO}_2^{\bullet}$ rate coefficient. It turns out the rate coefficient calculated this way is almost exactly equal to $-\lambda_{\text{smallestCSE}}/[O_2]$ (see \mathbf{V}). Perhaps the reason for this is simply that the BW-analysis remains valid because the CSEs never cross (at least below 1500 K) with the IEREs, not even at 10^{-5} bar (see Fig. 25). Given that a single eigenvalue determines the high-temperature kinetics, one could argue that the system has effectively been reduced to a single well, with the



intermediate wells having merged with that of the reactants.

Figure 25: CSEs plotted as a function of temperature and pressure for the 3-ethylallyl system. Figures taken from (III).

Another interesting feature in these reactions is that the high-temperature rate coefficient is pressure-independent (this is also illustrated in Fig. 25). Klippenstein and co-workers have discussed the reasons behind this as well.¹⁶ As temperature is increased, the peroxyl adduct begins to approach what Klippenstein calls its stabilisation limit (see Fig. 26). At the stabilisation limit, a significant chunk of the peroxyl's Boltzmann population is above the reaction threshold(s). Once this happens, collisions continuously try to repopulate the reactive states that are depleted by reactions to re-establish a Boltzmann distribution. So although increasing pressure will increase collisional relaxation from reactive states, there will be a compensating increase in the rate at which reactive states are repopulated. As can be seen from Fig. 26, at the stabilisation limit activating collisions start to become as likely as deactivating ones.

From the point of view of combustion modelling, the emergence of a pressure-independent rate coefficient that is easily obtained from the smallest CSE is very useful. To model the reactivity of, say, 1,3-dimethylallyl, one only needs to plot $-\lambda_{\text{smallestCSE}}/[O_2]$ as a function of temperature and then fit a modified Arrhenius expression to the result. If there are multiple product channels, the expression can simply be multiplied with the branching ratio of each channel to obtain channel-specific rate coefficients. The only drawback with this approach, from what I can tell, is that the user needs to know if he/she is working in the post-avoided-crossing (post-equilibrium) region. This condition should be frequently fulfilled in combustion systems. The simplification this approach provides is obvious. The number of BW coefficients grows rapidly with system size (there is a BW rate coefficient from each well to the other wells and sinks), and it is not realistic to provide a pressuredependent parameterisation of each of them to combustion modellers. The number of reactions they can accommodate is quite limited in models that fully couple chemistry with continuum-mechanics. The results we have obtained suggest that it is often sufficient to give a few Arrhenius expressions. For the allylic systems studied in this thesis, these expressions are given in Table 5.

	Fable	5:	Modif	ied Ar	rhenius	paramet	ers for	the p	roduct	chanr	nels	of the a	llylic	systems
S	tudie	d ii	n this	thesis.	Note	that the	expon	ential	param	eter is	s in	calories	See	articles
(III),	$(\mathbf{V}$), and	(\mathbf{XII})	about	the detail	ls of th	e diffe	erent pr	oduct	cha	annels.		

$k(T) = AT^m \mathrm{e}^{-E'_{\mathrm{a}}/RT}$									
Reaction	$A~(\mathrm{cm^3~s^{-1}})$	m	$E'_{\rm a} \ ({\rm cal} \ {\rm mol}^{-1})$						
3-ethylallyl									
$R \longrightarrow P1E$	$1.72 \cdot 10^{-18}$	1.26	2360						
$R \longrightarrow P1Z$	$4.36 \cdot 10^{-19}$	1.41	3280						
$R \longrightarrow P2$	$2.93\cdot 10^{-27}$	3.41	-3490						
	1,3-dimethy	lallyl							
$R \longrightarrow P1E$	$1.66 \cdot 10^{-18}$	1.26	3030						
$R \longrightarrow P1Z$	$2.88 \cdot 10^{-18}$	1.22	3710						
$R \longrightarrow P2RR$	$1.02 \cdot 10^{-29}$	4.02	-2500						
$R \longrightarrow P2SR$	$5.27 \cdot 10^{-30}$	4.08	-1750						
	1,1-dimethy	lallyl							
$R \longrightarrow P1$	$1.46 \cdot 10^{-19}$	1.71	780						
$R \longrightarrow P3$	$2.09 \cdot 10^{-28}$	3.76	-2530						
$R \longrightarrow P4$	$3.56 \cdot 10^{-18}$	0.79	7020						
$R \longrightarrow P6$	$3.18 \cdot 10^{-18}$	0.77	5510						



Figure 26: The stabilisation limit for 1,3-dimethyallylperoxyl (Int1E, $C_5H_9O_2^{\bullet}$). R here refers to the separated reactants, whose zero-kelvin enthalpy is set to zero, and ts1EP1E refers to the formally-direct transition state. Figure taken from (**V**)

4.3 Reactions of Propargylic Radicals with Oxygen Molecules

I present here results for the two propargylic radicals studied in this thesis (1- and 3methylpropargyl, II and I) and some unpublished data for propargyl and 3-ethylpropargyl. For propargyl, we have only performed computations. The experimental data we use for fitting is from Slagle and Gutman and Atkinson and Hudgens.^{12,71} Since the publication of articles (I) and (II), trace fitting was introduced in MESMER, which makes a global fit of these results easier and less arbitrary. Several bug-fixes have also been implemented in MESMER since the publication of the articles that will have a small effect on the results. To make the comparisons between the propargylic radicals as consistent as possible, I have refitted the results in (I) and (II) with the most recent MESMER version. Therefore, there might be some very small differences in the values reported here and in the publications. A publication is being prepared where the four propargylic radicals are systematically studied. A potential energy profile for the 1-methylpropargyl $+ O_2$ reaction is shown in Fig. 27. The essential features of the profile are the same for all propargylic radicals. One of the products shown in profile, methylketene, was observed in the experiments and its formation rates matched the decay rate of 1-methylpropargyl. The equivalent product was observed in the other systems. The other product, a formylic (methanoylic) species, reacts instantly⁷² with O₂ upon formation under our high-[O₂] conditions and so cannot be detected. I have considered more product channels in my calculations than those shown in the profile, particularly for propargyl, but these channels are kinetically irrelevant, especially under the conditions of our experiments.



Figure 27: Potential energy profile for the 1-methylpropargyl + O_2 reaction. The energies are in kJ mol⁻¹. Figure taken from (II).

The experimental and computational results for the propargylic systems are listed in Table 6 and displayed graphically in Fig. 29. As demonstrated by Moradi et al., addition to the CH₂-end of propargyl is barrierless, whereas addition to the H $-C\equiv$ -end appears to have a small barrier. These findings are consistent with our experiments. Therefore, we have used ILT and conventional TST to get the TS state sums for the CH₂- and H $-C\equiv$ -additions,

respectively. The trace fits yield fairly consistent parameters for the studied systems. The value of $\langle \Delta E \rangle_{\rm down,300~K}$ increases with radical size for both He and N₂, which is as one would expect. Interestingly, 1-methylpropargyl has a slightly smaller $\langle \Delta E \rangle_{\rm down,300~K}^{\rm (He)}$ value than 3-methylpropargyl. However, since 1-methylpropargyl has a larger canonical recombination rate coefficient (at least according to the fits), the fall-off curves for 1- and 3-methylpropargyl end up crossing. The order makes sense at the high-pressure limit. In 1-methylpropargyl the methyl group is next to the dominant radical centre, so I would except it to be more reactive than 3-methylpropargyl. It is not clear, though, as to why collisional energy transfer should be more efficient for 3-methylpropargyl. There are some obvious differences in the structures; the methyl group rotation is free in 3-methylpropargyl, but hindered by about 10 kJ mol⁻¹ in 1-methylpropargyl, 3-methylpropargyl is effectively linear, 1-methylpropargyl is not. That said, it is hard to know if any of these factors are directly linked to collisional energy transfer. Definite answers require running trajectories.

Table 6: Optimised master equation model parameters using trace fitting approaches. The values in brackets for the energies are computed results.

Parameter	Propargyl	1-Methylpropargyl	3-Methylpropargyl	3-Ethylpropargyl	
$A (10^{-13} \text{ cm}^3 \text{ s}^{-1})^{\text{a}}$	1.98	12.2	7.27	12.1	
m	-1.33	-1.29	-1.44	-1.44	
$\langle \Delta E \rangle^{(\text{He})}$ (cm ⁻¹)	87.2	127	137	178	
(D/down,300 K (Chi)	0.01.2	0.201	101	110	
n	0.812	0.301	0	0	
$\Delta_{\rm r} H_0^{\ominus}$ (kJ mol ⁻¹)(Int1p)	-72.91 (-75.48)	-79.80 (-84.14)	-75.08 (-78.43)	-78.41 (-78.90)	
$\Delta_{\rm r} H_0^{\ominus}$ (kJ mol ⁻¹)(ts01a)	3.601(12.78)	2.097(7.989)	2.796(7.679)	2.831(5.464)	
$\Delta_{\rm r} H_0^{\bigotimes}$ (kJ mol ⁻¹)(ts12a) ^a	7.275 (9.260)	2.437 (3.836)	0.4230 (1.460)	-12.83 (-0.3761)	
$\langle \Delta E \rangle_{\text{down,300 K}}^{(N_2)}$ (cm ⁻¹)	206	260	283	247	

a In case of multiple ts12a transition structures, the lower energy one was fitted and the energy difference held fixed to the computed value.

The canonical recombination rate coefficient is much smaller for propargyl than for any of the alkyl-substituted propargyls. This is very similar to the behaviour of allyl in the allylic systems and shows how big an effect simple methyl-substitution can have on rate coefficients.

As to the high-temperature reactivity, it appears to be mainly determined by the value of the latter TS (ts12a) and to a smaller degree by t01a. All the fitted energies are in good agreement with ROHF-CCSD(T)/CBS//MN15/Def2TZVP values, which is a bit surprising, given that many of the transition structures exhibited multi-reference character. For example, for ts12a we noticed that our Hartree-Fock calculations often converged to a different solution if we used a different initial guess. For ts01a, the MN15 functional was not able to find the correct transition structure and we used M08HX instead to locate it. The T1 diagnostics were also relatively large, above 0.03. Furthermore, when we tried to employ unrestricted wave-function methods, both of these transition structures had huge spin contaminations. The fitted energy for ts12a in 3-ethylpropargyl + O₂ differs quite significantly from the calculated value and we need to double-check the fit. Our experience has been that changing the initial guesses can lead to different results. When multiple parameters are simultaneously fit, there is no guarantee one obtains the global minimum. Thus, it is advisable to try different sets of initial guesses. If some parameters are known relatively well, like well-depths, it can help if these are fixed in initial fitting runs and only the more uncertain parameters are floated. The well-depths can be included in later runs after one has obtained reasonable values for the other parameters.

Like for the allylic systems, we notice that a pressure-independent rate coefficient with weak, positive temperature dependence arises at higher temperatures for the propargylic systems. The reasons for this are the same as for the allylic systems, so the discussion will not be repeated here. A comparison of the CSE plots shown in figures 25 and 28 show that they are qualitatively the same. It is interesting that the same behaviour emerges even though the mechanisms are different. It may well be this behaviour is encountered quite frequently and master equation modellers should expend some effort to analyse the CSE-curves and check if single-exponential behaviour re-emerges at elevated temperatures. As mentioned in the previous section, surprisingly simple rate coefficient descriptions can be extracted.



Figure 28: CSEs plotted as a function of temperature and pressure for the propargyl + O_2 system. The experiments are by Slagle and Gutman and Atkinson and Hudgens.^{12,71} The ME simulations are unpublished results.



Figure 29: The rate coefficients for the reactions between propargylic radicals and oxygen molecules as a function of temperature and pressure. The measurements for propargyl are by Slagle and Gutman and Atkinson and Hudgens.^{12,71}

5 Conclusions

Laser-photolysis photoionisation mass spectrometry has been used to study reactions between resonance-stabilised hydrocarbon radicals and oxygen molecules. Both propargylic and allylic radicals have been studied and interesting structure-relationships have been observed. Most of the reactions have not been studied before, at least not extensively as a function of temperature and pressure, but where previous measurements exist, they are in reasonably good agreement with the present results (within a factor of two). The experimental work was complemented with quantum chemical calculations and master equation simulations. A particular focus of the work was to synergistically combine experiments and computations to compensate for the shortcomings of the other. The experiments were used to fix collisional energy transfer parameters, obtain state sums for barrierless reactions, and to adjust energies of key transition states if needed. The recently introduced trace fitting was employed and compared with good success to a more traditional fitting approach. After parameter optimisation, the master equation models were able to reproduce experimental findings and, presumably, extrapolate well to conditions relevant to practical application. The modelling work was also informative in rationalising the experimental findings.

It was found during the studies for each reaction that a phenomenological rate coefficient arises at high temperatures that is independent of pressure and has weak, positive temperature dependence. This behaviour is opposite to the low-temperature $R + O_2^{\bullet} \longrightarrow RO_2^{\bullet}$ recombination rate coefficients, which all exhibit negative temperature dependence and are pressure dependent. In these reactions, the high-temperature reactivity is governed by a single eigenvalue (the least negative one). This eigenvalue can be used to obtain simple phenomenological expressions for the different product channels and there is no need to provide pressure-dependent Bartis-Widom rate coefficients for all of the elementary steps. However, many of the Bartis-Widom rate coefficients appear to be valid at high temperatures, even after chemically significant eigenvalues begin to converge with the internal energy relaxational eigenvalues.

Except for 2-methylallyl, all the radicals react fairly fast with O₂ at elevated temperatures. The phenomenological rate coefficients for the five-carbon allylic radicals are in the range $5 \cdot 10^{-16} - 2 \cdot 10^{-14}$ cm³ s⁻¹ and the propargylic ones in the range $2 \cdot 10^{-15} - 4 \cdot 10^{-14}$ cm³ s⁻¹. Thus, the oxygen reactions constitute of major sink of these radicals in combustion systems. It is certainly incorrect to assume that larger allylic radicals are as unreactive as plain allyl (C₃H₅•).

Finally, high-quality experiments have been performed and the results are suitable for benchmarking purposes.

A Derivation of the TST Rate Coefficient¹

A.1 The Microcanonical Rate Coefficient

The number of phase space points in the reactant region, $N_{\rm R}$, can be obtained by integrating the density of phase space points $\xi(\boldsymbol{\Gamma}, t)$ over the phase space of the reactant,

$$N_{\rm R} = \int \xi(\boldsymbol{\Gamma}, t) \mathrm{d}\boldsymbol{\Gamma} \;. \tag{A.1}$$

Here $d\boldsymbol{\Gamma} = d\boldsymbol{q}d\boldsymbol{p}$. Differentiating this with respect to time and using the continuity equation

$$\frac{\partial \xi(\boldsymbol{\Gamma}, t)}{\partial t} = -\boldsymbol{\nabla} \cdot \xi(\boldsymbol{\Gamma}, t) \dot{\boldsymbol{q}}$$
(A.2)

gives

$$-\frac{\mathrm{d}N_{\mathrm{R}}}{\mathrm{d}t} = -\int \frac{\partial \xi(\boldsymbol{\Gamma}, t)}{\partial t} \mathrm{d}\boldsymbol{\Gamma} -\frac{\mathrm{d}N_{\mathrm{R}}}{\mathrm{d}t} = \int \boldsymbol{\nabla} \cdot \xi(\boldsymbol{\Gamma}, t) \dot{\boldsymbol{q}} \mathrm{d}\boldsymbol{\Gamma} .$$
(A.3)

Applying Gauss's theorem yields the flux expression

$$-\frac{\mathrm{d}N_{\mathrm{R}}}{\mathrm{d}t} = \int \xi(\boldsymbol{\Gamma}, t) \dot{\boldsymbol{q}} \cdot \boldsymbol{n} \mathrm{d}\boldsymbol{S} , \qquad (A.4)$$

where S is some arbitrary dividing surface (a transition state) that separates the reactants and the products and n is a unit vector normal to this surface. If the dividing surface is defined by the function f(q), then a vector normal to this is given by $\nabla f(q)$, so the equality above can be expressed as

$$-\frac{\mathrm{d}N_{\mathrm{R}}}{\mathrm{d}t} = \int \xi(\boldsymbol{\Gamma}, t)\delta(f(\boldsymbol{q}) - q_{\mathrm{rc}})(\boldsymbol{\nabla}f(\boldsymbol{q}) \cdot \dot{\boldsymbol{q}})\mathrm{d}\boldsymbol{\Gamma} .$$
(A.5)

Here δ is the delfa function and $q_{\rm rc}$ is some arbitrary reaction coordinate $q_{\rm rc} = q_{\rm rc}(\boldsymbol{q})$. The last equality needs to be slightly modified because we are not interested in the *overall* flux through the dividing surface but rather the *reactive* flux. To take this into account, we introduce the *characteristic function of reaction* $\chi(\boldsymbol{\Gamma})$ that contains all the dynamical information. This gives

$$-\frac{\mathrm{d}N_{\mathrm{R}}}{\mathrm{d}t} = \int \chi(\boldsymbol{\Gamma})\xi(\boldsymbol{\Gamma},t)\delta(f(\boldsymbol{q}) - q_{\mathrm{rc}})(\boldsymbol{\nabla}f(\boldsymbol{q})\cdot\dot{\boldsymbol{q}})\mathrm{d}\boldsymbol{\Gamma}.$$
 (A.6)

 $\chi(\boldsymbol{\Gamma})$ can be defined in several ways.⁷⁵ Here we use the following definition: $\chi(\boldsymbol{\Gamma}) = 1$ if a trajectory initiated from the dividing surface at t = 0 goes directly to products (without recrossing the dividing surface) and was part of the reactant ensemble at $t \to -\infty$. Otherwise, $\chi(\boldsymbol{\Gamma}) = 0$. Note that the flux expression is independent of the location of the dividing surface. Although the overall one-way flux is dependent on the dividing surface location, $\chi(\boldsymbol{\Gamma})$ makes sure that the reactive flux is always the same. If the dividing surface

¹The derivation is largely based on the material presented in refs 38,73,74

is put deep into the reactant valley, the overall flux through the dividing surface will be large, but most trajectories will recross the dividing surface before (if ever) ending up in the product valley. Similarly, if the dividing surface is put deep into the product valley, then most trajectories that cross the dividing surface will in fact have originated from the product rather than reactant side of the potential energy surface.

Phenomenologically, the time-dependent unimolecular rate coefficient is defined as the ratio of the negative time derivative of the reactant population and the reactant population, so classically,

$$k(t) = \frac{-\frac{\mathrm{d}N_{\mathrm{R}}}{\mathrm{d}t}}{N_{\mathrm{R}}} = \frac{\int \chi(\boldsymbol{\Gamma})\xi(\boldsymbol{\Gamma}, t)\delta(f(\boldsymbol{q}) - q_{\mathrm{rc}})(\boldsymbol{\nabla}f(\boldsymbol{q}) \cdot \dot{\boldsymbol{q}})\mathrm{d}\boldsymbol{\Gamma}}{\int \xi(\boldsymbol{\Gamma}, t)\mathrm{d}\boldsymbol{\Gamma}} .$$
(A.7)

The "no recrossing assumption" of TST is realised by stating that $\chi(\boldsymbol{\Gamma}) = u(\boldsymbol{\nabla} f(\boldsymbol{q}) \cdot \dot{\boldsymbol{q}})$ at t = 0 (*u* is the Heaviside step function). That is to say, all trajectories that cross the dividing surface at t = 0 in the reactant \rightarrow product direction are assumed to be reactive. Note that making this assumption means that the reactive flux through the dividing surface is now dependent on its location. Since making this assumption also means that the reactive flux is necessarily overestimated (some trajectories recross), the optimal location of the dividing surface is where the reactive flux obtains its minimum value.

The equilibrium assumption in the microcanonical case is realised by stating that

$$\xi(\boldsymbol{\Gamma}, t) = \frac{\delta(\mathcal{H} - E)\delta(J - J')}{\int \delta(\mathcal{H} - E)\delta(J - J')\mathrm{d}\boldsymbol{\Gamma}} \,. \tag{A.8}$$

Here the denominator is a normalisation constant (volume of the (E, J) surface) and it cancels out in the expression for k. As mentioned in the main text, the equilibrium assumption removes the time-dependency from the rate coefficient (the ratio of phase space points crossing the dividing and the total number of phase space points in the reactant valley is a constant), so the microcanonical TST expression is

$$k(E,J) = \frac{\int \delta(\mathcal{H} - E)\delta(J - J')\delta(f(\boldsymbol{q}) - q_{\rm rc})(\boldsymbol{\nabla}f(\boldsymbol{q}) \cdot \dot{\boldsymbol{q}})u(\boldsymbol{\nabla}f(\boldsymbol{q}) \cdot \dot{\boldsymbol{q}})\mathrm{d}\boldsymbol{\Gamma}}{\int \delta(\mathcal{H} - E)\delta(J - J')\mathrm{d}\boldsymbol{\Gamma}} .$$
(A.9)

The expression can be further simplified by demanding that the reaction coordinate is separable and orthogonal to the rest of the coordinates. This leads to the following simplifications:

$$\dot{q}_{\rm rc} = \frac{p_{\rm rc}}{\mu} \tag{A.10}$$

$$\mathcal{H} = \mathcal{H}^* + \frac{p_{\rm rc}^2}{2\mu} = \mathcal{H}^* + E_{\rm rc} \tag{A.11}$$

$$\delta(f(\boldsymbol{q}) - q_{\rm rc}) = \delta(q_{\rm rc} - q_{\rm rc}') \tag{A.12}$$

$$\boldsymbol{\nabla} f(\boldsymbol{q}) \cdot \dot{\boldsymbol{q}} = \frac{p_{\rm rc}}{\mu} \,. \tag{A.13}$$

Here \mathcal{H}^* is the constrained Hamiltonian for all the degrees of freedom but $(q_{\rm rc}, p_{\rm rc})$ and μ is the reduced mass for the motion along the reaction coordinate. The TST expression is now

$$k(E,J) = \frac{\int \delta(\mathcal{H}^* - (E - E_{\rm rc})\delta(J - J')\delta(q_{\rm rc} - q'_{\rm rc})(\frac{p_{\rm rc}}{\mu})u(p_{\rm rc})\mathrm{d}\boldsymbol{\Gamma}}{\int \delta(\mathcal{H} - E)\delta(J - J')\mathrm{d}\boldsymbol{\Gamma}} .$$
(A.14)

The integral over the reaction coordinate is straightforward to compute and the integral over its conjugate momenta can be evaluated by making the change of variable

$$E_{\rm rc} = \frac{p_{\rm rc}^2}{2\mu} \to \frac{\mathrm{d}E_{\rm rc}}{\mathrm{d}p_{\rm rc}} = \frac{p_{\rm rc}}{\mu} \ . \tag{A.15}$$

Further progress is made by noting that the E- and J-resolved density of states is defined as

$$\rho(E,J) = \frac{1}{h^{n+1}} \int \delta(\mathcal{H} - E)\delta(J - J') \mathrm{d}\boldsymbol{\Gamma} , \qquad (A.16)$$

where n + 1 is the number of degrees of freedom in the system (including the reaction coordinate). Plugging in the density of states expression yields

$$k(E,J) = \frac{\int_0^\infty \left(\int \delta(\mathcal{H}^* - (E - E_{\rm rc})\delta(J - J')\mathrm{d}\boldsymbol{\Gamma}^*\right)\mathrm{d}\boldsymbol{E}_{\rm rc}}{\int \delta(\mathcal{H} - E)\delta(J - J')\mathrm{d}\boldsymbol{\Gamma}}$$
$$= \frac{\int_0^\infty \rho^{\ddagger}(E - E_{\rm rc}, J)\mathrm{d}\boldsymbol{E}_{\rm rc}}{h\rho_{\rm react}(E, J)} .$$
(A.17)

The superscript ‡ denotes the transition state. Note that the step function has been omitted because the lower limit of integration is set to zero (as opposed to minus infinity). Computing the final integral yields the RRKM expression

$$k(E,J) = \frac{N^{\ddagger}(E,J)}{h\rho_{\text{react}}(E,J)}, \qquad (A.18)$$

where N^{\ddagger} is the sum of states of the transition state for a given E and J.

A J-averaged microcanonical rate coefficient is obtained by integrating over angular momentum,

$$k(E)_{J} = \frac{\int_{0}^{\infty} \rho_{\text{react}}(E, J)k(E, J)dJ}{\int_{0}^{\infty} \rho_{\text{react}}(E, J)dJ}$$

$$k(E)_{J} = \frac{\int_{0}^{\infty} N^{\dagger}(E, J)dJ}{h\int_{0}^{\infty} \rho_{\text{react}}(E, J)dJ}$$

$$k(E)_{J} = \frac{N^{\dagger}(E)_{J}}{h\rho_{\text{react}}(E)_{J}}.$$
(A.19)

Because forward and backward reactions share the same transition state $(N^{\ddagger}(E, J))$, their TST rate coefficients are related by

$$k_{\rm f}(E,J)\rho_{\rm react,f}(E,J) = k_{\rm b}(E - \Delta_{\rm r}E,J)\rho_{\rm react,b}(E - \Delta_{\rm r}E,J) , \qquad (A.20)$$

where $\Delta_{\mathbf{r}} E$ is the reaction energy. This expression applies even if one of the reactions is bimolecular.

A.2 The Canonical Rate Coefficient

The derivation of the canonical rate coefficient is started here from equation (A.7) and making the TST assumptions, except now the density of phase space points is defined as

$$\xi(\boldsymbol{\Gamma}, t) = \frac{\mathrm{e}^{-\beta \mathcal{H}}}{\int \mathrm{e}^{-\beta \mathcal{H}} \mathrm{d}\boldsymbol{\Gamma}} \,. \tag{A.21}$$

Plugging this into equation (A.7) yields

$$k(\beta) = \frac{\int \delta(f(\boldsymbol{q}) - q_{\rm rc}) (\boldsymbol{\nabla} f(\boldsymbol{q}) \cdot \dot{\boldsymbol{q}}) u(\boldsymbol{\nabla} f(\boldsymbol{q}) \cdot \dot{\boldsymbol{q}}) e^{-\beta \mathcal{H}} \mathrm{d}\boldsymbol{\Gamma}}{\int e^{-\beta \mathcal{H}} \mathrm{d}\boldsymbol{\Gamma}} = \frac{\int \delta(f(\boldsymbol{q}) - q_{\rm rc}) (\boldsymbol{\nabla} f(\boldsymbol{q}) \cdot \dot{\boldsymbol{q}}) u(\boldsymbol{\nabla} f(\boldsymbol{q}) \cdot \dot{\boldsymbol{q}}) e^{-\beta \mathcal{H}} \mathrm{d}\boldsymbol{\Gamma}}{h^{n+1} Q_{\rm react}(\beta)} .$$
(A.22)

We have used the canonical partition function definition

$$Q(\beta) = \frac{1}{h^{n+1}} \int e^{-\beta \mathcal{H}} d\boldsymbol{\Gamma} .$$
 (A.23)

The familiar form of the canonical TST expression is obtained by again demanding that the reaction coordinate be separable and orthogonal to the other coordinates. We also shift the potential energy function of the reduced Hamiltonian \mathcal{H}^* by the reaction threshold $\Delta_r E_0^{\ddagger}$, so

$$\mathcal{H}^* = \mathcal{T}^* + V' + \Delta_{\rm r} E_0^{\ddagger} , \qquad (A.24)$$

where $V = V' + \Delta_{\rm r} E_0^{\ddagger}$ and the "shifted" reduced Hamiltonian is $\mathcal{H}'^* = \mathcal{T}^* + V'$. Now

$$k(\beta) = \frac{\int_0^\infty \left(\int e^{-\beta \mathcal{H}^*} d\boldsymbol{\Gamma}^*\right) e^{-\beta E_{\rm rc}} dE_{\rm rc}}{h^{n+1} Q_{\rm react}(\beta)}$$
$$= \frac{\int_0^\infty \left(\int e^{-\beta \mathcal{H}^*} d\boldsymbol{\Gamma}^*\right) e^{-\beta \Delta_{\rm r} E_0^{\dagger}} e^{-\beta E_{\rm rc}} dE_{\rm rc}}{h^{n+1} Q_{\rm react}(\beta)}$$
$$= \frac{1}{h\beta} \frac{Q^{\dagger}(\beta)}{Q_{\rm react}(\beta)} e^{-\beta \Delta_{\rm r} E_0^{\dagger}}. \tag{A.25}$$

The reverse rate coefficient for a given reaction can be obtained from the equilibrium constant. For example, the rate coefficients of bimolecular recombination and unimolecular dissociation $(A + B \Longrightarrow AB)$ are related by

$$K(\beta) = \frac{k_{\rm rec}(\beta)}{k_{\rm dis}(\beta)} \frac{p^{\ominus}}{RT} = \frac{k_{\rm rec}}{k_{\rm dis}V^{\ominus}} .$$
(A.26)

Here $p^{\ominus} = 1$ bar and $V^{\ominus} = \frac{RT}{p^{\ominus}}$ (ideal-gas behaviour has been assumed). The expression for the equilibrium constant is

$$K(\beta) = \frac{Q_{AB}(\beta)}{Q_A(\beta)Q_B(\beta)V^{\ominus}} e^{-\beta\Delta_r E} , \qquad (A.27)$$

which can be plugged to the previous equation to obtain

$$k_{\rm rec}(\beta) = k_{\rm dis}(\beta) \frac{Q_{\rm AB}(\beta)}{Q_{\rm A}(\beta)Q_{\rm B}(\beta)V^{\ominus}} e^{-\beta\Delta_{\rm r}E} .$$
(A.28)

Using the canonical TST expression gives

$$k_{\rm rec}(\beta) = \frac{1}{h\beta} \frac{Q^{\ddagger}(\beta)}{Q_{\rm A}(\beta)Q_{\rm B}(\beta)} e^{-\beta\Delta_{\rm r}E_{\rm rec}^{\ddagger}} , \qquad (A.29)$$

where $\Delta_{\rm r} E_{\rm rec}^{\ddagger} = \Delta_{\rm r} E_{\rm dis}^{\ddagger} - \Delta_{\rm r} E$.

B Derivation of the FTST Rate Coefficient for an Atom-Diatom System²

B.1 The Canonical Rate Coefficient

The starting point of the derivation is equation (A.22),

$$k(\beta) = \frac{\int \delta(f(\boldsymbol{q}) - q_{\rm rc}) (\boldsymbol{\nabla} f(\boldsymbol{q}) \cdot \dot{\boldsymbol{q}}) u(\boldsymbol{\nabla} f(\boldsymbol{q}) \cdot \dot{\boldsymbol{q}}) \mathrm{e}^{-\beta \mathcal{H}} \mathrm{d}\boldsymbol{\Gamma}}{h^{n+1} Q_{\rm react}(\beta)} .$$
(B.1)

Separation of the modes gives the FTST-expression

$$k(\beta, r) = \frac{Q_{\text{cons}}(\beta)}{Q_{\text{react}}(\beta)} \frac{1}{h^{n+1}} \dots$$
$$\dots \int \delta(f(\boldsymbol{q}_{\text{tr}}) - r) (\boldsymbol{\nabla} f(\boldsymbol{q}_{\text{tr}}) \cdot \boldsymbol{q}_{\text{tr}}) u(\boldsymbol{\nabla} f(\boldsymbol{q}_{\text{tr}}) \cdot \boldsymbol{q}_{\text{tr}}) e^{-\beta \mathcal{H}_{\text{tr}}} \mathrm{d} \boldsymbol{q}_{\text{tr}} \mathrm{d} \boldsymbol{p}_{\text{tr}}$$
$$= \frac{Q_{\text{cons}}(\beta)}{Q_{\text{react}}(\beta)} \mathcal{F}_{c}(\beta, r) . \tag{B.2}$$

Here n + 1 is the number of transitional modes, including the reaction coordinate, \mathcal{F}_c is the canonical flux through the dividing surface, and r is the reaction coordinate. From here on, the subscripts "tr" are dropped. Only the transitional modes are investigated. The reaction coordinate is chosen to be the distance between the H-atom and an arbitrary point d on the O–O bond R. The studied system is depicted in Figure 30. The kinetic



Figure 30: The rotating body-fixed frame. The triatomic system is in the xz-plane. energy for the translational modes is given by

$$2\mathcal{T} = \sum_{i=1}^{3} m_i \dot{\boldsymbol{q}}_{\text{cart},i}^2 + 2\boldsymbol{\omega} \sum_{i=1}^{3} m_i \boldsymbol{q}_{\text{cart},i} \times \dot{\boldsymbol{q}}_{\text{cart},i} + \boldsymbol{\omega}^{\mathrm{T}} \boldsymbol{I} \boldsymbol{\omega} .$$
(B.3)

 $^{^{2}}$ The derivation is largely based on the material presented in refs^{7,76}

Here $\boldsymbol{q}_{\text{cart},i}$ is the Cartesian position vector of atom *i* in the rotating frame, m_i is its mass, $\boldsymbol{\omega} = (\omega_x, \omega_y, \omega_z)$ gives the angular velocities of the Cartesian axes, and \boldsymbol{I} is the instantaneous moment of inertia tensor of the whole system. The cartesian coordinates are related to the Jacobi coordinates $(\theta, R, r_{\text{cm}})$ by the following expressions:

$$\begin{aligned} x_{\rm H} &= 0 & x_{\rm O_1} &= -\frac{R}{2}\sin(\theta) & x_{\rm O_2} &= \frac{R}{2}\sin(\theta) \\ y_{\rm H} &= 0 & y_{\rm O_1} &= 0 & y_{\rm O_2} &= 0 \\ z_{\rm H} &= -\frac{2m_{\rm O}}{M}r_{\rm cm} & z_{\rm O_1} &= \frac{m_{\rm H}}{M}r_{\rm cm} - \frac{R}{2}\cos(\theta) & z_{\rm O_2} &= \frac{m_{\rm H}}{M}r_{\rm cm} + \frac{R}{2}\cos(\theta) & . \end{aligned}$$

Here M is the total mass $2m_{\rm O} + m_{\rm H}$. The kinetic energy of the transitional modes can be expressed more compactly in matrix form

$$\begin{aligned} 2\mathcal{T} &= \begin{pmatrix} \omega_{x} & \omega_{y} & \omega_{z} & \dot{\theta} & \dot{r}_{\rm cm} \end{pmatrix} \\ & \begin{pmatrix} I_{r} + I_{R} \cos^{2}(\theta) & 0 & -I_{R} \cos(\theta) \sin(\theta) & 0 & 0 \\ 0 & I_{r} + I_{R} & 0 & -I_{R} & 0 \\ -I_{R} \cos(\theta) \sin(\theta) & 0 & I_{R} \sin^{2}(\theta) & 0 & 0 \\ 0 & -I_{R} & 0 & I_{R} & 0 \\ 0 & 0 & 0 & 0 & \mu \end{pmatrix} \begin{pmatrix} \omega_{x} \\ \omega_{y} \\ \omega_{z} \\ \dot{\theta} \\ \dot{r}_{\rm cm} \end{pmatrix} \\ &= \dot{\boldsymbol{Q}}_{\rm cm}^{\rm T} \boldsymbol{A}_{\rm cm} \dot{\boldsymbol{Q}}_{\rm cm} , \end{aligned}$$
(B.4)

where $I_r = \mu r_{\rm cm}^2 = \frac{2m_{\rm O}m_{\rm H}}{2m_{\rm O}+m_{\rm H}}r_{\rm cm}^2$, $I_R = \mu_R R^2 = \frac{m_O}{2}R^2$, and $A_{\rm cm}$ is the inverse G-matrix in centres-of-mass coordinates. The kinetic energy is not yet fully expressed in terms of generalised velocities because there are no angles that correspond to the angular velocities $\boldsymbol{\omega}$. The linear transformation needed to get from $\dot{\boldsymbol{Q}}_{\rm cm}$ to generalised velocities $\dot{\boldsymbol{q}}_{\rm cm}$ is⁷⁷

$$\begin{pmatrix} \omega_x \\ \omega_y \\ \omega_z \\ \dot{\theta} \\ \dot{r}_{cm} \end{pmatrix} = \begin{pmatrix} -\sin(\Theta)\cos(\Psi) & \sin(\Psi) & 0 & 0 & 0 \\ \sin(\Theta)\sin(\Psi) & \cos(\Psi) & 0 & 0 & 0 \\ \cos(\Theta) & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \Phi \\ \dot{\Theta} \\ \dot{\psi} \\ \dot{\theta} \\ \dot{r}_{cm} \end{pmatrix}$$

$$\dot{\boldsymbol{Q}}_{cm} = \boldsymbol{S} \dot{\boldsymbol{q}}_{cm} .$$
(B.5)

 \mathbf{SO}

$$2\mathcal{T} = \dot{\boldsymbol{q}}_{\rm cm}^{\rm T} \boldsymbol{S}^{\rm T} \boldsymbol{A}_{\rm cm} \boldsymbol{S} \dot{\boldsymbol{q}}_{\rm cm} = \dot{\boldsymbol{q}}_{\rm cm}^{\rm T} \boldsymbol{a}_{\rm cm} \dot{\boldsymbol{q}}_{\rm cm} . \tag{B.6}$$

The Lagrangian for the centres-of-mass system is

$$\mathcal{L} = \frac{1}{2} \dot{\boldsymbol{q}}_{\rm cm}^{\rm T} \boldsymbol{a}_{\rm cm} \dot{\boldsymbol{q}}_{\rm cm} - V(r_{\rm cm}, \theta) , \qquad (B.7)$$

from which the momenta corresponding to $\boldsymbol{q}_{\rm cm}$ can be obtained,

$$\boldsymbol{p}_{\rm cm} = \frac{\partial \mathcal{L}}{\partial \dot{\boldsymbol{q}}_{\rm cm}} = \boldsymbol{S}^{\rm T} \boldsymbol{A}_{\rm cm} \boldsymbol{S} \dot{\boldsymbol{q}}_{\rm cm} = \boldsymbol{a}_{\rm cm} \dot{\boldsymbol{q}}_{\rm cm} . \tag{B.8}$$

Since the components of angular momentum in a body-fixed frame are defined by

$$\boldsymbol{J} = \frac{\partial \mathcal{L}}{\partial \boldsymbol{\omega}} , \qquad (B.9)$$

these components are the first three components of

$$\frac{\partial \mathcal{L}}{\partial \dot{\boldsymbol{Q}}_{\rm cm}} = \boldsymbol{A}_{\rm cm} \dot{\boldsymbol{Q}}_{\rm cm} = \boldsymbol{A}_{\rm cm} \boldsymbol{S} \dot{\boldsymbol{q}}_{\rm cm} = \boldsymbol{p}_J . \tag{B.10}$$

Thus, \boldsymbol{p}_{cm} and \boldsymbol{p}_J are related by

$$\boldsymbol{p}_{\mathrm{cm}} = \boldsymbol{S}^{\mathrm{T}} \boldsymbol{p}_{J}$$

 $\rightarrow \boldsymbol{p}_{J} = (\boldsymbol{S}^{\mathrm{T}})^{-1} \boldsymbol{p}_{\mathrm{cm}} .$ (B.11)

The centres-of-mass reaction coordinate $r_{\rm cm}$ is related to the more general reaction coordinate r by the simple geometric relation

$$r = f(\theta, r_{\rm cm}) = \left(r_{\rm cm}^2 + d^2 - 2r_{\rm cm}d\cos(\theta)\right)^{\frac{1}{2}} .$$
(B.12)

In principle, if the oxygen pivot point is moved a distance +d along the bond from the centre of mass, there will be another pivot point at a distance -d, so the general reaction coordinate should in fact be defined as

$$r = \begin{cases} (r_{\rm cm}^2 + d^2 - 2r_{\rm cm}d\cos(\theta))^{\frac{1}{2}}, & 0 \le \theta \le \frac{\pi}{2} \\ (r_{\rm cm}^2 + d^2 + 2r_{\rm cm}d\cos(\theta))^{\frac{1}{2}}, & \frac{\pi}{2} < \theta \le \pi \end{cases}$$

However, in practice only the first case needs to be considered. The value of θ can be limited to the range $[0, \pi/2]$. The resulting flux through the dividing surface can be multiplied by two to obtain the total flux. This can be done because the diatomic fragment is homonuclear. The function for r can be inverted to obtain

$$r_{\rm cm} = F(\theta, r) = d\cos(\theta) \pm \left(r^2 - d^2\sin^2(\theta)\right)^{\frac{1}{2}}$$
 (B.13)

Here we will only consider cases where r is so much larger than d that the expression in the square-root is never negative and the negative root is unphysical. The Jacobian of the transform is

$$\frac{\partial r_{\rm cm}}{\partial r}\frac{\partial \theta}{\partial \theta} - \frac{\partial r_{\rm cm}}{\partial \theta}\frac{\partial \theta}{\partial r} = r\left(r^2 - d^2\sin^2(\theta)\right)^{-\frac{1}{2}} . \tag{B.14}$$

Taking the total differential of $r_{\rm cm}$ reveals that the general and centres-of-mass velocities are related by the linear transform $\dot{q}_{\rm cm} = \mathcal{J}_v \dot{q}$, where

$$\boldsymbol{\mathcal{J}}_{v} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & \frac{\partial F(\theta, r)}{\partial \theta} & \frac{\partial F(\theta, r)}{\partial r} \end{pmatrix} .$$
(B.15)

Replacing $\dot{\boldsymbol{q}}_{\mathrm{cm}}$ with $\boldsymbol{\mathcal{J}}_{v}\dot{\boldsymbol{q}}$ in the kinetic energy expression yields

$$2\mathcal{T} = \dot{\boldsymbol{q}}_{cm}^{T} \boldsymbol{a}_{cm} \dot{\boldsymbol{q}}_{cm}$$

$$2\mathcal{T} = \dot{\boldsymbol{q}}^{T} \mathcal{J}_{v}^{T} \boldsymbol{a}_{cm} \mathcal{J}_{v} \dot{\boldsymbol{q}}$$

$$2\mathcal{T} = \dot{\boldsymbol{q}}^{T} \boldsymbol{a} \dot{\boldsymbol{q}} .$$
(B.16)

Since

$$\boldsymbol{p} = \frac{\partial \mathcal{L}}{\partial \dot{\boldsymbol{q}}} = \boldsymbol{a} \dot{\boldsymbol{q}} \to \dot{\boldsymbol{q}} = \boldsymbol{a}^{-1} \boldsymbol{p} = \boldsymbol{g} \boldsymbol{p} ,$$
 (B.17)

the kinetic energy expression in terms of conjugate momenta is

$$2\mathcal{T} = \boldsymbol{p}^{\mathrm{T}}\boldsymbol{g}^{\mathrm{T}}\boldsymbol{a}\boldsymbol{g}\boldsymbol{p}$$

$$2\mathcal{T} = \boldsymbol{p}^{\mathrm{T}}\boldsymbol{g}\boldsymbol{p} , \qquad (B.18)$$

where we have used ag = 1 and $g^{T} = g$. From the above equations it can be seen that

$$p = \mathcal{J}_v^{\mathrm{T}} a_{\mathrm{cm}} \mathcal{J}_v \dot{q}$$

$$p = \mathcal{J}_v^{\mathrm{T}} a_{\mathrm{cm}} \dot{q}_{\mathrm{cm}}$$

$$p = \mathcal{J}_v^{\mathrm{T}} p_{\mathrm{cm}}$$

$$\rightarrow p_{\mathrm{cm}} = (\mathcal{J}_v^{\mathrm{T}})^{-1} p . \qquad (B.19)$$

The Jacobian for this transform is

$$\frac{1}{\frac{\partial F(\theta, r)}{\partial r}} = \left[r \left(r^2 - d^2 \sin^2(\theta) \right)^{-\frac{1}{2}} \right]^{-1} , \qquad (B.20)$$

so clearly the $(r, p_r) \rightarrow (r_{\rm cm}, p_{\rm r,cm})$ transformation is canonical because $drdp_r = dr_{\rm cm}dp_{\rm r,cm}$. The Hamiltonian with the general reaction coordinate is

$$\mathcal{H} = \frac{1}{2}\boldsymbol{p}^{\mathrm{T}}\boldsymbol{g}\boldsymbol{p} + V(r,\theta) = \frac{1}{2}\boldsymbol{p}^{\mathrm{T}}\boldsymbol{a}^{-1}\boldsymbol{p} + V(r,\theta) .$$
(B.21)

To evaluate the canonical flux through the dividing surface, it is helpful to define a momentum integral \mathcal{P} and solve it first.

$$\mathcal{F}_{c}(\beta, r) = \frac{1}{h^{n+1}} \int \delta(r - r^{\ddagger}) (\nabla r \cdot \dot{q}) u (\nabla r \cdot \dot{q}) e^{-\beta \mathcal{H}} dq dp$$

$$= \frac{1}{h^{n+1}} \int \delta(r - r^{\ddagger}) \dot{r} u(\dot{r}) e^{-\beta \mathcal{H}} dq' dr dp dp_{r}$$

$$= \frac{1}{h^{n+1}} \int \delta(r - r^{\ddagger}) \left(\int \dot{r} u(\dot{r}) e^{-\beta \mathcal{T}} dp dp_{r} \right) e^{-\beta V} dq' dr$$

$$= \frac{1}{h^{n+1}} \int \delta(r - r^{\ddagger}) \mathcal{P} e^{-\beta V} dq' dr . \qquad (B.22)$$

Here q' refers to all the generalised coordinates, excluding the reaction coordinate. The Heaviside step function $u(\dot{r})$ is non-zero when

$$\dot{r} = \frac{\partial \mathcal{H}}{\partial p_{\rm r}} = \frac{\partial \mathcal{T}}{\partial p_{\rm r}} = \sum_{j=1}^{5} g_{5j} p_j > 0 , \qquad (B.23)$$

from which we get the condition

$$p_r > p_r^* \tag{B.24}$$

where

$$p_r^* = -\frac{\sum_{j=1}^4 g_{5j} p_j}{g_{55}} \,. \tag{B.25}$$

We can now integrate \mathcal{P} over the reaction coordinate momentum to get

$$\mathcal{P} = \int \dot{r} u(\dot{r}) e^{-\beta T} d\mathbf{p}' dp_r$$

=
$$\int \left(\int_{p_r^*}^{\infty} \frac{\partial T}{\partial p_r} e^{-\beta T} dp_r \right) d\mathbf{p}'$$

=
$$\int \left(\int_{\mathcal{T}^*}^{\infty} e^{-\beta T} d\mathcal{T} \right) d\mathbf{p}'$$

=
$$\frac{1}{\beta} \int e^{-\beta T^*} d\mathbf{p}' .$$
 (B.26)

The expression for the constrained kinetic energy $(\dot{r} = 0)$ is

$$2\mathcal{T}^* = \boldsymbol{q'}^{\mathrm{T}} \boldsymbol{a'} \boldsymbol{q'} , \qquad (B.27)$$

where a' is equal to a except that the fifth row and column is missing. The corresponding G-matrix is the inverse of a',⁷ meaning

$$2\mathcal{T}^* = \mathbf{p'}^{\mathrm{T}}\mathbf{g'}\mathbf{p'} = \mathbf{p'}^{\mathrm{T}}\mathbf{a'}^{-1}\mathbf{p'} = \mathbf{p'}^{\mathrm{T}}\mathbf{S}^{-1}\mathbf{A'}^{-1}(\mathbf{S}^{\mathrm{T}})^{-1}\mathbf{p'} = \mathbf{p'}^{\mathrm{T}}\mathbf{S}^{-1}\mathbf{G'}(\mathbf{S}^{\mathrm{T}})^{-1}\mathbf{p'}.$$
 (B.28)

(**S** and \mathcal{J} commute, so the order of operation can be reversed). To complete the momentum integral, we make the transformation $\boldsymbol{p} \to \boldsymbol{p}_J$ which has the Jacobian $\sin(\Theta)$. The momentum integral in the transformed coordinates is

$$\mathcal{P} = \frac{\sin(\Theta)}{\beta} \int e^{-\frac{1}{2}\beta \boldsymbol{p}_{J}^{T} \boldsymbol{G}' \boldsymbol{p}_{J}'} d\boldsymbol{p}_{J}' .$$
(B.29)

The matrix A' is symmetric and has the block structure

$$\begin{pmatrix} \boldsymbol{I} & \boldsymbol{C} \\ \boldsymbol{C}^{\mathrm{T}} & \boldsymbol{D} \end{pmatrix} = \begin{pmatrix} I_r + I_R \cos^2(\theta) & 0 & -I_R \cos(\theta) \sin(\theta) & 0 \\ 0 & I_r + I_R & 0 & -I_R \\ -I_R \cos(\theta) \sin(\theta) & 0 & I_R \sin^2(\theta) & 0 \\ 0 & -I_R & 0 & I_R + \mu \left(\frac{\partial F(\theta, r)}{\partial \theta}\right)^2 \end{pmatrix}.$$
(B.30)

G' is similarly symmetric and has the block form

$$\begin{pmatrix} \boldsymbol{X} & \boldsymbol{Y} \\ \boldsymbol{Y}^{\mathrm{T}} & \boldsymbol{Z} \end{pmatrix} = \begin{pmatrix} \frac{1}{I_{r}} & 0 & \frac{\cos(\theta)}{I_{r}\sin(\theta)} & 0 \\ 0 & \frac{I_{R} + \mu \left(\frac{\partial F(\theta, r)}{\partial \theta}\right)^{2}}{\mu (I_{r} + I_{R}) \left(\frac{\partial F(\theta, r)}{\partial \theta}\right)^{2} + I_{r}I_{R}} & 0 & \frac{I_{R}}{\mu (I_{r} + I_{R}) \left(\frac{\partial F(\theta, r)}{\partial \theta}\right)^{2} + I_{r}I_{R}} \\ \frac{\cos(\theta)}{I_{r}\sin(\theta)} & 0 & \frac{I_{r} + I_{R}\cos^{2}(\theta)}{I_{r}\sin^{2}(\theta)} & 0 \\ 0 & \frac{I_{R}}{\mu (I_{r} + I_{R}) \left(\frac{\partial F(\theta, r)}{\partial \theta}\right)^{2} + I_{r}I_{R}} & 0 & \frac{I_{r} + I_{R}}{\mu (I_{r} + I_{R}) \left(\frac{\partial F(\theta, r)}{\partial \theta}\right)^{2} + I_{r}I_{R}} \end{pmatrix}.$$
(B.31)
Expansion of the exponent yields

$$\mathcal{P} = \frac{\sin(\Theta)}{\beta} \int \left(\int_{-\infty}^{\infty} e^{-\frac{1}{2}\beta \left(\mathbf{2} \mathbf{J}^{\mathrm{T}} \mathbf{Y} p_{\theta} + \mathbf{Z} p_{\theta}^{2} \right)} \mathrm{d}p_{\theta} \right) e^{-\frac{1}{2}\beta \mathbf{J}^{\mathrm{T}} \mathbf{X} \mathbf{J}} \mathrm{d}\mathbf{J}$$

$$= \frac{\sin(\Theta)}{\beta} \int \left(\int_{-\infty}^{\infty} e^{-\frac{1}{2}\beta \left((p_{\theta} + \mathbf{J}^{\mathrm{T}} \mathbf{Y} \mathbf{Z}^{-1}) \mathbf{Z} (p_{\theta} + \mathbf{Z}^{-1} \mathbf{Y}^{\mathrm{T}} \mathbf{J}) \right)} \mathrm{d}p_{\theta} \right) e^{-\frac{1}{2}\beta \mathbf{J}^{\mathrm{T}} (\mathbf{X} - \mathbf{Y} \mathbf{Z}^{-1} \mathbf{Z} \mathbf{Z}^{-1} \mathbf{Y}^{\mathrm{T}}) \mathbf{J}} \mathrm{d}\mathbf{J}$$

$$= \frac{\sin(\Theta)}{\beta} \left(\frac{2\pi}{\beta} \right)^{\frac{1}{2}} |\mathbf{Z}|^{-\frac{1}{2}} \int e^{-\frac{1}{2}\beta \mathbf{J}^{\mathrm{T}} (\mathbf{X} - \mathbf{Y} \mathbf{Z}^{-1} \mathbf{Y}^{\mathrm{T}}) \mathbf{J}} \mathrm{d}\mathbf{J} .$$
(B.32)

It is useful to investigate the remaining exponent.

$$\begin{aligned} \boldsymbol{X} - \boldsymbol{Y}\boldsymbol{Z}^{-1}\boldsymbol{Y}^{\mathrm{T}} & (B.33) \\ &= \begin{pmatrix} \frac{1}{I_{r}} & 0 & \frac{cos(\theta)}{I_{r}\sin(\theta)} \\ 0 & \frac{I_{R} + \mu \left(\frac{\partial F(\theta, r)}{\partial \theta}\right)^{2}}{\mu (I_{r} + I_{R}) \left(\frac{\partial F(\theta, r)}{\partial \theta}\right)^{2} + I_{r}I_{R}} - \frac{I_{R}^{2}}{(I_{r} + I_{R}) \left(\mu (I_{r} + I_{R}) \left(\frac{\partial F(\theta, r)}{\partial \theta}\right)^{2} + I_{r}I_{R}\right)} & 0 \\ & \frac{cos(\theta)}{I_{r}\sin(\theta)} & 0 & \frac{I_{r} + I_{R}\cos^{2}(\theta)}{I_{r}I_{R}\sin^{2}(\theta)} \end{pmatrix} \end{aligned}$$
(B.34)

$$= \begin{pmatrix} I_r & 0 & I_r \sin(\theta) \\ 0 & \frac{1}{I_r + I_R} & 0 \\ \frac{\cos(\theta)}{I_r \sin(\theta)} & 0 & \frac{I_r + I_R \cos^2(\theta)}{I_r I_R \sin^2(\theta)} \end{pmatrix}$$
(B.35)
$$= \mathbf{I}^{-1}$$
(B.36)

So the exponent is just the inverse of the moment of inertia matrix. Further progress can be made by making the diagonalisation $I \rightarrow I_{d}$,

Now the momentum integral is

$$\mathcal{P} = \frac{\sin(\Theta)}{\beta} \left(\frac{2\pi}{\beta}\right)^{\frac{1}{2}} |\boldsymbol{Z}|^{-\frac{1}{2}} \int e^{-\frac{1}{2}\beta \left(\frac{J_x^2}{I_{xx}} + \frac{J_y^2}{I_{yy}} + \frac{J_z^2}{I_{zz}}\right)} d\boldsymbol{J} .$$
(B.39)

To obtain the results in terms of the magnitude of total angular momentum, yet another coordinate transform is needed, this time from cartesian to spherical, giving

$$\mathcal{P} = \frac{\sin(\Theta)}{\beta} \left(\frac{2\pi}{\beta}\right)^{\frac{1}{2}} |\mathbf{Z}|^{-\frac{1}{2}} \int_0^\infty \int_0^{2\pi} \int_0^\pi \mathrm{e}^{-\beta E_{\mathrm{rot}}} J^2 \sin(\nu) \mathrm{d}\nu \mathrm{d}\eta \mathrm{d}J \,. \tag{B.40}$$

where

$$E_{\rm rot} = \frac{J^2}{2} \left(\left[\frac{\sin^2(\eta)}{I_{xx}} + \frac{\cos^2(\eta)}{I_{yy}} \right] \sin^2(\nu) + \frac{\cos^2(\nu)}{I_{zz}} \right) .$$
(B.41)

Now what remains is to solve the coordinate-part of the flux integral. Integration over the reaction coordinate and the Euler angles can be done analytically, giving

$$\mathcal{F}_{c}(\beta,r) = \frac{1}{h^{n+1}} \int_{0}^{2\pi} \int_{0}^{\pi} \int_{0}^{2\pi} \int_{0}^{\pi} \int_{0}^{\infty} \delta(r-r^{*}) \frac{\sin(\Theta)}{\beta} \left(\frac{2\pi}{\beta}\right)^{\frac{1}{2}} |\mathbf{Z}|^{-\frac{1}{2}} \dots$$
$$\dots \int_{0}^{\infty} \int_{0}^{2\pi} \int_{0}^{\pi} e^{-\beta E_{rot}} J^{2} \sin(\nu) d\nu d\eta dJ e^{-\beta V} dr d\theta d\Phi d\Theta d\Psi$$
$$= \frac{4\pi}{h^{5}} \left(\frac{2\pi}{\beta}\right)^{\frac{3}{2}} \int_{0}^{\pi} |\mathbf{Z}|^{-\frac{1}{2}} \left(\int_{0}^{\infty} \int_{0}^{2\pi} \int_{0}^{\pi} e^{-\beta E_{rot}} J^{2} \sin(\nu) d\nu d\eta dJ\right) e^{-\beta V} d\theta .$$
(B.42)

The remaining integrals are best solved numerically. Analytical solutions exist for the integrals over η and ν , but they tend to be complicated.⁷ To obtain a *J*-dependent flux, the order of integration can be changed in the above expression and the integration over *J* omitted. This gives

$$\mathcal{F}_{c}(\beta,J,r) = \frac{4\pi J^{2}}{h^{5}} \left(\frac{2\pi}{\beta}\right)^{\frac{3}{2}} \int_{0}^{\pi} |\boldsymbol{Z}|^{-\frac{1}{2}} \left(\int_{0}^{2\pi} \int_{0}^{\pi} e^{-\beta E_{rot}} \sin(\nu) d\nu d\eta\right) e^{-\beta V} d\theta .$$
(B.43)

This expression will be useful in the derivation of the microcanonical rate coefficient.

To summarise, the canonical rate coefficient for the $H^{\bullet} + O_2$ reaction is

$$k(\beta, r) = \frac{Q_{\text{cons}}(\beta)}{Q_{\text{react}}(\beta)} \mathcal{F}_{c}(\beta, r) .$$
(B.44)

This expression can be optimised with respect to r to find minimum value for $k(\beta, r)$. However, a canonical minimisation does not provide the smallest $k(\beta, r)$ because the minimisation should in fact be done with respect to E and J. This will be considered next.

B.2 The Microcanonical Rate Coefficient

The canonical rate coefficient of a reaction can be obtained by averaging the microcanonical rate coefficient over E and J,

$$k(\beta, r) = \frac{1}{Q_{\text{react}}(\beta)} \int_0^\infty \int_0^\infty k(E, J, r) \rho_{\text{react}}(E, J) e^{-\beta E} dJ dE .$$
(B.45)

Using the RRKM-expression

$$k(E, J, r) = \frac{N(E, J, r)}{h\rho_{\text{react}}(E, J)}$$
(B.46)

and changing the order of integration, this simplifies to

$$k(\beta, r) = \frac{1}{hQ_{\text{react}}(\beta)} \int_0^\infty \int_0^\infty N(E, J, r) e^{-\beta E} dE dJ$$

$$k(\beta, r) = \frac{1}{hQ_{\text{react}}(\beta)} \int_0^\infty L[N(E, J, r)] dJ .$$
(B.47)

The sum of states divided by the Planck constant can be expressed as the convolution

$$h^{-1}N(E,J,r) = \int_{0}^{E} \rho_{\rm cons}(\epsilon)h^{-1}N_{\rm tr}(E-\epsilon,J,r)\mathrm{d}\epsilon$$
(B.48)

$$= \int_{0}^{E} \rho_{\rm cons}(\epsilon) \mathcal{F}_{\rm mc}(E - \epsilon, J, r) \mathrm{d}\epsilon , \qquad (B.49)$$

where $\mathcal{F}_{mc}(E - \epsilon, J, r)$ is the microcanonical flux through the dividing surface. Here it has been assumed that the conserved modes have no angular momentum. Replacing

 $h^{-1}N(E, J, r)$ in equation (B.47) with the convolution yields

$$k(\beta, r) = \frac{1}{Q_{\text{react}}(\beta)} \int_0^\infty L\left[\int_0^E \rho_{\text{cons}}(\epsilon) \mathcal{F}_{\text{mc}}(E - \epsilon, J, r) \mathrm{d}\epsilon\right] \mathrm{d}J \tag{B.50}$$

$$= \frac{1}{Q_{\text{react}}(\beta)} \int_{0}^{\infty} L[\rho_{\text{cons}}(E,r)] L[\mathcal{F}_{\text{mc}}(E,J,r)] dJ$$
(B.51)

$$= \frac{Q_{\rm cons}(\beta)}{Q_{\rm react}(\beta)} \int_0^\infty L[\mathcal{F}_{\rm mc}(E,J,r)] \mathrm{d}J \;. \tag{B.52}$$

Comparison with equation (B.2) shows that

$$\mathcal{F}_{\rm c}(\beta, r) = \int_0^\infty L[\mathcal{F}_{\rm mc}(E, J, r)] \mathrm{d}J , \qquad (B.53)$$

or with the J-dependent canonical flux,

$$\mathcal{F}_{c}(\beta, J, r) = L[\mathcal{F}_{mc}(E, J, r)].$$
(B.54)

This transform can be inverted to obtain an expression for the microcanonical flux. We will use the transform

$$L^{-1}\left[t^{-n}e^{-ct}\right](s) = \frac{u(s-c)(s-c)^{n-1}}{\Gamma(n)}.$$
 (B.55)

Applying this to the problem at hand yields

$$\mathcal{F}_{\rm mc}(E,J,r) = L^{-1}[\mathcal{F}_{\rm c}(\beta,J,r)] \tag{B.56}$$

$$=\frac{4\pi J^2}{h^5 \Gamma(\frac{3}{2})} (2\pi)^{\frac{3}{2}} \int_0^\pi |\mathbf{Z}|^{-\frac{1}{2}} \left(\int_0^{2\pi} \int_0^\pi u \left(E - E_{\rm rot} - V \right) \dots \right)$$
(B.57)

$$\dots \left(E - E_{\rm rot} - V\right)^{\frac{1}{2}} \sin(\nu) \mathrm{d}\eta \mathrm{d}\nu \bigg) \mathrm{d}\theta \;. \tag{B.58}$$

The microcanonical flux can be convolved with the conserved mode to obtain the microcanonical rate coefficient

$$k(E, J, r) = \frac{4\pi J^2}{h^5 \Gamma(\frac{3}{2})\rho_{\text{react}}(E, J)} (2\pi)^{\frac{3}{2}} \int_0^E \rho_{\text{cons}}(\epsilon, r) \int_0^\pi |\mathbf{Z}|^{-\frac{1}{2}} \dots$$
(B.59)

$$\dots \left(\int_0^{2\pi} \int_0^{\pi} u \left(E - \epsilon - E_{\rm rot} - V \right) \left(E - \epsilon - E_{\rm rot} - V \right)^{\frac{1}{2}} \sin(\nu) \mathrm{d}\nu \mathrm{d}\eta \right) \mathrm{d}\theta \mathrm{d}\epsilon \quad (B.60)$$

$$=\frac{2^{\frac{9}{2}}J^{2}\pi^{2}}{\nu_{\text{harm}}h^{6}\rho_{\text{react}}(E,J)}\int_{0}^{E}\int_{0}^{\pi}|\boldsymbol{Z}|^{-\frac{1}{2}}...$$
(B.61)

$$\dots \left(\int_0^{2\pi} \int_0^{\pi} u \left(E - \epsilon - E_{\rm rot} - V \right) \left(E - \epsilon - E_{\rm rot} - V \right)^{\frac{1}{2}} \sin(\nu) \mathrm{d}\nu \mathrm{d}\eta \right) \mathrm{d}\theta \mathrm{d}\epsilon \;. \tag{B.62}$$

Note that $\rho_{cons}(\epsilon)$ is simply the density of states of the diatom harmonic oscillator.

The integral can be solved by crude Monte Carlo integration,

$$\int_{0}^{E} \int_{0}^{\pi} |\mathbf{Z}|^{-\frac{1}{2}} \left(\int_{0}^{2\pi} \int_{0}^{\pi} u \left(E - \epsilon - E_{\rm rot} - V \right) \left(E - \epsilon - E_{\rm rot} - V \right)^{\frac{1}{2}} \sin(\nu) \mathrm{d}\nu \mathrm{d}\eta \right) \mathrm{d}\theta \mathrm{d}\epsilon$$
$$\approx \frac{V}{N} \sum_{i=1}^{N} G(\epsilon_{i}, \theta_{i}, \nu_{i}, \eta_{i}) , \qquad (B.63)$$

where

$$G(\epsilon, \theta, \nu, \eta) = |\mathbf{Z}|^{-\frac{1}{2}} u \left(E - \epsilon - E_{\text{rot}} - V \right) \left(E - \epsilon - E_{\text{rot}} - V \right)^{\frac{1}{2}}$$
(B.64)

$$V = \int_0^E \int_0^\pi \int_0^{2\pi} \int_0^\pi \sin(\nu) \mathrm{d}\nu \mathrm{d}\eta \mathrm{d}\theta \mathrm{d}\epsilon = 4\pi^2 E , \qquad (B.65)$$

and N is the number of Monte Carlo points. The arguments of $G(\epsilon,\theta,\nu,\eta)$ are sampled from

$$\epsilon = E \cdot x_1 \tag{B.66}$$

$$\theta = \frac{\pi}{2} \cdot x_2 \tag{B.67}$$

$$\eta = 2\pi \cdot x_3 \tag{B.68}$$

$$\nu = \arccos(2 \cdot x_4 - 1) . \tag{B.69}$$

Here x_i is a random value in the range [0,1]. Due to the symmetry of the interaction potential, θ can be sampled in the range $[0, \pi/2]$.

C Trajectory Calculations

The trajectories are run in a centres-of-mass frame where $r = r_{\rm cm}$.

To reduce the dimensionality of the trajectory calculations, one can make the coordinate transform $(\Phi, \Theta, \Psi, p_{\Phi}, p_{\Theta}, p_{\Psi} \rightarrow q_J, q_M, q_K, J, M, K)$, where J is the magnitude of total angular momentum and M and K are the projection of total angular momentum on the space- and body-fixed z-axes, respectively. Because angular momentum is conserved, M and J are cyclic coordinates. The generating function needed to make the canonical transformation has been presented by Augustin and Miller⁷⁶ and it is

$$F_2(\Phi,\Theta,\Psi,J,M,K) = \Phi M + \Psi K + J \arccos\left(\frac{J^2 \cos(\Theta) - MK}{[(J^2 - K^2)(J^2 - M^2)]^{\frac{1}{2}}}\right)$$
(C.1)

$$-M \arccos\left(\frac{M\cos(\Theta) - K}{[\sin(\Theta)(J^2 - M^2)^{\frac{1}{2}}]}\right)$$
(C.2)

$$-K \arccos\left(\frac{K\cos(\Theta) - M}{[\sin(\Theta)(J^2 - K^2)^{\frac{1}{2}}]}\right) .$$
(C.3)

The momenta conjugate to Euler angles are obtained from

$$p_{\Phi} = \frac{\partial F_2}{\partial \Phi} = M \tag{C.4}$$

$$p_{\Theta} = \frac{\partial F_2}{\partial \Theta} = \frac{1}{\sin(\Theta)} \left((J^2 - K^2) \sin^2(\Theta) - (K\cos(\Theta) - M)^2) \right)^{\frac{1}{2}}$$
(C.5)

$$p_{\Psi} = \frac{\partial F_2}{\partial \Psi} = K \tag{C.6}$$

and the new coordinates from

$$q_J = \frac{\partial F_2}{\partial J} = \arccos\left(\frac{J^2 \cos(\Theta) - MK}{[(J^2 - K^2)(J^2 - M^2)]^{\frac{1}{2}}}\right)$$
(C.7)

$$q_M = \frac{\partial F_2}{\partial M} = \Phi - \arccos\left(\frac{M\cos(\Theta) - K}{[\sin(\Theta)(J^2 - M^2)^{\frac{1}{2}}]}\right)$$
(C.8)

$$q_K = \frac{\partial F_2}{\partial K} = \Psi - \arccos\left(\frac{K\cos(\Theta) - M}{\left[\sin(\Theta)(J^2 - K^2)^{\frac{1}{2}}\right]}\right) , \qquad (C.9)$$

the last of which is useful to rearrange to

$$K\cos(\Theta) - M = (J^2 - K^2)^{\frac{1}{2}}\sin(\Theta)\cos(\Psi - q_K)$$
. (C.10)

These expressions can be used together with $\boldsymbol{p}_J = (\boldsymbol{S}^{\mathrm{T}})^{-1} \boldsymbol{p}$ (see equation (B.11)) to

obtain the body-fixed components of angular momentum,

$$J_x = -\frac{\cos(\Psi)p_{\Phi}}{\sin(\Theta)} + \sin(\Psi)p_{\Theta} + \frac{\cos(\Psi)\cos(\Theta)p_{\Psi}}{\sin(\Theta)}$$
(C.11)
$$= \frac{\cos(\Psi)}{\sin(\Theta)} \left(K\cos(\Theta - M)\right) + \frac{\sin(\Psi)}{\sin(\Theta)} \left((J^2 - K^2)\sin^2(\Theta) - (K\cos(\Theta) - M)^2\right)^{\frac{1}{2}}$$
(C.12)

$$J_y = \frac{\sin(\Psi)p_{\Phi}}{\sin(\Theta)} + \cos(\Psi)p_{\Theta} - \frac{\sin(\Psi)\cos(\Theta)p_{\Psi}}{\sin(\Theta)}$$
(C.13)

$$= -\frac{\sin(\Psi)}{\sin(\Theta)} \left(K\cos(\Theta - M) \right) + \frac{\cos(\Psi)}{\sin(\Theta)} \left((J^2 - K^2) \sin^2(\Theta) - (K\cos(\Theta) - M)^2 \right)^{\frac{1}{2}}$$
(C.14)

$$J_z = p_{\Psi} = K . \tag{C.15}$$

Applying equation (C.10) simplifies the expressions to

$$J_x = (J^2 - K^2)^{\frac{1}{2}} \cos(q_K) \tag{C.16}$$

$$J_y = -(J^2 - K^2)^{\frac{1}{2}} \sin(q_K) \tag{C.17}$$

$$J_z = K {.} (C.18)$$

The Hamiltonian in the transformed coordinates is

$$\mathcal{H} = \frac{1}{2I_r} \left(J^2 - K^2 + \frac{2K(J^2 - K^2)^{\frac{1}{2}}\cos(q_K)\cos(\theta)}{\sin(\theta)} + \frac{K^2\cos^2(\theta)}{\sin^2(\theta)} \right)$$
(C.19)

$$+\frac{1}{2I_r}\left(p_{\theta}^2 - 2(J^2 - K^2)^{\frac{1}{2}}\sin(q_K)p_{\theta}\right) + \frac{1}{2I_R}\left(p_{\theta}^2 + \frac{K^2}{\sin^2(\theta)}\right)$$
(C.20)

$$+\frac{p_R^2}{2\mu_R} + \frac{p_r^2}{2\mu} + V(r, R, \theta) , \qquad (C.21)$$

where

$$V(r, R, \theta) = V(r, \theta) + 2\mu_R \pi^2 \nu_{\text{harm}}^2 (R - R_{\text{eq}})^2 .$$
 (C.22)

Here it has been assumed that the harmonic potential is decoupled from the two-dimensional potential provided by Harding et al.⁴¹ This is, of course, a very bad approximation at short centres-of-mass separations, but the purpose is here is to compare trajectory results with TST, so the details of the potential are not essential. What matters is that the potential is the same for both.

The equations of motions are obtained the standard way,

$$\dot{\boldsymbol{q}} = \frac{\partial \mathcal{H}}{\partial \boldsymbol{p}}$$
 $\dot{\boldsymbol{p}} = -\frac{\partial \mathcal{H}}{\partial \boldsymbol{q}}$. (C.23)

The trajectories are started from a centres-of-masses distance r = 30 Å. The initial conditions are microcanonically sampled as follows (*E* and *J* fixed):

1. The orientation of the fragments are set by $q_K = 2\pi x_1$ and $\theta = \pi x_2$, where x_i is a random number in the range [0,1].

- 2. The diatom distance is initially set to its equilibrium value R = 1.2075 Å, and then K is sampled from $K = (2x_3 1)J$. Afterwards, the initial rotational energy $E_{\rm rot}$ is calculated from the Hamiltonian by setting $p_{\theta} = p_{\rm r} = p_{\rm R} = 0$.
- 3. The energy of the diatom vibration is set by

$$E_{\rm vib} = (E - E_{\rm rot})x_4 . \qquad (C.24)$$

The position and momentum are then set by

$$R = R_{\rm eq} + \left(\frac{E_{\rm vib}}{2\pi^2 \mu_R \nu_{\rm harm}^2}\right)^{\frac{1}{2}} \cos(2\pi x_5) \tag{C.25}$$

$$p_R = -(2\mu_R E_{\rm vib})^{\frac{1}{2}} \sin(2\pi x_5)$$
 (C.26)

4. The energy associated with the internal diatom rotation is sampled from

$$E_{\rm int} = (E - E_{\rm rot} - E_{\rm vib})x_6$$
 . (C.27)

The corresponding momentum is obtained by solving

$$\frac{1}{2I_r} \left(p_\theta^2 - 2(J^2 - K^2)^{\frac{1}{2}} \sin(q_K) p_\theta \right) + \frac{p_\theta^2}{2I_R} = E_{\text{int}}$$
(C.28)

for p_{θ} . This is a quadratic equation and the positive and negative roots are randomly chosen.

5. Finally, the translational energy is obtained from

$$E_{\text{trans}} = E - \mathcal{H}(q_K, \theta, r, R, K, p_\theta, p_R, p_r = 0) , \qquad (C.29)$$

which is solved for p_r to get

$$p_r = -(2\mu E_{\rm trans})^{\frac{1}{2}}$$
 (C.30)

Only the negative root is taken as we are interested in reactive collisions. Since the trajectories are initiated from r = 30 Å (the interaction potential is virtually zero), it is fair to assume that any trajectory with $p_r > 0$ will never make it to the product valley.

At each step, it is checked that $\mathcal{H} \leq E$, and if $\mathcal{H} > E$, the whole sampling procedure is restarted. When the initial conditions are set like this, the average initial energy associated with each mode are related by $\langle E_{\rm vib} \rangle \approx 2 \langle E_{\rm int} \rangle \approx 2 \langle E_{\rm trans} \rangle$.

The purpose of the trajectory calculations was to obtain an estimate for the number of trajectories that recross the variationally optimised dividing surface at a given E and J. This information was used to calculate a dynamic correction factor

$$\chi(E,J) = \frac{N_{\text{norecross}}}{N_{\text{norecross}} + N_{\text{recross}}} , \qquad (C.31)$$

where $N_{\text{norecross}}$ and N_{recross} are the number of trajectories that cross the dividing surface only once and more than once, respectively. This correction factor was then used to compute a canonical rate coefficient from

$$k(\beta) = \frac{1}{hQ(\beta)_{\text{react}}} \int_0^\infty \int_0^\infty \chi(E, J) N_{\text{FTST}}^{\ddagger}(E, J) e^{-\beta E} dJ dE .$$
(C.32)

The trajectories were run in batches of 560. If the value of $\chi(E, J)$ changed by less than 1%, the trajectory runs for the specified E and J were terminated. An individual trajectory was terminated when it was deemed reactive (100 kJ mol⁻¹ down in the HO₂• potential well), unreactive (returned back to the initial centres-of-mass distance 30 Å), or when the energy of the trajectory differed more than 1% from the initial energy. The number of trajectories for a given E and J that failed due to energy conservation or other numerical issues were always negligible and often zero.

The codes used in the trajectory and FTST calculations can be inspected here: https://github.com/ttpekkan/git

D Inverse Laplace Transform

The canonical rate coefficient of a reaction can be expressed in terms of the Laplace transform of the *J*-averaged state sum $N^{\ddagger}(E)_J$ of the TS,

$$k(\beta) = \frac{\int_0^\infty \int_0^\infty \rho_{\text{react}}(E, J) k(E, J) \mathrm{e}^{-\beta E} \mathrm{d}J \mathrm{d}E}{\int_0^\infty \int_0^\infty \rho_{\text{react}}(E, J)) \mathrm{d}J \mathrm{e}^{-\beta E} \mathrm{d}E}$$
(D.1)

$$=\frac{\int_0^\infty \rho_{\text{react}}(E)_J k(E)_J \mathrm{e}^{-\beta E} \mathrm{d}E}{\int_0^\infty \rho_{\text{react}}(E)_J \mathrm{e}^{-\beta E} \mathrm{d}E}$$
(D.2)

$$=\frac{\int_0^\infty N^{\ddagger}(E)_J \mathrm{e}^{-\beta E} \mathrm{d}E}{hQ(\beta)} \tag{D.3}$$

$$=\frac{L[N^{\ddagger}(E)_J]}{hQ_{\text{react}}(\beta)}.$$
(D.4)

This procedure can be inverted to obtain $N^{\ddagger}(E)_J$ from the canonical rate coefficient. For example, if one wanted to obtain the TS state sum for a A + B recombination reaction, one can obtain it from

$$N^{\ddagger}(E)_J = hL^{-1}[k_{\rm dis}(\beta)Q_{\rm AB,rovib}(\beta)] .$$
 (D.5)

The equilibrium constant relates the recombination and dissociation rate coefficients,

$$K(\beta) = \frac{k_{\rm rec}(\beta)}{k_{\rm dis}(\beta)} \frac{p^{\ominus}}{RT} = \frac{k_{\rm rec}(\beta)}{k_{\rm dis}(\beta)} \frac{1}{V^{\ominus}} , \qquad (D.6)$$

 \mathbf{SO}

$$N^{\ddagger}(E)_{J} = hL^{-1} \left[\frac{k_{\text{rec}}(\beta)}{K(\beta)V^{\ominus}} Q_{\text{AB,rovib}}(\beta) \right]$$
(D.7)

$$= hL^{-1} \left[k_{\rm rec}(\beta) \frac{Q_{\rm A,trans}(\beta) Q_{\rm B,trans}(\beta)}{Q_{\rm AB,trans}(\beta) V^{\ominus}} \frac{Q_{\rm AB,rovib}(\beta)}{Q_{\rm AB,rovib}(\beta)} Q_{\rm A,rovib}(\beta) Q_{\rm B,rovib}(\beta) e^{\beta \Delta_{\rm r} E} \right]$$
(D.8)

$$= h \left(\frac{2\pi\mu}{h^2}\right)^{\frac{3}{2}} L^{-1} \left[k_{\rm rec}(\beta) \left(\frac{1}{\beta}\right)^{\frac{3}{2}} Q_{\rm A,B,rovib}(\beta) e^{\beta \Delta_{\rm r} E} \right] .$$
(D.9)

Here $p^{\ominus} = 1$ bar and V^{\ominus} are the standard pressure and volume, respectively, and μ is the reduced mass of the recombining fragments. If the canonical recombination rate coefficient is expressed in modified Arrhenius form

$$k_{\rm rec}(\beta) = A \left(\frac{\beta_0}{\beta}\right)^m e^{-\beta E'_{\rm a}} , \qquad (D.10)$$

one obtains

$$N^{\ddagger}(E)_{J} = Ah\beta_{0}^{m} \left(\frac{2\pi\mu}{h^{2}}\right)^{\frac{3}{2}} L^{-1} \left[\left(\frac{1}{\beta}\right)^{m+\frac{3}{2}} e^{-\beta(E_{a}^{\prime}-\Delta_{r}E)} Q_{A,B,rovib}(\beta) \right]$$

$$= \frac{Ah\beta_{0}^{m}}{\Gamma(m+\frac{3}{2})} \left(\frac{2\pi\mu}{h^{2}}\right)^{\frac{3}{2}} \int_{0}^{E} u(\epsilon + \Delta_{r}E - E_{a}^{\prime})(\epsilon + \Delta_{r}E - E_{a}^{\prime})^{m+\frac{1}{2}} \rho_{A,B,rovib}(E-\epsilon) d\epsilon$$

(D.11)

E Torsional Coupling

The starting point of the derivation is the kinetic energy expression of the coupled internalexternal rotation system,

$$2\mathcal{T} = \begin{pmatrix} \boldsymbol{\omega} & \dot{\boldsymbol{q}}_{\text{int}} \end{pmatrix} \begin{pmatrix} \boldsymbol{I} & \boldsymbol{C}^{\mathrm{T}} \\ \boldsymbol{C} & \boldsymbol{I}_{\text{int}} \end{pmatrix} \begin{pmatrix} \boldsymbol{\omega} \\ \dot{\boldsymbol{q}}_{\text{int}} \end{pmatrix} = \dot{\boldsymbol{Q}}^{\mathrm{T}} \boldsymbol{A} \dot{\boldsymbol{Q}} .$$
(E.1)

Here $\boldsymbol{\omega} = (\omega_x, \omega_y, \omega_z)$, \boldsymbol{I} is the moment of inertia tensor, \boldsymbol{C} contains the coupling terms between internal and external rotations, and $\boldsymbol{I}_{\text{int}}$ are the inertial moments about a given bond and their coupling terms. Like in Appendix B, the relationship between \boldsymbol{Q} and the generalised Euler velocities is given by $\dot{\boldsymbol{Q}} = \boldsymbol{S} \dot{\boldsymbol{q}}$ (see equation B.5), so

$$2\mathcal{T} = \dot{\boldsymbol{Q}}^{\mathrm{T}} \boldsymbol{A} \dot{\boldsymbol{Q}} = (\boldsymbol{S} \dot{\boldsymbol{q}})^{\mathrm{T}} \boldsymbol{A} \boldsymbol{S} \dot{\boldsymbol{q}} = \dot{\boldsymbol{q}}^{\mathrm{T}} \boldsymbol{a} \dot{\boldsymbol{q}} .$$
(E.2)

As shown in Appendix B, $\dot{\boldsymbol{q}} = \boldsymbol{a}^{-1}\boldsymbol{p}$, which gives

$$2\mathcal{T} = \boldsymbol{p}^{\mathrm{T}}\boldsymbol{g}\boldsymbol{p} , \qquad (\mathrm{E.3})$$

where $\boldsymbol{g} = \boldsymbol{a}^{-1}$. Now we have the Hamiltonian

$$\mathcal{H} = \frac{1}{2} \boldsymbol{p}^{\mathrm{T}} \boldsymbol{g} \boldsymbol{p} + V(\boldsymbol{q}_{\mathrm{int}})$$
(E.4)

and the partition function for the coupled system is obtained from

$$Q(\beta) = \frac{1}{h^n} \int \int \left(e^{-\frac{1}{2} \boldsymbol{p}^{\mathrm{T}} \boldsymbol{g} \boldsymbol{p} \beta} \mathrm{d} \boldsymbol{p} \right) e^{-V(\boldsymbol{q}_{\mathrm{int}})\beta} \mathrm{d} \boldsymbol{q} .$$
(E.5)

The integrals over the momenta and Euler angles $(|\boldsymbol{a}| = \sin(\Theta)|\boldsymbol{A}| = \sin(\Theta)|\boldsymbol{G}|^{-1})$ can be done analytically, giving

$$Q(\beta) = 8\pi^2 \left(\frac{2\pi}{\beta h^2}\right)^{\frac{n}{2}} \int |\boldsymbol{A}|^{\frac{1}{2}} \mathrm{e}^{-V(\boldsymbol{q}_{\mathrm{int}})\beta} \mathrm{d}\boldsymbol{q}_{\mathrm{int}} .$$
(E.6)

Since

$$Q(\beta) = L[\rho(E)] \tag{E.7}$$

can be inverted to give

$$\rho(E) = L^{-1}[Q(\beta)], \qquad (E.8)$$

we get

$$\rho(E) = 8\pi^2 \left(\frac{2\pi}{h^2}\right)^{\frac{n}{2}} L^{-1} \left[\left(\frac{1}{\beta}\right)^{\frac{n}{2}-1} \int |\boldsymbol{A}|^{\frac{1}{2}} \frac{1}{\beta} e^{-V(\boldsymbol{q}_{\rm int})\beta} \mathrm{d}\boldsymbol{q}_{\rm int} \right]$$
(E.9)

$$= 8\pi^2 \left(\frac{2\pi}{h^2}\right)^{\frac{n}{2}} \frac{1}{\Gamma(\frac{n}{2}-1)} \int_0^E \int (E-\epsilon)^{\frac{n}{2}-2} u(\epsilon - V(\boldsymbol{q}_{\text{int}}) |\boldsymbol{A}|^{\frac{1}{2}} \mathrm{d}\boldsymbol{q}_{\text{int}} \mathrm{d}\epsilon \;. \tag{E.10}$$

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