AFRL-RV-PS-TR-2019-0160 **AFRL-RV-PS-TR-2019-0160**

STATE-RESOLVED AEROTHERMODYNAMIC MODELING FOR AIR USING QCT DATA

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20 December 2018

Final Report

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REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE *(DD-MM-YYYY)* 20-12-2018	**2. REPORT TYPE** Final Report	**3. DATES COVERED** *(From - To)* 21 Jun 2017 – 20 Dec 2018

4. TITLE AND SUBTITLE
State-Resolved Aerothermodynamic Modeling for Air Using QCT Data

5a. CONTRACT NUMBER
FA9453-17-2-0081

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
62601F

6. AUTHOR(S)
Thomas E. Schwartzentruber

5d. PROJECT NUMBER
1010

5e. TASK NUMBER
PPM00035156

5f. WORK UNIT NUMBER
EF133295

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Regents of the University of Minnesota
200 Oak Street SE, Suite 224
Minneapolis, MN 55455-2009

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Air Force Research Laboratory
Space Vehicles Directorate
3550 Aberdeen Avenue SE
Kirtland AFB, NM 87117-5776

10. SPONSOR/MONITOR'S ACRONYM(S)
AFRL/RVBN

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AFRL-RV-PS-TR-2019-0160

12. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Recently, due to continued advancements in computational chemistry and large-scale parallel computing, molecular level physics can be investigated using ab-initio computations. The most common analysis technique is called Quasi-Classical-Trajectory (QCT) analysis, wherein a large number of individual molecular collisions are simulated using a potential energy surface (PES) that dictates the forces on individual atoms comprising the molecules. Since the molecular systems of interest for air are small (typically 2-4 atoms), the PES can be fit to highly accurate electronic structure calculations. In the past 5 years a number of such results have been reported. The challenge now is to reduce this huge amount of data into accurate, yet tractable, models for predictive hypersonic flow simulations. The goal of the grant research was to develop accurate, yet tractable, models for both the direct simulation Monte Carlo (DSMC) particle method as well as for continuum computational fluid dynamics (CFD) methods.

15. SUBJECT TERMS

hypersonics, state-resolved, quasiclassical trajectory, air model, direct simulation Monte Carlo, computational fluid dynamics, potential energy surface, collisional cross sections, non-equilibrium, reproducing kernel Hilbert space, quasi-steady-state

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** Dr. Raymond Bemish
a. REPORT Unclassified	**b. ABSTRACT** Unclassified	**c. THIS PAGE** Unclassified	Unlimited	16	**19b. TELEPHONE NUMBER** *(include area code)*

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. 239.18

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ACKNOWLEDGMENTS

This material is based on research sponsored by Air Force Research Laboratory under agreement number FA9453-17-2-0081. The U.S. Government is authorized to reproduce and distribute reprints for Governmental purposes notwithstanding any copyright notation thereon.

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FINAL GRANT REPORT

State-resolved Aerothermodynamic Modeling for Air Using QCT Data

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Grant Period: 06/21/2017 through 12/20/2018

1.1 Introduction

Recently, due to continued advancements in computational chemistry and large-scale parallel computing, molecular level physics can be investigated using ab-initio computations. The most common analysis technique is called Quasi-Classical-Trajectory (QCT) analysis, wherein a large number of individual molecular collisions are simulated using a potential energy surface (PES) that dictates the forces on individual atoms comprising the molecules. Since the molecular systems of interest for air are small (typically 2-4 atoms), the PES can be fit to highly accurate electronic structure calculations [1-3]. In the past 5 years a number of such results have been reported [4-7]. The challenge now is to reduce this huge amount of data into accurate, yet tractable, models for predictive hypersonic flow simulations. The goal of the grant research was to develop accurate, yet tractable, models for both the direct simulation Monte Carlo (DSMC) particle method [8,9] as well as for continuum computational fluid dynamics (CFD) methods [10].

1.2 Required Quasi-Classical-Trajectory (QCT) data

Each particle in a collision represents a particular species that can be an atom, diatom, or polyatomic molecule. Each particle has a molecular mass (m), a center-of-mass velocity vector (v_x, v_y, v_z), and internal energies (ε_{rot} and ε_{vib}) if it is a diatomic or polyatomic molecule. Particles can also have electronic energy (ε_{el}) and, for ionized flows, particles can also represent free electrons. In order to model collisions between particles, one requires probabilities that particles will transition to a new energy state or possibly react to form new product species. Since internal energy states are quantized, such transitions can be written in the following form [11]:

$$A_2(j_1, v_1) + B_2(j_2, v_2) \rightarrow A_2(j_1', v_1') + B_2(j_2', v_2') \ , \tag{1}$$

where A_2, B_2 are two molecules with initial internal energy states $(j_1, v_1), (j_2, v_2)$ and final internal energy states $(j_1', v_1'), (j_2', v_2')$, respectively. Here j_1, j_2, j_1', j_2' represent the rotational quantum numbers, while v_1, v_2, v_1', v_2' represent the vibrational quantum numbers.

The required state-to-state transition probabilities are referred to by:

$$P(g;j,v \to j',v') = \frac{\sigma(g;j,v \to j',v')}{\sigma(g;j,v)} \quad (2) \qquad \sigma(g;j,v) = \sum_{j',v'} \sigma(g;j,v \to j',v') \quad (3)$$

Here, the numerator is the cross-section of transitioning to/from specific internal energy states and the denominator is the total cross-section, which is the summation of all possible transitions. The relative velocity of the collision pair is denoted by *g*. If these probabilities can be obtained, they can be used directly within the DSMC method. Note that the impact parameter and scattering angle of colliding particles has been integrated-out of the cross-sections (σ). In a dilute gas, impact parameters and therefore scattering angles are almost completely random, and such integration/averaging over impact parameter is an accurate assumption.

Therefore, modeling requires probabilities that are a function of the relative collision velocity *g* (or relative translational energy ε_{rel}), and the pre- and post-collision internal energy states. It is important to note that although internal energies are quantized (*j,v* quantum numbers), treating them as continuous energy modes (ε_{rot} and ε_{vib}) is also accurate.

1.3 Research Accomplishments

From SOW: *Collect existing QCT data from the literature in addition to ongoing QCT research from University of Minnesota groups and collaborators. Much of this collision data (pre- and post-collision states of billions of collisions) is stored at the University of Minnesota in .hdf5 file format.*

From SOW: *Determine the most suitable representation of the significant amount of QCT data, such as relevant averages taken over specific energy modes. Infer the most important physical trends from the data.*

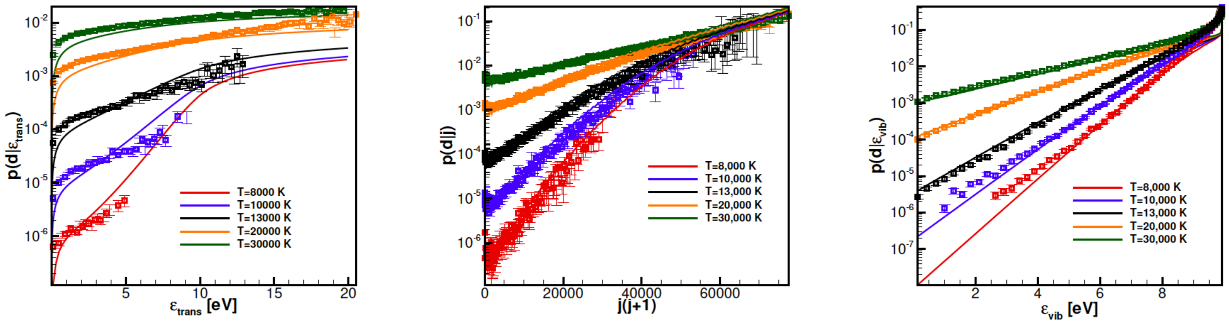
As shown in Fig. 1, a large amount of QCT collision data has been generated and processed. This involves using the pre- and post-collision state data to generate the probabilities discussed above, which are required for modeling. While the probabilities are highly-dimensional, we have found that formulating "conditional" probabilities is the best approach for model reduction. For example, the following conditional probabilities are plotted in Fig. 1:

$$p(d|\epsilon_{trans}) = \sum_{v}^{v_{\max}} \sum_{j}^{j_{\max}(v)} p(d \mid \epsilon_{rel}, \epsilon_v, \epsilon_{rot}) f(j,v;T) \quad (4)$$

$$p(d|j) = \sum_{v=0}^{v_{\max}} \int_0^\infty p(d \mid \epsilon_{rel}, \epsilon_v, \epsilon_{rot}) \left(\frac{\epsilon_{rel}}{k_B T}\right) \exp\left[-\frac{\epsilon_{rel}}{k_B T}\right] d\left(\frac{\epsilon_{rel}}{k_B T}\right) f(j,v;T) \quad (5)$$

$$p(d|v) = \sum_{j=0}^{j_{\max}} \int_0^\infty p(d \mid \epsilon_{rel}, \epsilon_v, \epsilon_{rot}) \left(\frac{\epsilon_{rel}}{k_B T}\right) \exp\left[-\frac{\epsilon_{rel}}{k_B T}\right] d\left(\frac{\epsilon_{rel}}{k_B T}\right) f(j,v;T) \quad (6)$$

These conditional probabilities represent the probability of dissociation given a fixed a value of ε_{rel} (ε_{trans}) , or ε_{rot} , or ε_{vib} , while averaging over Boltzmann distributions of the other quantities at a corresponding temperature. When the data are plotted in this manner, very clear trends are evident. As seen in Figs. 1b and 1c, the dissociation probability clearly scales exponentially with rotational and vibrational energy.



(a) Reaction probability as function of relative translational energy.

(b) Reaction probability as function of rotational energy.

(c) Reaction probability as function of vibrational energy.

Figure 1: Conditional reaction probabilities. Symbols denote QCT results and solid lines represent new model results.

From SOW: *Construct analytical expressions that best fit the physical trends and QCT data, and use these expressions to create new models for DSMC.*

Based on the clear physical trends observed (such as those shown in Fig. 1), we developed the following probability model:

$$\begin{aligned} p(d \mid \epsilon_{rel},\epsilon_v,\epsilon_{rot}) &= C_1 \overbrace{\left[\frac{\epsilon_{rel}+\epsilon_{int}-\epsilon_d^{\text{eff}}}{\epsilon_d}\right]^{\alpha} \frac{\epsilon_d}{\epsilon_{rel}}}^{\text{I : Collision Energy}} \; \overbrace{\exp\left[\beta\frac{\epsilon_{rot}^{\text{eff}}}{\epsilon_d}\right]}^{\text{II: Rotational Energy}} \\ &\quad \times \underbrace{\exp\left[\gamma\frac{\epsilon_v}{\epsilon_d}\right]}_{\text{III: Vibrational Energy}} \; \underbrace{\exp\left[\delta\frac{|\epsilon_{int}-\epsilon_d|}{\epsilon_d}\right]}_{\text{IV: Internal Energy}} \qquad \epsilon_{rel}+\epsilon_{int}\geq\epsilon_d^{\text{eff}} \\ &= 0 \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{otherwise} \end{aligned} \tag{7}$$

The expression consists of four terms. The first term controls the influence of translational energy on the probability of dissociation. Essentially, the first term ensures that the collision energy is greater than the dissociation energy. This form and the power-law dependence is somewhat common in the literature, and we find it fits the data well. The additional term ($\varepsilon_d/\varepsilon_{rel}$) ensures that for high-translational energy the collisions result in "fly-by" collisions rather than reactions, as physically expected. The second and third terms model an exponential dependence on both rotational and vibrational energy, with fitting parameters γ and β that set the slopes seen in Figs. 1b and 1c. The fourth term controls the influence of internal energy and specifically accounts for the difference between bound ($\varepsilon_{int} < \varepsilon_d$) and quasi-bound molecules ($\varepsilon_{int} > \varepsilon_d$). As shown in Fig. 1, this rather-simple expression fits a wide range of QCT data accurately. While other functional forms for the probability may also fit the data well (high-order polynomials for example), the above expression has the advantage of being analytically integrable. As described later in this report, this allowed us to formulate analytically consistent DSMC *and* CFD models.

From SOW: *At the same time, use the multidimensional fitting techniques to* ***directly fit the QCT data****, and incorporate the fast-evaluation technique into DSMC.*

The new probability model (cross-section model) clearly fits the conditional probabilities well (Fig. 1). However, it may also be of interest to fit each individual state-resolved cross-section accurately. Therefore, we also investigated the accuracy of our model against the raw QCT state-resolved cross-section data. Specifically, instead of plotting an integrated result (conditional probability), we analyzed the correlation between individual cross-sections by plotting the ratio of $p(d|\varepsilon_{rel}, \varepsilon_{vib}, \varepsilon_{rot})$/p-QCT in Fig. 2, for a large number of individual cross-sections.

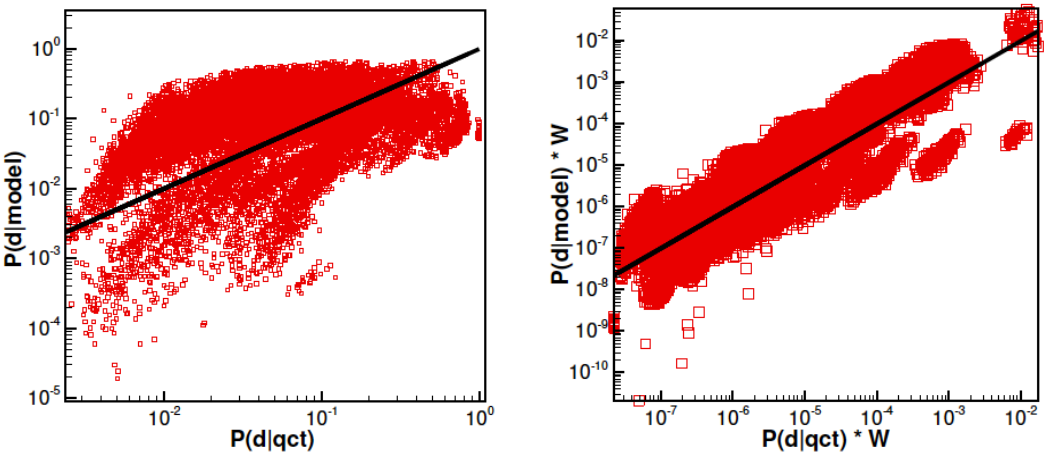


Figure 2: Correlation of estimated dissociation cross-section using the model and QCT simulations. Black line indicates slope of unity for reference.

In Fig. 2, the correlation between the cross-section using the proposed model and raw QCT data is shown. The ratio of the reaction probabilities from the model and QCT is centered around unity for a significant number of data points, however noticeable deviation of the data points from unity also exists. Figure 2a shows the correlation when the model is fit to raw QCT data using a least-squares approach where each cross-section has the same weight towards the accuracy of the fit. Figure 2b shows the correlation when the model is fit to raw QCT data where the importance of each cross-section in the fit is weighted by its Boltzmann statistical weight (at a temperature of 10,000 K). We find no noticeable increase in accuracy using such weighting, and conclude that our simple probability expression captures conditional probabilities very accurately and captures individual state-resolved probabilities within one order of magnitude. If for certain applications, high accuracy for all state-specific cross-sections is required, one may fit using high-order polynomials, or high-order expansions (perhaps using the terms in our expression), or even neural network fits to the raw QCT data.

In fact, this grant involved collaboration with a computational chemistry group at the University of Basel, Switzerland, led by Prof. Markus Meuwly. The MN student funded on the current AFRL project visited the University of Basel. It was decided that the MN student funded on the current AFLR grant would continue to focus on the above analytical probability model, while Basel researchers focused on a neural network approach. Their approach led to the following publication:

> *Koner, D., Unke, O.T., Boe, K., Bemish, R.J., and Meuwly, M., "Exhaustive state-to-state cross sections for reactive molecular collisions from importance sampling simulation and a neural network representation", J. Chem. Phys., 150, 211101 (2019).*

Therefore, fitting QCT data with a neural network, is in-fact a viable alternative. The advantage is an increase in accuracy at the state-resolved cross-section level, while the disadvantage is cost, complexity, and the fact that it cannot be integrated to formulate a continuum model for CFD. As shown below, we believe that the accuracy of the analytical probability model is more than sufficient for accurate DSMC and CFD simulations.

From SOW: *At the same time, use the multidimensional fitting techniques to directly fit the QCT data, and* ***incorporate the fast-evaluation technique*** *into DSMC.*

A second collaboration with University of Basel researchers involved fitting the Potential Energy Surface (PES) using an advanced kernel-based fitting approach [12-14]. This technique has two important benefits. First, it is a general multidimensional fitting procedure that can be automated instead of requiring the significant amount of researcher time/effort currently involved in fitting multidimensional surfaces. Second, the technique to evaluate the curve-fit for any point in the multidimensional space is extremely fast. The technique accomplishes a near-complete tradeoff, where much of the parameters required for an evaluation are pre-determined and stored compactly in memory and only a few floating point operations are required. That is, computational cost is drastically reduced while the memory required for the algorithm is drastically increased. This is particularly exciting since current QCT calculations are limited by floating point operations and large amounts of memory (RAM) lies unused.

The technique could be used to create new multidimensional potential energy surfaces (PESs) for each type of collision involving air species, using the electronic structure data from the Truhlar group [1-3]. When writing the proposal, we had reason to believe that a dramatic (possibly 10x) speedup in QCT and DMS calculations could be achieved using this technique.

During the collaborative visit, when the MN student funded under this AFRL grant visited the University of Basel, this kernal-based approach was investigated. Although the kernal-based approach was successful for $N+N_2$ collisions, it was unfortunately not successful for diatom-diatom collisions, such as N_2+N_2. The reason is actually evident in the paper listed below. Without going into the details, the number of parameters that require pre-computing and storage for the kernal-based technique scales with $\sim 2^{(2d)}$, where d is the dimension of the problem (number of degrees of freedom for a molecular configuration). This can be seen in Eq. 11 in the paper below (the parameters are labelled as γ). For a three-atom system, d=3 and the kernal-based method works very well. However, for a four-atom system, *d*=6, and the number of parameters required becomes > 4000. This is now *more* parameters than the global polynomial curve fits used by the Truhlar group for their PESs. As a result, for our systems of interest (N4 and N2O2), the kernal-based method did not offer increased computational efficiency. It is also noted that the computational cost analysis presented in Fig. 2 of the paper below corresponds to *d*=1. Therefore, unfortunately this aspect of the proposal was unsuccessful, but it was worth the try, and we now understand what the limitation is.

> *Unke, O.T. and Meuwly, M., "Toolkit for the construction of reproducing kernal-based representations of data: Application to multidimensional potential energy surfaces", Journal of Chemical Information and Modeling, 2017, 57 (8), pp. 1923-1931.*

From SOW: *Perform demonstration DSMC simulations to investigate the accuracy and efficiency of the new DSMC models, compared to prior DSMC models.*

As part of the grant research, we were actually able to create both new DSMC and new CFD models. This is a direct result of the fact that we were able to formulate a simple (yet accurate) analytical probability model. A new continuum-level dissociation rate expression was analytically obtained by integrating the probability model (described earlier). No new free parameters are introduced and the molecular and continuum models are mathematically consistent. The new continuum model captures (i) the influence of translational energy, rotational energy, and vibrational energy on dissociation, (ii) the distributions of rotational and vibrational energy in the gas, in addition to (iii) non-Boltzmann effects including overpopulation (and depletion) of high vibrational energy states during rapid excitation (and quasi-steady-state dissociation).

For comparison, the widely used Park model is a standard Arrhenius rate model but uses an `effective' temperature (T_{eff}) that is empirically set as the geometric mean of T and T_V:

$$k(T,T_V) = A T_{eff}^{\eta} \exp\left[-\frac{\varepsilon_d}{k_B T_{eff}}\right], \quad T_{eff} = \sqrt{T\ T_V} \tag{8}$$

In contrast, our new model derives analytically from kinetic theory, specifically using the molecular-level model expressions based on QCT/DMS ab-initio results presented earlier in this report. The new dissociation rate expression is:

$$k(T, T_{rot}, T_v) = AT^{\eta} \exp\left[-\frac{\epsilon_d}{k_B T}\right] * \left[\mathrm{H}(\epsilon_d, 0, 1) + \mathrm{H}(\epsilon_d^{\max}, \epsilon_d, 2)\right] \tag{9}$$

$$\eta = \alpha - \frac{1}{2}; \quad (10) \quad A = \frac{1}{S}\left(\frac{8k_B}{\pi\mu_C}\right)^{1/2} \pi b_{\max}^2 C_1 \Gamma[1+\alpha]\left(\frac{k_B}{\epsilon_d}\right)^{\alpha-1} \qquad (11)$$

$$\mathrm{H}(x, y, n) = \frac{\exp[(-1)^{n-1}}{\mathrm{Z}^{QSS}(T_{rot}, T_v)} \frac{\exp\left[x\delta_{rot}\right] \mathrm{g}^{QSS}(\delta_{vr}) - \exp\left[y\delta_{rot}\right] \mathrm{g}^{QSS}(\delta_v - y\delta_{rot}/\epsilon_d)}{k_B \theta_{rot} \delta_{rot}}; \tag{12}$$

where

$$\delta_{rot} = -\frac{1}{k_B T_{rot}} + \frac{1}{k_B T} + \frac{\beta - \theta_{CB} + (-1)^n \delta}{\epsilon_d} - \frac{\theta_{CB}}{k_B T} + \frac{\delta_{rot}^{NB}}{\theta_{rot} k_B}; \tag{13}$$

$$\delta_v = -\frac{1}{k_B T_v} + \frac{1}{k_B T} + \frac{\gamma + (-1)^n \delta}{\epsilon_d} + \frac{\delta_v^{NB}}{\theta_v^m k_B} \quad (14) \quad \delta_{vr} = \delta_v - \delta_{rot} \qquad (15)$$

While the details of the derivation and full description of all terms is omitted for brevity (contained in listed publications), a few aspects of the model warrant discussion. First, the new model consists of a standard Arrhenius rate expression based on the translation temperature, T. The influence of rotational and vibrational energy on the dissociation rate is contained in a separate term, $H = H(T, T_{rot}, T_v)$. The function H contains effects due to the average rotational and vibrational energy state of the gas, as well as non-Boltzmann effects. The two H terms contain the contribution from bound molecules and quasi-bound molecules, respectively. Second, the parameter α is seen to appear in the translational temperature exponent, the parameter β appears in the rotational energy contribution term, and the parameter γ appears in the vibrational energy contribution term. Recall, from the probability model that these parameters were based on QCT data and therefore no additional free parameters have been introduced in the above continuum rate expression. In fact, as expected from the exponential dependence described previously, the controlling function H consists of exponential functions containing contributions from rotational energy δ_{rot} and vibrational energy δ_v. Third, non-Boltzmann effects due to overpopulation and depletion simply appear as additional individual terms δ_v^{NB} and δ_{rot}^{NB}.

While the above dissociation rate expression may appear to be complex, it is important to note that it is simply a function of T, T_{rot}, and T_v (as well as a number of molecular parameters based on QCT and DMS results). Therefore, this expression can be used in standard large-scale CFD simulations (especially if trans-rotational equilibrium is assumed: $T = T_{rot}$). Finally, since the new model is analytically derived from kinetic theory, DSMC and CFD models should now agree precisely in the near-continuum limit (a necessity for a hybrid CFD-DSMC code).

New model results are compared with the standard Park models, and new model results are also compared with QCT and DMS ab-initio results. Perhaps the most important comparisons are shown in Fig. 3. A zero-dimensional relaxation integration code was developed to test the new continuum models. This allows us to directly compare both standard Park model results and new model results with DMS calculations for rovibrational excitation and dissociation. Figure 3a shows significant differences between the Park model solution and the results of DMS for nitrogen dissociation. Note that the plots show average rotational energy and vibrational energy (not T_{rot} and T_{v}), and that although temperatures are expected to approach an equilibrium value, the average energies in rotational and vibrational modes are not expected to asymptote to the same value. The most important discrepancy is that the effective dissociation rate predicted by the Park model is significantly faster than the DMS result. One main reason for this difference is that the non-preferential energy removal does not remove enough vibrational energy from the gas, resulting in a much higher average vibrational energy, and therefore a higher rate of dissociation. In Fig. 3b, an adiabatic simulation is shown, which approaches a post-shock temperature of approximately 15,000 K. The same trends are evident, where the Park model predicts the vibrational energy content of the gas to be too high, and as a result predicts a faster dissociation rate than observed in the ab-initio DMS calculations.

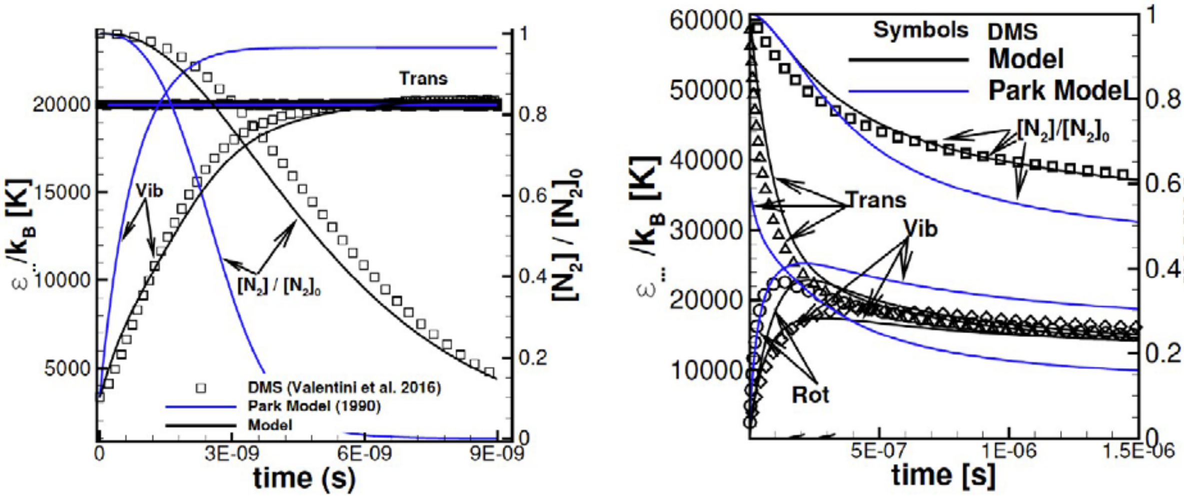


Figure 3 – Zero-dimensional rovibrational excitation and dissociation in nitrogen comparing DMS results with the Park model and the new model. (a) Isothermal relaxation. (b) Adiabatic relaxation.

1.4 Publications Resulting from this Grant

Singh, N. and Schwartzentruber, T.E., "Non-Boltzmann Vibrational Energy Distrubtions and Coupling to Dissociation Rate," Journal of Physical Chemistry A, submitted 2019 – under review.

Singh, N. and Schwartzentruber, T.E., "Consistent Continuum-Kinetic Dissociation Model, Part I: Kinetic Formulation," Journal of Physical Chemistry A, submitted 2019 – under review.

Singh, N. and Schwartzentruber, T.E., "Consistent Continuum-Kinetic Dissociation Model, Part II: Continuum Formulation," Journal of Physical Chemistry A, submitted 2019 – under review.

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