Comparison of quantum mechanical and empirical potential energy surfaces and computed rate coefficients for N_2 dissociation

Richard L. Jaffe[1], David. W. Schwenke[2],

NASA Ames research Center, Mail Stop 230-3, Moffett Field, CA 94035-1000

Simone Venturi[3], Marco Panesi[4],

University of Illinois at Urbana-Champaign, Urbana, IL 61801

and

Maninder Grover[5] and Thomas E. Schwartzentruber[6]

University of Minnesota, Minneapolis, MN 55455

Introduction

Physics-based modeling of hypersonic flows is predicated on the availability of chemical reaction rate coefficients and cross sections for the collisional processes. This approach has been built around the use of quantum mechanical calculations to describe the interaction between the colliding particles. In this approach a potential energy surface (PES) is computed by solving the electronic Schrödinger equation and collision cross sections are determined for that PES using classical, semiclassical or quantum mechanical scattering methods. The rate coefficients are computed by integrating the thermally weighted cross sections. State-to-state rate coefficients are determined by only integrating over a thermal distribution of collisional energies. Finally, thermal rate

[1] Senior Research Scientist, Aerothermodynamics Branch, Mail Stop 230-3. Associate Fellow AIAA. richard.jaffe@nasa.gov

[2] Senior Research Scientist, NAS Applications Branch, Mail Stop 258-3

[3] Graduate Student, Department of Aerospace Engineering, University of Illinois at Urbana-Champaign, 104 Wright St., Urbana, IL 61801.

[4] Assistant Professor, Department of Aerospace Engineering, University of Illinois at Urbana-Champaign, 306 Talbot Lab, 104 Wright St., Urbana, IL 61801, Senior Member AIAA

[5] Graduate Student, Department of Aerospace Engineering and Mechanics, University of Minnesota, Minneapolis, MN 55455, Student Member AIAA

[6] Associate Professor, Department of Aerospace Engineering and Mechanics, University of Minnesota, Minneapolis, MN 55455 Senior Member AIAA

coefficients are determined by summation of the state-to-state rate coefficients for reactions of molecules in all relevant ro-vibrational energy levels. If the flow is in thermal non-equilibrium, the translational, vibrational and rotational energy modes can be represented in different ways: three unique temperatures can be used to describe the distributions, the populations of individual ro-vibrational energy levels can be determined by solving the Master Equation, or through the use of direct simulation in particle-based Monte Carlo sampling. The PES-to-rate coefficient approach had been proposed and attempted in the early days of digital computing, but it is only in the last 15 years that computer hardware and software have been up to the task of calculating accurate interatomic and intermolecular potentials.

Recently several new "first principles" potential energy surfaces to describe ro-vibrational energy transfer and dissociation in molecular nitrogen have become available. These have been computed by solving the quantum mechanical Schrödinger equation for the electronic energy of three or four nitrogen atoms at a large number of geometric arrangements. The resulting energies are fit to an analytical expression for rapid interpolation of the energy for any arbitrary geometry and have been used in quasiclassical trajectory (QCT) calculations to determine collision cross sections and reaction rate coefficients for inelastic and dissociative processes. Examples for $N_2 + N$ collisions are the PESs from NASA Ames Research Center[1-2] and from the Universidade de Coimbra in Portugal[3]. For $N_2 + N_2$ collisions there are PESs from NASA Ames[4], the University of Minnesota[5] and the University of Perugia[6].

Possibly the earliest example of a PES dates to 1931 with the empirical potential of Eyring and Polanyi[7] for the interaction of three hydrogen atoms, which was based on the theoretical Valence Bond theory treatment of London[8] for H_3. This was later made more general by Sato's[9,10] addition of an overlap parameter and used for QCT of atom-diatom exchange reactions involving hydrogen and halogen atoms. Hence the acronym LEPS. The H_3 LEPS potential was used by Erying and others for Transition State Theory[11] calculations of rate coefficients and by Karplus et al. for QCT calculations of atom-diatom collisions[12]. Lagana et al.[13] generated a LEPS potential

for N_2 + N collisions that has been used by Esposito and coworkers[14] for QCT calculations of state-to-state N_2 energy transfer and dissociation rate coefficients.

Each research group has their own recipe for devising the geometric grid, computing the electronic energy (i.e., the atomic orbital basis set expansion and treatment of electron correlation effects used in solving the electronic Schrödinger equation) and defining the analytic expression used to represent the PES. As a result, it is likely that there will be differences between the potentials and between QCT rate coefficients computed using each PES.

With all these potentials available for use, the obvious questions arise, such as: How do these PESs compare? How sensitive are QCT cross sections or rate coefficients to the accuracy of the PES? Most importantly, what cross sections or rate coefficients should be used for Discrete Simulation Monte Carlo (DSMC) and Computational Fluid Dynamics (CFD) flow field calculations? In this presentation comparisons will be made between the different PESs and between thermal and phenomenological rate coefficients computed using them. The most complete datasets of cross sections and rate coefficients have been obtained using the NASA Ames[4] and University of Minnesota[5] PESs for N_2 + N_2, so those comparisons will be the major emphasis of this proposed paper. Most of the rate coefficient comparisons will be made for thermal dissociation and rovibrational energy transfer (i.e., rovibrational relaxation)[4,15]. However, work at Ames[16] and Minnesota[17] have used 0-d Master Equation and Monte Carlo models to compute phenomenological dissociation rate coefficients, which take into account energy other collisional processes such as relaxation and recombination. For the proposed study, we will also compare these processes. As both the NASA Ames and U. Minnesota potentials are independent and free from empirical calibration, the results of these comparisons should provide validation of this aspect of the physics-based approach to hypersonic chemistry models.

Results

        As an example of PES comparisons, the Minnesota[5] and Ames[4] PES for rectangular N_4 geometries are shown in Figure 1. In this arrangement, two N_2 molecules (both with bond length r) are a distance R apart. R (in bohr) is plotted along the x-axis and r (in bohr) is plotted along the y-axis. Each contour line represents a constant value of the N_4 potential energy relative to the energy of two N_2 molecules at $r = r_e$ and $R = \infty$. The red line represents zero energy and each successive blue line represents an increase in energy of 5 kcal/mol. The green line on the bottom plot is the locus of points with $r = R$ (square geometries). One can see that for the two cases (NASA and Minnesota) the PESs are quite similar. For the low energy region around the $r \cong r_e$ and $R \geq 5$ bohr, the channel in the NASA PES is narrower in r and shallower in R. Other small differences can be seen throughout the contour plots. The differences between these potentials will be analyzed in greater detail in the proposed paper.

        Figure 2 shows a comparison of thermal rate coefficients for $N_2 + N \rightarrow N + N + N$. The QCT rate coefficients from NASA[1,2] and Bari University[14] are compared with the experimental result of Appleton et al.[18] and the 2-temperature hypersonic chemistry model developed by Park[19,20] which is currently the de facto standard for aerothermodynamic modeling. Appleton's shock-tube experiments were carried out for a temperature range of 8000 K to 15,000 K and have a published uncertainty of $\pm 37\%$. The NASA rate coefficients were computed for $7500 < T < 25,000$ K. The Bari data were computed for $1000 < T < 10,000$ K using the LEPS potential of Lagana et al.[13]. The overall agreement between Ames, Appleton and Park is quite good. The Bari data are in reasonable agreement with the other data sets for low temperatures, but extrapolation of their results to higher temperature leads to large differences.

        Figure 3 shows a comparison of thermal rate coefficients for $N_2 + N_2 \rightarrow N + N + N_2$. The NASA[4] and Minnesota[15] values are compared with Appleton[18] and the Park 2-T model[19,20]. Again, the overall agreement between these data sets is good. We

will include more detailed comparisons dissociation and energy transfer rate coefficients in the proposed paper.

The calculations of the potential energy surfaces and rate coefficients do not contain empirical parameters that can be adjusted to reproduce specific experimental data. The fact that there is generally good agreement between the experimental dissociation rate coefficients[18] and the computed QCT rate coefficients provides validation of the physics-based computational approach.

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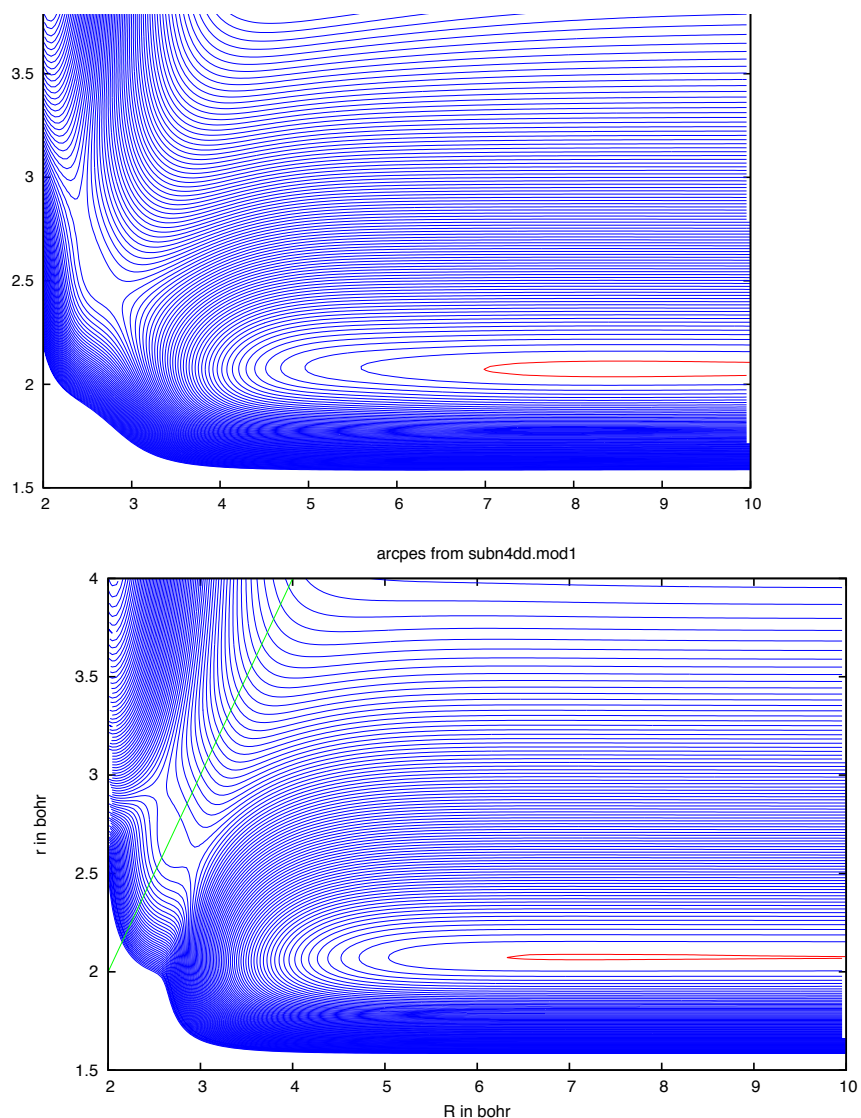
Figures

Figure 1. Comparison of the U. Minnesota[5] (top) and NASA[4] Ames (bottom) PESs for rectangular geometries of N_4. N atoms are at the corners of a rectangle. The potential energies are relative to two N_2 molecules with bond lengths at $r = r_e$ and $R = \infty$. Blue and red lines represent constant energy contours. The red contour has zero energy and each successive blue line represents a 5 kcal/mol increase in energy.
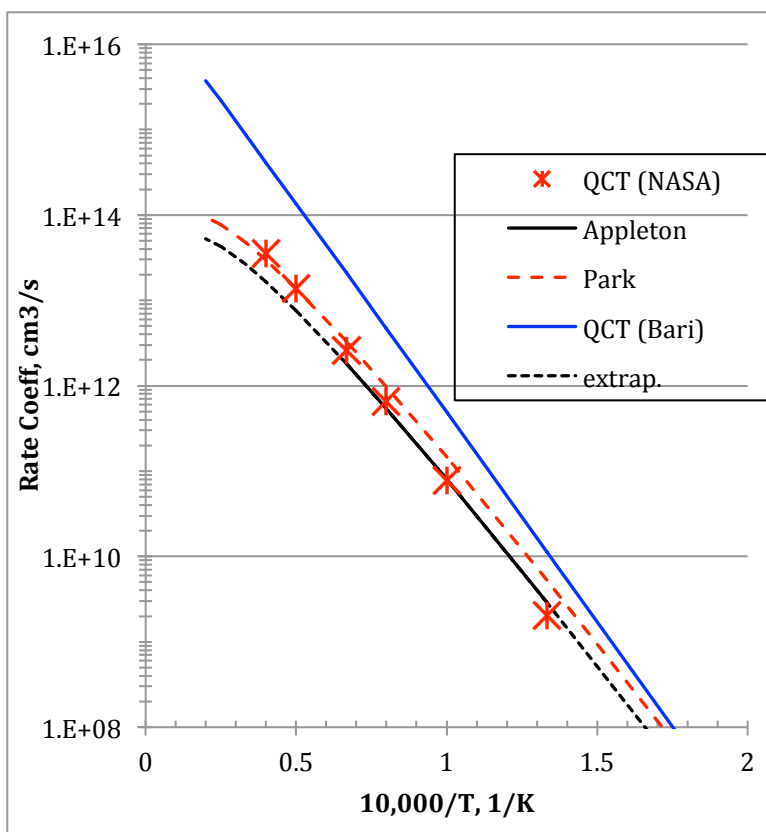
Figure 2. Thermal rate coefficients for $N_2 + N \rightarrow N + N + N$. Computed rate coefficients using the QCT method from NASA Ames[1,2] and Bari University[14] are compared, along with values from Appleton's shock-tube experiment[18] and Park's 2-T model[19,20]. The Appleton experimental data was obtained for $8000 < T < 15,000$ K (solid line) and extrapolated to lower and higher temperatures (dashed line).
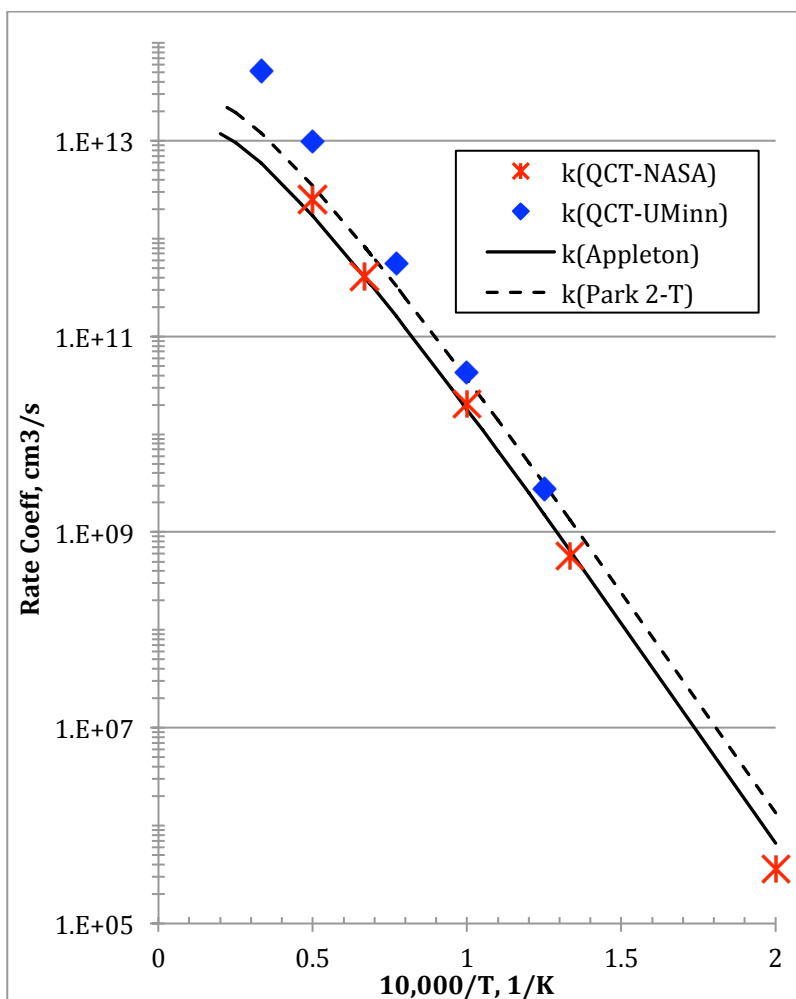
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