CHEMISTRY MODELING FOR AEROTHERMODYNAMICS AND TPS

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ABSTRACT

Recent advances in supercomputers and highly scalable quantum chemistry software render computational chemistry methods a viable means of providing chemistry data for aerothermal analysis at a specific level of confidence. Four examples of first principles quantum chemistry calculations will be presented. The study of the highly nonequilibrium rotational distribution of nitrogen molecule from the exchange reaction N + N_2 illustrates how chemical reactions can influence the rotational distribution. The reaction C_2H + H_2 is one example of a radical reaction that occurs during hypersonic entry into a methane containing atmosphere. A study of the etching of Si surface illustrates our approach to surface reactions. A recently developed web accessible database and software tool (DDD) that provides the radiation profile of diatomic molecules is also described.

1. INTRODUCTION

In an aerocapture mission, there is a trade off between the mass of the propellant needed for orbital insertion and the mass of the Thermal Protection System (TPS) needed to shield against aerodynamical heating. Thus the design of such a mission must include careful aerothermal analysis carried out at a specific level of confidence. This in turn calls for a corresponding level of confidence in the chemistry data used in the analysis.

The chemistry data needed in aerothermal analysis include chemical reaction rates, radiation emission and absorption probabilities, and probabilities of surface catalytic reactions. There are two sources for these data, laboratory measurements and first principles quantum chemistry calculations. Traditionally, experimental measurements were the major source of data. However, measurements of high temperature radical reactions and photoemission probabilities for high-lying rotational and vibrational states of a molecule pose experimental problems due to the difficulties in the unambiguous

measurement of a specific reaction rate or molecular transition probability at a high temperature. Under such circumstances, first principles calculations frequently are the only source of reliable data. While first principles calculations have been used in the past to provide selected data, the approach has been plagued by the lengthy turn-around time. Recently, the availability of powerful new supercomputers such as Project Columbia at Ames Research Center and the development of highly scalable chemistry software make quantum chemistry calculations more efficient than those of even just a few years ago. Thus first principles calculations can now be used as a reliable source of chemistry data for aerothermal analysis.

To illustrate recent advances in modern quantum chemistry methods and how they can be used to serve the need of mission design for planetary probes, this paper presents examples of four recent chemistry calculations. The rotational temperature of N_2 is a determining factor of its radiation profile and has to be included in the calculation of the radiative heat load to a vehicle or probe during high velocity entry into a nitrogen-containing atmosphere. Our calculation of the N+N_2 exchange reaction is carried out to reconcile the rotational temperature of N_2 observed in a recent shock tube experiment [1]. The ethynyl radical C_2H is an important intermediate product in the entry shock of a methane containing atmosphere and the H_2 + C_2H reaction presented in this paper illustrates current quantum chemical capability in calculating high temperature radical reactions. The etching of a silicon surface by halogens serves as an example of a computational study of surface catalytic reactions. A newly developed web-based tool, Dynamic Database for Diatomics (DDD) provides the user with the unprecedented capability of determining the complete radiation profile of a diatomic molecule.

Even with recent software and hardware advances, the amount of chemistry data required in aerothermal analysis is still far too numerous for a reasonable turn-around time.

In this respect, the recent sensitivity study of thermochemical modeling by Bose et al. [2] for Titan atmospheric entry points to sensitivity analysis as an important tool in selecting a subset of chemical data particularly important in reducing the uncertainties in the modeling. Sensitivity studies are especially important as a guide to selecting the needed data before quantum chemistry calculations are carried out.

2. N + N$_2$ EXCHANGE REACTION

In a recent shock tube experiment using nitrogen gas, Fujita et al. [1] measured the rotational and vibrational temperatures using the N$_2$ second positive and N$_2^+$ first negative bands and found significant nonequilibrium between the measured rotational and translational temperatures. So far, proposed explanations [3,4] of this nonequilibrium rotational distribution using N$_2$–N$_2$ collisions require physically unrealistic features in the N$_2$–N$_2$ interaction potential and are likely to be unreliable [5]. Thus it is likely that the large Δj transitions indicated in the shock tube data of Reference [1] do not come from N$_2$–N$_2$ collisions. Instead, our study [5] shows that the N + N$_2$ exchange reaction can lead to large Δj transitions at the high-temperature regime of the experiment.

In the atom exchange reaction

$$N + N_2(v,j) \rightarrow N_2(v',j') + N, \qquad (1)$$
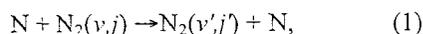
the N-N bond in the original N$_2$ molecule is broken and a new N-N bond is formed. Due to the nature of the N + N$_2$ interaction potential [6], the new N$_2$ molecule may result in a highly-excited rotational state in comparison with the rotational state of the original molecule.

A theoretical determination of exchange scattering must be based on a quantum mechanical description. For example, the N–N$^+$ resonance charge exchange [7] would be underestimated by almost an order of magnitude using classical mechanics. The first *ab initio* potential energy surface for the N–N$_2$ system (denoted as WSHDSP PES) that includes variation in the interatomic separation distances of the N$_2$ molecules and the first quantum dynamics study of the cumulative reaction probabilities and chemical reaction rates of the N + N$_2$ exchange reaction have recently been reported by our group [6].

The WSHDSP PES [6] for N–N$_2$ is constructed from the results of high-level quantum electronic structure calculations. These calculations are primarily based on the same methods [8] that were used earlier to determine the *ab initio* data for the construction of the very accurate N–N$_2$ rigid-rotor PES of Stallcop et al. [9]; long-range dispersion force data and nearly 4000 *ab initio* data points are applied to construct the N–N$_2$ WSHDSP PES. This potential has a number of special features. In particular, strong enhancements in the collision cross section due to

the formation of a short-lived metastable N$_3$ state have been reported [10,11].

2.1 Rotational Excitation

State-to-state cross sections for scattering energies at 2.5 eV are presented in Fig. 1 to illustrate the distribution of rotational state excitation. Note that we plot two sets of cross sections, one with nuclear spin of the N$_3$ system properly accounted for and the other without spin. N$_3$ obeys the Bose-Einstein statistics. Since the incorporation of nuclear spin introduces rapid oscillations in the cross sections, the underlying features in the cross sections are more easily recognizable using the data without nuclear spin. Note, however, the rapidly varying cross sections of even versus odd j states in N$_2$ will be reflected in its radiation profile.
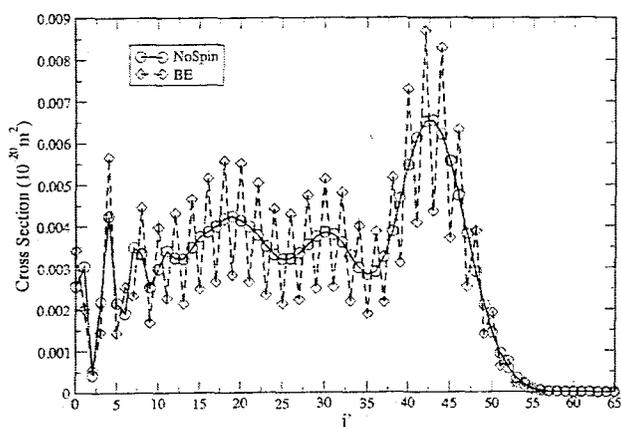

FIG. 1. State-to-state cross sections for exchange scattering with rotational excitation from initial ground rotational and vibrational state of N$_2$, N + N$_2$(v=0, j=0) $\rightarrow$ N$_2$(v'=0, j') + N, vs. j' for total scattering energy at 2.5 eV. The symbols o and $\Diamond$ represent the results obtained by neglecting nuclear spin and using Bose-Einstein statistics for the nuclear spin, respectively. The discrete data points are connected by straight line for clarity.

Fig. 2 shows the cross section $\sigma_{vj' \leftarrow vj}$ for scattering from a ($v = 0, j = 0$) initial ro-vibrational state to various final ro-vibrational states. The curves of $\sigma_{0j' \leftarrow 00}$ for low-lying final ro-vibrational states, such as ($v' = 0, j' = 0$) and ($v' = 0, j' = 2$) states, have weak oscillating behavior arising from the formation of short-lived metastable N$_3$ states [10,11]. Note that the cross section for $j = 0 \rightarrow j' = 48$ is larger than for $j = 0 \rightarrow j' = 2$ at most energies. The variation of the large cross sections for producing high j' with kinetic energy verifies that the N+N$_2$ exchange reaction is quite efficient for producing high rotational states of N$_2$ molecules.

The kinetic energies and average energies of the rotational state distributions of our studies are comparable to the translational and rotational temperatures of the experiment of [1]. For example, in our study the average N_2 rotational energy for a total scattering energy at 3.0 eV corresponds to rotational temperature (T_r) at 5200 K; the kinetic energy in Fig. 2 corresponds to translational temperatures in the range 33,000 K to 50,000 K. Considering that the vibrational and rotational motions are not coupled for low vibrational excitations, we conclude that T_r for the lower vibrational states is close to the value 4500 K found from the rotational distribution in [1]. Furthermore, the translational temperature of the experiment, estimated [1] to be above 40,000 K, falls within our estimate of 33,000 K to 50,000 K.
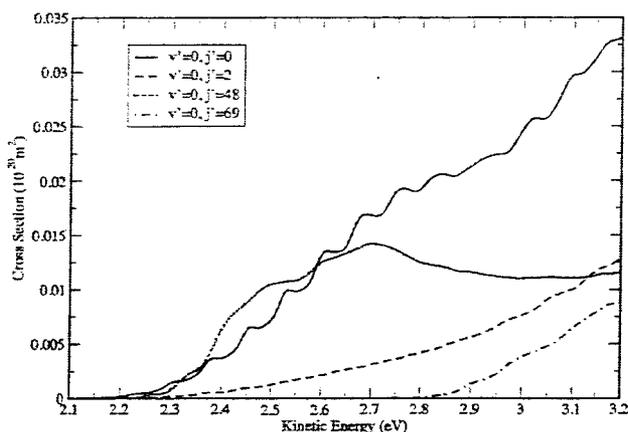

FIG. 2. State-to-state cross sections for exchange scattering with rotational state excitation from initial ground rotational and vibrational state of N_2, $N + N_2(v = 0, \ j = 0) \rightarrow N_2(v' = 0, j') + N$, vs. j' for total scattering energy at 2.5 eV.

The above results for rotational excitation indicate that the exchange reaction of $N + N_2$ collisions provides a mechanism to pump N_2 molecules at low rotational states into N_2 molecules at higher rotational states. Because this exchange reaction has a propensity for producing highly excited rotational states, it provides a route that may lead to a nonequilibrium rotational temperature behind a strong shock.

2.2 Vibrational Excitation

The cross section for v' excitation from a $(v = 0, j = 0)$ initial ro-vibrational state is obtained by summing over all the final rotational states; i.e.,

$$\sigma^*_{v' \leftarrow 00} = \sum_{j'} \sigma_{v'j' \leftarrow 00}. \tag{2}$$

The values of $\sigma^*_{v' \leftarrow 00}$ are shown in Fig. 3 for $v' = 0-3$. This figure shows that significant vibrational excitation of

N_2 is produced by exchange reactions at higher kinetic energies.
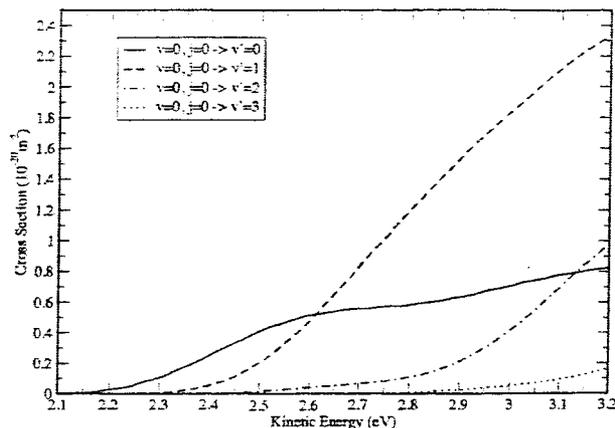
FIG. 3. Cross sections for exchange scattering with vibrational excitation from initial ground rotational and vibrational state of N_2, $N + N_2(v = 0, j = 0) \rightarrow N_2(v') + N$ as a function of kinetic energy; $v' = 0-3$.

3. $C_2H + H_2$ REACTION

Hydrogen is a major component in the atmosphere of all giant planets and methane is a minor component. The Titan atmosphere also contains 2-8% methane. The ethynyl radical C_2H is an intermediate product of methane chemistry upon high temperature shock. The $H_2 + C_2H$ reaction is an important step leading to acetylene, C_2H_2.

$$H_2 + C_2H \rightarrow C_2H_2 + H. \tag{3}$$
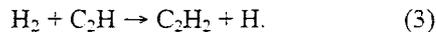
Because this reaction also plays an important role in combustion chemistry, extensive experimental studies have been reported in the literature [12-21]. Thus it is a good candidate for benchmarking the capability of first principles calculations of radical reactions of interest to giant planet missions. For this study, the first ever seven dimensional (7D) quantum dynamics calculation is carried out. This is done by fixing two of the nine dimensional space based on quantum chemistry transition state calculation, thus reducing the nine-degree-of-freedom calculation to a seven-degree-of-freedom calculation. Then, using the time-dependent wave packet method [22,23], we calculate the initial state selected reaction probabilities for angular momentum $J=0$; these results are used with J-shifting and energy averaging to determine the rate constant. Fig. 4 compares the thermal rate constants from the present calculation with those from various experimental measurements. It is seen that in most cases the calculated rate constants not only agrees with the measured data to within experimental error, but also reproduce the temperature dependence over a wide range of temperatures. There are two exceptions. The

single measurement of Renlund et al. [13] disagrees with both the calculated rate constant and all other measurements in the temperature range by almost an order of magnitude. Also, the high temperature data of Kruse and Roth [19] not only are higher than the calculated curve but also are higher than the general temperature dependence extrapolated from the lower temperature data. The present result clearly demonstrates our 7D reduced-dimensional calculations can yield accurate rate constants for radical reactions.
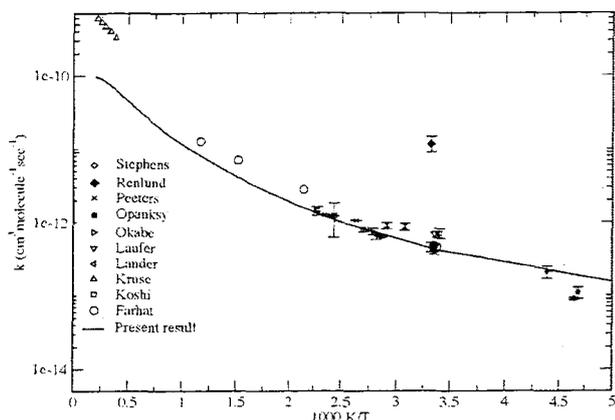

FIG. 4. Calculated rate constant of $H_2 + C_2H \rightarrow C_2H_2 + H$ vs. inverse temperature. Also presented are various experimental results from $\lozenge$ [12], $\blacklozenge$ [13], $\times$ [14], $*$ [15], $\triangleright$ [16], $\triangledown$ [17], $\triangleleft$ [18], $\triangle$ [19], $\square$ [20], and $\bigcirc$ [21].

4. ETCHING OF A Si SURFACE

The etching of a Si surface by halogens is used to illustrate our approach to the study of surface catalytic reactions. In these studies molecular dynamics (MD) simulations were used to investigate etching of Si surfaces by halogen species [24,25]. For complete descriptions of surface reactions taking place during the etching (and epitaxial growth) process, it is necessary to understand the bonding structures and stabilities of chemisorbed halogen species on the Si surface. MD studies today can reproduce short time behavior of an etching process quite successfully. Generally speaking, simulation calculations are consistent with experiments.

MD calculations provide detailed understanding of the local physics and chemistry taking place during the adsorption and subsequent desorption of halogen species from the exposed Si surfaces. First and second chlorination (and fluorination) steps of surface Si atoms were analyzed separately, and the role played by surface vacancies was investigated. Steric effects coming from repulsive forces among the halogen atoms were found to be quite significant. Results indicate that the second step that leads to the formation of doubly chlorinated species

is very important in the overall etching process. In MD simulations, energies and forces are calculated employing existing empirical potential functions for systems containing Si and halogen species. These potentials are based on two- and three-body interactions.

In general, calculations were carried out in two steps. First we used a simulated annealing procedure based on a MD method. For complete equilibration, the temperature of the system was first increased and then linearly cooled down to a low temperature limit. Typical runs in these cases were about a picosecond long. The final configuration of the low temperature result was then used as an input to a minimization routine based on a quasi-Newton algorithm to find the local minimum. This method is very efficient in finding low-lying minima for systems containing large numbers of moving particles.

Fig. 5 illustrates the mechanisms of surface defect etching of Si(001)-2×1 surface using MD simulations. Our results show that MD calculations provide an atomic level understanding of the etching process, which is the removal of halogenated Si particles from the surface region. Furthermore, the outcome of these studies strongly indicates that MD simulations are able to predict the thermodynamics and energetics of surface etching.
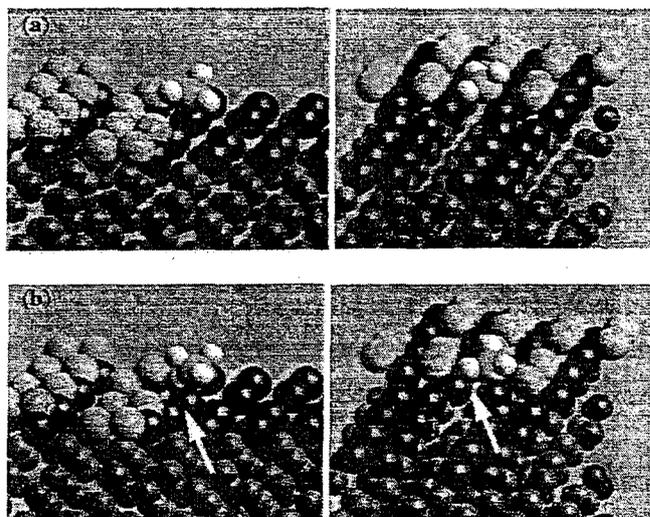

FIG. 5. Etching of SiF_3 from A type step edge. (a) The side and front views of the sample at the beginning of a room temperature MD trajectory calculation. (b) Same as in (a) at the end of the MD trajectory. The arrows indicate the dimerization of the lower step edge Si atoms as the SiF_3 on the top is etched away.

5. DYNAMIC DATABASE FOR DIATOMICS

A proper account of re-entry heating requires an accurate description of radiation effects. The radiation field is due to emission from atoms and molecules that are either

heated by the shock layer or formed by reactions. Both neutrals and ions will participate. The transitions of importance are electronic, and modeling requires a database of opacity data for each species expected to be present in the flow field.

Our present focus is on the opacity data of diatomics. The diatomics involved depend on the entry atmosphere, and the number of species can be quite large. For example, entry into the earth's atmosphere produces excited states of CN, NO, N_2, as well as their ions.

The conventional way to obtain the opacity data is from experimental analysis. This, however, is a slow process requiring many man years for a single diatomic. The measurements produce line positions and line strengths. While the line positions can be obtained with a very high degree of accuracy, line strengths are much more difficult to measure accurately. In fact, many spectroscopic studies do not even attempt to measure line strengths.

Another source of opacity data is from calculations carried out from first principles. In contrast to experimental measurements, theory can yield accurate line strengths without too much difficulty, but accurate line positions are much more difficult. However, progress has been made on that front; see, for example, Polyansky et al. [26]. In the past, a calculation for a single diatomic also required a number of man-years of work. Now we can exploit the recent increases in computer power to introduce a new paradigm whereby automatic computation of accurate opacities for diatomics becomes possible. We call our software package for carrying this out DDD: dynamic database for diatomic molecules.

DDD will be accessible as a world-wide-web interface, and will work in one of two ways. The first mode, the retrieval mode, occurs when a request for data by a user is for a diatomic for which calculations had been previously carried out. In this case DDD will return the data essentially instantly in one of several forms indicated by the user. The second mode, the data creation mode, occurs when a request for data is for a diatomic with no stored data. In this case DDD will start the necessary calculations to determine the opacity required by the user. Depending on the diatomic and the load on the parallel computers, this calculation may require a few minutes to several days. If the calculations are not completed in a short period of time, DDD will inform the user that calculations are being carried out, and will e-mail the user when the calculations are completed.

We have been testing our preliminary version of DDD, and the results are quite promising. In Table I we present some preliminary results for CN, T_e, the electronic excitation energy, ω_e, the vibrational frequency in the harmonic approximation, and B_e, the rotational constant for a rigid rotor. These are low-order spectroscopic constants describing the line positions, but our

calculations also yield line strengths. Numbers in parenthesis are experimental values from Huber and Herzberg [27]. The agreement is quite satisfactory for this level of calculation. Of interest is the large number of states that are predicted for which experiments have not been carried out. Note that these calculations were carried out without any user intervention after the initial specification of the atoms C and N.

The algorithm for DDD is quite complicated. Given a database for atoms, consisting of orbital occupations of the ground and valence excited states, DDD constructs a preliminary list of binding configurations of the diatomic. These orbital occupations are then used in trial calculations. Based on these results, more sophisticated calculations are carried out on the strongly bound levels, and potential energy curves, transition moment curves, and coupling matrix elements are computed. For these calculations, the highly reliable multi-reference configuration interaction method is used. These are then used in a coupled rotation-vibrational-electronic code [28] to generate a line list.

TABLE I: Summary of Electronic States of CN. Numbers in parenthesis are from [27].

	$T_e(\mathrm{cm}^{-1})$	ω_e	B_e
$^4\Sigma^+$	67917	1073	1.316
$^2\Pi_r$	67620	1351	1.174
$^4\Pi_r$	66585	2393	1.714
$^2\Delta_r$	60704 (60096)	1549 (1239)	1.375(1.383)
$^2\Sigma^-$	59638	1242	1.347
$^2\Sigma^+$	59439 (59151)	1721 (1681)	1.456(1.487)
$^2\Phi_r$	59291	931	1.095
$^2\Pi_r$	58747	2187	1.429
$^4\Sigma^-$	52655	1260	1.348
$^2\Pi_r$	51761 (54486)	1133 (1004)	1.045(1.162)
$^4\Delta_r$	46864	1309	1.367
$^4\Pi_r$	44243	923	1.104
$^4\Sigma^+$	36466	1326	1.367
$^2\Sigma^+$	27128 (25752)	2059 (2163)	1.868(1.973)
$^2\Pi_i$	8401 (9245)	1766 (1812)	1.642(1.715)
$^2\Sigma^+$	0 (0)	2028 (2068)	1.818(1.900)

6. CONCLUDING REMARKS

This paper illustrates the capability of present day first principles quantum chemistry calculations. By making use of the recent advances in hardware and software, first principles calculations can now provide reliable chemistry data needed for aerothermal analysis of aerocapture missions and other entry problems. The $N + N_2$ calculation supports the experimental observation by Fujita et al. [1] of strong nonequilibrium between the kinetic and rotational temperatures of a high-energy shock. Furthermore, our theoretical calculations provide insight into the origin of this nonequilibrium and indicate that future aerothermal modeling of high-velocity entry should incorporate these nonequilibrium conditions. The scatter in the measured $C_2H + H_2$ reaction data at high

temperatures illustrates the risk of using limited experimental data. First principles calculations can be validated by comparisons with available low-temperature experimental data and, moreover, provide otherwise unavailable high-temperature data. Our capability is not limited to gas-phase studies, as illustrated by the silicon etching study. The techniques of this work can be used to study surface catalytic reactions. The web-based DDD is a pioneering tool that provides a powerful means for the aerothermodynamicists to do their modeling of radiation heat load. We also point out that sensitivity analysis should be used as a guide for selecting the critical subset of required data. This approach will significantly shorten the turn around time, minimize the computational effort, and maximize the benefit of the calculations.

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