# Theoretical study of thermodynamic properties and reaction rates of importance in the high-speed research program

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# Introduction

One of the primary goals of NASA's high-speed research program is to determine the feasibility of designing an environmentally safe commercial supersonic transport airplane. The largest environmental concern is focused on the amount of ozone destroying nitrogen oxides ($NO_x$) that would be injected into the lower stratosphere during the cruise portion of the flight. The limitations placed on $NO_x$ emission require more than an order of magnitude reduction over current engine designs. To develop strategies to meet this goal requires first gaining a fundamental understanding of the combustion chemistry.

To accurately model the combustor requires a computational fluid dynamics approach that includes both turbulence and chemistry. Since many of the important chemical processes in this regime involve highly reactive radicals, an experimental determination of the required thermodynamic data and rate constants is often very difficult. Unlike experimental approaches, theoretical methods are as applicable to highly reactive species as stable ones. Also our approximation of treating the dynamics classically becomes more accurate with increasing temperature. In this article we review recent progress in generating thermodynamic properties and rate constants that are required to understand $NO_x$ formation in the combustion process. We also describe our one-dimensional modeling efforts to validate an $NH_3$ combustion reaction mechanism. We have been working in collaboration with Marty Rabinowitz at Lewis research center, to ensure that our theoretical work is focused on the most important thermodynamic quantities and rate constants required in the chemical data base.

## Outline

- Thermodynamic properties
  1. C-H bond dissociation energies of $CH_4$
  2. Resolution of the controversy concerning the C-H bond energy of acetylene
- Reaction rate constants
  1. Lifetime of $HN_2$ to unimolecular decay
  2. $C_2H_2 + C_2H_2 \rightarrow ?$
  3. propane + O → propyl + OH
- Modeling
  1. 1D modeling to validate an $NH_3$ combustion mechanism (H-N-O)
  2. 1D modeling of turbine combustors with $CH_4$ fuel to identify important H-C-N-O reactions.

## Calculation of heats of formation

Although the heat of formation is well known for many molecules, individual bond energies are often very uncertain. We have developed an inexpensive computational approach for predicting accurate (1 to 2 kcal/mole) C-C and C-H bond energies [1-2]. Currently we are attempting to assess the accuracy with which we can compute N-H, N-N, O-H and O-O bond energies [3]. An accurate knowledge of bond energies is required to model the chemistry occuring in jet engines. For purposes of calibration, we have studied the successive bond energies of methane [1]. These are compared with experiment in the following table. At a modest level of theory, our directly calculated values are about 2 kcal/mole too small after the inclusion of the vibrational zero-point energy (ZPT). However, 0.5 kcal/mole accuracy is achievable with very large calculations. When we add 2 kcal/mole to correct for deficiencies in the theoretical bond energies (column labeled estimate), excellent agreement is obtained with experiment. This gives us considerable confidence that our results for hydrocarbons and other systems, such as ketene [2] and methanol [4] are also very accurate.

## C-H dissociation energy in $C_2H_2$

There is currently considerable controversy regarding the C-H dissociation energy of acetylene, $D_0^0$(HCC–H). This is in large part due to the low and presumably very accurate value determined by Green, Kinsey and Field (GKF) [5] using Stark anticrossing spectroscopy. Their result, 126.647(2) kcal/mole, is claimed to be an *upper bound*, and is consistent with the 127±1.5 kcal/mole estimate of Segall *et al.* [6] obtained by measuring the kinetic energy (K.E.) of the hydrogen atom fragment using Doppler multiphoton ionization spectroscopy. However, these values are substantially smaller than previous theoretical estimates [7,8] and other recent experimental results, such as the $D_0$ value of 131.3±0.7 kcal/mole measured by Ervin *et al.* [9] using the techniques of negative ion photoelectron spectroscopy and gas phase proton transfer kinetics.

We undertook a systematic study of the C-H bond dissociation energy in acetylene with respect to improvements in the level of theoretical treatment [10]. Our best estimate for the $D_0$ value of 130.1±1.0 kcal/mole is in good agreement with the recent experiment of Ervin *et al.* [9] and previous theoretical calculations [7,8]. We believe our error bars to have a better than 90% probability of bracketing the correct $D_0$ value, and we therefore seriously question the recent upper bound inferred from Stark anticrossing spectroscopy [5]. Detailed theoretical studies of the $C_2H_2$ and $C_2H$ vibrational frequencies have also led us to revise upward the $D_0^0$ values determined from kinetic data.

| | |
|---|---|
| | Experimental |
| ≤126.647±0.002 | Stark anti-crossing spectroscopy |
| 127.±1.5 | $HCCH + h\nu \rightarrow C_2H + H(K.E.)$ |
| 124-127 | Kinetic data |
| 131.3±0.7 | $\Delta H_{acid}(HCCH) + EA(C_2H) - IP(H)$ |
| 132.±2 | $HCCH + h\nu \rightarrow C_2H(K.E.) + H$ |
| 132.6±1.2 | photoionization of HCCH |
| | Theoretical |
| 130.1±1.0 | MRCI |

## Reaction Rate Constants

The first step in determining an accurate rate constant is to compute the potential energy surface – that is, for "all" possible arrangements of the atoms, solve for the electronic energy. The surface must then be fit to an analytic form in order to solve for the nuclear motion on this surface using either classical or quantum mechanical scattering methods We are currently exploring the use of variational transition state approaches with tunneling corrections for determining qualitative (factor of 2-3) reaction rate constants and product branching ratios. One of the advantages of this method is that it requires only a small portion of the complete potential energy surface. This approach has been applied to determining the rate constant of the reaction of propane with atomic oxygen— see later discussion.

Several reactions are currently under study in our laboratory. For example, the reaction

$$H + O_2 \rightarrow HO + O$$

is being studied, since this reaction consumes most of the $O_2$ in typical hydrocarbon combustion. However, the rate constant for this reaction is uncertain by a factor of six at flame temperatures. A global potential energy surface(PES) has been developed and fitting is in progress [11-14].

Another molecule that we have studied extensively is $HN_2$, since it has been postulated as an important species in thermal De-$NO_x$ processes. A global PES has been developed for

$$H + N_2 \rightarrow HN_2$$

and an accurate lifetime has been computed for the $HN_2$ molecule [15-18].

The reaction of $C_2H_2$ with itself is postulated to be important in the final steps of hydrocarbon combustion. We believe that acetylene must first be converted to the vinylidene isomer ($CCH_2$) before reaction can occur— see later discussion.

The reaction

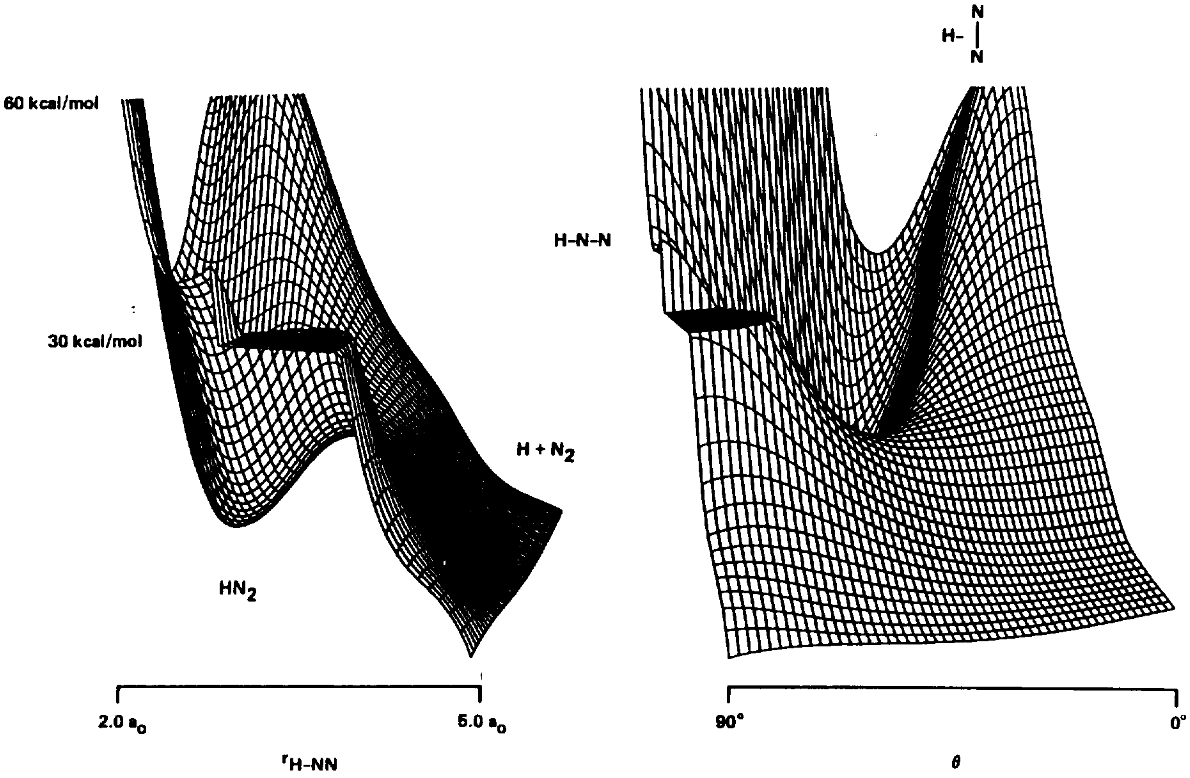
$$CH + N_2 \rightarrow HCN + N$$

is believed to be the rate determining step in "prompt $NO_x$" formation. A large number of stationary points have been located on this potential energy surface. Large-scale investigations of the surfaces are in progress. Finally, work is beginning on the $CH_3$+$O_2$ and $CH_3$+OH reactions to determine product branching ratios. Model studies have shown these to be important in the combustion of jet fuel.

## Global potential energy surface for $H+N_2 \rightarrow HN_2$

The $HN_2$ species has been postulated as an important intermediate in the thermal De-$NO_x$ process. The $HN_2$ species was found to be unstable with respect to $H+N_2$ by 3.0 kcal/mol, but quasibound by 12.2 kcal/mol due to a barrier to dissociation—see figure below. The computed $N_2$-H lifetime [17] (based on 1-D tunneling through an Eckart barrier) was five orders of magnitude smaller than the value assumed in the experimental analysis. Koizumi and Schatz (Northwestern) have fit this surface and carried out coupled channel calculations to determine the lifetime. These rigorous calculations confirm those based on a Wigner model of tunneling that indicate this radical has a very short lifetime to unimolecular decomposition [18].

This suggests that commonly used reaction mechanisms for $NO_x$ chemistry such as the Sandia reaction set [19] are incorrect.



## $C_2H_2+C_2H_2 \rightarrow$ ?

The reaction of $C_2H_2$ with itself is postulated to be important in the final steps of hydrocarbon combustion. It is exceedingly unlikely that any reaction takes place between two acetylene molecules at the temperatures of interest, but the vinylidene ($CCH_2$) isomer is only about 30 kcal/mol above acetylene, and a number of products can result from reaction of vinylidene with acetylene.

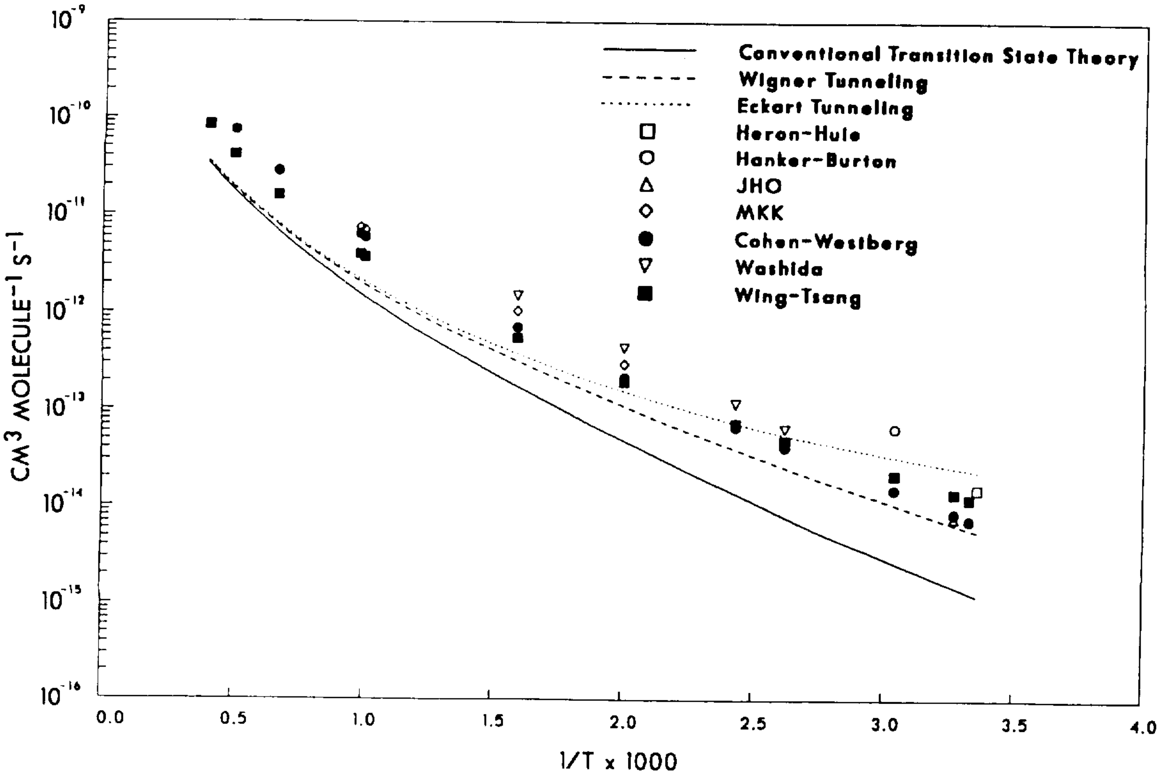
So far, seven stable isomers of $C_4H_4$ have been found using self-consistent-field (SCF) and multiconfigurational self-consistent-field (MCSCF) wave functions, as well as several stationary points that are not minima or are not stable with respect to symmetry-breaking nuclear distortions. The lowest energy $C_4H_4$ isomer is vinylacetylene, which is about 45 kcal/mol more stable than two acetylenes. Butatriene is about 10 kcal/mol higher in energy, and methylenecyclopropene is about 14 kcal/mol higher still. Another isomer, cyclobutadiene, is only a little more stable than two acetylenes. The other stationary points are much higher in energy. The energetics here are not fully refined at the correlated level, but correlation does not seem to have a significant effect on the thermochemistry.

Several pathways have been followed on this surface using large MCSCF configurational spaces, in preliminary attempts to find transition states for the first reaction steps of vinylidene with acetylene, but while these have yielded another fairly stable isomer, carbenecyclopropane, and transition states for some rearrangements have been found, the initial transition states have not yet been located. However, the investigation is at an early stage and there should not be a problem determining the reaction pathways.

## The Reaction of Propane with Atomic Oxygen

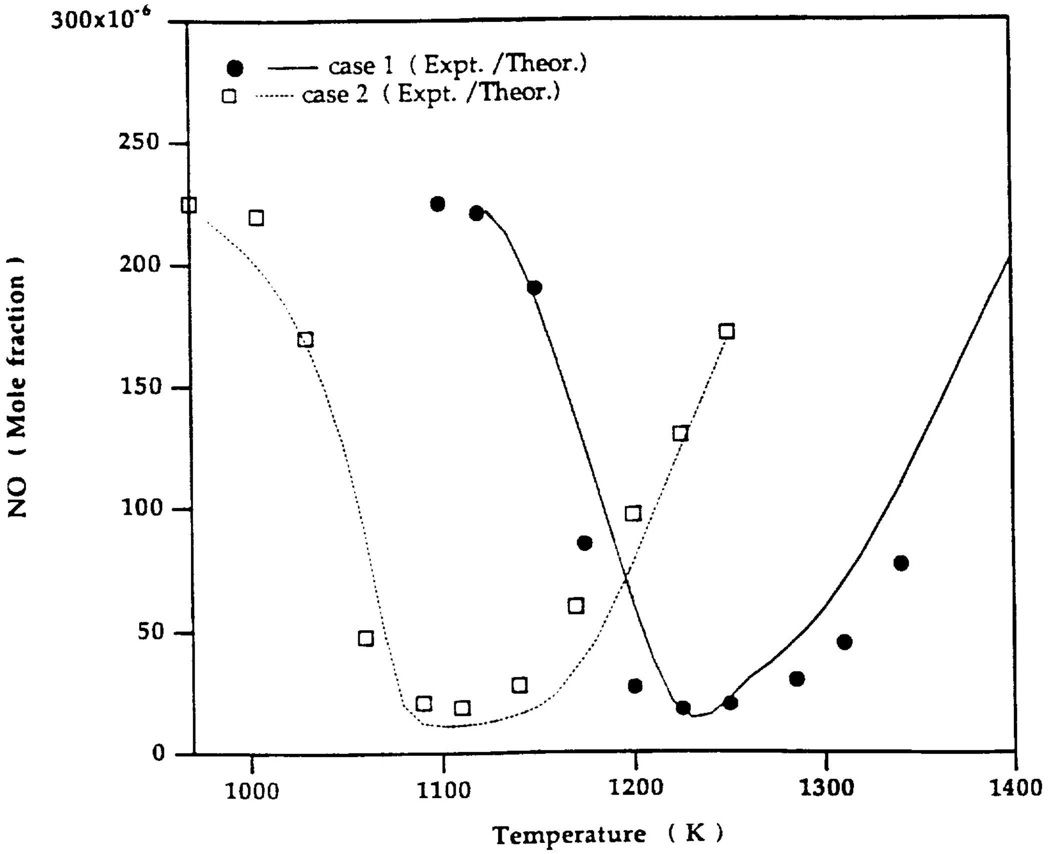
We have studied the hydrogen abstraction from the central carbon of propane by ground state oxygen [20]. The energy barrier on the potential energy surface was determined using SCF gradient methods. A more accurate barrier and exoergicity were determined using correlated methods. Furthermore, a correction factor to account for deficiencies in the basis set and electron correlation treatment was determined by carrying out large scale calculations for the analogous reaction $H_2 + O \rightarrow H + OH$. This correction lowers the saddle point and product energies by 4.66 kcal/mol relative to the reactants. The final computed energies are 4.36 kcal/mol for the barrier and 7.00 for the exoergicity. These compare favorably with the experimentally determined values of 5.0 and 7.0 kcal/mol.

The potential energy profile, molecular geometries and vibrational frequencies were used for a transition state theory calculation of the rate constant for the hydrogen abstraction reaction. Two approximate treatments of tunneling were carried out. The Wigner model assumes that the energy barrier is an inverted parabola truncated at the reactant and product energy limits. The Eckart model uses a potential energy function based on a modified hyperbolic secant. It can be seen from the figure that the transition state theory calculations with either tunneling model agree with the experimental data to within a factor of two over the entire temperature range (300-2000K). Greater than a factor of two accuracy in the rate would require a global surface, which is exceedingly difficult for a system with this many atoms.



# Thermal de-$NO_x$

Experiment of Lyon and Hardy [21] showing NO removal by ammonia injection. The process works in a narrow temperature range, and oxygen must be present for $NH_2$ formation. Initial conditions of experiment are: NO=225 ppm, $NH_3$=450 ppm, $O_2$=1.23%, remainder He. The pressure is 1.1 atm and the observations are made at 0.1 sec. Case two is similar to case one except for 225 ppm $H_2$ displacing an equal amount of He. Modeling shown here uses the reaction mechanism of Miller and Bowman [19], with a long lifetime for $N_2H$ ($\tau=10^{-4}$ sec). Calculations assume a plug flow reactor, and are simialr to Miller and Bowman [19]. The same calculations done with a shorter $N_2H$ lifetime, in an attempt to match the theoretical value of the lifetime ($< 10^{-9}$ sec), are unable to reproduce the experimental results.



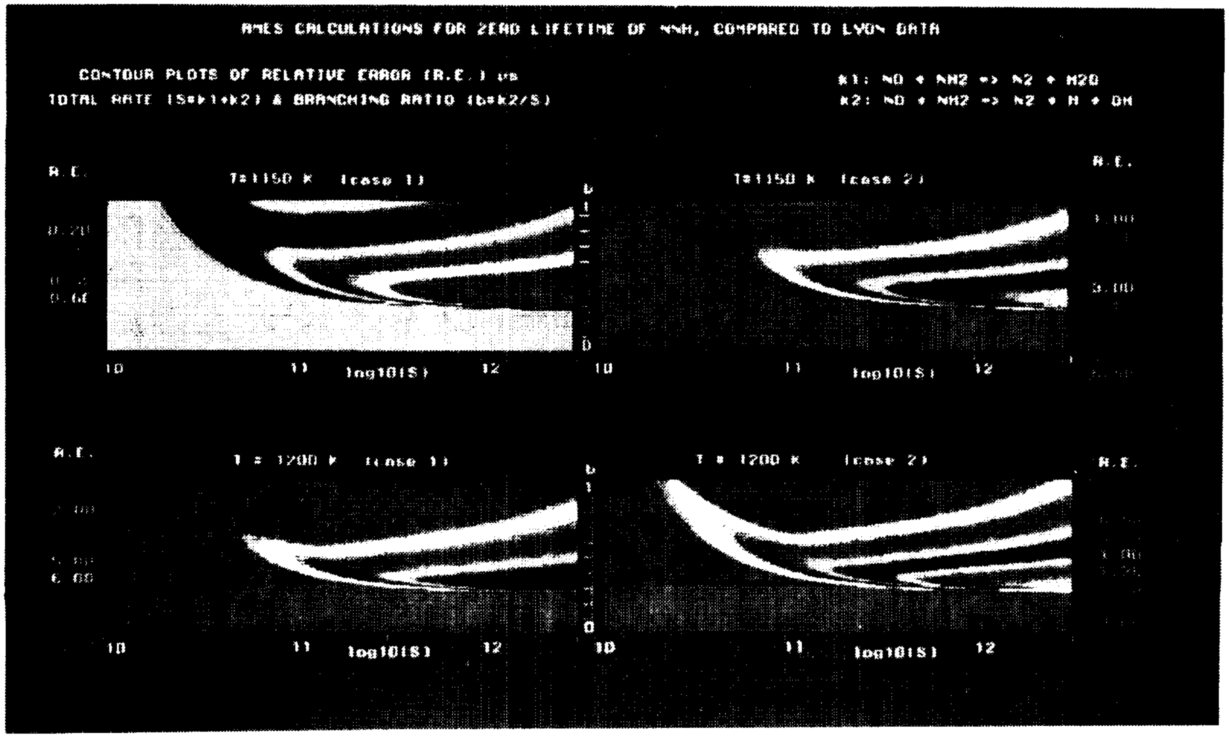
## Thermal de-NOx, no $N_2H$

In the limit of very short $N_2H$ lifetimes (< $10^{-9}$ sec), we can assume a spontaneous decay of $N_2H$ into $N_2$ and $H$. The $NO$ removal mechanism then hinges on two important reactions:

$$NO + NH_2 \rightarrow N_2 + H_2O \tag{1}$$
$$NO + NH_2 \rightarrow N_2 + H + OH \tag{2}$$

where the second reaction replaces $NO + NH_2 \rightarrow N_2H + OH$. The first equation has a chain terminating character, while the second is chain branching and will be important at low temperatures (combined with $NH_3 + OH \rightarrow NH_2 + H_2O$). A systematic study is performed in an attempt to find a consistent reaction mechanism, without $N_2H$, that explains the data. The parametric variables are the total forward rate of reactions (1) and (2), $S = k_1 + k_2$ and the branching ratio $b = k_2/S$. At two temperatures for which there is simultaneous experimental data for cases 1 and 2, we plot the deviation from the experimental result as a function of both the total rate and the branching ratio. The contour plots are for the Relative Error, defined as R.E. $= |NO - NO^*|/NO^*$, where $NO^*$ is the experimental value observed. The ordinates are the total rate (x axis, in $log_{10}$ units, and ranging from 10 to 13), and branching ratio (y axis, ranging from 0 to 1). Valid regions are for small R.E. (blue regions), and are mutually exclusive for T = 1150 K. A narrow overlap may exist at T = 1200 K, without convincing evidence. The disagreement at T = 1150 K is due to the fact that for most values of $S$ and $b$, the production of $NH_2$ is not sufficiently fast to start the $NO$ removal. Calculations were performed for a plug flow reactor.

These results indicate that the presence of reaction (2) cannot by itself explain the experimental data. Since the assumption of a plug flow reactor may be invalid, partial recirculation zones in the reactor may be able to introduce radicals early in the stream and speed up the removal of $NO$ at low temperatures. The same systematic series of calculations should be done also for Perfectly Stirred and Partially Stirred reactors.



## Conclusions

Computational chemistry techniques have utility in computing accurate thermodynamic properties such as C-H bond energies. Accurate C-H bond energies have been computed for methane, ethylene, ketene, acetylene, and methanol. Reaction rates can be computed at least to within a factor of two. The reactions currently under study in our laboratory include $H+O_2 \rightarrow HO+O$, $H+N_2 \rightarrow HN_2$, $C_2H_2$ with itself, $CH+N_2 \rightarrow HCN+N$, $CH_3+OH$, and $CH_3+O_2$. Our calculations demonstrate that the $HN_2$ molecule has a short lifetime ($<10^{-9}$ sec) to unimolecular decomposition. We are presently trying to incorporate this fact into model studies of the effect of $NH_3$ on NO removal. We have been working in close collaboration with Marty Rabinowitz at Lewis to ensure that we are addressing the key chemical issues involved in reducing NO emission in jet engines.

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