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COMPUTED POTENTIAL ENERGY SURFACES FOR CHEMICAL REACTIONS

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Ames Research Center
Moffett Field, California 94035

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16. Abstract

Quantum mechanical methods have been used to compute potential energy surfaces for chemical reactions. The reactions studied were among those believed to be important to the NASP and HSR programs and included the recombination of two H atoms with several different third bodies, the reactions in the thermal Zeldovich mechanism, the reactions of H atom with O_2, N_2, and NO, reactions involved in the thermal De-NO_x process, and the reaction of $CH(^2\Pi)$ with N_2 (leading to "prompt NO"). These potential energy surfaces have been used to compute reaction rate constants and rates of unimolecular decomposition. An additional application was the calculation of transport properties of gases using a semiclassical approximation (and in the case of interactions involving hydrogen inclusion of quantum mechanical effects).

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This cooperative research project has been funded from 7/1/87 to 12/31/93. During this 6.5 year period the main emphasis of the research has been the computation of potential energy surfaces (PES's) for chemical reactions.

These calculations are based on the Born-Oppenheimer approximation, which assumes that because the electrons move much more rapidly than the nuclei, the electronic motion is able to adjust instantaneously to the motion of the nuclei. Thus, the electronic and nuclear motions are separable, and the nuclear motion problem, which controls such physical observables as reaction rate constants, product branching ratios, and product ro-vibrational energy distributions, is solved in two steps.

The first step is the computation (by quantum mechanics) of the energy of the system as a function of the positions of the nuclei. This calculation may be carried out at a large number of nuclear geometries (each individual geometry is referred to as a point on the PES) and an interpolating function is then obtained which reproduces the computed energies at all the points and varies smoothly between them. Alternatively, codes exist to compute not only the energies but also the derivatives of the energy with respect to the coordinates of the nuclei. These algorithms permit locating a point or points on the potential energy surface at which all the first derivatives are zero (a stationary point) and then computation of the second derivatives characterizes the curvature of the PES at the stationary point. Typically in PES's for chemical reactions the stationary points are of two types: i) a minimum which is a point at which the curvature is positive in all directions and ii) a saddle point which is a point at which the curvature is positive for all but one direction which has a negative curvature. Typically saddle points correspond to the barriers separating reactants and products of a chemical reaction. These methods can also characterize the minimum energy path between a given saddle point and adjacent minima. Thus, the pathway that the nuclear motion takes during a chemical reaction may be defined.

Given the PES, the motion of the nuclei on this surface may be computed by

classical or quantum mechanical methods to give reaction rate constants and other information, which can be used in modelling a wide range of chemical processes.

The chemical reactions which have been studied during the course of this work were selected from reactions which were believed to be important in the National Aerospace Plane (NASP) and High Speed Research (HSR) programs, as well as reactions which are important in shock layers in front of hypersonic vehicles, and more recently reactions which lead to formation of aromatic species, which are believed to be precursors to soot formation in combustion of aliphatic fuels.

In addition to the work on combustion reactions, some work was also undertaken on transitional metal systems, in order to complete projects which were started under a previous cooperative agreement. This work was described in detail in previous progress reports and will not be further referenced here. In this report we will summarize the work on chemical reactions. Since all of this work has been discussed in previous progress reports and has been published in the open literature, we will give here only a brief summary of this work plus a list of publications from which the interested reader may obtain further details of this work.

The first paper [1] describes calculations for the reactions of N + O_2 and O + N_2. These reactions are believed to be important in high temperature air as e.g. in a shock layer in front of a hypersonic aircraft. These reactions are also important in the HSR program, since they constitute the thermal Zeldovich mechanism for NO production in combustion.

Papers 2 and 3 are benchmark calculations for two atom-diatom reactions which have been extensively studied by theory. The reaction of $O(^3P)$ + H_2 [2] is important in combustion, and the reaction of F + H_2 [3] is important in laser chemistry.

Papers 4, 9, and 14 discuss the reaction

$$H + O_2 \rightarrow HO + O \tag{1}$$

which is a very important chain branching reaction in combustion.

Paper 5 discusses the reaction of the electronically excited ^1D state of the O

atom with H_2. Unlike the reaction of ground state O with H_2 [2], which has a barrier, the excited state surface correlates with the singlet ground state surface of H_2O and has no barrier. This system was studied because of an interest in the use of electronically excited reactants to enhance the rate of H_2 combustion in SCRAM jet engines.

Papers 6, 11, 15, and 16 describe calculations of the potential energy surface and rate of unimolecular decay of the HN_2 species. The interesting result of this work is that the HN_2 species has a much shorter lifetime than had been previously assumed by DOE scientists in models of thermal De-NO_x, which is a process in which NO is converted to N_2 and H_2O by addition of NH_3 to combustion processes. This process has also been considered as a means to reduce NO emmisions in the HSR program.

Paper 8 discusses the potential surface for N_2H_2. The NASA interest in this system derives from the possible role of HN_2 in a chaperone mechanism for recombination of two H atoms to give H_2 with N_2 as a third body. Interest in these recombination processes derived from the importance of such reactions in SCRAM jet engines. A related system which was studied is H + NO [10], [12]. This system may be important in wind tunnel experiments to study SCRAM jets, since the need to heat the air to high temperatures results in NO formation by the thermal Zeldovich mechanism [1]. Other recombination reactions which were studied are H + H + H_2O [13] and H + H + Ar [20].

Paper 7 was written for presentation at a NATO workshop on dynamics.

Paper 18 made use of the potential for H + N_2 [11] to compute transport properties. This work was in collaboration with Dr. E. Levin who later became a co-principal investigator on this cooperative agreement.

The remaining papers are related to the HSR program. Here there is a need to obtain both thermochemical information (heats of formation etc.) and rate information. Paper 17 discusses calculations of the bond energies of CH_3OH. An important contibution from this paper is an estimate of the heat of formation of CH_2OH. Paper 21 describes calculations for several reaction pathways on the CH_3OH potential energy surface in the reaction of CH_3 with OH. Several of these pathways had not been characterized before, including the $^1CH_2$ + H_2O chan-

nel. The production of singlet methylene ($^1CH_2$) by this reaction has important mechanistic implications, since singlet methylene is very reactive and could be involved in NO production and soot formation among other possibilities. Paper 22 describes some features of the PES for CH_3O. This work has been used by Dr. F. Temps to model experiments on highly vibrationally excited CH_3O.

Papers 19, 24, and 25 describe the PES's for several reactions which are important in the nitrogen chemistry which goes on in combustion. In a collaborative study with Schatz the computed PES for NH + NO [19] will be used to compute product branching ratios.

Paper 23 describes calculations for the reaction of $CH(^2\Pi)$ with N_2. This reaction is believed to be the source of "prompt NO". Under rich conditions, prompt NO is an important NO source in combustion. The present calculations are the first to characterize the reaction pathway for this important process. Previous work had assumed pathways with little or no barrier. However, the current calculations show significant ($\approx$ 20 kcal/mol) barriers in agreement with the activation energy measured at high temperature. Tamar Seideman is currently using this surface in dynamics calculations on this system.

Paper 26 discusses the CH_3 + O_2 reaction. This system is complicated in that there is a surface crossing and more than one surface has to be included in the dynamics treatment. Truhlar and coworkers are planning to study this system.

Transport Properties of Gases
Investigator: Dr. Eugene Levin

During the time period from 1 July 1992 to 31 December 1993, the research work was entirely focused on the determination of the transport properties of gases (e.g., viscosity, diffusion, thermal conductivity, etc.) from the collision cross-sections of the constituent species. The calculation of the collision cross-sections from the scattering phase shifts required knowledge of the potential energy surface describing the interaction of the colliding particles. The phase shifts were then obtained from a uniform semiclassical description of the scattering due to Stallcop which includes the principal quantum mechanical effects of tunneling and

resonance.

Calculations were completed for H-H_2, H-H, H-Ar, H-N_2, H-H_2O, H_2-H_2, H_2-N_2, and N_2-N_2. For interactions involving hydrogen atoms or molecules, the results obtained from the semiclassical method were compared with quantum mechanical determinations from the Schroedinger equation and corrections to the transport properties at low temperatures were incorporated. The results have been published for H-N_2 [18] and H-H_2 [27]. Additional papers are in preparation.

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