



AFRL-AFOSR-VA-TR-2023-0452

Molecular processes at the extreme temperatures relevant for the hypersonic flight regime

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09/19/2023
Final Technical Report

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Air Force Research Laboratory
Air Force Office of Scientific Research
Arlington, Virginia 22203
Air Force Materiel Command

REPORT DOCUMENTATION PAGE

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1. REPORT DATE 20230919		2. REPORT TYPE Final		3. DATES COVERED	
				START DATE 20190601	END DATE 20230531
4. TITLE AND SUBTITLE Molecular processes at the extreme temperatures relevant for the hypersonic flight regime					
5a. CONTRACT NUMBER		5b. GRANT NUMBER FA9550-19-1-0266		5c. PROGRAM ELEMENT NUMBER	
5d. PROJECT NUMBER		5e. TASK NUMBER		5f. WORK UNIT NUMBER	
6. AUTHOR(S) Otoniel Denis Alpizar					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Universidad Autonoma de Chile Av. Pedro de Valdivia 425 Santiago 00000 CL				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Office of Scientific Research 875 N. Randolph St. Room 3112 Arlington, VA 22203			10. SPONSOR/MONITOR'S ACRONYM(S) AFRL/AFOSR IOS		11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-AFOSR-VA-TR-2023-0452
12. DISTRIBUTION/AVAILABILITY STATEMENT A Distribution Unlimited: PB Public Release					
13. SUPPLEMENTARY NOTES					
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15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR		18. NUMBER OF PAGES 12
a. REPORT U	b. ABSTRACT U	c. THIS PAGE U			
19a. NAME OF RESPONSIBLE PERSON ROGER GREENWOOD				19b. PHONE NUMBER (Include area code) 000-000-0000	

Standard Form 298 (Rev. 5/2020)
Prescribed by ANSI Std. Z39.18

Final Performance Report

Grant Number: FA9550-19-1-0266

Research Title: Molecular processes at the extreme temperatures relevant for the hypersonic flight regime

PI Name: Otoniel DENIS ALPIZAR

Period of Performance: 01 Jun 2019 - 31 May 2023

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1 Summary

In hypersonic flight or during atmospheric reentry, the temperature of the gases around the spacecraft increases enormously. The energy is redistributed through complex molecular interactions, and understanding such processes is crucial for using aerothermodynamics models. This project has been focused on investigating the dynamics of reactions occurring near the surface of vehicles during atmospheric reentry. For this purpose, potential energy surfaces have been developed to study reactions of interest for the hypersonic regime (e.g., $\text{CN}+\text{N}$, N_2+C , and $\text{CO}+\text{C}$). Dynamics have been carried out using quasiclassical methods, and rate coefficients have been reported at temperatures as high as 20000 K. In addition, vibrational relaxation processes have been analyzed in these and other systems. The results obtained here will have relevance for the application of aerothermodynamic models.

2 Accomplishments

2.1 Research Objectives

In hypersonic flight or during atmospheric reentry, the temperature of the gases around the spacecraft reaches tens of thousands of degrees Kelvin. Energy is redistributed through complex processes, such as changes in the chemical composition of the gases, redistribution through vibrational, translational, rotational, and electronic modes, emission and absorption of radiation, dissociation, and ionization. Understanding how these processes occur is critical to, for example, the correct design of the ship's thermal protection system.

Aerothermodynamic studies use chemical models which require knowledge of the reactive rate coefficients of many reactions as a function of temperature [1]. For example, Park's 20-species model [2] includes 23 reactions, whereas Martin *et al* [1] considered 158 reactions. However, the rates are unavailable or limited to low or intermediate temperatures for many of these reactions.

Due to the large amount of N, O, Ar, and C in the atmospheres of Earth and also on Mars, understanding reactions involving such elements (e.g., N_2+C , $CO+C$, and $CO+O$) are of great interest. Therefore, the main objective of this research project is to investigate the dynamics of reactions occurring near the surface of vehicles during atmospheric reentry.

2.2 Details of accomplishments during this reporting period

2.2.1 Major activities

- A new PES was developed for the CN_2 complex (published, see Ref. [3]).
- The dynamics of the $CN+N$ and N_2+C were studied, and new reactive rate coefficients were reported (published, see Ref. [3] and [4]).
- The PES of $CO+O$ reaction was studied (unpublished).
- The C_2O complex was analyzed, and new PESs were developed for this system (article in preparation).
- The dynamics for $CO+C$ were studied (paper in preparation).

- The existence of two-center three-electron bonds in C_2O and CN_2 was proposed (paper submitted to the Int. J. Quantum Chem.: QUA-2023-0274).
- The vibrational relaxation time for H_2O was determined from quantum calculations (article in preparation).

2.2.2 Specific objectives

The specific objectives of the project are developing full-dimensional potential energy surfaces at a high level of theory for reactions crucial for reactions that take place around a spacecraft during the reentering to the atmosphere; analyzing the vibrational, rotational, and kinetic energy transfer for such reactions at high temperatures; determine rate coefficients from quasiclassical trajectories method depending on vibrational and translational temperatures; computing vibrational relaxation time at high temperatures; and studying the non-adiabatic dynamics in the cases required.

2.2.3 Significant results

- We reported new rate coefficients at high temperatures for reactions used in the aerothermodynamics models.
- We developed new potential energy surfaces for several systems (CN_2 , C_2O , CO_2 , and H_2 -Ar) and, in some cases, for more than one electronic state.
- We proposed a two-center two-electron (2c-3e) bonds for explain stability of CN_2 and C_2O in their ground states.

2.2.4 Other achievements

We started new collaborations that have already yielded results:

- We collaborated with Prof. Hua Gou (University of New Mexico) to study the N_2+C reaction. A joint paper has already been published (see Ref [4]).
- We collaborate with theoretical and experimental groups at the University of Bordeaux (France) to study H_2O relaxation with Ar. The results of the vibrational relaxation times are shown in Section 5.

2.3 Dissemination activities

- Oral presentation: “Molecular processes at the extreme temperatures relevant to the hypersonic flight regime” at the 2023 AFOSR/ONR/HVSI Annual High-Speed Aerodynamics Portfolio Review. USA. July 24-28, 2023.
- Oral presentation: “Molecular processes at the extreme temperatures relevant to the hypersonic flight regime”. AFOSR/HVSI/ONR High-Speed Aerodynamics Annual Review, USA. July 18-22, 2022.
- Poster: “Study of the $\text{CN}(^2\Sigma) + \text{N}(^4S)$ Reaction at High Temperatures”. AFOSR Molecular Dynamics/ Theoretical Chemistry Program Review (Online), EE.UU. March 24-26, 2022.
- Seminar: “Molecular collision studies at extreme conditions” at Universidad Autónoma de Chile. Chile, May, 2022
- Oral presentation: “Molecular reactions studies at extreme conditions: $\text{CN}+\text{N}$ ” at the Brainstorm III (online workshop). Santiago. Chile, June, 2021
- Oral presentation: “Molecular Collisions in Extreme Conditions: From Interactions in the Interstellar Medium to the High Temperatures of the Hypersonic Flight Regime.” III Workshop Vincúlate, Santiago, Chile. November 6-7, 2020.

3 Impacts

Development of the principal discipline(s) of the project

We reported reaction rate coefficients and analyzed the redistribution of energy through vibrational, translational, and rotational of reactions that are used in aerothermodynamics models. Furthermore, we also developed PES at a high level of theory, which are available to the community.

Impact in this reporting period on the development of human resources

Thanks to this project, it has been possible to develop a new area of research at Universidad Autónoma de Chile. It has allowed the training of young researchers, increasing their academic opportunities. The two post-docs (Rodrigo Urzua and Ricardo Pino) involved in the project already have

permanent positions, one at Universidad Autónoma de Chile and the other at Universidad Arturo Prat (Chile). With these researchers in their new academic jobs, it will be possible to consolidate this line of research in the country.

4 Changes

4.1 Problems or delays

This project was initially scheduled for completion in May 2022. However, mainly due to the closure of universities in Santiago due first to the social outbreak in Chile and later because of the COVID-19 pandemic, an extension was requested and approved, with May 31, 2023, as the project end date.

5 Technical Updates

5.1 Methodology

Each reaction investigated during the execution of this project was based on a methodology that includes three steps, as detailed below:

1. The correlation diagrams of the system are analyzed, and the electronic states of the complex to be studied are selected. For each electronic state of interest, thousands of ab initio energies are calculated at many geometrical configurations of the system. These calculations are performed at the high level of theory, e.g., MRCI+Q or MRCI-F12+Q.
2. Each grid of ab initio energies calculated (each corresponding to a given electronic state) is fitted to an analytical function: the potential energy surface (PES). This fit can be performed by cubic splines, least squares, and kernel-based methods. The procedure we developed for triatomic systems uses a combination of least-squares (to describe the angular part) and kernel methods (for the radial part) for each asymptotic channel (AB+C, BC+A, and CA+B), which are then fitted together using a switching function.
3. Finally, the developed PES is used to study the reaction's dynamics and determine the rate coefficients. We use the quasiclassical trajectories (QCT) method [5]. At a given temperature, thousands of trajectories were run for a large set of initial conditions, from which the rate coefficients are obtained. We also investigate the dynamics at fixed

initial vibrational states to analyze the out-of-equilibrium dynamics. The calculated rates are compared with experimental values (generally available only for a narrow range of temperatures), and from this comparison, we analyzed whether it is necessary to include non-adiabatic dynamics to study the system.

5.2 Main results

In this section, each proposed reaction is analyzed. This includes those that are correlated in the three complexes of interest (C_2O , CO_2 , CN_2), as well as for the H_2O+Ar .

CO+C

The reaction $CO + C$ in the ground states of the CO and C is connected with the channel $C_2 + C$ through $1^3A''$, $2^3A''$ and $1^3A'$ electronic states of C_2O , see Figure 1. Therefore, for these three electronic states, at each asymptotic channel ($CO + C$ and $C_2 + C$), a regular grid of *ab initio* energies was computed at a large set of geometrical configurations (using the Jacobi coordinates r , R , and θ). Such calculations were performed at the MRCI+Q/aug-cc-pVTZ level of theory as implemented in the Molpro package[6]. The reference wave functions were obtained from previous SA-CASSCF.

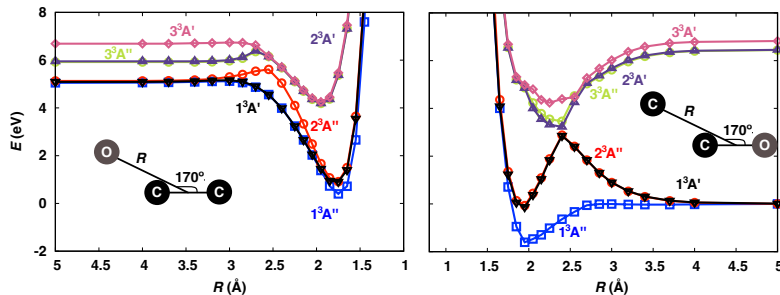


Figure 1: Energy dependency with R of the analytical PES (solid lines) at the $1^3A''$, $2^3A''$, and $1^3A'$ electronic states for $CO + C$ at $r_{N_2} = 1.25 \text{ \AA}$ at several angular configurations. A set of *ab initio* energies (not used in the fit) is also included (points). The zero of energy corresponds to the full atomization.

Each asymptotic channel was fitted to $V_i(R, r, \theta) = \sum_l C_l(R, r) \cdot P_l(\cos \theta)$, and the global PES for each electronic state ($1^3A''$, $2^3A''$ and $1^3A'$) is ex-

pressed as $V(\mathbf{y}) = \sum_{i=1}^3 \omega_i(\mathbf{y})V_i(\mathbf{y})$, where, V_i is the PES of each channel, $C^aO + C^b$, $C^bO + C^a$, and $C_2 + O$ (with the superscript a and b used to identify the C atoms), and they are mixing smoothly using a distance-dependent switching function, $\omega_i(\mathbf{y}) = \frac{e^{-(y_i/a)^4}}{\sum_{i=1}^3 e^{-(y_j/a)^4}}$ where $\mathbf{y} = (y_1, y_2, y_3)$ is the vector of inter-atomic distances of the C_2O molecule, and the parameter a was chosen to minimize the root means square deviation. Figure 2 shows a contour plot of the analytical PES for each electronic state.

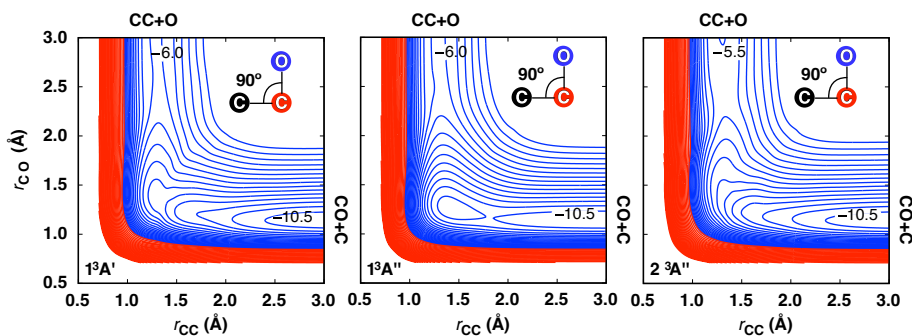


Figure 2: Contour plot of the potential energy surface of C_2O (energies in eV).

These surfaces were used to compute the rate coefficients of the $CO + C$ reaction using the QCT method as employed in Ref [3]. $CO + C \rightarrow C_2 + O$ is an endothermic reaction that, at low temperatures, is closed (as shown in Figure 1). Even at 10000 K, the rate coefficients are relatively low, 3.42×10^{11} ($1^3A''$), 4.63×10^{12} ($2^3A''$) and 5.52×10^{12} ($1^3A'$). Furthermore, Figure 3 shows the probability distribution of the rovibrational energy of the formed C_2 at 10000 K. C_2 may be formed with rovibrational energies larger than the dissociation energy due to the existence of a centrifugal barrier.

Furthermore, we also studied the formation of the C_2O and also for CN_2 complexes in their ground state. First, optimization was done at the CCSD(T) level. Later, the nature of the chemical bonding at the CASSCF level was analyzed using the electronic localization function (ELF) for both compounds. The ELF topological analysis indicates the possible existence of two-center two-electron (2c-3e bonds); see Figure 4. The delocalization between the basins of these compounds helps to confirm these results. Furthermore, reso-

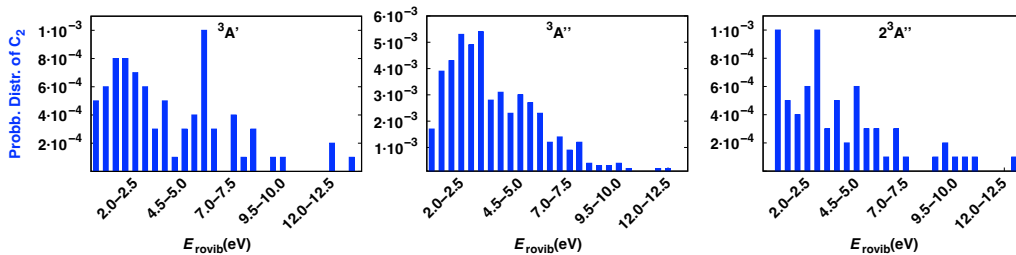


Figure 3: Probability distribution of the final states of C_2 from the $CO+C \rightarrow C_2+O$ reaction at 10000 K.

nance structures based on the valence bond model proposed by Pauling help to explain schematically the 2c-3e nature of the bonds. Certain resonance structures have allowed us to describe the triplet nature and the excess of electrons in the monosynaptic basins. Additionally, the ionic nature of the proposed resonance structures shows a charge shift character. To our knowledge, this is the first time that the existence of two different 2c-3e bonds in triatomic molecules has been proposed.

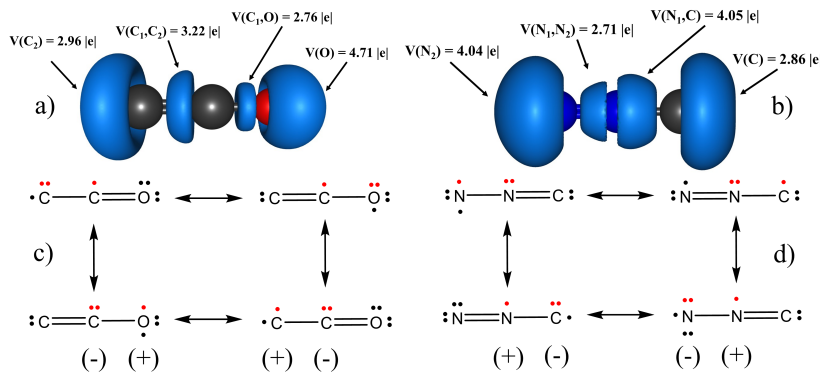


Figure 4: ELF isosurfaces for a) C_2O b) N_2C in their ground states and their respective proposed resonance structures (c and d) according to the Valence bond approach and ELF results. Red dots represent the electrons that participate in the 2c-3e bond.

O_2+C

The ground state of CO_2 , unlike C_2O and CN_2 , is a singlet, which correlates the reaction of O_2+C with the ground state of CO and the 1D excited state of O . For this study we performed a set of ab initio calculations at the MRCI level of theory and fitted the surface following the same steps described above

for C_2O . Figure 5 shows a contour plot for this system.

[7]

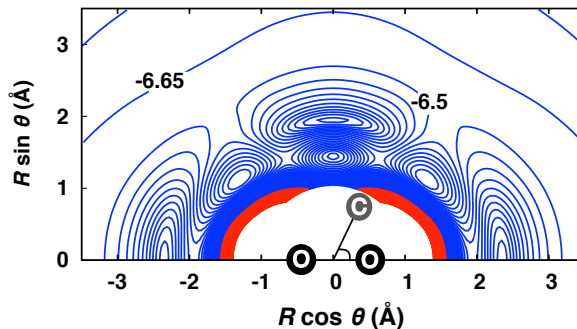


Figure 5: Contour plot of the potential energy surface of O_2+C at $r_e = 1.208 \text{ \AA}$ (energies in eV).

For the dynamics, we used the QCT method. At the same time as we were doing this work, a paper investigating this reaction with a PES at the same level of theory as ours was published. Our rates were in good agreement with those published. However, they extended their work to 5 electronic states of the complex, which makes it difficult to publish this research.

CN+N and N_2+C

The CN+N, and N_2+C reactions were analysed in detail in Ref [3] and [4]. A new energy surface for the $^3\text{A}''$ electronic state of CN_2 at the MRCI-F12 level of theory was developed. This surface was then employed in QCT calculations to study the CN+N and N_2+C reactions. In both cases, the vibrations and rotational analysis of the formed molecule were studied.

Figure 6 (Left panel) shows a comparison of the computed rates for the $\text{N}_2+\text{C}\rightarrow\text{CN}+\text{N}$ reaction with available data [8, 9, 10]. The agreement is quite good, and the inclusion of non-adiabatic dynamics seems not to be necessary. However, experimental data are limited at low and intermediate temperatures, while our calculations report the rates up to 20000 K. Furthermore, the dynamics out equilibrium was also analyzed. From the state $\nu = 0, j = 0$, the rates are lower than the thermal ones. In the case of the CN+N reaction, the calculations from the initial vibrational $\nu = 1, 2$, and 3 of CN do not show important differences, as seen in Figure 6 (Right panel).

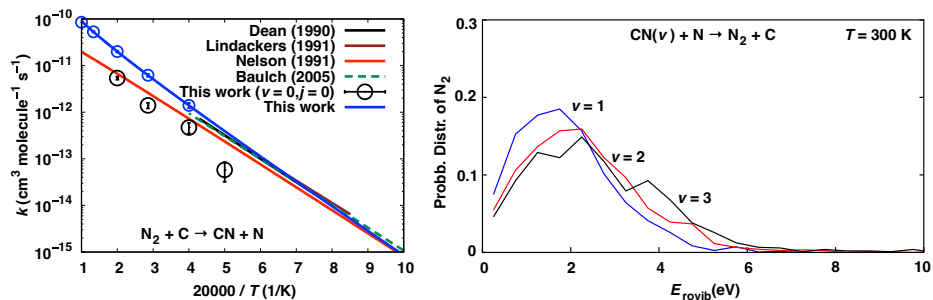


Figure 6: Left Panel: Rate coefficients of the $\text{N}_2 + \text{C} \rightarrow \text{CN} + \text{N}$ reaction. Experimental data from Ref. [8, 9, 10] are also included. Furthermore, the rates for the fixed initial $\nu = 0, j = 0$ state of N_2 are also shown. Right Panel: Probability distribution of the final rovibrational energy of N_2 from the $\text{CN} + \text{N}$ reaction at different initial vibrational states of CN at 300 K.

$\text{H}_2\text{O} + \text{Ar}$

The vibrational relaxation time (τp) of $\text{H}_2\text{O} + \text{Ar}$ was computed as for $\text{CO} + \text{Ar}$ [11], from the rate coefficients for the bending transition $1 \rightarrow 0$. The developed PES includes the bending motion of H_2O . The relaxation rate coefficients were computed using the rigid bender close-coupling method, using the same code employed to study $\text{H}_2\text{O} + \text{H}$ [12]. The averaged vibrational relaxation time from 1800 and 4100 K was experimentally reported by Kung and Center [13] to be $4.9 \times 10^{-7} \text{ atm s}$, while from our calculation, this value in the [1800, 2500] K is $5.99 \times 10^{-7} \text{ atm s}$. However, this work shows a strong dependence of τp with the temperature; see Figure 7.

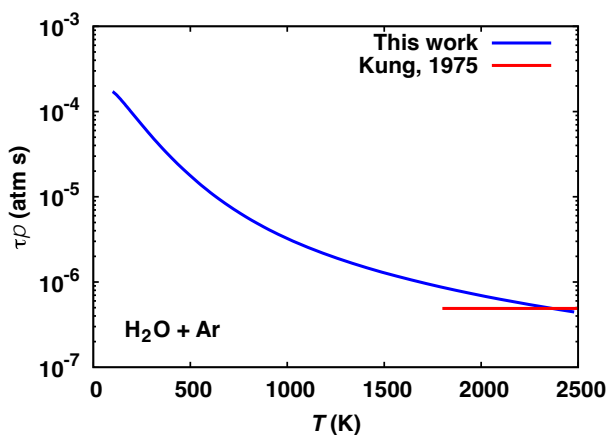


Figure 7: Vibrational relaxation time of $\text{H}_2\text{O} + \text{Ar}$.

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