Ab Initio Electronic Structure Calculations of CNN for CN Excitation Studies

Eric C. Geistfeld*
NASA Postdoctoral Fellow at NASA Ames Research Center, Moffett Field, CA, 94035, USA

David W. Schwenke †
NASA Ames Research Center, Moffett Field, CA, 94035, USA

The CN molecule is an important contributor to radiative heat flux in shock layers around vehicles entering Titan's atmosphere. Current data for heavy particle (de)excitation rate coefficients of CN leads to uncertainties in the population of CN in its first and second excited states. This in turn leads to uncertainties in the radiative heat flux predicted by Computational Fluid Dynamics (CFD) simulations of Titan atmospheric entry. This work performs ab initio electronic structure calculations of the CNN complex to create Potential Energy Surfaces (PESs) that correlate to the ground and first and second excited states of CN. Specifically, the state combinations of CN(X,A,B) + N($^4S^o$) correlate to six states of CNN (three Quintet A" and three Triplet A"). Initial calculations of these states suggest that heavy particle (de)excitation of CN by N atoms is likely to proceed through collinear geometries on triplet surfaces. Complete PESs will show all of the reaction pathways in detail, and will be used in nonadiabatic dynamics calculations to evaluate improved rate coefficients and reduce uncertainty in the radiative heat flux during Titan entry.

I. Nomenclature

α_r = Repulsive Diatomic Potential Energy Term Fitting Parameter
α_s, C_j = Short Range Diatomic Potential Energy Term Fitting Parameters
a_{LR}, R_{LR}, r_d = Long Range Triatomic Potential Energy Term Fitting Parameters
C_{ijk}, p_1, p_2 = Short Range Triatomic Potential Energy Term Fitting Parameters
CAS = Complete Active Space
δ = Long Range Diatomic Potential Energy Term Fitting Parameter
i^2c-MRCI = Improved Internally Contracted Multi Reference Configuration Interaction
MCHF = Multi Configuration Hartree Fock
PES = Potential Energy Surface
$V_{LRCutoff}$ = Long Range Diatomic Potential Energy Term Cutoff Parameter
Z_S = Atomic Number of Species S

II. Introduction

Titan's atmosphere is composed mostly of N_2 with a small amount of CH_4. So, shock layers around craft entering Titan's atmosphere will contain a variety of molecules formed from H, C, and N atoms, including the cyanogen radical CN. Sensitivity analysis has shown that the radiative heat flux predicted by computational fluid dynamics (CFD) simulations of Titan entry has up to 14% uncertainty due to the rate coefficients for collisional (de)excitation reactions that control the population of CN in its first and second excited states.[1]

$$\mathrm{CN}(\mathrm{A}\ ^2\Pi) + \mathrm{M} \longleftrightarrow \mathrm{CN}(\mathrm{B}\ ^2\Sigma_g^+) + \mathrm{M} \tag{1}$$

CN and its reactions with different collision partners have been studied for years in multiple experimental and theoretical contexts because of its importance in kinetics for combustion, and astrophysics applications.[2, 3, 4, 5, 6, 7]

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*NASA Postdoctoral Fellow, Aerothermodynamics Branch, AIAA Member
†Senior Research Scientist, Supercomputing Branch

Recently, attention has focused on their importance in atmospheric entry problems.[8, 9, 10, 11, 1] The red and violet emission bands due to decay from the first and second excited states, respectively, are known to be large sources of radiative heat flux on capsules entering Titan's atmosphere. So, the population of CN in its first and second excited states predicted by Computational Fluid Dynamics (CFD) calculations is very important, but rate coefficient data for reaction 1 is relatively sparse. The age and relatively small amount of data that does exist leads to uncertainties in the rate parameters of reaction 1 for CFD chemistry models.

The goal of the current work is to provide improved rate coefficient data for these reactions from first principles quantum chemistry calculations. We focus first on heavy particle (de)excitation of CN by nitrogen atoms. The first step of this process is to create ab initio adiabatic Potential Energy Surfaces (PESs) of CNN that correspond to the ground, first excited, and second excited states of CN. Adiabatic PESs are constructed by calculating single point energies and state couplings by solving the Schrödinger equation under the Born-Oppenheimer approximation then fitting functional forms to them. The diatomic-atomic state of the CNN system can change when following adiabatic states and the state couplings can be jagged and discontinuous. The next step is to form diabatic states from the adiabatic states that have better defined diatomic-atomic character and smooth and continuous state couplings. While a set of diabatic states is not unique, a good set of them will make nonadiabatic dynamics calculations much easier. Finally, the nonadiabatic dynamics calculations will determine the CN heavy particle (de)excitation rate coefficients at conditions relevant to shock layers around vehicles entering Titan's atmosphere. Rate data for other reactions involving one C atom and two N atoms like exchange, dissociation, and recombination can then be calculated as well.

III. Methodology

A. Electronic Structure Calculations

We use the new electronic structure code Massively Parallel Electron Correlation (MPEC) to calculate ab initio single point energies using the Improved Internally Contracted Multi Reference Configuration Interaction with Singles and Doubles (i^2c-MRCI(SD)) method.[12] I^2c-MRCI(SD) calculations require reference orbitals, which we generated using the Multi Configuration Hartree Fock (MCHF) method to optimize a set of Complete Active Space (CAS) orbitals.

The number of states of each symmetry produced by different combinations of CN and N are summarized in Table 1. While there are many states, the quintet A" and triplet A" manifolds are those that link the CN(X,A,B)+N($^4S^o$) states.

	CN(X)	CN(A)	CN(B)
N($^4S^o$)	One A" (Quintet,Triplet)	One A", One A' (Quintet,Triplet)	One A" (Quintet,Triplet)
N($^2D^o$)	Three A", Two A' (Triplet, Singlet)	Five A", Five A' (Triplet,Singlet)	Three A", Two A' (Triplet, Singlet)

Table 1 Possible CNN states from combinations of CN and N, formatted as "Number of states of each spatial symmetry in C_s (Possible Spin States) "

Figure 1 is a correlation diagram that shows the CN+N, C+N+N, and N_2+C asymptotes of the CNN complex and how the quintet and triplet A" adiabatic surfaces connect them at the CAS level. The lowest three asymptotes of quintet A" symmetry correspond to CN(X,A,B)+N($^4S^o$), but the triplet A" states have eight intermediate minima corresponding to CN(X,A)+N($^2D^o$). So, to form a good set of diabatic states for modelling reaction 1, we need at least 3 quintet A" states and 11 triplet A" states.

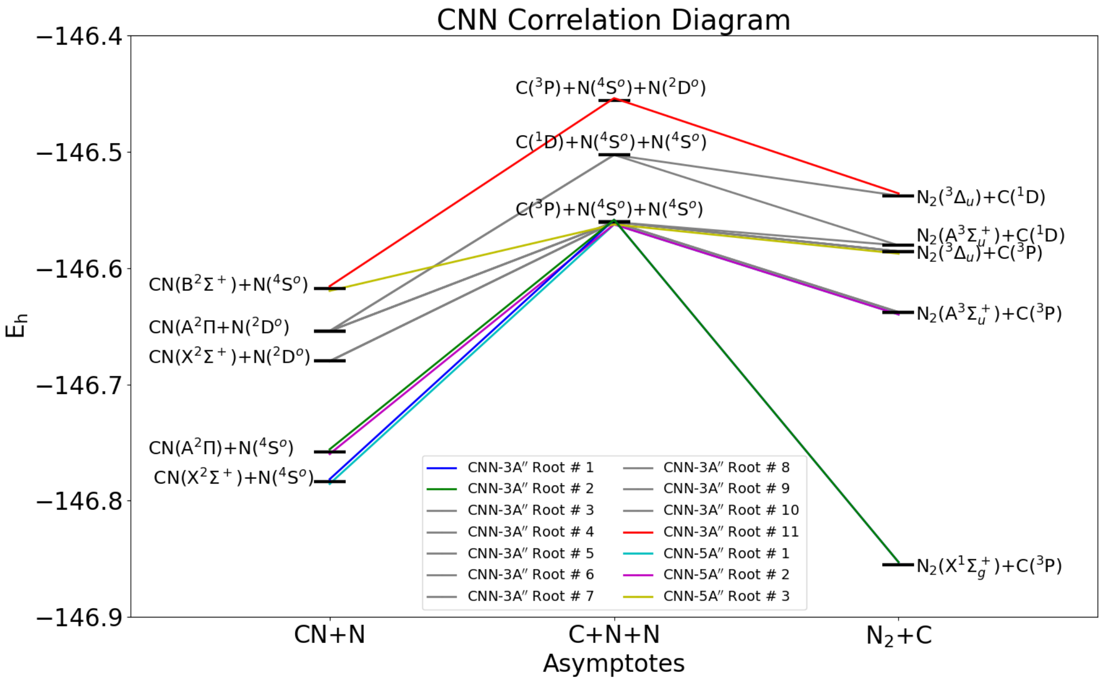

Fig. 1 CNN correlation diagram, showing CAS energies of important states for CN+N, C+N+N, and N$_2$+C asymptotes.

Because there are 24 possible states each of quintet and triplet A" symmetry that correspond to the atomic asymptotes C(^{3}P)+N(^{4}S^o)+N(^{4}S^o), C(^{1}D)+N(^{4}S^o)+N(^{4}S^o), and C(^{3}P)+N(^{4}S^o)+N(^{2}D^o), reference orbitals were generated for the lowest 24 states of both of these symmetries at a large number of geometries of the CNN system.

To generate orbitals, we used MPEC's MCHF CAS mode with the augmented-correlation-consistent-polarized-valence-triple-zeta (aug-ccpvtz) basis sets of Dunning.[13] For diatomic CN calculations shown here we constrain three orbitals to be doubly occupied - one N 1s, one C 1s, and one N 2s - and use an active space of 7 orbitals, one C2s and all of the 2p orbitals for each atom. For diatomic N$_2$ calculations we constrain 4 orbitals to be doubly occupied - two N 1s and two N 2s - and use an active space consisting of 6 orbitals, all the 2p orbitals for each atom. For the triatomic calculations we constrain 6 orbitals to be doubly occupied - two N 1s, one C 1s, two N 2s, and one C2s - and use an active space consisting of all the 2p orbitals for each atom.

B. Functional Forms

Single point energies are fit to functional forms to create analytical representations of PESs. The functional form used for the triatomic PESs in the current work is:

$$V = V^{CN}(R_{1,2}) + V^{NN}(R_{2,3}) + V^{CN}(R_{3,1}) + V^{3-Body}(R_{1,2}, R_{2,3}, R_{3,1}) \tag{2}$$

where the first three terms represent the potential energy of the different possible diatoms formed from combinations of C (atom 1), N (atom 2), and N (atom 3) the last term represents the three-body contribution to the energy. [14].

1. Diatomic

The diatomic potential terms are functions of the form $V(R_{1-2}) = V_{Rep} + V_{SR} + V_{LR}$ as described in Ref. [14]. Here the repulsive term is:

$$V_{Rep}(R) = Z_1 Z_2 \frac{e^{(-\alpha_r R)}}{R} \tag{3}$$

where α_r is determined from non-linear least squares fitting. The short range term is:

$$V_{SR}(R) = R^n e^{(-\alpha_s R)} \sum_j C_j (R - R_{eq})^j \tag{4}$$

where n and the number of terms in the summation over j were determined from trial and error, and α_s and C_j are determined from non-linear least squares fitting. Finally, the long range term is zero for R less than a cutoff distance $R_{LRcutoff}$ and for $R \geq R_{LRcutoff}$ is:

$$V_{LR}(R) = -\frac{C_8}{R^8 + \delta^8} - \frac{C_{10}}{R^{10} + \delta^{10}} \tag{5}$$

for CN, and

$$V_{LR}(R) = -\frac{C_6}{R^6 + \delta^6} - \frac{C_8}{(R^4 + \delta^4)^2} - \frac{C_{10}}{(R^2 + \delta^2)^5} \tag{6}$$

for N_2, where C_m are determined from $r^m (V_{LRcutoff} - V_\infty)$ and the terms in m come from the multipole expansion. The cutoff distance is determined by where the potential stops changing appreciably, and δ is determined from non-linear least squares fitting.

The I^2c-MRCI(SD) energies of CN and NN have been fit to functions of these forms and the internal energy states of the molecules have been calculated using the WKB approximation. Although the full expression in Eqn. 2 is fit to the triatomic data, two body terms with fitting parameters from high quality diatomic calculations or experiment can be used in the final PES.

2. Triatomic

Fitting the three-body term proceeds in a similar manner where the third term in Eqn. 2 is decomposed into short range and long range contributions:

$$V^{3Body} = V^{LR}(R_1, r_1, \theta_1) + V^{LR}(R_2, r_2, \theta_2) + V^{LR}(R_3, r_3, \theta_3) + V^{SR}(R_1, R_2, R_3) \tag{7}$$

where r_i is the vector from atom i to the center of mass of j and k, R_i is the vector from atom j to atom k, and θ_i is the angle between r_i and R_i. The long range terms are:

$$V^{LR} = -C_6 P_1 \cos(\theta) \frac{e^{-a^{LR}(R - R^{LR})}}{r^6 + r_d^6} \tag{8}$$

where C_6, a^{LR},R^{LR}, and r_d are parameters determined through fitting and P_1 is a Legendre polynomial. [14] The short range terms are:

$$V^{SR} = \sum_\alpha e^{(-p_1 r_i^2 - p_2 R_i^2)} \sum_{ijk} C_{ijk} r_\alpha^i R_\alpha^j P_k(cos(\theta)) \tag{9}$$

where α is 1, 2, or 3, and the parameters p_1, p_2, and C_{ijk} are determined through fitting. The limits on the ijk sum can be adjusted freely, and the weights of each point in the non-linear least square fitting are adjusted to ensure good fits near transition states.

Once fitting parameters are determined for the adiabatic energies, the functional form of Eqn. 2 and its analytical derivatives provide the necessary information for adiabatic dynamics calculations. For nonadiabatic dynamics calculations, similar analytical forms must be fit to the diabatic energies and couplings.

C. Dynamics Calculations

Once the triatomic MRCI energies and state couplings are computed, transformed to a diabatic basis, and fit with functional forms, they can be used in nonadiabatic dynamics simulations of CN+N collisions. These dynamics simulations will use Tully's fewest switches surfaces hopping method to determine rate coefficients for reaction 1 and others.[15]

IV. Results

This section presents the results of the electronic structure calculations so far. First the diatomic potentials of CN in the states of interest are shown, then different cuts of adiabatic single point energies for the triatomic CNN system are shown and specific geometries where (de) excitation reactions are likely to occur are discussed.

A. Diatomic Potentials

The i^2c-MRCI energies of the CN molecule in its ground and first and second excited states were fit with functional forms, and the rovibrational states of the CN molecule in these states were determined from them. The diatomic potential curves from the calculations with the aug-cc-pv5Z basis set are visible in Fig. 2, and information about the JV states is in Table 2. This data can be used to compare spectroscopic parameters based on these fits to other CN data. Although the triatomic calculations only used the aug-cc-pvTZ basis, these diatomic fits can also be used in the final PESs to improve performance without requiring calculations using the larger basis set for all triatomic geometries.

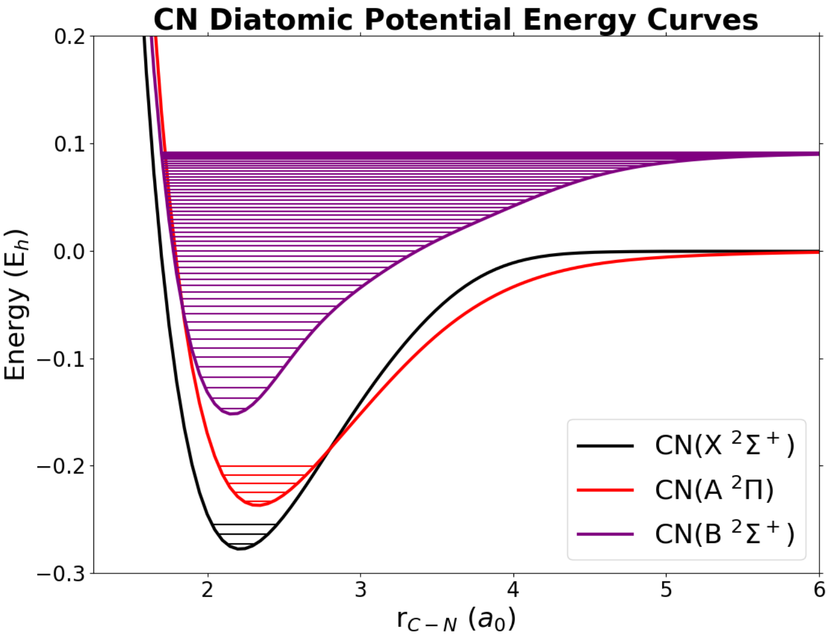

Fig. 2 Diatomic potential energy curves of the ground and first and second excited states of CN from MRCI data, shown with select vibrational levels of the first rotational level for each electronic state.

CN State	# JV States (#j,max #v)	# Bound	# Quasibound
CN($X^2\Sigma_g^+$)	7356 (262,49)	5535	1821
CN($A^2\Pi$)	7288 (244,53)	5747	1541
CN($B^2\Sigma_g^+$)	7716 (214,57)	6222	1494

Table 2 JV state information for CN(X,A,B)

B. Triatomic Single Point Energies

The i^2c-MRCI(SD) surfaces are in progress, but the preliminary MCHF CAS calculations show interesting and important features of the CNN system.

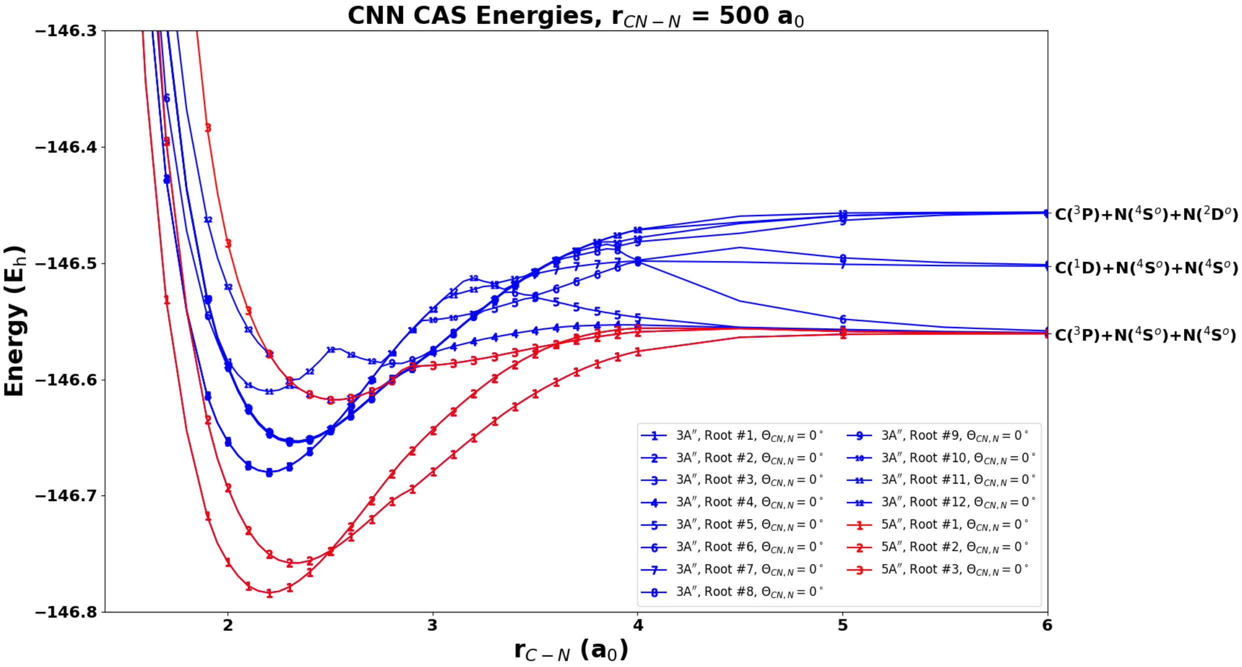

Fig. 3 Cuts of the three lowest quintet A" manifolds of CNN, sweeping in CN bond distance with the second N atom kept far away.

Figure 3 shows cuts of the Triplet and Quintet A" potential energy surfaces at the CAS level where the free N atom is kept far away and the C-N bond length is varied. Because the third atom is far away, one might expect the minima of these curves to be closely match the diatomic curves. However, because these calculations are performed for a lower symmetry than those in Fig. 2 the curves do not always match well. The adiabatic curves for the first two roots are not able to cross each other like the potentials for CN(X) and CN(A) do, and the third state does not asymptote to a different energy than the first two, like CN(B) should, as shown in Fig. 2 for example. The electronic character of the adiabatic states changes with geometry and they do not directly represent the corresponding diatomic curves. Diabatic curves formed from the set of adiabatic states will have well defined electronic character and properly resolve these differences to make non-adiabatic dynamics calculations easier.

1. Topological Features of the CNN Surfaces

This section uses adiabatic CAS energies to suggest expected reaction pathways for the CNN system. Figures 4 and 5 show sweeps of the Quintet and Triplet A" single point energies respectively at the CAS level where the CN is fixed near its ground state equilibrium bond length (r_{C-N} = 2.20 a$_0$) and the free N atom is brought towards/away from the CN center of mass at three different angles.

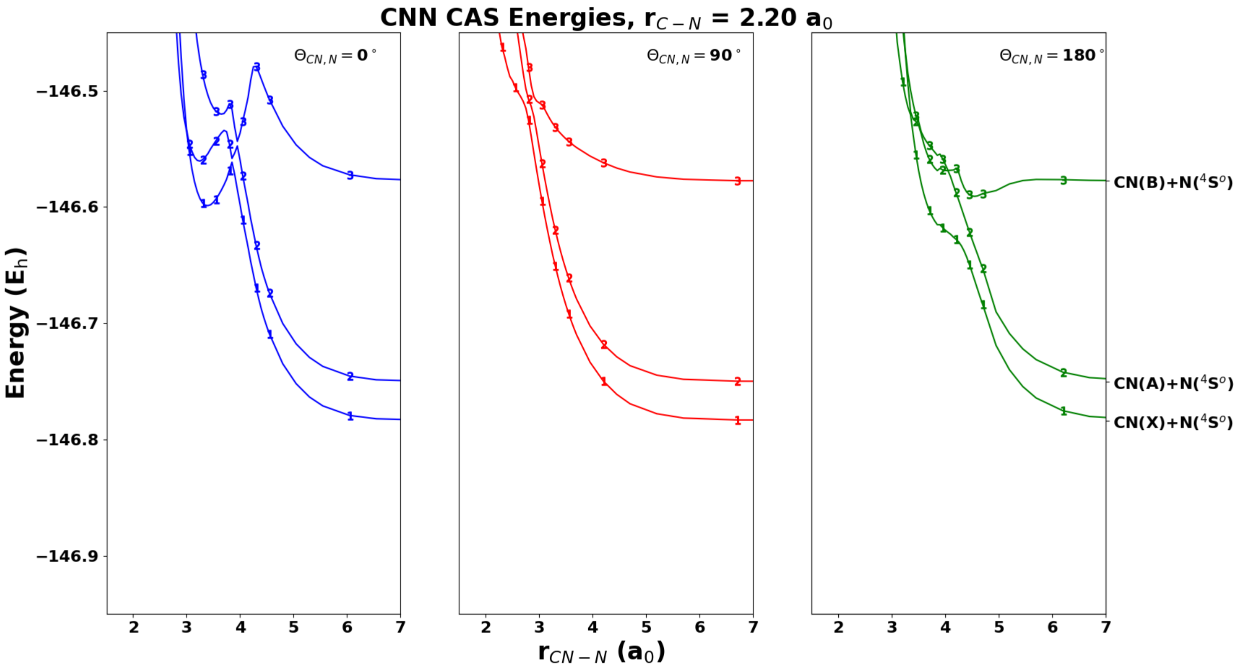

Fig. 4 Cuts of the three lowest Quintet A” manifolds of CNN, sweeping in CN-N distance with the CN bond length fixed at 2.20 a_0. The subplots are labeled by angle and the curves are labeled by state number.

Although the adiabatic states are inconvenient for dynamics calculations and not strictly chemically meaningful here, their avoided crossings show us meaningful aspects of the CNN complex for studying heavy particle (de)excitation. In regions where adiabatic states have avoided crossing, diabatic states will cross, and their couplings will be large. These regions on the PESs are where heavy particle (de)excitation occurs.

The green and blue lines in Fig. 4 show that there are several avoided crossings at intermediate distances of 3.5-6 a_0 for the first three Quintet A” states at collinear geometries, while for the perpendicular bisector geometries shown by the red lines there is only one avoided crossing near 3 a_0. In general the avoided crossings of all three states are surround by regions of close coupling of either states 1 and 2 or 2 and 3, and the avoided crossings of all three states are at lower energies at the collinear geometries. Diabatic curves drawn through these avoided crossings would themselves cross at those points, representing regions where the CN molecules has a higher probability to change electronic state.

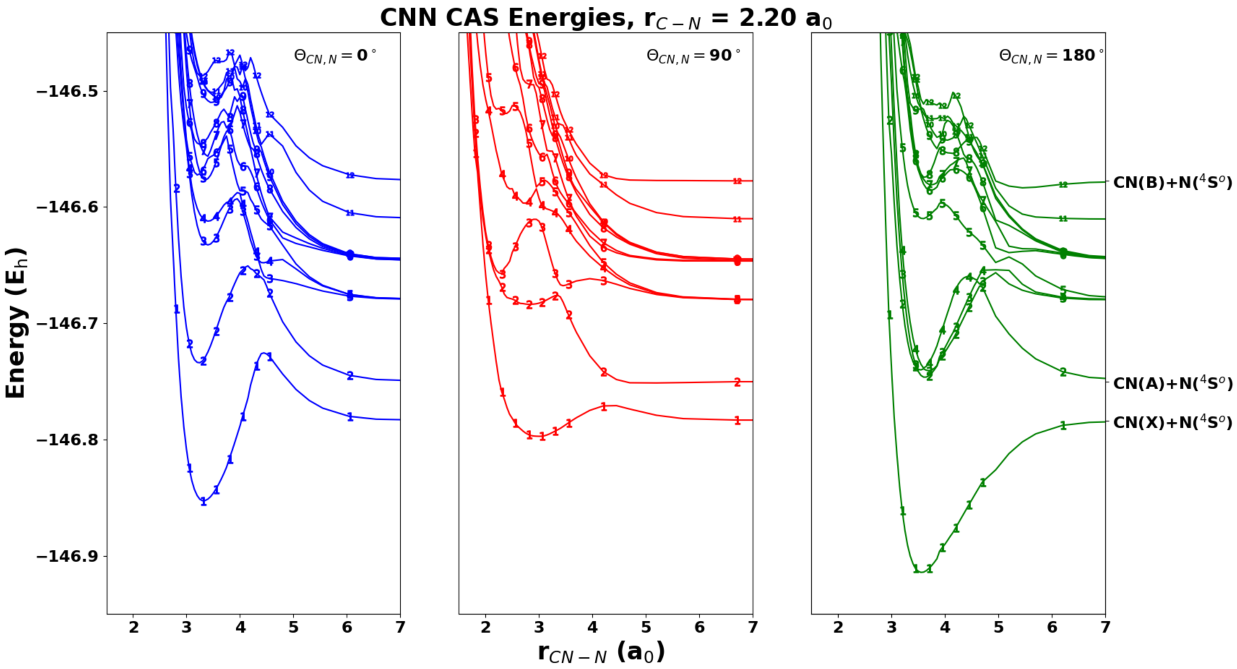

Fig. 5 Cuts of the twelve lowest Triplet A" manifolds of CNN, sweeping in CN-N distance with the CN bond length fixed at 2.20 a_0. The subplots are labeled by angle and the curves are labeled by state number.

Figure 5 shows similar features to Fig. 4, with avoided crossings between the relevant states occuring at lower energies at collinear geometries. This is most apparent comparing the higher lying states in the red curves to those in blue and green. From 3-5 a_0 the blue and green curves show large regions of close coupling with multiple avoided crossings and some minima corresponding to C-N-N and N-C-N triatoms. In contrast, the red curves are mostly repulsive with avoided crossings at higher energies and between fewer states at a time. Comparing Figs. 4 and 5 the avoided crossings on the triplet surfaces are lower than those on the quintet surfaces regardless of the angle of approach.

The features of Figs. 4 and 5 suggest that the heavy particle (de)excitation in reaction 1 is likely to occur through collinear geometries on triplet surfaces because that is where the states of interest are most closely coupled at the lowest energies. Whether this is counteracted by the larger statistical weight of the quintet surfaces, such that the overall rate of heavy particle excitation is larger from quintet states, must be determined from dynamics calculations.

V. Conclusions and Further Work

This work aims to produce ab initio PESs that describe the CNN complex and allow nonadiabatic dynamics simulations of CN (de)excitation by N atoms. The electronic structure calculations to form the PESs are underway. Diatomic potentials based on ab intio data points have been created, and reference orbitals have been generated at a large number of triatomic geometries for the symmetries of interest.

The data from the reference orbitals shows multiple avoided crossings at collinear arrangements, suggesting that collisional (de)excitation of CN by N atoms is likely to proceed through these geometries. The same data shows more avoided crossings at lower energies on triplet A" as opposed to quintet A", but the overall contributions to the heavy particle excitation rate by quintets and triplets may be similar once statistical weights are applied to results from dynamics calculations. Once the i^2c-MRCI(SD) PESs are completed, thorough analysis will show possible reaction pathways in detail, and nonadiabatic dynamics simulations will determine improved rate coefficients for the (de)excitation of CN by N atoms that can be used in CFD simulations to lower uncertainties in radiative heat flux predictions for atmospheric entry to Titan.

The broader capability to calculate adiabatic PESs for electronically excited states and transform them to a diabatic basis is an essential one for studying molecules relevant to radiation in shock layers. The advantage of MPEC is its design features that make it particularly well suited for these purposes. There is a vast amount of future work possible. Other systems like C_2N_2 and HCN are of interest for Titan, and the excited states of compounds involving Hydrogen, Helium, Carbon, Nitrogen, and Oxygen will be relevant to atmospheric entry for most destinations in our solar system.

Acknowledgments

The work of Eric Geistfeld was financially supported by the NASA Postdoctoral Program Fellowship and the Entry Systems Modeling Project. Computational resources supporting this work were provided by the NASA High-End Computing (HEC) Program through the NASA Advanced Supercomputing (NAS) Division at Ames Research Center.

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