Dynamics of hydrogen + methane

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Dynamics of H + CH$_4$

by

Edgar E. Arcia

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Two new potential energy surfaces were developed to describe the abstraction and exchange reactions of H with CD$_4$ at two relative collisional energies (35 Kcal/mol and 56 Kcal/mol). This new surface was evolved from the surface by Valencich-Chapman-Bunker (VCB), which was chosen because it was the only six-atom surface that gave substitution via the Walden inversion mechanism. Tabular terms in the VCB surface were replaced with functional fits and the switches were modified to avoid discontinuity problems. Quasiclassical trajectories were run and cross section to reactions were calculated. Our first surface (V5) gave cross section to abstraction too high and it preferred a non collinear transition state. Substitution followed a path that we called substitution via failed abstraction, where the attacking H tries to abstract an H', rotates and the H' leaves the CH$_4$ system. The best surface (V6) gives cross sections that agree well with experimental values. In this surface, a collinear transition state is preferred for abstraction of D by H. Three mechanisms for substitution were identified: (1) substitution via Walden inversion, (2) substitution with retention of configuration via a trigonal bipyramidal intermediate, and (3) front side substitution (FSS). The majority of substitution events followed the FSS mechanism. Two new transition states were found at the MP2/6-311G** level of theory, by a restricted geometry search. One leads to abstraction through an “L-configuration.” The second transition state leads to sideways-substitution. The two transition states are higher in energy than the collinear abstraction and the trigonal bipyramidal intermediate. The first surface (V5) gave a cross section to abstraction too high and preferred a non collinear transition state.
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Simple chemical reactions can be used as prototypes for more complicated ones. The world's most studied reaction\(^1\), hydrogen exchange in \(H_2\), is an example.

\[
H' + H_2 \rightarrow HH' + H
\]  

(1-1)

It is important to understand prototypical reactions for several reasons, among them:

a. they typify a process for an entire class of reactions, the most simple example establishes norms and trends for the class,

b. it is most likely to be well characterized experimentally and understood first,

c. with only a few complications, the prototype is expected to be more amenable to theoretical investigation,

d. theory can deal with conditions that may not be attainable in the laboratory, where experimental measurement of some aspects of the problem may be difficult, ambiguous or impossible,

e. even when definitively treated, simple, well studied systems remain important for testing and evaluating new and competing theoretical methods, and
it is also important to evaluate the applicability of generalizations developed from simple systems to more complicated situations to establish theoretical limits and to evolve the model.

A recent comparison of high resolution experimental data on the $\text{H}_3$ system provides a detailed assessment of the applicability and quality of quantum mechanical (QM) and quasi-classical trajectory (QCT) calculations. The QM results are finally in excellent agreement with all aspects of the experiments. The QCT results are also very good, including the angular distributions of individual vibrational levels. The correct potential energy surface (PES) is required, of course, and some differences were noted when information on individual rotational states was available.

The $\text{CH}_3$ system, as a prototypical hydrocarbon reaction, can be thought of as the next level of complexity. This system and its isotopomers contain a polyvalent atom; the reactive possibilities are here inherently more complex and interesting than in the three atom system. Most collisions are unreactive, but as the translational energy of the hydrogen atom is increased two reactive processes are possible: abstraction (equation 1-2) and substitution (equation 1-3). At larger relative collisional energies, decomposition of $\text{CH}_4$ also can occur.

$$
\text{H} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2 \quad (1-2)
$$
$$
\text{H'} + \text{CH}_4 \rightarrow \text{CH}_3\text{H'} + \text{H} \quad (1-3)
$$
Both reactions have large activation energies (~13 and ~40 kcal/mol respectively), and the reactants are both relatively light. This has prohibited experimental study of this reaction with molecular beam equipment, but recent advances in laser technology have made it possible to probe the reactive products of individual collisions between atoms and molecules in this reaction.  

Valentini and his group have determined the vibrational and rotational distributions of HD produced by reaction of H with D₂ and with CD₄ by Coherent Anti-Stokes Raman Scattering (CARS) spectroscopy, where the H had 36.8 kcal of translational energy. The activation energy for abstraction from CD₄ is similar to that for D₂. However, reaction (1-2) was remarkably less probable than (1-1), σ_{abs} = 0.15 Å² and σ_{subs} = 1.2 Å², respectively. Other issues are the relatively low vibrational excitation of the HD product, and an apparent positive correlation of excitation in rotational with vibrational excitation. Most bimolecular reactions show a decrease in rotational energy as the vibrational excitation of the product increases.

Bersohn and coworkers used polarized dissociating light and Resonance Enhanced Multiphoton Ionization (REMPI) to measure the velocity distribution of D atoms displaced from CD₄ by H atoms with 56 kcal of translational energy, reaction (1-3). Even at this higher energy the reaction cross section is very small, σ_{subs} = 0.084 Å². When CH₃D replaced CD₄, the cross section decreased to 0.04 Å². Since the probability did not decrease by a factor of 4, this is taken as evidence of a concerted substitution mechanism which involves most of the molecule. The measured velocity anisotropy
parameter implied a typical reactive scattering angle of either $25^\circ$ or $155^\circ$.

Each of these experiments is a window on a different process occurring in the same system at different energies. We will simulate reactions of H atoms with CD$_4$ and CH$_3$D using sampling conditions representative of these two experimental conditions. We will calculate the reaction cross sections, distributions of energies in the products, orientation requirements, and find microscopic mechanisms for both products at each energy. If these calculations compare well with the direct experiments, we will then provide information relevant to older experiments which used flash photolysis and nuclear transmutation. In these experiments the relative energy of only the first collision was known. Energy exchange, product decomposition and wall reactions are serious complications in these cases.

We want to develop a new potential energy surface (PES) that describes the chemistry of reactions (1-2) and (1-3) accurately, and agrees with experimental and \textit{ab initio} data. This includes barrier height to reaction, geometry of transition states, vibrational frequencies at these geometries, reaction cross sections, etc. In addition, we will calculate information which is not yet experimentally accessible such as the cross section for abstraction in Bersohn's experimental system.

Our potential description is based on an earlier surface developed by Valencich, Chapman and Bunker,$^9,10$ VCB, because it was the only PES used in a three dimensional, six-atom dynamical study of this system which exhibited an inversion mechanism for substitution.

There are several documented problems$^{11-14}$ associated with the VCB surface, and
our first set of objectives address these problems. We group these problems into three categories: (1) computational problems, (2) fundamental problems, and (3) problems with the form of the model.

(1) Computational Problems

When a problem is solvable in principle, but is awkward to implement, we refer to it as a computational problem. For example, internal energy in the reactants was not included in the early simulation work. Avoiding internal state sampling simplified the coding process, and computing resources were focused on a variety of translational energy ranges and isotopic combinations.

Normal mode stretches have high frequencies, and a large portion of the zero point energy is attributable to them. Frequencies associated with modes that are involved in the reactive process therefore change significantly along a reaction path. To test for sensitivity to this influential form of internal energy, a series of trajectories were repeated with and without twice the zero point energy of methane in stretches only. While the outcome of an individual event could change as a result of this test, energy in stretches had the same statistical effect on reactive probabilities as increasing the relative collisional energy by the same amount in this system. This computer experiment was the basis for ignoring internal energy in the reactants and the probability of reaction was studied as a function of translational energy only.

Standard techniques have since been developed to sample internal energy states appropriate to the experimental conditions in a routine manner, and this
issue is examined in this project.\textsuperscript{15}

Another computational problem has to do with limits. The general utility of a potential surface\textsuperscript{10,11,15} is enhanced if it does not contain terms which are subject to limit condition problems. For convenience we discuss three types of limit problems.

A type 1 (T1) limit difficulty develops with a potential which contains an angular term. The derivative of the potential with respect to an involved coordinate then contains a term divided by the \textit{sine} of that angle and is subject to floating divide problems as the angle goes to zero. We employed a series expansion as angles approach the limiting values of zero and \(\pi\) radians to eliminate floating divide T1 problem.

Functions which index a variable by an on/off condition, like defining a particular angle with respect to the shortest or longest bond, introduce discontinuities in the potential when the index changes. We term this limit problem as type 2 (T2). An example of the complications introduced by attempts to work around this problem is discussed by Truhlar\textsuperscript{11} \textit{et al.}

A third type (T3) of awkwardness concerns functions which have a desired behavior for one range (say in the negative direction) of the variable and an extremely undesirable behavior in the other. The harmonic representation of a diatomic bond is an example of such a function. While this description is appropriate for small changes in the bond length, it is not a useful description for a bond involved in a reaction because it cannot be broken. Angular functions
have similar problems when bonds break.

The angular portion, \( F(2\rho) \), of the abstraction term in the VCB surface (see next chapter for a mathematical description), is a cosine function of the attack angle, \( \rho \). \( F(2\rho) \) goes to zero independent of energy as the attack angle goes to 45 deg. For larger angles \( F(2\rho) \) is kept at zero to prevent the cosine function from making H abstraction possible at very large angles. This function is replaced by a hyperbolic tangent fit to remedy this T3 situation.

(2) Fundamental Problems

Variational transition state theory calculations and normal mode sampling procedures require that the potential include harmonic terms in the description of stretches and bends. The linear interpolation procedure used with the tabular functions present in the VCB surface derail these procedures.

The original abstraction description in VCB summed three terms, each of which is dependent upon only one variable: \( r_{CHa} \), \( r_{CHb} \), or \( r_{Hab} \). The attacking ligand, \( H_a \), was defined as the H furthest from the carbon. The hydrogen being abstracted, \( H_b \), was identified as the closest to \( H_a \). While this clearly makes possible T2 limit problems, no serious problems developed in simulating reactions (1-2) and (1-3). Since all trajectories were initiated with a particular \( H_a \) designation, this index was not changed during the course of a trajectory because it was clear which H was the “attacking” species. Four possible \( H_2 \) pairs were evaluated and no difficulties were experienced when the identity of \( H_b \)
changed.

In simulating reaction (1-2) in reverse,\textsuperscript{10} however, difficulty with this on/off designation of two hydrogens was encountered. Firstly, the identification \( H_a \) changed with rotation of either reactant. In addition, as the \( H_2 \) approach brought it equivalently near to more than one \( H \), choosing the \( b \) index became problematic. Even though this situation is a problem with the switches, it actually addresses a more fundamental issue of equivalence. A considerable effort is required to define the potential to make the hydrogens as equivalent as possible.\textsuperscript{9,11,15}

We will examine all ten pairs of \( H_2 \), not just four, retaining the “a” and “b” designation for each pair. This makes the potential surface better suited to a variational transition state theory treatment, because the mathematical treatment of each hydrogen is more equivalent. Making these functions depend on all three distances: \( r_{CHa} \), \( r_{CHb} \), or \( r_{HaHB} \), can gradually turn on and off a bonding pair contribution. This modification will also give us greater flexibility in the position, shape and duration of the barrier to abstraction.

(3) Problems with the Form of the Model

The original formulation of abstraction due to Valencich and Bunker\textsuperscript{9} was modified in the VCB version\textsuperscript{10} to include a repulsive interaction between the nonreactive hydrogens and the two hydrogens involved in forming the new bond. This was included to prevent formation of \( H_n \) clusters when the back reaction, \( CH_3 + H_2 \), was studied. When all ten possible \( H_2 \) pairs are considered, however,
some CH$_3$/H$_2$ repulsions will be unreasonably large unless this term depends upon the H$_2$ bond length as well. This function will be multiplied by a hyperbolic tangent function of r$_{He}$ to ensure that unrealistic repulsions are not contributed by inappropriate pairs. In addition, the form of the H$_n$ repulsive function generates limit problems of type 3, so we will replace its form with an exponential term.

Besides determining the outcome of an individual trajectory, the width of the barrier, and the shape of the PES, determine the reaction exothermicity, as well as the vibrational frequencies of reactants, products and transition states. In general, we want to manipulate the character of the abstraction path without changing the substitution process and *vice versa*. 

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CHAPTER 2

Mathematical Model

A. Valencich-Chapman-Bunker (VCB) Surface

We base our description on the Valencich-Chapman-Bunker (VCB) potential energy surface. This surface is chosen because it is a six-atom description that gives substitution by the Walden inversion mechanism.

This surface is composed of three terms:

\[ \text{VCB} = A + B + R \]  \hspace{1cm} (2-1)

The A term defines a three-body abstraction. The B term describes the hybridization-based bonding interactions between the hydrogens and the carbon. The R term defines angular repulsions between H-C-H'.

![Naming convention used in the abstraction term A](image)

**Figure 2-1** Naming convention used in the abstraction term A

The abstraction term A is the sum of the product of an angular function, \( F(\rho) \),
with the sum of a Morse, a hyperbolic tangent and a hyperbolic secant function, which depend on the bond distances between H\textsubscript{a}, H\textsubscript{b} and the C. The sum is over H\textsubscript{a} and the four hydrogens in CH\textsubscript{4}. H\textsubscript{a} is the hydrogen atom most distant from the carbon, H\textsubscript{b} is the hydrogen being abstracted, and \( \rho \) is the angle formed by the hydrogens and the carbon (H\textsubscript{a}-C-H\textsubscript{b}), as in Figure 2-1.

\[
A = \sum_{a=b} \left\{ D_{H_2} * F(\rho_{H_2CH_4}) * \left( M(r_{H_2H_0}) + T(r_{CH_4}) + S(r_{CH_4}) \right) + HRe \rho \right\} \tag{2-2}
\]

Each of the functions are defined in the following equations and the values of the constants are listed in Table 2-1.

\[
HRe \rho = k_{SC} \left\{ \sum_{i \neq a, b} (r_{H_iH_i} - 1.21\text{Å})^2 + \sum_{j \neq a, b} (r_{H_jH_j} - 1.21\text{Å})^2 \right\}; \quad r_{HH} < 1.21 \text{Å} \tag{2-3}
\]

\[
F(\rho) = \frac{1}{2} \left( 1 + \cos(2\rho) \right); \quad \rho < \frac{\pi}{2} \tag{2-4}
\]

\[
M(r_{H_aH_b}) = \exp(-\beta (r - r_0)) \left( \exp(-\beta (r - r_0)) - 2 \right) \tag{2-5}
\]

\[
T(r_{C-H_a}) = c_1 \left( 1 - \tanh(c_2 r - c_3) \right) \tag{2-6}
\]

\[
S(r_{C-H_a}) = c_4 \sech(c_5 r + c_6) \tag{2-7}
\]

The B term is a product of a well depth function \( D(\xi) \) with a sum of unitary Morse
functions. The D function is tabular. $\xi$ is the hybridization of the carbon and it is defined as a sum of switches (equations 2-10 and 2-11).

$$B = D(\xi) \sum_{i=1}^{5} M(r_{CH_i}) \tag{2-8}$$

$$M(r_{CH_i}) = \exp[-\beta (r - r_0)] \left\{ \exp[-\beta (r - r_0)] - 2 \right\} \tag{2-9}$$

$$\xi = \sum_{i=1}^{5} S(r_{CH_i}) \tag{2-10}$$

$$S(r_{CH_i}) = -M(r_{CH_i}); \quad r_{CH_i} \geq r_0$$

$$= 1 \quad r_{CH_i} < r_0 \tag{2-11}$$

The angular repulsion term is a sum over all H-C-H possible pairs. It is a product of switches, as defined in the B term (equation 2-11), and an R($\theta$) function, which is also tabular.

$$R = \sum_{i=1}^{4} \sum_{j>i} S(r_{CH_i}) \times S(r_{CH_j}) \times R(\theta_{H_iH_j}) \tag{2-12}$$

The switches turn off the angular repulsions and decrease the hybridization of the carbon as the bond length increases.
Table 2-1  Values of constants used in the VCB surface.

<table>
<thead>
<tr>
<th>A Term</th>
<th>B and D Terms</th>
</tr>
</thead>
<tbody>
<tr>
<td>D_{H2}</td>
<td>109.5 kcal</td>
</tr>
<tr>
<td>k_{SC}</td>
<td>358.5 kcal</td>
</tr>
<tr>
<td>β</td>
<td>1.94 Å⁻¹</td>
</tr>
<tr>
<td>r_0</td>
<td>0.7417 Å</td>
</tr>
<tr>
<td>c_1</td>
<td>1.8</td>
</tr>
</tbody>
</table>

B. Improvements to the VCB Surface

1. D(ξ) Functional Fit

We replaced the D tabular function with two functional fits. This makes it possible to use our surface in transition state theory calculations, where first and second derivatives must be continuous. In general, both fits are products of polynomial sums and hyperbolic functions.

\[ D_1(\xi) = D_0 + \frac{D_T}{2} \left[ 1 + \text{Tanh}(B_T(\xi - X_T)) \right] + D_{s_1} \text{Sech}(B_{s_1}(\xi - X_{s_1})) + D_{s_2} \text{Sech}(B_{s_2}(\xi - X_{s_2})) \]  

(2-13)

This functional fit has slightly higher values than the tabular data, \( \xi < 2.8 \). Also, \( D_1 \) intentionally decreases more rapidly than the tabular function for \( \xi > 4.5 \) (Figure 2-2).

A second functional fit \( D_2(\xi) \) was developed by an undergraduate student: \(^{16}\)

\[ D_2(\xi) = D_0 + D_1 \xi + D_2 \xi^2 + \frac{D_3 + D_4 \xi}{\text{Exp}\left( U_1(U_2 - \xi)^2 \right)} \]  

(2-14)

\( D_2(\xi) \) is also a very good fit to the tabular data, and it peaks slightly higher than \( \xi=4.00 \). Figure 2-2 compares \( D_1, D_2 \) and tabular D functions.
Figure 2-2  Well depth as a function of the hybridization at the carbon (\( \xi \)). VCB tabular function (\( \bullet \)), D1 (broken line) and D2 (solid line).

Table 2-2. Constants to define functional fits \( D1(\xi) \) and \( D2(\xi) \). Units as indicated.

<table>
<thead>
<tr>
<th>( D1(\xi) )</th>
<th>( D2(\xi) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_0 ) 105.5 kcal</td>
<td>( \bar{U}_1 ) 1.11</td>
</tr>
<tr>
<td>( D_T ) 0.66 kcal</td>
<td>( U_2 ) 3.27</td>
</tr>
<tr>
<td>( D_{S1} ) 12.2 kcal</td>
<td>( \bar{D}_2 ) -3.2787 kcal</td>
</tr>
<tr>
<td>( D_{S2} ) 5.2 kcal</td>
<td>( D_3 ) -33.94 kcal</td>
</tr>
<tr>
<td>( \bar{D}_1 ) 3.35 kcal</td>
<td>( \bar{D}_4 ) 8.8994 kcal</td>
</tr>
<tr>
<td>( X_T ) 4.65 kcal</td>
<td>( X_{S1} ) 3.9</td>
</tr>
<tr>
<td>( X_{S2} ) 4.55 kcal</td>
<td></td>
</tr>
</tbody>
</table>
2. R(θ) Functional Fit

Fits to the R(θ) tabular function gave two functions, one that fits well at the low end of the data (small angles), and a second that fits the high end (large angles) well.

\[
R_{1_{low}}(\theta_{H,CH}) = \text{Tanh}((0.85\theta)^4)^* \left( d_1 + s_1\theta + s_2\theta^2 + \frac{d_2 + s_3\theta + s_4\theta^2}{e^{\theta}} \right) \\
R_{1_{high}}(\theta_{H,CH}) = \left[ 1 - \text{Tanh}((1.25\theta)^2) \right]^* \left( s_5\theta^2 + s_6\theta^3 + s_7\theta^4 \right)
\]  

(2-15) (2-16)

![Figure 2-3](image)

**Figure 2-3** Angular repulsion functions. VCB tabular function (●), R1\text{low} (dashed line), R1\text{high} (solid line).

We used a sum of both because angles important to the dynamics (near zero, around 90-120 and 180 deg) were fitted well in this way (see Figure 2-4).
\[ R_1(\theta_{H_iCH_j}) = U_L \cdot R_{1_{low}}(\theta) + U_H \cdot R_{1_{high}}(\theta) \]  \hspace{1cm} (2-17)

**Figure 2-4** Angular repulsion function. VCB tabular function (●), \( R_{1_{low}} + R_{1_{high}} \) (solid line).

**Table 2-3.** Constants to define functional fits \( R_{1_{low}} \) and \( R_{1_{high}} \). Units as indicated.

<table>
<thead>
<tr>
<th>( d_1 ) kcal</th>
<th>( d_2 ) kcal</th>
<th>( s_1 ) kcal/rad</th>
<th>( s_2 ) kcal/rad^2</th>
<th>( s_3 ) kcal/rad</th>
<th>( s_4 ) kcal/rad^2</th>
<th>( s_5 ) kcal/rad^3</th>
<th>( s_6 ) kcal/rad^3</th>
<th>( s_7 ) kcal/rad^4</th>
</tr>
</thead>
<tbody>
<tr>
<td>-45611.12</td>
<td>52810.16</td>
<td>15170.94</td>
<td>-1385.26</td>
<td>18463.20</td>
<td>16021.47</td>
<td>27.175</td>
<td>319.47</td>
<td>216.914</td>
</tr>
</tbody>
</table>

We also have fits of the same functional form as equation (2-13), but did not use them in the dynamics simulation.
3. Abstraction Term Modifications

The abstraction term $A$ was modified in several ways. All ten possible pairs of $H_a-H_b$ were considered. This makes all hydrogen atoms more nearly equivalent and makes the surface better suited to variational transition state theory calculations. The angular function was changed to a hyperbolic tangent function, for a better limit behavior.

$$F[ho(H_aCH_b)] = \frac{D_{H_2}}{2} \cdot \{1 - \tanh[p \cdot (Q_0 - \rho)]\}$$ (2-18)

The $T(r_{CHa})$ and $S(r_{CHa})$ functions were made to depend on all bond lengths, and a second secant hyperbolic function was added. These changes were included to have a more flexible function to position and shape the barrier to abstraction.

$$T1 = \frac{U_{T1}}{8} \left\{1 - \tanh[B_{T1}(r_{CHa} - C_{T1})]\right\} \left\{1 - \tanh[B_{T2}(r_{CHb} - C_{T2})]\right\}$$ (2-19)

$$S1 = U_{S1} \text{Sech}[B_{S1}(r_{CHa} - C_{S1})] \text{Sech}[B_{S2}(r_{CHb} - C_{S2})]$$ (2-20)

$$S2 = U_{S2} \text{Sech}[B_{S4}(r_{CHa} - C_{S4})] \text{Sech}[B_{S5}(r_{CHb} - C_{S5})]$$ (2-21)
A tangent hyperbolic switch was added to the repulsion term RH to avoid contributions from unrealistic H-H pairs (when H_b is one of the "unreacting" methyl hydrogens.)

\[
T2(r_{H_aH_b}) = \frac{1}{2} \left\{ 1 - \tanh \left( B_{T4} \ r_{H_aH_b} - U_{T2} \right) \right\}
\]  

(2-22)

The HRep term was replaced with an exponential fit, EAREp, based on \textit{ab initio} calculations (Gaussian 92 suite of programs),\textsuperscript{18} where an H_2 molecule was moved in close to a CH\textsubscript{3} radical (Figures 2-5 and 2-6). Single point calculations at the MP4 level of theory using the 6-311G** basis set were carried out. An H_2 molecule was moved toward one of the hydrogens in the methyl radical, keeping all atoms in the same plane and the H\textsubscript{2} molecule collinear with one of the C-H bonds in CH\textsubscript{3}.

\[
EAREp = D_{EA} \left\{ \sum_{i=a,b} \exp(-B_{EA} \ r_{H_iH_i}) + \sum_{j=a,b} \exp(-B_{EA} \ r_{H_bH_j}) \right\}
\]

(2-23)

![Diagram of system used to model the RH term](image-url)
Figure 2-6  Back hydrogen repulsion functions. EARep (solid line), RHrep in VCB (dashed line), PMP4 single point calculations with Gaussian-92 (▲).

Table 2-4. Constants to define EARep function. Units as indicated.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{EA}$</td>
<td>1314.59881</td>
<td>kcal</td>
</tr>
<tr>
<td>$B_{EA}$</td>
<td>4.17582</td>
<td>Å⁻¹</td>
</tr>
</tbody>
</table>
A beta version of Venus,\textsuperscript{17} a general dynamics program, was modified to include our potential description. Modifications to print extra output related to the CH\textsubscript{5} system were done, and the end condition tests had to be expanded to distinguish between abstraction and substitution events. This program can run a trajectory, perform a normal mode analysis and follow the minimum energy path. Although Venus has no graphical user interface, and its input is somewhat awkward, it has a good normal mode sampling routine.

An individual trajectory is started by selecting initial conditions. We used normal mode sampling of the vibrational motion, and the rotational motion was sampled from a classical distribution appropriate for 300 K. The classical equations of motion are solved by a combined fourth-order Runge-Kutta integrator and sixth-order Adams-Moulton predictor-corrector algorithm. Each potential term and its first derivative are calculated analytically. We necessarily included changes to Venus to use the potential forms discussed in Chapter 2.

Energy conservation was checked for each potential term coded in the program. Total energy changes of not more than 0.05 kCal were assumed to indicate energy conservation (for runs at about 35 to 65 kCal). Larger energy changes were taken as an
indication of a programing error, and the code was then checked for errors. The average energy change was 0.001 kCal or less. One test suggested by van Gunsteren and Mark\textsuperscript{20} is that the root mean square fluctuation of the total energy, $E_{\text{tot}} = E_{\text{kin}} + E_{\text{pot}}$, of the system should be small compared to the root mean square fluctuation of the kinetic energy $\Delta E_{\text{kin}}$ or potential energy $\Delta E_{\text{pot}}$. For one trajectory where tabular functions were used (VCB surface, see Chapter 4), $\Delta E_{\text{tot}} = 0.0304$ kCal and $\Delta E_{\text{pot}} = 6.714$ kCal, meaning that total energy was conserved.

The program was written in standard Fortran and compiled with the DEC-Fortran 90 compiler. The default math library was used instead of fast\_math, for better accuracy. Batches of 2,000 trajectories were run on a Dec-Alpha workstation with a minimal printout, so that statistics could be collected.

**Visualization of trajectories**

Trajectories that were thought to be interesting were re-run with a detailed printout of the coordinates at every 50 or 100 integration steps. Initially, a NeXT\textsuperscript{®} application ChemView was written to read-in the output from Venus. This program displayed atoms as meshed-spheres and it was difficult to track each hydrogen. The program did not include an option to stop the trajectory or to change the camera position between frames. Improvements were made and a surface was rendered on each sphere, but the execution
speed was lowered considerably.

Due to the problems described above, a new program was found (freeware on the Internet). Moviemol\textsuperscript{19} is a visualization program that runs on PC’s and SGI’s. It displays atoms as circles, and by selecting a different atom number for the attacking hydrogen, tracking of substitution was easy. A disadvantage was that graphic output was cartoon-like (circles and lines), and data had to be moved from a Unix workstation to a PC. A program was written to convert the Venus output to moviemol format.

A third program, also available as freeware, was used to visualize trajectories: Xmol\textsuperscript{21}. This program uses the standard xyz format, can read Gaussian input and output files, and runs on the X-windows system. The only disadvantage is that it produces postscript output for graphics, which makes it difficult to incorporate into word processing or presentation software. Xmol was used to check trajectories and decide which one should be used for figures or presentations.

The last program used for visualization was Review\textsuperscript{22}. It is a program that runs on MS-Windows. It permits the user to change the camera position or stop the animation at any frame. It allows generation of a series of files to create images of the animation, with an external 3D rendering program. Pov-Ray\textsuperscript{23} was used for ray tracing, which creates targa image files that can easily be imported into word processing or presentation software, or converted to other formats, including flic and mpeg movie formats.
CHAPTER 4

VCB Surface

We used Mathematica to make surface plots of symmetry constrained reactions of H + CD₄. For modeling abstraction, the H₄-H₆ and C-H₆ bond lengths were varied systematically and the energy was minimized with respect to the angle β (see Figure 2-1). A 3-D plot and a surface plot of the resultant potential energy surface was produced (Figures 4-1 and 4-2). In these plots the barrier formed a ridge along the H-H bond coordinate. The same procedure was used to create figures for the substitution via the Walden inversion mechanism (Figures 4-3 and 4-4).

Table 4-1

<table>
<thead>
<tr>
<th></th>
<th>35 kCal/mol</th>
<th>56 kCal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>VCB</td>
<td>Experimental¹</td>
</tr>
<tr>
<td>σₘₐₓ (Å²)</td>
<td>0.141 ± 0.014</td>
<td>0.14 ± 0.03</td>
</tr>
<tr>
<td>σₘᵦₑₑ (Å²)</td>
<td>0.034 ± 0.007</td>
<td>—</td>
</tr>
</tbody>
</table>

¹ Ref. 5
² Ref. 6
Figure 4-1  VCB 3D surface for collinear abstraction, generated with Mathematica where the energy was minimized with respect to the angle $\beta$ for each point.

Figure 4-2  VCB surface plot for collinear abstraction, generated with Mathematica where the energy was minimized with respect to the angle $\beta$ for each point.

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Figure 4-3  VCB 3D surface for inverting substitution, generated with Mathematica where the energy was minimized with respect to the angle $\beta$ for each point.

Figure 4-4  VCB surface for inverting substitution, generated with Mathematica where the energy was minimized with respect to the angle $\beta$ for each point.
The VCB surface was coded for Venus. Trajectories of \( \text{H} + \text{CD}_4 \) at two relative collisional energies of 35 and 56 \( \text{kCal/mol} \) were run. These two energies are the same as in Valentini’s and Bersohn’s experiments.\(^5,6\) Cross section to abstraction at the lower energy compares well to experimental values. Substitution at the higher energy gives a cross section almost three times larger than the experimental value (Table 4-1).

Abstraction events had an average initial angle \( \rho \) of 18.9 deg, with a range of 0 to 46 deg (Figure 4-5). We followed individual trajectories that had initial \( \rho \) angles of 2.1, 21.1 and 46.0 deg. In all of these trajectories, the value of \( \rho \) was between 10 and 15 deg at the position of closest approach, given by the value of the angle when the distance Ha-C is at its minimum in Figures 4-6 through 4-8. This indicates a bent arrangement for the dominant geometry at the closest approach (GCA). Appendix B contains movies of these trajectories.

![Figure 4-5](image-url)  
**Figure 4-5** Distribution of initial \( \rho \) angle in trajectories that gave abstraction, using VCB surface.
Figure 4-6  Trajectory for which abstraction occurred, initial angle $\rho=2.1$ deg.

Figure 4-7  Trajectory for which abstraction occurred, initial angle $\rho=21.1$ deg.
Substitution events show a distribution of initial angle $\rho$ with two averages, 64.6 and 156.5 deg, suggesting two mechanisms (Figure 4-9). Similar to abstraction, these trajectories show an angle that oscillates around 90 and 170 deg, respectively, near the transition states (Figures 4-10 and 4-11). The first set of trajectories substitute with retention of configuration, via a trigonal bipyramidal intermediate, where the attacking H is in the axial position, and the D leaving is in the equatorial position. The other mechanism is the Walden inversion, where the D leaving is in the axial position. Movies of these trajectories are shown in Appendix B.
Figure 4-9   Distribution of initial $\phi$ angle in trajectories that gave substitution, using VCB surface.

Figure 4-10   Trajectory for which substitution occurred, initial angle $\phi=69.0$ deg.
A trajectory study by Valentini\textsuperscript{24} with a modified VCB surface gave interesting results. For the D and R tabular functions and S(r) switch they substituted spline fits, moved the $M(r_{HH})$ outside the angular function in the A term and omitted the HRep term.

$$A_M = \sum_{a\neq b} \left\{ D_{H2} F(\rho_{H_aCH_b}) T(r_{CH_a}) + S(r_{CH_a}) \right\} + M(r_{HH}) \quad (4-1)$$

They compared two methods of selecting initial conditions: normal mode sampling and the adiabatic switch method (AS). The AS method starts with the reactants stationary and greatly separated using an approximate Hamiltonian, $H_0$, where the normal modes of vibration are separable. The modified reactive Hamiltonian, $H_1$, which is non-
separable and anharmonic, is turned on slowly. Valentini concluded that there was no
difference between normal mode or AS sampling methods (Table 4-2). They also ran
trajectories without zero point energy (ZPE), which gave an increase in the cross section to
abstraction.

We also ran trajectories without the Hrep terms and with the $M(r_{th})$ function
moved outside of the angular switch, $F(\rho_{HeCHa})$. When this calculation failed to agree with
their computation, we examined two additional VCB modifications. In one set, we
retained Hrep terms but moved the $M(r_{th})$ outside of the angular switch. The original
abstraction $A$ function was retained in the second, but the $R$ and $D$ tabular terms were
replaced with functional fits $R_{1high}$ and $D_2$ (equations 2-14 and 2-15). Not one of these
three calculations reproduced Valentini's cross sections. Cross sections in the variants
that we tried increased, but are still significantly smaller than theirs (Table 4-2). Initial
angle distributions for abstraction events are similar and wider compared to our runs of
the original VCB surface.

There are several complicating aspects of their work that make it difficult to locate
the source of the different predictions of these calculations. Firstly, the actual equation
for $H_0$ was not given. The application of spline fits to surface descriptions is known to be
fraught with problems.29 The details of when the relative translational motion was
introduced during the course of the transition from $H_0$ to $H_1$ were not specified. In
addition, the forces on the atoms were obtained by the difference in the values of the
potential rather than by coding derivatives. We will make our input data and derivative
Cross sections for substitution are increased significantly in the variants with the

tabular functions. For the set where functional fits replaced the tabular functions,

substitution was decreased by a factor of five compared to the original VCB surface

(Table 4-3). Valentini did not report cross sections for substitution in his study, so we can

not compare our results to theirs.

Table 4-2 Comparison of calculated cross sections ($\sigma_{ab, Å^2}$) to abstraction of D by H

in CD₄, in modified VCB surfaces at 35 kCal/mol of relative collisional energy.

<table>
<thead>
<tr>
<th></th>
<th>Normal Mode Sampling</th>
<th>Adiabatic Switch Sampling</th>
<th>Without ZPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>VCB</td>
<td>0.141 ± 0.014</td>
<td></td>
<td>0.141 ± 0.014¹</td>
</tr>
<tr>
<td>M-VCB²</td>
<td>1.29</td>
<td>1.43</td>
<td>2.03</td>
</tr>
<tr>
<td>M-VCB³</td>
<td>0.418 ± 0.034</td>
<td></td>
<td></td>
</tr>
<tr>
<td>mVCB⁴</td>
<td>0.460 ± 0.033</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R1D2-VCB</td>
<td>0.198 ± 0.022</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

¹ Collisional energy was increased by the value of the ZPE to keep the total energy the same
² Ref. 24
³ Morse term outside angular function, no HRep term, constants as in ref (24). 12,000 runs using Venus.
⁴ Morse term outside angular function, no other changes. 12,000 runs using Venus.
Table 4-3  Comparison of calculated cross section ($\sigma_{\text{subs}}$) to substitution of D by H in CD$_4$, and ratios of inversion to retention of configuration, in modified VCB surfaces at 35 kCal/mol of relative collisional energy and normal mode sampling of vibrational energy.

<table>
<thead>
<tr>
<th>Surface</th>
<th>$\sigma_{\text{subs}}$ (Å$^2$)</th>
<th>N inversion/ N retention</th>
</tr>
</thead>
<tbody>
<tr>
<td>VCB</td>
<td>0.034 ± 0.007</td>
<td>1.40</td>
</tr>
<tr>
<td>M-VCB$^1$</td>
<td>0.614 ± 0.042</td>
<td>1.82</td>
</tr>
<tr>
<td>mVCB$^2$</td>
<td>1.864 ± 0.066</td>
<td>1.38</td>
</tr>
<tr>
<td>R1D2-VCB</td>
<td>0.007 ± 0.004</td>
<td>0$^3$</td>
</tr>
</tbody>
</table>

$^1$ Morse term outside angular function and no HRep term, constants as in ref (24). 12,000 runs using Venus.

$^2$ Morse term outside angular function, no other changes. 12,000 runs using Venus.

$^3$ Only three events out of 12,000 runs, all retention of configuration.

All surfaces have similar initial angle distributions, showing both mechanisms. The surface R1D2-VCB gave only three substitutions with retention of configuration. One event had an initial angle of 27 deg. Even though the angle was small, it oscillated around 80 deg near the transition state (Figure 4-12). The incoming H is in the equatorial position and the leaving D is in the axial position, which leads to retention of configuration.

In the original VCB study, trajectories without ZPE were run because limited testing with extra energy in stretch motion affected the cross section in the same manner seen by adding translational energy, and it was computationally less expensive. In our runs, we see no change in the cross section for abstraction, both at the same total energy, with and without ZPE energy included (Table 4-4). Distributions of the initial angle $\rho$ are very similar, with and without ZPE, at both energies. The cross section to substitution...
more than triples at 35 KCal but it is the same at 56 Kcal (Table 4-4). This demonstrates
the sensitivity of reactive processes in the vicinity of a reaction threshold. The
distributions of the initial angle $\rho$ at both energies show the retention and inversion of
configuration mechanisms, but the Walden inversion is greatly enhanced in the absence
of ZPE (Table 4-5).

The preference of the Walden inversion mechanism in the absence of ZPE can be
explained by noting that the transition state is the same for both mechanisms. A trigonal
bipyramid (TBP) can decompose by loss of either an equatorial or an axial position.

Figure 4-12  Trajectory for which substitution occurred, initial angle $\rho=27.3$
deg with R1D2-VCB surface.

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Decomposition of a bond is promoted by stretching motion of that bond. In the TBP transition state, the axial bonds are extended and that always favors the inversion process. When ZPE is included, at the same total energy, the three equatorial ligands are much more likely to be vibrating and inversion is less likely.

Table 4-4  Cross section (\(\sigma\)) to reaction of H + CD\(_4\) in VCB surface with and without zero point energy (ZPE) at two relative collisional energies.

<table>
<thead>
<tr>
<th>Energy</th>
<th>35 kCal/mol</th>
<th>56 kCal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>With ZPE(^1)</td>
<td>No ZPE(^2)</td>
</tr>
<tr>
<td>(\sigma_{abs} (\text{Å}^2))</td>
<td>0.141 ± 0.014</td>
<td>0.141 ± 0.014</td>
</tr>
<tr>
<td>(\sigma_{subst} (\text{Å}^2))</td>
<td>0.034 ± 0.007</td>
<td>0.117 ± 0.013</td>
</tr>
</tbody>
</table>

\(^1\) ZPE was included in normal vibration mode motion.

\(^2\) ZPE was included in relative translational motion.

Table 4-5  Ratio of substitution events via Walden inversion mechanism to retention of configuration, with and without ZPE, at two relative collisional energies for the VCB surface.

<table>
<thead>
<tr>
<th>Energy</th>
<th>with ZPE</th>
<th>no ZPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>35 KCal</td>
<td>1.4</td>
<td>15.6*</td>
</tr>
<tr>
<td>56 KCal</td>
<td>1.21</td>
<td>2.64</td>
</tr>
</tbody>
</table>

* Cross section to reaction increased 3.4 times
CHAPTER 5

V5 SURFACE

We developed functional fits to D and R tables and modified the abstraction term A of VCB surface. The V5 surface for abstraction is constructed as follows:

\[ V5 = A + B + R \] (5-1)

\[ A = \sum_{\alpha=1}^{4} \sum_{\omega=0}^{1} \left\{ D_{H_\alpha} F[\rho] \left( M[r_{H_\alpha H_\omega}] + T1 + S1 + S2 \right) + T2[r_{H_\alpha H_\omega}] \right\} \text{HRep} \] (5-2)

Where the terms are defined by the equations:

- B \quad D1, equation 2-13
- R \quad R1, equation 2-17
- F[\rho] \quad equation 2-18
- M[r_{H_\alpha H_\omega}] \quad equation 2-5
- T1 \quad equation 2-19
- S1 \quad equation 2-20
- S2 \quad equation 2-21
- T2[r_{H_\alpha H_\omega}] \quad equation 2-22

All ten possible pairs were considered to make the hydrogens nearly equivalent. The HRep term was multiplied by a switch to avoid unrealistic contributions from pairs where both hydrogens were the non-reactive atoms. The constants for T1, S1, S2 and T2 are listed in Table 5-1.
Mathematica was used to make energy-minimized plots of V5 for collinear abstraction (Figures 5-1 and 5-2), in the same way as was done for the VCB surface. A transition state $TS_M$ for collinear abstraction was obtained from these plots.

The character of $TS_M$ was refined, without symmetry restrictions, by scanning the surface with Venus. A frequency analysis always gave eleven real frequencies, one big negative frequency, and a variable number of small negative frequencies (−300 cm$^{-1}$ or less). We animated a series of trajectories that started from the same TS, but with one quanta of energy in a different individual normal mode. This showed that the motion in modes with small imaginary frequencies amounted to rotational decomposition of the complex and probably arose from round off error.
Figure 5.1  3-D plot of back angle-minimized V5 surface for collinear abstraction (with Mathematica)

Figure 5.2  Surface plot of back-angle minimized V5 PES for collinear abstraction (with Mathematica)
We also performed *ab initio* calculations to find the transition state (TS) for collinear abstraction, T1. The TS was found at the MP2 level of theory with a 6-311G** basis set. The frequency analysis was done at the MP4 level of theory at the geometry obtained at the lower level.

The transition state of V5, T1-V5, compares well to our *ab initio* calculations and to others reported in the literature. The H-H and C-H bonds are both about 0.1 Å longer than *ab initio* geometries. The angle to the back hydrogens is still unrelaxed, 109 deg. versus 103 deg. Energetics compare well to *ab initio* and experimental data (Table 5-2).

The normal mode analysis of T1-V5 compares well to most *ab initio* data. The real frequencies differed by less than 300 cm\(^{-1}\). The critical imaginary frequency is about 100 cm\(^{-1}\) higher than calculated values (Table 5-3), with the exception of the POL-CI value, which is markedly lower than the other values. The other frequencies differ from each other also by about 100 cm\(^{-1}\).

**Table 5-2** Transition state geometry for collinear abstraction

<table>
<thead>
<tr>
<th>Model</th>
<th>(r_{C-H}) (Å)</th>
<th>(r_{H-H}) (Å)</th>
<th>(\beta) (deg)</th>
<th>Barrier (Kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V5</td>
<td>1.50</td>
<td>1.00</td>
<td>109.0</td>
<td>13.48</td>
</tr>
<tr>
<td>MP2(^1)</td>
<td>1.400</td>
<td>0.873</td>
<td>103.55</td>
<td>15.53(^5)</td>
</tr>
<tr>
<td>MP2(^2)</td>
<td>1.409</td>
<td>0.873</td>
<td>103.2</td>
<td>17.6</td>
</tr>
<tr>
<td>QCISD(^2)</td>
<td>1.390</td>
<td>0.899</td>
<td>103.7</td>
<td>16.3</td>
</tr>
<tr>
<td>PMP4(^3)</td>
<td>1.50</td>
<td>0.88</td>
<td>103.0</td>
<td>15.5</td>
</tr>
<tr>
<td>POL-CI(^4)</td>
<td>1.47</td>
<td>0.92</td>
<td>102.44</td>
<td>15.9 (extr. 13.5)</td>
</tr>
</tbody>
</table>

\(^1\) Ref. 14
\(^2\) Ref. 25
\(^3\) This work
\(^4\) Ref. 12
\(^5\) Using PMP4 SDTQ/6-311G**//UMP2/6-31G**
Table 5-3  Normal mode analysis of the transition state for collinear abstraction.
Harmonic frequencies in cm$^{-1}$

<table>
<thead>
<tr>
<th>Modes</th>
<th>V5</th>
<th>POL-Cl$^1$</th>
<th>MP2$^2$</th>
<th>QCISD$^2$</th>
<th>MP2$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a$_1$</td>
<td>1108</td>
<td>995</td>
<td>1093</td>
<td>1111</td>
<td>1044</td>
</tr>
<tr>
<td>a$_1$</td>
<td>2001</td>
<td>1960</td>
<td>1958</td>
<td>1764</td>
<td>1969</td>
</tr>
<tr>
<td>a$_1$</td>
<td>3015</td>
<td>3228</td>
<td>3125</td>
<td>3090</td>
<td>3133</td>
</tr>
<tr>
<td>e</td>
<td>701</td>
<td>592</td>
<td>544</td>
<td>534</td>
<td>589</td>
</tr>
<tr>
<td>e</td>
<td>1278</td>
<td>1146</td>
<td>1142</td>
<td>1152</td>
<td>1216</td>
</tr>
<tr>
<td>e</td>
<td>1547</td>
<td>1534</td>
<td>1463</td>
<td>1459</td>
<td>1459</td>
</tr>
<tr>
<td>e</td>
<td>3156</td>
<td>3404</td>
<td>3287</td>
<td>3236</td>
<td>3297</td>
</tr>
<tr>
<td>a$_1$</td>
<td>1632i</td>
<td>974i</td>
<td>1639i</td>
<td>1529i</td>
<td>1500i</td>
</tr>
</tbody>
</table>

$^1$ Ref. 12
$^2$ Ref. 25
$^3$ This work

Dynamics - Abstraction

We ran trajectories of H + CD$_4$ at 35 and 56 Kcal/mol of relative collisional energy and of H + CH$_3$D at the higher energy to compare with experimental data.

Cross section to abstraction are listed in Table 5-4. V5 cross section is about five times the experimental value at the lower energy. The initial angle $\rho$ distribution (Figure 5-3) is wide, with a range of 0 to 60 deg and a maximum of 20-25 deg, which is at a higher value than for the VCB surface (maximum of 18 deg). The distributions for trajectories with ZPE included and for trajectories without ZPE are very similar. The initial angle distribution at the higher energy is very similar to the corresponding VCB distribution.
Figure 5-3  Distribution of initial $\theta$ angle in trajectories that gave abstraction, using V5 surface.

Table 5-4  Cross section ($\text{Å}^2$) to abstraction of D by H in CD$_4$, at 35 Kcal/mol of relative collisional energy

<table>
<thead>
<tr>
<th>System</th>
<th>VCB</th>
<th>V5</th>
<th>CARS</th>
</tr>
</thead>
<tbody>
<tr>
<td>H + CD$_4$</td>
<td>0.141 ± 0.014</td>
<td>0.701 ± 0.045</td>
<td>0.14$^1$</td>
</tr>
<tr>
<td>H + C$_2$H$_6$</td>
<td></td>
<td></td>
<td>1.5$^2$</td>
</tr>
<tr>
<td>H + C$_3$H$_8$</td>
<td></td>
<td></td>
<td>2.9$^2$</td>
</tr>
</tbody>
</table>

$^1$ Ref. 5
$^2$ Ref. 26
We made movies several trajectories which had initial angles of about 2, 25 and 45 deg at the low energy. For all the trajectories followed, a non-collinear geometry at closest approach (GCA) was observed. The angle $\rho$ near the GCA oscillated around 10-15 deg, typical examples are shown in Figures 5-4 through 5-6.

**Figure 5-4** Variation of the angle $\text{H}_\text{a}$-$\text{C}$-$\text{H}_\text{b}$ and bondlengths in a trajectory for an abstraction event with initial angle $\rho$ 2.0 deg, in V5 surface.
Figure 5-5  Variation of the angle $H_a$-$C$-$H_b$ and bondlengths in a trajectory for an abstraction event with initial angle $\rho$ 28.6 deg, in V5 surface.

Figure 5-6  Variation of the angle $H_a$-$C$-$H_b$ and bondlengths in a trajectory for an abstraction event with initial angle $\rho$ 46.2 deg, in V5 surface.
At the higher energy, the GCA prefers an angle of about 20 deg. In a trajectory where the initial angle $\rho$ is 6.6 deg, the angle first increases to $\sim 25$ deg and then comes down to $\sim 18$ deg near the GCA (Figure 5-7). In a second trajectory, the angle $\rho$ starts at 24.7 deg, increases to $\sim 33$ deg and then goes down to $\sim 18$ deg at the GCA (Figure 5-8). In a trajectory with initial $\rho$ 41.4 deg, the angle oscillates between 5 and 35 deg through the region of strong interaction (Figure 5-9).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5_7}
\caption{Variation of the angle $\text{H}_2\text{C}-\text{H}_b$ and bondlengths in a trajectory for an abstraction event with initial angle $\rho$ 6.6 deg, in V5 surface. $\text{E}_{\text{rel}} = 56$ KCal/mol}
\end{figure}
Figure 5-8  Variation of the angle $H_a$-$C$-$H_b$ and bondlengths in a trajectory for an abstraction event with initial angle $\rho$ 24.7 deg, in V5 surface. $E_{rel} = 56$ KCal/mol

Figure 5-9  Variation of the angle $H_a$-$C$-$H_b$ and bondlengths in a trajectory for an abstraction event with initial angle $\rho$ 41.4 deg, in V5 surface. $E_{rel} = 56$ KCal/mol
This behavior (non-collinear geometry at closest approach for abstraction) prompted us to examine the possibility of a non-collinear transition state. Starting at the collinear TS geometry, Ha was moved up and down (towards one of the methyl H’s), but keeping the C-Ha distance unchanged. Table 5-5 compares the results with ab initio data. Although the symmetry is now different, the real frequencies compare just as well with \textit{ab initio} data. The frequency of the critical mode, however, has increased by 400 cm\textsuperscript{-1}.

![Figure 5-10](image)

\textbf{Figure 5-10} Labeling of angles for non-collinear abstraction. A negative $\rho$ angle is displayed.

\begin{table}[h]
\centering
\begin{tabular}{lcccc}
\hline
Model & $r_{C-Hb}$ (Å) & $r_{H_a-Hb}$ (Å) & $\rho$ (deg) & $\beta$ (deg) & Barrier (Kcal/mol) \\
\hline
V5 & 1.49 & 1.01 & -10 & 109.0 & 13.06 \\
MP2\textsuperscript{1} & 1.400 & 0.873 & 0 & 103.55 & 15.53\textsuperscript{4} \\
PMP4\textsuperscript{2} & 1.50 & 0.88 & 0 & 103.0 & 15.5 \\
POL-CI\textsuperscript{3} & 1.47 & 0.92 & 0 & 102.44 & 15.9 (extr. 13.5) \\
\hline
\end{tabular}
\caption{Actual transition state geometry for non-collinear abstraction compared with \textit{ab initio} collinear transition states.}
\end{table}

\textsuperscript{1} Ref. 14
\textsuperscript{2} This work
\textsuperscript{3} Ref. 12
\textsuperscript{4} Using PMP4 SDTQ/6-311G**//UMP2/6-31G**

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Table 5-6  Comparison of normal mode analysis of the transition state for non-collinear abstraction in V5 surface to *ab initio* collinear transition states. Harmonic frequencies in cm$^{-1}$

<table>
<thead>
<tr>
<th>Modes</th>
<th>V5</th>
<th>POL-CI</th>
<th>MP2$^1$</th>
<th>QCISD</th>
<th>MP2$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_1$</td>
<td>1073</td>
<td>995</td>
<td>1093</td>
<td>1111</td>
<td>1044</td>
</tr>
<tr>
<td>$a_1$</td>
<td>1605</td>
<td>1960</td>
<td>1958</td>
<td>1764</td>
<td>1969</td>
</tr>
<tr>
<td>$a_1$</td>
<td>3048</td>
<td>3228</td>
<td>3125</td>
<td>3090</td>
<td>3133</td>
</tr>
<tr>
<td>$e$</td>
<td>551</td>
<td>592</td>
<td>544</td>
<td>534</td>
<td>589</td>
</tr>
<tr>
<td>$e$</td>
<td>1251, 1307</td>
<td>1146</td>
<td>1142</td>
<td>1152</td>
<td>1216</td>
</tr>
<tr>
<td>$e$</td>
<td>1548, 1543</td>
<td>1534</td>
<td>1463</td>
<td>1459</td>
<td>1459</td>
</tr>
<tr>
<td>$e$</td>
<td>3179, 3174</td>
<td>3404</td>
<td>3287</td>
<td>3236</td>
<td>3297</td>
</tr>
<tr>
<td>$a_1$</td>
<td>2027i</td>
<td>974i</td>
<td>1639i</td>
<td>1529i</td>
<td>1500i</td>
</tr>
</tbody>
</table>

1  Ref 0 Thanh
2  This work

*Ab initio* calculations (single points at the PMP4/6-311G** level of theory) show that by moving away from a collinear transition state the energy increases immediately. The V5 surface behaves differently, the energy actually decreases slightly until $\rho$ is 10 degrees, and then it starts to increase'(Figure 5-11). This means the geometry indicated in Table 5-2 is not a true transition state. This lower energy for non-collinear abstraction (and an almost flat potential until 15 deg) explains why the cross section to abstraction is too high compared to the experimental value. Additionally, the minimum is located by moving the attacking hydrogen down, towards the two other hydrogens (Figure 5-12). While the actual barrier is lower by less than 0.5 kcal, its influence is significant because a collinear arrangement at closest approach has vanishing probability.
Figure 5-11 Comparison of Surface V5 with PMP4 single points *ab initio* calculations for non-collinear abstraction

Figure 5-12 Angle dependence of V5 for non-collinear abstraction
Dynamics - Substitution

Mathematica was used to make plots for the Walden inversion substitution reactive path in the same manner as before (Figures 5-13 and 5-14). Table 5-7 lists the geometry parameters of the transition state for substitution and compares it to \textit{ab initio} calculations (see also Figure 5-14).

Table 5-7 Transition state geometry for Walden inversion substitution

<table>
<thead>
<tr>
<th>Model</th>
<th>( r_{C-\text{Ha}} )</th>
<th>( r_{C-\text{Hb}} )</th>
<th>( r_{C-\text{H'}} )</th>
<th>Barrier (KCal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V5</td>
<td>1.50</td>
<td>1.50</td>
<td>1.08</td>
<td>40.6</td>
</tr>
<tr>
<td>POL-CI(^1)</td>
<td>1.414</td>
<td>1.414</td>
<td>1.077</td>
<td>34.5</td>
</tr>
<tr>
<td>MP2(^2)</td>
<td>1.34</td>
<td>1.34</td>
<td>1.088</td>
<td>39.25(^3)</td>
</tr>
</tbody>
</table>

\(^1\) Ref. 13
\(^2\) This work, MP2/6-311G**
\(^3\) PMP4/6-311G**//MP2/6-311G**

The transition state in V5 has longer C-H bondlengths than theoretical calculations, and the barrier to reaction is higher compared to the POL-CI calculation, but very close to the MP2 calculation. The frequency analysis is not in as good agreement to theoretical data. Three of the frequencies are about 1000 cm\(^{-1}\) too high. The imaginary frequency is 250 cm\(^{-1}\) higher than the MP2 value and 1000 cm\(^{-1}\) higher than the POL-CI calculation (Table 5-8).

Computed cross sections for substitution are summarized in Table 5-9 for collisions of H with CD\(_4\) and CH\(_3\)D. Both cross sections compare well with the experimental values. The isotope effect is well represented, the cross section for substitution of D in CH\(_3\)D is almost half of the substitution of D in CD\(_4\).
Figure 5-13  V5 3D surface for Walden inversion substitution, generated with Mathematica where the energy was minimized with respect to the angle \( \beta \) for each point.

Figure 5-14  V5 surface for Walden inversion substitution, generated with Mathematica where the energy was minimized with respect to the angle \( \beta \) for each point.
Table 5-8  Normal mode analysis of the transition state for \(D_{3h}\) substitution. Harmonic frequencies in cm\(^{-1}\).

<table>
<thead>
<tr>
<th>Modes</th>
<th>V5</th>
<th>POL-CI(^1)</th>
<th>MP2(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a_1)</td>
<td>1046</td>
<td>1130</td>
<td>1334</td>
</tr>
<tr>
<td>(a_1)</td>
<td>1667</td>
<td>1439</td>
<td>1681</td>
</tr>
<tr>
<td>(a_1)</td>
<td>3338</td>
<td>3218</td>
<td>3054</td>
</tr>
<tr>
<td>(e)</td>
<td>511</td>
<td>958</td>
<td>865</td>
</tr>
<tr>
<td>(e)</td>
<td>2114</td>
<td>1223</td>
<td>1371</td>
</tr>
<tr>
<td>(e)</td>
<td>2700</td>
<td>1451</td>
<td>1409</td>
</tr>
<tr>
<td>(e)</td>
<td>3455</td>
<td>3422</td>
<td>3254</td>
</tr>
<tr>
<td>(a_1)</td>
<td>2493i</td>
<td>1487i</td>
<td>2221i</td>
</tr>
</tbody>
</table>

\(^1\)  Ref. 13  
\(^2\)  This work, MP2/6-311G**  
\(^3\)  PMP4/6-311G**/MP2/6-311G**

Table 5-9  Cross section (Å\(^2\)) to substitution of D by H in CD\(_4\) and CH\(_3\)D at 56 KCal/mol of relative collisional energy.

<table>
<thead>
<tr>
<th>System</th>
<th>VCB</th>
<th>V5</th>
<th>LIF(^1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H + CD(_4)</td>
<td>0.222 ± 0.018</td>
<td>0.105 ± 0.017</td>
<td>0.084</td>
</tr>
<tr>
<td>H + CH(_3)D</td>
<td>0.067 ± 0.012</td>
<td>0.040</td>
<td></td>
</tr>
</tbody>
</table>

\(^1\)  Ref. 6

The initial angle \(\rho\) with CD\(_4\) has a different distribution (Figure 5-15) than the VCB surface, Figure 4-9. At the lower energy, much smaller angles are reactive on V5 than on VCB. Half of these events have impact parameters, \(b\), less than 0.9 Å\(^2\), and no initial angles above 90 deg produce substitution. The distribution ranges from 11 to 38 deg, for the normal mode sampling. For trajectories at the same total energy but without sampling vibrational motion, the distribution ranges from 23 to 47 deg.
Figure 5-15  Distribution of initial angle $\rho$ for substitution events in CD$_4$ on surface V5, with and without ZPE, at 35 KCal/mol relative collisional energy

At the high energy with CD$_4$, the distribution of the initial angle shows a peak at 30 deg, with a range of 10 to 70 deg. (Figure 5-16). Five events with angles about 160-170 deg followed the Walden inversion mechanism, ten events followed a trigonal bipyramidal intermediate, with angles ranging from 40 to 70 deg., and the rest (22 events) followed a different mechanism, as did all the trajectories at the lower energy.

The initial angle distribution of substitution of H or D in CH$_3$D (Figure 5-17) is similar to the CD$_4$ distribution. From this figure it is not completely clear how to assign the mechanism followed. Movies of all the trajectories at both energies were observed to decide what mechanism was followed. In the H + CH$_3$D trajectories, there were four events with substitution of D by H and 18 substitutions of H by H via Walden inversion,
two events of substitution of D by H and 10 events of H by H via a bipyramidal intermediate, and the rest of the trajectories (13 of D by H and 68 of H by H) followed the new mechanism (Figure 5-17).

![Graph](image-url)

**Figure 5-16** Distribution of initial angle \( \rho \) for substitution events in \( \text{CD}_4 \) on V5 surface at 56 KCal/mol of relative collisional energy

The third mechanism was called substitution via failed abstraction. In these events, the attacking H clearly initiates the abstraction process with the nearest deuterium. As the poorly aimed path brings the C-D-H group into a bent and extended GCA, H continues to move in and the \( a \) and \( b \) designations change. As the HD bond lengthens, the D leaves and H binds to the C. Figure 5-18 gives a graphical interpretation of this
mechanism. In these events, the initial angle $\rho$ is relatively small, about 30 deg, and the initial impact parameter, $b$, is greater than $0.8 \text{Å}^2$.

**Figure 5-17** Initial angle distribution for substitution of H/D by H in CH$_3$D, at a relative collisional energy of 56 kcal/mol.
Figure 5-18 Substitution by failed abstraction, V5 surface
Knowing that abstraction on surface V5 took place mainly through a non-collinear transition state, our efforts were directed to develop a new surface where abstraction would proceed via a collinear transition state. The abstraction term A was modified mainly by changing the constants and by replacing the HRep term with a functional fit to \textit{ab initio} data. The bonding term B was replaced with a different functional fit and the repulsion term R used only the fit that reproduced the high angles well.

\[ V6 = A + B + R \]  

\[ A = \sum_{a=b} \left\{ D_{H2} F[\rho] \left[ M[r_{Ha_Hb}] + T1 + S1 + S2 \right] + T2[r_{Ha_Hb}] \text{EARep} \right\} \]  

Where the terms are defined by the equations:

- B \quad \text{D2, equation 2-14}
- R \quad \text{R1, equation 2-15}
- F[\rho] \quad \text{equation 2-18}
- M[r_{Ha_Hb}] \quad \text{equation 2-5}
- T1 \quad \text{equation 2-19}
- S1 \quad \text{equation 2-20}
- S2 \quad \text{equation 2-21}
- T2[r_{Ha_Hb}] \quad \text{equation 2-22}
- \text{EARep} \quad \text{equation 2-23}
Changes in T1 were as to make Hₐ and H₅ nearly equivalent (constants are the same). The constants in T2(r_{HₐH₅}) were chosen so that when ρ=33 (or Hₐ-H₅-C is 90 degrees) the repulsion term is off for H₅ but it is on for Hₐ. The angular function of the term A favors abstraction within a cone. In the VCB surface, F(ρ) = 0.5 for ρ = 45 deg. In V5 we chose the same angle to be the midpoint. In this new surface, V6, we chose one fourth of the angle between two hydrogens in methane (109.47/4) as the midpoint of the cone. In this manner, an attacking Hₐ will not have an overlap of cones to decide which H in methane it can abstract.

<table>
<thead>
<tr>
<th>Table 6-1</th>
<th>Constants used in the abstraction term A of V6. Units as indicated.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>T1 function</strong></td>
<td></td>
</tr>
<tr>
<td>Uₜ₁ 2.5</td>
<td>Bₜ₁ 11.06 Å⁻¹</td>
</tr>
<tr>
<td></td>
<td>Bₜ₂ 11.06 Å⁻¹</td>
</tr>
<tr>
<td></td>
<td>Bₜ₃ 0.00 Å⁻¹</td>
</tr>
<tr>
<td><strong>S1 function</strong></td>
<td></td>
</tr>
<tr>
<td>Uₛ₁ 2.25</td>
<td>Bₛ₁ 0.494 Å⁻¹</td>
</tr>
<tr>
<td></td>
<td>Bₛ₂ 0.62 Å⁻¹</td>
</tr>
<tr>
<td></td>
<td>Bₛ₃ 0.88 Å⁻¹</td>
</tr>
<tr>
<td><strong>S2 function</strong></td>
<td></td>
</tr>
<tr>
<td>Uₛ₂ 0.15</td>
<td>Bₛ₄ 0.00 Å⁻¹</td>
</tr>
<tr>
<td></td>
<td>Bₛ₅ 1.50 Å⁻¹</td>
</tr>
<tr>
<td></td>
<td>Bₛ₆ 0.75 Å⁻¹</td>
</tr>
<tr>
<td><strong>T2 function</strong></td>
<td></td>
</tr>
<tr>
<td>Bₜ₄ 3.41 Å⁻¹</td>
<td>Uₜ₂ 4.71 Å</td>
</tr>
<tr>
<td><strong>F(ρ)</strong></td>
<td>p 10.0 rad⁻¹</td>
</tr>
</tbody>
</table>
Plots of collinear abstraction were produced in the same way as it was done with the other surfaces (Figures 6-1 and 6-2). A transition state was located from these plots and we used this geometry as a starting point to do a surface scan with Venus to locate the true transition state, T1 V6. The transition state reported refers to the TS found by using Venus. We report the geometry and the classical barrier to reaction for abstraction in Table 6-2. A frequency analysis was carried out at this geometry, which gave one negative frequency (~ 1800 cm$^{-1}$) that leads to abstraction of a hydrogen. As with the other surfaces, V6 also gave three small negative frequencies (~200 and ~60 cm$^{-1}$) that correspond to internal rotations of the complex (Table 6-3).

The transition state geometry compares well with \textit{ab initio} calculations. The bond between the carbon and the hydrogen being abstracted (H$_b$) agrees with the MP2$^{14}$ and PMP4$^{27}$ values and differs by 0.07 Å with the POL-CI$^{12}$ and by 0.10 Å with our own PMP4 calculations (Table 6-2). The H$_a$-H$_b$ distance is longer by 0.20 - 0.23 Å compared to all the calculations. The angle to the non-reactive hydrogens is still unrelaxed in our surface (by ~ 6 deg). The barrier height is lower than the calculated by MPX methods, but higher than the extrapolated value of the POL-CI calculation.$^{12}$

The frequency analysis compares relatively well (Table 6-3). The imaginary frequency is too high (by about 300 cm$^{-1}$). Four of the other frequencies agree well, either within the range of the reported \textit{ab initio} frequencies or less than 50 cm$^{-1}$ difference. Of the $e$ modes, one is ~ 100 cm$^{-1}$ and the other is ~200 cm$^{-1}$ higher, and one of the $al$ modes is ~400 cm$^{-1}$ lower.
Figure 6-1  3D plot of back angle-minimized V6 surface for collinear abstraction (with Mathematica)

Figure 6-2  Surface plot of angle-minimized V6 PES for collinear abstraction (with Mathematica)
Table 6-2  Transition state geometries for collinear abstraction

<table>
<thead>
<tr>
<th>Model</th>
<th>$r_{C-H}$ (Å)</th>
<th>$r_{H-H}$ (Å)</th>
<th>$\beta$ (deg)</th>
<th>Barrier (Kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V5</td>
<td>1.5</td>
<td>1.00</td>
<td>109.0</td>
<td>13.48</td>
</tr>
<tr>
<td>V6</td>
<td>1.40</td>
<td>1.12</td>
<td>108.9</td>
<td>14.8</td>
</tr>
<tr>
<td>MP2</td>
<td>1.400</td>
<td>0.873</td>
<td>103.55</td>
<td>15.53</td>
</tr>
<tr>
<td>PMP4</td>
<td>1.405</td>
<td>0.872</td>
<td>103.0</td>
<td>15.07</td>
</tr>
<tr>
<td>POL-CI</td>
<td>1.47</td>
<td>0.92</td>
<td>102.44</td>
<td>15.9 (extr. 13.5)</td>
</tr>
</tbody>
</table>

1 Ref. 14
2 Ref. 27
3 PMP4 (SDTQ)/6-311G**//UMP2/6-311G**, this work
4 Ref. 12

Table 6-3  Normal mode analysis of the transition state for collinear abstraction.
Harmonic frequencies in cm$^{-1}$

<table>
<thead>
<tr>
<th>Modes</th>
<th>V6</th>
<th>POL-CI</th>
<th>MP2</th>
<th>QCISD</th>
<th>MP2</th>
</tr>
</thead>
<tbody>
<tr>
<td>a1</td>
<td>1051</td>
<td>995</td>
<td>1093</td>
<td>1111</td>
<td>1044</td>
</tr>
<tr>
<td>a1</td>
<td>1513</td>
<td>1960</td>
<td>1958</td>
<td>1764</td>
<td>1969</td>
</tr>
<tr>
<td>a1</td>
<td>3173</td>
<td>3228</td>
<td>3125</td>
<td>3090</td>
<td>3133</td>
</tr>
<tr>
<td>e</td>
<td>788</td>
<td>592</td>
<td>544</td>
<td>534</td>
<td>589</td>
</tr>
<tr>
<td>e</td>
<td>1424</td>
<td>1146</td>
<td>1142</td>
<td>1152</td>
<td>1216</td>
</tr>
<tr>
<td>e</td>
<td>1550</td>
<td>1534</td>
<td>1463</td>
<td>1459</td>
<td>1459</td>
</tr>
<tr>
<td>e</td>
<td>3231</td>
<td>3404</td>
<td>3287</td>
<td>3236</td>
<td>3297</td>
</tr>
<tr>
<td>a1</td>
<td>1821i</td>
<td>974i</td>
<td>1639i</td>
<td>1529i</td>
<td>1500i</td>
</tr>
</tbody>
</table>

1 Ref. 12
2 Ref. 25
3 PMP4 (SDTQ)/6-311G**//UMP2/6-311G**, this work

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**Dynamics - Abstraction**

We ran trajectories of H + CD$_4$ at 35, 50 and 56 Kcal/mol of relative collisional energy and H + CH$_3$D at the higher energy to compare with experimental data. We also ran trajectories for D + CH$_4$ at 35 Kcal/mol and T + CH$_4$ at 65 Kcal/mol of relative collisional energy.

Cross sections to abstraction are listed in Table 6-4. With the changes introduced in the definition of V6, its $\sigma_{\text{ab}}$ agrees very well with the measured value. The initial angle $\rho$ is wide, with a range of 0 to 55 deg and a maximum of 30 deg, which is higher when compared to VCB and V5 (Figure 6-3). With increasing of relative collisional energy, the distribution gets a little wider. Another difference is that when a simulation without zero point energy (but added to the relative collisional energy), neither abstraction nor substitution reactive events were recorded out of 8,000 trajectories.

**Table 6-4** Cross section (Å$^2$) to abstraction of D by H in CD$_4$, at 35 Kcal/mol of relative collisional energy

<table>
<thead>
<tr>
<th>System</th>
<th>VCB</th>
<th>V5</th>
<th>V6</th>
<th>CARS</th>
</tr>
</thead>
<tbody>
<tr>
<td>H + CD$_4$</td>
<td>0.141 ± 0.014</td>
<td>0.701 ± 0.045</td>
<td>0.151 ± 0.015</td>
<td>0.14$^1$</td>
</tr>
<tr>
<td>H + C$_2$H$_6$</td>
<td></td>
<td></td>
<td></td>
<td>1.5$^2$</td>
</tr>
<tr>
<td>H + C$_3$H$_8$</td>
<td></td>
<td></td>
<td></td>
<td>2.9$^2$</td>
</tr>
</tbody>
</table>

$^1$ Ref. 12  
$^2$ Ref. 25

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Figure 6-3 Distribution of initial $\rho$ angle in trajectories that gave abstraction at three different collisional energies, using V6 surface.

We made movies of trajectories ($E_{rel} = 35$ Kcal) with initial angles of 2.7, 9.5, 16.5, 33.5, and 52.9 degrees. These angles were chosen as to be representative of the initial angle $\rho$ distribution. In the first trajectory (Figure 6-4), the angle $\rho$ starts at 2.7 deg, increases to about 11 deg and then decreases to about 3 deg in the GCA. In the second trajectory, the initial angle is 9.5 deg, then it oscillates and at the GCA state $\rho$ is 4.4 deg (Figure 6-5). The third trajectory behaves similarly: the angle starts at 16.5 deg, it oscillates and then comes down to about 6 deg in the GCA (Figure 6-6). This behavior is in contrast to trajectories in the V5 surface, where the angle $\rho$ at the GCA was around 15 deg.
Figure 6-4  Variation of the angle $H_2$-C-H$_b$ and bond lengths in a trajectory for an abstraction event with initial angle $\phi$ 2.7 deg, in V6 surface.

Figure 6-5  Variation of the angle $H_2$-C-H$_b$ and bond lengths in a trajectory for an abstraction event with initial angle $\phi$ 9.5 deg, in V6 surface.
A trajectory with an initial angle $\rho$ 33.5 deg also behave similarly to the others. In this case, the angle just decreased to about 5 deg in the GCA, and then increased and oscillated around 10 deg (Figure 6-7). This trajectory shows vibrational excitation of the HD product, by the oscillating bond lengths (both C-H).

For the trajectory with an initial angle of 52.9 deg, the angle $\rho$ decreases to 1.5 deg at the GCA and then it oscillates around 10 deg (Figure 6-8). This trajectory demonstrated that even with an initial angle that is large ($\sim$ 50 deg), the GCA preferred is almost collinear ($\rho$ oscillates around 5 deg). The preferred collinear TS in V6 surface, as opposed to non-collinear TS in V5 surface, accounts for the reduction in the cross section to reaction when both surfaces are compared.
Figure 6-7  Variation of the angle $H_1\text{-}C\text{-}H_2$ and bondlengths in a trajectory for an abstraction event with initial angle $\rho$ 33.5 deg, in V6 surface.

Figure 6-8  Variation of the angle $H_1\text{-}C\text{-}H_2$ and bondlengths in a trajectory for an abstraction event with initial angle $\rho$ 52.9 deg, in V6 surface.
At the higher energies, a preference of a collinear GCA is also observed. Figures 6-9 and 6-10 show the evolution of the angle $\rho$ and the bondlengths in trajectories with 50 Kcal/mol and 56 Kcal/mol of relative collisional energy, respectively. In both cases, $\rho$ at the transition state is around 5 degrees.

Figure 6-9  Variation of the angle $H_a\text{-}C\text{-}H_b$ and bondlengths in a trajectory for an abstraction event with initial angle $\rho$ 25.46, in V6 surface. $E_{\text{rel}} = 50$ KCal/mol
Valentini measured the quantum state population distribution of the HD \((v', J')\) product. In our analysis, we partitioned the vibrational energy into bins and approximated the rotational quantum number (Equation 6-3) and obtained a vibration-rotation distribution.

\[
J^2 \approx \frac{2J J_{rot} E_{rot}}{\hbar^2}
\]  

\text{(6-3)}
The V6 distribution for \( v' = 0 \) compares qualitatively well with the experimental one, after the latter was scaled to fit in the same graph (Figure 6-11). The population of \( J' = 1 \) and 2 in V6 are lower than the experimental values, and the deep in \( J' = 5 \) may be due to not enough events (more trajectories are needed). For \( v' = 1 \) the distribution in V6 does not follow the trend in the experiment (Figure 6-12). In V6 it peaks at \( J' = 2, 3 \), while in the experiment it peaks at \( J' = 5 \), with measurable population for higher rotational states.

**Figure 6-11** Quantum state population distribution of the HD\((v' = 0, J')\) product of the abstraction of D by H in CD\(_4\) at 35 Kcal/mol relative collisional energy. The experimental values were scaled to fit the plot.
Dynamics - Substitution

Mathematica was used to make plots for the substitution reactive path in the same manner as for the other surfaces (Figures 6-11 and 6-12). Again, using the transition state obtained with Mathematica, Venus was used to scan the potential energy surface and determined the true transition state. The geometry of the transition state is listed in Table 6-5.

Figure 6-12  Quantum state population distribution of the HD(v'=1,J') product of the abstraction of D by H in CD₄ at 35 Kcal/mol relative collisional energy. The experimental values were scaled to fit the plot.
Figure 6-13  V6 3D surface for Walden inversion substitution, generated with Mathematica, where the energy was minimized with respect to the angle β for each point.

Figure 6-14  V6 surface for Walden inversion substitution, generated with Mathematica, where the energy was minimized with respect to the angle β for each point.
Table 6-5  Transition state geometry for substitution

<table>
<thead>
<tr>
<th>Model</th>
<th>$r_{\text{C-Ha}}$</th>
<th>$r_{\text{C-Hb}}$</th>
<th>$r_{\text{C-H'}}$</th>
<th>Barrier (KCal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V5</td>
<td>1.50</td>
<td>1.50</td>
<td>1.08</td>
<td>40.6</td>
</tr>
<tr>
<td>V6</td>
<td>1.556</td>
<td>1.556</td>
<td>1.093</td>
<td>27.30</td>
</tr>
<tr>
<td>MP2$^1$</td>
<td>1.34</td>
<td>1.34</td>
<td>1.088</td>
<td>39.25$^2$</td>
</tr>
<tr>
<td>PMP4$^3$</td>
<td>1.33</td>
<td>1.33</td>
<td>1.08</td>
<td>38.97</td>
</tr>
<tr>
<td>POL-CI$^4$</td>
<td>1.414</td>
<td>1.414</td>
<td>1.077</td>
<td>34.5</td>
</tr>
</tbody>
</table>

$^1$ This work, MP2/6-311G**
$^2$ PMP4/6-311G*/MP2/6-311G**
$^3$ Ref. 27
$^4$ Ref. 13

The transition state in V6 has even longer bondlengths than V5 and all the theoretical calculations. The barrier to reaction is 7 Kcal lower than the POL-CI calculation, and 12 Kcal lower than the other methods.

The frequency analysis does not agree very well with theoretical calculations. The imaginary frequency is $\sim 40$ cm$^{-1}$ higher than the POL-CI calculation, but both differ from the MP2 calculation by $\sim 700$ cm$^{-1}$. One of the $e$ modes agrees with the POL-CI value but is $\sim 200$ cm$^{-1}$ higher than the MP2. Two modes are off by about 1500 cm$^{-1}$, other two by about 100-200 cm$^{-1}$. The lowest frequency also differs by $\sim 400$ cm$^{-1}$.

Cross sections to reaction are listed in Table 6-7. For substitution of D in CD$_4$, the cross section is slightly higher, but inclusion of error bars makes the $\sigma$'s overlap. When considering H + CH$_3$D, our cross section is in better agreement with experiment, and again, they overlap when the error bars are included.
Table 6-6 Normal mode analysis of the transition state for collinear substitution. Harmonic frequencies in cm\(^{-1}\).

<table>
<thead>
<tr>
<th>Modes</th>
<th>V6</th>
<th>POL-CI(^1)</th>
<th>MP2(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a(_t)</td>
<td>1246</td>
<td>1130</td>
<td>1334</td>
</tr>
<tr>
<td>a(_t)</td>
<td>2953</td>
<td>1439</td>
<td>1681</td>
</tr>
<tr>
<td>a(_i)</td>
<td>2956</td>
<td>3218</td>
<td>3054</td>
</tr>
<tr>
<td>e</td>
<td>419</td>
<td>958</td>
<td>865</td>
</tr>
<tr>
<td>e</td>
<td>1806</td>
<td>1223</td>
<td>1371</td>
</tr>
<tr>
<td>e</td>
<td>2936</td>
<td>1451</td>
<td>1409</td>
</tr>
<tr>
<td>e</td>
<td>3064</td>
<td>3422</td>
<td>3254</td>
</tr>
<tr>
<td>a(_i)</td>
<td>1520</td>
<td>1487i</td>
<td>2221i</td>
</tr>
</tbody>
</table>

\(^1\) Ref. 13

\(^2\) This work, MP2/6-311G**

Table 6-7 Cross section (Å\(^2\)) to substitution of D by H in CD\(_4\) and CH\(_3\)D at 56 Kcal/mol of relative collisional energy.

<table>
<thead>
<tr>
<th>System</th>
<th>VCB</th>
<th>V5</th>
<th>V6</th>
<th>LIF(^1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H + CD(_4)</td>
<td>0.222 ± 0.018</td>
<td>0.105 ± 0.017</td>
<td>0.099 ± 0.013</td>
<td>0.084 ± 0.014</td>
</tr>
<tr>
<td>H + CH(_3)D</td>
<td>0.067 ± 0.012</td>
<td>0.035 ± 0.007</td>
<td>0.040 ± 0.015</td>
<td></td>
</tr>
</tbody>
</table>

\(^1\) Ref. 6

The initial angle \(\rho\) distribution in V6 is similar to the distribution of V5 surface, which was not expected (Figure 6-15). We expected that the events that substituted through failed abstraction will not develop in this new surface. The majority of the events (84.0%) have small initial angle \(\rho\), less than 60 deg. There are also events that follow substitution with retention of configuration through a bipyramidal intermediate.
(8.9 %) and events with inversion of configuration, via the Walden inversion mechanism (7.1 %). As before, the initial angle is one indication of the mechanism followed, and together with the initial and final impact parameters a decision was taken as to what mechanism was followed.

![Figure 6-15](image)

**Figure 6-15** Initial angle $\rho$ distribution for substitution of a D by H in CD$_4$, at a relative collisional energy of 56 KCal/mol.

We prepared movies of the events that follow this third mechanism. Figure 6-16 shows the evolution of the bondlengths and angle $\rho$ for a trajectory with initial $\rho$ 15.7 deg. Figure 6-17 shows the same information for a trajectory with initial $\rho$ 27.7 deg. In both trajectories, the angle $\rho$ at the transition state is around 30-40 degrees. This mechanism corresponds to front side substitution.
Figure 6-16 Variation of the angle $H_a$-$C$-$H_b$ and bondlengths in a trajectory for a substitution event with initial angle $\theta$ 10.7 deg, in V6 surface. $E_{rel} = 56$ KCal/mol

Figure 6-17 Variation of the angle $H_a$-$C$-$H_b$ and bondlengths in a trajectory for a substitution event with initial angle $\theta$ 27.7 deg, in V6 surface. $E_{rel} = 56$ KCal/mol
The mechanism for front side substitution does not involve a trigonal bipyramidal intermediate like the Walden inversion or retention mechanisms. In this mechanism, the incoming hydrogen is almost aimed at the carbon. The transition state is formed when the attacking hydrogen is sideways with one deuterium, substituting by simply "pushing" it out of the CD₄ molecule. Figure 6-18 illustrates this mechanism.

Figure 6-18  Front side substitution mechanism. (a) Attacking hydrogen aims at the carbon. (b) Attacking hydrogen forms a transition state, where the H and the deuterium are sideways. (c) Attacking H bonds to the carbon and the deuterium leaves.

Predictions

As specified earlier, trajectories of D + CH₄ and T + CH₄ were run. Table 6-8 lists the cross sections to reaction for the first reaction at 35 Kcal/mol and for the second reaction at 65 Kcal/mol. In principle, the experiment of D + CH₄ is possible by CARS, but has not been done. The cross section to substitution in T + CH₄ agrees well with the values reported by Raff, but for abstraction our cross section is about half. Since our cross section to abstraction in the H + CD₄ system is very good, and a decrease in o(abs)
is expected with an increase in energy, we believe the predicted value using V6 is more realistic.

Table 6-8 Cross section to reaction (Å²) for D + CH₄ and T + CH₄ at two relative collisional energies in V6 surface.

<table>
<thead>
<tr>
<th>System</th>
<th>E_{rel} (Kcal/mol)</th>
<th>Abstraction of D</th>
<th>Substitution of D</th>
</tr>
</thead>
<tbody>
<tr>
<td>D + CH₄</td>
<td>35</td>
<td>0.313 ± 0.027</td>
<td>0.344 ± 0.028</td>
</tr>
<tr>
<td>T + CH₄</td>
<td>65</td>
<td>0.445 ± 0.025</td>
<td>1.073 ± 0.039</td>
</tr>
<tr>
<td>T + CH₄₁</td>
<td>65</td>
<td>0.95</td>
<td>1.1</td>
</tr>
</tbody>
</table>

¹ Ref. 28
Chapter 7

Ab Initio Calculations

Since substitution in surface V6 was mainly by front side substitution, we did calculations at the MP2 level of theory, using 6-311G** basis set, to find a transition state where the attacking hydrogen was sideways. To avoid falling back to the collinear abstraction transition state, a restricted geometry was used. The angle $H_a-H_b-C$ and the dihedral $H_a-H_b-C-H'$ were held constant at 90 deg. The $C-H_b$ and $H_a-H_b$ bond distances were allowed to change, together with the $C-H'$ bondlengths. With these restrictions, a transition state was found (TS3, Figure 7-1). A frequency analysis gives one negative frequency (Table 7-1), which leads to abstraction of $H_b$. 

Figure 7-1  Transition state 3 (TS3)
Table 7-1  Geometry of the transition state 3 (TS3). Bondlengths in Å and angles in degrees.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_{C-H_b}$</td>
<td>1.447</td>
</tr>
<tr>
<td>$r_{H_a-H_b}$</td>
<td>0.970</td>
</tr>
<tr>
<td>$r_{C-H'}$</td>
<td>1.086</td>
</tr>
<tr>
<td>Angle $\beta$</td>
<td>105.69</td>
</tr>
<tr>
<td>Frequency $v_{TS3}$ (cm$^{-1}$)</td>
<td>2548i</td>
</tr>
<tr>
<td>Potential Energy (Kcal/mol)</td>
<td>42.55$^1$</td>
</tr>
</tbody>
</table>

$^1$ PMP4//MP2 geometry

Another transition state was found by letting $H_a$ and $H_b$ “slide” along a line parallel to the $H_a-H_b$ bond, and keeping the same constraints as before. The frequency analysis shows one negative frequency which leads to hydrogen exchange. The geometry parameters are listed in Table 7-2.

Figure 7-2  Transition state 4 (TS4)
Table 7-2  Geometry of the transition state 4 (TS4). Bondlengths in Å and angles in degrees.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>r C- bond (Ha-Hb)</td>
<td>0.978</td>
</tr>
<tr>
<td>r H_i-H_b</td>
<td>1.565</td>
</tr>
<tr>
<td>r C-H'</td>
<td>1.119</td>
</tr>
<tr>
<td>Angle β</td>
<td>116.75</td>
</tr>
<tr>
<td>Frequency v_{TS4} (cm$^{-1}$)</td>
<td>2709i</td>
</tr>
<tr>
<td>Potential Energy (Kcal/mol)</td>
<td>56.62$^1$</td>
</tr>
</tbody>
</table>

$^1$ PMP4//MP2 geometry

These two new transition states allow for non-collinear abstraction and for front-side substitution, even though the energies are ~ 30 Kcal and ~ 15 Kcal higher, respectively, than the more favorable transition states.
CHAPTER 8

Conclusions

Based on the VCB surface, a new potential energy surface was developed to describe the abstraction and exchange reactions of H + CH₄. Changes were incorporated to improve the description of the abstraction channel, but the substitution channel was affected too. Microscopic mechanisms were identified and two new transition states were found by ab initio calculations, through restricted geometries.

We ran trajectories of the original VCB surface, with and without zero point energy included. Both results are identical and reproduce the experimental cross section to abstraction. Valentini and coworkers²⁴ reported calculations on a modified VCB surface, which we were not able to reproduce. In our runs of the modified VCB surface, as outlined by Valentini, we observed an increase in the cross section to abstraction. A benefit of Valentini's study is that there is no statistical difference between normal mode sampling and the adiabatic switch method of selecting initial conditions.

We improved the VCB description of the potential energy surface by allowing all hydrogens to abstract each other, as to make all hydrogen more equivalent. Functional fits replaced the tabular functions in VCB. Terms with limit problems were replaced by functions that have no discontinuities in the first derivatives. The angular terms were approximated by a series expansion in the limit of β → 0 and π. A switch function was added to avoid contributions of unrealistic pairs in the back hydrogen repulsions.
The V5 surface gave cross section to abstraction that were five times too big compared to measured values. This is due to a preferred non-collinear transition state. Cross section to substitution agree very well with experimental values, for H + CD₄ and for H + CH₃D. Three mechanisms were identified: substitution with inversion of configuration via Walden inversion, substitution with retention of configuration via a trigonal bipyramidal intermediate, and substitution by failed abstraction (SFA). This mechanism (SFA) arises from the non-collinear transition state for abstraction, in which the incoming H tries to abstract, but the HD product rotates and the H binds to the carbon and the deuterium leaves.

Improvements to V5 resulted in the V6 surface. In V6, the abstraction term was modified so the contributions from the r_{C-Ha} and r_{C-Hb} were the same if the identities of Hₐ and Hₐ were to be interchanged. The back-hydrogen repulsion function was replaced by an exponential fit to \textit{ab initio} data, and the D and R functional fits were changed.

Cross section to abstraction on surface V6 agree very well with experimental values. The abstraction mechanism prefers a collinear transition state, as observed from movies of the reactive events and by plots of the potential energy versus the angle of attack. Analysis of the quantum states of the HD product agree qualitatively for the v'=0 state, but differ for the v'=1 state. Vibrational states with v'=2 and v'=3 were also observed.

Cross sections to substitution fall within the error bars of the experimental data. The initial angle distribution shows two distinct regions: angles around 30-40 degrees and angles around 170 degrees. Movies of the reactive trajectories show three mechanisms,
as the V5 surface did. Substitution by Walden inversion and substitution with retention of configuration via a trigonal bipyramidal intermediate were observed. The majority of the substitution events followed a third mechanism: front-side substitution.

The front-side mechanism suggested that another transition state has to be identified. Ab initio calculation at the MP2/6-311G** level of theory were carried out on geometry restricted configurations. Two new transition states were found: TS3, which leads to abstraction, and TS4, which leads to substitution. Both can be described as an “L” and a “sideways” transition states.

**Further Work**

Not so good agreement in the frequency analysis, especially for substitution, suggests that refinements in the functional fits of the bonding and/or angular repulsion terms are needed. In the bonding term, the $D(\xi)$ function is multiplied by an inverse Morse function. $D(\xi=3)$ should be higher than $D(\xi=5)$ because CH$_3$ is a stable radical and a carbon with five ligands is thought to be a transition state. In the $D(\xi)$ functions used, the opposite is true.

The hybridization at the carbon in the trigonal bipyramidal transition state is about 4.5. When an attacking H starts to interact with the CH$_4$ molecule, one of the H bonds should start to break, keeping the hybridization almost constant, since the mechanism requires that one hydrogen comes in and the hydrogen on the opposite side starts to leave. This can be accounted for by changing the switch function to calculate the total hybridization at the carbon.
The barrier to substitution is too low in V6 compared to ab initio calculations which can be increased by modifying the bonding and/or angular repulsion terms also. The switches used in the angular repulsion term and to calculate the total hybridization at the carbon can also be modified to either increase the barrier height to substitution or to move inside the transition state to substitution.
REFERENCES


16. D. L. Thomlinson, now a medical doctor


19. *Moviemol* for PC MS-DOS Ver. 1.1 by K. Hermansson and L. Ojamae


APPENDIX A

Mathematica Notebooks
VCB: DTab.RTab.So
Abstraction

■ General Functions

\[
\text{rmeH}[y_, b_] := \sqrt{y^2 + \text{rch}^2 - 2 \cdot y \cdot \text{rch} \cdot \cos[b]}
\]

\[
\text{Ang34}[b_] := \arccos[1.0 - 1.5 \cos[b - \pi / 2]]
\]

\[
\text{R1}[x_, y_, \text{gama}_] := \sqrt{(x \cdot \cos[\text{gama}] + y)^2 + (x \cdot \sin[\text{gama}])^2}
\]

\[
\text{R13}[x_, y_, b_, \text{gama}_] := \sqrt{(\text{R1}[x, y, \text{gama}]^2 + \text{rch}^2 - 2 \cdot \text{R1}[x, y, \text{gama}] \cdot \text{rch} \cdot \cos[b - \rhoo[x, y, \text{gama}]])}
\]

\[
\text{R14}[x_, y_, b_, \text{gama}_] := \sqrt{(\text{R1}[x, y, \text{gama}]^2 + \text{rch}^2 - 2 \cdot \text{R1}[x, y, \text{gama}] \cdot \text{rch} \cdot \cos[b + \rhoo[x, y, \text{gama}]])}
\]

\[
\rhoo[x_, y_, \text{gama}_] := \arctan\left(\frac{x \cdot \sin[\text{gama}]}{x \cdot \cos[\text{gama}] + y}\right)
\]

■ D Hybridization Term

\[
\text{mch}[y_] := \exp[\text{chb} \cdot (\text{recH} - y)] \cdot (-2.0 + \exp[\text{chb} \cdot (\text{recH} - y)])
\]

\[
\text{recH} := 1.09
\]

\[
\text{chb} := 1.83
\]

\[
\text{s}[x_] := \exp[\text{chb} \cdot (\text{recH} - x)] \cdot (2.0 - \exp[\text{chb} \cdot (\text{recH} - x)]) /; x > \text{recH}
\]

\[
\text{s}[x_] := 1.0 /; x \leq \text{recH}
\]

\[
\text{bonds}[x_, y_, \text{gama}_] := 3 \cdot \text{s}[\text{rch}] + \text{s}[y] + \text{s}[\text{R1}[x, y, \text{gama}]]
\]
\]
\[ dtD[x_\_, y_\_, gama_\_] := sD[\text{Floor}[1 + (\text{bonds}[x, y, gama] - 2.0)/.05]] + \\
\quad (sD[\text{Floor}[2 + (\text{bonds}[x, y, gama] - 2.0)/.05]]) - \\
\quad sD[\text{Floor}[1 + (\text{bonds}[x, y, gama] - 2.0)/.05]]) (\text{bonds}[x, y, gama] - 2.0 - \\
\quad .05 \text{Floor}[(\text{bonds}[x, y, gama] - 2.0)/.05])/.05 \\
\]
\[ DFit[x_\_, y_\_, gama_\_] := \\
\quad dtD[x, y, gama] (3.0 \text{mch}[rch] + \text{mch}[y] + \text{mch}[R1[x, y, gama]]) \]
\[ sR_s = \{ 0.000, 0.013, 0.055, 0.134, 0.256, \\
0.435, 0.687, 1.029, 1.476, 2.039, \\
2.729, 3.558, 4.5448, 5.708, 7.06, \\
8.609, 10.390, 12.543, 15.375, 19.36, \\
24.998, 32.554, 41.817, 52.059, 62.287, \\
71.658, 79.770, 86.670, 92.631, 97.922, \\
102.707, 107.066, 111.058, 114.742, 118.166, \\
121.356, 124.325, 127.079, 129.604, 131.871, \\
133.841, 135.495, 136.833, 137.876, 138.657, \\
139.221, 139.609, 139.852, 139.9678, 139.967, \\
139.853, 139.619, 139.260, 138.773, 138.135, \\
137.291, 136.157, 134.659, 132.776, 130.553, \\
128.006, 125.384, 122.531, 119.514, 116.296, \\
112.820, 109.033, 104.928, 100.557, 96.018, \\
92.075, 86.869, 82.438, 78.159, 74.029, \\
70.028, 66.146, 62.388, 58.767, 56.296, \\
51.982, 48.825, 45.814, 42.941, 40.107, \\
37.621, 35.197, 32.937, 30.810, 28.794, \\
19.021, 17.798, 16.683, 15.667, 14.738, \\
10.833, 10.424, 10.031, 9.644, 9.271, \\
8.923, 8.602, 8.303, 8.014, 7.73, \\
7.449, 7.172, 6.899, 6.631, 6.371, \\
6.116, 5.866, 5.621, 5.382, 5.148, \\
4.919, 4.695, 4.474, 4.257, 4.045, \\
3.837, 3.634, 3.437, 3.244, 3.057, \\
2.874, 2.696, 2.523, 2.356, 2.197, \\
2.043, 1.898, 1.764, 1.642, 1.53, \\
1.429, 1.337, 1.252, 1.171, 1.095, \\
1.023, 0.955, 0.892, 0.832, 0.775, \\
0.719, 0.665, 0.615, 0.569, 0.53, \\
0.497, 0.467, 0.438, 0.410, 0.380, \\
0.350, 0.320, 0.290, 0.260, 0.230, \\
0.199, 0.167, 0.141, 0.110, 0.090, \\
0.070, 0.050, 0.030, 0.010, 0.0, \\
0.0\};\]
sR1[b_] := sRs[[Floor[b 180. / Pi]]] + (sRs[[1 + Floor[b 180. / Pi]]] - sRs[[Floor[b 180. / Pi]]]) (-Floor[b 180. / Pi] + b 180. / Pi)

RFit[x_, y_, b_, gama_] := 3.0 sw[rch] sw[y] sR1[b] + sw[rch] sw[R1[x, y, gama]] (sR1[b - rho[x, y, gama]] + 2.0 sR1[b + rho[x, y, gama]] + 3.0 sw[rch]^2 sR1[Ang34[b]]

rch := 1.09
sw[x_] := s[x]

- Abstraction Terms

- General Terms

fA1[b_] := 54.5 (1. + Cos[2.0 b])

T2[r_] := 1/(2(1.0 - Tanh[b t4 r - ut2]))

M1[x_] := Exp[1.94 (.7417 - x)] (-2.0 + Exp[1.94 (.7417 - x)])

T1[z_] := 1.8 (1. - Tanh[1.18 z - 2.3])
S1[y_] := 0.09 Sech[14.475 y - 26.5]

HHRep[r_] := 358.5 (r - 1.21)^2 /; r < 1.21;
HHRep[r_] := 0.0 /; r ≥ 1.21

Abs12[x_, y_, b_, gama_] :=
fA1[rho[x, y, gama]] (M1[x] + T1[R1[x, y, gama]] + S1[y]) +
T2[x] (3.0 HHRep[rmeH[y, b]] + HHRep[R13[x, y, b, gama]] +
2. HHRep[R14[x, y, b, gama]])

Abs13[x_, y_, b_, gama_] := fA1[b - rho[x, y, gama]]
(M1[R13[x, y, b, gama]] + T1[R1[x, y, gama]] + S1[rch]) +
T2[R13[x, y, b, gama]] (HHRep[x] + 2. HHRep[R14[x, y, b, gama]] +
2. HHRep[rmeH[rch, Ang34[b]]] + HHRep[rmeH[y, b]])

Abs14[x_, y_, b_, gama_] := fA1[b + rho[x, y, gama]]
(M1[R14[x, y, b, gama]] + T1[R1[x, y, gama]] + S1[rch]) +
T2[R14[x, y, b, gama]] (HHRep[R13[x, y, b, gama]] +
HHRep[R14[x, y, b, gama]] + HHRep[x] +
2. HHRep[rmeH[rch, Ang34[b]]] + HHRep[rmeH[y, b]])
AbsVCB[x_, y_, b_, gama_] :=
Abs12[x, y, b, gama] + Abs13[x, y, b, gama] + 2. Abs14[x, y, b, gama]

- Constants

bt4 := 3.80; ut2 := 5.36;
VZero := 422.54

VCB[x_, y_, b_, gama_] := DFit[x, y, gama] + RFit[x, y, b, gama] +
AbsVCB[x, y, b, gama] + VZero

FindMinimum[VCB[1.0, 1.47, b, 0.0], {b, 1.09 Pi/180, 110 Pi/180}]

OpenWrite["VCB—En"]
OpenWrite["VCB—All"]
OpenWrite["VCB—An"]

Date[]
For[ t = 0.5, t < 2.5, t += 0.1,
For[u = 0.75, u < 3.5, u += 0.1,
List1 =
    FindMinimum[VCB[t, u, b, 0.], {b, 1.85, 1.9}];
List1 >> "VCB-All";
WriteString["VCB-En", List1[[1]], ", "];
WriteString["VCB-An", List1[[2]], ", "];
Write["VCB-En", "], "];
WriteString["VCB-En", ", "];
Write["VCB-An", "], "];
WriteString["VCB-An", ", "]
Date[]
Close["VCB—En"]
Close["VCB—An"]
Close["VCB—All"]
VCB: DTab.RTab.So

Substitution

■ General Functions

\[
\begin{align*}
\text{rmeH}[y_-, b_+] & := \sqrt{y^2 + \text{rch}^2 - 2 \cdot y \cdot \text{rch} \cos[b]} \\
\text{R13}[x_-, b_+] & := \sqrt{x^2 + \text{rch}^2 - 2 \cdot x \cdot \text{rch} \cos[\pi - b]} \\
\text{R23}[y_-, b_+] & := \sqrt{y^2 + \text{rch}^2 - 2 \cdot y \cdot \text{rch} \cos[b]} \\
\text{R34}[b_+] & := \sqrt{2 \cdot \text{rch}^2 - 2 \cdot \text{rch} \cos[\text{Ang34}[b]]} \\
\text{Ang34}[b_+] & := \arccos\left[1.0 - 1.5 \cos[b - \pi / 2.\] \right]
\end{align*}
\]

■ D Hybridization Term

\[
\begin{align*}
\text{mch}[y_] & := \exp[\text{chb} (\text{recH} - y)] (-2.0 + \exp[\text{chb} (\text{recH} - y)]) \\
\text{recH} & := 1.09 \\
\text{chb} & := 1.83 \\
\text{s}[x_] & := \exp[\text{chb} (\text{recH} - x)] (2.0 - \exp[\text{chb} (\text{recH} - x)]) /; x > \text{recH} \\
\text{s}[x_] & := 1.0 /; x \leq \text{recH}
\end{align*}
\]

\[
\text{bonds}[x_-, y_+] := 3 \text{s}[\text{rch}] + \text{s}[y] + \text{s}[x]
\]
\[ \text{sD} = \{105.479, 105.524, 105.588, 105.674, 105.773, \\
105.883, 106.007, 106.148, 106.307, 106.482, \\
106.673, 106.897, 107.102, 107.343, 107.601, \\
107.870, 108.147, 108.433, 108.745, 109.101, \\
109.515, 110.004, 110.501, 111.330, 111.851, \\
112.189, 112.763, 113.352, 113.961, 114.586, \\
115.217, 115.840, 116.440, 117.005, 117.525, \\
117.998, 118.385, 118.698, 118.918, 119.056, \\
119.098, 119.085, 119.045, 118.978, 118.885, \\
118.766, 118.620, 118.477, 118.248, 118.022, \\
117.864, 117.491, 117.186, 116.854, 116.496, \\
116.018, 115.699, 115.261, 114.796, 114.305, \\
113.787, 113.242\}; \\
\]

\[ \text{dT}[x_, y_] := \text{sD[Floor}[1 + (\text{bonds}[x, y] - 2.0)/.05]] + \\
(\text{sD[Floor}[2 + (\text{bonds}[x, y] - 2.0)/.05]]) - \\
\text{sD[Floor}[1 + (\text{bonds}[x, y] - 2.0)/.05]]) (\text{bonds}[x, y] - 2.0 - \\
.05 \text{Floor}[(\text{bonds}[x, y] - 2.0)/.05])/.05 \\
\]

\[ \text{DFit}[x_, y_] := \text{dT}[x, y] (3.0 \text{mch}[x] + \text{mch}[y] + \text{mch}[x]) \]

- **Angular Repulsion Term**

\[ \text{sRs} = \{0.000, 0.013, 0.055, 0.134, 0.256, \\
0.435, 0.687, 1.029, 1.476, 2.039, \\
2.729, 3.558, 4.5448, 5.708, 7.06, \\
8.609, 10.390, 12.543, 15.375, 19.36, \\
24.998, 32.554, 41.817, 52.059, 62.287, \\
71.658, 79.770, 86.670, 92.631, 97.922, \\
102.707, 107.066, 111.058, 114.742, 118.166, \\
121.356, 124.325, 127.079, 129.604, 131.871, \\
133.841, 135.495, 136.833, 137.876, 138.657, \\
139.221, 139.609, 139.852, 139.9678, 139.967, \\
139.853, 139.619, 139.260, 138.773, 138.135, \\
137.291, 136.157, 134.659, 132.776, 130.553, \\
128.006, 125.384, 122.531, 119.514, 116.296, \\
112.820, 109.033, 104.928, 100.557, 96.018, \\
92.075, 86.869, 82.438, 78.159, 74.029, \\
70.028, 66.146, 62.388, 58.767, 56.296, \\
51.982, 48.825, 45.814, 42.941, 40.107, \}
\]
\begin{verbatim}
37.621,  35.197,  32.937,  30.810,  28.794,
26.874,  25.057,  23.363,  21.797,  20.352,
19.021,  17.798,  16.683,  15.667,  14.738,
13.896,  13.111,  12.417,  11.808,  11.285,
10.833,  10.424,  10.031,  9.644,  9.271,
8.923,   8.602,  8.303,   8.014,   7.73,
7.449,   7.172,   6.899,   6.631,   6.371,
6.116,   5.866,   5.621,   5.382,   5.148,
4.919,   4.695,   4.474,   4.257,   4.045,
3.837,   3.634,   3.437,   3.244,   3.057,
2.874,   2.696,   2.523,   2.356,   2.197,
2.043,   1.898,   1.764,   1.642,   1.53,
1.429,   1.337,   1.252,   1.171,   1.095,
1.023,   0.955,   0.892,   0.832,   0.775,
0.719,   0.665,   0.615,   0.569,   0.53,
0.497,   0.467,   0.438,   0.410,   0.380,
0.350,   0.320,   0.290,   0.260,   0.230,
0.199,   0.167,   0.141,   0.110,   0.090,
0.070,   0.050,   0.030,   0.010,   0.0,
0.0};
sR1[b_] := sRs[[Floor[b 180./Pi]]] + (sRs[[1 + Floor[b 180./Pi]]] -
   sRs[[Floor[b 180./Pi]]]) (-Floor[b 180./Pi] + b 180./Pi)

RFit[x_, y_, b_] := 3.0 sw[rch] sw[y] sR1[b] +
   3.0 sw[rch] sw[x] sR1[\pi - b] + 3.0 sw[rch]^2 sR1[Ang34[b]]

rch := 1.09

sw[x_] := s[x]

\section*{Abstraction Terms}

\subsection*{General Terms}

\begin{verbatim}
  fA1[b_] := 54.5 (1. + \cos[2.0 b])
  T2[r_] := \frac{1}{2} (1.0 - \tanh[bt4 r - ut2])
  M1[x_] := \exp[1.94 (.7417 - x)] (-2.0 + \exp[1.94 (.7417 - x)])
\end{verbatim}
\end{verbatim}
\[ T_1(z) := 1.8 (1 - \tanh(1.18 z - 2.3)) \]

\[ S_1(y) := 0.09 \text{Sech}(14.475 y - 26.5) \]

\[ \text{HHRep}[r] := 358.5 (r - 1.21)^2 \; /; \; r < 1.21; \]

\[ \text{HHRep}[r] := 0.0 \; /; \; r \geq 1.21 \]

\[ \text{Clear[Abs13, Abs23, Abs34]} \]

\[ \text{Abs13}[x, y, b] := a_1[x - b] (M_1[R_{13}[x, b]] + T_1[x] + S_1[rch]) + \]
\[ T_2[R_{13}[x, b]] (2 \cdot \text{HHRep}[R_{13}[x, b]] + 2 \cdot \text{HHRep}[R_{34}[b]] + \]
\[ \text{HHRep}[R_{23}[y, b]]) \]

\[ \text{Abs23}[x, y, b] := a_1[b] (M_1[R_{23}[y, b]] + T_1[y] + S_1[rch]) + \]
\[ T_2[R_{23}[y, b]] (2 \cdot \text{HHRep}[R_{23}[y, b]] + 2 \cdot \text{HHRep}[R_{34}[b]] + \]
\[ \text{HHRep}[R_{13}[x, b]]) \]

\[ \text{Abs34}[x, y, b] := a_1[Ang_{34}[b]] (M_1[R_{34}[b]] + T_1[rch] + S_1[rch]) + \]
\[ 2 T_2[R_{34}[b]] (\text{HHRep}[R_{34}[b]] + \text{HHRep}[R_{13}[x, b]] + \]
\[ \text{HHRep}[R_{23}[y, b]]) \]

Only Hydrogen 1 can abstract!

\[ \text{AbsVCB}[x, y, b] := 3 \text{Abs13}[x, y, b] \]

\[ \text{Constants} \]

\[ b_{t4} := 3.80; \; u_{t2} := 5.36; \]

\[ V_{Zero} := 422.54 \]

\[ V_{CB}[x, y, b] := DFT[x, y] + RFT[x, y, b] + \text{AbsVCB}[x, y, b] + V_{Zero} \]
OpenWrite["VCB-s-En"]
OpenWrite["VCB-s-All"]
OpenWrite["VCB-s-An"]

Date[]

For[ t = 1.0, t < 4.0, t += 0.05,
    For[u = 1.0, u < 4.0, u += 0.05,
        List1 =
            FindMinimum[VCB[t, u, b], {b, 1.85, 1.9}];
        List1 >> "VCB-s-All";
        WriteString["VCB-s-En", List1[[1]], ", "];
        WriteString["VCB-s-An", List1[[2]], ", "];
        Write["VCB-s-En"", ", "];
        WriteString["VCB-s-En", " ""];
        WriteString["VCB-s-An", "]
        WriteString["VCB-s-An", " "
        WriteString["VCB-s-An", ""]
        Date[]
        Close["VCB-s-En"]
        Close["VCB-s-An"]
        Close["VCB-s-All"]
V5: D2.R1.So

Abstraction

- General Functions

\[ \text{rmeH}[y, b] := \sqrt{y^2 + \text{rch}^2 - 2y \text{rch} \cos[b]} \]

\[ \text{Ang34}[b] := \arccos[1.0 - 1.5 \cos[b - \pi/2]] \]

\[ \text{R1}[x, y, \text{gama}] := \sqrt{(x \cos[\text{gama}] + y)^2 + (x \sin[\text{gama}])^2} \]

\[ \text{R13}[x, y, b, \text{gama}] := \sqrt{\text{R1}[x, y, \text{gama}]^2 + \text{rch}^2 - 2 \text{R1}[x, y, \text{gama}] \cdot \text{rch} \cdot \cos[b - \text{rho}[x, y, \text{gama}]]} \]

\[ \text{R14}[x, y, b, \text{gama}] := \sqrt{\text{R1}[x, y, \text{gama}]^2 + \text{rch}^2 - 2 \text{R1}[x, y, \text{gama}] \cdot \text{rch} \cdot \cos[b + \text{rho}[x, y, \text{gama}]]} \]

\[ \text{rho}[x, y, \text{gama}] := \arctan\left[\frac{x \sin[\text{gama}]}{x \cos[\text{gama}] + y}\right] \]

- D Hybridization Term

\[ \text{recH} := 1.09 \]

\[ \text{chb} := 1.83 \]

\[ \text{DFit}[x, y, \text{gama}] := \text{dtD}[x, y, \text{gama}] (3.0 \text{mch}[\text{rch}] + \text{mch}[y] + \text{mch}[\text{R1}[x, y, \text{gama}]]) \]

\[ \text{mch}[y] := \exp[chb (\text{recH} - y)] (-2.0 + \exp[chb (\text{recH} - y)]) \]

\[ \text{dtD}[x, y, \text{gama}] := 105.5 + \frac{0.66 (1. + \tanh[3.35 (\text{bonds}[x, y, \text{gama}] - 4.65)])}{2.} + \frac{12.2}{2.} + \frac{5.2}{\cosh[2. (\text{bonds}[x, y, \text{gama}] - 3.9)]} \]

\[ \frac{5.2}{\cosh[3.25 (\text{bonds}[x, y, \text{gama}] - 4.55)]]} \]
\[ s[x_] := \exp\left(\text{chb}(\text{recH} - x)\right) \left(2.0 - \exp\left(\text{chb}(\text{recH} - x)\right)\right) /; x > \text{recH}; \]
\[ s[x_] := 1.0 /; x \leq \text{recH} \]

\[ \text{bonds}[x_, y_, \text{gama}_] := 3s[rch] + s[y] + s[Rl[x, y, \text{gama}]] \]

\textbf{Angular Repulsion Term}

\[ sR[b_] := 1385.26 \text{Tanh}\left([0.85 b]^4\right) \left(-32.92604 + \frac{38.12292}{\exp[b]} + \frac{13.3283 b}{\exp[b]} - b^2 + \frac{11.56568 b^2}{\exp[b]}\right) + \]
\[ (1.0 - \tanh[(1.25 b)^2]) \left(27.175 b^2 + 319.47 b^3 + 216.914 b^4\right) \]

\[ \text{RFit}[x_, y_, b_, \text{gama}_] := 3.0 s[wch] s[w[y] sR[b] + \]
\[ s[wch] s[w[Rl[x, y, \text{gama}]] (sR[b - \rho[x, y, \text{gama}]] + \]
\[ 2.0 sR[b + \rho[x, y, \text{gama}]])) + s[y] s[w[Rl[x, y, \text{gama}]] \]
\[ sR[\rho[x, y, \text{gama}]] + 3.0 s[wch]^2 s[R[\text{Ang34}[b]]] \]

\[ rch := 1.09 \]
\[ s[w[x_] := s[x] \]

\textbf{Abstraction Terms}

\textbf{General Terms}

\[ fA1[b_] := 54.75 (1. + \text{Tanh}[10. (.785398 - b)]) \]
\[ T2[r_] := \frac{1}{2} (1.0 - \text{Tanh}[bt4 r - ut2]) \]
\[ M1[x_] := \exp[1.94 (.7417 - x)] (\text{-}2.0 + \exp[1.94 (.7417 - x)]) \]
\begin{align*}
T_1(x, y, z) & := \frac{u_{11} (1. - \tanh[b_{11} (z - c_{11})]) \times (1. - \tanh[b_{12} (y - c_{12})]) \times (1. - \tanh[b_{13} (x - c_{13})])}{2 \times 2 \times 2} \\
S_1(x, y, z) & := u_{11} \left( \text{sech}[(b_{11} (z - c_{11}))^2] \times \text{sech}[(b_{12} (y - c_{12}))^2] \times \text{sech}[(b_{13} (x - c_{13}))^2] \right) \\
S_2(x, y, z) & := u_{12} \left( \text{sech}[(b_{14} (z - c_{14}))^2] \times \text{sech}[(b_{15} (y - c_{15}))^2] \times \text{sech}[(b_{16} (x - c_{16}))^2] \right)
\end{align*}

\begin{align*}
\text{HHRep}[r] & := 358.5 (r - 1.21)^2 \quad ; \quad r < 1.21; \\
\text{HHRep}[r] & := 0.0 \quad ; \quad r \geq 1.21
\end{align*}
Abs12[x_, y_, b_, gama_] := fAl[rho[x, y, gama]] (M1[x] + T1[x, y, R1[x, y, gama]] + S1[x, y, R1[x, y, gama]] + S2[x, y, R1[x, y, gama]] + T2[x] (3.0 H H Rep[rmeH[y, b]] + H H Rep[R13[x, y, b, gama]] + 2. H H Rep[R14[x, y, b, gama]])

Abs13[x_, y_, b_, gama_] := fAl[b - rho[x, y, gama]] (M1[R13[x, y, b, gama]] + T1[R13[x, y, b, gama], rch, R1[x, y, gama]] + S1[R13[x, y, b, gama], rch, R1[x, y, gama]] + S2[R13[x, y, b, gama], rch, R1[x, y, gama]]) + T2[R13[x, y, b, gama]] (H H Rep[x] + 2. H H Rep[R14[x, y, b, gama]] + 2. H H Rep[rmeH[rch, Ang34[b]]] + H H Rep[rmeH[y, b]])

Abs14[x_, y_, b_, gama_] := fAl[b + rho[x, y, gama]] (M1[R14[x, y, b, gama]] + T1[R14[x, y, b, gama], rch, R1[x, y, gama]] + S1[R14[x, y, b, gama], rch, R1[x, y, gama]] + S2[R14[x, y, b, gama], rch, R1[x, y, gama]]) + T2[R14[x, y, b, gama]] (H H Rep[R13[x, y, b, gama]] + H H Rep[R14[x, y, b, gama]] + 2. H H Rep[rmeH[rch, Ang34[b]]] + H H Rep[rmeH[y, b]])

Abs23[x_, y_, b_, gama_] := fAl[b] (M1[rmeH[y, b]] + T1[rmeH[y, b], rch, y] + S1[rmeH[y, b], rch, y] + S2[rmeH[y, b], rch, y]) + T2[rmeH[y, b]] (H H Rep[rmeH[y, b]] + H H Rep[x] + 2. H H Rep[rmeH[rch, Ang34[b]]] + H H Rep[R13[x, y, b, gama]])

Abs34[x_, y_, b_, gama_] := fAl[Ang34[b]] (M1[rmeH[rch, Ang34[b]]] + T1[rmeH[rch, Ang34[b]], rch, rch] + S1[rmeH[rch, Ang34[b]], rch, rch] + S2[rmeH[rch, Ang34[b]], rch, rch]) + 2. T2[rmeH[rch, Ang34[b]]] (H H Rep[rmeH[rch, Ang34[b]]] + H H Rep[rmeH[y, b]] + H H Rep[R13[x, y, b, gama]])

AbsV5[x_, y_, b_, gama_] := Abs12[x, y, b, gama] + Abs13[x, y, b, gama] + 2. Abs14[x, y, b, gama] + 3.0 (Abs23[x, y, b, gama] + Abs34[x, y, b, gama])

- Constants

p := 10.; g := 3.1415926; hafpi := 1.5707963
bt4 := 3.80; ut2 := 5.36;
DEFINITION OF Vab# by parameters for hole fillers:

\[ V_6 = V_{ab5} + R_2 + D_1 \]

\[ \text{ut1} = 12.5; \]
\[ \text{bt1} = 0.0; \text{ct1} = 1.6; \]
\[ \text{bt2} = 1.12; \text{ct2} = 0.79; \]
\[ \text{bt3} = 0.88; \text{ct3} = 0.6; \]
\[ \text{us1} = 0.78; \]
\[ \text{bs1} = 0.0; \text{cs1} = 1.88; \]
\[ \text{bs2} = 0.99; \text{cs2} = 0.64; \]
\[ \text{bs3} = 1.06; \text{cs3} = 0.12; \]
\[ \text{us2} = 0.085; \]
\[ \text{bs4} = 1.00; \text{cs4} = 1.70; \]
\[ \text{bs5} = 0.0; \text{cs5} = 0.47; \]
\[ \text{bs6} = 2.15; \text{cs6} = 0.70; \]

\[ V_{\text{Zero}} := 416.8 \]

\[ V_5[x_, y_, b_, \text{gama}_] := \text{DFit}[x, y, \text{gama}] + \text{RFit}[x, y, b, \text{gama}] + \]
\[ \text{AbsV5}[x, y, b, \text{gama}] + V_{\text{Zero}} \]
V5 - Substitution

- **General Functions**

\[
\text{rmeH}[y\_, \ b\_] := \sqrt{y^2 + \text{rch}^2 - 2 \cdot y \text{rch} \cos[b]}
\]

\[
\text{Ang34}[b\_] := \arccos\left[1.0 - 1.5 \cos\left(b - \frac{\pi}{2}\right)\right]
\]

\[
\text{R1}[x\_, \ y\_, \ \text{gama}\_] := \sqrt{(x \cos[\text{gama}] + y)^2 + (x \sin[\text{gama}])^2}
\]

\[
\text{R13}[x\_, \ y\_, \ b\_, \ \text{gama}\_] := \sqrt{\text{R1}[x, y, \text{gama}]^2 + \text{rch}^2 - 2 \cdot \text{R1}[x, y, \text{gama}] \cdot \text{rch} \cos[b - \text{rho}[x, y, \text{gama}]]}
\]

\[
\text{R14}[x\_, \ y\_, \ b\_, \ \text{gama}\_] := \sqrt{\text{R1}[x, y, \text{gama}]^2 + \text{rch}^2 - 2 \cdot \text{R1}[x, y, \text{gama}] \cdot \text{rch} \cos[b + \text{rho}[x, y, \text{gama}]]}
\]

\[
\text{rho}[x\_, \ y\_, \ \text{gama}\_] := \arctan\left[\frac{x \sin[\text{gama}]}{x \cos[\text{gama}] + y}\right]
\]

- **D Hybridization Term**

\[
\text{recH} := 1.09
\]

\[
\text{chb} := 1.83
\]

Clear [DFit]

\[
\text{DFit}[x\_, \ y\_] := \text{dtD}[x, y] (3.0 \text{mch[rch]} + \text{mch}[y] + \text{mch}[x])
\]

\[
\text{mch}[y\_] := \exp[\text{chb}(\text{recH} - y)] (-2.0 + \exp[\text{chb}(\text{recH} - y)])
\]

\[
\text{dtD}[x\_, \ y\_] := 105.5 + \frac{0.66 (1. + \tanh[3.35 (\text{bonds}[x, y] - 4.65)])}{2.} + 12.2 \text{Sech}[2. (\text{bonds}[x, y] - 3.9)] + 5.2 \text{Sech}[3.25 (\text{bonds}[x, y] - 4.55)]
\]

\[
\text{s}[x\_] := \exp[\text{chb}(\text{recH} - x)] (2.0 - \exp[\text{chb}(\text{recH} - x)]) /; x > \text{recH};
\]

\[
\text{s}[x\_] := 1.0 /; x \leq \text{recH}
\]

\[
\text{bonds}[x\_, \ y\_] := 3 \text{s[rch]} + \text{s}[y] + \text{s}[x]
\]
Angular Repulsion Term

\[
\begin{align*}
\text{sR}[b_] & := 1385.26 \text{Tanh}(0.85 \, b^4) \left(-32.92604 + \frac{38.12292}{\text{Exp}[b]} + 10.95169 \, b + \frac{13.3283 \, b}{\text{Exp}[b]} - b^2 + \frac{11.5656 \, b^2}{\text{Exp}[b]}\right) + (1.0 - \text{Tanh}((1.25 \, b)^2))(27.175 \, b^2 + 319.47 \, b^3 + 216.914 \, b^4) \\
\text{RFit}[x_-, y_-, b_] & := 3.0 \, \text{sw}[rch] \, \text{sw}[y] \, \text{sR}[b] + \text{sw}[y] \, \text{sw}[x] \, \text{sR}[\pi] + 3.0 \, \text{sw}[x] \, \text{sw}[rch] \, \text{sR}[\pi - b] + 3.0 \, (\text{sw}[rch])^2 \, \text{sR}[\text{Ang34}[b]] \\
\text{rch} & := 1.09 \\
\text{sw}[x_] & := \text{s}[x]
\end{align*}
\]

Abstraction Terms

General Terms

\[
\begin{align*}
\text{fA1}[b_] & := 54.75 \, (1. + \text{Tanh}(10. \, (0.785398 - b))) \\
\text{T2}[r_] & := \frac{1}{2} \, (1.0 - \text{Tanh}(bt4 \, r - ut2)) \\
\text{M1}[x_] & := \text{Exp}(1.94 \, (0.7417 - x)) \, (-2.0 + \text{Exp}(1.94 \, (0.7417 - x))) \\
\text{T1}[x_-, y_-, z_-] & := \frac{1}{8} \, \text{utl} \, (1. - \text{Tanh}(bt1 \, (z - ct1))) \, (1. - \text{Tanh}(bt2 \, (y - ct2))) \, (1. - \text{Tanh}(bt3 \, (x - ct3))) \\
\text{S1}[x_-, y_-, z_-] & := \text{us1} \, \text{Sech}((bs1 \, (z - cs1))^2) \, \text{Sech}((bs2 \, (y - cs2))^2) \, \text{Sech}((bs3 \, (x - cs3))^2) \\
\text{S2}[x_-, y_-, z_-] & := \text{us2} \, \text{Sech}((bs4 \, (z - cs4))^2) \, \text{Sech}((bs5 \, (y - cs5))^2) \, \text{Sech}((bs6 \, (x - cs6))^2) \\
\text{HHRep}[r_] & := 358.5 \, (r - 1.21)^2 \, /; \, r < 1.21; \\
\text{HHRep}[r_] & := 0.0 \, /; \, r \geq 1.21
\end{align*}
\]
Definitions

Abs13[x_, y_, b_] := fAl[π - b] (M1[rmeH[x, π - b]] +
T1[rmeH[x, π - b], rch, x] + S1[rmeH[x, π - b], rch, x] +
S2[rmeH[x, π - b], rch, x]) + T2[rmeH[x, π - b]] *
(2.HHRep[rmeH[x, π - b]] + 2.HHRep[rmeH[rch, Ang34[b]]] +
HHRep[rmeH[y, b]])

Abs23[x_, y_, b_] := fAl[b] (M1[rmeH[y, b]] + T1[rmeH[y, b], rch, y] +
S1[rmeH[y, b], rch, y] + S2[rmeH[y, b], rch, y]) +
T2[rmeH[y, b]] (2.HHRep[rmeH[y, b]] +
2.HHRep[rmeH[rch, Ang34[b]]] + HHRep[rmeH[x, π - b]])

Abs34[x_, y_, b_] := fAl[Ang34[b]] (M1[rmeH[rch, Ang34[b]]] +
T1[rmeH[rch, Ang34[b]], rch, rch] +
S1[rmeH[rch, Ang34[b]], rch, rch] +
S2[rmeH[rch, Ang34[b]], rch, rch]) +
2. T2[rmeH[rch, Ang34[b]]] (HHRep[rmeH[rch, Ang34[b]]] +
HHRep[rmeH[y, b]] + HHRep[rmeH[x, π - b]])

AbsV5[x_, y_, b_] := 3.0 (Abs13[x, y, b] + Abs23[x, y, b] + Abs34[x, y, b])

Constants

p := 10.; g := 3.1415926; hafpi := 1.5707963
bt4 := 3.80; ut2 := 5.36;

DEFINITION OF Vab# by parameters for hole fillers;
V6=Vab5+R2+D1
\begin{verbatim}
ut1 = 12.5;
b1t = 0.0; ct1 = 1.6;
b2t = 1.12; ct2 = 0.79;
b3t = 0.88; ct3 = 0.6;
us1 = 0.78;
bs1 = 0.0; cs1 = 1.88;
bs2 = 0.99; cs2 = 0.64;
bs3 = 1.06; cs3 = 0.12;
us2 = 0.085;
bs4 = 1.00; cs4 = 1.70;
bs5 = 0.0; cs5 = 0.47;
bs6 = 2.15; cs6 = 0.70;
VZero := 416.8
V5[x_, y_, b_] := DFit[x, y] + RFit[x, y, b] + AbsV5[x, y, b] + VZero
\end{verbatim}
V6: D1.R2.sD
Abstraction

- General Functions

\[ r_{meH}(y, b) := \sqrt{y^2 + rch^2 - 2 \cdot y \cdot rch \cdot \cos(b)} \]
\[ \text{Ang34}(b) := \arccos\left(1.0 - 1.5 \cos(b - \pi / 2)\right) \]
\[ R1(x, y, \gamma) := \sqrt{(\cos(\gamma) + y)^2 + (\sin(\gamma) y)^2} \]
\[ R13(x, y, b, \gamma) := \sqrt{R1(x, y, \gamma)^2 + rch^2 - 2 \cdot R1(x, y, \gamma) \cdot rch \cdot \cos(b - \rho(x, y, \gamma))} \]
\[ R14(x, y, b, \gamma) := \sqrt{R1(x, y, \gamma)^2 + rch^2 - 2 \cdot R1(x, y, \gamma) \cdot rch \cdot \cos(b + \rho(x, y, \gamma))} \]
\[ \rho(x, y, \gamma) := \arctan\left(\frac{x \sin(\gamma)}{x \cos(\gamma) + y}\right) \]

- D Hybridization Term

\[ \text{recH} := 1.086 \]
\[ \text{chb} := 1.83 \]
\[ D\text{Fit}(x, y, \gamma) := d\text{tD}(x, y, \gamma) (3.0 \cdot mch[rch] + mch[y] + mch[R1(x, y, \gamma)]) \]
\[ mch[y] := \exp[chb (\text{recH} - y)] (-2.0 + \exp[chb (\text{recH} - y)]) \]
\[ d\text{tD}(x, y, \gamma) := 71.153 + 24.859 \cdot \text{bonds}[x, y, \gamma] - 3.2787 \cdot \text{bonds}[x, y, \gamma]^2 + 8.8994 \cdot \text{bonds}[x, y, \gamma] - 33.94 \]
\[ \exp[1.1105 (3.2699 - \text{bonds}[x, y, \gamma]^2)] \]
\[ \text{bonds}[x, y, \gamma] := 3 \cdot \text{sd}[rch] + \text{sd}[y] + \text{sd}[R1(x, y, \gamma)] \]
\[ \text{sd}[y] := 0.5 \left(1 - \tanh\left(-\frac{3.0}{y^3 + 0.001} + y - \text{recH}\right)\right) \]
Angular Repulsion Term

\[ sR[b_] := 1385.26 \text{Tanh}[(.85 b)^4] \left( -32.92604 + \frac{38.12292}{\text{Exp}[b]} + 10.95169 b + \frac{13.3283}{\text{Exp}[b]} \right) \]

\[ \text{RFit}[x_, y_, b_, \text{gama}_] := 3.0 \text{sw[rch]sw[y]sR[b]} + \text{sw[rch]sw[R1[x, y, gama]]}(sR[b - \text{rho}[x, y, \text{gama}]] + 2.0 sR[b + \text{rho}[x, y, \text{gama}]]) + \text{sw[y]sw[R1[x, y, gama]]sR[\text{rho}[x, y, \text{gama}]]} + 3.0 \text{sw[rch]}^2 sR[\text{Ang34}[b]] \]

\[ \text{rch} := 1.09 \]

\[ \text{sw}[x_] := \text{sd}[x] \]

Abstraction Terms

General Terms

\[ fA1[b_] := 54.75 (1. + \text{Tanh}[10 \cdot (.785398 - b)]) \]

\[ T2[r_] := \frac{1}{2} \left( 1.0 - \text{Tanh}[b_{14} r - \text{ut2}] \right) \]

\[ M1[x_] := \text{Exp}[1.94 (.7417 - x)] (-2.0 + \text{Exp}[1.94 (.7417 - x)]) \]

\[ T1[x_, y_, z_] := \frac{1}{2.2} (\text{ut1} (1. - \text{Tanh}[b_{11} (z - \text{ct1})]) * (1. - \text{Tanh}[b_{12} (y - \text{ct2})]) * (1. - \text{Tanh}[b_{13} (x - \text{ct3})])) \]

\[ S1[x_, y_, z_] := \text{us1} (\text{Sech}[(b_{11} (z - \text{cs1}))^2] * \text{Sech}[(b_{12} (y - \text{cs2}))^2] * \text{Sech}[(b_{13} (x - \text{cs3}))^2]) \]

\[ S2[x_, y_, z_] := \text{us2} (\text{Sech}[(b_{14} (z - \text{cs4}))^2] * \text{Sech}[(b_{15} (y - \text{cs5}))^2] * \text{Sech}[(b_{16} (x - \text{cs6}))^2]) \]

\[ \text{HHRep}[r_] := \text{rda} \cdot \text{Exp}[-(b_{1a} \cdot r)] \]

Abs12[x_, y_, b_, gama_] :=
\[ fA1[\text{rho}[x, y, \text{gama}]](\text{M1}[x] + T1[x, y, R1[x, y, \text{gama}]]) + S1[x, y, R1[x, y, \text{gama}]] + S2[x, y, R1[x, y, \text{gama}]] + T2[x] * (3 \cdot \text{HHRep}[\text{rmeH}[y, b]] + \text{HHRep}[R13[x, y, b, \text{gama}]] + 2 \cdot \text{HHRep}[R14[x, y, b, \text{gama}]] \]
Abs13[x_, y_, b_, gama_] :=
  fA1[b - rho[x, y, gama]] * (M1[R13[x, y, b, gama]] +
    T1[R13[x, y, b, gama],rch,R1[x,y,gama]] +
    S1[R13[x, y, b, gama],rch,R1[x,y,gama]] +
    S2[R13[x, y, b, gama],rch,R1[x,y,gama]]) +
  T2[R13[x, y, b, gama]] *
    (HHRep[x] + 2.*HHRep[R14[x, y, b, gama]] +
     2.*HHRep[rmeH[rch, Ang34[b]]] + HHRep[rmeH[y, b]])

Abs14[x_, y_, b_, gama_] :=
  fA1[b + rho[x, y, gama]] * (M1[R14[x, y, b, gama]] +
    T1[R14[x, y, b, gama],rch,R1[x,y,gama]] +
    S1[R14[x, y, b, gama],rch,R1[x,y,gama]] +
    S2[R14[x, y, b, gama],rch,R1[x,y,gama]]) +
  T2[R14[x, y, b, gama]] * (HHRep[R13[x, y, b, gama]] +
    HHRep[R14[x, y, b, gama]] + HHRep[x] +
    2.*HHRep[rmeH[rch, Ang34[b]]] + HHRep[rmeH[y, b]])

Abs23[x_, y_, b_, gama_] :=
  fA1[b] * (M1[rmeH[y, b]] +
    T1[rmeH[y, b],rch,y] + S1[rmeH[y, b],rch,y] +
    S2[rmeH[y, b],rch,y]) +
  T2[rmeH[y, b]] * (2.*HHRep[rmeH[y, b]] + HHRep[x] +
    2.*HHRep[rmeH[rch, Ang34[b]]] + HHRep[R13[x, y, b, gama]])

Abs34[x_, y_, b_, gama_] :=
  fA1[Ang34[b]] * (M1[rmeH[rch, Ang34[b]]] +
    T1[rmeH[rch, Ang34[b]],rch,rch] +
    S1[rmeH[rch, Ang34[b]],rch,rch] +
    S2[rmeH[rch, Ang34[b]],rch,rch]) +
  2.*T2[rmeH[rch, Ang34[b]]] *
    (HHRep[rmeH[rch, Ang34[b]]] + HHRep[rmeH[y, b]] +
     HHRep[R13[x, y, b, gama]])

AbsV6[x_, y_, b_, gama_] :=
  Abs12[x, y, b, gama] +
  Abs13[x, y, b, gama] + 2.*Abs14[x, y, b, gama] +
  3.*(Abs23[x, y, b, gama] + Abs34[x, y, b, gama])
- Constants

\[ p := 10.; \ g := 3.1415926; \ hafpi := 1.5707963; \]
\[ \text{bt4} := 3.41; \ \text{ut2} := 4.71 \]
\[ \text{rda} := 1314.59881; \]
\[ \text{bda} := 4.17582; \]

DEFINITION OF \( V_{ab#} \) by parameters for hole fillers;
\[ V_6 = V_{ab5} + R_2 + D_1 \]
\[ \text{ut1} := 2.5; \]
\[ \text{bt1} := 11.06; \ \text{ct1} := 2.04; \]
\[ \text{bt2} := 11.06; \ \text{ct2} := 2.04; \]
\[ \text{bt3} := 0.; \ \text{ct3} := 1.; \]
\[ \text{us1} := 2.25; \]
\[ \text{bs1} := 0.494; \ \text{cs1} := 0.; \]
\[ \text{bs2} := 0.620; \ \text{cs2} := 0.15; \]
\[ \text{bs3} := 0.88; \ \text{cs3} := 0.25; \]
\[ \text{us2} := 0.15; \]
\[ \text{bs4} := 0.; \ \text{cs4} := 1.7; \]
\[ \text{bs5} := 1.5; \ \text{cs5} := 1.1; \]
\[ \text{bs6} := 0.75; \ \text{cs6} := 1.03; \]

\[ V_{Zero} := 423.6 \]

\[ V_6[x_-, y_-, b_-, gama_] := \]
\[ \text{DFit}[x, y, gama] + \text{RFit}[x, y, b, gama] + \text{AbsV6}[x, y, b, gama] + V_{Zero} \]
V6: D1.R2.Sd

Substitution

■ D Hybridization Term

\[
\begin{align*}
\text{recH} & := 1.086 \\
\text{chb} & := 1.83 \\
\text{DFit}[x_-, y_] & := \text{dtD}[x, y] (3.0 \text{mch}[\text{rch}] + \text{mch}[y] + \text{mch}[x]) \\
\text{mch}[y_] & := \exp[\text{chb} (\text{recH} - y)] (-2.0 + \exp[\text{chb} (\text{recH} - y)]) \\
\text{dtD}[x_, y_] & := 71.153 + 24.859 \text{bonds}[x, y] - 3.2787 \text{bonds}[x, y]^2 + \\
& \quad \frac{8.8994 \text{bonds}[x, y] - 33.94}{\exp[1.1105 (3.2699 - \text{bonds}[x, y])^2]} \\
\text{bonds}[x_, y_] & := 3 \text{sd}[\text{rch}] + \text{sd}[y] + \text{sd}[x] \\
\text{sd}[y_] & := 0.5 \left(1 - \tanh\left(-\frac{3.0}{y^3 + 0.001} + y - \text{recH}\right)\right) \\
\end{align*}
\]

■ Angular Repulsion Term

\[
\begin{align*}
\text{sd}[y_] & := 0.5 \left(1 - \tanh\left(-\frac{3.0}{y^3 + 0.001} + y - \text{recH}\right)\right) \\
\text{sR}[b_] & := 1385.26 \tanh\left(0.85 b\right)\left(-32.92604 + \frac{38.12292}{\exp[b]} + 10.95169 b + \\
& \quad \frac{13.3283 b}{\exp[b]} - b^2 + \frac{11.56568 b^2}{\exp[b]}\right) \\
\text{RFit}[x_, y_, b_] & := 3.0 \text{sw}[\text{rch}] \text{sw}[y] \text{sR}[b] + \text{sw}[y] \text{sw}[x] \text{sR}[\pi] + \\
& \quad 3.0 \text{sw}[x] \text{sw}[\text{rch}] \text{sR}[\pi - b] + 3.0 \text{sw}[\text{rch}]^2 \text{sR}[\text{Ang34}[b]] \\
\text{rch} & := 1.086 \\
\text{sw}[x_] & := \text{sd}[x] \\
\end{align*}
\]
Abstraction Terms

General Terms

\[ f_{A1}[b_] := 54.75 \left( 1 + \tanh[p \left( 0.477658 - b \right)] \right) \]

\[ \text{Ang34}[b_] := \arccos\left[ 1.0 - 1.5 \cos[b - \pi/2.] \right] \]

\[ M1[x_] := \exp[1.94(\pi/2 - x)] \left(-2.0 + \exp[1.94(\pi/2 - x)]\right) \]

\[ ut1 \left( 1 - \tanh[bt1(z - ct1)] \right) \left( 1 - \tanh[bt2(y - ct2)] \right) \]

\[ T1[x_\_, y_\_, z_] := \frac{222}{\left( 1 - \tanh[bt3(x - ct3)] \right)} \]

\[ S1[x_\_, y_\_, z_] := \text{us1} \left( \text{sech}[bs1(z - cs1)]^2 \right) \text{sech}[bs2(y - cs2)]^2 \]

\[ S2[x_\_, y_\_, z_] := \text{us2} \left( \text{sech}[bs4(z - cs4)]^2 \right) \text{sech}[bs5(y - cs5)]^2 \]

\[ rmeH[y_\_, b_] := \sqrt{y^2 + \text{rch}^2 - 2. \text{rch} \cos[b]} \]

\[ \text{HHRep}[r_] := \text{rda} \exp[-\text{bdar} r] \]

\[ T2[r_] := \frac{1}{2} \left( 1.0 - \tanh[bt4 r - ut2] \right) \]

\[ \text{Abs13}[x_\_, y_\_, b_] := f_{A1}[\pi - b] \left( M1[rmeH[x, \pi - b]] + T1[rmeH[x, \pi - b], \text{rch}, x] + S1[rmeH[x, \pi - b], \text{rch}, x] + S2[rmeH[x, \pi - b], \text{rch}, x] + T2[rmeH[x, \pi - b]] \right) \]

\[ (2. \text{HHRep}[rmeH[x, \pi - b]] + 2. \text{HHRep}[rmeH[\text{rch}, \text{Ang34}[b]]] + \text{HHRep}[rmeH[y, b]]) \]

\[ \text{Abs23}[x_\_, y_\_, b_] := f_{A1}[b] \left( M1[rmeH[y, b]] + T1[rmeH[y, b], \text{rch}, y] + S1[rmeH[y, b], \text{rch}, y] + S2[rmeH[y, b], \text{rch}, y] + T2[rmeH[y, b]] \right) \]

\[ (2. \text{HHRep}[rmeH[y, b]] + 2. \text{HHRep}[rmeH[\text{rch}, \text{Ang34}[b]]] + \text{HHRep}[rmeH[x, \pi - b]]) \]
\[
\text{Abs34}[x_-, y_-, b_] := fA1[Ang34[b]] (M1[rmeH[rch, Ang34[b]]] + T1[rmeH[rch, Ang34[b]], rch, rch] + S1[rmeH[rch, Ang34[b]], rch, rch] + S2[rmeH[rch, Ang34[b]], rch, rch]) + \\
2. \text{T2}[rmeH[rch, Ang34[b]]] (HHRep[rmeH[rch, Ang34[b]]] + HHRep[rmeH[y, b]] + HHRep[rmeH[x, \pi - b]])
\]

\[
\text{AbsV6}[x_-, y_-, b_] := 3.0 (\text{Abs13}[x, y, b] + \text{Abs23}[x, y, b] + \text{Abs34}[x, y, b])
\]

- Constants

\[
\text{rch} := 1.086; \text{p} := 10.; \text{g} := 3.1415926; \text{haFpi} := 1.5707963 \\
\text{rda} := 1314.59881; \text{bda} := 4.17582; \\
\text{bt4} := 3.41; \text{ut2} := 4.71;
\]

DEFINITION OF Vab# by parameters for hole fillers:
\[
V6 = Vab5 + R2 + D1
\]

\[
\text{ut1} := 2.50; \text{us1} := 2.25; \text{us2} := 0.15; \\
\text{bt1} := 11.06; \text{ct1} := 2.04; \\
\text{bt2} := 11.06; \text{ct2} := 2.04; \\
\text{bt3} := 0.00; \text{ct3} := 1.00; \\
\text{bs1} := 0.494; \text{cs1} := 0.00; \\
\text{bs2} := 0.62; \text{cs2} := 0.15; \\
\text{bs3} := 0.88; \text{cs3} := 0.25; \\
\text{bs4} := 0.00; \text{cs4} := 1.70; \\
\text{bs5} := 1.50; \text{cs5} := 1.10; \\
\text{bs6} := 0.75; \text{cs6} := 1.03;
\]

\[
VZero := 423.3
\]

\[
V6[x_-, y_-, b_] := \text{DFit}[x, y] + \text{RFit}[x, y, b] + \text{AbsV6}[x, y, b] + VZero
\]
APPENDIX B

Trajectory Movies
Abstraction in VCB surface, $\gamma_{\text{initial}} = 2.1$ deg
Abstraction in VCB surface, $\theta_{\text{initial}} \approx 21.1 \, \text{deg}$
Abstraction in VCB surface, $\theta_{\text{initial}} = 46.0 \text{ deg}$
Substitution in VCB surface, $p_{\text{initial}} = 69.0\,\text{deg}$
Substitution in VCB surface, $\psi_{\text{initial}} = 171.9^\circ$ deg