Quantum Chemical Studies of Radical Cation Rearrangement, Radical Carbonylation, and Homolytic Substitution Reactions

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Abstract

Quantum chemical calculations have been performed to investigate radical cation rearrangement, radical carbynylation, and homolytic substitution reactions of organic molecules.

The rearrangement of the bicyclopropyliadiene radical cation to the tetramethyleneethane radical cation is predicted to proceed with stepwise disrotatory opening of the two rings. Each ring opening is found to be combined with a striking pyramidalization of a carbon atom in the central bond.

The isomerization of the norbornadiene radical cation to the cycloheptatriene radical cation (CHT+), initialized by opening of a bridgehead–methylene bond, is investigated. The most favorable path involves concerted rearrangement to the norcaradiene radical cation followed by ring opening to CHT+. The barrier of this channel is found to be significantly reduced upon substitution of the methane group with C(CH3)2.

Stepwise mechanisms are predicted to be favored over concerted isomerization for the McLafferty rearrangement of the radical cations of butanal and 3-fluorobutanal. The barrier for the concerted rearrangement is found to be lowered by 17.2 kcal/mol upon substitution, a result which is rationalized by the calculated dipole moments and atomic charges.

Recent experiments showed that photoinitiated carbynylation of alkyl iodides with [13C]carbon monoxide may be significantly enhanced by using small amounts of ketones that have σ* character of their excited triplet state. DFT calculations show the feasibility of an atom transfer type mechanism, proposed to explain these observations. Moreover, the computational results rationalize the observed differences in yield when using various alcohol solvents.

Finally, following photolysis of methylidiole, recent electron spin resonance spectroscopy experiments demonstrated that the S2,2 reaction 'CD3 + SiD3CH3 → CD3SiD3 + 'CH, proceeds with high selectivity over the energetically more favorable D abstraction. The role of geometrical effects, especially the formation of prereactive complexes between methylsilane and methylidiole is studied, and a plausible explanation for the experimentally observed paradox is presented.

Keywords: quantum chemistry, coupled-cluster, density functional theory, meta-GGA, reaction mechanism, potential energy surface, isomerization, fragmentation, dissociation, condensation, addition, SH2, hydrogen abstraction, iodine atom transfer, complex, weakly interacting system, hyperfine coupling constant

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List of papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals I–VI:

I **Bicyclopropylidene radical cation: A rehybridization ring opening to tetramethylenethane**
Norberg, D.; Larsson, P.-E.; Dong, X.-C.; Salhi-Benachenhou, N.; Lunell, S.
DOI: 10.1002/qua.20082

II **Isomerization pathways from the norbornadiene to the cycloheptatriene radical cation by opening a bridgehead–methylene bond: A theoretical investigation**
Norberg, D.; Larsson, P.-E.; Salhi-Benachenhou, N.
DOI: 10.1039/b612791f

III **McLafferty rearrangement of the radical cations of butanal and 3-fluorobutanal: A theoretical investigation of the concerted and stepwise mechanisms**
Norberg, D.; Salhi-Benachenhou, N.
DOI: 10.1002/jcc.20797

IV **Radical carbonylation with $[^{11}$C]carbon monoxide promoted by oxygen-centered radicals: experimental and DFT studies of the mechanism**
Itsenko, O.; Norberg, D.; Rasmussen, T.; Långström, B.; Chatgilialoglu, C.
DOI: 10.1021/ja0707714
V  Direct ESR evidence for $S_{H2}$ type reaction of methyl radical with methylsilane and methylgermane in a low temperature solid: A deuterium labeling study
DOI:10.1016/j.cplett.2005.04.091

VI  $S_{H2}$ reaction vs. hydrogen abstraction/expulsion in methyl radical–methylsilane reactions: Effects of prereactive complex formation
Norberg, D.; Shiotani, M.; Lunell, S.
Submitted to J. Phys. Chem. A.

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My contribution to the Papers I–VI:

I  Performed the computational work. Significantly contributed to the interpretation of the results and to the writing of the manuscript.

II  Partially formulated the research project. Performed the computational work. Significantly contributed to the interpretation of the results and to the writing of the manuscript.

III  Formulated the research project. Performed the computational work. Interpreted the results and wrote the manuscript, under the supervision of Nessima Salhi-Benachenhou.

IV  Performed the computational work. Partially contributed to the interpretation of the computational results and to the writing of the computational part of the manuscript.

V  Performed the computational work. Significantly contributed to the interpretation of the computational results and to the writing of the computational part of the manuscript.

VI  Partially formulated the research project. Performed the computational work. Significantly contributed to the interpretation of the results and to the writing of the manuscript.
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Abbreviations

3F-Bu⁺ 3-fluorobutanal radical cation
AO Atomic orbital
B3LYP Hybrid GGA DFT functional
B97-1 Hybrid GGA DFT functional
BCP Bicyclopropylidene
BCP⁺ Bicyclopropylidene radical cation
BHandHLYP Hybrid GGA DFT functional
BHE⁺ Bicyclo[2.2.1]hepta-2-ene-5-yl-7-yl-7-ylum radical cation
BO Born–Oppenheimer approximation
BOOB di-tert-butyl peroxide
Bu⁺ Butanal radical cation
CC Coupled-cluster
CCD CC with double excitations
CCSD CC with single and double excitations
CCSD(T) CCSD with perturbative triple excitations
CHT⁺ Cycloheptatriene radical cation
CI Configuration interaction
CID CI with double excitations
CISD CI with single and double excitations
D⁺ Distonic isotooluene radical cation
DFT Density functional theory
ENDOR Electron-nuclear double resonance
ESP Electrostatic potential
ESR Electron spin resonance
GGA Generalized gradient approximation
HF Hartree–Fock
Hfccc Hyperfine coupling constant
IRC Intrinsic reaction coordinate
KS Kohn–Sham
LDA Local density approximation
MK Merz–Singh–Kollman
MLR McLafferty rearrangement
MO Molecular orbital
MPn Møller–Plesset perturbation theory of n th order
MPWKCIS1K Hybrid meta-GGA DFT functional
N⁺ Norbornadiene radical cation
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>NBO</td>
<td>Natural bond orbital</td>
</tr>
<tr>
<td>NCD⁺</td>
<td>Norcaradiene radical cation</td>
</tr>
<tr>
<td>PCM</td>
<td>Polarizable continuum model</td>
</tr>
<tr>
<td>PES</td>
<td>Potential energy surface</td>
</tr>
<tr>
<td>PET</td>
<td>Positron emission tomography</td>
</tr>
<tr>
<td>PMP2</td>
<td>Spin projected MP2</td>
</tr>
<tr>
<td>Q⁺</td>
<td>Quadricyclane radical cation</td>
</tr>
<tr>
<td>QCISD</td>
<td>Quadratic CI with single and double excitations</td>
</tr>
<tr>
<td>RHF</td>
<td>Restricted HF</td>
</tr>
<tr>
<td>SCF</td>
<td>Self-consistent field</td>
</tr>
<tr>
<td>SE</td>
<td>Schrödinger equation</td>
</tr>
<tr>
<td>SıH₂</td>
<td>Bimolecular homolytic substitution</td>
</tr>
<tr>
<td>TME⁺</td>
<td>Tetramethyleneethane radical cation</td>
</tr>
<tr>
<td>TS</td>
<td>Transition structure</td>
</tr>
<tr>
<td>UEG</td>
<td>Uniform electron gas</td>
</tr>
<tr>
<td>UHF</td>
<td>Unrestricted HF</td>
</tr>
<tr>
<td>WFT</td>
<td>Wavefunction theory</td>
</tr>
<tr>
<td>XC</td>
<td>Exchange-correlation</td>
</tr>
<tr>
<td>ZPVE</td>
<td>Zero-point vibrational energy</td>
</tr>
<tr>
<td>Å</td>
<td>Ångström</td>
</tr>
</tbody>
</table>
Applied quantum chemistry is the field of theoretical chemistry which uses the rules of quantum mechanics to investigate the properties and reactions of atoms and molecules. The number of publications on quantum chemical applications has grown rapidly during the recent decades, a fact that in part can be explained by the ever lasting development of computer technology which allows for the study of molecular systems of more realistic size than was possible in the early days of quantum chemistry. However, the development of quantum chemical methods, efficient computational algorithms, and easy-to-use friendly-interfaced computational program packages are also important factors for the nowadays widespread use of quantum chemistry.

One particularly useful aspect of quantum chemistry is that one may study the mechanisms of chemical reactions in detail. This contingency has been utilized extensively in this thesis and, therefore, some elementary facts on reaction mechanisms as well as on their interpretation are here introduced.

The reaction mechanism is the detailed and ordered specification of chemical processes that take place in the reacting molecules. Among others, such chemical processes may be breaking and formation of bonds. A complete specification of the reaction mechanism includes a characterization of the composition, structure and energy of the reactants, reaction intermediates, products, and transition states. Computationally, these compounds are known as stationary points and each one is represented by a single optimized structure. If the vibrational frequency spectrum of the stationary point contains only real valued frequencies then it is an energy minimum and any small deviation in its geometry will be associated with increased energy. In the reaction mechanism, the reactants, intermediates, and products are all energy minima. The stationary point corresponding to the transition state, the so-called transition structure (TS), has got one imaginary frequency. A small distortion of the geometry in the direction of the vibration corresponding to the imaginary frequency leads to decreased energy while distortion in any other direction is associated with increased energy. Thus, the TS is an energy maximum in one direction, and to be properly included in the reaction mechanism it must smoothly connect one minimum to another via the paths of steepest energy descent emerging from the imaginary vibration.

Once all of the relevant stationary points have been located and characterized one may construct the energy profile for the reaction mechanism. This profile displays diagrammatically the relative energies of the stationary
points. The highest point on the profile defines the activation energy for the total reaction.

In case there are alternative mechanisms available for the same total reaction, one may judge their relative importance by the corresponding energy profiles. Figure 1 displays two examples of energy profiles which both describe the reaction of reactant A to product B. The profile (a) involves a single TS, transforming A to B in a single, concerted, elementary step, while (b) includes two TSs and, thus, proceeds stepwise via the intermediate C. The stepwise reaction is associated with the stationary point, TS2, of highest relative energy so the most plausible mechanism will be the concerted one. In this sense, by comparing different alternative mechanisms for a reaction, one may identify the minimum energy path of the reaction, that is, the mechanism which requires the least amount of activation energy to proceed.

In addition to the activation energy, energy profiles also provide information on the reaction energy. The reaction energy is the difference in energy between the products and the reactants (Figure 1). If Gibbs relative energies are used to obtain the energy profiles, a negative reaction energy signals that the reaction is exergonic and that it will occur spontaneously, and the equilibrium population will therefore be shifted towards the products. Moreover, if there are several exergonic mechanisms that lead from the reactant to different products, the equilibrium population will be shifted towards the product of lowest Gibbs energy.

![Figure 1. Schematic example of energy profiles of the (a) concerted, and (b) stepwise mechanisms for the reaction of A to B.](image)

In this thesis, quantum chemistry has been applied to some reactions involving radicals in order to elucidate their mechanisms. A radical is a mole-
cule which has an unpaired electron. The presences of unpaired electrons tend to make radicals highly reactive and they often react in a way that leads to electron pairing.

In industrial applications, radical reactions are important for, e.g., the synthesis of polymers, such as polyethylene, Teflon and polystyrene, but also for the production of gasoline from petroleum. Moreover, radical reactions may be very useful in other applications of organic chemistry because they may dramatically decrease the time needed for performing syntheses. The latter advantage is extensively utilized in the experiments of Paper IV, where the synthesis of carbonyl-$^{13}$C-labeled compounds is enhanced by a radical based mechanism.

Radical reactions are also of vital importance, and ubiquitous, in the chemistry of living subjects. For instance, radicals are intermediates produced in the normal course of metabolism. However, because of their reactivity, high concentrations of radicals may also be harmful to biological systems.

The fact that radicals are highly reactive makes them difficult to investigate experimentally. Even though there are experimental methods, such as electron spin resonance (ESR) spectroscopy or mass spectrometry, for studying the structures of radicals, as well as the fate of their reactions, the reactions often occur so fast that the details of the underlying mechanisms are lost. Therefore, complementary quantum chemical investigations may be of high value and, sometimes, the only means for acquiring detailed information on the mechanisms for radical reactions.

The reactions studied in Papers I–III are rearrangement reactions of positively charged radicals, so-called radical cations. In a rearrangement, or isomerization, a single molecule undergoes intramolecular chemical processes. Thus, in Paper I, the ring opening of the bicycloprenylidene radical cation to the tetramethyleneethane radical cation was investigated. In Paper II, three channels for the isomerization of the norbornadiene radical cation ($N^+$) to the cycloheptatriene radical cation were studied, which all start by cleavage of one bridgehead–methylenes bond. Moreover, the effect of substituting the methylene hydrogen atoms in $N^+$ with methyl groups on the lowest energy path was investigated. The investigation of radical cation isomerizations is concluded with Paper III, where the McLafferty rearrangement of the butanal radical cation, and the effect of substituting the β-carbon atom with fluorine, were studied.

The remaining radical reactions studied in this thesis are bimolecular, meaning that two species collide, and as a result react to form new compounds. Hence, in Paper IV, quantum chemical calculations were carried out to validate a proposed mechanism for the observed ketone or alkoxyl radical enhanced radical carbonylation synthesis of carbonyl-$^{13}$C-labeled compounds. Finally, the computations in Papers V and VI were performed to investigate the origin of the bimolecular homolytic substitution reaction ob-
served by ESR between the methyl radical and methylsilane or methylger-
mane.

Chapter 2 provides an overview of the theory behind the quantum chemi-
cal calculations performed in this thesis. Chapters 3–7 subsequently summa-
rize the main results of Papers I–VI, while Chapter 8 provides their main conclusions. The thesis is concluded with a summary in Swedish.
2 Quantum chemical methods

The Schrödinger equation\(^1\) (SE) provides the basic physical foundation for quantum chemistry. For a system composed of \(N\) nuclei and \(n\) electrons described by the wavefunction \(\Psi\) and governed by a time-independent non-relativistic Hamiltonian (\(H\)) the SE takes the form

\[
H \Psi = E \Psi, \tag{2.1}
\]

where \(E\) is the energy of the state described by \(\Psi\). In turn, for this kind of system, \(H\) is (in atomic units) given by

\[
H = -\sum_{i=1}^{n} \frac{1}{2} \nabla_i^2 - \sum_{A=1}^{N} \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^{n} \sum_{A=1}^{N} \frac{Z_A}{r_{iA}}
\]

\[+ \sum_{i=1}^{n} \sum_{j>i}^{n} \frac{1}{r_{ij}} + \sum_{A=1}^{N} \sum_{B>A}^{N} \frac{Z_A Z_B}{r_{AB}}, \tag{2.2}\]

where \(M_A\) is the mass of nucleus \(A\) divided by the mass of the electron and \(Z_A\) is the atomic number of nucleus \(A\). \(r_{iA}\), \(r_{ij}\) and \(r_{AB}\) are the distances between electron \(i\) and nucleus \(A\), between electrons \(i\) and \(j\), and between nuclei \(A\) and \(B\), respectively. The first two terms in Eq. (2.2) are operators for the kinetic energy of the electrons and of the nuclei while the final three terms are the operators for nuclear–electron, electron–electron and nuclear–nuclear potential energies.

The methods applied to the chemical reactions investigated in this thesis are all based on the Born–Oppenheimer approximation\(^2\) (BO). Within the BO, the kinetic energy operators for the nuclei are removed from \(H\) and the SE is solved for a fixed set of nuclei. The SE with the BO is usually referred to as the electronic SE, and the resulting wavefunctions as electronic states. In this thesis, the electronic ground state is addressed, that is, the lowest energy solution to the electronic SE.

The commonly used concept of potential energy surfaces (PES) stems directly from the use of the BO. For a given electronic state, the PES is the energy landscape formed by solving the electronic SE for all possible nu-
clear coordinates. In that sense, the electronic energies provide the potential surface on which the nuclei move.

Unfortunately, further approximations are required because the electronic SE is impossible to solve analytically for systems containing more than one electron. In modern quantum chemistry, there are mainly two branches of methods available to proceed from this point. In the first branch, the aim is to compute the wavefunction as accurately as possible. In the second nowadays overwhelmingly popular branch, the aim is to find the optimal electron density of the system. The methods defined by the former and the latter branches are generally referred to as wavefunction theory (WFT) and density functional theory (DFT) based methods, respectively. WFT based methods without empirical parameters are also referred to as \textit{ab initio} methods.

In the following, the underlying details of WFT and DFT are briefly outlined with special emphasis on the particular methods that have been used in this thesis. For detailed accounts of WFT and DFT, the reader is referred to the books of Szabo and Ostlund\textsuperscript{3}, and Yang and Parr\textsuperscript{4}, respectively. Moreover, the book on DFT by Koch and Holthausen\textsuperscript{5} can be recommended as introductory reading for chemists starting to do quantum chemical calculations.

2.1 Hartree–Fock theory

The starting point for the WFT methods employed in this thesis is provided by Hartree–Fock (HF) theory. In this theory, the \( n \)-electron wavefunction of a molecular system is represented by a single Slater determinant\textsuperscript{6}, \( \Psi_{\text{SD}} \).

\[
\Psi_{\text{SD}} = \frac{1}{\sqrt{n!}} \begin{vmatrix}
\chi_1(x_1) & \chi_2(x_1) & \cdots & \chi_n(x_1) \\
\chi_1(x_2) & \chi_2(x_2) & \cdots & \chi_n(x_2) \\
\vdots & \vdots & \ddots & \vdots \\
\chi_1(x_n) & \chi_2(x_n) & \cdots & \chi_n(x_n)
\end{vmatrix},
\]

(2.3)

constructed from \( n \) occupied one-electron wavefunctions, \( \chi(x) \), called molecular orbitals (MOs). The MOs contain the spatial distribution of the electrons as spatial functions \( \psi(r) \). Moreover, since the electronic Hamiltonian gives no reference to the two distinct spin states exhibited by electrons, the spatial functions are augmented with so-called spin functions, \( \alpha(\omega) \) and \( \beta(\omega) \). Because of this, MOs – defined as \( \chi(x) = \psi^\alpha(r)\alpha(\omega) \) or \( \psi^\beta(r)\beta(\omega) \) – are also referred to as spin orbitals. In \( \chi(x) \), \( x \) denotes the electron spatial and spin coordinates, \( r \) and \( \omega \), respectively. \( \Psi_{\text{SD}} \) meets the requirement of being antisymmetric with respect to interchange of two electron coordinates and, moreover, it fulfills the Pauli exclusion principle.

14
According to the variation principle, the best wavefunction is the one that minimizes the energy $\langle \Psi | H | \Psi \rangle$.\(^3\) In HF theory, the optimal MOs that minimize $\langle \Psi_{SD} | H | \Psi_{SD} \rangle$ are found by solving the set of $n$ one-electron canonical HF equations:

$$f(i)\chi(x_i) = \varepsilon\chi(x_i), \ i = 1 \ldots n,$$

where $\varepsilon$ is the energy of the MO $\chi$ occupied by electron $i$ and $f(i)$ is the so-called Fock operator [Eq. (2.5)] that acts only on the electron $i$.

$$f(i) = -\frac{1}{2} \nabla_i^2 - \sum_{A=1}^{N} \frac{Z_A}{r_{iA}} + V^{HF}(i)$$  \hspace{1cm} (2.5)

The first term in Eq. (2.5) computes the kinetic energy for the electron $i$, and the second term computes the potential energy between this electron and the fixed nuclei. The final term, the so-called HF potential, calculates in an average fashion the Coulomb potential energy between electron $i$ and all other electrons. Hence, HF theory is a mean-field theory that does not take into account the instantaneous interactions between the electrons. In addition, the HF potential also includes another interaction between the electrons, so-called exchange interaction, that does not have a classical counterpart. The exchange interaction arises as a consequence of the antisymmetric nature of the total wavefunction and occurs only between electrons with the same spin. Furthermore, it has the effect of reducing the overall electron–electron repulsion in the system. The calculation of the HF potential for electron $i$ requires prior knowledge of all other occupied MOs. The HF equations are therefore non-linear and have to be solved iteratively in a process known as the self-consistent field (SCF) procedure.

In Eq. (2.4), the HF equations are written in terms of MOs. However, in order to perform actual calculations, the spin parts of the MOs $\chi(x)$ have to be integrated out. This transforms the HF equations into a set of equations involving only the spatial parts $\psi(r)$ of the MOs. If one forces the $\alpha$ and $\beta$ electrons to occupy pairwise the same spatial part, which is done for closed-shell species in this thesis, the procedure is called restricted HF (RHF). On the other hand, if the $\alpha$ and $\beta$ electrons are associated with different spatial parts, the procedure leads to the unrestricted HF (UHF) equations, which are employed for radicals in this thesis.

UHF has the advantage over RHF to allow for a proper account of spin polarization, a feature which is very important for, e.g., the study of dissociation reactions or in the prediction of equilibrium geometries and hyperfine interactions of radicals.

However, a disadvantage of UHF is that the corresponding wavefunction is not an eigenfunction of the total spin operator for the electrons. This
means that UHF wavefunctions may be contaminated with spin states of higher multiplicity. Thus, one way of measuring the quality of an UHF calculation is to compare the computed expectation value of $S^2$ to the theoretical one. If the spin contamination is large, the usefulness of the UHF wavefunction will be limited since expectation values for other properties will also be an admixture of the properties of the different states contributing to this contamination effect.\textsuperscript{7}

For both RHF and UHF, the spatial parts of the MOs, $\psi(r)$, are expanded in a set of known basis functions:

$$\psi_j = \sum_{\mu=1}^{K} c_{j\mu} \phi_{\mu}.$$  \hspace{1cm} (2.6)

This procedure is known as the linear combination of atomic orbitals. In Eq. (2.6), $K$ is the number of basis functions used in the expansion and $c_{j\mu}$ is the expansion coefficient for the basis function $\phi_{\mu}$ in the MO $\psi_j$. This transforms the HF integro-differential equations into sets of matrix equations developed by Roothaan\textsuperscript{8} for RHF and by Pople and Nesbet\textsuperscript{9} for UHF. These matrix equations are solved in the SCF procedure by varying the expansion coefficients until an optimal set of coefficients have been found.

In general, the number of basis functions is much larger than the number of electrons present in the system which implies that only a fraction of the resulting MOs will be occupied with electrons. The remaining, unoccupied, MOs are referred to as virtual. The HF energy obtained with an infinite number of basis functions is called the HF limit energy. This is the best possible energy that can be obtained with the use of a single Slater determinant. The difference between the exact non-relativistic energy and the HF limit energy is referred to as the correlation energy. This quantity is always negative and, thus, the HF energy is always overestimated compared to the exact energy. Moreover, because a practical computation involves a basis set with a finite number of basis functions, the corresponding energy will be above the HF limit energy, according to the variation principle.

Correlation energy can be divided into dynamic and static correlation. Dynamic correlation is the part associated with the instantaneous electron–electron interactions not covered by HF. Static correlation, on the other hand, is associated with the deficiency of using only a single Slater determinant as the wavefunction during the MO optimization. For most systems, the lack of dynamical correlation is the main deficiency of the HF approximation. Static correlation might, however, become important when two, or more, Slater determinants formed from different sets of MOs are close in energy. In these cases, it may be necessary to use linear combinations of Slater determinants to represent the wavefunction during the MO optimization. An example of such a multi-reference method is provided by the com-
plete active space SCF method. The methods used in this thesis are all of single-reference character, meaning that the MOs are optimized by using a single Slater determinant for the wavefunction.

2.1.1 Configuration interaction

A Slater determinant formed from MOs is usually denoted a configuration. Thus, the Slater determinant formed from the $n$ HF optimized MOs of lowest energy – the ground state HF wavefunction – is called the HF configuration, $\Psi_{HF}$. Exchanging one of the occupied MOs in $\Psi_{HF}$ with a virtual MO creates another configuration, albeit of higher energy. Such other configurations are called excited configurations. In particular, excited configurations which differ by one MO relative to $\Psi_{HF}$ are singly excited ($\Psi_{S}$) while those differing by two and three MOs are doubly ($\Psi_{D}$) and triply ($\Psi_{T}$) excited configurations, respectively, and so forth.

In the configuration interaction (CI) method, the wavefunction is described as a linear combination of $\Psi_{HF}$ and excited configurations,

$$\Psi_{CI} = C_{HF}\Psi_{HF} + \sum_{S} C_{S}\Psi_{S} + \sum_{D} C_{D}\Psi_{D} + \sum_{T} C_{T}\Psi_{T} + \ldots \quad (2.7)$$

The $\Psi_{CI}$ ground state expansion coefficients are the elements of the eigenvector to the Hamiltonian matrix of lowest energy. A Hamiltonian matrix is built with elements of the type $<\Psi_{A}|H|\Psi_{B}>$, where $\Psi_{A}$ and $\Psi_{B}$ are the configurations $\Psi_{HF}$, $\Psi_{S}$, $\Psi_{D}$, and so forth. In fact, given a complete set (an infinite number) of MOs, diagonalization of the corresponding CI Hamiltonian matrix (the full CI matrix) yields the exact non-relativistic energy of the ground state and of all the excited states within the BO approximation. Unfortunately, the number of configurations grows fast with the number of MOs and the expansion in Eq. (2.7) is therefore truncated in actual CI calculations.

For ground state calculations, $\Psi_{HF}$ is usually the most important configuration, that is, the one with the largest coefficient. On the other hand, Bril-louin’s theorem states that $\Psi_{HF}$ does not mix with the singly excited configurations in the CI matrix, $<\Psi_{HF}|H|\Psi_{S}> = 0$. Therefore, truncation of Eq. (2.7) after the second term does not improve over HF theory. Thus, for ground state calculations, at least doubly excited configurations have to be included to improve the HF description of the system. The inclusion of the first and the third terms in Eq. (2.7) defines the CID method – the CI method with double excitations (doubles). However, the doubles do mix with the singles, so the latter configurations can indirectly influence the ground state properties of the system. The inclusion of the first three terms in Eq. (2.7) defines the CISD method.
A drawback with all truncated CI methods is that they are not size consistent. A method that is size consistent delivers the same energy for a system composed of two infinitely separated species as the sum of the energies of the isolated species.

An illustrative example on the failure of truncated CI to be size consistent is provided by the calculation of the energy of a non-interacting \( \text{H}_2 \) dimer (\( \text{H}_2 - \text{H}_2 \) with infinite separation) and the energy of two isolated \( \text{H}_2 \) molecules with the CID method. If CID was size consistent, it should deliver the same energy in both instances. For the isolated \( \text{H}_2 \) molecule, the CID expansion contains all doubly exited configurations. However, for the non-interacting dimer, excitations of all four electrons, which correspond to doubly excited configurations in the monomers, correspond to quadruple excitations and will not be included in the model. Thus, the energy of the dimer will not be equal to the sum of the energies of the monomers, but larger. Moreover, this erroneous behavior increases with the size of the system.

There are truncated CI methods which try to solve this problem by including quadruple excitations (e.g., the QCISD method). Actually, the quadruply excited configurations solve the problem for any system with 2 electrons. Nevertheless, as soon as the number of electrons becomes larger, the erroneous behavior persists and a limiting number of 50 electrons has been suggested for performing accurate calculations with such methods. However, whereas the truncated CI methods have the deficiency of not being size consistent they are variational, that is, they deliver energies that are upper bounds to the exact non-relativistic energy.

### 2.1.2 Møller–Plesset perturbation theory

Perturbation theory is a technique to acquire more accurate wavefunctions and energies by successive perturbations of an idealized model system with known eigenstates and eigenvalues. The Hamiltonian, \( \mathbf{H}^{(0)} \), ground state wavefunction, \( \Psi^{(0)} \), and ground state energy, \( E^{(0)} \), of the model system are said to be of zeroth order. The counterparts for the real system can then be written

\[
\mathbf{H} = \mathbf{H}^{(0)} + \mathbf{V},
\Psi = \Psi^{(0)} + \Psi^{(1)} + \Psi^{(2)} + \ldots,
E = E^{(0)} + E^{(1)} + E^{(2)} + \ldots
\]

(2.8)

where \( \mathbf{V} \) is the perturbation which leads to the Hamiltonian of the exact non-relativistic system while \( \Psi^{(A)} \) and \( E^{(A)} \) are the \( A^{th} \) correction to the zeroth order wavefunction and energy, respectively. In Møller–Plesset (MP) perturbation theory, which is a special case of Rayleigh–Schrödinger perturbation theory, \( \mathbf{H}^{(0)} \) is defined as the sum of one-electron Fock operators given in Eq. (2.5) while \( \Psi^{(0)} \) is the Slater determinant with HF optimized occupied
For this model system, the zeroth order MP energy (MP0) is given by the sum of the \( n \) occupied MO energies,

\[
E_{\text{MP0}} = E^{(0)} = \langle \Psi_{\text{HF}} | \mathbf{H}^{(0)} | \Psi_{\text{HF}} \rangle = \sum_{j} \varepsilon_j .
\]  

(2.9)

The MP perturbation which leads to the correct Hamiltonian is given by

\[
\mathbf{v} = \sum_{i=1}^{n} \sum_{j>i}^{n} \frac{1}{r_{ii'}} - \sum_{i} v^{HF}(i) ,
\]  

(2.10)

where \( v^{HF}(i) \) is the HF potential felt by electron \( i \). Because

\[
E_{\text{MP1}} = E^{(0)} + E^{(1)} = \langle \Psi_{\text{HF}} | \mathbf{H}^{(0)} | \Psi_{\text{HF}} \rangle + \langle \Psi_{\text{HF}} | \mathbf{V} | \Psi_{\text{HF}} \rangle = \langle \Psi_{\text{HF}} | \mathbf{H}^{(0)} + \mathbf{V} | \Psi_{\text{HF}} \rangle = E_{\text{HF}},
\]  

(2.11)

\( E^{(1)} \) is simply the correction that gives the HF energy. Thus, corrections to higher orders are required to improve on HF.

While the calculations of \( E_{\text{MP0}} \) and \( E_{\text{MP1}} \), only require the HF configuration, all higher order corrections include excited configurations. In particular, the second order MP correction to the energy is given by

\[
E^{(2)} = \sum_{J \neq \text{HF}} \frac{\langle \Psi_{J} | \mathbf{V} | \Psi_{\text{HF}} \rangle \langle \Psi_{\text{HF}} | \mathbf{V} | \Psi_{J} \rangle}{E^{(0)} - E_{J}} ,
\]  

(2.12)

and the MP2 energy is computed as \( E_{\text{MP1}} + E^{(2)} \). The sum in Eq. (2.12) formally runs over all excited configurations \( J \). However, by virtue of Brillouin’s theorem and due to the orthogonality of occupied and virtual HF MOs it can be shown that the terms involving singly excited configurations are zero. Moreover, due to the two-particle nature of \( \mathbf{V} \) introduced by the \( r_{i2}^{-1} \) terms, triply and higher excited configurations do not mix with \( \Psi_{\text{HF}} \). Thus, only terms involving doubly excited configurations participate in the summation in Eq. (2.12).

For systems which are reasonably well described by the HF configuration, \( e.g., \) closed-shell and open-shell species which exhibit low degrees of spin contamination and/or multi-configurational character, MP2 is usually a good choice of method. On the other hand, for systems where the HF configuration is heavily spin contaminated, the MP2 method can be highly erroneous and the results from such calculations must be viewed with precaution.
2.1.3 Coupled-cluster theory

In coupled-cluster (CC) theory,\textsuperscript{7,14} the wavefunction is defined by

\[ \Psi_{\text{CC}} = e^X \Psi_{\text{HF}}, \]  

(2.13)

which is known as the exponential ansatz. \( X \) is the so-called cluster operator given by

\[ X = X_1 + X_2 + X_3 + \ldots + X_n, \]  

(2.14)

where \( n \) is the number of electrons in the system. The various operators \( X_i \) generate the singly, doubly, triply excitations, and so forth, from the HF configuration. For example, \( X_2 \) generates all possible doubly excited configurations by

\[ \Psi_{\text{HF}}^{X_2} = \sum_{a<b} \sum_{r<s} t_{ab\rightarrow rs} \Psi_{\text{HF}} = \sum_{a<b} \sum_{r<s} \Psi_{ab\rightarrow rs}. \]  

(2.15)

In Eq. (2.15), the coefficient, or the amplitude \( t_{ab\rightarrow rs} \) represents the probability for the two electrons in the HF optimized occupied MOs \( a \) and \( b \) to interact and to become excited into the virtual MOs \( r \) and \( s \). The generation of the singly (\( X_a\rightarrow r \Psi_{\text{HF}} = t_{a\rightarrow r} \Psi_{a\rightarrow r} \)), triply (\( X_{abc\rightarrow rst} \Psi_{\text{HF}} = t_{abc\rightarrow rst} \Psi_{abc\rightarrow rst} \)) excited configurations, and so forth, are represented similarly, each with its own amplitude.

If the full cluster operator in Eq. (2.14) is employed, \( \Psi_{\text{CC}} \) becomes equivalent with the full CI wavefunction. However, also the CC wavefunction has to be truncated to make calculations amenable for most systems and the use of \( X = X_2 \) defines the CCD method while the CCSD method is obtained by \( X = X_1 + X_2 \).

The most important difference between CC and CI lies in the form of the truncated wavefunctions. For instance, after Taylor expansion, the CCD wavefunction takes the form:

\[ \Psi_{\text{CCD}} = e^X \Psi_{\text{HF}} = \left( 1 + X_2 + \frac{X_2^2}{2!} + \frac{X_2^3}{3!} + \ldots \right) \Psi_{\text{HF}}. \]  

(2.16)

By comparison of CC with CI, the first two terms in the CCD expansion in Eq. (2.16) define the wavefunction of the CID method. The remaining terms generate quadruply, hextuply excited configurations, and so forth, by independent excitations promoted by two or more cluster operators of lower orders. Configurations generated by such independent excitations are known as disconnected clusters while configurations generated by a single operator are
termed connected clusters. Hence, $X_{ab\rightarrow rs}X_{cd\rightarrow tu}\Psi_{HF}$ is a disconnected quadruple cluster while $X_{abcd\rightarrow rs tu}\Psi_{HF}$ is a connected one.

Returning to the example of the non-interacting $H_2$ dimer, it can be seen that the CCD method, defined for this system by the first three terms within the parentheses in Eq. (2.16), properly takes into account the quadruply excited configurations through the disconnected clusters. Indeed, the presence of disconnected clusters renders all truncated CC methods size consistent and it is precisely the lack of disconnected clusters that makes truncated CI non-size consistent.\(^7\)

It has been shown that the inclusion of connected triples, or even quadruple or higher excitations for special cases, might be necessary in order to achieve very high accuracy with CC theory for certain properties.\(^{15}\) However, due to the computational cost in terms of time requirements and computational resources, the methods cannot be routinely applied for large systems, and especially not for investigations of complex reactions, involving many stationary points that need to be addressed. In such cases, the so-called CCSD(T) method constitutes an alternative approach. In this method, the connected triples amplitudes are computed in a single step with perturbation theory.

CCSD(T) has been frequently used for predicting electronic energies of stationary points optimized at lower levels of theory in many of the papers presented in this thesis. This method has been shown\(^{16}\) to be quite insensitive to spin contamination in the reference UHF wavefunction as compared to, e.g., the MP2 method. A good example is provided by the recent study of Hemelsoet et al.\(^{17}\) who investigated the performance of a large number of methods to predict the reaction enthalpy at 298 K for hydrogen abstraction from benzene by the methyl radical. Even though the UHF wavefunction of the phenyl radical (one of the product species) was heavily spin contaminated ($<S^2> = 1.4$, as compared to 0.75 for a pure double state), CCSD(T) gave an enthalpy of reaction only 1.6 kcal/mol higher than experiment. In contrast, MP2 overestimated the reaction enthalpy by 24.7 kcal/mol, clearly indicating that this method should be avoided for prediction of energetic properties involving compounds with high spin contamination.

### 2.2 Density functional theory

Whereas WFT based methods focus on finding an optimal wavefunction for the system, DFT based methods focus on finding the optimal electron density ($\rho$) of the system. In DFT, the energy, and all other properties, are computed with so-called functionals of $\rho$. A functional is simply a function which takes another function as argument and delivers a number. Hohenberg and Kohn showed in a first theorem that the knowledge of the exact density makes it possible to compute exactly all ground state properties of the sys-
In a second theorem they proved that the functional of the density that delivers the exact energy obeys the variational principle. These two theorems placed DFT on solid physical grounds.

Hence, from a formal point of view, the problem of finding an optimal wavefunction, which depends on $3n$ electronic spatial coordinates, is reduced to the problem of locating the corresponding density which only depends on 3 spatial coordinates. However, despite this formal simplicity of DFT, its main problem is that the form of the exact energy functional is unknown. This disappointing fact has two critical consequences. First, it turns out that any approximate DFT method is non-variational. Second, because the form of the exact energy functional is unknown, there is no systematic strategy for constructing approximations to improve the description of the system similar to that in WFT where, for instance, CC provides an improvement over HF. Instead, the hierarchy of approximations used in DFT is based more or less on physical considerations of how the density behaves in molecular systems. Moreover, the vast majority of DFT methods include one or several empirically determined parameters.

Nevertheless, even though the exact energy functional is unknown, Kohn and Sham developed a scheme for optimization of the density given an approximate form of this functional. This scheme, known as the Kohn–Sham (KS) scheme, underlies virtually all DFT methods used today and, in particular, those used in this thesis. Moreover, if the exact energy functional was known, this scheme would lead to the exact density of the system.

The KS scheme is orbital based and starts by introducing a fictive system composed of $n$ non-interacting electrons moving in an external potential, $v_S$. Such a system is exactly described by a single Slater determinant and the optimal orbitals are given by the set of equations

$$
\left\{-\frac{1}{2} \nabla^2 + v_S(r)\right\}\psi_j(r) = \epsilon_j \psi_j(r),
$$

and the density is constructed from the orbitals by

$$
\rho_S(r) = \sum_j |\psi_j(r)|^2.
$$

What Kohn and Sham realized was that one can find a formal expression for the effective potential that transforms the density of the non-interacting system of electrons into the density for the real system of interacting electrons. For this purpose, they proposed a separation of the exact unknown energy functional, $E[p(r)]$, into some parts that one knows how to compute and one part that is unknown:
\[ E[\rho(r)] = T_s[\rho(r)] + E_{\text{nuc-el}}[\rho(r)] + J[\rho(r)] + E_{\text{XC}}[\rho(r)], \quad (2.19) \]

or in terms of orbitals:

\[
E[\rho(r)] = -\frac{1}{2} \sum_{j}^{n} \left\langle \psi_j(r) \right| \nabla^2 \left| \psi_j(r) \right\rangle - \sum_{A}^{N} \int \frac{Z_A}{|r - R_A|} \left| \psi_j(r) \right|^2 \, dr \\
+ \frac{1}{2} \sum_{j}^{n} \sum_{j'}^{n} \int \left| \psi_j(r) \right|^2 \frac{1}{|r - r'|} \left| \psi_{j'}(r') \right|^2 \, dr \, dr' + E_{\text{XC}}[\rho(r)].
\]

(2.20)

The first term in the partitioning of \( E[\rho(r)] \) is the functional for the kinetic energy of the system of non-interacting electrons while the second and the third terms are functionals for nuclear–electron and electron–electron Coulomb interaction, respectively. The final term, \( E_{\text{XC}}[\rho(r)] \), referred to as the exchange-correlation (XC) functional, is defined as to contain all of what is unknown. In particular, this functional includes the non-classical effects of both exchange and correlation, but also a portion of the kinetic energy which is not covered by \( T_s[\rho(r)] \). Furthermore, \( E_{\text{XC}}[\rho(r)] \) is also designed to correct for the self-interaction error in \( J[\rho(r)] \), an error which arises from the fact that the latter functional allows for one electron to interact with itself.

Next, because the expressions Eq. (2.19) and Eq. (2.20) are written for the exact energy functional, the variation principle is applicable. It can be shown that the set of orbitals that minimizes the energy has to fulfill the following equations:

\[
\begin{bmatrix}
-\frac{1}{2} \nabla^2 - \sum_{A}^{N} \frac{Z_A}{|r - R_A|} + \int \frac{\rho(r')}{|r - r'|} \, dr' + v_{\text{XC}}(r) \\
\end{bmatrix} \psi_j(r) = E_j \psi_j(r)
\]

(2.21)

where \( v_{\text{XC}}(r) \) is the so called XC potential defined by the functional derivative of \( E_{\text{XC}}[\rho(r)] \),

\[ v_{\text{XC}}(r) = \frac{\partial E_{\text{XC}}[\rho(r)]}{\partial \rho(r)}. \]

(2.22)

The final three terms in the Hamiltonian in Eq. (2.21) define an effective one-body potential, \( v_{\text{eff}}(r) \). Hence, by choosing \( v_S(r) = v_{\text{eff}}(r) \) in Eq. (2.17), the effective potential which transforms the density of the non-interacting system into the real density has been found. The equations (2.17) with \( v_S(r) = v_{\text{eff}}(r) \) are generally referred to as the KS equations and the resulting orb-
tals are called KS orbitals. As was the case with HF, the one-electron Hamiltonian in the KS equations depends on the orbitals that are to be found so even these equations have to be solved iteratively. However, an important difference between HF and KS is that, if the exact expression for $E_{\text{XC}}[\rho(r)]$ was known, the KS equations would provide the exact non-relativistic ground state solution within the space spanned by a given basis set, including all electron correlation effects that are missing in HF.

Hence, within the KS methodology, the approximation lies in the way that the XC functional is formulated. The next section briefly summarizes the main hierarchies of approximations available for DFT today and introduces the particular functionals employed in this thesis in some detail.

### 2.2.1 Exchange-correlation functionals

The approximate forms of the XC functional can broadly be divided based upon how much explicit information on the density that is included. In the simplest category, the XC energy is computed only with reference to the local value of the density $\rho(r)$ at the position $r$. These methods belong to the local density approximation (LDA) and treat the electron density as a uniform electron gas (UEG). However, LDA methods are theoretically sound only for systems where the density is slowly varying, such as in large metal surfaces, and do not perform well for molecules, in which the density can be far from slowly varying. Therefore, the next hierarchy of XC functionals, which often uses LDA as the starting point, incorporates also information on the gradient of the density $\nabla \rho(r)$ at position $r$. Such methods belong to the generalized gradient approximation (GGA). Finally, a third category of XC functionals, the so-called meta-GGA functionals, go one step further. In addition to depend on $\rho(r)$ and $\nabla \rho(r)$, they also depend on the Laplacian of the density $\nabla^2 \rho(r)$, and/or on the kinetic energy density of the KS orbitals $\tau(r)$ given by

$$\tau(r) = \frac{1}{2} \sum_{j}^{\text{oCC}} | \nabla \psi_j(r) |^2 .$$ (2.23)

In summary, the LDA, GGA and meta-GGA forms of the XC functional can by expressed, respectively, as:

$$E^{\text{LDA}}_{\text{XC}}[\rho(r)] = \int f(\rho(r)) \, dr$$ (2.24)

$$E^{\text{GGA}}_{\text{XC}}[\rho(r)] = \int f(\rho(r), \nabla \rho(r)) \, dr$$ (2.25)

$$E^{\text{meta-GGA}}_{\text{XC}}[\rho(r)] = \int f(\rho(r), \nabla \rho(r), \nabla^2 \rho(r), \tau(r)) \, dr$$ (2.26)
Usually, the XC functional is divided into two parts:

\[ E_{XC}[\rho(r)] = E_X[\rho(r)] + E_C[\rho(r)], \tag{2.27} \]

where \( E_X[\rho(r)] \) and \( E_C[\rho(r)] \) are functionals for the exchange energy and the correlation energy, respectively.

The main advantage of LDA is that the expression for the exchange energy is known exactly:

\[ E_X^{\text{LDA}}[\rho(r)] = \int \rho(r) \varepsilon_X^{\text{LDA}}(\rho(r)) \, dr, \tag{2.28} \]

where

\[ \varepsilon_X^{\text{LDA}} = \varepsilon_X^{S} = -\frac{3}{4} \sqrt{\frac{3 \rho(r)}{\pi}} \tag{2.29} \]

is the Slater exchange energy density.\(^{20}\) To this date, no exact expression is known for the LDA correlation energy and the most widely used approximation of this functional was developed by Vosko, Wilk and Nusair (VWN)\(^{21}\) on the basis of quantum Monte Carlo simulations performed on the UEG by Ceperley and Adler.\(^{22}\)

GGA exchange functionals are often formulated by a so-called enhancement factor to the LDA exchange:\(^{23}\)

\[ E_X^{\text{GGA}}[\rho(r)] = E_X^{\text{LDA}} - \int F[x] \rho(r) \, dr, \tag{2.30} \]

where \( F[x] \) is the enhancement factor and \( x \) is the reduced density gradient defined by

\[ x = \frac{\left| \nabla \rho(r) \right|}{\rho(r)^{4/3}}. \tag{2.31} \]

Two particular functionals for GGA exchange, which are formulated with an enhancement factor, have been employed in this thesis. The first one, called B88, was developed by Becke\(^{24}\) and the corresponding enhancement factor is given by

\[ F[x] = F^{\text{B88}}[x] = \frac{bx^2}{1 + 6bx \sinh^{-1} x}, \tag{2.32} \]
where the parameter $b$, which is equal to 0.0042, was found from a fitting procedure against the HF exchange energies computed for the noble gas atoms. The second GGA exchange functional is based on the PW91 enhancement factor proposed by Perdew and Wang:

\[
F[x] = F_{\text{PW91}}[x] = \frac{bx^2 - (b - \beta)x^2e^{-cx^2} - 10^{-6}x^d}{1 + 6bx\sinh^{-1}x - \frac{10^{-6}x^d}{A_x}}, \quad A_x = \frac{3}{2}\sqrt{\frac{3}{4\pi}},
\]

(2.33)

where $\beta = 5(36\pi)^{-5/3}$, $b = 0.0042$, $c = 1.6455$ and $d = 4$. The particular version of the PW91 exchange functional used in this thesis was developed by Adamo and Barone who modified the parameters $b$ and $d$ of this functional to 0.0046 and 3.73, respectively, by a fitting procedure to the rare gas dimers ($\text{He}_2$ and $\text{Ne}_2$) in order to improve the behaviour of this functional in low-density and large-gradient regions. The modified PW91 exchange functional is hereafter denoted “MPW”.

Two particular versions of the functional for GGA correlation have been employed: LYP and PW91. A special feature of the LYP functional, proposed by Lee, Yang and Parr and based on the approximate correlation energy formula for He atoms derived by Colle and Salvetti, is that it does not contain any LDA component.

Finally, one type of functional for meta-GGA correlation has been used. This functional, developed by Krieger, Chen, Iafrate and Savin, is denoted KCIS. The KCIS correlation functional includes reference to the kinetic energy density of the orbitals while the Laplacians are omitted and can be expressed as

\[
E_{\text{KCIS}}[\rho(r)] = \int f(\rho(r), \nabla \rho(r), \tau(r)) \, dr.
\]

(2.34)

In Eq. (2.34), $f$ is defined by

\[
f = \rho(r)e^{\text{GGAGAP}(\rho(r), \nabla \rho(r))} - \frac{\tau(r)^W}{\tau(r)} \rho(r)e^{\text{GGAGAP}(\rho(r), \nabla \rho(r))},
\]

(2.35)

where $\tau(r)^W$ is the so-called Weizäcker kinetic energy density given by

\[
\tau(r)^W = \frac{1}{8} \frac{|\nabla \rho(r)|^2}{\rho(r)}.
\]

(2.36)
For further reading, the reader is referred to the original reference\textsuperscript{29} and to the papers by Kurth, Perdew and Blaha\textsuperscript{30} and by Toulouse, Savin and Adamo\textsuperscript{31} who validate this functional. However, it is noted that a special feature of KCIS has to do with the $e_c^{\text{GGAGAP}}$ functional which is the correlation energy per particle of a UEG with a gap in the excitation spectrum. In contrast to the UEG, whose spectrum consists of a continuum of states, molecular or atomic spectra consist of discrete occupied energy levels up to the highest occupied molecular orbital and unoccupied energy levels up to the ionization threshold followed by a continuum of states. Therefore the gap introduced in the excitation spectrum in KCIS has been suggested to be more appropriate for molecular and atomic applications\textsuperscript{31}.

The most successful DFT methods available to date, in terms of chemical applications, are the so-called hybrid DFT methods.\textsuperscript{7} These methods incorporate a fraction of HF exchange (computed from KS orbitals) in the XC functional and rely on the adiabatic connection method which asserts that HF exchange arises as a natural component in the DFT exchange energy.\textsuperscript{5} In this thesis, four different hybrid DFT methods have been employed: B3LYP, BHandHLYP, MPWKCIS1K and B97-1. The first three methods are built up of the exchange and correlation functionals described above and will be briefly outlined below. The B97-1 method is a re-parameterized\textsuperscript{32} version of the 10-parameter hybrid GGA functional called B97 introduced by Becke.\textsuperscript{33} The B97-1 method was used in Paper VI for optimizing weakly bounded complexes since it was recently found\textsuperscript{34} to be promising for this purpose.

The B3LYP method is a 3-parameter hybrid GGA-functional and has the same form as that devised by Becke\textsuperscript{35} in 1993 for the B3PW91 functional:

$$E_{XC}^{\text{B3PW91}} = (1-a)E_X^S + aE_X^{\text{HF}} + bE_X^{\text{B88}} + E_C^{\text{VWN}} + cE_C^{\text{PW91}}. \quad (2.37)$$

The parameters in the B3PW91 functional ($a = 0.20$, $b = 0.72$ and $c = 0.81$) were determined from a linear least-square fit to the atomization energies, ionization potentials and proton affinities given for the atoms and molecules in Ref. 36. The B3LYP functional,\textsuperscript{37} is defined by setting $E_C^{\text{PW91}} = E_C^{\text{LYP}} - E_C^{\text{VWN}}$ in Eq. (2.37) and by using the same values for parameters $a$, $b$ and $c$, which results in the following expression:

$$E_{XC}^{\text{B3LYP}} = (1-a)E_X^S + aE_X^{\text{HF}} + bE_X^{\text{B88}} + (1-c)E_C^{\text{VWN}} + cE_C^{\text{LYP}}. \quad (2.38)$$

B3LYP is by far the most widely employed DFT method for applied quantum chemistry and many evaluations\textsuperscript{7} have proved that it is a reliable functional for general purpose use.
Whereas B3LYP includes 20% exact HF exchange, the second hybrid GGA-functional BHandHLYP\textsuperscript{38,39} employs 50% and is defined by:

\[ E_{\text{XC}}^{\text{BHandHLYP}} = 0.5E_{\text{X}}^\text{S} + 0.5E_{\text{X}}^\text{HF} + 0.5E_{\text{X}}^\text{B88} + E_{\text{C}}^\text{LYP}. \]  

(2.39)

Thus, compared to B3LYP in Eq. (2.38), BHandHLYP is given by the parameters \( a = 0.5, b = 0.5 \) and \( c = 1. \)

Finally, the MPWKCIS1K method, developed recently by Zhao, González-García and Truhlar,\textsuperscript{40} includes the above mentioned modified PW91 GGA functional (MPW) for exchange and the KCIS meta-GGA functional for correlation:

\[ E_{\text{XC}}^{\text{MPWKCIS1K}} = 0.59E_{\text{X}}^\text{MPW} + 0.41E_{\text{X}}^\text{HF} + E_{\text{C}}^\text{KCIS}. \]  

(2.40)

The amount of HF exchange (41%) was set by Truhlar and co-workers\textsuperscript{40} by minimizing the root-mean-square energy of Eq. (2.40) against the Kinetics\textsuperscript{9} database. This database contains forward and reverse barrier heights, and energies of reactions, for the three reactions in the BH6 database.\textsuperscript{41} Thus, MPWKCIS1K was developed for the purpose of yielding reliable predictions of kinetics. Indeed, in an evaluation of a large number of DFT functionals for predicting barrier heights for both hydrogen and non-hydrogen transfer reactions, the MPWKCIS1K functional was found to be one of the top three candidates.\textsuperscript{40} This method was even found to outperform the quadratic configuration interaction method QCISD for this purpose.\textsuperscript{40} Therefore, this method has been chosen in some of the papers for the prediction of activation and reaction energies.

### 2.3 Basis sets

The collection of mathematical functions that are used to expand the spatial part of the MOs (see Eq. (2.6)) constitutes the basis set and sets the limit for the one-electron space that can be covered in a calculation. Usually, basis functions are Gaussian shaped functions of the form:

\[ G_{ijk}(r_A, \alpha) = x^iy^jz^ke^{-\alpha r_A^2}, \]  

(2.41)

constructed to mimic the exact one-electron wavefunctions which appear when the SE is solved for the hydrogen atom. In Eq. (2.41), \( i, j \) and \( k \) are non-negative integers, \( \alpha \) is a positive real number, and \( r_A \) is the position of the electron relative to nucleus \( A \). By choosing the appropriate values for the parameters \( i, j \) and \( k \) in Eq. (2.41) one can form functions that display the
same symmetries as, e.g., the s-, p- and d-type wavefunctions of the hydrogen atom.

However, because of the exponential $-r^2$ dependence, single Gaussians are not good approximations to the hydrogenic atomic orbitals (AOs). First, they do not reproduce the cusp at the position of the nucleus. Second, they fall off too rapidly with distance. Therefore, basis functions ($\varphi$) are constructed as linear combinations of several Gaussians:

$$\varphi_A = \sum_s C_s G_{ijk}(r_A, \alpha_s) = \sum_s C_s x^i y^j z^k e^{-\alpha_s r^2_A}, \quad (2.42)$$

where the coefficients $C_s$ and exponents $\alpha_s$ are optimized in order to improve the description at the nucleus as well as to improve the fall off behavior with distance. A basis function formed by such a linear combination of Gaussians is called a contracted Gaussian and each Gaussian function is in turn referred to as a primitive Gaussian.

Basis sets can be divided in three categories: minimal, multiple-Z and split-valence (or valence-multiple-Z). These reflect the number of contracted Gaussians used to model the different AOs.

In a minimal basis set, each AO is modeled by one contracted Gaussian. Hence, these basis sets constitute the minimum number of basis functions that can possibly be used.

On the other hand, a multiple-Z basis set models the AOs by linear combinations of contracted Gaussians. This increases the number of basis functions and, hence, increases the flexibility of the one-electron space.

In the split-valence basis sets, core AOs are modeled by a single contracted Gaussian while valence AOs are modeled by linear combinations of such functions. The split-valence scheme is motivated by the fact that it is valence electrons that are mostly involved in, e.g., the formation of chemical bonds so increased flexibility in the corresponding AOs should be more important than for core AOs.

In addition, one may increase the description even further by augmenting the basis set with polarization and diffuse functions. The former are Gaussians of one or more quantum number higher than for the valence electrons. For example, a polarization function on carbon would be a d-type Gaussian since its valence AOs are of p-type. The use of polarization functions is highly motivated for studying chemical reactions because they allow for a better description of the wavefunction in regions where chemical bonds are broken and formed. Diffuse functions, which are Gaussians with small exponents $\alpha$, are designed to describe regions far away from the nucleus. Such functions may therefore be important to use for systems containing loosely bound electrons, such as anions.
There are two types of schemes for the contraction of primitives: segmented and general. In the segmented contraction scheme, used in the popular collection of basis sets developed by Hehre, Stewart and Pople, different primitives are used to model different AOs of same angular momentum. This means, for example, that the primitives used to model 1s AOs are different from those used for 2s. In contrast, the general contraction scheme, used in the also popular collection of so-called correlation-consistent basis sets developed by Dunning, the same primitive Gaussian is used to model all AOs of the same angular momentum. However, even if the primitives in the latter scheme are the same, they appear with different coefficients in the contracted Gaussians.

In this thesis, two Pople type basis sets, 6-31G and 6-311G, and one correlation-consistent basis set, cc-pVDZ, have been used.

The 6-31G basis set is a split-valence double-Z basis set and it models core AOs with a single contracted Gaussian composed of six primitives. The valence orbitals are represented by two basis functions: one contracted Gaussian of three primitives and one uncontracted primitive.

The 6-311G basis set is a split-valence triple-Z basis set and also models core AOs with a single contracted Gaussian composed of six primitives. However, the valence orbitals are represented by three basis functions: one contracted Gaussian of three primitives and two uncontracted primitives.

Moreover, diffuse functions and/or polarization functions of d- and/or f-type have often been added to both of the latter basis sets for atoms heavier than hydrogen while polarization functions of p-type in general have been added for the hydrogen atoms. For instance, the notation 6-311+G(2df,2p) means that the Pople type split-valence triple-Z basis set is augmented with diffuse functions (+ sign) and one f-type and a set of two d-type polarization functions for heavy atoms, while a set of two p-type polarization functions is added for hydrogen atoms.

The correlation-consistent cc-pVDZ basis set is a split-valence double-Z basis set and includes polarization functions for all atoms in its definition. This is the simplest of a series of correlation-consistent basis sets available which can be denoted cc-pVXZ, X = D, T, Q, 5, 6..., where, e.g., “Q” indicates that it is a split-valence quadruple-Z basis set. Diffuse functions added to these basis sets are denoted with the prefix “AUG-“, and a prefix “C” denotes that functions are added in order to describe more accurately the core orbitals, as in cc-pCV6Z.

Finally, the LanL2DZ basis set was employed for the iodine atoms in Papers IV, V and VI. This basis set uses the Los Alamos effective core potential to model all the core orbitals while it employs a double-Z description for the valence orbitals. In some calculations this basis set is supplemented with the d-type polarization and p-type diffuse functions of Check et al., in which cases it is referred to as LanL2DZdp.
It is a well-known fact that WFT based predictions with high accuracy for certain properties might require both a highly correlated method and a very large basis set. For example, in a study of the performance of different coupled-cluster methods, Helgaker et al.\textsuperscript{15} showed that rigorous predictions, that is, predictions that do not rely on fortuitous agreement or on agreement because of favourable error cancellation, of atomization energies to chemical accuracy (error $\sim 1$ kcal/mol\textsuperscript{15}) could be accomplished with CCSDTQ/cc-pCV6Z. Since this is an extremely high level of computation, it is not a tractable choice for hardly any system of realistic size with today's computer resources. Fortunately though, in the same investigation\textsuperscript{15}, the authors found that much lower levels of theories seem to be required for rigorous predictions of accurate relative energies of more importance for chemical reactions. Thus, the mean absolute error in calculated reaction enthalpies at 0 K for a set of isogyric reactions was, within chemical accuracy, 0.6 kcal/mol at the CCSD(T)/cc-pCVQZ level of theory.\textsuperscript{15}

As mentioned, the CCSD(T) method has been used frequently for the prediction of electronic energies in this thesis. In most of the papers, the 6-311+G(d,p) basis set is employed for this purpose. The main objective has not been to calculate energetics to chemical accuracy, but rather to explore and compare different mechanisms from a more qualitative point of view and it is assumed that this basis set gives sufficiently accurate results for this purpose.

In contrast to WFT, DFT based methods have proven more forgiving to the size of the basis set.\textsuperscript{7} In particular, it has been pointed out that the accuracy of predicted geometries for minima with such methods does not improve significantly when basis sets are increased beyond triple-Z.\textsuperscript{7} Moreover, it has been indicated that the addition of diffuse functions to a double-Z basis set may be more important than enlargement to triple-Z for improving the accuracy of predicted barrier heights and reaction energies with DFT.\textsuperscript{46}

In this thesis, DFT has primarily been used for the optimization of geometries and the calculation of vibrational frequencies of stationary points. However, in Papers III and IV, DFT was used for the prediction of energies as well. Typically, the geometries of stationary points have been optimized with the 6-31G(d,p) or 6-311+G(d,p) basis sets and a comparison made in Paper II between the stationary points optimized with B3LYP in conjunction with these two basis sets showed very small differences in the computed geometrical parameters.
2.4 Electronic structure analysis

Atomic partial charges
In a real molecular system, the charge is continuously smeared out over the whole space and atomic partial charges are therefore to a large extent a theoretical construct. Indeed, the magnitude of an atomic partial charge depends solely on the computational scheme used for its derivation. However, in order to understand, in a qualitative sense, the structure and reactivity of molecules, atomic partial charges might be useful to compute.

There are several different schemes available for deriving atomic partial charges and this section describes two schemes which have been used in this thesis.

In 1955, Mulliken\textsuperscript{47} derived an orbital based scheme for the calculation of atomic partial charges.\textsuperscript{7} This scheme is derived by first expanding the expression for the total number of electrons, \( n \), in AO components:

\[
\begin{align*}
    n &= \sum_{j}^{N} \int \psi_j(r)\psi_j(r)dr = \sum_{j}^{N} \sum_{r,s} \int c_{jr} \phi_r(r) c_{js} \phi_s(r)dr \\
    &= \sum_{j}^{N} \left( \sum_{r} c_{jr}^2 + \sum_{r \neq s} c_{jr} c_{js} S_{rs} \right). 
\end{align*}
\]  

In Eq. (2.43), \( r \) and \( s \) are AO indices, \( c_{jr} \) is the coefficient for basis function \( \phi_r \) in MO \( \psi_j \) and \( S_{rs} \) is the overlap integral between AOs \( r \) and \( s \) defined by

\[
S_{rs} = \int \phi_r(r) \phi_s(r)dr.
\]  

In Eq. (2.43), the overlap integral is a measure of the extent to which the AOs \( \phi_r \) and \( \phi_s \) overlap in space (\( S = 0 \) for orthogonal orbitals, \( S = 1 \) for fully overlapping orbitals). In Mulliken’s scheme, also known as Mulliken population analysis, electrons belonging to a single basis function are associated with the atom on which that basis function is centered. That is, the first sum in the last line of Eq. (2.43) is straightforwardly divided up amongst the \( N \) atoms in the system. The second sum represents electrons shared between two different basis functions. For these terms, Mulliken proposed that the electrons should be divided evenly on the atoms on which the basis functions \( \phi_r \) and \( \phi_s \) are centered. Given these rules, one arrives at the following formula for computing the electron population, \( n_k \), for atom \( k \):
\[ n_k = \sum_j \left( \sum_{r \in k} c_{jr}^2 + \sum_{r,s \in k,s} c_{jr} c_{js} S_{rs} + \sum_{r \in k,s \in k} c_{jr} c_{js} S_{rs} \right) \]  

(2.45)

and the Mulliken atomic partial charge, \( q_k \), for atom \( k \) is defined as

\[ q_k = Z_k - n_k, \]

(2.46)

where \( Z_k \) is the charge of nucleus \( k \). By using Mulliken population analysis, it is also possible to compute Mulliken atomic partial spin for radicals. In this case, the Mulliken spin on atom \( k \) is computed from the difference between the \( \alpha \) and \( \beta \) electron populations of this atom \( (n_{k,\alpha} - n_{k,\beta}) \).

Whereas Mulliken’s scheme is based on a partitioning of the wavefunction in terms of the basis functions, the second approach employed in this thesis determines the atomic partial charges by fitting them to reproduce the electrostatic potential (ESP) at selected points \( r \) on a “molecular surface”. The molecular surface is obtained as the union of atom centered spherical surfaces with specified radii that are typically chosen as some multiple of the atom’s van der Waals radius. The exact ESP at position \( r \) is defined by

\[ V_{\text{ESP,exact}}(r) = \sum_{k}^{\text{nuclei}} \frac{Z_k}{|r - r_k|} - \frac{1}{|r - r'|} \int \frac{\Psi'(r')^2}{|r - r'|} \, dr', \]

(2.47)

where \( Z_k \) is the charge of nucleus \( k \) and \( \Psi \) is the electronic wavefunction. The atomic partial charges, \( q_{k,i} \), are then determined by minimizing the difference between the exact ESP and the ESP generated by the atomic partial charges [Eq. (2.48)].

\[ V_{\text{ESP,fit}}(r) = \sum_{k}^{\text{nuclei}} \frac{q_k}{|r - r_k|} \]

(2.48)

The particular ESP fitting scheme used in this thesis is that proposed by Merz, Singh and Kollman (MK).\(^{48}\)

**Natural bond orbital analysis**

The basic idea of the natural bond orbital (NBO) analysis\(^{49}\) is to produce orbitals, NBOs, which, in contrast to the delocalized canonical MOs, are localized to either one, two or three centres, \( e.g. \), atoms. In this thesis, only one- and two-centred NBOs were considered. Two basic types of NBOs exist: Lewis-type donors (\( \sigma_i \)) and non-Lewis-type acceptors (\( \sigma_j^* \)). In the formal localized Lewis structure picture, the \( \sigma_i \) orbitals are occupied with 1 or 2 electrons while the \( \sigma_j^* \) orbitals have no occupation. The NBOs generated in
the NBO analysis are constructed such as to maximize the occupancy of the donor orbitals, i.e., to achieve a set of orbitals which, as closely as possible, mimics the localized Lewis structure picture. However, in the actual NBO analysis, the optimal donor and acceptor NBOs will generally not have integer occupation numbers. A deviation from 0 of the occupancy for some acceptor NBO signals that the structure is stabilized by delocalization of electrons from some donor(s) into that acceptor orbital. The energetic stabilization, \( \Delta E^{(2)}_{i\rightarrow j^*} \), resulting from delocalization from \( \sigma_i \) to \( \sigma_j^* \) can be estimated by 2nd-order perturbation theory:

\[
\Delta E^{(2)}_{i\rightarrow j^*} = -q_i <\sigma_i|\mathbf{F}|\sigma_j^*>^2/(\epsilon_j^* - \epsilon_i),
\]

where \( \mathbf{F} \) is the Fock or Kohn-Sham operator, \( \epsilon_i = <\sigma_i|\mathbf{F}|\sigma_i> \) and \( \epsilon_j^* = <\sigma_j^*|\mathbf{F}|\sigma_j^*> \) are the orbital energies for the donor and acceptor NBOs, respectively, and \( q_i \) is the occupancy of the donor orbital \( \sigma_i \). A large value of \( \Delta E^{(2)}_{i\rightarrow j^*} \) indicates that delocalization from \( \sigma_i \) to \( \sigma_j^* \) is a substantial contributor to the energetic stabilization of the species.

**Hyperfine coupling constants**

Electron spin resonance (ESR) spectroscopy is an important technique to study radicals. The key ESR property calculated in this thesis is the isotropic hyperfine coupling constant (hfcc) which is the separation between two consecutive lines in the ESR spectrum observed for the given radical. This corresponds to the hyperfine splitting which is due to the interaction between the spin \( S \) of the unpaired electron and the spin \( I_N \) of any magnetic nucleus \( N \) present in the radical when an external magnetic field \( B \) is applied. The hyperfine splitting of a given magnetic nucleus of the radical is proportional to the unpaired spin density at the position of this nucleus. Thus the hfcc's provide an indication of the distribution of the unpaired electron spin throughout the radical.

For instance, in the simple case of the hydrogen atom, the hyperfine interaction is given by the following spin Hamiltonian:

\[
H = H_e + H_{\text{nucl}} + a_{\text{H}} S \cdot I_{\text{H}}
\]

where \( a_{\text{H}} \) is the hfcc of the proton and \( H_e \) and \( H_{\text{nucl}} \) are the electronic and nuclear Zeeman terms, respectively:

\[
H_e = (-e/2m_e)g_S^z B
\]

\[
H_{\text{nucl}} = (-e/2m_p)g_{\text{H}}^I I_{\text{H}} B
\]

* A magnetic nucleus is a nucleus with nonzero spin.
Here, \( m_e \) and \( m_p \) are the electron and the proton mass, respectively; \( g \) and \( g_{\text{H}} \) are dimensionless constants called the g-values of the electron\(^{\dagger} \) and the proton, respectively; \( S_z, I_{\text{H}} \) and \( B \) are the z-components of the electronic \( S \) and nuclear \( I_{\text{H}} \) spin angular momenta and of the external magnetic field \( B \).

Hence, the ESR spectrum of the hydrogen atom is:

\[
\text{Hence, the ESR spectrum of the hydrogen atom is:}
\]

where the dotted line shows what would be observed if there were no nuclear hyperfine interaction.

In general, the observed ESR spectra are much more complicated than the simple spectrum of the H atom, because there are many factors, such as the temperature dependence and various matrix (or solvent) effects, which influence the actual ESR experiment. Therefore the analysis of the observed ESR spectra is often difficult and complementary theoretical calculations are often necessary to provide a comprehensive understanding of the structure and the reactivity of radicals.

\(^{\dagger}\) It should be noted that the g-value of the free electron is \( g_e = 2.002319 \) but deviations from this value are observed in atomic and molecular environments.
3 Bicyclopropylidiene radical cation: Rearrangement to the tetramethyleneethane radical cation (I)

Bicyclopropylidene (BCP) is a tetrasubstituted ethylene in which one cyclopropane ring is connected to each of the ethylene carbon atoms (Figure 2a). The rich chemistry of this compound has made it interesting for synthetic applications. For example, BCP has proven to be a highly useful building block for the preparation of cyclopropyl-containing compounds.50

Figure 2. a) Bicyclopropylidene (BCP). b) Rearrangement of BCP$^+$ to the tetramethyleneethane radical cation (TME$^+$). c) Dis- and conrotatory alternatives for the motions of the hydrogen atoms during the ring openings in BCP$^+$.

The chemistry of the corresponding radical cation (BCP$^+$) was also extensively studied by means of ESR and electron-nuclear double resonance (ENDOR) measurements. The first studies indicated that BCP$^+$ is highly unstable and undergoes ring opening to the tetramethyleneethane radical cation (TME$^+$) (Figure 2b), a reaction which was observed to proceed rapidly in a CF$_3$CCl$_3$ matrix at 77 K.51 The corresponding $^1$H hfccs, 7.16 G and 8.05 G, were assigned to two sets of four equivalent protons in TME$^+$. In addition, the rearrangement from BCP$^+$ was suggested to follow a stepwise
mechanism similar to the disrotatory mode (Figure 2c) predicted for the isomerization of the methylenecyclopropane radical cation to the trimethylenemethane radical cation.  

Later ESR measurements showed that BCP$^+$ could be isolated in other matrices. In particular, the compound was observed to be stable up to 100 K in CFCl$_3$ and CF$_2$CICFCl$_2$ matrices while it rearranged to TME$^+$ at higher temperatures in the former matrix. Hfcs corresponding to two sets of four equivalent protons (22.4 G and 2.7 G) were observed for BCP$^+$ which are strikingly different from those found for TME$^+$. Moreover, the unequal magnitudes observed for the two sets of protons of BCP$^+$ suggested that, when it is ionized, BCP transforms from a planar compound to a species which is twisted about the central C–C bond. Twisting about ionized double bonds is characteristic for alkene radical cations, in particular, a torsion angle of ca. 25° is observed for the ethylene radical cation. It was also confirmed in ab initio calculations on BCP$^+$ which, on the one hand, predicted the torsion angle about this bond to be 32.8° at the HF/6-31G(d,p) level, as opposed to the 0° dihedral angle expected for D$_{2h}$ symmetric BCP. On the other hand, the calculations indicated, surprisingly, that the ionization of BCP involved only a minor elongation of the central C–C bond, 0.028 Å, a value which should be compared to the observed elongation of about 0.07 Å of ethylene when it is ionized. Hence, the expected weakening of the central C–C bond in BCP upon removal of a π electron seems to be partially counterbalanced by the cyclopropane moieties.

Even though a stepwise disrotatory pathway was suggested, there are many alternative mechanisms for the present rearrangement, e.g., concerted and/or conrotatory ring opening, which have not been considered. Therefore, a detailed investigation of the mechanism for the rearrangement of BCP$^+$ to TME$^+$ was undertaken in Paper I. Moreover, the electronic structure of BCP$^+$ was analyzed by means of the NBO method in order to rationalize the unusually short central C–C bond computed for this compound. The geometries of the stationary points were optimized with B3LYP/6-31G(d,p). Gibbs energies based on rigid rotor and harmonic oscillator approximations were subsequently obtained at 100 K and 1.0 atm from CCSD(T)/cc-pVDZ computed electronic energies and the B3LYP/6-31G(d,p) frequencies.

### 3.1 BCP$^+$ and TME$^+$

One minimum of BCP$^+$ (1) and two minima of TME$^+$ (2 and 3), see Figure 3, were located in Paper I.

It is noted that the main geometrical features computed for BCP$^+$ are reproduced at the DFT level. Hence, as indicated by the C3C1C1’C2’ dihedral angle, 1 is found to be twisted by 37.3° about the central C–C bond.
Moreover, the C1–C1’ bond length is predicted to be only 1.317 Å, consistent with the short bond optimized\textsuperscript{53} at the HF level.

Structures 2 and 3 of TME\textsuperscript{+} differ mainly by the value of the torsion angle about C1–C1’, 10.7° and 90.0° for the former and the latter species, respectively. The perpendicular compound 3 is found to be about 1.5 kcal/mol more stable than 2 at the CCSD(T) level. However, no TS which would connect the two TME\textsuperscript{+} compounds by internal rotation was found in the present study. A detailed analysis of the corresponding reaction path indicated, instead, the presence of a cusp at a torsion angle of ~42° on the energy profile. It was also found that the character of the singly occupied molecular orbital changes abruptly from one side of the cusp to the other. These facts indicate that an excited state PES might be crossing the radical cation ground state surface at this point.

Figure 3. B3LYP/6-31G(d,p) optimized geometries of the minimum energy structures obtained for BCP\textsuperscript{+}, 1, and TME\textsuperscript{+}, 2 and 3, with selected distances (Å) and dihedral angles (degrees).

The B3LYP calculated \textsuperscript{1}H hfccs of 1, 2 and 3 are displayed in Table 1 together with experimental values reported for BCP\textsuperscript{+} and TME\textsuperscript{+}. A close agreement is noted between the computed and experimental values of the hfccs for 1. Moreover, the calculated hfccs of 2 and 3 are both close to those obtained with ESR for TME\textsuperscript{+}.

<table>
<thead>
<tr>
<th>Table 1. B3LYP/6-31G(d,p) calculated \textsuperscript{1}H hfccs (in Gauss) for the compounds 1, 2 and 3 compared to experimental values. See Figure 3 for the atom labels.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogens</td>
</tr>
<tr>
<td>B3LYP</td>
</tr>
<tr>
<td>a</td>
</tr>
<tr>
<td>b</td>
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<tr>
<td>Exp.</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reference 53.  
\textsuperscript{b} Reference 51.
An NBO calculation was carried out on 1 in order to investigate the origin of the unusually short central C–C bond predicted for this compound. As outlined in Section 2.4, using perturbation theory, it is possible to estimate the stability exerted on a species from delocalization of electrons from Lewis type occupied NBOs into non-Lewis type unoccupied NBOs. It is found that the main electron delocalizations that stabilize this species comes from electron transfer from the distal (C2–C3 and C2’–C3’ in Figure 3) $\alpha$ and $\beta$ $\sigma$-bonds into non-bonding orbitals centered on C1 and C1’. Moreover, a large stabilizing interaction is computed for the delocalization of $\beta$ electrons from the proximal (C1–C2, C1–C3, C1’–C2’ and C1’–C3’ in Figure 3) $\sigma$-bonds into the same non-bonding orbitals centered on C1 and C1’. Thus, the NBO calculations indicate that the removal of one electron from the $\pi$-bond in BCP is partially compensated for by electron transfer from the $\sigma$-bonds in the cyclopropane rings into unoccupied orbitals located on the central carbon atoms in BCP$^+$. These hyperconjugation effects might therefore explain the short distance of the central C–C bond predicted for 1.

3.2 Rearrangement mechanism

Several pathways for the rearrangement of BCP$^+$ to TME$^+$ were investigated. In particular, both stepwise and concerted opening of the two rings were studied, with both disrotation and conrotation of the hydrogen atoms. However, all attempts of finding stationary points along these paths collapsed to one particular channel, which involves successive opening of the two rings with disrotation of the hydrogen atoms during each ring opening. The Gibbs energy profile for this path is displayed in Figure 4 where compounds 1, 6, 8, 2 and 3 are energy minima while species 5, 7, 9 and 10 are characterized as TSs. The total reaction is predicted to be highly exergonic, $-17.4$ kcal/mol, which explains why TME$^+$ becomes the dominant species in the ESR experiments at elevated temperatures. Moreover, the first ring opening is found to be rate-determining for the isomerization, with a computed activation energy of 7.3 kcal/mol for TS 5. It is also noted that this first ring opening proceeds stepwise via a shallow intermediate (6). In contrast, the second ring opening, which passes through TS 9, is predicted to be barrierless. It is finally noted that TS 9 connects to a planar bifurcation TS (10) which in turn connects to the TME$^+$ compound 2 by a small rotation about the central C–C bond in either direction (see also Figure 3).
Interestingly, each ring opening step is found to proceed with a striking rehybridization of the carbon atom in the central C–C bond closest to the bond which is broken. Hence, during the transformation of 1 to TS 5 (8 to TS 9), the central carbon atom changes hybridization from sp^2 to sp^3 character and further back to sp^2 when structure 8 (10) is formed. Indeed, this pyramidalization is found to be an essential part of the reaction coordinate in the lowest energy path. This fact is illustrated in Figure 5 which shows how the C2–C3 distance (solid line) and the C3C2C1C1’ dihedral angle (dashed line) change versus the energy during the transformation of 1 to 5 as traced out by the intrinsic reaction coordinate (IRC). The C2–C3 bond is the bond that is broken in this reaction and the C3C2C1C1’ torsion angle is used as a measure of the degree of pyramidalization of C1. As can be clearly seen in Figure 5, the rehybridization dominates over C2–C3 bond breaking almost until the point i2 is reached and only thereafter does the ring opening become the dominating reaction coordinate. To further analyze the impact of the pyramidalization on this first ring opening, a constrained optimization scan was performed at the B3LYP/6-31G(d,p) level. In that scan, the C3C2C1C1’ dihedral angle was held frozen to prevent C1 from undergoing rehybridization, while the C2–C3 bond was opened incrementally by 0.05 Å. Indeed, the corresponding energy profile showed that such a pathway is associated with a barrier that has approximately 12 kcal/mol higher energy than that

---

‡ The constrained optimization scan is unpublished work and is therefore not found in Paper I.
defined by TS 5, which further supports the significance of the rehybridization.

Figure 5. The C2–C3 distance (Å) and the variation of the C3C2C1C1’ dihedral angle (degrees) as taken from the B3LYP/6-31G(d,p) IRC path from 5 to 1. The relative energy is presented against the elongation of the C2–C3 distance (solid line) and the variation of the C3C2C1C1’ dihedral angle (dashed line). i1 and i2 are two intermediate points on the IRC path.
4 Isomerization of the norbornadiene radical cation to the cycloheptatriene radical cation (II)

The PES of C\textsubscript{7}H\textsubscript{8}\+. has been reported to contain an unusually large number of stable isomers including, e.g., the radical cations of norbornadiene (N\textsuperscript{+}), quadricyclane (Q\textsuperscript{+}), toluene, cycloheptatriene (CHT\textsuperscript{+}), and methylenecyclohexadiene. In particular, the facile rearrangement of Q\textsuperscript{+} to N\textsuperscript{+}, considered to be a prototype for one-electron oxidation reactions, has been studied extensively\textsuperscript{55-62} and was also given special attention\textsuperscript{63} due to its potential application for solar energy storage.

In ESR experiments\textsuperscript{64-66} it was shown that both Q\textsuperscript{+} and N\textsuperscript{+} could rearrange further to CHT\textsuperscript{+}. Starting from N\textsuperscript{+}, a multi-step mechanism via Q\textsuperscript{+} and the stable bicyclo[2.2.1]hepta-2-ene-5-yl-7-ylium radical cation\textsuperscript{67} (BHE\textsuperscript{+}) was later proposed\textsuperscript{68} to account for this transformation (Figure 6a).

\textbf{Figure 6.} a) The proposed\textsuperscript{68} multi-step mechanism via Q\textsuperscript{+} and BHE\textsuperscript{+} for the isomerization of N\textsuperscript{+} to CHT\textsuperscript{+}. b) The alternative route for the rearrangement of N\textsuperscript{+} to CHT\textsuperscript{+} which starts by cleavage of the bridgehead–methylene bond, as investigated in Paper II.

However, for the isomerization of N\textsuperscript{+} to CHT\textsuperscript{+}, there are alternative pathways which have not been considered. In particular, the neutral rearrangement of N to CHT was suggested\textsuperscript{69,70} to proceed by initial opening of the bridgehead–methylene bond but this mechanism has not been taken into
account for the corresponding radical cation isomerization. This fact motivated the study performed in Paper II. There, the rearrangement of N⁺ to CHT⁺ by opening of a bridgehead–methylene bond is investigated (Figure 6b). Moreover, a recent mass-spectral investigation of substituted norbornane β-amino alcohols showed that opening of the bridgehead–methylene bond becomes favoured if the methylene hydrogen atoms are substituted with methyl groups. Therefore, the corresponding rearrangement of a substituted version of N⁺ was also investigated in Paper II in which the two methylene hydrogen atoms are replaced by methyl groups.

Three rearrangement channels from N⁺ to CHT⁺ initialized by opening of a bridgehead–methylene bond were located in the present study. The first path: N⁺ – TS1 – NCD⁺ – TS2 – CHT⁺ involves concerted isomerization to the norcaradiene radical cation (NCD⁺) followed by ring opening to CHT⁺. In the second channel: N⁺ – TS3 – I₁ – TS4 – NCD⁺ – TS2 – CHT⁺, the opening of the bridgehead–methylene bond proceeds via a stable intermediate (I₁) before rearrangement to NCD⁺ whereas in the final path located here: N⁺ – TS3 – I₁ – TS5 – CHT⁺, the compound I₁ transforms to CHT⁺ in a single step. It is found that the first channel, which will be referred to in the following either as the “concerted channel” or the “lowest energy pathway”, involves the lowest activation energy and it will therefore be the main concern of this summary.

For the unsubstituted system, B3LYP and MP2 were used for geometry optimization. Gibbs energies based on rigid rotor and harmonic oscillator approximations were subsequently obtained at 100 K and 1.0 atm for the B3LYP optimized structures using CCSD(T) computed electronic energies and the B3LYP frequencies. For the substituted system, B3LYP was used throughout. All calculations were performed with the 6-311+G(d,p) basis set, unless otherwise is noted.

4.1 N⁺ and CHT⁺

The B3LYP and MP2 computed ¹H hfccs of N⁺ and CHT⁺ are given in Table 2. This table also includes pictures of these compounds with selected geometrical parameters as optimized at the two levels of theory. It is noted that both methods predict similar geometries for N⁺ and, moreover, yield ESR parameters in good agreement with those measured for this compound.

The situation is different for CHT⁺, as can be seen in Table 2. Hence, for this species, the ¹H hfccs computed with B3LYP are close to the experimental values. On the contrary, the ESR parameters computed with MP2 for CHT⁺ deviate both qualitatively and quantitatively from the measured ones. In particular, the MP2 ¹H hfccs for H₁ₐ and H₁₈ are 56.9 and 21.4 G, respectively, while the corresponding experimental value is 51.5 G for both
H atoms (see Table 2 for the labels). However, this deviation can be explained by the fact that a bent equilibrium structure is predicted for CHT$^+$ with this method, while B3LYP optimizes the compound to a planar geometry.

Table 2. $^1$H hfcc values (in Gauss) for N$^+$ and CHT$^+$ as computed with B3LYP/6-311+G(d,p) and MP2/6-311+G(d,p). Pictures are provided for both compounds with selected bond distances (in Ångström) and angles as optimized at the two levels of theory (MP2 within parentheses).

<table>
<thead>
<tr>
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<td>51.5</td>
<td>5.7</td>
<td>—</td>
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$^a$ $^1$H hfcc values assigned to an ESR spectrum of N$^+$ in a zeolite matrix at 175 K.$^{65}$

$^b$ $^1$H hfcc values assigned to an ESR spectrum of CHT$^+$ in a CF$_2$ClCFCl$_2$ matrix at 77 K.$^{72}$

A planar geometry for CHT$^+$ is consistent with all theoretical$^{68,73}$ and most experimental$^{57,72,74}$ observations of this compound. Only one ESR investigation on this ion, which was performed in a CCl$_3$CF$_3$ matrix at 70 K, indicated that the equilibrium structure might be slightly bent.$^{75}$ However, the authors of that study concluded that the observed non planar geometry probably reflects matrix effects.$^{75}$

One explanation for the non planar geometry found with MP2 for CHT$^+$ might be attributed to the large spin contamination of its reference wavefunction ($<S^2> = 1.023$). This suggests that the geometry might be an artefact of the computational method. However, a planar CHT$^+$ conformation obtained with MP2 is here found to be a shallow TS ($v_{im} = 54i$ cm$^{-1}$) for inversion between two bent conformers, with a PMP2//6-311+G(d,p) computed activation energy of 0.2 kcal/mol. This fact could indicate that the measured $^1$H hfccs are average values over the reaction path between two bent conformers, passing through a planar TS.
4.2 Isomerization mechanisms

Gibbs energy profiles for the three isomerization mechanisms from N$^+$ to CHT$^+$ investigated in Paper II are displayed in Figure 7.

![Gibbs energy profiles](image)

*Figure 7.* Gibbs energy profiles (in kcal/mol) computed from CCSD(T)/6-311+G(d,p) electronic energies and B3LYP/6-311+G(d,p) thermal corrections to Gibbs energy at 100.0 K and 1.0 atm for the three channels from N$^+$ to CHT$^+$ investigated in Paper II. Selected B3LYP/6-311+G(d,p) geometrical parameters are given for the compounds in the lowest energy pathway. Distances are given in Ångström.

It can be seen in Figure 7 that the pathway that proceeds with concerted opening of the bridgehead–methylene bond to NCD$^+$ (solid line) has the lowest activation energy, 28.9 kcal/mol. The path that transforms I1 to CHT$^+$ in a single step (dotted line) has the highest barrier, 37.1 kcal/mol, while the channel which involves stepwise conversion to NCD$^+$ *via* I1 (dashed line) is intermediate in this respect, 31.2 kcal/mol.

The rearrangement of N$^+$ to TS1 in the lowest energy pathway involves mainly an elongation of the bridgehead–methylene bond (C1–C5 in Figure 7) from 1.552 Å in N$^+$ to 2.366 Å in TS1. Moreover, the symmetry plane in N$^+$ that cuts the atoms C1, C2 and C5 is preserved throughout the uphill path which implies that TS1 has got C₅ symmetry. On the neutral PES, opening of the bridgehead–methylene bond in N was suggested to lead to a diradical isotoluene intermediate in which the C1–C5 bond is fully opened.⁶⁹,⁷⁰ On the PES of C₇H₈$, this diradical would correspond to a distonic compound (D$^+$)
which, furthermore, has been shown to be a stable minimum in many theoretical studies. However, the IRC calculation performed in the forward direction from TS1 predicts that the reaction coordinate breaks symmetry at C1–C5 ~ 3.8 Å before the distonic compound is formed. At that point, the methylene group starts to rotate in order to attain a favourable conformation for the formation of the C1–C7 bond in NCD+, the closure of which then becomes the dominating reaction coordinate in the final part of the IRC. Interestingly though, a constrained steepest descent optimization from TS1 where approximate C5 symmetry is enforced for the bond opening indicates that the formation of D+ is barrierless. This can be seen in Figure 8 which shows the converged IRC (solid line) and the constrained optimization scan (dashed line) versus the C1–C5 distance. This result suggests that there exist a branching point on the IRC which separates the continued formation of the distonic compound from the formation of NCD+.

Figure 8. The IRC calculation from TS1 to NCD+ (solid line), and the constrained optimization scan from TS1 where approximate C5 symmetry is enforced on the C1–C5 bond opening (dashed line), as a function of the C1–C5 distance. Both calculations are performed at the B3LYP/6-31G(d,p) level of theory. The energy of NCD+ is taken as zero.

In agreement with structural parameters reported at the MINDO/3 level, the ring opening of NCD+ to CHT+ is found to pass through an unsymmetric TS (TS2). Moreover, the corresponding activation energy, 8.6 kcal/mol, is close to the previously reported barriers for this step. However, whereas the earlier calculations predicted that CHT+ is much more stable (6–17 kcal/mol) than NCD+, the present computations indicate that the two compounds have the same energy (Figure 7). This is an interesting result
because the associated activation energy is even lower than the barrier predicted for the facile $Q^+$ to $N^+$ reaction (10.1 kcal/mol) at the same level of theory. This fact suggests that $NCD^+$ might be observable in ESR or ENDOR experiments on $CHT^+$.

Finally, by comparison of the activation energy for the concerted channel ($N^+ – TS1 – NCD^+ – TS2 – CHT^+$), 28.9 kcal/mol, with the barrier for the previously proposed multi-step mechanism, 24.3 kcal/mol, it is concluded that opening of the bridgehead–methylene bond in $N^+$ probably is associated with a too high barrier for the concerted channel to be competitive with the multi-step one. In the next section, the effects of substitution on the concerted and multi-step channels are presented and discussed.

4.3 Substitution effects on the concerted channel

The fact that cleavage of the bridgehead–methylene bond in ionized norbornane $\beta$-amino alcohols was observed to be favoured over other paths when the methylene hydrogen atoms were substituted with methyl groups could indicate that the concerted channel found in Paper II becomes competitive with the multi-step mechanism under such conditions. Therefore, a study of both the concerted channel and the multi-step path was here undertaken, where the H atoms at C$_1$ (see Figure 7 for the labels) are substituted with CH$_3$ groups.

The names of all structures involved in the multi-step mechanism are taken from reference and these are here (except for $Q^+$ and $BHE^+$) augmented with the prefix “MS-“. Furthermore, all of the substituted compounds in both channels are augmented with the suffix “-2CH$_3$”, in order to distinguish them from the unsubstituted structures.

By comparison of the B3LYP optimized substituted and unsubstituted stationary points for both channels some interesting facts can be noted. The largest structural changes upon substitution are noted for the bonds connected to the substituted methylene carbon. Typically, these bonds are elongated by 0.01–0.02 Å upon substitution while the other bond distances deviate by less than 0.01 Å from those in the unsubstituted molecules.

However, the most significant structural changes appear when the compounds $N^+$, $NCD^+$ and $TS1$ are substituted. These structures, together with their substituted analogues ($N-2CH$_3$+, $NCD-2CH$_3$+ and $TS1-2CH$_3$) are displayed in Figure 9 with selected geometrical parameters. First, the C$_1$–C$_2$ and C$_1$–C$_5$ bonds in $N-2CH$_3$+ are predicted to be 0.030 Å longer than in $N^+$, indicating a substantial weakening of the bridgehead–methylene bonds in the substituted norbornadiene radical cation. Second, the lateral C$_1$–C$_2$ and C$_1$–C$_7$ bonds in the cyclopropane moiety of $NCD^+$ increase from 1.543 to 1.602 and 1.593 Å, respectively, upon substitution. Hence, in $NCD-2CH$_3$, the symmetry is broken, and the cyclopropane moiety has attained a struc-
ture that corresponds to the $^2\text{B}_2$ electronic state (one short and two long bonds) of the cyclopropane radical cation, which is the highest energy product when cyclopropane undergoes Jahn–Teller distortion upon ionization.\textsuperscript{79} Finally, when TS1 is substituted, the $\text{C}_1$–$\text{C}_5$ distance is shortened by 0.357 Å, and the $\text{C}_5$ symmetry is broken. These facts indicate that the TS between the substituted norbornadiene and norcaradiene radical cations is much earlier than the corresponding unsubstituted TS.

Figure 9. B3LYP/6-311+G(d,p) optimized geometries of $\text{N}^+$, $\text{NCD}^+$ and TS1 together with their substituted analogues. Bond lengths are given in Ångström.

Figure 10 and Figure 11 display B3LYP energy profiles for the unsubstituted and substituted pathways, respectively. Both the concerted (solid lines) and the multi-step (dashed lines) channels are represented.

By inspection of the multi-step energy profiles it can be concluded that the present substitution only has minor influence on the relative energies of the stationary points. It is noted in Figure 10 that the rate-determining TS on the unsubstituted multi-step pathway is MS-TS2. Figure 11 reveals that the corresponding substituted TS (MS-TS2-2CH$_3$) remains the point of highest energy on the substituted energy profile. Moreover, the magnitudes of their relative energies are similar: 24.2 and 23.8 kcal/mol for MS-TS2 and MS-TS2-2CH$_3$, respectively.

In contrast, it is found that the added methyl groups exert a significant stabilizing effect on the TS for concerted rearrangement of the norbornadiene radical cation to the norcaradiene radical cation. Hence, the relative energy reduces from 26.7 kcal/mol for TS1 to 18.2 kcal/mol for TS1-2CH$_3$. This result has two consequences. First, it is in agreement with the experimental observation that substitution of the methylene H atoms with methyl groups in ionized norbornane β-amino alcohols makes the opening of the bridgehead–methylene bond favoured.\textsuperscript{71} Second, since the overall barrier
height for the concerted substituted pathway is 5.6 kcal/mol lower than that for multi-step isomerization, the concerted channel becomes the minimum energy path on the substituted PES.

**Figure 10.** B3LYP/6-311+G(d,p) energy profiles (in kcal/mol) for the concerted (solid line) and the multi-step (dashed line) pathways from N^+ to CHT^+.

**Figure 11.** B3LYP/6-311+G(d,p) energy profiles (in kcal/mol) for the concerted (solid line) and the multi-step (dashed line) pathways from substituted N^+ to CHT^+.
The McLafferty rearrangement (MLR) is defined as a combined transfer of a \( \gamma \)-hydrogen atom (\( H_\gamma \)) to a double bonded atom through a six-membered TS, and cleavage of the \( \alpha-\beta \) bond (\( C_2-C_3 \) in Figure 12). It is a commonly observed fragmentation reaction for radical cations in mass-spectrometric investigations of carbonyl compounds.\(^8\)

One general issue related to the MLR is whether the reaction type occurs concerted, or stepwise via distonic intermediates. Indeed, the main body of experimental studies is interpreted in terms of a stepwise mechanism.\(^8\) For example, the extensive study by Stringer \textit{et al.} on \(^{13}\)C and \(^2\)H labelled ketones clearly indicated a stepwise rearrangement of the corresponding radical cations.\(^8\)

However, there are also experimental reports that point toward a concerted mechanism.\(^8\) Thus, Stone \textit{et al.} observed that the loss of acetaldehyde from the benzyl ethyl ether radical cation proceeds without hydrogen scrambling.\(^8\) This observation, and subsequent Rice-Ramsperger-Kassel-Marcus theory rate calculations on the same reaction,\(^8\) indicated that the MLR of this compound is concerted.

Conflicting results are also found in the reports on quantum chemical investigations of MLR reactions.\(^8\) Hence, two \textit{ab initio} studies at the HF level of theory located stepwise pathways for the MLR of the butanal radical cation (\( \text{Bu}^+ \)) to the vinyl alcohol radical cation and ethylene (Figure 12). However, the concerted mechanism can not be ruled out because the corresponding TS was not found in these investigations.\(^9\)

In contrast, channels for both stepwise and concerted MLR of \( \text{Bu}^+ \) were located in a semi-empirical study. Moreover, the barrier for the concerted rearrangement was found to be lower than for the stepwise mechanism, suggesting that the MLR of \( \text{Bu}^+ \) proceeds concerted. However, the semi-empirically optimized O–H distances in the concerted TS is very short (0.96
and 0.99 Å with the MNDO and AM1 methods, respectively), and casts doubt on whether this TS really belongs to a concerted pathway.\textsuperscript{92}

In Paper III, the stepwise and concerted mechanisms of the MLR of Bu\textsuperscript{+} were therefore reinvestigated. To further expand the theoretical knowledge of MLR reactions, a substituted Bu\textsuperscript{+}, the 3-fluorobutanal radical cation (3F-Bu\textsuperscript{+}), was also studied in Paper III. This particular substitution was chosen primarily because it has been found that the replacement of one of the hydrogen atoms in the methyl radical with CF\textsubscript{3} results in a destabilization of the formed \textsuperscript{12}CH\textsubscript{2}CF\textsubscript{3} radical.\textsuperscript{93} This suggests that fluorine atoms at position 3 in Bu\textsuperscript{+} (Figure 12) should exert a destabilizing effect on the distonic compounds formed after H\textsubscript{2} transfer, and possibly also favour a concerted rearrangement channel where radical localization on C\textsubscript{4} is avoided.

In this work, the MP2 method was used for geometry optimization. The spin contamination of the MP2 reference wavefunctions were found modest for most structures, the largest value of \langle S^2 \rangle being 0.860 and 0.894 for the unsubstituted and substituted structures, respectively. Therefore, the MP2 geometries are assumed to be of good quality. However, some stationary points could not be located at this level and these were instead optimized with BH\textsuperscript{2}andHLYP. Gibbs energies based on rigid rotor and harmonic oscillator approximations were subsequently obtained at 298.15 K and 1.0 atm for the species on the PES of Bu\textsuperscript{+} from CCSD(T) electronic energies and MP2 (or BH\textsuperscript{2}andHLYP) frequencies. For the compounds on the PES of 3F-Bu\textsuperscript{+}, MPWKCIS1K electronic energies were employed to obtain the Gibbs energies. B3LYP was used for the calculations of dipole moments, atomic spin densities and charges. The 6-311+G(d,p) basis set was used throughout.

5.1 McLafferty rearrangement of the butanal radical cation (III)

In Figure 13, the four channels of the MLR of Bu\textsuperscript{+} investigated in Paper III are a concerted mechanism, (1): (B) – (H) – (K) – (Products), and three stepwise channels: (2): (B) – (C) – (D) – (G) – (K) – (Products), (3): (B) – (C) – (D) – (L) – (K2) – (Products) and (4): (B) – (C) – (D) – (M) – (E) – (F) – (K2) – (Products), where (Products) refers to the vinyl alcohol radical cation and ethylene.

Compound (B) is the cyclic conformer of Bu\textsuperscript{+} while species (D) and (E) are cyclic and linear forms of the distonic compound in the stepwise routes, respectively. Finally, (K) and (K2) are two weakly bounded post-dissociation complexes. Of the TSs, (C) is the one for H\textsubscript{2} transfer while (M) is the TS that connects the two distonic species. Finally, (L), (F) and (G) are TSs for the C\textsubscript{2}–C\textsubscript{3} bond cleavage and (H) is the concerted TS.
Figure 13. Mechanisms of the McLafferty rearrangement of the butanal radical cation.

5.1.1 Concerted McLafferty rearrangement of Bu⁺

All attempts of optimizing the concerted TS, (H), with MP2 failed and collapsed to TSs involved in the stepwise pathways, a result which was also repeated with B3LYP. However, when using instead BHandHLYP, the sought TS was located. The optimized geometrical parameters of (H) (Figure 14) differ substantially from those obtained for the corresponding semi-empirical⁹² TS. In particular, both the O–H₇ and C₂–C₃ distances are very long (1.927 and 2.692 Å, respectively), implying that the concerted channel is highly asynchronous.

Figure 14. BHandHLYP/6-311+G(d,p) optimized geometry of the concerted TS (H) for the McLafferty rearrangement of the butanal radical cation. Distances are in Ångström.

To explore further the PES in the region of the concerted rearrangement, 2-dimensional constrained optimization scans were performed with B3LYP
(Figure 15a) and BHandHLYP (Figure 15b). These scans probed the PES for C$_2$–C$_3$ and O–H$_y$ distances varying from ca. 1.5 to 2.9 Å and from ca. 1.2 to 2.0 Å, respectively. At the converged points of the BHandHLYP scan, MP2 (Figure 15c) and spin-projected MP2 (PMP2, Figure 15d) single-point calculations were carried out to obtain approximate topologies of the PES for these methods as well.

The cause of the failure of B3LYP to locate (H) is obvious in Figure 15a. In order for the concerted TS to exist, there must be a local energy maximum that separates this channel from the stepwise one. On the B3LYP profile, no such local maximum exists. The point of highest energy on this energy profile is found at maximum O–H$_y$ and C$_2$–C$_3$ distances and the surface goes downhill in all directions moving towards lower values of these parameters. Similarly, the MP2 and PMP2 profiles also lack local maxima which explain why the concerted TS could neither be located with MP2. In contrast, Figure 15b reveals that the BHandHLYP profile have the required local maximum (V$_{_{\text{LMAX}}}$ in the figure) which explains why (H) could be located with this method.

![Figure 15. 2-dimensional energy profiles of the PES region for concerted rearrangement of Bu$^+$ at the various levels of theory. The concerted and the stepwise channels are highlighted with dotted and solid lines, respectively. Distances are in Ångström and energies in kcal/mol.](image-url)
5.1.2 Isomerization mechanisms

Gibbs energy profiles for the concerted pathway, (1), and the three stepwise channels, (2) – (4), are displayed in Figure 16.

A very high barrier, 37.7 kcal/mol, is predicted for the concerted rearrangement. During the transformation from (B) to (H), the calculated dipole moment increases from 5.6 to 103.3 D, indicating the presence of an unfavorable charge separation in the concerted TS which could be one explanation of the high relative energy of (H).

In contrast, the stepwise channels are found to be associated with much lower barriers. In particular, the barrier for the Hγ transfer is predicted to be only 2.2 kcal/mol, indicating that distonic compounds should be formed readily in MLR reactions. Following path (2) for cleavage of the C2–C3 bond implies initial rearrangement of (D) to the C5 symmetric complex (K) through a barrier of 16.9 kcal/mol. The complex (K) is stabilized by a weak bond formed between Hγ and the electron rich π-orbitals in the ethylene fragment (Figure 13). The facts that (K) is located 3.8 kcal/mol below (Products) and that the reverse activation energy back to (D) is rather high, 8.6 kcal/mol, might indicate that this complex plays an important role in the MLR of Bu+. Indeed, a similar complex formed prior to addition of the hydroxyl radical to acetylene has recently been experimentally observed.94 In path (3), the C2–C3 bond is broken via TS (L) which connects to the second complex (K2). The activation energy for this process, 13.6 kcal/mol, is 3.3 kcal/mol lower than for C2–C3 bond cleavage in path (2). Finally, in path (4), distonic (D) first rearranges to the 4.1 kcal/mol less stable linear distonic compound (E). The C2–C3 bond is subsequently cleaved via TS (F) with an activation energy of 9.8 kcal/mol. Also (F) is found to connect to (K2).

Because the structure with highest relative energy dictates the overall barrier height for each pathway it can be concluded that the stepwise paths (3) and (4) constitute the most plausible mechanisms for the MLR of Bu+ in the gas phase.
5.1.3 Redistribution of spin and charge

Mulliken atomic spin densities and atomic charges computed according to the MK protocol were obtained for all stationary points. Atomic group charges were obtained by summing the MK atomic charges of the hydrogens into their adjacent heavy atom.

Interestingly, a net 0.3 positive charge is transferred from the vinyl alcohol fragment into the ethylene fragment during transformation of (B) to the concerted TS (H). At the same time, the negative charge on the oxygen atom increases from −0.1 to −0.3. Indeed, this supports the idea that an unfavorable charge separation is built up in (H). During the downhill conversion to (K) in the concerted channel the positive charge is transferred back to the vinyl alcohol fragment via the H₇ transfer. Combining these facts with the observation that the spin density resides on the vinyl alcohol fragment during the whole isomerization from (B) to (K) implies that the C₂–C₃ and C₄–H₇ bond breaking steps in the concerted channel are of heterolytic nature.

In contrast, all of the stepwise pathways are found to proceed with homolytic bond cleavages. In particular, the H₇ transfer results in a complete localization of the spin at C₄ in (D) while the positive charge is distributed on the

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**Figure 16.** CCSD(T)//MP2 (CCSD(T)//BHandHLYP for (G) and (H)) Gibbs energy profiles (in kcal/mol) at 298.15 K and 1.0 atm for the concerted and stepwise McLafferty rearrangement of the butanal radical cation. All calculations have been done employing the 6-311+G(d,p) basis set.
other atoms. This confirms that cyclic (D) is distonic, a conclusion which also holds for linear (E). Regarding the cleavage of the C\textsubscript{2}–C\textsubscript{3} bond, the three paths can be divided in two groups. In channel (2), essentially all of the spin density and positive charge is fully transferred to the vinyl alcohol fragment in complex (K) which means that the electronic structure of (K) is product like. Therefore this complex may be characterized as an ion-molecule complex. On the contrary, in paths (3) and (4), the spin and charge are not fully located on the vinyl alcohol fragment until the compound has dissociated completely. In particular, the magnitudes of the atomic spin densities and group charges of C\textsubscript{3} and C\textsubscript{4} in complex (K\textsubscript{2}) are both 0.2 which shows that this complex is not product like and may therefore not be called an ion-molecule complex.

5.1.4 Substitution effects on the stepwise and concerted paths

The mechanisms located in Paper III for the MLR of 3F-Bu\textsuperscript{+} are displayed in Figure 17. One concerted channel: (3F-1) was found, as were three stepwise pathways: (3F-3), (3F-4) and (3F-5).

The names of the stationary points and paths on the substituted PES were chosen to be consistent with those on the PES of Bu\textsuperscript{+}. Thus, (3F-B) corresponds to substituted (B) and path (3F-1) is the substituted analogue of channel (1) and so forth (see further Figure 13 and Figure 17).

No substituted path corresponding to channel (2) was found since the substituted TS corresponding to (G) could not be located. Because of the lower symmetry of fluoroethylene compared to ethylene, the difference between (3F-3) and (3) on the one hand, and between (3F-4) and (4) on the other hand, is that the complex (K\textsubscript{2}), which is a common stationary point in the unsubstituted channels, is replaced by two distinct structures: (3F-K\textsubscript{2D}) and (3F-K\textsubscript{2E}) for the substituted paths (3F-3) and (3F-4), respectively (Figure 17).

Path (3F-5) emerges as a new channel from (3F-E-LM), which corresponds to (E) in the unsubstituted case, due to the possibility of hydrogen bonding between the F atom and the O–H\textsubscript{y} moiety. Thus, (3F-E-GM) is formed from (3F-E-LM) via internal rotation about the C\textsubscript{1}–C\textsubscript{2} bond through TS (3F-N), and (3F-K\textsubscript{3}) is a complex created through TS (3F-Q) when the C\textsubscript{2}–C\textsubscript{3} bond in (3F-E-GM) is broken.
Comparing the geometrical parameters of the substituted minima with the corresponding unsubstituted compounds reveals that the largest structural changes take place when (B) and (K) are substituted (Figure 18). In particular, the inter-fragment O–H$_y$ distance in (3F-B) is predicted to be 0.350 Å longer than in (B), indicating that the substituted species should be less susceptible to H transfer. Moreover, the complex (3F-K) is tilted away from C$_s$ symmetry as reflected, for instance, by the fact that the C$_1$–C$_2$–C$_3$–C$_4$ (C$_1$–C$_2$–C$_4$–C$_3$) dihedral angle is -87.2° (87.2°) in (K) and -63.0° (113.3°) in (3F-K). This geometrical change is driven by a favorable interaction between the F atom and the hydrogen atom H$_{2a}$ in the substituted complex (Figure 18).
Figure 18. MP2/6-311+G(d,p) optimized geometries of (B) and (K) together with their substituted counterparts. Distances are given in Ångström.

For the TSs the largest geometrical changes take place when (C), (L), (F) and (H) are substituted with the F atom (Figure 19). For TS (3F-C), a C_4–H_y (O–H_y) distance of 1.162 Å (1.562 Å) is computed which is 0.013 Å (0.103 Å) longer (shorter) than in (C), indicating that the substituted TS for H_y transfer is later than its unsubstituted counterpart. On the contrary, the two TSs (3F-L) and (3F-F) for C_2–C_3 bond cleavage are earlier than their unsubstituted counterparts as the C_2–C_3 distance in these species are shortened by 0.113 Å and 0.107 Å compared to (L) and (F), respectively.

However, the largest structural change is found for the concerted TS. This TS becomes much earlier with respect to the C_2–C_3 bond cleavage when it is substituted since this partial bond is shortened from 2.692 Å in (H) to 2.496 Å in (3F-H). Moreover, the computed C_4–H_y and O–H_y distances in (3F-H) of 1.087 and 2.323 Å, respectively, indicate that the substituted concerted rearrangement is even more asynchronous than its unsubstituted counterpart.

Thus, from a structural point of view, the hydrogen transfer seems less favorable while the likelihood of C_2–C_3 bond cleavage increases in the substituted system compared to the unsubstituted system.

Figure 19. MP2/6-311+G(d,p) optimized geometries (BHandHLYP/6-311+G(d,p) for (H) and (3F-H)) of the TSs (C), (L), (F) and (H) together with their substituted counterparts. Distances are given in Ångström.
Gibbs energy profiles for the concerted substituted pathway: (3F-1) and the three stepwise substituted channels: (3F-2) – (3F-4) are displayed in Figure 20. Interestingly, the predicted activation energy for the concerted substituted channel, 20.5 kcal/mol, is reduced by 17.2 kcal/mol as compared to the unsubstituted case. Again the relative energy can be related to the dipole moment. Hence, for (3F-H), the computed dipole moment is 12.1 D which is significantly lower than that of (H) (103.3 D), indicating that the unfavorable charge separation is reduced in the substituted concerted TS.

However, even the barriers for H\textsubscript{γ} transfer and C\textsubscript{2}–C\textsubscript{3} bond cleavages in the stepwise routes are largely influenced by the substitution. In particular, and in sharp contrast to the unsubstituted system, the H\textsubscript{γ} transfer is predicted to be the rate-determining step for all substituted channels. The corresponding activation energy, 4.9 kcal/mol, is 2.7 kcal/mol higher than for the unsubstituted H\textsubscript{γ} transfer. Hence, despite the reduction of the barrier for the concerted rearrangement, this mechanism cannot compete with stepwise fragmentation even with this particular substitution.

Finally, it is observed in Figure 20 that the hydrogen bonded structure (3F-E-GM) in path (3F-5) is the most stable species on the substituted PES and the equilibrium population is therefore predicted to be shifted towards this compound at room temperature. However, since complex (3F-K3) is the second most stable structure this complex might play an important role for the MLR of 3F-Bu\textsuperscript{+}.

**Figure 20.** MPWKCIS1K//MP2 (MPWKCIS1K//BHandHLYP for (3F-H)) Gibbs energy profiles (in kcal/mol) at 298.15 K and 1.0 atm for the concerted and stepwise McLafferty rearrangement of the 3-fluorobutanal radical cation. All calculations have been done employing the 6-311+G(d,p) basis set.
Positron emission tomography (PET) has emerged as a useful tool for investigation of biochemical processes in a living subject in a non-invasive manner. By introducing a positron emitting radionuclide in a compound (tracer) capable, for example, of binding to a certain protein, one may achieve valuable information on the in vivo location and function of that protein from this molecular imaging technique.

Amongst the common positron emitting radionuclides (i.e., $^{11}$C, $^{15}$O and $^{18}$F), $^{11}$C is probably the most versatile candidate due to the synthetic diversity of carbon chemistry. However, since $^{11}$C has a short half-life ($t_{1/2} = 20.4$ min), synthetic protocols allowing for rapid incorporation into the tracer are a prerequisite.

Only a few $^{11}$C-labeled compounds are available as starting materials for $^{11}$C-labeling synthesis and among them, $[^{11}$C]carbon dioxide$^{95,96}$ and hydrogen $[^{11}$C]cyanide$^{97,98}$ have previously been employed for labeling of aliphatic ester functionalities $R[^{11}$C]O$_2$R' (R, R' = alkyl) in the carbonyl position. However, these synthetic routes are associated with time consuming multi-step protocols which decrease the radiochemical yield of the products.

$[^{11}$C]carbon monoxide ($[^{11}$C]O) was until recently not much used for labeling because of difficulties in handling it in microscale. However, after development of suitable equipment,$^{99}$ it has proved to be a useful labeling reagent.$^{100}$

A synthetic route which has shown to be successful for creating carboxylic acids, esters and amides starting from unlabeled CO is the atom transfer radical carbonylation type reaction, widely studied by Ryu and co-workers.$^{101}$ Figure 21 illustrates the complex reaction mechanism occurring in a one-pot fashion, which involves (i) radical initiation by photolysis of alkyliodides, (ii) two reversible steps of chain propagation, and (iii) ionic quenching with the help of a base in order to shift the acyliodide to the desired acyl derivative.
Figure 21. Reaction mechanism of the one-pot procedure based on the iodine atom transfer carbonylation.

Whereas the radical carbonylation reaction provides generality in the sense that a large number of products may be formed, it is not directly applicable to the synthesis of $^{11}$C-labeled compounds due to the requirement of irradiation for several hours. However, it was recently shown that a modification of the radical-based approach involving the use of strong bases, or small amounts of suitable photochemical sensitizers (ketones), could lead to efficient production of aliphatic [carbonyl-$^{11}$C]esters with much shorter reaction times (5-7 min). Improved yields were also observed in reactions employing oxygen nucleophiles when acetone was used as a solvent and it was initially suggested that the ketones promote the photolysis of alkyliodides (step $i$ in Figure 21) by energy transfer from the excited triplet state.

In Paper IV, the radical carbonylation synthesis of aliphatic [carbonyl-$^{11}$C]esters was further investigated, with particular focus on the mechanism of action of the added ketones.

Eight different ketones were selected for this purpose. Four of these had $n\pi^*$ character of their low-lying triplets while the remaining ketones had $\pi\pi^*$ triplets. In all 8 cases, 10–20 nmol of $[^{11}C]$O were mixed with a CH$_3$OH/THF§ (1:1 v/v) solution containing 0.2 M 1-iodopentane and 0.01 M ketone and irradiated for 6 min and the radiochemical yield of methyl [carbonyl-$^{11}$C]hexanoate was measured [Eq. (6.1)].

---

§ Tetrahydrofuran
C₅H₁₁I + [¹¹C]O + CH₃OH $\xrightarrow{\text{Ketone}}$ C₅H₁₁–[¹¹C]O–OCH₃

(6.1)

The results of these experiments showed that the most efficient ketones had nπ* character of their triplets (25–59% yield) while the ketones with ππ* triplets were much less efficient (1–14% yield). It is known that carbonyl triplets can, in addition to acting as energy donors, abstract hydrogen atoms from their surroundings. Indeed, the efficiency by which the nπ* ketones promote the reaction in Eq. (6.1) was found to correlate well with their hydrogen abstracting abilities. This indicated that the ketones do not promote the C–I bond homolysis in the alkyliodides by direct energy transfer, but rather act in a more indirect manner by abstracting hydrogen atoms from one of the species in the reaction mixture, which in turn abstracts iodine from alkyliodide.

The latter hypothesis was strengthened in a new set of experiments on the reaction in Eq. (6.1) where the ketones were replaced with di-tert-butyl peroxide (BOOB). It is known that BOOB readily forms BO* radicals upon photolysis and that the formed alkoxyl radicals abstract hydrogens with similar efficiency as the benzophenone triplet (the ketone that resulted in the second highest radiochemical yield of the reaction in Eq. (6.1)). Indeed, the results showed that the ester was readily formed under this condition, although the radiochemical yield indicated that the efficiency depended on the balance between the concentrations of CH₃OH and THF. Further experiments using another peroxide (di-cumyl-peroxide) confirmed the importance of hydrogen abstraction for efficient ester production. Moreover, exchanging the CH₃OH alcohol against ethanol or 2-propanol in the presence of BO* radicals resulted in good radiochemical yields of the ester and high conversion of [¹¹C]O. However, low yield and [¹¹C]O conversion were obtained when benzyl or allyl alcohols were used.

Based on these observations, a mechanism was proposed for the investigated radical carbonylation reactions:

\[
\begin{align*}
\text{BOOB} + h\nu & \rightarrow 2\text{BO}^* \\
\text{BO}^* + \text{SH} & \rightarrow \text{BOH} + \text{S}^* \\
\text{S}^* + \text{RCH}_2\text{I} & \rightleftharpoons \text{SI} + \text{RCH}_2^* \\
\text{RCH}_2^* + \text{CO} & \rightleftharpoons \text{RCH}_2\text{C(O)}^* \\
\text{RCH}_2\text{C(O)}^* + \text{RCH}_2\text{I} & \rightleftharpoons \text{RCH}_2\text{C(O)}\text{I} + \text{RCH}_2^* \\
\text{RCH}_2\text{C(O)}\text{I} + \text{CH}_3\text{OH} & \rightarrow \text{RCH}_2\text{C(O)}\text{OCH}_3 + \text{HI}
\end{align*}
\]

Accordingly, the reaction sequence is initiated through Eqs. (6.2) – (6.4) where an alkoxyl radical first abstracts a hydrogen atom from either alcohol.

** It should be mentioned that experiments performed in ethanol resulted in high ester yields irrespective of whether THF was present or not.
or THF (SH = solvent molecule) which is followed by iodine atom transfer from the alkyliodide to $S^*$. The sequence continues with two equilibrium reactions – carbonylation [Eq. (6.5)], and acyliodide formation via iodine atom transfer from the alkyliodide [Eq. (6.6)]. Finally, the aliphatic \textit{[carbonyl-$^{11}$C]ester} is produced by quenching with alcohol [Eq. (6.7)].

\section{DFT calculations on the mechanism}

In order to provide a theoretical validation for the proposed mechanism, DFT calculations were performed on the reactions in Eqs. (6.4) – (6.6) using ethanol as a model for the solvent compound involved in the radical mechanism and ethyliodide as the model alkyliodide. In particular, the reactions addressed were: (6.8) the iodine transfer from ethyliodide to the 1-hydroxyethyl radical, (6.9) the carbonylation of the ethyl radical, and (6.10) the formation of the acyliodide by iodine transfer from ethyliodide.

\[ \cdot \text{OH} + \cdot \text{I} \rightleftharpoons \text{OH} \cdot \text{I} + \cdot \text{CH}_2\text{CH}_3 \] \hspace{1cm} (6.8)

\[ \cdot \text{CH}_2\text{CH}_3 + \text{CO} \rightleftharpoons \text{O} \cdot \text{CH}_2\text{CH}_3 \] \hspace{1cm} (6.9)

\[ \cdot \text{O} + \cdot \text{I} \rightleftharpoons \cdot \text{O} + \text{CH}_2\text{CH}_3 \] \hspace{1cm} (6.10)

Moreover, to understand better why both ethanol and 2-propanol gave high product yields and high conversion of \textit{[}$^{11}$C\textit{]}O while benzyl and allyl alcohols gave low yields and conversion, also the iodine transfer reactions from ethyliodide to the (6.11) carbon centered radicals derived from 2-propanol (1-hydroxy-1-methylethyl radical) and (6.12) allyl alcohol (1-hydroxy-1-vinylmethyl radical) were investigated.

\[ \cdot \text{OH} + \cdot \text{I} \rightleftharpoons \cdot \text{OH} + \cdot \text{CH}_2\text{CH}_3 \] \hspace{1cm} (6.11)

\[ \cdot \text{OH} + \cdot \text{I} \rightleftharpoons \cdot \text{OH} + \cdot \text{CH}_2\text{CH}_3 \] \hspace{1cm} (6.12)

Gas phase zero-point vibrational energy (ZPVE) corrected SCF energies were obtained at the MPWKCIIS1K/6-311+G(2df,2p)[H, C and O at-
oms]/LanL2DZdp[I atoms] level at geometries optimized with MPWKCIS1K/6-31+G(d)/LanL2DZdp. In order to take bulk solvation effects into account, single-point SCF calculations where performed at the gas phase optimized structures with MPWKCIS1K/6-311+G(2df,2p)/LanL2DZdp using the polarizable continuum model\textsuperscript{7,107} (PCM) with the standard parameters for ethanol.

For the carbonylation reaction, gas phase Gibbs energies were obtained based on rigid rotor and harmonic oscillator approximations. To estimate the corresponding free energy differences in ethanol solvent, solvation energies were computed as the difference between the gas phase energy of the optimized structure and the energy of the solvated structure. Then, to obtain the free energies in solution, a thermodynamic cycle\textsuperscript{7} was applied using these solvation energies and the gas phase Gibbs energies.

The results for the reactions in Eqs. (6.8) – (6.12) are summarized in Table 3. In general, only minor differences between the computed SCF and PCM-SCF energies are noted for these reactions.

Table 3. Reaction barriers ($\Delta E^\ddagger$) and reaction energies ($\Delta E_r$), in kcal/mol, for the reaction of carbon-centered radicals with ethyliodide [Eqs. (6.8), (6.10) – (6.12)] and for the carbonylation reaction [Eq. (6.9)]. Mulliken spin and charge on the reacting carbon atoms in the isolated carbon-centered reactant radicals.\textsuperscript{a} All energies are corrected for the ZPVE.

<table>
<thead>
<tr>
<th>Iodine transfer reactions</th>
<th>Carbonylation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Eq.</td>
</tr>
<tr>
<td>$\Delta E^\ddagger$</td>
<td>SCF</td>
</tr>
<tr>
<td></td>
<td>PCM-SCF</td>
</tr>
<tr>
<td>$\Delta E_r$</td>
<td>SCF</td>
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<tr>
<td></td>
<td>PCM-SCF</td>
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<tr>
<td>Spin</td>
<td>SCF</td>
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<td></td>
<td>PCM-SCF</td>
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<tr>
<td>Charge</td>
<td>SCF</td>
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<tr>
<td></td>
<td>PCM-SCF</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The SCF and PCM-SCF Mulliken spin and charge for the ethyl radical are 1.07 (1.07) and -0.17 (-0.20), respectively. \textsuperscript{b} The spin on the oxygen is 0.23. \textsuperscript{c} The spin on the terminal carbon is 0.70.

The first reaction in the sequence given by Eqs. (6.8) – (6.10) is the iodine transfer from CH$_3$CH$_2$I to CH$_3$CH(OH). For this reaction, two TSs were located, one which was nearly linear with respect to the C–I–C axis and a second one which was bent (Figure 22). However, while the channel proceeding through the linear TS was associated with a low barrier, 8.9 kcal/mol, the activation energy for the path with the bent TS was much higher, 25.5 kcal/mol. This result is consistent with barriers predicted previ-
ously \(^{108}\) for linear arrangements for other iodine transfer reactions. Therefore, only linear TSs were considered for the remaining iodine transfer reactions investigated in Paper IV.

Figure 22. The a) linear and b) bent TS optimized for the reaction: \(\text{CH}_3\text{CH(OH)} + \text{CH}_3\text{CH}_2\text{I} \leftrightarrow \text{CH}_3\text{CHIOH} + \cdot\text{CH}_2\text{CH}_3\). The energies are relative to the reactants and the PCM corrected energies are given within parentheses.

Although the iodine transfer reaction in Eq. (6.8) was found to be slightly endothermic (2.7 kcal/mol, Table 3), the reverse reaction is expected to be unimportant because the iodohydrin (\(\text{CH}_3\text{CHIOH}\)) is assumed to dissociate into acetaldehyde and HI [Eq. (6.13)].

\[
\text{HO} \quad \leftrightarrow \quad \text{O} \quad + \quad \text{HI} 
\]

(6.13)

To verify this assumption, DFT calculations were carried out on the HI elimination reaction from \(\text{CH}_3\text{CHIOH}\), in the same manner as described above for the carbonylation. However, when the SCF and PCM-SCF relative energies were inspected, it was noted that they differed significantly, indicating that the gas phase optimized geometries might not be representative for the geometries in ethanol. Therefore, the geometries were re-optimized with the PCM model. The resulting energy profiles are displayed in Figure 23a while the gas phase and ethanol optimized TSs are given in Figure 23b.

Indeed, inspection of the latter figure shows that the TS undergoes significant changes in its geometry upon reoptimization with PCM. As concluded from the TS geometry, the reaction is asynchronous in both phases where the elongation of the C–I bond is the major reaction coordinate in the uphill path. However, the reaction is substantially more asynchronous in ethanol; C–I being 3.61 Å (3.09 Å) in ethanol (gas phase).

Inspection of Figure 23a reveals that the reaction has a substantial barrier in the gas phase, the SCF (Gibbs) activation energy being 22.2 (21.6) kcal/mol. The high barrier may be rationalized by the atomic charges as computed for this TS with the MK scheme. In the TS, a significant amount of negative charge, \(-0.6\), is found on the iodine, which creates a charge sepa-
ration in the system that is unfavourable in the gas phase. In contrast, when the PCM model is applied, the SCF-PCM (Gibbs, solvent) activation energy drops to 9.5 (10.4) kcal/mol, as seen in Figure 23a. A larger amount of negative charge, −0.9, is found on the iodine compared to the gas phase which indicates the stabilizing effect of a polar solvent on a charge separated structure.

A continued inspection of Figure 23a shows that the reaction involves a post-dissociation complex. In the gas phase, the SCF energy of this complex is 2.3 kcal/mol lower than the products. However, since the complete reaction involves a significant increase in entropy (1 → 2 species), the products are located 4.8 kcal/mol below the complex on the gas phase Gibbs energy profile. Moreover, when the bulk solvation effect is taken into account, the post-dissociation complex is located 2.0 kcal/mol above the products, even at the SCF level. The free energies of the reaction in solution increase this difference further, making the products 10.0 kcal/mol (Gibbs, solvent) more stable than the complex.

To summarize, when the free energies of the reaction in solution are used to describe the HI elimination from CH₃CHIOH, the reaction is exergonic by −3.8 kcal/mol and proceeds with an activation energy of 10.4 kcal/mol. Hence, it appears that this reaction will drive the equilibrium in Eq. (6.8) in the forward direction and confirms that its reverse reaction will be less important under the experimental conditions.

![Figure 23](image.png)

Figure 23. a) Energy profiles (in kcal/mol) for HI elimination from CH₃CHIOH and the TSs optimized in (b) gas phase and in (c) ethanol using the PCM model. MK charges are shown in italics style. All SCF energies are corrected for ZPVE.

The next step in the investigated reaction sequence is the carbonylation of CH₃CH₂⁺ [Eq. (6.9)], which is computed to have a free energy barrier in solution of 13.4 kcal/mol. The free energy barrier is predicted to be 1.7 kcal/mol lower in ethanol than in the gas phase (Table 3). Moreover, the
reaction goes from being endergonic, 0.1 kcal/mol, in the gas phase to being exergonic, −4.0 kcal/mol, in ethanol. Thus, also this step of the proposed mechanism seems to be favored under the experimental conditions.

The final step in the studied sequence of reactions is the iodine transfer from ethyliodide to the acyl radical [Eq. (6.10)]. Table 3 reveals that the barrier for this reaction is low, 7.0 kcal/mol, and that it is slightly endothermic, 0.4 kcal/mol. Even though this step is somewhat disfavoured in ethanol ($\Delta E^\ddagger = 8.1$ kcal/mol, $\Delta E_r = 1.7$ kcal/mol), the reverse reaction is expected to be unimportant under experimental conditions, owing to the consumption of acyliodide by the nucleophile (alcohol).

The computed energy profiles described above for the reactions in Eqs. (6.8) – (6.10) are in good agreement with the high yields of esters and high conversion of $[^{11}C]O$ observed when ethanol was used as solvent and nucleophile. To confirm that the theoretical model also agrees favorably with experimental results for 2-propanol and allyl alcohol, the iodine transfer reactions from ethyliodide to the corresponding carbon-centered radicals were addressed next.

As can be seen in Table 3, the barrier for the iodine transfer from ethyliodide to the 1-hydroxy-methylethyl radical [Eq. (6.11)] is found to be slightly higher than for the corresponding reaction with the 1-hydroxyethyl radical, 0.8 (PCM-SCF) and 1.0 (SCF) kcal/mol. In addition, the former reaction is more endothermic than the latter, 1.7 (PCM-SCF) and 1.9 (SCF) kcal/mol. To confirm that even the reverse reaction of Eq. (6.11) will be unimportant under experimental conditions, the HI elimination from 2-hydroxy-2-iodopropane [Eq. (6.14)] was also investigated.

\[
\text{I} \quad \text{OH} \quad \text{O} \quad + \quad \text{HI}
\]

Eqs. (6.8) – (6.14)

These calculations were performed in the same manner as those for the HI elimination from 1-hydroxy-1-iodoethane. Interestingly, the predicted free energies of the reaction in solution shows that this HI elimination proceeds with a barrier of only 2.5 kcal/mol, which is 7.9 kcal/mol lower than the barrier for HI elimination from 1-hydroxy-1-iodoethane. Moreover, the computed reaction energy, −10.5 kcal/mol, reveals that this reaction is also significantly more exergonic. Inspection of the TS for HI elimination from 2-hydroxy-2-iodopropane reveals that the MK charge on the iodine is 0.1 more negative than in the TS for HI elimination from 1-hydroxy-1-iodoethane. This again signifies the stabilizing effect by a polar solvent on a charge separated compound. Hence, the iodohydrin dissociation in Eq. (6.14) should efficiently drive the equilibrium in Eq. (6.11) forward, which is in good agreement with the experimental observations.
The final reaction addressed was the iodine transfer from ethyliodide to the carbon-centered radical derived from allyl alcohol, the 1-hydroxy-1-vinylmethyl radical [Eq. (6.12)]. This reaction is associated with the highest barrier of all iodine transfer reactions investigated, 21.1 (22.5) kcal/mol in ethanol (gas phase). Moreover, the reaction is endothermic by 17.3 kcal/mol in ethanol. These unfavorable energetics agree well with the low yields and low [\(^{11}\)C]O conversions observed in the experiments with allyl and benzyl alcohols.

In summary, for all reactions addressed computationally in Paper IV, the energy profiles are in good agreement with the experimental observations. In particular, they provide an explanation for the observed high yields and conversions of [\(^{11}\)C]O when ethanol and 2-propanol are employed, but also rationalize the low yields and conversions observed for allyl and benzyl alcohol. Thus, the mechanism proposed in Paper IV for the radical carbonylation reactions is well supported by the DFT computations.

6.2 Atomic spin and NBO analysis

To investigate further the origin of the differences in barrier heights calculated for the iodine transfer reactions addressed in Paper IV, the Mulliken atomic spins on the reacting carbon atoms in the reactant carbon-centered radicals were analyzed (see Table 3).

It might be expected that the magnitude of the atomic spin on the reacting carbon atom should correlate with the barrier height in the sense that larger spin would lead to a lower barrier. However, as can be see in Table 3, that is not the case for those reactions. For instance, the reacting carbon in the acyl radical has the second lowest spin, 0.68, but the iodine transfer reaction [Eq. (6.10)] is associated with the lowest barrier, 7.0 kcal/mol. Moreover, the barrier for the iodine transfer from ethyliodide to the 1-hydroxy-methylethyl radical is 9.9 kcal/mol but the atomic spin value of the reacting carbon atom, 0.90, is much larger than it is for the acyl radical.

Therefore, in order to gain a better understanding of the differences in the activation energies, NBO calculations were performed on all reactant species and TSs. The NBO calculations were done in gas phase at the level of theory used to obtain the gas phase energies.

As outlined in Section 2.4, using NBO, it is possible to estimate the stability originating from delocalization of electrons from Lewis type occupied orbitals into non-Lewis type unoccupied orbitals.

One large stabilizing interaction found in all TSs corresponds to an oxygen lone pair to C–I (\(\sigma^*\)) antibonding orbital hyperconjugation term. This type of hyperconjugation interaction is illustrated in Figure 24 for the TSs of the 1-hydroxyalkyl radical [Eqs. (6.8), (6.11) and (6.12)] and acyl radical [Eq. (6.10)] reactions. The magnitude of this effect is larger for the acyl...
radical reaction than for the 1-hydroxyalkyl reactions. This might be attributed to the fact that the two orbitals are in the same plane for the acyl radical TS whereas they are slightly out of plane in the 1-hydroxyalkyl radical TSs.

As for the reactants, only the 1-hydroxy-1-vinylmethyl radical was found to have significant stabilizing interactions and two of these were particularly strong. The first one corresponds to a C–C π bonding orbital to radical-carbon atom-centered virtual orbital interaction while the second describes an interaction between a radical-carbon atom-centered occupied orbital and a C–C π* antibonding orbital. Indeed, these interactions correspond to the two major resonance forms of this radical.

In summary, the above described hyperconjugative effects calculated with NBO lead to the following stability ordering of the TSs involved in the iodine transfer reactions: 1-hydroxyalkyl radicals < acyl radical. Combining this trend with the large stabilizing interactions found in the 1-hydroxy-1-vinylmethyl radical results in a good rationalization of the computed barrier heights (Table 3) by the NBO results.

Figure 24. Hyperconjugation in the TSs for iodine atom transfer from ethyliodide to acyl and 1-hydroxyalkyl radicals.
7 S$_{H2}$ type reaction between the methyl radical and methylsilane or methylgermane

A bimolecular homolytic substitution (S$_{H2}$) reaction converts a radical, $R_1^\cdot$, into a new radical, $R_2^\cdot$, by the reaction

$$R_1^\cdot + AR_2 \rightarrow [R_1---A---R_2]^\cdot \rightarrow R_1A + R_2^\cdot.$$

Such reactions are fundamentally important in radical chemistry since they are elementary steps in many chemical reactions with various types of radicals such as ROO$^\cdot$, tert-BuO$^\cdot$, Me$_2$N$^\cdot$ and Me$^\cdot$ and it is known, in general, that S$_{H2}$ reactions may proceed on multivalent atoms such as Si, Sn, O, S, Se, Te, Mg, Hg, B, N, and P.

The experimental study presented in Paper V constitutes the first ESR spectroscopic evidence for an S$_{H2}$ reaction involving methyl radical attack on methylsilane and methylgermane. The ESR experiments were carried out at low temperatures for a solid solution containing ca. 1 mol% of methyliodide in solid methylsilane and the methyl radicals were generated by photolysis of methyliodide. The ESR-spectra revealed that the S$_{H2}$ reaction in Eq. (7.2) proceeds at 77 K with high selectivity over the competitive deuterium (D) abstraction, at the initial stage of the reaction. On the other hand, only the product of hydrogen abstraction, the methylsilyl radical (•SiH$_2$CH$_3$), could be observed for the unlabeled compounds. It was suggested that slow D abstraction, owing to the large kinetic isotope effect observed for the hydrogen abstraction by the methyl radical from methylsilane ($k_{Si-H}/k_{Si-D}$ = 5200), makes it possible to observe the S$_{H2}$ reaction in Eq. (7.2).

$$^{*}CD_3 + SiD_3CH_3 \rightarrow ^{*}CD_3SiD_3 + ^{*}CH_3$$

ESR measurements under the same conditions with methylgermane showed that the S$_{H2}$ reaction, $^{*}CD_3 + GeD_3CH_3 \rightarrow CD_3GeD_3 + ^{*}CH_3$, proceeded also for that compound at the initial stage of the reaction.

In order to investigate the origin of the observed S$_{H2}$ reactions, DFT and ab initio calculations were performed in Papers V and VI. In Paper V, the main objective was to study the energy profiles for the deuterated systems. In Paper VI, the computations were extended to investigate further the PES governing the methyl radical attack on silicon in methylsilane from different
C–Si–C angles. Moreover, an extensive search for different SiH₃CH₃/CH₃I complexes was also undertaken in order to investigate the molecular arrangement of the reactants prior to photolysis.

7.1 Energy profiles for the deuterated systems (V)

As Schiesser and co-workers¹¹¹,¹¹² have pointed out, there are, in principle, two conceivable mechanisms, backside and frontside, for the S₂H2 reaction between the methyl radical and methylsilane or methylgermane. In the backside mechanism, the methyl radical attacks the heteroatom in a collinear conformation whereas in the frontside mechanism, the attack angle is bent (Figure 25). However, these authors did not locate a TS for the frontside mechanism for these systems, other than at the uncorrelated HF level. In particular, all attempts of optimizing such a TS with MP2 collapsed to a TS for hydrogen expulsion from silicon (or germanium).¹¹²

![Figure 25. Frontside and backside mechanisms for the S₂H2 reaction.](image)

In Paper V, channels were located for the backside S₂H2 reaction (7.3) and the hydrogen abstraction (7.4):

\[
\begin{align*}
CH₃XH₃ + \cdot CH₃ & \rightarrow \cdot CH₃ + XH₂CH₃ \\
CH₃XH₃ + \cdot CH₃ & \rightarrow \cdot XH₂CH₃ + CH₄
\end{align*}
\]

(7.3) (7.4)

Here, X is C, Si or Ge. The TSs for the S₂H2 reactions, as optimized with B3LYP/6-31+G(d,p), are displayed in Figure 26. It can be seen that all TS structures are nearly collinear and have D₃h symmetry. This contrasts previously optimized TSs with MP2 of this reaction for X = Si and Ge.¹¹¹ Indeed, those structures were found to be slightly distorted away from symmetry in the sense that the X–C distances are unequal. Instead, structures of D₃h symmetry were found to correspond to shallow hypervalent minima.¹¹¹

![Figure 26. B3LYP/6-31+G(d,p) optimized TSs for the S₂H2 reactions addressed in Paper V.](image)
CCSD(T)/AUG-cc-pVDZ//B3LYP/6-31+G(d,p) ZPVE corrected energies were obtained for the stationary points involved in the S\textsubscript{H2} reactions and D abstractions of the following deuterated systems:

- \( \text{CH}_3\text{XD}_3 + \cdot\text{CH}_3 \) (7.5)
- \( \text{CH}_3\text{XD}_3 + \cdot\text{CD}_3 \) (7.6)
- \( \text{CD}_3\text{XD}_3 + \cdot\text{CH}_3 \) (7.7)

Note that the S\textsubscript{H2} reaction of Eq. (7.7) is the reverse of Eq. (7.6), which in turn is the S\textsubscript{H2} reaction observed by ESR for \( X = \text{Si} \) and Ge. As can be seen in Table 4, the barriers for the \( X = \text{C} \) systems are considerably higher than for the \( X = \text{Si} \) and Ge systems. For the hydrogen abstractions, this result is in agreement with the fact that the dissociation energy of an sp\textsuperscript{3} hybridized C–H bond is ca. 10 kcal/mol larger than for the Si–H bond.\textsuperscript{113} Moreover, regardless of isotopic system and identity of \( X \), the D abstraction is found to be energetically much more favorable than the S\textsubscript{H2} reaction. In particular, for the reaction in Eq. (7.6) with \( X = \text{Si} \), the barriers for the D abstraction and S\textsubscript{H2} reaction are 8.8 and 22.0 kcal/mol, respectively. Also, although the latter S\textsubscript{H2} reaction is exothermic by 0.9 kcal/mol, which supports the advantageous usage of the deuterated \( \cdot\text{CD}_3 \) radical as a reactant, the D abstraction is exothermic by 13.3 kcal/mol.

**Table 4.** ZPVE corrected activation energies (\( E_a \)) and reaction energies (\( \Delta E \)), in kcal/mol, for the S\textsubscript{H2} reactions and the deuterium abstraction reactions in Eqs. (7.5), (7.6) and (7.7). The energies were calculated with CCSD(T)/AUG-cc-pVDZ//B3LYP/6-31+g(d,p).

<table>
<thead>
<tr>
<th>System</th>
<th>( X )</th>
<th>( S\textsubscript{H2} )</th>
<th>( \Delta E )</th>
<th>D atom abstraction</th>
<th>( E_a )</th>
<th>( \Delta E )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3\text{XD}_3 + \cdot\text{CH}_3 )</td>
<td>C</td>
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<td>Ge</td>
<td>20.9</td>
<td>0.0</td>
<td></td>
<td>6.8</td>
<td>-17.1</td>
</tr>
<tr>
<td>( \text{CH}_3\text{XD}_3 + \cdot\text{CD}_3 )</td>
<td>C</td>
<td>49.3</td>
<td>-1.1</td>
<td></td>
<td>14.3</td>
<td>-3.2</td>
</tr>
<tr>
<td></td>
<td>Si</td>
<td>22.0</td>
<td>-0.9</td>
<td></td>
<td>8.8</td>
<td>-13.3</td>
</tr>
<tr>
<td></td>
<td>Ge</td>
<td>20.1</td>
<td>-0.9</td>
<td></td>
<td>6.3</td>
<td>-17.9</td>
</tr>
<tr>
<td>( \text{CD}_3\text{XD}_3 + \cdot\text{CH}_3 )</td>
<td>C</td>
<td>50.4</td>
<td>1.1</td>
<td></td>
<td>15.1</td>
<td>-2.3</td>
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<tr>
<td></td>
<td>Si</td>
<td>22.9</td>
<td>0.9</td>
<td></td>
<td>9.4</td>
<td>-12.5</td>
</tr>
<tr>
<td></td>
<td>Ge</td>
<td>21.0</td>
<td>0.9</td>
<td></td>
<td>6.8</td>
<td>-17.1</td>
</tr>
</tbody>
</table>

7.1.1 Translational energy of the methyl radical

In order to rationalize why the S\textsubscript{H2} reactions for \( X = \text{Si} \) and Ge really proceed despite their much higher barriers compared with the competitive D abstractions, one may observe that there will be excess energy available in the \( \cdot\text{CH}_3 \) and I\textsuperscript{*} fragments following photolysis of CH\textsubscript{3}I. The binding energy
of the C–I bond in CH₃I has been experimentally determined to be between 53.0 and 55.0 kcal/mol. By using this interval for the binding energy, a photolytic energy corresponding to a wavelength of 365 nm (the shortest wavelength of the high intensity lines in the light source used in the ESR measurements), and the Newtonian laws of conservation of both momentum and total energy, the kinetic energy of the *CH₃ fragment was calculated to be 20.9 – 22.6 kcal/mol. In these calculations, it was assumed that all of the excess energy is transferred to the translational degrees of freedom for the dissociating fragments, an assumption which is supported by reference 114. The difference between the ZPVE corrected binding energies of CH₃I and CD₃I was estimated using B3LYP/6-31+G(d,p)/LanL2DZ[I atoms] to be ca. 1 kcal/mol which makes the kinetic energy values applicable on the deuterated case as well.

Thus, given a favorably ordered sample prior to photolysis of methyliodide, the computed kinetic energies indicate that the methyl radical might have sufficient energy to cross the barriers for the S₁Η₂ reactions for the X = Si and Ge systems (Table 4). This can be one reason why the S₁Η₂ reaction really proceeds at 77 K.

7.2 Can complex formation promote the S₁Η₂ reaction? (VI)

In order to answer the title question, further quantum chemical calculations for the X = Si system were undertaken in Paper VI. In particular, an extensive search for SiH₃CH₃/CH₃I complexes was combined with a detailed investigation of the PES governing the methyl radical attack at silicon in methylsilane from different C–Si–C angles.

In this work, channels were located with B3LYP in conjunction with the larger 6-311+G(d,p) basis set for (7.8) the backside S₁Η₂ mechanism which exchange the two methyl radicals, (7.9) the hydrogen abstraction from silicon, and (7.10) hydrogen expulsion from silicon.

\[
\begin{align*}
\text{CH₃SiH₃} + \cdot\text{CH₃} & \rightarrow [\text{TS1}]^\ddagger \rightarrow \cdot\text{CH₃} + \text{SiH₂CH₃} & (7.8) \\
\text{CH₃SiH₃} + \cdot\text{CH₃} & \rightarrow [\text{TS2}]^\ddagger \rightarrow \text{CH₃SiH₂}^\cdot + \text{CH₄} & (7.9) \\
\text{CH₃SiH₃} + \cdot\text{CH₃} & \rightarrow [\text{TS3}]^\ddagger \rightarrow \text{CH₃SiH₂CH₃} + \cdot\text{H}^\cdot & (7.10)
\end{align*}
\]

As can be seen in Figure 27, the geometry of the TS for the S₁Η₂ reaction is again predicted to be collinear and to have D₃h symmetry. In contrast, the reactions in Eqs. (7.9) and (7.10) proceed through TSs which have got much steeper C–Si–C angles; 109.8 and 99.2° for TS2 and TS3, respectively. The main difference between the latter channels is the orientation of the methylsilane fragment relative to the attacking methyl radical. Hence, the methylsi-
lane fragment in the TS for hydrogen expulsion is rotated ca. 60° about the Si–C₂ axis compared to the TS for hydrogen abstraction.

Figure 27. B3LYP/6-311+G(d,p) optimized TSs for the reactions (7.8) – (7.10). Bond lengths are given in Ångström.

CCSD(T)/6-311+G(d,p)//B3LYP/6-311+G(d,p) ZPVE corrected energy profiles for the reactions in Eqs. (7.8) – (7.10) are displayed in Figure 28. For comparison, the relative ZPVE corrected B3LYP/6-311+G(d,p) energies are given within parentheses in this figure.

Figure 28. ZPVE corrected CCSD(T)/6-311+G(d,p)//B3LYP/6-311+G(d,p) energy profiles (in kcal/mol) for the reactions (7.8) – (7.10). The relative ZPVE corrected B3LYP/6-311+G(d,p) energies are given within parentheses.

In agreement with the results of Paper V, the present calculations predict that the hydrogen abstraction requires much less activation energy, 10.8 kcal/mol, than the S₃H₂ reaction, 25.7 kcal/mol. Moreover, whereas the reaction energy of the identity reaction in Eq. (7.8) is nil, the hydrogen abstraction is found to be highly exothermic, −11.4 kcal/mol. It is worth to note that the hydrogen expulsion reaction, although not visible in the ESR spectrum, is predicted to proceed through a barrier of 24.5 kcal/mol, which is lower by 1.2 kcal/mol than that of the S₃H₂ reaction. Nevertheless, the former reaction
is endothermic by 4.2 kcal/mol which makes it less important. B3LYP is here noted to reproduce the CCSD(T) energy profiles qualitatively.

7.2.1 Attack of *CH₃ at Si in SiH₃CH₃ from different angles

The large difference between the C–Si–C angle in TS₁ (180.0°) compared with TS₂ (109.8°) and TS₃ (99.2°) might imply that the Sₙ2 reaction could proceed in a wide range of C–Si–C angles before the other channels become activated. To investigate this possibility closer, two sets of B3LYP/6-31+G(d,p) constrained optimization scans were carried out in order to study the PES governing the methyl radical attack at silicon in methylsilane from different C–Si–C angles. In all scans, the Si–C₁ distance was decreased from 5.0 Å, incrementally by 0.1 Å, to 1.8 Å (see Figure 29a for the labels). A total of 24 C–Si–C angles were studied, ranging from 60° to 175°, with an interval of 5°, while the final two angles were set to 179° and 179.9°.

In the first set of scans, D₀, the C₁–Si–C₂–Hₐ dihedral angle was held frozen at 0°, implying that the methyl radical approached the Si atom such that abstraction of Hₐ had maximum probability to succeed at C–Si–C angles close to 110°. In the second set of scans, D₁₈₀, the same dihedral angle was set to 180° so that the methyl radical approached the Si atom in between two Si hydrogens (H₉ and H₃), making hydrogen abstraction least probable for C–Si–C angles close to 110°. The different molecular arrangements for the D₀ and D₁₈₀ sets of scans are exemplified in Figure 29b for C–Si–C = 145°.

![Figure 29. a) Structures of methylsilane and methyl radical with labels used in the discussion. b) Initial conformations of the D₀ and D₁₈₀ scans with C–Si–C = 145°. In the D₀ (D₁₈₀) set of scans, C₁–Si–C₂–Hₐ was held frozen at 0° (180°).](image)

A 2-dimensional energy profile was constructed from the D₀ set of scans (Figure 30, left). This profile shows how the energy changes versus the Si–C₁ distance and the C–Si–C angle. As clearly seen in this figure, there are distinct regions on the PES which lead to different products. These reactions, and the C–Si–C angles where they proceed, are summarized in Figure 30, right.

Thus, the backside Sₙ2 reaction is found to proceed in the range 179.9° ≥ C–Si–C ≥ 145° (with barriers between 17.1 – 22.6 kcal/mol). In agreement with the collinear geometry of TS₁, the reaction is most favorable at 179.9°.
At C–Si–C = 140° (24.6 kcal/mol), the reaction leads to expulsion of one Si hydrogen atom, and to formation of dimethyldisilane.

At the attack angle 135°, the hydrogen abstraction from silicon comes into play. This reaction prevails in the range 135° ≥ C–Si–C ≥ 90° (6.0 – 9.8 kcal/mol) and is predicted to be most favorable at 110°, in agreement with the geometry optimized for TS2.

Finally, in the range 85° ≥ C–Si–C ≥ 60°, the SiH2 reaction again becomes activated, but now via the frontside mechanism. However, the corresponding barriers, 22.7 – 42.3 kcal/mol, are much larger than for the backside mechanism. Moreover, all attempts of optimizing the TS for the frontside SiH2 reaction with B3LYP failed.

![Figure 30. 2-dimensional plot of the energy versus the Si–C1 distance and the C–Si–C angle for the B3LYP/6-31+G(d,p) constrained optimization scans in the D0 set.](image)

A 2-dimensional energy profile was constructed from the D180 set of scans (Figure 31) in the same manner as described for the D0 set of scans.

As can be seen in this figure, the backside SiH2 reaction proceeds within a wider range of C–Si–C angles: 179.9 – 140°. The corresponding barriers, 18.0 – 21.6 kcal/mol, are found to be slightly higher for the most linear angles, but slightly lower for the steepest angles, as compared to the backside SiH2 activation energies in the D0 set of scans.

None of the scans in the D180 set leads to hydrogen abstraction. This can be explained by the fact that the methyl radical approaches the Si atom in between the hydrogens Hb and Hc (Figure 29b). Instead, in the range 135° ≥ C–Si–C ≥ 115° (19.5 – 20.9 kcal/mol), a reaction is observed which seems to lead to the formation of a hypervalent minimum ([CH3SiH3CH3]*). However, despite considerable effort, all attempts of optimizing the hypervalent minimum resulted in expulsion of one of the Si hydrogen atoms, leading to the formation of dimethyldisilane. In the range 110 – 90° (17.4 – 18.8
kcal/mol), the reaction proceeds directly to hydrogen expulsion from silicon. In agreement with TS3, this reaction has a minimum barrier at 100°.

In the range $85° \geq \text{C–Si–C} \geq 60°$, the frontside $\text{SiH}_2$ mechanism is activated. Again, the corresponding barriers, 22.5 – 42.3 kcal/mol, are considerably higher than those found for the backside $\text{SiH}_2$ reaction.

From the analysis of the two sets of scans, it is concluded that the backside mechanism for the $\text{SiH}_2$ reaction is active within the approximate range $180° \geq \text{C–Si–C} \geq 140°$, with preference for the most linear angles. Moreover, the scans indicate that the hydrogen abstraction from silicon proceeds in the range $90° – 135°$, but only if methylsilane and the methyl radical are oriented such that the methyl radical approaches one of the hydrogens in methylsilane. Finally, at $\text{C–Si–C}$ angles steeper than 90°, the frontside mechanism for the $\text{SiH}_2$ reaction is activated. However, the corresponding barrier increases rapidly with decreasing angles of attack so that this mechanism seems to be of minor importance for the present $\text{SiH}_2$ reaction.

![Figure 31. 2-dimensional plot of the energy versus the Si–C₁ distance and the C–Si–C angle for the B3LYP/6-31+G(d,p) constrained optimization scans in the D180 set.](image)

7.2.2 Complexes formed between $\text{SiH}_3\text{CH}_3$ and $\text{CH}_3\text{I}$

A preliminary search for $\text{SiH}_3\text{CH}_3/\text{CH}_3\text{I}$ complexes was performed with B97-1/6-311+G(2df,2p)/[H, C, Si atoms]/LanL2DZ[I atoms]. At this level, 11 complexes (1 – 11) were found. When these structures were re-optimized with MP2/6-311+G(2df,2p)/LanL2DZ, which is the production level of the complex geometries in Paper VI, complex 11 collapsed to complex 5. The 10 (11) optimized MP2 (B97-1) complexes are displayed in Figure 32 with selected geometrical parameters.

In general, MP2 and B97-1 give similar qualitative predictions of the geometries of the complexes. The most noteworthy deviation in geometry between the two methods is found for complex 2. At the B97-1 level, this
complex has a conformation in which the methyl moiety in methyliodide points towards the Si–C bond in methylsilane, while at the MP2 level, the two molecular fragments attain a nearly parallel conformation relative to one another with respect to the C–I and Si–C bonds (Figure 32).

![Figure 32](image)

*Figure 32.* MP2 and B97-1 optimized SiH₃CH₃/CH₃I complexes. The 6-311+G(2df,2p)/LanL2DZ basis set was used throughout. Bond lengths are given in Ångström and the B97-1 values are given within parentheses.

The best estimates of the electronic energies of the MP2 complexes were obtained with CCSD(T)/6-311++G(3df,3pd)/LanL2DZdp. At this level, the relative energies of the complexes 1 to 10 increase from 0.00 to 2.15
kcal/mol, indicating that the energy differences between the complexes are small.

Of the various located MP2 complexes, 5 (1.27 kcal/mol) and 6 (1.27 kcal/mol), are of direct importance for the $S_{\text{H}2}$ reaction in Eq. (7.8) and the hydrogen abstraction in Eq. (7.9), respectively. In complex 5, the methyl moiety of methyliodide points collinearly towards the Si atom in methylsilane. Hence, photodissociation of methyliodide in this complex would lead to methyl radical attack at silicon with an approximate $\text{C–Si–C}$ angle of 180°. Bearing in mind that this was found to be the most favorable attack angle for the backside $S_{\text{H}2}$ reaction, it seems likely that this complex could account for a large fraction of the observed $S_{\text{H}2}$ reactions. Moreover, 5 was found to be the lowest energy linear conformer.

As for complex 6, whereas this compound indeed has the most favorable conformation for the hydrogen abstraction of all complexes optimized with MP2, a detailed inspection of Figure 32 reveals, nevertheless, that it is not perfect in this sense. This is reflected by the fact that $\text{H}_a–\text{C}_1–\text{I} = 168.8°$, which implies that the methyl moiety in methyliodide is not directed exactly towards an $\text{Si}$ hydrogen, but rather points towards the $\text{Si–H}_a$ bond. Moreover, because the $\text{C–Si–C}$ angle in this complex, 73.7°, is very steep, and because it was found that the hydrogen abstraction proceeds favorably only in the range $90° \leq \text{C–Si–C} \leq 135°$, this could indicate that photodissociation of methyliodide in 6 might not lead to hydrogen abstraction with full efficiency.

Finally, it is interesting to note that the B97-1 optimized complex 11 (Figure 32), which also has got a molecular arrangement in favor of hydrogen abstraction from silicon, becomes unstable at the MP2 level. Indeed, with MP2, complex 11 collapsed to 5. Since MP2, in general, is preferable over DFT for weakly interacting systems, and because the B97-1 optimized $\text{C–Si–C}$ angle in 11 is rather steep, 137.6°, the stability of the molecular arrangement in 5 with respect to deviations in this angle from linearity seems to be significant.

These findings provide a reasonable explanation of the $S_{\text{H}2}$ reaction in Eq. (7.2) observed by ESR in Paper V.
In this thesis, quantum chemical calculations have been used to increase the understanding of the mechanisms of a number of organic radical reactions. The main conclusions of these investigations are here summarized.

In Paper I, the mechanism for the opening of the two cyclopropane rings in the bicyclopropylidene radical cation (BCP⁺) to the tetramethylenethane radical cation was studied. The reaction path was found to proceed with stepwise opening of the rings. The first ring opening was predicted to proceed with an activation energy of 7.3 kcal/mol, whereas no barrier was found for the second ring opening. Each ring opening was found to be accompanied by a striking pyramidalization of one carbon atom on the central C–C bond together with a disrotation of the hydrogen atoms. NBO calculations were performed to rationalize the unusually short distance predicted for the central C–C bond in BCP⁺.

In Paper II, the rearrangement of the norbornadiene radical cation (N⁺) to the cycloheptatriene radical cation (CHT⁺) by opening one bridgehead–methylene bond in N⁺ was investigated. Three channels were located for this isomerization. The lowest energy pathway involves a concerted rearrangement to the norcaradiene radical cation (NCD⁺), followed by ring opening to CHT⁺. It was found that the reaction path from N⁺ to NCD⁺ has a branching point that prevents the formation of distonic isotoluene. The predicted activation energy of this channel, 28.9 kcal/mol, is 4.6 kcal/mol higher than the barrier for the multi-step pathway previously proposed for this reaction. However, substitution of the methylene group in N⁺ with C(CH₃)₂ was found to reverse the ordering of the rate-determining TSs of the concerted and multi-step channels and the concerted rearrangement becomes the minimum energy path on the substituted PES.

In Paper III, the concerted and stepwise mechanisms of the McLafferty rearrangement of the butanal radical cation (Bu⁺) and the 3-fluorobutanal radical cation (3F-Bu⁺) were studied. One concerted channel and three stepwise pathways were located for both Bu⁺ and 3F-Bu⁺. The two lowest energy channels found for Bu⁺ proceed stepwise and the Cα–Cβ bond cleavage steps were found to be rate determining for this reaction, with barriers of 11.1 and 11.4 kcal/mol. Interestingly, the barrier for the concerted rearrangement is lowered from 37.7 to 20.5 kcal/mol upon substitution. The dipole moment of the concerted substituted TS (3F-H), 12.1 D, was found to
be significantly smaller than that of the unsubstituted TS (H), 103.2 D. This indicates that an unfavorable charge separation is partially removed upon substitution of the concerted TS and provides an explanation for the low relative energy of (3F-H). A charge separated structure for (H) is, moreover, supported by calculated atomic charges. However, despite this reduction of the barrier, it was found that concerted rearrangement cannot compete with stepwise fragmentation even with this particular substitution.

In Paper IV, a synthetic methodology for labeling ¹¹C-radiotracers for positron emission tomography (PET) was presented. It was found experimentally that dialkylperoxides or ketones with nπ* character of their excited triplet state accelerate the photoinitiated radical carbonylation of alkyliodides with [¹¹C]carbon monoxide ([¹¹C]O). High product yields and high conversion of [¹¹C]O were obtained using either ethanol or 2-propanol as solvent. In contrast, low yield and conversion were obtained when using allylic and benzylic alcohols. On the basis of these observations, an atom transfer type mechanism was proposed for the reaction. Accordingly, the reaction sequence starts with hydrogen abstraction from one of the solvent molecules (SH) by the photoexcited ketone, or by the alkoxy radical formed by photolysis of the peroxide. The solvent derived carbon centered radical, S*, then abstracts the iodine atom from an alkyliodide (RI). Subsequently, [¹¹C]O adds to R* and forms an acyl radical, R[carbonyl-¹¹C*]O, which in turn abstracts the iodine atom from another alkyliodide yielding an acyliodide, R[carbonyl-¹¹C](O)I. Finally, an aliphatic [carbonyl-¹¹C]ester is produced by quenching of the acyliodide with alcohol. DFT calculations were undertaken to study the proposed mechanism using ethanol as a model for the solvent compound involved in the radical mechanism and ethyliodide as the model alkyliodide. Bulk solvation effects were taken into account by the polarizable continuum model, using the standard parameters for ethanol. The calculated energetics support the feasibility of the mechanism. The first iodine atom transfer step, \( \text{CH}_3\text{C}(\cdot)\text{HOH} + \text{CH}_3\text{CH}_2\text{I} \rightarrow \text{CH}_3\text{CHIOH} + \text{CH}_3\text{CH}_2\cdot \), was predicted to be slightly endothermic, but the process was found to be efficiently driven by the subsequent more exergonic dissociation of the iodohydrin, \( \text{CH}_3\text{CHIOH} \rightarrow \text{CH}_3\text{CHO} + \text{HI} \). For neither of these reactions, the computed activation energy exceeds ca. 10 kcal/mol, when solvent effects are taken into account. The calculations further rationalized the observed high yield and conversion when 2-propanol was used as solvent and, also, the poor yields for the allylic and benzylic alcohols.

Paper V reports on the first ESR observation of an \( \text{S}_{\text{II}}\text{2} \) reaction between a deuterated methyl radical and methylsilane or methylgermane, \( \text{CH}_3\text{XD}_3 + \cdot\text{CD}_3 \rightarrow \cdot\text{CH}_3 + \text{XD}_3\text{CD}_3, \ X = \text{Si} \) or Ge, following the photolysis of methyliodide. It was observed that the \( \text{S}_{\text{II}}\text{2} \) reaction proceeds with high selectivity over the competitive D abstraction from the X atom, at the initial stage of the reaction. In Papers V and VI, quantum chemical calculations were performed to investigate the origin of the observed \( \text{S}_{\text{II}}\text{2} \) reaction. The computa-
tions performed in Paper V predict that the D abstraction is energetically much more favorable than the S\textsubscript{H\textsubscript{2}} reaction, regardless of system and isotopic composition of the reactants. In particular, for X = Si, the barriers for the observed S\textsubscript{H\textsubscript{2}} reaction and the corresponding D abstraction reaction are 22.0 and 8.8 kcal/mol, respectively. Moreover, the latter reaction is substantially more exothermic than the former. However, the translational energy of the methyl radical, created by the photolysis of methyl iodide, was estimated to be 22 kcal/mol. This indicates that the methyl radical, despite these unfavorable energetics, have sufficient energy to cross the barrier for the S\textsubscript{H\textsubscript{2}} reaction, given a favorable initial orientation of the reactants prior to photolysis.

In Paper VI, the PES governing the methyl radical attack on silicon in methylsilane from different C–Si–C angles was studied. Moreover, to investigate the molecular arrangement of the reactants prior to photolysis of methyl iodide, an extensive search for different SiH\textsubscript{3}CH\textsubscript{3}/CH\textsubscript{3}I complexes was undertaken. It was found that the backside mechanism for the S\textsubscript{H\textsubscript{2}} reaction may proceed favorably in a wide range of C–Si–C angles, 140–180°, while the hydrogen abstraction reaction is active in the range 90–135°. For steeper C–Si–C angles, the frontside S\textsubscript{H\textsubscript{2}} mechanism is activated. However, the latter mechanism is probably unimportant for the present S\textsubscript{H\textsubscript{2}} reaction due to high barriers along its reaction paths. Interestingly, one of the located complexes, 5, corresponds to the collinear arrangement where the methyl moiety in methyl iodide points towards silicon in methylsilane. Photolysis of methyl iodide in this complex would thus lead to methyl radical attack at silicon with an approximate C–Si–C angle of 180°. Indeed, this was found to be the most favorable attack angle for the backside S\textsubscript{H\textsubscript{2}} reaction. Moreover, the calculations indicated that complex 5 is rather stable towards deviations from linearity. One complex, 6, has a favorable orientation for the hydrogen abstraction. However, in this complex, the C–Si–C angle is very steep, 73.7°. Since the hydrogen abstraction reaction proceeds favorably only in the range 90° ≤ C–Si–C ≤ 135°, photodissociation of methyl iodide in 6 may not lead to hydrogen abstraction with full efficiency. These data provide a reasonable explanation of the S\textsubscript{H\textsubscript{2}} reaction observed in Paper V.

Ett användningsområde där kvantkemiska studier kan vara mycket värdefulla som komplement till experimentella observationer är undersökningen av kemiska reaktionsmekanismer. I en kemisk reaktion omvandlas en eller flera molekyler till nya molekyler. På molekylär nivå så karaktäriseras den kemiska reaktionen av dess reaktionsmekanism, vilken är en detaljerad beskrivning av de förändringar som sker i de ingående molekyllernas struktur under reaktionens gång. Ett exempel på en sådan förändring kan vara bildandet av en ny kemisk bindning.

I den här avhandlingen har just mekanismer undersöks med kvantkemiska metoder för ett antal olika reaktioner som innehåller radikaler. Vanliga stabila molekyler innehåller i de flesta fall ett jämnt antal elektroner som dessutom parvist upptar samma område. En radikal är istället en molekyl som innehåller en oparad elektron. Denna egenskap gör att radikaler ofta är mycket reaktiva. Även om det finns experimentella metoder för att studera radikalers
struktur, egenskaper och reaktionsförlopp så gör deras reaktivitet att de underliggande detaljerna i dess reaktionsmekanismer ofta inte är mätbara. Därför kan kompletterande kvantkemiska beräkningar vara av mycket stor betydelse och ibland den enda framkomliga vägen för att få detaljerade kunskaper om mekanismer för radikalreaktioner.


I delarbete I undersöktes mekanismen för omlagringen av bicyklopropylidenradikalkationen ($\text{BCP}^+$) till tetrametylenetanradikalkationen ($\text{TME}^+$) (Figu A). $\text{BCP}^+$ innehåller två cyklopropanringar som är kopplade till varsin kolatom på ett etenfragment. Experimentella studier har visat att de två ringarna öppnas redan vid låga temperaturer vilket resulterar i bildandet av $\text{TME}^+$. Reaktionsförloppet är dock så snabbt att man inte kunde säga hur mekanismen gick till i detalj, till exempel om ringarna öppnades en i taget eller samtidigt. Beräkningarna som utfördes i delarbete I gav förslag på en reaktionsmekanism. I denna öppnas ringarna stegvist. Dessutom kunde man se två andra strukturella förändringar som var viktiga för mekanismen. I anslutning till varje ringöppning så genomgår kolatomen i den centrala kol–kol-bindningen en så kallad pyramidalisering, det vill säga den strukturella omgivningen till kolatomen går från att vara plan till att vara pyramidiformad. Dessutom förutsades vätatomerna som är kopplade till de två kolatomer vars bindning bryts rotera i motsatta riktningar under ringöppningsprocesserna.
I delarbete II studerades omlagringen av norbornadienradikalkatjonen \((N^+)^\) till cykloheptatrienradikalkatjonen \((CHT^+)\). Även denna omlagring har observerats experimentellt, utan att en detaljerad reaktionsmekanisk kunnat fastslås. Det finns flera tänkbara mekanismer för denna omlagring och i detta arbete undersökt tre stycken som alla startar med att en specifik bindning i \(N^+\) bryts (Figur B). Resultaten visade att den mest gynnsamma av dessa mekanismer fortfarande har en högre barriär än en annan mekanism som tidigare hade studerats kvantkemiskt. Själva omlagringmekanismen som lokaliseras i delarbete II visade sig däremot vara intressant ur ett teoretiskt perspektiv, för i det första steget, som även är hastighetsbestämmande för denna mekanism, bryts den molekylära symmetrin trots att det finns möjlighet att nå en produkt utan detta symmetribrott. Baserat på experimentella observationer av ett system av närliggande struktur till \(N^+\) verkade det troligt att den mekanism som lokaliseras i delarbete II kunde bli ännu mer gynnsam om man bytte ut väteatomerna på metylenpositionen mot metylgrupper. Mekanismen undersökt därför med detta utbyte. Intressant nog så visade det sig att detta utbyte har en dramatisk effekt på mekanismen och att barriären blir lägre än för den mekanism som tidigare lokaliserats för omlagringen av \(N^+\) till \(CHT^+\) med samma utbyte.

I delarbete III undersökte mekanismen för McLafferty-omlagringen för radikalkatjonerna av butanal \((Bu^+)\) och 3-fluorbutanal \((3F-Bu^+)\). I det generella fallet så innebär en McLafferty-omlagning att ett väte i \(\gamma\)-position \((H_\gamma)\) överförs till en dubbelbunden atom \((X)\) samtidigt som kol–kol-bindingen i \(\alpha–\beta\)-positionen bryts. För både \(Bu^+\) och \(3F-Bu^+\) är \(X\) en syreatom och den totala omlagringen leder till att molekylerna delas upp i två fragment, ett som är en radikalkation och ett som är neutralt laddat utan att vara en radikal (Figur C). Frågeställningen för detta arbete var huruvida omlagringen sker med samtidig överföring av \(H_\gamma\) och \(C_\alpha–C_\beta\) bindningsbrytning eller om de

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**Figur A.** Omlagringen av bicyklopropylidenradikalkatjonen \((BCP^+)\) till tetrametylenetanradikalkatjonen \((TME^+)\) som undersöks i delarbete I.

**Figur B.** Omlagring av norbornadienradikalkatjonen till cykloheptatrienradikalkatjonen. Bilden övre pilen indikerar den bindning som bryts initialt i de mekanismer som undersöks i delarbete II.

**Figur C.** Omlagring av butanal \((Bu^+)\) till 3-fluorbutanal \((3F-Bu^+)\). Bilden övre pilen indikerar den bindning som bryts initialt i de mekanismer som undersöks i delarbete III.

Figur C. McLafferty-omlagringen av butanalradikalkationen som studeras i delarbetet III.

I delarbete V presenterades för första gången experimentella bevis för den så kallade S_H2-reaktionen mellan den deutererade (D) metylradikalen och metylsilan eller metylgerman, \( \text{CH}_3\text{XD}_3 + ^*\text{CD}_3 \rightarrow ^*\text{CH}_3 + \text{XD}_3\text{CD}_3, \ X = \text{Si eller Ge} \). Under den inledande fasen efter fotodissociation av metyljodid (\( \text{CD}_3\text{I} + \text{hv} \rightarrow ^*\text{CD}_3 + \text{I} \)) så observerades S_H2-reaktionen med högt utbyte i förhållande till en konkurrerande reaktion i vilken en D-atom överförs till metylradikalen. Den senare reaktionen brukar i allmänhet kallas för en abstraktionsreaktion. Beräkningarna i delarbetena V och VI utfördes i syfte att förklara detta utfall. Förbryllande nog så befann sig S_H2-reaktionen vara betydligt mer ogynnsam än D-abstraktionen för både \( X = \text{Si eller Ge} \). Det tydde på att en möjlig förklaring till det experimentella utfallet kunde härröras från hur molekylerna i reaktionsblandningen var ordnade i förhållande till varandra innan fotodissociationen av metyljodid. Det vill säga att de låg ordnade på så sätt att D-abstraktionsreaktionen försvårades i den inledande fasen, trots att den var mer gynnsam. Den idén fick stöd av en uppskattning av hur stor rörelseenergin hos metylradikalen borde vara just efter fotodissociationen. Det visade sig att rörelseenergin förutsådes vara tillräckligt stor för att S_H2-reaktionen skulle kunna ske. I delarbete VI undersökt dessa närmare. Där studerades dels hur metyljodid och metylsilan ligger ordnade i förhållande till varandra innan fotodissociation av metyljodid, dels vid vilka C–Si–C-vinklar som de olika reaktionerna kan ske när metylradikalen attackerar kiselatomen i metylsilan. Beräkningarna visade att S_H2-reaktionen är aktiv för C–Si–C vinklar mellan 140 – 180° medan väteabstraktionen kan ske mellan 90 – 135°. Intressant nog hittades ett komplex där metyldelen av metyljodid ligger riktad mot kiselatomen i metylsilan. Detta komplex är linjärt med avseende på C-, Si- och I-atomerna i systemet och dessutom visade sig komplexet vara förhållandevis stabilt mot avvikelser från den linjära formen. Eftersom komplexet är linjärt skulle fotodissociation av metyljodid leda till att metylradikalen rör sig mot kiselatomen i metylsilan med en C–Si–C-vinkel på ca 180° vilket befanns vara den mest gynnsamma vinkeln för S_H2-reaktionen. Utöver detta hittades ett komplex som har en ordning som skulle kunna vara gynnsam för väteabstraktionen. I detta komplex är dock C–Si–C = 73.7° vilket är utanför området där väteabstraktionen förutsådes ske. Detta tyder på att väteabstraktionen inte bör äga rum med full effektivitet från detta komplex. Beräkningarna i delarbete VI kan alltså ge en möjlig förklaring till den observerade S_H2-reaktionen, det vill säga att en initial ordning i reaktionsblandningen kan ligga bakom det höga utbytet i den inledande fasen efter fotodissociation av metyljodid.
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11 References


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