Molecular Motion in Frustrated Lewis Pair Chemistry: insights from modelling

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To my family.
Mechanisms of reactions of the frustrated Lewis pairs (FLPs) with carbon dioxide (CO$_2$) and hydrogen (H$_2$) are studied by using quantum chemical modelling. FLPs are relatively novel chemical systems in which steric effects prevent a Lewis base (LB) from donating its electron pair to a Lewis acid (LA). From the main group of the periodic table, a variety of the electron pair donors and acceptors can create an FLP and the scope of the FLP chemistry is rapidly expanding at present. Representative intermolecular FLPs are phosphines and boranes with bulky electron-donating groups on phosphorus and bulky electron-withdrawing groups on boron – e.g., the $t$Bu$_3$P/B(C$_6$F$_5$)$_3$ pair. The intramolecular FLPs feature linked LB and LA centers in one molecule.

Investigations of the FLP reaction mechanisms were carried out using the transition state (TS) and the potential energy surface (PES) calculations plus the Born-Oppenheimer molecular dynamics (BOMD) as an efficient and robust implementation of general ab initio molecular dynamics scheme. In BOMD simulations, quantum and classical mechanics are combined. The electronic structure calculations are fully quantum via the density functional theory (DFT). Molecular motion at finite (non-zero) temperature is explicitly accounted for at non-quantized level via Newton’s equations. Due to recent advancements of computers and algorithms, one can treat fairly large macromolecular systems with BOMD and even include significant portion of the first solvation shell surrounding a large reacting complex in the molecular model.

Main results are as follows. It is shown that dynamics is significant for understanding of FLP chemistry. The multiscale nature of motion – i.e., light molecules such as CO$_2$ or H$_2$ versus a pair of heavy LB and LA molecules – affects the evolution of interactions in the reacting complex. Motion which is perpendicular to the reaction coordinate was found to play a role in the transport of the activated complex through the TS-region. Regarding the heterolytic cleavage of H$_2$ by $t$Bu$_3$P/B(C$_6$F$_5$)$_3$, FLP simulated in gas phase and with explicit solvent, it was found that (i) the reaction path includes shallow quasi-minima “imbedded” in the TS-region, and (ii) $t$Bu$_3$P/B(C$_6$F$_5$)$_3$ are almost stationary while proton- and hydride-like fragments of H$_2$ move toward...
phosphorous and boron respectively. For binding of CO$_2$ by tBu$_3$P/B(C$_6$F$_3$)$_3$ FLP, it was found that (i) the reacting complex can “wander” along the “potential energy wall” that temporarily blocks the path to the product, and (ii) the mechanism can combine the concerted and two-step reaction paths in solution. The discovered two-step binding of CO$_2$ by tBu$_3$P/B(C$_6$F$_3$)$_3$ FLP involves solvent-stabilized phosphorus-carbon interactions (dative bonding). These and other presented results are corroborated and explained using TS and PES calculations. With computations of observable characteristics of reactions, it is pointed out how it could be possible to attain experimental proof of the results.
List of Publications

This thesis is based on the following publications, referred to in the text by their Roman numerals.

I. *Ab initio* dynamics trajectory study of the heterolytic cleavage of \( \text{H}_2 \) by a Lewis acid \([\text{B}(\text{C}_6\text{F}_5)_3]\) and a Lewis base \([\text{tBu}_3\text{P}]\)
Maoping Pu and Timofei Privalov

II. How frustrated Lewis acid/base system pass through transition-state region: \( \text{H}_2 \) cleavage by \( \text{tBu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3 \)
Maoping Pu and Timofei Privalov

III. *Ab initio* molecular dynamics study of hydrogen cleavage by a Lewis base \([\text{tBu}_3\text{P}]\) and a Lewis acid \([\text{B}(\text{C}_6\text{F}_5)_3]\) at mesoscopic level
Maoping Pu and Timofei Privalov

IV. Multiple-path of \( \text{CO}_2 \) binding by a Lewis acid \([\text{B}(\text{C}_6\text{F}_5)_3]\) and a Lewis base \([\text{tBu}_3\text{P}]\): the energy landscape perspective
Maoping Pu and Timofei Privalov

V. Uncovering the role of intra- and intermolecular motion in frustrated Lewis acid/base chemistry: *ab initio* molecular dynamics study of \( \text{CO}_2 \) binding by phosphorus/boron frustrated Lewis pair \([\text{tBu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3]\)
Maoping Pu and Timofei Privalov

VI. *Ab initio* molecular dynamics with explicit solvent discovers a two-step pathway in the Frustrated Lewis Pair reaction
Maoping Pu and Timofei Privalov
Publications not included in this thesis

VII. **Binding of CO$_2$ by a Mes$_2$PCH$_2$CH$_2$B(C$_6$F$_5$)$_2$ species: an involvement of the ground state species in a low-energy pathway**
Maoping Pu and Timofei Privalov

VIII. **Toward controlling water oxidation catalysis: tunable activity of Ruthenium complexes with axial imidazole/DMSO ligands**
Lei Wang, Lele Duan, Beverly Stewart, Maoping Pu, Jianhui Liu, Timofei Privalov, Licheng Sun

IX. **Chemistry of intermolecular frustrated Lewis pairs in motion: emerging perspectives and prospects**
Maoping Pu and Timofei Privalov

Parts of this thesis build upon

**Dynamical analysis of chemical activity of sterically encumbered Lewis acid/Lewis base pairs**
Maoping Pu

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Contents

List of Publications ........................................................................................................ VII
Abbreviations .................................................................................................................. X
1. Introduction ............................................................................................................... 1
2. Computational methodology ..................................................................................... 3
   2.1 Basic theory ............................................................................................................ 3
   2.2 Wavefunction methods ......................................................................................... 5
   2.3 Density functional theory ..................................................................................... 6
   2.4 Basis set ............................................................................................................... 9
   2.5 Transition state theory ......................................................................................... 10
   2.6 Ab initio molecular dynamics .............................................................................. 13
   2.7 Solvent models ..................................................................................................... 14
3. Background information ......................................................................................... 16
4. What is an FLP? The tBu3P/B(C6F5)3 pair as an example .................................... 18
5. Molecular motion in the reaction of tBu3P/B(C6F5)3 with H2 ................................ 21
6. Molecular motion in tBu3P/B(C6F5)3 plus CO2 reaction ....................................... 29
7. Concluding remarks ............................................................................................... 37
Sammanfattning på svenska ..................................................................................... 39
Acknowledgements ..................................................................................................... 41
References ..................................................................................................................... 42
Abbreviations

AIMD \( \textit{ab initio} \) molecular dynamics
BO Born-Oppenheimer
BOMD Born-Oppenheimer molecular dynamics
BSSE basis set superposition error
DFT density functional theory
DFT-D dispersion corrected density functional theory
eq equation
FLP frustrated Lewis pair
FMO frontier molecular orbital
GGA generalized gradient approximation
HF Hartree-Fock
HK Hohenberg-Kohn
HOMO highest occupied molecular orbital
KS Kohn-Shaw
LUMO lowest unoccupied molecular orbital
LYP Lee-Yang-Parr
MD molecular dynamics
MEP minimum energy pathway
NAC near attack conformer
NEB nudged elastic band
PE potential energy
PES potential energy surface
QC quantum chemistry
RC reaction coordinate
RH Roothaan-Hall
SCF self-consistent field
TF Thomas-Fermi
TS transition state
TST transition state theory
vdW van der Waals
1. Introduction

A chemical reaction is a process in which transformation(s) of molecule(s) take place. To reveal the mechanism of a reaction, one has to determine its characteristics by experiment and/or theory. Depending on the magnitude of timescales and properties of interest, exploration might be more straightforward with theory rather than with experiment. Pursuit of deeper understanding of molecules and reactions between them can benefit from rapid advancement of scientific computing.

Molecular motion can be understood in terms of normal modes, coupling between them, mode-populations and energy-flows. Therefore, the challenge of mechanistic study based on molecular motion is twofold - firstly, one needs to understand which modes are responsible for the chemical process of interest and characterize the reaction-pathway, and secondly, to figure out how the system might proceed along the reaction path. This challenge can be met but with approximations regarding how electrons and nuclei are described. Rephrasing what was said by Dirac back in 1929, the underlining physical laws which govern interactions between molecules are known - e.g., the Schrödinger equation - however, the application of the governing laws to studies of chemical transformations requires approximations.

A combination of reasonable approximations and statistical mechanics has led to the transition state theory (TST) which is widely used to describe chemical reaction mechanisms. At present, TST is computationally affordable for systems with (many) hundreds of atoms. Starting from the late 1980s, with the advent of sufficiently powerful computers and development of quantum-chemical methodologies suitable for time-resolved modelling of large chemical systems, it is possible to perform “virtual experiments” with molecules in silico. The first principle (ab initio) branch of molecular dynamics allows the insight at the atomic level and pico-second timescales. This complements continuous advancement of chemical experiment towards microscopic timescales.

The aim of the work presented in this thesis is to investigate the role of molecular motion in mechanisms of chemical reactions involving frustrated Lewis pairs (FLPs). FLPs are novel chemical systems in which steric bulk prevents ordinary Lewis neutralization. Reactions, studied with means of
theory, are the heterolytic H₂ cleavage and CO₂ capture by representative FLP, tBu₃P/B(C₆F₅)₃. We found and rationalized some mechanistic effects which can arise due to multiscale molecular motion in FLP reactions.

This thesis is organized as follows. In Chapter 2, the computational methodologies are presented; Chapter 3 concisely provides background information. Chapter 4 presents results regarding tBu₃P/B(C₆F₅)₃ frustrated Lewis pair. Chapters 5 and 6 present the results regarding mechanisms of H₂ cleavage and CO₂ binding by tBu₃P/B(C₆F₅)₃, respectively; Concluding remarks are given in Chapter 7.
2. Computational methodology

2.1 Basic theory

The time-dependent Schrödinger equation,\(^1\) (Eq. 1), is the starting point of the non-relativistic \textit{ab initio} quantum chemical (QC) theory; the Hamiltonian \(\hat{H}\) is given by Eq. 2 in atomic units.

\[
\hat{H}\Psi(t, R, r) = \frac{i\hbar}{\partial t} \frac{\partial \Psi(t, R, r)}{\partial t}. \quad \text{(Eq. 1)}
\]

\[
\hat{H} = T_e + T_n + V_{en} + V_{ee} + V_{nn} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_{i}^{2} - \sum_{A=1}^{M} \frac{1}{2M_{A}} \nabla_{A}^{2} - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_{A}}{r_{iA}} + \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{1}{r_{ij}} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_{A}Z_{B}}{R_{AB}}. \quad \text{(Eq. 2)}
\]

In Eq. 1, the molecular wavefunction \(\Psi(t, R, r)\) depends on all electronic and nuclear coordinates \((r)\) and \((R)\), and time \((t)\); \(\nabla\) is the Laplace operator; \(M_{A}\) is the mass of nucleus \(A\) with the charge \(Z_{A}\); \(N\) and \(M\) are the total numbers of electrons and nuclei; \(r_{iA}\), \(r_{ij}\), and \(R_{AB}\) are the electron-nucleus, electron-electron and nucleus-nucleus distances, respectively; \(T_{e}\) and \(T_{n}\) are electronic and nuclear kinetic energies, respectively; \(V_{en}, V_{ee}\) and \(V_{nn}\) are the electron-nucleus, electron-electron, nucleus-nucleus interaction (Coulomb) energies.

With the ansatz \(\Psi(t, R, r) = \Psi(r, R) e^{iEt/\hbar}\) where \(E\) is the total energy of the isolated molecular system, the time-independent form of the Schrödinger equation reads

\[
\hat{H}\Psi(r, R) = E\Psi(r, R). \quad \text{(Eq. 3)}
\]

At the non-relativistic level, the Schrödinger equation is complete but impractical for treatment of polyatomic systems - hence, necessity of approximations.

The Born-Oppenheimer (BO) approximation makes use of one fundamental characteristic of molecules - the several orders of magnitude sepa-
ration between the timescales of the electronic and nuclear dynamics. Because of the mass difference between nuclei and electrons, e.g., a proton is 1836 times heavier than an electron, the timescale of the reorganization of the electrons of a molecule in response to a change in nuclei positioning is several orders of magnitude smaller than the shortest timescale of nuclear dynamics. The essence of BO approximation is that electrons adiabatically follow the motion of nuclei in molecules; thus, the molecular wavefunction \( \Psi(r, R) \) could be written as

\[
\Psi(r, R) = \phi(r \mid R)\chi(R), \quad \text{(Eq. 4)}
\]

where \( \chi(R) \) is the nuclear wavefunction and \( \phi(r \mid R) \) is the electronic wavefunction which is parametrically dependent on nuclear configuration. Therefore,

\[
\hat{H}_e\phi(r \mid R) = E_e(R)\phi(r \mid R). \quad \text{(Eq. 5)}
\]

In the electronic Schrödinger equation (Eq. 5), \( \hat{H}_e \) is the electronic Hamiltonian - i.e., \( \hat{H} \) in Eq. 2 without \( T_n \) and \( V_{nn} \). \( E_e(R) \) is the electronic energy of the system.

For a system with the known Hamiltonian \( \hat{H} \), the functional \( E[\Psi] \) given by Eq. 6 allows finding of an approximation to the ground state, \( (E_0, \Psi_0) \), at any given level of accuracy. The variational principle states that \( E[\Psi] \geq E_0 \) for \( \Psi \neq \Psi_0 \); \( E[\Psi] = E_0 \) if and only if \( \Psi \) is exactly the true ground state wavefunction, \( \Psi_0 \), of \( \hat{H} \).

\[
E[\Psi] = \frac{\langle \Psi \mid \hat{H} \mid \Psi \rangle}{\langle \Psi \mid \Psi \rangle} \geq \frac{\langle \Psi_0 \mid \hat{H} \mid \Psi_0 \rangle}{\langle \Psi_0 \mid \Psi_0 \rangle} = E_0. \quad \text{(Eq. 6)}
\]

In quantum chemistry, the variational method is often applied to finding an approximation to the exact solution of the Schrödinger equation. One seeks the minimal value of the functional \( E[\Psi_{\text{trial}}] \) with respect to the variation of all parameters in the trial wavefunction \( \Psi_{\text{trial}} \). Thus, the obtained wavefunction is the best approximation to the exact ground state \( \Psi_0 \); the expectation value of the energy in such an approximate state is strictly an upper bound to the true ground state energy of the system.
2.2 Wavefunction methods

The Hartree–Fock (HF) method is an approximate method of finding the wavefunction and the energy of a stationary state of the quantum system. The idea is to replace the complicated many-electron problem by a set of one-electron problems in which electron-electron repulsion is treated in an average way. With the Pauli principle in mind, the exact \( N \)-electron wavefunction is approximated by a single Slater determinant (Eq. 7) - \( i.e. \), an antisymmetric product of one-electron wave functions.\(^3\)

\[
\varphi(r | R) = \varphi(x_1, \ldots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \phi_1(x_2) & \cdots & \phi_1(x_N) \\ \phi_2(x_1) & \phi_2(x_2) & \cdots & \phi_2(x_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(x_1) & \phi_N(x_2) & \cdots & \phi_N(x_N) \end{vmatrix}. \tag{Eq. 7}
\]

In Eq. 7, \( \phi_i \) is an orbital function which obeys effectively the one-electron Fock equation; \( x_i \) denotes the spatial and spin coordinate of the \( i \)-th electron.

The expectation value of the electronic Hamiltonian is

\[
E_{1HF} = \left\langle \varphi(r | R) | \hat{H}_e | \varphi(r | R) \right\rangle = \sum_{i=1}^{N} H_i + \frac{1}{2} \sum_{i,j=1}^{N} \left( J_{ij} - K_{ij} \right). \tag{Eq. 8}
\]

where \( H_i \) is the sum of kinetic and potential energies of \( i \)-th electron interacting with all nuclei; the Coulomb integral \( J_{ij} \) describes electrostatic repulsion between \( i \)-th and \( j \)-th electrons \( \left( J_{ij} = <\phi_i(x_1)\phi_j(x_2) | 1/r_{12} | \phi_j(x_1)\phi_i(x_2) > \right) \); the exchange integral \( K_{ij} \) is the result of Pauli exclusion principle requiring that wavefunction must be antisymmetric with respect to the permutation of the coordinates of any two electrons such as a pair of \( i \)-th and \( j \)-th electrons \( \left( K_{ij} = <\phi_i(x_1)\phi_j(x_2) | 1/r_{12} | \phi_j(x_1)\phi_i(x_2) > \right) \).

The mean field assumption is central to the HF-method - the contribution of the electron in the single orbital to the system’s total energy is that of the electron exposed to the mean electric field of all the other electrons. Such a description lacks the proper correlation of the motion of electrons. However, the effect known as electron exchange (Pauli repulsion) is fully accounted
for in the HF-method and the exact HF exchange energy could be a justifiable component of the hybrid density functionals (see below Section 2.3).

The correlation energy can be defined as the difference between the true electronic energy and the HF-energy. A general approach to treat correlation effect uses a truncated expansion of the wavefunction with several Slater determinants. Such an expansion can be constructed in several ways - e.g., the configuration interaction (CI), multi-configurational self-consistent field (MCSCF), and coupled cluster (CC) methods to name just a few. The CI-method deals with linear combination of the determinants based on HF-orbitals with some occupied spin-orbitals replaced by unoccupied spin-orbitals. The number of the occupied-unoccupied orbital permutations is equal to the expansion order of the “excited” determinant. The variational method is used to compute the coefficients of the “excited” determinants in the expansion. The MCSCF-method uses the optimized molecular orbitals and is thus useful in cases where the HF-wavefunction is a poor approximation - e.g., near-degeneracy of configurations in which chemical bonds break (transition-states) or excited electronic states. In comparison to the CI-method and the MCSCF-method with either the complete or restricted active spaces (CAS- or RAS- MCSCF), arguably a better correlated method is the coupled cluster (CC) method. Last but not least, it is worth mentioning the technique that splits the molecular Hamiltonian into the soluble part and a perturbation - e.g., the Møller-Plesset perturbation theory.

2.3 Density functional theory

The density functional theory (DFT) aims to describe polyatomic (molecular) system on the basis of its electron density $\rho(r)$. For an ensemble of $N$ electrons with the wavefunction $\psi$, the electron density is defined as $\rho(r) = \sum_{i=1}^{N} \int |\psi(x_i)|^2 dx_1 dx_2 ... dx_N$ where $x_i$ is the collective notation for the spatial and spin coordinate of the $i$-th electron. At present, DFT is a widely used approach for studies of large systems. An advantage of DFT is that it is considerably faster than any other methods in the realm far beyond the HF-approximation.

An early precursor to modern DFT is the Thomas-Fermi (TF) model of an atom - a system with many electrons but only one nucleus with charge $Z$. It is an instructive example of the kinetic energy of electrons, electron-electron and electron-nucleus interactions expressed as density functionals. To be specific, the energy of electrons in the TF-model is
\[ E[\rho] = T[\rho] + V_{\text{en}}[\rho] + V_{\text{ee}}[\rho]. \]  
(Eq. 9)

where \( T[\rho] \) is the kinetic energy density functional (Eq. 10), \( V_{\text{en}}[\rho] \) and \( V_{\text{ee}}[\rho] \) are the electron-nucleus and electron-electron density functionals given by (Eq. 11) and (Eq. 12), respectively.

\[ T[\rho] = \frac{3\hbar^2}{10m_e} \left( \frac{3}{8\pi} \right)^{2/3} \int \rho(r)^{5/3} \, d^3r, \]  
(Eq. 10)

\[ V_{\text{en}}[\rho] = \int \rho(r) \frac{Ze^2}{r} \, d^3r, \]  
(Eq. 11)

\[ V_{\text{ee}}[\rho] = \frac{1}{2} e^2 \int \frac{\rho(r)\rho(r')}{|r-r'|} \, d^3r \, d^3r'. \]  
(Eq. 12)

In order to describe polyatomic (molecular) systems solely in terms of the electron density, an elaborate theoretical framework has been built upon two Hohenberg-Kohn (HK) theorems. In principle, the knowledge of the electron density is all that is necessary for a complete determination of molecular properties. The first HK-theorem shows that electron density uniquely determines ground state properties of a many-electron system. The importance of it is that the use of functionals of the electron density can reduce the problem of \( N \) electrons with \( 3N \) spatial coordinates to only \( 3 \) spatial coordinates. The first HK-theorem had been extended to the case of excited states as well. The second HK-theorem provides that the correct ground state electron density indeed minimizes the energy functional of the system. Based on the two HK theorems, the energy of a system is given by

\[ E_{\text{sys}}[\rho] = \int \rho(r) v(r) dr + F[\rho]. \]  
(Eq. 13)

where \( v(r) \) is the external potential felt by the electrons - e.g., \( v(r) = V_{\text{en}}[\rho] \) for an isolated molecular system. The functional \( F[\rho] \) combines the kinetic energy, \( T[\rho] \), and the electron-electron interaction, \( V_{\text{ee}}[\rho] \), functionals – i.e., \( F[\rho] = T[\rho] + V_{\text{ee}}[\rho] \).

The Kohn-Sham (KS) DFT formulation is based on the idea that the many-body problem of interacting electrons could be resolved by making use of the system of non-interacting electrons in an effective potential. The
effective potential includes the external potential and the Coulomb interaction between electrons which gives rise to the exchange and correlation effects. Specifically, KS-DFT uses an ensemble of non-interacting electrons as a “simple” reference system because of its known kinetic energy functional, $T_0[\rho]$, and introduces the exchange-correlation functional, $E_{xc}[\rho]$. With that and $J[\rho]$ accounting for the classical Coulomb repulsion, $F[\rho]$ reads:

$$F[\rho] = T_0[\rho] + J[\rho] + E_{xc}[\rho].$$  \hspace{1cm} (Eq. 14)

The difficulty of KS-DFT is devising the actual exchange-correlation functional $E_{xc}[\rho]$. The local density and local spin-density approximations (LDA and LSDA) are arguably the two simplest treatments. Being derived from analyses of free electron gas, LDA relates to the TF-model described above. If both the density and its gradient are taken into account, one arrives at the generalized gradient approximation (GGA) method - still local, but more accurate for molecular geometries and the ground-state energies. Examples of popular exchange and correlation functionals are the Becke’s 1988 exchange functional and the Lee-Yang-Parr (LYP) functional, respectively. Furthermore, one can include the second derivative of the electron density in the exchange-correlation model - i.e., meta-GGA functionals such as Minnesota functionals.

Another possible approach is hybrid DFT functionals. An example is B3LYP defined as Eq. 15, where $a = 0.8$, $b = 0.72$ and $c = 0.81$.

$$E_{xc}^{B3LYP} = aE_{xc}^{LSDA} + (1 - a)E_{xc}^{HF} + bE_{xc}^{B88} + cE_{xc}^{LYP} + (1 - c)E_{xc}^{VWN}. \hspace{1cm} (Eq. 15)$$

In Eq. 15, LSDA is the local spin exchange functional to uniform electron gas, B88 is the Becke 88 exchange functional, LYP is a GGA correlation functional and VWN is the Vosko-Wilk-Nusair local density approximation correlation functional.

The so-called dispersion force (aka van der Waals force), $E_D$, arises from electron correlation in interacting objects (molecules) and it asymptotically decays as $1/R^6$. Such an interaction is not described properly by the LDA and GGA DFT methods. A way to correct for this is to use the semi-empirical correction, $E_{DFT-D} = E_{DFT} + E_D$, where $E_D$ is calculated by using atomic empirical dispersion coefficients derived either from experiments or high level \textit{ab initio} calculations. Computational efficiency is the main ad-
vantage of the empirical methods. One of the examples is the DFT-DN methods developed by Grimme. It is also possible to construct DFT functionals which account for the dispersion forces, e.g., the so-called Minnesota family of functionals.

The accuracy of DFT in describing energetics and structures, has been benchmarked against accurate experiments and higher-level wavefunction calculations. In the diverse barrier height database (DBH24) which includes six nucleophilic substitutions, six unimolecular reactions, six associations and six hydrogen transfers reactions, the mean unsigned error (MUE, or average absolute deviation) of barrier heights computed with B3LYP is 4.2 kcal/mol with MG3S basis set. For ten van der Waals complexes, e.g. OCS-CO$_2$ dimer, B3LYP with aug-cc-PVTZ basis set gives MUE of 1.20 kcal/mol for binding energy while the dispersion corrected method B3LYP-D2 reduces MUE to 0.47 kcal/mol. For hydrogen bonding, MUE is reduced from 1.6 kcal/mol (B3LYP) to 0.23 kcal/mol (B3LYP-D3) in the database of 23 hydrogen-bonded dimers including water dimer.

2.4 Basis set

The variational method yields a set of $N$ coupled integro-differential HF equations for $N$ spin-orbitals. To simplify numerical implementation of the self-consistent-field (SCF) approach, it is convenient to express molecular orbitals using the basis set expansion. With a given basis set of either Gaussian- or Slater-type, the Roothaan-Hall (RH) matrix equations replace the set of integro-differential HF equations.

$$\varphi_i = \sum_{\mu=1}^{N_{bas}} c_{\mu i} \chi_\mu .$$  \hspace{1cm} (Eq. 16)

Here $\varphi_i$ is molecular (or atomic) wavefunction, $c_{\mu i}$ is orbital coefficient, and $\chi_\mu$ is basis set functions which could be in principle any functions.

Finite basis sets are susceptible to give the basis set superposition error (BSSE). In calculation of the interaction energy of two units, the units of the complex may have somewhat expanded basis set in comparison to the individual unit. Take the helium dimer as an example. It is shown that the interaction energy – i.e., the energy difference between the dimer and the sum of helium atoms – becomes smaller and the helium-helium distance longer as the size of the basis set increases. With the counterpoise method
(Eq. 17), one can correct for BSSE using the larger basis set, AB, for calculation of monomers A and B.

\[ E_{\text{int}} = E(AB)^{AB} - E(A)^{AB} - E(B)^{AB}. \]  

(Eq. 17)

### 2.5 Transition state theory

Simply put, the transition state theory (TST) is a “marriage” between quantum and classical mechanics with the former describing electrons and the latter describing nuclei. Back in 1935, Eyring formulated and implemented the seminal idea that “The forces between atoms are due to the motion and distribution of electrons and must be calculated, therefore, using quantum mechanics. However, after this is done the nuclei themselves can be assumed to move under the influence of their forces according to classical mechanics, it must be possible, therefore, to calculate the reaction rates by the methods of statistical mechanics.”

![Scheme 1](image)

**Scheme 1.** An illustration of the potential energy surface for a reaction with the transition state; \( \delta \) is the characteristic barrier “length”, \( E_0 \) is the zero-level energy difference between the reactant and transition state.

In addition to the Born-Oppenheimer (BO) approximation, the so-called quasi-equilibrium assumption is particularly noteworthy – i.e., TS is assumed to be in equilibrium with the reactants. By definition, on the potential energy surface a TS-structure has one (and only one) negative eigenvalue of the matrix of second derivatives of energy (the hessian matrix). Additionally, it is assumed that TS is the point of no return - i.e., any trajectory that reaches TS proceeds further to product without re-crossing at the TS-area. With
the probability and the lifetime of the TS denoted by \( C' \) and \( \tau \), Eq. 18 is a general expression for the reaction rate constant, \( k \).

\[
\frac{C'}{\tau} = k. \tag{Eq. 18}
\]

With the quasi-equilibrium assumption, the probability of the TS at temperature \( T \) can be derived using statistical mechanics. The TS lifetime is the characteristic “length” of the barrier divided by the mean “decomposition” velocity of the TS, i.e. \( \bar{v} = (\kappa_B T / m^*)^{1/2} \) where \( m^* \) is the effective mass. Making use of partition functions \( Q \), Eq. 18 reads

\[
k = \frac{\kappa_B T}{h} \frac{Q^T Q^R Q^V}{Q^T Q^R Q^A Q^B Q^V} e^{-E_0/RT}. \tag{Eq. 19}
\]

where, \( Q_T, Q_R, Q_V \) are translational, rotational and vibrational partition functions, respectively; \( # \) stands for TS and A, B denote reactants.

The so-called universal “frequency” factor \( \kappa_B T / h \) where \( \kappa_B \) and \( h \) are the Boltzmann and Planck’s constants, depends only on temperature \( T \); it can be interpreted as inverse “lifetime” of TS - qualitatively speaking, an effective duration of the system in the TS region.

The non-recrossing and the neglect of tunneling are assumptions which are easy to go beyond, at least in theory. With the transmission coefficient \( \gamma(T) \), added a posteriori correction for the recrossing of the TS-area \( \Gamma(T) \), tunneling \( \kappa(T) \) as well as other effects \( g(T) \).

Presently, there are a number of computational means for location of TS. One of methods is the nudged elastic band method with climbing image (NEB-CI). In the NEB methods, minimum energy path (MEP) is described as a “string” with a number of discrete “images” connecting reactant- and product-configurations. With fictional spring interactions added to ensure the separation between adjacent images, the optimization of all images is executed. The advantage of the method is that NEB-CI is proven to converge to the true MEP in the multidimensional configurational space of the system albeit with rather high computational expense and slow convergence of the path as a whole.

Using the ideal gas model, the total partition function \( Q \) (nuclei only) of \( N \) molecules is \( Q = q^N \) where each \( q \), the individual molecular partition
function, is the product of molecular translational, rotational, and vibrational
partition functions—i.e., \( q_t, q_r, \) and \( q_v \), respectively.\(^\text{22}\)

Based on the analytical energy expressions for the free particle in a
box, rigid body rotor and one-dimensional harmonic oscillator, the individual
partition functions \( q_t, q_r, \) and \( q_v \), are as follows.

The translational partition function:

\[
q_t = \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} V.
\]  
(Eq. 20)

where \( V \) is the volume to which the motion of molecule is constrained,
\( q_t = \left( \frac{2\pi m k T}{h^2} \right)^{1/2} L \) if the molecule is constrained to move along a single axis
over the length \( L \).

The rotational partition function:

\[
q_r = \frac{\sqrt{\pi}}{\sigma} \frac{\sqrt[3]{8\pi^2 I_A k_B T}}{h} \frac{\sqrt[3]{8\pi^2 I_B k_B T}}{h} \frac{\sqrt[3]{8\pi^2 I_C k_B T}}{h}.
\]  
(Eq. 21)

where \( \sigma \) is the symmetry index of the molecule, \( I_A, I_B, I_C \) are the three
principle moments of inertia of the molecule.

The vibrational partition function:

\[
q_v = \prod_{k=1,3N-6} \frac{e^{-\nu_j^2/2 k_B T}}{1-e^{-\nu_j^2/2 k_B T}}.
\]  
(Eq. 22)

where \( \nu_j \) is the frequency of the \( j \)th harmonic vibration of the molecule.

Kramers’ approach reduced the total phase space of a system to the
two-dimensional space—i.e., the reaction coordinate \( x(t) \) and its time deriva-
tive \( \dot{x}(t) \).\(^\text{23, 24}\) All other degrees of freedom give rise to the linear damping
force and the energy-exchanging bath (fluctuations). In such a model, the
actual “motion” in the reduced two-dimensional space, \( \{ x(t), \dot{x}(t) \} \), is de-
scribed by the Langevin equation

\[
M\ddot{x} = -\frac{\partial U(x)}{\partial(x)} - \gamma M\dot{x} + \varepsilon(t).
\]  
(Eq. 23)
where, $U$ is the potential energy corresponding to the reaction coordinate, $-\gamma Mx$ and $\xi(t)$ are the damping and fluctuating forces. One typically considers the damping force as weak-, medium- and strong- scenarios. An expression formally similar to TST can be obtained in the intermediate-to-strong friction scenarios.\(^{20}\)

### 2.6 Ab initio molecular dynamics

As a method, the *ab initio* molecular dynamics (AIMD) can explicitly simulate molecular motion. Unlike molecular dynamics (MD) using the parameterized *force-fields* to describe the inter- and intra-molecular interactions, AIMD computes system’s evolution with forces calculated (updated) at *ab initio* electronic structure level “on-the-fly”. Resultant trajectories can capture molecular transformations in time-resolved fashion. An ensemble of the molecular trajectories could then be used in order to extract essential characteristics of the process and derive the mechanism.

Relatively high computational cost often arises for large systems because the electronic structure, and thus the forces, is calculated at each time step in AIMD simulations.\(^{25}\) On the other hand, a substantial gain in computational efficiency can be attained from the neglect of the quantization of nuclear motion.

The AIMD implementation, used in the work described in this thesis, is the Born-Oppenheimer molecular dynamics (BOMD). This is a hybrid classical-/quantum-method in which classical equations of motion are integrated for all atoms of the system and the forces acting on atoms, $\vec{F}_{i}^{BO}$, are derived from the BO energy which is the function of molecular geometry. The BO energy is obtained via the standard variational SCF procedure using “conventional” density functionals and basis sets.\(^{26}\) The position and the velocity of i-th atom are updated according to integration algorithm e.g., velocity Verlet with a proper timestep, $\delta t$, as shown by Eqs. 25 - 26.

\[
m_{i}\ddot{a}_{i} = \vec{F}_{i}^{BO}. \quad (\text{Eq. } 24)
\]

\[
r(t + \delta t) = r(t) + v(t)\delta t + \frac{1}{2}a(t)\delta t^2, \quad (\text{Eq. } 25)
\]

\[
v(t + \delta t) = v(t) + \frac{1}{2}[a(t) + a(t + \delta t)]\delta t. \quad (\text{Eq. } 26)
\]
The critical advantage of BOMD with DFT is that it can efficiently provide insight into “chemistry in motion” of really large systems with manageable computational time for a comprehensive ensemble of trajectories. However, the approach is insufficient in cases where quantum effects (e.g., tunneling) dominate and/or the separation of the electronically adiabatic PESs is small. For reasons of brevity, other AIMD formulations such as the Ehrenfest molecular dynamics and the Car-Parrinello molecular dynamics were not discussed.

In MD simulations in general, the states in which it is possible to find the system and their probabilities must be evaluated. A combination of all possible states constitutes the ensemble of the system. The microcanonical ensemble, i.e. NVE, represents the system in which the number of particles, N, volume, V, and the total energy, E, are constant. It is the simplest to simulate provided that the integration procedure accurately conserves the total energy while the evolution of the system involves the potential energy being converted into kinetic energy and vice versa. Instead of the total energy, the temperature in the canonical ensemble, NVT, could be kept constant in simulation. It corresponds to a system in thermal equilibrium with heat bath. Simulations of NVT ensembles make use of thermostat models such as a simple rescaling of velocities, Berendsen Nosé-Hoover and Langevin thermostats. The work described in this thesis involves NVT- and NVE-type modelling; to maintain NVT ensemble we use the Langevin thermostat with the relaxation (damping) time $\tau \approx 1.5$ to 2 ps.

A part of the work described in this thesis involves calculation of infrared (IR) activity (spectra) of chemical systems. The IR spectra for the stationary structures and transient structures along the MEP, was computed using the standard harmonic frequency analysis and on the basis of BOMD trajectories.

The BOMD-based IR-spectra were computed using the Fourier transform of the autocorrelation function of the time-dependent total dipole moment $\langle \mathbf{d}(\tau) \mathbf{d}(t+\tau) \rangle$ as follows:

$$I(\omega) = \int \hat{d}(\tau) \hat{d}(t+\tau) e^{-i\omega t} dt.$$  \hspace{1cm} (Eq. 27)

### 2.7 Solvent models

Continuum solvation model treats the solvent molecules as a uniform medium with a dielectric constant $\varepsilon$ and a cavity for solute M in the medium.
example, the Onsager model simply uses the spherical cavity in the polarizable medium that is calculated to be in accord with the dipole moment of the solute – i.e., the simplest formulation of the so-called Self-Consistent Reaction field (SCRF). Modern continuum solvent models use the SCRF approach with vdW-surface for the cavity shape and parameterized interactions.

For describing solvent effect on processes with finite timescales, the dielectric constant $\epsilon$ could in principle be considered as time-dependent – i.e. the solvent may have different timescales of response versus electronic configuration or geometrical change at different reaction stages.

In explicit solvation model, the solvent molecule is added one at a time until the property of interest no longer change (converged). The solvent and solute molecules are allowed to interact with each other and all the interaction in principle can be calculated explicitly. For the sake of computational cost, different theoretical methods can be used to describe solute and solvent e.g., QM/MM, quantum mechanics for the solute and molecular mechanics for the solvent.
3. Background information

More than half a century ago, Brown pointed out that steric effect arising from bulky substituents of a Lewis base (LB) and a Lewis acid (LA) may not only hinder the formation of a classical LB-LA adduct but drive a chemical reaction. New manifestations of steric effect have come to light with the discovery of (Mes)$_2$P(C$_6$F$_4$)B(C$_6$F$_5$)$_2$ species, Mes = C$_6$H$_2$Me$_3$, which reversibly cleave H$_2$. Nowadays, the term “frustrated Lewis pair” (FLP) describes (i) a pair of bulky LB and LA molecules which do not form the quenched Lewis adduct for steric reasons - i.e., intermolecular FLPs, and (ii) a molecule which includes unquenched LB and LA centers – i.e., intramolecular FLPs. To mention just a few notable applications of FLPs are H$_2$ activation; binding of CO, NO, CO$_2$, N$_2$O, and SO$_2$, olefins, dienes, and alkynes; stoichiometric and catalytic hydrogenations; CO$_2$ reduction.

The work presented in this thesis deals with two FLP reactions - i.e., heterolytic cleavage of H$_2$, [1], and CO$_2$ capture, [2], by tBu$_3$P/B(C$_6$F$_5$)$_3$. According to experiments, exposure of the stoichiometric mixture of tBu$_3$P and B(C$_6$F$_5$)$_3$ to an atmosphere of H$_2$ at 1 atm pressure and 25°C, results in facile formation of [tBu$_3$PH][HB(C$_6$F$_5$)$_3$] salt (ion pair) - i.e., reaction [1]. A solution of tBu$_3$P/B(C$_6$F$_5$)$_3$ covered with an atmosphere of CO$_2$ gives zwitterionic tBu$_3$P(CO)OB(C$_6$F$_5$)$_3$ with high yield - i.e., reaction [2].

This thesis primarily focuses on the mechanistic aspects which underline chemical reactions [1] and [2] and, in the interest of space, leaves behind computational details and technicalities described in Methodological sections of the attached Papers. That being said, it deserves a brief mentioning that (i) all herein described calculations were performed using DFT-D functional theory with sufficiently large basis sets; (ii) BSSE and other possible sources of errors were estimated and found to be at acceptably low level; (iii) all BOMD and TS calculations were carried out using the commercially
available software Terachem v1.5 on the in-house computers with NVIDIA TESLA C2070 and C2075 GPUs; (iv) all PE-calculations were carried out using Gaussian 09 on resources provided by National Supercomputer Center (NSC, Linköping, Sweden).
4. What is an FLP? The $t$Bu$_3$P/B(C$_6$F$_5$)$_3$ pair as an example

Prior to dealing with the mechanisms of reactions [1] and [2], it is instructive to qualitatively access structural characteristics of the $t$Bu$_3$P/B(C$_6$F$_5$)$_3$ FLP. Two mechanistically relevant local minima are shown in Figure 1. In min 1, the phosphorous atom faces the boron atom - i.e. face-to-face configuration. The phosphorous atom faces one of the three C$_6$F$_5$ groups of B(C$_6$F$_5$)$_3$ in min 2. The gas phase energy of min 1 is circa 4 kcal/mol lower than the energy of min 2.

![Figure 1. PES minima of $t$Bu$_3$P/B(C$_6$F$_5$)$_3$ pair with (A) phosphorous facing boron, and (B) $t$Bu$_3$P facing one of three C$_6$F$_5$ groups of B(C$_6$F$_5$)$_3$.](image)

As described in Paper I, BOMD trajectories were initiated from min 1 in gas phase in order to estimate structural characteristics of the FLP at room temperature. It was found that $t$Bu$_3$P readily moves from the boron-facing position to the periphery of B(C$_6$F$_5$)$_3$ and above one of the three C$_6$F$_5$ groups followed by transition back to the boron-facing position. In Figure 2 areas A and B correspond to min 1 and min 2. The overall picture and the evolution specifically within area A are illustrated in Figures 3 and 4 with overlays of BOMD snapshots. It is observed (in silico) that gas phase trajectories of the $t$Bu$_3$P/B(C$_6$F$_5$)$_3$ pair remain confined in area A around min 1 for a period of time of the order of 10 picoseconds.
Figure 2. An illustration of the dynamics of the tBu₃P/B(C₆F₅)₃ pair including two representative trajectories with 50 ps duration per trajectory. Parameter χ describes the deviation from strictly face-to-face alignment in the tBu₃P/B(C₆F₅)₃ pair.

Figure 3. An illustration of the evolution of tBu₃P/B(C₆F₅)₃ pair over a long period of time involving both face-to-face and other configurations around min 1 and min 2 as shown in Figure 2.
In Paper I, the host-guest model has been devised in which the reaction-suitable LB / LA conformations were obtained from the dynamics of the \( t\text{Bu}_3\text{P}/B(C_6\text{F}_5)_3 \) in gas phase. However, a shortcoming of gas phase BOMD conformational analysis of \( t\text{Bu}_3\text{P}/B(C_6\text{F}_5)_3 \) is that, qualitatively speaking, \( t\text{Bu}_3\text{P}/B(C_6\text{F}_5)_3 \) has no other molecular “partners” to interact with.\(^{47,48}\) Thus, the gas phase FLP model was extended using the solvent cage treated explicitly at high quantum-chemical level in the BOMD simulations - \( i.e. \) the solute-solvent molecular clusters in Papers III and VI.

**Figure 4.** The view from the top (A) and from the side (B) of the dynamics of the \( t\text{Bu}_3\text{P}/B(C_6\text{F}_5)_3 \) pair in the face-to-face configuration – area A as shown in Figure 2.
5. Molecular motion in the reaction of $t\text{Bu}_3\text{P}/\text{B(C}_6\text{F}_5)_3$ with $\text{H}_2$

The mechanism of $[1]$ was investigated using PE-calculations and at time-resolved level using BOMD simulations in gas phase and with explicit solvent – Papers I – III.

Figure 5. The optimized (A) vdW-complex comprised of reactants and (B) the product of $[1]$; B3LYP-D3/6-311g** level of theory. All distances are in Å.

Figure 6. The 2D-PES $E(\text{P}^-\cdot\text{H}, \text{B}^-\cdot\text{H})$ of $\{t\text{Bu}_3\text{P} + \text{H}_2 + \text{B(C}_6\text{F}_5)_3\}$ system, with the projections of MEP and TS. The energy is in kcal/mol.
Figure 7. The TS-structure of [1]. All distances are in Å.

Figure 5 shows optimized geometries of the initial complex in which reactants are at the van der Waals (vdW) range from each other and the product of [1]. The calculated structure of [tBu3PH][HB(C6F5)3] in [1] is consistent with the published crystal structure. Figure 6 shows the two-dimensional PES E(P·H, B·H) of {tBu3P +H2 + B(C6F5)3} system with the MEP and TS projected on the P·H/B·H distances plane. Connecting {tBu3P +H2 + B(C6F5)3}vdW with [tBu3PH][HB(C6F5)3], MEP of [1] features the TS-structure in which the H-H bond length is almost the same as that in the initial vdW-complex with nearly unperturbed H2; and the B···H and P···H distances are longer than the onset of strong chemical interaction. The height of the reaction-barrier represented by the TS, Figure 7, is circa 5 kcal/mol with respect to {tBu3P +H2 + B(C6F5)3}vdW.

Figure 8. Simplified representations of (A) the reaction coordinate (RC) and (B) the relevant mode which is orthogonal to RC; H2 almost moves as a whole in both modes; timescales are symbolized by $\tau^{{\text{RC}}}$ and $\tau^{{\perp}}$. 

{tBu3P + H2 + B(C6F5)3}^{\text{TS}}
The entry into the saddle on 2D-PES $E(P^-H, B^-H)$ – i.e. MEP-segment \{$tBu_3P + H_2 + B(C_6F_5)_3\}^{vdW} \rightarrow TS$ – lacks the curvature; however, the MEP-segment “TS $\rightarrow$ product” has steeply declining slope (Figure 6). In the direction perpendicular to the MEP, the saddle of 2D-PES has low curvature as well. The small magnitude of the vibrational frequency of \{$tBu_3P + H_2 + B(C_6F_5)_3\}^{TS}$, $\nu^{RC}\approx -50 \text{ cm}^{-1}$, indicates that the reaction coordinate (RC) is predominated by motion of heavy masses. The RC and the relevant mode which is orthogonal to RC correspond to the symmetric and anti-symmetric normal modes of $P^-H-H^-B$, respectively.

![Figure 9. (A) One of the reactive trajectories of \{$tBu_3P + H_2 + B(C_6F_5)_3\}$ system projected on the PES $E(P^-H, B^-H)$. (B) The same trajectory versus MEP. The segment in green is the H-H bond breaking; the $B^-P$ distance stays nearly frozen on the short timescale of the $H_2$ cleavage.](image-url)
In papers I and II, different initial conditions were used for BOMD simulations of reaction \([1]\) and the obtained results – \textit{i.e.}, the reactive and non-reactive trajectories – are similar. Typical reaction-scenario, Figure 9, is that the trajectory is trapped in the TS-region for a period of time (about 350 fs). Qualitatively, \(\tau^\text{RC} \sim \tau^\text{BP}\), where \(\tau^\text{BP}\) is the timescale of the closing of the phosphine-borane “pocket” formed by relatively heavy \(t\text{Bu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3\). Quantitatively, \(\tau^\text{BP}\) is \textit{circa} half-picosecond and \(\tau^\perp\) has the order of 100 fs.

\[\text{Figure 10.}\] The PES \(E(P-H, B-H | B-P)\) calculated for \(B-P = 4.6 \text{ Å}\); the potential energies are displayed relative to the product (in kcal/mol). The contour line spacing is one \(\kappa_B T\) at \(T = 300 \text{ K}\).

Interpretation of trajectory-data requires consideration of several dimensions. As shown in Figure 9 A, a representatively reactive trajectory enters the TS-region alongside MEP but collisional events within the structurally loose transient complex make the trajectory crisscross the saddle of PES \(E(P-H, B-H | B-P)\) for a short but non-negligible period of time. This is consistent with the shallow minima on PES \(E(P-H, B-H | B^-P)\) for \(B^-P \approx [B^-P]^{TS}\), shown in Figure 10. During the typical time spent by trajectories in the TS-region, the dynamics of \(\{t\text{Bu}_3\text{P} + \text{H}_2 + \text{B}(\text{C}_6\text{F}_5)_3\}\) system is localized (“wrapped”) around a large segment of MEP that belongs to the TS area, Figure 9 B. However, trajectories drastically deviate from the MEP at the event of the heterolytic H-H bond cleavage – \textit{i.e.}, \(t\text{Bu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3\) are almost stationary while proton- and hydride-like fragments of \(\text{H}_2\) move toward phosphorous and boron respectively (trajectory-segment in green in Figure 9 B). Note that this segment does not overlap with the TS-region.
Figure 11. (A) A snapshot from BOMD simulation of the solute-solvent cluster including \( t\text{Bu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3 \), surrounded by 85 toluenes. (B) A qualitative PES \( E(\text{P}^\cdots\text{H}, \text{B}^\cdots\text{H}) \) of solvent-caged \( \{t\text{Bu}_3\text{P} + \text{H}_2 + \text{B}(\text{C}_6\text{F}_5)_3\} \) system with typical \([\text{B}^\cdots\text{P}] \approx 5.3 \, \text{Å}\); see details in Paper III. The energy scale is in kcal/mol.

In order to qualitatively rationalize results of BOMD simulations described above, a part of Paper II deals with more elaborate PE-calculations and analysis – i.e., the PES \( E(\text{P}^\cdots\text{H}, \text{B}^\cdots\text{H} \mid \text{B}^\cdots\text{P}) \) calculated for fixed values of the \( \text{B}^\cdots\text{P} \) distance. It is noteworthy that for \([\text{B}^\cdots\text{P}] \approx [\text{B}^\cdots\text{P}]_{\text{TS}} \), the PES \( E(\text{P}^\cdots\text{H}, \text{B}^\cdots\text{H} \mid \text{B}^\cdots\text{P}) \) has shallow local minima at \( \text{P}^\cdots\text{H}/\text{B}^\cdots\text{H} \) distances which are fairly close to those of the TS-structure – see an example in Figure 10.
Figure 12. (A) Plots of P–H and B–H distances versus time for representative BOMD trajectory of \{tBu3P + H2 + B(C6F5)3\} surrounded by 30 toluenes, the insert shows mean values of the B–P and H–H distance with the corresponding standard deviations σ for 0 - 450 fs time interval. (B) A snapshot of the solvent-caged \{tBu3P + H2 + B(C6F5)3\} system with P–B distance larger than 5 Å.

A shortcoming of gas phase BOMD analysis of the FLP reactions such as [1] is that, qualitatively speaking, tBu3P/B(C6F5)3 have no other molecular “partners” to interact with except H2 and each other. This is inefficient because interactions within tBu3P/B(C6F5)3 are non-covalent and thus have the same order of magnitude as the non-covalent solute-solvent interactions. Results of BOMD simulation of H2 cleavage by tBu3P/B(C6F5)3 FLP surrounded by explicit solvent molecules, Figure 11 A, are reported in paper III. It is shown that (i) the first solvation shell is mechanismically non-
innocent and because of that H₂ activation can begin at considerably larger phosphine-borane separation than portrayed by BOMD simulations in gas phase, and (ii) structurally diffuse but nonetheless well expressed an intermediate state of LB⁻⁻H₂⁻⁻LA type is present in the reaction pathway of [I].

According to the PE-calculations, tBu₃P/B(C₆F₅)₃ could cooperatively “trap” H₂, Figure 11 B. Room temperature BOMD simulations with explicit solvent have shown, albeit at qualitative level, that such a “pocket” has much large timescale of response to forces along RC compare to the motion of H₂. Thus, dynamics of H₂ exhibits quasi-periodic P⁻⁻H/B⁻⁻H distances change despite the stochastic perturbation from solvent, Figure 12 A. The solvent-caged intermediate, {tBu₃P⁻⁻H₂⁻⁻B(C₆F₅)₃}, is broadened structurally but is not fully “smeared out” by solvent; and, it appears to have distinctive IR signature primarily because of the induced dipole moment of H₂ (Figures 6 and 7 in Paper III).

![Scheme 2. The MO-diagram based on the electronic structure analysis of the stationary PES points and TS of reaction [I] (left); an illustration of HOMO and electrostatic interactions (based on Mulliken charges) in {tBu₃P + H₂ + B(C₆F₅)₃} at P⁻⁻B distances typical for the TS-region (right).](image)

Prior to the work in this thesis, interactions in the TS of [I] are rationalized by the “electric field” model and the cooperative MO-interactions – i.e., the lone pair of a Lewis base, Lp(LB), interacts with the σ* of H₂ and a unoccupied orbital of a Lewis acid interacts with the σ orbitals of H₂. However, σ(H₂), is substantially lower in energy than the HOMO of {Lp(LB) + σ*(H₂)} composed mainly by Lp(LB) and σ*(H₂) (Scheme 2).
Furthermore, the shape and the spatial extent of \{Lp(LB) + σ*(H_2)\} is suitable for an overlap with the boron-centered LUMO(LA). Thus, a possible rationale of interactions underlining the mechanism of reaction [1] is that HOMO of \{Lp(LB) + σ*(H_2)\} interacts with the LUMO of a Lewis acid, B(C_6F_5)_3, and it is also involved in electrostatic interactions which stabilize the \{LB–H_2\} complex. Qualitatively speaking, in the TS-region of \{tBu_3P + H_2 + B(C_6F_5)_3\} system B(C_6F_5)_3 may be looked at as a “counter-ion” of sorts due to the partially positive charges on boron and carbons (Scheme 2 and Figure 13). That being said, one should keep in mind that at the DFT level it is problematic to resolve the question about the relative weight of the electronic configurations which might correspond to \{Lp(LB) + σ*(H_2)\}↔LUMO(LA) or σ(H_2)↔LUMO(LA) interactions.
6. Molecular motion in \( t\text{Bu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3 \) plus \( \text{CO}_2 \) reaction

Similar to the mechanism of [1], the mechanism of reaction [2] was investigated using PE-calculations and BOMD in gas phase and with explicit solvent – Papers IV - VI.

![Diagram of molecular motion](image)

**Figure 14.** Representative vdW-complexes with different orientation of \( \text{CO}_2 \) within the \( t\text{Bu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3 \), TS\(^\perp\) for vdW\(^\perp\) → product and TS\(^\parallel\) for vdW\(^\parallel\) → product. All distances are in Å.
In agreement with crystal structure, the calculated structure of tBu3P-C(O)O-B(C6F5)3 product has O…B and P…C distances of 1.589 Å and 1.926 Å and bent carbon dioxide with the C-O bonds measuring about 1.30 and 1.22 Å. For comparison, C-O bonds are 1.17 Å in the geometry optimized isolated CO2. Figure 14 shows examples of initial complexes with vdW-range distances between reactants and the corresponding TS-structures with different orientation of CO2 in the FLP. Figure 15 shows an ensemble of structurally distinct but energetically near-degenerate MEPs of [2]; MEPs are reasonably separated in the TS-area and converge in the binding funnel at C…P ≈ 2.0 Å.

An interaction of the lone pair of phosphorus, Lp(P), with the LUMO - orbital of CO2, \( \pi^*(CO_2) \), gives rise to \{Lp(P) + \pi^*(CO_2)\} molecular orbital which is the predominant component of the HOMO for the TS-configuration. The predominant component of the LUMO is localized on
B(C₆F₅)₃ with the boron-centered \( p \)-component “mixed” with the orbitals of the perfluoro aromatic rings. In addition to MO-interaction, electrostatic interactions between atoms with partially positive and negative charge, \( i.e. \) \( O^{δ-}/B^{δ+} \) and \( O^{δ-}/C^{δ+} \) and \( O^{δ-}/F^{δ-} \), could be mechanistically important as well (Figure 16).

**Figure 16.** The electrostatic potential surface (EPS) of \( tBu_3P\ldots C(O)O\ldots B(C_6F_5)_3 \) at the TS-region; red to blue gradation represents ESP values from the lowest negative to the most positive.

The timescale of the evolution of \( tBu_3P/B(C_6F_5)_3 \) pair, \( τ_{BP} \), plays a role in the mechanism of reaction [2]. In Paper V, we examined the potential energy of \( \{tBu_3P + CO_2 + B(C_6F_5)_3\} \) system versus \( P\ldots C \) and \( B\ldots O \) distances with the \( B\ldots P \) distance as a parameter – \( i.e. \) PESs \( E(P\ldots C, B\ldots O | B\ldots P) \) in Figure 17. We found that for the \( B\ldots P \) distances close to the value in the TS-structure, \( [B\ldots P]_{TS} \approx 5.4 \) Å, the shape of \( E(P\ldots C, B\ldots O | B\ldots P) \) is such that only a very small energy-change arises from the contraction of \( P\ldots C \) together with the elongation of \( B\ldots O \); however, the direction towards the area of the product-like \( P\ldots C \) and \( B\ldots O \) distances are met with steeply rising slope of \( E(P\ldots C, B\ldots O | B\ldots P) \). Limited translational motion of \( CO_2 \) within \( tBu_3P/B(C_6F_5)_3 \) is therefore possible. As Figure 17 shows, the product-like energy well begins to form on \( E(P\ldots C, B\ldots O | B\ldots P) \) for \( B\ldots P < 5.0 \) Å. In the dynamical sense, the \( B\ldots P \) distance constraint corresponds to the limit \( τ_{BP} \to \infty \) and the finite \( τ_{BP} \) has the meaning of “dynamical frustration” of the chemical step in [2].

A brief account of the dynamics results presented in Paper V is that both reactive and non-reactive trajectories typically stray far away from MEP for sub-picosecond duration – \( e.g. \), circa 0.75 ps for trajectories in blue
and green in Figure 18. The TS-recrossing has relatively large magnitude in accordance with the spatial dimensions of the phosphine–borane donor-acceptor “pocket” and involves extended excursions to regions afar from the saddle area. In terms of the evolution of C–P and B–O distances with time, it is intuitively reasonable to describe such patterns as “caged roaming”.

**Figure 17.** PESs $E(P\cdots C, B\cdots O | B\cdots P)$ at selected values of $B\cdots P$ distance; the potential energy is displayed relative to the marked local minimum (in kcal/mol); the contour line spacing is 1 kcal/mol.

According to MEP calculations, the passage through the saddle region involves monotonous closing of the phosphine–borane “pocket” with matched shortening of both $tBu_3P\cdots CO_2$ and $C(O)O\cdots B(C_6F_5)_3$ distances (Figure 18 B). The process is more complicated than this in its details – CO$_2$ moves in the phosphine–borane “pocket” and sequential $tBu_3P \leftrightarrow CO_2$ and $C(O)O \leftrightarrow B(C_6F_5)_3$ collisions occur on the smaller timescale than the closing of the “pocket” (Figure 19). In terms of how $C\cdots P/B\cdots O$ distances behave *versus* time - shortening of $P\cdots C$ together with the elongation of the $O\cdots B$ and
vice versa - dynamics involves the mode which is orthogonal to the direction of MEP in the saddle region (Figure 19).

**Figure 18.** (A) Representative BOMD reactive trajectories projected on the PES $E(\text{P...C, B-O})$. (B) A comparison of the reactive trajectory (blue) with the ensemble of MEPs (solid and dashed red lines).
The above described behavior of trajectories gives rise to a quasi-intermediate in which the trapped CO₂ collides with LB and LA which constitute the FLP. An evidence of the quasi-intermediate being present in the reaction path of [2] is the histogram of the dipole moment \( \langle d \rangle \), in Debye) of snapshots of many trajectories initiated from the TS-region of [2] at room temperature (Figure 20). According to MEPs of [2], the probability distribution given by such a histogram is expected to include only two contributions – the product \( \langle d \approx 14 \text{ Debye} \rangle \) and vDW-complex in the reactants-area \( \langle d < 3 \text{ Debye} \rangle \). The local maximum in the area \( 5 \text{ Debye} < d < 9 \text{ Debye} \) in Figure 20 arises due to the “caged roaming” - see details in Paper V.

**Figure 19.** An overlay of BOMD snapshots from the phase of the TS-region transit with the simplified portrayal of how CO₂ moves relative to \( \text{tBu}_{3}P/\text{B(C}_6\text{F}_5)_3 \).

**Figure 20.** Histogram of the dipole moment \( \langle d \rangle \), in Debye) of BOMD snapshots of many trajectories initiated from the TS-region of [2] at room temperature – see details in Paper V.
Scheme 3. (A) The one-step reaction path with the TS-configuration, \([LB^-\text{C}(O)O^-\text{LA}]^\#\), describing asynchronously (dynamically) concerted P-C/O-B bonding. (B) The two-step reaction scenario with \{tBu_3P^-\text{CO}_2\}^D as the intermediate - the first reaction step is the dative P-C bonding followed by the O-B bonding as the second reaction step; \(D^D\) and \(D^\text{vdW}\) are dipole moments of \{tBu_3P^-\text{CO}_2\}^D and \{tBu_3P + \text{CO}_2\}^\text{vdW}, respectively.

Figure 21. A snapshot from the reaction-dynamics calculations showing geometrically persistent \{tBu_3P + \text{CO}_2\}^D intermediate accompanied by \(\text{B(C}_6\text{F}_5)_3\) in dichloromethane; for the sake of clarity, the frontal and background parts of the solvation shell are not shown. In the displayed structure, P–B distance is more than 7Å, O–B distances are more than 5Å and the OCO bending angle is circa 135°.

Data presented in Papers IV–V unraveled the dynamically concerted reaction pathway of [2], Scheme 3A. In addition to that, Paper VI presents
evidence of the two-step pathway in which solvent is directly involved, Scheme 3B. In the discovered two-step pathway of [2], an attack of \( t\text{Bu}_3\text{P} \) on CO\(_2\), takes place in the first reaction step followed by the oxygen-boron bonding in the second reaction step. The intermediate \( \{t\text{Bu}_3\text{P} \cdots \text{CO}_2\}\)\(_D\) has persistent phosphorus-carbon bonding, \( [\text{P} \cdots \text{C}] \approx 2.0 \) Å, and characteristic IR-absorption spectrum.

Figure 21 shows typical BOMD snapshot of the reacting complex composed of the intermediate \( \{t\text{Bu}_3\text{P} \cdots \text{CO}_2\}\)\(_D\) plus B(C\(_6\)F\(_5\))\(_3\) in dichloromethane. In BOMD simulations reported in Paper VI, solvent is described explicitly. The rationalization of the two-step pathway of [2] is that the solvent stabilizes the intermediate which results from nucleophilic attack of phosphorus Lewis base on CO\(_2\). The latter had been explored in some detail in Paper VI. It was found that \( \{\text{LB} \cdots \text{CO}_2\}\)\(_D\) correspond to a minimum of the solvated potential energy for several phosphorous LBs. Specifically, BOMD simulations with explicit solvent affirmed that formation of \( \{t\text{Bu}_3\text{P} \cdots \text{CO}_2\}\)\(_D\) is possible and provided the necessary trajectory-data for computations of the BOMD-based IR spectra. The latter is corroborated by IR-calculations using the harmonic frequency analysis.
Prior to the work summarized in this thesis, explicit inquiries into the effect of molecular motion on the FLP reaction mechanisms have not been undertaken. Therefore, it is quite likely that we have exposed only the tip of an iceberg with regard to molecular motion effects in FLP chemistries.

On the basis of simulations which take into account explicit interactions between: (i) $t\text{Bu}_3\text{P}$ and $B(\text{C}_6\text{F}_5)_3$, (ii) $t\text{Bu}_3\text{P}/B(\text{C}_6\text{F}_5)_3$ pair and the third molecule such as $\text{H}_2$ or $\text{CO}_2$, and (iii) solute and solvent, it appears that both $t\text{Bu}_3\text{P}/B(\text{C}_6\text{F}_5)_3$ as a pair as well as the encounter and reacting complexes of $\{t\text{Bu}_3\text{P} + X + B(\text{C}_6\text{F}_5)_3\}$ type have multitude of mechanistically relevant configurations. Furthermore, for reactions [1] and [2] two essential factors are (i) the timescale of relative motion of $t\text{Bu}_3\text{P}/B(\text{C}_6\text{F}_5)_3$, $\tau_{BP}$, and (ii) the timescale, $\tau_X$, of motion involving molecule $X$ within the reacting complex of $\{t\text{Bu}_3\text{P} + X + B(\text{C}_6\text{F}_5)_3\}$ type. Implications of the difference in magnitudes of $\tau_{BP}$ and $\tau_X$ are as follows. For the heterolytic cleavage of $\text{H}_2$ by $t\text{Bu}_3\text{P}/B(\text{C}_6\text{F}_5)_3$, the reaction path along which $\text{H-H}$ bond could be broken includes shallow minima “imbedded” in the transition-state region. $t\text{Bu}_3\text{P}/B(\text{C}_6\text{F}_5)_3$ are almost stationary while proton- and hydride-like fragments of $\text{H}_2$ move toward phosphorous and boron respectively. For binding of $\text{CO}_2$ by $t\text{Bu}_3\text{P}/B(\text{C}_6\text{F}_5)_3$, the reacting system can “wander” along the “potential energy wall” blocking the product configuration from the transition-state region. The mechanism of $\text{CO}_2$ binding by the FLP can combine the dynamically concerted and two-step reaction paths in solution. The discovered two-step binding of $\text{CO}_2$ by $t\text{Bu}_3\text{P}/B(\text{C}_6\text{F}_5)_3$ FLP involves solvent-stabilized phosphorus-carbon interactions (dative bonding).

Based on calculations summarized in this thesis, the duration of the passage through the TS-region by $\{t\text{Bu}_3\text{P} + X + B(\text{C}_6\text{F}_5)_3\}$ reacting complex depends on the conformational inertia of LB/LA pair. The latter relates to molecular mass of LB and LA molecules, as well as that of solvent molecules, which can be changed within certain range by isotope-substitution. Thus, accurate rate measurements for the isotopically heavier LB/LA pairs and solvent versus the “normal” ones might verify the mechanisms of [1] and [2] described herein.

For detection of quasi-intermediate of $\{t\text{Bu}_3\text{P} + X + B(\text{C}_6\text{F}_5)_3\}$ type, promising observables could be infrared (IR) absorption and Raman spectra.
For example, the computed IR spectra contains characteristic H$_2$-stretch bands - the polarized H$_2$ becomes IR active due to the charge separation in the quasi-intermediate of \{tBu$_3$P + H$_2$ + B(C$_6$F$_5$)$_3$\} type. For CO$_2$, calculations indicate substantial red-shift of the characteristic vibrational line.
Syftet med denna avhandling är att med kvant-kemiska beräkningar kasta ljus över de mekanismer som är aktiva för reaktion mellan frusterade Lewis par (FLPs) och koldioxid (CO$_2$) och/eller väte. Intresset för FLP har på den senaste tiden ökat då man kan utnyttja situation när man har steriska hinder för att en Lewis bas (LB) ska donera sina elektroner till en Lewis syra (LA) för olika kemiska reaktioner. Från huvudgrupperna i det peridiska systemet kan man finna många olika elektron par donatorer och acceptorer som kan skape FLP. Typexempel av intermolykylära FLP är fosfiner och borater med stora elektron donerade grupper på fosfor och stora elektron dragande grupper på bor, t.ex. paret tBu$_3$P/B(C$_6$F$_5$)$_3$. Det är de intermolykylära egenskaper hos FLP som binder samman LB och LA centrumen i en och samma molekyl.


Ett flertal viktiga resultat har framkommit i denna studie. Vi kan visa att dynamiken är en av nycklarna till att förstå kemin hos FLP. Den multi dimensionella naturen hos rörelser som påverkar bildandet av interaktion i de reaktiva komplexen, vilket är mest tydlig för lätta molekyler som CO$_2$ och H$_2$ som samverkar med molekylpar av tunga LB och LA. Våra beräkningar visar att rörelses mönster som är vinkelrätta mot reaktionskoordinaterna är nyckel till de omvandlingar som sker av de aktiva komplexen genom regionen av övergångstillstånd. Simulering av gas fasen och verkligen lösningsmedel gav i fallet med heterolitisk klyvning av H$_2$ med tBu$_3$P/B(C$_6$F$_5$)$_3$ FLP att den vägen som reaktionen passerade grunda kvasi-minimuma som var ”inbäddade” i regionen av övergångstillstånd. Den tidigare nämnda modelering gav i fallet bindning av CO$_2$ till tBu$_3$P/B(C$_6$F$_5$)$_3$ FLP att: (i) de
reaktiva komplexen kan “vandra” längs “väggar av potentiell energi” som tillfälligt blockerade reaktionväg och att (ii) mekanismen kan kombinera den som har samordnad P-C och O-B bidningen plus två-steg reaktionsväg i lösningsmedlet. Upptäckten av två-steg bindningen av CO₂ till tBu₃P/B(C₆F₅)₃ FLP innehåller lösningsmedel-stabiliserade fosfor-kol interaktioner. Dessa och de andra presenterade resultaten är bekräftas och förklaras genom övergångstillstånd beräkningar. Genom beräkningar karateristik hos reaktionerna som är mätbar vill vi visa ett sätt att med experiment bevisa att de föreslagna reaktionerna mekanismen är riktiga.
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