A THEORETICAL APPROACH TO THE FORMATION OF GLYCINE IN THE INTERSTELLAR GAS PHASE

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Zusammenfassung

Glycin ist die einfachste der essentiellen Aminosäuren und repräsentiert damit eines der grundlegenden Bausteinmoleküle des Lebens. Wegen seiner zentralen biologischen Bedeutung wurde nach der ersten Labormessung des Millimeterwellenspektrums in der Gasphase 1978 eine ausgedehnte Durchmusterung des interstellaren Raumes gestartet. In den Sternenstehungsgebieten des Orion und des Sagittarius B2 wurden einige spektrale Rotationsübergänge beobachtet, die von zwei verschiedenen Konformationen des Glycins herrühren könnten. Aufgrund seiner biologischen Signifikanz ist die zweifelsfreie Beobachtung sowie die Aufklärung seiner Bildung im interstellaren Raum von immenser Bedeutung; nicht nur für die interstellare Chemie im allgemeinen, sondern vor allem im Hinblick auf die Frage nach dem Ursprung des Lebens auf der Erde.

Diese Arbeit repräsentiert, verglichen mit den zahlreichen experimentellen und theoretischen Untersuchungen seit über 25 Jahren, einen alternativen Ansatz zum Problem der Molekülbildung in der interstellaren Gasphase. Dieser wird mit quantenchemischen Methoden am Beispiel der Bildung von Glycin durchgeführt. Dabei wurden zwei mögliche Zerfallsprozesse retrospektiv als Bildungspfade zugrunde gelegt und die involvierten molekularen Spezies, Reaktanden, vier verschiedene Konformationen des Produktmoleküls, sowie zwei Kandidaten möglicher Übergangszustände im Hinblick auf die Kalkulation der Intrinsischen Reaktionskoordinate optimiert. Diese dient zur Charakterisierung des resultierenden Bildungspfades.

Die Optimierung der in den gewählten Reaktionspfaden zugehörigen Spezies umfaßt ihre Geometrie und Totalenergie, die ein-Elektronenenergien und Symmetrien der involvierten Molekülorbitale auf der zugehörigen Hyper-fläche der Potentialenergie, sowie ihre fundamentalen Schwingungsfrequenzen. Die in Frage kommenden Verbindungen sind die mesomeren Konfi-

gurationen der interstellar beobachteten Spezies CH_4N^+ und die ionischen und radikalen Strukturen der COOH-Gruppe des Bildungsweges 1, sowie die Reihe folgender Moleküle ${}^+CH_2COOH$, ${}^-CH_2COOH$ im Singlett- und Triplettzustand, ${}^+CH_2COOH$, und Essigsäure CH_3COOH , sowie Ammoniak NH_3 , und Formen der Amino Gruppe ${}^+NH_2$, ${}^-NH_2$, und ${}^+NH_2$, welche zum zweiten Bildungspfad gehören. Glycin selbst bietet mehrere verschiedene Rotationskonformere zur Untersuchung, davon wurden vier der stabilsten Konformationen hier berechnet.

Mit dieser Information wurden einige ausgewählte Molekülorbitalkorrelationsdiagramme aufgestellt, die als erstes Kriterium im Hinblick auf die Klassifizierung einer Reaktion als erlaubt oder verboten anzusehen sind, wobei die Symmetrieeigenschaften der involvierten Molekülorbitale besondere Berücksichtigung finden.

Alle Optimierungen wurden auf der Grundlage der Hartree-Fock Näherung mit den Basissätzen 3-21G, 4-31G und 6-31G durchgeführt, gefolgt von störungstheoretischen Møller-Plesset Rechnungen zweiter Ordnung. Dabei fand das Gaussian Programm Anwendung.

Abstract

Glycine as the simplest of the amino acids represents one of the essential building blocks of life. Because of its central biological significance there have been started an extensive search in interstellar space since the first laboratory determination of the millimeter wave spectrum of the gaseous molecule in 1978. In the star forming regions of Orion and Sagittarius B2 a few spectral rotational transitions were observed, which may correspond to two different conformeres of NH_2CH_2COOH . Hence, the doubtless detection and furthermore, the knowledge of its formation in space would be of importance not only for interstellar chemistry, but also for the question of the origin of life on Earth.

Compared with the investigations of various scientists over the last 25 years, this work represents an alternative approach to molecular formation in the interstellar gas phase, here with special consideration of glycine, using quantum mechanical tools. Starting with two different possible paths of formation, the involved reactants, four different conformations of the product molecule as well as possible intermediates were optimized. Two decomposition processes available e.g., via mass spectrometrical fragmentation were chosen retrospectively as paths of formation.

The optimization of the molecules relevant to the selected reaction path I and II comprises the geometry, the total energy, the one-electron energy and the symmetry of the molecular orbitals involved in the chemical reaction on the corresponding potential energy surface, as well as their fundamental vibrational frequencies. The species in question are both mesomeric configurations of the interstellar observed species CH_4N^+ and ionic/radical species COOH derived from formic acid HCOOH according to path of formation number I, as well as the series of compounds ${}^+CH_2COOH$, ${}^-CH_2COOH$ in singlet and triplet state, ${}^-CH_2COOH$, and acetic acid ${}^-CH_3COOH$, ammonia ${}^-NH_3$,

and versions of the amino group ${}^+NH_2$, ${}^-NH_2$, and ${}^\cdot NH_2$ corresponding to the second path of glycine synthesis. Glycine itself offers several different rotational conformations to investigate, four of the most stable conformeres have been calculated and are presented here. The results relevant to glycine include also two definite transition structures with consideration of computing the intrinsic reaction coordinate, which characterizes the desired route of formation.

With this information some selected molecular orbital correlation diagrams could be composed, which represent a first criterion, whether the considered chemical reaction is classified as allowed or forbidden, taking specific note of the symmetry properties of the molecular orbitals involved.

All optimizations were performed via ab initio Hartree-Fock approximation with the basis sets 3-21G, 4-31G and 6-31G, followed by Møller-Plesset second order perturbation calculations using the gaussian 92 program.



für meinen Dad und D., die beide wissen was diese Arbeit für mich bedeutet

for my Dad and D., who both are knowing what this work matters to me WE LIVE IN A UNIVERSE OF CHANCE, BUT NOT OF ACCIDENT. George Wald

I awoke the next day to a sound like sizzling bacon, the noise made by ice melting in a pan on a primus. In the months after Antarctica, I often heard it in the boneless moments between sleep and consciousness; then memories ached like an old wound. Sunshine was pouring through the window. Steve brought tea to our bunks. Some of the ice must have been brackish, as it was salty. I made up a jug of milk for our breakfast cereal, and that was salty too. I wasn't having much luck with breakfasts. But it didn't matter. Nothing mattered. We basked on our veranda, and a flock of Antarctic terns flew by, their high-pitched chirp exotically foreign after the coarse squawk of the skuas. Later, we took the boats out and followed a minke whale around the bergs, sailing through Daliesque arches and poking into cold blue grottoes. The sun was low, and the honeyed air was so still that the growlers and bergy bits were barely moving. It was a golden evening. A day like that made everything worthwhile.

from Sara Wheeler's TERRA INCOGNITA — Travels in Antarctica

YOU WAIT. EVERYONE HAS AN ANTARTIC. Thomas Pynchon

This work is mine.

THE RAVEN AND THE FIRST MEN

According to the First Nations legend, life on earth began when the Raven flew down from the heavens thousand of years ago. The earth was covered with snow. He stole the sun from the gods and made rivers, oceans, thick green forest, and many animals. Then he found a clamshell on a sandy beach. He opened it and coaxed its inhabitants, five men, out of their dark prison into the land he created, promising them peace, harmony and prosperity.

retold by J.M. Brown & A.R. Miller

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Introduction

The question how life had been formed is one of the challenging problems of our time. It is the question of ourselves, our origin. There are two alternative hypotheses concerning the formation of life, to be more precise, the formation of biotic and prebiotic structures being indispensable for each living organism we know. They make their contribution to the comprehension of our precursors' origin (i) on our home planet Earth, i.e. the *in situ* formation [1], [2], known as the *Oparin-Haldane hypothesis*, and (ii) beyond our living space in the interstellar environment. Here the possibility of transferring those precursors and seeds via meteoritic or cometary impacts is discussed (see e.g. Oro 1961 [299], Anders 1989 [297] and Chyba et al. 1990, 1992 [298], [179]). Also the concept of cosmic delivery of living organisms, the so-called theory of *panspermia* has been reconsidered, first introduced by the Greek philosopher Anaxagoras about 500 B.C. and in 1907 taken up by Arrhenius [208], who proposed a specific model for those seeds of life.

Investigation of impact caused craters of the Moon and other solar system bodies suggests the surface of primitive Earth was intensively bombarded by planetesimal debris throughout the first 700 million years after planetary formation [264]. The evidence for the first forms of life is determinated 300 million years after the heavy bombardment, provided by geological studies of fossilized microorganisms [300], [262]. The close sequential phases of that external bombardment and the appearance of primitive organisms favors the idea that extraterrestrial matter could have initiated the first step of life.

The nature of terrestrial life as we know it, implicates the property of *chiral-ity* of a molecular species responsible for the physico-chemical effect of *optical activity*, caused by an asymmetric carbon atom. Classical, a chiral molecule and its mirror image, defined by left (L) or right (D) optical-rotatory dispersion, have been considered as nearly energetically equivalent. Accordingly, in

laboratory synthesis both versions of molecules are formed in racemic mixtures. Although both enantiomeres have the same chemical and geometrical composition, they show a different mode of biochemical action within a living organism. That might be one reason for their alternative natural incidence.

Protein molecules consist up to 20 different amino acids in L configuration. Some amino acids of the opposite D type do occur in cell walls of certain bacteria. Thinking of the 74 amino acids found in samples of the Murchison Meteorite, only 8 are present in proteins, 11 have other biological roles, and the remaining 55 have been found only in extraterrestrial samples [242], [243]. The polynucleotides contain sugars in D configurations only. Clearly, at some point evolution must have selected specific configurations for complex protein synthesis and the stereoselectivity of catalytic enzymes. In that way such handedness is not only preserved, but might have led to definite biological phaenotypes as well as to certain physiological and biochemical processes in terrestrial living systems. It is still an open question why and how such configurations so successfully overcame the opposite type. The most controversial theory discusses symmetry breaking via parity-violating weak interactions. However, glycine as the simplest amino acid shows no optical activity because of the lack of an asymmetric carbon center.

The role of chirality in the origin of life and its origin itself has been extensively discussed and investigated by many scientists of various working fields (see for example [231], [17], [235], [234], [226], [238], [239], [227], [237], [241], [228], [223], [233], [232], [230], [240], [229], and references therein).

Latest technical developments in the field of radioastronomy show definite detections and searches for spectroscopical hints of complex organic molecular species like the long chain cyanopolyynes [249], amino acids [248], [247], [4], [280], acetic acid [246], esters [245], and recently of the first identification of a sugar [244] in the interstellar gas phase of dense clouds. Together with explorations of our solar system and most manifold theoretical as well as experimental investigations on the origin of life it gives us the understanding that life can be considered as a natural result of evolution in the cosmos. That information allows us also to presume that the appearance of extrater-restrial forms of life may very well occur on other planets, which are orbiting some of thousands million stars in our home galaxy.

About twenty-five years of theoretical investigations have pursued the aim to clarify the formation of the spectroscopically identified molecular species and includes calculations applying alternative reaction mechanisms considered to be in effect under astrophysical conditions.

Observations of the TMC-1 dark cloud, for example, present plenty of unsaturated carbon chain compounds, including the cyanopolyynes, various cumulene carbenes and their derivatives [249], [281], [257], [255], [251], [252], [261], [250]. In such an environment interstellar chemistry can proceed, where dust grains effectively shield molecules from external UV radiation, while cosmic rays are able to penetrate, initiating various ion-molecule interactions. Those reactions are often supplemented by neutral-neutral processes, producing many complex organic species. Ion-molecule reactions dominate the gas phase synthesis in interstellar clouds because most of those exothermic reactions have no activation barriers, whereas endothermic reactions are almost entirely suppressed because of the low temperature in dark clouds. In regions like the peripheries of dense molecular clouds and diffuse interstellar clouds, as well as in circumstellar shells, photochemical reactions via ultraviolet ionization will play an important role for dissociation processes and molecular destruction studied by Bates & Spitzer [302], Prasad & Tarafdar 1983 [304], Omont 1987 [303], van Dishoeck [301], for example.

Chemical evolution was studied via various chemical formation routes modeled by Herbst & Klemperer 1973 [186], Huntress & Mitchell 1979 [108], Mitchell et al. 1979 [273], Wamsley et al. 1980 [274], Herbst et al. 1983, 1984 [271], [272], Leung et al. 1984 [256], Millar & Freeman 1984 [275], [276], Millar & Nejad 1985 [278], Herbst & Leung 1986 [277], Millar et al. 1987 [187], Herbst 1987 [253], Prasad et al. 1987 [260], Herbst & Leung 1989, 1990 [254], [279], and Millar et al. 1997 [258], and with respect to the physical and chemical conditions of the ambient cloud by Pineau des Forêts et al. 1991 [283] and Lee et al. 1998 [284], among many others.

Association reactions are important in various astronomical regions for increasing molecular complexity and as a first step to condensation [288]. Theories were presented for two mechanisms for the gas phase, the *three-body process* being in satisfactory agreement with a variety of laboratory studies [287], and the *radiative association mechanism* proposed by Williams in 1972 [105] and Herbst and Klemperer in 1973 [186]. Calculations of rate constants for that association mechanism have been performed by several groups like Bass et al. 1979 [290], Huntress & Mitchell 1979 [108], Bates 1983, 1991 [289], [291], [292], Herbst 1985, 1987 [295], [296], [115], Winnewisser & Herbst 1987 [109], Bates & Herbst 1988 [287], [116], Smith 1989 [293], Dunbar 1990 [294], Herbst & Dunbar 1991 [117].

More non-traditional pathways of extraterrestrial formation of organic compounds offer the possibility for exothermic reactions with energy barriers to take place via the mechanism of molecular chemical tunneling comprehensively investigated by Goldanskii 1979, 1997 [269], [270], and coworker 1989 [201] as well as by Gray et al. 1980 [282], among others.

The methodological procedure of those theoretical investigations bases almost entirely on the calculation of rate constants of the considered reactions via (i) experimentally measured rate coefficients and — if not available or chemically inaccessible — by (ii) theoretical estimates and determinations. Those results have often been compared with laboratory measurements and observed abundances of the molecular species in question, showing a differing grade of correspondence.

Thinking of the wide-ranging abundance of amino acids and other prebiotic molecules found in extraterrestrial material like the Murchison meteorite [45] as well as their probable existence in the interstellar gas phase, the central question arises of their origin. In the special case of glycine the link between the existence in meteorites and in the gas phase and its interstellar chemistry could become more strengthened, if interstellar glycine would be ultimately detectable. Spectroscopical evidence for glycine with recently found abundances of about 10^{-10} in Sagittarius B2 [263] has not yet been verified. At present it is not clear, whether the still outstanding identification of glycine is a question of technique or real interstellar presence.

From the point of view of interstellar synthesis it is open to question, whether glycine and other large organic molecules may be formed via gas phase reactions considered so far for interstellar chemistry [5]. An alternative is that complex organic molecules are chemically created in the interior of icy grain mantles provided a source of free energy is available to drive the chemical transformations [34]. The paths of formation of amino acids in interstellar gas and dust are not yet established. Recently Chakrabarti & Chakrabarti 2000, [267] explored the possibility of production of adenine and some simple amino acids like glycine during a molecular cloud collapse based on hydrodynamical calculations. Very recently Charnley [305] proposed the creation of protonated glycine in hot molecular cores. An alternative synthesis in the solid phase via irradiation of interstellar grain mantels is suggested by Bernstein and coworker [306]. A differentiated detailed approach via STRECKER type synthesis is the theoretical treatment via quantum chemical methods of Arnaud and coworker 2000 [268]. They consider both, equilibrium and non-equilibrium reactions in solution according to the Miller experiment [1]

representing the conditions on the primordial earth, as well as in vacuo with respect to the interstellar gas phase.

While the investigations mentioned above start with the basic requirement that collision of two molecular species leads definitely to a product, assuming a specific underlying reaction mechanism, the work presented here uses a completely different approach and represents the preceding step on the way of theoretical research how chemical compounds may form. It formulates a detailed theoretical study of two single molecules meeting in the gas phase for the special case of glycine synthesis. In order to clarify, if a new chemical bonding can be created between them and the reaction can actually happen, it is necessary to investigate the involved molecular orbitals, their relative energetical positions on the energy scale as well as their symmetry. The complete analysis would then lead to an adequate mechanism of reaction.

The first chapter delineates the embedding THE ASTROPHYSICAL SITUATION of the present theoretical investigation within the complex coherence of scientific endeavors. The CHEMICAL PATH gives a view of a differentiated approach of the problem of chemical molecular formation in the interstellar gas phase, followed by the description of the quantum chemical METHODS used in this work. The Approach gives information about the obtained results, which were discussed also with respect to continuing efforts, which are worth striving for.

Chapter 1

The astrophysical situation

To comprehend how this contribution of research is embedded in the continuity of the successive insight of physical and chemical evolutionary processes in interstellar space, it is important to be aware of the present astrophysical situation.

To begin with the complex trail of chemical evolution on the cosmic scale, it may be classified into five stages [39], [40]:

- 1. The first stage starts with the *Big Bang*, i.e. with the appearance of matter in form of elementary particles, proceeding to the formation processes of stars and planets, and continues in synthesizing the essential chemical elements like carbon, nitrogen, and oxygen via nuclear fusion within the stars.
- 2. The second stage characterizes the condensation of the first organic molecular structures formed on the surface of grains and in the gas phase of circumstellar shells of evolved stars, in the interstellar medium, in comets, meteorites, and in planetary primordial atmospheres.
- 3. On the third stage more complex building block molecules are produced up to prebiotic structures like the simplest amino acids precursors of proteins and nucleic acids in the astrophysical scenarios mentioned above.
- 4. The next step is represented by the molecular evolution on early earth or similar environments like extraterrestrial planets right to the de-

velopment of precellular structures. Chirality, self-organization, self-reproduction, and the genetic code begin to play an essential role on that primitive biological stage.

5. Finally the *advanced* fifth level of life, perhaps more advanced than we know it so far from unicellular structures (microorganisms) to multicellular organisms.

In the course of scientific research two alternative theories arose, outlining the circumstances, which favor the formation of the seed of life, the initiating and furthermore the evolution of what we know as terrestrial life. For obvious reasons the first aim of investigations represents the in situ formation of the building blocks of life on the primordial earth. On the other hand there have been increasing grounds for the assumption that biological precursor molecules from space would have been injected via impacts of meteorites, particularly evolved carbonaceous chondrites like the Murchison meteorite.

The probable situation on the primordial earth

In the beginning of 1950 Stanley Miller and Harold Urey [41] started their famous experiment on the formation of life on earth. A reaction chamber filled with methane, molecular nitrogen with traces of ammonia, water and hydrogen, represents the reducing primordial atmosphere on earth as well as liquid water — so to speak, as the early ocean. These mixture of earthly chemical compounds were set out electrical charges of high voltage corresponding to the thunder lightnings hitting the oceans on early earth. After several weeks the authors could verify substances like amino acids and other building block molecules of life.

Comparing the experimental results of Miller & Urey with the chemical analysis of the Murchison meteorite, one finds conspicuous correspondence in the class of compounds as well as in their concentrations[315], supporting the hypothesis that initial biological relevant molecules can also be formed under interstellar conditions and be able to contaminate the earth' surface via meteoritic impact.

Current knowledge is based on the assumption that the primordial atmosphere had a different composition as postulated decades before [212], [213], [84], various following experiments [214], [216], [215], [84], [217], showed that

the required relevant prebiotic chemical substances can be formed under very different conditions. A certain amount of energy, in the form of electrical discharges, ultra violet, ionized or cosmical radiation, seems to play the essential role besides the required C, H, O, and N containing species which have to be present [36].

Generally this *prebiotic chemistry* also requires large quantities of starting ingredients. Those compounds at a low concentration cannot play their prebiotic role. However, some of the starting material may also have been supplied by meteoritic or cometary impacts or might even have been formed together with monomers of biological relevance in the primitive submarine hot springs [316]. Such contributions will still need to be investigated.

On the other hand, even if a sufficient amount of those required reactants would had been available under primordial conditions as well as their desired prebiotic products like the amino acids, so what about their stability against electrical discharges or the UV light, which intensities were much stronger than at present? It is also known, that already at that time the whole water of the terrestrial ocean had been filtered by so-called submarine apertures, with temperatures from $300 - 350^{\circ}C$, where amino acids will be already decomposed, provided that the formed prebiotic stuff was distributed or solved in sea water (according to Miller's experiment). And additionally, what are the respective roles of the processes in the gas phase and in solution, and what is the influence of temperature? How far can prebiotic chemistry evolve in the absence of liquid water? It has to be noted emphatically, that obviously there exist a difference between the chemical investigations in solution and in gas phase. Variations of Miller's experiment showed that the formation of the molecules in question depends sensitively of the reacting C, N, and O bearing compounds, i.e. under so-called reducing conditions the amount of the desired product molecules is negligible. In the case of gas phase reactions it seems to be most important to have carbon, nitrogen, oxygen and hydrogen around, despite of their composition, as well as a certain amount of energy (see above). And more generally, to what extent can these experimental results be transferred to real planetary, cometary, and interstellar environments?

Extraterrestrial prebiotic chemistry in our solar system

Although the earth has generally been considered to be the only body in our solar system where organic and inorganic compounds in presence of abundant liquid water could be transformed into prebiotic stuff, those investigations allows us to expect precursors of biomolecules exist at least in the whole universe under appropriate conditions, for instance, in our solar system on such places like some of the Jovian moons, especially on Europa. Recently Levy et al. report on a simulation of prebiotic synthetic processes on Europa and other ice-covered planets and satellites [7]. Besides adenine and guanine, a simple set of amino acids dominated by glycine were found in substantial yields under these simulated conditions. In 1979, when the Voyager spacecraft returned pictures from the surface of Europa, one of the Jovian satellites, consisting apparently of water ice, speculations about a subsurface ocean appeared (McKinnan 1997 and references therein [13]). Recent observations of Europa and Callisto via the Galileo spacecraft in late 1995 strengthened the hypothesis of such an subsurface ocean [8], [9], [10], [11], [12], [14] (and references therein) and led to further speculations that those conditions might possibly had been supported the origin and evolution of life [42], [43]. One potential source of the essential organic compounds on the Jovian moons would be impacts of carbonaceous chondrites, which had shown to contain amino acids, purines, pyrimidines, and polymers [44], [45]. And Jupiter itself could harbor progenitors of molecules with biochemical relevance after the Shoemaker-Levy impact in 1994.

The assumptions of the key scenario of the *micrometeorites* from Antarctica of Maurette et al. [35] which are based on experimental measurements describe each micrometeorite as an *individual* very tiny "chondritic chemical reactor" to generate amino acids and other organic compounds on the early earth via hydrolysis of their carbonaceous components. Antarctic meteorites are known since 1969 including carbonaceous chondrites that contain organic compounds of extraterrestrial origin. Such a single micrometeorite of a size about 100 microns is typically composed of millions of tiny mineral grains. Such grains include potential catalysts like oxides and sulphides of various metals as well as clay minerals and are embedded into the carbonaceous component. This component exists as an ultra thin shell around the mineral grains and protect them against mechanical and chemical damage during the passage through the terrestrial atmosphere or on earth' surface, and avoiding fast dilution of the reactants in water after the impact — one of the major objections facing all *primordial soup models*.

An even more important exogenous source of organic material could be comets [179] which contain large amounts of hydrogencyanide and formaldehyde among others, the main components to synthesize the simplest amino acids, e.g. via Strekker type synthesis and other simple organic compounds [211], [47], [46]. Suggestions concerning the development of prebiotic material in comets and their contribution to terrestrial oceans [31] are in noticeably accordance with Giotto's and Vega's observations during the return of Hallev's comet in 1985/1986 (Kissel et al. 1986 [32], Kissel and Krüger 1987 [33]) as well as the fact that life appeared on earth at a time where the influx of cometary and meteoritic material was more distinct and larger than now. Greenberg considers cometary grains as seeds of life's origin. Such interstellar dust aggregates along with its fluffy morphological structure, i.e. its huge specific surface provide necessary conditions for the onset of life. Just as the occurrence of such large quantities of liquid water should have been brought by comets during the major impact era ending about 4 billion years ago [34]. Recent observations of the two bright comets, Hyakutake and Hale-Bopp, allowed to identify more than 25 parent species and to improve the understanding of cometary out gassing [170], [181], [182], [171], [180], [173], [183].

Cosmic ray and cosmic ray-induced ultraviolet light are two most effective energy sources for the formation of organic compounds in space [218]. With the aim to study the possibility of formation of amino acids in the cometary environment, Kasamatsu et al. [48] investigated the prebiotic synthesis experimentally by irradiating several ice-mixtures with high energy protons. Amino acids such as glycine and D- and L- alanine were detected in every product mixture after hydrolysis. The results of this and similar experimental investigations verify the possible formation of amino acid precursors in interstellar dust grains and cometary nuclei by cosmic radiation as well as by vacuum ultraviolet light [218], [36].

Such organics like hydrogencyanide and formaldehyde are key ingredients of the prebiotic chemistry. Furthermore, in the presence of liquid water under terrestrial-like conditions, they can give rise to the building blocks of living systems. Similar processes are expected in present planetary environment, like Titan [49], [191], [194], Europa [7], [193], [42], [43], Ganymede and Callisto [192], [190], but in the absence of liquid water. In aqueous solution HCN can evolve to a tetramere. A reaction with a fifth molecule of hydrogencyanide can produce adenine, one of the purine bases, which, like the pyrimidine bases, are the one of the essential constituents of the nucleotides, building blocks of the nucleic acids. HCN polymerization can also

compose complex oligomeres. After hydrolysis those oligomeres release the purine bases adenine and guanine, as well as pyrimidine bases and amino acids. Some other experimental data suggests that the chemistry of hydrogencyanide could even directly provide polypeptides, fragments of proteins [38]. In aqueous solution HC_3N can act as an agent forming the pyrimidine bases cytosine and uracil just as sugars can be made out of formaldehyde [37]. In addition, C_2N_2 can react via condensation to biopolymers. Though it must be emphasized that all of the prebiotic syntheses require very restricted physical-chemical conditions, a chemistry in aqueous solution with a narrow range of pH, for instance, corresponds to only a strictly limited number of environmental conditions.

Interstellar chemical complexity

In the 1980's Marcel Devienne [50] started an impressing experiment, which enables us several years after Miller & Urey to presume that even such complex molecules like amino acids could be formed not only within the depth of an meteorite or on the surface of any ice-covered dust grain, but also in the interstellar gas phase. In a high vacuum chamber of $10^{-7} - 10^{-9}$ Torr the surface of a very pure graphite target was bombarded with molecular beams of nitrogen and hydrogen in the presence of a residual humidity. The molecular beams comprise a density of $10^9 - 5 \times 10^{14}$ molecules per cm^2 sec and energies up to 20 keV. During the impact several sputtering particles would be formed both of neutral and ionic character. The ionic species were separated and detected using a tandem mass spectrometer. A comparison between the mass spectra of resulting species and already known species verify the remarkable formation of 20 different amino acids as well as five different sugars and nicotinamide among other compounds. This experimental situation, i.e. its physical conditions as well as the collision of graphite particles of macroscopical size with gas phase molecules, corresponds also with the astrophysical scenario of dust-and-gas-interaction in the interstellar space.

When we think of interstellar chemical complexity then we may think of its beginning, species being formed within and expelled by the envelopes of evolved stars, novae and supernovae as shown by observations. Although the original molecules are typically dissociated by the interstellar radiation field reaching a sufficient distance from the star, while the condensed material survives in form of ubiquitous dust absorbing most of the radiation in space.

The first polyatomic molecule detected in the interstellar gas phase had been ammonia (NH_3) [128]. Although several authors tackled that problem theoretically with different methods (see e.g. [186], [187], [189]), the mechanism of synthesis is still not clarified definitely. Observations in the infrared, radio, millimeter and sub-millimeter range show a large variety of more complex organic molecules in the gas phase, present in the dense interstellar medium [172], [168], [195], where they are sufficiently shielded from UV radiation. These include organic species such as nitriles, especially the long chain polyinnitriles, just as aldehydes, alcohols, acids, ethers, ketones, amines, and amides as well as various long chain hydrocarbon compounds. In the range of quiescent dark clouds and star-forming region there exist a large compositional manifoldness of such molecular species, as well as large gradients of abundance on small spatial scales within each type of cloud [172], [169], [167], [166]. Others like PAHs, fullerenes, and diamonds [175] are expected to be present in the interstellar gas phase and on dust grains embedded in diffuse and dense clouds. The formation and distribution of such complex species in the gas and solid state is also far from comprehension [185]. Carbon, for instance, is locked as CO and C_2H_2 in the envelopes of carbon rich late-type stars. C_2H_2 is regarded as precursor for the PAHs [318], which themselves might act as intermediates [178] and as chemical catalysts, thought to be one component of the organic dust [317]. Dust particles in general represent important chemical catalysts, by gathering atoms, ions and molecular fragments out of the surrounding gas [197], [200], [199], [198] allowing an active chemistry on their huge morphologic surfaces at very low temperatures. The widespread presence of aromatic structures are well documented by numerous observations with the Infrared Space Observatory (ISO) [184]. Characterization of the Diffuse Interstellar Bands (DIBs) suggests and supports the existence of PAHs and fullerenes (see e.g. [177], [165], [176], [196]). A variety of complex aromatic networks is suggested for the chemistry on carbonaceous grains [174].

Although studies of surface reactions are not yet as quantitative and precise as studies of gas phase reactions, an active chemistry on grain surfaces is assumed. In cold environments at 10K atoms like H, D, C, O, and N have sufficient mobility passing the grain surface, e.g. via quantum tunneling predicted by Goldanskii and coworker (1989) [201] to meet a reaction partner. Formation of the simple mantle such as H_2O, NH_3 , and CH_4 may be explained by exothermic hydrogen addition reaction without an activation barriers [204], [202], [205], [207]. More complex molecules like CH_3OH as well as various unidentified organics suggests reaction processes in and on the ice mantles. Processes like ultraviolet irradiation, cosmic ray bombard-

ment, and temperature variations may alter the grain mantle composition. Analogous laboratory experiments show that irradiation processes lead to the formation of radicals, complex molecules and organic refractory material [203], [210], [209], [206]. Therefore, grain chemistry may be considered even more important in high energy environments.

Some decades ago Hoyle and Wickramssinghe (1976) [86] already proposed that the physical conditions inside dense molecular clouds favor the formation of amino acids and complex organic compounds. Now there exist astronomical evidence in terms of some detected spectral transitions of glycine in the Sgr B2 massive star forming region of Miao et al. 1994 [3] and Combes et al. 1996 [4] as well as of acetic acid [246] and a first sugar [244] supporting this hypothesis. Although those observations do not verify doubtlessly the existence of such complex species in the interstellar gas phase, they have posed serious problems for present-day theories of molecule formation in space. The gas phase reaction schemes normally considered for dense cloud chemistry do not provide pathways of formation for such complex molecules. Several laboratory experiments suggest new reaction networks in which amino acids and other large organic species are synthesized inside of icy grain mantels by photoprocesses via direct and scattered ultra violet starlight. Frequent chemical explosions of the processed mantels would eject large fragments of organic dust into the ambient cloud. Large dust fragments sputter into smaller parts, which photodissociate into individual molecules. In this way exploding grain mantels may solve the longstanding molecule desorption problem for interstellar dense cloud chemistry [5].

In view of those unsolved difficulties the question arises what different procedure may be used to elucidate the outstanding problems of the formation of more complex molecular species under astrophysical conditions. Quantum chemical methods allow to study chemical reactions and their underlying mechanisms in detail, which is often impossible via experiment. Especially for gas phase reactions this procedure is most appropriate to computate the individual species in detail. These theoretical tools enable the researcher to calculate all critical parameters of the intrinsic mechanism of the reaction.

Chapter 2

The Chemical Pathway

What is a molecule? It is a minimum on the potential energy surface.

PRIMAS

To comprehend how molecules could be formed one has to examine the chemical pathway in particular as well as the underlying reaction mechanism. The chemical pathway describes all elementary steps covering the transformation of starting reactants via transition state and possibly intermediate species into final products.

The investigation of the reaction mechanism requires the knowledge of the geometrical structure of all involved species including information about their energetical contents and stereochemistry. This knowledge is necessary to investigate the approach of two reacting species in detail, whether their collision would give rise to a formation of a new chemical bonding and thus a chemical reaction would really occur.

The prediction of the reactivity of the involved molecules includes the examination of the corresponding molecular orbitals and their energetical as well as their spatial arrangement, i.e. their symmetry. Considering an approach of two molecular species along its chemical pathway means to follow a selective path over the virtual potential energy surface of the corresponding molecular system.

2.1 The concept of the n-dimensional molecular potential energy surface

A potential energy surface (PES) of a molecular system can be thought of as a topographical map describing the terrain on which the reacting molecules have to move on their route to a transition state and then onward toward the geometrical arrangement of the product molecule(s). On this virtual map one can pursue the motions of the involved nuclei and their electrons in dependency of their mutual distances on one of those possible routes, the so-called reaction coordinate. The reaction coordinate as an appropriate intersection of the PES is characterized by the different energetical states of the participating species which correlate with the above mentioned distinctive configurations and conformations of the molecular system. These distinguished states or so-called critical points have to be studied in detail, e.g. via molecular orbital calculations.

The potential energy surface describes the variation in the total electronic energy of the molecule as a function of the nuclear N coordinates or 3N-6 (for nonlinear molecules) internal coordinates, respectively, within the Born-Oppenheimer approximation [69], and hence it determines the forces on the nuclei. For a given configuration of the atomic nuclei, the total electronic energy can now be calculated ab initio using a hierarchy of quantum chemical methods (see Chapter 4). To investigate a reacting molecular system transforming into the product molecule(s) means to follow one of several possible reaction paths according to different reaction mechanisms within a 3N-6 dimensional (!) configuration space for a single reaction. There may be multiple symmetry related paths, different versions of the same mechanism for one reaction, as well as competing reactions. So the question arises of the exact definition of a reaction path, and how does one select such an adequate pathway. The latter is still an active field of research (see e.g. Kraka & Dunning [88], Truhlar & Gordon [89], and Page [90].

Some fundamental considerations lead to the concept of the chemical reaction path and will be outlined in the next section.

2.2 The chemical reaction path

In 1935 Eyring postulated a chemical pathway of reaction as the motion along a unique line passing through a saddle point on the PES which determines the course of a chemical reaction. This line was identified with the minimal energy reaction path (MERP). Although discussions around the concept of MERP have been continuing up to the present, Eyring's notion has in fact remained unchanged [91], [92]. Among the reaction paths particularly important are those for which the energy barrier is a minimum. Referring to Mezey [93] certain paths that fulfill this condition are the above mentioned minimum energy paths defined by the following properties: these MERPs follow the direction of the steepest descent [120] which connects two adjacent minima passing through the saddle point on the PES in the 3N-6-dimensional configuration space as the total reaction path [83].

The projection of the total reaction path onto the configurational space represents the MERP. Accordingly the arc length along the MERP is the reaction path or reaction coordinate [119], [95] and depicts the continuous transformation of the nuclear geometrical configuration reflecting the motion of the reactant to the product in the course of the chemical reaction.

The definition given by Fukui [97], [98], [118] of the *intrinsic reaction co-ordinate* (*IRC*) is also a steepest descent pathway and seems to be most useful for the purpose one is here confronted with: it can be defined as the path traced by a classical particle sliding with infinitesimal velocity from a transition state toward both minima, characterizing the initial and the final state(s), and is orthogonal to any equipotential contour surface crossed (see also section 4.1.9).

The methods for obtaining the steepest descent path or some approaching reaction coordinate fall into two categories:

Methods that starts at the transition state

...and evolve to reactants and product(s). In such methods the procedure consists of two parts:(i) the computation of the transition state and (ii) the determination of the pathway to reactants and products. For location of the transition state, the most common technique is to minimize the gradi-

ent norm corresponding to the PES ([121], [122], and see also references in section 3.1.6). The difficulty is that such a minimization can lead to any stationary point, minimum or maximum, or even to non-stationary points [52]. The search may be more difficult, if there are secondary minima in the neighborhood of the required saddle point. Sometimes symmetry can be used directly to optimize the structure of an intermediate that should lie very close to the transition structure [125]. Once the transition structure is found, the procedure to obtain the steepest descent path proceeds via the calculation of the IRC (see also section 4.1.9 for details).

Procedures that link reactants and product(s)

Those methods attempt to use some form of interpolation, generally linear, between reactants and product(s). The internal coordinates shared by both reactants and product(s) may be varied linearly and simultaneously from initial structures to final structure(s), leading to a linear internal coordinate path that smoothly connects reactants and product(s). All the internuclear distances themselves may be varied linearly resulting in *linear synchronous transit* pathway [63].

Moreover a lot of potential energy surfaces seem to possess points where the reaction path bifurcates, it splits itself near a valley ridge inflection point, delineating a very unstable point on the PES, or just regarding the direct and the reverse reaction, crosses one or more equivalent paths or simply becomes unstable.

According to Baker [99], bifurcation is often associated with symmetry breaking. A bifurcation or branching point can be regarded as a point of the reaction path where symmetry breaking is energetically favored; for example, consider a molecular inversion caused by an internal rotation. If the symmetry breaking occurs while following the steepest descent path for a reaction process, then a path bifurcation results therefrom. Following Pearson [123], at such stationary points there have to exist at least two products which are transformed into each other by some symmetry operations.

If a steepest descent path comes to a point where the followed valley turns into a ridge, then this point is called a *valley ridge inflection* (VRI). Such points have often been mixed up with bifurcation points, because the region around them is unstable. During the computation, if the actual calcu-

lated path deviates slightly from its theoretically correct route, it can diverge strongly. Most of the time the VRIs have been studied in the context of symmetry [99], [102], [124].

Notions and concepts like bifurcation, branching points and valley ridge inflection [103], which illustrates and characterizes the complexity of a multidimensional potential energy surface and its analytical and numerical treatment, has partially been studied by Baker [99], Bosh [100], Schlegel [101], and Valtazanos [102].

With the aim to study a chemical reaction path in detail we consider two colliding molecular species

$$A + B \longrightarrow AB^* \rightleftharpoons C + D$$

A and B represent the reacting species, AB^* the transition state, and C and D symbolizes the possible product compounds, which could dissociate into the initiating molecules again under appropriate physical and chemical conditions. That general chemical reaction is designated as a reaction in absolute chemical equilibrium, but as we know, in most cases of chemical reactions the equilibrium lies on one side of the reaction, or the reaction is an entirely irreversible one.

The localization of the critical points

In order to explore an appropriate path of reaction, one has to locate and characterize its minima and saddle points. Minima are points of stable equilibrium geometrical structures representing the initial and the final states of the transformation process. Saddle points are intermediate highly excited and thus unstable points associated with transition state structures. Both they are stationary or so-called critical points of the energy function, part of the PES. Mezey [94], Müller [95], and Schlegel [96] based their differentiation on the investigation of the eigenvalues of the corresponding Hessian matrix (see section 4.1.5 for details).

First of all one has to optimize the geometrical parameters of the involved molecular species with respect to symmetry as well as their total electronic energy, here realized via ab initio quantum chemical methods. In case of the desired minima one starts with an initial molecular configuration according to a certain point somewhere on the n-dimensional potential energy surface of the system, which leads to the next lying stable configuration point, presenting an energy minimum. Besides, it is throughout probable that there exist several stable geometries belonging to a single molecular structure varying in the arrangements of atoms or functional groups as well as in bonding lengths and/or angles. These different mesomere structures may correspond to distinguished conformations of the molecule, which would be transformed into each other via internal rotations, if at least one simple bonding exist and where no rotational barriers are to expect.

Both minima and saddle points are characterized by a zero gradient. However, unlike a minimum, a first order saddle point must be a maximum along the reaction path, and a minimum for all displacements perpendicular to the path. That means, it has to be a maximum in one (and only one) direction. In general, this direction is not known in advance and must be determined during the course of the optimization. In opposition to the determination of the energy minima of the PES, the search for the first order saddle points, which corresponds to the transition state structures, is a much more complex problem, moreover direct experimental verification is not possible in this case. Hence, the quantum chemical calculations are the only source of direct information on the geometrical arrangement and the energetics of transition states, like it is outlined in section 4.1.6. Additionally, several algorithms have been proposed to deal with the problem of locating transition structures [96], [95] among others.

Since the minima and saddle point are well defined points on the energy surface, it should be possible to define a unique reaction path. The steepest descent path from the saddle point to the minima can be defined easily as shown above, but it depends on the particular choice of the coordinate system. Cartesian coordinates would yield a different path than internal coordinates. Moreover, internal coordinates are not unique, since a number of different sets of bond lengths, angles and torsions can represent the same structure. Whereas an intrinsic reaction path or intrinsic reaction coordinate can be defined independently of the coordinate system [28]. Since the classical equations of motion can be defined in any coordinate system, and since they must yield the same trajectory, this definition of the IRC is unique. An intrinsic reaction coordinate features the mathematical and geometrical properties of the energy surface, like minima, maxima and saddle points. Considerable care should be taken not to overvalue the chemical or physical

meaning of the reaction coordinate. Since molecules have been more than infinitesimal kinetic energy, a classical trajectory will not follow the intrinsic reaction path and may deviate quite widely from it. The IRC represents, however, a convenient measure of the progress of a molecule in a reaction [96].

2.3 Reaction mechanisms of astrophysical interest

In order to take the astrophysical situation into account, one has to consider some reaction mechanisms, which particularly be used in chemical modeling under the conditions of the interstellar gas phase. In general, one proceeds from two-body collisions. For example, three of the most important and chemically effective mechanisms are outlined here.

2.3.1 Ion-molecule-mechanism

One of the most investigated chemical reaction mechanisms in theoretical astrophysics is the reaction of a charged species, preferably a kation, colliding with a neutral molecule. Numerous contributions of comprehensive theoretical, experimental and spectroscopical study are available in [309], [311], [312], and [310].

Since molecular hydrogen is the major component in the interstellar space, polyatomic ions can be built up rapidly by exothermic ion-molecule reactions of the type

$$A^{+} + H_{2} \longrightarrow AH^{+} + H$$

$$AH^{+} + H_{2} \longrightarrow AH_{2}^{+} + H$$

$$(1)$$

$$(2)$$

where A^+ represents any ion. Another mode of synthesis, but of less much efficiency, is

$$A^+ + H_2 \rightleftharpoons (AH_2^+)^* \longrightarrow AH_2^+ + h\nu$$
 (3)

 $(AH_2^+)^*$ is a short-lived collision complex, which can stabelize itself by in-

frared emission [186].

Those polyatomic ions, which do not react rapidly with other components are destroyed primarily by recombination with electrons. These reactions are highly exothermic and usually lead to decomposed neutral products. Among the neutral species formed by recombination reactions are CH, NH, OH, H_2O , NH_3 , and H_2CO [219]. Less reactive compounds like NH_3 and H_2O can react efficiently only with ions, while more reactive species such as OH and CH may react in some certain cases with neutral atoms and molecules as well as with ions.

2.3.2 Neutral-neutral-mechanism

These neutral-neutral reactions produce a wider variety of neutral components. The reaction happens between atoms and free radicals. Their major contribution is the destruction of radicals and the formation of diatomical species like molecular oxygen and nitrogen, cyanide and nitrogen monoxide, for example [308], [307].

Many of those neutral-neutral reactions have no activation barriers, so the temperature dependence can be ignored in this case [186].

2.3.3 Radiative-association-mechanism

Radiative association is thought to play a significant, dominant role in the gas phase chemistry of dense and diffuse interstellar clouds [105], [106], [186], [107], [108], [109], [117] and has been used in a number of models (e.g., [110]) to investigate the chemical pathway of an assortment of complex molecules. Since laboratory measurements of the desired rate coefficients for radiative association processes have been difficult, several scientists tackled the problem via theoretical determinations like [111], [112], [113] and is discussed in the following reviews [114], [109].

In the majority of these calculations, radiative association proceeds via an intermediate complex, which exists in the vibrational continuum of the electronic ground state. The excited complex stabilizes by radiating the surplus energy from the ground state to lower vibrational levels of the exited state. A different version of the mechanism the collision complex formed initially on its ground state potential surface and crosses efficiently onto an excited surface relaxing radiatively via electronic emission to stable levels of the electronic ground state.

The basic mechanism assumed for radiative association can be described by the processes [116]:

$$A^+ + B \longrightarrow A^+ B^*$$
 (1)

$$A + B^* \longrightarrow A^+ + B + e^- \tag{2}$$

$$A + B^* \longrightarrow A^+ + B + e^-$$
 (2)
 $A + B^* \longrightarrow A^+B + h\nu + e^-$ (3)

The symbol A^+B^* delineates a complex, or species with sufficient energy to redissociate into reactants. A more complicated mechanism in which the complex dissociates into different products as in the original reactants has presented by Herbst [115].

Further types of formation pathways like insertion reactions, the charge transfer mechanism and condensation reactions also take part in reaction networks of the interstellar chemistry.

Chapter 3

The methods

3.1 Ab initio molecular orbital theory

Ab initio molecular orbital theory is concerned with predicting the properties of atomic and molecular systems. It is based upon the fundamental laws of quantum mechanics and uses a variety of mathematical transformation and approximation techniques to solve the fundamental equations.

3.1.1 Schrödinger's equation

For the problem of geometry optimization I am interested in, an equation is needed, which depends on the position of the particles independent of time.

Entities like nuclei and electrons are characterized by both particle-like and wave-like properties. The time-independent Schrödinger equation [68] describes a particle or collection of particles like a molecular system via the wavefunction Ψ , which represents a function of the coordinates of all the particles in the system

$$\mathbf{H}\Psi(\vec{r}) = E\Psi(\vec{r}) \tag{3.1}$$

The molecular Hamiltonian \mathbf{H} is given as

$$\mathbf{H} = \mathbf{T} + \mathbf{V} \tag{3.2}$$

where the operator for kinetic energy T is the sum of one-particle operators concerning all particles of the molecular system:

$$\mathbf{T} = -\frac{h^2}{8\pi^2} \sum_{k} \frac{1}{m_k} \left(\frac{\partial^2}{\partial x_k^2} + \frac{\partial^2}{\partial y_k^2} + \frac{\partial^2}{\partial z_k^2} \right). \tag{3.3}$$

The sum is over all particles k, i.e. nuclei and electrons, with m_k , the mass of particle k and Planck's constant h.

The potential energy V denotes the Coulomb interaction between every single pair of charged particles:

$$\mathbf{V} = \frac{1}{4\pi\varepsilon_0} \left[-\sum_{i}^{el} \sum_{I}^{nu} \left(\frac{Z_I e^2}{r_{iI}} \right) + \sum_{i}^{el} \sum_{j(3.4)$$

where ε_0 delineates the dielectric constant and $r_{iI} = |\vec{r}_i - \vec{r}_I|$ the distance of electron i and nucleus I; r_{ij} and R_{IJ} have corresponding meanings. Z stands for the atomic number and e for the elementary charge.

The energy and many other properties can be obtained by solving the Schrödinger equation for Ψ , adapted to the appropriate boundary conditions. Different wavefunctions are solutions to it, corresponding to different stationary states of the molecular system.

3.1.2 Born-Oppenheimer approximation

The Born-Oppenheimer approximation [69] facilitates the solution of the Schrödinger equation. The general molecular problem is simplified by separating nuclear and electronic motions. This separation is reasonable since

the mass of a typical nucleus is thousand times larger than that of an electron. Consequently the nuclei move very slowly in regard to the electrons whereas the electrons react instantaneously to changes in nuclear position. Thus, the electron distribution within a molecular system depends on the position of the nuclei, and not on their velocities, i.e. the electronic motion can be described as occurring in a field of fixed nuclei.

The separation of nuclei and electrons leads to the definition of the electronic Hamiltonian (from now on assuming atomic units):

$$H^{el} = -\frac{1}{2} \sum_{i}^{el} \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial Z_i^2} \right) - \mathbf{V}. \tag{3.5}$$

In accordance to the Born-Oppenheimer approximation the Schrödinger equation may be formulated for the motion of the electrons

$$H^{el}\Psi^{el}(\vec{r}, \vec{R}) = E^{eff}(\vec{R})\Psi^{el}(\vec{r}, \vec{R}).$$
 (3.6)

The electronic Hamiltonian H^{el} corresponds to the motion of electrons only in the field of fixed nuclei. Ψ^{el} is the electronic wavefunction which depends on the electronic coordinates \vec{r} as well as the nuclear coordinates \vec{R} . The effective electronic energy $E^{eff}(\vec{R})$ depends on all the relative nuclear coordinates, delineating the potential surface according to the nuclear motion for a polyatomic molecule [70].

$$H^{nu} = T^{nu}(\vec{R}) + E^{eff}(\vec{R}) \tag{3.7}$$

The Hamiltonian H^{nu} characterizes the vibrational, rotational and translational states of the nuclei. For predicting the vibrational or rotational spectra of molecules it is necessary to solve the nuclear Schrödinger equation at least approximately.

For the ongoing problem of optimizing the molecular geometry, theory will be focused entirely on solving the electronic wavefunction.

3.1.3 Hartree-Fock approximation

The molecular orbital theory uses one-electron functions or *orbitals* to approximate the full wavefunction Ψ . A molecular orbital is a function $\psi(\vec{r})$ of spatial coordinates, denoted by \vec{r} , of a single electron. To complete the description of an electron, the spin coordinates have to be included. With the spin function $\alpha(\xi)$, Ψ delineating an n-electron system is decomposed into the so-called $Hartree\ product$

$$\Psi = \psi_1(\vec{r}_1)\alpha(\xi) \cdot \psi_2(\vec{r}_2)\alpha(\xi) \cdots \psi_n(\vec{r}_n)\alpha(\xi). \tag{3.8}$$

To use the *Hartree-Fock approximation* an antisymmetric product of oneelectron functions is required. The simplest antisymmetric function in terms of molecular orbitals is a determinant.

A closed shell n-electron system contains pairs of electrons with opposite spin according to the electronic spin functions $\alpha(\xi)$ and $\beta(\xi)$ are assigned to n/2 molecular orbitals:

$$\Psi = \frac{1}{\sqrt{n!}} \begin{bmatrix}
\psi_{1}(\vec{r}_{1})\alpha(1) & \psi_{1}(\vec{r}_{1})\beta(1) & \dots & \psi_{\frac{n}{2}}(\vec{r}_{1})\alpha(1) & \psi_{\frac{n}{2}}(\vec{r}_{1})\beta(1) \\
\psi_{1}(\vec{r}_{2})\alpha(2) & \psi_{1}(\vec{r}_{2})\beta(2) & \dots & \psi_{\frac{n}{2}}(\vec{r}_{2})\alpha(2) & \psi_{\frac{n}{2}}(\vec{r}_{2})\beta(2)
\end{bmatrix} \\
\vdots & \vdots & \vdots & \vdots & \vdots \\
\psi_{1}(\vec{r}_{i})\alpha(i) & \psi_{1}(\vec{r}_{i})\beta(i) & \dots & \psi_{\frac{n}{2}}(\vec{r}_{i})\alpha(i) & \psi_{\frac{n}{2}}(\vec{r}_{i})\beta(i) \\
\psi_{1}(\vec{r}_{j})\alpha(j) & \psi_{1}(\vec{r}_{j})\beta(j) & \dots & \psi_{\frac{n}{2}}(\vec{r}_{j})\alpha(j) & \psi_{\frac{n}{2}}(\vec{r}_{j})\beta(j)
\end{bmatrix} \\
\vdots & \vdots & \vdots & \vdots & \vdots \\
\psi_{1}(\vec{r}_{n})\alpha(n) & \psi_{1}(\vec{r}_{n})\beta(n) & \dots & \psi_{\frac{n}{2}}(\vec{r}_{n})\alpha(n) & \psi_{\frac{n}{2}}(\vec{r}_{n})\beta(n)
\end{bmatrix} (3.9)$$

Each row represents all possible assignments of an electron i to all orbital spin combinations. The factor $\frac{1}{\sqrt{n!}}$ is necessary for normalization. The *Slater determinant* [73] is fully antisymmetric under the exchange of any pair of electrons, because the effect of interchanging a pair of rows causes the determinant to change sign.

For a molecular orbital it is not possible to be occupied by two electrons of the same spin, because the wavefunction eq. 3.9 vanishes if two columns are identical [71]. This is called the *Pauli principle* [72].

The next step in this procedure is to introduce the molecular orbital expansion and determining the corresponding coefficients based on the *variational* principle or variational theorem [71]. Solving the Hartree-Fock equation using the iterative process of the self-consistent-field (SCF) procedure [152] yields the molecular orbitals $\psi_i(\vec{r})$.

$$F\psi_i(\vec{r}) = \varepsilon_i \psi_i(\vec{r}) \tag{3.10}$$

where F delineates the Fock operator, here for closed shell systems

$$F = h + \sum_{l=1}^{n/2} (2J_l - K_l)$$
(3.11)

with J_l and K_l defined in terms of their effects on $\psi(\vec{r})$:

the Coulomb operator J_l

$$J_{l}\psi(\vec{r}) = \int \frac{\psi_{l}^{*}(r')\psi_{l}(r')}{|\vec{r} - \vec{r}'|} dV'\psi(\vec{r})$$
 (3.12)

and the exchange operator K_l

$$K_{l}\psi(\vec{r}) = \int \frac{\psi_{l}^{*}(r')\psi_{l}(r')}{|\vec{r} - \vec{r}'|} dV'\psi(\vec{r})$$
(3.13)

which represents the quantum mechanical correction term taking into consideration the effects of spin correlation.

A further restriction involves expanding the molecular orbitals in terms of basis functions ϕ_i , linear combinations of a pre-defined set of one-electron functions according to the linear combination atomic orbital (LCAO) method [74].

Thus an individual molecular orbital is defined as

$$\psi_i = \sum_{\mu=1}^{N} c_{\mu i} \phi_{\mu} \tag{3.14}$$

 $c_{\mu i}$ represent the molecular orbital expansion coefficients. The basis functions ϕ_i are also chosen to be normalized.

For orbital expansion an appropriate set of basis functions has to be selected, with that the coefficients $c_{\mu i}$ may then be adjusted to minimize the total electronic energy calculated from the many-electron wavefunction. The resulting value of the energy will then be as close as possible to the exact energy E_0 of the ground state of the system within the selected limitations, i.e. the exact solution of the Schrödinger equation.

$$E(\Phi_1, \Phi_2, \dots, \Phi_N) \ge E_0 \tag{3.15}$$

The equality sign shall be applied only in case Ψ is the exact ground state function.

For the *closed shell* wavefunction eq. 4.9 the Hartree-Fock equations turn into the *Roothaan-Hall equations* [74], [75] offering an opportunity to solve that problem.

$$\sum_{\nu=1}^{N} (F_{\mu\nu} - \epsilon_i S_{\mu\nu}) c_{\mu i} = 0 \qquad \mu = 1, 2, \dots, N$$
 (3.16)

 ϵ_i delineate the *one-electron energy* of a molecular orbital ψ_i , $S_{\mu\nu}$ representing the elements of a $N \times N$ matrix is termed the *overlap matrix*

$$S_{\mu\nu} = \int \phi_{\mu}^{*}(1)\phi_{\nu}(1)dx_{1}dy_{1}dz_{1}$$
 (3.17)

and $F_{\mu\nu}$ describes the elements of $N \times N$ Fock matrix

$$F_{\mu\nu} = H_{\mu\nu}^{core} + \sum_{\lambda=1}^{N} \sum_{\sigma=1}^{N} P_{\lambda\sigma} [(\mu\nu|\lambda\sigma) - 1/2(\mu\lambda|\nu\sigma)]. \tag{3.18}$$

The matrix $H_{\mu\nu}^{core}$ stands for the energy of a single electron in a field of pure nuclei

$$H_{\mu\nu}^{core} = \int \phi_{\mu}^*(1) \mathbf{H}^{\mathbf{core}}(1) \phi_{\nu}(1) dx_1 dy_1 dz_1$$

$$\mathbf{H^{core}}(1) = -\frac{1}{2} \left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \right) - \sum_{A=1}^M \frac{Z_A}{r_{1A}}.$$
 (3.19)

with the atomic number Z_A of atom A.

 $P_{\lambda\sigma}$ (eq. 3.18) represents the density matrix and $(\mu\nu|\lambda\sigma)$ the two-electron repulsion integrals

$$(\mu\nu|\lambda\sigma) = \int \int \phi_{\mu}^{*}(1)\phi_{\nu}(1) \left(\frac{1}{r_{12}}\right) \phi_{\lambda}^{*}(2)\phi_{\sigma}(2) dx_{1} dy_{1} dz_{1} dx_{2} dy_{2} dz_{2}$$
 (3.20)

The conditions of normalization are

$$\sum_{\mu=1}^{N} \sum_{\nu=1}^{N} c_{\mu i}^{*} S_{\mu \nu} c_{\nu i} = 1.$$
 (3.21)

Open shell systems

The spin restricted Hartree-Fock (RHF) theory [76], [77] is generally used for closed shell state calculations. For open shell-systems like radicals or triplet states with electrons not completely assigned to molecular orbitals in pairs, the Roothaan-Hall equations has to be modified. The restricted open shell Hartree-Fock (ROHF) method [85] as well as the spin unrestricted Hartree-Fock (UHF) method [78] describe two ways of modification.

In the *ROHF theory* a single set of molecular orbitals is used with doubly and singly occupied orbitals. The according coefficients $c_{\mu i}$ are still defined by the equation for expansion eq. 4.14 as well as their optimized values are still obtained via the procedure of the variational principle eq. 4.15.

In the approach of the *UHF theory* different spatial orbitals are assigned to α and β electrons. Thus there exist two distinct sets of molecular orbitals. The previously doubly occupied orbital ψ_1 is now divided into two distinct orbitals ψ_1^{α} and ψ_1^{β} , defined by two sets of coefficients

$$\psi_i^{\alpha} = \sum_{\mu=1}^{N} c_{\mu i}^{\alpha} \phi_{\mu} \qquad \qquad \psi_i^{\beta} = \sum_{\mu=1}^{N} c_{\mu i}^{\beta} \phi_{\mu}$$
 (3.22)

The coefficients are varied independently and lead to modified *Roothaan-Hall* equations [78] according to the *UHF theory*

$$\sum_{\nu=1}^{N} (F_{\mu\nu}^{\alpha} - \epsilon_i^{\alpha} S_{\mu\nu}) c_{\mu i}^{\alpha} = 0$$

$$\sum_{\nu=1}^{N} (F_{\mu\nu}^{\beta} - \epsilon_{i}^{\beta} S_{\mu\nu}) c_{\mu i}^{\beta} = 0 \qquad \mu = 1, 2, \dots, N$$
 (3.23)

The corresponding Fock matrices are specified [70] by

$$F^{\alpha}_{\mu\nu} = H^{core}_{\mu\nu} + \sum_{\lambda=1}^{N} \sum_{\sigma=1}^{N} [(P^{\alpha}_{\lambda\sigma} + P^{\beta}_{\lambda\sigma})(\mu\nu|\lambda\sigma) - P^{\alpha}_{\lambda\sigma}(\mu\lambda|\nu\sigma)]$$

$$F_{\mu\nu}^{\beta} = H_{\mu\nu}^{core} + \sum_{\lambda=1}^{N} \sum_{\sigma=1}^{N} [(P_{\lambda\sigma}^{\alpha} + P_{\lambda\sigma}^{\beta})(\mu\nu|\lambda\sigma) - P_{\lambda\sigma}^{\beta}(\mu\lambda|\nu\sigma)]$$
(3.24)

with the density matrix $P_{\mu\nu}$, which is also divided into two parts

$$P^{\alpha}_{\mu\nu} = \sum_{i=1}^{\alpha occ} c^{\alpha *}_{\mu i} c^{\alpha}_{\nu i} \qquad P^{\beta}_{\mu\nu} = \sum_{i=1}^{\beta occ} c^{\beta *}_{\mu i} c^{\beta}_{\nu i} \qquad (3.25)$$

where βocc and αocc denote the involved occupied orbitals. The integrals $S_{\mu\nu}$ and $H^{core}_{\mu\nu}$ appearing in the UHF treatment have the same definition as for closed shell calculations.

Since the *RHF* function is a special case of the *UHF* function, the *UHF* theory will supply a lower optimized energy than *RHF* theory. However, *UHF* functions have the disadvantage not being true eigenfunctions of the total spin operator, which exact wavefunctions necessarily are.

In this work both procedures of *RHF* and *UHF theory* are used to calculate the radical and ionic form of the involved species.

3.1.4 Møller-Plesset Perturbation Theory

A further approach to electron correlation used here is Møller-Plesset Perturbation Theory. The central idea in the perturbation technique is to use a known unperturbed or so-called zeroth-order Schrödinger equation

$$\mathbf{H}\Psi^0 = E^0 \Psi^0 \tag{3.26}$$

solving the Schrödinger equation related to an expanded or perturbed problem. In that respect Perturbation Theory is based upon dividing the Hamiltonian into two parts:

$$\mathbf{H} = \mathbf{H_0} + \lambda \mathbf{V} \tag{3.27}$$

The Schrödinger equation with $\mathbf{H_0}$ is assumed soluble exactly. $\lambda \mathbf{V}$ is a perturbation \mathbf{V} is the perturbation operator and not related to the potential energy (eq. 3.4). The assumption is that \mathbf{V} is a small perturbation to $\mathbf{H_0}$ so that the perturbed wavefunction and energy can be expressed as a power series in \mathbf{V} in terms of the parameter λ :

$$\Psi = \Psi^0 + \lambda \Psi^1 + \lambda^2 \Psi^2 + \lambda^3 \Psi^3 + \dots \tag{3.28}$$

$$E = E^{0} + \lambda E^{1} + \lambda^{2} E^{2} + \lambda^{3} E^{3} + \dots$$
 (3.29)

The perturbed wavefunction and energy are substituted back into the zeroth order Schrödinger equation:

$$(\mathbf{H_0} + \lambda \mathbf{V})(\Psi^0 + \lambda \Psi^1 + \dots) = (E^0 + \lambda E^1 + \dots)(\Psi^0 + \lambda \Psi^1 + \dots)$$
 (3.30)

After expanding the products, one can equate the coefficients on each side of the equation for each power of λ , leading to a series of relations representing successively higher orders of perturbation. After some rearranging one gets the first three equations corresponding to powers and orders, respectively, of 0,1, and 2 of λ :

$$(\mathbf{H_0} - E^0)\Psi^0 = \mathbf{0}$$

$$(\mathbf{H_0} - E^0)\Psi^1 = (E^1 - \mathbf{V})\Psi^0$$

$$(\mathbf{H_0} - E^0)\Psi^2 = (E^1 - \mathbf{V})\Psi^1 + E^2\Psi^0$$
(3.31)

So far, this is the presentation of general perturbation theory results. In 1934, Møller and Plesset proposed a perturbation treatment of atoms and molecules in which the unperturbed wave function is the Hartree-Fock function.

In this particular case of the $M\emptyset$ ller-Plesset (MP) Perturbation Theory [79], [80] $\mathbf{H_0}$ is defined as the sum of the one-electron Fock operators:

$$\mathbf{H_0} = \sum_{i}^{n} F^i \tag{3.32}$$

When recollecting the Slater determinant as an antisymmetrized product of the spin orbitals (eq. 3.9) expanded in terms of ϕ_i , each term involves a different permutation of the electrons among the spin orbitals. The determinant is an eigenfunction of the $MP\mathbf{H_0}$

$$\mathbf{H_0}\Psi_0 = \left(\sum_{i=1}^n \varepsilon_i\right)\Psi_0 \tag{3.33}$$

The eigenfunctions of the unperturbed Hamiltonian $\mathbf{H_0}$ are the zeroth-order wave functions, thus the Hartree-Fock ground state function Ψ_i is one of the zeroth-order wave functions, and the zeroth-order energy is just the sum of the MO energies

$$E_0^0 = \langle \Psi_0^0 | \mathbf{H_0} \Psi_0^0 \rangle = \sum_{i}^{n} \varepsilon_i$$
 (3.34)

The MP first-order correction E_0^1 is

$$E_0^1 = \langle \Psi_0^0 | \mathbf{H}' | \Psi_0^0 \rangle \tag{3.35}$$

The perturbation $\mathbf{H}'(=\lambda \mathbf{V})$ see eq. 3.27) is the difference between the true molecular electronic Hamiltonian \mathbf{H} and \mathbf{H}^0 ; $\mathbf{H}' = \mathbf{H} - \mathbf{H}^0$. Thus one obtains

$$E_{0}^{0} + E_{0}^{1} = \langle \Psi_{0}^{0} | \mathbf{H}_{0} | \Psi_{0}^{0} \rangle + \langle \Psi_{0}^{0} | \mathbf{H}' | \Psi_{0}^{0} \rangle = \langle \Psi_{0}^{0} | \mathbf{H}^{0} + \mathbf{H}' | \Psi_{0}^{0} \rangle = \langle \Psi_{0}^{0} | \mathbf{H} | \Psi_{0}^{0} \rangle$$
(3.36)

 $\langle \Psi_0^0 | \mathbf{H} | \Psi_0^0 \rangle$ is the variational integral for the Hartree-Fock determinant Ψ_0^0 and therefore it is equal to the Hartree-Fock energy E_{HF}

$$E_0^0 + E_0^1 = E_{HF}. (3.37)$$

To improve the Hartree-Fock energy, it is necessary to use the second-order energy correction E_0^2 [85]

$$E_0^2 = \sum_{s \neq 0} \frac{|\langle \Psi_s^0 | \mathbf{H}' | \Psi_0^0 \rangle|^2}{E_0^0 - E_s^0}$$
 (3.38)

where Ψ_s^0 and E_s^0 are solutions of $\mathbf{H_0}\Psi_s^0 = \mathbf{E_s^0}\Psi_s^0$. The unperturbed wavefunctions Ψ_s^0 represents all possible Slater determinants (see eq. 4.9) formed from n different spin orbitals. Each unperturbed wavefunction can be classified by the number of its containing virtual orbitals, and this number is called the excitation level. Taking the molecular energy as

$$E_0^0 + E_0^1 + E_0^2 = E_{HF} + E_0^2$$

results in a calculation designated as $M\emptyset$ ller-Plesset perturbation theory of the second-oder (MP2).

To perform a MP electron correlation calculation, one first chooses a basis set and carries out a Hartree-Fock calculation to obtain Ψ_0 and E_{HF} as well as virtual orbitals. That is followed by the computation of the second-order energy correction E^2 evaluating the integrals over spin orbitals in terms of integrals over the basis functions. Naturally using a finite, incomplete set of basis functions to expand the spin orbitals, the HF calculation will then produce the approximate energy value and will yield a finite number of virtual orbitals.

The value of E^2 will always be negative. Lowering the energy is what the exact correction should do, although the Møller-Plesset perturbation theory correction is capable to overcorrect it, since it is not variational. The third and fourth order energy correction can be also derived (e.g. [87]), but since higher order corrections may be positive and in order to get closer to the true (negative) energy of the molecular system, here I confine this procedure to the second-order correction.

A remark why it is reasonable to use the Møller-Plesset (MP) perturbation calculations. MP calculations are much faster than Configuration Interaction (CI) calculations. The energy gradient in MP2 calculations is readily evaluated analytically [82], and this allows MP2 geometry optimization to be done easily and allows of MP2 vibrational frequencies.

Although offering a high computational efficiency, MP calculations are not variational and can produce an energy below the true energy of the molecular system; especially when MP calculations of third or higher order are applied.

MP2 calculations on closed shell molecules typically yield 85% to 95% of the basis set correlation [80] and substantially improve the accuracy of equilibrium geometry and vibrational frequency predictions. The errors in MP2 predicted equilibrium single bond length are reduced by a factor of 2 or 3 [81].

Because of their computational efficiency and the good results they provide for molecular properties, MP2 calculations have become the method of choice for dealing with the effects of electron correlation on molecular ground state equilibrium properties.

3.1.5 Geometry optimization

Application of molecular orbital theory requires a specification of molecular geometry, as it is necessary for the detailed investigation of the chemical pathway. With those tools mentioned above it is now possible to calculate the total energy of the molecular system and its corresponding geometric parameters like bond lengths and bond angles devoted to a well-defined molecular symmetry.

The geometry of a nonlinear molecule with N nuclei is defined by 3N-6 independent nuclear coordinates and its electronic energy is a function of these 3N-6 coordinates. Particularly the equilibrium geometry according to the nuclear configuration minimizes the molecular electronic energy including nuclear repulsion.

The equilibrium geometry represents one stable molecular configuration of the system and accordingly a stationary point on the potential energy surface (PES). Saddle points denoting transition states, characterize other *critical* points on the PES.

Such critical points of a given function f(q) are those points of the configurational space in which the values of all first derivatives of the function relative to any independent variable q_i are equal to zero. In any critical point of a PES described by the coordinates $(q_1, q_2, ..., q_{3N-6})$ the first derivatives of energy E with respect to all coordinates (the gradients) become equal to zero:

$$\vec{g}radE \equiv \left(\frac{\partial E}{\partial q_1}, \frac{\partial E}{\partial q_2}, \frac{\partial E}{\partial q_3}, \dots, \frac{\partial E}{\partial q_{3N-6}}\right) = (0, 0, 0, \dots, 0) \equiv 0$$
 (3.39)

To characterize the nature of such extremum points of a molecular system on the PES one has to investigate the curvature in these points. That means, the second derivatives of the energy have to be calculated with respect to all coordinates in the extremum region. In its general form the set of second derivatives of the energy constitutes the *Hessian matrix H*:

$$\mathbf{H} = \begin{pmatrix} \frac{\partial^2 E}{\partial q_1^2} & \frac{\partial^2 E}{\partial q_1 \partial q_2} & \cdots & \frac{\partial^2 E}{\partial q_1 \partial q_{3N-6}} \\ \frac{\partial^2 E}{\partial q_2 \partial q_1} & \frac{\partial^2 E}{\partial q_2^2} & \cdots & \frac{\partial^2 E}{\partial q_2 \partial q_{3N-6}} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 E}{\partial q_{3N-6} \partial q_1} & \frac{\partial^2 E}{\partial q_{3N-6} \partial q_2} & \cdots & \frac{\partial^2 E}{\partial q_{3N-6}^2} \end{pmatrix}$$
(3.40)

When the Hessian matrix has at least one zero eigenvalue the corresponding critical point is called a *degenerate critical point*. It is generally assumed that the degenerate critical points of a PES are of no great significance for the analysis of reaction mechanisms [83], hence I will consider only *nondegenerate* critical points, i.e. in which the Hessian matrix has no zero eigenvalues.

Supposing the matrix of eq. 3.40 is positively definite, i.e. all its eigenvalues are positive, then the correlating point is a minimum and corresponds to a stable molecular geometry or an intermediate.

In case there exits one (and only one) negative eigenvalue in the considered matrix H, then this point is the first-order saddle point (the order of critical points is determined by the number of negative eigenvalues of the matrix H). It characterizes structurally the transition state of the reaction.

3.1.6 Transition State Theory

Transition State Theory (TST) is based on the assumption that a reaction proceeds from one to another energy minimum via an intermediate maximum [51]. The Transition State (TS) is the configurational point of a molecular system on the PES which describes the change of configuration from the reactant(s) to the product(s), while the corresponding geometrical configuration on the energy maximum is called the *transition structure*. Within standard TST the *transition state* and *transition structure* are equivalent. This is not necessarily the case for more refined models although both terms were often used interchangeably.

The reaction proceeds via a reaction coordinate leading from the reactant(s) to the product(s) along a path where the energy is as low as possible, and the TS is the point where the energy has a maximum.

The total energy of a TS is defined as

$$E(q) = E(q_1, q_2, \dots, q_{3N-6})$$
(3.41)

with the first derivative of energy for any critical point given in eq. (3.39).

A point on the PES of reacting system corresponds to a transition state if the following conditions are satisfied additionally [52]: i) The force constant matrix of this point has a negative value (Murrell-Laidler Theorem [53]) ii) it represents the highest energy along a total reaction path linking the initial reactant(s) and product(s) in the configurational space iii) and it has the minimal energy among all those points on the PES which meet the criteria mentioned above.

In other words in the multidimensional case it is thus a first order saddle point on the potential energy surface, a maximum in the reaction coordinate direction and a minimum along all other coordinates.

Transition state structure optimization

It is emphasized that the localization of a transition state, that means first-order saddle points and their corresponding transition structures requires an exceedingly complex search, on the basis of the manifoldness of the configurational space, which increases with rising number of nuclei in the molecular system. There are *no* general methods which guarantee to succeed. Many different strategies have been proposed, most of them can be divided into two general categories, those based on interpolation between two minima and those using only local information.

There exist a number of different methods for direct localization of transition state points which do not require a calculation of the whole PES [54], [55],[56]. The Newton-Raphson scheme [57] as well as the minimization procedure of McIver & Komornicki [52] using a nonlinear optimization, are methods which converges to the desired stationary point only if the initial geometry is located in a region on the PES sufficiently close to this point.

Another group of methods [58], [59], [60], [61] approaching to those saddle points starts its search from a minimum and proceeds uphill toward a saddle

point. In this case an evaluation of the energy gradient as well as the Hessian matrix eq.(3.26) is necessary.

Some other schemes for locating a transition state are considered in detail in [62], [63], and [64].

3.1.7 Molecular orbital correlation diagrams

Geometrical and energetical optimization of molecular species being involved in a chemical reaction represents the first step of studying the chemical pathway. In order to predict the interaction of two colliding molecules and to decide whether such an interaction would really lead to a reaction, one can use the Woodward-Hoffmann Rules based on the *Conservation of Orbital Symmetry* [65].

The classification of chemical reactions as allowed or forbidden by the symmetry of the orbitals involved, dates back to the earliest days of Quantum Chemistry. In 1928, Wigner and Witmer [16] formulated rules for the formation of diatomic molecules, based on the group theoretical characterization of the orbitals of its constituents atoms. The newly conceived molecular orbital (MO) description of diatomic molecules [236], [18] was systematized by Mulliken [19], who related their MOs as linear combinations of the atomic orbitals (AOs) of the separated atoms on one side of a correlation diagram to those of a *united atom* on the other side. Walsh [20] later extended the correlation diagram approach to polyatomic molecules, taking specific note of how the symmetry properties of the MOs of an initially linear molecule varies with molecular geometry, and showing how this variation can be used to explain the conformation preferentially adopted by the molecule. Bader demonstrated formally in his pioneering paper of 1962 [21] how the energetically favored mode of fragmentation of a non-linear polyatomic molecule can be deduced from the symmetry properties of its molecular orbitals and of its vibrational coordinates.

The reasons for prevailing of the *Woodward-Hoffmann Rules* among that number of methods for the systematic characterization of organic reactions as being either *allowed* or *forbidden* would seem to be: their wide applicability, their beautiful simplicity and the immense authority with which they were presented [26].

In this scheme the outermost electrons of a reacting specie, named frontier electrons [23] play a decisive role within a chemical reaction [65], i.e. for the reactivity, and occupy the Highest Occupied Molecular Orbital (HOMO) of the reactant. The concept of Woodward & Hoffmann's approach is that the MOs of the product must be generated smoothly from MO's of the reactant(s) having the same symmetry properties.

Let one consider a ground state reaction with closed shell reactants should be transfered into a closed shell product. If the occupied MOs of the educt(s) are converted into occupied MOs of the product retaining at least one symmetry element along the reaction pathway, the reaction is called *symmetry allowed*. However, the frontier electrons of the educt(s) are not necessarily delivered to the HOMO of the product. The condition set by both Woodward & Hoffmann and by Fukui [23], [66], [67] for classifying a ground state reaction as *allowed*, if the energy of the HOMO decreases as the reaction occurs.

In contrary to the *allowedness*, the notion of *forbiddance* poses no problem. Whenever the electronic configuration of the reactant and product fail to correlate in the highest common symmetry point group, their interconversion is *forbidden* by orbital symmetry conservation along any pathway that retains that symmetry point group.

Similar considerations are applied to excited state reactions, though it has long been recognized that orbital symmetry arguments should be used with caution when considering photochemical reactions [22], [24].

In a bimolecular reaction the two reactant molecules are set up — by Woodward & Hoffmann as well as by Fukui — in the appropriate geometry for generating the expected product. The judgement as to whether the energy of the frontier electrons increases or decreases is made on different grounds in the two methods: Woodward & Hoffmann construct a correlation diagram between the occupied orbitals of the reactants and the product, taking their symmetry properties explicitly into account, disregarding the unoccupied orbitals. Fukui's approach, which is shared by other perturbation treatments of reactivity [25] (Chaps. 3-5, 7), focuses its attention primarily on the stabilization, as the reaction is under way, of a bonding orbital of one reactant, usually its HOMO by its interaction with an (antibonding) orbital of the other, ordinarily its LUMO.

The construction of a molecular orbital correlation diagram requires the knowledge of the energy levels as well as the symmetry of the involved molec-

ular orbitals of the reacting species and product(s). Then one has to classify both sets of energy levels according to symmetry. The levels of same symmetry are connected, followed by the rule that only levels of unlike symmetry are allowed to cross.

In this work the molecular orbital correlation treatment is applied for as a first criterion to prove, whether the selected reaction pathways could really occur under symmetry conditions.

3.1.8 Intrinsic reaction coordinate calculation

The optimization methods described in sections 3.1.3 – 3.1.6 concentrate on locating stationary points on the potential energy surface (PES). The important points for discussing chemical reactions are minima, corresponding to reactant(s) and product(s), as well as saddle points, corresponding to transition state structures. Once a transition state (TS) has been located, it should be verified that it indeed connects the desired minima. An inspection of the according atomic motions may be a strong indication that the correct TS is found. A strict proof requires a determination of the *Minimum Energy Reaction Path* (MERP) from the TS to the related minima. If the MERP is located in mass-weighted coordinates, it is called the *Intrinsic Reaction Coordinate* (IRC). Fukui [28] introduced the concept of the IRC defined as a classical trajectory of a system's motion over the PES:

the IRC path is defined by the differential equation

$$\frac{d\mathbf{x}}{ds} = -\frac{\vec{g}}{|\vec{g}|} = \vec{v} \tag{3.42}$$

here \mathbf{x} is the (mass-weighted) coordinate, s is the path length and \vec{v} the (negative) normalized gradient. \vec{g} denotes the vector of the first 3N derivatives of the potential of N nuclear coordinates. Determining the IRC requires solving the equation above starting from a geometry slightly displaced from the TS along the normal coordinate in direction to the imaginary frequency.

Another method following the IRC, which does not rely on the integration of the differential equation, has been developed by Gonzales and Schlegel [29]. The idea is to generate points on the IRC via a series of constrained optimizations.

The TS corresponds to the energy being a maximum in one direction and a minimum in all other directions. The according frequency and thus its vibration along the eigenvector with a negative eigenvalue will formally be imaginary. That eigenvector is the direction leading downhill from the transition state towards the reactant(s) (reverse reaction path) and the product(s) (forward reaction path). At the TS the eigenvector for the imaginary frequency is the reaction coordinate. The whole reaction path may be calculated by sliding downhill to each side from the TS. This can be performed by taking a small step along the TS eigenvector calculating the gradient and taking a small step in the negative gradient direction. The negative of the gradient always points downhill, and by taking a sufficiently large number of such steps a stationary point according to a TS is eventually reached [27]. This is equivalent to a steepest descent minimization, but there exist more efficient methods (for more details see references below).

The basic idea in the reaction path methods is considering only the energy surface in the immediate vicinity of a suitable one-dimensional coordinate which usually (but not necessarily) is taken as the IRC. The reaction path potential may be generated by a series of frequency calculations appertaining to the points along the IRC.

As it is said in detail in the preceding chapter the desired aim is to find a distinct reaction path, which leads from definite reactants via a specified transition state to a definite product. It is important to note that the symmetry properties characterizing the transition state of such an reaction are predetermined by the symmetry of its initial and final states. The according transition vector representing just a small section of the reaction path retains all symmetry elements of the TS. Regarding the reaction path as the steepest descent line from the saddle point to the minima corresponding to the reactants and product(s), the nuclear configuration symmetry of the transforming structures of reactants and product(s) needs to be unchanged [28], [153], [22], [154].

Chapter 4

The Approach

This approach is based on the question, when two molecules meet in the gas phase will they actually react to a new chemical compound? And which criterions have to be fulfilled that they really do? In that sense this procedure is divided into some certain steps. First some selected paths of chemical formation are considered. This is followed by optimization of the configurations and conformations of each participating molecular species like the alternative reactants and the product, representing definite points on the corresponding potential energy surface. With the obtained information some selected molecular orbital correlation diagrams are composed and discussed. They present a first criterion for the considered reactions, to be classified as allowed or forbidden. The next important step is the extraordinarily difficult determination of the adequate transition structure according to the transition state of the reaction. Thereafter the computation of the intrinsic reaction coordinate has to be performed, which would give information about the path of formation and the underlying reaction mechanism.

4.1 The considered chemical paths of formation

With reference to the results of Devienne's experiment, the formation of glycine and related compounds as well as the processes of decomposition verifying the synthezised products via mass spectrometrical methods some

of the ways of fragmentations are based retrospectively as ways of formations.

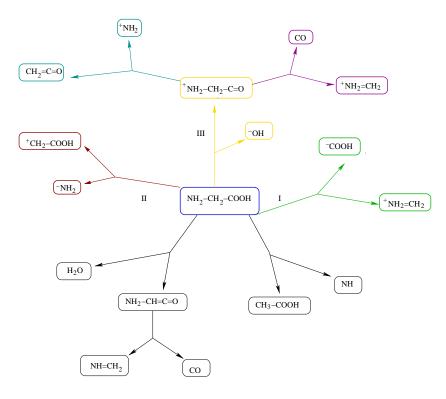


Figure 4.1: mass spectrochemical decomposition of glycine

By picking out just two principle different ways of formation (path I and II), which offer a synthesis just out of two components, it is useful to expand both general pathways, distinguishing a number of distinctive chemical reactions (a), (b), to be possibly in effect under interstellar conditions of the gas phase:

- I. (a) ${}^{+}NH_{2}CH_{2} + {}^{-}COOH \longrightarrow NH_{2}CH_{2}COOH$ (b) ${}^{+}NHCH_{3} + {}^{-}COOH \longrightarrow NH_{2}CH_{2}COOH$ (c) ${}^{+}NH_{2}CH_{2} + HCOOH \longrightarrow NH_{2}CH_{2}COOH + H^{+}$ II. (a) $CH_{3}COOH + NH_{3} \longrightarrow NH_{2}CH_{2}COOH + H_{2}$
- (b) ${}^+CH_2COOH + NH_3 \longrightarrow NH_2CH_2COOH + H^+$
 - (c) ${}^{+}CH_{2}COOH + {}^{-}NH_{2} \longrightarrow NH_{2}CH_{2}COOH$
 - (d) $\cdot CH_2COOH + \cdot NH_2 \longrightarrow NH_2CH_2COOH$
 - (e) ${}^-CH_2COOH + {}^+NH_2 \longrightarrow NH_2CH_2COOH$

The state of the initial species involved in each path may vary in multiplicity and charge, while the product molecule glycine may be formed as one of different conformeres. Those conformeres varies in the spatial arrangement of their molecular constituents, presenting the same geometrical structure. Although they can be transfered into each other via internal rotation, each conformere has a distinct total energy and represents an individual minimum on the potential energy surface.

Considering four different conformations of the product molecule, then each variation (a), (b), and (c) of path number I may split into further four different possible ways of formation. Consistently, there would be the total of twelve distinctive chemical reactions to investigate.

4.2 Optimization of the involved species

According to path I, the mesomeric structures of the reacting species CH_4N^+ , methyleneamine ${}^+NH_2CH_2$ and methylimine ${}^+NHCH_3$ as well as the carboxyl bearing systems ${}^-COOH$, ${}^+COOH$, ${}^+COOH$ and formic acid HCOOH are computed here. As initial molecules of path II are subject of investigation: acetic acid CH_3COOH and its ionic and radical forms of the organic acid and their reaction partners ammonia NH_3 as well as related species (see above). The molecular optimizations include the total energies, the geometrical parameters in terms of internal coordinates, as well as the fundamental vibrational frequencies. These calculations are the basis for the further computations of the transition state structures and the intrinsic reaction coordinate.

All computations were performed via Hartree-Fock (HF) approximation with different basis sets of 3-21G, 4-31G and 6-31G followed by second order perturbation Møller-Plesset (MP2) calculation using the ab initio program gaussian 92. The values shown in most of the following tables are according to MP2/HF6-31G calculations.

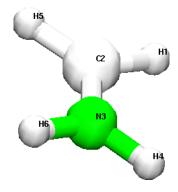


Figure 4.2: planar methyleneamine

4.2.1 The CH_4N^+ species

 CH_4N^+ is observed in the mesomeric form of CH_3NH^+ in the massive star forming region of Sagittarius B2, besides related ionic and neutral species like $HCNH^+$, CH_2NH [157], [155] and CH_3NH_2 [156], which had not been detected in any other object for many years. For the mesomeric form ${}^+NH_2CH_2$ does not exist any result of detection, but it is presumed to play a key role as an intermediate product in the formation of methylenimine CH_2NH [158] and other interstellar N-bearing molecules [163]etc.

In recent years several theoretical investigations have been made with respect to the stable configurations of the CH_4N^+ species. In the last years various authors obtained a stable singlet state for the planar methyleneamine $CH_2NH_2^+$ (see e.g. [141], [142], [144], [149], [146] and [137]. The spiro configuration (see figure 4.3) is a further alternative, but may play only a role as a transition state of a chemical reaction [144].

Methyleneamine ${}^{+}NH_{2}CH_{2}$

The following tables show the results of optimizations for the total energies and internal coordinates as well as the fundamental vibrational frequencies according the shown molecular structures.

Table 4.1: Total energy according to the different basis sets

basis set	charge	multiplicity	symmetry	total energy [hartree]
HF3-21G/MP2	+1	$\operatorname{singlet}$	C_s	-94.05693
HF4-31G/MP2	+1	singlet	C_s	-94.44414
HF6-31G/MP2	+1	singlet	C_s	-94.54001

Table 4.2: Internal coordinates via HF6-31G/MP2

bondlength	[Å]	bondangle	[deg]
r_{CH}	1.0869	α_{H1CN}	119.90
r_{CN}	1.2978	α_{CNH4}	121.92
r_{CH5}	1.0869	α_{H1CH5}	120.19
r_{NH4}	1.0229	α_{NCH5}	119.90
r_{NH6}	1.0229	α_{CNH6}	121.92
		α_{H4NH6}	116.15

Table 4.3: Vibrational frequencies: via HF 6-31G/MP2

vib. mode	$[cm^{-1}]$	vib. mode	$[cm^{-1}]$	vib. mode	$[cm^{-1}]$
1A'	1019.7	2A"	1085.7	3A"	1104.2
4A"	1186.4	5A'	1414.1	6A'	1498.5
7A'	1646.1	8A'	1804.5	9A'	3209.0
10A'	3337.8	11A'	3489.7	12A'	3598.9

The spiro configuration

Table 4.4: Internal coordinates and total energy via HF6-31G/MP2

bondlength	[Å]	bondangle	[deg]
r_{CH}	1.0819	α_{H1CN}	121.34
r_{CN}	1.3539	α_{CNH4}	121.67
r_{CH5}	1.0820	α_{H1CH5}	117.36
r_{NH4}	1.0045	α_{NCH5}	121.29
r_{NH6}	1.0047	α_{CNH6}	121.79
		α_{H4NH6}	116.53
total energy		-94.23453	[hartree]

There exist a comparing study by Krumrey and coworker [220] of the vibrational frequencies calculated in this work with the frequencies determined via the classical GF formalism of Wilson for both planar and spiro configurations

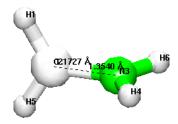


Figure 4.3: spiro conformation of methyleneamine

of methyleneamine as well as for methylimine. The results of both different investigations are in reasonable agreement.

Methylimine CH_3NH^+

For this mesomeric structure exist two different states of multiplicity, the singlet state and the triplet state. As one can see, the values for the total energy of the singlet state are lower than for the triplet state and therewith this state of the species is energetically more stable than the latter.

Table 4.5: Total energy according to the different basis sets

basis set	charge	multiplicity	symmetry	total energy [hartree]
HF3-21G/MP2	+1	$\operatorname{singlet}$	C_1	-94.05693
HF4-31G/MP2	+1	singlet	C_1	-94.44419
HF6-31G/MP2	+1	$\operatorname{singlet}$	C_1	-94.54001
HF3-21G/MP2	+1	triplet	C_1	-93.91768
HF4-31G/MP2	+1	triplet	C_1	-94.30154
HF6-31G/MP2	+1	$\operatorname{triplet}$	C_1	-94.39802

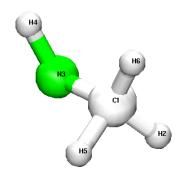


Figure 4.4: singlet methylimine

Table~4.6: Internal~coordinates/singlet~state~via~HF6-31G/MP2

bondlength	[Å]	interatomic/dihedral angle	[deg]
r_{CH2}	1.0865	α_{H2CN}	119.85
r_{CH3}	1.2979	δ_{H2NH4}	149.04
r_{NH4}	1.0227	$lpha_{H5CN}$	121.86
r_{H5C}	2.0329	δ_{H5H2H6}	88.24
r_{H6C}	1.0871		

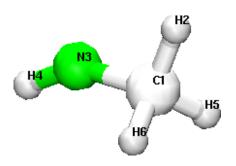


Figure 4.5: triplet methylimine

Table 4.7: Internal coordinates/triplet state via HF6-31G/MP2

bondlength	[Å]	interatomic angle	[deg]	dihedral angle	[deg]
r_{CH}	1.1001	α_{H2CN}	108.54	δ_{H2NH4}	179.91
r_{CN}	1.4294	α_{CNH4}	149.56	δ_{H4NH5}	128.17
r_{NH4}	1.0303	α_{NCH5}	108.81	δ_{H4NH6}	102.19
r_{CH5}	1.1027	α_{NCH6}	108.80	δ_{H5H2H6}	60.33
r_{CH6}	1.1027	α_{H5CH6}	110.64	δ_{H2CH4}	121.23

The comparison of the vibrational frequencies of both configurations of ${}^+NH_2CH_2$ and ${}^+NHCH_3$ in the singlet state shows very good accordance within the HF6-31G/MP2 computation. From this results one can draw the conclusion, that both structures have a very similar geometrical conformation.

Table 4.8: Vibrational frequencies via HF3-21G/MP2

species	singlet state	triplet state		$^+NH_2CH_2$
vib. mode	$[cm^{-1}]$	$[cm^{-1}]$	vib. mode	$[cm^{-1}]$
1A	1019.7	145.9	1A'	1019.7
2A	1085.1	635.3	2A'	1085.7
3A	1103.9	967.4	3A'	1104.2
4A	1185.7	1107.8	4A'	1186.4
5A	1414.3	1127.3	5A"	1414.1
6A	1498.3	1461.7	6A'	1498.5
7A	1645.6	1462.5	7A"	1646.1
8A	1804.0	1482.7	8A'	1804.5
9A	3210.3	3008.6	9A'	3209.0
10A	3339.6	3112.9	10A'	3337.8
11A	3490.1	3134.4	11A'	3489.7
12A	3599.7	3480.6	12A'	3598.9

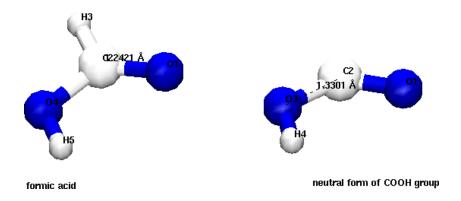


Figure 4.6: formic acid and carboxylat group $\cdot COOH$

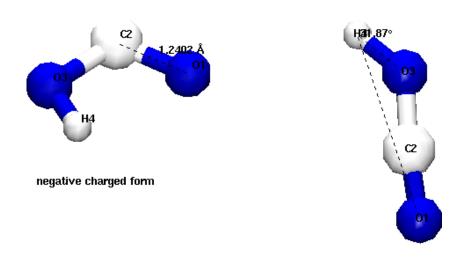
4.2.2 The COOH bearing species

Formic acid and related species

These species represent the second group of reactants according to path I. Formic acid HCOOH and the ionic species ^+COOH have already been identified in star forming regions. Formic acid seems to play a role in grain surface chemistry seeded by carbon monoxide [305]. The optimization procedure includes the total energy, which characterizes their energetical position on the PES, the corresponding geometrical parameters in terms of internal coordinates as well as the fundamental vibrational frequencies.

Table 4.9: Total energy of formic acid and related species

basis set	molecular species	symmetry	total energy [hartree]
HF6-31G/MP2	HCOOH	C_s	-189.00771
HF6-31G/MP2	$COOH^-$	C_s	-188.37254
	COOH.	C_s	-188.35489
	$COOH^+$	C_s	-188.07950



positive charged form

Figure 4.7: carboxylat group — ^-COOH and ^+COOH

Table 4.10: Internal coordinates of the neutral species via MP2/HF/6-31G

species	НСООН	$\cdot COOH$		НСООН	$\cdot COOH$
bondlength	[Å]	[Å]	interatomic angle	[deg]	[deg]
$r_{C=O}$	1.2437	1.2197	α_{OCH}	125.90	
r_{C-H}	1.0911		α_{OCO}	124.94	131.01
r_{C-O}	1.3915	1.3717	α_{HCO}	109.14	
r_{O-H}	0.9858	0.9911	α_{COH}	110.92	113.97

The intramolecular distances and bond angles of both species are comparable. The presence of a non-bonded electron at the $\cdot COOH$ radical refer to a high reactivity of this species.

Table 4.11: Internal coordinates of the charged species via MP2/HF/6-31G

species	^-COOH	$^{+}COOH$		^-COOH	$^{+}COOH$
bondlength	[Å]	[Å]	interatomic angle	[deg]	[deg]
$r_{C=O}$	1.2621	1.1721	α_{OCO}	108.14	170.97
r_{C-O}	1.6527	1.2510	α_{COH}	102.74	127.63
r_{O-H}	0.9973	0.9983			

The difference of the total energies as well as the intramolecular geometries of the these both charged species is conspicuous, as it is also shown in figure 4.7.

With decreasing number of valence electrons, molecular stability is reduced.

Table 4.12: Vibrational frequencies of formic acid and related species

HCOOH			^-COOH	$\cdot COOH$	$^{+}COOH$
vib. mode	$[cm^{-1}]$	vib. mode	$[cm^{-1}]$	$[cm^{-1}]$	$[cm^{-1}]$
1A'	598.3	1A'	341.8	577.0	481.0
2A"	668.3	2A"	584.5	604.0	490.1
3A"	1042.0	3A'	593.9	1014.4	923.8
4A'	1051.2	4A'	1068.1	1299.5	1180.6
5A'	1303.9	5A'	1532.5	1815.1	2287.2
6A'	1427.9	6A'	3385.9	3482.1	3439.3
7A'	1669.6				
8A'	3194.5				
9A'	3587.3				

As referred to the different shape of the ^+COOH species compared with ^-COOH and ^+COOH , it is noteworthy that the single vibrational frequencies differ with decreasing number of valence electrons up to about $400cm^{-1}$ with one another, like it is indicated in the table above.

Acetic acid and related species

The existence of acetic acid CH_3COOH in the interstellar space was supposed to be uncertain, while its isomere methyl formate $HCOOCH_3$, was already found in 1987 with large abundances in hot cores of giant molecular clouds, like Orion [313], [314]. Since 1997 there has been claimed evidence for its observation in the Large Molecule Heimat Source of Sagittarius B2. Its interstellar synthesis is still not clarified, but thought to be involved in chemical grain-surface interactions.

Acetic acid and its related forms ${}^-CH_2COOH$, ${}^+CH_2COOH$ and ${}^+CH_2COOH$ belong to the initiating molecular species of formation path II. The optimizations presented here include the total energy, the geometrical parameter as well as the fundamental vibrational frequencies.

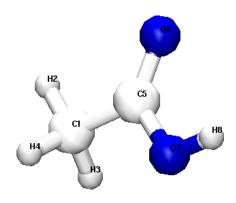


Figure 4.8: acetic acid CH_3COOH

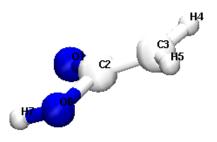
Table 4.13: Total energy of formic acid and related species

basis set	molecular species	multiplicity	total energy [hartree]
HF6-31G/MP2	CH_3COOH	$\operatorname{singlet}$	-228.13084386660
HF6-31G/MP2	$^-CH_2COOH$	singlet	-227.50864
	$^-CH_2COOH$	$\operatorname{triplet}$	-227.15476
	$\cdot CH_2COOH$	dublet	-227.47301
	$^{+}CH_{2}COOH$	$\operatorname{singlet}$	-227.15476

Table 4.14: Internal coordinates of acetic acid via MP2/HF/6-31G

bondlength	$[\mathrm{\AA}]$	interatomic angle	[deg]	dihedral angle	$[\deg]$
$r_{C=C}$	1.5082				
$r_{C=O}$	1.2486				
r_{C-H2}	1.0935	α_{CHH}	110.01	$\delta_{H4CH2H3}$	120.09
r_{C-H3}	1.0969	α_{CCH}	108.93	δ_{CCH2H3}	-119.97
r_{C-H4}	1.0968	α_{CCO}	126.84	δ_{O6CCH3}	120.31
r_{C-O}	1.4035	α_{OCO}	122.04	δ_{O7CCH2}	179.71
r_{O-H8}	0.9851	α_{COH}	109.65	$\delta_{H8O7CO6}$	0.01

The ${}^-CH_2COOH$ species can exist with two different spins, in the singlet and the triplet state. As it is shown in the figure 4.9, its change of multiplicity changes the structure as well. The singlet species presents a planar shape, while the triplet species shows a torsional rotated CH_2 group on the C-C axis out of the molecular plane as the most stable configuration.



singlet -CH2COOH

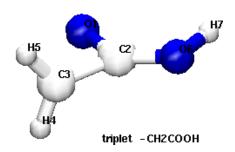


Figure 4.9: ${}^-CH_2COOH$ in the singlet and triplet state

Table 4.15: Internal coordinates of the singlet and triplet state of the $^-CH_2COOH$ and of $^+CH_2COOH$ via HF6-31G/MP2

$-CH_2COOH$	singlet state	triplet state	$^{+}CH_{2}COOH$
bondlength	[Å]	 [Å]	 [Å]
$r_{C=C}$	1.3815	1.4423	1.4424
$r_{C=O}$	1.2987	1.3034	1.3033
r_{C-H4}	1.0879	1.0883	1.0883
r_{C-H5}	1.0868	1.0883	1.0883
r_{C2-O6}	1.5070	1.2961	1.2961
r_{O6-H7}	0.9847	0.9943	0.9944
interatomic angle	[deg]	$[\deg]$	$[\deg]$
α_{CCO1}	133.15	82.28	82.28
α_{CCO6}	113.02	140.89	140.88
α_{CHH}	119.01	120.51	120.50
α_{CCH5}	121.30	119.74	119.74
α_{OCO}	113.82	136.82	136.82
α_{COH7}	100.95	119.31	119.31
dihedral angle	[deg]	$[\deg]$	$[\deg]$
δ_{O1CCH4}	0.	89.57	89.56
δ_{O6CCH5}	0.	90.43	90.43
$\delta_{O1CO6H7}$	0.	0.	0.01
δ_{H5CCO1}	180.	-89.57	-89.56

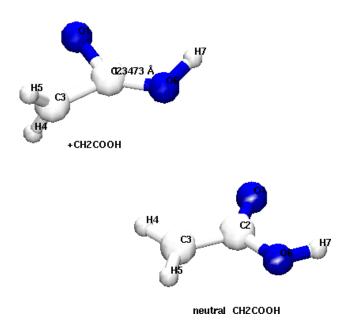


Figure 4.10: ${}^{+}CH_{2}COOH$ and ${}^{\cdot}CH_{2}COOH$

Comparison with the internal coordinates of triplet state of ${}^-CH_2COOH$ with ${}^+CH_2COOH$ show a striking agreement as well as their total energies (!).

Table 4.16: Internal coordinates of CH₂COOH via HF6-31G/MP2

bondlength	[Å]	interatomic angle	[deg]	dihedral angle	[deg]
$r_{C=C}$	1.4856	α_{CCO1}	126.92		
$r_{C=O}$	1.2210	α_{CCO6}	109.73		
r_{C-H4}	1.0833	α_{CHH}	121.55	δ_{O1CCH4}	-0.06
r_{C-H5}	1.0830	α_{CCH5}	120.54	δ_{O6CCH5}	-0.06
r_{C2-O6}	1.3900	α_{OCO}	123.34	$\delta_{O1CO6H7}$	-0.01
r_{O6-H7}	0.9854	α_{COH7}	109.55	δ_{H5CCO1}	179.94

The configuration of ${}^{\cdot}CH_2COOH$ shows nearly planarity like the singlet version of ${}^{-}CH_2COOH$. But the total energies of both species show no correlation.

Table 4.17: Vibrational frequencies of acetic acid and related systems via HF6-31G/MP2

species	CH_3COOH	$\cdot CH_2COOH$	$^-CH_2COOH$	triplet	$^{+}CH_{2}COOH$
vib. mode	$[cm^{-1}]$	$[cm^{-1}]$	$[cm^{-1}]$	$[cm^{-1}]$	$[cm^{-1}]$
1A	102.3	158.9	416.3	405.0	405.0
2A	423.7	428.8	428.6	421.0	421.0
3A	549.1	517.4	442.2	545.6	545.6
4A	567.8	584.1	530.0	655.9	656.1
5A	652.8	659.0	634.4	824.7	824.5
6A	845.0	795.3	687.7	966.2	966.0
7A	1027.3	893.1	731.8	1075.6	1075.6
8A	1122.8	992.1	1028.2	1105.2	1105.1
9A	1191.0	1189.7	1191.8	1134.5	1134.5
10A	1370.7	1383.3	1252.8	1443.6	1443.5
11A	1482.5	1495.1	1492.7	1518.1	1518.1
12A	1550.5	2105.1	1742.0	1777.5	1777.2
13A	1554.1	3229.7	3179.1	3194.4	3194.5
14A	1721.1	3369.1	3273.3	3331.6	3331.8
15A	3090.2	3598.5	3580.9	3481.7	3481.4
16A	3173.6				
17A	3205.8				
18A	3596.0				

As one can clearly see the vibrational frequencies of the ${}^-CH_2COOH$ triplet species are nearly in perfect agreement with the frequencies of the ${}^+CH_2COOH$ singlet species — as well as their structural geometrical parameters!

4.2.3 NH_3 and related species

Ammonia was the first polyatomic molecule detected in the interstellar space [128]. Also after differentiated investigations like those from Herbst and coworker 1987 [189]) the formation mechanism is still not completely clarified. The molecular radical NH_2 is the only system of the treated species here ${}^-NH_2$, ${}^+NH_2$, and ${}^+NH_2$, which is already observed. NH_2 and NH_3 play an important role in the formation pathways of other N-bearing compounds like ${}^+NH_2CH_2$ (investigated in this work), $CH_3NH_3^+$, NH_2CHO , and NH_2CN [158]. NH_2 itself is considered to be formed via ion-molecule reactions and photolysis of NH_3 [326].

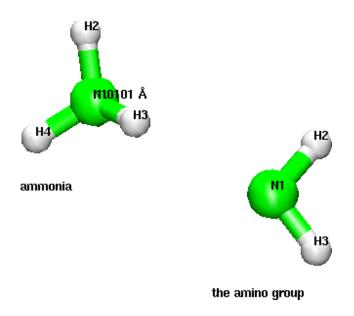


Figure 4.11: NH_3 and the amino group NH_2

Table 4.18: Total energy of ammonia and the amino group systems via HF6-31G/MP2

species	charge	multiplicity	symmetry	total energy [hartree]
NH_3	0	singlet	C_{3v}	-56.16463
$-NH_2$	-1	$\operatorname{singlet}$	C_{2v}	-55.45525
$\cdot NH_2$	0	dublet	C_{2v}	-55.49096
$+NH_2$	+1	singlet	C_s	-55.10307

The calculation of the total energies confirm ammonia NH_3 as the most stable molecule of this amino group series. The species ${}^-NH_2$ and ${}^+NH_2$ with one hydrogen atom and one electron less, respectively, have nearly the same total energy, while the positive charged ${}^+NH_2$ show a difference of about 0.4 hartree, corresponding to 10.9 eV. Remarkable is the different symmetry point group according to ${}^+NH_2$ in regard to ${}^+NH_2$ and ${}^-NH_2$. The reason for lies in the two single N-H bondings, presenting different lengths.

Table 4.19: Internal coordinates for the NH_3 and related systems via HF6-31G/MP2

geometrical parameters	species			
bondlength [Å]	NH_3	$-NH_2$	$\cdot NH_2$	$+NH_2$
r_{N-H2}	1.01007	1.06224	1.00022	1.05106
r_{N-H3}	1.01007	1.06224	1.00022	1.05117
r_{N-H4}	1.01007			
interatomic angle [deg]				
α_{H2NH3}	114.23	100.09	143.48	113.68
α_{H2NH4}	114.23			
α_{H3NH4}	114.23			
dihedral angle [deg]				
δ_{H2H3H4}	60.			

Table 4.20: Vibrational frequencies of ammonia via HF6-31G/MP2

vib. mode	$[cm^{-1}]$	vib. mode	$[cm^{-1}]$
$1A_1$	702.0	$4A_1$	3567.7
2E	1748.8	$5\mathrm{E}$	3765.3
3E	1748.8	6E	3765.3

Ammonia presents two pairs of degenerated frequencies because of its high symmetry according to symmetry point group C_{3v} .

Table 4.21: Vibrational frequencies of the amino group systems via HF6-31G/MP2

species	$^-NH_2$	$\cdot NH_2$	$^+NH_2$	
vib. mode	$[cm^{-1}]$	$[cm^{-1}]$	$[cm^{-1}]$	vib. mode
A_1	1585.0	1097.8	1441.5	A'
A_1	2993.8	3674.7	3203.1	A'
B_2	3091.1	3998.2	3339.9	A'

The optimization of the total energy, the corresponding geometrical parameters as well as the frequencies of the molecular systems according to path II is necessary for the concluding calculation of the intrinsic reaction coordinate.

4.2.4 Glycine

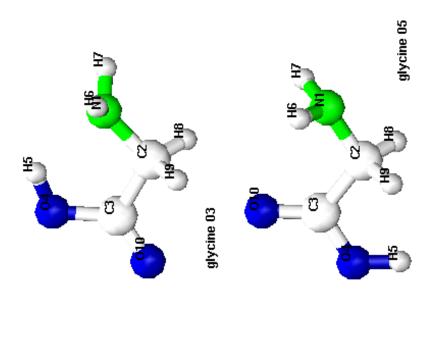
Although there exist only a few spectral lines of observation, which might give reference to glycine in the interstellar gas phase, the clarification of the chemical path of formation is of importance in view of its large abundances in meteoritic and cometary matter. The crystal structure of glycine was originally determined by Albrecht & Corey in 1939 [321] and additionally refined via X-radiation methods by Marsh 1957 [320]. Since then, many structural investigations have followed via refined experimental microwave technique by Brown and coworker in 1978 [324] and Godfrey and coworker in 1995 [325] also with respect to its several conformations by Neville and coworker [222] as well as via theoretical methods by Császár [323]. For obvious reasons glycine was calculated in aqueous solution by Alper and coworker [319], where it is present in zwitterionic form ${}^+NH_3CH_2COO^-$, but as well as a single molecule without interactions via molecular orbital theoretical methods, e.g. by Vishveshwara & Pople 1976 [322].

Conformational isomeres

Table 4.22: Total energies of four different conformations via HF6-31G/MP2

conformation	symmetry	total energy [hartree]
glycine 02	C_s	-283.23310
glycine 03	C_s	-283.23068
glycine 04	C_s	-283.23060
glycine 05	C_s	-283.22106

The differences between the single conformere range up to approximately 1.204×10^{-2} hartree corresponding to 0.329 eV. The corresponding geometrical parameters are listed below



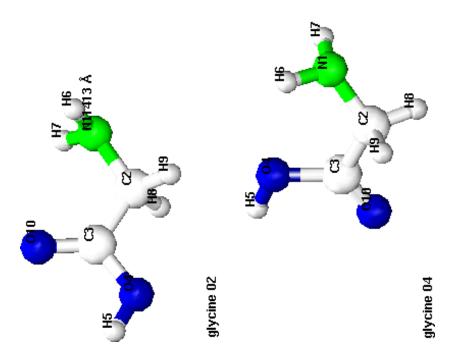


Figure 4.12: NH_2CH_2COOH Conformation 02, 03, 04, and 05

Table 4.23: Internal coordinates of glycine conformations via HF6-31G/MP2

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$					
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		4			
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	bondlength [A]	gly02		gly04	gly05
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	r_{N-C}	1.4640	1.4844	1.4667	1.4624
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	r_{C-C}	1.5278	1.5456	1.5295	1.5418
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	r_{C-O4}	1.3999	1.3820	1.4031	1.4086
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		0.9852	0.9994	0.9851	0.9818
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	r_{N-H6}	1.0161	1.0153	1.0157	1.0164
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	r_{N-H7}	1.0160	1.0153	1.0160	1.0164
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$r_{C=O}$	1.2486	1.2462	1.2492	1.2412
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	r_{C2-H8}	1.0984	1.0984	1.0969	1.1010
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	r_{C2-H9}	1.0984	1.0984	1.1001	1.1009
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$					
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	α_{NCC}	114.85	110.67	117.25	115.02
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	α_{CCO4}	110.98	114.21	112.22	115.43
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	α_{CCO10}	126.41	122.65	125.52	124.88
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	α_{COH}	110.06	106.16	109.50	112.76
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	α_{OCO}	122.60	123.13	122.20	119.67
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	α_{H6NH7}	110.84	111.30	111.04	110.62
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	α_{H6NC}	113.71	114.71	113.39	113.36
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$lpha_{NCH8}$	109.61	111.67	109.61	108.93
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	α_{H8CH9}	106.35	107.09	106.74	106.83
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	α_{CCH9}	108.03	107.74	107.18	108.41
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	dihedral angle [deg]				
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		-179.93	0.04	-26.67	-179.87
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		0.07	-179.96	155.75	0.15
δ_{H6NCC} 64.05 114.57 60.18 63.62 δ_{H6NCH9} -57.77 -5.48 -61.57 163.9 δ_{H6NCH8} -174.14 -125.39 -177.96 -174.49		0.00	-180.00	-0.33	-179.96
δ_{H6NCH9} -57.77 -5.48 -61.57 163.9 δ_{H6NCH8} -174.14 -125.39 -177.96 -174.49		64.05	114.57	60.18	63.62
δ_{H6NCH8} -174.14 -125.39 -177.96 -174.49	_	-57.77	-5.48	-61.57	163.9
		-174.14	-125.39	-177.96	-174.49
00011	δ_{CCOH}	-180.00	0.00	-178.00	0.06

Table 4.24: Vibrational frequencies of the different conformeres

	gly02	gly03	gly04	gly05
vib. mode	$[cm^{-1}]$	$[cm^{-1}]$	$[cm^{-1}]$	$[cm^{-1}]$
1A'	77.5	26.0	43.2	92.9
2A'	250.2	267.6	263.2	248.1
3A'	257.9	328.4	288.3	257.4
4A'	460.6	508.7	471.3	409.9
5A'	519.7	532.6	525.7	457.8
6A'	627.1	629.9	609.8	553.6
7A'	645.1	797.3	668.3	637.0
8A'	760.8	867.4	760.2	779.4
9A'	869.0	878.9	838.0	857.4
10A'	937.6	940.8	934.5	940.1
11A'	1087.1	1084.2	1117.9	1115.5
12A"	1166.5	1193.5	1147.8	1175.1
13A'	1217.5	1204.8	1236.1	1210.3
14A"	1330.2	1361.8	1359.2	1227.6
15A'	1408.7	1379.2	1409.8	1401.6
16A'	1424.6	1398.7	1416.6	1417.7
17A"	1537.8	1544.4	1540.4	1544.5
18A"	1714.4	1736.8	1702.4	1736.0
19A'	1762.8	1752.5	1762.6	1764.4
20A'	3090.4	3087.5	3081.1	3058.9
21A'	3141.4	3144.6	3146.7	3110.0
22A'	3552.1	3336.5	3553.3	3549.0
23A'	3593.4	3565.8	3597.0	3622.1
24A'	3667.8	3679.8	3671.1	3663.8

The similarities of the vibrational frequencies result from the unchanged functional groups within the molecule. By way of contrast, the rotational spectrum varies very clearly from conformere to conformer because of the different moments of inertia.

4.2.5 MO correlation diagrams — results

According to the instructions outlined in section 3.1.8 molecular orbital correlation diagrams some selected diagrams for two different pathways of formation in the ground state were composed and are briefly discussed here.

The following four diagrams give information about the reaction path I, corresponding to the four different conformations of the product molecule, i.e. type 02, 03, 04, and 05 of glycine.

(a)
$${}^{+}NH_{2}CH_{2} + {}^{-}COOH \longrightarrow NH_{2}CH_{2}COOH$$

Diagram number 1 shows the MO correlation scheme according to glycine 02. The orbitals of educts correlates with the orbitals of the product of same symmetry, i.e. MOs with A' symmetry are connected with each other as well as the MOs with A'' symmetry. As one can see there exist no intersections of the correlation lines according to the same symmetry. Thus this reaction is called symmetry allowed. The other diagram number 2 differs in the alternative conformation of the product molecule. The energetical position of each MO of the different types of glycine varies only slightly, so that the those reaction types are as well symmetry allowed.

Reaction path II is considered in diagram number 3 and 4.

(c)
$${}^{+}CH_{2}COOH + {}^{-}NH_{2} \longrightarrow NH_{2}CH_{2}COOH$$

(e)
$${^-}CH_2COOH + {^+}NH_2 \longrightarrow NH_2CH_2COOH$$

Here we meet a different situation. This time the product molecule is considered as the glycine 02, the most stable conformere. The energetical position of the involved MOs of ${}^-CH_2COOH$ varies against those of ${}^+CH_2COOH$ according to their different total energies. The same is valid for ${}^+NH_2$ and ${}^-NH_2$.

Considering path II c the MOs of the reacting species in the ground state could not be entirely connected with the corresponding MOs of the product molecule. Instead of some MOs of the ground state correlate with MOs of the exited state. That means, these reactions are symmetry forbidden in the ground state. It may exist an activation barrier. If distortion of the considered MOs could occur or the involved species would be elevated in the exited state, the reaction might happen after all. It is emphasized, that these results are obtained with methods via HF6-31G/MP2 calculations.

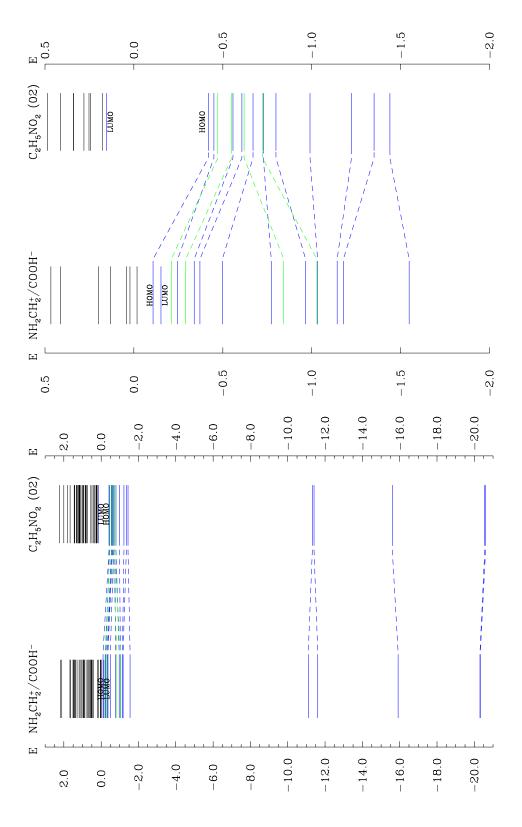


Figure 4.13: Diagram 1 81

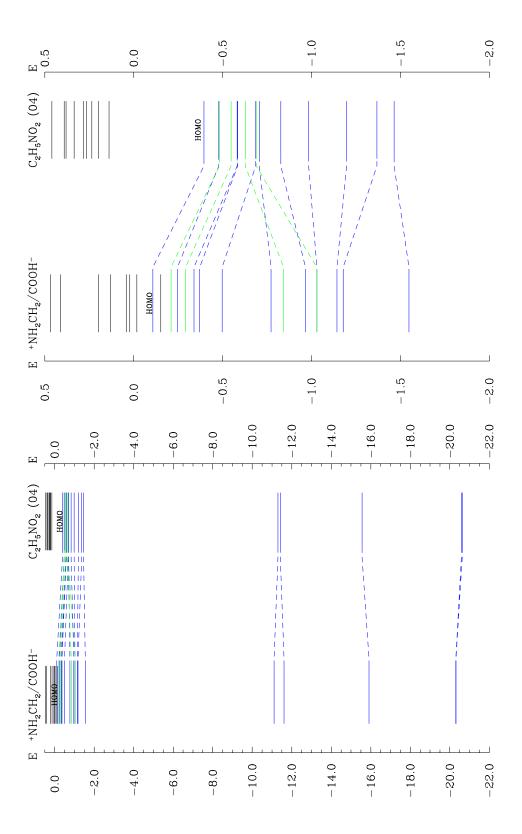


Figure 4.14: Diagram 2 82

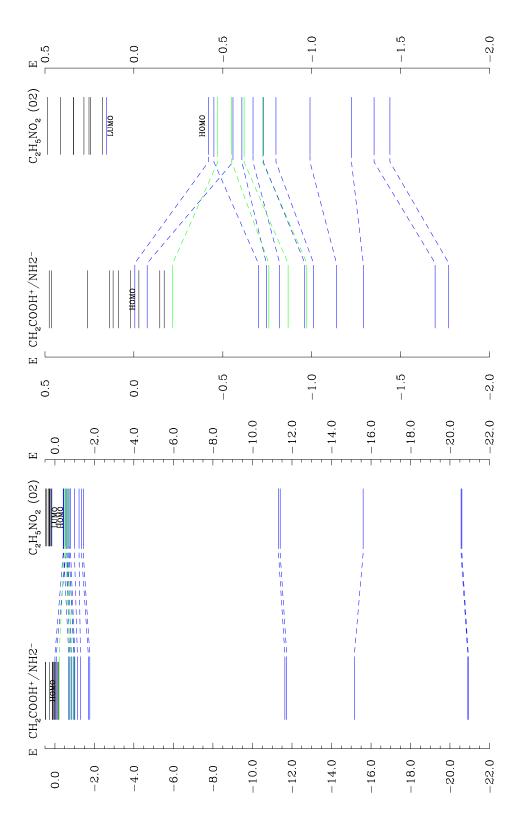


Figure 4.15: Diagram 3

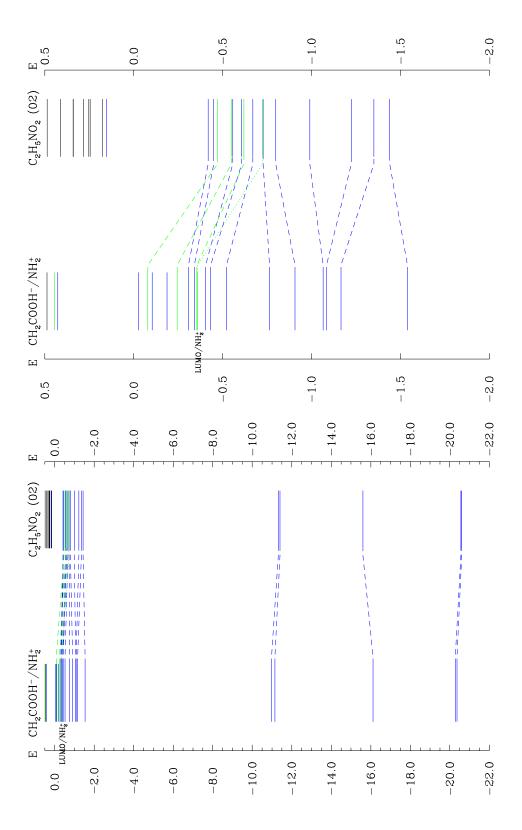


Figure 4.16: Diagram 4 84

4.2.6 The next steps

After examination of the molecular orbital correlation diagrams, the next step in this procedure is the determination of the transition structure, which connects the initial state molecules with the final product. When actually obtained, there exist basically two different approaches to obtain an intrinsic reaction coordinate as outlined in detail in chapter The Chemical Pathway. One procedure uses a form of linear or quadratic interpolation, leading to an internal coordinate path that connects reacting and product molecules. Other methods start at the transition state, provided an adequate transition structure has actually been located on the PES. It proceeds along the steepest descent path down to the desired product and in reversion to unknown reactants.

Transition states configurations

Emanating from the glycine conformation type 02 the following transition structures have been derived. This procedure was performed step by step beginning with a small basis set (here 3-21G) based on the Hartee-Fock approximation. The resulting structure of that completed computation was inserted into the next calculation with the next larger basis set and so on. After completion of those Hartree-Fock based computations, a calculation of the second order Møller-Plesset type was added.

Table 4.25: Total energies of transition structures derived from glycine 02

configu	ration	basis set	total energy [hartree]
glycii	ne 02	HF6-21G/MP2	-283.23310
trans gl	ycine I	HF3-21G	-281.22219
trans gl	ycine II	HF3-21G	-280.60543
transition	structure	HF3-21G	-281.03486
		HF4-31G	-282.19483
		HF6-21G/MP2	-283.05366

This computation led to a definite transition structure according to the last molecular configuration shown in figure 4.17.

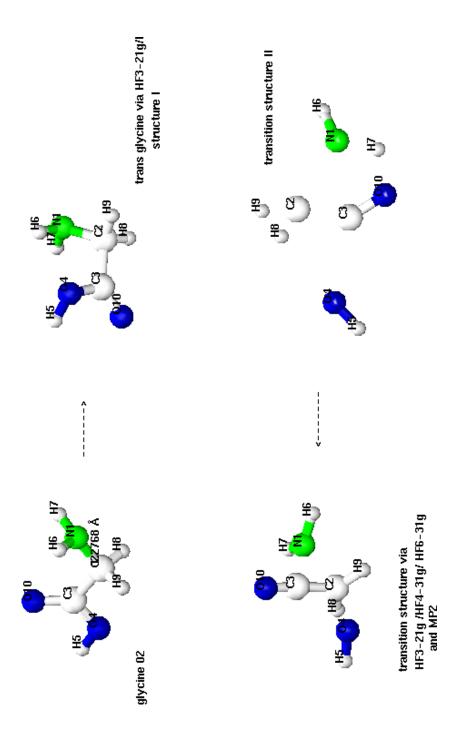


Figure 4.17: glycine 02 transition structure via HF and MP2 calculation with different basis sets $\,$

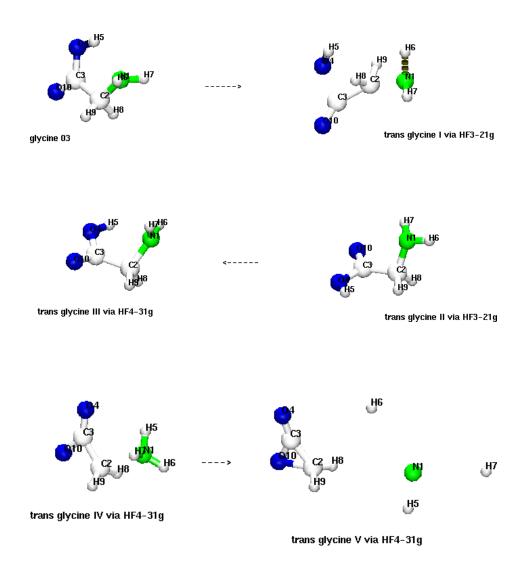


Figure 4.18: glycine 03 transition structure via HF calculation with different basis sets $\,$

Table 4.26: Total energies of transition structures derived from glycine 03

configuration	basis set	total energy [hartree]
glycine 03	HF6-21G/MP2	-283.23068
trans glycine I	HF3-21G	-281.01225
trans glycine II	HF3-21G	-281.22633
trans glycine III	HF4-31G	-282.37549
trans glycine IV	HF4-31G	-282.30703
trans glycine V	HF4-31G	-281.52423

Starting the search with the glycine type 03 led to a transition structure (trans glycine II) via HF3-21G computation. Since the basis set is a very small one, that structure could not be esteemed as corresponding to a real transition state. Continuing calculations with the larger basis set 4-31G show a successive decomposition of the compound into several molecular and atomic fragments (according to trans glycine IV and V) and has been aborted at this point.

Table 4.27: Total energies of transition structures derived from glycine 04

configuration	basis set	total energy [hartree]
glycine 04	HF6-21G/MP2	-283.23060
trans glycine I	HF3-21G	-280.53558
trans glycine II	HF3-21G	-281.25530
trans glycine II	HF4-31G	-282.28556
trans glycine II	HF6-31G	-282.57449
trans glycine II	$\mathrm{HF}6\text{-}31\mathrm{G/MP2}$	-283.12796

That successive computation procedure has succeeded in yielding a real transition state structure, shown in figure 4.19.

Table 4.28: Total energies of transition structures derived from glycine 05

configuration	basis set	total energy [hartree]
glycine 05	HF6-21G/MP2	-283.22106
trans glycine I	HF3-21G	-281.22597
trans glycine II	HF4-31G	-282.26904
trans glycine III	HF4-31G	-282.13185
trans glycine IV	HF4-31G	-281.74758

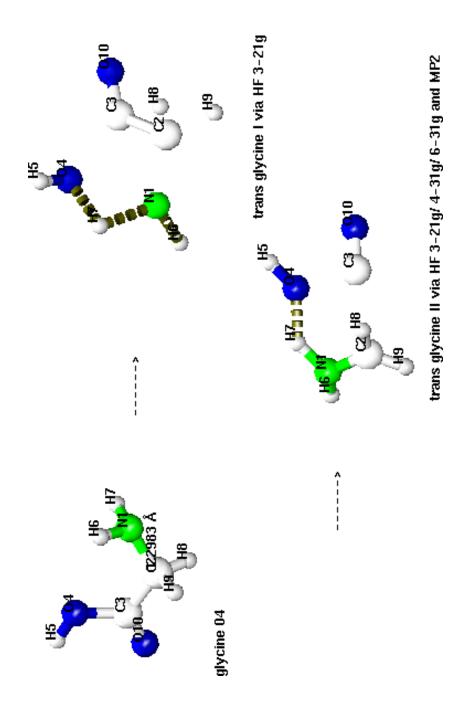


Figure 4.19: glycine 04 transition structure via HF calculation with different basis sets $\,$

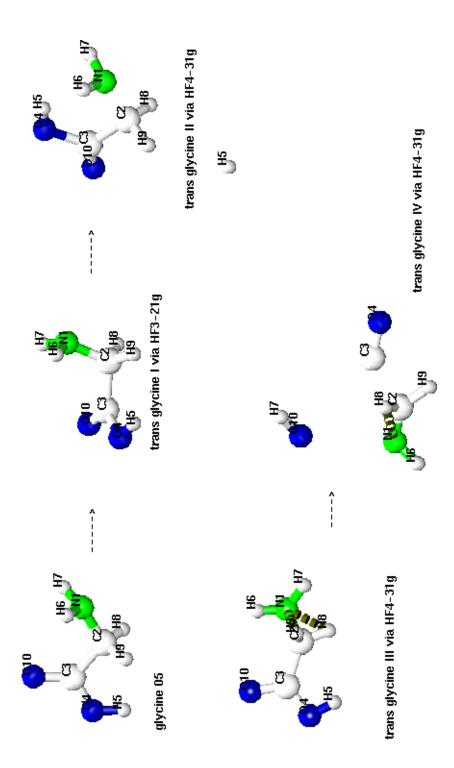


Figure 4.20: glycine 05 transition structure via HF calculation with different basis sets $\,$

The stepwise calculations derived from glycine type 05 led to a gradual decomposition of the amino acid as it is shown in figure 4.20, and has been aborted after complete decay, like the computation procedure of the glycine 04 type.

The different computations yield two transition state structures derived from the glycine conformation $type\ 03$ and $type\ 05$ via HF3-21G optimization, which cannot esteemed as transition structures corresponding to a real transition state, because of the small basis set. However, the transition state optimizations using the conformation $type\ 02$ and $type\ 04$ as start configurations are completed via HF 6-31G followed by a perturbation calculation of second order Møller-Plesset.

The following table compares the geometrical parameter of the starting molecule with those of the resulting two transition state structures. These structures corresponding to certain points on the PES can be used now as starting points for intrinsic reaction coordinate calculations.

Table 4.29: Internal coordinates of the transition structures via HF6-31G/MP2

geometrical parameters	species			
bondlength [Å]	gly 02	trans gly 02	gly 04	trans gly 04
r_{N-C}	1.4640	1.8497	1.4667	1.3195
r_{C-C}	1.5278	1.4254	1.5295	2.3234
r_{C-O4}	1.3999	2.2284	1.4031	1.9127
r_{O-H5}	0.9852	0.9895	0.9852	0.9812
r_{N-H6}	1.0161	1.0212	1.0157	1.0153
r_{N-H7}	1.0160	1.0216	1.0160	1.0845
$r_{C=O}$	1.2486	1.1826	1.2492	1.2046
r_{C2-H8}	1.0984	1.0841	1.0969	1.0796
r_{C2-H9}	1.0984	1.0824	1.1001	1.0871
interatomic angle [deg]				
α_{NCC}	114.85	75.06	117.25	95.88
α_{CCO4}	110.98	80.89	112.22	78.67
α_{CCO10}	126.41	172.05	125.52	168.817
α_{COH}	110.06	109.89	109.50	109.45
$lpha_{OCO}$	122.60	112.45	122.20	112.20
α_{H6NH7}	110.84	113.16	111.04	120.18
α_{H6NC}	113.71	116.37	113.39	119.96
α_{NCH8}	109.61	100.48	109.61	117.63
α_{H8CH9}	106.35	119.45	106.74	118.81
α_{CCH9}	108.03	119.39	107.18	108.94
dihedral angle [deg]				
δ_{NCCO4}	-179.93	174.51	-26.67	41.39
δ_{NCCO10}	0.07	168.09	155.75	-151.56
δ_{OCOH5}	0.00	77.40	-0.33	10.04
δ_{H6NCC}	64.05	110.31	60.18	102.62
δ_{H6NCH9}	-57.77	-7.30	-61.57	-13.81
δ_{H6NCH8}	-174.14	-130.61	-177.96	-176.88
δ_{CCOH}	-180.00	95.43	-178.00	-172.65

The most conspicuous differences for the configurations of glycine 04 and trans glycine 04 consists in the N-C and the C-C distances. These values exceed the usual range of bonding lengths between carbon atoms, as well as carbon and nitrogen within a molecule, respectively. Hence, it follows that the molecule has separated into an association of molecular building blocks at this point.

These building blocks are methyleneamine ${}^+NH_2CH_2$, carbon monoxide $C \equiv O$, and the hydroxy group ${}^-OH$. For the configurations of glycine 02 and its transitional candidate one can note as well the unusual large distances of N-C and of C-O4, whereas the C-C distance is shorter as in the original molecule, which is also an indication of specific molecular separation. Here the association of the transition state configuration consists of an amino group NH_2 , cumulene $CH_2C = O$ and a hydroxy group ${}^-OH$ as it is shown in figure 4.19 and 4.20.

Table 4.30: Vibrational frequencies of 2 different transition structures derived from two conformation types of glycine

	gly02	ts gly02	gly04	ts gly04
vib. mode	$[cm^{-1}]$	$[cm^{-1}]$	$[cm^{-1}]$	$[cm^{-1}]$
1A	77.5	-1013.7	43.2	-581.3
2A	250.2	258.7	263.2	115.3
3A	257.9	281.6	288.3	179.5
4A	460.6	338.1	471.3	217.0
5A	519.7	448.0	525.7	353.9
6A	627.1	586.0	609.8	390.1
7A	645.1	604.6	668.3	412.2
8A	760.8	688.3	760.2	539.9
9A	869.0	755.7	838.0	592.0
10A	937.6	841.9	934.5	719.3
11A	1087.1	896.2	1117.9	987.7
12A	1166.5	991.7	1147.8	1012.9
13A	1217.5	1011.3	1236.1	1048.2
14A	1330.2	1172.4	1359.2	1126.7
15A	1408.7	1237.3	1409.8	1440.4
16A	1424.6	1283.6	1416.6	1465.8
17A	1537.8	1540.6	1540.4	1598.0
18A	1714.4	1720.2	1702.4	1723.2
19A	1762.8	1993.5	1762.6	1790.9
20A	3090.4	3232.7	3081.1	2550.9
21A	3141.4	3362.5	3146.7	3219.7
22A	3552.1	3475.3	3553.3	3360.3
23A	3593.4	3497.6	3597.0	3623.0
24A	3667.8	3621.8	3671.1	3639.0

As indicated before, the vibrational frequencies are of necessity for the continuing computations of the intrinsic reaction coordinate. Under laboratory conditions transition state structures are not accessible because of their low stability, whereas their existence under interstellar conditions seems to be possible by all means. Thus most of these vibrational frequencies calculated here could be used for the infrared detection project of SOFIA, which shall be started in 2002. Those infrared observations may then support the endeavors of doubtless identifying of glycine, its transition structures, as well as its possible progenitors.

Chapter 5

Discussion and outlook

Referring to the beginning of this work, the observation of more complex molecular species has posed serious problems for present-day theories of molecular synthesis in space. Although there still exist only spectroscopical hints in the special case of glycine, one cannot neglect the large abundances of amino acids and related prebiotic molecules in the meteoritic and cometary composition.

The aim of this work is to present an alternative approach as a contribution to understand the complex problem of molecular formation with special consideration of glycine in the interstellar gas phase.

The procedure starts with some selected chemical routes of formation representing intersections through the virtual map of the 24-dimensional potential energy surface of glycine. These pathways includes molecular species, which are already observed in some cases in the interstellar gas phase. The performance of the optimization of those involved molecules indicates the next step within the technical procedure characterizing the formation process and yields a number of new results of molecular geometrical properties of the reacting gaseous species. These are in particular (i) the transfer of the mesomeric structures of the planar methyleneamine ${}^+NH_2CH_2$ and the non-planar methylimine CH_3NH^+ changing from the singlet to the triplet state. It is conspicuous that the values of the fundamental frequencies of both configurations are the same in the HF6-31G calculations, also recognizable via the total energy in that approximation. (ii) The striking similarities between the negative charged species of ${}^-CH_2COOH$ in its triplet state and

the positive version of ${}^+CH_2COOH$ in its singlet state in the geometrical parameter, the vibrational frequencies and therewith in the values of the total energy.

Four of the most stable conformations of the product molecule glycine itself known so far are verified by the calculations presented here, as well as the vibrational frequencies corresponding to each conformation. The total energies of the four different conformations, they differ in the range of 2.42×10^{-3} – 1.2×10^{-2} corresponding to 0.06 - 0.33 eV compared with the most stable and statistically most abundant conformation of glycine (gly 02).

The following step in this procedure presents the construction of molecular orbital (MO) correlator diagrams. The application of such a diagram offers a new optional tool in astrophysical examination of the chemical process of molecular formation and represents a first test, whether the molecules in question may really give rise to a chemical reaction. In case the investigated chemical reaction would be symmetry forbidden, one can spare the large scaled and time intensively ongoing computations of the intrinsic reaction coordinate. The test has been performed in the ground state, and can be also performed for the exited state, which corresponds to photochemical conditions.

The application of these MO correlation diagrams show alternative results for the chemical pathways in question. In the case of pathway number Ia

$$^{+}NH_{2}CH_{2} + ^{-}COOH \longrightarrow NH_{2}CH_{2}COOH$$

considering different conformations of the product molecule glycine (according to diagram 4.1 and 4.2), the reaction appears to be possible under symmetry conditions or *symmetry allowed*, independent, which conformation of glycine would be formed.

The MO correlation diagrams of selected pathways number IIc and IIe show differing results (corresponding to diagram 4.3 and 4.4).

(c)
$${}^{+}CH_{2}COOH + {}^{-}NH_{2} \longrightarrow NH_{2}CH_{2}COOH$$

(e)
$${^-}CH_2COOH + {^+}NH_2 \longrightarrow NH_2CH_2COOH$$

Both versions of pathway number II consider the most stable conformation type of glycine (02). In case of IIc the MOs of the reacting species in the

ground state could not be entirely connected with the corresponding MOs of the product molecule. Thus the reaction is *symmetry forbidden* in the ground state. It may exist an activation barrier. If the involved MOs could be distorted or the participating species would be elevated in the exited state, the reaction might happen after all. Contrary to IIc, pathway IIe is *symmetry allowed* in the ground state.

To continue this procedure presented here the next necessary step is the finding of the adequate transition state. The presented transition state structures correlating to the glycine system on the potential energy surface (PES) as well as their corresponding vibrational frequencies has been calculated here for the first time.

The figures 4.17 - 4.20 represent the performed computations approaching to the transition state and illustrate the change of the molecular shape during a series of calculations. Each computation started with a minimum on the PES according to an individual conformation of the glycine molecule applying a small basis set. The computations proceeds with a higher basis set in case the preceding calculation has come to a reasonable end.

Starting with the conformation type 02 of glycine (compare figure 4.17) the computation led via a geometrically distorted glycine, here delineated as trans glycine structure I, and a loose association of several highly excited molecular fragments trans glycine II eventually to a transition structure consisting of the associated molecular fragments OH, $CH_2 = C = O$ and NH_2 in a first step via HF3-21G approximation. This transition structure could be verified as a real transition state via the following computations with the next larger basis sets 4-31G and 6-31G, concluded by a second order perturbation calculation due to Møller-Plesset. Compared with the initiating conformation the resulting transition structure indicates a difference of total energy of 0.179 hartree according to 4.89 eV.

The computations initiated by the conformation types 03 and 05 of glycine (compare figure 4.18 and 4.20) led in a first step to molecular varied shape of glycine, of very similar value for the total energy: 03 trans glycine II with -281.22633 hartree and 05 trans glycine I with -281.22597 hartree. Both structures were obtained via a concluded HF3-21G calculation. The continuing computations with the higher basis set 4-31G led via different geometrical arrangements of molecular fragments finally to a decomposition of glycine and were aborted at that point.

Emanating from the glycine conformation type 04 (compare figure 4.19) also a real transition structure has been derived. The performed calculation is directed via a highly exited, nearly decomposed trans glycine I with a total energy of -280.53558 hartree and succeed in a transition structure of associated molecular fragments of C = O, OH and NH_2CH_2 , here trans glycine II, via HF3-21G. This result has been confirmed by the following computations via HF4-31G and HF6-31G, as well as by a perturbation calculation of second order Møller-Plesset. This structure shows a difference of total energy of 0.103 hartree corresponding to 2.8 eV compared with the starting conformation of glycine. It is emphasized again, that transition state computations are still beyond routine.

The first step of the formation process described by the optimizations of the reactants and product configurations and conformations are completed, while the procedure to obtain the adequate transition structures is demonstrated. In case of the resulting two transition state structures, it is necessary to check, whether the particular transition structure connects actually the minima of the desired educts. Therewith one has to take into account that the geometry of such a transition state structure of a reacting system pre-determines the stereochemical outcome of reaction. The position of the transition state structure on the PES influences the energy distribution of the chemical transformation.

The computation proceeds from two selected pathways I and II, mentioned above and considered in more detail in the beginning of this chapter. Looking at the resulting transition state structures trans glycine II in figure 4.19 and the transition state structure in figure 4.17, they seem to refer two different pathways of fragmentation and formation:

(IIIb)
$$CH_2 = C = O + {}^{+}NH_2 \longrightarrow {}^{+}NH_2CH_2CO$$

(IIIa)
$${}^{+}NH_{2}CH_{2}CO + {}^{-}OH \longrightarrow NH_{2}CH_{2}COOH$$

and

(IIIc)
$$C = O + {}^{+}NH_2CH_2 \longrightarrow {}^{+}NH_2CH_2CO$$

(IIIa)
$${}^{+}NH_{2}CH_{2}CO + {}^{-}OH \longrightarrow NH_{2}CH_{2}COOH$$
.

The calculation of the intrinsic reaction coordinate and thus the doubtless and accurate assignment of the transition structures would exceed the scope of this work and is part of continuing research.

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