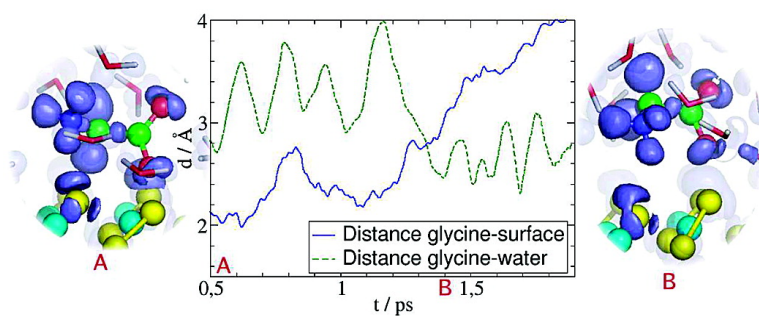


Glycine on a Wet Pyrite Surface at Extreme Conditions

Christian Boehme, and Dominik Marx

J. Am. Chem. Soc., **2003**, 125 (44), 13362-13363 • DOI: 10.1021/ja0359714 • Publication Date (Web): 10 October 2003

Downloaded from <http://pubs.acs.org> on March 30, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 4 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

Glycine on a Wet Pyrite Surface at Extreme Conditions

Christian Boehme* and Dominik Marx

Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, 44780 Bochum, Germany

Received May 6, 2003; E-mail: Christian.Boehme@theochem.ruhr-uni-bochum.de

The “iron–sulfur world” (ISW) scenario¹ is an intriguing recent proposal in the controversial field of “Origin of Life” research. At the very heart of the ISW is the idea that prebiotic chemistry has taken place in the deep sea near volcanoes (hydrothermal vents), at the interface between extremely hot and pressurized water and Fe/S minerals such as pyrite, Fe^{II}S₂. In the complex reaction chain leading from carbon monoxide to proteins, the formation of the peptide bond is a key step. It has been demonstrated that this reaction, which is usually unfavorable in water, can be carried out in the presence of FeS, H₂S, and CO in aqueous solution at somewhat elevated temperature and pressure.² While this is a major success for the ISW, the mechanism of this unusual reaction is not yet understood. Furthermore, pressure and temperature of this experiment (2 bar and 100 °C) were much lower than the extreme conditions proposed for the ISW. In an effort to contribute to the discussion we present ab initio molecular dynamics (MD) simulations³ of the simplest amino acid, glycine (GLY: CH₂NH₂COOH) at the water/pyrite interface, which can easily be carried out at ISW conditions. Our aim is to understand the very first step of pyrite-assisted peptide bond formation, which is the adsorption of GLY on the pyrite surface and its possible activation. The results are not only interesting in the context of the ISW but also explore novel chemistry under unusual conditions.

The Car–Parrinello simulations³ were carried out with the CPMD program.⁴ The electronic structure is described by density functional theory using the PBE functional,⁵ Vanderbilt ultrasoft pseudopotentials,⁶ and a plane wave basis set with a cutoff of 25 Ry. Periodic boundary conditions were applied to an orthorhombic supercell of $\sim(10.8 \times 10.8 \times 18.9)$ Å³. The (001) pyrite surface is represented by nine atomic layers (24 Fe and 48 S atoms), with the three lowest layers held fixed at optimized bulk positions. In the condensed phase simulations, a lamella of 35 water molecules was added which, at the thermostated temperature of 500 K, corresponds to a pressure of about 200 bar (20 MPa).

Contrary to the gas phase, the prevalent form of GLY in ambient water is its zwitterion, which is not even a stationary point in vacuum.⁷ However, in our vacuum optimizations of GLY on pyrite it turns out to be a minimum. This stabilization of the zwitterion is the result of its adsorption mode: The primary interaction between surface iron and the attached carboxylate oxygen of GLY, O_{gly}, is supported by an additional weak hydrogen bond of the protonated amino group to surface sulfur. The resulting surface binding energy of 13.3 kcal·mol⁻¹ is small in terms of a chemical bond, suggesting weak electrostatic interactions, and not so much the formation of strong coordinative bonds. This is confirmed by the electron localization function (ELF)⁸ analysis (Figure 1). ELF isosurfaces at high $\eta(\mathbf{r}) = \eta^*$ enclose so-called “localization domains” in 3D space \mathbf{r} , typically found at covalent bonds and free electron pairs. While the left part of Figure 1 is a superimposed picture of the separately optimized free neutral GLY and the free pyrite surface, the right part shows adsorbed zwitterionic GLY; note that in the former case the proton forms the hydroxyl group, whereas in the

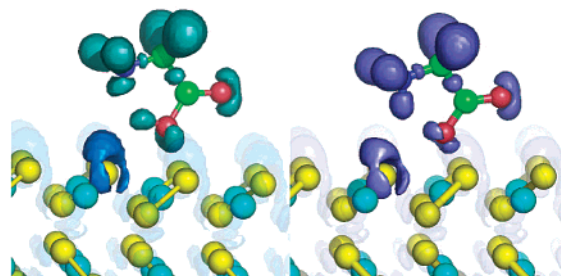


Figure 1. ELF isosurfaces at $\eta^* = 0.85$ of free neutral GLY superimposed onto that of the free pyrite surface (left) and total ELF of zwitterionic GLY adsorbed on pyrite (right). Iron atoms are cyan, sulfur yellow, oxygen red, nitrogen blue, carbon green, and hydrogen white.

latter it protonates the amino group. Significant are the deformation of the free electron pairs of the sulfur atom closest to the $-\text{NH}_3^+$ group (highlighted in dark blue) and of O_{gly} upon adsorption. Both can be explained as a compression of the corresponding free electron pairs of S and O_{gly}, resulting from close contact to the electrostatically attractive closed shell centers H_{gly} and Fe, respectively. In particular no localization domain between O_{gly} and the surface iron atom is found, which would indicate a coordinative bond. Similarly, analysis of Boys–Wannier localized orbitals does not show topological changes upon adsorption.

Even though the bidentate adsorption of the zwitterion, mediated by the carboxylate and ammonium groups, is of moderate strength, the molecule desorbs easily in a gas-phase MD simulation at 500 K. The process starts with the conversion to the neutral form by internal proton transfer after only 0.2 ps. In the resulting binding mode the neutral form is 1.9 kcal·mol⁻¹ lower in energy than the zwitterion (after optimization). The adsorption energy of the neutral form in this mode is only 3.2 kcal·mol⁻¹, and therefore, desorption follows swiftly after another 0.3 ps. However, this desorption mechanism is certainly not viable in a protic solvent where the zwitterion is clearly favored. To get information on the retention time and desorption mechanism of GLY under ISW conditions, MD simulations were carried out at the interface of pyrite and compressed hot water. At these conditions the desorption takes significantly longer (about 1.5 ps) and turns out to be water-assisted. The desorption process sets in during one of the irregular oscillation periods when GLY approaches its turning point $d(\text{Fe}-\text{O}_{\text{gly}}) \approx 2.8$ Å after about 1.3 ps, see Figure 2. Just after GLY starts to oscillate back to the surface a nearby water molecule forms a stabilizing hydrogen bond to O_{gly} which weakens the Fe–O_{gly} interaction; note the short oxygen–oxygen distance of $d(\text{O}_{\text{gly}}-\text{O}_{\text{wat}}) \approx 2.7$ Å. This leads to the detachment of the carboxylate group, followed by breaking the stabilizing contact S–H_{gly} half a picosecond later at 1.8 ps. Earlier close contacts with water molecules, in particular at 0.8 ps, did not result in desorption. Detailed analysis shows that the O_{gly}–O_{wat}–H_{wat} angles were too large for the formation of a sufficiently strong hydrogen bond, i.e., larger than 20° compared to less than 10° in the desorption case. Interestingly, it is found in

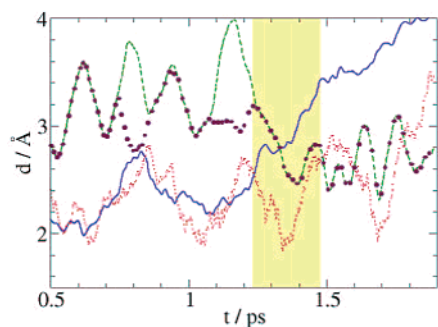


Figure 2. Interatomic distances for desorption of zwitterionic GLY from pyrite in hot pressurized water: Fe–O_{gly} (solid line, blue), O_{gly}–O_{wat} (dashed line, green), O_{gly}–O_{wat,closest} (circles, maroon), S–H_{gly} (dotted line, red); the detachment event is highlighted.

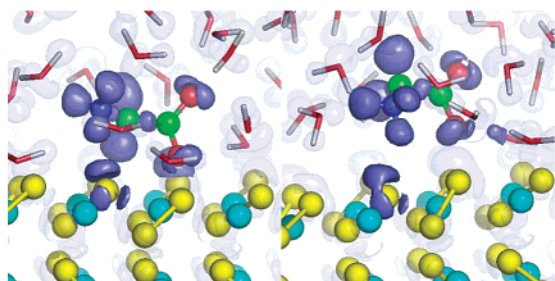


Figure 3. ELF isosurfaces at $\eta^* = 0.85$ of GLY in water after 0.55 ps (left) and 1.40 ps (right).

another MD run (not shown) that the detachment of GLY occurs more easily if the stabilizing contact between the $-\text{NH}_3^+$ group and the surface breaks first.

The described desorption mechanism manifests itself also in electronic structure changes. In Figure 3 one can see that at 0.55 ps—when GLY is still adsorbed—the deformation of the free electron pair of the surface sulfur closest to the $-\text{NH}_3^+$ group is even more pronounced than the one observed in the gas phase, owing to the shorter S–H_{gly} distance of 2.01 Å compared to 2.47 Å in the optimized gas-phase structure. Furthermore, a deformation of the free electron pair of O_{gly} is visible, again indicating the closed shell contact to surface Fe. Already at 1.40 ps, i.e., at the onset of desorption, the bonding pattern has changed significantly: The free electron pair of sulfur is almost relaxed to its unperturbed shape, and the ELF close to O_{gly} shows no longer the Fe–O_{gly} close contact. Instead, the second electron pair of O_{gly} is deformed by an approaching water molecule, and the localization domain of the closer water hydrogen is clearly deformed toward O_{gly}, thus indicating the newly formed hydrogen bond. Notwithstanding the complex desorption process, the retention time of GLY on pyrite

remains relatively short, even at ISW conditions. As catalysis of the direct peptidization of two GLY on the surface requires their simultaneous adsorption, the fast desorption militates against such a mechanism. An initial reaction of GLY with an anchor molecule like COS is an alternative, and might allow for peptidization via a thio acid HS(O)CNHCH₂COOH, as speculated.^{1,2,9} First indications for the GLY activation necessary in both cases can be seen in our simulations: In “ISW water” the average N–H distance of the proton that is hydrogen-bonded to the surface is 1.060 Å as opposed to 1.047 Å in free GLY. This suggests an increased acidity of this proton and therefore a possible attack of the now more negatively charged nitrogen atom, e.g. on a coadsorbed COS molecule, resulting in the aforementioned thio acid.

To summarize, for the first time ab initio MD has been used to investigate a system relevant to ISW at ISW conditions, including bulk water at high pressure and temperature. The simulations show that GLY easily desorbs from a pyrite/water interface through hydrogen-bond assistance. The retention time is only of the order of a picosecond, and the surface bonding is best understood as a relatively weak electrostatic interaction. However, we have found indications of GLY activation due to the interaction with the surface and thus for a possible reaction with a suitable anchor molecule like COS. Improving pyrite surface binding of GLY in this way could be a necessary premise for efficient peptidization.

Acknowledgment. We are indebted to Bernd Meyer for providing the pseudopotentials. Rechnerverbund-NRW (Aachen), SSCK (Karlsruhe), and BOVILAB@RUB (Bochum) are gratefully acknowledged for providing computational resources. We also thank DFG and FCI for support.

References

- (1) Wächtershäuser, G. *Prog. Biophys. Mol. Biol.* **1992**, *58*, 85–201.
- (2) Huber, C.; Wächtershäuser, G. *Science* **1998**, *281*, 670–672.
- (3) (a) Marx, D.; Hutter, J. *Ab initio Molecular Dynamics: Theory and Implementation*. In *Modern Methods and Algorithms of Quantum Chemistry*, Vol. 1; Grotendorst, J., Ed.; John von Neumann Institute for Computing: Jülich, 2000 <http://www.theochem.ruhr-uni-bochum.de/go/cprev.html>. (b) Car, R.; Parrinello, M. *Phys. Rev. Lett.* **1985**, *55*, 2471–2474.
- (4) Hutter, J.; Alavi, A.; Deutsch, T.; Bernasconi, M.; Goedecker, S.; Marx, D.; Tuckerman, M.; Parrinello, M. “CPMD”, MPI für Festkörperforschung and IBM Zurich Research Laboratory, 1995–1999.
- (5) (a) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868. (b) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1997**, *78*, 1396.
- (6) Vanderbilt, D. *Phys. Rev. B* **1990**, *41*, 7892.
- (7) Pulkkinen, S.; Noguera, M.; Rodríguez-Santiago, L.; Sodupe, M.; Bertran, J. *Chem.-Eur. J.* **2000**, *6*, 4393–4399.
- (8) Savin, A.; Nesper, R.; Wengert, S.; Fassler, T. F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1809–1832.
- (9) Keller, M.; Blochl, E.; Wächtershäuser, G.; Stetter, K. O. *Nature* **1994**, *368*, 836–838.

JA0359714