



**HAL**  
open science

# Arginine interactions with anatase TiO (100) surface and the perturbation of Ti NMR chemical shifts - a DFT investigation: relevance to Renu-Seeram bio solar cell

Rainer Koch, Andrew S. Lipton, Slawomir Filipek, Venkatesan  
Renugopalakrishnan

## ► To cite this version:

Rainer Koch, Andrew S. Lipton, Slawomir Filipek, Venkatesan Renugopalakrishnan. Arginine interactions with anatase TiO (100) surface and the perturbation of Ti NMR chemical shifts - a DFT investigation: relevance to Renu-Seeram bio solar cell. *Journal of Molecular Modeling*, 2010, 17 (6), pp.1467-1472. 10.1007/s00894-010-0853-y . hal-00625154

**HAL Id: hal-00625154**

**<https://hal.science/hal-00625154>**

Submitted on 21 Sep 2011

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Arginine interactions with anatase TiO<sub>2</sub> (100) surface and the perturbation of <sup>49</sup>Ti NMR chemical shifts – a DFT investigation: relevance to Renu-Seeram bio solar cell

*Dedicated to Prof. Paul von Rague Schleyer on the occasion of his 80<sup>th</sup> birthday*

**Received:** 06.07.2010 / **Accepted:** 01.09.2010

Rainer Koch<sup>1,✉</sup>, Andrew S. Lipton<sup>2</sup>, Slawomir Filipek<sup>3</sup>, and Venkatesan Renugopalakrishnan<sup>4,5</sup>

<sup>1</sup>Institute for Pure and Applied Chemistry and Center of Interface Science, University of Oldenburg, P.O. Box 2503, D-26111 Oldenburg, Germany

<sup>2</sup>Pacific Northwest National Laboratory, Richland, WA, USA

<sup>3</sup>International Institute of Molecular and Cell Biology, 4 Ks. Trojdena Street, 02-109 Warsaw and Faculty of Chemistry, University of Warsaw, 02-093 Warsaw, Poland

<sup>4</sup>Children's Hospital, Harvard Medical School, Boston, MA 02115, USA

<sup>5</sup>Dept. of Chemistry and Chemical Biology, Northeastern University, Boston, MA 02115, USA

✉Phone: +49-441-798-3653; Fax: +49-441-798-3329; Email: rainer.koch@uni-oldenburg.de

## Abstract

Density functional theoretical calculations have been utilized to investigate the interaction of the amino acid arginine with the (100) surface of anatase and the reproduction of experimentally measured <sup>49</sup>Ti NMR chemical shifts of anatase. Significant binding of arginine through electrostatic interaction and hydrogen bonds of the arginine guanidinium protons to the TiO<sub>2</sub> surface oxygen atoms is observed, allowing attachment of proteins to titania surfaces in the construction of bio-sensitized solar cells. GIAO-B3LYP/6-31G(d) NMR calculation of a three-layer model based on the experimental structure of this TiO<sub>2</sub> modification gives an excellent reproduction of the experimental value (-927 ppm) within +/- 7 ppm, however, the change in relative chemical shifts, EFGs and CSA suggest that the effect of the electrostatic arginine binding might be too small for experimental detection.

**Keywords** TiO<sub>2</sub> · NMR simulation · DFT · Amino acid binding

## Introduction

Interaction of  $\text{TiO}_2$  with the mutants of bacteriorhodopsin (bR) is important in the design of efficient biosensitized solar cells (BSSC). Application of biologically-derived, inexpensive light harvesting protein sensitizers for sensitizing titanium dioxide ( $\text{TiO}_2$ ) nano particles and fibers, instead of the traditional, toxic and expensive chemical based dyes in dye-sensitized solar cells (DSSCs), is an attractive proposition.

Protein-sensitized solar cells emulate the design of DSSCs except that the dye molecules are replaced by light harvesting biomolecules as sensitizer. The impetus for this replacement comes from potentially high efficiency of conversion that light harvesting protein complexes promise, their ability to self-assemble on a surface [1], their low cost of production by biotechnology and room temperature processing and their long lifetimes even at higher temperature ( $100^\circ\text{C}$ ) [2]. An interesting candidate for a protein sensitizer is bacteriorhodopsin (bR) which is a trans-membrane protein found in the archae *Halobacterium salinarum* [3]. Absorption of photon in bR occurs principally through the chromophoric group and the charge separation that occurs eventually leads to shedding of electrons. Upon absorption of light, there is a shift of electron density from the  $\beta$ -ionone ring of the chromophore toward the Schiff base, which is comparable to a  $2.6 \text{ \AA}$  displacement of a single electron down the polyene chain [4] and is in the opposite direction of the initial photovoltage spike that is observed in bR [5]. This short duration charge shift is a critical component of the primary event because it sets in motion events that lead to the photoisomerization of the chromophore [6].

$\text{TiO}_2$  has been in the focus of numerous investigations since the demonstration of the original DSSC photovoltaic cell [7]. Researchers have proposed the possibility of using hybrid architecture of nanoparticles and nanofibres [8-12] to facilitate the better electron transport. Given the advancement in electrospinning for generating large surface-to-volume ratio nanofibres in larger-scale [13], the electrospun  $\text{TiO}_2$  nanofibres have been shown to increase solar energy efficiency up to 6.2 % in DSSC [14].

The basic hypothesis for the design of such a BSSC, for which we propose the name Renu-Seeram Cell is that bR is attached by chemisorption to  $\text{TiO}_2$ , and upon photoexcitation ejects electrons into the conduction band of semiconducting metal oxide completing the circuit and

electrons flow from counter electrode to the conductive ITO glass plate. An iodide electrolyte recharges bR.

In order to shed some light on this interaction, we set out to investigate computationally the binding of arginine, which has been identified as a potential terminal amino acid in bR, on the (100) (or identical by symmetry the (010)) surface of TiO<sub>2</sub> anatase [15] in order to derive a model for the interaction of TiO<sub>2</sub> to bR mutants.

## Methods

All calculations were carried out using the Gaussian 03 [16] suite of programs. Density functional theory (DFT) with the hybrid B3LYP functional [17-19] in combination with Pople's 6-31G(d) [20, 21] was used for the optimizations of the ground state geometries of a TiO<sub>2</sub> anatase model, arginine and a complex of arginine on anatase and the simulation of the chemical shifts. The default convergence criteria and integration grid of the program were used. The nature of all found local minimum structures was confirmed by the lack of an imaginary harmonic vibrational frequency [22]. Absolute magnetic shieldings were determined with the GIAO (gauge-including atomic orbital) method [23-25] as implemented in Gaussian 03. The obtained shielding tensors were referenced against titanium tetrachloride to yield relative chemical shifts. This approach has been used successfully for the determination of chemical <sup>49</sup>Ti shifts previously [26]. The simulations of NMR tensor parameters were performed using the SIMPSON program [27]

## Results and discussion

When a protein such as bR or its mutants is brought onto a surface such as anatase or ZnO, it will be either covalently attached or chemisorbed. It is therefore reasonable to expect subtle electronic perturbations of <sup>49</sup>Ti chemical shift anisotropy (CSA or  $\Delta\sigma$ ) and the quadrupole coupling,  $C_q$ , which provide useful tools to probe subtle interactions at the atomic level. It should be possible to compare the DFT derived changes in electric field gradient and CSA with experimental values [28].

TiO<sub>2</sub> surfaces have been thoroughly studied, both experimentally and theoretically [29-40]. Also, the adsorption of small molecules on TiO<sub>2</sub> surface has been reported in the literature recently [41-52]. Based on previous experience with the calculation of <sup>49</sup>Ti NMR chemical shifts [25], we have started to explore a suitable model for the TiO<sub>2</sub> (100) surface on which the bR is attached [15]. This surface is one of the two major cleavage planes, together with the (101) surface. It possesses small grooves formed by oxygen atoms on either side of the groove along with both Ti and O atoms at the bottom. Several repeat unit cells are required for reliable and consistent data, since there are relative chemical shifts in the range of several hundred ppm for individual Ti atoms. The model employed herein to represent the (100) surface of anatase consists of 30 TiO<sub>2</sub> units, terminated with 12 hydrogen atoms (Fig. 1). It has been taken from the crystal structure of TiO<sub>2</sub> anatase [53] and the positions of all surface and added hydrogen atoms are kept fixed during the optimization, only allowing the amino acid to move freely on the surface.

<Figure 1>

The well-established B3LYP/6-31G(d) level of theory has been chosen because of its previously demonstrated superior performance in the <sup>49</sup>Ti NMR determination [26]. Herein, relative chemical shifts of the Ti atoms of this model are computed compared against the available experimental NMR data. In our model there are four titanium atoms which have a “complete” oxygen-saturated environment – in the middle layer of the side-on view of Fig. 1 – which can serve as representatives of the bulk titanium atoms. These Ti atoms are calculated to have isotropic chemical shifts (relative to TiCl<sub>4</sub>) between -921 and -922 ppm, in excellent agreement with the experimental value for anatase of -927 ppm [26]. Shifts of those titanium atoms on the surface which have five oxygen contacts are in the range of -450 to -530 ppm.

In a previous study, the positively charged arginine and lysine amino acid residues have been identified as potential binding groups as they reside at the cytoplasmic surface of bR [15]. For this reason we have chosen arginine as a model for bR in this binding investigation. Different orientations of arginine on the surface have been modeled with the most stable ones reported herein (Fig. 2): In structure 1, arginine possesses two hydrogen bonds bridging the groove, originating from each of the terminal nitrogen atoms and pointing towards the central oxygen atoms in our model. This orientation is stabilized relative to the separated TiO<sub>2</sub> surface and arginine by about 160 kJ mol<sup>-1</sup>. The largest part of this energy can be attributed to attractive electrostatic interaction between the positively charged arginine N terminus and the surface

oxygen atoms. The importance can be seen in the increasing tilting of arginine towards the surface in the following structures 2-5, thus bringing the third partially charged nitrogen atom of the guanidinium group closer to the negatively charged oxygen atoms. Structure 2 exhibits this slightly tilted position across the groove and has a third hydrogen bond which lowers the energy by an additional  $60 \text{ kJ mol}^{-1}$ . Orientations 3 and 4 are quite similar to each other, being stabilized by 250 and  $254 \text{ kJ mol}^{-1}$ , respectively. Both trade the docking across the gap formed by the surface oxygen atoms in favor of one intramolecular and two hydrogen bonds to oxygen atoms on the same side of the groove.

The most stable arrangements are the last two presented in Fig. 2. They are  $266$  and  $272 \text{ kJ mol}^{-1}$  respectively more stable than the separate molecules and adopt an orientation which allows additional weak hydrogen contacts across the groove. Structure 5 forms such a bond at about  $2.6 \text{ \AA}$  from the previously uninvolved third nitrogen atom, in addition to the two strong bonds at about  $1.9 \text{ \AA}$ , while the most stable structure 6 possesses four contacts at  $1.7$ ,  $2.1$ ,  $2.4$  and  $2.4 \text{ \AA}$  (see also Fig. 3). Both orientations retain the intramolecular hydrogen bond. These data illustrate that the attachment at an oxygen-based channel is in fact the most likely position but it appears preferentially to form as many hydrogen bonding interactions with oxygen atoms on both sides of this trough as possible, even at the expense of their individual strength. In addition, the latter structures are closer to the surface, leading to increased electrostatic stabilization.

<Figure 2>

Starting from this final orientation 6, we also derived the chemical shifts for both the loaded anatase ( $^{49}\text{Ti}$ ) and the amino acid ( $^{13}\text{C}$ ). In Table 1 are given the  $^{13}\text{C}$  chemical shifts of arginine under the influence of the anatase attachment. One can clearly see that the carbon atoms which are close to a new hydrogen bond (atoms 3 and 8) are shifted to a higher field by up to  $12 \text{ ppm}$ .

<Table 1>

<Figure 3>

The relative  $^{49}\text{Ti}$  chemical shifts of the four central Ti atoms with oxygen saturation (see above) are influenced by the arginine attachment by only a few ppm (between 1 and 9 ppm, values range from -913 to -928 ppm). This appears too small to be easily detectable in a standard NMR experiment. However, the surface titanium atoms are much stronger influenced: the induced changes in relative chemical shifts range from -83 to +93 ppm

For comparison we have simulated the experimental parameters previously obtained for bulk anatase with those predicted by quantum mechanical calculations using the most stable orientation 6 (Fig. 2). These data are depicted in Fig. 4 for each NMR active isotope of titanium. The experimental values [26] of quadrupole coupling constant,  $C_q$ , previously measured for anatase are 4.94 and 4.04 MHz for the 47 and 49 isotopes respectively. The asymmetry parameter for each was 0.06, as these systems are nearly axially symmetric one would expect it near zero. The chemical shielding anisotropy (CSA) was 117 ppm with an asymmetry parameter of 0.1 and all three Euler angles fixed at  $0^\circ$  (coincident principle axis systems). These parameters are contrasted with those for the model systems in Table 2. We define the shielding anisotropy as  $\Delta\sigma = \delta_{33} - \frac{1}{2}(\delta_{11} + \delta_{22})$ , where the elements of the shielding tensor are ordered as  $|\delta_{33} - \delta_{\text{iso}}| \geq |\delta_{11} - \delta_{\text{iso}}| \geq |\delta_{22} - \delta_{\text{iso}}|$ ; and  $\delta_{\text{iso}}$  is the trace of the tensor  $\delta$ .

<Figure 4>

<Table 2>

It is clear from the data in Fig. 4 that the level of theory seems to overestimate both the electric field gradient (EFG) and the CSA. The  $^{47}\text{Ti}$  (nuclear spin 5/2) data is dominated by the quadrupolar coupling which is directly proportional to the EFG tensor and therefore shows the effects of this parameter, while in the  $^{49}\text{Ti}$  (nuclear spin 7/2) data it is evident that the CSA interaction dominates this lineshape at the simulated magnetic field. The key point is that the effects are similar for the models with and without the arginine present. The implication is that the electrostatics of the Ti atoms on the surface are not strongly impacted by the binding of the amino acid. Although it is possible with some effort to experimentally distinguish surface atoms from the bulk, measuring such a surface effect with NMR seems difficult, despite the above mentioned calculated changes in relative chemical shifts.

## Conclusions

The nature of the attachment of arginine on the anatase (100) surface is clearly based on electrostatic interaction together with hydrogen bonds. It appears that an increased number of these weak interactions lead to stabilization of the complex between our (100) anatase model and the amino acid, indicating that the attachment of bR onto a TiO<sub>2</sub> surface is possible in the Renu-Seeram Cell [54]. Additionally, the small energetic changes between some of the found orientations suggest that one can expect dynamic behavior of arginine on the surface. The correct DFT reproduction of <sup>49</sup>Ti NMR chemical shifts for anatase gives confidence in the reliability of the employed approach for the evaluation of this property. Detailed computational investigation of both <sup>13</sup>C (arginine) and <sup>49</sup>Ti (TiO<sub>2</sub>) NMR data show very little change in predicted relative chemical shifts upon binding. This is further confirmed by the simulation of the titanium spectra based on experimental and calculated data. It suggests that NMR investigation of the protein binding on titania nanoparticles seems unfeasible. Other techniques such as SERS on TiO<sub>2</sub> [55] might give additional insight into the attachment mode.

## Acknowledgments

RK gratefully acknowledges generous allocation of computer time at the Center for Scientific Computing, Uni Oldenburg and financial support by the Deutsche Forschungsgemeinschaft DFG.

## Supporting material available

Cartesian coordinates of the B3LYP/6-31G(d)-optimized structures of anatase-arginine complexes are available in the Supporting Information



## References

1. Das R, Kiley PJ, Segal M, Norville J, Yu AA, Wang LS, Trammell A, Evan Reddick L, Kumar R, Stellacci F, Lebedev N, Schnur J, Bruce BD, Zhang S, Baldo M (2004) *Nano Lett* 4:1079-1083
2. Kiley P, Zhao X, Vaughn M, Baldo MA, Bruce BD, Zhang S (2005) *PLoS Biology* 3:e230
3. Oesterhelt D, Stoekenius W (1971) *Nature New Biol* 233:149-152
4. Birge RR, Gillespie NB, Izaguirre EW, Kusnetzow A, Lawrence AF, Singh D, Song QW, Schmidt E, Stuart JA, Seetharaman S, Wise KJ (1999) *J Phys Chem B* 103:10746-10766
5. Trissl HW (1985) *Biochim Biophys Acta* 806:124-135
6. Zadok U, Khatchaturians A, Lewis A, Ottolenghi M, Sheves M (2002) *J Am Chem Soc* 124:11844-11845
7. Regan BO, Grätzel M (1991) *Nature* 353:737-740
8. Onozuka K, Ding B, Tsuge Y, Naka T, Yamazaki M, Sugi S, Ohno S, Yoshikawa M, Shiratori S (2006) *Nanotechnology* 17:1026-1031
9. Pavasupree S, Ngamsinlapasathian S, Nakajima M, Suzuki Y, Yoshikawa S (2006) *J Photochem Photobiol A: Chem* 184:163-169
10. Pavasupree S, Ngamsinlapasathian S, Suzuki Y, Yoshikawa S (2006) *J Nanosci Nanotechnol* 6:3685-3692
11. Suzuki Y, Ngamsinlapasathian S, Yoshida R, Yoshikawa S (2006) *Cent Eur J Chem* 4:476-488
12. Asagoe K, Ngamsinlapasathian S, Suzuki Y, Yoshikawa S (2007) *Cent Eur J Chem* 5:1-15
13. Ramakrishna S, Fujihara K, Teo WE, Yong T, Ma Z, Ramaseshan R (2006) *Materials Today* 9:40-50
14. Song MY, Ahn YR, Jo SM, Kim DY (2005) *Appl Phys Lett* 87:113113-1-113113-2
15. Thavasi V, Lazarova T, Filipek S, Kolinski M, Querol E, Kumar A, Ramakrishna S, Padrós E, Renugopalakrishnan V (2009) *J Nanosci Nanotech* 9:1679-1687
16. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JA Jr, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Bakken V, Adamo C,

- Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, and Pople JA, (2004) Gaussian 03, Revision C02. Gaussian Inc, Wallingford CT
17. Becke AD (1988) *Phys Rev A* 38:3098-3100
  18. Becke AD (1993) *J Chem Phys* 98:5648-5652
  19. Lee C, Yang W, Parr RG (1988) *Phys Rev B* 37:785-789
  20. Hariharan PC, Pople JA (1973) *Theor Chim Acta* 28:213-222
  21. Pietro WJ, Francl MM, Hehre WJ, DeFrees DJ, Pople JA, Binkley JS (1982) *J Am Chem Soc* 104:5039-5048
  22. The artificially constrained hydrogen atoms of the anatase model produce distinct vibrations with negative wavenumbers; these frequencies were neglected as they are not important for the binding of arginine on the surface.
  23. Ditchfield R (1974) *Mol Phys* 27:789-807
  24. Wolinski K, Hinton JF, Pulay P (1990) *J Am Chem Soc* 112:8251-8260
  25. Cheeseman JR, Frisch MJ, Devlin FJ, Stephens PJ (2000) *J Phys Chem A* 104:1039-1046
  26. Koch R, Bruhn T (2006) *J Mol Model* 12:723-729
  27. Bak M, Rasmussen JT, Nielsen NC (2000) *J Magnetic Res* 147:296-330
  28. Larsen FH, Farnan I, Lipton AS (2006) *J Magn Res* 178:228-236
  29. Onda K, Li B, Zhao J, Jordan KD, Yang J, Petek H (2005) *Science* 308:1154-1158
  30. Fernandez-Garcia M, Belver C, Hanson JC, Wang X, Rodriguez JA (2007) *J Am Chem Soc* 129:13604-13612
  31. Asahi R, Taga Y, Mannstadt W, Freeman A (2000) *J Phys Rev B: Condens Matter* 61:7459-7465
  32. Vittadini A, Casarin M, Selloni A (2007) *Theor Chem Acc* 117:663-671
  33. Vittadini A, Selloni A, Rotzinger FP, Graetzel M (1998) *Phys Rev Lett* 81:2954-2957
  34. Diebold U (2003) *Appl Phys A* 76:681-687
  35. Hadjiivanov KI, Klissurski DG (1996) *Chem Soc Rev* 25:61-69
  36. Ramamoorthy M, Vanderbilt D (1994) *Phys Rev B: Condens Matter* 49:16721-16727

37. Lazzeri M, Vittadini A, Selloni A (2001) *Phys Rev B: Condens Matter* 63:155409/1-155409/9
38. Kubo T, Orita H, Nozoye H (2007) *J Am Chem Soc* 129:10474-10478
39. Koitaya T, Nakamura H, Yamashita K (2009) *J Phys Chem C* 113:7236-7245
40. Morgan BJ, Watson GW (2009) *J Phys Chem C* 113:7322-7328
41. Topoglidis E, Cass AEG, Gilardi G, Sadeghi S, Beaumont N, Durrant JR (1998) *Anal Chem* 70:5111-5113
42. Duncan WR, Prezhdo OV (2008) *J Am Chem Soc* 130:9756-9762
43. Li J, Wu L, Zhang Y (2001) *Chem Phys Lett* 342:249-258
44. Sheka EF, Nikitina EA, Zayets VA, Ginzburg IY, Schoonman J (2005) *J Nanopart Res* 7:171-186
45. De Angelis F, Fantacci S, Selloni A, Nazeeruddin MK, Graetzel M (2007) *J Am Chem Soc* 129:14156-14157
46. Duncan WR, Prezhdo OV (2007) *Annu Rev Phys Chem* 58:143-184
47. Duncan WR, Craig CF, Prezhdo OV (2007) *J Am Chem Soc* 129:8528-8543
48. Lundqvist MJ, Nilsing M, Lunell S, Aakermark B, Persson P (2006) *J Phys Chem B* 110:20513-20525
49. Raghunath P, Lin MC (2009) *J Phys Chem C* 113:8394-8406
50. Zhang J, Zhang M, Han Y, Li W, Meng X, Zong B (2008) *J Phys Chem C* 112:19506-19515
51. Oviedo J, Sanchez-de-Armas R, San Miguel MA, Sanz JF (2008) *J Phys Chem C* 112:17737-17740
52. Morandeira A, Lopez-Duarte I, Martinez-Diaz MV, O'Regan B, Shuttle C, Haji-Zainulabidin NA, Torres T, Palomares E, Durrant JR (2007) *J Am Chem Soc* 129:9250-9251
53. Wagemaker M, Gordon JK, Van Well AA, Mutka H, Mulder FM (2003) *J Am Chem Soc* 125:840-848
54. Kang et al. have very recently reported that hydroxylation of a rutile TiO<sub>2</sub> (110) surface significantly increases binding energies of proteins. For details see Kang Y, Li X, Tu Y, Wang Q, Ågren H (2010) *J Phys Chem C* 114:14496-14502
55. Musumeci A, Gosztola D, Schiller T, Dimitrijevic NM, Mujica V, Martin D, Rajh T (2009) *J Am Chem Soc* 131:6040-6041

**Tables****Table 1** Relative  $^{13}\text{C}$  chemical shifts (in ppm) of arginine before and after attachment to a  $\text{TiO}_2$  anatase surface

Atom number	arginine	arginine on anatase	difference
1	34.8	33.0	-1.8
2	52.0	58.1	6.1
3	162.6	173.6	11.0
5	29.0	29.9	0.9
6	44.2	44.0	-0.2
8	140.5	152.9	12.4

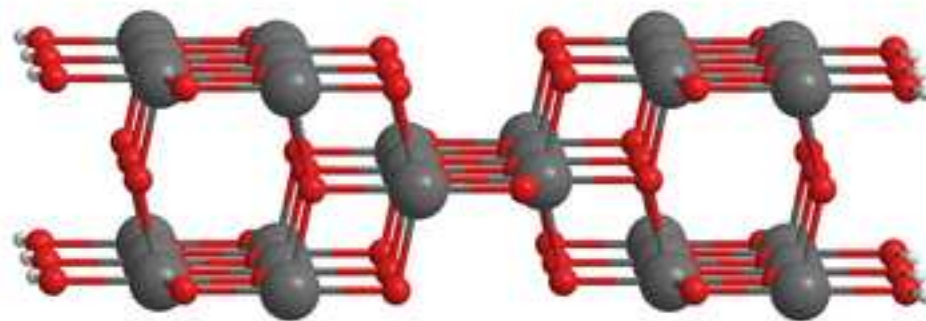
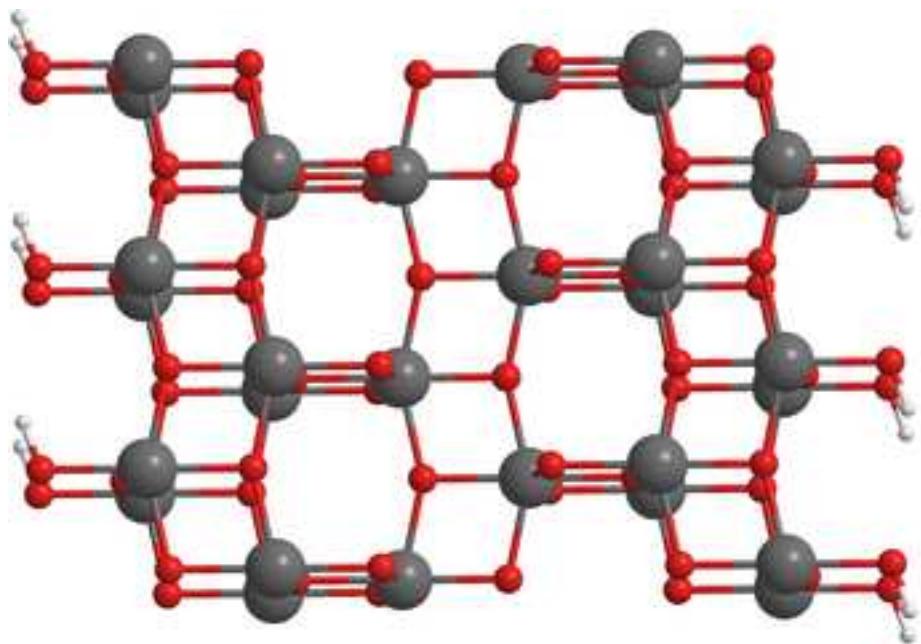
**Table 2** NMR tensor parameters for anatase, experimental and model systems

System	$C_q$ (MHz) $^{47}\text{Ti}/^{49}\text{Ti}$	$\eta_q$	$\delta_{\text{iso}}$ (ppm)	$\Delta\sigma$ (ppm)	$\eta_\sigma$	$\alpha$	$\beta$	$\gamma$
Expt [26]	4.94/4.04	0.06	-927	117	0.10	0	0	0
Anatase $\text{TiO}_2$ (Fig. 1)	7.5/6.1	0.66	-923	446	0.19	0	86	180
Orientation 6 (Fig. 2)	8.4/6.8	0.68	-923	422	0.19	188	87	182

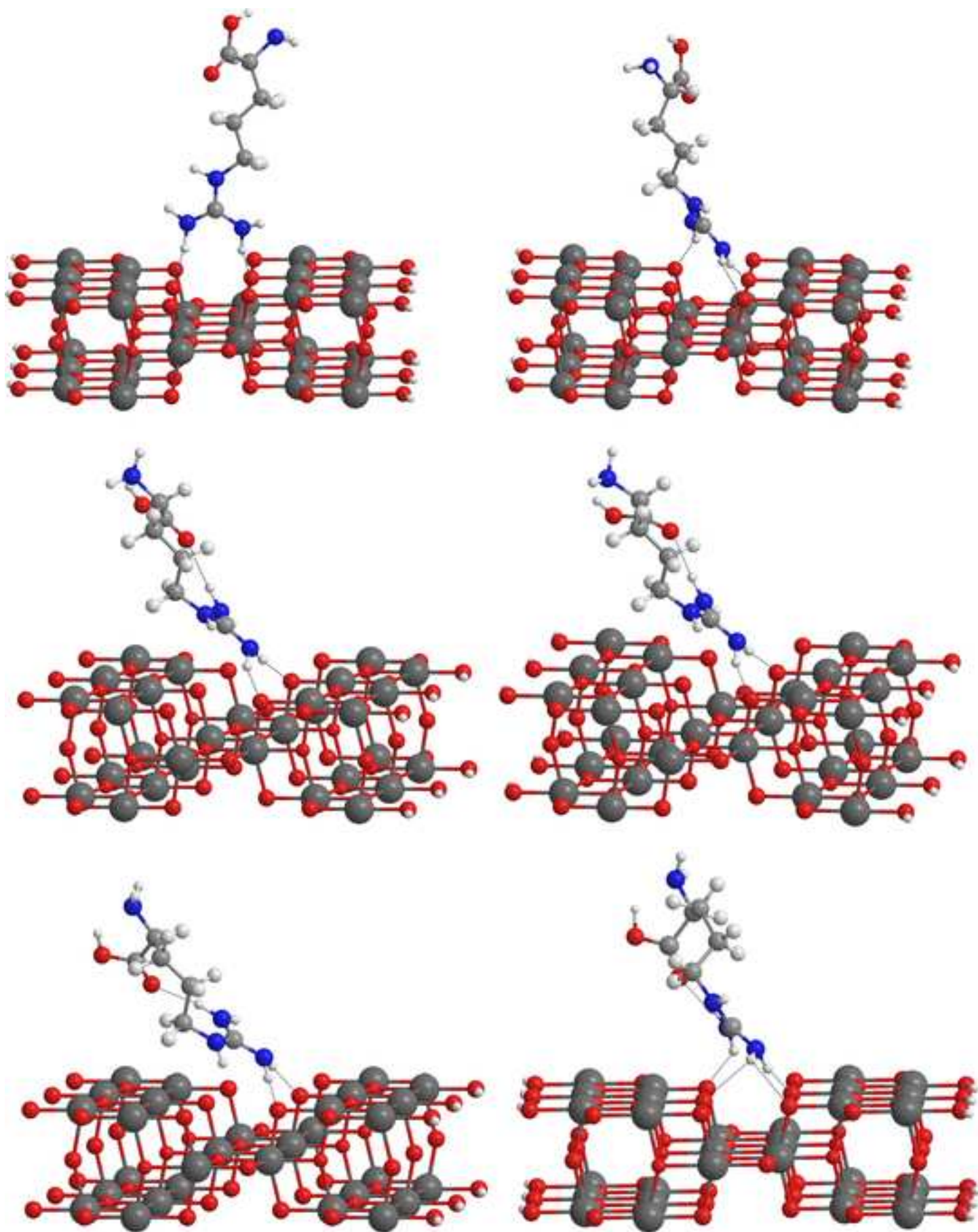
## Figure captions

- Fig. 1** Model of (100) TiO<sub>2</sub> anatase surface, top (left) and side (right) views; oxygen atoms in red, titanium atoms in grey
- Fig. 2** Different orientations of arginine on the anatase (100) surface model: 1 (top left), 2 (top right), 3 (middle left), 4 (middle right), 5 (bottom left) and 6 (bottom right). Hydrogen bonds are shown
- Fig. 3** Numbering scheme for arginine used in Table 1. The groove oxygen atoms are also shown, allowing easier identification of the hydrogen bonds
- Fig. 4** Ideal pulse simulations at 21.1 T (900 MHz for <sup>1</sup>H) of solid-state NMR spectra for the experimental values for anatase (**a** + **d**), the model with no arginine on the surface (**b** + **e**), and the surface Ti atom with arginine bound (**c** + **f**) with the first column showing <sup>49</sup>Ti and the second <sup>47</sup>Ti NMR spectra

**Figure 1**  
[Click here to download high resolution image](#)

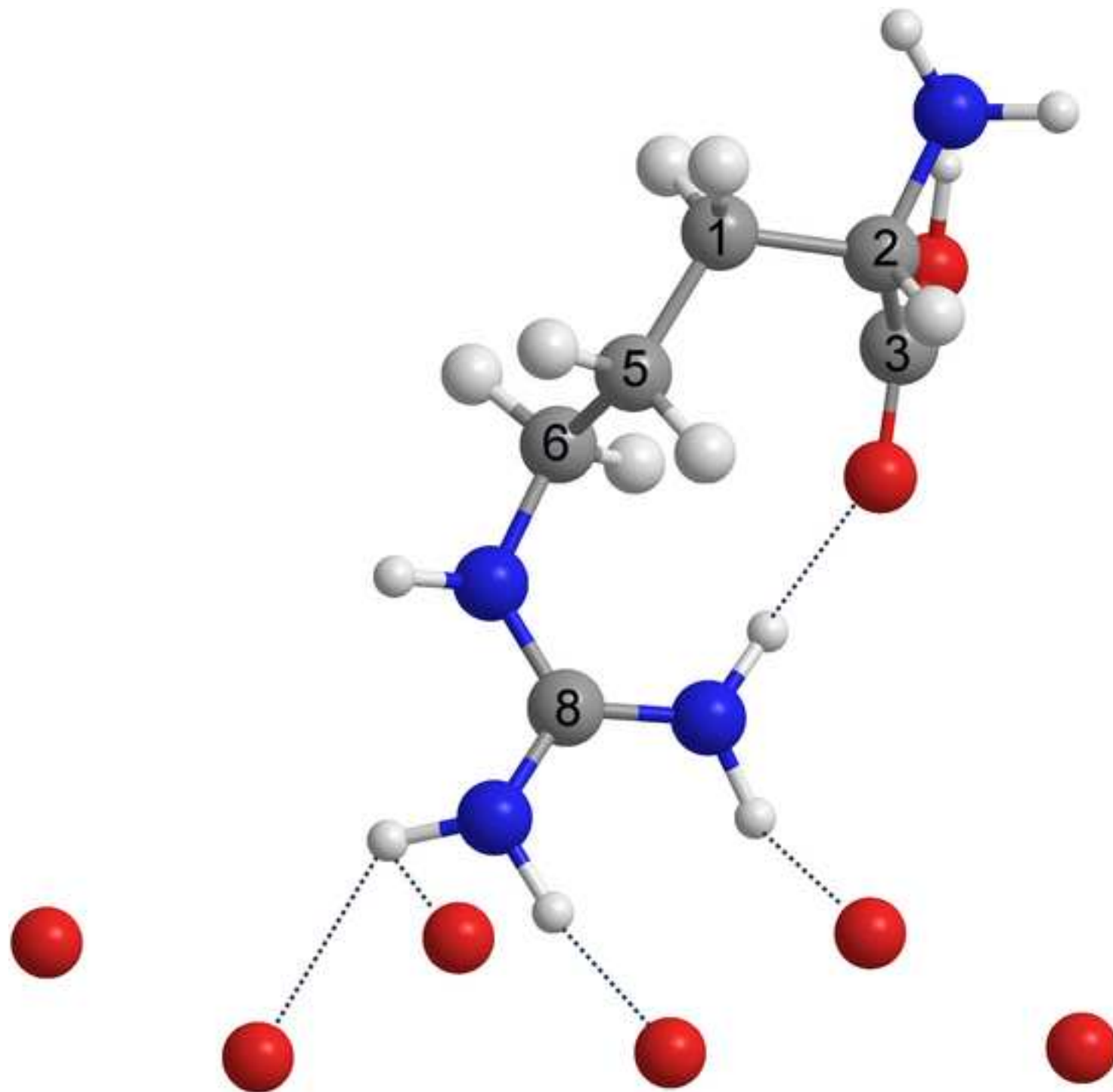


**Figure 2**  
[Click here to download high resolution image](#)

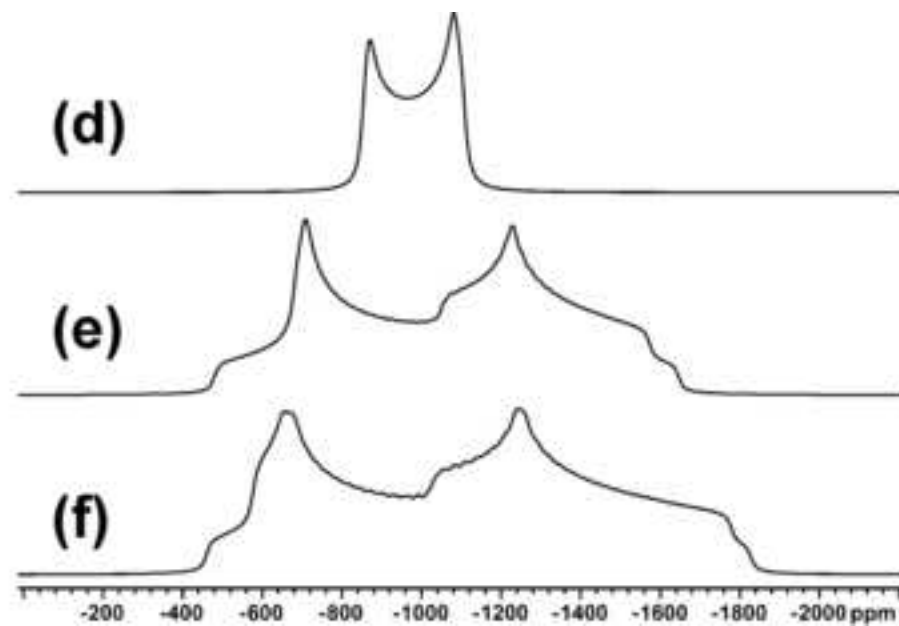
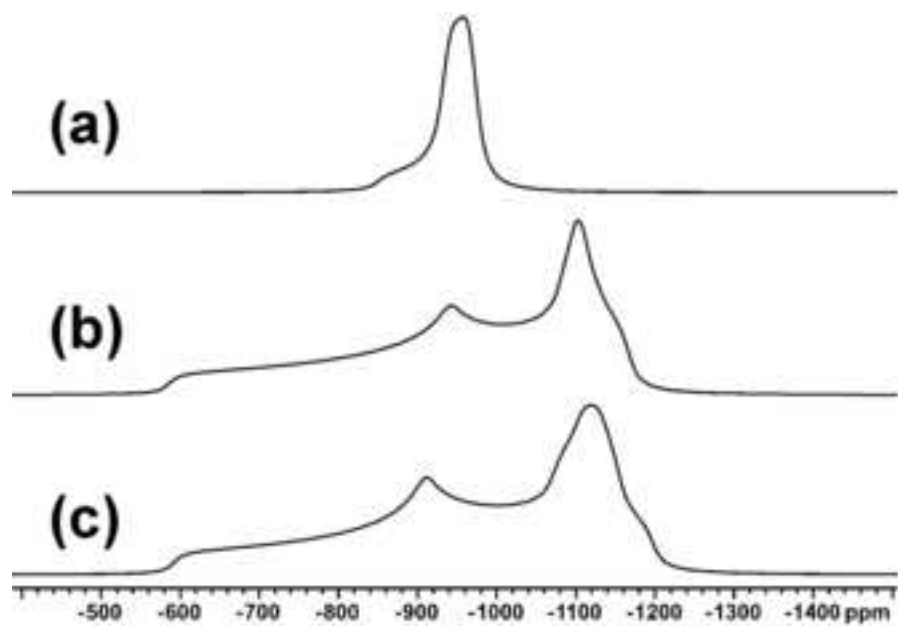




**Figure 3**  
[Click here to download high resolution image](#)



**Figure 4**  
[Click here to download high resolution image](#)



Supporting Information to

# **Arginine interactions with anatase TiO<sub>2</sub> (100) surface and the perturbation of <sup>49</sup>Ti NMR Chemical Shifts – A DFT investigation: Relevance to Renu Seeram Bio Solar Cell**

*RAINER KOCH<sup>1,\*</sup>, ANDREW S. LIPTON<sup>2</sup>, SLAWOMIR FILIPEK<sup>3</sup>, V. RENUGOPALAKRISHNAN<sup>4,5</sup>*

<sup>1</sup> *Institute for Pure and Applied Chemistry and Center of Interface Science, University of Oldenburg, P.O. Box 2503, D-26111 Oldenburg, Germany (rainer.koch@uni-oldenburg.de)*

<sup>2</sup> *Pacific Northwest National Laboratory, Richland, WA, USA*

<sup>3</sup> *International Institute of Molecular and Cell Biology, 4 Ks. Trojdena Street, 02-109 Warsaw, Poland*

<sup>4</sup> *Children's Hospital, Harvard Medical School, Boston, MA 02115, USA*

<sup>5</sup> *Dept. of Chemistry and Chemical Biology, Northeastern University, Boston, MA 02115, USA*

**Total energies (in a.u.) and Cartesian coordinates of B3LYP/6-31G(d)-optimized orientations (see Figure 2 in the main manuscript)**

Orientation 1

Total energy: -31066.951363

C	2.627823	-1.759249	8.710844
C	1.427658	-1.741932	7.754781
C	1.801725	-1.693354	6.271207
N	0.563738	-1.678733	5.485248
C	0.415518	-1.260118	4.214046
N	-0.799129	-0.997356	3.734712
C	2.226841	-1.838219	10.196963
N	3.310936	-1.616320	11.165597
C	1.554068	-3.187073	10.552215
O	1.752064	-3.562582	11.819417
O	0.876105	-3.825277	9.777592
N	1.469011	-1.080969	3.416039
O	-1.501028	-1.294819	1.111538
Ti	-1.215708	-0.881603	-0.755730
O	-1.723912	-0.546474	-2.591014
Ti	-3.692809	-0.740228	-2.511634
O	-3.184605	-1.075357	-0.676351
Ti	-3.469926	-1.488573	1.190918
O	-4.030780	0.317962	1.589837
Ti	-6.000678	0.124173	1.669264

O	-6.507887	0.459439	-0.166059
Ti	-6.223556	0.872571	-2.033290
O	-8.191467	0.678984	-1.953977
O	-5.660723	-0.933789	-2.432316
Ti	-5.891402	-2.818176	-2.799355
O	-6.175753	-3.231351	-0.932137
Ti	-5.668562	-3.566670	0.903182
O	-7.636477	-3.760229	0.982475
O	-4.253669	1.066300	-2.112693
Ti	-4.024979	2.950494	-1.745573
O	-3.516845	2.615309	0.089719
Ti	-1.547935	2.808964	0.010399
O	-2.056069	3.144149	-1.824893
O	-3.921533	-2.624418	-2.878751
Ti	-3.360705	-4.430956	-3.277693
O	-2.852504	-4.766169	-1.442424
Ti	-0.883603	-4.572443	-1.521798
O	-1.391807	-4.237228	-3.357077
O	-5.328619	-4.624510	-3.198373
O	-5.992894	2.756942	-1.666253
Ti	-6.555701	4.563286	-1.267232
O	-6.840024	4.150157	0.600001
Ti	-6.332804	3.814866	2.435317
O	-8.300721	3.621349	2.514653
O	-4.585799	4.757035	-1.346632
O	-5.437837	-1.682173	1.270202
O	-3.698603	-3.372775	0.823833
Ti	-3.137729	-5.179309	0.424937

O	-1.168821	-4.985644	0.345606	O	5.207003	1.996850	-2.494233
O	-5.105634	-5.372987	0.504206	Ti	5.437728	3.881242	-2.127245
O	-7.859316	-3.011730	-2.720036	O	5.944882	3.545999	-0.291903
O	-8.523615	4.369730	-1.187913	Ti	5.660492	3.132922	1.575332
Ti	-3.802070	2.202117	1.957056	O	7.628411	3.326432	1.496025
O	-1.833160	2.395766	1.877721	O	7.737724	0.384017	-2.972517
O	-5.769985	2.008565	2.036351	O	4.132047	-3.694020	-3.579782
O	-4.362891	4.008649	2.356034	O	8.069863	-3.306689	-3.738470
O	-7.968590	-0.069412	1.748552	O	4.022657	-0.751677	0.888738
Ti	1.316976	-2.494274	-1.234231	Ti	3.461829	1.054872	1.287628
O	0.753145	-0.688024	-0.835213	O	1.492917	0.861254	1.366980
Ti	0.984831	1.196474	-0.468268	O	5.761851	-2.442354	0.442357
O	2.953740	1.390121	-0.547652	O	5.429780	1.248401	1.208316
Ti	3.239079	1.803321	-2.414921	O	4.354884	-4.442431	0.122770
O	1.270168	1.609681	-2.335571	O	3.690590	2.939160	1.654714
Ti	5.769807	0.190494	-2.893203	Ti	3.129719	4.745696	2.053604
O	6.276957	-0.144810	-1.057871	O	2.621536	5.080854	0.218320
Ti	5.992563	-0.557961	0.809346	Ti	0.652630	4.887162	0.297651
O	7.960480	-0.364416	0.730057	O	-1.316276	4.693470	0.376982
O	3.799902	-0.003243	-2.813814	O	5.097633	4.939261	1.974301
Ti	3.571165	-1.887441	-3.180883	O	3.467821	3.687535	-2.047849
O	3.285797	-2.300651	-1.313609	Ti	2.907034	5.494097	-1.648959
Ti	3.793963	-2.635855	0.521671	O	0.938121	5.300488	-1.569603
O	1.825045	-2.829401	0.601045	O	4.874953	5.687607	-1.728275
O	5.539113	-1.693911	-3.260196	O	7.405647	4.074754	-2.206560
Ti	6.101950	-3.500257	-3.659166	O	1.602253	-2.081061	-3.101529
O	6.609138	-3.835524	-1.823838	O	1.160812	4.552013	2.132942
Ti	6.324784	-4.248639	0.043394	O	0.421023	3.002722	-0.069209
O	8.292699	-4.055094	-0.035940	O	1.085224	-4.378760	-1.601195

O	-0.651934	-2.687891	-1.154829
O	-0.984082	1.002857	-0.388934
H	-8.250488	-2.176429	-2.527638
H	-8.582658	1.514287	-1.761578
H	-8.914788	5.205030	-0.995515
H	-8.027655	-2.924925	1.174849
H	-8.359777	0.765879	1.940964
H	-8.691882	4.456673	2.707017
H	8.128889	-0.451304	-3.164892
H	8.461048	-4.142001	-3.930845
H	8.351657	-1.199733	0.537695
H	8.683872	-4.890413	-0.228304
H	8.019572	2.491108	1.303655
H	7.796807	3.239432	-2.398936
H	1.471680	-1.066916	10.406138
H	2.411075	-2.926181	12.189678
H	3.581372	-0.636905	11.211805
H	4.142258	-2.149208	10.910950
H	3.231673	-0.852021	8.569268
H	3.272899	-2.616189	8.474906
H	0.833509	-2.640992	7.947640
H	0.794930	-0.872005	7.980218
H	2.370280	-0.786918	6.031539
H	2.419017	-2.564617	6.008361
H	-0.253640	-2.075206	5.929966
H	2.286532	-1.656953	3.546267
H	1.351299	-0.581124	2.514891
H	-1.562454	-0.816238	4.369529
H	-0.964145	-0.976327	2.703114

Orientation 2

Total energy: -31066.975348

	O	6.202858	3.373063	0.290817			
	Ti	5.708732	3.036655	2.129497			
	O	7.679046	3.172447	2.255451			
	O	4.227349	-0.205173	-2.326721			
	Ti	3.979680	-2.094470	-2.653036			
	O	3.484609	-2.430986	-0.814420			
	Ti	1.513299	-2.566849	-0.940424			
	O	2.008370	-2.230333	-2.779040			
	O	3.932206	3.518930	-1.724635			
	Ti	3.389394	5.353750	-1.448861			
	O	2.894256	5.017270	0.389744			
	Ti	0.922954	4.881360	0.263664			
	O	1.418094	5.217842	-1.574951			
	O	5.359707	5.489527	-1.322885			
	O	5.949994	-1.958695	-2.527060			
	Ti	6.494789	-3.793379	-2.802707			
	O	6.793141	-4.075217	-0.913361			
	Ti	6.298985	-4.411650	0.925306			
	O	8.269302	-4.275913	1.051285			
	O	4.522484	-3.929293	-2.928810			
	O	5.459025	1.147129	1.802999			
	O	3.736370	2.900587	2.003390			
	Ti	3.193512	4.735388	2.279205			
	O	1.222203	4.599520	2.153187			
	O	5.163817	4.871299	2.405178			
	O	7.874790	3.790631	-1.472555			
	O	8.465102	-3.657599	-2.676730			
	Ti	3.783865	-2.712809	1.075038			
	O	1.812555	-2.848661	0.949022			
C		-2.353146	-2.989991	7.980144			
C		-1.240760	-2.678343	6.960803			
C		-1.746609	-2.092584	5.640054			
N		-0.636769	-2.010694	4.690288			
C		-0.336345	-1.044498	3.793942			
N		0.589440	-1.288347	2.880563			
C		-1.873157	-2.911156	9.442685			
N		-2.734331	-3.558893	10.444078			
C		-1.663726	-1.441640	9.890277			
O		-1.804023	-1.262218	11.205703			
O		-1.381162	-0.541226	9.129411			
N		-0.938330	0.162200	3.849546			
O		1.517415	0.875361	1.550944			
Ti		1.218063	1.157139	-0.338457			
O		1.713204	1.493704	-2.177046			
Ti		3.684504	1.629638	-2.050951			
O		3.189363	1.293073	-0.212362			
Ti		3.488714	1.011295	1.677039			
O		4.031552	-0.823514	1.401246			
Ti		6.003853	-0.687573	1.527389			
O		6.497997	-0.351113	-0.311276			
Ti		6.199637	-0.069278	-2.200621			
O		8.169948	0.066532	-2.074640			
O		5.654817	1.765422	-1.924973			
Ti		5.904477	3.654854	-1.598531			

O	5.754180	-2.577026	1.200990	O	-4.112495	4.836825	-1.928584
O	4.326671	-4.547637	0.799300	O	-8.055112	4.565097	-2.180645
O	7.974165	-0.551755	1.653347	O	-4.013004	0.494439	1.197245
Ti	-1.299009	2.856009	-0.188961	Ti	-3.470193	-1.340374	0.921419
O	-0.753189	1.021405	-0.464587	O	-1.498880	-1.204556	1.047440
Ti	-1.003858	-0.868088	-0.791148	O	-5.735618	2.247972	1.397650
O	-2.975167	-1.003921	-0.917208	O	-5.440542	-1.476130	0.795458
Ti	-3.274537	-0.722128	-2.806604	O	-4.308237	4.218544	1.799429
O	-1.303226	-0.586290	-2.680578	O	-3.717933	-3.229746	0.595039
Ti	-5.789650	0.976792	-2.656866	Ti	-3.175077	-5.064546	0.319218
O	-6.283735	0.640365	-0.818178	O	-2.679958	-4.728008	-1.519381
Ti	-5.985312	0.358553	1.071160	Ti	-0.708651	-4.592114	-1.393354
O	-7.955628	0.222773	0.945215	O	1.262655	-4.456220	-1.267326
O	-3.817344	1.112699	-2.530776	O	-5.145391	-5.200339	0.193253
Ti	-3.569629	3.001981	-2.204412	O	-3.522258	-2.611426	-3.132971
O	-3.270230	2.720195	-0.315009	Ti	-2.979487	-4.446250	-3.408800
Ti	-3.765332	2.383702	1.523603	O	-1.008174	-4.310442	-3.282779
O	-1.794014	2.519443	1.649619	O	-4.949805	-4.581988	-3.534758
O	-5.539976	2.866224	-2.330374	O	-7.464884	-2.883042	-3.385013
Ti	-6.084799	4.700892	-2.054678	O	-1.598317	3.137800	-2.078389
O	-6.578922	4.364432	-0.216007	O	-1.203770	-4.928663	0.445249
Ti	-6.280539	4.082581	1.673332	O	-0.458062	-2.702705	-1.066733
O	-8.250853	3.946817	1.547345	O	-1.048274	4.745497	0.137577
O	-5.244860	-0.857885	-2.932565	O	0.672302	2.991807	-0.062894
Ti	-5.494566	-2.747303	-3.259055	O	0.967455	-0.732266	-0.665143
O	-5.988656	-3.083790	-1.420380	H	8.257663	2.938300	-1.593796
Ti	-5.690237	-3.365678	0.468947	H	8.552839	-0.785802	-2.195881
O	-7.660555	-3.501418	0.342999	H	8.847976	-4.509930	-2.797971
O	-7.759967	0.841042	-2.782825	H	8.061925	2.320121	2.134187



H	8.357052	-1.404082	1.532123
H	8.652163	-5.128254	0.930004
H	-8.142832	1.693384	-2.661555
H	-8.437997	5.417430	-2.059378
H	-8.338505	1.075107	1.066496
H	-8.633726	4.799154	1.668624
H	-8.043415	-2.649076	0.464274
H	-7.847744	-2.030698	-3.263743
H	-0.888506	-3.392965	9.526650
H	-2.120273	-2.131655	11.557497
H	-2.611312	-4.568251	10.450671
H	-3.718940	-3.374939	10.253533
H	-2.763561	-3.989937	7.793408
H	-3.182184	-2.279391	7.856629
H	-0.540621	-1.960723	7.393230
H	-0.681035	-3.601789	6.750279
H	-2.556586	-2.706823	5.217110
H	-2.153771	-1.093762	5.814846
H	-0.068294	-2.844068	4.606995
H	-1.226355	0.548712	4.737070
H	-0.810890	0.824952	3.080684
H	0.721820	-2.200324	2.430760
H	0.860410	-0.507624	2.259087

Orientation 3

Total energy: -31066.985208

C	-2.658439	-3.795205	7.366669
C	-1.526480	-3.533199	6.356897
C	-1.955314	-2.971429	4.995252
N	-0.787140	-2.611639	4.206145
C	-0.428692	-1.386364	3.762623
N	0.622808	-1.305155	2.960278
C	-2.959352	-2.627586	8.337055
N	-4.054193	-2.934775	9.278146
C	-3.272908	-1.274126	7.638477
O	-4.421075	-0.725646	8.009981
O	-2.517858	-0.740570	6.842946
N	-1.094415	-0.287554	4.165931
O	1.547629	0.900181	1.643441
Ti	1.282228	1.165315	-0.253428
O	1.810861	1.478246	-2.086859
Ti	3.781027	1.596839	-1.929437
O	3.252394	1.283908	-0.096007
Ti	3.517795	1.018774	1.800863
O	4.047440	-0.823824	1.552728
Ti	6.018606	-0.705232	1.710215
O	6.546244	-0.392398	-0.123309
Ti	6.281832	-0.127216	-2.020106
O	8.251010	-0.008739	-1.862812
O	5.750208	1.715290	-1.772148
Ti	6.012605	3.605539	-1.460769

O	6.277038	3.340401	0.436031
Ti	5.749420	3.027617	2.269568
O	7.718601	3.146075	2.426834
O	4.310678	-0.245760	-2.177549
Ti	4.050270	-2.135890	-2.488769
O	3.521707	-2.448773	-0.655309
Ti	1.551529	-2.567295	-0.812641
O	2.080093	-2.254411	-2.646101
O	4.041469	3.486965	-1.618216
Ti	3.511850	5.329573	-1.370101
O	2.983221	5.016726	0.463345
Ti	1.013052	4.898157	0.305938
O	1.541684	5.211006	-1.527518
O	5.481031	5.448017	-1.212812
O	6.019451	-2.017449	-2.331480
Ti	6.551050	-3.859938	-2.579437
O	6.815454	-4.125123	-0.682640
Ti	6.287805	-4.437931	1.150885
O	8.256988	-4.319528	1.308177
O	4.579880	-3.978501	-2.736885
O	5.486974	1.137274	1.958135
O	3.778190	2.908901	2.112118
Ti	3.248525	4.751490	2.360275
O	1.278349	4.632964	2.202928
O	5.217698	4.870068	2.517559
O	7.981786	3.723982	-1.303481
O	8.520231	-3.741492	-2.422148
Ti	3.787012	-2.713951	1.241615
O	1.816835	-2.832461	1.084271

O	5.756194	-2.595501	1.398880	O	-3.985723	4.878643	-1.969044
O	4.316623	-4.556566	0.993535	O	-7.926073	4.641599	-2.283761
O	7.987786	-0.586748	1.867484	O	-3.979606	0.567911	1.201850
Ti	-1.220513	2.889340	-0.162966	Ti	-3.449987	-1.274690	0.953682
O	-0.687889	1.046921	-0.410886	O	-1.479808	-1.156215	1.111031
Ti	-0.951295	-0.843379	-0.722399	O	-5.688349	2.339611	1.355848
O	-2.921470	-0.961870	-0.879788	O	-5.419204	-1.393113	0.796408
Ti	-3.186890	-0.696722	-2.776653	O	-4.248907	4.300640	1.761279
O	-1.216713	-0.578225	-2.619298	O	-3.710467	-3.164896	0.642398
Ti	-5.687676	1.027338	-2.685916	Ti	-3.180804	-5.007485	0.394234
O	-6.215254	0.714535	-0.852370	O	-2.652192	-4.694581	-1.439207
Ti	-5.950780	0.449376	1.044421	Ti	-0.682018	-4.576029	-1.281851
O	-7.919963	0.330929	0.887164	O	1.288155	-4.457477	-1.124496
O	-3.716504	1.145895	-2.528482	O	-5.149985	-5.125945	0.236958
Ti	-3.456050	3.036010	-2.217213	O	-3.447349	-2.586853	-3.087924
O	-3.190601	2.770868	-0.320341	Ti	-2.917772	-4.429465	-3.336097
Ti	-3.719195	2.458008	1.513113	O	-0.947593	-4.311000	-3.178747
O	-1.749012	2.576407	1.670458	O	-4.886957	-4.547870	-3.493367
O	-5.425264	2.917587	-2.374488	O	-7.387708	-2.823784	-3.402624
Ti	-5.956893	4.760061	-2.126482	O	-1.485871	3.154487	-2.059862
O	-6.484510	4.447226	-0.292953	O	-1.210630	-4.888944	0.551594
Ti	-6.220075	4.182027	1.603838	O	-0.418694	-2.685810	-0.970279
O	-8.189256	4.063597	1.446539	O	-0.957042	4.779635	0.148525
O	-5.156080	-0.815145	-2.933926	O	0.749663	3.007797	-0.005571
Ti	-5.418524	-2.705379	-3.245353	O	1.018885	-0.724900	-0.565067
O	-5.946107	-3.018241	-1.411819	H	8.358392	2.866868	-1.409705
Ti	-5.681637	-3.283477	0.484962	H	8.627635	-0.865855	-1.969036
O	-7.650822	-3.401884	0.327700	H	8.896838	-4.598605	-2.528373
O	-7.656860	0.908922	-2.843188	H	8.095214	2.288967	2.320587

H	8.364407	-1.443858	1.761277
H	8.633584	-5.176652	1.201912
H	-8.033459	1.766046	-2.736935
H	-8.302693	5.498715	-2.177511
H	-8.296575	1.188046	0.993427
H	-8.565864	4.920716	1.552802
H	-8.027417	-2.544759	0.433959
H	-7.764303	-1.966658	-3.296371
H	-2.046856	-2.424898	8.911749
H	-4.768025	-1.335260	8.721722
H	-3.716655	-3.136080	10.215107
H	-4.596725	-3.739365	8.969555
H	-2.393390	-4.650935	7.997280
H	-3.586475	-4.075944	6.844873
H	-0.805536	-2.831054	6.789866
H	-0.982007	-4.472132	6.192460
H	-2.539924	-3.722854	4.444059
H	-2.581036	-2.091239	5.116727
H	-0.211285	-3.369819	3.861466
H	-1.603794	-0.264329	5.043623
H	-0.930354	0.584194	3.670418
H	0.860512	-2.090949	2.330292
H	0.830088	-0.405228	2.494582

Orientation 4

Total energy: -31066.986802

	O	6.292367	3.326000	0.465727
	Ti	5.763909	3.004588	2.297529
	O	7.733435	3.116397	2.455338
	O	4.315395	-0.239812	-2.167614
	Ti	4.049433	-2.127414	-2.489309
	O	3.520028	-2.448922	-0.657585
	Ti	1.549506	-2.560790	-0.815461
	O	2.078910	-2.239282	-2.647184
	O	4.057154	3.490522	-1.587548
	Ti	3.532951	5.333269	-1.329175
	O	3.003481	5.011798	0.502536
	Ti	1.032966	4.899882	0.344585
	O	1.562440	5.221355	-1.487135
	O	5.502477	5.445064	-1.171343
	O	6.018959	-2.015621	-2.331477
	Ti	6.545143	-3.858256	-2.589692
	O	6.808845	-4.134743	-0.694410
	Ti	6.280356	-4.456180	1.137379
	O	8.249884	-4.344425	1.295214
	O	4.573627	-3.970163	-2.747683
	O	5.495908	1.116781	1.975619
	O	3.792333	2.892528	2.139534
	Ti	3.268083	4.735256	2.397949
	O	1.297562	4.623383	2.240058
	O	5.237602	4.847185	2.555776
	O	7.998162	3.714235	-1.271725
	O	8.514669	-3.746459	-2.431859
	Ti	3.784632	-2.725405	1.237823
	O	1.814109	-2.837263	1.079935
C		-2.681384	-3.916582	7.285736
C		-1.549785	-3.652090	6.273580
C		-1.977529	-3.082598	4.909976
N		-0.824568	-2.692936	4.111194
C		-0.446832	-1.440508	3.766266
N		0.613754	-1.299769	2.983353
C		-3.112695	-2.718165	8.170519
N		-4.355649	-3.032311	8.898711
C		-3.365543	-1.429594	7.355429
O		-4.645688	-1.106044	7.236460
O		-2.466554	-0.789583	6.836836
N		-1.104564	-0.364350	4.236716
O		1.555873	0.892991	1.659838
Ti		1.291173	1.169430	-0.235515
O		1.820647	1.490986	-2.067210
Ti		3.791159	1.602926	-1.909244
O		3.261684	1.281370	-0.077549
Ti		3.526384	1.004931	1.817803
O		4.050614	-0.837806	1.559411
Ti		6.022125	-0.725871	1.717442
O		6.550604	-0.404408	-0.114346
Ti		6.286894	-0.127924	-2.009627
O		8.256418	-0.016096	-1.851789
O		5.760684	1.714728	-1.751411
Ti		6.028636	3.602440	-1.429557

O	5.754159	-2.613605	1.395630	O	-3.965936	4.907657	-1.930187
O	4.308828	-4.568159	0.979485	O	-7.906978	4.683917	-2.245991
O	7.991650	-0.614036	1.875255	O	-3.972331	0.579384	1.216723
Ti	-1.206499	2.900257	-0.135339	Ti	-3.448128	-1.263356	0.958297
O	-0.679289	1.057689	-0.393516	O	-1.477603	-1.151533	1.116190
Ti	-0.948249	-0.830072	-0.715506	O	-5.675865	2.355204	1.380653
O	-2.918769	-0.941911	-0.873438	O	-5.417689	-1.375129	0.800480
Ti	-3.183488	-0.665456	-2.768786	O	-4.230663	4.309722	1.796885
O	-1.212965	-0.553612	-2.610888	O	-3.714161	-3.151032	0.636537
Ti	-5.679204	1.065398	-2.668335	Ti	-3.189914	-4.993760	0.378116
O	-6.207623	0.743967	-0.836525	O	-2.660461	-4.672230	-1.453590
Ti	-5.943850	0.467505	1.058750	Ti	-0.689941	-4.560331	-1.295691
O	-7.913379	0.355707	0.900949	O	1.280578	-4.448432	-1.137791
O	-3.707687	1.177299	-2.510358	O	-5.159440	-5.105570	0.220296
Ti	-3.441679	3.064885	-2.188613	O	-3.449501	-2.553058	-3.090533
O	-3.176931	2.788437	-0.293258	Ti	-2.925339	-4.395809	-3.348963
Ti	-3.706367	2.466952	1.538461	O	-0.954814	-4.283996	-3.191070
O	-1.735838	2.578698	1.696349	O	-4.894869	-4.507564	-3.506776
O	-5.411239	2.953111	-2.346432	O	-7.390550	-2.776684	-3.406319
Ti	-5.937452	4.795731	-2.088168	O	-1.471155	3.176709	-2.030718
O	-6.465910	4.474267	-0.256375	O	-1.219394	-4.881871	0.536019
Ti	-6.202177	4.197766	1.638900	O	-0.421063	-2.672652	-0.973643
O	-8.171703	4.085985	1.481058	O	-0.937473	4.788012	0.186628
O	-5.153023	-0.777230	-2.926602	O	0.764023	3.012060	0.022600
Ti	-5.421021	-2.664928	-3.248506	O	1.022276	-0.718245	-0.557630
O	-5.949445	-2.986419	-1.416707	H	8.372249	2.856624	-1.382729
Ti	-5.685677	-3.262957	0.478557	H	8.630523	-0.873710	-1.962792
O	-7.655207	-3.374715	0.320752	H	8.888757	-4.604070	-2.542863
O	-7.648733	0.953631	-2.826150	H	8.107529	2.258792	2.344312

H	8.365753	-1.471643	1.764269
H	8.623961	-5.202047	1.184170
H	-8.022813	1.811253	-2.715119
H	-8.281078	5.541530	-2.134962
H	-8.287472	1.213322	1.011992
H	-8.545792	4.943601	1.592099
H	-8.029283	-2.517092	0.431790
H	-7.764626	-1.919061	-3.295287
H	-2.289533	-2.478896	8.854138
H	-5.117269	-1.766425	7.823163
H	-4.297048	-2.797082	9.885796
H	-4.602001	-4.016402	8.829221
H	-2.366060	-4.709026	7.973572
H	-3.570593	-4.299610	6.761614
H	-0.823882	-2.960106	6.713788
H	-1.014887	-4.593111	6.095023
H	-2.544618	-3.842150	4.353195
H	-2.626103	-2.216663	5.018766
H	-0.285166	-3.432658	3.678231
H	-1.615370	-0.380881	5.116229
H	-0.898471	0.534368	3.813192
H	0.869960	-2.048640	2.313898
H	0.803398	-0.374710	2.562924

Orientation 5

Total energy: -31066.9912520

C	-2.774003	-4.655526	6.333961	O	6.364219	3.254976	0.615942
C	-1.601920	-4.385070	5.370478	Ti	5.834087	2.879788	2.437004
C	-1.924001	-3.789757	3.983936	O	7.805426	2.955050	2.593852
N	-0.769213	-3.135881	3.387392	O	4.326116	-0.187484	-2.132427
C	-0.442772	-1.836349	3.560454	Ti	4.029660	-2.058608	-2.517487
N	0.678535	-1.385727	3.003672	O	3.498582	-2.433875	-0.696504
C	-3.370647	-3.436359	7.088675	Ti	1.526247	-2.509179	-0.853419
N	-4.240113	-3.916385	8.176421	O	2.057325	-2.133912	-2.674401
C	-4.264826	-2.566809	6.176678	O	4.128136	3.524559	-1.425244
O	-5.557735	-2.810952	6.297225	Ti	3.633700	5.365491	-1.103120
O	-3.831641	-1.734984	5.390644	O	3.102556	4.990261	0.717851
N	-1.187882	-1.030434	4.334123	Ti	1.130228	4.914912	0.560860
O	1.591929	0.857821	1.737864	O	1.661375	5.290144	-1.260121
Ti	1.328172	1.202755	-0.146361	O	5.605037	5.440738	-0.946250
O	1.859322	1.578067	-1.967313	O	6.000998	-1.983362	-2.360617
Ti	3.831647	1.653440	-1.810306	Ti	6.497417	-3.824219	-2.682583
O	3.300498	1.278128	0.010646	O	6.760174	-4.169182	-0.798430
Ti	3.564254	0.933194	1.894870	Ti	6.230012	-4.544395	1.022618
O	4.058717	-0.907728	1.572727	O	8.201351	-4.469187	1.179490
Ti	6.032042	-0.832378	1.729796	O	4.524088	-3.899542	-2.839612
O	6.562194	-0.457139	-0.091250	O	5.535590	1.008498	2.051727
Ti	6.299428	-0.112179	-1.975402	O	3.860696	2.804312	2.279967
O	8.270764	-0.036898	-1.818526	Ti	3.366213	4.645225	2.602131
O	5.802984	1.728695	-1.653435	O	1.393879	4.569916	2.445203
Ti	6.101431	3.599893	-1.268216	O	5.337546	4.720607	2.759002
				O	8.072769	3.675141	-1.111345
				O	8.468754	-3.748969	-2.525713
				Ti	3.762241	-2.778853	1.187773
				O	1.789906	-2.854146	1.030847



O	5.733580	-2.703599	1.344620	O	-3.872084	5.079032	-1.700470
O	4.256670	-4.619794	0.865685	O	-7.816751	4.928423	-2.014351
O	8.003379	-0.757090	1.886649	O	-3.941357	0.646800	1.297454
Ti	-1.141546	2.968388	0.018533	Ti	-3.446920	-1.194123	0.975277
O	-0.644100	1.127581	-0.303396	O	-1.474584	-1.118865	1.132207
Ti	-0.943557	-0.743645	-0.688749	O	-5.616208	2.442687	1.525711
O	-2.915889	-0.818917	-0.845718	O	-5.418293	-1.269349	0.818423
Ti	-3.179664	-0.473968	-2.729937	O	-4.139428	4.358844	2.004732
O	-1.207329	-0.398689	-2.573001	O	-3.743448	-3.065318	0.590149
Ti	-5.647426	1.291653	-2.564773	Ti	-3.248968	-4.906230	0.267978
O	-6.177517	0.916444	-0.743703	O	-2.717841	-4.530943	-1.552986
Ti	-5.914689	0.571504	1.140445	Ti	-0.745508	-4.455609	-1.396047
O	-7.886028	0.496253	0.983606	O	1.226824	-4.380275	-1.239108
O	-3.674095	1.366969	-2.407758	O	-5.220306	-4.981494	0.111119
Ti	-3.377594	3.238076	-2.022649	O	-3.476171	-2.345090	-3.115050
O	-3.113790	2.893133	-0.138423	Ti	-2.981776	-4.186024	-3.437231
Ti	-3.644899	2.517889	1.682556	O	-1.009439	-4.110775	-3.280301
O	-1.672560	2.593071	1.839479	O	-4.953116	-4.261232	-3.594081
O	-5.348965	3.162849	-2.179505	O	-7.420843	-2.495587	-3.428910
Ti	-5.845413	5.003689	-1.857490	O	-1.405258	3.313335	-1.865717
O	-6.375544	4.628449	-0.036438	O	-1.276636	-4.830907	0.424920
Ti	-6.112756	4.283471	1.847708	O	-0.446135	-2.584465	-1.010638
O	-8.084093	4.208238	1.690828	O	-0.842024	4.839609	0.403864
O	-5.151010	-0.549196	-2.886792	O	0.830787	3.043625	0.175509
Ti	-5.449503	-2.420377	-3.272059	O	1.028780	-0.668382	-0.531836
O	-5.979601	-2.795645	-1.451003	H	8.433003	2.816005	-1.252332
Ti	-5.716778	-3.140660	0.433131	H	8.631016	-0.896037	-1.959512
O	-7.688119	-3.215872	0.276290	H	8.828989	-4.608104	-2.666699
O	-7.618766	1.216432	-2.721625	H	8.165666	2.095921	2.452843

H	8.363628	-1.616222	1.745680
H	8.561575	-5.328331	1.038463
H	-7.978993	2.075577	-2.580610
H	-8.176998	5.787560	-1.873339
H	-8.246268	1.355390	1.124632
H	-8.444328	5.067378	1.831853
H	-8.048341	-2.356726	0.417311
H	-7.781066	-1.636440	-3.287893
H	-2.547949	-2.799980	7.440580
H	-5.621578	-3.448017	7.065897
H	-4.254425	-3.270584	8.963043
H	-3.950423	-4.825101	8.528549
H	-2.400653	-5.336531	7.108811
H	-3.586671	-5.192387	5.824583
H	-0.898515	-3.704493	5.868038
H	-1.051525	-5.321445	5.224914
H	-2.228781	-4.585788	3.295486
H	-2.754513	-3.085540	4.040458
H	-0.304177	-3.597067	2.609724
H	-2.046428	-1.317290	4.799568
H	-0.944688	-0.049490	4.361210
H	1.067967	-1.967441	2.234636
H	0.745004	-0.391575	2.743126

Orientation 6

Total energy: -31066.993420

	O	-6.132716	-3.387032	-0.680774
	Ti	-5.619045	-3.655320	1.163742
	O	-7.580921	-3.901300	1.247281
	O	-4.329324	0.926902	-1.982953
C	Ti	-4.153714	2.826490	-1.669920
C	O	-3.639104	2.558361	0.174567
C	Ti	-1.676236	2.804465	0.091000
O	O	-2.190846	3.072593	-1.753487
C	O	-3.893450	-2.773573	-2.642544
C	Ti	-3.281965	-4.574474	-2.989103
N	O	-2.767287	-4.842630	-1.144639
C	Ti	-0.804430	-4.596458	-1.228262
N	O	-1.319111	-4.328301	-3.072736
N	O	-5.243840	-4.820448	-2.905538
N	O	-6.115589	2.580517	-1.586354
O	Ti	-6.729049	4.381171	-1.239711
O	O	-7.004463	4.013990	0.638426
Ti	Ti	-6.490764	3.745731	2.482938
O	O	-8.452643	3.499794	2.566518
Ti	O	-4.765191	4.627394	-1.323361
O	O	-5.441409	-1.755376	1.476669
Ti	O	-3.655135	-3.408949	1.080140
O	Ti	-3.043605	-5.209843	0.733627
Ti	O	-1.080739	-4.963731	0.650047
O	O	-5.005466	-5.455942	0.817144
Ti	O	-7.819149	-3.265778	-2.475333
O	O	-8.690924	4.135195	-1.156147
O	Ti	-3.915419	2.191094	2.052809
Ti	O	-1.952551	2.437191	1.969227

O	-5.877296	1.945122	2.136349	O	4.187795	-3.637952	-3.307355
O	-4.526898	3.991991	2.399404	O	8.113526	-3.145726	-3.474539
O	-8.016774	-0.200725	1.906887	O	3.990053	-0.572880	1.074797
Ti	1.337017	-2.450370	-0.999035	Ti	3.378568	1.228032	1.421303
O	0.722537	-0.649838	-0.652394	O	1.415696	0.981966	1.504902
Ti	0.901134	1.250132	-0.339542	O	5.776289	-2.226529	0.678256
O	2.864000	1.496225	-0.423173	O	5.340480	1.473982	1.337747
Ti	3.140429	1.863505	-2.301347	O	4.426018	-4.273386	0.415297
O	1.177561	1.617418	-2.217751	O	3.554245	3.127714	1.734301
Ti	5.715771	0.308790	-2.731495	Ti	2.942717	4.928611	2.080808
O	6.229400	0.040517	-0.886966	O	2.428059	5.196711	0.236330
Ti	5.953915	-0.326690	0.991156	Ti	0.465197	4.950571	0.319910
O	7.915793	-0.080723	0.907622	O	-1.497666	4.704431	0.403490
O	3.751911	0.062579	-2.647857	O	4.904592	5.174596	1.997259
Ti	3.576254	-1.837013	-2.960840	O	3.316091	3.763113	-1.988362
O	3.299797	-2.204303	-1.082661	Ti	2.704646	5.564038	-1.641855
Ti	3.814439	-2.472450	0.761814	O	0.741774	5.317981	-1.558253
O	1.851559	-2.718442	0.845433	O	4.666528	5.809969	-1.725415
O	5.538164	-1.591061	-3.044398	O	7.241835	4.255226	-2.155566
Ti	6.151652	-3.391715	-3.390989	O	1.613384	-2.083080	-2.877239
O	6.665318	-3.659951	-1.546465	O	0.979853	4.682480	2.164395
Ti	6.389872	-4.027119	0.331670	O	0.286677	3.050663	0.007141
O	8.351748	-3.781154	0.248091	O	1.158354	-4.350331	-1.311907
O	5.102315	2.109455	-2.384904	O	-0.625853	-2.696433	-0.915387
Ti	5.279954	4.009294	-2.072006	O	-1.061738	1.004067	-0.255961
O	5.793586	3.741081	-0.227469	H	-8.233704	-2.436531	-2.307245
Ti	5.518102	3.373950	1.650668	H	-8.669611	1.263941	-1.647653
O	7.479984	3.619881	1.567117	H	-9.105480	4.964441	-0.988059
O	7.677650	0.554733	-2.815053	H	-7.995482	-3.072052	1.415346

H	-8.431344	0.628511	2.074990
H	-8.867189	4.329064	2.734572
H	8.092199	-0.274533	-2.983118
H	8.528094	-3.974983	-3.642604
H	8.330354	-0.909985	0.739569
H	8.766304	-4.610418	0.080037
H	7.894528	2.790612	1.399058
H	7.656379	3.425958	-2.323631
H	1.734812	-4.440889	6.888678
H	4.867479	-4.262910	7.054976
H	3.304701	-5.664914	8.089558
H	3.232262	-4.397773	9.131275
H	1.638584	-2.754103	8.680570
H	3.138758	-2.017304	8.131872
H	0.746614	-2.267809	6.240263
H	0.746172	-1.019813	7.466088
H	2.714343	0.069635	6.503942
H	2.933067	-1.217482	5.326966
H	0.782268	0.804856	5.402717
H	1.653657	-2.360185	4.028187
H	0.778032	-2.062561	2.569031
H	-0.318877	1.144710	3.266111
H	-0.736352	-0.307960	2.521065