

# A computational analysis for amino acid adsorption

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## ABSTRACT

In this study we have systematically investigated the effects of surface configuration and molecular state for the adsorption of methionine ( $C_5H_9NO_2S$ ) on a graphite surface using two model force fields, AMBER 3 and MM+. Computational results were compared with experimental results.

A commercial computational chemistry software (HyperChem™) was utilized in this study. Parameter sets for the force fields, AMBER 3 and MM+, were employed together with methionine in its non-ionic and zwitterionic state to investigate the molecular adsorption on a graphene sheet, a graphene sheet with hydrogen termination, as well as double layers of graphite with and without hydrogen termination.

The results show that the model produces excellent qualitative results regarding inter-molecular configuration. Using the AMBER3 force field and methionine in its zwitterionic state adsorbed on a single graphite sheet leads to results which clearly resemble the experimental results and show hydrogen bonding between neighboring methionine molecules through the amino and carboxyl groups. Dimers are formed when two molecules are anti-parallel to each other, and parallel molecules are the building blocks of molecular rows.

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## 1. Introduction

Understanding the underlying principles of molecular self-assembly has evolved in the last twenty years and is becoming an increasing focus in computational chemistry [1–3]. Experimental methods have produced a wide variety of molecules and substrate combinations where different degrees of molecular nanostructures can be produced, from one-dimensional wire structures to two dimensional networks, and three-dimensional, chemically selective pyramidal structures [4–11]. Ideally, these examples are geared towards progress in the fields of molecular electronics, biosensors, and medical applications [12–14]. In recent years, interest in molecular self-assembly on surfaces has shifted from metal substrates to graphene, hexagonal boron nitride, or similar structures [15,16]. The results of the present study have the potential to complement the aforementioned experimental work.

A major sticking point for many experimental studies and the application of their results is the understanding of the inter-molecular geometries and forces. Even the best experimental techniques, like Scanning Tunneling Microscopy (STM), Atomic Force Microscopy (AFM), Quantitative Low-Energy Electron Diffraction (LEED), or Scanned-Energy Mode Photoelectron Diffraction (PhD), are either not fully or only under special circumstances capable of determining positions, orientations, and inter-molecular spacing of complex entities like porphyrins, amino acids, or other relevant functional biomolecules [17–21]. In

order to resolve these issues, a combination of experimental techniques together with computational approaches can deliver additional information on adsorption sites, molecular orientation, and bond lengths [22–24]. This paper describes the approach of a computational analysis of methionine molecules (see Fig. 1) adsorbed on graphite modeled with two force field parameter sets and four substrate configurations. Our focus is on providing a computational model for the adsorption and interactions of methionine and the graphite substrate. With the help of a commercially available software package, HyperChem™, [25,26] and selective parameter sets, we compare qualitative and quantitative results of these calculations with experimental results and other computational approaches [27,28].

In previous work, we have shown that the amino acid methionine can be self-assembled into regularly spaced molecular wires under ambient conditions where spacing between rows can be regulated by adsorbate concentration [27]. These structures suggest the systematic formation of methionine dimer molecules due to the fact that all rows have the same width. These wires have an 18 Å width and a 45 Å spacing between each wire for a specific coverage as shown in Fig. 2. The make-up of each wire is found to be a dimer chain of methionine in parallel and anti-parallel configuration. The very consistent spacing between the rows suggests long ranged interactions between the methionine molecules.

## 2. Method and model

The computational results presented in this study have been obtained by performing molecular mechanics calculations using the commercially

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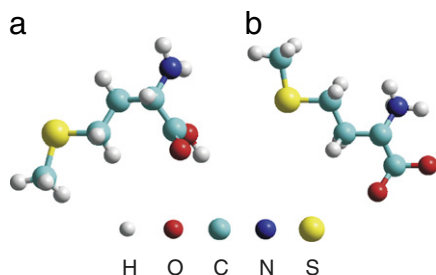


Fig. 1. Methionine molecule in a) non-ionic form and b) zwitterionic form.

available software package HyperChem 7.5. We specifically choose the two aforementioned force field parameter sets of AMBER3 and MM+. The results of these calculations yield potential energies of the molecule–substrate system from which we can deduce adsorption energies, bonding energies, and optimized inter-molecular configurations. In general, the system's energy consists of a sum of energy contributions depending on the parameter set of the chosen force field:

$$E = \sum_{\text{bond-stretching}} E + \sum_{\text{bond-bending}} E + \sum_{\text{dihedral}} E + \sum_{\text{out-of-plane}} E + \sum_{\text{non-bonded}} E + \sum_{\text{Coulomb}} E.$$

One of the force fields used is the universal MM+ force field which is built on an extension of MM2, a force field established by N.L. Allinger in 1977 and expanded multiple times since then [29–31]. It is a force field which can be applied to many situations but lacks the accuracy of force fields aimed at specific cases. AMBER, on the other hand, was developed especially suitable for amino acids. It was introduced by P. Kollman's group and is mostly used for nucleic acids and proteins, thus very applicable to the present case of amino acids [32–35]. The main differences between the two force field parameter sets are: MM+ has higher than quadratic terms for the bond energies and the angle calculations. Furthermore, for the Coulomb interaction it uses dipoles instead of point charges. The non-bonding van-der-Waals term has exponential form. On the other hand, AMBER3 has explicit hydrogen bonding terms in 10–12 form [26].

For the optimization of the individual molecules all forces described in the equation above are employed to find the energetically best configuration. Since the self-assembly of methionine molecules does not lead to chemical bonding between two molecules, the optimization of the adsorption geometry is only governed by the non-bonding forces included in the last two terms. These involve van-der-Waals repulsive forces at close range, Lennard–Jones long range attractive interaction, electrostatic Coulomb forces, and hydrogen bonding terms.

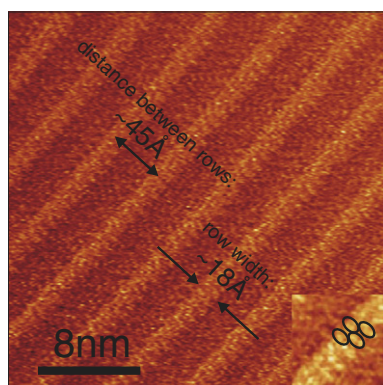


Fig. 2. STM image of methionine on graphite surface. At coverage of about 40% a row spacing of 45 Å can be observed. The width of the rows (~18 Å) is determined by the length of two methionine molecules facing each other. Inset shows individual methionine molecules imaged as elliptical features [27].

We chose the system of the amino acid methionine on a graphite surface to extend the scope of our previous work [27,36]. Additionally, there are other experimental results for this amino acid and other similar amino acids available for comparison [37,38]. The graphite substrate was simulated in four different configurations: (i) a single layer of graphene with a lattice constant of 1.4 Å (SG), (ii) a single layer of graphene with hydrogen-terminated dangling bonds (SGH), (iii) a double layer of graphite with inter-planar separation of 3.41 Å (DG), and (iv) a double layer of graphite with hydrogen-terminated dangling bonds (DGH). All templates have a dimension of 60 Å × 60 Å. This size guarantees that there are no significant boundary effects observed for the adsorption of methionine around the center of the template. The methionine molecule was modeled in its non-ionic state and in its zwitterionic state. Although amino acids are not found in their zwitterionic state from gas phase, [39] previous experiments have shown that methionine during the adsorption on surfaces can be found in its zwitterionic state [37]. Both configurations of methionine are depicted in Fig. 1.

In order to allow more general comparisons of the adsorption under different conditions (temperature, solvent etc.) and with other calculations as well as limit the parameter space, all calculations were performed in vacuo and at a temperature of zero K [40].

The calculations carried out in this study yield a comparison of the total energy of the methionine molecules and the surfaces for different configurations. In a first step the graphite surfaces were constructed with the atomic structure and C–C bond length according to bulk graphite. The methionine molecules were geometry-optimized using the respective force field parameters for these calculations. The adsorption energy was determined and evaluated. For the subsequent calculations, this first methionine molecule was fixed with its center of mass at the origin of our coordinate system. Then a second optimized molecule was positioned on a 20 Å × 20 Å grid with a step width of 0.1 Å around the origin and the energies of each of these configurations was recorded. This second molecule was oriented in two different configurations extracted from experimental results, namely parallel to the stationary molecule and antiparallel to it. These two configurations simulate the width of the dimer rows (antiparallel) and orientation along the dimer rows (parallel).

### 3. Results and discussion

Our calculations yield adsorption energies, geometries of single molecules, inter-molecular binding energies, and preferred geometric configurations between two molecules. These results were analyzed regarding self-consistency among the different molecules and surface configurations, and compared to experimental findings of our previous work as well as with more powerful computational approaches (like DFT) and other experimental results [8,27,28].

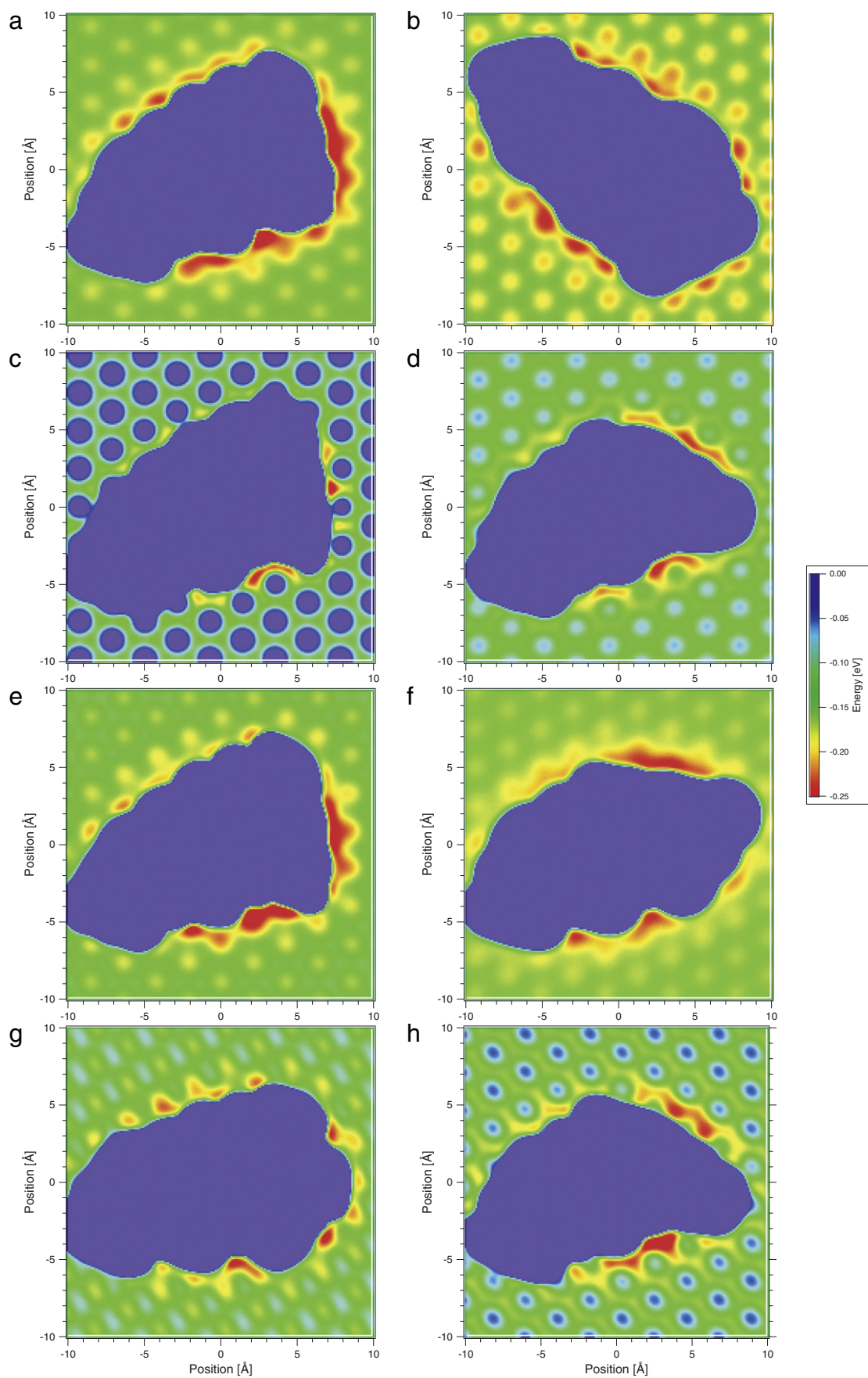
#### 3.1. Adsorption energy

Adsorption energies were found by comparing the potential energy of the molecule–substrate system with methionine far removed from

Table 1

Adsorption energies for the two force field parameter sets AMBER 3 and MM+. The surface configurations are described as follows: SG (single graphene surface), SGH (single graphene surface with hydrogen termination), DG (double layer of graphite surface), DGH (double layer of graphite with hydrogen termination).

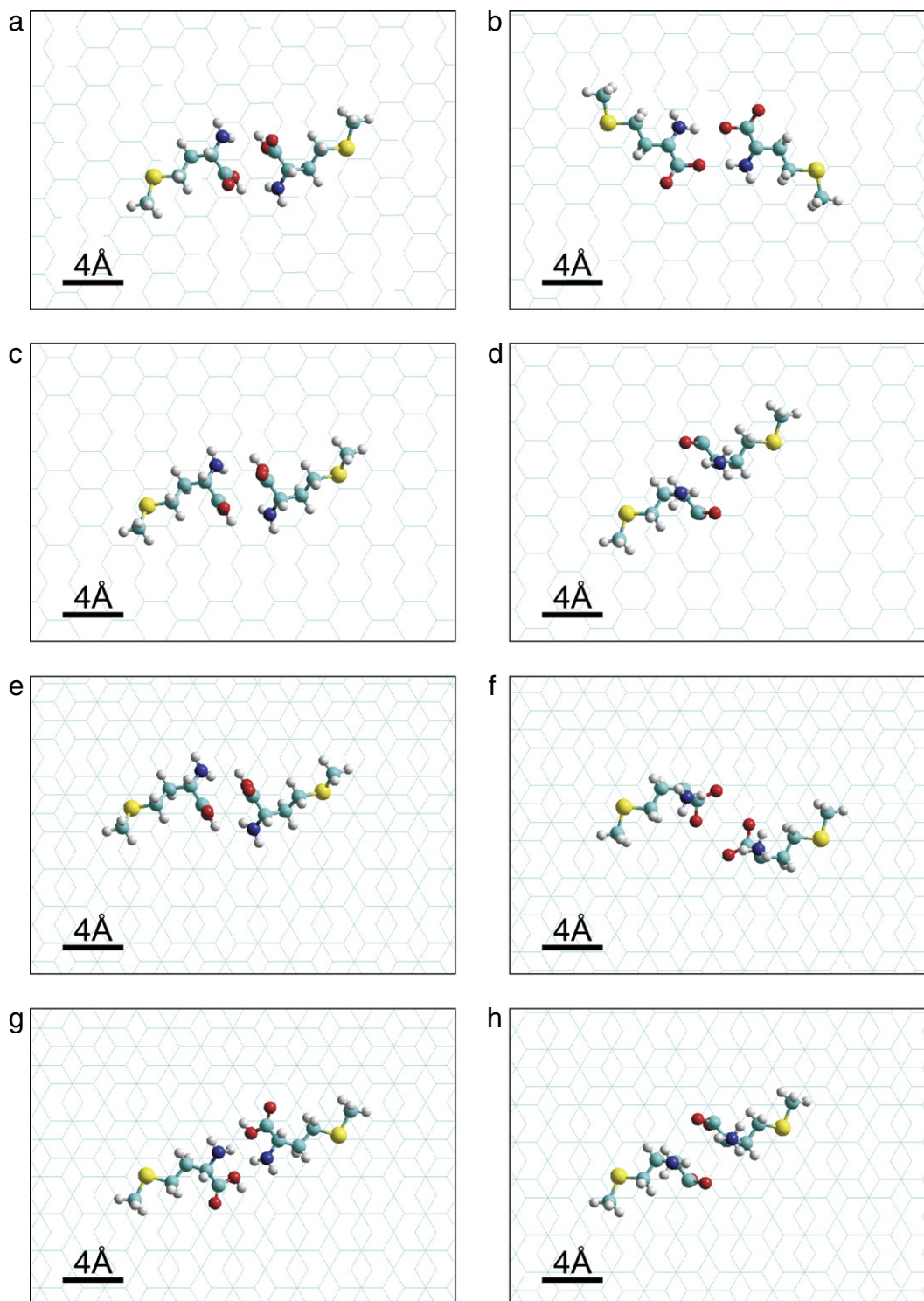
	Adsorption energies for single methionine molecules [eV]							
	AMBER 3		MM+		AMBER 3		MM+	
	SG	SGH	DG	DGH	SG	SGH	DG	DGH
non-ionic	0.39	0.34	0.43	0.38	0.74	0.72	0.83	0.53
zwitterionic	0.44	0.30	0.46	0.32	0.65	0.62	0.81	0.46



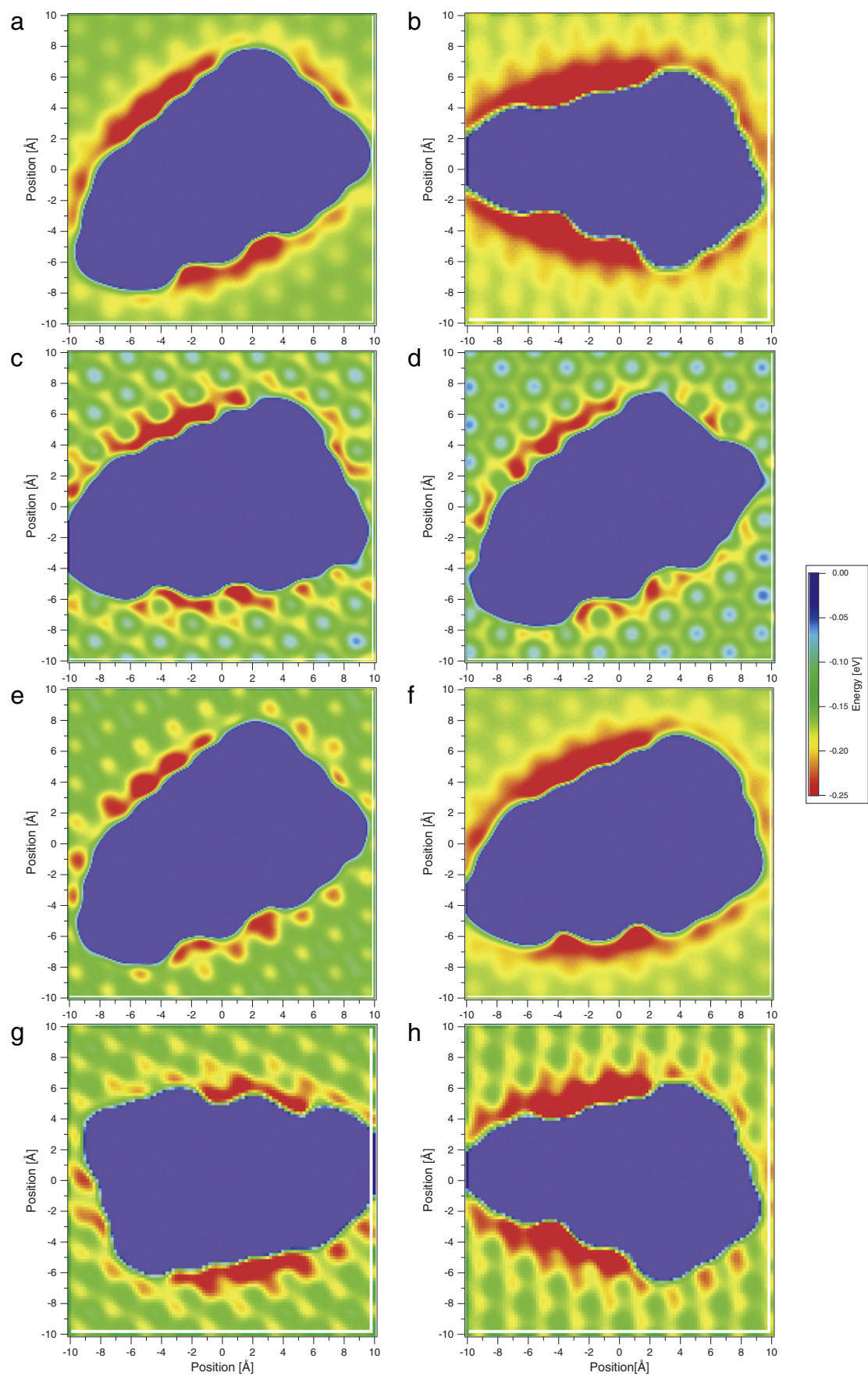
**Fig. 3.** Energy maps for anti-parallel dimers using the AMBER 3 parameter set. The figures correspond to the four surface configurations (SG, SGH, DG, and DGH) with the two molecular states (non-ionic and zwitterionic) a) SG non-ionic, b) SG zwitterionic, c) SGH non-ionic, d) SGH zwitterionic, e) DG non-ionic, f) DG zwitterionic, g) DGH non-ionic, and h) DGH zwitterionic.

the substrate, and therefore outside of the influence of the substrate, to the energetically most favorable configuration of the molecule when interacting with the different substrate configurations. Table 1 summarizes the results for the two different force field parameter sets with the four different substrates and two molecular configurations. Previous calculations of different amino acids adsorbed on carbon nanotubes using DFT have produced adsorption energies of about 0.5 eV [40].

Our results using AMBER3 are fairly close to these values. Furthermore, the previous study also indicates that amino acids in zwitterionic form produce higher adsorption energies on a graphene-like surface due to the polar nature of the molecule which is confirmed with our results (compare SG with SGZ). However, when the substrate is hydrogen-terminated, the overall adsorption energies decrease as can be expected. The use of a double layer graphite results in overall slightly higher



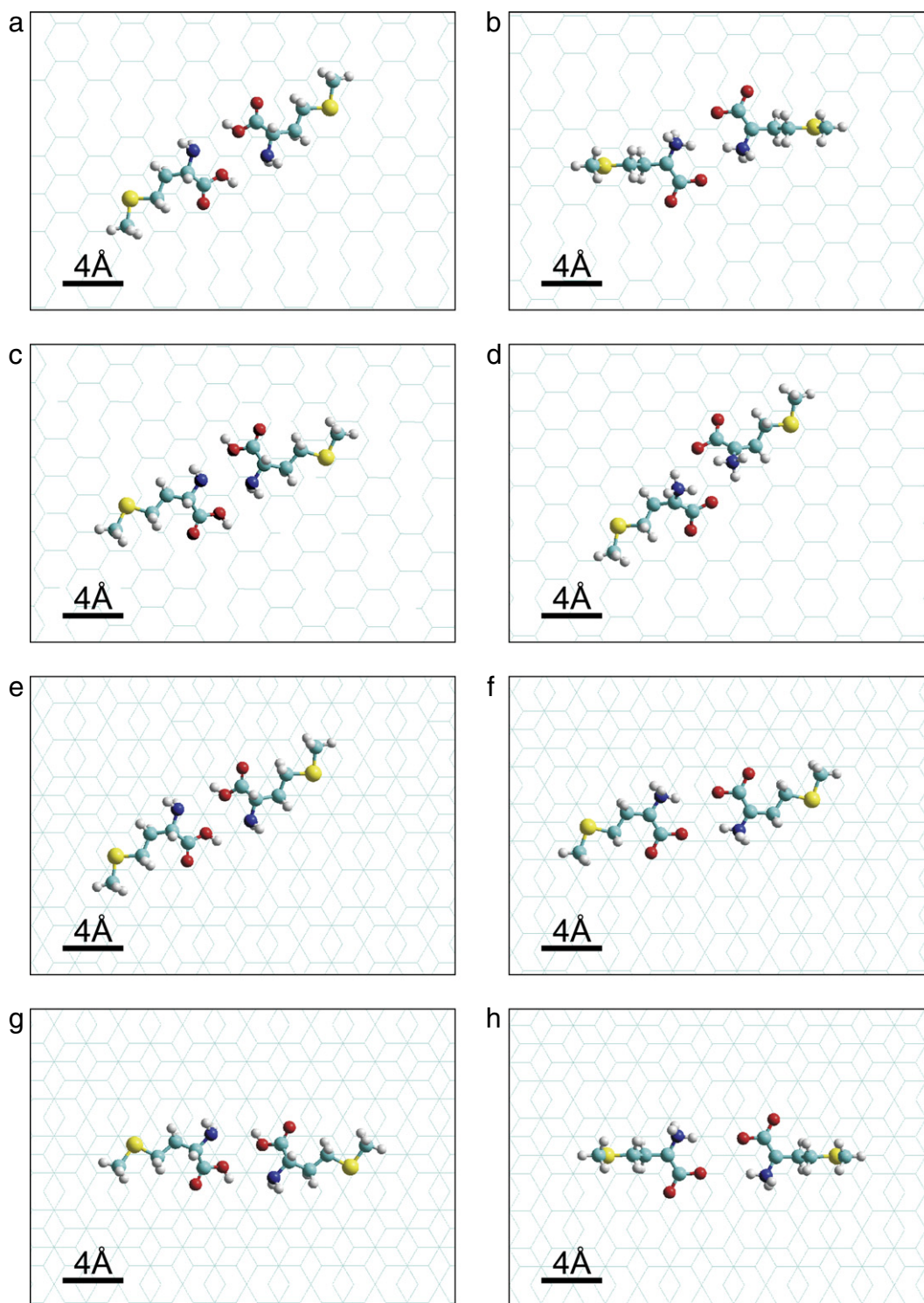
**Fig. 4.** Optimized configurations for anti-parallel dimers using the AMBER 3 parameter set deduced from the corresponding energy maps in Fig. 3. The figures correspond to the four surface configurations (SG, SGH, DG, and DGH) with the two molecular states (non-ionic and zwitterionic) a) SG non-ionic, b) SG zwitterionic, c) SGH non-ionic, d) SGH zwitterionic, e) DG non-ionic, f) DG zwitterionic, g) DGH non-ionic, and h) DGH zwitterionic.



**Fig. 5.** Energy maps for anti-parallel dimers using the MM+ parameter set. The figures correspond to the four surface configurations (SG, SGH, DG, and DGH) with the two molecular states (non-ionic and zwitterionic) a) SG non-ionic, b) SG zwitterionic, c) SGH non-ionic, d) SGH zwitterionic, e) DG non-ionic, f) DG zwitterionic, g) DGH non-ionic, and h) DGH zwitterionic.

adsorption energies due to more interactions between the substrate atoms and the amino acid. The parameter set MM+ follows the same general trend of lower adsorption energies for the hydrogen-terminated substrates and higher energies for the double layer of graphite, but two features stand out: the adsorption energies are generally higher and the zwitterionic conformer of methionine does not lead to a higher adsorption energy when compared to the non-ionic case. One

explanation is that the overall adsorption geometry is the driving factor of these energies. In all cases methionine is lying at on the substrate, as has been found in previous studies on methionine and other amino acids [27,37,38,41]. One important aspect in the differences of the adsorption energies is the configuration of the amino and carboxyl groups. When these groups are mostly in-plane, i.e. parallel to the surface, then the overall adsorption energy is higher. That can be seen



**Fig. 6.** Optimized configurations for anti-parallel dimers using the MM+ parameter set deduced from the corresponding energy maps in Fig. 5. The figures correspond to the four surface configurations (SG, SGH, DG, and DGH) with the two molecular states (non-ionic and zwitterionic) a) SG non-ionic, b) SG zwitterionic, c) SGH non-ionic, d) SGH zwitterionic, e) DG non-ionic, f) DG zwitterionic, g) DGH non-ionic, and h) DGH zwitterionic.

when comparing the data from Table 1 with the configurations of the molecules on the substrate as depicted in Fig. 4 for AMBER3, and Fig. 6 for MM+. The aforementioned in-plane configuration of carboxyl and amino group coincides with higher adsorption energies in the SGZ and DGZ cases for AMBER3.

### 3.2. Anti-parallel configuration

Experimental findings of the adsorption of methionine on a graphite substrate have shown rows of constant width (about 18 Å) separated by a varying amount depending on the amino acid concentration [27]. These findings can only be explained by a structure of molecular dimers lined up to produce these rows (cf. Fig. 2). Therefore, these dimers are comprised of two molecules in anti-parallel orientation, preferably with the energetically-favorable configuration of the amino and carboxyl group facing each other. The calculations for this situation were accomplished by keeping one molecule stationary, moving a second molecule (oriented at 180° with respect to the first one) around on a 20 Å × 20 Å grid in 0.1 Å increments, and recording the total potential energy of the system. The results are energy maps as can be seen in Fig. 3 for AMBER 3 and in Fig. 5 for MM+. The pronounced blue/purple areas in the center are energetically very unfavorable (and sometimes practically impossible) configurations where the molecules are either too close together or even intermingled with each other which corresponds to physically unrealistic situations. The energetically most favorable positions for the second molecule with a lowest total energy are indicated by the red areas. The deduced inter-molecular configurations from the energy maps can be seen in Fig. 4 for AMBER 3, and in Fig. 6 for MM+. The binding energies are determined by the difference between two molecules at their lowest energy (red regions) and two non-interacting molecules adsorbed on the surface but very far apart. The corresponding energy values are listed in Table 2.

The binding between the amino acid molecules in this anti-parallel configuration is governed by the interaction between the amino groups and carboxyl groups. The geometries of these configurations lead to the width of a molecular row of about 18 Å as seen in the experimental results (cf. Fig. 2). Only three of the 16 configurations with different force fields, surface configurations, and molecular states show confirmed hydrogen bonding with molecules at the lowest total energy according to the HyperChem calculations. They are depicted by an asterisk in Table 2. For the AMBER3 force field they are the zwitterionic molecule on a single graphene template (SG-Z) and the non-ionic molecule on the double sheet of graphite with hydrogen termination (DGH-NI). For the MM+ force field, the only configuration at lowest energy and with hydrogen bonds between the two methionine molecules occurs for the zwitterionic molecule on the double graphite sheet (DG-Z).

Experimental studies of hydrogen bond energies yielded energies of about 0.08 eV [42,43]. The energies in Table 2 are in general agreement with these values, especially considering that force field calculations have been shown to underestimate these energies [44]. The main difference between the binding energies of different configurations lies in the geometric positioning of two anti-parallel molecules.

**Table 2**

Table for binding energies of two methionine molecules in anti-parallel configuration. The asterisks indicate established hydrogen-bonding found using HyperChem.

	Binding energies for anti-parallel configuration [eV]							
	AMBER 3				MM+			
	SG	SGH	DG	DGH	SG	SGH	DG	DGH
Non-ionic	0.108	0.137	0.098	0.074*	0.061	0.047	0.044	0.052
Zwitterionic	0.043*	0.098	0.046	0.079	0.044	0.067	0.039*	0.026

The orientation of the carboxyl and amino groups with respect to the surface is an important factor in the ability to enable hydrogen bonds to the other partner in the dimer configuration. The preferred hydrogen bond length is about 2 Å which yields binding energies of about 0.1 eV. As one can see in Figs. 4 and 6, the positions of the two molecules yield mostly very favorable dimer configurations possibly enabling hydrogen bonds between the two molecules. However in most cases, a traditional hydrogen bond with bond length around 2 Å could not be established. The modeling of the experimental dimer configuration leads to an interplay between commensurability between molecule and substrate and an intermolecular attraction between two methionine molecules. In previous studies the phenomenon of hydrogen bond length between molecules adsorbed on surfaces has been explained by surface adsorption and a commensurate configuration, which can cause a stretching of the hydrogen bonds and therefore a change in energy [45,46].

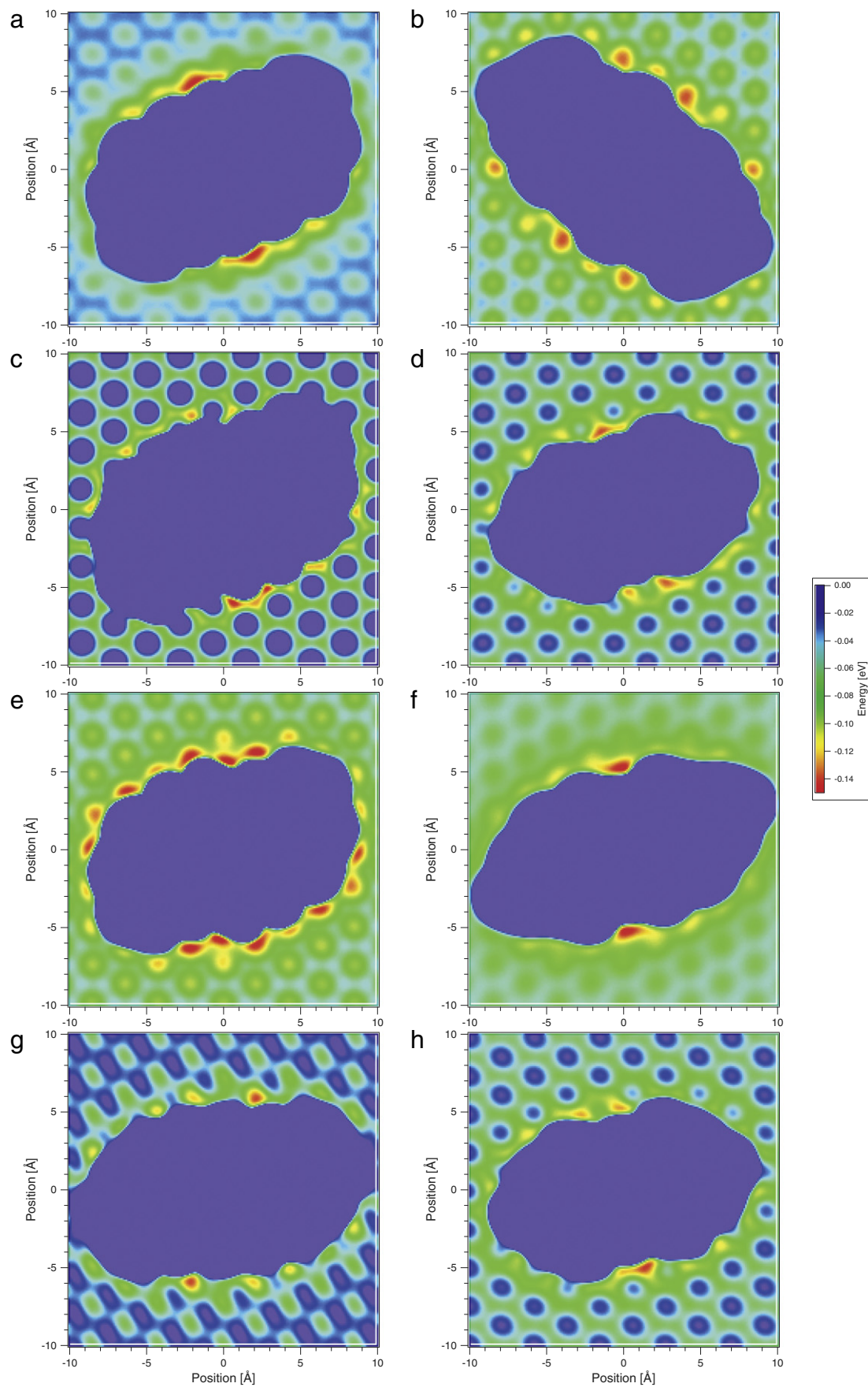
Overall, both force field parameter sets and all surface configurations lead to qualitatively and quantitatively excellent agreement with the experimental results of dimer formation. The calculations confirm the involvement of the amino and carboxyl groups in the interactions between individual methionine molecules in anti-parallel configuration for three aforementioned situations (AMBER3: SG-Z and DGH-NI, MM+: DG-Z). The width of a molecular row of 18 Å could be confirmed with these calculated configurations.

### 3.3. Parallel configuration

The analysis of the inter-molecular configurations where two methionine molecules are parallel is mimicking the molecules along the molecular rows. Similar to the previous anti-parallel case, we kept one molecule stationary, moved the second molecule (in this case oriented the same way as the stationary one) on a 20 Å × 20 Å grid in 0.1 Å increments, and produced energy maps as can be seen in Fig. 7 for AMBER 3, and in Fig. 9 for MM+. From these maps, we deduced the inter-molecular bonding configurations as seen in Figs. 8 and 10, respectively. The binding energies are summarized in Table 3. Additionally, in this configuration, we have tabulated the inter-molecular distances to compare it to previous experimental results (see Table 4).

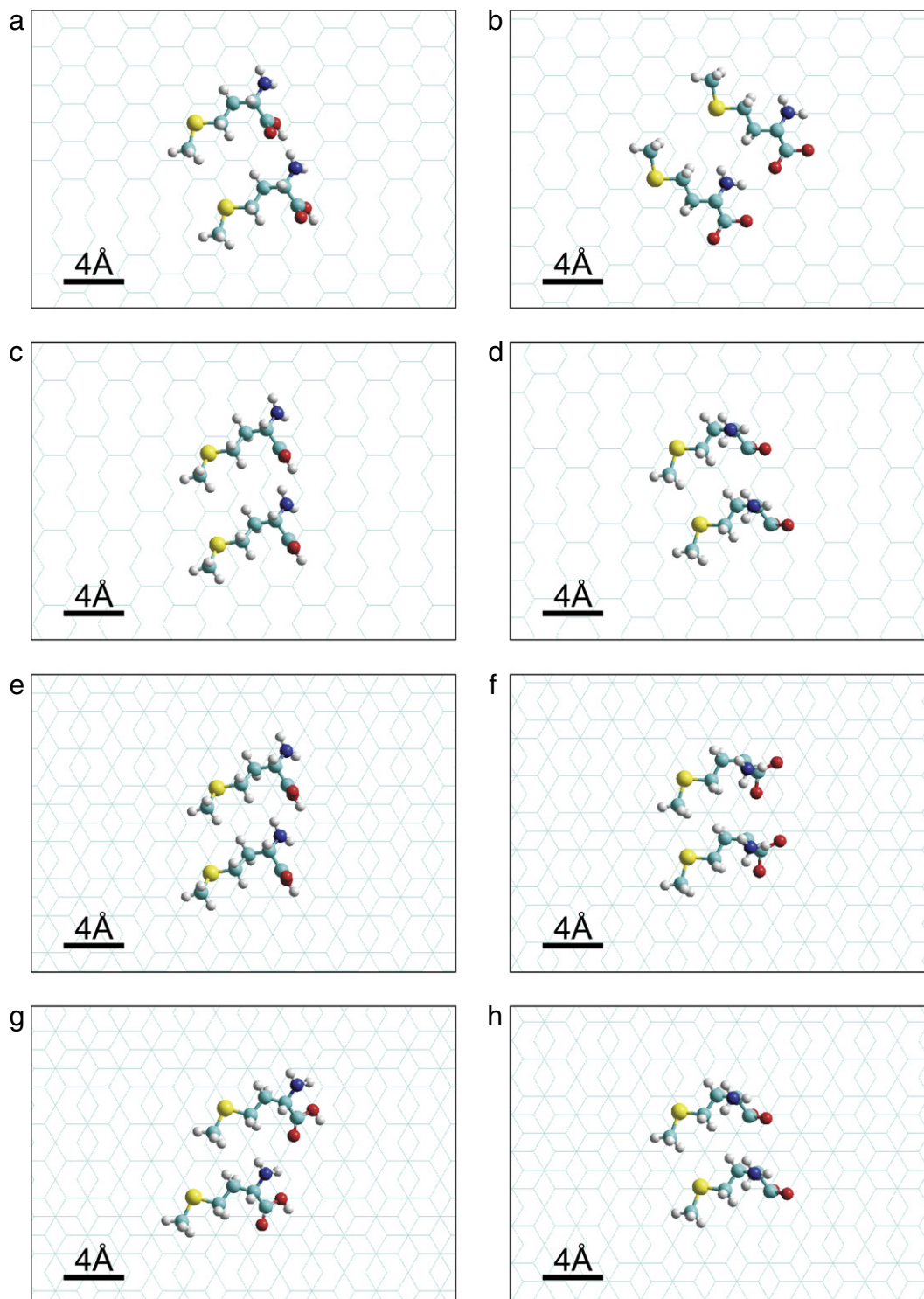
The most striking feature of this analysis is that the energetically-most favorable configuration in all cases is the situation where two molecules are positioned side-by-side. This feature had been deduced from our previous experimental finding due to the fact that the methionine rows have always the same width of two molecules which could not be accomplished if two parallel molecules would not be positioned next to each other in their lowest energy configuration [27]. In this parallel configuration, there are multiple binding possibilities between neighboring molecules by the means of hydrogen bonding. However, only two of the 16 situations investigated show hydrogen bonds at the lowest energy configurations. These are the two molecular configurations (non-ionic and zwitterionic) when using AMBER3 and a single graphene sheet (SG-NI and SG-Z). In these situations, the hydrogen bonds occur between the amino group of one molecule and the carboxyl group of a neighboring molecule. No hydrogen bonding could be found between the side chains of neighboring molecules. For all other configurations the distance between suitable atoms in neighboring molecules is not conducive to establish any hydrogen bonds according to HyperChem. As mentioned in the section about the anti-parallel configuration, a stretching of hydrogen bonds between adsorbed molecules is possible, but cannot be confirmed in this study.

Comparing the spacing between neighboring molecules (see Table 4), the average is 6.0 Å with a standard deviation of 0.5 Å. The individual values are highly correlated with the initial adsorption geometry of the methionine molecule, and a general trend regarding molecular configuration, surface, or force field cannot be deduced. This intermolecular spacing is strongly dependent on the surface as has



**Fig. 7.** Energy maps for parallel molecules using the AMBER 3 parameter set. The figures correspond to the four surface configurations (SG, SGH, DG, and DGH) with the two molecular states (non-ionic and zwitterionic) a) SG non-ionic, b) SG zwitterionic, c) SGH non-ionic, d) SGH zwitterionic, e) DG non-ionic, f) DG zwitterionic, g) DGH non-ionic, and h) DGH zwitterionic.



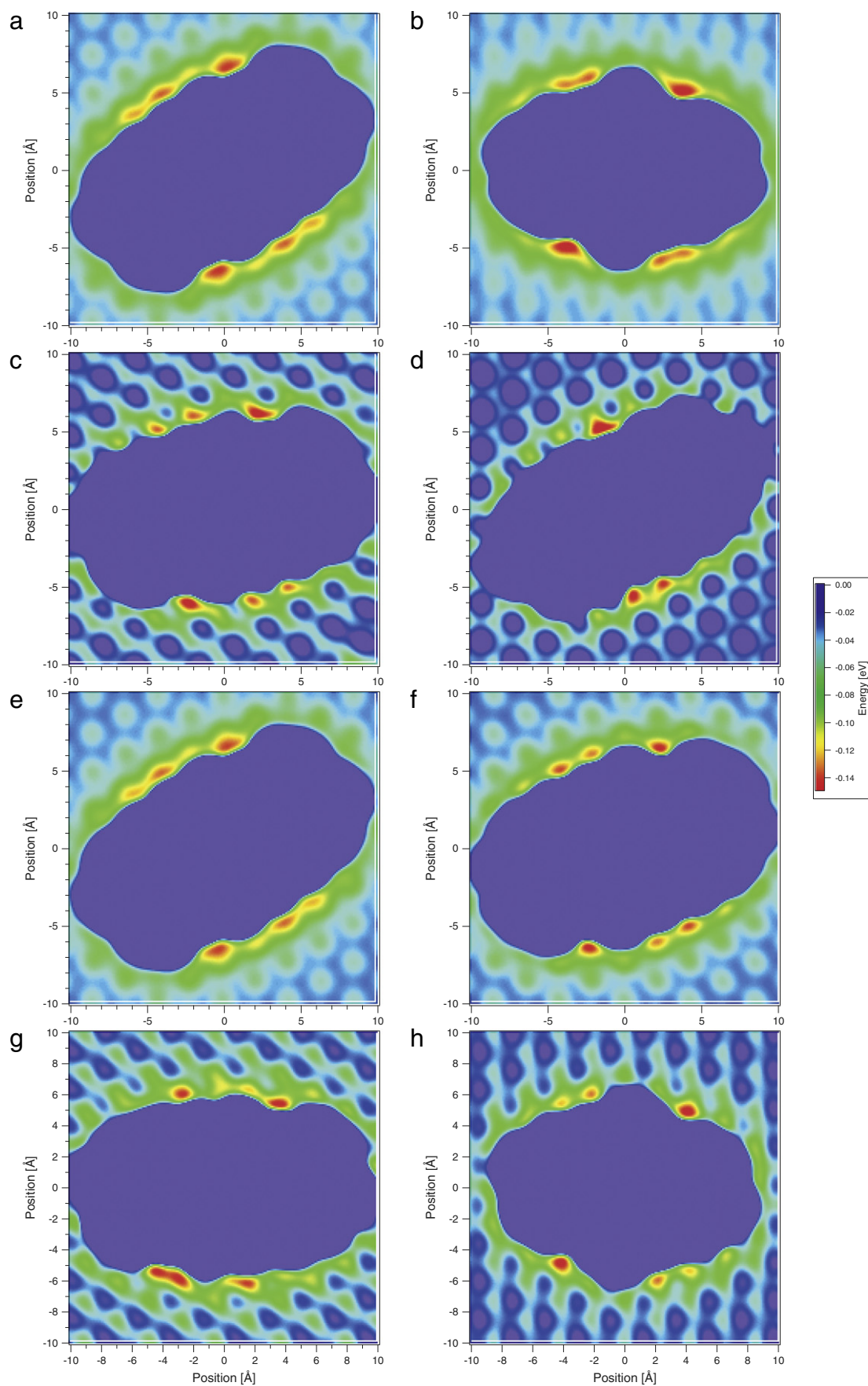


**Fig. 8.** Optimized configurations for parallel molecules using the AMBER 3 parameter set deduced from the corresponding energy maps in Fig. 7. The figures correspond to the four surface configurations (SG, SGH, DG, and DGH) with the two molecular states (non-ionic and zwitterionic) a) SG non-ionic, b) SG zwitterionic, c) SGH non-ionic, d) SGH zwitterionic, e) DG non-ionic, f) DG zwitterionic, g) DGH non-ionic, and h) DGH zwitterionic.

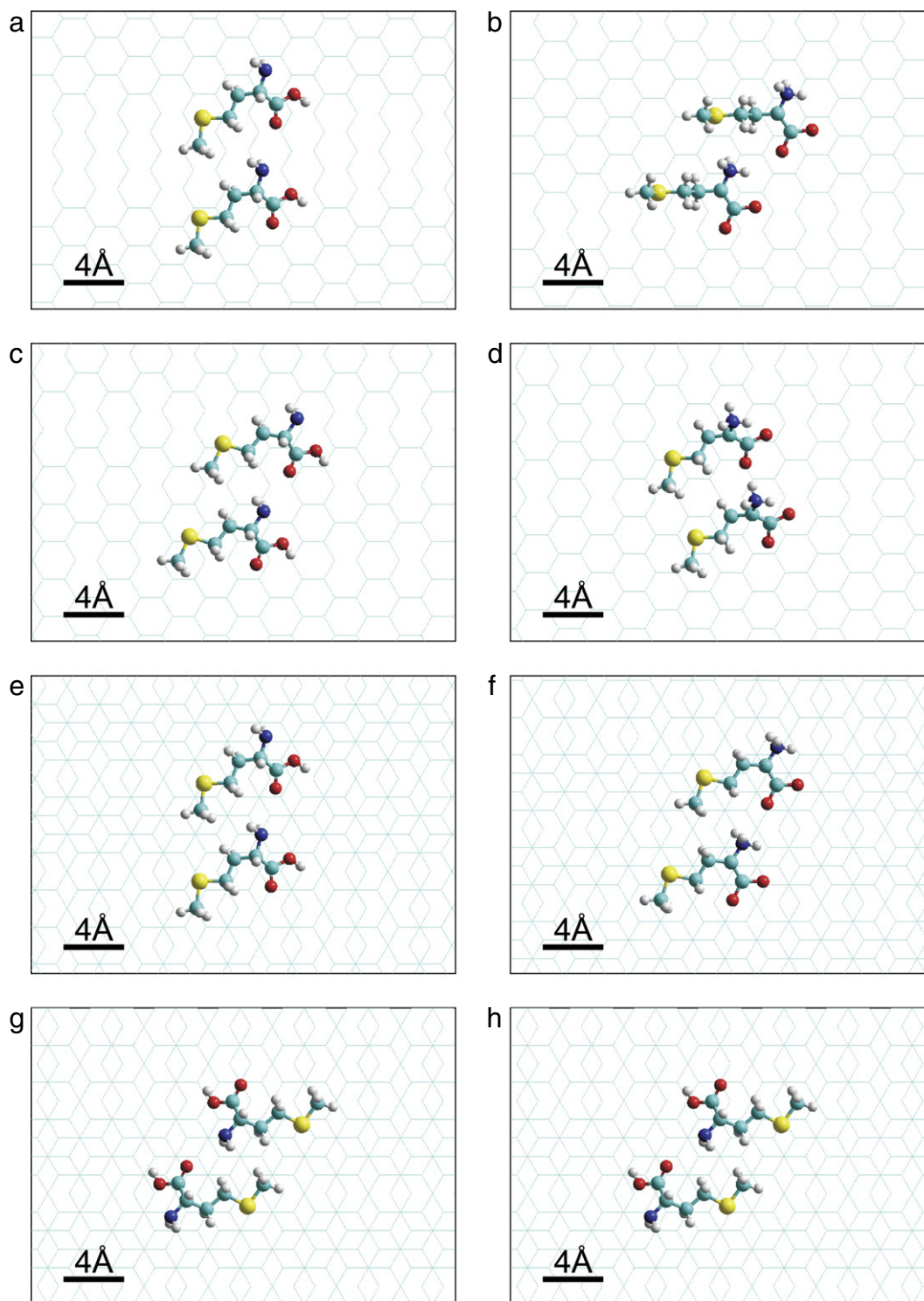
been shown in experimental studies of methionine on graphite (8.4 Å) or methionine on Ag(111) with a separation of 5.4 Å [27,37]. In our case, a 40% higher spacing was expected from the experiments, so the full effect of commensurability of methionine and graphite has not been accounted for in this study.

The parallel configuration calculations confirmed that two methionine molecules prefer to adsorb side-by-side. This finding was expected

due to the fact of experimentally found methionine rows of constant width which can only be understood if the carboxyl and amino sides face each other or the side chains face each other, but not with mixed configurations. The calculations confirm that mixed configurations are indeed energetically not favorable. The intermolecular distances are slightly off from experimental results most likely due to the fact of missing surface commensurability of these molecules in the calculations.



**Fig. 9.** Energy maps for parallel molecules using the MM+ parameter set. The figures correspond to the four surface configurations (SG, SGH, DG, and DGH) with the two molecular states (non-ionic and zwitterionic) a) SG non-ionic, b) SG zwitterionic, c) SGH non-ionic, d) SGH zwitterionic, e) DG non-ionic, f) DG zwitterionic, g) DGH non-ionic, and h) DGH zwitterionic.



**Fig. 10.** Optimized configurations for parallel molecules using the MM+ parameter set deduced from the corresponding energy maps in Fig. 9. The figures correspond to the four surface configurations (SG, SGH, DG, and DGH) with the two molecular states (non-ionic and zwitterionic) a) SG non-ionic, b) SG zwitterionic, c) SGH non-ionic, d) SGH zwitterionic, e) DG non-ionic, f) DG zwitterionic, g) DGH non-ionic, and h) DGH zwitterionic.

#### 4. Conclusion

Previous studies on amino acid interaction indicate possible hydrogen bonding mechanism between amino and carboxyl groups. Table 5 summarizes the energies and bond lengths for the situations of our study where hydrogen bonds could be established. The energies and bond lengths are consistent with previous studies [42,43]. In the anti-parallel case this binding mechanism was found for AMBER 3 and

SG-Z and DGH-NI, and for MM+ and DG-Z, in the parallel case for AMBER3 and SG-NI and SG-Z. One can see that only one of the 16 situations produces hydrogen bonds in the anti-parallel and parallel case, which is the configuration of using the AMBER3 force field with the molecule in zwitterionic form and the substrate as a single sheet of graphene (SG-Z). Therefore our conclusion is that this situation describes the experimental system the best. Since the AMBER force field was developed specifically suitable for amino acids and MM+ is a

**Table 3**

Table for binding energies of two methionine molecules in parallel configuration. The asterisks indicate established hydrogen-bonding found using HyperChem.

	Binding energies for parallel configuration [eV]							
	AMBER 3				MM +			
	SG	SGH	DG	DGH	SG	SGH	DG	DGH
Non-ionic	0.092*	0.073	0.056	0.073	0.092	0.105	0.091	0.026
Zwitterionic	0.042*	0.069	0.081	0.076	0.109	0.120	0.097	0.108

**Table 4**

Table for the inter-molecular spacing of two methionine molecules in parallel configuration.

	Inter-molecular spacing for parallel configuration [Å]							
	AMBER 3				MM +			
	SG	SGH	DG	DGH	SG	SGH	DG	DGH
Non-ionic	5.85	6.03	5.61	6.26	6.50	6.48	6.51	6.49
Zwitterionic	7.00	5.22	5.20	5.19	6.22	5.41	6.80	6.39

**Table 5**

Table of binding energies and hydrogen bond lengths for the situations of established hydrogen bonds between two methionine molecules. SG-Z: single graphene layer with methionine in zwitterionic form; DGH-NI: double graphite substrate with hydrogen termination and methionine in non-ionic form; DG-Z: double graphite substrate with methionine in zwitterionic form; SG-NI: single graphene layer with methionine in non-ionic form.

	Established hydrogen bonds between two methionine molecules				
	Anti-parallel		Parallel		
	AMBER 3		MM +	AMBER 3	
	SG-Z	DGH-NI	DG-Z	SG-NI	SG-Z
Energy [eV]	0.043	0.074	0.039	0.092	0.042
Bond length [Å]	2.02	2.16	2.89	2.07	2.63

more general force field, it comes as no surprise that AMBER3 performs better in our study. Also, it has been found that methionine is in its zwitterionic form adsorbing on other surfaces, therefore supporting our findings [37].

## 5. Summary

We studied the adsorption of methionine on graphite using two common force field parameter sets with the molecule in its non-ionic and zwitterionic configurations. As substrates, we modeled the graphite with four different approaches, as single sheet, as a hydrogen-terminated single sheet, as a double layer, and as a hydrogen-terminated double layer. This study shows that molecular mechanics calculations can confirm the experimental results of molecular rows made out of dimers very well. The geometry of the experimental finding is reproduced accordingly. Calculated binding energies between individual molecules and the substrate as well as between the two molecules were found to be in good agreement with previous studies using DFT calculations [40,42,43]. Overall, the experimental finding could best be described by using the force field AMBER3 with methionine in its zwitterionic form adsorbed on a single sheet of graphene. Additional to the geometric agreement of calculation and experiment, we found that the binding between neighboring methionine molecules is facilitated through hydrogen bonds between the carboxyl and amino groups. Furthermore, the calculations suggest that methionine is adsorbed in its zwitterionic state. In a follow-up study it would be interesting to see if this force field and substrate configuration can be used to model or predict experimental results for other amino acids adsorbed on graphite.

The present study shows that experimental results can be confirmed using computational inexpensive methods of molecular mechanics

calculations instead of higher-order computations such as Density Functional Theory. These DFT calculations are often not available to experimentalists (like our group) or are too time-intensive or too reliant on large computational capacity. Nevertheless, in a future study a comparison with results from DFT is desirable in order to test the robustness of our calculations.

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