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Theoretical studies on force titration of amino-group-terminated self-assembled monolayers

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Abstract

The structures of (3-aminopropyl)triethoxysilane (APTES), 4-aminothiophenol (4-ATP) and 4-mercaptopyridine (4-MP) self-assembled monolayers (SAMs) are studied by quantum mechanics in order to explain the force titration curves of these amino-group-terminated SAMs. The surface charges and electrostatic surface potentials derived from the ab initio calculations can give satisfactory explanations for the experimental results. We also propose a simple model to simulate the force titration process. The force between the tip and sample can be estimated according to the slope coefficient of the curve of energy versus distance. This curve can lead to a better understanding of the force titration curves of amino-group-terminated SAMs.

Keywords: Chemical force microscopy; Force titration; Ab initio calculation; Genetic algorithm

1. Introduction

Chemical force microscopy (CFM) [1], which uses a chemically modified tip as the force probe, is a new variant of atomic force microscopy (AFM) [2]. With CFM, one can investigate intermolecular interactions on the nanometre scale and map a chemically inhomogeneous surface. It has demonstrated great capabilities in chemical specification and identification. Force titration, a new titration concept recently proposed by us [3, 4] and Lieber et al. [5] independently, is a novel use of CFM for characterizing the dissociation properties of surface functional groups like COOH, NH₂, etc. We have studied COOH- [3, 4], NH₂- [6, 7] and pyridyl- [8] terminated self-assembled monolayers (SAMs) by means of this technique. [3, 4, 6-8] give details of the force titration experiments. Fig. 1(a) shows the typical force titration behavior of (3-aminopropyl)triethoxysilane (APTES) SAMs (surface functional group is NH₂) on silicon using an OH-terminated tip. It shows a repulsive force at low pH and an attractive force at high pH. When using an APTES SAM-modified tip and surface to measure the adhesion force between them, the same shape of force titration curves was obtained by both us and Lieber et al. [5]. Protonation of the surface amino groups results in a repulsive

force while the dominant attractive force arises from the van der Waals' interaction between the tip and the sample when both interaction groups are neutral. However, for the case of 4-aminothiophenol (4-ATP) SAMs (surface functional group is NH_2) on gold, the force titration curve obtained with a 4-ATP SAM-modified tip is more complicated (see Fig. 1(b)) [7]. There is an attractive force at low pH although the 4-ATP molecules are protonated, while there is a repulsive force at high pH value although the 4-ATP molecules are in neutral form. Results for 4-mercaptopyridine (4-MP) SAMs (where the surface functional group is a pyridyl group) are similar to those for 4-ATP SAMs (see Fig. 1(c)) [8].

In order to explain the phenomena mentioned above, *ab initio* calculations were carried out to clarify the electronic structures of the APTES, 4-ATP and 4-MP molecules, and to determine the Mulliken charges and the electrostatic surface potentials (ESPs). A simple model to simulate the force titration process is also proposed. The energy versus distance profile between the tip and sample can be obtained from the model. The slope coefficient of the curve corresponds to the interaction force between the probe tip and the sample.

In this paper, in order to simplify the calculations, we do not explain the force titration curve of APTES SAMs obtained with an OH-terminated tip (Fig. 1(a)). But we give a satisfactory explanation for the force titration curve of APTES SAMs obtained with an APTES SAM-modified tip, whose variation is just like that of Fig. 1(a). The two adhesive forces are also of the same order of magnitude.

2. Method

Electronic structures of both the neutral and protonated forms of APTES, 4-ATP and 4-MP SAM molecules (Fig. 2) were calculated by using the GAUSSIAN 94 software package [9]. The basis set in HF minimization was LANL1DZ, and both the Mulliken charges and the ESPs were obtained. The total charge on the nitrogen atom and its bonded hydrogen atoms can be considered as the surface charge of the SAM molecule. The surface charge plays the main role in determining the electrostatic force between the molecules on the tip and the sample, and can be used to interpret the force titration curve. For each molecule, the ESP was calculated in a plane perpendicular to the molecular axis at which the distance from the center of the plane to the nitrogen atom is 1.5 Å.

In order to simulate the process of force titration, the molecules on the tip and sample were rotated and translated to make the two molecules lie along the Z-axis. The nitrogen atoms were placed at the origin of the coordinate axis and the barycentrics of the two molecules placed separately on the two half axes. Then the two molecules were separated gradually over a distance range from 2 to 30 Å in a stepwise manner. For each conformation, minimization was performed with the separated distance firmly retained by using a genetic algorithm [10] in order to find the global minimum. The variables are twist angles. Then the total energy of the system was evaluated for each global conformation by using the MM3 force field. The total energy includes three parts, which are E_{tip} , E_{sample} and E_{inter} .

$$E_{\text{total}} = E_{\text{tip}} + E_{\text{sample}} + E_{\text{inter}} \quad (1)$$

$$E_{\text{tip}} = E_{\text{vdw}} + E_{\text{torsion}} + E_{\text{hb}} + E_{\text{coulombic}} \quad (2)$$

$$E_{\text{sample}} = E_{\text{vdw}} + E_{\text{torsion}} + E_{\text{hb}} + E_{\text{coulombic}} \quad (3)$$

where E_{total} is the total energy, E_{tip} and E_{sample} are the energies of the tip and sample, respectively, which can be expressed separately by means of by Eqs. (2), (3). E_{vdw} , E_{torsion} , E_{hb} and $E_{\text{coulombic}}$ stand for the van der Waals' energy, torsional energy, hydrogen-bond energy and electrostatic energy, respectively. E_{inter} is the interaction energy between the tip and sample, which plays the main role in determining the shape and of the force titration curve. Other energetic terms are omitted for simplicity.

The ionic strength of the buffer solution was kept at 0.01 M [5-8], so that the dielectric constant in our calculation was replaced by that of water, 80.

3. Results and discussion

3.1. Surface charge of SAM molecule

The surface charges obtained from ab initio calculations of APTES, 4-ATP and 4-MP molecules are $0.606e$, $0.607e$ and $0.035e$ at low pH (protonated form), and $-0.090e$, $-0.298e$ and $-0.909e$ (e is electronic charge) at high pH (neutral form), respectively. So, for APTES SAMs, when the sample approaches the tip there is a repulsive force at low pH and an attractive force at high pH. But for 4-MP SAMs, there is an attractive force at low pH and a repulsive force at high pH. The calculated surface charges of both protonated and neutral forms of APTES SAMs are consistent with the experimental results. As for 4-MP, although it is expected to be neutral at high pH, the polarization arising from the conjugation between the nitrogen atom and the pyridine ring results in a negative surface charge. At low pH, although the nitrogen atom of 4-MP SAM is protonated, the good conjugation disperses the positive charge effectively to the pyridine ring. As a result, the surface charge is only $0.035e$. However, similar reasoning relying only on use of surface charges fails to account for the force titration curve of 4-ATP SAMs.

3.2. ESP

Fig. 3 shows the electrostatic surface potentials in the plane 1.5 \AA away from the nitrogen atoms. The ESP can accurately evaluate the repulsive force between the molecules on the tip and the sample. According to our model, the larger the ESP value, the larger the repulsive force and the larger the area distributed, the larger the repulsive force. For APTES, the largest values are $18.1 e\text{\AA}^{-1}$ in neutral form (Fig. 3(a)) and $11.79 e\text{\AA}^{-1}$ in protonated form (Fig. 2(b)). But the protonated form has a broader area distributed, and so the repulsive force is larger than that of the neutral form. For 4-ATP, although the protonated form has more area distributed,

the ESP is much smaller than that of the neutral form [the largest values are $18.05 e\text{\AA}^{-1}$ in the neutral form (Fig. 3(c)) and $8.809 e\text{\AA}^{-1}$ in the protonated form (Fig. 3(d)), respectively]. So, the neutral form should contribute to a larger repulsive force than the protonated form. For 4-MP, the neutral form (Fig. 3(e)) not only has the larger ESP values, but also more area distributed compared with the protonated form (Fig. 3(f)). Consequently this results in a larger repulsive force than for the protonated form.

3.3. Energy versus distance

Fig. 4 shows the energy versus distance profile between two SAM molecules. In the curve for the APTES SAMs (Fig. 4(a)), although the protonated form has lower interaction energy, the neutral form has a deeper potential well than the protonated form. The deeper the potential well, the larger the adhesive force. For 4-ATP (Fig. 4(b)) and 4-MP SAMs (Fig. 4(c)), both the protonated forms have deeper potential wells and lower total energies. So the protonated forms contribute to larger forces. We can estimate the adhesive forces from the curves because the slope coefficient of the curves represents the force. For example, the curve of 4-MP SAMs (protonated form) has a slope coefficient of $1.8 (4.5/2.5 \times 1.8) \text{ kJ mol}^{-1} \text{\AA}^{-1}$. By using an estimation of 10 molecules on the tip, the total force can be calculated to be $3 \times 10^{-10} \text{ N}$, which is the same order of magnitude as the force measured experimentally. Table 1 lists the slope coefficients and estimated forces for all three systems. Most of the estimated forces are of the same order of magnitude as the experimentally measured ones, except for the neutral form of APTES SAM. The reason is that, for APTES SAM, there are more molecules on the tip.

4. Conclusion

In this paper, three theoretical models are proposed to explain the force titration curves of amino- group-terminated SAMs. The simple surface charge model can qualitatively explain the force titration curves of APTES and 4-MP SAMs; however, it fails to explain the force titration curve of 4-ATP. The ESP model can qualitatively explain the adhesive interactions for all three systems.

The third model provides a reasonable approach to simulate the force titration process. From the profile of the energy versus separation distance, we can estimate the adhesive force. Although this model can also qualitatively explain the adhesive interaction of all three systems, this model is too simple to calculate the adhesive force accurately. A more complicated model, using molecular dynamics to simulate the process of force titration and considering the effect of the solution, is under investigation.

Acknowledgements

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System name	Form	Slope coefficient (kJ mol ⁻¹ Å ⁻¹)	Estimated force (10 ⁻⁹ N)	Experimental force (10 ⁻⁹ N)
APTES SAMs	neutral form	0.8	0.15	8.0 ^a
	protonated form	0.5	0.1	0.1
4-ATP SAMs	neutral form	0.8	0.15	0.7
	protonated	0.5	0.1	0.1
4-MP SAMs	neutral form	0.6	0.1	0.01
	protonated form	1.8	0.3	0.4

^aFor APTES SAMs, the experimental forces in this table are obtained with an OH-terminated tip. However, the forces obtained with an

Table 1.

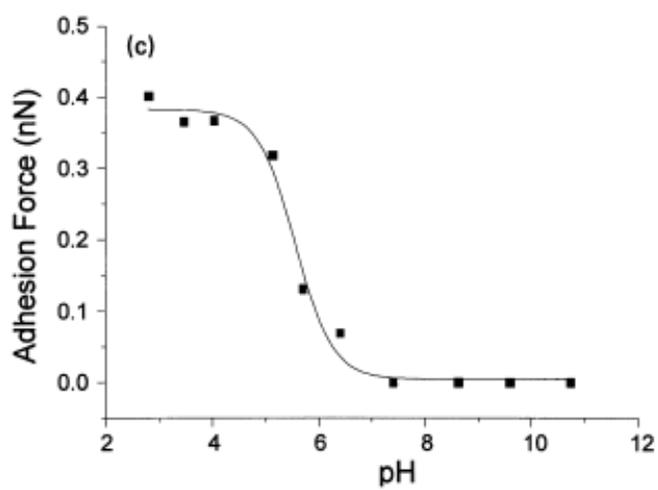
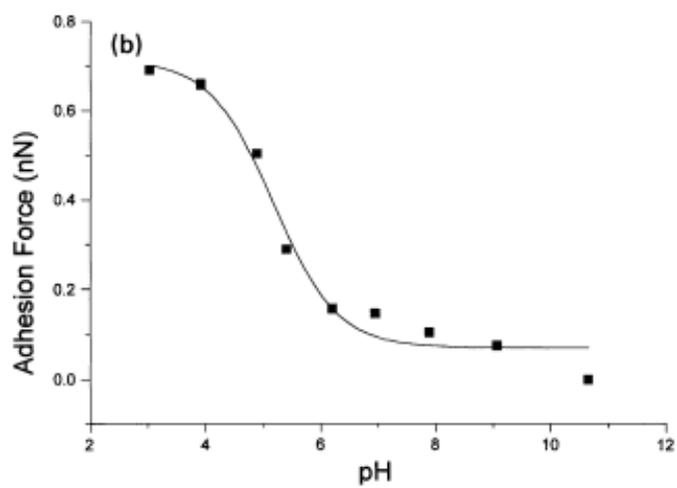
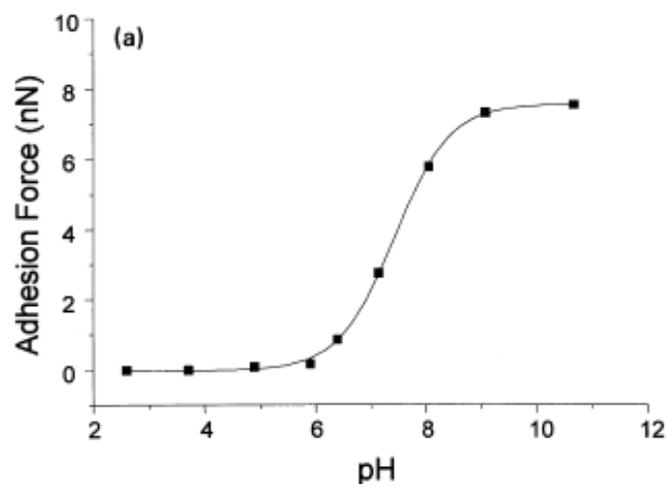


Fig. 1.

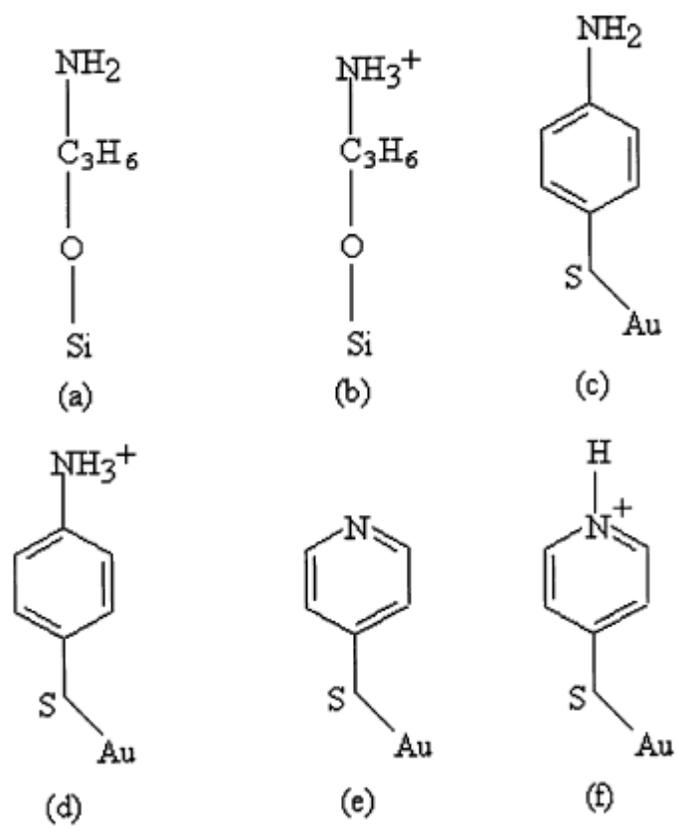


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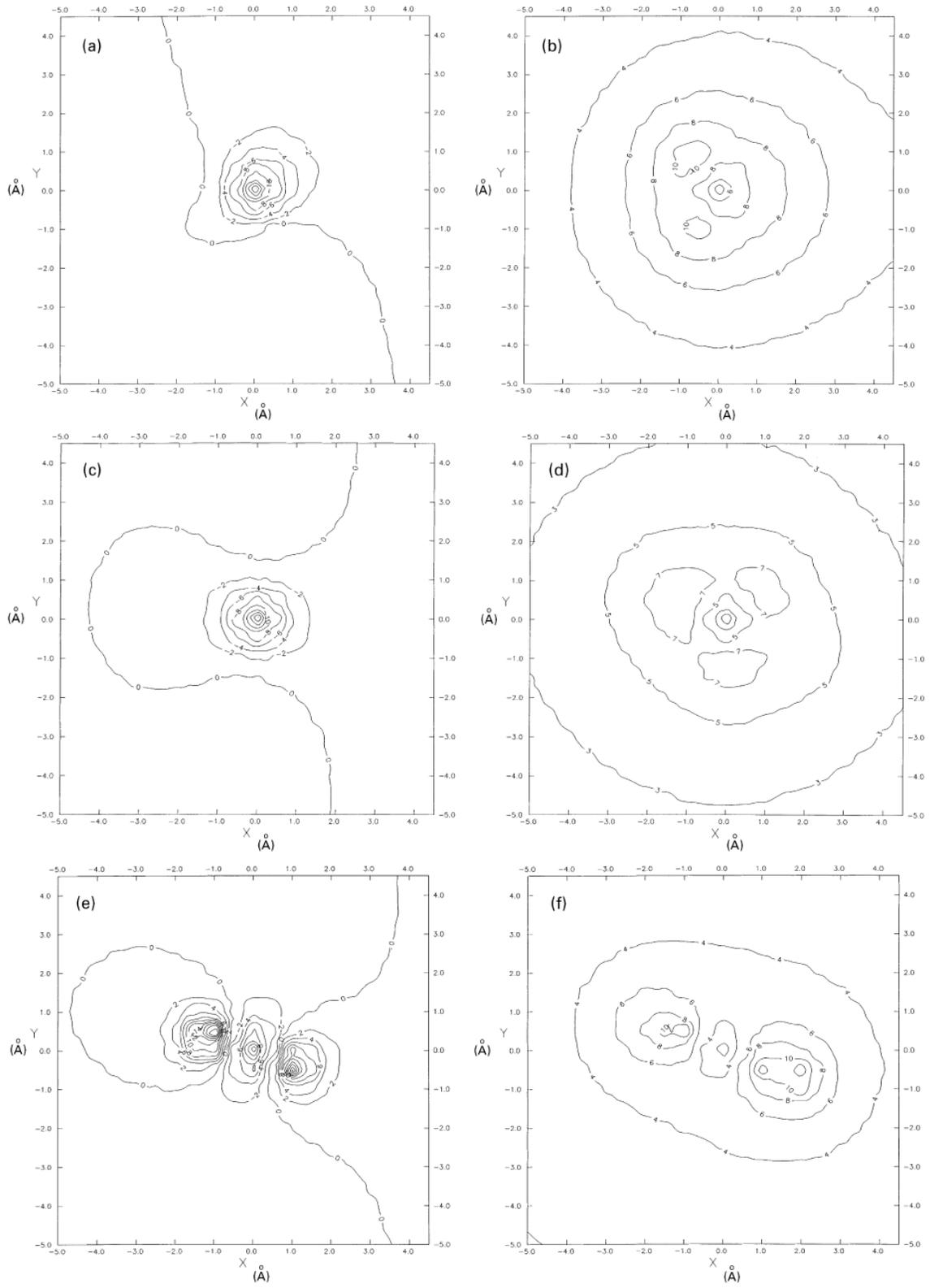
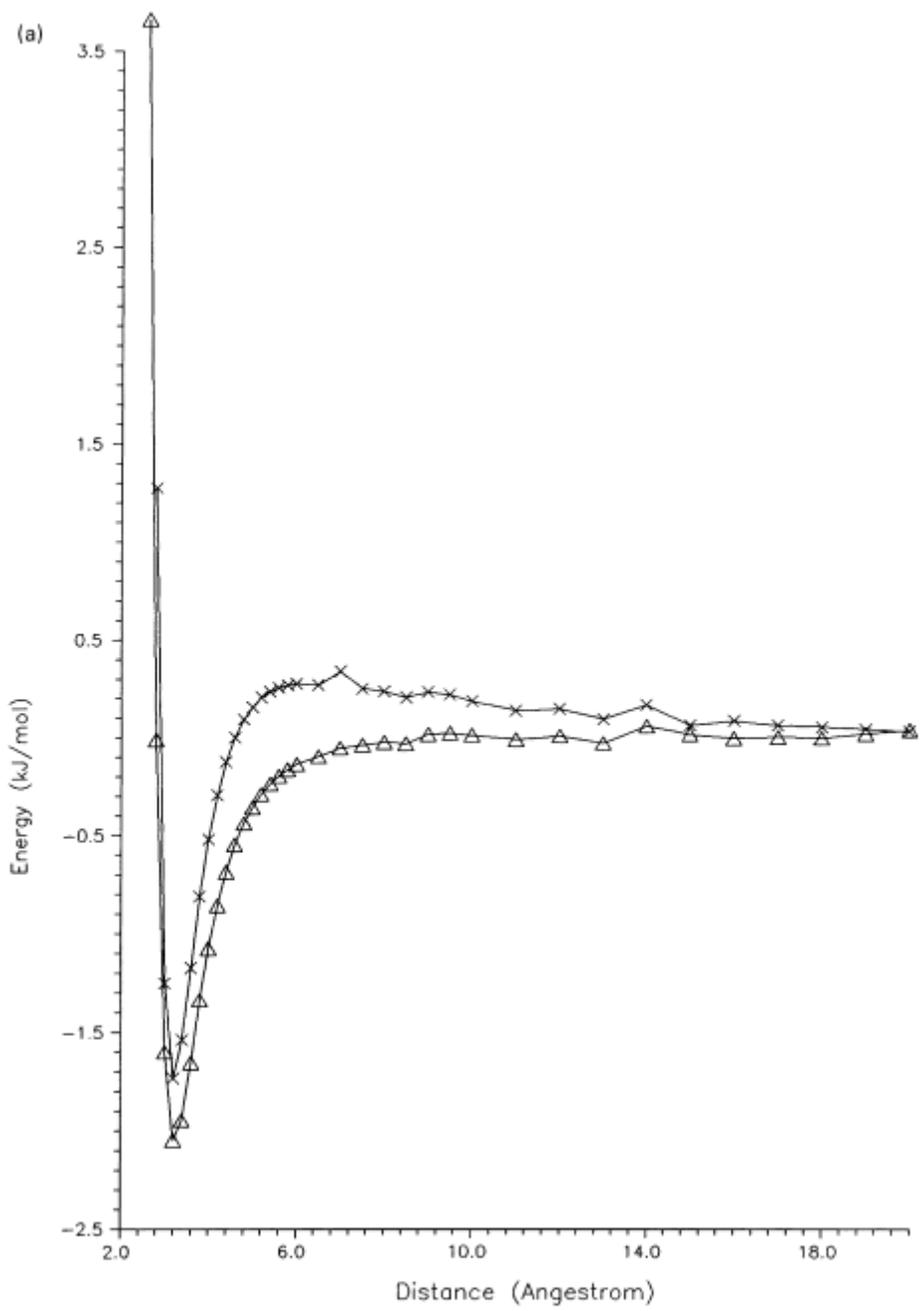
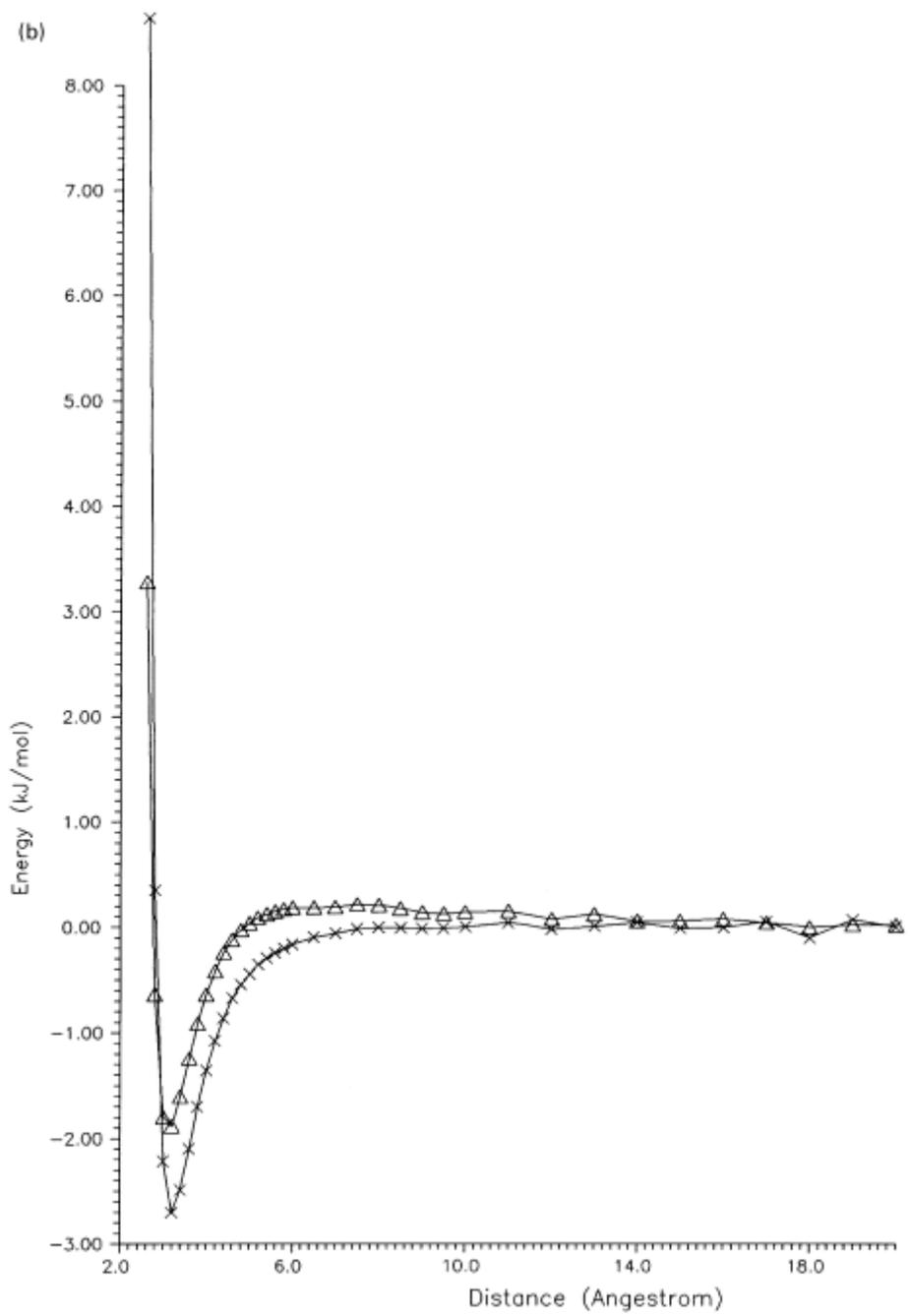


Fig. 3.





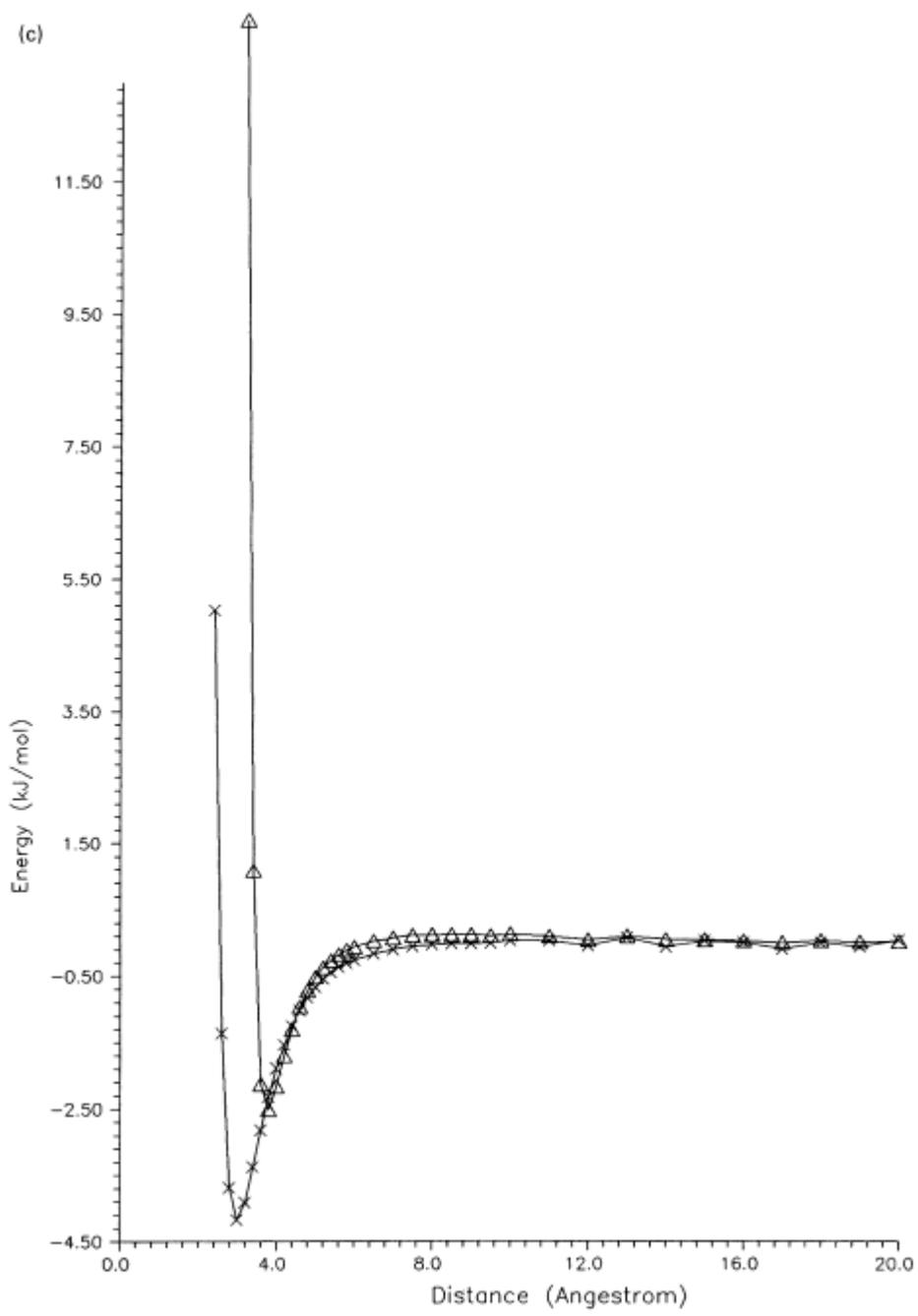


Fig. 4.