Solvent effect on the crystal morphology of 2,6-diamino-3,5-dinitropyridine-1-oxide: A molecular dynamics simulation study

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ABSTRACT

The attachment energy (AE) calculations were performed to predict the growth morphology of 2,6-diamino-3,5-dinitropyridine-1-oxide (ANPyO) in vacuum. The molecular dynamics (MD) method was applied to simulate the interaction of trifluoroacetic acid solvent with the habit faces and the corrected AE model was adopted to predict the growth habit of ANPyO in the solvent. The results indicate that the growth morphology of ANPyO in vacuum is dominated by $(1\,1\,0)$, $(1\,0\,0)$, $(1\,0\,-1)$ and $(1\,1\,-2)$ faces. The corrected AE energies change in the order of $(1\,1\,0) > (1\,0\,-1) > (1\,1\,-2) > (1\,0\,0)$, which causes the crystal morphology to become very close to a flake in trifluoroacetic acid solvent and accords well with the results obtained from experiments. The radial distribution function analysis shows that the solvent molecules adsorb on the ANPyO faces mainly via the solvent–crystal face interactions of hydrogen bonds, Coulomb and Van der Waals forces. In addition to the above results, the analysis of diffusion coefficient of trifluoroacetic acid molecules on the crystal growth faces shows that the growth habit is also affected by the diffusion capacity of trifluoroacetic acid molecules. These suggestions may be useful for the formulation design of ANPyO.

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1. Introduction

Explosives are widely used for both military and civilian applications. In order to reduce the unexpected accidents due to environmental stimuli, such as rough handling, fragment impact and thermal cook-off, there is strong requirement for explosives having both good thermal stability impact and shock insensitivity and better explosive performance in modern ordnance. The sensitivities of explosive versus external stimuli are affected greatly by crystal morphology including crystal shape and size. The growth habit of explosive is determined by both the internal structure factors and the external conditions. A great number of researches have been carried out experimentally and theoretically, and solvent has been found to be one of the most important external factors determining the morphology [1–3].

Experimental approaches and computational simulations are the main methods which are used to research the crystal morphology. However, the former are expensive and time consuming, and,

especially, the experimental results cannot provide enough microscopic details about how the solvents interact with the explosive crystal. In contrast, computational models can be used to obtain more detailed insights into the effect of solvent on the morphology of explosives and the interaction of solvent with explosives. Among the many computational methods, molecular dynamics (MD) simulation is a powerful approach for investigating the mechanism of crystallization, because it could give us atomic-scale information. And many studies on crystal growth simulation using the MD method have been reported [4–7].

In recent years, the studies on 2,6-diamino-3,5-dinitropyridine-1-oxide (ANPyO) have become one of the hotspots in insensitive explosive researches. The structure of ANPyO is similar to that of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), making it potential insensitive high energy explosive candidate with heat resistance, low mechanical and thermal sensitivity [8]. Ritter and Licht reported the synthesis of ANPyO by the nitration of 2,6-diaminopyridine followed by oxidation using H_2O_2 in acetic acid [9]. However, the method has the disadvantages of low yields, high impurity contents and high danger coefficient. Some researchers focused on the improvement of synthesis of ANPyO [10–12].

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Compared with experimental studies, few theoretical researches on ANPyO have been done [13–16]. Liu et al. performed a periodic DFT calculation of ANPyO to obtain its optimized structure, the insight into the chemical properties and the theoretical lattice energy of the crystal [13]. The work of Ju et al. was trying to investigate theoretically the structures and the binding energies of the ANPyO dimers by first-principle methods [14]. However, the studies which have been done at the molecular level before were unconcerned with the effect of solvents on the morphology of ANPyO. ANPyO possesses symmetrical molecular structure and exhibits strong chemical stability, resulting in a low solubility or insolubility in common organic solvents, therefore, the annealed solvents used for ammonium nitrate explosives are not generally suitable for ANPyO. According to the previous study [12], trifluoroacetic acid was chosen as solvent for ANPyO recrystallization in this study, and MD simulations were carried out for the first time to explore the morphology modification of ANPyO induced by solvent. In addition, we also performed the diffusion coefficients calculation of trifluoroacetic acid molecules on the habit crystal faces to probe the effect of stirring on the crystal growth of ANPyO. This provides the fundamental information on the potential morphological changes in the stage of the design of a crystallization process.

2. Theories and MD simulation details

2.1. Attachment energy model

The growth morphology algorithm is based on the attachment energy (AE) method and can predict the shape of a crystal more accurately than the BFDH method because it takes the energetics of the system into account. The AE model was proposed by Hartman and Bennema based upon period bond chain (PBC) theory [17]. The AE method attempts to simulate crystal habits as obtained under non-equilibrium growth conditions. It relates the relative growth rate of a given surface to the potential energy per unit cell gained if a new layer of material attaches to the surface in vacuum.

The attachment energy, E_{att}, is defined as the energy released on attachment of a growth slice to a growing crystal surface. E_{att} is computed as [18]:

$$E_{att} = E_{latt} - E_{slice} \qquad (1)$$

where E_{latt} is the lattice energy of the crystal, E_{slice} is the energy of a growth slice of thickness d_{hkl}. The relative growth rate in vacuum of the crystal surface, R_{hkl}, is assumed to be proportional to the absolute value of attachment energy:

$$R_{hkl} \propto \left| E_{att} \right| \qquad (2)$$

In other words, the crystal surfaces with smaller absolute value of the attachment energies grow slower and, therefore, are more morphologically important.

2.2. Simulation details

All calculations were performed using the program Materials Studio 3.0 (Accelrys Inc., USA) [19]. The initial structure of ANPyO unit cell was taken from the experiment by Hollins et al. [20], which crystallized in the monoclinic space group of $C2/c$ with five independent lattice parameters $a = 14.864$ Å, $b = 7.336$ Å, $c = 7.509$ Å, $\alpha = \gamma = 90°$, and $\beta = 111.67°$. There are two irreducible molecules in the unit cell, and the model was built with Visualizer module and the optimization of the unit cell was performed in the COMPASS force field [21].

The AE model was used to predict the crystal morphology of ANPyO in vacuum, acquiring the main stable crystal faces with different Miller indices $(h\,k\,l)$. Then, the ANPyO crystal was cleaved along the main stable faces $(1\,1\,0)$, $(1\,0\,0)$, $(1\,0\,-1)$ and $(1\,1\,-2)$, which were extended to 3D periodic superstructures of 2.253 nm × 2.486 nm × 3.633 nm, 2.201 nm × 2.253 nm × 3.460 nm, 2.934 nm × 2.792 nm × 2.915 nm, and 2.768 nm × 3.315 nm × 3.189 nm, respectively. The $(1\,1\,0)$ and $(1\,0\,0)$ super cells include 54 ANPyO molecules (1080 atoms in total) while the $(1\,0\,-1)$ and $(1\,1\,-2)$ super cells consist of 64 ANPyO molecules (1280 atoms in total). A solvent layer filled with 100 random distributed trifluoroacetic acid molecules was built with the layer density set to be 1.535 g/cm^3 by the Amorphous Cell tool. Geometry optimization, followed by MD simulations (100 ps with time step 1 fs at 288 K, using the Andersen thermostat [22]) for the solvent layer was done to make trifluoroacetic acid molecules uniformly distribute in the solvent layer.

In order to investigate the effect of solvent on the crystal morphology, the interfacial model was employed, which is composed of an ANPyO crystal layer and a trifluoroacetic acid solvent layer. In the study, the solvent layer was adsorbed on the $(h\,k\,l)$ crystal face along c axis. A vacuum slab thickness of 20 Å was built above the solvent layer to eliminate the effect of additional free boundaries on the structure. The crystal layer was constrained along a, b, and c axis directions during the MD simulation process. The schematic view of the starting conformations for ANPyO face–trifluoroacetic acid solvent interfacial models is shown in Fig. 1.

The energy minimization for the interfacial model was carried out using a molecular mechanic method (MM) before the MD simulations, which were carried out using the Discover module in Materials Studio along with the use of COMPASS force field [21]. The COMPASS force field is a powerful *ab initio* force field which has been parameterized and validated using condensed phase properties, in addition to various *ab initio* and empirical data for molecules in isolation. Consequently, this force field enables the accurate and simultaneous prediction of structural, conformational, vibrational, and thermophysical properties for a broad range of molecules in isolation or condensed phases under a wide range of conditions of temperature and pressure [23,24].

All MD simulations were carried out at 288 K in the NVT ensemble [25]. The coupling to the heating bath was carried out using the Nose thermostat [26]. MD simulation was started by taking initial velocities from a Maxwell distribution. The solution to Newton's Laws of Motion was based on assumptions as follows: periodic boundary condition and time average is equivalent to the ensemble average. Integral summation was carried out with a Verlet velocity integrator [27]. The nonbonding interactions in each system, as well as the Van der Waals force and electrostatic force were computed using an atom-based summation method and the Ewald summation method, respectively, with a cutoff radius of 0.95 nm (spline width: 0.10 nm; buffer width: 0.05 nm). When any interaction pair moves more than half this distance, the neighbor list is recreated. Tail corrections were used to calculate the potential energy contributions from interactions between atoms separated by distances longer than the nonbonding cutoff. The time step was set to 1 fs, equilibration stage ran for 200,000 fs, and then the production stage ran for 300,000 fs, the data were collected for subsequent analysis at the same time. The trajectory was recorded every 500 fs.

3. Results and discussion

3.1. ANPyO crystal morphology in vacuum

Fig. 2 shows the crystal morphology of ANPyO in vacuum calculated by the AE model using Forcefield assigned charges and the Compass force field, and Table 1 lists the relevant parameters of the main crystal habit faces of ANPyO.
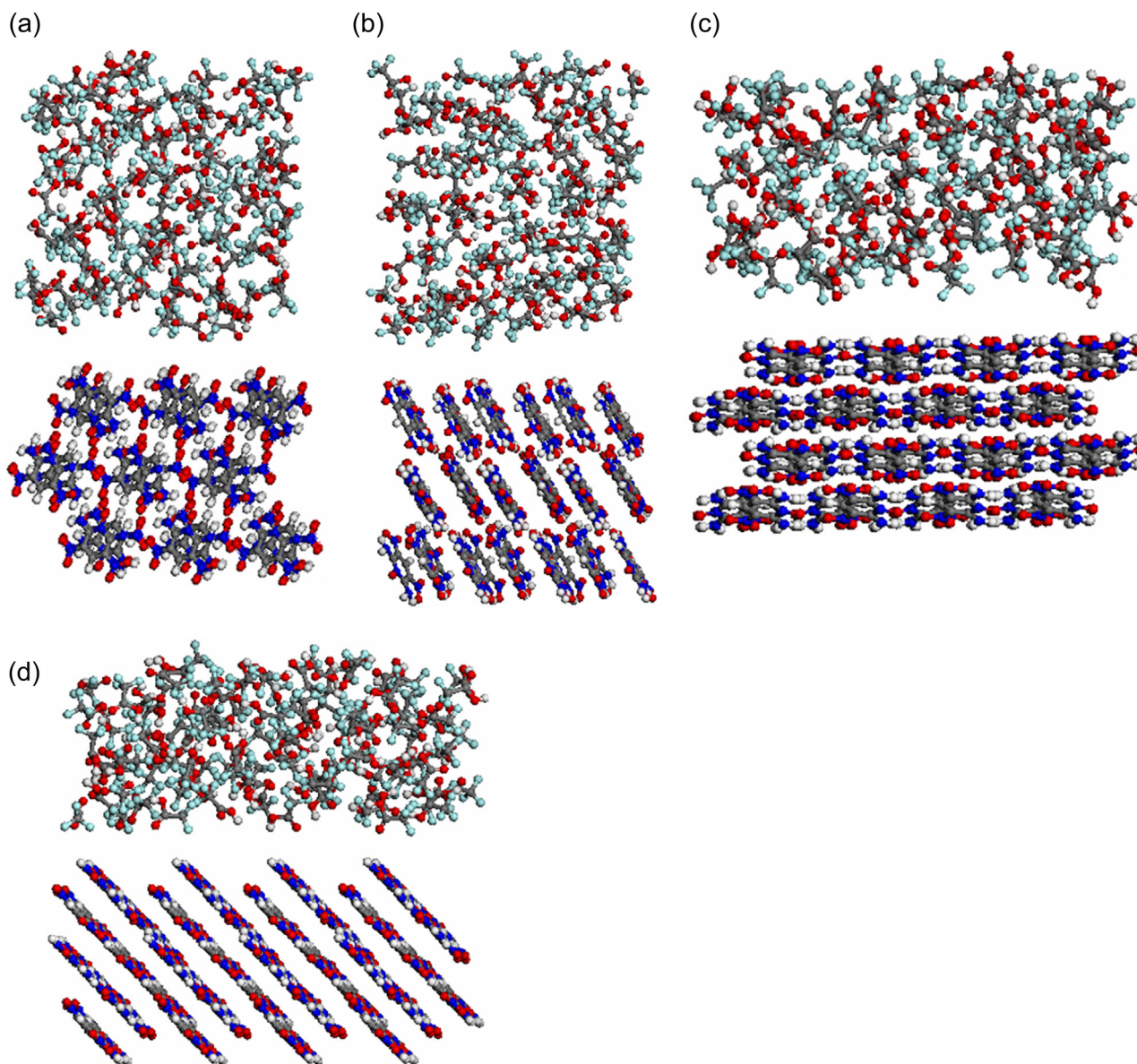
(a)

(b)

(c)

(d)

Fig. 1. The schematic view of the starting conformations for ANPyO face–trifluoroacetic acid solvent interfacial model. (a), (b), (c) and (d) correspond to (1 1 0), (1 0 0), (1 0 −1) and (1 1 −2) faces, respectively.

From Fig. 2, it can be seen that the prediction of the crystal shape according to the AE model results in a shape similar to the ellipsoid and the ratio between the longest and the shortest diameter of the habit is 2.349. The morphology of ANPyO crystal in vacuum is dominated by the four faces of (1 1 0), (1 0 0), (1 0 −1) and (1 1 −2).

Table 1 demonstrates that there are four main stable faces existing in ANPyO crystal. The total habit face area of (1 1 0) face is above 40% and (1 1 0) face has the largest interplanar

distance (d_{110} = 6.91 Å) which indicating that it is morphologically the most important face of ANPyO crystal. The attachment energy of (1 1 0) face is calculated to be −16.62 kcal/mol comprised of the Van der Waals force (−13.43 kcal/mol) and the electrostatic interaction (−3.19 kcal/mol). The (1 1 −2) face is the smallest existing face, which has 6.24% area. The (1 0 −1) and (1 0 0) faces occupy the second and third largest facet areas, respectively.

Table 1
The parameters of the main crystal habit faces of ANPyO.[a]

h k l	Multiplicity	d_{hkl} [b]	D [c]	E_{att} (total)	E_{att} (vdW)	E_{att} (electr)	R_{hkl}	S (%)[d]
(1 1 0)	2	6.91	16.62	−16.62	−13.43	−3.19	1	40.70
(1 0 0)	4	6.48	25.76	−25.76	−16.66	−9.10	1.55	17.38
(1 0 −1)	4	5.22	26.14	−26.14	−19.34	−6.81	1.57	35.69
(1 1 −2)	2	3.72	32.21	−32.21	−27.79	−4.42	1.94	6.24

[a] All energies are in kcal/mol, distance is in Å, and area in Å².

[b] Interplanar distance.

[c] The center-to-plane distance between the growth origin and the growth face.

[d] The percentage of the total habit face areas occupied by all symmetry images of the facet.
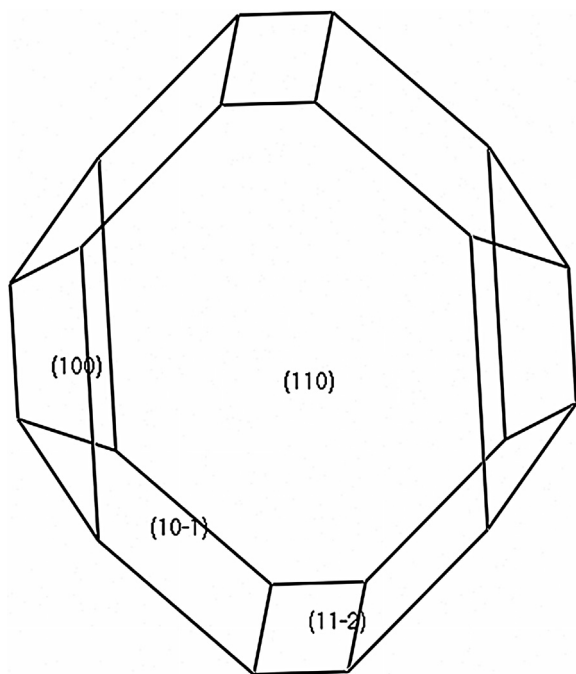
Fig. 2. The predicted ANPyO crystal morphology in vacuum by the AE model.

3.2. Interaction energies and the solvent effect on ANPyO crystal morphology

Most crystals are grown from solution and the solvent affects the crystal morphology by its different interaction energies with different faces of a crystal. And the stronger the interaction, the larger the absolute value of the interaction energy. The equilibrium configurations of trifluoroacetic acid adsorbing on different ANPyO crystal faces are presented in Fig. 3.

As can be seen from Fig. 3, trifluoroacetic acid molecules have contacted closely with the four ANPyO crystal faces, which includes extensive interactions between the solvent and crystal faces. Consequently, all the trifluoroacetic acid molecules have to be removed from the crystal faces before they can grow. The process requires an expenditure of energy and the energy increases with the strength of interaction. Therefore, the interaction reduces the growth rate of certain crystal faces. And finally trifluoroacetic acid modifies the crystal shape of ANPyO by its different interaction with different crystal faces.

The interaction energy E_{int} between the solvent layer and the crystal face can be used to construct the energy correction term E_s for the vacuum attachment energy E_{att} and calculated using the following relationship:

$$E_{int} = E_{tot} - E_{surf} - E_{solv} \tag{3}$$

where E_{tot} is the total energy of the solvent layer and the crystal face, E_{surf} is the energy of the crystal face without the solvent layer, and E_{solv} is the energy of the solvent layer without the crystal face.

The modified attachment energy E'_{att} can be carried out using the following formula:

$$E'_{att} = E_{att} - E_s \tag{4}$$

According to the AE model, the relative growth rate of the crystal surface in solution, R'_{hkl}, is taken to be proportional to the absolute value of the modified attachment energy E'_{att}:

$$R'_{hkl} \propto \left| E'_{att} \right| \tag{5}$$

Myerson and Toyokura [28] have used the solvent accessible areas on crystal face as a measure of solvent binding. The accessible solvent surface A_{acc} is obtained by calculating the Connolly surface. For the Connolly surface calculation, the grid interval was set to be 0.15 Å at a probe radius of 1.0 Å in this paper. Thus, the energy correction term E_s which describes the energy of solvent binding on the crystal habit face $(h k l)$ can be calculated using the following equation:

$$E_s = E_{int} \times A_{acc}/A_{box} \tag{6}$$

where A_{acc} is the accessible solvent surface of the crystal face in the unit cell, and A_{box} is the total crystal face area in the simulation box.

The calculated results for the ANPyO face–trifluoroacetic acid solvent interfacial models are summarized in Table 2.

From the analysis results of Table 2, it can be found that all of the interaction energies of ANPyO face–trifluoroacetic acid systems are negative, which indicates that the adsorption of trifluoroacetic acid on ANPyO faces is exothermic and thermodynamically favorable, in agreement with the illustration of Fig. 3. The interaction strength of trifluoroacetic acid with different crystal faces can be compared in the following sequence: $(1 1 -2) > (1 1 0) > (1 0 -1) > (1 0 0)$. The energy correction term E_s not only lies on the interaction energy E_{int} but also relates to the accessible solvent surface of the crystal face in the unit cell A_{acc} and the total crystal surface area in the simulation box. Taking E_s into account, the modified attachment energies E'_{att} of ANPyO change in the order of $(1 1 0) > (1 0 -1) > (1 1 -2) > (1 0 0)$, which suggests that in trifluoroacetic acid solution the ANPyO crystal would grow more rapidly in the $(1 0 0)$ direction while slowly in the $(1 1 0)$ direction, accordingly expresses the $(1 1 0)$ face in the particle shape. The final crystal morphology in trifluoroacetic acid calculated based on the modified attachment energy model is depicted in Fig. 4, in which the total facet area of $(1 1 0)$ face is remarkably increased while that of $(1 0 -1)$, $(1 1 -2)$ and $(1 0 0)$ faces diminished compared with the results of the AE model, and the crystal shape is very close to a flake, which is consistent with the observed morphology of ANPyO crystal [12].

3.3. Radial distribution function of the interfacial model

The radial distribution function (RDF) gives a measure of the probability that, given the presence of an atom at the origin of an arbitrary reference frame, there will be an atom with its center located in a spherical shell of infinitesimal thickness at a distance, r, from the reference atom. The RDF has found applications in structural investigations of both solid and liquid packing, in studying specific interactions such as hydrogen bonding. Usually, in radial distribution function graph $g(r)$–r, the peak which is within 0.35 nm mainly consists of chemical bond and hydrogen bond, while the peak which is outside of 0.35 nm is mainly composed of Coulomb and Van der Waals forces.

In order to analyze the solvent–crystal interactions clearly, the interface structure between ANPyO $(1 1 0)$ face and trifluoroacetic acid molecules was explored with RDF(s), as shown in Fig. 5. Only the outermost layer of ANPyO molecules which was nearest to the solvent was considered in the following RDF(s) analysis. The RDF(s) graphs of two pairs of atoms were plotted, which are hydrogen atoms in trifluoroacetic acid molecules to oxygen atoms and nitrogen atoms of nitro-group in ANPyO molecules respectively denoted as $H_{solvent}-O_{ANPyO}$ and $H_{solvent}-N_{ANPyO}$ pairs. Similar RDF(s) can be obtained when analyzing other interfacial model systems comprising trifluoroacetic acid and the other three crystal faces.

As shown in Fig. 5, there are sharp peaks in $r = 0.17$ nm and 0.27 nm, which means that the strong hydrogen bonds exist between O, N and H. In the interval of 0.30–1.0 nm, wide peaks can be observed in $g(r)_{O-H}-r$ and $g(r)_{N-H}-r$, which indicates that the Coulomb and Van der Waals forces also exist. That is to say,
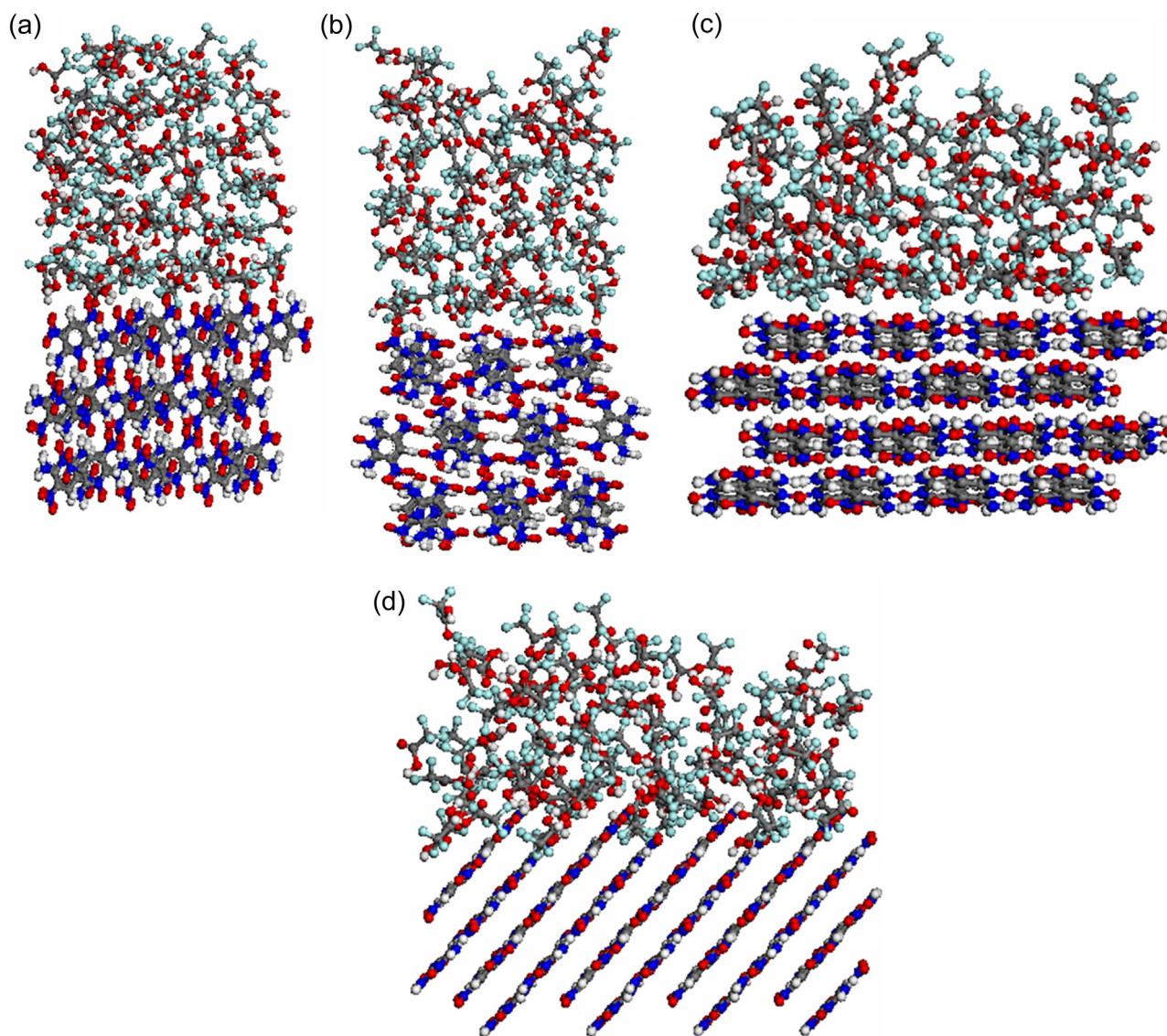
Fig. 3. The equilibrium configurations of trifluoroacetic acid adsorbing on different ANPyO crystal faces at 288 K. (a), (b), (c) and (d) correspond to (1 1 0), (1 0 0), (1 0 −1) and (1 1 −2) faces, respectively.

trifluoroacetic acid molecules adsorb on the ANPyO faces mainly via the solvent–crystal interactions of hydrogen bonds, Coulomb and Van der Waals forces.

3.4. The solvent molecules diffusion capacity

According to the prediction of the modified attachment energy model, the ANPyO crystal in trifluoroacetic acid presents a flake and the predominant face is (1 1 0), which is in agreement with the experimental results obtained under agitation 20 r/s by Zhiwei [12].

However, the simulation results of the interaction energy between the ANPyO crystal faces and the solvent showed that the adsorption energy of the solvent on the (1 1 −2) face is the largest. Thus it can be seen that the solvent molecules diffusion capacity also plays a role in the growth of various ANPyO crystal faces, which involves the diffusion coefficient (D) of solvent molecules on different crystal faces. The D of trifluoroacetic acid molecules on various ANPyO crystal faces was calculated using the well-known Einstein diffusion equation. According to this equation, the three-dimensional diffusion coefficient of a molecule can be evaluated as the derivative

Table 2
Interaction energies of the interfacial models and modified attachment energies of ANPyO crystal faces.[a]

h k l	E_{tot}	E_{solv}	E_{surf}	E_{int}	A_{acc}	A_{box}	E_s	E'_{att}	R'_{hkl}
(1 1 0)	−341.43	4921.16	−5093.54	−169.04	141.83	560.10	−16.43	−0.19	1
(1 0 0)	−373.43	4863.23	−5115.78	−120.88	192.48	495.89	−13.03	−12.73	67
(1 0 −1)	−1127.42	4958.07	−5920.93	−164.56	193.76	819.17	−14.18	−11.96	62.95
(1 1 −2)	−945.90	5020.56	−5728.77	−237.70	266.41	917.59	−19.96	−12.25	64.47

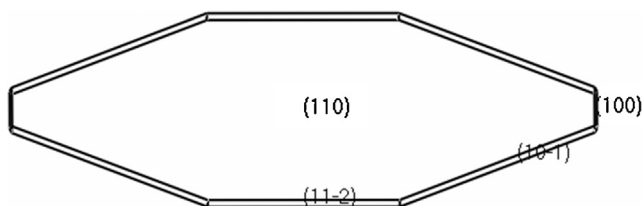[a] All energies are in kcal/mol, areas in Å².

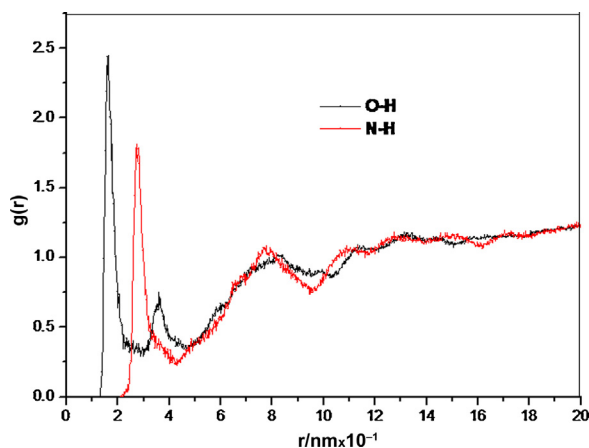**Fig. 4.** The predicted ANPyO crystal morphology in trifluoroacetic acid by the modified AE model.

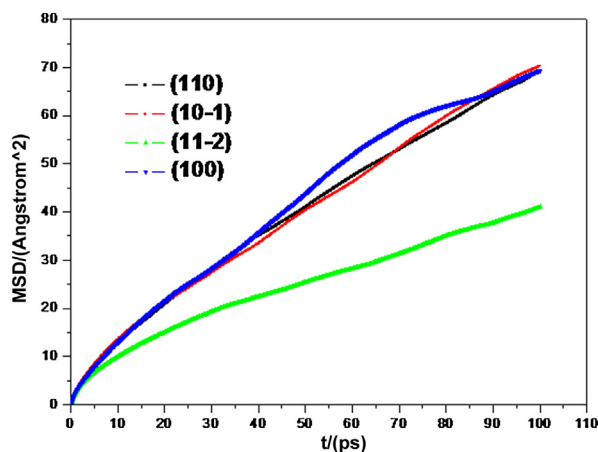**Fig. 5.** Radial distribution function of the interfacial model of CF$_3$COOH and ANPyO (1 1 0) face.

Fig. 6. The MSD of trifluoroacetic acid molecules on (1 1 0), (1 0 −1), (1 1 −2) and (1 0 0) faces at 288 K.

of its mean square displacement (MSD) with respect to time as follows:

$$D = \frac{1}{6} \lim_{t \to \infty} \frac{d}{dt} \sum_{i=1}^{N} \left\langle \left| r_i(t) - r_i(0) \right|^2 \right\rangle \qquad (7)$$

where r_i denotes the position vector of the particle, and the angular brackets denote an ensemble average. So the limiting slope of the MSD as a function of time can be used to evaluate the D of a particle undergoing random Brownian motion in three dimensions. The MSD was calculated using the Discover module from the production runs of MD simulation. Fig. 6 shows the MSD of trifluoroacetic acid molecules on the (1 1 0), (1 0 −1), (1 1 −2) and (1 0 0) faces at 288 K.

The diffusion coefficients of trifluoroacetic acid molecules on (1 1 0), (1 0 −1), (1 1 −2) and (1 0 0) faces were estimated from the slope of the MSD to be 1.07×10^{-9} m^2/s, 1.09×10^{-9} m^2/s, 5.81×10^{-10} m^2/s and 1.13×10^{-9} m^2/s, respectively. These results indicate that trifluoroacetic acid molecules diffuse more easily on (1 1 0), (1 0 −1) and (1 0 0) faces and the diffusion coefficient of the solvent on (1 1 0), (1 0 −1) and (1 0 0) faces was about 2 times larger than that on the (1 1 −2) face. Without stirring, the number of solvent molecules moving to the (1 1 −2) crystal face would be reduced and the ability of solvent molecules blocking the reaction sites would be decreased, causing the (1 1 −2) crystal faces to diminish or disappear.

4. Conclusions

In this study, the MD simulations of a solvent layer of trifluoroacetic acid with the ANPyO habit crystal faces were investigated by introducing the interfacial model. The effect of the solvent on the growth morphology of ANPyO was reported by a corrected AE model. The major results can be summarized as follows:

(1) The prediction of the crystal shape of ANPyO in vacuum according to the AE model results in a shape similar to the ellipsoid and the crystal morphology is dominated by four faces of (1 1 0), (1 0 0), (1 0 −1) and (1 1 −2). Taking the energy correction term into account, the modified attachment energies of ANPyO change in the order of (1 1 0) > (1 0 −1) > (1 1 −2) > (1 0 0), and the crystal shape become very close to a flake in trifluoroacetic acid solvent.
(2) The RDF analysis indicates that the solvent molecules adsorb on the ANPyO faces mainly via the solvent–crystal faces interactions of hydrogen bonds, Coulomb and Van der Waals forces.
(3) The calculation of the diffusion coefficients of trifluoroacetic acid molecules near the crystal growth faces showed that the solvent molecules diffuse more easily on (1 1 0), (1 0 −1) and (1 0 0) faces than (1 1 −2) face and the growth habits of ANPyO are also affected by the diffusion capacity of trifluoroacetic acid molecules.

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