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Predicting crystal growth morphology of molecular crystals

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Abstract : Predicting the growth morphology of molecular crystals is an important step in controlling process parameters in chemical and pharmaceutical industries. Here we present a computational method to predict growth morphology of molecular crystals, derived from internal crystal structure. The habit contrlloing energetic were obtained using first-principles method. Our approach takes into account of molecular orientation and other internal parameters on growth shape. It also takes into account of surface relaxation, possible reconstruction and different surface terminations of the habit facets on the growth morphology. Surface roughness at $T = 0$ K is quantified in terms of difference in lateral attachment energies of molecules in facet's unit cell. The growth morphologies of urea and succinic acid were computed from the presented model. The relaxed morphologies obtained using Hartree-Fock method gives an excellent agreement with the as grown crystals from vapour phase. **© Global Scientific Inc.**

Keywords : Urea crystal; Succinic acid crystal; Hartman-Perdok; Attachment energy; Growth morphology.

INTRODUCTION

The study and manipulation of forms of crystals have attracted immense interest of artists and academicians since the Bronze Age[1]. The relationship between the crystallization forms and its internal structure have been captured the interest of scientists long before the crystal structure could be determined from diffraction data. Scientists are eager to understand nature's mechanism by which crystals grown in different shapes. This will enable the engineer to manipulate the crystallization processes to obtain a desired shape of crystals. The forms of the crystals is of great relevance in many industrial processes and has a direct impact on the separation efficiency and the stability of crystalline chemicals, the bioavailability and the effective delivery of drugs, etc. The mechanism that determine the size, shape and properties of crystals are key to addressing challenges as diverse as treating disease, designing new materials etc.

The growth theory of Hartman and Perdok (HP) is employed to compute crystals shape[2-5]. However, HP theory does not take into account of molecular orientation, surface scaling factor[6], surface relaxation of habit faces and the effects of solvents on relative growth rate. A slab of a given orientation (*hkl*) may possess many surface terminations, but HP theory does not take care of the effect of surface termination on the attachment energy. Failure of the HP theory is often ascribed to the effect of solvent or additives[7]. It is conjectured that the atomic structure at the solid-liquid interface determines growth shape. Therefore, an atomic scale study of the interfaces is important to model the effects of impurities and surfactants on crystal forms.

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METHODOLOGY

The crystal growth theories generally treat a single interfacial state, flat facet or rough, or the transition between them, but a single closed surface can have both type of surface structure. It is interesting to note from ref.[8] that monomers or dimmers of molecules are adsorbed during the growth of $ZnCd(SCN)_4$ crystal. Motivated from above study, a model is presented to calculate the formation and lateral attachment energies of the growth units in the presence of neighbour ghost atoms on the each facet *i.e.* energy of growth units in slab were calculated by converting all neighbouring growth units into vacancy. A growth unit diffuses towards interfacial regions through mother nutrient and the transient growth units were formed near the interfaces. The growth units reorient itself according to the atomic structure of the facets before its get adsorbed. The formation energy (FE) of the transient growth unit is the energy released when a transient growth unit is formed from free growth unit in the interfacial region. In case, unit cell consist of multiple molecules, lateral attachment energy (LAE) of each molecule may differ and depend on relative orientation of the molecules and the internal struc-

ture of the facet. The LAE of the transient molecules are the energies released when transient molecules were absorbed on the facet, which may be define as

$$E_{LAE}^{(hkl)} = \frac{1}{2}(E_{crystal} - E_{formation}^{(hkl)}) \qquad (1)$$

where $E_{crystal}$ is bulk cohesive energy of the crystal and $E_{formation}^{(hkl)}$ is the FE of the transient molecule. Figure 1(a) shows a typical assembly of transient urea molecule in (001) face (b) shows the vivid description of the (001) face in which the transient molecule is encircled. The facet's growth rate is determined by adsorption of molecules having lowest LAE. This is in the contrast to the HP model, where each molecule in a unit cell has equal LAE in spite of different neighbouring interfacial ghost atoms. Surface docking models also does not take into account of FE of the solvent molecules/impurity atoms.

To calculate habit controlling energies of different faces, following methodology has been employed. The slabs of d_{hkl} thickness were created and structurally optimized to obtain relaxed structure slabs. In the relaxed slab, the un-relaxed transient energy of molecules was calculated in the presence of neighbouring ghost atoms. To calculate the relaxed structure and energy of transient molecule, structure of un-relaxed transient mol-

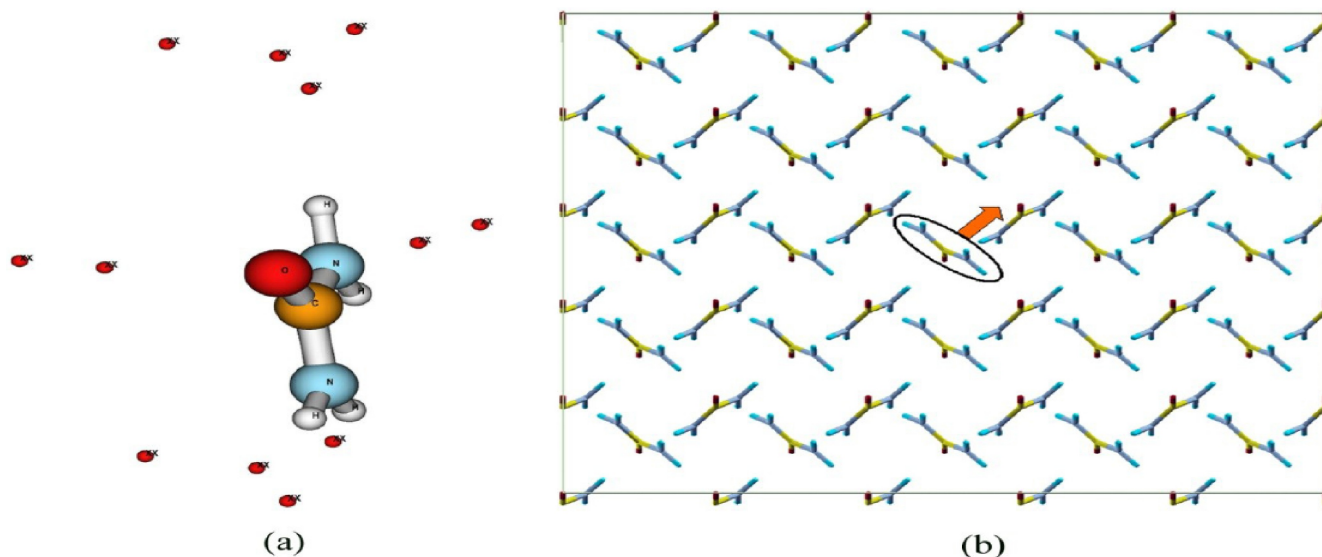(a)   (b)

Figure 1 : Schematic illustration of the model in which the growth of a crystal layer proceeds stepwise (a) shows a typical transient urea molecule in the (001) facet of urea crystal. The vacancies (small red) are labelled by XX. The energy difference between a transient molecule and a free molecule in vapour is defined as formation energy (FE). The growth units in the vapour diffuse towards interfacial regions through mother nutrient and transient growth units are formed near the solid-vapour interface and eventually get incorporated into the growing step at the kink sites after reorienting themselves according to the atomic structure of the interface (b) shows the pictorial description of the interfacial structure of (001) facet in which the transient molecule is encircle. The attachment energy (AE) of the transient molecule is calculated by subtracting energy of whole interface from the energy of the interface without the transient molecule.

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ecule has been optimized in the presence of neighbouring ghost atoms. This is needed because the crystal growth progresses since free molecules get absorbed on the facets. LAE of molecules were calculated using equation (1) shows an aggregate effect of lateral binding of the molecules in 3-D crystal. The transient molecules were formed near the interfaces have lower energies compared to free molecules in vapour/solution. Our model reveals that the crystal growth process is favourable event as the formation of transient molecules near the interfaces is exothermic process. The un-relaxed formation energy of the molecule is the energy difference between un-relaxed transient molecules in a slab and a free molecule and the energy difference between relaxed transient molecules in slab and free molecule in vapour/solution is defined as relaxed formation energy. The un-relaxed and relaxed formation and lateral attachment energy of transient molecules are well defined quantity within this model, and play a similar role for the morphology calculation as in un-relaxed formation and attachment energies in rigid models[9,10]. We, admittedly, though a thorough statistical mechanics should be employed to get more sophisticated results about lateral binding but the presented method deals in average manner at zero temperature. Hartree-Fock (HF) and density functional theory (DFT) with hybrid exchange-correlation functional using all electrons Gaussian basis set was employed and a counterpoise (CP) correction method[11] was used to correct the basis set superposition error in molecular crystals.

COMPUTATIONAL METHOD

All calculations were carried out with CRYSTAL03 program[12]. It is an *ab initio* code based on linear combination of atomic orbitals (LCAO) program for the treatment of periodic systems. The basis set employed for carbon, nitrogen and oxygen is $s(6)sp(2)sp(1)$ and for the hydrogen atom it is $s(2)s(1)$ ("6-21G"). Crystalline orbitals are represented as linear combinations of Bloch functions and are evaluated over a regular three-dimensional mesh in reciprocal space. Each Bloch functions are built from atom-centred atomic orbitals, which are contractions (linear combinations with constant coefficient) of Gaussian-type functions (GTF), each GTF being the product of a Gaussian times a real solid spheri-

cal harmonic. 6-31G molecular all-electron basis set has been employed in the present calculation. The level of accuracy in evaluating the Coulomb and exchange series is controlled by five thresholds[12], for which values of 10^{-10}, 10^{-10}, 10^{-10}, 10^{-10}, 10^{-20} were used for the Coulomb and exchange series. The DFT exchange-correlation contribution is evaluated by numerical integration over the cell volume. The SCF ends when the root mean square (RMS) of the change in eigenvalues from two subsequent cycles is less than 10^{-10} or the change in the absolute value of the total energy is less than 10^{-9}. The shrinking factors along the reciprocal lattice vectors were set to 4, 4, 4, corresponding to 8 reciprocal space points of the irreducible Brillouin zone at which the Hamiltonian matrix was diagonalized. To calculate the relaxed structure of 3-D bulk crystal and 2-D slabs of various orientations, we started with experimental crystal structure[13,14] as initial guess structure. Both lattice and atomic coordinates have been fully relaxed by means of energy gradients. The geometry optimization is performed by means of a quasi-Newton algorithm in which the quadratic step is combined with a parabolic fit. Geometry convergence is tested on the RMS and the absolute value of the largest component of the gradients and estimated displacements. The threshold for the maximum force, the RMS force, the maximum atomic displacement, and the RMS atomic displacement on all atoms have been set to 0.00045, 0.00030, 0.00180, and 0.00120 au, respectively. The optimization is successfully complete when the four conditions are simultaneously satisfied.

We have employed Hartree-Fock (HF) and density functional theory (DFT) methods with hybrid exchange-correlation functional (B3LYP) to obtain optimized slice structure and habit controlling energetics. An important issue connected with calculated lattice and slice energy is the basis-set superposition error (BSSE). The BSSE arises because two molecules which are bound together make use of the basis function on the neighbouring atoms to enhance the quality of their own basis sets, beyond the quality used for the isolated molecule calculation. In fact, in calculating the wave function and total energy of a molecular crystal with a finite basis set, the description of molecule *A* in the crystal will be improved by the variational freedom provided by the functions of the adjacent molecule *B*, and vice

versa. As a consequence, the energy content of A and B in the crystalline environment turns out to be overestimated, as if an extra binding occurred between A and B. This error is commonly corrected via the counterpoise (CP) method, as proposed by Boys and Bernardi[11], by supplementing the basis set of an isolated molecule with the functions of an increasing number of ghost atoms belonging to the surrounding array of molecules that would be present in the crystal. The ghost atoms are points in space with an associated basis set, but lacking a nuclear charge so allowing better description of the electron density in the vacancies. We have utilized CRYSTAL03 program to calculate BSSE both using HF and DFT method. For BSSE correction to the lattice energy, the monomer energy is calculated by placing ghost atoms in a cluster surrounding the monomer at the atomic positions obtained from the crystal structure optimization at the same computational level.

RESULTS AND DISCUSSION

The formation of mounds during growth arises from diffusion bias[15,16], as can be demonstrated by considering the stability during deposition of two-dimensional islands having a single molecular-layer height. If incoming molecules deposited atop the island experience a barrier to diffusion over the island's edge, then the next molecular layer may nucleate before the previous layer completes, thereby leading to growth and the eventual appearance of mounds. If, however, this step-ledge barrier is negligibly small, then the molecular layer completes before the next one nucleates so that the growth is layer by layer, yielding a relatively smooth surfaces. In view of the above, surface roughness at zero temperature is defined as the difference in the attachment energies (lateral binding) of molecules in a unit cell. This is because, the molecules having higher lateral binding have higher growth rate compared to the molecules those having lower lateral binding. Thus, uneven attachment energies of molecules in facet's unit cell create a barrier leads to rough surfaces even at zero temperature.

Effects of bond strength and temperature on crystal surface morphology at fixed supersaturations were studies by Bennema *et al.* and R.F. Xiao *et al.*[17,18]. Surface roughness is a function of (ϕ / kT) at fixed super-saturation, where ϕ is lateral bond strength. At zero temperature, thermal roughness of facets vanishes but the atomic roughness at zero temperature need not be zero and it is controlled by the strength of the coupling of the crystal surface to the underlying lattice[19,20] *i.e.* at zero temperature, surface atomic roughness depends on details of the interaction. The atomic roughness at zero temperature vanishes for those facets having either single growth unit or the orientation of facets were such that all growth units (in case of multiple growth units) in facet's unit cell have equal LAE. Thus, roughness at zero temperature is proportional to the difference in binding energies of growth units in a facet's unit cell.

To quantify the surface roughness at zero temperature, we have used a criterion similar to BCF[21], originally defined for thermal roughening. The surface roughness R_s (a geometrical factor, which characterized surface roughness) at zero temperature can be define in terms of lateral binding of growth units in facets unit cell as

$$R_s = \frac{(E_{max}^{att} - E_{min}^{att})}{E_{max}^{att}} \qquad (2)$$

where E_{max}^{att} and E_{min}^{att} are the maximum and minimum lateral binding strength of growth units in crystal facets.

The growth morphologies of urea[10,22,23] and beta-succinic acid[24-27] crystals are well studied due to its simple molecular structure using HP theory based on semi-empirical force-field method. Recently we had studied the growth morphology of urea crystal from HP model[28] and the effect of surface relaxation on the growth morphology using *ab-initio* method but the calculated shape does not well match with experimental shape. Docherty *et al.*[22] and Boek *et al.*[23] have considered only experimentally observed facets and does not considered surface relaxation for calculating shape of urea crystal. Ashley *et al.*[10] have considered the others facets for calculating relaxed and un-relaxed growth shapes but they predicted the appearance of (101) and (200) and underestimated (111) face. Morphology of succinic acid crystal is also widely studied but none of these have considered (101) and other facets.

First, we studied the growth morphology of urea crystal and considered 9 low index faces for calculating FE and LAE of the transient molecules. The results are presented in TABLE 1. Figure 2 (a)-(h) shows

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TABLE 1 : Un-relaxed and relaxed formation and lateral attachment energies (kcal/mol) of transient molecules in different facets of urea crystal for various Hamiltonian.

Hamiltonian	Faces (*hkl*)	Un-relaxed formation energy of molecule		Un-relaxed LAE of molecule		Relaxed formation energy of molecule		Relaxed LAE of molecule	
		(M1)	(M2)	(M1)	(M2)	(M1)	(M2)	(M1)	(M2)
HF	(200)	-7.23		-7.03		-11.29	-11.18	-5.00	
	(110)	-12.14	-6.31	-4.58	-7.49	-15.54	-15.71	-2.88	-5.39
	(101)	-4.63	-4.63	-8.33	-8.33	-8.84	-7.89	-6.23	-6.23
	(001)	-8.94	-8.94	-6.17	-6.17	-12.38	-12.07	-4.46	-4.46
	(111)	-1.33	-9.08	-9.98	-6.11	-6.00	-4.67	-7.65	-4.47
	(100)	-9.26	-9.26	-6.02	-6.02	-13.06	-12.95	-4.12	-4.12
	(210)	-8.94	-5.98	-6.18	-7.66	-12.73	-12.57	-4.28	-5.55
	(201)	-1.29	-1.29	-10.00	-10.00	-6.00	-4.85	-7.65	-7.65
	(211)	-1.01	-5.10	-10.14	-8.10	-5.68	-4.44	-7.81	-5.27
B3LYP	(200)	-8.15		-9.43				-7.92	
	(110)	-13.27	-7.10	-6.87	-9.95	-10.52	-10.30	-5.65	-8.35
	(101)	-4.66	-4.66	-11.18	-11.18	-8.84	-7.89	-9.56	-9.56
	(001)	-9.31	-9.31	-8.85	-8.85	-12.38	-12.07	-7.47	-7.47
	(111)	-1.08	-9.47	-12.96	-8.77	-12.36	-11.84	-11.17	-7.58
	(100)	-10.13	-10.13	-8.44	-8.44	-13.06	-12.95	-7.03	-7.03
	(210)	-9.76	-6.65	-8.62	-10.18	-10.19	-9.82	-7.22	-8.59
	(201)	-1.23	-1.23	-12.89	-12.89	-6.00	-4.85	-11.08	-11.08
	(211)	-0.85	-5.22	-13.08	-10.89	-10.76	-8.34	-11.28	-9.33

TABLE 2 : Un-relaxed and relaxed formation and lateral attachment energies (kcal/mol) of transient molecules in different facets of succinic acid crystal for various Hamiltonian.

Hamiltonian	Faces (*hkl*)	Un-relaxed formation energy of molecule		Un-relaxed LAE of molecule		Relaxed formation energy of molecule		Relaxed LAE of molecule	
		(M1)	(M2)	(M1)	(M2)	(M1)	(M2)	(M1)	(M2)
HF	(002)	-1.49		-11.66		-1.75		-11.53	
	(010)	-8.00	-8.00	-8.40	-8.40	-9.79	-9.79	-7.51	-7.51
	(011)	-4.73	-4.17	-10.04	-10.32	-5.13	-4.91	-9.84	-9.94
	(020)	-9.08		-7.86		-10.37		-7.22	
	(100)	-8.25	-8.25	-8.28	-8.28	-12.84	-14.68	-5.98	-5.06
	(101)	-8.97	-8.94	-7.92	-7.93	-10.93	-10.93	-6.94	-6.94
	(110)	-6.06	-5.35	-9.37	-9.73	-9.73	-8.03	-7.54	-8.39
	(111)	-10.68	-9.45	-7.06	-7.68	-12.45	-11.64	-6.18	-6.58
B3LYP	(002)	-0.01		-16.57		-0.78		-16.18	
	(010)	-8.08	-8.08	-12.53	-12.53	-9.62	-9.62	-11.76	-11.76
	(011)	-3.22	-2.47	-14.96	-15.34	-4.51	-3.15	-14.32	-15.00
	(020)	-9.39		-11.88		-10.76		-11.19	
	(100)	-7.97	-7.97	-12.59	-12.59	-12.11	-15.46	-10.52	-8.84
	(101)	-9.10	-9.07	-12.02	-12.04	-10.98	-10.98	-11.08	-11.08
	(110)	-5.03	-4.19	-14.06	-14.48	-9.06	-7.40	-12.04	-12.87
	(111)	-11.16	-9.95	-10.99	-11.60	-12.86	-12.03	-10.14	-10.56

following slabs of urea crystal. (200) facet represented the irreducible growth for (100) and two surface terminations are possible of the (200) facet. The label of the surface atoms are 10(H) and 12(H). (110) facet is either terminated by 2(C) or 5(N) surface atom. The M1 molecule has lower LAE and the growth rate of (110) is limited by the adsorption of the M1 molecules. Thus, surface of (110) is a mixture of flat (F) and rough facet. There exists one termination for (101) facet label by 4(O) surface atom. Both M1 and M2 molecules have equal LAE and the surface texture of (101) is flat. (001) facet has two terminations labelled by

2(C) and 10(H) atoms. Both M1 and M2 molecules have equal LAE and the interface is F-facet. One surface termination is possible for (111) facet which is characterized by 5(N) surface atom. The M2 molecule has lower LAE and the growth of the facet is limited by adsorption of M2 molecules. We have also considered slightly high index facets for calculating the FE and LAE. (210) face has two terminations and the surface atoms are 7(N) and 8(N). The M1 molecule has lower LAE compared to M2 and the morphology of the facet is dominated by adsorption of M1 molecules. (201) face is terminated by the surface atom

Figure 2 : Relaxed slabs geometry of urea crystal (a) (100), (b) (110), (c) (101), (d) (001), (e) (111), (f) (210), (g) (201) and (h) (211). The unit cell molecules in (a), (c), (d) and (g) slabs were coplanar but unit cell molecules in (b), (e), (f) and (h) slabs were non-coplanar.

Figure 3 : Predicted growth morphologies of urea crystals using Hartree-Fock method (a) un-relaxed and (b) relaxed structure. The relaxed morphology has an excellent agreement with experimentally grown crystal from vapour[22].
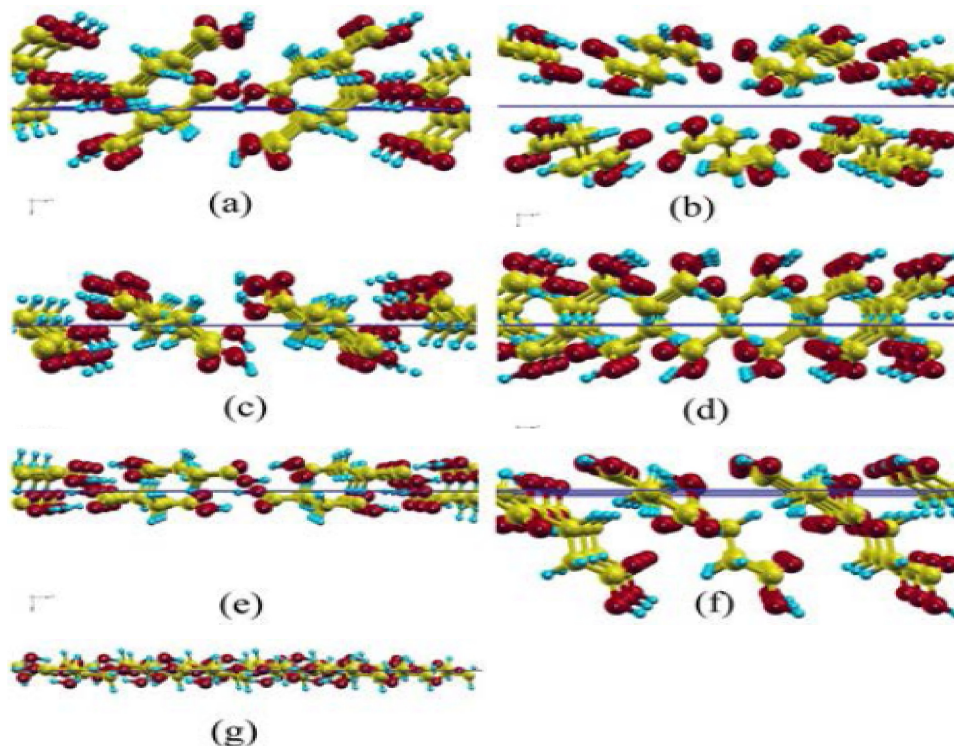
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Figure 4 : Relaxed slabs geometry of succinic acid crystal (a) (001), (b) (010), (c) (011), (d) (100), (e) (101), (f) (110) and (g) (111). Relative orientation molecule in unit cell of (a), (b) and (e) slabs were either 0 or 180° but molecules in unit cell of (c), (d), (f) and (g) slabs have different orientation than (a), (b) and (e).
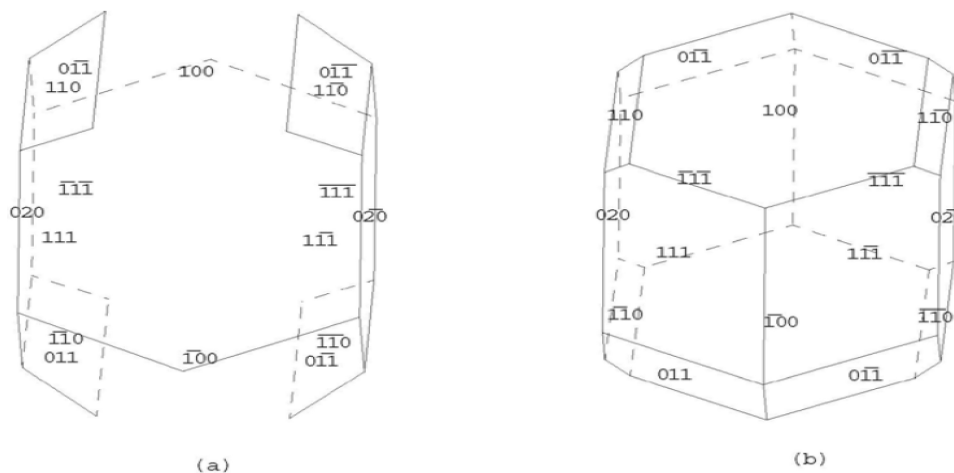

Figure 5 : Predicted growth morphologies of β-succinic acid crystal using Hartree-Fock method (a) un-relaxed and (b) relaxed structure. The relaxed morphology has an excellent agreement with experimentally grown crystal using vapour[24-26].

1(C). M1 and M2 have same LAE and the interfacial state of the facet is flat. Finally we considered (211) facet, in which two surface termination are possible and the morphology of the facet is dominated by the adsorption of M2 molecules.

The un-relaxed and relaxed growth morphologies calculated using HF method has excellent agreement with the experimentally grown crystals[22]. Figure 3 shows the (a) un-relaxed (b) relaxed morpholo-

gies of the urea crystal obtained using HF method. TABLE 1 reveals that the surface relaxation of crystal faces gives growth morphology close to the experimental results.

Second, we studied the growth morphology of succinic acid crystal and considered 8 low index facets for calculating FE and LAE. In TABLE 2, we report the FE and LAE of the various facets of succinic acid crystal. (020) and (002) faces represented the irreducible

growth for (010) and (001) facets. Two surface terminations are possible for (002) facet. (010) facet has two possible terminations and label of surface atoms are 8(C) and 22(H). Both M1 and M2 molecules have equal LAE and the interface of (010) is flat. (011) face have only one termination by 14(O) surface atom. M1 and M2 have comparable LAE but M1 molecule has offered lower LAE and the interfacial state of (011) is rather flat. (100) have two surface termination and the LAE of M2 molecule is lower compared to M1 and growth rate of (100) face is limited by adsorption of M2 molecule. (101) face have also two possible surface termination and both M1 and M2 have same LAE and feature of the facet is flat. (110) face has terminated by 15(O) surface atom and the M1 molecule has lower LAE and the morphology of the face is dominated by the adsorption of the M1 molecule. Finally (111) facet is only one surface termination and the label of the surface atom is 14(O). The growth rate of the (111) facet is limited by the incorporation of M1 molecules on the facet. Figure 4 (a)-(g) shows the above discussed slabs of succinic acid crystal.

The un-relaxed and relaxed growth shape of succinic acid crystal calculated from HF theory has excellent agreement with the experimentally grown crystal[24-26]. Figure 5 shows (a) un-relaxed (b) relaxed growth morphology of the succinic acid crystal obtained from HF method. The relaxed FE and LAE of the succinic crystal are presented in TABLE 2 and it reveals that relaxation of the facets in succinic acid crystal gives

TABLE 3 : Computed surface roughness at T=0 K of various facets of urea and succinic acid crystals.

Crystal	Faces (*hkl*)	Surface roughness (R_s) at 0 K
Relaxed shape of urea crystal (data was presented in TABLE 1)	(001), (101), (201) and (200)/(100)	0.00
	(110)	0.47
	(111)	0.42
	(210)	0.23
	(211)	0.32
Relaxed shape of succinic acid crystal (data was presented in TABLE 2)	(101), (002) and (010)/(020)	0.00
	(011)	0.01
	(100)	0.15
	(110)	0.10
	(111)	0.06

growth morphology close to experimental results.

Eq. (2) is used to calculate surface roughness at 0 K, $R_s = 0$ for those facets having single growth unit in a unit cell or when all growth units have equal LAE. In case of relaxed morphology of urea crystal at 0 K, $R_s =$ 0 for (001), (101), (101) and (200)/(100) facets since both molecules in a unit cell were same LAE. TABLE 3 shows the calculated surface roughness using equation (2) of several facets of urea and succinic acid crystal. The vapour grown crystals like urea and succinic acid were obtained at low temperature (at 203 K)[22] and low super-saturation. It is assumed that the system was growing at low supersaturation (σ) and therefore that screw dislocations would be the dominant growth site for all habit faces. Hence, the relative growth rates are determined on the basis of the thermodynamics of incorporating molecules at kink sites. The growth rate depends on σ but shape of crystal is weakly dependent on σ *i.e.* at very low σ, the relative growth rates of facets are independent of the σ[29]. Since the vapour grown crystal morphologies were free from solvent and other impurity effects hence there were no lateral interaction between solid-fluid at interface and growth rate is uniquely defined by strength of lateral interaction between solid-solid. Thus, vapour grown crystal shapes were due to mainly determine from the internal factor like LAE and molecular orientation factor, which were implicitly taken into our consideration while calculating growth morphology. The LAE calculated at 0 K is the habit controlling factor, though a weak temperature dependence of LAE of molecule can not be ruled out. From above, however shapes of crystal weakly depend on temperature but the texture of facets changes due to increases of thermal surface roughness as a function of temperature. TABLE 4 present the calculated and measured number of facets, forms present, relative facets and forms area in experimental and predicted morphology of urea and succinic acid crystal. It reveals that excellent agreements between our predicted morphologies and with as vapour grown crystals were obtained.

Success of HF theory for molecular crystals is due to the fact that molecular crystals have been dominated by hydrogen binding and electron-correlation energies is less pronounced compared to ionic and covalent bonded crystals. The molecule crystals also possess dispersion energies DFT with hybrid functional overes-

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TABLE 4 : Calculated and measured number of facets, forms present and relative facets and forms area in experimental and predicted morphology of urea and succinic acid crystal.

Crystal	Data from Experimental morphologies[22,26]				Data from our calculated morphologies			
	No. of facets present	Forms present	Relative facets area	Relative forms area	No. of facets present	Facets present	Relative facets area	Relative forms area
Urea		{111}	1.00	1.00	10	{111}	1.00	1.00
		{001}	3.18	1.59		{001}	3.39	1.69
	10	{110}	6.12	6.12		{110}	6.38	6.38
Succinic acid	12	{110}	1.00	1.00	12	{110}	1.00	1.00
		{011}	2.08	2.08		{011}	1.70	1.70
		{010}	5.87	2.93		{010}	5.78	2.89
		{111}	5.45	5.45		{111}	5.95	5.95
		{010}	10.92	5.46		{010}	11.07	5.53

timated the habit controlling energies. Our calculated growth morphologies of the urea and succinic acid crystals are better agreements with experimental results than the Hartman and Bennema model which are based on semi empirical method.

SUMMARY AND CONCLUSION

In summary, we presented a model to predict the growth morphology of molecular crystals. The habit controlling enegetics were obtained using periodic *ab initio* total energy calculations. The effects of different possible surface terminations and surface relaxation or even reconstruction have been studied. A comparison of the predicted growth morphology of the urea crystals grown by sublimation reveals excellent agreement. The calculated morphology of succinic acid crystal has an excellent agreement with the as grown crystals by sublimation. In both cases, the calculated growth morphologies reproduced all experimentally observed forms and excellent match of relative facets area.

ACKNOWLEDGEMENTS

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