Molecular Dynamics

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Asymmetric Crystal Growth of α-Resorcinol from the Vapor Phase: Surface Reconstruction and Conformational Change Are the Culprits**

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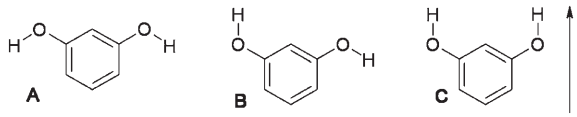
A fundamental issue in crystal growth is the challenge of disentangling the relative contributions of the intrinsic crystal structure and the various external factors, such as the effects of solvent, to the resulting morphology of the crystal. Crystals of polar molecules in noncentrosymmetric space groups often exhibit asymmetric growth along the polar axis. The cause of this asymmetric growth is a mystery but has commonly been attributed to solvent effects, the inherent contribution of the crystal forces being relegated to mere modulation of the morphology.[1–3] The archetypical example in this context is probably the unidirectional crystal growth of α-resorcinol (space group $Pna2_1$) along the polar axis in aqueous solvents.[4,5] Recently, asymmetric crystal growth from the vapor phase has been observed for a number of polar crystals, including α-resorcinol.[6,7] In view of this finding, it has been proposed that asymmetric crystal growth along the polar axis may be an intrinsic feature of polar crystals, which may be modulated by solvent effects. For the particular case of α-resorcinol, "self-poisoning" has been suggested as the underlying cause for the observed asymmetric growth.[8]

We show herein, by means of molecular-dynamics simulation, that for the case of α-resorcinol the surfaces bounding the [011] polar axis undergo reconstruction when equilibrated and exhibit marked asymmetry in terms of their crystalline order. The slower-growing (011) surface shows extensive disorder akin to melting, whilst the $(0\bar{1}\bar{1})$ surface remains essentially crystalline. Also, we observe that molecules at the disordered surface can adopt different conformations arising from rotation of the hydroxy groups. The presence of disordered layers and molecules with "rogue" conformations at the (011) surface are expected to significantly hinder crystal growth at this surface relative to the $(0\bar{1}\bar{1})$ surface, which would be entirely consistent with experimental observations. The asymmetry in the surface reconstruction of the polar faces of α-resorcinol may be a general feature of polar surfaces and possibly the root cause of the asymmetric growth of polar crystals from the vapor phase.

The resorcinol molecule can exist in three possible conformations, which are shown in Scheme 1. The molecular



Scheme 1. The three possible conformations of resorcinol and the molecular axis used to define the dipole moment.

conformation in the α form[9,10] of resorcinol is the symmetric structure **A**. In the β,[10,11] the other polymorph of resorcinol, the molecular conformation is the asymmetric structure **B**. The α form is the stable phase at room temperature and pressure. The α→β transition occurs at a relatively low temperature; the reported temperature, which varies from 337[12] to 369 K,[13] is probably dependent on the quality of the crystals, which would influence the extent of superheating/supercooling. The transition can also be induced by pressure at about 0.5 GPa.[14] The (011) and $(0\bar{1}\bar{1})$ faces of α-resorcinol that limit the [011] polar axis are shown in Figure 1. The (011) face mostly exposes the phenyl rings, whilst the $(0\bar{1}\bar{1})$ face is rich in hydroxy groups.

An important aspect concerning the growth kinetics of polar crystal faces is the inherent stability of the faces. The energy of the surfaces that terminate the polar axis diverges when they are in their structurally pristine state. Such surfaces

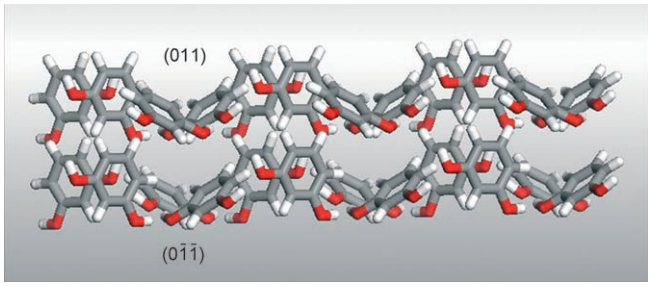


Figure 1. Molecular packing at the (011) and $(0\bar{1}\bar{1})$ faces of α-resorcinol.

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(often termed type 3[15]) cannot exist in this state and will undergo reconstruction in a bid to minimize their free energy. This aspect, whilst being well appreciated for the polar surfaces of ionic systems,[16,17] appears to have received little attention with respect to molecular systems. Clearly, the resulting reconstruction will influence the growth kinetics of the affected surfaces. If, for whatever reason, the surface reconstruction for any two faces limiting a polar axis is asymmetric, then this situation will be reflected in the relative growth rates of the polar faces. On the basis of this thesis, we investigated the stability of the (011) and $(0\bar{1}\bar{1})$ faces of α-resorcinol using molecular-dynamics simulation at various temperatures ranging from 243 to 303 K, with the expectation that the surface reconstruction of the two faces would be asymmetric. As there is scope for the resorcinol molecule to undergo a conformational change, we also investigated the relative stability of the different conformations to ascertain whether conformational change needs to be considered in the crystal-growth process.

The relative stabilities of the three molecular conformations, ascertained using quantum-mechanical density functional theory (DFT), are given in Table 1. The calculations predict that conformer **B** (that found in the β phase) is the most stable, followed by **A**, and then **C**. This order seems reasonable, as the interaction energy of the dipoles of the O–H bonds is minimized for conformer **B**. The predicted populations of the three conformers as a function of temperature at equilibrium are shown in Figure 2. This plot reveals that the relative population of conformer **B** is higher than that of conformer **A** at all temperatures in the gas phase. The potential energy barrier to interconversion of the conformers (that is, the rotational barrier about the C–O bonds) was estimated to be about 18 kJ mol^{-1} (equivalent to about 7 kT at 298 K). Whilst both conformational states **A** and **B** would be well-populated at equilibrium under ambient conditions, their rate of interconversion is relatively slow because of the high torsional barrier. Nevertheless, in the vapor-phase crystal-growth experiments, even if the source material is pure α-resorcinol, there is a possibility of some interconversion to yield the asymmetric conformer **B**. These molecules will have to convert to the symmetric conformer **A** before or at the point of integration into the crystal surfaces of α-resorcinol, which could become the rate-limiting step as the interconversion kinetics are relatively slow.

Table 1: Relative energies (ΔU)[a] and dipole moments (μ)[b] of the three conformers of resorcinol.

Conformer	ΔU [kJ mol^{-1}]	$\Delta U + E_0$ [kJ mol^{-1}]	μ [debye]
A	0.83	0.63	−2.27
B	0.00	0.00	+0.06
C	2.76	2.54	+2.37

[a] The relative energies were obtained from DFT calculations using the B3LYP hybrid functional and the 6-31G** basis set. E_0 is the zero-point energy correction. [b] The dipole moment along the axis shown in Figure 1.

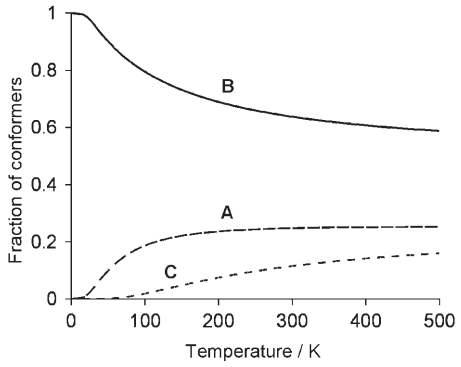

Figure 2. Relative populations of resorcinol conformers **A**, **B**, and **C** (see Scheme 1) as a function of temperature.

A snapshot of the equilibrated crystal slab exposing the (011) and $(0\bar{1}\bar{1})$ faces to vacuum at 283 K is shown in Figure 3. There is marked asymmetry in the crystalline order at the polar surfaces. We also notice that some of the molecules at the (011) surface adopt the **B** conformation, which is characteristic of the β phase. Furthermore, a small number of the molecules at this surface readily detach and then reintegrate. At temperatures lower than 283 K, the surface reconstruction on both surfaces is minimal, presumably because the kinetic energy is insufficient to overcome the strong hydrogen bonding that characterizes the crystalline phases of resorcinol. At higher temperatures, although the structural disorder sets in at the slower-growing (011) surface, ultimately the entire crystal slab becomes disordered. This complete disorder results simply from the limitation that, in the simulations, we are only able to investigate a relatively thin slab (width of ca. 5.8 nm) with a high surface-to-volume ratio.

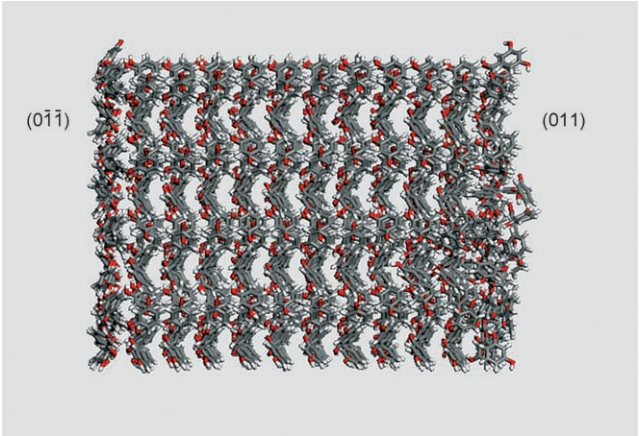

Figure 3. Snapshot of the equilibrated crystal slab of α-resorcinol, showing the marked asymmetry in the crystalline order at the polar surfaces $(0\bar{1}\bar{1})$ and (011).

The molecular density of the equilibrated slab is shown in Figure 4. The data confirm marked reconstruction of the (011) face relative to the $(0\bar{1}\bar{1})$ face, with the first layer (and to some extent the second layer also) of the (011) face showing complete loss of structure, and the topmost layer of the $(0\bar{1}\bar{1})$

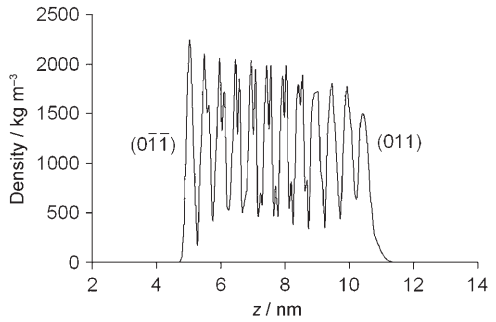

Figure 4. Molecular density of resorcinol molecules as a function of the position along the [011] direction (the *z* axis of the summation cell) in the equilibrated crystal slab of α-resorcinol.

face showing only limited distortion. Although reconstructed surfaces are generally considered to be ordered, there are other examples of particular surfaces of materials being disordered, or even partially molten, at temperatures well below the melting point; the (0001) surface of hexagonal ice (Ih) is a well-known example.[18]

The extensive disorder at the (011) face relative to the $(0\bar{1}\bar{1})$ face suggests that the rate of growth at the (011) surface is significantly hindered. The crystal growth from vapor could be a two-step process: adsorption of molecules at the surface, followed by reorientation and integration into the growing lattice. We expect such a process to be followed at the $(0\bar{1}\bar{1})$ face, where surface reconstruction is minimal and the topmost layer is essentially crystalline, although not entirely equivalent to the α-resorcinol structure. In contrast, at the (011) surface, where the topmost layer and parts of the second layer are highly disordered or effectively molten, crystal growth will proceed as if it were from the melt. Within the confines of the disordered layers, the diffusion rate of individual molecules will be extremely limited and the period for molecular orientation significantly extended relative to that in vacuum. Furthermore, as some of the molecules at the disordered surface can adopt conformations other than that in α-resorcinol, an additional step of conformational change is required before a molecule can be integrated into the crystalline surface. Molecules with rogue conformations may also serve to poison the growing surface. These considerations all point to asymmetric crystal growth, with the $(0\bar{1}\bar{1})$ surface growing significantly faster than the (011) surface, as observed experimentally.

The asymmetry in the surface reconstruction must arise either from an asymmetry in the fundamental driving forces at the two surfaces or as a result of the surfaces responding differently to otherwise identical or similar driving forces. The driving force at each surface would be the free energy for the surface in its pristine condition. Whilst surface energies can be quantified by molecular simulation, such a calculation is unfortunately not possible for polar surfaces. One cannot obtain a unique surface energy for each polar surface, as cleavage of the bulk crystal creates both surfaces.

There is another possibility that could complicate the emerging molecular picture, that is, the possibility of a layer of the β phase forming on the slower-growing (011) surface during the sublimation experiments and inhibiting subsequent deposition. The α→β transition temperature (337–369 K) falls within the range of temperatures employed in the reported gradient-sublimation crystal-growth experiments for α-resorcinol,[6] namely a source temperature of 363 K and deposition temperatures in the range 298–343 K. Thus, indeed, there is scope for β-phase nucleation. Surface diffraction or spectroscopy may help to rule out this possibility.

Finally, we note that the proposed explanation for the asymmetric crystal growth of α-resorcinol from the vapor phase in itself neither sheds any light nor challenges the significance of surface–solvent interactions in the crystal growth of α-resorcinol from solution, as promoted by previous studies.[19,20] In solution, we would expect a polar solvent, the fluid phase, to undergo a more substantive structural reorganization (relative to reconstruction of the crystal surface) in a bid to minimize the surface dipole and the associated interfacial free energy. Should this thesis prove to be so, it will relegate the significance of surface reconstruction in favor of surface–solvent effects.

Experimental Section

Electronic structure calculations: The calculations were carried out using DFT with the B3LYP functional[21] and the 6-31G** basis set within the computer code GAMESS-UK.[22] For each conformer, the geometry was optimized and the zero-point energy was estimated by calculating the vibrational frequencies at the optimized geometry. The torsional energy barrier was calculated by varying the C-C-O-H torsion angle in steps of 20°, with reoptimization of the other geometrical variables at each step. The maxima in the potential energy were observed when either or both of the O–H bonds were perpendicular to the plane of the molecule.

Molecular-dynamics simulations: The simulations were carried out using GROMACS.[23] The system consisted of a crystal slab of α-resorcinol comprising 768 molecules with the (011) and $(0\bar{1}\bar{1})$ faces exposed to vacuum. The system employed three-dimensional periodic boundaries, and simulations were carried out in the NVT (constant number of particles, volume, and temperature) ensemble. The force field employed was that which had been optimized by us earlier to reproduce the crystalline phases of resorcinol.[24] The electrostatic forces were evaluated using a pseudo-two-dimensional version[25] of particle-mesh Ewald summation at a precision of 10^{-5} to eliminate the interaction of the slab with its periodic images. The dimensions of our simulation cell were typically $4.3 \times 4.5 \times 20.8\ \text{nm}^3$ ($x \times y \times z$). The thickness of the crystal slab was about 5.8 nm. The cutoff for both the van der Waals interactions and the real part of the particle-mesh Ewald summation was 1.2 nm. All the bonds in the system were constrained, which enabled a time step of 2 fs. The simulations were carried out at 243, 263, 283, and 303 K. The starting crystal-slab configuration for each temperature was obtained from an equilibrated bulk crystal at the same temperature. The simulation time was typically 10 ns, but at 283 K it was 15 ns. The last 5 ns was used for calculating the equilibrium properties.

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