

Crystal morphology prediction and morphology variation in NaIO_4 and $\text{NaIO}_4 \cdot 3\text{H}_2\text{O}$

L. J. SOLTZBERG* AND ERIN MADDEN

Department of Chemistry, Simmons College, 300 The Fenway, Boston, MA 02115, USA.

E-mail: lsoltzberg@simmons.edu

(Received 20 January 1999; accepted 4 June 1999)

Abstract

Attachment energies computed with only Coulomb potentials have been utilized to predict crystal morphologies for NaIO_4 , sodium iodate, and the hydrate $\text{NaIO}_4 \cdot 3\text{H}_2\text{O}$, sodium iodate trihydrate [actually $\text{Na}(\text{H}_3\text{O})(\text{IO}_3)(\text{OH})_3$]. As with other previously studied water-soluble ionic compounds, these two systems exhibit a systematic relationship between the early growth morphology and that of mature crystals; this relationship can in each case be reproduced by adjusting one attachment energy value. Morphology prediction for these two substances is of particular interest because $\text{NaIO}_4 \cdot 3\text{H}_2\text{O}$ is a polar crystal and involves extensive hydrogen bonding, and because obtaining the observed morphology for NaIO_4 involved consideration of solvent desorption at the growing faces.

1. Introduction

Docherty *et al.* (1991) have summarized the various approaches to crystal morphology prediction. Geometry-based approaches date back to the 19th century; such methods consider that densely packed faces (generally low-index faces) are less hospitable to the addition of new solute molecules than high-index faces, which would be more 'rough' on the atomic scale. While such an approach does yield the observed morphologies in many cases, it tends to fail for crystals involving directional forces, as with many molecular crystals.

Morphology prediction methods that incorporate specific intermolecular interactions improve upon the performance of the geometric approach. Considerable success in predicting the morphologies of molecular crystals has been achieved through the use of the 'attachment energy' method. Here, the growing crystal is considered to consist of the bulk crystal (that which has already grown) and a crystal slice of a certain orientation (hkl) with thickness (d_{hkl}) about to attach to the bulk. The energy of the bulk is computed by summing atom–atom potentials over a sufficiently large volume to achieve convergence. The slice energy is similarly computed, and the attachment energy is taken as the difference between the bulk energy and the slice energy;

that is, the bulk energy of the crystal per mole is the sum of the slice energy and the attachment energy. The attachment energy can be computed for any crystal direction. Directions corresponding to high attachment energies are assumed to grow rapidly and thus do not appear as faces in the mature crystal, while those directions with low attachment energies become the bounding faces of the crystal.

We have recently summarized the computational issues involved in the attachment-energy method and have suggested that, for ionic crystals, it may be possible to dispense with all short-range forces, retaining only the Coulomb potential, for which no special parameterizations are needed (Soltzberg *et al.*, 1998). In the present work, we apply the Coulomb-only attachment-energy method to two particularly challenging examples. $\text{NaIO}_4 \cdot 3\text{H}_2\text{O}$ involves extensive hydrogen bonding but, nonetheless, its observed morphology is successfully predicted using only Coulomb interactions; in addition, this crystal (space group $R3$) is polar. For NaIO_4 (space group $I4_1/a$), although structurally simpler than the hydrate, morphology prediction did not initially yield agreement with the experimentally observed morphology; a simple allowance for solvent affinity at the growing faces did give a reasonable approximation to the observed morphology.

The attachment-energy method has been applied to several ionic crystals in recent years (Hartman & Strom, 1989; Gay & Rohl, 1995; Roberts *et al.*, 1995). Those studies have taken into account not only the Coulombic attractive forces in such crystals, but also short-range attractive and repulsive forces. The method, which has been described in detail by Telfer *et al.* (1996), involves refining an initial set of X-ray or neutron diffraction atomic coordinates plus the parameters of the various potentials against a group of experimental data including elastic constants, dielectric constants and phonon frequencies. The structure and potentials thus obtained (the 'refined structure') are then used for the computation of attachment energies. In the present work, we have dispensed with the short-range potentials and thus with the refinement process, and have used only the Coulomb interactions computed from published X-ray or neutron diffraction atomic coordinates. This approach has given satisfactory results in the

cases studied, presumably because Coulomb interactions dominate the lattice energy in the ionic compounds chosen.

2. Experimental

Crystals of the title compounds were grown by controlled cooling from solutions saturated at various starting temperatures. The apparatus and method for growing crystals have been described previously (Soltzberg *et al.*, 1994, 1998). In the present work, we grew crystals in small beakers, with paraffin oil on the surface to prevent evaporation. Crystal growth was recorded using a microscope-mounted video camera and a time-lapse video cassette recorder. $\text{NaIO}_4 \cdot 3\text{H}_2\text{O}$ crystals were grown in the temperature range 296–303 K. Crystals of NaIO_4 were grown in the range 318–323 K. Hill (1928) has reported that periodate solutions take on the order of hours to days to equilibrate, so we held the stock solution at the appropriate starting temperature for 1 week before growing crystals.

Morphologies of resulting crystals were determined using optical goniometry to establish the identity of crystal faces.

3. Computations

The starting point for crystal morphology prediction consists of unit-cell dimensions and atomic coordinates obtained from X-ray or neutron diffraction studies. In the present work, we utilized coordinates from X-ray diffraction studies for both NaIO_4 (Kalman & Cruickshank, 1970) and $\text{NaIO}_4 \cdot 3\text{H}_2\text{O}$ (Abrahams & Bernstein, 1978).

Since we employed only the Coulomb potential, the only information needed in addition to the structural

data was the charge on each atom in the structure. It has been shown that predicted morphologies can be sensitive to the charge separation within a polyatomic anion (Hartman & Strom, 1989). Experimental evidence based on charge distributions determined from very accurate X-ray diffraction data, such as the work of Maslen *et al.* (1995) on inorganic systems, shows that formal charges certainly are too large. In the present work, we employed charges computed by fitting to the electrostatic potential map derived from *ab initio* wave functions. We used the *MacSPARTANPlus* software (Wavefunction Inc., 1997) with wave functions computed at the 3-21G* level.

The atomic coordinates and charges were then used as input to *MARVIN* (Gay & Rohl, 1995). *MARVIN* was developed specifically for calculating crystal energies from structural data and employs algorithms that implement the two-dimensional and three-dimensional Ewald sum (Ewald, 1921); this method greatly reduces the computational cost of calculating atom–atom interactions among multiple unit cells and makes it practical to carry out such calculations even on a desktop computer.

For each (hkl) of interest,† *MARVIN* computes the attachment energy and the surface energy, which is related to the attachment energy as $\gamma \equiv ZE_{\text{att}}d_{hkl}/2V$, where γ is the surface energy, Z is the number of molecules or formula units per unit cell, d_{hkl} is the interplanar spacing, and V is the unit-cell volume (Hartman & Bennema, 1980; Rohl & Gay, 1996). It is generally found that, except for submicrometre crystals, the attachment energy is a better predictor of morphology than the surface energy (Bennema, 1993). The essential idea for predicting morphology from the attachment energy is that growth rate is roughly proportional to the attachment energy. Visualization of the morphology is based on Wulff's theorem (Brice, 1973), as implemented in the software *SHAPE* (Dowty & Richards, 1994).

4. Results and discussion

Fig. 1 summarizes our results and should be compared with similar findings for six compounds previously reported by Soltzberg *et al.* (1998). As with the other crystals reported in that work, there is a difference between the observed early- and late-growth morphologies that can be understood on the basis of a change in the relative growth rate of one growth direction. In the case of NaIO_4 , the difference is subtle, appearing as a difference in the relative sizes of the $\{112\}$ and $\{101\}$ forms. The observed late-growth morphology agrees

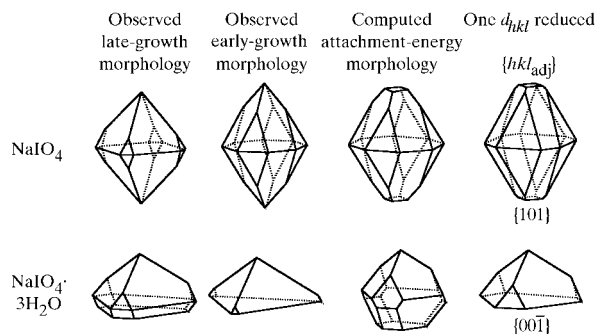


Fig. 1. Observed and predicted morphologies. The renderings have the standard clinographic orientation, with the a axis emerging from the page, the b axis roughly horizontal but tilted slightly from the page, and the c axis nearly vertical but tilted very slightly out of the page. The computed attachment-energy morphology for NaIO_4 is based on attachment energies scaled by the estimated H_2O adsorption energy, as explained in the text. $\{hkl_{\text{adj}}\}$ is the face whose relative growth rate is adjusted to model the early-growth morphology.

† The growth directions investigated are, generally speaking, low-index planes, subject to the Bravais–Friedel–Donnay–Harker (BFDH) condition, which adjusts plane spacing for translational symmetry elements that result in extra planes of atoms (Docherty *et al.*, 1991).

with that reported by Deshpande *et al.* (1982) for two large crystals grown over a period of several days. This morphology is also consistent with that reported by Groth (1908).

The morphology difference between early- and late-growth crystals is more pronounced in the hydrate. Newly appearing and rapidly grown crystals look like simple squat trigonal pyramids, with tiny [101] faces becoming visible at the corners as the crystals age. Mature large crystals show additional faces around the base. Crystals of both types were illustrated by Groth (1908); the polar character is obvious in both types of morphology.

Prediction of morphology for both these compounds presented challenges not encountered with any of the substances that we studied previously. The hydrate is a polar crystal, but the straightforward computation of attachment energies cannot give a polar morphology. Fig. 2 shows a bulk crystal and two slices, hkl and $hk\bar{l}$. If the internal structure in the slice is the same as the structure in the bulk, it is clear that there will be no difference in the interaction of the bulk with either slice, even if the internal structure is polar. The polarity of the crystal structure can only affect the attachment energy if there is some structural difference between the bulk and the slice. There is, indeed, reason to expect that charge separation would be greater in the bulk than in the slice; *abinitio* computations on NaCl clusters show that charge separation increases with cluster size. Docherty *et al.* (1993) successfully predicted the polar morphology of urea crystals by considering the polarization of a free urea molecule to be different from that of the molecule in the bulk crystal. To test this strategy for $\text{NaIO}_4 \cdot 3\text{H}_2\text{O}$, we computed *abinitio* atomic charges for one and two formula units from the unit cell; the resulting charges are shown in Table 1. We scaled the resulting charges to bring the cation to integer charge (+1), in keeping with usual practice (see, for example, Telfer *et al.*, 1996). We utilized the 'impurity' feature of MARVIN to incorporate the two charge sets by entering two different versions of each atom, designating the atoms in the slice as 'impurities' and assigning them different charges from the atoms in the bulk crystal. This approach produced a good approximation to the observed morphology of late-growth crystals, as seen in Fig. 1. Artificial reduction of the attachment energy for $(00\bar{1})$ changed the

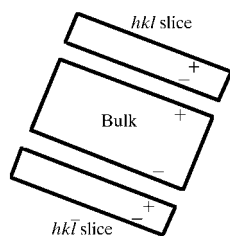


Fig. 2. Interactions of a polar bulk crystal with hkl and $hk\bar{l}$ slices.

Table 1. Atomic charges used for the bulk crystal and the crystal slice in $\text{NaIO}_4 \cdot 3\text{H}_2\text{O}$

	q (bulk)	q (slice)
Na	+1.0000	+1.0000
I	+2.5191	+2.3824
O	-1.1250	-1.0872
H	+0.5480	+0.5253
H _{hydronium}	+0.7992	+0.7265
O _{hydronium}	-0.8106	-0.6147

morphology to resemble that of early growth crystals of this material.

Since we did not employ any interatomic potentials other than electrostatic potentials, the extensive hydrogen bonding in $\text{NaIO}_4 \cdot 3\text{H}_2\text{O}$ might have been expected to be problematic; however, this was not the case. The success of the morphology prediction for this substance suggests that, at least with respect to the energetics of the crystal, electrostatic interactions can account for the effects due to hydrogen bonding. Indeed, Buckingham (1997) has commented on the utility of an electrostatic view of hydrogen bonding.

Morphology prediction for the anhydrous compound initially gave poor results, as shown in Fig. 3(a). The fact that NaIO_4 forms a hydrate suggested that the process of removal of water from the growing faces of the crystal might affect the growth kinetics for the anhydrous material. This idea had been employed in another morphology study (Wireko *et al.*, 1987). In that study of the growth of α -resorcinol along its polar c axis, the binding energy of a water molecule to different crystal faces was estimated by systematically computing its interaction energy with the crystal at a variety of sites and for a variety of orientations. Sayle *et al.* (1996) have employed MARVIN in a simplified version of this strategy. We applied this latter approach to the morphologically important $\{004\}$, $\{101\}$ and $\{112\}$ faces of NaIO_4 . We used MARVIN to compute the effect of placing a water molecule 2.49 Å (the average Na—O distance in the crystal) and 52.49 Å above various surface Na^+ ions on these faces and took the difference between the 2.49 and 52.49 Å energies to be an estimate of the interaction energy with each face. We then crudely scaled the attachment energies for these faces by dividing by the interaction energies, since tight binding of the solvent to a face would retard the growth of that

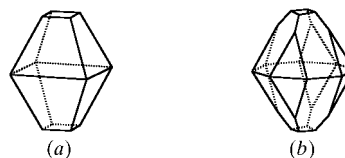


Fig. 3. (a) Predicted morphology for NaIO_4 using attachment energies. (b) Predicted morphology for NaIO_4 using attachment energies scaled by the estimated H_2O adsorption energies.

Table 2. Interaction energies of a water molecule with the morphologically important faces of NaIO₄

	<i>hkl</i>		
	101	112	004
E_{total} (H ₂ O at 2.49 Å) (eV)	-130.5110	-130.4709	-132.9555
E_{total} (H ₂ O at 52.49 Å) (eV)	-130.0850	-129.7657	-132.4828
ΔE (adsorption energy) (eV)	-0.4260	-0.7052	-0.4727
ΔE (adsorption energy) (kJ mol ⁻¹) [†]	-2.57	-4.25	-2.85
$E_{\text{attachment}}$ (eV mol ⁻¹) [†]	-1.1324	-1.7353	-1.7590
$E_{\text{attachment}}$ (scaled) (eV mol ⁻¹) [†]	-0.44	-0.41	-0.62

[†] These particular energy values have been divided by the number of unit cells in the MARVIN computation (4) and the number of formula units in the unit cell (4) to put them on a per-mole basis.

face. The resulting estimates of the binding energy are shown in Table 2 and the improvement in the predicted morphology is shown in Fig. 3(b); that morphology is also shown in Fig. 1. Artificial reduction of the attachment energy for {101} changed the relative prominence of {101} and {112} to resemble that shown by early growth crystals of NaIO₄.

The two crystals presented in this study introduce features not encountered in our previous work. The inclusion of a compound and its hydrate, with attendant strong hydrogen bonding, and the inclusion of a polar crystal extend the range of crystal environments encompassed by this study. The persistence of the early-growth/late-growth morphology differentiation and its apparent correspondence to an increase in the growth rate of all directions except one under conditions of rapid growth (Soltzberg *et al.*, 1998) begin to suggest that this phenomenon may indeed have some generality among ionic crystals.

The authors are grateful to The Petroleum Research Fund and to the Simmons College Fund for Research for support of this work. We thank Drs Gillian Telfer, Robert Hammond and Kevin Roberts of Heriot-Watt University, Edinburgh, for instructive discussions. We also thank Drs Andrew Rohl and David Gay for making available the MARVIN software and for clarification of various points regarding its application.

References

- Abrahams, S. C. & Bernstein, J. L. (1978). *J. Chem. Phys.* **69**, 4234–4237.
- Bennema, P. (1993). *J. Chem. Soc. Faraday Disc.* **95**, 37–54.
- Brice, J. C. (1973). *The Growth of Crystals from Liquids*, pp. 81–84. Elsevier: New York.
- Buckingham, A. D. (1997). *Theoretical Treatments of Hydrogen Bonding*, edited by D. Hadzi, pp. 1–12. Chichester: John Wiley.
- Deshpande, V., Suryanarayana, S. V. & Deshpande, V. T. (1982). *J. Cryst. Growth*, **57**, 113–117.
- Docherty, R., Clydesdale, G., Roberts, K. J. & Bennema, P. (1991). *J. Phys. D.* **24**, 89–99.
- Docherty, R., Roberts, K. J., Saunders, V., Black, S. & Davey, R. J. (1993). *Faraday Discuss.* **95**, 11–25.
- Dowty, E. & Richards, R. P. (1994). *SHAPE*, Version 4.2. 521 Hidden Valley Rd, Kingsport, TN 37663, USA.
- Ewald, P. (1921). *Ann. Phys.* **64**, 253–287.
- Gay, D. H. & Rohl, A. L. (1995). *J. Chem. Soc. Faraday Trans.* **91**, 925–936.
- Groth, P. (1908). *Chemische Krystallographie*, Vol. 2, pp. 176–181. Leipzig: Wilhelm Engelmann.
- Hartman, P. & Bennema, P. (1980). *J. Cryst. Growth*, **49**, 145–156.
- Hartman, P. & Strom, C. S. (1989). *J. Cryst. Growth*, **97**, 502–512.
- Hill, A. E. (1928). *J. Am. Chem. Soc.* **50**, 2678–2962.
- Kalman, A. & Cruickshank, D. W. J. (1970). *Acta Cryst.* **B26**, 1782–1785.
- Maslen, E. N., Streltsov, V. A. & Streltsova, N. R. (1995). *Acta Cryst.* **B51**, 929–939.
- Roberts, K. J., Telfer, G. B., Jackson, R. A., Wilde, P. J. & Meenan, R. (1995). *J. Chem. Soc. Faraday Trans.* **91**, 4133–4138.
- Rohl, A. L. & Gay, D. H. (1996). *J. Cryst. Growth*, **166**, 84–90.
- Sayle, D. C., Gay, D. H., Rohl, A. L., Catlow, R. A., Harding, J. H., Perrin, M. A. & Nortier, P. (1996). *J. Mater. Chem.* **6**, 653–660.
- Soltzberg, L. J., Carneiro, O., Joseph, G. S., Khan, Z., Meretsky, T. D., Ng, M. M. & Ofek, S. A. (1998). *Acta Cryst.* **B54**, 384–390.
- Soltzberg, L. J., Fappiano, S. A., Griffith, L. D., Hidek, L. E., Ofek, S. A. & Suarez, L. L. (1994). *Acta Cryst.* **B50**, 518–524.
- Telfer, G. B., Wilde, P. J., Jackson, R. A., Meenan, P. & Roberts, K. J. (1996). *Philos. Mag. B*, **73**, 147–152.
- Wavefunction Inc. (1997). *MacSpartan Plus*, Version 1.1.9. 18401 Von Karman Ave., Irvine, CA 92612, USA.
- Wireko, F. C., Shimon, L. J. W., Frolow, F., Berkovitch-Yellin, Z., Lahav, M. & Leiserowitz, L. (1987). *J. Phys. Chem.* **91**, 472–481.