

Interionic potentials and epitaxy on NaCl(001) and KBr(001)

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Abstract. Using a variety of interionic potentials, we compute the configurations of adsorbed NaCl and KBr monomers on NaCl(001) and KBr(001) surfaces. In our best estimate, the monomer adsorbs with the cation nearly on top of the surface anion and is tilted by 33–55° from the vertical.

Recently, Duan *et al* [1, 2] have probed the structure and dynamics of alkali halide (001) surfaces during crystal growth by the use of elastic and inelastic He scattering. Both homoepitaxy (such as NaCl on NaCl) and heteroepitaxy (such as KBr on NaCl [2]) have been studied. Well defined maxima in the specular scattered intensity are generally seen for coverages that correspond to a multiple of a deposited monolayer. One notable exception to this behaviour is that no maximum is seen for a monolayer of KBr on NaCl, and even the maximum corresponding to two deposited KBr layers is weak. As the KBr/NaCl deposition proceeds, the surface diffraction peaks of bulk NaCl are gradually replaced by those of bulk KBr. After several layers are deposited, KBr grows happily with six KBr units on top of seven NaCl units, since the ratio of the cation–anion distances $d(\text{KBr}) = 3.298 \text{ \AA}$ and $d(\text{NaCl}) = 2.821 \text{ \AA}$ is close to $\frac{7}{6}$. A detailed explanation of the diffraction structure seen for less than five deposited monolayers in this system, as well as for NaCl/NaCl, KBr/KBr, and NaCl/KBr, can give considerable information on interionic potentials, which can in turn be used for cluster calculations.

Stimulated by these experiments, we have begun calculations of alkali halide growth structures, using the conjugate gradient method code of the International Mathematical and Statistical Library (IMSL-UMCGG) to look for minimum-energy configurations. By varying the starting configuration, we can discover the significant local minima, including the absolute minimum.

The first results we report here are obtained using the model potentials of Bjorklund and Spears (BS) [3], who have carried out systematic calculations of alkali halide surface structures. In the BS model, relaxation and rumpling of the virgin substrate are neglected, and the substrate ions are not allowed to shift or polarize during the growth process. The intramolecular potential is $V_{\text{att}}(r) + V_{\text{rep}}(r)$, with

$$V_{\text{att}}(r) = -e^2/r - \frac{1}{2}(e^2/r^4)(\alpha_+ + \alpha_-) - (2e^2/r^7)\alpha_+\alpha_- - C/r^6 \quad (1)$$

$$V_{\text{rep}}(r) = A \exp(-r/\rho). \quad (2)$$

This is the usual Rittner model with Born–Mayer repulsion and dipole–dipole van der Waals attraction. The electronic polarizabilities α_i are taken from Tessman *et al* [4] and are listed

in table 1, column (1). The van der Waals coefficients C are listed in table 2, column (1); they are computed using the Slater-Kirkwood formula with the effective electron number [5] and Tessman polarizabilities at $\lambda = 5893 \text{ \AA}$. The range parameters ρ and preexponentials A , taken from Spears [6], are listed in table 3, column (1), and table 4, column (1g). This set of parameters gives a reasonably good fit of molecular properties and can be used with some confidence.

Table 1. Electronic polarizabilities α_i in \AA^3 taken from Tessman: (1) for $\lambda = 5893 \text{ \AA}$; (2) for $\lambda = \infty$.

	(1)	(2)
K^+	1.334	1.201
Na^+	0.408	0.255
Br^-	4.158	4.130
Cl^-	2.960	2.974

Table 2. Van der Waals constants C in eV \AA^6 for various approximations (see text): (1) Slater-Kirkwood, with α from table 1, column (1); (2) Mayer (values in parentheses are estimated by square root combination).

	(1)	(2)		(1)	(2)
KK	50.32	15.17	NaBr	41.11	8.74
NaNa	6.07	1.05	NaCl	30.16	6.99
KNa	17.34	(4.0)	BrBr	313.70	125.45
KBr	122.62	37.45	ClCl	166.30	75.05
KCl	89.70	29.96	BrCl	228.40	(97.0)

Table 3. Born-Mayer range parameter ρ in \AA for various approximations (see text): (1) gas, Spears; (2) combination rules, BS; (3) Huggins-Mayer.

	(1)	(2)	(3)		(1)	(2)	(3)
KK	—	0.278	0.3394	NaBr	0.3496	0.331	0.3394
NaNa	—	0.240	0.3394	NaCl	0.3293	0.316	0.3394
KNa	—	0.258	0.3394	BrBr	—	0.532	0.3394
KBr	0.3651	0.365	0.3394	ClCl	—	0.461	0.3394
KCl	0.3469	0.347	0.3394	BrCl	—	0.494	0.3394

Following BS, repulsive pair potentials of the same form as equation (2) are used for the adsorbate-substrate interaction, with the parameters listed in tables 3, column (2), and 4, column (2gs) and (2sg). These parameters are little more than educated guesses, especially for the cation-cation and anion-anion pairs. They are obtained using a geometrical average combination rule for the potentials, which leads to

$$A_{ij} = (A_{ii} A_{jj})^{1/2} \quad (3)$$

$$\rho_{ij}^{-1} = \frac{1}{2}(\rho_{ii}^{-1} + \rho_{jj}^{-1}). \quad (4)$$

Table 4. Born-Mayer preexponential A in eV for various approximations (see text): (1g) gas, Spears; (2g) gas, combination rules, Spears; (1s) bulk substrate, BS; (2s) bulk substrate, combination rules, BS; (2gs), adsorbate-substrate, BS; (2sg) substrate-adsorbate, BS; (3) Huggins-Mayer.

	(1g)	(2g)	(1s)	(2s)	(2gs)	(2sg)	(3)
KK	—	3360	—	2118	2668	2668	1374
NaNa	—	1622	—	845	1171	1171	256
KNa	—	2335	—	1338	1685	1853	593
KBr	2882	2878	1684	1697	2137	2285	2456
KCl	2873	2840	1790	1790	2255	2255	1686
NaBr	1917	2000	1023	1072	1485	1443	1061
NaCl	1963	1973	1118	1131	1567	1424	728
BrBr	—	2465	—	1359	1830	1830	4390
ClCl	—	2400	—	1513	1906	1906	2069
BrCl	—	2432	—	1434	1931	1806	3014

In detail, the procedure used by BS to obtain the adsorbate-substrate parameters is as follows. First find ρ_{ij} and A_{ij} that give the best combination-rule fit to the set of ρ_{ij} and A_{ij} determined by Spears [6] for all the alkali halide molecules. The values of interest here are reported in column (2) of table 3 and column (2g) of table 4. Next, determine A_{ij} ($i \neq j$) for the bulk crystals, using van der Waals and Born-Mayer forces for nearest neighbours only, with the same C and ρ as in the molecule. From these values, which are listed in column (1s) of table 4, obtain by a best fit of the combination rules the values listed in column (2s). Finally, when K is in the adsorbate and Na in the substrate, for instance, combine A_{KK} from column (2g) with A_{NaN_a} from column (2s) to obtain the A value reported in column (2gs) on the KNa line, and similarly construct the A value in column (2sg) when K is in the substrate and Na in the adsorbate.

Using this scheme, we find, in general agreement with BS, that the intramolecular distance in the $M'X'$ adsorbed molecule differs by less than 1% from the gas-phase value. As shown in figure 1, the adsorbate cation M' sits on top of the substrate anion X at a distance that is greater than the corresponding distance in the solid (and even greater than the distance in the free molecule). The energy is a minimum when the tilt angle θ is close to zero, but the minimum is very broad and the energy increases by less than 1 meV until θ reaches a critical value. One can almost picture X' as a hard ball that can rotate freely around the M' pivot until it makes contact with the substrate. However, a simple hard-balls picture is not adequate, because the longer range of the halogen-halogen repulsion is what favours the attachment with M' down and X' away from the surface.

In assessing the validity of this simple model, we have considered first the effect of the polarization induced in the substrate by the adsorbed molecule. (We still neglect the polarization induced in the molecule by the substrate.) The laterally averaged force can be represented by the image potential

$$V_{\text{im}}(\{r_i\}) = -\frac{1}{2} \frac{\epsilon - 1}{\epsilon + 1} \sum_{ij} \frac{e_i e_j}{|r_i - r'_j|} \quad (5)$$

where r'_i is the position of the image of the charge e_i . The dielectric constants of interest [7] are $\epsilon(\text{KBr}) = 4.90$, $\epsilon(\text{NaCl}) = 5.90$. We find that the attractive image force brings the molecule a little closer to the surface, and that a smaller (or zero) tilt angle θ is favoured in all the cases we have examined. Correspondingly, the adsorbate cation M' sits nearly (or

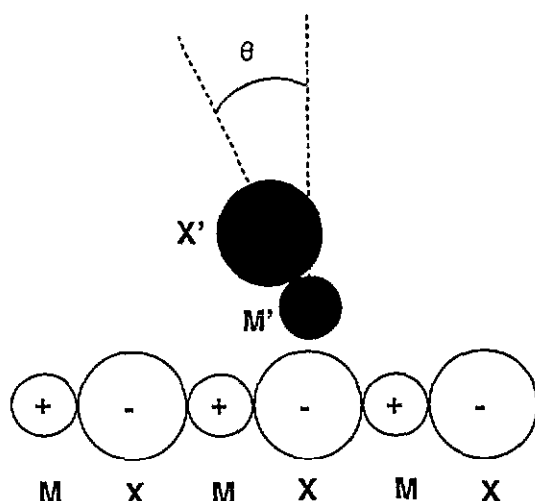


Figure 1. Schematic drawing of a surface ion row in the (110) direction (open circles) and of the adsorbed monomer (black circles).

exactly) on top of the substrate anion X. However, if M' is kept fixed at about 3 \AA above the surface, the restoring torque exerted by the image force around $\theta = 0$ is small, and the molecule is again almost free to rotate around M' .

We have considered next the van der Waals attraction between each adsorbate ion and the substrate. We keep only its lateral average, which to a good approximation is

$$- (\pi/4)(C_{iX} + C_{iM})[1/a^2 z_i^4 + 1/3d^3(z_i + a/2)^3] \quad (6)$$

where a is the MX separation. This interaction brings M' and X' even closer to the surface. Although it hardly changes the $M'X'$ distance, it gives in all cases we have examined a non-zero tilt angle θ . The image and van der Waals forces have opposite effects on θ , but the net result of their action is to increase θ significantly. Thus we do not agree with BS, who, on the basis of earlier work by Hove [8] on adsorbate migration, claim that the effect of these forces is negligible.

The final results of the modified BS model are reported in table 5, column (1).

Alternative sets of A_{ij} and ρ_{ij} parameters have been obtained by Narayan and Ramaseshan (NR) [9] for the alkali halide solids. As recognized by Shanker and Agrawal [10], the NR method is equivalent to Smith's [11] theory of deformable ions. Hence the NR parameters obey the Smith combination rules

$$\rho_{ij} = \frac{1}{2}(\rho_{ii} + \rho_{jj}) \quad (7)$$

$$(A_{ij}/\rho_{ij})^{\rho_{ij}} = (A_{ii}/\rho_{ii})^{\rho_{ii}/2}(A_{jj}/\rho_{jj})^{\rho_{jj}/2}. \quad (8)$$

Kumar and Shanker [12] have obtained excellent fits of many molecular properties by using NR-type potentials. However, the values of A and ρ are in general quite different for the molecule and the corresponding solid. Thus a BS-type interpolation to obtain the adsorbate-substrate parameters appears even more questionable in this case. For this reason, and

Table 5. Adsorbed molecule binding energy ϵ_b in eV, nuclear coordinates (x, z) in Å, internuclear separation d_a in Å, and tilt angle θ in degrees for two model potentials (see text): (1) BS; (2) Huggins–Mayer. The z coordinate is normal to the surface and the x coordinate is along the MXMXMX row in figure 1, with origin on the second M ion. For comparison, the internuclear separations in the gas (in the solid) are 2.821 (3.292) for KBr, 2.666 (3.147) for KCl, 2.502 (2.989) for NaBr, and 2.361 (2.820) for NaCl.

	(1)		(2)			(1)		(2)	
KBr/KBr					KBr/NaCl				
ϵ_b	0.43	—	0.70	—	ϵ_b	0.38	—	0.38	—
d_a, θ	2.83	46°	2.84	93°	d_a, θ	2.83	42°	2.96	100°
K (x, z)	2.83	3.23	3.07	3.22	K (x, z)	2.57	3.19	2.89	3.17
Br (x, z)	0.78	5.21	0.23	3.04	Br (x, z)	0.71	5.31	-0.03	2.66
NaCl/KBr					NaCl/NaCl				
ϵ_b	0.56	—	0.84	—	ϵ_b	0.44	—	0.79	—
d_a, θ	2.39	55°	2.39	88°	d_a, θ	2.34	33°	2.39	96°
Na (x, z)	2.69	2.71	2.91	2.75	Na (x, z)	2.62	2.71	2.55	2.70
Cl (x, z)	0.71	4.05	0.52	2.80	Cl (x, z)	1.30	4.70	0.17	2.43

because some of the reported fits are beset by errors [13], we have not pursued the use of these parameters.

An obvious flaw of all the schemes described so far is that the interionic distances in the adsorbate do not approach the bulk values as the adsorbed layer thickens. Although the BS interpolation scheme may be acceptable for a single adsorbed molecule, we really need better potentials to describe epitaxy and crystal growth.

Tosi and Doyama [14] have proposed several closely related sets of potentials that accurately reproduce the crystal lattice parameter and compressibility of the alkali halide solids, as well as the internuclear distance, electric dipole, binding energy, and vibrational frequency of the corresponding molecules. In the simplest parametrization, a single Born–Mayer term

$$W_{\text{rep}}(r) = B \exp(-r/\rho) \quad (9)$$

is used to describe the repulsive forces in the crystal, and is also applied to the molecule. The intramolecular repulsion is then $(B/6) \exp(-r/\rho)$. This model completely disregards the repulsion between negative ions that can be important to the equilibrium configuration of an adsorbed molecule.

In a more refined model of the crystal, Tosi and Doyama include the second-neighbour repulsion, according to

$$W_{\text{rep}}(r) = 6[b_+b_- \exp(-r/\rho) + (\beta_{++}b_+^2 + \beta_{--}b_-^2) \exp(-r\sqrt{2}/\rho)] \quad (10)$$

where $\beta_{++} = 1.25$ and $\beta_{--} = 0.75$ are the Pauling factors (also, $\beta_{+-} = 1$). The parameters b_+, b_- and ρ enable one to find the potential between any ion pair. Two versions of this model are described by Tosi [15]. In the original Huggins–Mayer form, $\rho = 0.3394$ Å and the $A_{ij} = \beta_{ij}b_i b_j$ coefficients are listed in table 4, column (3). A better fit to experimental data was obtained by Tosi and Fumi [16] by allowing ρ to vary from salt

to salt. Unfortunately this set of parameters is incomplete for our purposes, because ρ is not defined for the Br-Cl and K-Na pairs.

The van der Waals interaction in the solid is described by the sum of dipole-dipole and dipole-quadrupole terms:

$$W_{\text{vdw}}(r) = -C'/r^6 - D'/r^8. \quad (11)$$

Neglecting three-body forces, C' and D' are related to the corresponding interionic constants C and D by

$$C' = 6.5952C_{+-} + 0.90335(C_{++} + C_{--}) \quad (12)$$

$$D' = 6.1457D_{+-} + 0.40005(D_{++} + D_{--}). \quad (13)$$

The Mayer values of $C_{ij}(i, j = \pm)$ used by Tosi [15] are reproduced in table 2, column (2); the corresponding values of D have been computed from

$$D_{ij} = (9C_{ij}/16\pi)(\hbar^2/2me^2)^{1/2}(\sqrt{\alpha_i} + \sqrt{\alpha_j}) \quad (14)$$

using the Tossman values of the polarizabilities. Tosi also reports a set of free-ion values for C_{+-} and C_{--} are about one half of the Mayer values, while the C_{++} are about the same. We have not used these small values, because they are based on the London approximation, which is now believed to be an underestimate.

Polarization forces vanish in the bulk solid at equilibrium but are important in the molecule and on the surface. Tosi and Doyama represent these forces in the molecule as

$$V_{\text{dip}}(r) = -(e/r^2)(m_+ + m_-) - (2/r^3)m_+m_- + m_+^2/2\alpha_+ + m_-^2/2\alpha_- \quad (15)$$

where m_+ and m_- are the induced dipoles, to be computed (see below). In addition, they include a modification of the repulsion due to the induced dipole, of the form $em_-B_{\text{def}}(r)$, where $B_{\text{def}}(r)$ can be expressed in terms of the Szigeti effective charge e^* , the repulsive potential $W_{\text{rep}}(r)$, and the equilibrium nearest-neighbour distance d in the solid. When equation (9) is used, $B_{\text{def}}(r) = B_{\text{def}}(0) \exp(-r/\rho)$, with

$$B_{\text{def}}(0) = (1/2\alpha_-)(1 - e^*/e) \exp(d/\rho)(1/\rho - 2/d). \quad (16)$$

The value of $(1 - e^*/e)$ is 0.26 for KBr, 0.20 for KCl, 0.31 for NaBr, and 0.26 for NaCl. Using equation (10) one obtains essentially the same values of $B_{\text{def}}(r)$ for the r values of interest. The equilibrium values of m_+ and m_- are determined by minimizing $V_{\text{dip}}(r) + em_-B_{\text{def}}(r)$. The procedure of minimizing with respect to the induced moments can be implemented numerically in the general case of surfaces and clusters. In the case of the molecule it leads to a modified Rittner model [14].

We report in table 5, column (2) the results of calculations using the model just described, with the image and van der Waals forces included as for the results of column (1). It can be seen that, in contrast to the BS model, the adsorbed molecules are predicted to lie nearly flat on the surface. This illustrates the critical role of the XX' repulsion in determining the tilt angle θ .

Another set of A , ρ , α and C parameters that fit both the solids and the molecule has been given recently by Gowda and Benson [17]. These parameters are determined separately by a best fit for all the anion-cation pairs, without regard to independent theoretical estimates. They differ markedly from the BS parameters we have used in one respect: the van der Waals constants C are an order of magnitude larger. The range parameters are approximately consistent with the combination rule (7), so that it would be possible to determine the missing values by independently assigning one of the ρ_{ii} . Unfortunately, in carrying out the best fit to the data the second-neighbour repulsion in the solid has been neglected. This is precisely the interaction that we need to estimate more accurately for our surface configuration studies. Gowda and Benson even find that this interaction is unimportant in their studies of the alkali halide dimers [18].

In conclusion, we regard the results reported in table 5, column (1), as our best estimate of the adsorbed monomer configurations. The monomer adsorbs with the cation nearly on top of the surface anion and is tilted $33\text{--}55^\circ$ from the vertical. An analogous conclusion has been reached by Polanyi *et al* [19] in their models of HBr adsorption on LiF, and is supported in their case by direct evidence from angular resolved photoemission. The fact that a monomer does not lie flat on the surface of its own kind (NaCl on NaCl, for instance) is not surprising, given the mismatch of the internuclear spacings in the molecule and in the solid. This mismatch is due to the Rittner polarization force, which cancels for a complete monolayer. The image force, which favours $\theta = 0$, is also greatly reduced for a complete monolayer. In all the cases we have studied the internuclear separation of the adsorbed monomer, d_a , is close to that in the gas phase (see values in the caption of table 5). For a KBr monomer on NaCl the internuclear spacings match well, but a mismatch would occur if a complete, unrumpled overlayer were to form. The possibility of a highly rumpled monolayer of KBr on NaCl can only be discussed by comparing the energy of various growth structures. More reliable cation-cation and anion-anion potentials are needed for this comparison.

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