

Deriving empirical potentials for molecular ionic materials

R. A. JACKSON¹, P. A. MEENAN², G. D. PRICE³, K. J. ROBERTS⁴, G. B. TELFER⁴ AND P. J. WILDE¹

¹Department of Chemistry, Keele University, Keele, Staffs ST5 5BG, UK

²Experimental Station, E I DuPont de Nemours & Co, Wilmington, DE 19880-0304, USA

³Department of Geological Sciences, University College London, Gower St, London WC1E 6BT, UK

⁴Department of Pure and Applied Chemistry, Strathclyde University, Glasgow G1 1XL, UK

Abstract

The procedure for deriving interatomic potentials for molecular ionic materials, using empirical fitting procedures, is described. Potentials are obtained for carbonates, phosphates and perchlorates, and used to calculate crystal and lattice properties which are compared with available experimental data.

KEYWORDS: interatomic potentials, ionic materials, carbonates, phosphates, perchlorates.

Introduction

MOLECULAR ionic materials, exemplified by carbonates, phosphates and perchlorates, pose particular challenges to computer modellers, because of the mixture of bonded and non-bonded interactions that have to be accounted for in any potential model obtained. There is, however, a strong motivation for applying computer modelling to these materials, as this technique can provide important and useful information, which includes crystal and lattice properties, but also defect structure, and crystal growth morphology. Potential models, a prerequisite of any computer modelling study, can be parameterised in two ways: parameters may be calculated directly, by, e.g. quantum mechanical methods, or they may be obtained by empirical fitting. It is this latter method that is applied in this paper, suitably adapted to the particular problems of molecular ionic materials.

Empirical fitting

The process of empirical fitting of potentials has been described elsewhere (see, for example, Jackson, 1990; Gale, 1995a) but a brief description will be given here. Essentially what is involved is a requirement that the potential reproduces the crystal structure and a number of specified properties. The

potential parameters (for bonded and non-bonded interactions) are therefore varied in a systematic manner until this is achieved. For inorganic materials, values of the ionic charges have usually been fixed, with formal values being employed. This approach is clearly not appropriate for the ions within a molecular ion, but it is reasonable to require that the overall ion charge takes the appropriate formal value. Hence, in the fitting process, charges for ions within the molecular ion are varied, subject to the overall ionic charge being constrained. In the work reported in this paper, empirical fitting was carried out using the GULP program (Gale, 1995b). Specific details of parameters and properties involved are given in the later sections where the potentials are described.

TABLE 1. Potential parameters for calcium carbonate

Short Range Potential Parameters:			
Interaction	A(eV)	$\rho(\text{\AA})$	C(eV \AA^6)
Ca-O	8839.3	0.23813	0.0
C-O	3088.4	0.12635	0.0
O-O	36010.8	0.19756	0.0

Charges (f e l): $q(\text{Ca}) = 2.0$, $q(\text{C}) = 0.99805$, $q(\text{O}) = -0.99935$

Force Constants: $k_0 = 9.3179 \text{ eV rad}^{-2}$; $k_t = 1.1392 \text{ eV}$

TABLE 2. Comparison of observed and calculated lattice parameters for aragonite

Structure parameter	Observed value	Calculated value
a (Å)	4.96	4.96
b (Å)	7.96	7.80
c (Å)	5.74	5.70
α, β, γ (degrees)	90.0	90.0

A general potential model for molecular ionic materials

The potential model used is closely related to that used for inorganic materials, with necessary adaptations to model covalent interactions within the molecular ion group. For clarity, non-bonded and bonded interactions are considered separately.

Non-bonded interactions

The potential has the following form:

$$V_{nb}(r_{ij}) = q_i q_j / r_{ij} + A \exp(-r_{ij}/\rho) - C r_{ij}^{-6}$$

where q_i, q_j are charges on ions i and j (which are not part of the same molecular ion), and A, ρ , and C are parameters whose values are obtained for each ion pair involved. In this paper, they are obtained by empirical fitting.

Bonded interactions

The important interactions are bond-stretching, bond-bending and torsional interactions:

$$V_b(r_{ij}, \theta, \phi) = 0.5k_s(r_{ij} - r_0)^2 + 0.5k_b(\theta - \theta_0)^2 + k_t[1 - S \cos(n\phi)]$$

where k_s, k_b and k_t are bond-stretching, bond-bending and torsional force constants respectively, and r_0, θ_0 are equilibrium bond lengths and angles respectively. Values of force constants are usually calculated by

TABLE 3. Potential parameters for calcium phosphate

Short Range Potential Parameters:			
Interaction	A(eV)	ρ (Å)	C(eV Å ⁶)
Ca-O	9065.102	0.2381	0.0
O-O	55559.36	0.2185	27.89

Charges (l e l): $q(\text{Ca}) = 2.0, q(\text{P}) = 1.454264, q(\text{O}) = -1.113566$

Force Constants: $k_s = 8.597 \text{ eV } \text{Å}^{-2}; k_b = 14.58 \text{ eV } \text{rad}^{-2}$

empirical fitting, but for bond-stretching force constants, experimental spectroscopic values may be available. It should be noted that for bonded interactions defined by the harmonic function given above, electrostatic interactions are not included.

Results of potential fitting

Carbonates. A potential was empirically fitted to the crystal structure, elastic and dielectric constants of the calcite phase of calcium carbonate (Jackson and Price, 1992). The parameters are reported in Table 1. Note that, exceptionally, a Buckingham potential was used to describe the bonded C-O interaction. The potential was tested by using it to calculate the aragonite structure, and the observed and calculated lattice constants are given in Table 2. An acceptable level of agreement was obtained. An interesting further point concerned the lattice energies of calcite and aragonite. The potential predicted that aragonite should have a slightly higher stability than calcite, but that when the free energy is calculated, calcite has higher stability. Thus the enhanced stability of calcite is shown to be entropic in origin.

Phosphates. Here the potential was fitted to the structure of calcium phosphate (Roux *et al.*, 1978). The P-O bonds are represented by a harmonic bond-stretching potential, and O-P-O bond angles are defined by a bond-bending term. Non-bonded potentials are parameterised for Ca-O and O-O interactions, but ignored for interactions involving P since it is assumed to be well-screened by the O atoms. However, all non-bonded atoms are allowed to interact electrostatically. The potential parameters obtained are given in Table 3, and Table 4 gives the agreement between calculated and experimental lattice parameters. In Tables 5 and 6, the potential has been transferred to strontium phosphate (Redden and Buerger, 1969) and to magnesium phosphate (Nord and Kierkegaard, 1968), neither of which were used in the fitting process. In all cases, agreement obtained between calculated and experimental lattice parameters is acceptable, indicating that the potential derived is transferable within these systems.

TABLE 4. Comparison of observed and calculated lattice parameters for calcium phosphate

Structure Parameter	Observed Value	Calculated Value
a, b, c (Å)	6.928	6.882
α, β, γ (degrees)	44.512	44.152

TABLE 5. Comparison of observed and calculated structure parameters for strontium phosphate

Structure Parameter	Observed Value	Calculated Value
a, b, c (Å)	7.28	7.28
α, β, γ (degrees)	90.0	90.0

TABLE 6. Comparison of observed and calculated structure parameters for magnesium phosphate

Structure Parameter	Observed Value	Calculated Value
a (Å)	7.596	7.898
b (Å)	8.231	8.685
c (Å)	5.078	5.174
α, γ (degrees)	90.0	90.0
β (degrees)	94.11	94.05

TABLE 7. Potential parameters for sodium perchlorate

Short Range Potential Parameters:			
Interaction	A(eV)	ρ (Å)	C(eV Å ⁶)
Na-O	866.245	0.2841	13.484
O-O	3485.8	0.2457	11.981

Charges (l e l): $q(\text{Na}) = 1.0$, $q(\text{Cl}) = 0.914424$, $q(\text{O}) = -0.478606$
 Force Constants: $k_s = 1.5913 \text{ eV \AA}^{-2}$; $k_b = 1.267 \text{ eV rad}^{-2}$

TABLE 8. Comparison of observed and calculated lattice parameters for sodium perchlorate

Structure Parameter	Observed Value	Calculated Value
a (Å)	7.085	6.972
b (Å)	6.526	6.424
c (Å)	7.048	7.052
α, β, γ (degrees)	90.0	90.0

Perchlorates. The potential was obtained by fitting to the orthorhombic phase of sodium perchlorate (Hermann and Ilge, 1931). It was defined in exactly the same way as the phosphate potential described

above. The potential parameters obtained are given in Table 7, and the lattice parameters obtained are given in Table 8 (with the experimental values for comparison). As a test of transferability, the

TABLE 9. Metal — oxygen parameters for transferred potentials

Interaction	A (eV)	ρ (Å)	C (eV Å ⁶)
Cs—O	15085.4788	0.2549	0.0
K—O	4865.9525	0.2549	0.0
Rb—O	8053.2102	0.2549	0.0
Mg—O	859.9522	0.3012	0.0
Sr—O	510.2696	0.3736	0.0

TABLE 10. Comparison of observed and calculated structure for the cubic phase of sodium perchlorate

Structure Parameter	Observed Value	Calculated Value
a, b, c (Å)	7.25	6.66
α, β, γ (degrees)	90.0	90.0

TABLE 11. Comparison of observed and calculated structure parameters for caesium perchlorate

Structure Parameter	Observed Value	Calculated value
a (Å)	9.823	10.201
b (Å)	6.009	5.902
c (Å)	7.764	7.991
α, β, γ (degrees)	90.0	90.0

TABLE 12. Comparison of observed and calculated structure parameters for potassium perchlorate

Structure Parameter	Observed Value	Calculated value
a (Å)	8.866	9.206
b (Å)	5.666	5.520
c (Å)	7.254	7.289
α, β, γ (degrees)	90.0	90.0

TABLE 13. Comparison of observed and calculated structure parameters for rubidium perchlorate

Structure Parameter	Observed Value	Calculated Value
a (Å)	9.252	9.668
b (Å)	5.789	5.662
c (Å)	7.472	7.602
α, β, γ (degrees)	90.0	90.0

parameters obtained were used in the energy minimisation of the cubic phase of sodium perchlorate (Wartchow and Berthold, 1978) and also potassium, rubidium and caesium perchlorate (Johansson and Lindqvist, 1977; Granzin, 1988). Note that in the latter three cases, a potential for the appropriate metal - oxygen interaction was fitted, and

these potentials are given in Table 9. The calculated lattice parameters are compared with the experimental values in Tables 10-13. Comparisons of calculated and experimental (Hausuhl, 1990) elastic constants for rubidium, potassium and caesium perchlorates are given in Tables 14-16.

Agreement is reasonably good in all cases, except

TABLE 14. Comparison of observed and calculated elastic constants for caesium perchlorate

Index	Observed Value (10^{11} dyne cm^{-2})	Calculated Value (10^{11} dyne cm^{-2})
C11	2.242	2.019
C22	2.034	1.412
C33	2.526	2.177
C12	1.591	0.922
C13	0.822	0.578
C23	0.934	0.458
C44	0.346	0.295
C55	0.488	0.612
C66	0.877	0.721

TABLE 15. Comparison of observed and calculated elastic constants for potassium perchlorate

Index	Observed Value (10^{11} dyne cm^{-2})	Calculated Value (10^{11} dyne cm^{-2})
C11	2.842	2.361
C22	2.924	1.789
C33	3.717	2.951
C12	1.787	1.079
C13	0.999	0.625
C23	1.167	0.428
C44	0.621	0.162
C55	0.912	0.903
C66	1.139	0.743

TABLE 16. Comparison of observed and calculated elastic constants for rubidium perchlorate

Index	Observed Value (10^{11} dyne cm^{-2})	Calculated Value (10^{11} dyne cm^{-2})
C11	2.511	2.253
C22	2.519	1.611
C33	3.252	2.596
C12	1.746	1.013
C13	0.810	0.614
C23	1.016	0.471
C44	0.454	0.241
C55	0.668	0.759
C66	1.024	0.754

for the structure reported in Table 10. Here the 10% underestimate of the lattice parameter can be explained by the fact that this is a high temperature structure, and it will be necessary to carry out free energy calculations to see if the potential performs better once temperature is included.

Conclusions

The results presented in this paper show that empirical fitting procedures can be successfully used to obtain potentials which reproduce the structures and elastic properties of molecular ionic materials. These potentials are now being used in morphological calculations, where the calculation of surface and attachment energies are used to predict crystal growth morphology (Jackson *et al.*, 1994, in preparation)

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