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# Computer modelling of ammonium nitrate: I. Development of potentials and calculation of lattice properties

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**Abstract.** The computer modelling of ammonium nitrate is described. Interatomic potentials are derived for ammonium and nitrate molecular ions, using empirical fitting to ammonium halides and alkali nitrates, and are used to calculate crystal and lattice properties which are compared with available experimental data. The potentials are then used to model the low temperature phase (phase V) of ammonium nitrate.

## 1. Introduction

Molecular ionic materials pose particular challenges to computer modelling 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, defect structure and crystal growth morphology [1, 2]. Potential models, a prerequisite of any computer modelling study, can be parametrized in one of two ways: parameters may be calculated directly, by, e.g., quantum mechanical methods, or they may be obtained by empirical fitting. It is the latter method that is applied in this paper.

Ammonium nitrate is an important industrial compound. It exists in a number of phases [3], and, since it has both a molecular anion and a molecular cation, it presents a particular challenge to the development of a potential model. The procedure adopted in this paper is to obtain potentials for the ammonium and nitrate groups separately, by fitting to ammonium bromide and potassium nitrate. The potentials are then evaluated by transferring to ammonium chloride and sodium nitrate respectively, and are finally transferred to the low temperature phase of ammonium nitrate.

## 2. 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.

### 2.1. 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  $A, \rho$  and  $C$  are parameters whose values are obtained for each ion pair involved. In this paper, they are obtained by empirical fitting.

## 2.2. Bonded interactions

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

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

where  $k_s, k_b$  and  $k_t$  are bond-stretching, bond-bending and torsional force constants respectively, and  $r_0, \theta_0$  are equilibrium bond lengths and bond angles respectively. Parameters  $S$  and  $n$  relate to the sign and phase of the torsion, and are set to +1 and 0.0 respectively. Values of force constants are usually calculated by 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.

## 3. Empirical fitting for molecular ionic materials

The process of empirical fitting of potentials has been described elsewhere [4, 5] 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 and energy minimization were carried out using the GULP program [6], which calculates lattice properties analytically for a given potential, including the elastic constants reported later.

## 4. Potential fitting to ammonium halides and alkali nitrates

### 4.1. Ammonium halides

A potential was empirically fitted to the crystal structure of ammonium bromide [7]. Note that the crystal structure is disordered with respect to the direction of the ammonium ion. This disorder was modelled in the fitting process by making use of the partial occupancy facility in the GULP code. The ammonium potential obtained was transferred to ammonium chloride, and the hydrogen–chloride ion potential fitted to the  $\text{NH}_4\text{Cl}$  structure [8]. The potential parameters obtained for both materials are given in table 1, and the resulting calculated lattice parameters are compared with experimental values in table 2. For the structure not involved in fitting ( $\text{NH}_4\text{Cl}$ ), agreement of 0.1% is observed, confirming transferability of the ammonium potential. In addition, calculated elastic constants for both compounds are given in table 3, and compared with available experimental values. It should be noted that elastic constants were not used in the fitting, and that this level of agreement is typical for molecular ionic compounds [1, 2].

**Table 1.** Short range potential parameters for NH<sub>4</sub>Br and NH<sub>4</sub>Cl. Charges ( $|e|$ ):  $q_{Br}, q_{Cl} = -1.0$ ,  $q_N = -0.65536$ ,  $q_H = 0.41384$ . Bonding force constants:  $k_s(\text{N-H}) = 5.1632 \text{ eV \AA}^{-2}$  ( $r_0 = 1.01 \text{ \AA}$ ),  $k_b(\text{H-N-H}) = 0.35526 \text{ eV rad}^{-2}$  ( $\theta_0 = 109.47^\circ$ ).

| Interaction | A (eV)    | $\rho$ (Å) | C (eV Å <sup>6</sup> ) |
|-------------|-----------|------------|------------------------|
| H-H         | 4.0261    | 0.7969     | 2.0325                 |
| H-Br        | 47 339.58 | 0.1978     | 124.5464               |
| H-Cl        | 6497.92   | 0.2513     | 168.3309               |

**Table 2.** Comparison of calculated and experimental lattice parameters for NH<sub>4</sub>Br and NH<sub>4</sub>Cl.

| Parameter          | Calculated | Experimental | % difference |
|--------------------|------------|--------------|--------------|
| NH <sub>4</sub> Br |            |              |              |
| $a = b = c$        | 4.0706     | 4.0594       | 0.28         |
| NH <sub>4</sub> Cl |            |              |              |
| $a = b = c$        | 3.8638     | 3.8600       | 0.10         |

**Table 3.** Elastic constants for NH<sub>4</sub>Br and NH<sub>4</sub>Cl (units:  $10^{11} \text{ dyne cm}^{-2} = 10 \text{ GPa}$ ).

|                    | 1        | 2        | 3        | 4        | 5        | 6        |
|--------------------|----------|----------|----------|----------|----------|----------|
| NH <sub>4</sub> Br |          |          |          |          |          |          |
| 1                  | 3.423 14 | 0.759 84 | 0.759 84 | 0.000 00 | 0.000 00 | 0.000 00 |
| 2                  | 0.759 84 | 3.423 14 | 0.759 84 | 0.000 00 | 0.000 00 | 0.000 00 |
| 3                  | 0.759 84 | 0.759 84 | 3.423 14 | 0.000 00 | 0.000 00 | 0.000 00 |
| 4                  | 0.000 00 | 0.000 00 | 0.000 00 | 0.676 02 | 0.000 00 | 0.000 00 |
| 5                  | 0.000 00 | 0.000 00 | 0.000 00 | 0.000 00 | 0.676 02 | 0.000 00 |
| 6                  | 0.000 00 | 0.000 00 | 0.000 00 | 0.000 00 | 0.000 00 | 0.676 02 |
| NH <sub>4</sub> Cl |          |          |          |          |          |          |
| 1                  | 3.781 04 | 0.955 54 | 0.955 54 | 0.000 00 | 0.000 00 | 0.000 00 |
| 2                  | 0.955 54 | 3.781 04 | 0.955 54 | 0.000 00 | 0.000 00 | 0.000 00 |
| 3                  | 0.955 54 | 0.955 54 | 3.781 04 | 0.000 00 | 0.000 00 | 0.000 00 |
| 4                  | 0.000 00 | 0.000 00 | 0.000 00 | 0.887 52 | 0.000 00 | 0.000 00 |
| 5                  | 0.000 00 | 0.000 00 | 0.000 00 | 0.000 00 | 0.887 52 | 0.000 00 |
| 6                  | 0.000 00 | 0.000 00 | 0.000 00 | 0.000 00 | 0.000 00 | 0.887 52 |

Experimental values (NH<sub>4</sub>Cl) ( $10^{11} \text{ dyne cm}^{-2}$ ):  $c_{11} = 4.74$ ,  $c_{12} = 1.64$ ,  $c_{44} = 1.43$ .

#### 4.2. Alkali nitrates

A potential was empirically fitted to the  $\alpha$ -phase of potassium nitrate at 25 °C [9], the lowest temperature phase of the compound. The nitrate potential obtained was transferred to sodium nitrate with the sodium–oxygen potential parameters being fitted to the NaNO<sub>3</sub> structure [10]. The fitted parameters are shown in table 4, and the comparison between the experimental and calculated structures is shown in table 5. Agreement of about 1% is observed for the NaNO<sub>3</sub> structure, and it is noted that this structure is of lower symmetry than the one used in the fitting, which gives further confidence in the validity of the transferred potential. In table 6, calculated values of the elastic constants are given. For the NaNO<sub>3</sub> structure, a negative value of  $c_{24}$  is expected from the symmetry.

**Table 4.** Short range potential parameters for KNO<sub>3</sub> and NaNO<sub>3</sub>. Charges ( $|e|$ ):  $q_K, q_{Na} = 1.0$ ,  $q_N = 0.6329$ ,  $q_O = -0.5464$ . Bonding force constants:  $k_s(\text{N-O}) = 48.597 \text{ eV \AA}^{-2}$  ( $r_0 = 1.24 \text{ \AA}$ ),  $k_b(\text{O-N-O}) = 14.5815 \text{ eV rad}^{-2}$  ( $\theta_0 = 120.0^\circ$ ),  $k_t(\text{O-N-O-O}) = 1.1392 \text{ eV}$ ,  $\varphi = 0.0^\circ$ .

| Interaction | A (eV)  | $\rho$ (Å) | C (eV Å <sup>6</sup> ) |
|-------------|---------|------------|------------------------|
| O–O         | 36000.8 | 0.197 46   | 24.0                   |
| O–N (nb)    | 5050.4  | 0.112 64   | 0.0                    |
| O–K         | 5900.6  | 0.2549     | 0.0                    |
| O–Na        | 3200.6  | 0.2390     | 0.0                    |

**Table 5.** Comparison of calculated and experimental lattice parameters for KNO<sub>3</sub> and NaNO<sub>3</sub>.

| Parameter         | Calculated | Experimental | % difference |
|-------------------|------------|--------------|--------------|
| KNO <sub>3</sub>  |            |              |              |
| <i>a</i>          | 5.4282     | 5.4142       | 0.26         |
| <i>b</i>          | 9.1673     | 9.1659       | 0.02         |
| <i>c</i>          | 6.4277     | 6.4309       | −0.05        |
| NaNO <sub>3</sub> |            |              |              |
| <i>a</i>          | 5.0183     | 5.0710       | −1.04        |
| <i>b</i>          | 5.0183     | 5.0710       | −1.04        |
| <i>c</i>          | 16.9489    | 16.8250      | 0.74         |

**Table 6.** Elastic constants for KNO<sub>3</sub> and NaNO<sub>3</sub> (units:  $10^{11} \text{ dyne cm}^{-2} = 10 \text{ GPa}$ ).

|                   | 1        | 2         | 3        | 4         | 5        | 6        |
|-------------------|----------|-----------|----------|-----------|----------|----------|
| KNO <sub>3</sub>  |          |           |          |           |          |          |
| 1                 | 3.763 93 | 1.888 53  | 1.328 96 | 0.000 00  | 0.000 00 | 0.000 00 |
| 2                 | 1.888 53 | 2.899 06  | 1.326 40 | 0.000 00  | 0.000 00 | 0.000 00 |
| 3                 | 1.328 96 | 1.326 40  | 0.990 12 | 0.000 00  | 0.000 00 | 0.000 00 |
| 4                 | 0.000 00 | 0.000 00  | 0.000 00 | 0.798 29  | 0.000 00 | 0.000 00 |
| 5                 | 0.000 00 | 0.000 00  | 0.000 00 | 0.000 00  | 0.671 67 | 0.000 00 |
| 6                 | 0.000 00 | 0.000 00  | 0.000 00 | 0.000 00  | 0.000 00 | 0.862 96 |
| NaNO <sub>3</sub> |          |           |          |           |          |          |
| 1                 | 5.368 27 | 2.468 86  | 2.512 92 | 0.781 21  | 0.000 00 | 0.000 00 |
| 2                 | 2.468 86 | 5.368 27  | 2.512 92 | −0.781 21 | 0.000 00 | 0.000 00 |
| 3                 | 2.512 92 | 2.512 92  | 2.255 10 | 0.000 00  | 0.000 00 | 0.000 00 |
| 4                 | 0.781 21 | −0.781 21 | 0.000 00 | 0.982 37  | 0.000 00 | 0.000 00 |
| 5                 | 0.000 00 | 0.000 00  | 0.000 00 | 0.000 00  | 0.982 37 | 0.781 21 |
| 6                 | 0.000 00 | 0.000 00  | 0.000 00 | 0.000 00  | 0.781 21 | 1.449 70 |

## 5. Transfer of the potential to ammonium nitrate

The potential parameters for the ammonium and nitrate ions were transferred to ammonium nitrate to try to reproduce the lowest temperature phase, phase V [3]. However it was found that the crystal structure could not be reproduced by just fitting the cross parameters for H...O and H...N (nitrate). The parameters for the H...H intermolecular potential also had to be adjusted to produce a reasonable fit to the experimental data. This change in the potential can be considered reasonable when considering the difference between the ammonium halide

**Table 7.** Short range potential parameters for  $\text{NH}_4\text{NO}_3$ . Charges ( $|e|$ ):  $q_N = 0.6329$ ,  $q_O = -0.5464$ ,  $q_H = 0.41384$ . Bonding force constants:  $k_s(\text{N-O}) = 48.597 \text{ eV \AA}^{-2}$  ( $r_0 = 1.23 \text{ \AA}$ ),  $k_b(\text{O-N-O}) = 14.5815 \text{ eV rad}^{-2}$  ( $\theta_0 = 120.0^\circ$ ),  $k_t(\text{O-N-O-O}) = 1.1392 \text{ eV}$ ,  $\varphi = 0.0^\circ$ ;  $k_s(\text{N-H}) = 5.1632 \text{ eV \AA}^{-2}$  ( $r_0 = 1.01 \text{ \AA}$ ),  $k_b(\text{H-N-H}) = 1.85526 \text{ eV rad}^{-2}$  ( $\theta_0 = 109.47^\circ$ ).

| Interaction | $A$ (eV) | $\rho$ ( $\text{\AA}$ ) | $C$ ( $\text{eV \AA}^6$ ) |
|-------------|----------|-------------------------|---------------------------|
| O-O         | 36040.8  | 0.19756                 | 24.0                      |
| O-N (nb)    | 5050.4   | 0.11264                 | 0.0                       |
| H-O         | 2756.0   | 0.19800                 | 0.0                       |
| H-H         | 155.13   | 0.02330                 | 0.0                       |
| N-H (nb)    | 14750.89 | 0.25000                 | 31.9                      |

(nb denotes 'non-bonded').

**Table 8.** Comparison of calculated and experimental lattice parameters for  $\text{NH}_4\text{NO}_3$ .

| Parameter | Calculated | Experimental | % difference |
|-----------|------------|--------------|--------------|
| $a$       | 8.0354     | 7.8850       | 1.91         |
| $b$       | 8.0545     | 7.9202       | 1.70         |
| $c$       | 9.5638     | 9.7953       | -2.36        |

**Table 9.** Elastic constants for  $\text{NH}_4\text{NO}_3$  (units:  $10^{11} \text{ dyne cm}^{-2} = 10 \text{ GPa}$ ).

|   | 1        | 2        | 3        | 4        | 5        | 6        |
|---|----------|----------|----------|----------|----------|----------|
| 1 | 3.338 18 | 1.321 90 | 1.888 83 | 0.000 00 | 0.000 00 | 0.000 00 |
| 2 | 1.321 90 | 3.353 08 | 1.894 19 | 0.000 00 | 0.000 00 | 0.000 00 |
| 3 | 1.888 83 | 1.894 19 | 5.967 52 | 0.000 00 | 0.000 00 | 0.000 00 |
| 4 | 0.000 00 | 0.000 00 | 0.000 00 | 2.065 86 | 0.000 00 | 0.000 00 |
| 5 | 0.000 00 | 0.000 00 | 0.000 00 | 0.000 00 | 1.783 69 | 0.000 00 |
| 6 | 0.000 00 | 0.000 00 | 0.000 00 | 0.000 00 | 0.000 00 | 1.562 52 |

system to which the potential was fitted, and the ammonium nitrate system. Ammonium nitrate is hydrogen bonded and this partial donation of electron density from the oxygen to the hydrogen means that the electronic environment of the hydrogen is different in the two systems, leading to a change in the intermolecular potential. The fact that the O...O potential did not have to be changed also indicates that the hydrogen bonding has a greater effect on the environment of the hydrogen than the oxygen. The overall potential is given in table 7. Comparison of the calculated and experimental lattice parameters is given in table 8; as can be seen, the reproduction of the crystal structure is achieved to within a few per cent. The elastic constants have also been calculated, and are given in table 9.

## 6. Conclusions

This paper describes the empirical fitting and subsequent transfer of potentials for materials containing ammonium and nitrate molecular ions. Agreement between experimental and calculated lattice parameters is good, indicating that, as far as reproduction of structure is concerned, the potentials for the ions transfer well into other compounds for which data are available. When transferred to phase V of ammonium nitrate, satisfactory reproduction of the experimental structure is obtained.

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