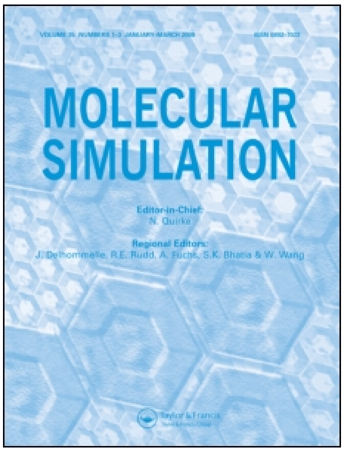

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PAIR POTENTIALS FROM *AB INITIO* CALCULATIONS FOR USE IN MD SIMULATIONS OF MOLTEN ALKALI CARBONATES

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Ab initio calculations at the Hartree-Fock SCF level have been carried out to determine the pair interaction between the alkali ions and the carbonate ion. A distinction has been made between terms in the metal ion - carbonate ion interaction which have different physical origins, such as static coulomb interaction, short-range repulsion and electronic polarization. The additivity of the pair interaction is investigated in 3-body calculations. It is shown that for these 3-body systems pairwise addition of 2-body interactions from which polarization effects have been omitted is superior to pairwise addition of the full Hartree-Fock interactions. A model potential based on these modified interactions has been constructed. Results of MD simulations show that both structural and dynamical properties are well described by these pair potentials.

KEY WORDS: *Ab initio* pair potentials, molten alkali carbonate, molecular dynamics.

I. INTRODUCTION

The study of structural and dynamical properties of molten salts is one of the first fields that have been studied systematically by Molecular Dynamics techniques. The comparatively simple alkali halides [1,2] turned out to be very well suited to explore the merits and pitfalls of the MD method. Apart from this new insights in the structure and the diffusion mechanism in molten salts were obtained. As a result a great deal of knowledge has been acquired on how to deal with ionic systems, such as how to handle the long-range forces. These developments have enabled the use of MD methods in various fields of inorganic chemistry. This has included the study of alumina, silicates, and borates [3], as well as more complicated molten salts like nitrates and nitrites [4,5].

The present study deals with molten alkali carbonates. These salts are being used as electrolytes in fuel cells. Therefore, a more specific knowledge of their physical and chemical properties is desired. For example, it is known that the conductivity of mixtures of these salts depends very critically on their composition. However, there is no model to explain this specific dependence. Secondly, a better knowledge of transport of ions and solvated molecules is required to elucidate the mechanisms of the electrochemical reactions in the fuel cell [6].

The quality of an MD simulation depends primarily on the modelling of the interaction between the particles. For an n-body system this interaction can be decomposed in 2-, 3-,.., n-body terms. The 2-body term, interaction between two isolated particles, will be the dominant term but the 3-body interaction, which involves electronic polarization, is usually not negligible. The inclusion of polarization introduces some considerable difficulties. In general, the polarization cannot be a constant, free-body polarization but must be damped at small interionic separations to avoid the "polarization catastrophe". Secondly, an iterative self-consistent scheme is necessary to account for induced dipole - induced dipole interactions. Recently, however, a method has been suggested which seems to go round this difficulty by treating the induced dipole as a dynamical variable [7].

In most simulations, effective 2-body potentials have been used in which averaged many-body effects have been incorporated. In many cases this is quite feasible as in a disordered system like a molten salt or a glass polarization effects will tend to cancel. For these ionic, inorganic systems mentioned above usually a potential is adopted which contains the long-range Coulombic interaction, based on effective charges, and a Born-Mayer-Huggins (BMH) term to account for short range repulsion, using effective ionic radii. The parameters are usually obtained by fitting structural or dynamical data. In some cases, where experimental data are scarce, this limits the value of the MD results. Secondly, since the effective parameters obtained from such a fit are only valid as fitting parameters, few conclusions can be drawn as to the relative importance of separate terms in the interaction energy, nor can they *a priori* be transferred to related systems, e.g. mixtures. Addition of new terms like polarization and dispersion would require a redetermination of all parameters.

Quantum chemistry provides valuable tools to study the interaction between a limited set of particles. A 2-body interaction can be calculated quite accurately as only a limited set of geometries needs to be considered. The number of relevant geometries increases rapidly with the number of atoms. This, as well as the increasing number of electrons, makes that usually only 2- and 3-body terms are taken into account. Here, we use the HF-SCF method to study the metal ion - carbonate interaction with some detail. In the simulation of the molten alkali carbonates this interaction is the most critical one as it is a delicate balance of electrostatic attraction and short range repulsion. The other interactions are dominated by electrostatic repulsion. First Hartree-Fock (HF-SCF) calculations were performed on the "supermolecule" $M^+ - CO_3^{2-}$ (M = Li, Na, K). To enable a decomposition of this true 2-body interaction energy the same calculations were carried out for a system where the M^+ ion is replaced by a point charge. Next, we study the (3-body) interaction between M^+ and a carbonate ion polarized by a second M^+ ion.

In section IV we attempt to base a model potential on the *ab initio* calculations. In general this is a difficult step. Model potentials use effective atomic properties like atomic radii and atomic partial charges. These cannot be obtained from quantum chemical molecular calculations without introducing some arbitrariness. The dependence of the Mulliken charges on the basis set are well known. Alternative schemes to determine the partial charges have been developed, e.g. by requiring that they conserve the local dipole [8] or by numerically integrating the electronic density within a volume around the atom. Here as well some choices should be made beforehand. We have found it preferable to fit terms in the interaction energy to simple expressions such as the BMH and Coulomb terms mentioned above. The disadvantage of this procedure is that monomeric (atomic) parameters are used to fit dimeric (supermolecule) interactions. In general, these parameters will change when one of the monomers is replaced, i.e. the parameters are not transferable. By fitting the parameters to energy terms that are to a great extent transferable this problem of non-transferability is largely overcome. In section V some preliminary results of MD simulations on molten sodium carbonate are presented.

II. COMPUTATIONAL DETAILS OF THE *AB INITIO* CALCULATIONS

All calculations have been carried out in the Hartree-Fock Self Consistent Field (HF-SCF) scheme [9]. Several systems have been investigated. First the isolated CO_3^{2-} ion was studied, assuming a planar geometry of D_{3h} geometry with C–O distance kept fixed at 0.127 nm [10,11]. This CO_3^{2-} geometry was used in all subsequent calculations. The interaction between a metal ion and a carbonate ion was examined for three different orientations of the metal ion with respect to the carbonate ion. The carbonate ion has been drawn in Figure 1. The metal ion is placed either on the z-axis, resulting in a system of C_{3v} symmetry, or on the positive or negative x-axis, resulting in a system with C_{2v} symmetry. To enable a distinction between Coulomb and polarization effects on the one hand, and overlap and bonding effects on the other hand, we also studied the interaction between CO_3^{2-} and a point charge Q with charge $+e$.

Three-body effects were investigated in a system consisting of two metal ions and a carbonate ion. A metal ion (Li^+, Na^+ or K^+) was put at a fixed position with respect to the carbonate ion, while a second metal ion of the same type approached the carbonate on the negative x-axis. Two cases were considered. In the first the metal ion is positioned on the positive x-axis at 0.30 nm (Li, Na) or 0.35 nm (K) from the C atom. This results in a system with overall C_{2v} symmetry, and therefore it will be denoted by "3-body C_{2v}". In the second case, the metal ion is put on the line making an angle of 60 degrees with the positive x-axis. The distance to the C atom is 0.22 nm in case of Li^+, 0.28 nm in case of Na^+ and 0.30 nm for K^+. This system will be referred to as 3-body C_s.

Large, contracted, Gaussian type basis sets have been employed. The standard set consisted of the (9,5) set of Huzinaga for carbon contracted to (5,3). The oxygen (9,5) set of Huzinaga [12] was extended with an additional p-function with an exponent optimized for O^- by Dunning and Hay [13], and contracted to (5,4). For Li^+ and Na^+ the larger Huzinaga sets [14] were taken. The exponents of the outermost s-functions

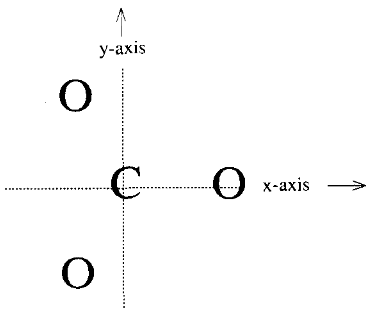

Figure 1 Geometry and orientation of the carbonate ion in the xy plane. The same orientation is assumed throughout this work.

were scaled to $0.17/a_0^2$ and $0.07/a_0^2$ for Li^+ and to $0.21/a_0^2$ and $0.07/a_0^2$ for Na^+. The resulting (9) and (12,6) sets were contracted to (5) and (7,3), respectively. For K^+ the Wachters (14,9) set [15] was used, contracted to (8,5). Here, the two outermost s-functions were replaced by s-functions with exponents $0.12/a_0^2$ and $0.046/a_0^2$. To test the stability of the results with respect to the basis set additional calculations were carried out with additional d-type polarization functions on C and O. The respective exponents, $0.75/a_0^2$ and $0.85/a_0^2$, were taken from Dunning and Hay [13].

III. RESULTS OF THE *AB INITIO* CALCULATIONS

The results of the calculations on CO_3^{2-} are summarized in Table 1. It is shown that the addition of polarization functions contributes significantly to the description of the binding in CO_3^{2-}. The binding energy at the assumed geometry increases by 283 kJ/mol. The Mulliken charge distribution can be used to illustrate the change, despite its arbitrary character. There is a charge transfer of about 0.45 *e* from C p-functions to C d-functions (+0.2 *e*) and to O p- and d-functions, increasing the gross charges on the ions. That this charge corresponds only to a different use of the basis functions and not to a significant physical charge reduction is demonstrated by the results obtained by numerical integration of the electron density. A sphere around the central C atom, bisecting the C–O distances only loses 0.04 *e* of electronic charge. This procedure also reveals that the number of electrons near the central C atom is much smaller than predicted by the Mulliken analysis. This is not an uncommon feature of the Mulliken population analysis as the basis functions of a central atom are usually relatively better used in the description of the electron distribution than the functions of outer atoms.

The results of the calculations on the M^+-CO_3^{2-} system are displayed in Figure 2 and summarized in Table 2. It should be noted that points which in Figure 2 look like a local minimum may very well be the saddle points on the potential surface, since only a small part of the potential surface has been investigated. In fact, in all three systems the minimum on the positive x-axis corresponds to such a saddle point. Among the configurations studied the one with the metal ion on the negative x-axis results in the deepest minimum, regardless of the kind of metal ion. The binding energies are largest and the bond lengths smallest in the Li systems. In this system the binding energy is also most sensitive to the orientation of the metal ion to the carbonate ion. Note that the binding energies are very large, in the order of 1000 kJ/mol as is usual for an ionic bond, and that the differences between the minima are smaller than 150 kJ/mol. These values should be compared to the value of the thermal

Table 1 Total energy, Mulliken and integrated charges of the isolated carbonate ion.

	Standard basis set	*+pol. functions*
Total energy/(hartree)	−262.26902	−262.37667
Mulliken charges/(*e*)		
C	0.76	1.01
O	−0.92	−1.00
Integrated charges[a]/(*e*)		
C	2.42	2.46
O	−1.47	−1.49

[a] Charge within 0.0635 nm of the C nucleus is assigned to C.

Table 2 Binding energies[a] and bond lengths[b] of M^+-CO_3^{2-} systems.

		z-axis	*pos. x-axis*	*neg. x-axis*
Li^+ CO_3^{2-}				
	E	995	1054	1140[c]
	R	0.18	0.28	0.21[c]
Na^+ CO_3^{2-}				
	E	929	926	1019
	R	0.21	0.32	0.25
K^+ CO_3^{2-}				
	E	825	810	884
	R	0.23	0.35	0.28

a. Energies in kJ/mol

b. Lengths in nm

c. The values obtained using a basis set without diffuse s-functions on Li are 1133 kJ/mol and 0.21 nm; when this set is extended with polarization functions on C and O the values are 1159 kJ/mol and 0.205 nm.

energy kT which is about 10 kJ/mol for systems at about 1200 K. The bond lengths increase by 0.03–0.04 nm from Li to Na, and by 0.02–0.03 nm from Na to K. The shape of the repulsion is similar in all systems.

The basis set effects have been studied in the binding region of CO_3^{2-} and Li^+ (Li on the negative x-axis). It is shown in Figure 3 that the use of polarization functions or the omission of diffuse metal s-functions only slightly affects the binding. Using polarization functions results in considerable lower total energies, but this is almost completely due to an improvement of the description of the carbonate ion. The largest effect is on the repulsion, which is softer when a larger basis set is employed. In view of the large interaction energies it is not expected that basis set superposition errors play an important role. This is partially confirmed by the fact that the diffuse s-functions on the Li^+ ion are only of minor importance at distances near the minimum (compare curves A and B in Figure 3), which indicates that they are not used to improve the description of the carbonate ion. Somewhat suprisingly, it turns out that at large separations curves B and C coincide but curve A is below these two. A Mulliken population analysis of the wave function at a Li^+-CO_3^{2-} separation of 0.75 nm shows that the diffuse functions have an occupancy of 0.25. This was found to be due to a near-degeneracy effect. At infinite separation the HF energy difference between the Li^+-CO_3^{2-} and Li-CO_3^- systems is only 78 kJ/mol. For Na^+-CO_3^{2-} and K^+-CO_3^{2-} a similar effect is found, with energy separations of 129 kJ/mol and 208 kJ/mol, respectively. Since this near-degeneracy effect disappears at smaller distances, there is no reason to presume that the ionic bond description breaks down in this case.

The Hartree-Fock interaction energy in M^+-CO_3^{2-} systems can be decomposed in three terms:

$$V = V_{\text{Coulomb}} + V_{\text{induction}} + V_{\text{short range}}. \quad (1)$$

V_{coulomb} denotes the electrostatic interaction energy between the unperturbed change distributions of the (isolated) metal and carbonate ions, $V_{\text{induction}}$ is the induction energy that arises from induced multipole moments on either particle. $V_{\text{short range}}$ is the repulsion from the overlapping electron clouds. Note, that this decomposition does not include dispersion terms. This kind of interaction results from correlated electron movements that are not included at the Hartree-Fock level. The first two terms on the right hand side of (1) can to a good approximation be obtained from calculations on the system Q-CO_3^{2-}, where Q is point charge with charge $+e$. Using the HF wave

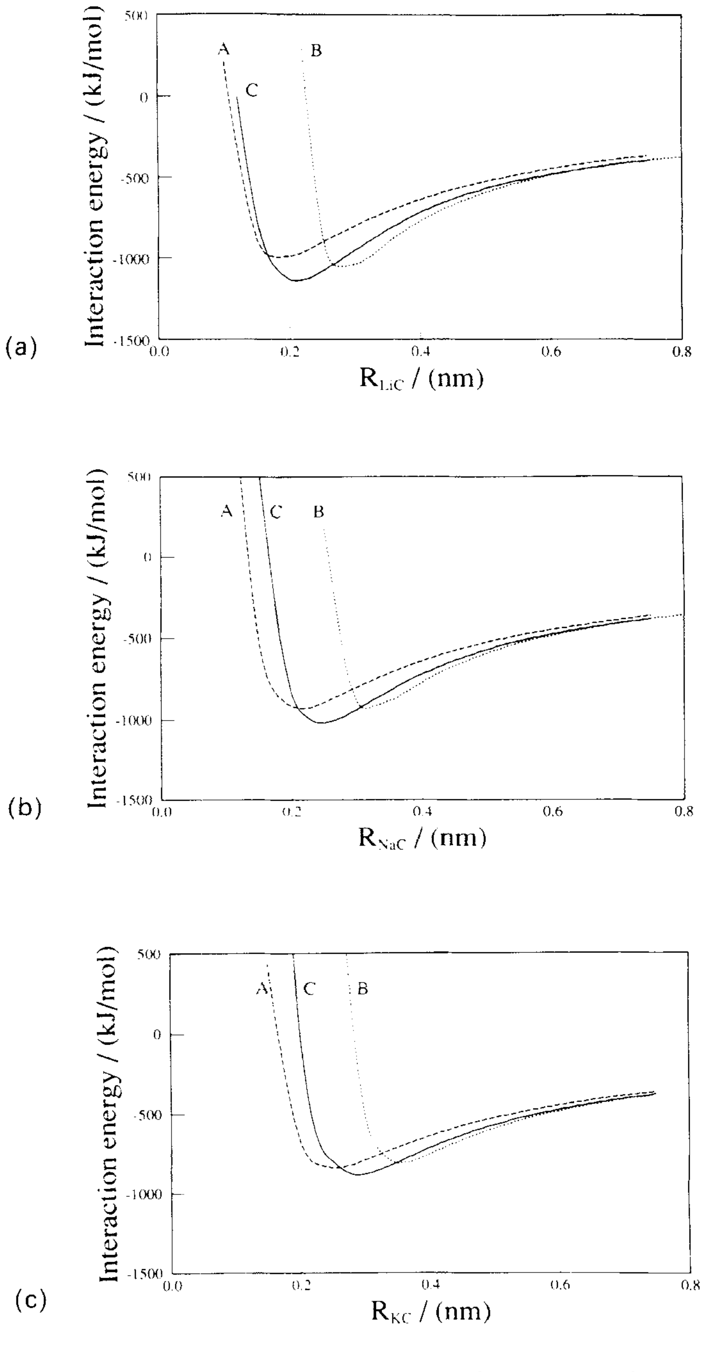

Figure 2 Hartree-Fock potential energy curves of Li^+-CO_3^{2-} (a), Na^+-CO_3^{2-} (b), and K^+-CO_3^{2-} (c), respectively. A is the interaction of the carbonate ion with a metal ion on the z-axis, B with a metal ion on the positive x-axis, and C with a metal ion on the negative x-axis.

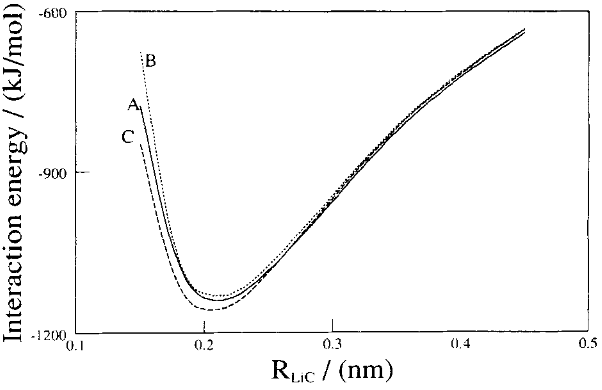

Figure 3 Hartree-Fock potential energy curves of Li^+-CO_3^{2-} hear the minimum A is obtained with the standard basis set, B with the same set but without the outer two s-functions on Li. C is obtained with a basis set without the outer two s-functions on Li, but with d-polarization functions on C and O.

function of unperturbed CO_3^{2-} as a trial function, $V_{coulomb}$ can be calculated from the energy in the first iteration of the SCF process. $V_{induction}$ is obtained from the energy of the fully relaxed system. The minor approximation in this scheme is that induced multipoles on the metal ion are neglected.

The different energy terms defined above are transferable to mixtures of molten alkali carbonates. The Coulomb interaction and the induction energy do not depend on the nature of the cation; the repulsion energy is the same for a specific carbonate-cation combination, irrespective of other ions in the melt.

In Figure 4 the total interaction energies of the respective metal ions with the carbonate ion are compared to the $V_{coulomb}$ and $V_{induction}$ (metal ion on the negative x-axis). At large distances, i.e. larger than 0.4 nm, the polarization contribution is almost negligible. However, it gradually increases with decreasing distance. At 0.2 nm

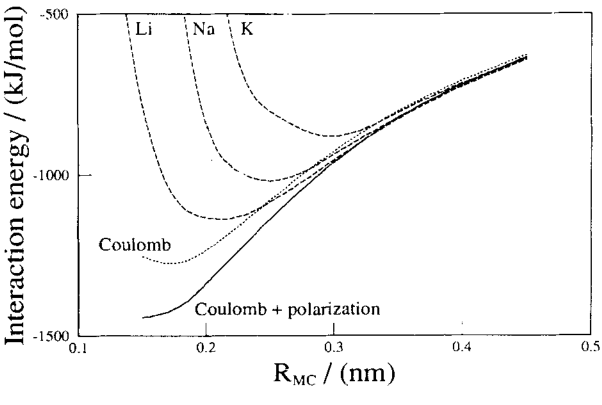

Figure 4 Potential energy curves of M^+-CO_3^{2-} systems compared with curve of Q-CO_3^{2-}. The metal ion or point charge is on the negative x-axis (see Figure 1). The dashed lines represent the interactions between M^+ and CO_3^{2-}, the dotted line labelled "Coulomb" represents the interaction between Q and a frozen CO_3^{2-} ion. The total interaction energy between Q and a (fully relaxed) CO_3^{2-} ion is represented by the solid line.

the polarization is 8% of the total Q–CO_3^{2-} interaction energy. The curves of the total interaction energy of the M^+–CO_3^{2-} systems coincide with the curve of the total interaction energy of Q–CO_3^{2-} at large distances. From Figure 4 the onset of the short range repulsion can be determined. This is at about 0.40, 0.35 and 0.30 nm for K, Na and Li, respectively. Along a distance of 0.05 nm the repulsion partially compensates the polarization, but at the potential minimum the repulsion is about twice as large as the polarization. This shows that at relevant separations repulsion and polarization are of comparative magnitude in all systems. Note, that the binding between the metal ion and the carbonate ion can be described in a fully ionic model. The total interaction energy curves of the M^+–CO_3^{2-} systems never drop significantly below that of the Q–CO_3^{2-} interaction, which means that covalency effects need not be considered explicitly but can be included in $V_{\text{short range}}$.

It may be assumed that the larger part of the polarization energy in the Q–CO_3^{2-} results from the induced dipole. This assumption is used to calculate the dipole polarizability of the isolated carbonate ions. The dipole polarizability α is assumed to be centered on the carbon atom and is computed in a finite field approach from:

$$V_{\text{induction}} = (1/2)\,\alpha/R_{QC}^4 \tag{2}$$

Values at $R_{QC} = 0.75$ nm have been used to find $\alpha = 4.30\cdot10^{-3}$, $6.10\cdot10^{-3}$, and $2.51\cdot10^{-3}\,\text{nm}^3$ with an ion on the negative x-axis, the positive x-axis and the z-axis respectively. This shows there is some anistropy in the polarizability. We approximate the trace of the polarizability tensor by the average of these values. Using this polarizability, the Clausius-Mosotti relation and the density of molten $Na_2CO_3^{2-}$ (1.94 g/cm^3 at 1200 K [16]) we predict an optical dielectric constant of 1.69. To our knowledge dielectric constants of molten carbonates have not been reported. For $NaNO_3$ the dielectric constant is of comparative magnitude: 1.9 [16].

The effect of 3-body terms in the interionic interaction is indicated in Figure 5. Pairwise addition of 2-body interaction energies in the C_{2v} M^+–CO_3^{2-}–M^+ system leads to overestimated interaction energies. This effect is largest for Li systems, smallest for K systems, and can be ascribed mainly to polarization effects which to a great extent cancel in the C_{2v} system. A similar effect has been found for the M^+–CO_3^{2-}–M^+ system with C_s symmetry. As cancelling of polarization is less effective in

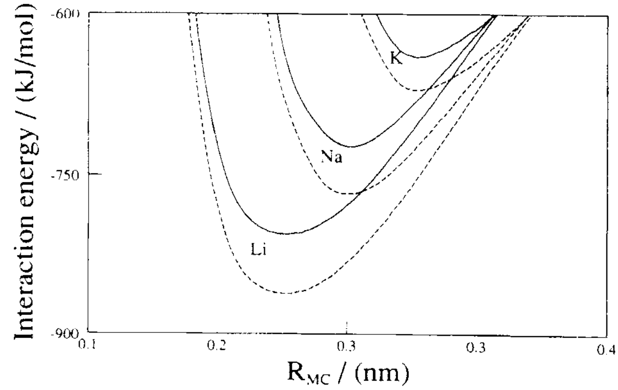

Figure 5 The potential energy curves of (M^+–CO_3^{2-})–M^+ of C_{2v} symmetry (see text). The solid lines represent the 3-body Hartree-Fock energy, the dashed lines are obtained by pairwise addition of Hartree-Fock 2-body interactions.

this case, the difference between the 3-body interaction energy and the interaction energy from pairwise addition of 2-body interactions is 40% smaller.

IV. MODEL POTENTIALS

The determination of a model potential based on the above *ab initio* calculations starts with the choice of an analytical form. This choice was based in the first place on the energy decomposition given in equation (1). Further demands are that the form is as simple as possible and that the resulting model potentials are transferable.

The Coulomb energy was assumed to be equal in all M^+–CO_3^{2-} systems and was obtained by fitting the expression:

$$V_{\text{Coulomb}} = \frac{Z_M Z_c}{r_{CM}} + \sum_{i=1}^{3} \frac{Z_M(2 + Z_C)}{3r_{CO_i}} \tag{3}$$

with $Z_M = 1.0e$, to the interaction energy of the $+e$ point charge and the unperturbed carbonate ion (Q–CO_3^{2-}) system. This means that we assume that the Coulomb interaction of the carbonate ion and the point charge can be described by a point charge distribution on the carbonate, with one point charge on each atom. The advantage of this approach is that the concept of atomic pair interactions can be used, under the condition that the geometry of the carbonate ion is constrained during the simulation. The outcome of a least squares fit is sensitive to the selection of points included in the fit. Large separations give rise to relatively large values of Z_C. On the other hand, the orientation of the point charge with respect to the carbonate ion was of minor importance. We have selected the range where the Coulomb term is the dominant term by far: interionic separations between 0.35 nm and 0.75 nm. Altogether sixteen points in all three directions considered were included. The resulting optimal point charge distribution (Table 3) differs from the one obtained by means of the Mulliken population analysis, as well as from the one found from a numerical integration of the Hartree-Fock density (Table 1), which again demonstrates the limited use of such analyses in the construction of model pair potentials.

The Hartree-Fock values of the short-range repulsion were obtained by subtracting the energy of the (relaxed) Q^+–CO_3^{2-} system at interionic separation R from the total HF interaction energy of the M^+–CO_3^{2-} system at the same separation. Altogether 35 points in the range 0.15–0.55 nm were included. At larger separations the repulsion is too small to be determined. For the short-range repulsion the interatomic Born-Mayer-Huggins form was chosen:

$$\begin{aligned} V_{\text{short range}} &= b\left(1 + \frac{Z_M}{n_M} + \frac{Z_C}{n_C}\right) \exp\left(\rho(\sigma_M + \sigma_C - r_{MC})\right) \\ &+ \sum_{i=1}^{3} b\left(1 + \frac{Z_M}{n_M} + \frac{Z_O}{n_O}\right) \exp\left(\rho(\sigma_M + \sigma_O - r_{MO_i})\right), \end{aligned} \tag{4}$$

where n_M, n_C and n_O are the number of electrons in the outer shell of the C, O and metal ion, respectively. b and ρ are constants. The parameters $\sigma_{M,C,O}$ (the "ionic radii") are the fit parameters to be determined in a least-squares fit of the repulsion energy. As from the M^+–CO_3^{2-} interaction only the sums $\sigma_M + \sigma_O$ can be determined, some choices regarding σ_M or σ_C and σ_O have to be made beforehand.

Table 3 Parameters[a] of the model pair potential of M^+–CO_3^{2-}.

Atom	*Z (e)*	*n*	*σ (nm)*
C	1.54	2.46	0.110
O	−1.18	7.18	0.133
Li	1.0	2.0	0.077
Na	1.0	8.0	0.107
K	1.0	8.0	0.139

[a] $b = 0.338 * 10^{-12}$ erg, $\rho = 34.5\ \mathrm{nm}^{-1}$

In this work values for σ_M are obtained from calculations on M^+–M^+ dimers. The short-range repulsion is then found by subtracting the Coulomb interaction energy of two $+e$ point charges from the total interaction energy. As can be seen in Figure 6, this seems to be a good approximation. The σ_M were found by a fit of:

$$V_{\text{short range}} = b\left(1 + 2\frac{Z_M}{n_M}\right)\exp\left(\rho(2\sigma_M - r_{MM})\right), \tag{5}$$

with all other parameters taken as above. A new fit of equation (4) to the repulsion in M^+–CO_3^{2-} yields the values of σ_C and σ_O listed in Table 3.

In Figure 7 the model potentials are compared to the *ab initio* ones for 2-body and 3-body systems. Since the model potential contains no polarization effects, the 2-body interaction is somewhat underestimated. Of course this effect is the largest for Li^+–CO_3^{2-}. In case of a 3-body system the interaction is still larger than found in an *ab initio* calculation, but this effect is smaller than when Hartree-Fock pair potentials are employed. It turns out that with the use of the value for σ_{Na} obtained above the repulsion between Na^+ and CO_3^{2-} is underestimated by the model. By enlarging σ_{Na} to 0.114 nm the short-range interaction in Na^+–CO_3^{2-} is represented just as well as in case of Li^+–CO_3^{2-} and K^+–CO_3^{2-}. This of course illustrates the point that monomeric parameters fitted to interaction in some dimer may not be transferred to other dimers. However, we expect little difficulty where it concerns the interaction between cations of different type, since the interaction is dominated by the Coulomb repulsion.

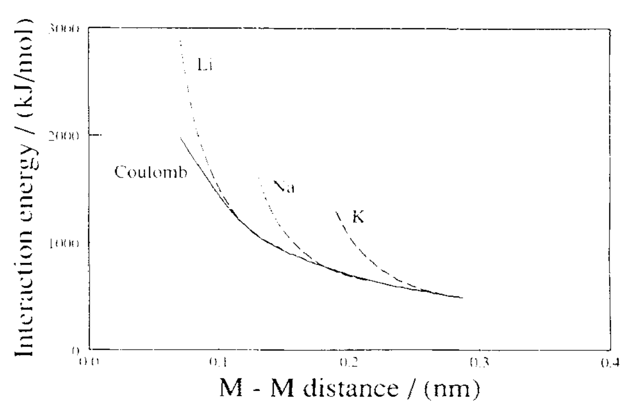

Figure 6 The Hartree-Fock interaction between alkali metal ions (dashed lines). The solid line is the interaction between two $+e$ point charges.

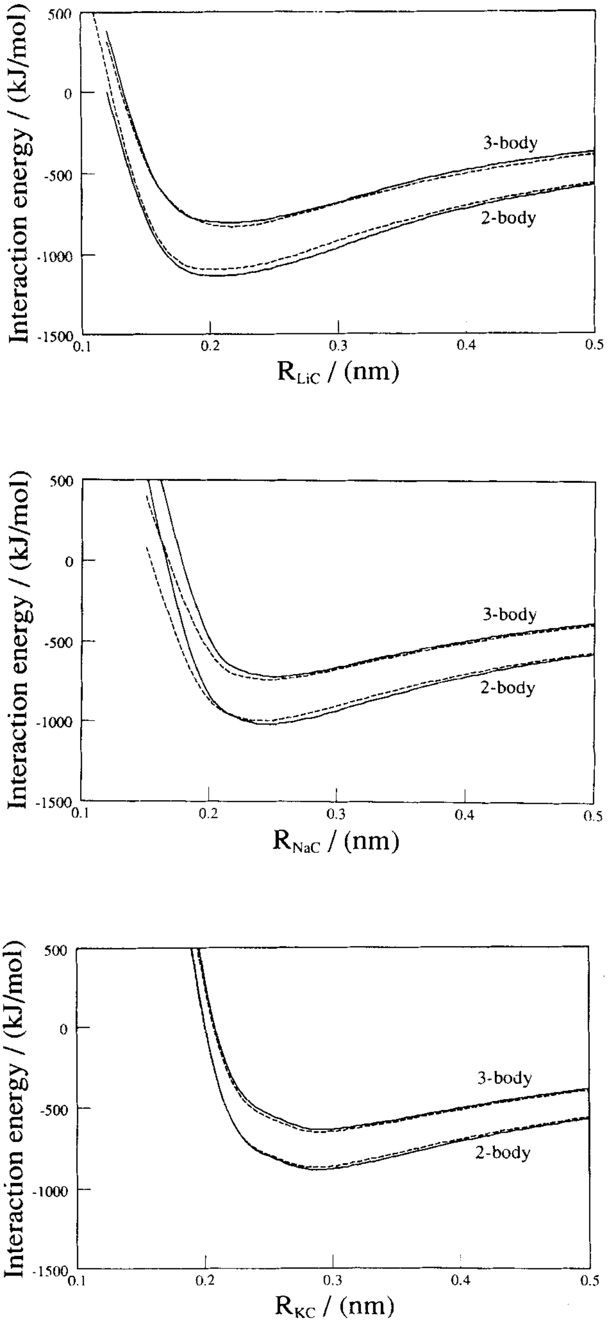

Figure 7 Hartree-Fock (solid lines) versus model (dashed lines) interaction energies, for M^+–CO_3^{2-} and M^+–CO_3^{2-}–M^+ (C_{2v} symmetry, see text).

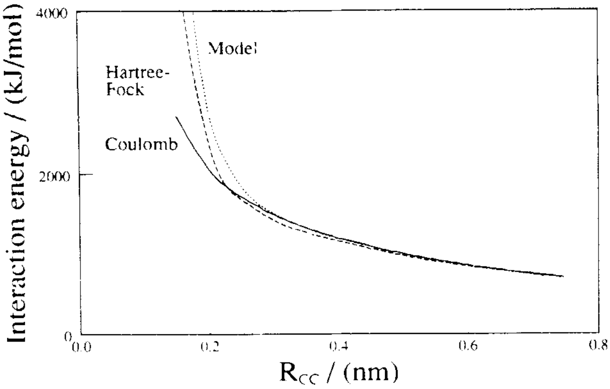

Figure 8 Interaction between two carbonate ions in an eclipsed configuration: Hartree-Fock (dashed line), full model potential (dotted line), and model Coulomb potential only (solid line).

Finally, it should be noted that the model represents well the repulsion between two carbonate ions, as is shown in Figure 8 for an eclipsed configuration of two carbonate ions. Here as well the interaction is dominated by the Coulomb interaction which is transferable.

In sect. III the polarizability of the carbonate ion was modelled by a dipole polarizability at the C position. This polarizability is quite anisotropic. Hence, a better approximation may be to put a dipole polarizability at all three oxygen centers in the carbonate ion. Taking the induced dipole - induced dipole interaction on the carbonate ion into account, it turns out that the polarizability caused by a point charge can be well represented in this model by an atomic polarization α_O of $1.2 \cdot 10^{-3}\,nm^3$.

V. MOLECULAR DYNAMICS SIMULATIONS

The present model potential (Table 2) was tested in an (N,V,T) Molecular Dynamics simulation of molten Na_2CO_3 at 1200 K. No polarization effects were taken into account. The Molecular Dynamics package GROMOS [17] was adapted to enable the use of a short-range BMH repulsion, and to use the Ewald method [18] to compute the Coulomb forces. 256 cations and 128 anions were considered in a basic cell with length $L = 2.28$ nm. The cut-off distance for the interactions was $L/2$; reciprocal space vectors were taken up to $|n|^2 \leqslant 27$, and the convergence parameter $\alpha = 5.6/L$ used.

The geometry of the carbonate ions was kept to the one used in the *ab initio* calculations. As the carbonate ion is planar and contains four atoms the SHAKE [19] method cannot be applied to all six distance constraints. The program has therefore been modified in the manner suggested by Ciccotti *et al.* [20].

The temperature was kept fixed by coupling to an external bath, adopting the method proposed by Berendsen *et al.* [21]. In this work the relaxation time was taken equal to the MD time step: 1 fs. After equilibrating at 2000 K, the system was annealed at 1200 K. The first 30000 time steps at this temperature were discarded; data were acquired from a subsequent run of 10000 steps. In this run the average total energy was -300 kJ/mol (omitting the C–O and O–O interactions within the CO_3^{2-}

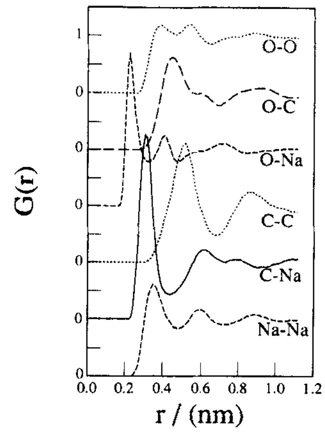

Figure 9 The pair correlation functions obtained from the MD simulation of the Na_2CO_3melt. The C–O and O–O correlations within the CO_3^{2-} ion have been omitted.

ion). The average pressure, calculated without the reciprocal part of the Coulomb interaction, was 13 kbar. Figure 9 shows the pair correlation functions in the simulated melt. There are very narrow and distinct Na–C and Na–O peaks. The position of the Na–O peak corresponds to an experimentally observed peak at 0.23 nm in the radial distribution curve inferred from x-ray diffraction measurements reported by Zarzycki [11]. According to this author this peak is not due to the internal O–O distances on the carbonate ion. The angular distribution functions (Figure 10) indicate that (a) the sodium atoms prefer positions 30° below or above the plane of the carbonate ion and (b) there is no great preference for a specific position in the CO_3^{2-} plane, although positions near an oxygen ion are slightly favoured over positions between two oxygen ions. This would be consistent with the peaks in the Na–O (at 0.22 nm) and Na–C (at 0.31 nm) pair correlations functions. Note that the position

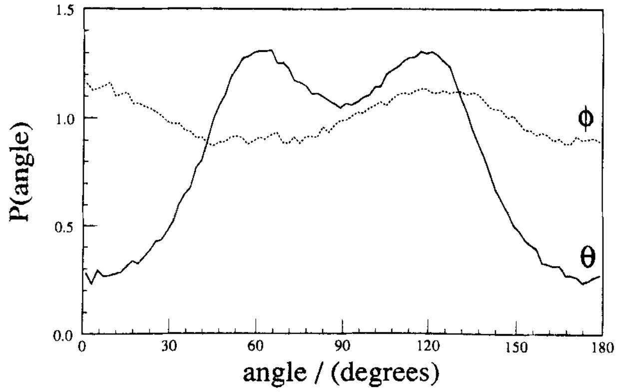

Figure 10 The angular distribution function of cations around a CO_3^{2-} ion. θ is the angle of the C–Na vector with respect to the normal to the carbonate plane. Φ is defined as the angle of the projection of the C–Na vector in the xy plane with the positive x-axis (see Fig. 1). $P(\theta) = m(\theta)/(n_R \sin\theta)$ and $P(\Phi) = m(\Phi)/n_R$, with m(x) the number of cations at angle x and n_R the coordination number at distance $R = 0.37$ nm.

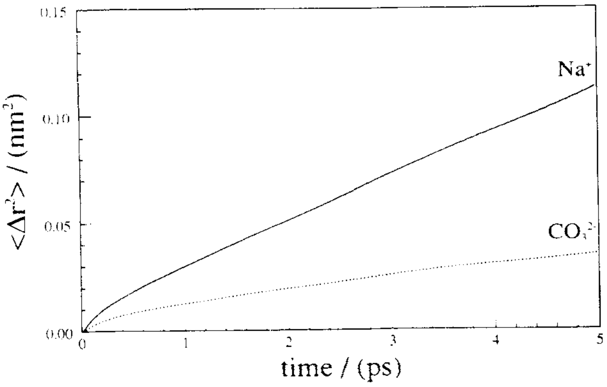

Figure 11 The mean square displacement of the Na^+ and the CO_3^{2-} ions in the MD simulation of a Na_2CO_3 melt.

between two oxygen ions and in the carbonate plane is the most favourable one when an isolated dimer is considered. Apparently the field of other ions is strong enough to overcome this preference. The coordination number of a carbonate ion by sodium ion within a range of 0.37 nm is seven. The first maxima in the pair correlation distribution functions of C–C and Na–Na are still in the region where Coulomb repulsion dominates the interaction.

The self-diffusion coefficients were calculated according to the Einstein equation:

$$D = 1/6\, d(<\Delta r^2>)/dt. \tag{6}$$

Here $<\Delta r^2>$ is the mean square desplacement which is shown in Figure 11. The diffusion coefficients of Na^+ and CO_3^{2-} are $3.4 \cdot 10^{-9}$ and $0.9 \cdot 10^{-9}$ m^2/s, respectively. Two sets of experimental data are available: measurements of Spedding and Mills [22] have yielded of $5.3 \cdot 10^{-9}$ and $3.0 \cdot 10^{-9}$ m^2/s for the diffusion coefficients for sodium and carbonate, respectively, whereas Djordjevic and Hills found the respecive values of $19.6 \cdot 10^{-9}$ and $27.9 \cdot 10^{-9}$ m^2/s [23]. Our results are in much better agreement with the values found by Spedding and Mills, and confirm the assumption that the results of Djordjevic and Hills are anomalous [6,22].

VI. CONCLUSIONS

Hartree-Fock calculations indicate a strongly ionic binding in M^+–CO_3^{2-} systems. This enables the decomposition of the interaction energies in a unified, i.e. not depending on the type of the cation, Coulomb interaction and induction energy. The short range repulsion can then be determined for each type of M^+–CO_3^{2-} system. It is then found possible to fit these interaction energies to simple expressions with "atomic" parameters. The potentials thus obtained can be used for simulations of all molten alkali carbonates and mixtures thereof.

As polarization effects tend to cancel in an environment of disordered ions, it is preferable to omit explicitly the induction energy from the pair potentials. The use of a model potential based on interaction energies without induction energy yields a better balance between the representations of the interaction in systems consisting of two and three ions, respectively. Additionally there is the advantage that in a later stage polarization may be included explicitly in the simulation, without having to remodel the Coulomb interaction and short-range repulsion.

Preliminary results of an MD simulation on molten NA_2CO_3 show that the radial distribution functions are well in agreement with the experimental data. The diffusion coefficients, which indicate that the Na^+ ions move faster than the carbonate ions are in good agreement with most experimental data.

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