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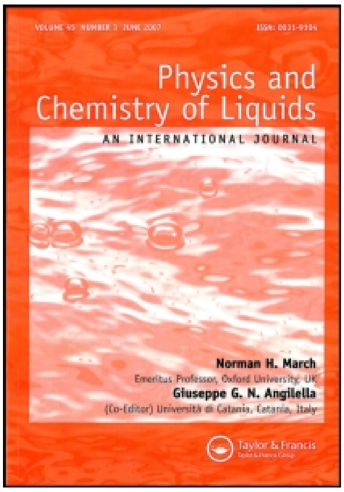

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Tests of the deformation-dipole model for metal–halide molecular clusters

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An ionic model that was originally built for chloroaluminate clusters by combining truncated expansions in classical multipoles and in quantal overlaps has been extensively applied to describe cohesion, structure, and vibrational spectra of a wide variety of molecular clusters in polyvalent metal halides [for a review see M.P. Tosi, *Phys. Chem. Liq.*, **43**, 409 (2005)]. In this work we test on simple ionic molecules two crucial aspects of the model, namely (i) the transferability of the overlap parameters for the halogen ions across families of halide compounds, and (ii) the anharmonicity in the halogen – metal ion interaction potential over a very broad range of interionic distances. Transferability is tested by means of a parallel discussion of alkali and alkaline-earth halide monomers near equilibrium. With regard to anharmonicity, the full potential energy curve yielded by the model for the sodium chloride monomer is compared with the results of quantum mechanical calculations for the ionic state of the molecule within a configuration-interaction approach.

Keywords: Ionic molecular clusters; Ionic models; Configuration-interaction calculations; Structure of molten salts

PACS numbers: 33.15.-6; 61.20.gY

1. Introduction

Calculations of the structure and other physical properties of molten salts and of ionic glasses and disordered solids have so far mainly relied on ionic models stemming from the early work of Born and Mayer [1] on cohesion in alkali halide crystals. The model ascribes the equilibrium state of the crystal at a given temperature and pressure to a balance of the net Coulomb attractions in the assembly of ions against quantum closed-shell overlap repulsions. A minimal requirement of such models is that they should give a reasonable account of cohesion not only in crystalline compounds but also in molecules and small clusters, and in turn the analysis of cohesive and vibrational

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properties of ionic systems in solid and molecular states has helped to determine useful model interactions (for a recent review see [2]).

In extending the Born–Mayer model to calculations of the potential energy curve of the alkali halide molecular monomers, Rittner [3] recognized the need to allow for the electronic polarization dipoles carried by the ions. For instance, in the NaCl molecule the polarization of the chlorine ion in the field of the sodium ion reduces the measured dipole moment to about one-half of the rigid-ion dipole that one would calculate from unitary charges located at the bond length distance. The Rittner model included only the polarization dipoles induced by electric fields and required a refitting of the overlap-repulsion parameters to account for the equilibrium state of the alkali halide molecules.

It was later shown by Tosi and Doyama [4] that essentially full consistency between the potential energy function of the crystal and that of the molecule near equilibrium is achieved in the alkali halides by allowing for the formation of electronic dipoles due not only to the local electric field but also to changes in the state of closed-shell overlap arising from relative displacements of the ions. Such a deformation-dipole model for alkali halide molecules has received basic justification from the work carried out by Brumer and Karplus [5] within quantum mechanical exchange perturbation theory. In essence, in this approach the potential energy curve of the molecule is constructed by combining a truncated expansion in classical multipoles with a truncated expansion in the overlap integrals. At low order in both expansions one recovers most terms in the expression for the molecular potential energy that are included in the deformation dipole model.

These ideas have been successfully extended to study a number of polyvalent metal halides in both pure and mixed liquid states. Charged or neutral microclusters are stable in many of these melts near freezing, so that the relationship between molecular states and molten states can be very direct. A remarkable example has been the development and use of such models to study the stability of molecular clusters in molten chloroaluminates [6]. Important examples of computer simulation work on metal–halide systems can be found in the work of Madden and coworkers (see for instance [7,8]).

In this work we test two crucial aspects of the background to such studies: (i) to what extent is it accurate to assume that the model parameters describing the halogen ions can be transferred between different families of compounds; and (ii) how accurate is the shape of the molecular potential energy predicted by the model at interionic separations far away from the equilibrium bond length. For these purposes we focus on the alkali halide monomers and use the results of ionic-model calculations on the alkaline-earth halides [9] and of quantum mechanical calculations on the NaCl monomer by a configuration interaction approach [10]. Comparisons with basic quantum mechanical calculations on the properties of the NaCl molecule near equilibrium have already been given elsewhere [2] and will be recalled below for completeness.

2. Relationship between alkaline-earth and alkali halides

Electrical deflection experiments on molecular beams of alkaline-earth dihalides by Klemperer *et al.* [11,12] revealed the presence of a large permanent dipole moment on several of these molecules (CaF_2, SrF_2, $SrCl_2$, BaF_2, $BaCl_2$, $BaBr_2$, and BaI_2). The dipole moment is associated with a bent molecular configuration, and a full account of the observed trends across the family of compounds has been given as arising from the interplay of the electronic polarizability of the cation and of the cation–anion bond length [9]. These theoretical results are also in good quantitative agreement with measurements of infrared spectra of alkaline-earth fluoride molecules trapped in a solid krypton matrix [13,14], showing that the molecular angle decreases progressively in going from CaF_2 to SrF_2 and BaF_2. A broader viewpoint on molecular shapes in alkaline-earth dihalides and in other sp-bonded triatomic molecules and clusters has been taken within pseupotential theories of electronic structure by Andreoni *et al.* [15].

The theoretical calculations on alkaline-earth halides [9] that we have recalled just above have been carried out within the deformation-dipole model, using interionic overlap potentials and overlap polarizabilities from the work of Yuen *et al.* [16] on crystalline properties of these compounds. In the calculations that we report below on alkali halide molecules, we have used the same values for the model parameters of the halogen ions.

The potential energy $U(r, m_+, m_-)$ of an alkali halide monomer as a function of the tinternuclear distance r and of the dipole moments m_+ and m_- carried by the two ions is written in the form

$$U(r, m_+, m_-) = -\frac{e^2}{r} - \frac{e(m_+ + m_-)}{r^2} - \frac{2m_+m_-}{r^3} + \frac{m_+^2}{2\alpha_+} + \frac{m_-^2}{2\alpha_-} + m_-B(r) + \varphi(r) \qquad (1)$$

where $\alpha_{+,-}$ are the electronic polarizabilities of the ions, $\varphi(r)$ is their short-range interaction energy due to interionic overlap repulsions, and the term $m\_B(r)$ makes allowance for an overlap deformation dipole located on the negative ion and pointing towards the positive ion. Minimization of the potential energy function with respect to the dipole moments yields their equilibrium values at any given value r of the bond length:

$$m_+(r) = \alpha_+\left(\frac{e}{r^2} + \frac{2m_-}{r^3}\right) \qquad (2)$$

and

$$m_-(r) = \alpha_-\left(\frac{e}{r^2} + \frac{2m_+}{r^3} - B(r)\right). \qquad (3)$$

The potential energy curve of the diatomic molecule is thus given by

$$U(r) = -\frac{e^2}{r} - \frac{e}{2r^2}[m_+(r) + m_-(r)] + \frac{1}{2}m_-(r)B(r) + \varphi(r) \qquad (4)$$

and this expression is to be minimized numerically with respect to the bond length r. The molecular dipole moment is given by

$$d(r) = er - [m_+(r) + m_-(r)] \qquad (5)$$

and expansion of $U(r)$ around its minimum yields the vibrational frequency ω. Rittner's model [3] is recovered by setting $B(r) = 0$.

The description of the model is completed by writing the short-range interaction energy in the form adopted by Yuen *et al.* [16],

$$\varphi(r) = f(\rho_+ + \rho_-)\exp\left(\frac{R_+ + R_- - r}{\rho_+ + \rho_-}\right) \qquad (6)$$

and by writing the function $B(r)$ in the form [4]

$$B(r) = \alpha_s \left| \frac{d\varphi(r)}{dr} \right| \tag{7}$$

where α_s is the short-range overlap polarizability. In equation (6) R_i are the ionic radii, ρ_i are the ionic stiffness parameters, and $f = 0.05\,e^2/\text{Å}^2$. The values of the model parameters that we have adopted for the alkali halide molecules, using data from [9,17,18], are reported in table 1.

Our results for the alkali halide molecules concerning the equilibrium bond length r_0, the equilibrium dipole moment $d(r_0)$, the molecular cohesive energy $U(r_0)$, and the vibrational frequency ω are reported in table 2. The corresponding experimental values are reported in parentheses whenever available, from [4,5,19,20] (see also Jordan [21]). It is seen from table 2 that the phenomenological theory reproduces the observed trends

Table 1. Model parameters for alkali and halogen ions.[a]

	Li	Na	K	Rb	Cs	F	Cl	Br	I
R_i (Å)	0.82	1.17	1.46	1.59	1.72	1.32	1.71	1.84	2.02
ρ_i (Å)	0.073	0.135	0.175	0.194	0.205	0.215	0.238	0.258	0.289
α_i (Å^3)	0.029	0.41	1.33	1.98	3.34	0.64	2.96	4.16	6.43
α_s (Å^3 e^{-1})	–	–	–	–	–	0.40	0.83	1.2	1.7

[a] The ionic radii R_i of the alkalis are from [17] and their hardness parameters ρ_i have been determined from a fit of the bond length in alkali chloride molecules. The electronic polarizabilities α_i are from [18]. All other parameters are from [9].

Table 2. Properties of the alkali halide molecular monomers (equilibrium bond length r_0, dipole moment $d_0 = d(r_0)$, dissociation energy $U_0 = -U(r_0)$ into separated ions, and vibrational frequency ω) from the deformation-dipole model and (in parentheses) from experiment.[a]

	r_0 (Å)	d_0 (Debye)	U_0 (eV)	ω (cm^{-1})
LiF	1.54 (1.564)	6.76 (6.28)	7.9 (7.8)	860 (867)
NaF	1.84 (1.926)	7.75 (8.12)	6.5 (6.5)	454 (492)
KF	2.11 (2.171)	8.21 (8.56)	5.8 (5.9)	344 (399)
RbF	2.21 (2.270)	8.16 (8.51)	5.6 (5.6)	292 (347)
CsF	2.30 (2.345)	7.48 (7.85)	5.4 (–)	272 (313)
LiCl	2.02 (2.020)	7.14 (7.08)	6.6 (6.5)	718 (569)
NaCl	2.36 (2.361)	8.89 (8.97)	5.5 (5.6)	343 (335)
KCl	2.67 (2.666)	9.99 (10.2)	4.8 (5.0)	247 (248)
RbCl	2.79 (2.786)	10.3 (10.5)	4.6 (4.8)	198 (207)
CsCl	2.91 (2.906)	10.0 (10.4)	4.5 (–)	180 (189)
LiBr	2.17 (2.170)	7.31 (7.23)	6.3 (6.3)	632 (512)
NaBr	2.52 (2.502)	9.29 (9.09)	5.2 (5.4)	282 (277)
KBr	2.83 (2.821)	10.6 (10.6)	4.6 (4.8)	194 (193)
RbBr	2.96 (2.945)	10.9 (–)	4.4 (4.6)	144 (150)
CsBr	3.09 (3.072)	10.8 (–)	4.2 (–)	126 (133)
LiI	2.34 (2.392)	7.12 (7.43)	5.9 (5.9)	568 (433)
NaI	2.72 (2.711)	9.44 (9.21)	4.9 (5.1)	247 (246)
KI	3.05 (3.048)	11.0 (11.0)	4.3 (4.5)	166 (173)
RbI	3.18 (3.177)	11.4 (–)	4.1 (4.3)	119 (125)
CsI	3.31 (3.315)	11.4 (12.1)	4.0 (–)	101 (109)

[a] The sources of the experimental data are as follows: (i) bond lengths, from microwave spectroscopic determinations reported in [19]; (ii) dipole moments, from data reported in [5]; (iii) binding energies, from thermochemical data reported in [4]; and (iv) vibrational frequencies, from spectroscopic measurements reviewed in [20].

and often is in good quantitative agreement with the experimental data. This degree of agreement is especially remarkable for the molecular dipole moments, which directly reflect the distortions of the electronic charge distribution. There also is a correlation between the error in the calculated bond length and the inaccuracies of the theory in the other calculated molecular properties: it is therefore a good practice to fit measured bond lengths in dealing with clusters in halides of polyvalent metals. Our results confirm that, given such minimal input from experiment to be used in determining the parameters that are appropriate to the metal ions across different families of compounds, the model has semiquantitative predictive value.

3. Relationship between phenomenology and basic theory for the NaCl molecule

It is well known that the two lowest adiabatic potential energy curves in the alkali halide monomers are both of ${}^1\sum^+$ symmetry and display an avoided crossing with an interchange of ionic and covalent character for the ground state (for a review see Jordan [21]). An estimate of the location r_X of the crossing can be obtained [22] from the ionization potential I of the alkali atom and the electron affinity A of the halogen atom by setting $I - A \approx e^2/r_X$, which yields $r_X \approx 9.45$ Å for NaCl. One can therefore safely view the molecular state near the equilibrium bond length at $r_0 = 2.361$ Å as being dominantly ionic. Here we examine how far away from the equilibrium state does the phenomenological theory account for the potential energy curve of the NaCl molecule.

Andreoni *et al.* [10] evaluated the potential energy curves and the ionization process of the NaCl monomer in configuration-interaction calculations based on a pseudopotential scheme for treating the field of the ionic cores in which the eight valence electrons of the molecule are moving. More specifically, the Coulomb, exchange, and core orthogonality effects of the assumed chemically inert core electrons of both sodium and chlorine were replaced by *ab initio* effective core potentials (ECP) reported by Wadt and Hay [23]. Further relevant information comes from a charge-density difference map between NaCl and $NaCl^+$ at the molecular equilibrium bond length, showing that in a vertical ionization process the electron that is being removed is strongly localized on the chlorine [10]. When the ionized molecule relaxes towards equilibrium, the hole left by the ionization process remains essentially localized and the binding of the molecular ion is primarily due to the polarization of the chlorine atom in the field of the sodium ion.

Some details of the method used in these calculations have been presented elsewhere by one of us [2]. We report in table 3 a comparison of the results of the basic theory with those of the phenomenological deformation-dipole model and with experimental data for the properties of the NaCl monomer (we have used for this purpose the data already reported in table 2 and the unpublished results in [10]). A comparison between the deformation-dipole model and the basic theory for the ionic state of the NaCl molecule over a very wide range of interatomic distance r is shown in figure 1. It is evident that the model is in excellent agreement with the theoretical predictions, not only at distances where the interionic overlap is becoming negligible but also at values of $r < r_0$, at which the molecular bond is compressed.

Table 3. Properties of NaCl molecular monomer (equilibrium bond length, dipole moment, dissociation energy into separated atoms or ions, and vibrational frequency) from experiment (EXP), configuration-interaction (CI) calculations, and deformation-dipole model (DDM).

	EXP	CI [10]	DDM
r_0 (Å)	2.361	2.382	2.36
d_0 (Debye)	8.97	10.00	8.89
D_e^{atoms} (eV)	4.1	4.11	–
D_e^{ions} (eV)	5.6	5.43	5.5
ω (cm^{-1})	335	378	343

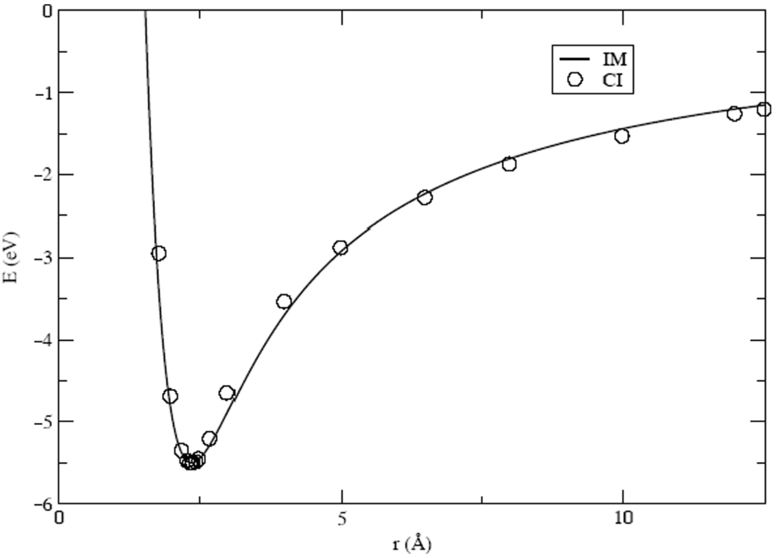

Figure 1. Potential energy curve of the ionic state of the NaCl molecular monomer from the deformation-dipole (IM) model (full line) and from configuration-interaction (CI) calculations (circles, from [10]).

4. Conclusions

In summary, we have quantitatively tested two important aspects of the usefulness of the deformation-dipole model in the study of ionic materials. First, we have seen that the model parameters can be usefully transferred not only between the different states of aggregation of these materials, as already demonstrated in previous work [4], but also between the different families of compounds. Second, we have checked the reliability of the model in accounting for strong anharmonicity against a basic quantum mechanical treatment of the potential energy curve of the NaCl monomer.

With regard to future applications of the present results, it is only fair to recall that electronic distortions of the outer electron shells of the ions have a rather modest role to play in the theory of the liquid structure of alkali halides near freezing at standard pressure [24]. However, these effects will certainly come to the fore even in these systems as the liquid density is lowered: specifically, in determining their liquid–gas coexistence curve and their critical behavior, and in quantitatively describing the transition in the bond character that must take place across the liquid–gas interface in going from a dissociated ionic liquid to a molecular gas. The latter topic is of considerable fundamental and practical interest at present.

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