Metal-halide molecular clusters: from fundamentals to model interactions

M. P. Tosi[a]

[a] Classe di Scienze, Scuola Normale Superiore, Pisa, Italy

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis
Taylor & Francis Group

Review

Metal-halide molecular clusters: from fundamentals to model interactions

M. P. TOSI*

Classe di Scienze, Scuola Normale Superiore, Pisa, Italy

Computer simulation studies of molten salts and disordered ionic solids employing phenomenological ionic models have proved useful in helping to understand the structure of these systems and their structure-dependent properties. A minimal requirement on such models is that they should give a reasonable account of cohesion in crystals and in molecules and small clusters of these compounds, and in turn the analysis of cohesive and vibrational properties of ionic systems in solid and molecular states has helped to determine useful model interactions. For an introduction to these topics the author first reports from the work carried out in the 1980s with W. Andreoni and G. Galli on what is learnt in Hartree-Fock and configuration–interaction calculations on the neutral and ionized monomer and dimer of NaCl. Then the author recalls how a deformation-dipole model was built for the cohesion of the neutral alkali halide monomers by combining a classical multipolar expansion with a quantum overlap expansion, and how this model relates to the theory of the cohesion and the vibrational spectrum of the alkali halide crystals. Finally, the author illustrates some applications to molecules and microclusters of polyvalent metal halides, from work carried out with Z. Akdeniz and coworkers. Transferability of model parameters for the halogen ions between different compounds and different aggregation states is crucial for these applications, and is achieved in the deformation-dipole model.

1. Background and outline

The study of the structure and other physical properties of molten salts and disordered ionic solids by computer simulation methods has so far mainly relied on phenomenological ionic models stemming from the seminal article published in 1932 by Born and Mayer [1] on cohesion in alkali halide crystals. The so-called Born model appeals to classical Coulomb interactions between ions carrying integer charges and ascribes the

*Email: tosim@sns.it

equilibrium state of the crystal at given temperature and pressure to a balance of the net Coulomb attractions against quantum closed-shell overlap repulsions that are taken to drop exponentially with increasing interionic distance (for a review see [2]). The pre-exponential factors in the overlap repulsive interactions contain ionic radii to which one can attribute meaning in terms of the measurable size of the electronic distribution of the ionic cores [3].

An early application of the Born model to the calculation of the potential energy curve of the alkali halide molecular monomers was given by Verwey and de Boer [4]. In extending the model to account for the dipole moment in the electronic ground state of these molecules, Rittner [5] recognized the need to allow for the electronic polarizability of the ions. For instance, in the NaCl monomer the polarization of the negative ion in the field of the positive ion reduces the measured dipole moment to about one-half of the rigid-ion value as determined from unit charges residing at the bond-length distance. The same effects of electronic polarization are met in the solid state in dealing with the energetics of the lattice defects that are responsible for charge and mass transport [6] and with the vibrations of the ions around their lattice sites [7]. In studying the latter the so-called shell model was developed (for a review see Cochran [8]). In brief, this model envisages each ion as having an outer shell of valence electrons that are elastically coupled to a rigid inner core, so that relative displacements of neighboring ions are accompanied by the formation of electronic dipoles due not only to the local electric field but also to changes in the state of closed-shell overlap. The shell model was further developed into a nonlinear deformation-dipole model and applied to the alkali halide molecular monomers by Tosi and Doyama [9].

What was learnt on the ionic interactions from these studies of alkali halide crystals and molecules has been applied with useful quantitative accuracy to study their molten state (for a review see [10]). The main characteristic feature of short-range order in alkali halide melts near freezing at standard pressure is the preservation of the alternation of charged species in space, and its details are well accounted for by means of interionic potentials developed from crystalline cohesive properties. Even more remarkably, these ideas have been successfully extended to study a number of polyvalent metal halides in both pure and mixed liquid states (for a review including up to trihalides see [11]). 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 much more direct than in fully dissociated ionic liquids such as the alkali halides. Important examples of computer simulation studies of metal-halide systems based on ionic models can be found in the work of Madden and coworkers (see for instance [12,13]).

In this short review the focus is on the theoretical study of molecular clusters *in vacuo* and the modelling of their static and dynamic structure. The report in section 2 is on only partly published work carried out in the 1980s [14, 15], in regard to what is learnt from fundamental quantum-mechanical studies of the monomer and dimer of NaCl that is illuminating in relation to phenomenological ionic models. Section 3 comprises how a parameter-free model was constructed for the alkali halide monomers [9], an outline of its theoretical justification [16], and a comparison of its results for the potential energy curve of the NaCl molecule near its minimum with those of the quantum-mechanical calculations and with experiment. In the same context comment on the relationship of these approaches to the theory of cohesion and

of the vibrational spectrum of the NaCl crystal is included. In section 4, the review covers some applications to microclusters of polyvalent metal halides. Section 5 concludes the review with a brief summary.

2. The NaCl microclusters: fundamentals

Much of the fundamental interest in the alkali halide monomers derives from the fact that the two lowest adiabatic potential energy curves, both of $^1\Sigma^+$ symmetry, display an avoided crossing with an interchange of ionic and covalent character (for a review see Jordan [17]). A detailed study of the avoided-crossing region has been given in configuration–interaction (CI) calculations on LiF [18,19]. An estimate of the location R_X of the crossing can be obtained [20] 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 $R_X \approx 9.45\,\text{Å}$ for NaCl. One can therefore safely view the molecular state near the equilibrium bond length at $R_e = 2.361\,\text{Å}$ as being dominantly ionic. The Hartree-Fock approach readily yields a fairly accurate account of the electronic ground state in this region, but needs to be transcended to obtain meaningful accuracy in describing ionization processes and the dissociation limit [14].

Andreoni *et al.* [14] studied the potential energy curves and the ionization process of the NaCl monomer in CI 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 [21]. In testing the accuracy of their ECP, these authors showed that at the generalized-valence-bond (GVB) level they yield close agreement with an all-electron calculation of the potential energy curve of the NaCl molecule, the relative error being 0.5% in R_e and 1% in the binding energy D_e. Further tests were made on the isolated atoms by Andreoni *et al.* [14]. In particular, the calculations on the sodium atom yield $I = 4.91\,\text{eV}$ for its ionization potential, against a measured value of 5.14 eV. All these tests indicate that the ECP scheme may introduce errors of a few tenths of an eV in calculations of energy differences.

The calculations of Andreoni *et al.* [14] on the NaCl molecule used 12 primitive Gaussians (three s and nine p) on sodium and 21 Gaussians (three s, twelve p, and six d) on chlorine. Their CI wavefunctions included all single and double excitations from self-consistent field – GVB orbitals [22]. A CI calculation starting from closed-shell GVB orbitals then yields the ionic-like state at all values of the bond length R. On the other hand, if the system is constrained to have two open shells with opposite spins, a CI calculation yields the atomic-like state upon choosing atomic orbitals as initial guesses. The degeneracy between these two states at crossing should be removed by further perturbative CI calculations. The electron affinity of the chlorine atom could then be estimated as $A \approx 3.6\,\text{eV}$ (in good agreement with the measured value $A = 3.615\,\text{eV}$) from the asymptotic form of the energy of the atomic-like ground state ($E_0(R) \rightarrow$ constant) and of the ionic-like first excited state ($E_1(R) \rightarrow$ constant $- e^2/R$) at values $R > R_X$ for the internuclear distance R in the molecule.

Table 1.   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 calculations (CI), and deformation dipole model (DDM).

	EXP [20,23]	CI [14]	DDM [9]
R_e (Å)	2.361	2.382	2.383
m (Debye)	9.00	10.	9.58
D_e^{atoms} (eV)	4.25	4.11	–
D_e^{ions} (eV)	5.75	5.43	5.71
ω_e (cm^{-1})	364.6	378.	402.

At the equilibrium internuclear distance R_e, which is found to lie at 2.382 Å against the measured value 2.361 Å, a shift of electronic charge density of $0.85e$ from Na to Cl is estimated from GVB Mulliken populations, the electron density being polarized in the direction opposite to the charge shift. As usual this method tends to underestimate the charge transfer, and indeed the amount of charge transfer obtained from GVB Mulliken populations approaches $0.99e$ as R is increased away from R_e. A comparison with experimental data for the equilibrium properties of the NaCl molecule, taken from Berry [20] and from Huber and Herzberg [23], is shown in the first two columns of table 1.

Contact with phenomenological models such as those of Rittner [5] and of Tosi and Doyama [9] can be made by writing the calculated dipole moment of the molecule as $\mu(R) = eR - \mu_e(R)$, where $\mu_e(R)$ is the "electronic dipole moment" associated with deformations of the closed-shell configuration of an assumed Cl$^-$ component of the molecule not too far from the equilibrium bond length. One obtains in this way an effective Cl$^-$ polarizability $\alpha_-(R)$, which is equal to about 3Å^3 for $R \approx 3$ Å: this is in good agreement with the value obtained from an analysis of the measured refractive index of alkali halide crystals [24]. It is also found that the polarizability function $\alpha_-(R)$ determined in this way *decreases* rapidly with decreasing internuclear distance below R_e. This behavior is the opposite of what one would obtain in a purely electrostatic model of the electronic dipole moment and provides direct evidence in favor of the phenomenological deformation-dipole model, which embodies quenching of the ionic deformability of the halogens with increasing interionic overlap (see section 3).

2.1.   *The ionized monomer and the neutral and ionized Na$_2$Cl and Na$_2$Cl$_2$ species*

Andreoni *et al.* [14] also carried out CI calculations on the NaCl$^+$ molecule in the two doublet states $^2\Pi$ and $^2\Sigma$, which are expected [17] to be the ground state and the first excited state, respectively. In fact the $^2\Sigma$ state, where the electron is removed from the σ-bond orbital of the NaCl molecule, is found to be unbound. The $^2\Pi$ state of the NaCl$^+$ species is instead obtained by removing an electron from the highest π orbital of the NaCl molecule and is found to be weakly bound by 0.44 eV against dissociation into Na$^+$ and Cl, in full agreement with the available data [23]. The minimum in the potential energy curve at the equilibrium bond length $R_e = 2.95$ Å is very shallow, in accord with the observation of broad bands in photoelectron spectra [25]. The calculated potential for adiabatic ionization of the NaCl molecule is 8.75 eV, to be compared with the value (8.93 ± 0.1) eV for the onset of the photoelectron spectral bands measured by Potts *et al.* [25].

A charge-density difference map between NaCl and NaCl$^+$ [14] shows that, in a vertical ionization process, the electron that is being removed is strongly localized on the chlorine site. When the molecule relaxes toward equilibrium after ionization, the hole left by the ionization process remains essentially localized on chlorine and the binding of the molecular ion is primarily due to the polarization of the chlorine atom in the field of the sodium ion. The Mulliken population on the chlorine site is 6.94e at $R = R_e$ and increases rapidly toward its dissociation-limit value of 7.0 as R increases.

Similar messages come from the calculations of Galli *et al.* [15] on the neutral and singly ionized states of Na_2Cl and Na_2Cl_2, using the Hartree-Fock method within a pseudopotential approach. Ionization is accompanied in both molecules by symmetry breaking, leading to a linear structure for Na_2Cl^+ and to a triangular shape for $Na_2Cl_2^+$.

Comparative examinations of the electron density maps of the neutral and ionized species are illuminating [15]. Thus, the Na_2Cl_2 dimer has a rhombic structure in which the binding arises from an accumulation of electronic charge along the Cl–Cl bond at the expense of polarization charge along the Na–Cl bond in the NaCl monomer. Ionization of the dimer yields a localized hole on one of the chlorines and is followed by symmetry breaking into a structure consisting of a linear Na_2Cl^+ unit to which a chlorine atom is very loosely attached at zero temperature. Release of this chlorine atom requires an activation energy of only a few hundredths of an eV.

These results suggest an explanation for mass spectroscopy data on a variety of alkali halide clusters, showing that chlorine-deficient ionized aggregates are more often observed than stoichiometric ones. Also there is broad agreement with experimental data on dissociation energies, ionization potentials, and equilibrium structural parameters, as discussed in detail in the original article of Galli *et al.* [15].

3. The NaCl molecule: phenomenological model

In their model for the alkali halide molecular monomers Tosi and Doyama [9] adopted a tight-binding viewpoint to express the potential energy of the ion pair through the multipolar expansion, including both classical electrostatic couplings and short-range overlap couplings between the various poles. Truncation of the expansion at the dipolar terms yields the potential energy $U(R, m_+, m_-)$ of the molecule as a function of the internuclear distance R and of the dipole moments m_+ and m_- carried by the two ions in the form

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

where $\alpha_{+,-}$ are the electronic polarizabilities of the ions, $\varphi(R)$ is their short-range inter-action energy (including overlap repulsions and van der Waals attractions), and the term $m_- B(R)$ makes allowance for an overlap deformation dipole located on the negative ion. The electronic dipole moment carried by the positive ion is in fact quite negligible in the NaCl molecule, so that one may, for the sake of simplicity, set $m_+ \approx 0$ to find

$$m_-(R) = \alpha_- \left[\frac{e}{R^2} - B(R) \right] \quad (2)$$

by minimization with respect to m_-, and

$$U(R) = -\frac{e^2}{R} - \frac{e}{2R^2}m_-(R) + \frac{1}{2}m_-(R)B(R) + \varphi(R). \tag{3}$$

In the same limit $\alpha_+ \ll \alpha_-$, the Rittner model is recovered by setting $B(R) = 0$. The electronic dipole on the halogen reduces in this case to the product of its polarizability times the electric field due to the charge of the sodium ion.

In their work Tosi and Doyama took $B(R)$ to be proportional to the overlap repulsive part of the short-range potential $\varphi(R)$, the proportionality factor being determined by the quantity $(1 - (e^*/e))$ where e^* is the so-called Szigeti effective charge [7] that enters the theory of the static dielectric constant of alkali halide crystals. The values of $(1 - (e^*/e))$ are in the range 0.1–0.3 for the alkali halides, and in particular $(1 - (e^*/e)) = 0.26$ for NaCl. It is then evident from equation (2) that the short-range deformation dipole cuts down the electrostatically induced dipole in an essentially exponential manner as the internuclear distance is decreased below its equilibrium value. Such a depression of the electrostatic dipole is supported by the CI calculations, as already stressed in section 2.

The most important consequence of including the short-range deformation dipole into the phenomenological theory is that *the model parameters become approximately transferable between different aggregation states and* (as we shall see in section 4) *between different halogen compounds*. Specifically, Tosi and Doyama were able to calculate the main properties of the alkali halide molecular monomers by exclusive use of model parameters that had been previously determined from the cohesive and dielectric properties of the alkali halide crystals. Their results for the NaCl molecule are reported in the third column of table 1, in comparison with experiment and with the theoretical results from the CI calculations of Andreoni *et al.* [14]. In contrast, in the Rittner model it was instead necessary to postulate a very sizable stiffening of the short-range overlap potential in going from the solid to the molecule and to redetermine the model parameters by fitting such molecular properties as the equilibrium internuclear distance and the vibrational frequency.

The nature of the molecular dipole moment in alkali halide diatomics has been examined in detail by Brumer and Karplus [16] from the viewpoint of quantum-mechanical exchange perturbation theory. These authors choose the ground states of the positive and negative ion as the zero-order basis and expand the molecular energy E to second order in their interaction potential V, i.e., $E = E^{(0)} + E^{(1)} + E^{(2)}$. Since exchange gives rise to contributions of second or higher order in the overlap integrals, $E^{(1)}$ and $E^{(2)}$ are in turn expanded to second order in the overlap, i.e., $E^{(1)} = E^{(1,0)} + E^{(1,2)}$ and $E^{(2)} = E^{(2,0)} + E^{(2,2)}$. Finally, V is treated by the multipolar expansion, yielding the electrostatic charge–charge interaction term from $E^{(1,0)}$ and the electrostatic charge–dipole interaction and the dipole–dipole van der Waals energy from $E^{(2,0)}$. The $E^{(1,2)}$ term can be represented as an exponential-like overlap repulsive energy term near the equilibrium bond length. Finally the $E^{(2,2)}$ term, which is ignored in the Rittner model, has the major effect of modifying the electronic polarizabilities of the ions through corrections which decay exponentially as the internuclear separation increases. This is the origin of the overlap deformation dipoles: they first arise in contributions to the molecular energy, which correspond to dipoles in the multipolar

expansion, and to second-order terms in the exchange perturbation expansion. Although the main focus of their work is on the molecular dipole moment, Brumer and Karplus [16] also show that inclusion of the deformation dipole yields improved values for the molecular spectroscopic constants. These give access to anharmonic terms in the potential energy curve of the molecule.

Evidence for ionic deformability has also come from quantum mechanical calculations of the cohesive energy of alkali halide crystals [26–29]. The main effect in the highly symmetric perfect-crystal configuration of a solid such as NaCl or NaF is a relative shrinkage of the electron density distribution of the negative ion, in substantial agreement with refined measurements by γ-ray diffractometry [30]. Such a "breathing distortion" of the charge density around the negative-ion site as a function of the lattice parameter is neglected in calculations based on the rigid-ion model. Electronic dipoles are induced on the ions in the crystal when ionic displacements from the perfect-crystal sites occur, as in lattice vibrations or in the neighborhood of lattice defects. Linearization of the deformation dipole model in these contexts yields the simplest version of the shell model [7,8].

4. Some extensions to microclusters of polyvalent metal halides

The extension of the deformation-dipole model to microclusters of polyvalent metal halides is straightforward [31]. The potential energy $U(\{\mathbf{r}_{ij}\}, \{\mathbf{m}_i\})$ as a function of the interionic bond vectors $\mathbf{r}_{ij}$ and of the dipole moments $\mathbf{m}_i$ carried by the ions is written as the sum of a Born–Mayer rigid-ion term, a classical polarization term, and a deformation-dipole term:

$$U(\{\mathbf{r}_{ij}\}, \{\mathbf{m}_i\}) = U_{BM}(\{\mathbf{r}_{ij}\}) + U_{pol}^{cl}(\{\mathbf{r}_{ij}\}, \{\mathbf{m}_i\}) + U_{dd}(\{\mathbf{r}_{ij}\}, \{\mathbf{m}_i^{(-)}\}). \tag{4}$$

The Born–Mayer term includes the Coulombic energy of ionic point charges and the overlap repulsive and van der Waals dipole–dipole interaction energies, the latter being often of some relevance only for the halogen ions:

$$U_{BM}(\{\mathbf{r}_{ij}\}) = \sum_{i \neq j} \left[\frac{z_i z_j e^2}{2 r_{ij}} + \frac{1}{2} \Phi_{ij}(r_{ij}) - \frac{C_{ij}}{2 r_{ij}^6} \right]. \tag{5}$$

Here the overlap repulsive interactions are expressed through individual (and transferable) ionic radii R_i and stiffness parameters ρ_i in the form proposed by Busing [32],

$$\Phi_{ij}(r_{ij}) = f (\rho_i + \rho_j) \exp[(R_i + R_j - r_{ij})/(\rho_i + \rho_j)] \tag{6}$$

where f is a constant arbitrarily chosen as $f = 0.05 \, e^2 \, \text{Å}^{-2}$. The classical polarization energy in equation (4) has the standard form

$$U_{pol}^{cl}(\{\mathbf{r}_{ij}\}, \{\mathbf{m}_i\}) = \sum_{i \neq j} \left[-\frac{z_i e \mathbf{r}_{ij} \cdot \mathbf{m}_j}{r_{ij}^3} + \frac{\mathbf{m}_i \cdot \mathbf{m}_j}{2 r_{ij}^3} - \frac{3(\mathbf{r}_{ij} \cdot \mathbf{m}_i)(\mathbf{r}_{ij} \cdot \mathbf{m}_j)}{2 r_{ij}^5} \right] + \sum_i \frac{m_i^2}{2\alpha_i}, \tag{7}$$

where α_i are the electronic polarizabilities of the ions. Finally, the third term in equation (4) accounts for deformation dipoles associated with each negative ion j and directed along each bond to its positive-ion neighbors i_j,

$$U_{\mathrm{dd}}(\{\mathbf{r}_{ij}\}, \{\mathbf{m}_i^{(-)}\}) = \frac{\alpha_{\mathrm{sr}}}{\alpha_-} \sum_{j,\,i_j} \mathbf{m}_j^{(-)} \cdot \hat{\mathbf{r}}_{i_j j} \left| \frac{\mathrm{d}\Phi_{i_j j}(r_{i_j j})}{\mathrm{d}r_{i_j j}} \right| \tag{8}$$

where α_{sr} is a short-range polarizability. Minimization of the molecular energy U with respect to the dipoles yields the dipole $\mathbf{m}_j^{(-)}$ on a halogen as

$$\mathbf{m}_j^{(-)} = \alpha_- \mathbf{E}_j(\{\mathbf{r}_{ij}\}, \{\mathbf{m}_i\}) + \alpha_{\mathrm{sr}} \sum_{i_j} \hat{\mathbf{r}}_{i_j j} \left| \frac{\mathrm{d}\Phi_{i_j j}(r_{i_j j})}{\mathrm{d}r_{i_j j}} \right|, \tag{9}$$

where $\mathbf{E}_j$ is the self-consistent electric field seen by the halogen. Each component of the deformation dipole in the second term on the RHS of equation (9) lies along a metal-halogen first-neighbor bond and points toward the metal ion. It is, therefore, opposite to the corresponding contribution to the electric-induction dipole, so that the net dipoles saturate as the ions deform in reaching their equilibrium positions.

The use of transferability of all model parameters for the halogen ions and of simple empirical rules for the ionic radii and the repulsive stiffness parameters for the positive ions has allowed us to obtain, with a single fitting parameter for each metal ion, a very good account of the structure of a variety of microclusters and reasonably good accounts of their cohesive and vibrational properties. A somewhat better quantitative account for the latter properties can be obtained by allowing for a moderate reduction of the nominal ionic valences, subject to overall charge compensation. This reduction tends to soften the calculated vibrational frequencies and to reduce the calculated binding energies relative to the free-ion state, while preserving the high quality of the structure calculations. In the following some selected examples are illustrated.

4.1. *Aluminum chloride and chloroaluminates*

The melts of alkali chloroaluminates, represented by the formula $(ACl)_{1-x}(AlCl_3)_x$ where A is an alkali, provide a striking example of systems in which the stability and coexistence of various complex anions depend strongly on composition. While the stoichiometric mixture at $x = 0.5$ can be regarded as a molten salt of alkali ions and tetrahedral $(AlCl_4)^-$ anions, the species $(AlCl_4)^-$, $(Al_2Cl_7)^-$, $(Al_3Cl_{10})^-$, and Al_2Cl_6 coexist in acidic melts in proportions which vary with the overall composition. The larger complex anions consist of $(AlCl_4)^-$ tetrahedra sharing corners, while Al_2Cl_6 is formed by two tetrahedra sharing an edge. The pure $AlCl_3$ melt consists of Al_2Cl_6 molecular dimers.

The view that melting of the pure $AlCl_3$ compound occurs from an ionic-like layered crystal structure into a molecular liquid of correlated Al_2Cl_6 dimers was proposed a long time ago on the basis of X-ray diffraction data and is consistent with the measured values of the thermodynamic melting parameters and of transport coefficients in the melt, as well as with Raman scattering data and *ab initio* calculations of vibrational frequencies (for a review of this evidence see [11]). The Al–Al bond length in the

mixed melts should directly reflect the proportion of edge-sharing to corner-sharing $(AlCl_4)^-$ tetrahedra, but the presently available neutron diffraction data are totally insensitive to the Al–Al interference [33].

Early simulation work by Rahman and coworkers showed extreme sensitivity of the predicted Al–Al bond length to the model adopted for the ionic interactions. For instance, Saboungi *et al.* [34] reported that in their simulation of liquid $NaAlCl_3$ the mean Al–Al bond length drops from 4.6 to 2.5 Å on allowing for the electrostatic induction of electronic dipole moments on the chlorine ions. One should also note that the formation of the double-bridged Al_2Cl_6 species results from the stabilization of bent Al–Cl–Al triplets and this is crucially dependent on halogen polarizability.

The use of the deformation-dipole model is essential in such a situation [31]. For instance, fitting of the measured bond length between Al and a terminal chlorine in the Al_2Cl_6 dimer leads to a value of 3.20 Å for the Al–Al bond length (to be compared with a value of 3.21 Å from experiment and of 3.26 Å from quantum chemistry calculations) and a value of 2.276 Å for the bond length between Al and a bridging chlorine (to be compared with the values 2.252 and 2.289 Å from the same sources). The original article [31] should be consulted for calculations of structure, energetics, and vibrational modes of the various Al-based neutral and charged microclusters.

4.2. *The stability of the $(AlF_5)^{2-}$ anion*

While a fourfold tetrahedral-like coordination is strongly stable for Al in chloride, bromide, and iodide melts [11], a fivefold-coordinated $(AlF_5)^{2-}$ species was first proposed by Gilbert and Materne [35] from Raman-scattering studies of liquid mixtures of NaF and AlF_3 with composition ranging from $NaAlF_4$ down to the industrially important cryolite material (Na_3AlF_6) and beyond. The stability of the $(AlF_5)^{2-}$ species is now supported by very extensive and detailed experimental studies of thermodynamic properties and Raman scattering spectra as functions of composition, temperature, and alkali-ion species in mixed melts of alkali and aluminum fluorides.

The $NaAlF_4$, Na_2AlF_5, and Na_3AlF_6 microclusters have been evaluated by Akdeniz *et al.* [36] within the deformation-dipole ionic model. The calculations show that the relatively uncommon fivefold coordination of the Al ion in the two latter clusters is stabilized by the alkali counterions in either double-bridged or triple-bridged configurations. For the $NaAlF_4$ cluster the model agrees with quantum chemistry calculations by Scholz and Curtiss [37] in predicting approximately equal stability for two structures consisting of an $(AlF_4)^-$ distorted tetrahedron binding an Na ion in an edge-bridged or a face-bridged configuration. It should be stressed that a multiplicity of energetically equivalent or closely similar sites for alkali ions in a microcluster can be interpreted as indicating that these positive ions will be mobile in dense disordered states of the material at finite temperature, including not only the molten state but also a possible superionic-glass state.

4.3. *Polymeric structures in Aluminum and Gallium halides*

The potential energy landscape for the $(Al_2Cl_7)^-$ anion is very complex (see for instance [31]). Four structures formed from corner-sharing tetrahedra are found to be almost degenerate in energy and differ only for internal rotations giving different relative orientations to the two terminal $AlCl_3$ groups. However, of these the only mechanically

stable structure is the C_2 one, which is obtained from a C_{2v} structure having an eclipsed arrangement of the terminal groups through opposite rotations of these groups by $30°$ around the $Al–Cl^B$ bond (with Cl^B denoting a bonding chlorine). The other structures have at least one imaginary vibrational frequency and therefore correspond to a multiplicity of saddle points separating equivalent true minima.

Similar structural properties, deriving from high freedom of rotation of molecular groups around internal bonds, have been found in a study of the series of $(Al_nCl_{3n+1})^-$ complex anions for $n \leq 4$ by the deformation-dipole model [38]. These systems form a chain-like polymeric series, with a binding-energy increment on addition of a further $AlCl_3$ monomer that rapidly converges to about $0.5\,eV$. Starting from a "stretched" configuration for the trimer, in which the metal ions and the bonding chlorines lie all in the same plane, a slightly more bound structure is found by rotations of the terminal groups out of the plane. Additional configurations for the trimer have a "winged" or a "cart" structure, as were first identified in semi-empirical molecular orbital calculations by Dymek *et al.* [39]. A "stretched" chain-like configuration is also obtained for the tetramer, in which all the metal ions and bonding chlorines that form its backbone lie in a single plane. Finally, the model calculations [38] show that these structural properties persist on replacing Al by Ga and/or Cl by Br.

With regard to the location of alkali counterions, an X-ray diffraction experiment on KAl_2Br_7 crystals [40] has reported an $Al–Br^B–Al$ bond angle of $109.3°$ and K–Br bond lengths in the range from 3.3 to $4.0\,Å$. The model calculations on the isolated KAl_2Br_7 microcluster [38] show a preferred location for the K ion in coordination to four terminal halogens and yield values of $112.6°$ for the $Al–Br^B–Al$ bond angle and of $3.74\,Å$ for the K–Br bond length. Again a multiplicity of sites at very nearly the same energy is found for both Na and K counterions around a polymeric anion, indicating high mobility for alkali-ion transport in condensed phases of these materials.

4.4. *Tetrahalides of actinide elements and halides of pentavalent elements*

Charge compensation within well-defined molecular units becomes progressively more frequent in the condensed phases of halides as the nominal valence of the metal ion increases. In comparison with the dissociated melts of alkali or alkaline-earth halides, the liquid phase in these molecular systems is characterized by a low freezing point and by high fluidity and very low electrical conductivity. Among trihalides, $AlCl_3$ and $FeCl_3$ melt from layered ionic structures into dimeric molecular liquids, with a change in coordination of the metal ion from sixfold to fourfold [11]. Other trihalides, such as $AlBr_3$ and $SbCl_3$, have a molecular-like structure already in the crystalline state, the basic molecular units being the dimer in the former compound and the monomer in the latter. Molecular-liquid behavior is well established among tetrahalides for $GeBr_4$ [41] and $ZrCl_4$ [42]. Typical molten-salt behavior is restored upon mixing with alkali halides: halogen donation to the polyvalent metal element gives rise to a liquid structure formed by complex anions and mobile alkali counterions.

The physical and chemical properties of actinide chloride melts are important in molten salt technology for applications in nuclear fuel recycling and in transmutation processes for minor actinide elements [43]. Little is known about the liquid structure of these compounds and even the structure of the tetrahalide molecular monomers in the vapor phase has been the object of repeated studies and interpretations. As summarized by Hargittai [44], the evidence from vapor-phase and matrix-isolation

infrared spectroscopy, from electron diffraction, and from photoelectron spectra has converged toward attributing a regular tetrahedral structure to the ThF_4, UF_4, $ThCl_4$, and UCl_4 molecules. Renewed thermochemical analyses of vapor-pressure data, that have been extended to other tetrahalides of Th and U as well as to tetrahalides of transuranic elements, offer no evidence from deviations from tetrahedral symmetry [45]. A regular tetrahedral structure is also predicted from quantum-chemical calculations on molecular actinide halides and from density-functional calculations on Th tetrahalide molecules [46–48].

Within an ionic molecular model, a distortion of a high-symmetry structural configuration of the molecule would be driven by the energy gain from the polarization of the metal ion in the electric field that the symmetry-breaking distortion induces at its site. The distortion would then be favored by a high electronic polarizability of the metal ion in combination with a short bond length. A case in point is that of the rare-earth trihalide monomers, for which a trigonal-pyramid configuration of the ground state has been explained by precisely this mechanism [49].

A study of MX_4 molecules by the deformation dipole model, for the cases M = Th, U, Np, Pu and Am and X = F, Cl, Br and I, has shown that the frequency of the ν_4 vibrational mode of the molecular tetrahedron is especially sensitive to the inclusion of the metal-ion polarizability in the calculations and that the available values of these mode frequencies are not compatible with a breaking of the T_d symmetry of the molecular ground state [50]. Whereas the Th halides show some deviations from the general behavior found in these calculations, for each halide the other actinide ions are found to have essentially the same effective valence (equal to about 3.6 in the tetrafluorides and 3.25 in the other tetrahalides) and to show some regular reduction of the ionic radius with increasing number of 5f electrons, the latter being a manifestation of the well-known actinide contraction [51]. The simple and reasonable trends that are predicted for these metal ions, for given input on the overlap and polarization parameters of the halogens, could be usefully extended to the whole series of transuranic elements and thus allow computer simulation studies of these halide compounds in the molten state.

An extension of these ideas to pentachloride and pentabromide molecules of Nb, Ta, Sb, and Mo, and to higher niobium-based halide clusters, has been given in [52]. The molecular monomers of these compounds have a D_{3h} trigonal-bipyramidal structure in the ground state, and the model calculations [52] yield an elongation of the axial bond length by about 1% relative to the equatorial bond length. This result is in agreement with electron diffraction data [44]. A C_{4v} square-pyramidal structure is found to be mechanically unstable against transformation into the D_{3h} shape. Finally, the calculated vibrational frequencies of the $NbCl_5$, Nb_2Cl_{10}, and $CsNbCl_6$ microclusters *in vacuo* are in good agreement with data from vibrational spectroscopy of the melts [53]. Insensitivity of vibrational modes to the state of aggregation is, of course, a signature of strong stability for microclusters.

5. Concluding remarks

Alkali halide systems, in a variety of aggregation states including molecular monomers and dimers, melts, and crystals, have been the subject of very many experimental and theoretical investigations since the early part of the past century. A unified

phenomenological model of the ionic interactions allows a theoretical description of the static and dynamic structure of all these systems, to useful quantitative accuracy in comparison with the available evidence. Quantum mechanical approaches provide basic justification for the model and shed light on its most important physical aspects.

In recent years these ideas have been extended to treat more complex ionic materials, with main attention paid to the halides of polyvalent metals and to mixed alkali – polyvalent metal halide systems. A few examples of work in this field of great richness and technical relevance have been reported upon in this short review. Developments toward other ionic materials, such as oxides, nitrates, and carbonates, are currently in progress.

Acknowledgments

References

[1] M. Born, J.E. Mayer. *Z. Phys.*, **75**, 1 (1932).
[2] M.P. Tosi. *Solid State Phys.*, **16**, 1 (1964).
[3] F.G. Fumi, M.P. Tosi. *J. Phys. Chem. Solids*, **25**, 31 and 45 (1964).
[4] E.J.W. Verwey, J.H. de Boer. *Rec. trav. chim.*, **59**, 23 (1940).
[5] E.S. Rittner. *J. Chem. Phys.*, **19**, 1030 (1951).
[6] N.F. Mott, M.J. Littleton. *Trans. Faraday Soc.*, **34**, 485 (1938).
[7] M. Born, Huang Kun. *Dynamical Theory of Crystal Lattices*, Clarendon, Oxford (1954).
[8] R.A. Cochran. *Crit. Rev. Solid State Sci.*, **2**, 1 (1971).
[9] M.P. Tosi, M. Doyama. *Phys. Rev.*, **160**, 716 (1967).
[10] M. Rovere, M.P. Tosi. *Rept. Progr. Phys.*, **49**, 1001 (1986).
[11] M.P. Tosi, D.L. Price, M.-L. Saboungi. *Ann. Rev. Phys. Chem.*, **44**, 173 (1993).
[12] M. Wilson, P.A. Madden. *Phys. Rev. Lett.*, **80**, 532 (1998).
[13] D.A. Keen, S. Hull, A.C. Barnes, P. Berastegui, W.A. Crichton, P.A. Madden, M.G. Tucker, M. Wilson. *Phys. Rev. B*, **68**, 014117 (2003).
[14] W. Andreoni, G. Galli, M.P. Tosi (Unpublished) (1986).
[15] G. Galli, W. Andreoni, M.P. Tosi. *Phys. Rev. A*, **34**, 3580 (1986).
[16] P. Brumer, M. Karplus. *J. Chem. Phys.*, **58**, 3903 (1973).
[17] K.D. Jordan. In *Alkali Halide Vapors: Structure, Spectra and Reaction Dynamics*, P. Davidovits, D.L. McFadden (Eds), p. 479, Academic, New York (1979).
[18] L.R. Kahn, P.J. Hay, I. Shavitt. *J. Chem. Phys.*, **61**, 3530 (1974).
[19] B.J. Botter, J.A. Kotter, J.C. Mulder. *Chem. Phys. Lett.*, **33**, 532 (1975).
[20] R.S. Berry. In *Alkali Halide Vapors: Structure, Spectra and Reaction Dynamics*, P. Davidovits, D.L. McFadden (Eds), p. 77, Academic, New York (1979).
[21] W.R. Wadt, P.J. Hay. *J. Chem. Phys.*, **82**, 284 (1985).
[22] W.J. Hunt, P.J. Hay, W.A. Goddard III. *J. Chem. Phys.*, **57**, 738 (1972).
[23] K.P. Huber, G. Herzberg. *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules*. Van Nostrand–Reinhold, New York (1979).
[24] J.R. Tessman, A.H. Kahn, W. Shockley. *Phys. Rev.*, **92**, 890 (1953).
[25] A.W. Potts, T.A. Williams, W.C. Price. *Proc. R. Soc. A*, **341**, 147 (1974).
[26] A. Zunger, A.J. Freeman. *Phys. Rev. B*, **16**, 2901 (1977).
[27] W. Andreoni, K. Maschke, M. Schlüter. *Phys. Rev. B*, **26**, 2314 (1982).
[28] G. Böbel, P. Cortona, C. Sommers, F.G. Fumi. *Acta Cryst. A*, **39**, 400 (1983).
[29] F. Gygi, K. Maschke, W. Andreoni. *Solid State Commun.*, **49**, 437 (1984).
[30] D.R. Yoder, R. Colella. *Phys. Rev. B*, **25**, 2545 (1982).
[31] Z. Akdeniz, M.P. Tosi. *Z. Naturforsch.*, **54a**, 180 (1999).

[32] W.R. Busing. *Trans. Amer. Crystallogr. Assoc.*, **6**, 57 (1970).
[33] Y.S. Badyal, D.A. Allen, R.A. Howe. *J. Phys.: Condens. Matter*, **6**, 10193 (1994).
[34] M.-L. Saboungi, A. Rahman, J.W. Halley, M. Blander. *J. Chem. Phys.*, **88**, 5818 (1988).
[35] B. Gilbert, T. Materne. *Appl. Spectrosc.*, **44**, 299 (1990).
[36] Z. Akdeniz, Z. Çiçek, M.P. Tosi. *Chem. Phys. Lett.*, **308**, 479 (1999).
[37] G. Scholz, L.A. Curtiss. *Theochem.*, **258**, 251 (1992).
[38] Z. Akdeniz, M. Çaliskan, Z. Çiçek, M.P. Tosi. *Z. Naturforsch.*, **55a**, 575 (2000).
[39] C.J. Dymek, J.S. Wilkes, M.A. Einarsrud, H.A. Øye. *Polyhedron*, **7**, 1139 (1988).
[40] E. Rytter, B.E.D. Rytter, H.A. Øye, J. Krogh-Moe. *Acta Cryst. B*, **29**, 1541 (1973).
[41] K.F. Ludwig, W.K. Warburton, L. Wilson, A.I. Bienenstock. *J. Chem. Phys.*, **67**, 604 and 613 (1987).
[42] G.M. Photiadis, G.N. Papatheodorou. *J. Chem. Soc. Dalton Trans.*, **1998**, 981 (1998).
[43] Y. Okamoto, F. Kobayashi, T. Ogawa. *J. Alloys Comp.*, **271**–**273**, 355 (1998).
[44] M. Hargittai. *Chem. Rev.*, **100**, 2233 (2000).
[45] R.J.M. Konings, D.L. Hildebrand. *J. Alloys Comp.*, **271**–**273**, 583 (1998).
[46] G.L. Malli, J. Styszynski. *J. Chem. Phys.*, **101**, 10736 (1994).
[47] G.L. Malli, J. Styszynski. *J. Chem. Phys.*, **109**, 4448 (1998).
[48] L. Gagliardi, C.-K. Skylaris, A. Willetts, J.M. Dyke, V. Barone. *Phys. Chem. Chem. Phys.*, **2**, 3111 (2000).
[49] Z. Akdeniz, Z. Çiçek, M.P. Tosi. *Z. Naturforsch.*, **55a**, 861 (2000).
[50] Z. Akdeniz, A. Karaman, M.P. Tosi. *Z. Naturforsch.*, **56a**, 376 (2001).
[51] M. Seth, M. Dolg, P. Fulde, P. Schwerdtfeger. *J. Amer. Chem. Soc.*, **117**, 6597 (1995).
[52] Z. Çiçek Önem, Z. Akdeniz, M.P. Tosi. *Z. Naturforsch.*, **57a**, 943 (2002).
[53] M.H. Brooker, G.N. Papatheodorou. In *Advances in Molten Salt Chemistry*, G. Mamantov (Ed.), Vol. 5, p. 26, Elsevier, Amsterdam (1983).