Molecular Modeling of the Structure and Dynamics of the Interlayer and Surface Species of Mixed-Metal Layered Hydroxides: Chloride and Water in Hydrocalumite (Friedel's Salt)

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Abstract

The dynamical behavior of Cl^- and H_2O molecules in the interlayer and on the (001) surface of the Ca-aluminate hydrate hydrocalumite (Friedel's salt) over a range of temperatures from -100 to $300°C$ is studied using the technique of isothermal-isobaric molecular dynamics computer simulations. This phase is currently the best available model compound for other, typically more disordered, mixed-metal layered hydroxides. The computed crystallographic parameters and density are in good agreement with available X-ray diffraction data and the force field developed for these simulations preserves the structure and density to within less than 2% of their measured values. In contrast to the highly ordered arrangement of the interlayer water molecules interpreted from the X-ray data, the simulations reveal significant dynamic disorder in water orientations. At all simulated temperatures, the interlayer water molecules undergo rapid librations (hindered hopping rotations) around an axis essentially perpendicular to the layers. This results in breaking and reformation of hydrogen bonds with the neighboring Cl^- anions and in a time-averaged nearly uniaxial symmetry at Cl^-, in good agreement with recent [35]Cl NMR measurements. Power spectra of translational, librational, and vibrational motions of interlayer and surface Cl^- and H_2O were calculated as Fourier transforms of the atomic velocity autocorrelation functions and compared with the corresponding spectra and dynamics for a bulk aqueous solution. The ordered interlayer space has significant effects on the motions. Strong electrostatic attraction between interlayer water molecules and Ca atoms in the principal layer makes the $Ca \cdots OH_2$ bond direction the preferred axis for interlayer water librations. The calculated diffusion coefficient of Cl^- as an outer-sphere surface complex is almost three times that of inner-sphere Cl^-, but is still about an order of magnitude less than that of Cl^- in bulk aqueous solution at the same temperature.

Introduction

Mixed-metal layered hydroxides (MMLHs), also called layered double hydroxides (LDHs) and "anionic clays", are among the few oxide-based materials with permanent anion exchange capacity developed through isomorphous substitution. They occur in many natural environments, are readily synthesized, and are receiving rapidly increasing attention for a wide variety of applications in catalysis, environmental remediation, and medicine. (e.g., Ulibarri et al., 1995; Newman and Jones, 1998, Schmassmann et al., 1993). They also play a key role in cement chemistry, due to their importance in controlling the chemical behavior of anionic species (Taylor, 1997). MMLHs have a layered structure typically based on that of brucite or portlandite. Substitution of +3 cations (often Al) for +2 cations (often Mg or Ca) in the principal hydroxide layer leads to a permanent positive charge. This charge is compensated by anions, which have associated water molecules, in the interlayer space and on the particle surfaces.

Hydrocalumite, $[Ca_2Al(OH)_6]Cl\cdot2H_2O$, also known as Friedel's salt, is unique among MMLHs, because it has not only an ordered Ca-Al distribution in the hydroxide layer, but well ordered Cl^- and water in the interlayer space. The interlayer order is due to coordination of the water molecules to Ca in the hydroxide layer, which results in an unusual 7-coordinate Ca environment. This phase occurs naturally (Fischer et al., 1980; Passaglia and Sacerdoti, 1988; Sacerdoti and Passaglia, 1988) and also forms by reaction of Cl-containing deicing salts with the calcium aluminates of Portland cement (Birnin-Yauri and Glasser, 1998).

Because of its structural order and occurrence as relatively large crystals, hydrocalumite is the only MMLH for which a single crystal structure refinement is available (Terzis, et al., 1987). Thus, it is currently the best model compound for understanding the structure and dynamical behavior of surface and interlayer water and anions in MMLHs. Such understanding

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is essential for full exploitation of the unique anion exchange capabilities of this important class of compounds. Recent [35]Cl NMR spectroscopic study of hydroalumite in our laboratory is broadly consistent with the structure determined by XRD, but has provided important new insight into the dynamical behavior of surface and interlayer Cl⁻ and has identified a previously unknown dynamical phase transition at 6°C (Kirkpatrick, et al., 1999). Below this temperature the Cl⁻ has triaxial symmetry, as expected from a rigid interlayer structure. Above this temperature the Cl⁻ symmetry is uniaxial or nearly so and can only be explained by relative motion (dynamical disorder) of the interlayer species at frequencies greater than about 10^5 Hz. Parallel NMR work on the analogous Mg,Al MMLH (a hydrotalcite-like compound) with Cl⁻ in the interlayer shows that this type of behavior may be common in this group of compounds.

In this paper, we present the first molecular dynamics (MD) computer simulations of hydrocalumite, with major emphasis on the interlayer structure and the contrasting dynamical behavior of the interlayer and surface species for the time scale from femtoseconds to hundreds of picoseconds. The results also provide a specific structural model for the motion of the interlayer species that causes the uniaxial Cl⁻ symmetry in the high temperature phase and demonstrate the unique capabilities of combined NMR and MD studies to understand the structure and dynamics of surface and interlayer species in water-rock systems.

There has been significant recent effort to model mineral-water interactions by computer simulation. There has been substantial progress in modeling the structure of water and hydrated interlayer cations in smectites (e.g., Chang et. al., 1997; Smith, 1998; Hartzell et al., 1998). Hydration and dehydration of clays has been simulated in some detail (Delville, 1995; Karaborni et al., 1996), and the molecular dynamics of proton binding to mineral oxide surfaces has also been studied (Rustad et al., 1998).

In many of these simulations, however, the atoms of the main oxide layers are treated as fixed in a rigid lattice, except for the degrees of freedom associated with swelling and lateral displacements of the lattice as a whole. This simplified approach saves substantial amounts of computer time and is efficient at providing useful structural information. However, it has inherent and substantial limitations for dynamic modeling of surface and interlayer species. Due to the immobility of the lattice atoms, there is no exchange of momentum and energy between the atoms of the main layers and the interlayer/surface species. Thus, in these models the imposed momentum and energy conservation laws *a priori* prevent accurate representation of the dynamics of such processes as hydrogen bonding, adsorption, and surface complexation. Surface diffusion rates can be overestimated, and the structure of the water layers at the interface can be distorted. Studies modeling ionic complexes in clays and MMLHs with all atoms in the system movable are beginning to appear in the literature (Aicken et al., 1997; Teppen et al., 1997, Hartzell et al., 1998; Newman et al, 1998; Williams et al., 1999), but to date these concern primarily questions of structure and swelling, and not the dynamics of interlayer and surface species.

The MD simulations reported here realistically model the dynamics of all main layer, interlayer and surface atoms on the time scale from 10^{-15} to 10^{-10} sec and are specifically aimed at probing the dynamic behavior of the interlayer and surface anions.

Simulation methods

The initial hydrocalumite structure for our simulations was taken from the X-ray diffraction results of Terzis et al. (1987), which has monoclinic C2/c symmetry. The MD simulation cell contains 2×2×1 crystallographic unit cells in the *a*, *b* and *c* directions,

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respectively. Except for the three dimensional periodic boundary conditions (e.g., Allen and Tildesley, 1987) imposed on the simulation supercell, there were no additional symmetry constraints. The structure was treated as triclinic, and all cell parameters, a, b, c, α, β, γ, were considered independent variables during the isothermal-isobaric MD simulations.

The total potential interaction energy of the simulated system consisted of a Coulombic term for all electrostatic interactions between partial charges on atoms and a Lennard-Jones (12-6) term modeling the van-der-Waals dispersive interactions:

$$U = \sum_{i,j} \left\{ \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} + 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] \right\} \tag{1}$$

where r_{ij} is the distance between atoms i and j, q_i, q_j are partial charges centered on these atoms, ε_{ij} and σ_{ij} are parameters of the Lennard-Jones interaction potential, and ε_0 is the dielectric permittivity of vacuum ($\varepsilon_0 = 8.85419\times10^{-12}$ F/m). The interaction parameters from the augmented ionic consistent valence force field (CVFF) within the Cerius[2] molecular modeling package (Molecular Simulations Inc., 1998) were used as a basis for construction of a force field to model all ion-ion and ion-water interactions in our simulations. However, the original force field was modified in several significant aspects.

For water-water interactions we used the flexible version of the simple point charge (SPC) interaction potential (Berendsen et al., 1981) as developed by Teleman et al., (1987). Lennard-Jones terms centered on the O atoms were assumed equivalent for both H_2O and OH-group oxygens, while those centered on the H atoms were ignored. The harmonic potential of the hydroxide OH-group stretching vibrations was also taken equivalent to that of H_2O.

Instead of placing full formal charges on the metal ions, we performed preliminary quantum-mechanical calculations to develop appropriate partial charges. The electronic structure

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of hydrocalumite was determined using periodic density functional theory (DFT) as implemented with the Dmol3 program (Delley, 1990). Heavy atom positions were those reported by Terzis et al. (1987). Appropriate positions for the structural hydrogens in the unit cell were derived by molecular mechanics optimization prior to the DFT calculation. A single point energy calculation was performed for the 88 atoms of the periodic cell that had been converted to P1 symmetry from the original monoclinic space group. Nonlocal corrections were implemented based on the generalized gradient approximation using the Perdew (1991) density functionals for both the electron exchange and correlation. The atomic basis functions included double numeric sets with polarization for all atoms including the hydrogens. A self-consistent field (SCF) and energy convergence (to 0.000001 Ha) were obtained after 20 iterations providing a total energy of −1066.066529 Ha (1 Ha = 2625.5 kJ/mol). A Mulliken analysis of the electron population was performed on the molecular orbitals to obtain the charges of the component atoms.

In order to make all charges consistent with the chosen water model and the full formal charge of −1 for the Cl⁻ anions, the calculated Mulliken charges on all atoms of the hydroxide layer were scaled up by about 30%. We consider this to be a justifiable procedure, because Mulliken analysis generally underestimates atomic partial charges (Chirlian and Francl, 1987; Woods et al., 1990; Teppen et al., 1997). The final set of interaction parameters used in our simulations is presented in Table 1. The Lennard-Jones parameters of unlike interactions were calculated according to the "arithmetic" combining rules:

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad ; \qquad \varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}} \quad . \tag{2}$$

A "spline cut-off" method was used to treat long range non-Coulomb interactions, and all long-range electrostatic interactions were treated using the Ewald summation method (e.g, Allen and Tildesley, 1987).

Molecular dynamics trajectories of all atoms were generated with a time step of 0.001 ps over a period of 100 ps after a preequilibration MD run of approximately the same length under any given conditions. An isothermal-isobaric molecular dynamics algorithm (Parrinello and Rahman, 1981) was used in all simulations, and the pressure was set equal to 1 bar. Simulations were performed for bulk crystals at temperatures between −100 and 500°C, for dehydrated crystals at 100°C, and for the interface of hydrocalumite with bulk liquid water. In the latter case the model crystal was initially cleaved in the interlayer along the (001) crystallographic plane; half of the Cl⁻ anions were left on each of the created surfaces, and the simulated periodic system consisted of 4 hydroxide layers (infinite in the a and b directions) interspersed in the c direction with a layer of water approximately 20 Å thick (Fig.1). This thickness is sufficiently large to effectively exclude direct interaction of one interface with the other. The number of water molecules in this layer was chosen to reproduce the density of bulk liquid water under ambient conditions ($\sim$1 g/cm^3). We have also performed MD simulations for a bulk NaCl aqueous solution with the same set of interaction parameters to compare the dynamics of Cl⁻ anions and H_2O molecules in the interlayer and in the interfacial region of hydrocalumite with the dynamics of the same species in the bulk aqueous solution. Every fourth time step during the simulations was recorded for further analysis. Thus, for every simulation we were able to analyze an equilibrium dynamic trajectory consisting of 25000 atomic configurations with a time resolution of 4×10^{-15} s. Power spectra of atomic motions in the translational, librational, and vibrational frequency ranges were calculated as Fourier transforms of the velocity autocorrelation functions for each type of atom.

Structural results

Although all atoms were treated as movable and the size and shape of the simulation cell were not constrained, the structural results demonstrate a remarkable ability of the modified force field to reproduce and preserve the structure and density of the simulated hydrocalumite crystals. The temperature dependencies of all crystallographic unit cell parameters and density are shown in Table 2. The monoclinic angle β and the density are about 2% smaller than in the X-ray results, but all other parameters at room temperature are well within 0.5% of their measured values (Terzis et al., 1987). Angles α and γ remain within 0.2° of their nominal value of 90°.

The principal layer consisting of Al(OH)$_6$ octahedra distributed in a hexagonal primitive sublattice and connected by Ca atoms is well reproduced and preserved in the MD simulations over the temperature range studied. At room temperature, the average Al-O distance is 1.92±0.05 Å and the average Ca-O distance is 2.58±0.05 Å compared to the experimental values of 1.912 Å and 2.41 Å, respectively (Terzis et al., 1987).

According to the X-ray data, the interlayer of composition [Cl·2H$_2$O]$^-$ also consists of a primitive hexagonal sublattice, with Cl$^-$ ions forming almost regular triangles of this lattice and water molecules located at the center of each triangle. The orientation of these water molecules is such that each Cl$^-$ is coordinated by four H atoms forming ordered chains of hydrogen bonds along the a crystallographic direction (Fig.2a). Each Cl$^-$ anion is additionally coordinated by six OH groups (three from two adjacent hydroxide layer). In our simulations these hydrogen bonds keep chlorine virtually immobile even at temperatures as high as 300°C.

The experimentally-observed 10-coordinate arrangement of H-bonds to Cl$^-$ is well reproduced in our MD simulations. However, in contrast to the highly ordered orientations of the

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interlayer H_2O molecules interpreted from the X-ray diffraction measurements (Fig.2a), the simulations reveal significant dynamic disorder in water orientations (Fig.2b). At all simulated temperatures, the interlayer water molecules undergo librations (hindered hopping rotations) around an axis essentially perpendicular to the layers. This results in breaking and reformation of hydrogen bonds with the neighboring Cl^- anions. At any instant each water molecule is still hydrogen bonded to 2 chlorides, but because of the hopping among the three possible pairs of chlorides, it is, on average, hydrogen bonded to each one about 2/3 of the time. From the perspective of the Cl^- ion, this results in a time-averaged nearly uniaxial symmetry. Although at any instant there are four H-bonds to the neighboring water molecules, averaged over time there are six H-bonds with 2/3 occupancy.

The variable temperature ^{35}Cl NMR experiments for hydrocalumite (Kirkpatrick et al., 1999) indicate the existence of a dynamical order-disorder phase transition near ~6°C. Below the transition temperature, the Cl^- ion is rigidly held in a triaxial environment, whereas above this temperature, the Cl^- is in a dynamically averaged uniaxial environment. The frequency of the atomic motion causing the dynamical averaging which results in the phase transition, must be greater than ~10^5 Hz. Thus, the librational frequencies for water of about 10^{13} Hz determined from the present MD simulations (see next section) are much more than sufficient to cause the dynamical averaging observed by NMR.

An interlayer structure with the experimentally observed triaxial Cl^- environment is not reproduced in our simulations starting with the high-temperature disordered structure, even at temperatures as low as –100°C. However, preliminary simulations at still lower temperatures starting from the ordered structure do indicate the existence of an order-disorder phase transition to a triaxial Cl^- environment, change of the space group from C2/c to P2/c, and an approximately

3% reduction in volume. Detailed analysis of this calculated phase transition and its relationship

to the phase transition observed in the NMR experiments (Kirkpatrick et al., 1999) requires more

extensive simulations, which are currently in progress and will be reported separately

(Kalinichev et al., 1999).

Anion and water dynamics in hydrocalumite

Power spectra of atomic motions in the translational, librational, and vibrational

frequency ranges, calculated as Fourier transforms of the atomic velocity autocorrelation

functions, allow comprehensive and detailed analysis of the dynamics in this material. The

spectral density of the hindered translational motions of Cl^- ions in the interlayer consists of two

distinct frequency bands centered at approximately 50 and 150 cm^{-1} (Fig. 3). Decomposition of

chloride velocities into components parallel and perpendicular to the interlayer plane indicates

that the 50 cm^{-1} band is associated with the "in-plane" motions of the anions, and the 150 cm^{-1}

band is associated with the hindered translational motions perpendicular to this plane. Because

each chloride ion is electrostatically bonded to neighboring water molecules and hydroxide

groups, these two $O \cdots Cl \cdots O$ modes of molecular motions are clearly analogous to the

intermolecular $O \cdots O \cdots O$ bending and stretching motions of water molecules in the hydrogen-

bonded network, respectively (e.g., Eisenberg and Kauzmann, 1969; Heinzinger, 1990). Two

weaker spectral peaks at ~110 and ~190 cm^{-1} are distinctly observable at lower temperatures

(Fig. 3c) but merge with the 150 cm^{-1} peak into one broad spectral band at ~150 cm^{-1} at higher

temperatures (Fig. 3a-b). The intensity of the stretching peak is greatly reduced for Cl^- ions on

the surface of hydrocalumite, where the shape of the Cl^- translational spectrum more closely

resembles the spectrum in a bulk aqueous solution (Fig. 3b). In the collapsed, dehydrated

hydrocalumite structure at high temperature, hindered translations in the plane of the interlayer are the only possible chloride motions, as shown by the very intense peak at ~50 cm^{-1} in Fig. 3a.

As for Cl$^-$, the translational dynamics of interlayer water in hydrocalumite is also much different from that of surface water molecules, which is in turn much closer to that of water molecules in the bulk solution (Fig. 4). The main differences are in the low-frequency range, below ~50 cm^{-1}. In particular, there are very low spectral intensities at $v = 0$ for translational motions for surface, and especially interlayer species, compared to the corresponding intensities for the same species in the bulk (Figs. 3b,4b). This result clearly indicates drastically reduced diffusion coefficients for these species. The shape of the translational spectrum for interlayer water molecules is also strongly correlated with the spectrum of Ca atoms in the main hydroxide layer, because each water molecule is quite strongly electrostatically bonded to a Ca atom. Thus, as proposed in the X-ray structure (Terzis et al, 1987), interlayer water molecules complete the seven-coordinated environment of Ca in the hydroxide layer (Fig. 5), with average Ca$\cdots$O(w) distances essentially equal to those of Ca–O in the main layer (~2.57 Å in our simulations).

The strong electrostatic attraction between the negatively charged oxygen atoms of interlayer H$_2$O molecules and positively charged Ca atoms in the hydroxide layer makes the Ca$\cdots$O(w) bond direction the preferred axis for H$_2$O librations (hindered rotations, Fig. 6). This is in sharp contrast to the molecular librations in bulk liquid water in which, on average, four equally strong H-bonds act on every water molecule to create almost isotropic librational environment. The result is much broader spectral peaks of these hindered rotations in water (e.g., Heinzinger, 1990; Kalinichev and Heinzinger, 1992). To some extent, this is also true for the H$_2$O molecules in the first adsorbed layer on the crystal/water interface (dashed line in Fig.6b). The calculated spectral bands of intramolecular bending and stretching vibrations of the

interlayer H_2O molecules (not shown) are also much narrower in comparison to the corresponding bands in bulk liquid water and shifted to higher frequencies, indicating significantly different hydrogen bonding environment in these two cases.

Although the general scheme for the interlayer water dynamics suggested by van der Pol et al., (1994) for hydrotalcite (Mg,Al MMLH with interlayer carbonate) based on ^{1}H NMR results is generaly confirmed by our simulations, our results show that the time-averaged direction of the C_2 symmetry axis of interlayer water molecules is neither preferably parallel (Marcelin et al., 1989), nor definitely perpendicular to the layers, but has some intermediate orientation.

Diffusion coefficients of Cl^- anions and water molecules calculated from mean square displacement of those species (Table 3) show that on the space and time scale of the simulations there is no statistically appreciable diffusion in the interlayer, which is experimentally known to be about 10^{-8} cm/s^2 (e.g., Buenfeld and Zhang, 1998). However, the simulations show two distinct types of surface Cl^- with diffusion rates differing by a factor of ~3. One type is strongly bonded directly to the OH groups of the hydroxide layer (inner-sphere surface complexing) and strongly preferred (~85% of all surface chlorides present). The other type has one molecular layer of water between the anion and surface hydroxides (outer-sphere surface complexing), making them much more mobile (see Fig. 1). These results are in good qualitative agreement with the [35]Cl^- NMR data for hydrocalumite under controlled relative humidity conditions. These observations show that at high humidity, when essentially bulk water is present, at least some of the surface Cl^- undergo rapid isotropic averaging, as indicated by the narrow NMR peak (Kirkpatrick et al., 1999). However, even the diffusion rates of the outer-sphere Cl^- are almost an order of magnitude less than that of Cl^- in bulk aqueous solution. The exchange of Cl^- between

inner-sphere and outer-sphere environments is clearly observable on the 100 ps time scale of our simulations. However, for a detailed comparison to the NMR data a quantitative analysis of the exchange dynamics is necessary, which would require more extended simulations.

The mobility of water molecules in all cases is greater than that of the corresponding chloride (Table 3). Inner-sphere and outer-sphere water molecules were defined as roughly corresponding, respectively, to the first and second molecular layers adjacent to the surface hydroxide layer. The calculated self-diffusion coefficients for water on the hydrocalumite surface in very good quantitative agreement with the results of recent molecular dynamics simulations of water in porous Vycor glass (Spohr et al., 1999), where the surface consists of disordered Si–O–H.

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Table 1. Parameters of the simulation model.

	σ_{ii} / Å	ε_{ii} / kJ/mol	q_i / e
Hydroxide layer			
Ca	2.558	5.732	1.6
Al	2.851	0.00188	2.06
O (hydroxide)	3.166	0.650	−1.15
H (hydroxide)	—	—	0.44
Interlayer			
Cl⁻	3.981	3.486	−1.0
O (water)	3.166	0.650	−0.82
H (water)	—	—	0.41

Table 2. Simulated crystallographic lattice parameters and density of hydrocalumite. (Statistical errors in the last significant figure are given in parentheses).

	Temperature					Experimental (25°C)
	−100°C	0°C	100°C	200°C	300°C	
a / Å	10.000(2)	10.024(2)	10.035(2)	10.053(2)	10.059(2)	9.979(3)
b / Å	5.770(2)	5.784(2)	5.797(2)	5.803(2)	5.807(2)	5.751(2)
c / Å	16.28(1)	16.33(1)	16.42(1)	16.55(1)	16.72(1)	16.320(6)
α / °	89.90(5)	90.07(5)	90.03(5)	90.00(5)	90.16(9)	90.0
β / °	101.95(5)	101.84(5)	101.78(5)	101.76(5)	101.65(5)	104.53(3)
γ / °	89.95(5)	90.01(5)	89.99(5)	89.99(5)	90.00(5)	90.0
V / Å^3	919.5(5)	926.5(5)	934.7(7)	945.0(7)	955.5(8)	906.6(4)
ρ / g/cm^3	2.027(1)	2.012(1)	1.994(1)	1.973(1)	1.951(1)	2.056(1)

Table 3. Calculated diffusion coefficients of interlayer and surface species (cm^2/s).

	Cl^-	H_2O
Interlayer	$\ll 10^{-7}$	$\ll 10^{-7}$
Surface (inner sphere)	8.1×10^{-7}	5.0×10^{-6}
Surface (outer sphere)	2.6×10^{-6}	1.3×10^{-5}
Bulk NaCl solution	1.1×10^{-5}	1.8×10^{-5}

Figure captions

to the paper of A.G.Kalinichev et al.

"Molecular modeling of the structure and dynamics of the interlayer and surface species of mixed-metal layered hydroxides: Chloride and water in hydrocalumite (Friedel's salt)"

Fig. 1. A snapshot of the simulation of hydrocalumite/water interface at 25°C.

Fig.2. Interlayer structure of hydrocalumite (view down the c direction): a) ordered structure from the X-ray diffraction data interpretation (Terzis et al., 1987); b) a snapshot of the orientationally-disordered structure resulting from the MD simulations at 0°C.

Fig.3. Spectral density of the interlayer Cl⁻ translational motions.

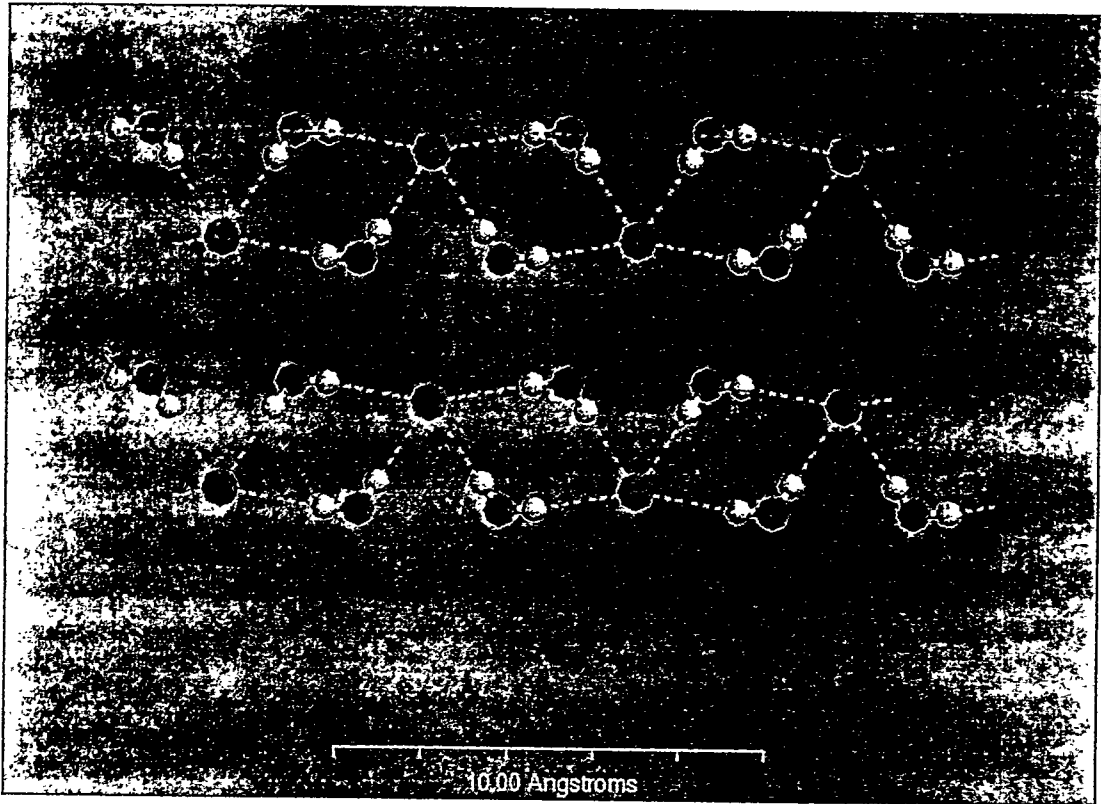Fig. 4. Spectral density of hindered translational motions of water molecules in the interlayer.

Fig. 5. Seven-coordinated environment of a Ca atom in the hydroxide layer and the $Ca-OH_2$ electrostatic bonding in hydrocalumite.

Fig. 6. Spectral density of H_2O molecular librations (hindered rotations) in the interlayer and on the surface of hydrocalumite.
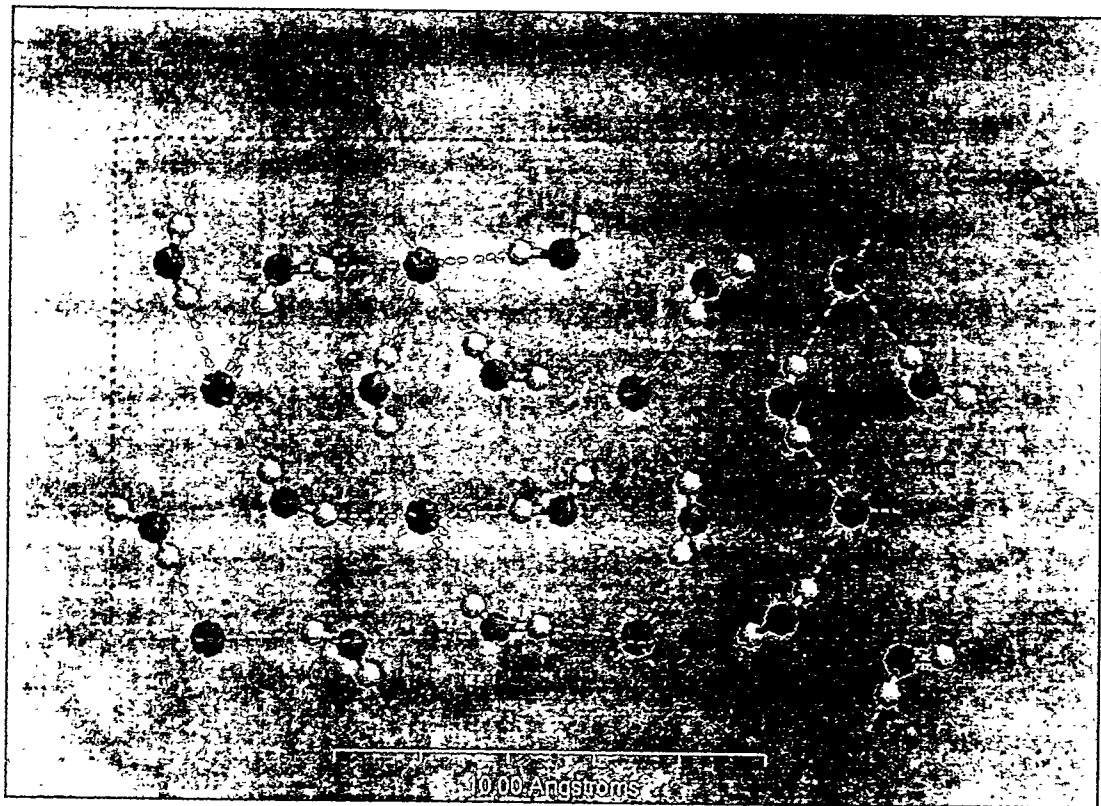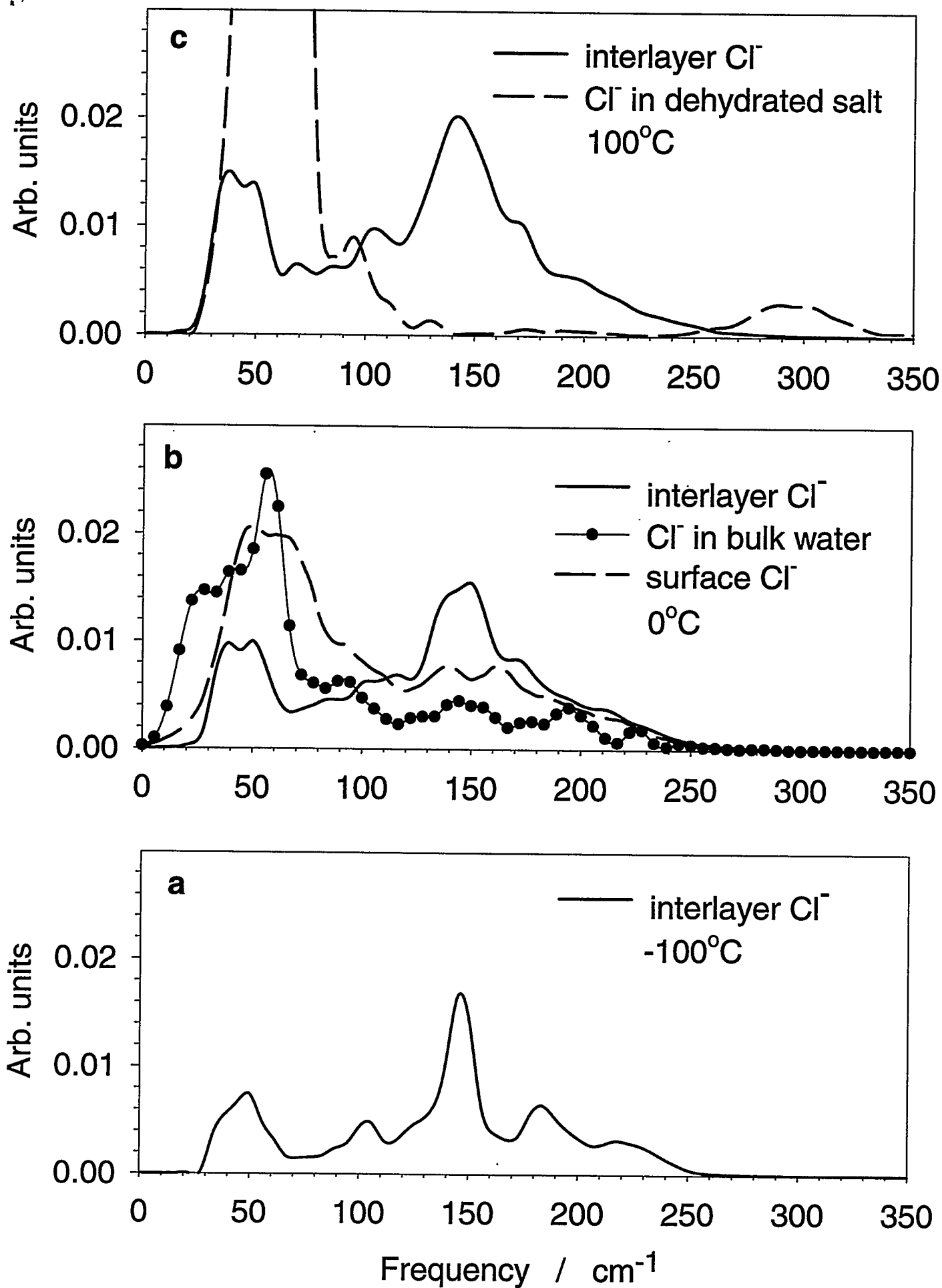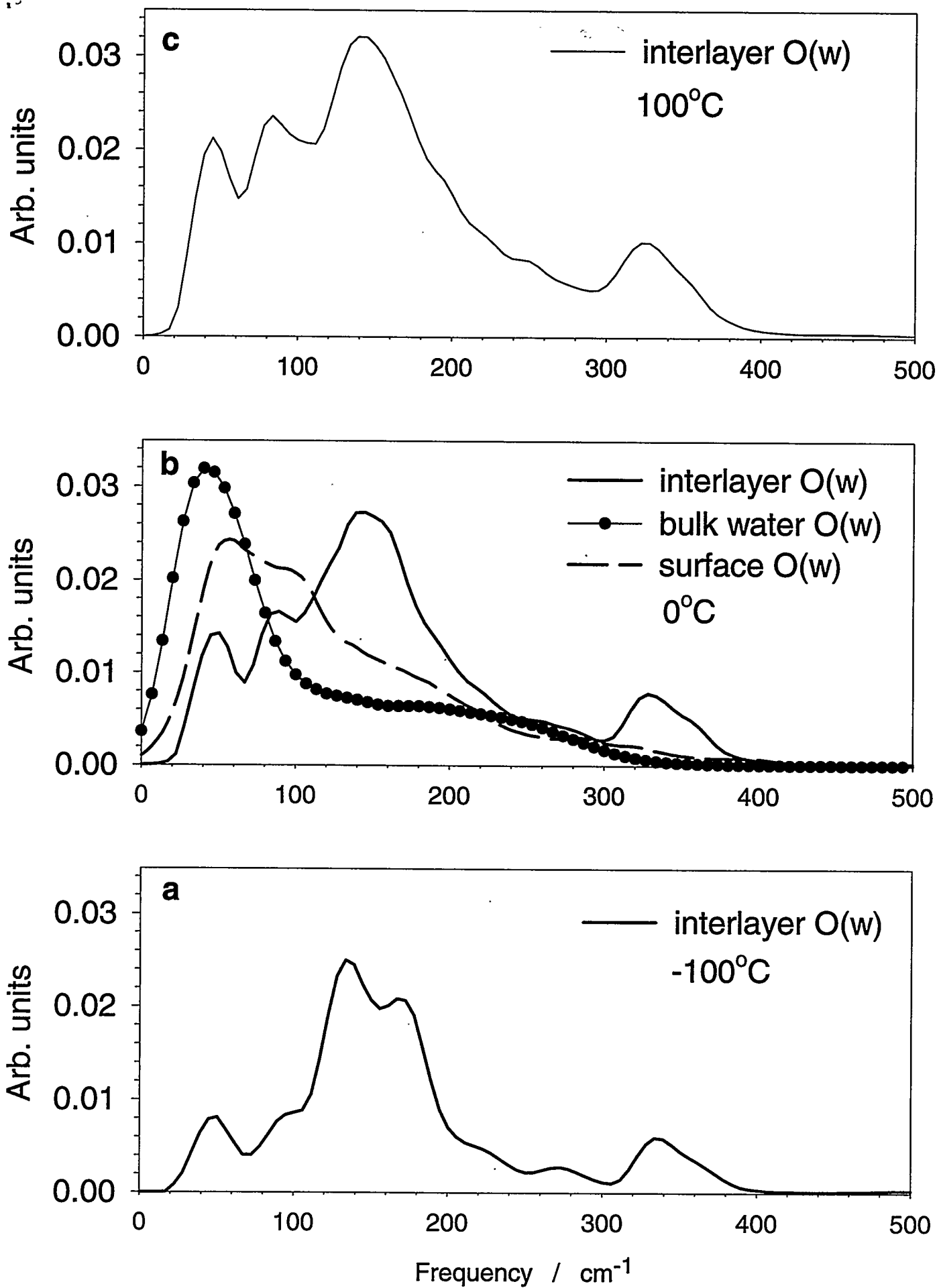
20.00 Angstroms

A. Kalinichev et al.   Fig.1

a

10.00 Angstroms

b

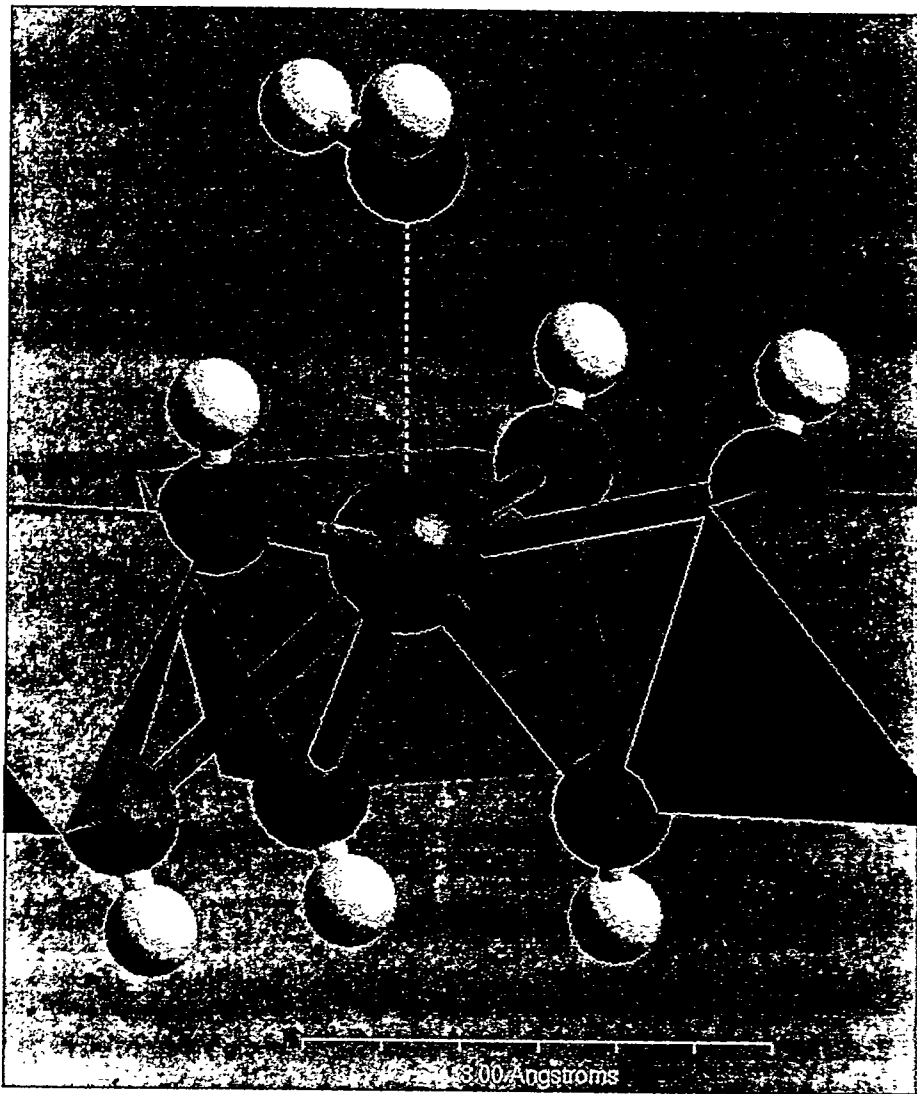

10.00 Angstroms

A.Kalinichev et al.   Fig.2

A. Kalinichev et al.   Fig. 3

A.Kalinichev et al.   Fig.4

A.Kalinichev et al.   Fig. 5.

A.Kalinichev et al.   Fig.6