5316 *J. Phys. Chem. B* **2007,** *111,* 5316−5321

Short-Range Order in Liquid Aluminum Chloride: Ab Initio Molecular Dynamics Simulations and Quantum-Chemical Calculations

A. L. L. East*,† and J. Hafner‡

Department of Chemistry and Biochemistry, University of Regina, Regina, Saskatchewan S4S 0A2, Canada, and Faculty of Physics and Center for Computational Materials Science Materialphysik, Universität Wien, Sensengasse 8, A-1090 Wien, Austria

Received: January 21, 2007; In Final Form: March 9, 2007

We use ab initio molecular dynamics simulations based on density-functional theory and quantum-chemistry calculations on molecular clusters to examine the structure of liquid $AlCl_3$. In the past, conflicting descriptions of the short-range-order in molten $AlCl_3$, based on either edge-sharing dimers or corner-sharing oligomers, have been proposed. This liquid also poses a simulation challenge, due to the possibility of ring-like trimers which can be metastable on the order of >10 ps. Simulations which begin with monomers, either random or ordered, appear to be able to produce proper ratios of ring-trimer to dimer-plus-tail molecular structures without the need to achieve long-time scale chemical equilibrium. Single-molecule calculations lend further support to the conclusion that the liquid is composed largely of edge-sharing dimers.

Introduction

Results from a neutron-scattering experiment on liquid $AlCl_3$ were published in 1994.[1] In that paper, Badyal et al. challenged the traditional notion that the liquid is composed of Al_2Cl_6 dimers, with edge-sharing tetrahedra based on four-coordinate Al atoms. Their first piece of evidence was the similarity in properties of liquid $AlCl_3$ with liquid $ZnCl_2$, whose structure is thought to be more network-like. Their second piece of evidence was their reverse Monte Carlo simulation of their measured structure-factor function $S(k)$, demonstrating a great deal of corner-sharing networks of three or more tetrahedra. However, Hutchinson et al.[2,3] have shown, via molecular dynamics simulations based on empirical force fields fit initially to crystal parameters, that $S(k)$ can be reproduced acceptably well by liquids composed largely by dimers. Their simulations began with melting from solid, a phase that features 6-coordinate Al atoms and is decidedly non-molecular. Very recently, Kirchner et al.[4] have performed Car−Parrinello molecular dynamics (MD) with gradient-corrected density-functional-theory (DFT) forces, beginning with an ensemble of “randomly distributed” $AlCl_3$ molecules. Their simulation resulted in a molecular liquid in which ∼50% of the molecules (but less than 50% of the original monomers) were in dimer form. While they did not compute $S(k)$, they did present radial pair correlation functions $g(r)$ that agreed closely with those of Hutchinson et al., having an only slightly increased Cl−Cl distance in the first $g_{\mathrm{ClCl}}(r)$ peak.

However, the Kirchner et al. paper also presented some interesting results for $AlCl_3$ clusters in the gas phase, apparently in an attempt to explain the existence of some larger molecular clusters found in their simulations. They used these results to conclude that the most stable form of gas-phase $AlCl_3$ clusters should be corner-sharing ring trimers, Al_3Cl_9, with a six-membered ring and four-coordinate Al atoms, analogous to 1,3,5-trioxane. They felt forced to conclude that one cannot make conclusions about the liquid based on cluster calculations. We will demonstrate that these conclusions are erroneous.

We are concerned, however, that in MD simulations chemical equilibration could be impeded by the so-called rare-event problem. Simply stated, a single chemical reaction with a potential-energy-surface barrier of ∼15 kJ mol^{-1} or greater should not normally be seen if one simulates a single molecule for only a handful of picoseconds of molecular time. Knowing this problem, and anticipating ring-opening barriers of this magnitude or greater, we found it surprising that Hutchinson et al.[2] (simulation 36 ps) and Kirchner et al.[4] (simulations of 10 and 1.4 ps) could produce $g(r)$ and $S(k)$ functions that seemingly agree well with experiment.

We have performed our own calculations of Al_2Cl_6 and Al_3Cl_9 molecules, and DFT-based ab initio MD simulations of the liquid, to improve upon the understanding of this liquid. In doing so, we demonstrate that two different liquid states are stable in a 10 ps simulation, and that single-molecule calculations are not in disagreement with reality, but in fact greatly assist the MD simulations in predicting the more stable of the two simulated states of liquid aluminum chloride.

Theoretical Methods

The ab initio molecular dynamics (AIMD) simulations were performed with the Vienna ab initio simulation package (VASP).[5] The level of theory was PW91, a gradient-corrected density functional theory (GGA DFT).[6] The calculations used Blöchl’s projector augmented wave technique,[7,8] applied to pseudopotentials appropriate for GGA DFT,[9,10] and a plane-wave basis set with an energy cutoff of 500 eV. Forces acting on the atoms are recalculated via the Hellmann−Feynman theorem after each MD move, i.e., the systems is always kept exactly on the Born−Oppenheimer surface. The liquid was mimicked by replicating a cubic unit cell using periodic boundary conditions, and calculations were restricted to the γ point. The unit cell contained 24 Al and 72 Cl atoms (24 $AlCl_3$ equivalents), with each atom having an isotope-averaged mass (26.982 amu for Al, 35.453 amu for Cl). The cell width was

---

* Corresponding author.
† University of Regina.
‡ Universität Wien.

10.1021/jp070517y CCC: $37.00

16.085 Å, to match the density of 1.277 g cm^{-3} employed by Hutchinson et al.;[2,3] the density used by Kirchner et al.[4] is only 6% less. The use of a smaller sample than that of Kirchner et al. (64 $AlCl_3$) allowed us to track the fate of each Al atom more easily, and it did not impede our ability to reproduce the experimental structure factor. Simulations were performed with the NVT (canonical) ensemble, using a Nosé thermostat[11] set for a thermal oscillation every 40 timesteps (SMASS = 0), and a Verlet velocity algorithm[12] with a usual timestep of 4 fs.

Simulation I began with 24 $AlCl_3$ monomers in a regular 3 × 3 × 3 array, but with three array locations vacant, and the monomers of the middle layer were rotated 90° upon their individual vertical axes to avoid large initial forces with the two layers on either side. This simulation ran at a temperature of $T = 600$ K for 4 ps, in 2 fs timesteps. Simulation II, a run originally intended to speed up equilibration, began from the structure taken at the $t = 132$ fs point of simulation I, and ran at temperatures that were linearly and continually reduced from 900 to 600 K over a 4 ps period, in 4 fs timesteps. Simulation III began from the structure taken from the end of simulation II, and ran at $T = 600$ K for 12 ps, in 4 fs timesteps. Simulation IV began from the structure taken from the end of simulation III, and ran at $T = 473$ K for 12 ps, in 4 fs timesteps. Simulation V began with eight Al_3Cl_9 ring trimers in a regular 2 × 2 × 2 array, with the trimer structure taken from a snapshot of the trimer ring seen in simulation III, and this simulation ran at $T = 600$ K for 12 ps, in 4 fs timesteps.

Single-molecule geometry optimizations were performed using the BLYP level of DFT,[13,14] the Ahlrichs TZVP basis set,[15] and the Gaussian03 code.[16] Vibrational frequencies were computed with analytic second derivatives, as is the default with Gaussian03. Thermal corrections for enthalpy and free energy were computed within the rigid-rotor and harmonic-oscillator approximations using BLYP molecular data. Improved electronic energies were obtained at BLYP-optimized geometries using the CCSD/CCSD(T) coupled-cluster levels of theory,[17] the same basis set, and the Gaussian03 or MOLPRO2002 codes.[18] All calculations were performed on a 32-bit-architecture Parallel Quantum Systems (Fayetteville, Ark.) computer at the University of Regina.

Using the data collected from the simulations, pair-correlation functions $g_{\alpha\beta}(r)$ were derived from histograms $n(r)$ of atom−atom distances via $g(r_i) = n(r_i)/N\rho V(r_i)$, where ρ is the particle density, $V(r_i)$ is the discrete shell volume considered for each discrete bin $n(r_i)$, and N is the number of reference atoms used to build $n(r)$. Bin width was 0.07 Å. Partial structure factors $S_{\alpha\beta}(k)$ were computed via direct summation of complex exponentials, as in eq 5 of ref 3. Total neutron-weighted structure factors $S(k)$ were computed as in eq 7 of ref 3, using the coherent neutron-scattering lengths {0.34, 0.96} for $\{b_{Al}, b_{Cl}\}$ and mole fractions {0.25, 0.75} for $\{c_{Al}, c_{Cl}\}$. It should be pointed out that because of stoichiometry and the much larger scattering length of Cl, the total structure factor is dominated by the contribution from the Cl atoms: the weighting factors for the partials are {0.029, 0.283, 0.691} for $\{w_{AlAl}, w_{AlCl}, w_{ClCl}\}$. Sampling for these functions was done over the last 10 ps of each 12 ps run.

Results

AIMD Simulations. Simulations I and II were runs designed to achieve first-level or short-time scale equilibration. Simulations III, IV, and V were hoped to be production runs, assuming no difficulties arising from possible second-level or long-time-scale equilibration. Figure 1 plots internal energy versus time for these five simulations. Simulation I (bold, solid line) demonstrates first-level convergence within 2 ps. The steady but more gradual decline of the energy of simulation II (bold dashed line) is due to the linearly decreasing temperature employed. The last three plots suggest that any possible long-time scale equilibration must either be invisible with respect to energy, or be occurring on a vastly greater time scale.

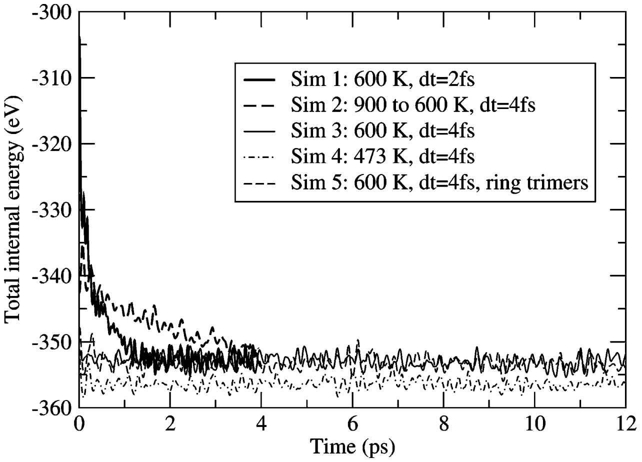

Figure 1. Time evolution of total energy during simulations.

TABLE 1: Link-Breaking and Link-Making Events in $(AlCl_3)_n$ Oligomers during Simulation III

timestep	time (ps)	event
50	0.2	addition: 1mer + 9mer → 10mer
300	1.2	fracture: 10mer → 8mer + 2mer
600	2.4	fracture: 8mer → 4mer + 4mer
700	2.8	fracture: 4mer → 2mer + 2mer
1400	5.6	fracture: 4mer → 2mer + 2mer
1400	5.6	fracture: 3mer → 2mer + 1mer (#11#20)(#12)
1500	6.0	addition: 1mer + 2mer → 3mer (#12)(#21#18)
1700	6.8	fracture: 3mer → 2mer + 1mer (#6#14)(#22)
1800	7.2	addition: 1mer + 2mer → 3mer (#22)(#13#9)
2000	8.0	fracture: 3mer → 2mer + 1mer (#22#13)(#9)
2100	8.4	addition: 1mer + 2mer → 3mer (#9)(#13#22)
2100	8.4	fracture: 3mer → 2mer + 1mer (#18#21)(#12)
2200	8.8	addition: 1mer + 3mer → 4mer (#12)(#8#16#24)
2950	11.8	fracture: 4mer → 3mer + 1mer (#24#16#8)(#12)

Link-making and link-breaking events were sufficiently rare, and our sample size sufficiently manageable that we made the effort to locate and document all such events in simulation III. This involved careful monitoring of the animations, and plotting of many atom−atom distances versus time. These events are tabulated in Table 1.

Link-breaking events outnumbered link-making events. This simulation began with one ring trimer, one monomer, one dimer, two chain trimers, and one nine-unit oligomer. At the end of the 12 ps run, the one ring trimer still existed, along with one monomer, seven dimers, and two chain trimers. Evidently, long-time scale equilibration is occurring and is resulting in a “dimer-plus-tails” liquid state or phase, consisting of very short oligomers of two or three units. Link-breaking events occurred only in chains of 3 or more $AlCl_3$ units. Link-making events involved only the attachment of a short-lived (recently produced)

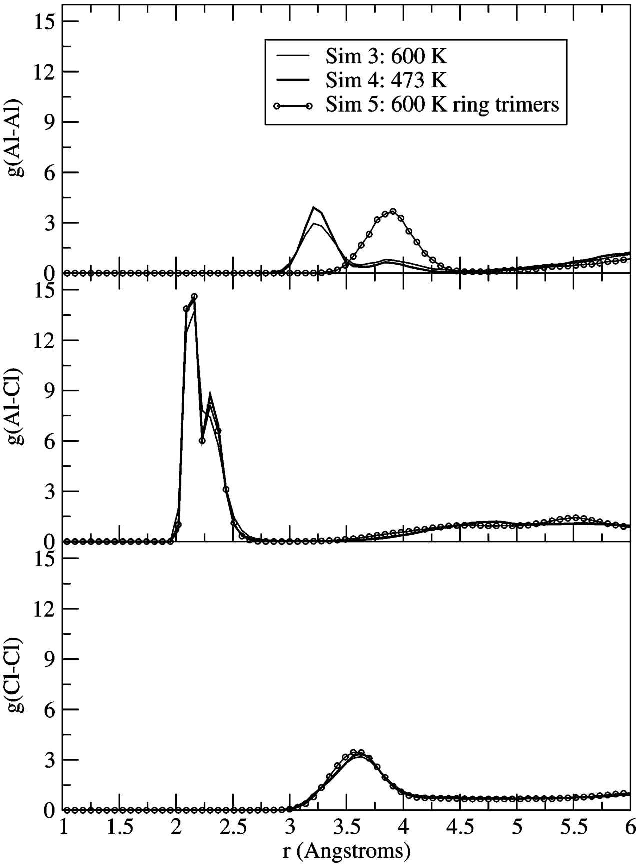

Figure 2. Radial correlation functions from simulation.

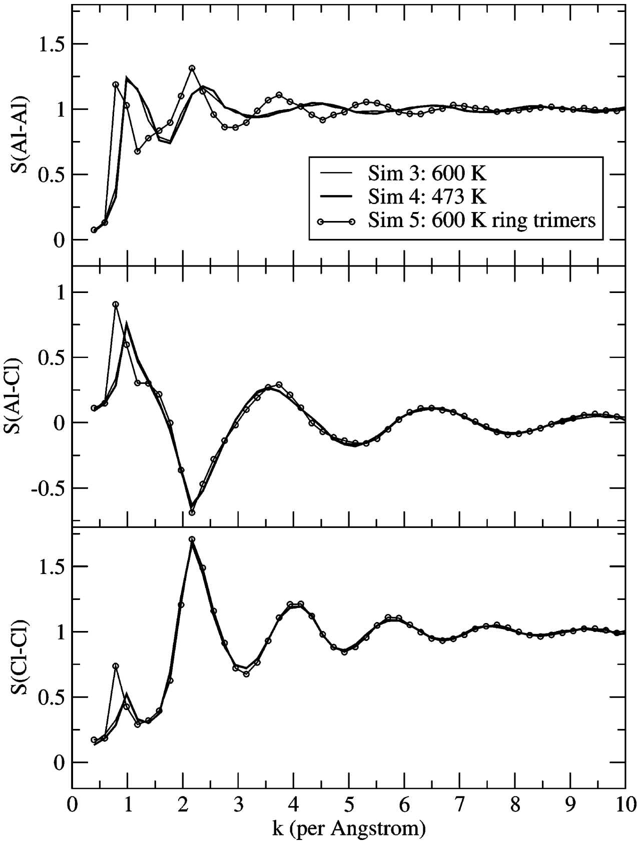

Figure 3. Partial structure factors from simulation. Simulations 3 and 4 provide nearly identical results.

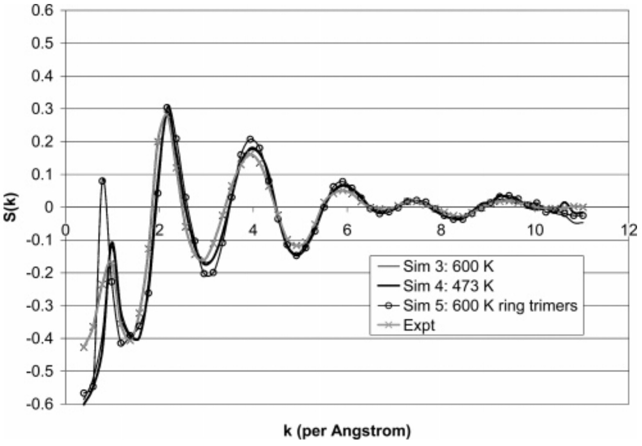

Figure 4. Total structure factors *S*(*k*). Simulations 3 and 4 provide indistinguishable results.

$AlCl_3$ monomer to an existing chain. Monomer lifetimes (when the monomer is truly free, i.e., when its Al atom is >5 Å from all other Al atoms) were observed to be less than 0.5 ps during this simulation.

Simulation IV continued from the end of simulation III, but at the lower temperature of 473 K used by experiment[1] and by Kirchner et al.[4] In the entire 12 ps run, very little change in molecular composition occurred, involving only the swapping of a monomer from a chain trimer to a dimer. Simulation V exhibited no link breaking or forming at all; all eight ring trimers were stable throughout the 12 ps simulation.

Figure 2 presents the pair-correlation functions $g_{\alpha\beta}(r)$ obtained from the three production runs, III, IV, and V. The $g_{\mathrm{AlAl}}(r)$ plot (top plot) is the only one that shows a clear difference between the ring trimer liquid and the dimer-plus-tails liquid, with ring trimers responsible for a 3.9 Å peak location. Note that the dimer-plus-tails simulations (III and IV) did have 3 of their 24 monomer units occupied in a single ring trimer, which produced the small bumps at 3.9 Å in their $g_{\mathrm{AlAl}}(r)$ plots. This is comparable to a small bump at 4.1 Å from the BLYP-based simulation of Kirchner et al.,[4] suggesting that a small number of ring trimers appeared in that simulation. The $g_{\mathrm{AlCl}}(r)$ and $g_{\mathrm{ClCl}}(r)$ plots demonstrate little difference between the three simulations. A small temperature effect can be seen in the $g_{\mathrm{AlCl}}(r)$ plot (middle plot): cooling the liquid from 600 to 473 K causes an improved separation of the peaks due to terminal Cl and bridging Cl atoms (2.15−2.20 and 2.30−2.35 Å, respectively). This improved separation more closely matches the separation seen in the plot arising from 600 K ring trimers.

Figure 3 presents the partial structure factors $S_{\alpha\beta}(k)$ from the three runs. Again, the distinction between a ring trimer phase and a dimer-with-tails phase is most evident in the top plot, $S_{\mathrm{AlAl}}(k)$, where the change in location of the first peak in $g_{\mathrm{AlAl}}(r)$ is reflected in a shift of the first two peaks and an out-of phase-oscillation at higher wavenumbers. Differences in the $S_{\mathrm{AlCl}}(k)$ and $S_{\mathrm{ClCl}}(k)$ partial structure factors are restricted to the prepeak at wave numbers of about 1 $\mathrm{Å}^{-1}$. For the ring-trimer phase, the prepeak is more pronounced and shifted to smaller wavenumbers. No temperature effect can be seen in the three plots.

Figure 4 presents the total structure factors *S*(*k*) from the three simulation runs and from experiment. The curve from Run III is almost co-incident with that of Run IV. Unfortunately, because of the predominant weighting factors, the dramatic differences in the Al−Al partial structure factor of simulation V are almost invisible in the total neutron-weighted *S*(*k*). A close comparison to the experimentally determined curve indicates a clear preference for the dimer-plus-tails structure: the broadness and asymmetry of the experimental prepeak ($k = 1$ Å^{-1}) seems to admit a small admixture from trimers, although this would worsen the agreement between theory and experiment in the 3−4 Å^{-1} region. The poor visibility in $S(k)$ of the decisive differences seen in the Al−Al correlations also explains why reverse Monte Carlo simulations fitting the total structure factor are ill-suited for exploring the short-range order in this liquid.

Single-Molecule Calculations. We chose to clarify and build upon the BLYP/TZVP exploratory calculations of Kirchner et al.,[4] by performing three dimer, three ring-trimer, and two chain-trimer optimizations at the same level of theory. Optimized results appear in Figure 5.

For the dimer, the D_{2h}-symmetry edge-dimer structure is a minimum-energy structure, but the two C_s-symmetry corner-sharing dimer structures (with an unfavorable 3-coordinate Al atom) are transition states for interconversion between two edge-sharing forms. We performed optimizations of versions of it: the imaginary frequency was 13i cm^{-1} for their version with six in-plane atoms, and 22i cm^{-1} for an internally rotated version with four in-plane atoms.

For the ring trimer, we tried optimizations of chair (C_{3v}), boat (C_s), and twist-boat (C_1) forms. The twist-boat was the global minimum, the C_{3v} chair form was slightly higher in energy, and the C_s structure was a transition state (imaginary frequency 8i cm^{-1}) for interconversion between twist-boat structures. For the chain trimer, we tried optimizing a dimer-plus-a-tail (edge-corner) trimer (C_1), with only four-coordinate Al atoms, and a symmetric edge−edge trimer (C_2) with a five-coordinate central Al atom, and they both optimized to the C_2-symmetry structure shown in the figure.

Table 2 compiles our computed reaction energies ΔE_{raw} for conversion of edge-dimers to other possible molecular forms, ignoring solvent effects which are presumed small. The BLYP reaction energies are endothermic, suggesting that dimers are the preferred forms. The CCSD(T) calculations are high-level benchmark calculations, and demonstrate that BLYP badly underestimates the benefit of dimers over monomers, and mildly overestimates the weak energetic preference for dimers over trimers. In fact, it appears the raw electronic energies of dimers and ring trimers are close to equal. However, entropy effects will further promote the formation of dimers over longer oligomers: Table 2 provides gas-phase entropy effects (last column) to demonstrate this. Although the entropy effects are smaller in the liquid phase than in the gas phase, it does appear that entropy will be the likely reason why the true liquid does not seem to possess substantial amounts of trimers.

Discussion

Badyal et al.[1] interpreted their structure factor function and associated fits to mean that the liquid-state features largely four-coordinate Al atoms. They pointed out that the large volume increase upon melting merely arises from the reduction from 6-fold- to 4-fold-coordination of the Al atoms, and does not in itself imply the formation of dimers. They pointed out that the first peak in the total pair correlation function $g(r)$, at 2.1 ± 0.4 Å, is due to overlap of two peaks, from Al atoms to bridged and nonbridged Cl atoms of the dimer. Their reverse-Monte Carlo simulations demonstrated that $S(k)$ could be fit by a liquid structure that has substantial polymeric corner-sharing structures, and that a signature feature of this would be in the $g_{\text{AlAl}}(r)$ partial pair distribution function, with a first peak at 3.7 Å. They also mentioned in a footnote that some ring trimers were produced by their simulation.

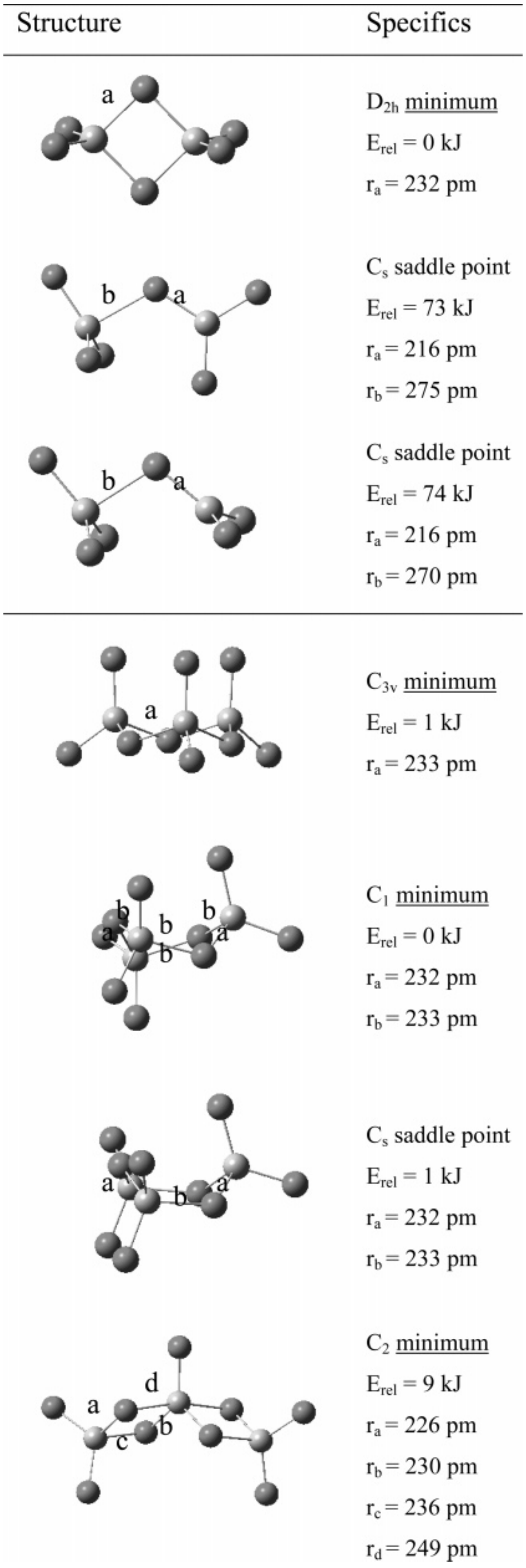

Figure 5. Optimized structures (with $r(\text{Al}-\text{Cl}_{\text{bridged}})$ values) and raw relative energies of Al_xCl_y clusters, from BLYP/TZVP calculations.

Unfortunately, it appears that due to the dominant weight of the Cl−Cl contrbutions, the overall structure factor $S(k)$ from neutron scattering is rather insensitive to a variety of structures observed in the various simulations. Simulations that are largely edge-sharing dimers (Hutchinson et al.[2]), largely corner-sharing polymers (Badyal et al.[1]), or a combination of the two (Kirchner et al.,[4] Hutchinson et al.'s V(I) of ref 3, and our Simulations I−IV), have all been able to produce acceptable mimics of S(k). A notable exception is the ring trimer structure, for which our

TABLE 2: Reaction Energies (kJ mol^{-1})

reaction	$\Delta E_{\rm raw}$ BLYP	$\Delta E_{\rm raw}$ CCSD[a]	$\Delta E_{\rm raw}$ CCSD(T)[a]	corrections[b] for $\Delta H_{298}^{\rm gas}$	further corrections[b] for $\Delta G_{298}^{\rm gas}$
$3Al_2Cl_6 \rightarrow 6AlCl_3$	242	353	366	−14	−137
$3Al_2Cl_6 \rightarrow$ 2-ring-Al_3Cl_9 (C_1)	20	−1	unknown[c]	+5	+37
$3Al_2Cl_6 \rightarrow$ 2-ring-Al_3Cl_9 (C_{3v})	21	6	4	+5	+45
$3Al_2Cl_6 \rightarrow$ 2-chain-Al_3Cl_9 (C_2)	39	18	11	+4	+40

[a] Calculated using BLYP-optimized structures. [b] Calculated using BLYP data and rigid-rotor/harmonic oscillator approximations. [c] Exceeds the memory capacity of our computer.

Simulation V demonstrates more significant differences in the 0.5−1.5 and 3−4 Å^{-1} regions. All simulations to date do agree that the Al atoms are largely four-coordinate. On the issue of the extent of corner-sharing versus edge-sharing, the empirical-potential result, like reverse Monte Carlo, can only offer a possible explanation for S(k); it has very little ability to suggest that it is producing the preferred structure, because of the ease of reproducing S(k) within a certain range of structure types. Hence, we place more weight on the DFT-based simulations, and believe that the liquid of the neutron-scattering experiment must consist predominantly of dimer and dimer-with-tail structures.

Next we discuss the issue of equilibration. The first of the papers by Hutchinson et al.[2] described two runs designed to test chemical equilibration. They used 960 atoms, density 1.277 g cm^{-3}, temperature 600 K, "extensive" equilibration, and 36 ps production runs. One run began from melting an ionic YCl_3 (six-coordinate Al) structure, which created dimers for 81% of Al atoms. A second run, from melting a dimeric (four-coordinate Al) Al_2Br_6 crystalline structure, kept the same dimers for 66% of Al atoms, with another 22% converting to dimers of different atoms (88% in dimers, total). This sounds somewhat successful; although chemical equilibrium had not been reached in at least one of these runs, the equilibrium percentage of Al atoms in dimers was narrowed to a range of 81−88%, given their potential functions. However, we should point out that the initial YCl_3 solid structure already possesses four-membered Al_2Cl_2 rings, and hence their initial structures in both cases were predisposed to producing dimer-plus-tails structures, rather than ring-trimer structures. We think that these simulations demonstrate that second-level equilibration of a dimer-plus-tails liquid phase is fathomable on a ∼50 ps time scale, suggesting that the barriers to tail formation are <15 kJ mol^{-1} (on the free energy surface, not the potential energy surface). On the other hand, their simulations do not address the possible metastability of ring trimers. Our simulation V demonstrates the error in assuming that complete chemical equilibration, in particular between ring trimers and dimer-plus-tail structures, can be achieved on a 10−50 ps time scale.

The equilibration test performed by Kirchner et al.[4] consisted of analyzing some unspecified properties of their 10-ps run in a variety of 1-ps data buckets, and observing consistency in the data. This does not preclude the possibility that a very slow equilibration process is merely beginning on this time scale.

Why did simulations beginning with random (Kirchner et al.[4]) or ordered (us) $AlCl_3$ monomers happen to produce a structure distribution that reproduced experiment so well, if the simulations used levels of theory than can produce two liquid "states" that are "metastable" to at least 10 ps? This is a really interesting question. It seems as if there is a kinetic effect: the most probable direction for a simulation begun from monomers is to head to the potential valley of dimers with corner-sharing tails, rather than the potential valley of ring trimers. The number of observed ring trimers was noticeably small from these simulations.

If there is a kinetic effect, then it temptingly leads to speculation about the true liquid: could the ring trimer form of the liquid constitute a metastable state or even an unique liquid phase? The energies of these two "phases" are quite similar at this level of theory, density, and 600 K temperature. We simply cannot simulate long enough to address this question. The liquid used for the experimental *S*(*k*) determination arose from sublimation of the solid, followed by condensation of the created vapor. The solid has a YCl_3-type structure (see, e.g., Hutchinson et al.[2]), with 6-coordinate Al atoms, and 4-membered or 12-membered rings of alternating Al and Cl atoms. Hence, there is an obvious kinetic reason for observing dimers (with 4-membered rings), rather than ring trimers (with 6-membered rings), in the experimental liquid also. The possibility of an experimentally synthesized metastable ring-trimer phase of liquid $AlCl_3$ is certainly intriguing, but it is more likely to have a lifetime of the order of microseconds than seconds, if it could be made at all.

Note that, without the availability of the experimental *S*(*k*) data, the simulations would be unable to conclude which form of the liquid is the more dominant one. We have demonstrated that single-molecule calculations allow the correct prediction, that dimers are more stable than ring trimers. This is at odds with the conclusions made by Kirchner et al.,[4] despite the use of an identical level of theory (BLYP/ TZVP) in the calculations. The reason for this is an unfortunate choice of "interaction energy" on their part. Their data in Tables 3 and 4 arise from the non-adiabatic definition, in which the oligomer is dissociated into monomers without structure relaxation, and they have mistakenly associated this with stabilization. The adiabatic definition, in which the oligomer is dissociated into relaxed monomers, is more appropriate when talking of a stabilization energy.[19,20] The two definitions give similar values for van der Waals complexes, but for strongly interacting monomers the distinction can become dramatic, as seen here. In the case of $(AlCl_3)_n$, the non-adiabatic interaction energy per monomer is stronger for the C_{3v} ring trimer than the edge dimer, as Kirchner et al. asserted: we obtain 112 and 104 kJ mol^{-1}, respectively, from BLYP/TZVP but ignoring the nearly constant basis-set superposition error. However, the adiabatic value, the one appropriate for discussion of relative stability, is stronger for the edge dimer (40 vs 37 kJ mol^{-1}). The CCSD(T) calculations suggest that the enthalpic differences between the two structural forms are actually very small: $\Delta E_{\rm raw}$ for 3 dimers → 2 C_{3v} trimers is +4 kJ mol^{-1}, instead of +21 from BLYP. However, the additional entropy effect will ensure that the dimers will be preferred. Hence, the ring trimer form is the metastable form, and this explains why this form contributes little to the experimental total structure factor.

Finally, we should clarify two other possible misconceptions that might arise from ref 4. First, there is only one stable dimer form. We have demonstrated (see Results) that the corner-sharing dimer they presented is a transition state, for interconversion between two edge-sharing forms. The possibility of the corner dimer being entropy-stabilized also seems unlikely, considering their statement that they saw little entropy effect on the "isomerization" energy in their Table 6. Hence, their statements that there are two "well-known" dimer structures, and that "neither the edge nor the corner dimer are unstable or transform into each other under temperature" are extremely perplexing. Second, their statements about the liquid being highly polarized are misleading. They seem to be referring to $AlCl_3$ monomers which "become polarized" in the dimer; it would be important to add that these polarizations essentially cancel in the dimers. The liquid is more likely to have limited conductivity, as Hutchinson et al. have suggested.[2]

Conclusions

The short-range order in liquid aluminum chloride is characterized by edge-sharing Al_2Cl_6 dimers, with some ability to maintain a small percentage of monomer tails which individually could exist on a ~10 ps time scale at 473−600 K. The experimental structure factor $S(k)$, derived from neutron-scattering data,[1] cannot discern between pure dimers and dimer-plus-tail structures. This places less weight on the empirical-force-field[2,3] and reverse-Monte Carlo[1] simulations for discerning between these latter two structures. As for the DFT-based MD simulations (ref 4 and this work), there are two indications that long-time scale equilibration has not been achieved on their 10−14 ps timescales: the first is the empirical-force-field work of Hutchinson et al.,[2] which demonstrates that equilibration of dimers with dimer-plus-tail structures requires a 50−100 ps time scale, and the second is our simulation of the ring-trimer liquid-phase that was stable for 12 ps. Despite this difficulty, the DFT-based MD simulations appear to generate realistic mimics of the equilibrium distribution of molecular structures when begun from a starting configuration of monomers, with short-time scale equilibration achievable in <10 ps.

The comparisons of simulated $S(k)$ data with experiment suggest that the liquid consists of few ring-trimer molecules. Traditional single-molecule thermochemical calculations predict the stability ordering to be dimers > ring-trimers > dimer-plus-tails. Contrary to what had been previously claimed,[4] traditional single-molecule calculations do not give erroneous predictions in this case, and in fact can lend valuable assistance in predicting the fate of metastable simulated phases.

Acknowledgment. B. Kirchner is thanked for clarification of the two definitions of "interaction energy" and additional discussions. P. Madden is thanked for providing a file of digitized data of the original experimental S(k) data. G. Kresse is thanked for the use of his structure factor program for elemental condensed phases, which we modified to generate partial structure factors for two-element materials. A.E. wishes to thank: the Canada Foundation for Innovation and the Government of Saskatchewan for funding of the supercomputer in Regina, the Natural Sciences and Engineering Research Council of Canada for an operating grant and travel expenses, the Austrian Science Funds and the Center for Computational Materials Science (University of Vienna) for supplemental sabbatical funding, and the members of the Computational Materials Science group for warm hospitality and many fruitful discussions.

References and Notes

(1) Baydal, Y. S.; Allen, D. A.; Howe, R. A. *J. Phys. Condens. Matter* **1994**, *6*, 10193.

(2) Hutchinson, F.; Walters, M. K.; Rowley, A. J.; Madden, P. A. *J. Chem. Phys.* **1999**, *110*, 5821.

(3) Hutchinson, F.; Wilson, M.; Madden, P. A. *Mol. Phys.* **2001**, *99*, 811.

(4) Kirchner, B.; Seitsonen, A. P.; Hutter, J. *J. Phys. Chem. B* **2006**, *110*, 11475.

(5) Kresse, G.; Furthmüller, J. *J. Phys. Rev. B* **1996**, *54*, 11169.

(6) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pedersen, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671.

(7) Blöchl, P. E. *Phys. Rev. B* **1994**, *50*, 17953.

(8) Kresse, G.; Joubert, D. *Phys. Rev. B* **1999**, *59*, 1758.

(9) Vanderbilt, D. *Phys. Rev. B* **1990**, *41*, 7892.

(10) Kresse, G.; Hafner, J. *J. Phys. Condens. Matter* **1994**, *6*, 8245.

(11) Nosé, S. *J. Chem. Phys.* **1984**, *81*, 511.

(12) Allen, M. P.; Tildesley, D. J. *Computer Simulations of Liquids*; Clarendon: Oxford, 1987.

(13) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(14) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(15) Schäfer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829. This traditional reference includes only the TZV basis set; the unpublished polarization-function exponents $\zeta_d^{Al} = 0.3$ and $\zeta_d^{Cl} = 0.65$ are commonly applied, as in Gaussian03, and were used here.

(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A. *Gaussian 03*, revision C.03; Gaussian, Inc.: Wallingford, CT, 2004.

(17) Bartlett, R. J. *J. Phys. Chem.* **1989**, *93*, 1697.

(18) Werner, H.-J.; Knowles, P. J.; Schutz, M.; Lindh, R.; Celani, P.; Korona, T.; Rauhut, G.; Manby, F. R.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Hetzer, G.; Lloyd, A. W.; McNicholas, S. J.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pitzer, R.; Schumann, U.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T. *MOLPRO 2002.6*; University of Birmingham: Birmingham, U.K., 2002.

(19) Xantheas, S. S. *J. Chem. Phys.* **1996**, *104*, 8821.

(20) Szalewicz, K.; Jeziorski, B. *J. Chem. Phys.* **1998**, *109*, 1198.