Isomers of (LiBr)$_n$ n = 4, 5, 8 and their interconversion

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Abstract. The structure and long-time dynamics of (LiBr)$_n$ n = 4,5,8 were studied by optimization and molecular dynamics. The ring structure, double ring stack for (LiBr)$_8$, was found to be the energy minimum. They are dynamically flexible and, particularly for (LiBr)$_4$ and (LiBr)$_5$, hardly isomerise into other isomers determined by optimization. (LiBr)$_8$ is probably a promising candidate to exhibit dynamic coexistence among a number of isomers.

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1. Introduction

Over the past years, there has been considerable effort to examine the structure and dynamics of alkali halide clusters. The equilibrium structures were studied by optimization methods and the dynamics by vibration frequency calculation of these equilibrium structures [1] and more recentlyby molecular dynamics [2,3,4]. NaCl and KCl were studied in order to examine the generality of the conclusion for Ar$_n$ [5] and it was reported that ionic clusters behaves rather differently.

It appears that the clusters studied so far, (NaCl)$_n$, (KCl)$_n$, (CsCl)$_n$ tends to maintain the cubic structure as their most favourable or lowest energy state [6] although (CsCl)$_n$ is known to adopt a structure different from the bulk solid. On the other hand, (NaI)$_n$ favours the ring [6].

We seek an understanding of (LiBr)$_n$ to obtain further information about clusters. Before we tackle the subject of coexistence, liquid-like and soft-solid like behaviour [2,3], we must know the isomers involved and their interconversion. We use the usual molecular dynamics and optimization to calculate the structure of the isomers, long-time-averaged temperature and bond length fluctuation (caloric and δ) curves and the time evolution of the isomerization at various energies. We choose (LiBr)$_4$ and (LiBr)$_5$ in order to

compare with KCl counterparts [3] and also examined the behaviour of (LiBr)$_8$ to extend the study to larger clusters.

2. Computational method

The structures of various isomers of (LiBr)$_n$, n = 4, 5, 8, were calculated by the steepest descent method with a guessed input geometry. Interconversion among structures was examined by molecular dynamics. The isomers were identified by quenching of the configuration by steepest descent optimization at regular intervals (50 - 500) over a trajectory of 50,000 time steps. Each time step is 0.003 ps. Dynamical properties were determined from averages over trajectories of 2 million time steps. As with KCl and NaCl, we used the Born-Mayer potential

$$V_{ij}(r) = A_{ij} exp(-r_{ij}/\rho),$$

to calculate the repulsive part of the system. The numerical values of the parameters are A_{++} = 42.95 eV, A_{--} = 2639.73 eV, A_{+-} = 378.16 eV and ρ = 0.3530 Å [7].

3. General results

Unlike KCl and NaCl clusters [1,2], the ring rather than the cube appears to be the most stable form among all cases considered. In the case of (LiBr)$_8$, the most stable structure is two well-stacked (LiBr)$_4$ rings. This indicates that the large difference in cation and anion sizes which are specified by the non-Coulombic forces significantly affect the structures of ionic clusters.

The structures of higher-energy isomers of LiBr clusters are very different from those of NaCl [1] and KCl [3] (see fig. 1). Most of them still maintain ring character.

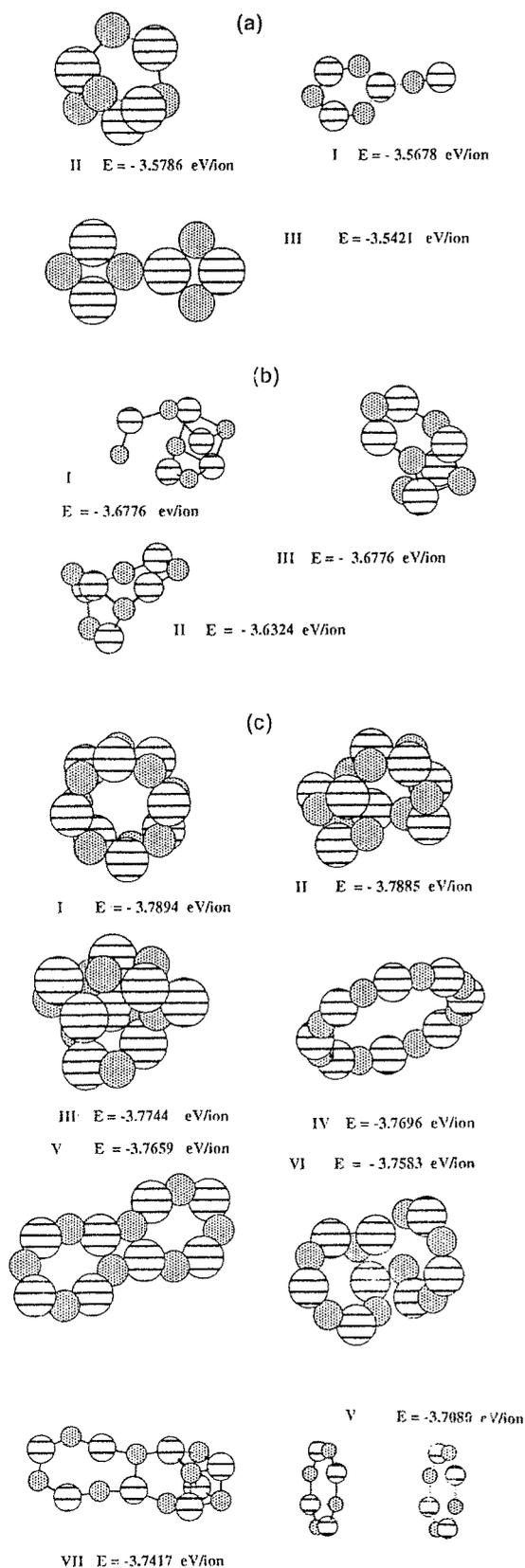* Present Address: Department of Chemistry, University of Oregon, Eugene, Oregon, USA

(a)

II E = -3.5786 eV/ion

I E = -3.5678 eV/ion

III E = -3.5421 eV/ion

(b)

I E = -3.6776 ev/ion

III E = -3.6776 eV/ion

II E = -3.6324 eV/ion

(c)

I E = -3.7894 eV/ion

II E = -3.7885 eV/ion

III E = -3.7744 eV/ion

IV E = -3.7696 eV/ion

V E = -3.7659 eV/ion

VI E = -3.7583 eV/ion

V E = -3.7089 eV/ion

VII E = -3.7417 eV/ion

Fig. 1. Structure and energy of LiBr clusters; (a) (LiBr)$_4$, (b) (LiBr)$_5$, (c) (LiBr)$_8$.

4. (LiBr)$_4$ results

The stability of the ring isomer (E = -3.708 eV/ion) is reflected by its caloric curve (fig. 2 left). It has no break or stationary regions. Regular quenching of the configuration along its MD trajectory indicates that it does not convert into other isomers.

On the other hand, molecular dynamics runs that start with the cube (E = -3.659 eV/ion) convert into the ring at E = -3.565 eV/ion. A sharp rise in the temperature is found in the caloric curve (fig. 2 left). From the regular quenching of the configuration along its MD trajectory, an irreversible conversion from the cube to the ring starts to occur at -3.565 eV/ion. The isomerization is accompanied by a small rise in δ (fig. 2 left) from 0.08 to 0.15 at that energy. At higher energies, the caloric curve coincides with that of the ring. A discontinunity occurs at E= -3.40 eV/ion where the cluster decomposes.

Quenching of the configuration along the MD trajectory above E = -3.45 eV/ion very infrequently (once in 60,000 time steps) exhibit chain structure. Presumably the vibrational amplitude of the ions becomes momentarily large to give a sharp jump in δ.

5. (LiBr)$_5$ results

The caloric curve (fig. 2 middle) of the (LiBr)$_5$ ring ($E = -3.7381$ eV/ion) indicates that the temperature of the cluster rises almostly linearly with its energy without any break and at a cluster energy of approximately -3.40 eV/ion, the cluster decomposes.

The δ curve (fig. 2 middle) shows its fluctuation with energy even though there is no isomerization at low energy. Infrequent isomerization to generate (I) and the chain but not (II) (fig. 1b) is possibly the result of the large vibrational amplitude of the ring at energy above -3.45 eV/ion.

6. (LiBr)$_8$ results

The caloric curve of the (LiBr)$_8$ double ring stack ($E = -3.7894$ eV/ion) (fig. 2 right) does not contain any discontinunity. However scattering of data was found for the caloric curve at approximately -3.675 eV/ion. The δ curve (fig. 4b) on the other hand shows rather large scattering of data. It indicates the large variations in vibrational amplitude or fast conversion between many short lived isomers.

Quenching of the cluster configuration over a trajectory of 500,000 steps below -3.740 eV/ion gives exclusively the double ring stack. The vibrations of this cluster are large enough to give a delta value of 0.1. Above -3.740 eV/ion, the next lowest energy isomer (E = -3.7885 eV/ion) starts to appear and the δ value starts to increase rapidly to 0.3. As the cluster energy increase beyond -3.685 eV/ion, the cluster begin to explore high-lying potential surfaces and reaches the high-energy isomers (II to VII) (fig 1c). The frequency of appearance and type of isomer also increases with cluster energy. Particularly isomers V and VI are definitely created as a result of the large-amplitude vibration of the two rings in the lowest-energy state. The cluster decomposes at ap-
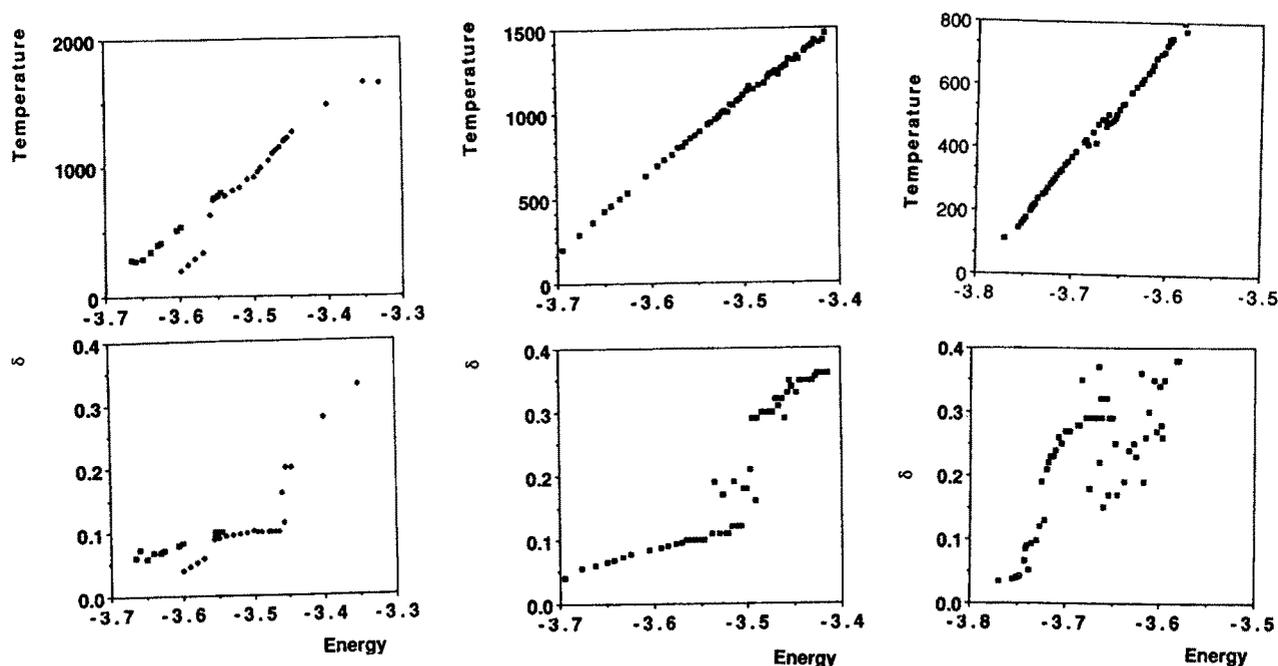
Fig. 2. Left. Caloric (above) and δ curve (below) of $(LiBr)_4$. Square. ring isomer; diamond. cube isomer. Middle. Caloric (above) and δ curve (below) of $(LiBr)_5$. Right. Caloric (above) and δ curve (below) of $(LiBr)_8$

proximately -3.450 eV/ion, by splitting of the double ring stack.

7. Conclusion

The behaviour of small lithium bromide clusters is different from their potassium chloride counterparts. The difference in cation and anion sizes gives rise to a ring as the minimum energy structure in LiBr clusters. These rings are stable in the sense that they have a long life time within a potential well. The flexible ring and ring-like isomers only favour occasional isomerization for larger clusters and the ring-like structure still occurs frequently in these higher energy isomers.

Given the infrequent appearance of the high energy isomers, we have to look for new conditions to promote isomerization. Hopefully we can use Monte Carlo simulation to generate those isomers found by simple optimization but not explored along a single MD trajectory. We would hope to promote such isomerization in future simulation studies by mode select excitation [3]. Alternatively we can start the MD run with a distorted initial geometry [2] and which might ensure a more thorough exploration of the cluster phase space. Otherwise the double ring of $(LiBr)_8$ is the only promising candidate to show any dynamic coexistence between a number of isomers.

8. Acknowledgement

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