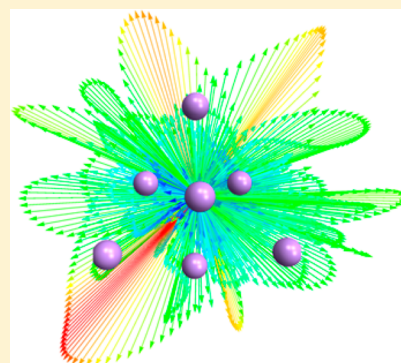


# Ab Initio Molecular Dynamics Study of Small Alkali Metal Clusters

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**ABSTRACT:** In this work, the dynamics of the clusters of the type  $M_3$  with  $M$  a metal alkaline atom from Li to Cs have been studied. Other heteroatomic mixed clusters like LiNaK and one bigger cluster,  $Na_7$ , have also been studied. It was found that the dynamics present interesting phenomena like pseudorotations and crossovers which could explain the differences between experimental and theoretical values of some electrical properties, like the electric dipole moment of alkali metal clusters.



## I. INTRODUCTION

In the last few decades, the study of small metallic atomic clusters has been a challenge area of research in both sides experimental and theoretical.<sup>1–3</sup> It is known that their properties range from those of molecules to the ones of solids, and they are often unique. From the theoretical point of view, small metal clusters have been extensively studied, in part because they are computationally easily affordable. It is known that their properties depend on the number of atoms and on the shape of the cluster. From the experimental side, measurement of cluster properties is a difficult task and deducing their actual geometry from experiments is almost always impossible. Hence, the interplay between theory and experiment is fundamental. Usually, the theoretical work starts search for the geometry of the most stable isomer. This task becomes more and more difficult as the number of atoms in the cluster increases. Most minimization techniques used in computational chemistry and implemented in many standard computational codes work well locating minima closed to the starting configuration but fail if one does not have a good guess of the stable geometry. Another strategy lately used are based on stochastic methodologies like simulated annealing,<sup>4,5</sup> genetic algorithm,<sup>6,7</sup> and big bang.<sup>8,9</sup> However, none of them ensures that the most stable structures are found. One of the main problems, besides the great number of variables to optimize, is the flatness of the potential energy surface. As a result of this, the system can easily go from one minimum to another, and it can be possible that during the time of an experimental measurement, the cluster coexists among different minima.

The alkali metal clusters are among the most studied ones from both the theoretical and the experimental point of view.<sup>1,10</sup> Geometry and other properties of the small members of the series have been extensively studied. However, for the heaviest members of the series,  $Rb_n$  and  $Cs_n$ , there are only few studies.<sup>11,12</sup> It is to notice that even for the small members of

the series there are still discrepancies between theory and experiment. For example, for a small cluster like  $Li_4$ , very exhaustive computational calculations of the dipole polarizability yields values higher in more than 10% with respect to the experimental one.<sup>13</sup> Very recently, an experimental work reports that all sodium clusters up to 200 atoms have a negligible, almost zero, dipole moment. This study includes the small member of the series,  $Na_3$ .<sup>14</sup> However, many theoretical calculations at different levels of theory predict that the most stable isomer of  $Na_3$  is triangular presenting a non negligible dipole moment in clear contradiction with the experiment.

There are theoretical evidence that some of these discrepancies can be related to the possibility of these clusters to easily move from one minimum to another on the potential energy surface and, therefore, the importance of their dynamical behavior. The development of very efficient exchange-correlation functionals in density functional theory (DFT) and the increasing computer power have made possible to do computer simulations of the type Born–Oppenheimer molecular dynamics (BOMD) of great accuracy in a reasonable time.<sup>15</sup> In contrast to the classical molecular dynamics, in the *ab initio* ones, the electronic Schrödinger equation is solved on the fly allowing for a more correct description of the main electronic characteristics like bond forming and breaking. In this way, for example, a new structure for the sodium heptamer has been found.<sup>16</sup> The thermal expansion of the clusters has also been obtained and proposed as a candidate to resolve the discrepancy in the dipole polarizabilities.<sup>17</sup> The regions of melting temperature of clusters of medium size has also been studied.<sup>18</sup> The heat capacities and the diffusive motion of atoms along the surface of a cluster have also been studied using

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BOMD methodology.<sup>19</sup> There are many other topics where the *ab initio* molecular dynamics, specially the popular Car–Parrinello, method has had a profound influence.<sup>20,21</sup>

In this work, we focus on the dynamics of the smallest members of the alkali metal clusters, the series  $M_3$  ( $M = \text{Li–Cs}$ ), an heteronuclear cluster,  $\text{LiNaK}$ , and the cluster  $\text{Na}_7$ . The motivations were experiments that showed that both  $\text{Na}_3$  and  $\text{Na}_7$  have null dipole moment<sup>14</sup> and the theoretical explanation given decades ago by Herzberg and Longuet-Higgins.<sup>22</sup> These systems present the phenomena of pseudorotation in which the atoms are interchanging their positions without a change in the total nuclear angular momentum of the system. It will be shown that the dynamics of the trimers are in some way more complicated than that. They present not only pseudorotation but also crossover. The crossover is the movement of the atoms going to the linear configuration and again to the angular one but on the opposite direction producing that the dipole moment vector points opposite to the original direction. We will show that the coupling of both phenomena produces a quasi periodic movement which is almost harmonic and could explain the absence of dipole moment even at a temperature as low as 20 K. The structure of this work is as follows. First some technical details of the calculations will be given. Then, the results will be shown with a general discussion of the kind of movements found in the dynamics at different total energies. A short discussion of the pseudorotation and crossover phenomena will be given. Unfortunately, for the type of methodologies used here, it is impossible to discuss the possible existence of a Berry phase of the wave function. We have done the calculations for all the alkali metal trimers and some heteronuclear clusters formed for the alkali metal atoms. Since the qualitative results are very similar in all cases, almost all the discussion will be centered around the sodium trimer. To finish, some results of the dynamics for the heptamer sodium cluster will be shown to demonstrate that the phenomena of pseudorotation and crossover can also occur in bigger systems.

## II. METHODOLOGY

Two different exchange–correlation functionals have been used, the B3PW91 and the B3LYP. Since the results showed negligible differences only the results with the B3PW91 functional will be shown. To have a guide about the reliability of our results, more demanding calculations of the type CCSD(T) have been done. For Li and Na the 6-311+G(d) basis set has been used. For K, Rb, and Cs, the Stuttgart pseudopotentials with their respective basis sets have been used.<sup>23</sup> On this way, first the geometries have been optimized and some of the most important electronic properties calculated. All the calculations have been done on the ground state which in all the systems corresponds to a spin multiplicity of two. Then, Born–Oppenheimer dynamics have been ran starting with different initial geometries constructed with random deviations of the triangular stable isomer. The total average nuclear kinetic energy has been kept fixed in each run at values of 100, 200, and 300 K, and in some cases, also some dynamics have been run at 20 K. The nuclear kinetic energy is expressed in units of temperature using the classical expression  $3(N - 5)/2kT = \sum_{i=1}^N (1/2)m_i v_i^2$  where the index  $i = 1, 2, \dots, N$  runs over the  $N$  atoms of the system. The integration time step was set at 2 fs, and the total time of the dynamics is 12 ps. However, most of the phenomena to be discussed here are well explained in a time as short as 8 ps. For each cluster at the given

temperature at least 10 dynamics with different initial conditions for initial velocities have been ran without finding any quantitative difference. It has also been monitored that the total nuclear kinetic energy conserves during the dynamics. To analyze the results, especially thinking of bigger clusters, the square distance deviation defined as

$$D(t) = \sum_{m=1}^N |\vec{R}_m(t) - \vec{R}_m(0)|^2$$

has been used. In the above expression  $\vec{R}_m(t)$  is the position vector of the atom  $m$  at the time  $t$ .  $D(t)$  is a measure of the global atomic displacement respect to the initial position. All calculations have been done using the G09 program.<sup>24</sup> To keep the total nuclear energy fixed the velocities have been scaled at each step. Since the G09 program only includes this type of thermostat in the ADMP (atom centered density matrix propagation) dynamics, we run the ADMP dynamics with the FULLSCF option which is equivalent to a BOMD dynamic.

## III. RESULTS AND DISCUSSION

**A. Ground State Equilibrium Structures.** In Table 1 and 2, the geometrical parameters, the dissociation energy per atom,

**Table 1. Geometrical Parameters (Interatomic Distance  $R$  and Angle), Dissociation Energy per Atom  $E_b$ , Dipole Moment  $\mu$ , and Smallest Frequency  $\nu_0$  in the Clusters  $M_3$  ( $M = \text{Li–Cs}$ ), with Symmetry  $C_{2v}$**

property	methodology	cluster				
		Li <sub>3</sub>	Na <sub>3</sub>	K <sub>3</sub>	Rb <sub>3</sub>	Cs <sub>3</sub>
$R$ [Å]	CCSDT	2.78	3.28	4.43	4.81	
	B3PW91	2.79	3.28	4.25	4.55	5.04
angle [deg]	CCSDT	71.9	81.3	94.4	95.3	
	B3PW91	72.5	85.1	86.5	90.9	93.2
$E_b$ [eV]	CCSDT	0.51	0.31	0.15	0.12	
	B3PW91	0.47	0.30	0.20	0.17	0.14
$\mu$ [D]	CCSDT	1.20	0.48	0.04	0.02	
	B3PW91	0.52	0.09	0.24	0.38	0.35
$\nu_0$ [cm <sup>-1</sup> ]	CCSDT	176	47	8	6	
	B3PW91	170	39	19	10	6

**Table 2. Interatomic Distance  $R$  and Dissociation Energy per Atom  $E_b$  in the Clusters  $M_3$  ( $M = \text{Li–Cs}$ ), with Symmetry  $D_{\infty h}$ <sup>a</sup>**

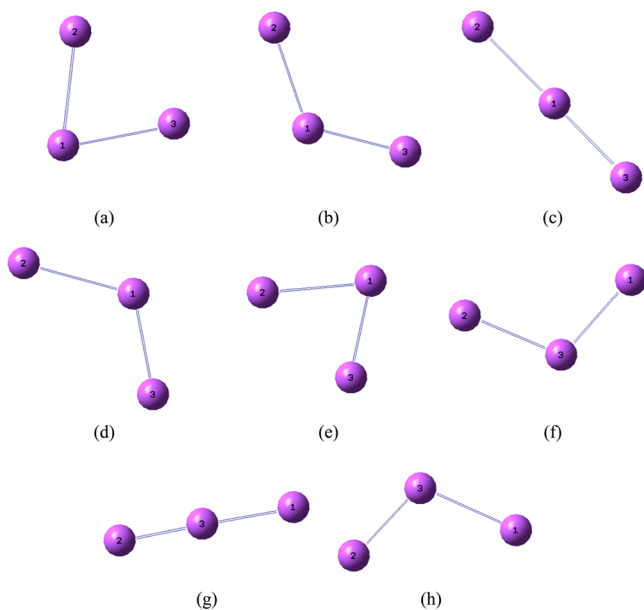
property	methodology	cluster			
		Na <sub>3</sub>	K <sub>3</sub>	Rb <sub>3</sub>	Cs <sub>3</sub>
$R$ [Å]	CCSDT	3.32	4.48	4.81	5.41
	B3PW91	3.32	4.29	4.57	5.06
$E_b$ [eV]	CCSDT	0.29	0.15	0.12	0.09
	B3PW91	0.29	0.19	0.16	0.14

<sup>a</sup>All the minimal frequencies calculated are lower than 10 cm<sup>-1</sup>.

the dipole moment, and the smallest harmonic frequency for the triangular and linear isomers are shown. The smallest frequencies for the linear isomers are not shown because all of them are, though positive, quite small compared to the expected accuracy of the method. At the CCSD(T) level of theory we did not find any stable angular isomer for  $\text{Cs}_3$ , and for  $\text{Li}_3$  was not found any linear isomer at any level of theory. In general, one can see that all properties follow a periodic trend

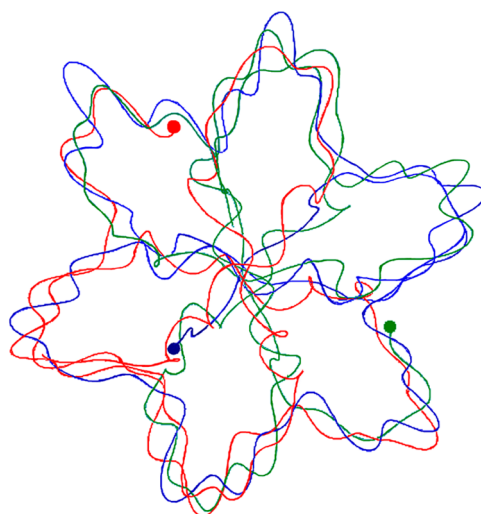
going down through the periodic table. This characteristic has been already exhaustively discussed.<sup>11</sup> The bond distances are relatively large and the dissociation energies small, confirming the known fact that those clusters are only weakly bonded. At the B3PW91 level of theory, in all cases the triangular isomer is more stable than the linear one. It is to notice that going down in the periodic table the differences are so small that for  $K_3$ – $Rb_3$  it is impossible to decide which is the most stable isomer. However, there is a clear trend to prefer the linear geometry when the size of the atom increases. Another manifestation of the weak bonds is the extremely small frequencies, which are also a clear indication of the flatness of the potential energy surfaces. The comparison between the Kohn–Sham calculations and the more sophisticated CCSD(T) ones shows that the agreement is reasonable for the lighter members of the series and deteriorates for Rb and Cs trimers. This is probably a consequence of the Jahn–Teller distortion presented in these clusters which also prevent them of being an equilateral triangle. All the triangular clusters present a non-negligible dipole moment in contrast with the already mentioned experimental measurements. However, it is to notice that there is a significant dispersion in the dipole moment values. For example, for  $Na_3$  the CCSD(T) methodology yields a value of 0.48 D whereas the B3PW91 calculation gives 0.09 D and the B3LYP functional gives 0.35 D.

**B. Dynamics.** Qualitatively, for all the studied clusters the phenomena to be discussed are very similar. Hence, almost all the presented results will be focused in the  $Na_3$  cluster. Figures 1–4 show different ways to analyze the global movement of the



**Figure 1.** Crossover and pseudorotation in  $Na_3$  cluster at 300 K (time step between consecutive images is 300 fs).

atoms through the dynamics. Figure 1 shows some snapshots of a representative dynamic for  $Na_3$ . This particular dynamic keeps the total average nuclear kinetic energy at 300 K. One can clearly see that the initial central sodium atom (labeled 1 in the figure) goes beyond the amplitude of the vibration and when passing through the linear configuration there is a crossover changing the atom that is in the middle position. Figure 2 shows the trajectory followed by each atom in the same dynamic. It is clear that the three atoms are equivalent,

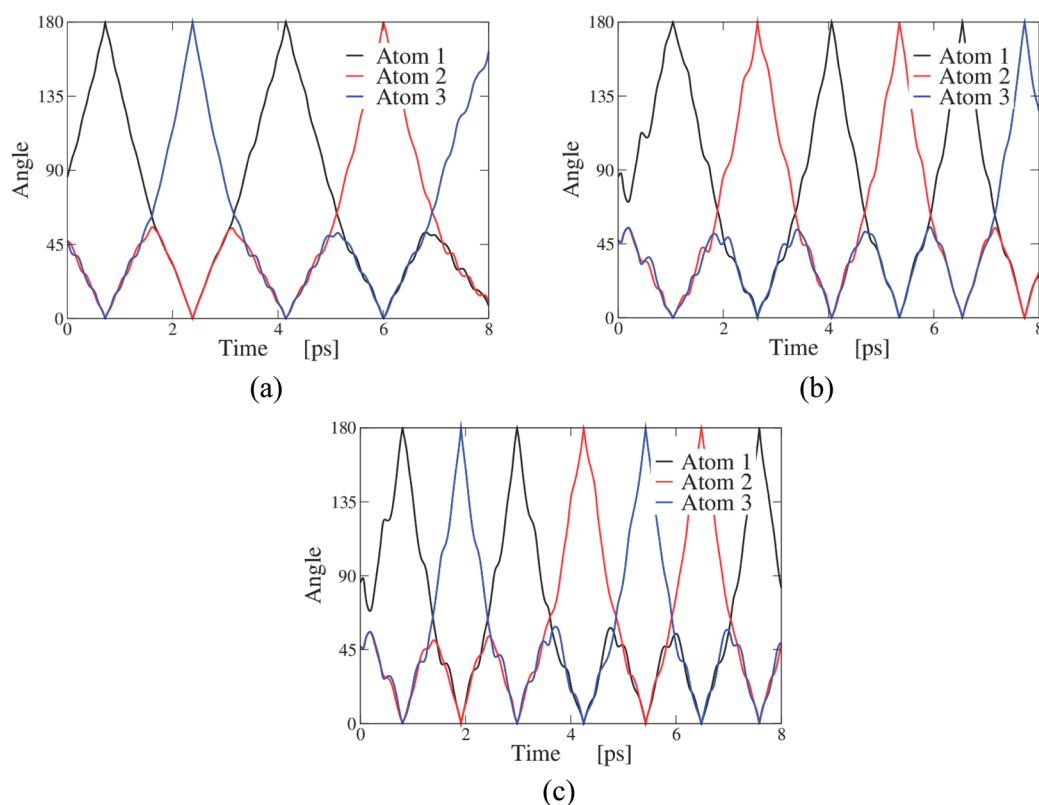


**Figure 2.** Trajectories of each sodium atom in the dynamic of  $Na_3$  cluster at 300 K in a period of 12 ps.

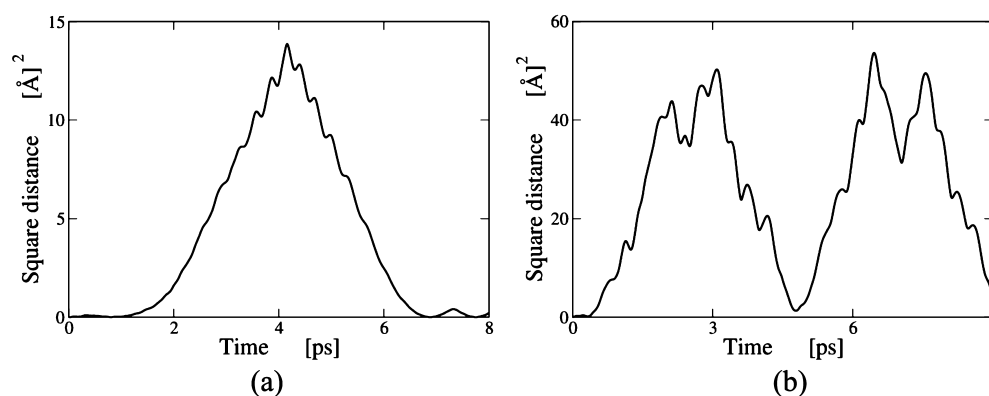
occupying the three of them the three corner of the triangle. There is not something as a central atom, and the system presents an almost circular symmetry in which the charge displacement is rotating, explaining in a qualitative way the absence of dipole moment in the experiment. Figure 3 shows the angles of  $Na_3$  along the dynamics at three different temperatures. Different colors are only to distinguish which atom is at the center. Every time the angle is  $60^\circ$  the cluster is near the forbidden equilateral triangle geometry which presents Jahn–Teller distortion and a conical intersection with an excited state producing the pseudorotation.<sup>22</sup> Figure 4 shows the square distance deviation at two different temperatures. Every time the square distance deviation approaches to zero means the cluster is close to its initial position. This clearly depends on the temperature, the larger the total nuclear kinetic energy the shorter the time to come back to the initial position.

The amplitude of the movement, measured as the maximum value of the square distance deviation, is also bigger at a higher temperature. It means the volume of the cluster increases at higher temperatures, which is a very reasonable result. It also implies that many other properties could depend on the temperature, for example, the dipole polarizabilities which would increase with the temperature.

We now separate the movement in two different phenomena which are coupled in the dynamics, the pseudorotation and the crossover. As it was already said, the pseudorotation consists in the interchanging of position among the atoms without a change in the nuclear angular momentum. As a visual example one can see the difference between snapshots e and f in Figure 1. At the beginning, snapshot e, the central atom appears to be the labeled 1, and in the following snapshot the central atom is the one labeled 3. Hence, the direction of the dipole moment has changed, and the system has not really rotated. In the three panels of Figure 3 one can observe the pseudorotation looking at the variation of the angles between 0 and  $60^\circ$  which are due to the pseudorotation. Note that the period of the pseudorotation depends on the temperature. The other movement, the crossover, which is coupled to the pseudorotation, consists in the movement of the central atom through the middle line going to the linear configuration and emerging to the other side, changing the direction of the dipole moment to the opposite side. In Figure 1, it is easy to see the



**Figure 3.** Angles along the time in the dynamics of  $\text{Na}_3$  cluster at different temperatures: (a) 100 K; (b) 200 K; (c) 300 K.

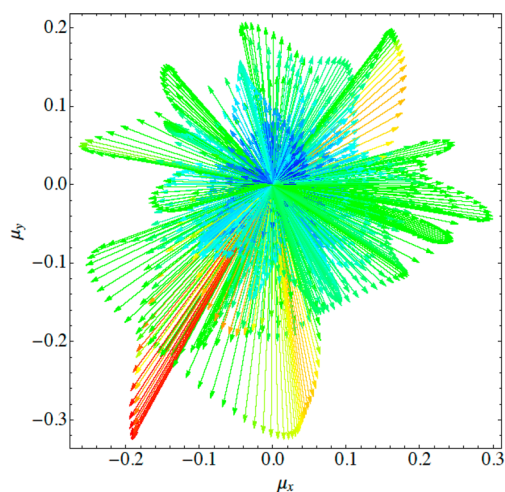


**Figure 4.** Square distance along the time in the dynamics of  $\text{Na}_3$  cluster at different temperatures: (a) 20 K; (b) 300 K.

phenomenon following the movement from snapshot a to snapshot e. It is this movement which explains that in Figure 2 all the atoms, in certain moment, go through the center of the system. In Figure 3, every time one angle is of 180 deg, it means the crossover is occurring. Note that it is perfectly possible to have pseudorotation without crossover. However, in the systems studied here, it is the combination of both movements which, in average, makes the dipole moment negligible. To graphic the point, Figure 5 shows the dipole moment vector at each step of the simulation. One can see that the dipole moment is rotating and very probably, in the time of an experimental measurement, the average is negligible. In Table 3, we show the results for the average of the dipole moment. One can see that the average of the components of the dipole moment is negligible in agreement with the experimental measurements. However, the average of the absolute value of the dipole moment vector is not zero. Their values are

approximately one-half of the values presented in Table 1 for the nonlinear isomers. A reasonable results because in the dynamics the systems are fluctuating with similar probability between the triangular isomers and the linear ones.

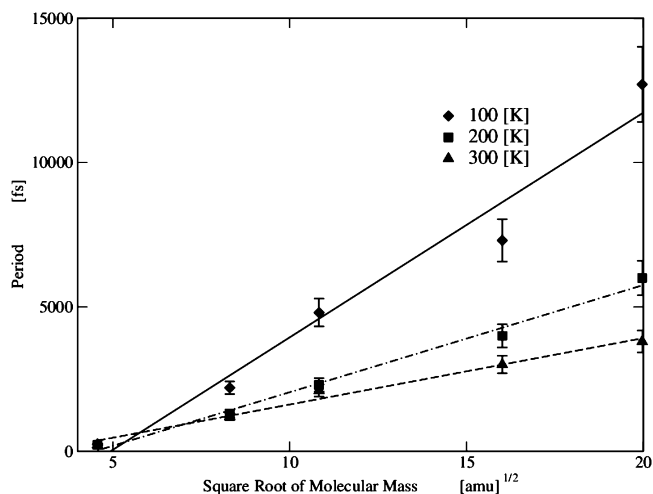
Until now, we have only presented results for  $\text{Na}_3$  because for the other members of the homonuclear alkali trimer series they are qualitatively similar. Only that, as expected, at the same energy, the movement is slower for the heavier members of the series. This is clear in Figure 6, where we show the period of movement for all the members of the series at the different temperatures versus the square root of the molecular mass. The period is defined as the lapse of time between a crossover or two consecutive pseudorotations. The heavier the element is the longer the period of movement. The dependence with the temperature is also very reasonable. The smaller the temperature is the longer the period. It is also interesting to note that the relationship is in a very good approximation a straight line



**Figure 5.** Dipole moment vectors every four steps in 8 ps dynamics of  $\text{Na}_3$  cluster at 300 K.

**Table 3.** Mean Dipole Moment Components  $\langle \mu_x \rangle$ ,  $\langle \mu_y \rangle$  and Module  $\langle |\mu| \rangle$ , in a Time Period of 16 ps at 100 K

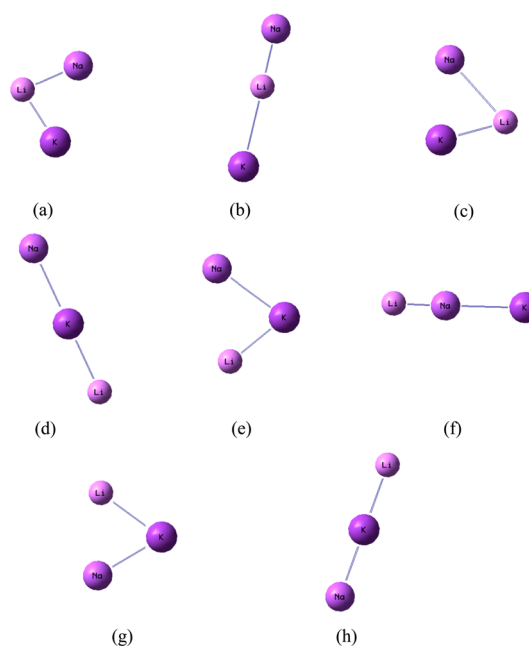
cluster	$\langle \mu_x \rangle$ [D]	$\langle \mu_y \rangle$ [D]	$\langle  \mu  \rangle$ [D]
$\text{Li}_3$	-0.01	0.01	0.19
$\text{Na}_3$	0.00	-0.02	0.21
$\text{K}_3$	0.02	-0.05	0.25
$\text{Rb}_3$	0.02	0.02	0.23
$\text{Cs}_3$	0.01	0.01	0.19



**Figure 6.** Period time at three different temperatures for all the clusters of the family  $M_3$  ( $M = \text{Li}-\text{Cs}$ ) versus the square root of the molecular mass.

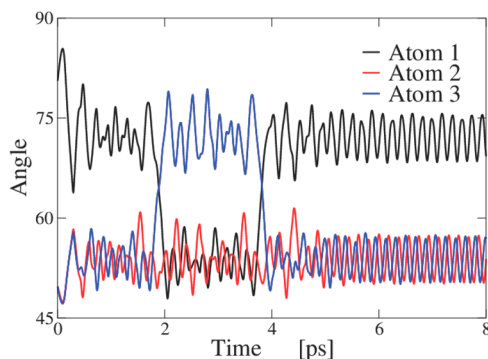
as it should be for a harmonic behavior. The regression coefficients are in all cases near to one. The greatest deviation is presented for one of the heaviest systems,  $\text{Rb}_3$ , at the lowest temperature.

In general, the phenomena of pseudorotation and crossover are not due to the symmetry of the systems. The pseudorotation is a quantum phenomenon due to the existence of a conical intersection and should be observable even at very low temperatures. The crossover is a dynamic phenomenon which depends on the temperature and should disappear at very low temperatures. To illustrate the point, Figure 7 shows some snapshots of one dynamic for the heteronuclear system



**Figure 7.** Snapshots in  $\text{LiNaK}$  molecular dynamics at 300 K (time step between consecutives images is 500 fs).

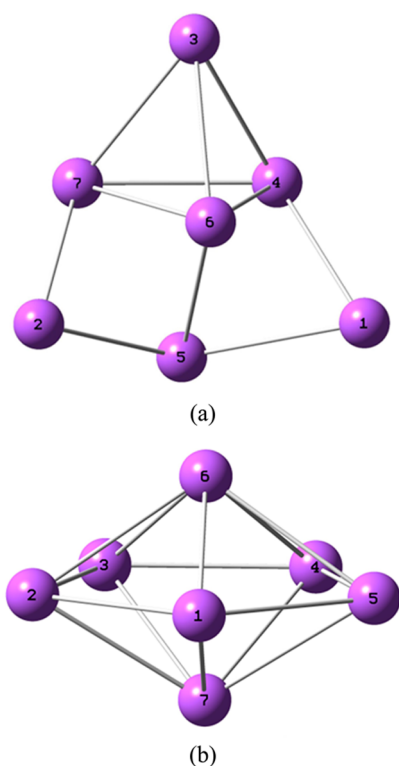
$\text{LiNaK}$ . Although this cluster has not symmetry, pseudorotation and crossover are observed. Likewise, a symmetric cluster like  $\text{Li}_3$  undergoes pseudorotation at temperatures as low as 20 K but does not undergo crossover (see Figure 8).



**Figure 8.** Angles of  $\text{Li}_3$  cluster at very low temperature, 20 K.

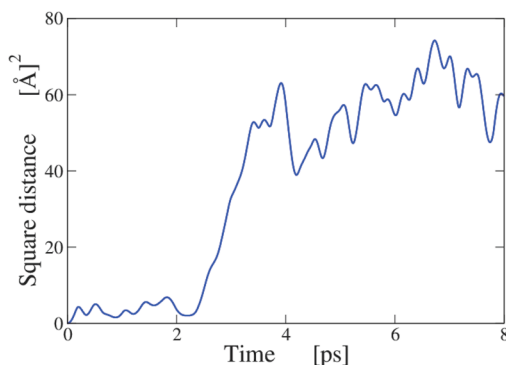
The dynamics are very similar for the other alkali metal trimers. Pseudorotation, when present, can explain by itself the close-to-zero average (with respect to the laboratory framework) dipole moment at low temperatures.

For bigger clusters the dynamics are more intricate but qualitatively they are similar to the ones of the trimers. The  $\text{Na}_7$  cluster has two low-lying isomers, one with  $D_{5h}$  symmetry and other with  $C_{3v}$  symmetry as shown in Figure 9. The later was found by Calaminici<sup>16</sup> using ab initio molecular dynamics similar to the ones used in this work. In this case, starting from the  $D_{5h}$  cluster, the dynamics also show both phenomena pseudorotation and crossover. However, its visualization it is complicated because the plane formed by the five atoms in the initial  $D_{5h}$  configuration is not conserved when coming back to the same original configuration. This is because the entire cluster must conserve the classical angular momentum. Hence, every time one of the axial atom changes position with one of the equatorial ones, all other atoms should move in such way



**Figure 9.** Two low lying isomers of the  $\text{Na}_7$  cluster: (a)  $D_{5h}$  symmetry; (b)  $C_{3v}$  symmetry.

that the angular momentum is conserved. In Figure 10, the square distance deviation of one dynamic at a kinetic energy of



**Figure 10.** Square distance along the time in the dynamic of  $\text{Na}_7$  cluster at 300 K.

300 K is shown. One sees that there are very clear picks which correspond at the moment of the crossover. Figure 11 shows the trajectories followed by each of the equatorial atoms projected on the plane they were at the initial time. It is clear to see the crossover among them. In this case, however, it is more difficult to separate both phenomena, but they again evidence why the average measured dipole should be negligible.

#### IV. CONCLUSIONS

In this work, the dynamics of the homo- and heteronuclear trimers of the alkaline metal atoms have been studied at an *ab initio* level. A bigger cluster,  $\text{Na}_7$ , has also been studied. The movement has been separated in two coupled phenomena, pseudorotation and crossover. Both depend on the temperature



**Figure 11.** Trajectories followed for every atom in the  $\text{Na}_7$  cluster projected on the equatorial plane in a period of 8 ps at 300 K.

and on the mass of the system. For the homonuclear trimers the periodic movement is in a good approximation harmonic. It has been shown by direct calculation of the time average of the dipole moment that both phenomena could explain the differences between the experimental measurements of this quantity and the static theoretical calculations. Other dynamic simulations in the bigger cluster,  $\text{Na}_7$ , yield the same conclusion. Hence, it is possible that the dynamic of the alkali metal clusters is the responsible for the negligible measured dipole moment.

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##### Notes

The authors declare no competing financial interest.

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