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Ab initio molecular dynamics of pseudorotating Li_5

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Abstract

The geometry of the Li_5 cluster has been optimized at the generalized valence bond (GVB) and complete active space self-consistent field (CASSCF) levels of theory utilizing ab initio molecular dynamics (AIMD) simulated annealing. The cluster is found to have a planar structure and pseudorotates on a time scale of picoseconds or faster at temperatures as low as 77 K. It is therefore quite likely that the pseudorotating Li_5 cluster observed in prior EPR experiments at 77 K is planar, though it was originally suggested to be a trigonal bipyramid. Vibrational frequencies have also been calculated for the optimized structure and for the pseudorotation transition state. © 1997 Elsevier Science B.V.

1. Introduction

The structures of metallic clusters are currently not well understood. Their geometries are often difficult or impossible to determine experimentally. Theoretical methods have been limited by the expense of sufficiently accurate calculations, and with traditional geometry optimization methods have been able to find only the local minima which are near initial guesses. While this approach works well for systems such as organic molecules for which ‘chemical intuition’ is a good starting point, it does not work nearly so well for the unique structures found in clusters. Compounding this problem, if the correct geometry of a cluster has relatively low symmetry, it may be overlooked easily; most researchers have restricted their searches to relatively high-symmetry geometries in order to reduce the problem to a tractable size and thus have searched only a limited subset of all possible geometries. Experimental methods, on the other hand, have recently been able to provide

some data on clusters but cannot probe their geometries directly. Experimental determination of cluster geometry has relied on the comparison of geometry-dependent properties such as vibrational and electronic spectra to theoretical values [1–3].

There has been some dispute recently over the ground structure of Li_5 . Most theoretical calculations show the C_{2v} planar ‘W’ structure to be the lowest in energy, with a C_{2v} distorted trigonal bipyramid slightly higher [4–6]; Boustani et al. find that the energy difference is 0.34 eV at the Hartree–Fock level of theory but is only 0.17 eV when computed using multireference doubles configuration interaction (MRD-CI) [5]. In 1993, Howard et al. [7] claimed the first experimental observation of the Li_5 cluster, which they formed in an adamantane matrix and identified via electron paramagnetic resonance (EPR) spectroscopy. All atoms in the cluster were found to be magnetically equivalent at temperatures as low as 77 K (the lowest temperature achieved in the study), and the structure was inferred to be a pseudorotating

trigonal bipyramid; the authors assert that planar Li_5 should have a high energy barrier to pseudorotation. Kawai et al. [8] investigated the Li_5 cluster using density functional theory in the local density approximation. Contrary to previous theory, they predicted that a distorted trigonal bipyramid was slightly lower in energy than the planar structure. However, they found a lower pseudorotation barrier for the planar structure (0.18 eV) than for the trigonal bipyramid (0.33 eV), indicating that pseudorotation should be easier in the planar structure. This, coupled with the finding that the isotropic spin population of the planar cluster is more consistent with that found in the EPR experiment led them to suggest that Li_5 may pseudorotate via the planar structure. We provide explicit evidence for such pseudorotation dynamics in this work.

We present a study of the structure of Li_5 with *ab initio* molecular dynamics (AIMD) simulated annealing utilizing the generalized valence bond (GVB) [9] and complete active space self-consistent field (CASSCF) [10] methods. After the structure was obtained, further AIMD simulations at constant temperature were performed to assess the ease with which pseudorotation may take place in a classical treatment of the nuclei. The transition state along the pseudorotation pathway was also optimized. Finally, we present computed vibrational frequencies for our structures.

2. Methods

The details of our GVB–AIMD method have been published previously [11,12]. In this work, we have solved for the electronic wavefunction at every time step, ensuring that the system remains on the Born–Oppenheimer potential energy surface. The CASSCF–AIMD algorithm is virtually identical, differing only in the calculation of the electronic wavefunction and related parameters. We treat the nuclei with classical molecular dynamics, using forces obtained by taking the analytic gradient of the energy and integrating the equations of motion numerically. For both the GVB and CASSCF simulations, we use an effective core potential with a valence double zeta basis set [13] and thus treat only the five valence electrons explicitly. In the GVB wavefunction, we

place four of those electrons in two GVB pairs (each described by two natural orbitals and perfect singlet pairing) [9] and the fifth goes into a singly-occupied orbital; the CASSCF wavefunction includes all doublet-state configurations of the five valence electrons in five orbitals. The GVB wavefunction thus contains a subset of the configurations present in the CASSCF wavefunction. The CASSCF calculations are done using the HONDO package [14], while the GVB perfect pairing calculations are performed using the Caltech suite of codes [15]. Vibrational frequencies are calculated by numerically differentiating the energy gradient to obtain the Hessian (second derivatives of the energy) matrix, which is diagonalized to obtain the frequencies. The transition state was found by local optimization of the C_{2v} structure within HONDO.

The simulated annealing approach [16] is a general method for finding the global minimum of a function. In simulated annealing, we start with a hot system and slowly cool it. The initial high temperature allows the system to overcome kinetic barriers which might otherwise prevent it from finding the global minimum, and the cooling, if done sufficiently slowly, ensures that the system eventually settles down into that minimum. Since simulated annealing is best thought of in terms of temperature, we perform our AIMD simulated annealing in the canonical ensemble instead of the microcanonical ensemble, using an adaptation of the Nosé–Hoover chain thermostat [17,18].

3. Results

Several simulations were performed at both the GVB and CASSCF levels of theory. Initial geometries were chosen randomly. An initial temperature of 1000 K was used, and the system was cooled by multiplying the temperature by a factor of 0.9 every 240 fs. A typical length for this cooling trajectory was 2.4 ps. After the system had settled down into a single minimum, the geometry was then refined with a traditional steepest descent optimization. In all cases, the final geometry was the planar ‘W’ structure shown in Fig. 1. Additional simulations were performed from initial geometries near the trigonal bipyramid found by other workers but all quickly

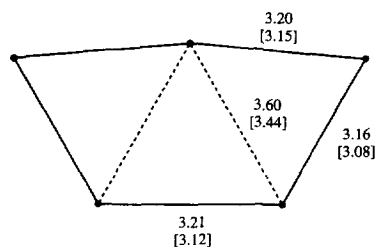


Fig. 1. Optimized geometry for the Li_5 cluster. Interatomic distances shown were calculated using the GVB wavefunction and the CASSCF wavefunction; the former is shown in brackets. All distances are given in Å.

converted to the planar structure. Traditional optimization of the trigonal bipyramid with a CASSCF wavefunction resulted in the structure shown in Fig. 2; its energy is 0.51 eV higher than that of the planar structure.

From the optimum planar geometry, new velocities were sampled from a 500 K temperature distribution. Using these new velocities, additional constant temperature simulations were performed using the CASSCF wavefunction, cooling by a factor of approximately 0.8 every 2.4 ps. Note that we use constant temperature dynamics where the system is connected to a heat bath in order to mimic properly the EPR experiments performed in a low (constant) temperature matrix. Pseudorotation was observable on a sub-picosecond timescale down to 113 K, and one pseudorotation event occurred during the 2.4 ps spent at the final temperature of 94 K. In Fig. 3(a) we show two distances between pairs of lithium atoms over the final 5 ps; each crossing of the curves represents a pseudorotation event. In Fig. 3(b), we show the distances between two pairs of lithium atoms in another constant temperature CASSCF–AIMD trajectory started from the optimized geometry at the actual EPR experimental temperature of 77 K. Over the 12 ps of simulation time, these curves cross three times, indicating three pseudorotation events.

Fig. 4(a) shows how these interatomic distances behave during pseudorotation in the context of the cluster as a whole. Similar trajectories obtained using the GVB wavefunction show much less pseudorotation, implying a significantly higher energy barrier. This increased barrier is not surprising and is almost certainly an artifact of the explicit pairing of elec-

trons in the GVB wavefunction, in which each electron may be thought of as occupying an interstitial one-electron orbital lying on an outer edge of the cluster [6,19], with singlet coupling of the two pairs of orbitals which adjoin the two acute angles. Since the identity of one of these acute angles changes upon each pseudorotation event (e.g., in Fig. 3(b), the angle centered on atom 5 is acute on the left while the angle centered on atom 4 is acute on the right), the singlet coupling must also change discontinuously at some point, resulting in a cusp in the potential energy surface at that point.

Fig. 4(b) shows the transition state structure along the pseudorotation pathway of the Li_5 cluster at the CASSCF level of theory. This geometry could not be optimized at the GVB level of theory due to its broken symmetry; taking the CASSCF structure with a GVB wavefunction, we obtain an estimated (upper bound) pseudorotation barrier of 0.14 eV at the GVB level. The overall bonding in the structure appears to be the same in this structure and in the minimum, as indicated by the very similar bond lengths and energies; this structure is found to be only 0.04 eV higher in energy at the CASSCF level than the minimum energy structure, much lower than the 0.18 eV barrier found using density-functional theory [8]. We may best understand the existence of this energy difference in the GVB formalism; note that there is but one acute angle in this structure, whereas the minimum energy structure has two, and it is across those two acute angles that electrons singlet-pair and thus are statically correlated in the GVB wavefunc-

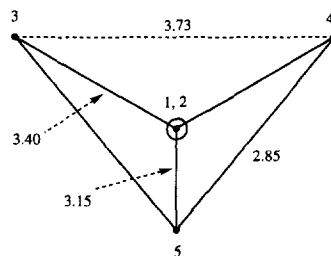


Fig. 2. Trigonal bipyramid local minimum structure for the Li_5 cluster. Atoms 1 and 2 are above and below the plane of the paper, respectively; they are represented by the dot inside a circle in the center of the diagram. Interatomic distances shown were calculated using the CASSCF wavefunction and are given in Å. The structure is C_{2v} instead of D_{3h} (in agreement with previous work) due to a Jahn–Teller distortion.

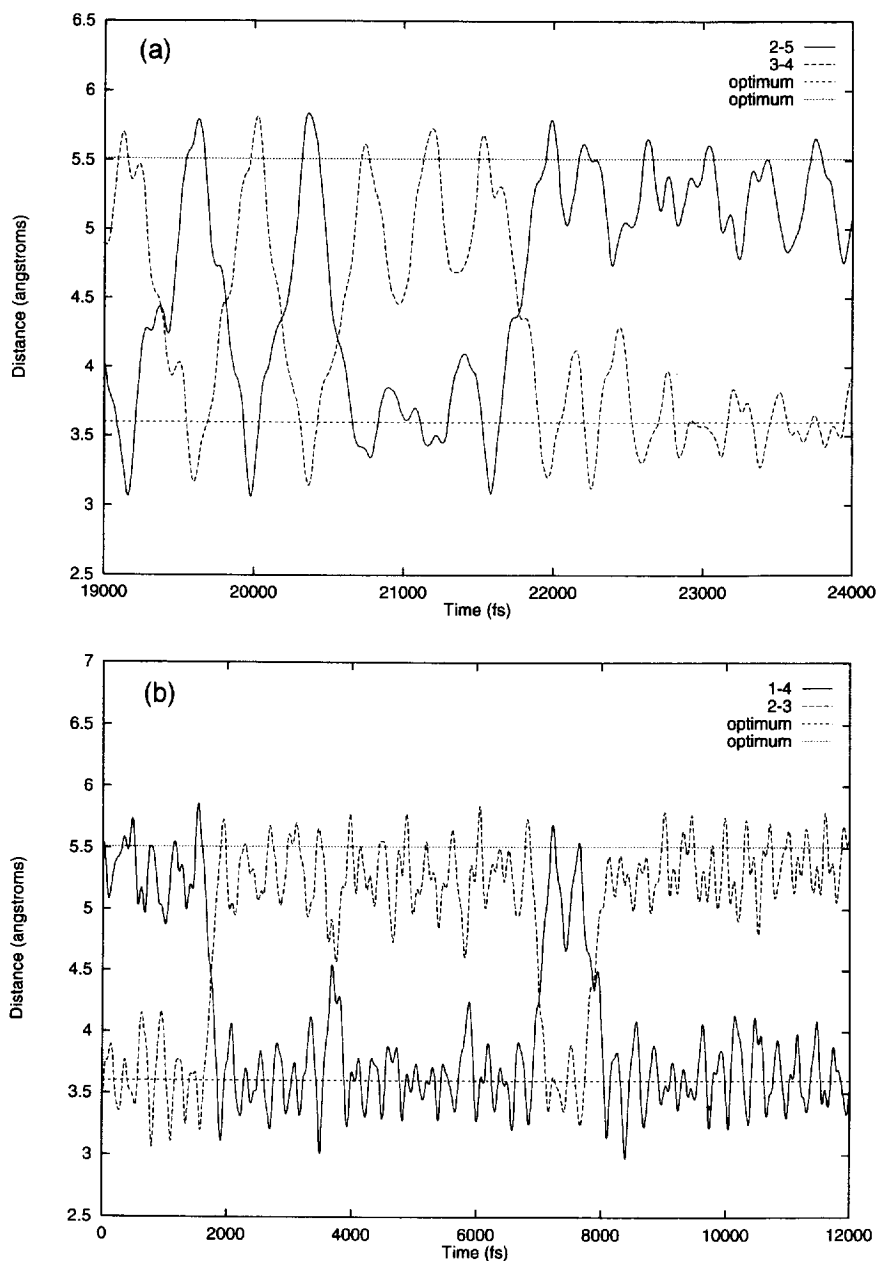


Fig. 3. (a) Interatomic distances for two pairs of atoms in the final 5 ps of a CASSCF-AIMD trajectory. The curves labeled '2-5' and '3-4' correspond to the distances between atoms 2 and 5 and atoms 3 and 4, respectively, as indicated in Fig. 4(a); the two horizontal lines labeled 'optimum' are the values of these distances in the optimized geometry. At 19.2 ps the temperature is reduced to 113 K, and at 21.6 ps the temperature becomes 94 K. The curves cross several times in the 2.4 ps spent at a temperature of 113 K, and once at a temperature of 94 K; each crossing denotes one pseudorotation event. (b) Interatomic distances for two pairs of atoms in a 12 ps CASSCF-AIMD trajectory, labeled as in Fig. 3(a). The temperature is held at 77 K for the duration of the trajectory. Again, each crossing denotes one pseudorotation event.

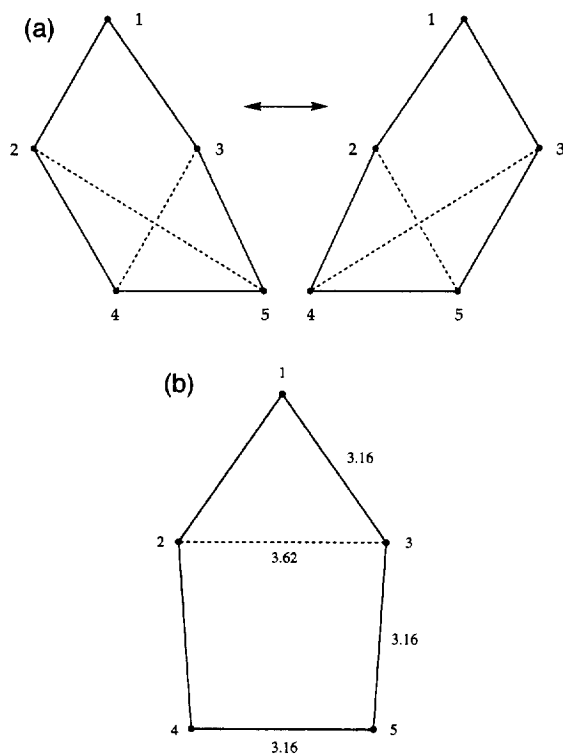


Fig. 4. (a) One pseudorotation event in the Li_5 cluster. The two dotted lines denote the distances plotted in Fig. 3(a); note that the 2–5 distance is longer on the left, while the 3–4 distance is longer on the right. (b) Transition state geometry for pseudorotation of the Li_5 cluster. Interatomic distances are given in Å.

tion. Increasing the angle to be slightly obtuse reduces the energy-lowering effect of this electron correlation, essentially increasing the total energy by partially breaking a 'bond'.

Vibrational frequencies were also calculated with the GVB and CASSCF wavefunctions for the optimum structure. The frequencies for this structure are summarized in Table 1. These computed frequencies are expected to be in general lower than the true frequencies, as the GVB and CASSCF electronic wavefunctions dissociate correctly (unlike the Hartree–Fock wavefunction, which dissociates to a limit which has 50% ionic character) but are bound less strongly than the true system due to incomplete treatment of electron correlation. This underestimation of the bond strength leads to a shallower potential well and thus to lower vibrational frequencies. It is worth noting that this line of reasoning does not

Table 1
Calculated vibrational parameters for Li_5 (planar)

Irreducible representation	Vibrational frequency (cm^{-1})	
	GVB	CASSCF
B_1	87	51
A_2	89	45
B_2^a	139	120
A_1	143	129
A_1	167	174
A_1	222	226
B_2	232	238
A_1	294	289
B_2	303	310

^a Mode corresponding to pseudorotation pathway.

necessarily apply to the frequency associated with the normal mode corresponding to the pseudorotation pathway at the GVB level of theory (the 139 cm^{-1} B_2 mode) due to the cusp in the potential energy surface discussed above; that frequency will likely not be underestimated by as much as the other frequencies, and may in fact be overestimated at the GVB level of theory. We see from Table 1 that the CASSCF level of theory does in fact predict a lower frequency for this mode, but by only 14%; greater discrepancies are found only in the out-of-plane bending modes, which have the two lowest frequencies. It is also worth noting that these are harmonic frequencies, and the relatively large anharmonicity along the pseudorotation pathway will likely cause the frequency which will be observed experimentally to be significantly lower.

In order to assess the accuracy of the CASSCF calculations compared to earlier MRDCI calculations

Table 2
Calculated vibrational parameters for Li_5 (transition state)

Irreducible representation	Vibrational frequency (cm^{-1}) CASSCF
B_2	79i
A_2	13
B_1	48
A_1	140
B_2	193
A_1	217
A_1	256
B_2	281
A_1	315

[5], the energies of the minima and the pseudorotation transition state were also computed using a multi-reference singles and doubles CI (MRSDCI) wavefunction, in which we include all single and double excitations from the CASSCF reference in the CI vector. The planar minimum remains lower in energy than the trigonal bipyramid, but now only by 0.07 eV, much less than the CASSCF value of 0.51 eV, suggesting that the trigonal bipyramidal structure might also be accessible. The barrier height for pseudorotation of the planar structure increases to 0.08 eV. Though this is double the CASSCF barrier height, it is still quite small and should not affect the observation of pseudorotation.

Since the trigonal bipyramidal structure at the MRSDCI level appears competitive with the planar structure, we also calculated its barrier to pseudorotation. At the CASSCF and MRSDCI levels, we find barriers of 0.57 eV and 0.72 eV, respectively. The transition state we find has a C_{2v} rectangular pyramidal structure, with base side lengths of 2.81 and 5.67 Å, and a base atom to apex distance of 3.60 Å. This is a Jahn–Teller stabilized distortion of the C_{4v} square pyramidal transition state suggested by Kawai [8]. As discussed below, the large barrier precludes any role for the trigonal bipyramid in pseudorotation.

Vibrational frequencies were also calculated at the CASSCF level of theory for the transition state. These frequencies are presented in Table 2. We note that except for the B_2 pseudorotation mode (which now has an imaginary frequency) and the A_2 out-of-plane bending mode, there are no dramatic changes.

4. Summary and conclusions

The geometry of the Li_5 cluster has been studied using ab initio molecular dynamics simulated annealing with GVB and CASSCF electronic wavefunctions. The optimum geometry for both wavefunctions is found to be a planar ‘W’ shape which is not remarkably different from that found previously. The previously described trigonal bipyramid geometry was not produced by any of the simulated annealing trajectories, and using traditional optimization methods was found to be 0.51 eV higher in energy than the planar structure at the CASSCF level of theory

and 0.07 eV higher with MRSDCI from the CASSCF reference. The MRSDCI barriers for pseudorotation for the planar and trigonal bipyramidal structures were found to be 0.08 eV and 0.72 eV, respectively, indicating that pseudorotation is only occurring through the planar structure, consistent with our CASSCF dynamics.

The pseudorotation dynamics of the Li_5 cluster were observed using constant temperature CASSCF–AIMD at a variety of temperatures. Pseudorotation was observed on a sub-picosecond time scale at temperatures as low as 113 K, and on a slightly longer (most probably order 1–10 ps) time scale at 94 K and at 77 K, the lowest temperature studied. We point out that this is a classical simulation of the nuclei and thus includes no tunneling effects. The pseudorotation barrier is sufficiently low – 0.04 eV – in these CASSCF–AIMD simulations that it is not necessary to invoke tunneling to explain the experimental findings; the pseudorotation process occurs classically on a much faster time scale than the time scale on which the EPR experiments are performed ($\tau_{EPR} \approx 10^{-8}$ s). Though these trajectories are, due to the effects of the thermostat, not ‘true’ trajectories in the sense that the isolated cluster could follow them, the experiments to which we compare were performed in a matrix; we therefore believe that the constant temperature dynamics (with its associated heat bath) are a better simulation of the system studied in the experiments than can be obtained with constant energy dynamics.

Finally, vibrational frequencies were calculated at both the GVB and CASSCF levels of theory for the optimized structure, and at the CASSCF level of theory only for the pseudorotation transition state. In general, we expect that these frequencies will be lower than the true vibrational frequencies, with the likely exception of the mode corresponding to the pseudorotation pathway. It is our hope that these values may soon be compared to a matrix-isolation vibrational spectrum of Li_5 .

In summary, we have shown via AIMD that low temperature pseudorotation of the five Li atoms in the Li_5 cluster occurs readily in the planar ‘W’ structure, which we find to be the global minimum energy structure on the GVB, CASSCF, and MRSDCI potential energy surfaces. Given the relatively small energy difference at the MRSDCI level of

theory, however, it is quite possible that the trigonal bipyramid is energetically accessible even if it is not the global potential energy minimum. However, the large predicted barrier to pseudorotation in the trigonal bipyramid suggests that either the trigonal bipyramid is not formed or that conversion of the trigonal bipyramid to the planar structure is facile. In either case, we suggest that it is not necessary to invoke a trigonal bipyramidal structure in order to explain the EPR finding of the magnetic equivalence of all 5 Li atoms.

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