# Internal Vibrations of the Li(NH$_3$)$_4$$^+$ Complex Analyzed from Ab Initio, Density Functional Theory, And the Classical Spring Network Model

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We report our theoretical findings regarding internal vibrations of the Li(NH$_3$)$_4$$^+$ complex which have been studied using three different methods, namely, a classical spring network model, density functional theory, and ab initio Hartree−Fock plus Møller−Plesset correlation energy correction truncated at second-order. The equilibrium Li···N and N···N distances are found to be 2.12 and 3.47 Å, respectively, in good agreement with the experimental data. The theoretically determined vibrational frequencies of the lowest modes are in good agreement with those extracted from inelastic X-ray scattering measurements. From group theory considerations, the internal vibrations of Li(NH$_3$)$_4$$^+$ complexes resemble those of a tetrahedral object. Further experimental investigation is suggested.

## I. Introduction

Li(NH$_3$)$_4$ complexes are commonly found in Li−ammonia solutions.[1] These solutions are of great interest because they can exhibit several phases depending on the concentration of Li. On the one hand, at low Li content, the solutions can be insulating with isolated excess electrons or with spin-paired electrons.[2] On the other hand, at high Li content, the solutions become metallic liquids with remarkable physical properties such as low density, low viscosity, and low freezing point.[3] A number of experimental studies have recently been carried out regarding the structural behavior of the Li−ammonia solutions. The structure factors of the liquid metals obtained from inelastic scattering experiments demonstrate that Li and four ammonia molecules form a stable Li(NH$_3$)$_4$ complex.[3,4] The formation of this complex is found to be independent of the Li concentration. It was suggested by several previous ab initio calculations that the complex possesses tetrahedral symmetry with the Li atom located at the center of a tetrahedral complex and one NH$_3$ molecule positioned at each corner of the tetrahedron.[5,6] The energetically most favorable orientation has the four NH$_3$ molecules arranged in such a way that their dipole moments point radially away from the central Li. The accuracy of this theoretical description of the complex in terms of its symmetry and molecular configuration has been confirmed experimentally.[1,7]

In addition, the experiments provided information on the dynamical behavior. Heat capacity measurements showed that Li−ammonia systems possess a higher Debye temperature than that predicted by the Dulong−Petit law.[8] This observation suggests significant contributions from internal vibrations of the complexes. Recently, inelastic X-ray scattering (IXS) experiments have been carried out to determine collective excitations in Li−ammonia solutions with varying Li content in the metallic liquid regime.[9] This high-resolution IXS experiment was carried out for a wide range of wave numbers. Apart from the collective excitations, the experiment also detected several vibrational modes corresponding to frequencies of 9, 18, 27, and 40 meV, respectively, which are higher than those of typical acoustic phonons in liquid metals and have thus been assigned to the internal vibration modes of the complex.[9]

The aim of this work is to illustrate from a theoretical point of view that the measured frequencies correspond indeed to the internal vibration modes. Our theoretical investigations took into account that the experimental studies were carried out in the metallic phase where the complexes exist in a positively charged state, such as Li(NH$_3$)$_4$$^+$ ion cores surrounded by a nearly free electron gas. In the present work, we make the reasonable assumption that the approximately homogeneous charge background due to the free electrons has negligible effects on the intracomplex interactions studied here. This assumption can be justified from the screening of electronic/ionic interactions by the high-/low-frequency dielectric constant in metal-ammonia solutions.

## II. Computational Details

In this work, we have employed three different theoretical approaches. First, we used density functional theory (DFT)[10,11] with the Becke three-parameter hybrid functionals (B3LYP)[12] in which the nonlocal correlation is provided by the LYP expression[13] and where the VWN functional III[14] is used for local correlation, as implemented in the Gaussian03 program

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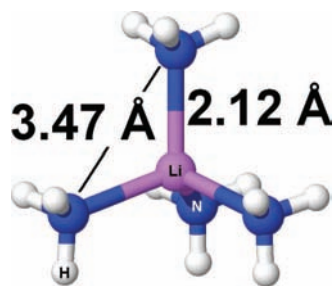# Department of Chemistry, Chulalongkorn University.

**Figure 1.** The fully relaxed molecular geometry of Li(NH$_3$)$_4^+$ as obtained from our density functional theory calculation at the B3LYP/6-311G(3df,3pd) level.

package.[15] To test the accuracy of this method in the present system, we furthermore carried out calculations using Hartree−Fock theory plus second-order Møller−Plesset perturbation theory (MP2),[16] which is implemented in Gaussian03 as well. Unconstrained relaxations of the atomic positions with respect to minimum energy and vibrational analysis at the equilibrium geometry have been carried out employing the 6-311G(3df, 3pd) basis set[17] for DFT calculations and the 6-31G(d,p) basis set[18] for the case of MP2. This treatment ensures fairly accurate interatomic interactions and includes correlation effects. Anharmonic effects were considered by performing numerical differentiation along the normal modes, as implemented in Gaussian03. Additionally, we also tested our computed frequencies against those obtained from velocity autocorrelation function analysis[19] of ab initio molecular dynamics simulations of a single Li(NH$_3$)$_4^+$ complex. In particular, we simulated a time frame of 4 picoseconds with 1-femtosecond time steps at a temperature of 300 K. The good agreement between the two very distinct approaches shows that anharmonic effects were properly treated in our study. Finally, we have applied a classical spring network model to analyze vibrations in the Li(NH$_3$)$_4^+$ complex. In the limit of small (harmonic) vibrations, this model should represent a reasonable approximation. We assume a perfect tetrahedral complex with Li$^+$ at the center and one NH$_3$ molecule at each corner. The bond lengths are taken from the DFT calculations. Li$^+$ and all four NH$_3$ units are assumed as point masses. The four springs connecting Li$^+$ and the NH$_3$ units possess a spring constant of 200 kJ mol$^{-1}$ Å$^{-2}$, while the spring constant for the NH$_3$···NH$_3$ interaction is set to 70 kJ mol$^{-1}$ Å$^{-2}$. These parameters are extracted from the work of Gurskii et al..[20] Naturally, this model is a rather simplistic portrait of the complex, neglecting any internal vibrations and twists that can occur in the NH$_3$ units. However, it is still very valuable in the sense that it allows us, in a straightforward way, to obtain useful information from a group theory viewpoint.

## III. Results and Discussion

The fully optimized structure obtained from our DFT calculations possesses tetrahedral symmetry with an equilibrium Li···N bond length of 2.12 Å and an equilibrium N···N distance of 3.47 Å (Figure 1), in good agreement with 2.06 (Li···N) and 3.49 Å (N···N), respectively, obtained from inelastic neutron scattering (INS) experiments.[1] The dipole moment of all four NH$_3$ molecules points radially away from the central Li ion. The bond lengths and distances obtained at the MP2 level of theory are 2.13 (Li···N) and 3.48 Å (N···N) and thus differ only by 0.01 Å from the DFT results.

At the equilibrium geometry, we proceeded to calculate the vibrational eigenfrequencies and corresponding eigenvectors from DFT and from ab initio, as well as from our classical spring
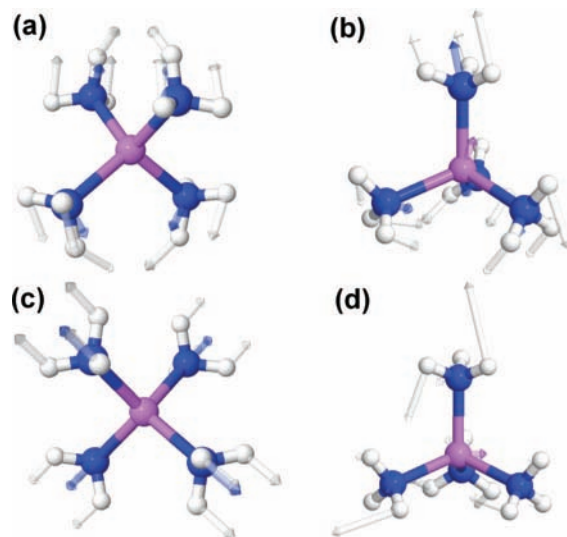


**Figure 2.** The eigenvectors as determined from ab initio and DFT for the four lowest energy modes listed in Table 1 are indicated by arrows. For the calculated DFT frequencies, the modes correspond to (a) 11, (b) 16, (c) 27, and (d) 40 meV.

**TABLE 1: The Vibrational Eigenfrequencies for the Four Lowest Modes in Units of meV from the IXS Experiment,[9] our DFT Study, Ab Initio MP2 Calculation, And the Classical Spring Network Model**

| IXS | DFT | MP2 | spring model |
|-----|-----|-----|--------------|
| 9 | 11 | 9 | 13 (E) |
| 18 | 16 | 14 | 17 (T$_2$) |
| 27 | 27 | 29 | 34 (A$_1$) |
| 40 | 40 | 43 | 47 (T$_2$) |

network model. The eigenfrequencies from the experiments and our various theoretical approaches are compared in Table 1, and the corresponding eigenvectors are displayed in Figure 2 (animations of the vibrational modes are available through the Supporting Information).

We note that there is generally good agreement between our theoretically determined vibrational frequencies and those measured experimentally. Furthermore, the relatively small difference between DFT and MP2 leads us to the conclusion that both approaches are equally successful here to properly describe the eigenmodes of the Li(NH$_3$)$_4^+$ complex.[21] In the following discussion, we therefore generally refer to the modes by their respective frequency in parentheses, citing the DFT results only.

The modes with the lowest frequency (11 meV) possess only pure angular vibrations (see Figure 2a) and are doubly degenerate. The modes illustrated in Figure 2b and d have different combinations of radial and angular vibrations and thus have distinguishable frequencies (16 and 40 meV, respectively). Both frequencies are in fact three-fold degenerate. Figure 2b shows only one eigenvector out of the three, analogous to Figure 2d. Finally, the mode displayed in Figure 2c contains only a pure radial vibration and is therefore nondegenerate (27 meV). The results in terms of frequencies are in good agreement with the experimental data[9] (Table 1). For the three-fold degenerate modes (16 and 40 meV), we observe from the ab initio and DFT calculations significant deformations of the NH$_3$ units in the form of internal vibrations and twisting. This is in contrast to the doubly degenerate (11 meV) and nondegenerate modes (27 meV) for which the NH$_3$ units essentially move as a rigid body. We have also identified four lower frequencies in our ab

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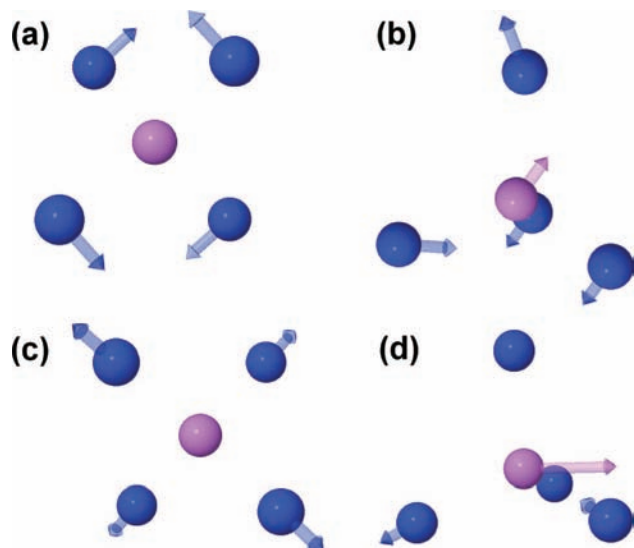


**Figure 3.** The eigenvectors as determined from the spring model for the four lowest energy modes listed in Table 1 are indicated by arrows. For the calculated spring model frequencies, the modes correspond to (a) 13, (b) 17, (c) 34, and (d) 47 meV.

initio calculations. Upon closer inspection, we found that the corresponding modes actually represent hindered rotations of the three hydrogen atoms of one $NH_3$ unit around the axis formed by the Li⋯N bond.

In order to gain further insight into the origin of the internal vibrational modes, we have also applied a spring network model for representing a $Li(NH_3)_4^+$ ion core. From symmetry considerations, we can deduce that there exist nine possible normal modes in the tetrahedral complex with the eigenvectors belonging to $A_1$, E, and two $T_2$ symmetry species.[22] The mode with $A_1$ symmetry is a totally symmetric mode, which allows only for pure radial vibration, as depicted in Figure 3c. The modes associated with the E irreducible representation are doubly degenerate and have only the pure angular vibrations; see Figure 3a. The modes associated with the $T_2$ irreducible representations are three-fold degenerate and have the combinations of radial and angular vibrations. For a tetrahedral object, there are two $T_2$ species, as shown in Figure 3b and d. Furthermore, group theory also indicates that all modes are Raman-active, but only the $T_2$ modes are also infrared active.[22] Thus, full investigation using Raman and infrared measurements can determine the correspondence between the modes and their symmetry classes. To the authors' knowledge, none of these experiments have yet been reported for the $Li(NH_3)_4$ complexes.

Next, we explicitly calculated the eigenfrequencies from the spring model by constructing the dynamical matrix and solving the corresponding secular equation for both the eigenfrequencies and the eigenvectors. The results of the eigenfrequencies are also listed in Table 1. It is remarkable that the eigenfrequencies determined from this rather simple model are in fairly good agreement with those from our ab initio and DFT calculation and hence with those from the IXS experiment.[9] The eigenvectors strongly resemble their corresponding partners in Figure 2; for example, Figure 3a resembles Figure 2a and so on. The discrepancies in terms of the frequencies can be understood if one considers that internal motion of the $NH_3$ units has been entirely neglected in the spring model, which treats them as rigid point masses, while the DFT calculations are able to take them fully into account. This finding is also consistent with another ab initio work which has previously shown that effects

due to internal motion in subunits of the complex are rather significant and nonadditive.[5]

## IV. Summary

In conclusion, we have used a simple spring model together with more sophisticated ab initio methods and density functional theory to calculate the internal vibrations of a $Li(NH_3)_4^+$ complex. The ab initio and DFT approaches both reproduce the actual complex geometry rather accurately. We find that the eigenfrequencies obtained from the DFT, ab initio, and the spring model are in good agreement with those obtained from the IXS experiment.[9] These results confirms that the vibrational modes detected by the IXS experiment do in fact correspond to the internal vibrations of the complex. From symmetry considerations, we also find that the vibration modes closely resemble those of a tetrahedral object. Further experimental studies, such as infrared measurements and Raman experiments, are suggested.

**Supporting Information Available:** Animations of the vibrational modes of the $Li(NH_3)_4^+$ complex corresponding to the four lowest frequencies, 11, 16, 27, and 40 meV, as determined by our density functional theory calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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