

Computational Analysis of the $\text{LiNH}_2\text{-Li}_2\text{NH}$ Solid Solution

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Introduction

The significant potential of hydrogen as a sustainable fuel can only be fulfilled if it is stored in a dense form [1]. Chemical methods avoid the need for extreme pressures or temperatures by reversibly bonding hydrogen to other elements. Liquid ammonia (NH_3) and solid materials such as lithium amides and imides have been considered for this purpose.

Lithium amide (LiNH_2) can be thermally decomposed to form lithium imide (Li_2NH). This process involves the synthesis of an intermediate lithium amide-imide solid solution, which can both allow the chemical storage of hydrogen and act as an ammonia decomposition catalyst [2]. There are several experimental studies on the properties of this solid solution [3, 4], but its atomic structure remains unknown. A recent paper by Makepeace and David [2] proposes using Raman spectroscopy to study the proportion of amide-imide groups present.

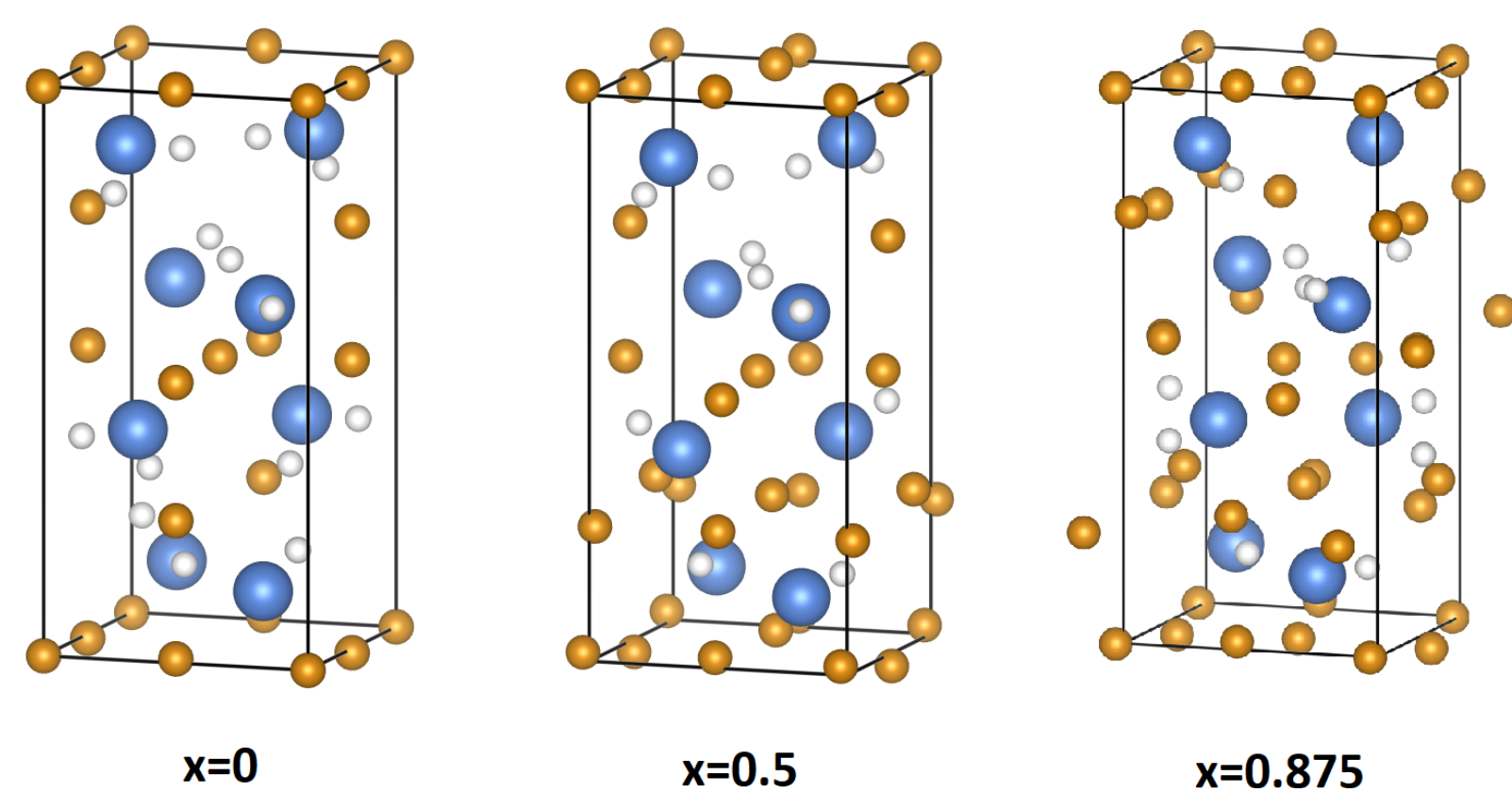
The work presented here uses computational modelling to complement experimental studies on the lithium amide-imide solid solution, with a focus on understanding its structure.

Material and Method

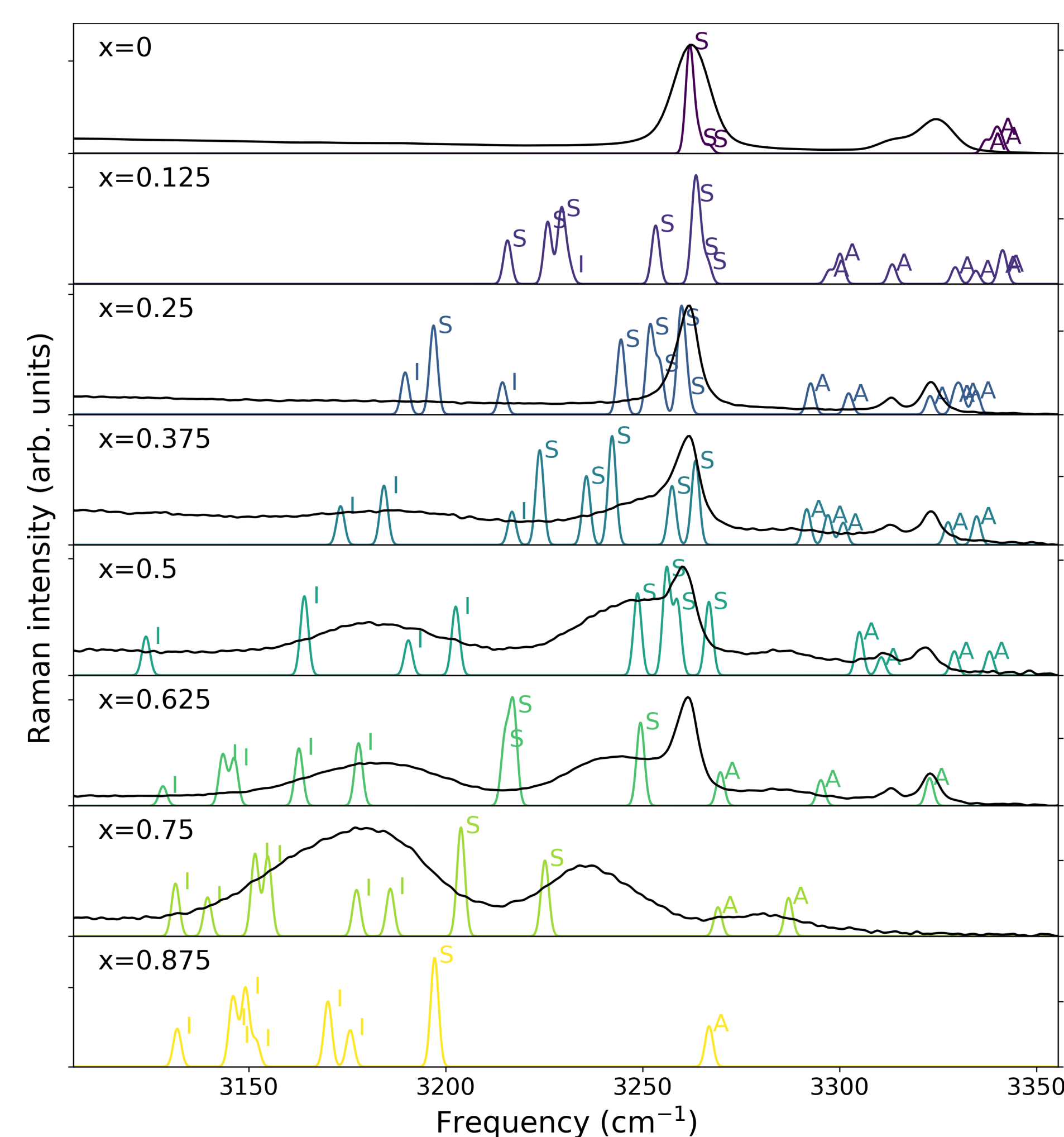
Possible structures of the lithium amide-imide solid solutions were modelled by progressively removing H atoms from the lithium amide cell and adding Li atoms, to produce cells with stoichiometries given by $\text{Li}_{1+x}\text{NH}_{2-x}$, with $0 < x < 0.875$.

First principles calculations were performed with CASTEP [5] on the different defect configurations available for each value of x . The lowest-energy configuration for each x was chosen as representative of that particular stoichiometry.

In general, we find that the lowest-energy configuration for each x value has all the defects close together: new Li atoms are placed at adjacent cubic sites, and H atoms are removed from sites close to those new Li atoms (see below).



Raman Results



The figure above compares our simulation results (colour) with experimental data (black) from Makepeace and David [2]. There is currently no experimental data for $x = 0.125$ and $x = 0.875$.

We observe three types of stretch: symmetric NH_2 stretches (S), asymmetric NH_2 stretches (A) and N-H 'imide' stretches (I). The number of I peaks increases with x , and these are concentrated at lower frequencies, as the solid solution's stoichiometry moves towards being 'imide-like'. On the other hand, S and A peaks decrease in number, but these are often grouped around the same frequencies – this is because the defects created in the solid solution are grouped together, so some regions of the solid solution remain 'amide-like' and produce peaks matching amide frequencies. Some lower-frequency S and A peaks arise from NH_2 groups that are surrounded by a mix of NH and NH_2 groups.

Overall, we see agreement between the experimental broadening of the peaks and the behaviour of the simulated peaks. Our results support the hypothesis that NH and NH_2 groups produce different Raman signals depending on whether they are in an amide-like, imide-like or non-stoichiometric local environment.

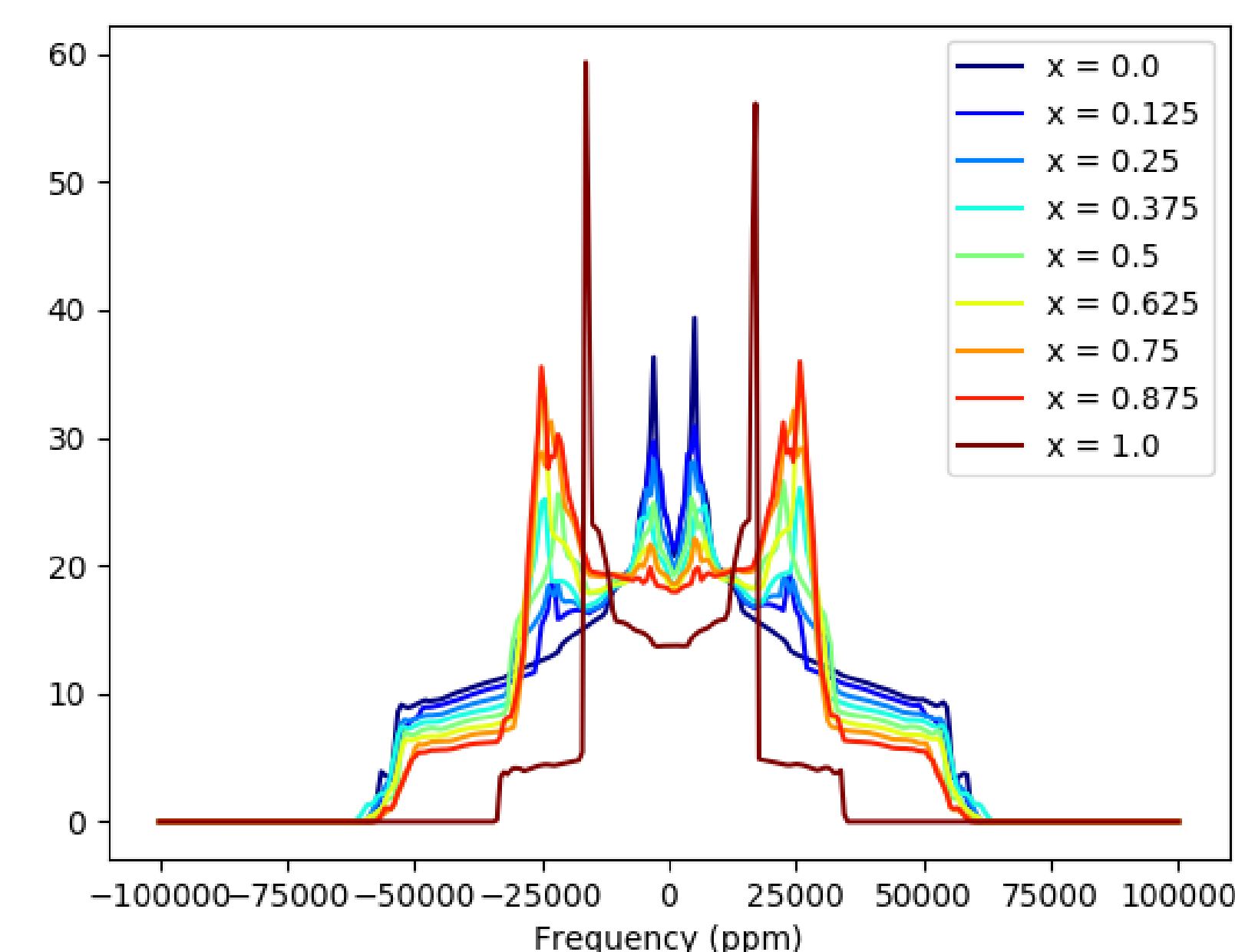
NMR Results

The two spectra below predict what the result of NMR quadrupolar (NQR) nitrogen spectra could look like for different values of x . It appears that the stoichiometry strongly influences the NMR spectrum, and thus it should be possible to use NMR spectra to determine the value of x .

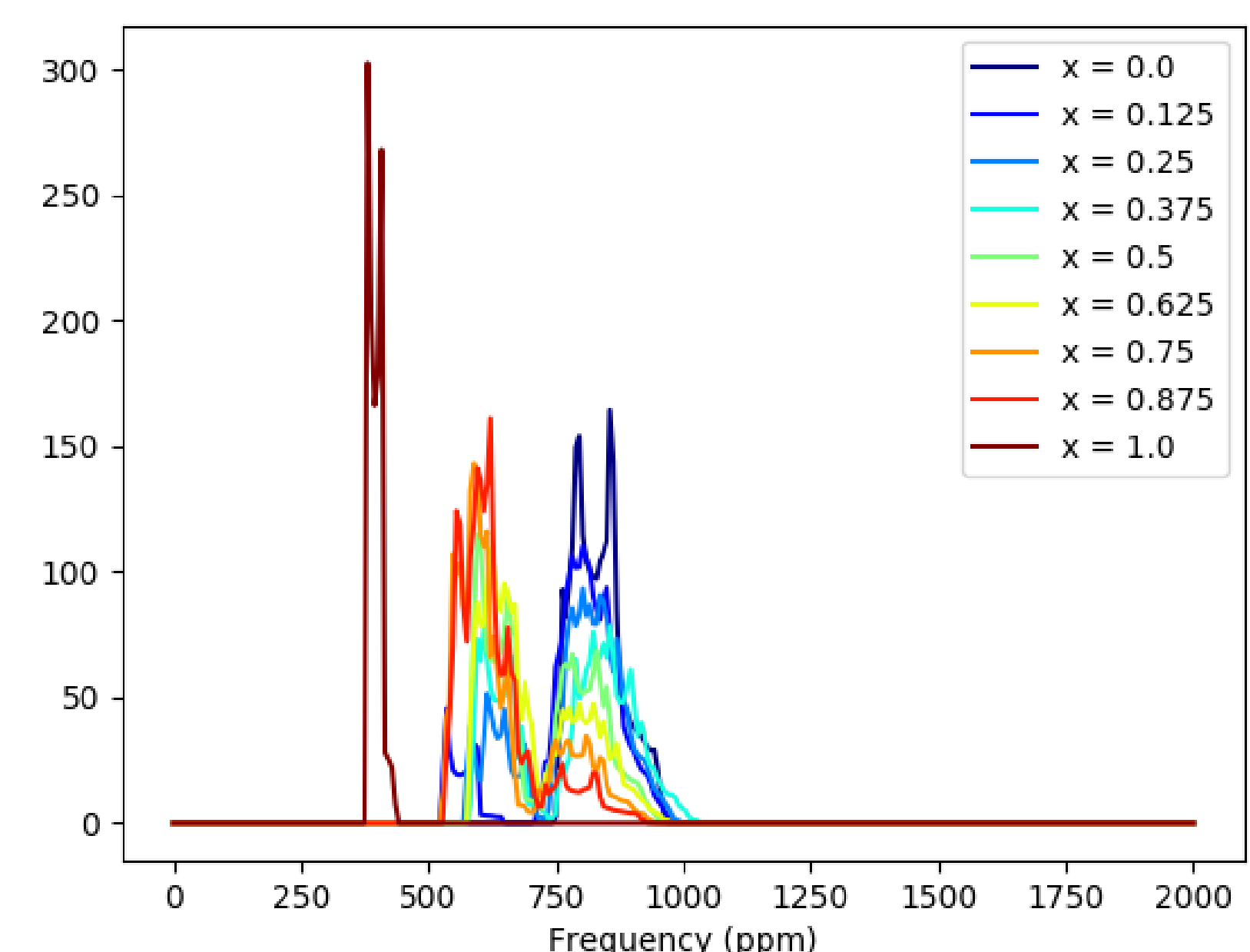
In addition, rotational dynamics should affect the width of both quadrupolar nitrogen lines and homo- and heterogeneous dipolar proton ones.

We therefore predict that static NMR should show strong differences between NH and NH_2 groups, and possibly indicate whether NH groups in non-stoichiometric samples tend to group together as predicted.

First-order NQR (static), $B \sim 10$ T



Second-order NQR (MAS), $B \sim 10$ T



Future Work

The next phase of our simulations will focus on surface behaviour. Understanding the surface behaviour of the lithium amide-imide solid solution is crucial to determining its capacity both as a hydrogen storage material and as a catalyst for ammonia decomposition.

We are currently developing a method to model surfaces of lithium amide, with an ultimate aim to extend this method to the lithium amide-imide solid solution. We hope to explore the surface behaviour of the solid solution across the whole stoichiometric range between lithium amide and lithium imide.

Conclusions

Our simulated Raman results show reasonable agreement with experimental data, and suggest that the behaviour of NH and NH_2 groups in the lithium amide-imide solid solution changes depending on their local environment. Further Raman studies of the solid solution will provide a deeper insight into the variations in behaviour of the amide and imide groups.

We also predict that NMR spectroscopy could provide significant insight into the behaviour of the NH and NH_2 groups in the solid solution. An experimental NMR study could potentially indicate if NH groups do indeed tend to cluster together, and complement the findings of this theoretical investigation.

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[1] *Energy Environ. Sci.* 5 (4 2012).

[2] *JPC C* 121.22 (2017).

[3] *Chem. Sci.* 6 (7 2015).

[4] *JACS* 129.6 (2007).

[5] *Zeitschrift für Kristallographie* 220 (2005).