

Theoretical XANES Study of the Activated Nickel (t-Amylisocyanide) Molecule

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Abstract. XANES is one of the most powerful techniques for investigating the active centres of non-crystalline systems such as synthetic catalysts and enzymes. We have investigated XANES for an active species in the Ni-catalyzed polymerization of isocyanides, the activated Ni (t-amylisocyanide) complex, using two of the most popular theoretical approaches. This is a very large cluster for which it is extremely difficult to derive a converged solution using the Finite Difference Method. The cluster has been linked to important chemical developments for catalysts for isocyanide polymerization. Predicted XANES for the nano-cluster are compared with experimental data, providing an important test for different theoretical approaches. Developments of a finite element method gave excellent agreement with the experimental data, while simpler models were relatively unsuccessful.

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INTRODUCTION

The activated nickel (t-amylisocyanide) molecule [1] is an important intermediate in the Ni-catalysed polymerization of isocyanides [2] which have shown remarkable efficiency as Mukaiyama epoxidation catalysts. XANES is a powerful technique for investigating the active centres of such non-crystalline synthetic catalysts and can help shed light on possible reaction mechanisms. The structure of the activated Ni (t-amylisocyanide) molecule (Figure 1) was determined by the solution of X-ray crystallographic structure with a relatively large disorder. A combination of XAFS and XANES studies was able to refine some bond lengths using a muffin-tin approach [1]. XANES analysis can provide valuable information not just about the location of atoms within a molecule, but also about the bonding between those atoms [3]. While the more symmetric inactive compound is amenable to structural investigation by these methods, large asymmetric molecules such as this activated complex provide a major challenge to XAFS and XANES FDM and muffin-tin prediction methods.

In the activated complex, $C_{31}H_{53}Cl_2N_5NiO_8$ or tri(tert-pentyl isocyanide)[benzylamino(tert-pentylamino)carbene] nickel(II) perchlorate [1, 4], the Ni is coordinated by 3 isocyanide C atoms of non-activated isocyanide ligands (middle left, top left, and top right). The 4th isocyanide (bottom right) has reacted with benzylamine, resulting in a coordinated carbene. The phenyl ring of the benzylamine (bottom) has a weak interaction with the Ni. The XAFS and XANES used here are from the Nickel K-edge.

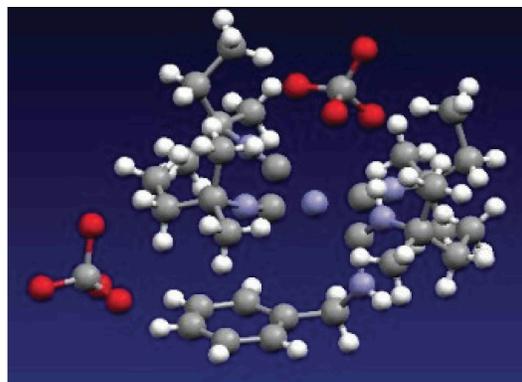


FIGURE 1. The activated nickel (t-amylisocyanide) molecule.

APPROACHES TO THEORETICAL XANES

We used two different approaches for providing theoretical XANES, namely FDMNES [5] and FEFF 8.2 [6]. No fitting was used to produce the FDMNES spectra, thus providing an objective test for this approach.

FEFF is the most commonly used program for calculating XAFS. It uses multiple scattering techniques over an approximate muffin-tin potential. FEFF can include inelastic and thermal effects, which gives it an advantage over FDMNES in the extended energy region. However, since the data on this molecule was taken at 5K, and the

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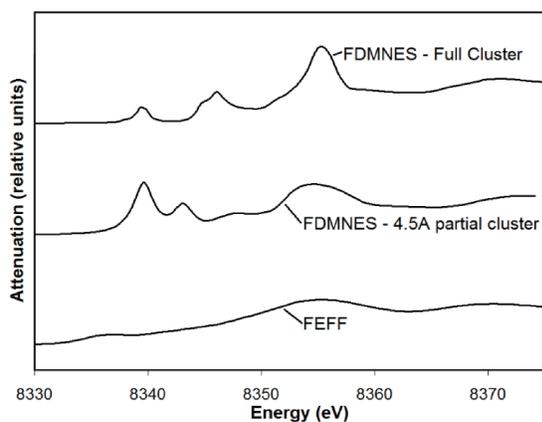


FIGURE 2. Predicted XANES curves from different theoretical approaches. Note the vastly different XANES seen from FDMNES when different cluster sizes are used. This was not true of the more symmetric non-activated cluster. FDMNES predicted a more sharply detailed structure than muffin-tin approaches, in good agreement with experiment at these energies.

oscillations occur in the near-edge region, thermal effects will be minimal.

FDMNES is a finite element method for calculating XANES, introduced by Yves Joly. One major advantage of this method is that it avoids using the muffin tin approximation. The FDMNES code had previously not been able to compute XANES for non-symmetric molecules of this size, and previous work on similar more symmetric molecules has only modelled partial clusters [7]. We have modified the FDMNES code to make it possible to model this cluster in its entirety. The predicted XANES spectra from FDMNES and FEFF are shown in Figure 2.

The FDMNES spectra was convolved with a 1.44 eV Lorentzian to take account of the core-hole width, then a 2 eV Lorentzian to simulate the effect of bandwidth. Two XANES spectra from FDMNES are plotted, a 4.5 Å cropped cluster, and the results from modelling the entire cluster. The difference in the results from these two cases emphasises the importance of full cluster modelling for accurate reproduction of XANES spectra. This could be due to changes in bonding which are only determined by performing the full theoretical analysis. Although the full cluster results from FEFF and FDMNES are similar above 8360 eV, below this the two spectra are very different. While FDMNES predicts the sharp resonance peaks characteristic of bound-bound transitions, FEFF predicts a relatively featureless fall toward the pre-edge.

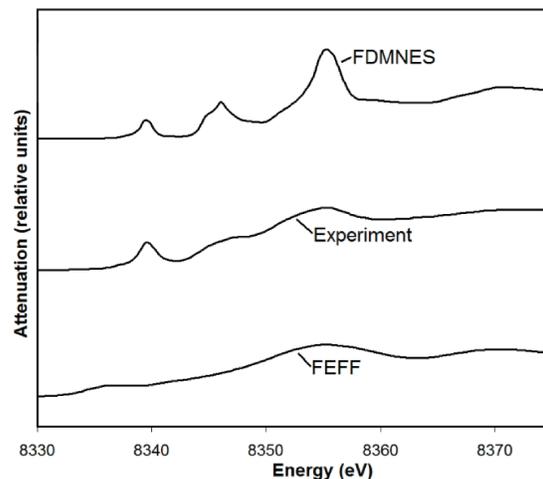


FIGURE 3. Comparison between theory and experiment. The middle curve is the experimental XANES taken at the nickel K-edge. FDMNES predicts the location of the peaks very well, although the higher energy peaks are too sharp. FEFF does not predict the sharp XANES features well.

COMPARISON BETWEEN THEORETICAL XANES SPECTRA AND EXPERIMENT

Comparisons between theoretical and experimental XANES spectra of large complex molecules provide a great test of different approaches to XAFS. Whereas in a symmetric crystalline environment certain assumptions may work well, modelling the X-ray absorption of complex single molecules requires a more general approach to XAFS. Studies like this are not only useful, but provide a bridge between fundamental physics and chemistry and biology.

The theoretically predicted XANES spectra of the Ni (t-amylisocyanide) molecule produced using FDMNES and FEFF are shown in Figure 3. Also plotted is the experimentally measured XANES, taken at the EXAFS station of DUBBLE/ESRF (BM 26) at a temperature of 5K.

ANALYSIS

As shown in Figure 3, the FDMNES prediction fits the experimental data much better than FEFF. The peak locations are modelled well by FDMNES, with a one to one correspondence. The shape and magnitude of the first pre-edge peak at 8339.5 eV is also well modelled. While the position of the higher energy peaks is correct, their magnitudes are too large.

As has been recently demonstrated [8], the magnitude of the above edge peaks can be improved by including thermal and inelastic effects in FDMNES. However, the question of how to accurately take account of inelastic effects in small molecules and nano-clusters remains open.

The fit between FEFF and experiment is significantly worse than FDMNES in the region shown. Only the hump at 8355 eV is in the correct position and it is far wider than the same feature in the experimental data. The pre-edge peak seen in the experimental data at 8339.5 eV is not predicted at all by FEFF and a very small bump at 8336 eV has taken its place which does not correspond to anything seen in the experimental data. FEFF does have advantages further above the edge where thermal and inelastic processes dominate, but it generally reproduces this by fitting the observed spectrum rather than by using an ab initio method.

The superiority of FDMNES in predicting the XANES of this molecule may relate to its spatial asymmetry, the avoidance of the muffin-tin approximation, the complexity of the system, or to particular assumptions involved.

CONCLUSION

Theoretical XANES curves were produced that showed remarkable agreement with experiment. The FDMNES code was altered so that it could fully model this large molecule without any fitting coefficient. Of the two theoretical approaches considered here, FDMNES best fits experiment. FEFF does not predict the shape and location of the features particularly well but is valuable further away from the edge, in the central XAFS region. FDMNES reproduced all the main features from the experimental data very well.

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