

Project Title:

Study for ultrafast dynamics of transition metal complexes

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Description of the project

1. Background and purpose of the project, relationship of the project with other projects

Recently, we have investigated ultrafast photo-excited dynamics of gold oligomers of $[\text{Au}(\text{CN})_2]_n$ in water. In this work, nuclear wave-packet motions induced by the gold-gold covalent bond formations in trimers and dimers were observed. In the case of trimer, considerable rising of the transient absorption signal due to structural change was recognized. DFT calculation has suggested that the change was bent-to-linear structural change of the excited-state trimer. Now, our interest is focused on larger oligomers in solution because we have recently found that much larger oligomers were generated by addition of the co-existing salts such as Et_4NCl in the water, and successfully recorded beat signals of wave-packet motions for those solutions (Fig. 1).

The frequencies were much smaller than those for trimer, clearly indicating that the vibrations are assignable to larger oligomers. Furthermore, considerable and slow rising was recognized on the transient absorption time-profiles, which

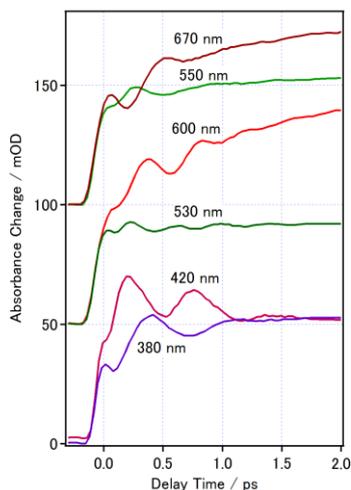


Figure 1. Femtosecond-picosecond transient absorption time profiles of $\text{K}[\text{Au}(\text{CN})_2]$ aqueous solution containing Et_4NCl . ($[\text{Au}] = 0.27 \text{ mol/dm}^3$, $[\text{Et}_4\text{NCl}] = 1.0 \text{ mol/dm}^3$, $\lambda_{\text{exc}} = 327 \text{ nm}$)

would be assignable to the structural change dynamics of the larger oligomers. To make the vibrational feature and the structural change dynamics clear, higher levels of calculations are required.

2. Specific usage status of the system and calculation method

Optimization of a structure of triplet $[\text{Au}(\text{CN})_2]$ tetramer was performed as well as normal mode analysis with DFT method in Gaussian 09 (b3lyp/lanl2dz). A polarizable continuum model (PCM) was employed using H_2O as solvent.

3. Result

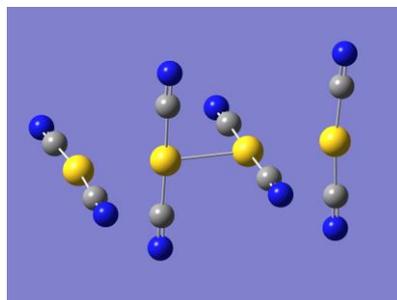


Figure 2. Optimized structure of triplet excited-state tetramer $[\text{Au}(\text{CN})_2]_4^-$.

A linear structure for excited tetramer was obtained as shown in Figure 2. Normal mode analysis showed that the frequencies were close to the experimental values obtained from the beat signals.

4. Conclusion

The structure and frequencies of excited-state tetramer were successfully determined by the theoretical calculations.

5. Schedule and prospect for the future

Calculations for the structural change dynamics and the effect of co-existing species are planned as future works. Larger oligomers are also target.