Project Title:

Exploring the Amplification of Small Molecular Motions into Large Structural Changes

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1. Background and purpose.

The main project for which RICC was used during this term was examination of the radical initiator azobisisobutyrilnitrile (AIBN). This material is known to photodecompose into radical ions following irradiation into a small absorption band at 345 nm (Figure 1, top). The resulting ions can be used for polymerization reactions. However, the dynamics of the decomposition have not been studied in detail. We were able to observe the decomposition by long-time irradiation of the sample at 365 nm, but we were unable to monitor this process on an ultrafast time-scale. Since the absorption at 345 nm is extremely weak, we performed DFT calculations to better understand the nature of this transition.

2. Specific usage

AIBN is simple enough that the calculations were performed on the workstation in our laboratory. The calculation indicated a transition with no oscillator strength at 365 nm, which could correspond to the weak transition that leads to decomposition. To better assess this possibility, we used GaussView, through RICC, to observe the calculated absorption spectra.

3. Results

The calculated absorption spectrum shows a single, strong band at 200 nm and nothing near 365 nm, which is consistent with the negligible strength of all other transitions (Figure 1, bottom). However, the calculated circular dichroism spectrum shows an additional feature at 365 nm, indicating that the transition is allowed for circularly polarized light.

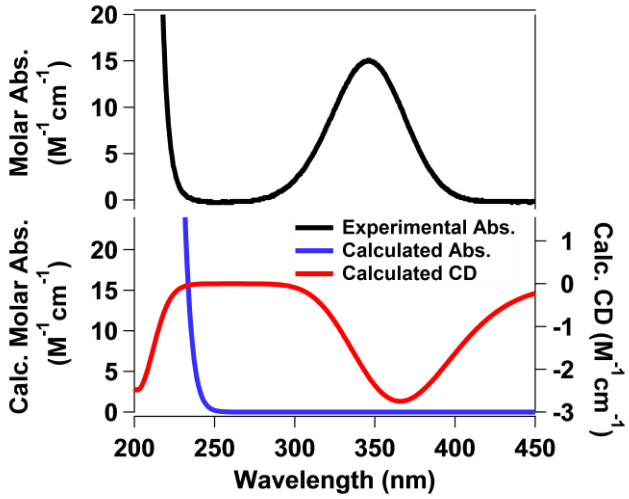

Figure 1. Experimental absorption spectrum (top) of AIBN compared with calculated (bottom) absorption and circular dichroism (CD) spectra.

4. Conclusion

The absorption band observed at 345 nm corresponds to the transition in AIBN that is sensitive to circularly polarized light. It is weakly sensitive to the randomly polarized light of the absorption experiment. We observed no signal from the ultrafast experiments because the excitation source for these experiments is plane-polarized.

5. Schedule and Future Prospects

The results of this work demonstrate the value of calculating spectra prior to attempting an experiment. Future studies are planned for investigating synthetic materials that undergo multiple, rapid structural changes, which we will examine using ultrafast spectroscopy. Calculations of the expected transient structures will be used to interpret the results. The synthesis of the first of these materials is complete, and calculations will begin after preliminary measurements.