Development of a Computer Program to Analyze the Renner-Teller Effect in NCO

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My current work is an ongoing effort stemming from efforts of Dr. David A. Gillett and others at the University of Oxford. Dr. Gillett first undertook the task of developing a computer program capable of analyzing experimental LMR spectra for the NCO free radical that he had collected. The linear structure of the NCO free radical presents itself as a prime candidate to study the Renner-Teller effect in a model system with just enough going on. Normally linear molecules will contain degenerate energy states too similar to each other to be distinguished, but the NCO free radical provides a gateway of insight into important molecular and rotational dynamics. *Gillett et al* initially started writing the source that we are still striving to tailor into a more complete Hamiltonian with the help of perturbation theory. It has been an arduous but methodical approach that allows us to fit a large number of molecular parameters to the spectral data.

Currently the program has the capability both to predict spectra and to fit molecular constants of the effective Hamiltonian to measured spectra by least squares analysis. When we solve for a good representation of the Hamiltonian we are rewarded with a large amount of information about the molecule. Some of the molecular parameters include: binding force constants, bond distances and bending amplitudes, electron distribution, and many other key factors helpful in understanding molecular structures and dynamics. The group has been successful in developing a program to mix any number of relevant states indiscriminately, but does not yet have a working method to assign and track all of the states that we are working with. A handful of the lowest lying energy states have been solved, but the current study aims at assigning the elegantly complex non-unique bands. The project still continues over 15 years since its original undertaking, and my current study now aims at systematically labeling the states that we analyze with our current effective Hamiltonian.

Bending in the $v_2 = 2 \ ^2\Pi$ level leads to a strong display of the Renner-Teller effect; the coupling between magnetic fields arising from vibrational and electronic angular momenta. In most molecular spectra the Renner-Teller effect is absent because there is no net electronic angular momentum. The unusually strong orbital motion of the unpaired electron in the conjugated p-system of the NCO free radical and the small overall size of the molecule leads to a significant and observable difference in the energy needed to move further away from the y axis relative to the x axis when the molecule bends.

A crucial part of adapting the current program for accurate Renner-Teller splitting will involve modifying how the program currently handles the spin-orbit coupling constant, Aso. The spin-orbit contribution has been previously determined and fit to spectral data for lower energy states, but the complex interactions in the $v_2=2$ ² Π state skew the expected results.

The problem for us arises because the spin-orbit coupling constant is dependent on the energy level of the unpaired electron p orbital, which is constantly changing as the molecule bends. Having both the Renner-Teller and spin-orbit effects present simultaneously in the $v_2 = 2^{2}\Pi$ level makes it difficult to properly label the states that arise.

The Renner-Teller effect largely quenches electronic spin-orbit interaction and the wavefunction can no longer be accurately represented with a case (a) basis. The angular momentum coupling between $\varepsilon \omega_2$ and Aso becomes close to the case (b) representation in the unique states. However, in the non-unique states, the coupling is more complex, because the spin-orbit effect is not quenched completely. Effectively splitting the ²Π non-unique states into a μ/κ basis by a rotation of the Hamiltonian matrix for those states makes the problem much easier to tackle. The rotation will allow us to keep using the same case (a) basis set up that was used for the previous states studied. This method will prove to be more advantageous and streamlined, and our focus is now on how to properly distinguish and track the states properly. When we are able to modify the program to combine the effects of the Aso interaction and the Renner-Teller effect simultaneously we hope to extend this model to even higher and more complex energy bands in the NCO free radical.

Not only will this project help us reach a better understanding of the energy patterns for NCO, but we are developing a universal model for an accurate effective Hamiltonian that can be used for similar linear systems. This will help us understand the basic molecular physics underlying these magnetic interactions. It will also allow us to better extend the predicted manifold of energy levels in these molecules, based on relatively few spectral transitions. Once we have completed work on this program we will hope to have a single program capable of labeling and solving multiple hot band energy mappings using a simple and consistent formatting.