

Research Summary

During the previous funding period (October 2018 through September 2019), the primary development from the project was the continued development and implementation of a new many-body potential energy function (termed *mbCO2*) capable of accurately and efficiently reproducing energies and structures of carbon dioxide systems.¹ In particular, nonadditive three-body interactions were added to the potential energy function and the anharmonic vibrational structure of the carbon dioxide dimer was explored. A reference set of CO₂ configurations was generated, and the potential energy of these molecules was calculated at the CCSD(T) level of theory. This level provides the most accurate results for most types of molecules including the carbon dioxide system and routinely achieves spectroscopic accuracy with experimental results. In our case, more than 20,000 three-molecule (trimer) CO₂ configurations were evaluated. Our in-house fitting software was then used to train the *mbCO2* potential energy function to the reference data. We included a base potential which accounts for the electrostatic, induction, and dispersion interactions for the trimer in the short- and long-range (see Fig. 1).

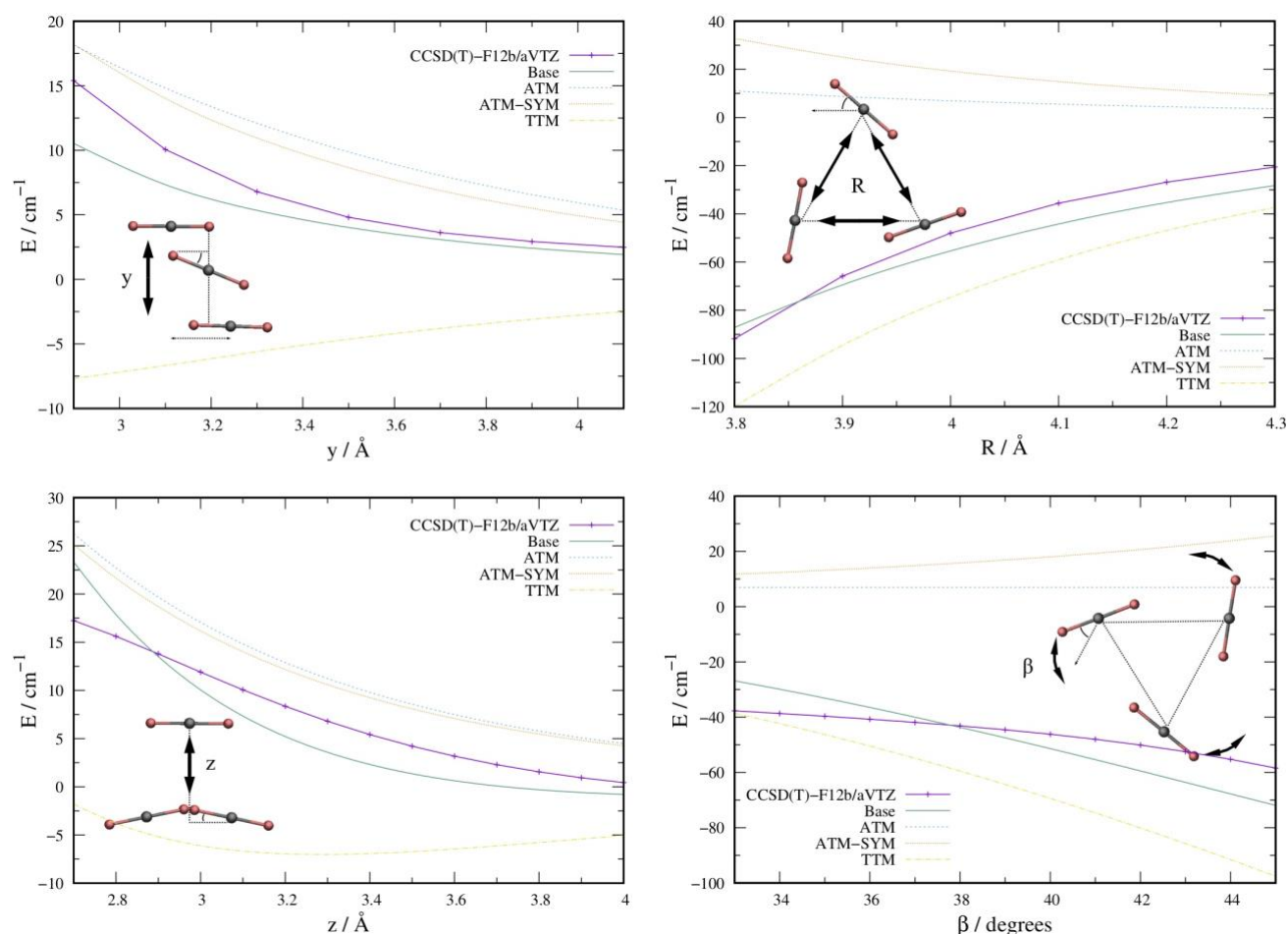


Figure 1. Potential energy surface scans in cm^{-1} of CO₂ trimer isomers are shown at the CCSD(T)-F12b/aug-cc-pVTZ level of electronic structure theory, as well as the Axilrod-Teller (ATM), Axilrod-Teller-SYM (ATM-SYM), Thole-type model (TTM), and base non-additive three-body potential energy functions. The barrel-shaped trimer energies are shown along the y and z distance coordinates (top left and bottom left, respectively). The cyclic trimer isomer energies are shown along the β angle coordinate (top right) and the R distance coordinate (bottom right)

A previously developed *mbCO2* potential function was also used to determine the vibrational frequencies for the CO₂ monomer (one-molecule) and dimer (two-molecule) systems. A combination of vibrational structure techniques including vibrational self-consistent field, vibrational second-order Møller-Plesset perturbation theory, and vibrational configuration interaction, were used alongside different coordinate representations. The different techniques and coordinate representations represent a hierarchy of methods at increasing accuracy. Combined with our potential energy surface, we have obtained vibrational frequencies, including the Fermi splitting, for the carbon dioxide monomer to within 4 wavenumbers of the experimental band positions. Additionally, the potential energy surface and vibrational structure methods were used to investigate the vibrational frequencies of the carbon dioxide dimer. For the intramolecular frequencies, the theoretical band assignments matched well with the monomer data, including the splitting due to in-phase and out-of-phase vibrations. For the intermolecular frequencies,

where experiment and theory in the literature are lacking, we were able to identify the positions of the large amplitude motions. These are complicated by their delocalized nature and Fermi resonance splitting of the overtone of the ν_a mode ($2\nu_a$) and the ν_c mode (see Fig. 2). This splitting partly explains the difficulty in identifying these modes experimentally.

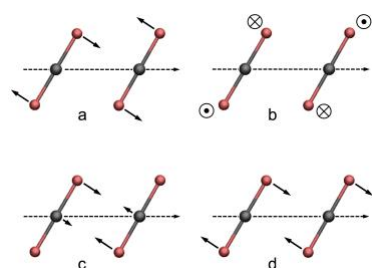


Figure 2. The four intermolecular vibrations of the CO₂ dimer.

Student Involvement

Nine undergraduate students participated in this project and each received research training in the use of computational chemistry software, computer programming, high performance computing, and physical chemistry approaches. Additionally, one Master's student also participated in the project. Two of the students attended the 2019 American Chemical Society (ACS) Spring National Meeting in Orlando, Fla. Two students participated in local conferences at California State University, Los Angeles. At each of these conferences, the students gained vital professional experience presenting their research and interacting with other scientists.

Future Research

The future research will focus on investigating the vibrational and electronic structure of clusters of carbon dioxide with more than three molecules. Specifically, the vibrational structure of the two low-lying trimer isomers shown in Fig. 1 will be solved using unmatched vibrational structure methods and potential energy surface near the complete basis set limit. We are also planning on performing dynamic simulations of carbon dioxide system at different pressures and temperatures to better understand its condensed phase properties. Static solid calculations will also be performed to corroborate these results. Lastly, additional interaction types will be included in the many-body potential function, including for argon atoms and methane molecules.

Related Products

During the previous funding period, the undergraduate students in the Sode group gave four (4) conference poster presentations. In this time, the PI also gave one (1) presentation at a national conference and a number of invited lectures. Also, one (1) journal article was published with an undergraduate co-author during the funding period.