

Research Summary

During the previous funding period (October 2017 through October 2018), the primary development was a new many-body potential energy function (termed *mbCO2*) capable of accurately and efficiently reproducing energies and structures of carbon dioxide systems.¹ 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, nearly 200,000 one-molecule (monomer) CO₂ configurations and almost 70,000 two-molecule (dimer) CO₂ configurations were evaluated at this level of theory. Our in-house fitting software was then used to train the *mbCO2* potential energy function to the reference data. The resulting many-body function reproduces the high level energies at a fraction of the computational cost of traditional electronic structure theory (see Fig. 1).

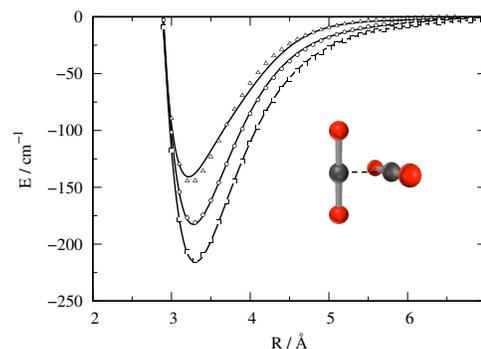


Figure 1. Potential energy surface scans for the crossed CO₂ dimer configuration. The reference energies are shown as geometric symbols. The solid lines represent the values obtained with the *mbCO2* energy function.

The *mbCO2* potential function was then used to determine the minimum energy structures of carbon dioxide clusters containing between three (trimer) to thirteen molecules. In some cases, where many structures exist with nearly degenerate energies, the *mbCO2* function can quickly and accurately determine the energetic ordering of the isomers. For instance, previous experimental and theoretical data disagree on the relative stability of the CO₂ trimers. Two structures, the barrel-shaped and cyclic trimer, are very close in energy; however, the *mbCO2* function has predicted that indeed the barrel-shaped structure is slightly more stable. This approach has also been extended to larger clusters.

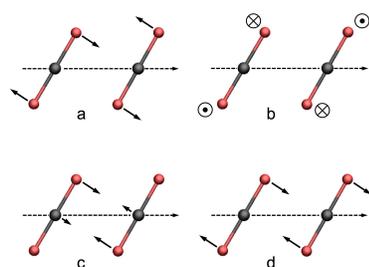


Figure 2. The four intermolecular vibrations of the CO₂ dimer.

The most recent efforts have focused on understanding the vibrational structure of small clusters of carbon dioxide molecules. This has been performed using the *mbCO2* function. The vibrational energy levels of the carbon dioxide monomer and dimer were explored and shown to agree well with experiment. Specifically for the monomer, the agreement is within four wavenumbers of the experimental band positions. Also, since the theoretical methods used in this work explicitly account for vibrational anharmonicity, Fermi resonance can be investigated. The interpretation of the dimer motions is complicated—especially for the intermolecular modes (see Fig. 2)—but newly developed theoretical approaches allowed for the accurate prediction of this spectrum as well. Notably, the dimer intermolecular spectrum is important for understanding van der Waals type interactions in similar systems and has only recently been studied thoroughly. Our results emphasize the

delocalized nature of these modes, which make them difficult to interpret and assign.

Student Involvement

Four 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. All but one of the students also presented his/her research at local, regional and/or national conferences. Three of the students attended the 2018 American Chemical Society (ACS) Spring National Meeting in New Orleans, La. Two students also attended the 2018 Florida Annual Meeting and Exposition (FAME) ACS Meeting in Palm Harbor, Fla. 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 including three-body and higher-order energy interactions into the *mbCO2* function to increase the accuracy and applicability of the model. The vibrational structure of the two low-lying trimer isomers will be explored, along with the thermodynamics of condensed phase CO₂ systems. Also, the function will be expanded to include interactions with argon atoms and methane molecules.

Related Products

During the previous funding period, the undergraduate students in the Sode group gave three (3) conference poster presentations. In this time, the PI also gave two (2) presentations at conferences. Also, one (1) journal article was published with an undergraduate co-author.