

Highly Accurate Bound Rovibrational Eigen-energies of Ozone Using the *ScalIT* Software Suite

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INTRODUCTION

In recent years, ozone and its isotopologues have been a topic of interest amongst many fields of research, due to its importance in atmospheric chemistry and its anomalous isotopic enrichment, or the so-called mass independent fractionation (MIF) effect. In the field of potential energy surface (PES) creation, debate of the existence of a potential barrier just under the dissociation energy (referred to as a potential “reef”) has plagued researchers for many years. Recently, Dawes *et al*¹ created a highly accurate PES, which attributes this reef to an avoided crossing. Subsequent calculations on this surface have shown improved agreement with experiment, but have been focused on only the vibrational spectrum. It is well known that reaction dynamics require extensive knowledge of the *ro*-vibrational spectrum, not just the vibrational states, especially in cases like ozone that assume a Lindemann-type mechanism. This work represents the start of the complete characterization of the rovibrational spectrum for various isotopologues of ozone on Dawes’ newly created PES, using a highly parallelized suite of exact quantum dynamics codes, *ScalIT*².

METHODS

ScalIT is a highly parallelizable modularized software suite, written in Fortran90 and MPI, that can create triatomic and tetraatomic full dimensional rovibrational Hamiltonians, and solve the time-independent nuclear Schrödinger equation for highly accurate bound rovibrational spectra. All calculations are exact to within the Born-Oppenheimer approximation. By default, *ScalIT* employs Jacobi coordinates, which represents an AB₂ molecule (Fig. 1), thus not incorporating all possible symmetry of an A₃ molecule. By plotting the wavefunctions in hyperspherical coordinates, one can identify the

physically real states as those exhibiting a totally symmetric six-fold azimuthal symmetry.

RESULTS AND DISCUSSION

This work calculates the entire bound vibrational and choice rovibrational spectrum of ¹⁶O₃ to high accuracy ($< 10^{-4}$ cm⁻¹), and compares to available theoretical and experimental results.

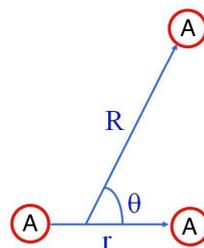


Figure 1. Schematic of a generic A₃ molecule described by Jacobi coordinates. Here, *r* represents the distance between the A₂ dimer, and *R* is the distance from the center of mass of *r* to the third A atom, with θ being the angle between.

CONCLUSIONS

Choice rovibrational states up to $J = 10$, and the entire vibrational spectrum of ¹⁶O₃ was calculated and converged to $< 10^{-4}$ cm⁻¹ using the Dawes PES and *ScalIT* software suite. This represents a starting point for the entire rovibrational spectrum for various isotopologues of ozone to serve as a database for future ozone research.

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¹ R. Dawes, P. Lolur, A. Li, B. Jiang, H. Guo. *J. Chem. Phys.* 139. 201103 (2013).

² C. Petty, B. Poirier. *Applied Mathematics.* 5. 2756-2763 (2013).