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Limited rotational and rovibrational line lists computed with highly accurate quartic force fields and *ab initio* dipole surfaces

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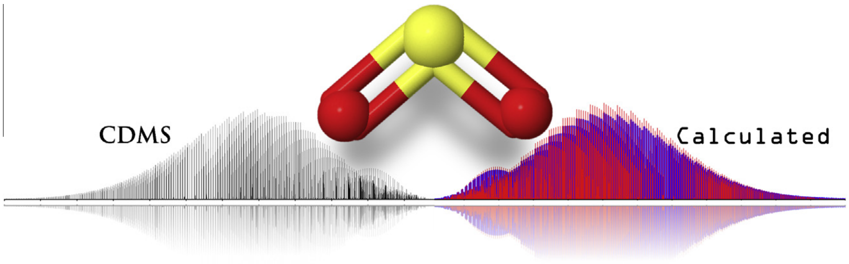
HIGHLIGHTS

- Quartic Force Fields (QFFs) yield highly accurate spectra including rotational structure.
- Infrared intensities (IR) are well determined using a CCSD(T) Dipole Moment Surface (DMS).
- Purely *ab initio* IR intensities agree extremely well with high-resolution experiment.
- Purely *ab initio* transition energies agree very well with high-resolution experiment.
- *Ab initio* purely rotational and rovibrational line lists should aid astronomers to assign lines.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, computational procedures are employed to compute the rotational and rovibrational spectra and line lists for H_2O, CO_2, and SO_2. Building on the established use of quartic force fields, MP2 and CCSD(T) Dipole Moment Surfaces (DMSs) are computed for each system of study in order to produce line intensities as well as the transition energies. The computed results exhibit a clear correlation to reference data available in the HITRAN database. Additionally, even though CCSD(T) DMSs produce more accurate intensities as compared to experiment, the use of MP2 DMSs results in reliable line lists that are still comparable to experiment. The use of the less computationally costly MP2 method is beneficial in the study of larger systems where use of CCSD(T) would be more costly.

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Introduction

The need for accurate but cost-effective computational reference data related to the rotational and rovibrational transitions of small astronomically significant molecules is growing rapidly as a result of an increase in the sub-millimeter to near-infrared telescopic power now being employed by the world's astronomers through telescopes such as the Herschel Space Observatory (HSO), the Stratospheric Observatory for Infrared Astronomy (SOFIA), the Atacama Large Millimeter Array (ALMA), and the upcoming James Webb Space Telescope (JWST). The rotational and rovibrational transitions present in observed astronomical spectra from these and related telescopes may correspond to interesting or previously undetected molecular systems which could provide fresh insights into the chemistry of the Interstellar Medium (ISM) as well as other astrophysical environments including exoplanet atmospheres in the future.

While many of the transitions observed are from small, common species such as water, carbon dioxide, ammonia, methane,

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methanol, and the like, reference data for these systems are essential in resolving various astronomical rotational and rovibrational spectra [1]. Global Potential Energy Surfaces (PESs) have been the standard means by which spectroscopically accurate rovibrational reference data has been generated. The best computational accuracies as compared to known experimental data have been achieved using this approach, but the use of experimental data is necessary in order to achieve 0.1 cm^{-1} or better accuracies [2–7]. Hence, these global PESs are not purely *ab initio* in nature, and this approach can not be employed for the study of astronomically significant molecules where experimental reference data is currently not available. Additionally, the number of points required to properly describe the global surface is understandably large and inflates the computational cost for the PES generation greatly.

Quartic Force Fields (QFFs) have long been used with great success for the *ab initio* computation of fundamental vibrational frequencies along with some of the lower frequency overtones and combination bands as well as spectroscopic constants for various small molecules [8–29]. This approach can accurately describe the potential region around the reference minimum necessary to model molecular vibrations and account for subsequent effects in the spectroscopic constants while averting the need to compute a global PES since the energy derivatives around the minimum are well-characterized. However, the computation of the Dipole Moment Surface (DMS), which is necessary in the computation of transition intensities, has not lent itself to a similar reduced formulation as the QFF has relative to the global PES. The reason for this is that there may be regions other than the geometrical minimum where the DMS is changing rapidly. As a result, significantly more points than those from the QFF are necessary to give a reliable surface required in the calculation of the intensities.

In light of these considerations, the computational cost of the *ab initio* calculations for the dipole moment components at each point on the surface is another important consideration. Even if the number of points on the surface where the dipole moment must be computed remains large, a lower cost method such as Møller–Plesset second-order perturbation theory (MP2) [30–32] could be employed if the quality of the dipole moment values does not decline drastically. MP2 scales on the order of N^5 where N is the number of basis functions while the coupled cluster method including singles, doubles, and perturbative triples [CCSD(T)], described in Refs. [33–35] called the "gold standard" [36,37] of quantum chemistry, scales as N^7. The use of MP2 over CCSD(T) can reduce the total computational cost for the creation of the DMS, but it is unclear as to how well an MP2 DMS may compare to one computed with CCSD(T) or to actual experimental results.

Recent work on both the *cis* and *trans* conformers of HOCO and DOCO [38,39], which are of interest to studies of the Martian atmosphere [40,41,22] and the ISM [42], has produced not only accurate descriptions of the vibrational frequencies for the fundamentals, combination bands, and overtones of less than 4000 cm^{-1}, but also reliable anharmonic intensities for these bands. Even though rotational or rovibrational structure was not included as a part of these studies, they represent a step towards a closer interaction between quantum chemists and astronomers as the techniques for the creation of accurate spectroscopic reference data are further expanded.

In the present work, we move beyond the level of computationally producing reliable intensities for only the pure vibrational bands and to explore the accurate computation of limited line lists without the use of global PESs. In this benchmark study, QFFs and *ab initio* dipole surfaces are employed to compute the pure rotational and rovibrational transitions, including both line positions and intensities, for a set of small, common astronomically significant molecules for which high-resolution experimental data exists: H_2O, CO_2, and SO_2 [43–45]. Experimental data from the HITRAN database [46] are compared with the rotational and rovibrational transitions computed from both CCSD(T) and MP2 dipole moment surfaces. As far as we know, QFF accuracies have never been tested for the computation of even a limited line list in which rotational structure is included. Thus, a benchmark as to how well the data generated from these *ab initio* methods compare to experiment and to each other (MP2 versus CCSD(T) for the DMS) is provided so that further studies may be undertaken for astronomically interesting molecules where experimental reference data is unavailable. Ultimately, this will provide astronomers with another tool with which they may analyze and assign astronomical spectra.

Computational details

Computation of the potential energy and dipole moment surfaces

Each of the three systems studied here (H_2O, CO_2, and SO_2) make use of QFFs in the calculation of the vibrational wavefunctions and eigenvalues. The H_2O QFF used here was originally reported in Ref. [47] and makes use of 3-point extrapolated [48] CCSD(T)/aug-cc-pVXZ (where X = T, Q, and 5) energies further corrected for core-correlation and scalar relativistic effects. This QFF will be referred to as the CRE QFF. The QFFs for the other two systems studied are refitted from their global potential energy surfaces: CO_2 from Ref. [5], and SO_2 from Ref. [7]. Both the CO_2 and SO_2 global potential surfaces are able to reproduce some high resolution experimental rovibrational transitions with better than 0.02 cm^{-1} accuracy. The step lengths utilized in each QFF are 0.005 Å for the bond lengths and 0.005 radians for the bond angles. All QFFs are transformed into a Morse-cosine set of coordinates. However, for CO_2, the bond angles require that their transformed coordinates be defined by the sine function of half the bond angle displacement so that the other linear configuration with $\angle O{-}C{-}O = 0.0^\circ$ cannot become a second minimum on the PES.

For each system, two dipole moment surfaces are constructed at the MP2 and CCSD(T) levels computed with the MOLPRO suite of computational chemistry programs [49]. The aug-cc-pVTZ and aug-cc-pV(T + d)Z (for the sulfur atom) basis sets [50–52] are used in our computations. The geometry grid used for the H_2O DMS is from Ref. [53], while the original CO_2 and SO_2 geometry grids in their global PES constructions are used [5,7]. Full 0–12th order polynomials are fitted to the effective charges on H atoms (in H_2O) and O atoms (in SO_2 and CO_2). There are 969 expansion coefficients for polynomials in terms of bond length displacements and displacements of the cosine of the bond angle [5].

On the original H_2O grid, 678 geometries are able to be utilized here. For those geometries where $\angle H{-}O{-}H$ is greater than 165° or less than 20°, a weighting of 0.001 is applied in order to focus on the lowest frequency bands. For points below 20,000 cm^{-1}, the fitting $\sigma(\text{rms}) = 3.4 \times 10^{-4}$ a.u. for non-zero MP2 dipole components and 3.0×10^{-4} a.u. for CCSD(T). The average fitting deviation is 0.047% and 0.054%, respectively. There are 579 CO_2 points and 819 non-zero dipole components [5]. For the MP2/aug-cc-pVTZ dipole components, the fitting rms is 1.1×10^{-5} a.u., and the average fitting deviation is as small as 0.0047%. For the CCSD(T)/aug-cc-pVTZ dipole components, the fitting rms is 1.2×10^{-4} a.u., and the average fitting deviation is 0.026%. There are 485 SO_2 points and 970 dipole components since one S=O bond is aligned along the x-axis. The weighting function takes a form similar to that for the H_2O global PES [54]. There are 770 dipole components for the 385 points below 30,000 cm^{-1}, and much smaller weights are required for points higher than 30,000 cm^{-1}. For the 770 MP2 dipole components, the fitting rms is 2.8×10^{-4} a.u., and the average fitting deviation is 1.1%. There were several points where one of the dipole components is very close to zero, which leads to the larger

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