


A LARGE-SCALE APPROACH TO MODELLING BIOSIGNATURES: FIRST STEPS


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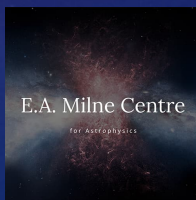
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ABSTRACT


This work presents the first steps to modelling spectra for biosignatures, using our code, Prometheus. The end goal is to create a source of synthetic rovibrational spectra for molecules, thus bridging the gap for missing data to help detect biosignatures. As a starting point however, only selected diatomics (O_2 and CO) with known spectra have been chosen in order to evaluate the accuracy of our method.


Our code uses the Transition-Optimised Shifted Hermite (TOSH) theory to account for anharmonicity. Our results show that this method can achieve results that are a better approximation than the ones produced through the basic harmonic method.

The present work however highlights the need for the theory to be adapted. The current approach still lags behind HITRAN spectral data, for example, as it does not yet truly consider vibration-rotation interactions.

FOCUS MOLECULES

Here we focus on two diatomics, which both have astrophysical importance and are biosignatures. They are:

 CO – plays a key role in interstellar molecular clouds. It can act as a coolant¹.

 O_2 – third most abundant element in the universe yet one of the most elusive molecules. Even now, a comprehensive picture of oxygen chemistry in interstellar environments is still missing². Figure 1. shows the Orion Nebula, one of few interstellar clouds where molecular oxygen has been detected.

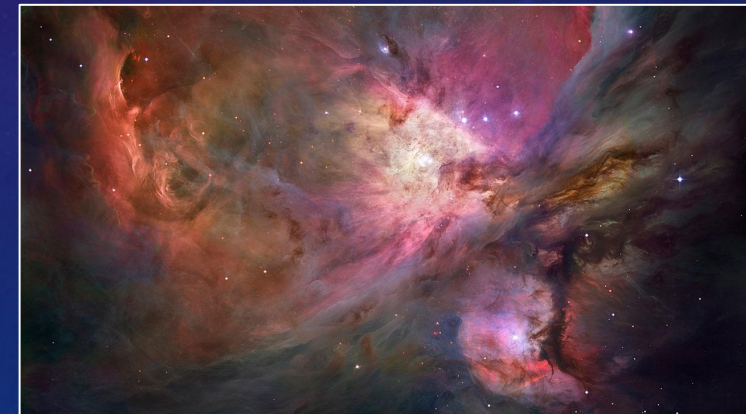


Figure 1. Credit: NASA/ESA/M.ROBERTO.

INTRODUCTION PT.1: BIOSIGNATURES

Currently our work focuses solely on the diatomic biosignatures contained within the catalogue described by Seager et al. (2016)³. A biosignature can simply be described as any molecule that is believed to be indicative of life. Further details about the classification derived by Seager et al. (2016) and used for this project can be found in the paper³. A digital version of the catalogue can be found [here](#).

INTRODUCTION PT.2: PROMETHEUS/ANALYTICAL ANHARMONIC APPROACH

The code we created is called Prometheus, it is designed to be simple to use and quickly produce approximate spectrums (currently only for diatomics). It also can create other figures such as fortrat diagrams. **Note:** A paper with a full evaluation and explanation of the code is under preparation.

Prometheus uses TOSH theory. This works by determining an “anharmonic” shift, σ , along the vibration coordinate Q . If the centre of the wavefunction is shifted by σ , the shape will remain the same, but the anharmonic correction can be incorporated into the wavefunction. More details can be found in the TOSH paper⁴.

METHOD PT.1: POTENTIAL ENERGY CURVE

Prometheus requires a potential energy curve for the chosen diatomic. The quality of this data is paramount as it will have a strong effect on the TOSH corrections and consequently the spectroscopic constants values. The key products of this section are the frequency, ω , the change in energy between vibrational levels, ΔE^{TOSH} , and the shift, σ . The shift is calculated by comparing, ΔE^{TOSH} , to second order vibrational perturbation theory, ΔE^{VPT2} , expressions. Further details can be found in the TOSH paper⁴.

METHOD PT.2: ROTATIONAL CONSTANTS

By incorporating a shift of the equilibrium distance, we now have a new value for the “vibrationally averaged” distance, r_0 . This is now expressed as, $r = r_e + \sigma$. From this we can calculate a new value for the rotational constant, using:

$$B_v = \frac{h^2}{8\pi^2 c \mu r^2}$$

Naturally as a single value is produced for, σ , the rotational constant for the upper and lower vibrational level is the same. We then use ΔE^{TOSH} to compute the band origin.

METHOD PT.3: SPECTRA

We can plot ro-vibrational transitions and use a Boltzmann distribution to obtain the relative intensities for each line. This combined with the typical rotational equations, using the spectroscopic constants obtained via TOSH, provide us with an approximate spectrum.

METHOD PT.4: COMPARISONS

The spectrums Prometheus produces can then be compared to different sources.

- ❁ **HITRAN2016:** data from HITRAN’s 2016 release. This was obtained from SpectralCalc as a csv file and read into the code. This data is currently acting as the optimal result (link [here](#)).
- ❁ **HARMONIC:** This is simply using Prometheus constants, calculated from the potential energy surface (PES), without any anharmonic corrections. For example, the band origin is the harmonic frequency, ω .

CO

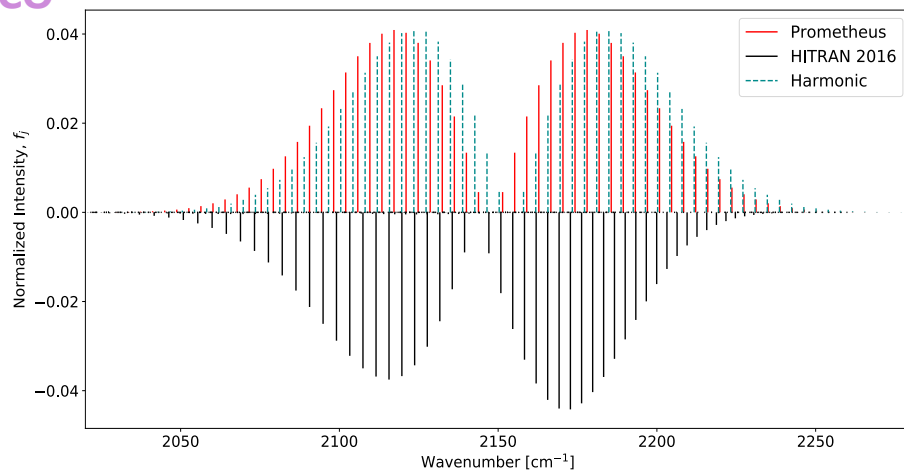


Figure 2. (Above) The comparison of CO spectra produced by Prometheus (Red), HITRAN 2016 (Black) and Harmonic (Dark Cyan).

CO DISCUSSION

In figure 2. we can see that the band origin of the harmonic spectrum is displaced the furthest of all the data, when compared to the HITRAN spectrum. Whereas Prometheus provides a very good approximation, being roughly less than 10 wavenumbers (0.5%) out. Before even considering the transition positions in depth, this clearly shows an anharmonic treatment is required for an accurate approximation.

Overall the distributions of Prometheus and HITRAN appear similar; however this is more of a global view of the spectra rather than a local look. On closer inspection, Prometheus often maps the wrong transition to HITRANs, possibly due to our constant rotation-vibration coupling model. This is exaggerated due to the position difference of the band origin.

O₂ DISCUSSION

Here the non-HITRAN2016 data (harmonic, Prometheus and NIST constants) have been arbitrarily normalized for ease of comparison. The HITRAN spectra contains structures that are not modelled in our approximate method.

Figure 3. highlights the fact that Prometheus fails to accurately model the Q branch when it is present. This is due to the TOSH theory predicting $B_0 = B_1$ thus reducing the Q branch transitions to one solitary frequency, rather than bunched transitions. This is not the case for the HITRAN2016 constants as the rotational-vibrational coupling constant is known, so differing rotational constants can be calculated ⁵.

When considering the overall spectrum, Prometheus still does a better approximation than the Harmonic method, despite the point mentioned previously. This is especially shown by the significant displacement of the Harmonic data from the other the other methods.

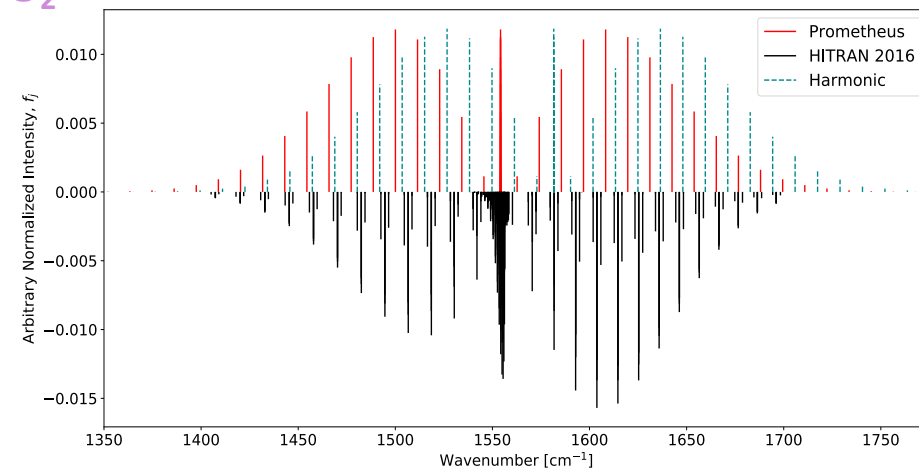
O₂

Figure 3. (Above) The comparison of O₂ spectra produced by Prometheus (Red), HITRAN 2016 (Black) and Harmonic (Dark Cyan).

CONCLUSIONS AND REFERENCES

ADDITIONAL O₂ DISCUSSION

The spectrum for O₂ is not only Raman active but, due to the spin of oxygen, every alternate rotational level is absent. This highlights the crucial need to consider extra phenomena, when modelling the spectra. This effect is currently being considered for implementation in Prometheus.

When reviewing the overall spectrum, Prometheus still does a better approximation than the Harmonic method, despite the points mentioned previously. This is especially shown by the significant displacement of the Harmonic data from the other the other methods.

KEY TAKEAWAY

As shown and discussed in [slide 3](#), the TOSH approximation produces full fundamental ro-vibrational spectra at higher accuracy than that of the harmonic approximation. It is also produced those both quickly and computationally cheaply.

A caveat is that the current theory does not accommodate for two differing vibrational constants for the upper and lower states. This leads to the incorrect suggestion that the vibration and rotation are independent. Which in turn leads to similar inaccuracies in the transition positions as the harmonic method. For further accuracy, this needs to be addressed.

The next steps for this work:

- ❁ Modify the theory to obtain a shift which varies with vibrational level, as opposed to being optimized for the fundamental, $0 \rightarrow 1$, vibrational transition.
- ❁ Create a means of evaluating the symmetry of a molecule and hence if its Raman active and/or IR active. This would include considering the phenomena arising due to properties such a spin.
- ❁ Adapt theory to roll out onto triatomic and eventually polyatomic biosignature molecules.

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REFERENCES

1. Whitworth, A. P. & Jaffa, S. E. A simple approach to CO cooling in molecular clouds. *Astron. Astrophys.* **611**, (2018).
2. Wang, J. *et al.* Molecular Oxygen in the Nearest QSO Mrk 231. *Astrophys. J.* **889**, 129 (2020).
3. Seager, S., Bains, W. & Petkowski, J. J. Toward a List of Molecules as Potential Biosignature Gases for the Search for Life on Exoplanets and Applications to Terrestrial Biochemistry. *Astrobiology* **16**, 465–485 (2016).
4. Lin, C. Y., Gilbert, A. T. B. & Gill, P. M. W. Calculating molecular vibrational spectra beyond the harmonic approximation. *Theor. Chem. Acc.* **120**, 23–35 (2008).
5. Pekeris, C. L. The Rotation-Vibration Coupling in Diatomic Molecules. *Phys. Rev.* **45**, 98–103 (1934).