An Ab-initio Potential Energy Surface for the HOPO Molecule

Ryan Mok, Sergey Yurchenko

Department of Physics & Astronomy, University College London, Gower Street, London WC1E 6BT.

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1. Intro: Why HOPO?

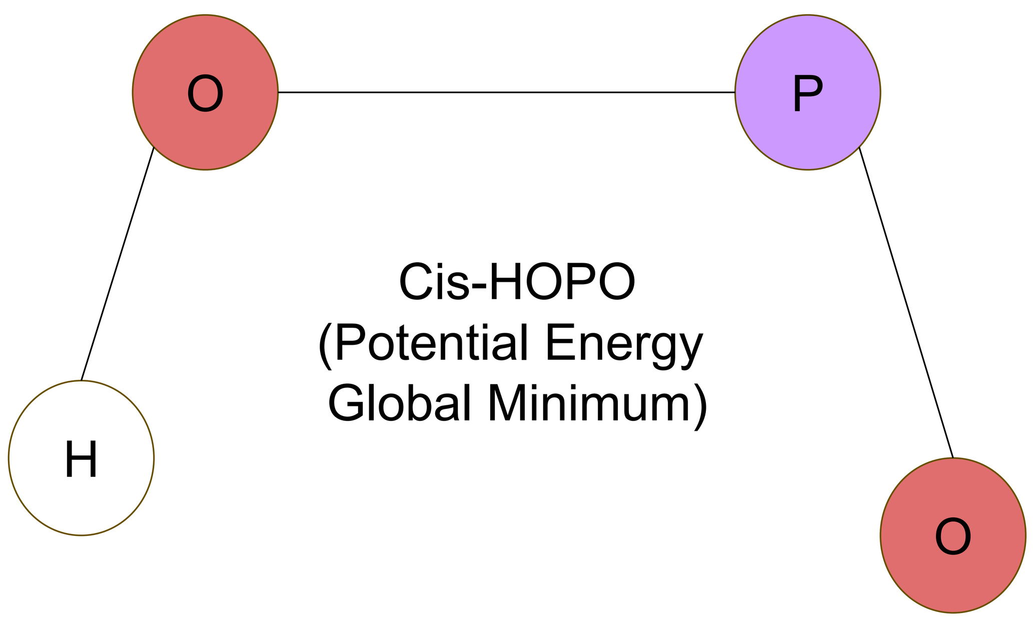
Lee et al. show evidence that the HOPO molecule may play a dominant role in transit and emission spectra for metallicity enriched hot-Jupiter and warm-Neptune atmospheres such as exoplanets HD 189733b and GJ1214b, respectively [1].

As a possible opacity source, Zilinskas et al. utilise HOPO data, analysing the atmosphere of 55 Cancri e [2]. For these reasons we aim to compute spectral data for HOPO.

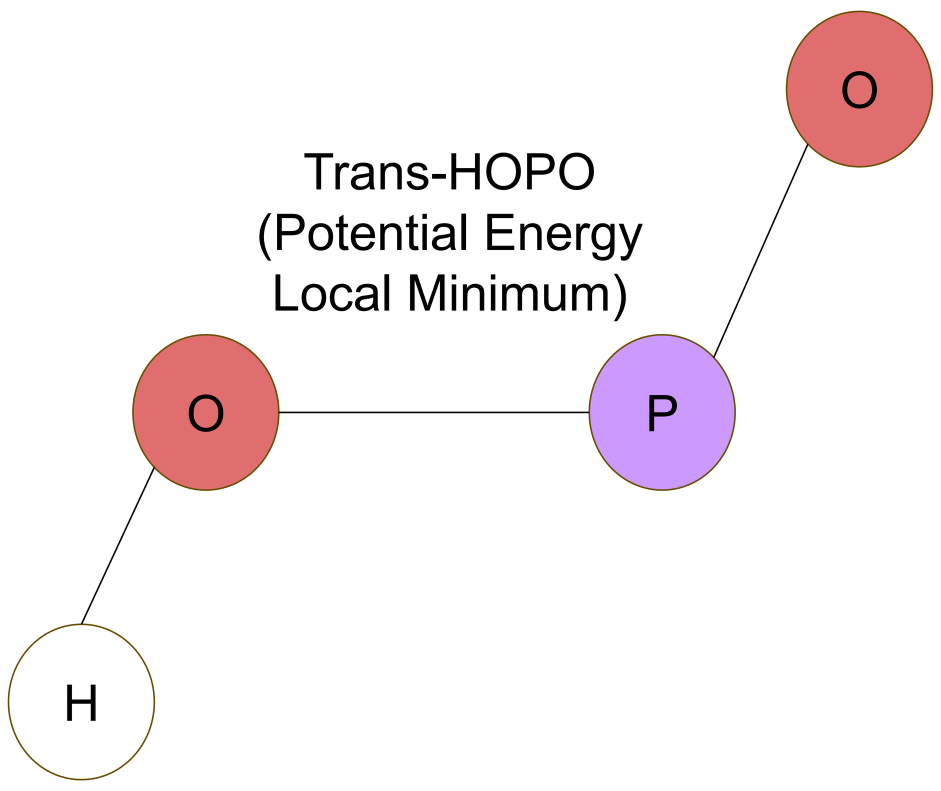
2. Objective + Approach

- A 4-atom polyatomic molecule, the potential energy surface is dependent on 6 internal degrees of freedom. We construct a six-dimensional potential energy surface for the ground electronic state, to be used for calculating a rovibrational spectrum of cis- and trans- HOPO.
- The electronic energy is calculated for a finite number of different nuclear geometries. Then we fit the calculated energies to some analytic function to obtain the potential energy surface (PES).

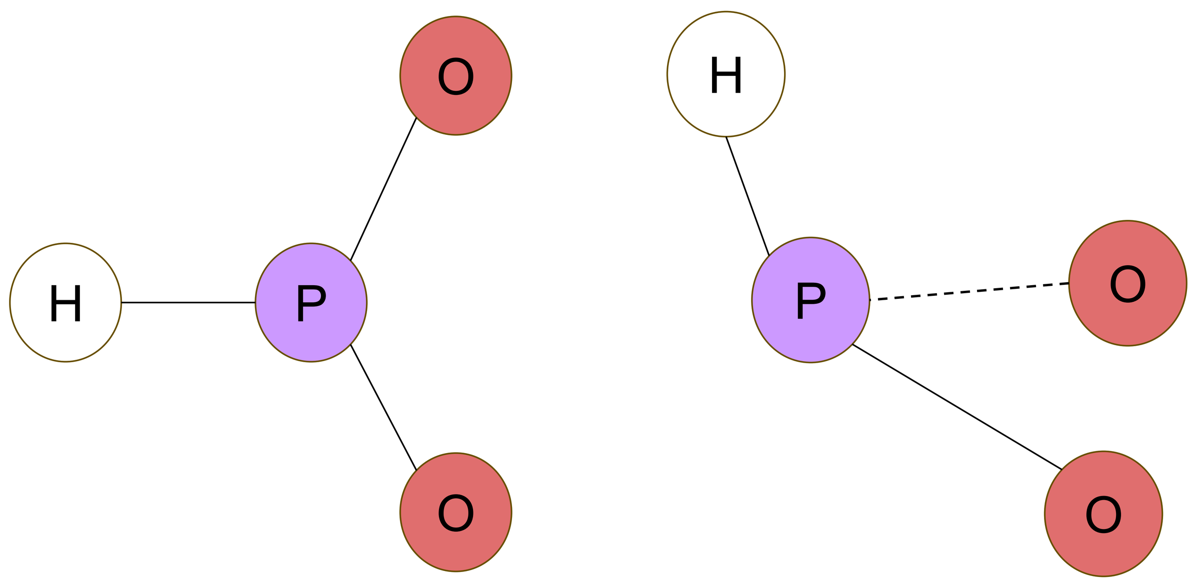
3. Main HOPO Isomers



The two lowest energy isomers in order are cis-HOPO and trans-HOPO

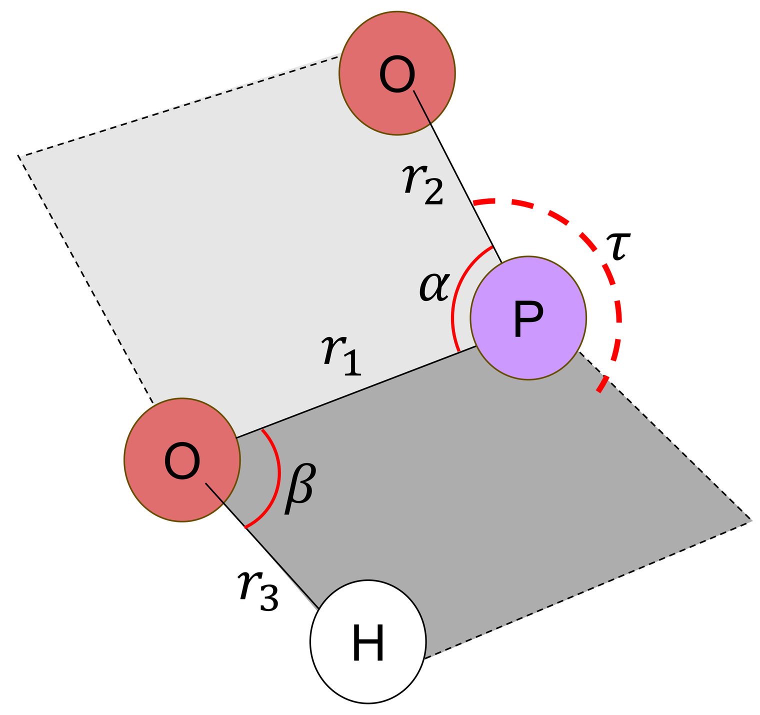


4. Other Isomers



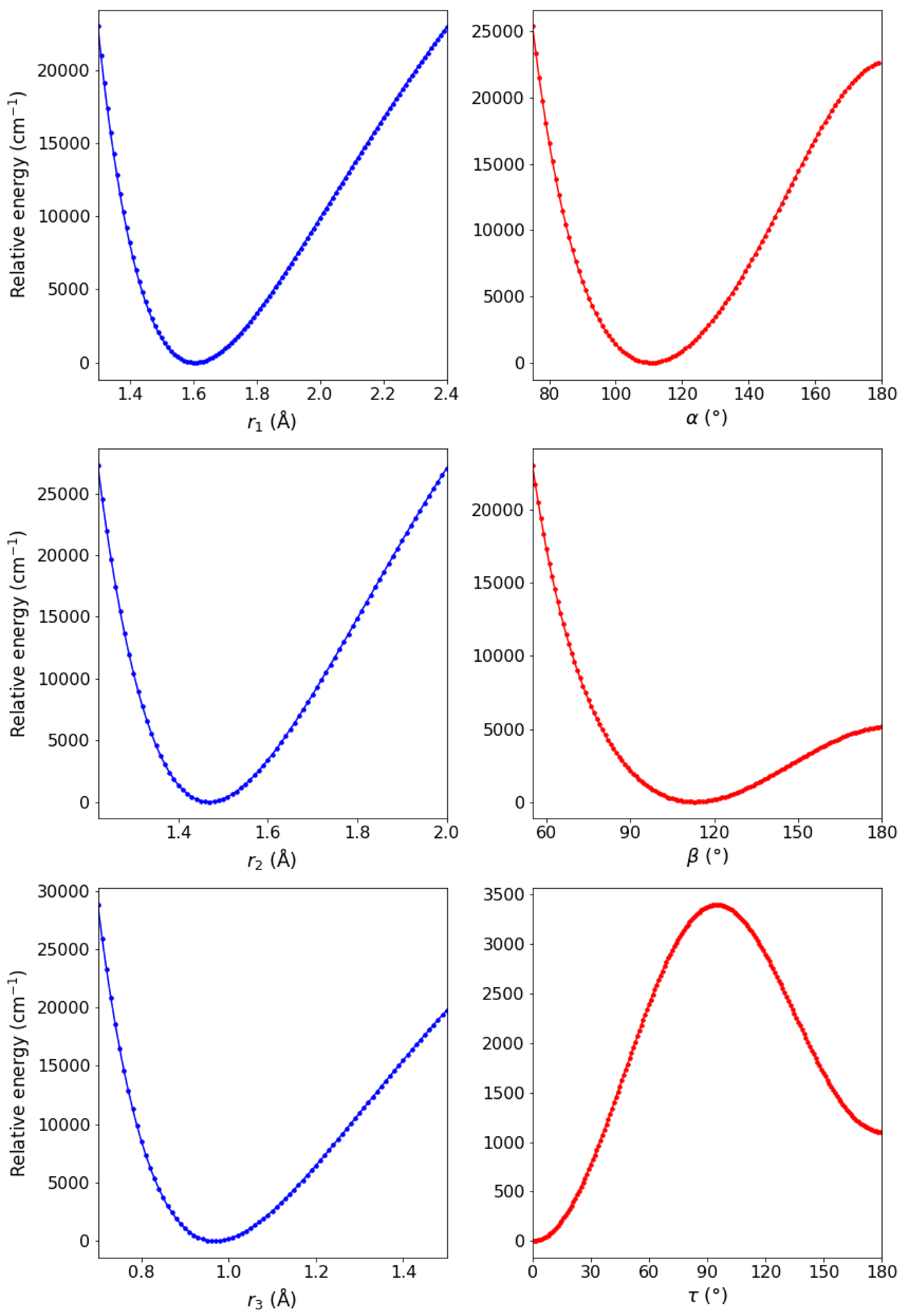
…and many more! However, transition barrier energies are too high, so we only consider the main two isomers [3].

5. Six Internal Coordinates:



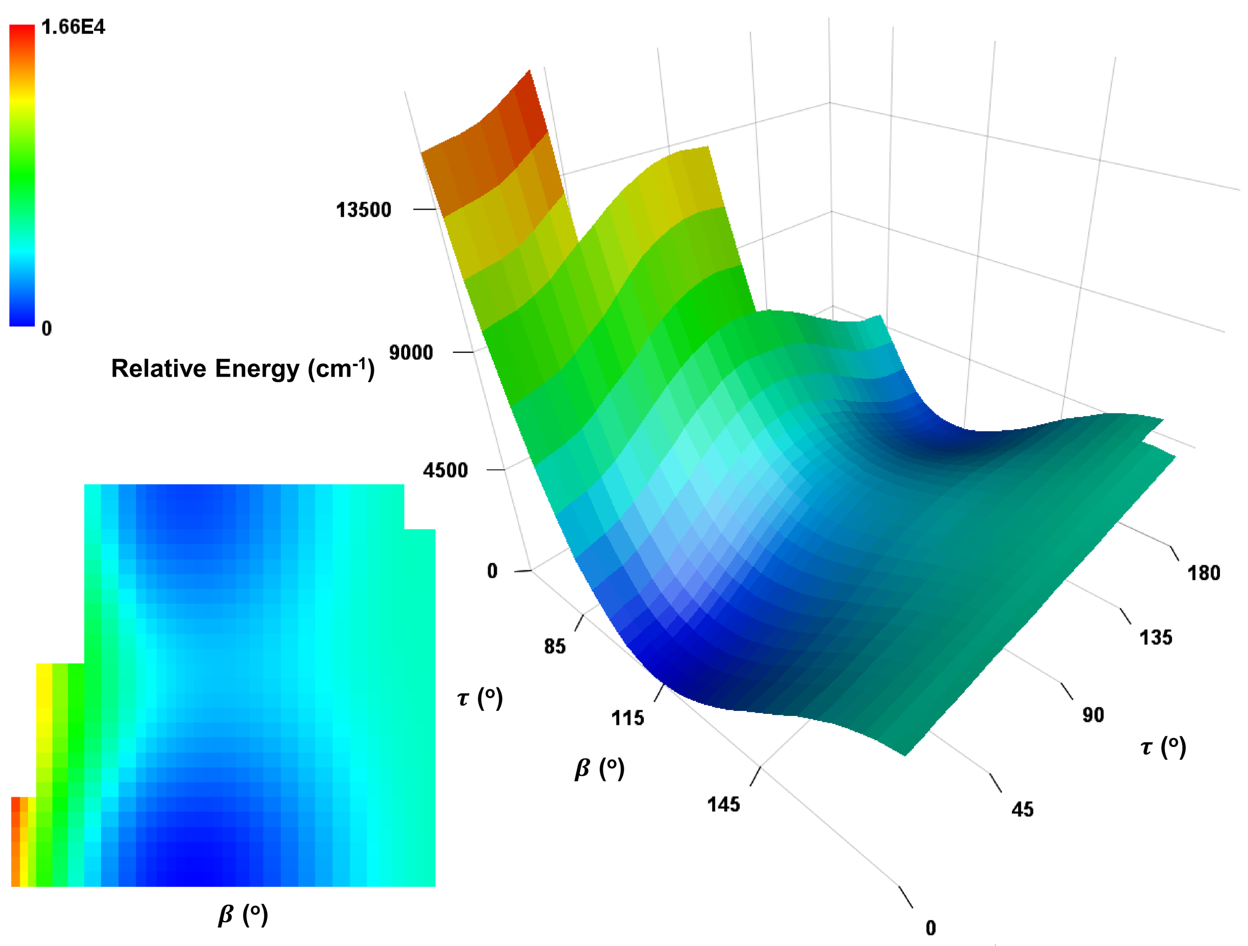
The PES is a function of these 6 coordinates!

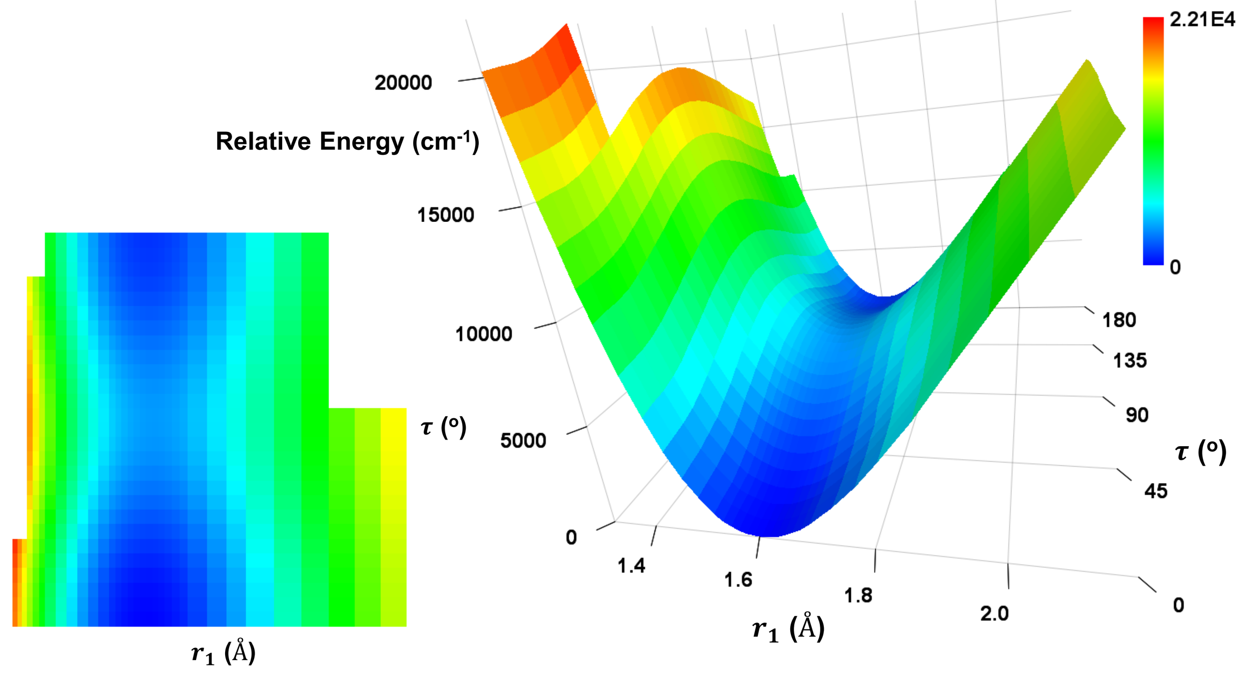
6. 1D Potential Curves

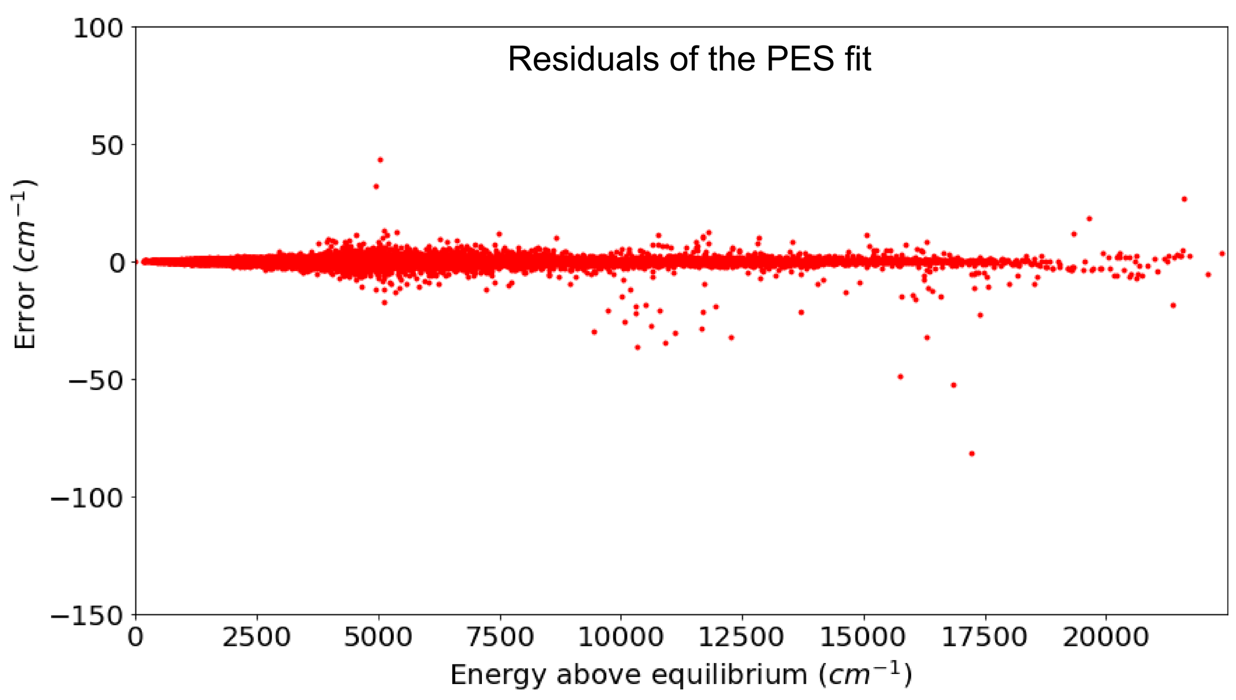


- Potential energies are calculated for 31,226 geometries at the CCSD(T)-F12b/cc-pVQZ-F12 level (energies up to 20,000 cm^{-1} relative to the minimum).
- The relatively shallow potential energy barriers of the β and τ coordinates complicate nuclear motion – leads to floppy molecule behaviour.

7. 2D Potential Surfaces







8. 6D PES Fit

- Calculated energies are fit to a sum-of-product series expansion function. The expansion is truncated to include up to 8th order terms.
- The fitted surface obtained has a weighted RMSD of 0.91 cm^{-1}. It contains 989 linear parameters and 8 non-linear parameters. The large number of parameters is required due to the lack of symmetry (there are no constraints on the values parameters can take).
- A plot of the residuals from the fitting can be observed in the graph below, which appears well distributed.

9. What's Next?

The PES constructed improves on previous calculations performed by Erfort et al. [4]. Computation of transition energies using the PES is under progress with the TROVE program.

A dipole moment surface has also been constructed, which allows calculation of transition intensities. In the future we hope the spectra of the HOPO molecule can be computed.

[1] Lee, E. K. H., Tsai, S.-M., Moses, J. I., Plane, J. M. C., Visscher, C., & Klippenstein, S. J. (2024). "A Photochemical Phosphorus–Hydrogen–Oxygen Network for Hydrogen-dominated Exoplanet Atmospheres". The Astrophysical Journal, 976(2), 231.

[2] Zilinskas, M., van Buchem, C. P. A., Zieba, S., Miguel, Y., Sandford, E., Hu, R., Patel, J. A., Bello-Arufe, A., Janssen, L. J., Tsai, S.-M., Dragomir, D., & Zhang, M. (2025). "Characterising the atmosphere of 55 Cancri e – 1D forward model grid for current and future JWST observations". Astronomy & Astrophysics, 697, A34.

[3] Y. Haitao, C. Yujuan, F. Honggang, H. Xuri, L. Zesheng, and S. Jiazhong, "Structures and stabilities of HPO2 isomers," Science in China Series B: Chemistry, vol. 45, no. 1, pp. 1–7, Dec 2002.

[4] S. Erfort, M. Tschope, G. Rauhut, X. Zeng, and D. P. Tew, "Ab initio calculation of rovibrational states for non-degenerate double-well potentials: cis–trans isomerization of HOPO," The Journal of Chemical Physics, vol. 152, no. 17, p. 174306, 05 2020.