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Publication date:
2012

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):

Underwood, D., Yurchenko, S. N., Tennyson, J., & Fateev, A. (2012). *Variationally computed ro-vibrational energies of sulphur trioxide*. Poster session presented at 22nd International Conference on High Resolution Molecular Spectroscopy, Prague, Czech Republic.

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Variationally Computed Ro-Vibrational Energies of Sulphur Trioxide

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Introduction

We present preliminary results of a collaboration between academic and industrial efforts.

We aim to create a high-temperature spectroscopic database for SO_3 which is essential in the analysis of complex data sets obtained through *in situ* measurements on industrial fuel units in power plants.



Ultimately, the results will be used in working to:

- increase the efficiency of electricity production by reducing NO_x emissions;
- optimising Ammonia consumption (Ammonia is used as a reductant);
- reducing material corrosion and;
- prolonging lifetimes of the selective catalytic reduction units.

Atmospheric & Astronomical significance:

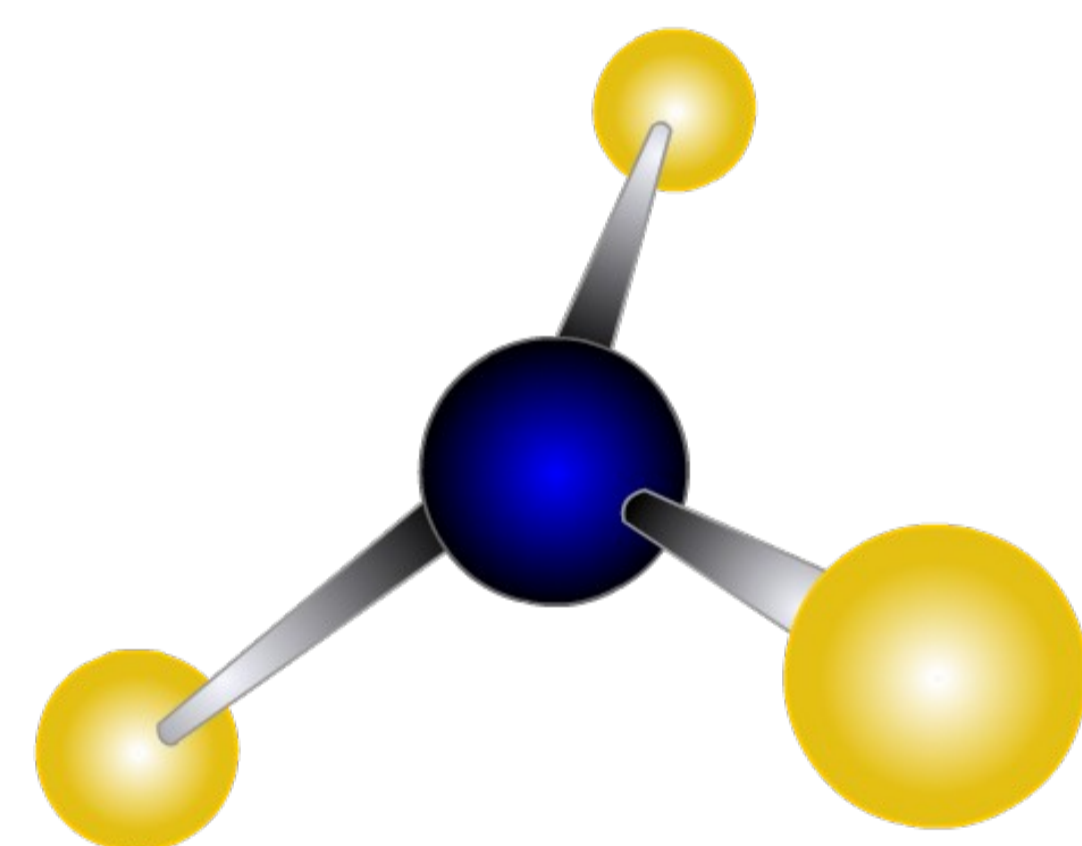
SO_3 is also a contributor to the formation of acid rain, and plays a significant role in atmospheric chemistry; it is also believed to be a constituent of atmospheres in astronomical environments, such as Venus and Io [1].

The Molecule

- A trigonal planar molecule that belongs to the D_3h point group.

- Has 4 fundamental vibrational modes:

- A_1' symmetric stretch
- A_1'' out-of-plane bend
- E' antisymmetric stretch
- E'' in-plane bend



Quantum Numbers: J, K, v_1, v_2, v_3, v_4

- Is composed entirely of spin-0 Bosons and therefore has only a single nuclear spin configuration and must exhibit an overall symmetric wavefunction.

- We therefore only have allowed ro-vibrational transitions between states of A_1' and A_1'' symmetries.

- SO_3 is a relatively heavy molecule with a small rotational constant ($B = 0.34854333(5)\text{cm}^{-1}$ [2]). Calculations of ro-vibrational energies up to high values of J are therefore necessary for large coverage in the production of synthetic spectra.

Computational Background and TROVE

- Potential Energy Surface used in this work computed using MOLPRO.

- Re-adjusted to an experimentally determined equilibrium bond length (1.41732 Angstroms [3]).

- PES is then used by TROVE [4] to calculate ro-vibrational wavefunctions and energy calculations.

- For SO_3 we define an active space such to maximise computational efficiency by the truncation of the Hamiltonian matrix blocks. This is based on the following:

- Calculations of ro-vibrational energies up to and including $10,000\text{cm}^{-1}$;
- SO_3 exhibits a polyad structure, and thus we can employ the polyad number [2]. We impose the condition on the quantum numbers that $P = 2(v_1 + v_3) + v_2 + v_4 \leq 14$
- Computational time is further reduced by noting that only energy levels of A_1' and A_1'' symmetry are required.

Results

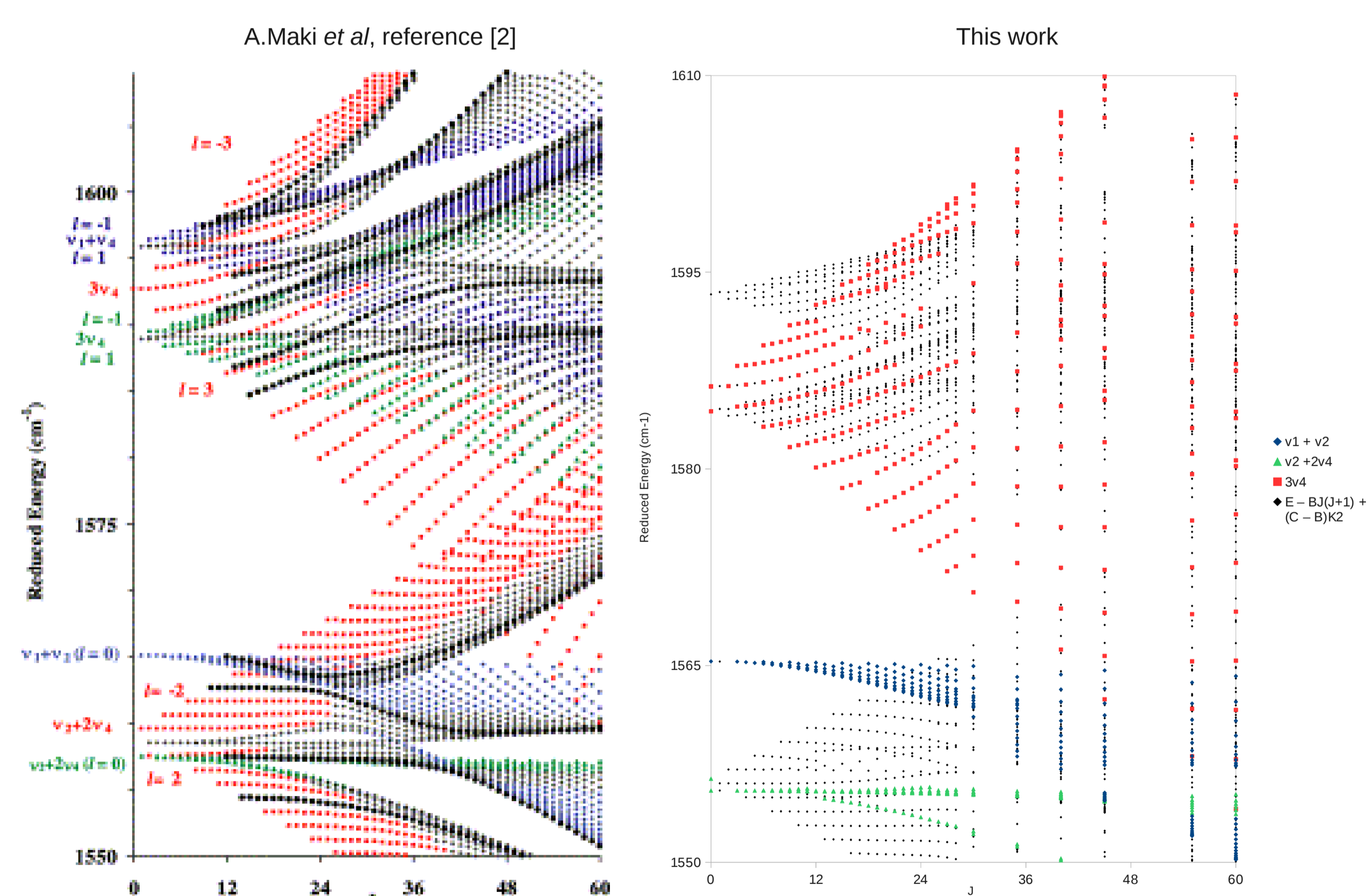
Fundamental Vibrations & Some Overtone/Combinations

	Experimental [2]	This Work	Martin [3]
v1	1064.924 cm^{-1}	1065.738 cm^{-1}	1064.219 cm^{-1}
v2	497.567 cm^{-1}	498.475 cm^{-1}	487.100 cm^{-1}
v3	1391.520 cm^{-1}	1387.428 cm^{-1}	1386.854 cm^{-1}
v4	530.086 cm^{-1}	528.580 cm^{-1}	527.321 cm^{-1}
2v2	995.018 cm^{-1}	995.346 cm^{-1}	970.366 cm^{-1}
2v3(l=2)	2777.871 cm^{-1}	2769.954 cm^{-1}	2770.080 cm^{-1}
2v4(l=0)	1059.814 cm^{-1}	1056.440 cm^{-1}	1054.702 cm^{-1}
2v4(l=2)	1060.452 cm^{-1}	1057.332 cm^{-1}	1055.383 cm^{-1}
v2 + v4	1027.902 cm^{-1}	1027.325 cm^{-1}	1013.453 cm^{-1}

Pure Rotational Energies

J	K	Experimental [2]	This Work	Difference
2	0	2.091 cm^{-1}	2.091 cm^{-1}	0.0003 cm^{-1}
4	0	6.970 cm^{-1}	6.971 cm^{-1}	0.001 cm^{-1}
6	0	14.638 cm^{-1}	14.640 cm^{-1}	0.002 cm^{-1}
8	0	25.093 cm^{-1}	25.097 cm^{-1}	0.003 cm^{-1}
10	0	38.336 cm^{-1}	38.341 cm^{-1}	0.005 cm^{-1}
20	0	146.333 cm^{-1}	146.354 cm^{-1}	0.021 cm^{-1}
40	0	323.876 cm^{-1}	323.923 cm^{-1}	0.046 cm^{-1}
60	0	1271.537 cm^{-1}	1271.704 cm^{-1}	0.167 cm^{-1}
70	30	1569.767 cm^{-1}	1569.969 cm^{-1}	0.201 cm^{-1}

Comparison of Reduced Energies ($E_{jk}' - E_{jk}''$) in 1550-1610 cm^{-1} Region



Next Step...

- We aim to complete the current work by calculating all ro-vibrational energies up to $J = 100$.
- To spectroscopically refine a new PES computed at the aug-cc-pVQZ-f12 level of theory.
- Calculations of an *ab initio* Dipole Moment Surface have already begun, using a aug-cc-pVTZ-f12 basis set, with preliminary intensity results for transitions up to $J = 20$. We will eventually calculate intensities up to $J = 100$ ($T = 300\text{K}$).

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Acknowledgements

The projects are supported by the ERC grant (Advanced Investigator Project 267219) and by Energinet.dk (Denmark, Project 10442).