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Publication date:
2012

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

Variationally Computed Ro-Vibrational Energies of Sulphur Trioxide

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Introduction

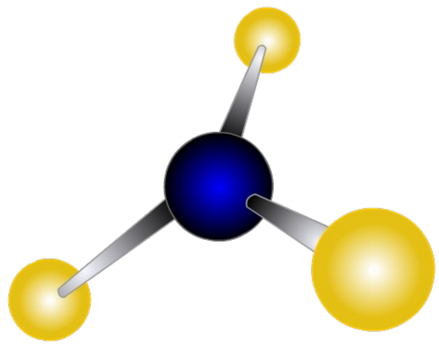
We present preliminary results of a collaboration between academic and industrial efforts.

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 point group.

- Has 4 fundamental vibrational modes:
  - A' symmetric stretch
  - A'' out-of-plane bend
  - E' antisymmetric stretch
  - E' in-plane bend

Quantum Numbers: J, K, v_1, v_2, $v_3^{l_3}$, $v_4^{l_4}$

- 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' and A'' symmetries.

- SO_3 is a relatively heavy molecule with a small rotational constant ($B = 0.34854333(5)cm^{-1}$ [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 $10{,}000cm^{-1}$;
  - SO_3 exhibits a polyad structure, and thus we can employ the polyad number [2]. We impose the condition on the quantum numbers that $P = 2(v1 + v3) + v2 + v4 \leq 14$
  - Computational time is further reduced by noting that only energy levels of A' and A'' symmetry are required.

Results

Fundamental Vibrations & Some Overtone/Combinations

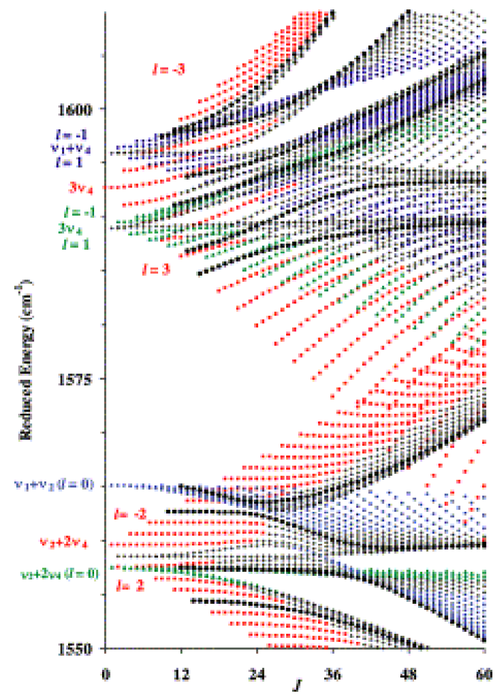
	Experimental [2]	This Work	Martin [3]
v1	$1064.924cm^{-1}$	$1065.738cm^{-1}$	$1064.219cm^{-1}$
v2	$497.567cm^{-1}$	$498.475cm^{-1}$	$487.100cm^{-1}$
v3	$1391.520cm^{-1}$	$1387.428cm^{-1}$	$1386.854cm^{-1}$
v4	$530.086cm^{-1}$	$528.580cm^{-1}$	$527.321cm^{-1}$
2v2	$995.018cm^{-1}$	$995.346cm^{-1}$	$970.366cm^{-1}$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

Pure Rotational Energies

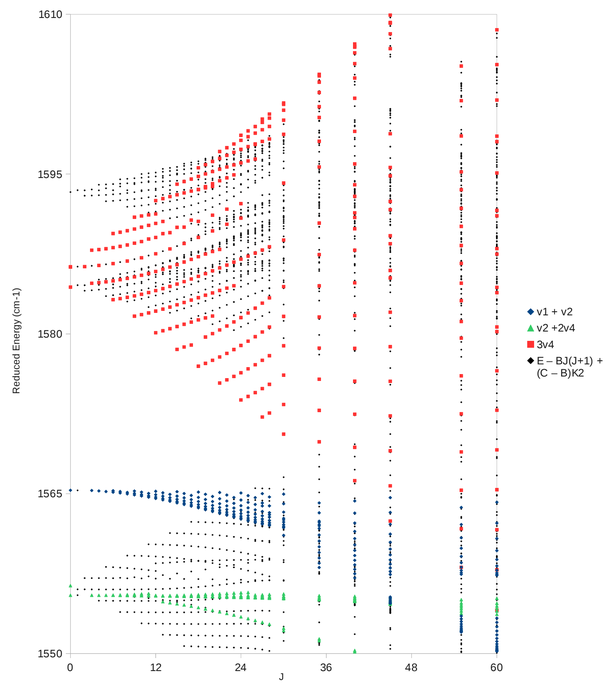
J	K	Experimental [2]	This Work	Difference
2	0	$2.091cm^{-1}$	$2.091cm^{-1}$	$0.0003cm^{-1}$
4	0	$6.970cm^{-1}$	$6.971cm^{-1}$	$0.001cm^{-1}$
6	0	$14.638cm^{-1}$	$14.640cm^{-1}$	$0.002cm^{-1}$
8	0	$25.093cm^{-1}$	$25.097cm^{-1}$	$0.003cm^{-1}$
10	0	$38.336cm^{-1}$	$38.341cm^{-1}$	$0.005cm^{-1}$
20	0	$146.333cm^{-1}$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

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

A.Maki *et al*, reference [2]



This work



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 = 300K).

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Acknowledgements

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