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Spectroscopically Accurate Line Lists for Application in Sulphur Chemistry

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Abstract

Monitoring sulphur chemistry is thought to be of great importance for exoplanets. Doing this requires detailed knowledge of the spectroscopic properties of sulphur containing molecules such as hydrogen sulphide (H_2S) [1], sulphur dioxide (SO_2), and sulphur trioxide (SO_3). Each of these molecules can be found in terrestrial environments, produced in volcano emissions on Earth, and analysis of their spectroscopic data can prove useful to the characterisation of exoplanets, as well as the study of planets in our own solar system, with both having a possible presence on Venus.

A complete, high temperature list of line positions and intensities for $H_2^{32}S$ is presented. The DVR3D program suite is used to calculate the bound ro-vibration energy levels, wavefunctions, and dipole transition intensities using Radau coordinates. The calculations are based on a newly determined, spectroscopically refined potential energy surface (PES) and a new, high accuracy, *ab initio* dipole moment surface (DMS). Tests show that the PES enables us to calculate the line positions accurately and the DMS gives satisfactory results for line intensities. Comparisons with experiment as well as with previous theoretical spectra will be presented. The results of this study will form an important addition to the databases which are considered as sources of information for space applications; especially, in analysing the spectra of extrasolar planets, and remote sensing studies for Venus and Earth, as well as laboratory investigations and pollution studies.

An *ab initio* line list for SO_3 was previously computed using the variational nuclear motion program TROVE [2], and was suitable for modelling room temperature SO_3 spectra. The calculations considered transitions in the region of 0-4000 cm^{-1} with rotational states up to J = 85, and includes 174,674,257 transitions. A list of 10,878 experimental transitions had relative intensities placed on an absolute scale,

and were provided in a form suitable for inclusion in standard atmospheric and planetary spectroscopic databases. The methods involved in computing the *ab initio* potential energy and dipole moment surfaces involved minor corrections to the equilibrium S-O distance, which produced a good agreement with experimentally determined rotational energies. However the purely *ab initio* method was not been able to reproduce an equally spectroscopically accurate representation of vibrational motion. We therefore present an empirical refinement to this original, *ab initio* potential surface, based on the experimental data available. This will not only be used to reproduce the room-temperature spectrum to a greater degree of accuracy, but is essential in the production of a larger, accurate line list necessary for the simulation of higher temperature spectra: we aim for coverage suitable for T $\leq$ 800 K.

Our preliminary studies on SO_3 have also shown it to exhibit an interesting "forbidden" rotational spectrum and "clustering" of rotational states; to our knowledge this phenomenon has not been observed in other examples of trigonal planar molecules and is also an investigative avenue we wish to pursue.

Finally, the IR absorption bands for SO_2 and SO_3 exhibit a strong overlap, and the inclusion of SO_2 as a complement to our studies is something that we will be interested in doing in the near future.
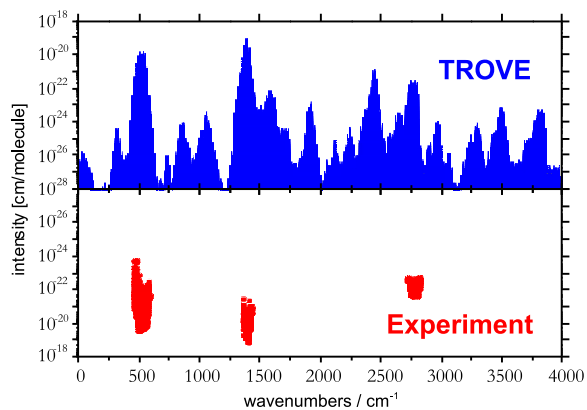
1. Figures

Figure 1: An overview of the T = 298.15 spectrum of SO_3; a comparison between our work and the normalised experimental data.

References

[1] A.A.A. Azzam, S.N. Yurchenko, J. Tennyson, M.-A. Martin, O. Pirali, J. Quant. Spectrosc. Radiat. Transf. (submitted).

[2] Daniel S. Underwood, S.N. Yurchenko, J. Tennyson, Phys. Chem. Chem. Phys., 2013, Advance Article (http://xlink.rsc.org/?doi=C3CP50303H)