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ExoMol molecular line lists – XVII. The rotation–vibration spectrum of hot SO₃

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ABSTRACT

Sulphur trioxide (SO₃) is a trace species in the atmospheres of the Earth and Venus, as well as being an industrial product and an environmental pollutant. A variational line list for ³²S¹⁶O₃, named UYT2, is presented containing 21 billion vibration–rotation transitions. UYT2 can be used to model infrared spectra of SO₃ at wavelengths longwards of 2 μm (ν < 5000 cm⁻¹) for temperatures up to 800 K. Infrared absorption cross-sections recorded at 300 and 500°C are used to validate the UYT2 line list. The intensities in UYT2 are scaled to match the measured cross-sections. The line list is made available in electronic form as supplementary data to this article and at www.exomol.com.

Key words: molecular data – opacity – astronomical data bases: miscellaneous – planets and satellites: atmospheres.

1 INTRODUCTION

SO₃ is known to exist naturally in the Earth’s atmosphere; its main natural source is volcanic emissions and hot springs (Michaud et al. 2005). However, SO₃ also plays a role in the formation of acid rain. The oxidation of SO₂ to SO₃ in the atmosphere, followed by subsequent rapid reaction with water vapour results in the production of sulphuric acid (H₂SO₄) (Calvert et al. 1985) with many adverse environmental effects (Kolb, Jayne & Worsnop 1994; Srivastava et al. 2004; Vahedpour et al. 2011). SO₃ is a natural product whose concentration in the atmosphere is significantly enhanced by human activity, particularly as a by-product of industrialization. SO₃ is observed in the products of combustion processes (Srivastava et al. 2004; Hietala & Merimaa 2014) and selective catalytic reduction units, where the presence of both is undesirable within flue gas chambers in large quantities, as well as other industrial exhausts (Rawlins et al. 2005; Fleig et al. 2012). The control of these outputs is therefore of great importance. The spectroscopic study of sulphur oxides can also provide insight into the history of the Earth’s atmosphere (Whitehill et al. 2013). All this means that observation of SO₃ spectra and hence concentrations provide a useful tool for understanding geological processes and controlling pollution.

Sulphur oxide chemistry has been observed in a variety of astrophysical settings. Within the Solar system, SO₃ is a constituent of the atmosphere of Venus (Craig et al. 1983; Zhang et al. 2010, 2012). Although SO₃ has yet to be observed outside our Solar system, it needs to be considered alongside other sulphur oxides, namely sulphur monoxide (SO) and SO₂, which are well known in several astronomical environments (Na, Esposito & Skinner 1990; Petuchowski & Bennett 1992; Martin et al. 2003, 2005; Visscher, Lodders & Fogley 2006; Belyaev et al. 2012; Adande, Edwards & Ziurys 2013; Belloche et al. 2013; Khayat et al. 2015). SO₃ chemistry has been considered in a number of environments including giant planets, brown dwarfs, and dwarf stars (Visscher et al. 2006). Unlike SO and SO₂, SO₃ is a symmetric species with no permanent dipole moment making it hard to detect in the interstellar medium. In practice, the identification of SO₃ in the infrared is hindered by the presence of interfering SO₂ where both species are found simultaneously; a number of their spectral features overlap, particularly the ν₃ bands of both molecules in the 1300–1400 cm⁻¹ (7.4 μm) region. From this point of view, SO₂ can also be seen as a spectral ‘weed’ with respect to the detection of SO₃. An understanding of the spectroscopic behaviour of both of these molecules within the same spectral window is therefore required to be able to correctly identify each species independently. In this context, we note that a number of line lists are available for SO₂ isotopologues (Huang, Schwenke & Lee 2014, 2016; Underwood et al. 2016); of particular relevance is the recent hot ExoAmes line list of Underwood et al. (2016).

The experimental spectroscopic studies of SO₃ have significant gaps, notably the absence of any measurement of absolute line intensities in the infrared. This may be attributed to its vigorous chemical reactivity which makes measurements difficult. SO₃ is a symmetric planar molecule with equilibrium S–O bond lengths of 1.417 32 Å and interbond angles of 120° (Ortigoso, Escribano &...
2 THEORETICAL METHOD

Computing a variational line list requires three components (Lodi & Tennyson 2010): a suitable potential energy surface (PES), dipole moment surfaces (DMS), and a nuclear motion program. The use of variational nuclear motion programs, which use basis functions to provide direct solutions of the rotation–vibration Schrödinger equation for a given PES, means that interactions between the levels associated with different vibrational states and the associated intensity stealing between these bands are automatically included in the calculation. In particular, the use of exact kinetic energy (KE) operators means that how well these effects are reproduced depends strongly on the PES used; the reader is referred to a recent study by Zak et al. (2016) for a discussion of this.

Here, the nuclear motion calculations are performed with the flexible, polyatomic vibration–rotation nuclear motion program TROVE (Yurchenko, Thiel & Jensen 2007). The ab initio DMS surface was adopted unaltered from our previous calculations (Underwood et al. 2013) (UYT); below we describe refinement of the PES. Both the ab initio PES and DMS were computed at the coupled-clusters (CCSD(T)-F12b) level of theory with appropriate triple-ζ basis sets, aug-cc-pVTZ-F12 and aug-cc-pV(T+d)Z-F12 for O and S, respectively.

The label F12b in the theoretical model denotes the use of explicitly correlated functions, which are designed to accelerate basis set convergence. The F12b variant is an efficient F12 implementation due to Adler, Knizia & Werner (2007). Use of CCSD(T)-F12b methods has been shown to give improved vibrational frequencies compared to standard CCSD(T) calculations (Martin & Kesharwani 2014) but their use for intensity calculations remains relatively untested. We return to this issue below.

2.1 Refining the potential energy surface

The refinement of the ab initio PES involved performing a least-squares fit to empirical ro-vibrational energies or observed transition frequencies. The procedure follows that described elsewhere (Yachmenev et al. 2011; Yurchenko et al. 2011; Sousa-Silva, Yurchenko & Tennyson 2013; Yurchenko & Tennyson 2014) and is based on adding a correction, ΔV, to the ab initio UYT PES, which
\[ \Delta V = \sum_{ijklm} \Delta f_{ijklm} \xi_i^k \eta^l \xi_j^m \xi_k^p \xi_l^q \xi_m^r \xi_n^s \] 

in terms of the same internal coordinates as UYT (Underwood et al. 2013):

\[ \xi_k = 1 - \exp(-\alpha(r_k - r_e)), \ \xi = 1, 2, 3, \] 

\[ \xi_4 = \frac{1}{\sqrt{6}}(2\alpha_{13} - \alpha_{1} - \alpha_{12}), \] 

\[ \xi_5 = \frac{1}{\sqrt{2}}(\alpha_{13} - \alpha_{12}), \] 

\[ \xi_6 = \sin \rho_e - \sin \overline{\rho}, \] 

where

\[ \sin \overline{\rho} = \frac{2}{\sqrt{3}} \sin[(\alpha_{13} + \alpha_{1} + \alpha_{12})/6]. \] 

\sin \rho_e is the equilibrium value of \sin \overline{\rho}, \alpha is a molecular parameter, and \Delta f_{ijklm} are expansion coefficients. Here, \( r_i \) is a bond length and \( \alpha_{ij} \) is an interbond angle. Further details of this functional form and symmetry relations between \( \Delta f_{ijkl} \) can be found elsewhere (Yurchenko et al. 2005b; Underwood et al. 2013).

The refined potential coefficients \( \Delta f_{ijkl} \) were determined using a least-squares fitting algorithm which uses the derivatives of energies with respect to \( \Delta f_{ijkl} \) computed via the Hellmann–Feynman theorem (Feynman 1939). The process starts by setting all \( \Delta f_{ijkl} = 0 \). The resulting refined PES is only an ‘effective’ one since it depends on any approximation in the nuclear motion calculations; it is therefore dependent on the levels of KE and PES expansion, and basis set used (see below). As a result of this, improving the nuclear motion calculation may lead to worse agreement with the observations.

The experimental data for the energies is taken from the extensive high resolution infrared studies of Maki and co-workers (Kaldor et al. 1973; Ortigoso et al. 1989; Chrysostom et al. 2001; Makie et al. 2001; Barber et al. 2002; Sharpe et al. 2003; Makie et al. 2004). The majority of these studies provide upper and lower energy states labelled by their vibrational normal mode and rotational \( (J, K) \) quantum numbers, which were validated using effective Hamiltonians. However, the bands studied by Maki et al. (2004) label transitions by rotational and vibrational quantum numbers, but do not list upper and lower energy levels. Combination differences were used to obtain energies for these bands using the experimental line positions reported by the accompanying publications; these are highlighted in Table 1. In matching experimental and computed energies, a number of experimentally derived energies were not included in the fit; these correspond to transitions excluded by Maki et al. (2004) from their Hamiltonian fits. A total of 119 energy levels for \( J \leq 5 \) were chosen from this set based on their reliability at reproducing the observed transitions, with the condition that they are physically accessible states with \( A' \) or \( A'' \) symmetry; any published values of experimentally derived purely vibrational terms (i.e. band centres) that are inaccessible were not included.

Table 1 shows the effect of the final potential refinement on the bands used in the refining procedure. The root mean square (rms) differences are calculated by matching all experimental lines for each band with calculated values via their quantum number assignments for all \( J \leq 5 \) available.

The rms differences calculated are slightly increased as a result of the refinement when including higher \( (J > 5) \) term values compared to the residuals in Table 3 for the \( v_1 + v_2 \) and \( v_1 + v_4 \) bands. The experimental energy levels used to refine these two bands were obtained using combination differences. However, for some rotationally excited levels within these bands, the quantum number labelling of the experimental transitions appears dubious: in particular there are a number of transitions whose labels are duplicated. These transitions were not included in the rms difference calculations but there must be some doubt about the validity of the quantum number assignments of the other transitions in these bands. This may well explain the increased rms difference.

Table 2 compares all published vibrational \( (J = 0) \) term values with those calculated with TROVE before and after refinement. There are some discrepancies introduced by the refinement procedure and in some cases deteriorations from the pre-refined values (e.g. \( 2v_2 \)).

The quality of the refinement can be assessed from Table 1, with the exception of \( 3v_2 \), for which there is no experimental band data available beyond the quoted vibrational term value (Maki et al. 2004). Table 3 lists all the \( J = 5 \) levels used in the refinement process, comparing with their final computed counterparts.

Our refined PES is given as Supplementary Information to this article.

### 2.2 Calculation using TROVE

In specifying a calculation using TROVE, it is necessary to fix a number of parameters. In particular, both the KE and PES are expanded as a Taylor series about the equilibrium geometry (Yurchenko et al. 2007). For UYT the expansions were truncated at fourth and eighth orders, respectively. Here, the KE expansion order was increased to sixth in order to allow better convergence. For the detailed description of the basis set see Underwood et al. (2013). Here, it suffices to define the maximal polyad number \( P_{\text{max}} \) used in TROVE to control...
the size of the basis set. The polyad number in the case of $SO_3$ in terms of the normal mode quantum numbers is given by

$$P = 2(n_1 + n_3) + n_2 + n_4,$$

(7)

where $n_1$, $n_2$, $n_3$, and $n_4$ are the normal mode quanta associated with the $v_1$, $v_2$, $v_3$, and $v_4$ vibrational modes. For the UYT2 calculations, the value of $P_{\text{max}}$ was set initially to 24 for the 1D primitive basis functions to form a product-type basis set, which was then contracted to $P_{\text{max}} = 18$ after a set of pre-diagonalizations of reduced Hamiltonian matrices and symmetrized. The value of $P_{\text{max}}$ used for UYT was 12. This increase was necessary to allow better convergence of the increased number of energies which is needed for high-temperature spectra. Only energies lying up to 10 000 cm$^{-1}$ above the ground state were considered as part of this study.

The high symmetry of $^{32}S^{16}O_3$, and the associated nuclear spin statistics, means that it is only necessary to consider transitions between $A'_1$ and $A''_1$ symmetries of the $D_{6h}$ point group used for the calculations. The final UYT2 line list consists of all allowed transitions between $0 < \nu \leq 5000$ cm$^{-1}$, satisfying the conditions $E' \leq 9000$ cm$^{-1}$, $E'' \leq 4000$ cm$^{-1}$, and $J \leq 130$. These parameters are designed to give a complete spectrum up to 5000 cm$^{-1}$ ($\lambda > 2$ mm) for temperatures up to about 800 K. Generating a complete line list with these parameters is computationally demanding and therefore requires special measures to be taken.

In terms of memory, diagonalization of the Hamiltonian matrices is the most computationally expensive part of the line list calculation. For each $J$, a matrix is built (Yurchenko et al. 2007, 2009) and then stored in the memory for diagonalization, using an appropriate eigensolver routine. TROVE uses a symmetry adapted basis set representation and allows splitting of each Hamiltonian matrix further into the six symmetry blocks ($A'_1$, $A'_2$, $E'$, $A''_1$, $A''_2$, and $E''$) which are dealt with separately. Since only the $A'_1$ and $A''_1$ symmetry species are allowed by the nuclear statistics of $^{32}S^{16}O_3$, only these symmetry blocks are diagonalized.

Memory requirements scale with the square of the dimension of the Hamiltonian matrix used for the calculations. For UYT2, the combined dimension $N_{\text{max}}$ of both $A'_1$ and $A''_1$ symmetries is 2692; for comparison, the UYT line list calculations used $N_{\text{max}} = 679$. The size of the largest matrix considered in the room-temperature calculations (for $J = 85$) is $N_{\text{max}} = 111$ 296, which is already surpassed by $J = 21$ for UYT2 for which the value of $N_{\text{max}} = 454$ 488. It became quickly apparent that the diagonalization techniques previously employed to determine the UYT wavefunctions would be impractical for UYT2.

Nuclear motion calculations were performed using both the Darwin and COSMOS high performance computing (HPC) facilities in Cambridge, UK. Each of the computing nodes on the Darwin cluster provide 16 CPUs across two 2.60 GHz 8-core Intel Sandy

### Table 2. Comparisons of vibrational ($J = 0$) terms for $SO_3$, between experimental values (Maki et al. 2001), and the ab initio (UYT) and refined (UYT2) PES. All values are in cm$^{-1}$.

<table>
<thead>
<tr>
<th>$v_2$</th>
<th>Obs.</th>
<th>UYT</th>
<th>UYT2</th>
</tr>
</thead>
<tbody>
<tr>
<td>497.57</td>
<td>498.48</td>
<td>497.56</td>
<td></td>
</tr>
<tr>
<td>530.09</td>
<td>528.59</td>
<td>530.09</td>
<td></td>
</tr>
<tr>
<td>995.02</td>
<td>995.35</td>
<td>993.67</td>
<td></td>
</tr>
<tr>
<td>1027.90</td>
<td>1027.35</td>
<td>1027.33</td>
<td></td>
</tr>
<tr>
<td>1059.81</td>
<td>1056.50</td>
<td>1059.48</td>
<td></td>
</tr>
<tr>
<td>1060.45</td>
<td>1057.38</td>
<td>1060.45</td>
<td></td>
</tr>
<tr>
<td>1064.92</td>
<td>1065.75</td>
<td>1066.49</td>
<td></td>
</tr>
<tr>
<td>1391.52</td>
<td>1387.45</td>
<td>1391.51</td>
<td></td>
</tr>
<tr>
<td>1492.35</td>
<td>1490.76</td>
<td>1488.47</td>
<td></td>
</tr>
</tbody>
</table>

*The value $L$ is given by $L = |l_1 + l_4|$, see Maki et al. (2004).*

### Table 3. Observed (Maki et al. 2001) minus calculated residuals for the $J = 5$ energy levels used in the refinement procedure. All values are in cm$^{-1}$. The corresponding values for $J \leq 5$ are given in Underwood (2016).

<table>
<thead>
<tr>
<th>State</th>
<th>$K$</th>
<th>Obs.</th>
<th>UYT2</th>
<th>Obs. – Calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_0$</td>
<td>3</td>
<td>8.885</td>
<td>8.886</td>
<td>−0.001</td>
</tr>
<tr>
<td>$v_2$</td>
<td>3</td>
<td>506.367</td>
<td>506.360</td>
<td>0.008</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>507.900</td>
<td>507.893</td>
<td>0.007</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>535.323</td>
<td>535.312</td>
<td>0.011</td>
</tr>
<tr>
<td>$v_1$</td>
<td>4</td>
<td>538.471</td>
<td>538.490</td>
<td>−0.020</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>539.561</td>
<td>539.560</td>
<td>0.001</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>540.677</td>
<td>540.685</td>
<td>−0.008</td>
</tr>
</tbody>
</table>

*The value $L$ is given by $L = |l_1 + l_4|$, see Maki et al. (2004).*
Bridge E5-2670 processors, and a maximum of 64 Gb of RAM. The advantage of moving eigenfunction calculations to the Darwin cluster is that an entire node can be dedicated to one calculation, spread across the 16 CPUs. Since multiple nodes can be accessed by a single user at any time, multiple computations were carried out simultaneously.

Diagonalization of matrices with \( J \leq 32 \) was possible using the LAPACK DSYEV eigensolver (Anderson et al. 1999), optimized for OpenMP parallelization across multiple (16) CPUs. For \( 32 < J \leq 90 \), a distributed memory approach was used with an message passing interface (MPI)-optimized version of the eigensolver, PDSYEV, which allowed diagonalizations across multiple Darwin/COSMOS nodes in order to make use of their collective memory. In order to diagonalize the matrix within the 36 h wall-clock limit, it was necessary to perform this method in three steps. First, for a given \( J \) and symmetry species \( \Gamma \), the Hamiltonian matrix was constructed and saved to disc. Secondly, the matrix was then read and diagonalized using PDSYEV across the number of nodes required to store the matrix in their shared memory. This produces a set of eigenvectors which were read in again to convert into the TROVE eigensolution format.

For \( J > 90 \), yet another approach was developed for use on the COSMOS shared memory machine. This method employed the PLASMA DSYTRDX routine (Kurzak et al. 2013) and, unlike the above procedure, constructed, diagonalized and stored wavefunctions to disc in a single process by extending both the standard wall-clock time and memory limits. For \( J = 130 \) (\( \Gamma = \Gamma' \)), a total of 52 h of real time was taken to construct and diagonalize the Hamiltonian matrix across 416 CPUs, and utilizing 3140 Gb of RAM.

While diagonalization dominates the memory requirements of the calculation, computing the line strengths, \( S(\nu_i \rightarrow \nu_f) \), is the major use of computer time. In principle, line strengths for all transitions obeying the rigorous electric dipole selection rules, \( \Delta \nu = \nu_f - \nu_i = 0, \pm 1 \) \( (\nu_f + \nu_i \geq 1) \) and \( \Gamma_i' \leftrightarrow \Gamma_f' \), were computed. In practice, this was modified to reduce the computational demands. First, calculations of the line strength only take into consideration eigenvector coefficients greater than \( 10^{-15} \). In addition to this a threshold value for the Einstein A coefficient of \( 10^{-15} \text{s}^{-1} \) dictates which transitions are kept. However, the number of linestrength calculations to be performed still remains very large and even with parallelization across multiple Darwin CPUs, performing the calculations proved to be both computationally expensive and difficult.

To help expedite these computations, an adapted version of TROVE was used which is optimized for performing calculations on graphical processing units (GPUs). The use of this implementation, known as GPU Accelerated INtensities (Al-Refaie, Tennyson & Yurchenko 2016), allowed for the computation of transition strengths for the more computationally demanding parts of the calculations. These calculations were performed on the Emerald GPU cluster, based in Southampton. In general, the calculation of transition strengths across multiple GPUs was much faster than the Darwin CPUs. For example, there are a total of 349 481 979 transitions for \( J' = 35 \), which took a total of 17 338 CPU hours to compute on the Darwin nodes, compared to 2053 GPU hours on the Emerald nodes for 346 620 894 transitions for the larger \( J' = 59 \) case. These GPU calculations were carried out for those \( \nu_i \leftrightarrow \nu_f \) pairs containing a large number of states, while the Darwin CPUs were reserved for the less computationally demanding sections.

21 billion transitions were calculated for UYT2, which is two orders of magnitude larger than UYT. Overall performing the computations needed for the UYT2 line list took us over 2 yr.

3 EXPERIMENTS

SO\(_2\) absorbance measurements at temperatures up to 500 C were performed at the Technical University of Denmark (DTU) using a quartz high-temperature gas flow cell (q-HGC). The cell has been described in detail by Grosch et al. (2013) and has recently been used for measurements with NH\(_2\) (Barton et al. 2015), S-containing gases (Grosch et al. 2015a) and some polycyclic aromatic hydrocarbon compounds (Grosch et al. 2015b).

Because SO\(_2\) is an extremely reactive gas and normally contains traces of SO\(_2\) if ordered from a gas supplier, it was decided to produce SO\(_3\) directly in the set-up. It is known that SO\(_2\) can react with O\(_3\) and form SO\(_3\):

\[
\text{SO}_2 + \text{O}_3 \rightarrow \text{SO}_3 + \text{O}_2. \tag{8}
\]

The rate constant for reaction (8) is temperature dependent: higher temperatures favour SO\(_3\) formation. However, at higher temperatures O\(_3\) starts to decompose into O\(_2\) and O:

\[
\text{O}_3(+M) \rightarrow \text{O}_2 + \text{O}(+M). \tag{9}
\]

Some O and O\(_2\) can contribute further in SO\(_3\) formation and ‘recycle’ O\(_3\):

\[
\text{SO}_2 + \text{O}(+M) \rightarrow \text{SO}_3(+M) + \text{O}. \tag{10}
\]

\[
\text{O} + \text{O}_2(+M) \rightarrow \text{O}_3(+M). \tag{11}
\]

If any water traces are present in the system, SO\(_3\) will rapidly be converted into sulfuric acid (H\(_2\)SO\(_4\)):

\[
\text{SO}_3 + \text{H}_2\text{O}(+M) \rightarrow \text{H}_2\text{SO}_4(+M). \tag{12}
\]

Other possible SO\(_3\) removal channels are:

\[
\text{SO}_3(+M) \rightarrow \text{SO}_2 + \text{O}(+M). \tag{13}
\]

These reactions are very prominent in a clean set-up with ‘active’ surfaces.

In the presence of O\(_2\), a reversible reaction (which is also temperature-dependent) takes place:

\[
2\text{SO}_2 + \text{O}_2(+M) \rightarrow 2\text{SO}_3(+M). \tag{14}
\]

However, SO\(_3\) formation through reaction (14) takes place at temperatures higher than 500 C. The experimental set-up is shown in Fig. 1. It can be divided into two parts: an SO\(_3\) generation part and a part for optical measurements.

The optical part of the set-up includes a high-resolution Fourier transform infrared (FTIR) spectrometer [Agilent 660 with a linearized broad-band mercury cadmium telluride (MCT) detector], the q-HGC and a light-source (Hawkeye, IR-Si217, 1385C) with a KBr plano-convex lens. The light source is placed in the focus of the KBr lens. The FTIR and sections between the FTIR/q-GHC and q-HGC/IR light source have been purged by CO\(_2\)/H\(_2\)O-free air obtained from a purge generator.

The O\(_2\)-generation part consists of a set of high-end mass-flow controllers (MFCs), an O\(_3\)-generator and a unit called the SO\(_3\)-reactor. MFCs (Bronkhorst) have been used to keep constant gas

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flows and mix gas flows of N₂, N₂+SO₂ and O₂+O₃ in desirable ratios. An O₃-generator (WEDECO GSO 30, water cooled, rated capacity at full load 100 g h⁻¹ of O₃ with use of O₂) was used to produce O₃ from O₂. Because of the high O₂ flow rate required for stable operation of the O₃-generator, only a part of the O₂+O₃ flow was used in the measurements. The ozone generator was operated at about 30 per cent (225 W) of the full load. The SO₃-reactor was used in the measurements. The ozone generator was operated at about 60 s at 1 ln min⁻¹. The gas residence time in the SO₃-reactor was about 30 per cent (225 W) of the full load. The SO₃-reactor was connected through a heated Teflon-line (inner diameter 4 mm, 50 mm. N₂ was a 50 cm heated quartz tube (20–200 C) with inner diameter of 20–200 C) to the inlet of the q-HGC. The gas residence time in the Teflon-line was about 0.8 s (at 1 ln min⁻¹) and some further (minor) conversion of SO₂ into SO₃ and at the same time mostly decompose O₃. The SO₃-reactor was connected through a heated Teflon-line (inner diameter 4 mm, T = 20–200 C) to the inlet of the q-HGC. The gas residence time in the Teflon-line was about 0.8 s (at 1 ln min⁻¹) and some further (minor) conversion of SO₂ into SO₃ also took place. Bottles with premixed gas mixture, N₂ + SO₂ (5000 ppm) (Strandmøllen) and N₂/O₂ (99.998 per cent) (AGA) have been used for reference and SO₂/SO₃ absorbance measurements. The main flow in the q-HGC was balanced with the two buffer flows of N₂ from q-HGC’s buffer parts. Most SO₂/SO₃ absorbance measurements were performed at 0.25–0.5 cm⁻¹ nominal spectral resolutions and around atmospheric pressure in the q-HGC. A few measurements were performed at a spectral resolution of 0.09 cm⁻¹. The measurements were performed in the following steps:

(i) N₂ + O₂ in q-HGC, reference spectra, ozone generator ‘off’;
(ii) N₂ + O₂ + SO₂ (2500 ppm) in q-HGC, absorption spectra, ozone generator ‘off’;
(iii) N₂ + O₂ + SO₂ + SO₃ + O₃ in q-HGC, absorption spectra, ozone generator ‘on’, initial SO₂ concentration 2500 ppm;
(iv) N₂ + O₂ + O₃, in q-HGC, ozone generator ‘on’ in order to measure O₃ traces in the q-HGC (addition step used only for some measurements).

O₃ has several absorption bands in 400–6000 cm⁻¹, which do not interfere with SO₂/SO₃ absorption bands. At each step, two measurements were made: with a light source (emission from the cell and light source) and without a light source (emission from the cell). Experimental absorption spectra SO₂/SO₃ were reconstructed in the way described in section 3.1 of Barton et al. (2015). Spectra of SO₂ measured in step 2 have been normalized and subtracted from the composite SO₂+SO₃ spectra obtained in step 3 in order to get the zero absorption signal in vicinity of the SO₂ bands as one can see in Fig. 2. It was further assumed that all SO₂ was consumed to produce SO₃ (i.e. no SO₂ losses channels). Note the various log 10-absorption scales on these figures. The extra (weak) broad feature in the region 1200–1285 cm⁻¹ is caused by the O₃ production in the O₃-generator.

Fig. 3 gives a comparison of our newly measured cross-sections in the 7.4 μm region with those available from the PNQL data base for SO₂ (upper) and SO₃ (lower).

4 OVERVIEW OF THE UYT2 LINE LIST


The energy levels listed in the states file are labelled with the quantum numbers summarized in Table 5 and are based on those recommended by Down et al. (2013) for ammonia with the simplification that one does not need to consider inversion. Only quantum numbers J, gTotal, Γ_total, and the counting index, n are rigorously defined. The remaining quantum numbers represent the largest contribution from rotational and vibrational components of the wavefunction expansion associated with a given state. TROVE provides local mode quantum numbers associated with the basis set construction scheme used (Underwood et al. 2013). The normal mode vibrational quantum numbers, n₁, n₂ and n₃, and their angular momentum projections L₃ = |l₃| and L₄ = |l₄| were obtained from the local mode quantum numbers via the correlation rules

\[ n₁ + n₃ = v₁ + v₂ + v₃, \]

\[ n₂ + n₄ = v₄ + v₅ + v₆, \]

and

\[ l₃ = -n₃, -n₃ + 2, \ldots, n₃ - 2, n₃, \]

\[ l₄ = -n₄, -n₄ + 2, \ldots, n₄ - 2, n₄, \]
Figure 2. Composite SO$_2$ + SO$_3$ + O$_3$ absorption spectrum at 300°C (blue) together with (normalized) SO$_2$ spectrum (olive) and the result of subtraction of SO$_2$ spectrum from the composite one (red): the vicinity of the $\nu_1$ (upper), $\nu_3$ (middle), and $\nu_1 + \nu_3$ (lower) bands of SO$_2$.

where $\nu_1$, $\nu_2$, and $\nu_3$ are three stretching mode quantum numbers, $\nu_4$ and $\nu_5$ are two deformational (asymmetric) bending mode quantum numbers and $\nu_6$ is the inversion local mode (TROVE) quantum number. The mapping between these quantum numbers for a particular level also required knowledge of the energy value and symmetry, since multiple levels may be labelled with the same local mode quantum numbers. In these ambiguous cases, the symmetric mode quantum numbers $n_1$ and $n_2$ were chosen for the lower energies, and $n_3$ and $n_4$ with the higher energies; it was assumed that $L_3$ and $L_4$ increase proportionally with the energies, and are multiples of 3 in the case of $A_1$ or $A_2$ symmetries, or otherwise for the $E$-type symmetry. This mapping is performed by hand at the $J=0$ stage of the calculation, and then propagated to $J > 0$.

The Einstein A coefficient for a particular transition from the initial state $i$ to the final state $f$ is given by

$$A_{if} = \frac{8\pi^2 \tilde{\nu}_{if}^3}{3h} (2J_i + 1) \sum_{A=X,Y,Z} |\langle \Psi_f | \bar{\mu}_A | \Psi_i \rangle |^2,$$

(19)

where $h$ is Planck’s constant, $\tilde{\nu}_{if}$ is the wavenumber of the line, $(hc \tilde{\nu}_{if} = E_f - E_i)$, $J_i$ is the rotational quantum number for the initial state, $\Psi^f$ and $\Psi^i$ represent the TROVE eigenfunctions of the final and initial states, respectively, $\bar{\mu}_A$ is the electronically averaged component of the dipole moment along the space-fixed axis $A = X, Y, Z$ (see also Yurchenko et al. 2005a).

In order to calculate the absorption intensity for a given temperature $T$, only five quantities are required (all provided by UYT2), the transition wavenumber $\tilde{\nu}_{if}$, the Einstein coefficient $A_{if}$, the lower (initial) state energy term value $\tilde{E}_i$, the total degeneracy of the upper (final) state $g_f = g_{ns}(J_f + 1)$, and the partition function $Q(T)$, as given by

$$I(f \leftarrow i) = \frac{A_{if} \ g_i \ \tilde{\nu}_{if}^3}{8\pi c \ Q \ \tilde{\nu}_{if}^3} \ exp \left( -\frac{c_3 \tilde{E}_i}{T} \right) \left[ 1 - exp \left( -\frac{c_3 \tilde{\nu}_{if}}{T} \right) \right].$$

(20)
Table 4. Extract from the UTY2 state file for SO₃; quantum numbers are specified in Table 5. The full table is available from http://cdsarc.u-strasbg.fr/cgi-bin/VizieR?-source=J/MNRAS/462/4300.

| n   | ̃E   | g   | J   | Γₜₜοτ | K   | v₁ | v₂ | v₃ | v₄ | v₅ | v₆ | n₁ | n₂ | n₃ | L₃ | n₄ | L₄ | Γₐₗib |
|-----|------|-----|-----|--------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1   | 0.0000 | 1   | 0   | 1     | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 1   |
| 2   | 993.6780 | 1   | 0   | 1     | 0   | 1   | 0   | 0   | 0   | 0   | 0   | 2   | 0   | 2   | 0   | 0   | 0   | 1   |
| 3   | 1059.4770 | 1   | 0   | 1     | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 2   | 0   | 1   |
| 4   | 1066.4970 | 1   | 0   | 1     | 0   | 1   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 1   | 1   |
| 5   | 1591.0349 | 1   | 0   | 1     | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 3   | 1   |
| 6   | 1919.6346 | 1   | 0   | 1     | 0   | 1   | 1   | 0   | 0   | 0   | 0   | 1   | 0   | 0   | 0   | 0   | 1   | 1   |
| 7   | 1981.9944 | 1   | 0   | 1     | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 4   | 0   | 4   | 0   | 0   | 0   | 1   |
| 8   | 2054.0505 | 1   | 0   | 1     | 0   | 1   | 0   | 0   | 0   | 2   | 2   | 0   | 2   | 0   | 0   | 2   | 0   | 1   |
| 9   | 2061.9334 | 1   | 0   | 1     | 1   | 0   | 1   | 0   | 0   | 0   | 0   | 0   | 2   | 1   | 2   | 0   | 0   | 1   |
| 10  | 2117.4659 | 1   | 0   | 1     | 0   | 1   | 0   | 0   | 0   | 4   | 0   | 0   | 0   | 0   | 4   | 0   | 1   | 1   |
| 11  | 2124.4973 | 1   | 0   | 1     | 1   | 1   | 0   | 0   | 0   | 2   | 2   | 0   | 1   | 0   | 0   | 2   | 0   | 1   |
| 12  | 2129.3331 | 1   | 0   | 1     | 1   | 1   | 0   | 0   | 0   | 2   | 0   | 0   | 1   | 2   | 2   | 1   | 1   |
| 13  | 2444.1614 | 1   | 0   | 1     | 0   | 1   | 1   | 0   | 0   | 0   | 3   | 2   | 0   | 2   | 0   | 0   | 3   | 1   |
| 14  | 2586.0493 | 1   | 0   | 1     | 0   | 1   | 0   | 0   | 0   | 0   | 5   | 0   | 0   | 0   | 0   | 5   | 1   | 1   |
| 15  | 2648.2382 | 1   | 0   | 1     | 0   | 1   | 0   | 0   | 0   | 3   | 0   | 1   | 0   | 0   | 0   | 3   | 1   |
| 16  | 2655.7551 | 1   | 0   | 1     | 1   | 0   | 0   | 0   | 0   | 2   | 0   | 0   | 0   | 2   | 0   | 0   | 1   | 1   |
| 17  | 2766.3812 | 1   | 0   | 1     | 0   | 1   | 0   | 2   | 0   | 0   | 0   | 0   | 0   | 2   | 0   | 0   | 0   | 1   |
| 18  | 2904.3481 | 1   | 0   | 1     | 0   | 1   | 0   | 0   | 0   | 2   | 0   | 0   | 2   | 1   | 1   | 1   | 1   |

Table 5. Quantum numbers used in labelling energy states.

<table>
<thead>
<tr>
<th>Quantum number</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>Counting index</td>
</tr>
<tr>
<td>̃E</td>
<td>Energy value (cm⁻¹)</td>
</tr>
<tr>
<td>g</td>
<td>Total degeneracy of the state</td>
</tr>
<tr>
<td>J</td>
<td>Vibrational quantum number</td>
</tr>
<tr>
<td>Γₜₜοτ</td>
<td>Angular momentum quantum number</td>
</tr>
<tr>
<td>K</td>
<td>Total symmetry in D₃h(M): 1 = A', 4 = A''</td>
</tr>
<tr>
<td>Γₐₗib</td>
<td>Projection of J on to the z-axis</td>
</tr>
<tr>
<td>Γₐₗ</td>
<td>Rotational symmetry in D₃h(M): 1 = A', 2 = A'', 3 = E', 4 = A', 5 = A'', 6 = E''</td>
</tr>
<tr>
<td>v₁, i = 1–6</td>
<td>Local mode vibrational quantum numbers</td>
</tr>
<tr>
<td>n₁, n₂, n₃, n₄</td>
<td>Normal mode vibrational quantum numbers</td>
</tr>
<tr>
<td>L₃, L₄</td>
<td>L projections of the vibrational angular momenta</td>
</tr>
<tr>
<td>Γₐₗib</td>
<td>Vibrational symmetry in D₃h(M): 1 = A', 2 = A'', 3 = E', 4 = A', 5 = A'', 6 = E''</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>f</th>
<th>i</th>
<th>Aᵢᵢ</th>
</tr>
</thead>
<tbody>
<tr>
<td>237007</td>
<td>249581</td>
<td>1.1253e-17</td>
</tr>
<tr>
<td>158430</td>
<td>148459</td>
<td>2.8358e-17</td>
</tr>
<tr>
<td>549592</td>
<td>568676</td>
<td>1.3725e-16</td>
</tr>
<tr>
<td>120670</td>
<td>112002</td>
<td>1.4546e-16</td>
</tr>
<tr>
<td>2080392</td>
<td>2117071</td>
<td>9.0696e-18</td>
</tr>
<tr>
<td>286088</td>
<td>302965</td>
<td>1.4938e-16</td>
</tr>
<tr>
<td>393104</td>
<td>377035</td>
<td>1.5764e-16</td>
</tr>
<tr>
<td>43637</td>
<td>49289</td>
<td>2.1375e-16</td>
</tr>
<tr>
<td>587986</td>
<td>607961</td>
<td>2.0370e-16</td>
</tr>
<tr>
<td>587868</td>
<td>647986</td>
<td>4.2068e-18</td>
</tr>
<tr>
<td>2007259</td>
<td>2043487</td>
<td>5.2490e-18</td>
</tr>
<tr>
<td>627725</td>
<td>648113</td>
<td>3.0673e-16</td>
</tr>
</tbody>
</table>

For a line list to be suitable for modelling spectra at a certain temperature, it is necessary for the partition function, Q, to be converged at this temperature. This is equivalent to stating that all energy levels that are significantly populated at the given temperature, T, must be considered. This convergence gives a metric upon which line list completeness can be gauged (Neale, Miller & Tennyson 1996).

Fig. 4 shows convergence of the partition function with Jₘₐₓ for different temperatures, T. Upon inspection, the value of Q is adequately converged at J = 130 for T ≤ 800 K. Table 7 shows the final values of Q obtained for selected temperatures alongside their estimated degree of convergence. As can be seen, the value of Q = 7908.906 at T = 298.15 K calculated from UYT2 is in agreement with the value of Q = 7908.266 obtained from UYT.

For the purposes of determining completeness of the line list, it is more appropriate to view the convergence of Q as a function of an energy cut-off, Eₘₐₓ. This is also shown in Fig. 4, from where it is clear that imposing this limit will have a non-negligible effect on a spectral simulation at T = 773.15 K, in particular; since the partition function is not fully converged at Eₘₐₓ = 4000 cm⁻¹ it is expected that levels with energies above this value will also be populated to some extent. This would be manifest as certain lines being missing from the spectrum, where transitions from levels contributing with some significance to the partition function are not included. Similarly, the truncation of calculations at J = 130 means that a number of potentially contributing energy levels are omitted.

where c₂ is the second radiation constant, and gₙₐ is the nuclear spin statistical weight factor (gₙₐ = 1 for ^12S^{16}O₃), c is the speed of light. The partition function Q is given by

\[ Q = \sum_i g_i \exp \left( -\frac{c_2 E_i}{T} \right). \]  (21)
Figure 4. Convergence of the partition function at different temperatures as a function of $J_{\text{max}}$ (upper) and $E_{\text{max}}$ (lower). The partition function increases monotonically with temperature.

Table 7. Values of the partition function, $Q$, for different temperatures, $T$. The degree of convergence is specified by $Q_{J=130} - Q_{J=129}/Q_{J=130} 	imes 100$.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$Q$</th>
<th>Degree of convergence (per cent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.15</td>
<td>7908.906</td>
<td>$6.27 \times 10^{-6}$</td>
</tr>
<tr>
<td>473.15</td>
<td>26 065.642</td>
<td>$8.50 \times 10^{-4}$</td>
</tr>
<tr>
<td>573.15</td>
<td>48 007.866</td>
<td>$3.62 \times 10^{-3}$</td>
</tr>
<tr>
<td>673.15</td>
<td>85 016.645</td>
<td>$9.99 \times 10^{-3}$</td>
</tr>
<tr>
<td>773.15</td>
<td>145 389.574</td>
<td>$2.12 \times 10^{-2}$</td>
</tr>
<tr>
<td>1000</td>
<td>437 353.233</td>
<td></td>
</tr>
</tbody>
</table>

from the partition sum at $T = 773.15$ K; at $J = 130$, the lowest energy lies around 4000 cm$^{-1}$. This means that the high-$T$ partition function obtained will be slightly lower than the fully converged value.

It is possible to quantify the completeness of the line list by assuming that the value of $Q$ at $J = 130$ is close enough to the ‘true’ value of the partition function at the given temperature. Fig. 5 shows the ratio of the value of the partition function at the 4000 cm$^{-1}$ cut-off and the assumed total partition function, $Q_{\text{total}}$. At $T = 773.15$ K, the line list is roughly 90 per cent complete. In reality, this is an upper limit due to the fact that there is a slight underestimation of $Q_{\text{total}}$ at this temperature. However, the contribution from the missing energies with $J > 130$, which all lie above 4000 cm$^{-1}$, can be estimated to be small enough not to affect $Q_{\text{total}}$ by more than 1 per cent below $T = 800$ K.

Figure 5. Ratios of $Q_{4000}$ to the assumed converged values $Q_{\text{total}}$ as a function of temperature.

Table 8. Comparison of calculated band intensities in cm molecule$^{-1} \times 10^{-18}$. Units are given in $10^{-18}$ cm molecule$^{-1}$.

<table>
<thead>
<tr>
<th>Band</th>
<th>Band intensity</th>
<th>UYT</th>
<th>UYT2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2v_2 - v_2$</td>
<td>0.66</td>
<td>0.62</td>
<td></td>
</tr>
<tr>
<td>$v_2$</td>
<td>3.71</td>
<td>3.39</td>
<td></td>
</tr>
<tr>
<td>$v_2 + v_4 - v_4$</td>
<td>0.58</td>
<td>0.54</td>
<td></td>
</tr>
<tr>
<td>$v_4$</td>
<td>5.95</td>
<td>5.37</td>
<td></td>
</tr>
<tr>
<td>$2(v_2 + v_0) - v_4$</td>
<td>0.41</td>
<td>0.44</td>
<td></td>
</tr>
<tr>
<td>$v_2 + v_4 - v_2$</td>
<td>0.53</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>$2(v_2 + v_0) - v_4$</td>
<td>0.87</td>
<td>1.17</td>
<td></td>
</tr>
<tr>
<td>$v_1 - v_4$</td>
<td>0.10</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>$v_3$</td>
<td>44.44</td>
<td>43.21</td>
<td></td>
</tr>
<tr>
<td>$2(v_3 + v_0) - v_0$</td>
<td>0.12</td>
<td>0.11</td>
<td></td>
</tr>
</tbody>
</table>

5 INTENSITY COMPARISONS

UYT (Underwood et al. 2013) made extensive intensity comparisons with the available, room temperature, high resolution, infrared spectra due to Maki and co-workers; in general finding good agreement. However, these experimental spectra are not absolute so the comparison is only for relative intensities. A comparison of the intensities predicted by the UYT and UYT2 line lists are summarized in Table 8. This comparison essentially shows that UYT2 reproduces the band intensities of UYT, showing that adjusting PES does not significantly alter the computed intensities, as has occasionally been found to happen (Al-Refaie et al. 2015b).

Since the comparison with the data of Maki and co-workers is only able to provide a measure of the quality of relative intensities within a particular band, an absolute intensity comparison is highly desirable. The new measured temperature-dependent DTU SO$_3$ cross-section data plus the room-temperature cross-sections in the PNNL (Pacific Northwest National Laboratory) data base (Sharpe et al. 2004) provide this possibility. For both data sets, there are discernible spectral features across four separate regions and it should be possible to make a semiquantitative analysis by comparing integrated intensities across a given spectral window. To make this comparison, cross-sections were generated from UYT2 using the ExoCross tool (Hill, Yurchenko & Tennyson 2013; Tennyson et al. 2016).

Fig. 6 shows comparisons between recorded cross-sections from PNNL at 298.15 K (25 C) and resolution 0.112 cm$^{-1}$, compared...
ExoMol XVII: line list for SO$_3$

Figure 6. Comparisons of the $\nu_2$ and $\nu_4$ bands (upper) and the $\nu_3$ band (lower) for PNNL (Sharpe et al. 2004) and simulated cross-sections at $T = 298.15$ K.

Fig. 6 shows a comparison of the $\nu_2$ and $\nu_4$ bands (upper) and the $\nu_3$ band (lower) for PNNL (Sharpe et al. 2004) and simulated cross-sections at $T = 298.15$ K.

with simulated cross-sections using the full UYT2 line list, based on a Gaussian profile of half-width at half-maximum (HWHM) = 0.1 cm$^{-1}$. Fig. 7 gives a similar comparison for the $\nu_1 + \nu_3$ and $2\nu_3$ bands.

Fig. 7 gives a similar comparison for the $\nu_1 + \nu_3$ bands (upper) and the $2\nu_3$ band (lower) for PNNL (Sharpe et al. 2004) and simulated cross-sections at $T = 298.15$ K.

The comparisons reveal that although band positions and features are fairly well represented, there is a clear tendency for the UYT2 data to overestimate the line intensities for both temperatures considered. In our experience of computing ab initio intensities, it is common for whole bands to have intensities which are over/underestimated by a constant factor (Lodi et al. 2008). However, we have not previously encountered a situation where the intensities of all the bands are shifted by a similar amount. There are a number of possibilities that could explain such a discrepancy. First, it is possible that the experimental cross-sections may be underestimated due to an overestimate of the SO$_3$ abundance; the calculation of cross-sections requires the knowledge of the species concentration within the length of the absorption cell (Barton et al. 2015). However, the fact that measurements at room temperature performed at DTU corroborate the PNNL data, and that similar discrepancies are observed for both data sets suggests that this is not the case. In this context, it is worth noting that a similar comparison for SO$_2$ yields good agreement between measured and ab initio absolute cross-sections (Underwood et al. 2016).

A second possible source of disagreement could be convergence issues with the partition function. Since the calculated intensities given by equation (20) depend on the scaling factor $Q(T)$, the incorrect computation of this value at the given temperature will would expect from the assumption made that all SO$_2$ consumed in the reaction (8) gives rise to SO$_3$. The comparisons reveal that although band positions and features are fairly well represented, there is a clear tendency for the UYT2 data to overestimate the line intensities for both temperatures considered. In our experience of computing ab initio intensities, it is common for whole bands to have intensities which are over/underestimated by a constant factor (Lodi et al. 2008). However, we have not previously encountered a situation where the intensities of all the bands are shifted by a similar amount. There are a number of possibilities that could explain such a discrepancy. First, it is possible that the experimental cross-sections may be underestimated due to an overestimate of the SO$_3$ abundance; the calculation of cross-sections requires the knowledge of the species concentration within the length of the absorption cell (Barton et al. 2015). However, the fact that measurements at room temperature performed at DTU corroborate the PNNL data, and that similar discrepancies are observed for both data sets suggests that this is not the case. In this context, it is worth noting that a similar comparison for SO$_2$ yields good agreement between measured and ab initio absolute cross-sections (Underwood et al. 2016).

A second possible source of disagreement could be convergence issues with the partition function. Since the calculated intensities given by equation (20) depend on the scaling factor $Q(T)$, the incorrect computation of this value at the given temperature will
lead to inaccurate values of absolute intensity. The difference in integrated cross-section intensities observed suggest that if the calculated value of \(Q(T)\) is incorrect, then it is smaller than the ‘true’ value, since the theoretical cross-sections are more intense than the experimentally observed values. This scenario can also be ruled out, due to two reasons. First, the agreement between \(Q(T)\) for both UYT and UYT2 is very good at \(T = 298.15\) K, where they are both adequately converged; the increased basis set size underlying the UYT2 calculations would undoubtedly account for any missing ro-vibrational energies in UYT. Secondly, and perhaps more interestingly, the analysis of several bands across different temperatures shows the cross-section discrepancies to be almost independent of the value of \(T\) (see below). This would not be expected if \(Q(T)\) were the source of the disagreement, since partition sums can be expected to converge differently as a function of temperature.

This strongly implies that the problem lies with the DMS. Despite experience of obtaining highly accurate ab initio dipole surfaces (Lodi, Tennyson & Polansky 2011; Polansky et al. 2015), defects in DMSs are by no means unknown (Al-Refaie et al. 2015b; Azzam et al. 2015; Pavlyuchko, Yurchenko & Tennyson 2015a). We therefore undertook a small series of new ab initio calculations to see if we could identify the source of this problem. These calculations were all performed with MOLPRO (Werner et al. 2012) at the CCSD(T) level using finite differences. First, we compared the original CCSD(T)-F12b with triple-\(\zeta\) basis sets (aug-cc-pVTZ-F12 on O and aug-cc-pV(T+d)Z-F12 on S) results with calculations performed at the more traditional CCSD(T) with the same basis sets. The results were very similar suggesting that use of F12b was neither the cause of the problem nor was it providing improved convergence. Secondly, we repeated the CCSD(T) using a larger quadrupole-zeta basis set (aug-cc-pVQZ-F12 on O and aug-cc-pV(Q+d)Z-F12 on S). The dipoles computed at this level proved to be somewhat smaller suggesting that the UYT DMS suffers from a lack of convergence in the one-particle basis set. Further work on this problem is left to a future study. Here, we adopt the more pragmatic approach of scaling our computed intensities.

It is not easy to make a rigorous analysis based on cross-section data available for \(\text{SO}_3\), as it is not immediately obvious what the contributions are from individual lines. In addition to this, both data sets contain varying degrees of noise within certain spectral regions, with the region around the \(\nu_3\) band generally providing the best signal. Pavlyuchko et al. (2015a) performed a fit of their DMS based on experimental intensity data for nitric acid, to better improve simulated intensities. The lack of absolute intensity measurements for \(\text{SO}_3\), coupled with the expensive computational demands of the line list calculation make this particularly difficult to perform here. Nevertheless, the best approach has been to compare integrated band intensities across fixed spectral windows to obtain scaling parameters for the each band. Table 9 summarizes the ratios of integrated intensities between simulated and recorded cross-sections for some available bands. These were obtained by explicit numerical integration over the wavenumber range of the corresponding regions.

Table 9. Intensities integrated over the corresponding band region for observed and calculated (UYT2) cross-sections as a function of temperature, \(T\). Intensity units are given in \(10^{-18}\) cm molecule\(^{-1}\).

<table>
<thead>
<tr>
<th>(T) (K)</th>
<th>Band</th>
<th>Integrated intensity</th>
<th>Obs./UYT2</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.15</td>
<td>(\nu_2 + \nu_4)</td>
<td>9.95</td>
<td>13.13</td>
</tr>
<tr>
<td></td>
<td>(\nu_3)</td>
<td>46.78</td>
<td>60.38</td>
</tr>
<tr>
<td></td>
<td>(\nu_3 + \nu_3)</td>
<td>0.71</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>(2\nu_3)</td>
<td>0.15</td>
<td>0.16</td>
</tr>
<tr>
<td>573.15</td>
<td>(\nu_2 + \nu_4)</td>
<td>10.26</td>
<td>13.53</td>
</tr>
<tr>
<td></td>
<td>(\nu_3)</td>
<td>46.79</td>
<td>59.62</td>
</tr>
<tr>
<td></td>
<td>(\nu_3 + \nu_3)</td>
<td>0.69</td>
<td>0.87</td>
</tr>
</tbody>
</table>
For most bands, there appears to be a fairly consistent shift in intensity values across different temperatures, however the overtone bands for \( T = 298.15 \) K suggest otherwise. The differences are quite subtle; for example, while the \( 2\nu_1 \) band has almost perfect agreement in integrated intensity across the band, the central \( \Omega \)-branch peak is not well represented by the UYT2 cross-sections. On the other hand, the DTU data at 573.15 K for the \( \nu_1 + \nu_3 \) band exhibits the same general shift as the \( \nu_2, \nu_4 \), and \( \nu_6 \) bands when care is taken to exclude the intensity due to contamination in the integration, but the same is not true at room temperature. The PNNL room-temperature cross-sections are well reproducible. Up to 400 measurements at DTU were performed several times and over different years, when the cell was used for other measurements. The data however are well reproducible. Up to 400 °C agreement in integrated absorption cross-sections between DTU and PNNL is from 0 per cent to 13 per cent for strongest bands, which is similar to PNNL’s uncertainty in the bands intensity. If the scaling factors for the two overtone bands at room temperature are ignored, then the remaining factors may be averaged and applied to all simulated cross-sections. This gives an average scaling factor of 0.76. The assumption made here is that the apparent better agreement in the room-temperature intensities for the \( \nu_1 + \nu_3 \) and \( 2\nu_1 \) are ‘accidental’, while the wide, coverage-consistent high-temperature cross-sections provide a more accurate description of the differences. Previous experience suggests that an ab initio DMS is more likely to overestimate rather than underestimate intensities (Schwenke & Partridge 2000; Tennyson 2014; Azzam et al. 2015). Without extra experimental data for more bands at different temperatures, it is difficult to ascertain whether the intensity overestimates seen here are consistent for all bands or vary with different vibrational transitions.

Figs 6 and 7 show the various bands at room temperature, with computed cross-sections multiplied by the averaged scaling factor. Figs 8 and 9 show the same for \( T = 573.15 \) K, which improve the simulated cross-sections, and demonstrate the implied temperature independent nature of the discrepancy. As can be seen in Fig. 7, using the averaged scaling factor (obtained from excluding the individual \( \nu_1 + \nu_3 \) and \( 2\nu_1 \) Obs./UYT2 ratios) improves the reproduction of the central band peak, though the \( P \)-branch does show some intensity differences. This appears to be common for multiple bands and is possibly due to our neglecting of pressure broadening when generating the cross-sections.

Fig. 10 shows the cross-sections calculated over the entire spectral range of \( 0 < \nu \leq 5000 \) cm\(^{-1}\), using a Gaussian profile of HWHM = 0.25 cm\(^{-1}\), for a number of different temperatures. All simulated cross-sections have been multiplied by the average scaling factor of 0.76. As can be seen, the region beyond 4500 cm\(^{-1}\) shows some anomalies for higher temperatures, for this reason it is recommended that this region be treated with caution.

6 CONCLUSION

The UYT2 line list contains 21 billion transitions, and a total of 18 million energy levels below 10 000 cm\(^{-1}\). This provides an improvement upon the initial room-temperature line list, UYT, in terms of both line positions and temperature coverage. Table 1 provides a measure of the improvement introduced by the PES refinement present in the UYT2 line list. The total rms deviation for the bands included in the potential adjustment is 1.35 cm\(^{-1}\), compared to 3.23 cm\(^{-1}\) for the unrefined PES of UYT. The majority of simu-

![Figure 10. Overview of the simulated cross-sections using UYT2, at \( T = 298.15, 473.15, \) and \( 773.15 \) K, with a Gaussian profile of HWHM = 0.25 cm\(^{-1}\). The dips in the cross-sections are progressively smoothed out with increasing temperature. For higher temperatures, the region beyond 4500 cm\(^{-1}\) appears anomalous, and should be treated with caution.](image-url)
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