ROOM TEMPERATURE LINE LISTS FOR CO_2 ISOTOPOLOGUES WITH *AB INITIO* COMPUTED INTENSITIES

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21 June 2016

Why CO_2?

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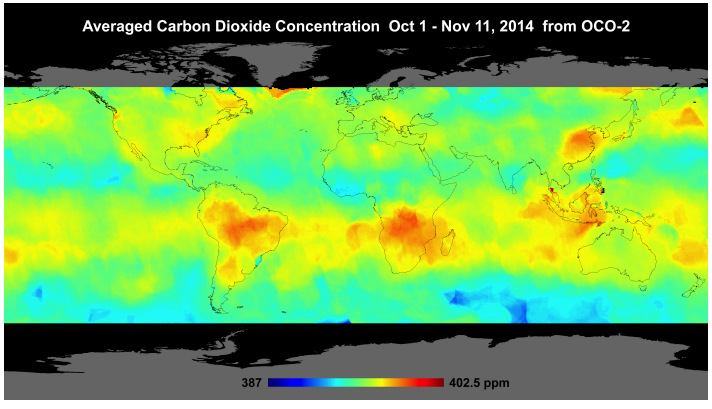
OCO-2 Space Mission

- sources, sinks and migrations of atmospheric CO_2
- influence of CO_2 on climate change

TCCON, NDACC

- validation of results from space missions
- fossil fuel emission, etc.



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Databases: HITRAN, CDSD

- Experiments leave spectral gaps
- Accurate line intensities challenging

  (especially for less abundant isotopologues)
- Multiple data sources may cause inconsistencies

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What is needed?

Dream line list:

- line positions accurate to 10^{-4} – 10^{-5} cm^{-1}
- covering all important bands (0 cm^{-1} –14 000 cm^{-1}) of CO_2
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State of the art:

- line positions: $10^{-2} - 10^{-9}$cm^{-1}

  (measurements & Effective Hamiltonian calculations (CDSD-296))
- several small spectral gaps - missing in HITRAN2012 and CDSD-296
- Experimental line intensities: $^{12}C^{16}O_2$: 1% (Devi *et. al*); other isotopologues: $>$2%
- ab initio computed intensities give the highest accuracy!

Recent progress

- CDSD-296 database (S. Tashkun and V. Perevalov)[1]
- NASA Ames line list (X. Huang *et. al*). Variational: Fitted PES (0.016 cm^{-1} accuracy, 0-13 000 cm^{-1}), *ab initio* DMS [2]
- Measurements in the 1.6 μm and 2.06 μm regions: Devi *et. al*[3], Jacquemart *et. al*[4], Karlovets *et. al*[5]

[1] S. A. Tashkun *et. al* JQSRT 152 (2015) 45–73.
[2] X. Huang *et. al* J. Chem. Phys. 136 (2012) 124311
[3] V. M. Devi *et. al* JQSRT 177 (2016) 117–144.
[4] D. Jacquemart *et. al* JQSRT 160 (2015) 1–9.
[5] E. V. Karlovets *et. al* JQSRT 136 (2014) 89–107.

Checklist

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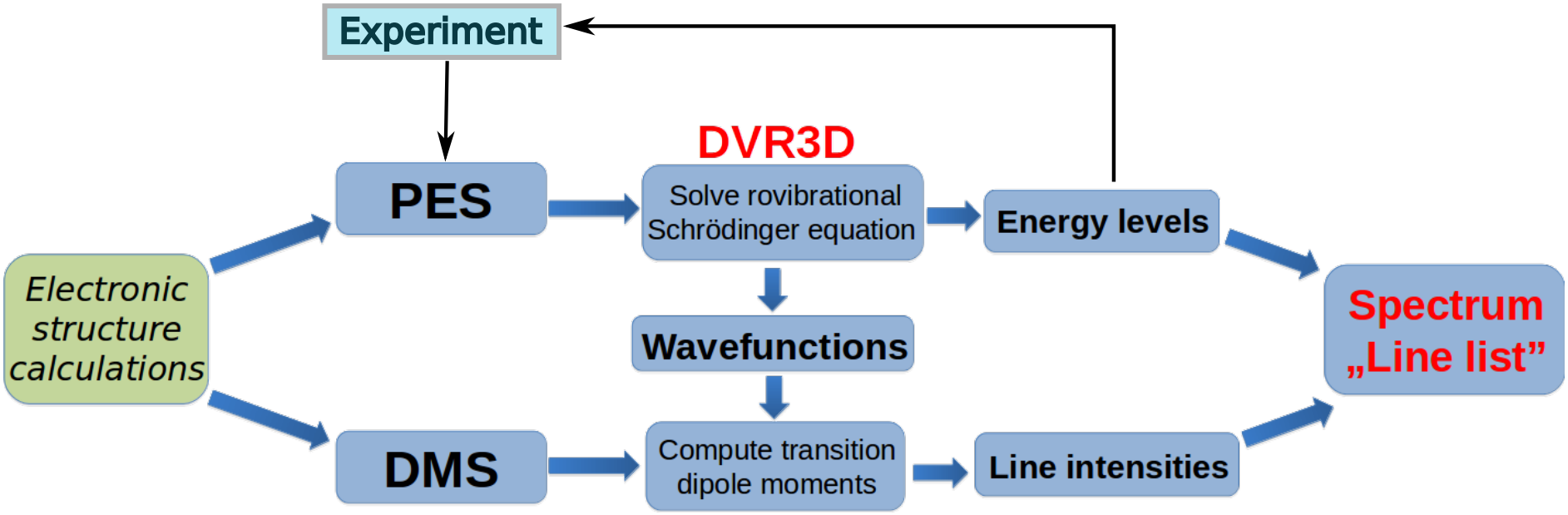
- reliability analysis

Present study

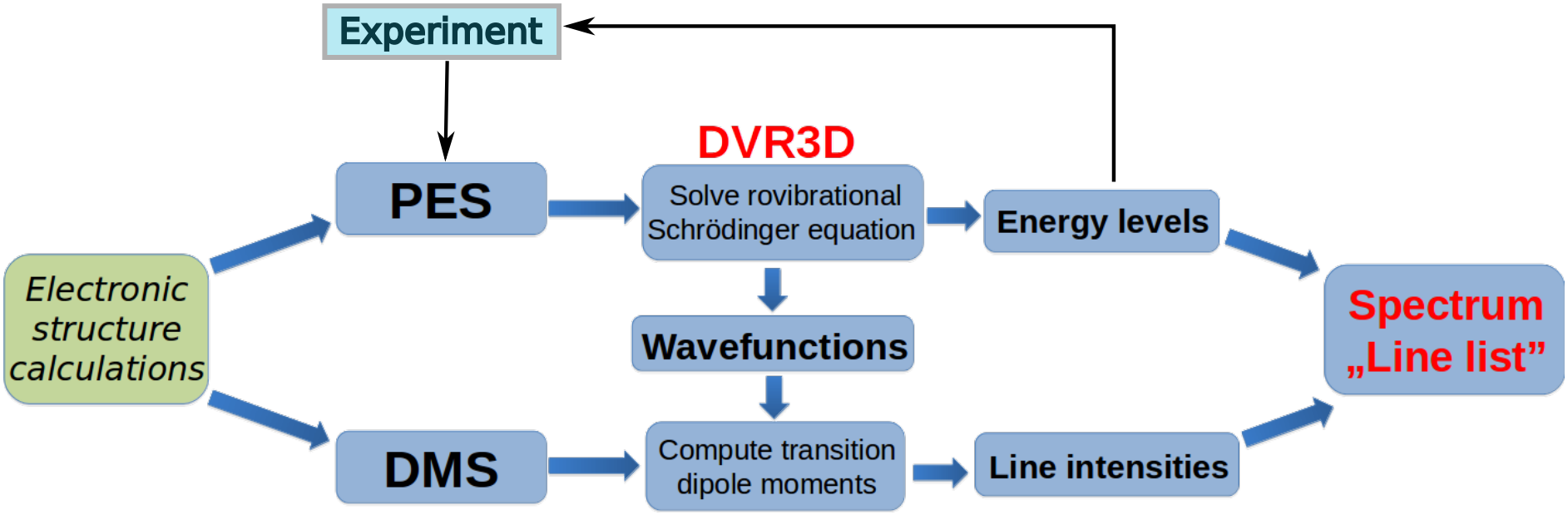
UCL-IAO line lists

1. 13 isotopologues of carbon dioxide ($^{12}C^{16}O_2$, $^{13}C^{16}O_2$:, $^{14}C^{16}O_2$:,$^{12}C^{17}O_2$:,$^{12}C^{18}O_2$, $^{13}C^{17}O_2$,$^{13}C^{18}O_2$,$^{16}O^{12}C^{18}O$, $^{16}O^{13}C^{17}O$, $^{16}O^{13}C^{18}O$, $^{16}O^{12}C^{17}O$, $^{17}O^{12}C^{18}O$, $^{17}O^{13}C^{18}O$)
2. Spectral region: 0-8000 cm^{-1}
3. *ab initio* Dipole Moment Surface (DMS)
4. line positions: Variational calculations & Effective Hamiltonian model (CDSD-296)

Theoretical scheme

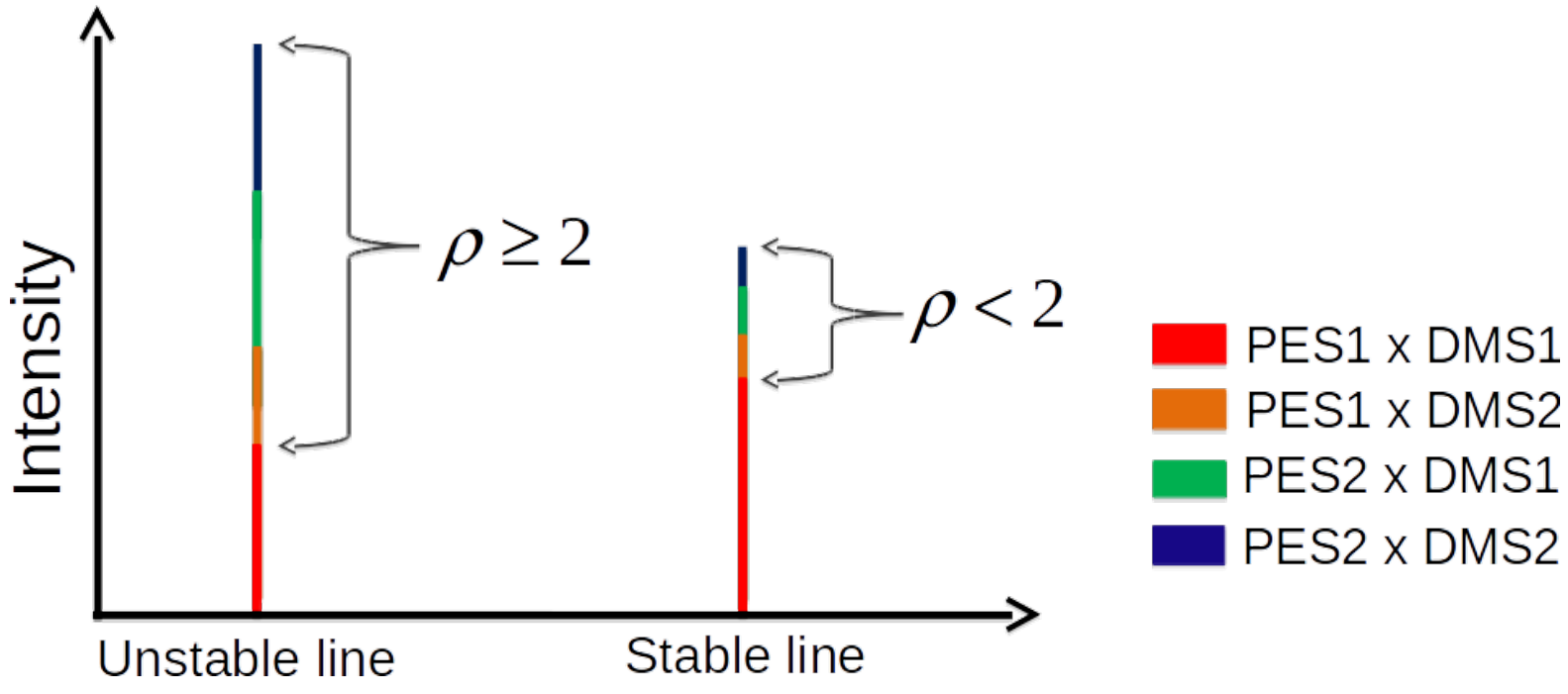


Four independent Line Lists for each isotopologue



Line sensitivity analysis - detecting resonances[6]

1. PES1: Ames-1 (semi-empirical) & DMS1: Ames (ab initio)
2. PES1: Ames-1 (semi-empirical) & DMS2: UCL (Ab initio)
3. PES2: UCL (ab initio fitted to Ames) & DMS1: Ames (ab initio)
4. PES2: UCL (ab initio fitted to Ames) & DMS2: UCL (ab initio)



[6]Zak *et. al* JQSRT 177, 31–42 (2016)

Scatter factor maps

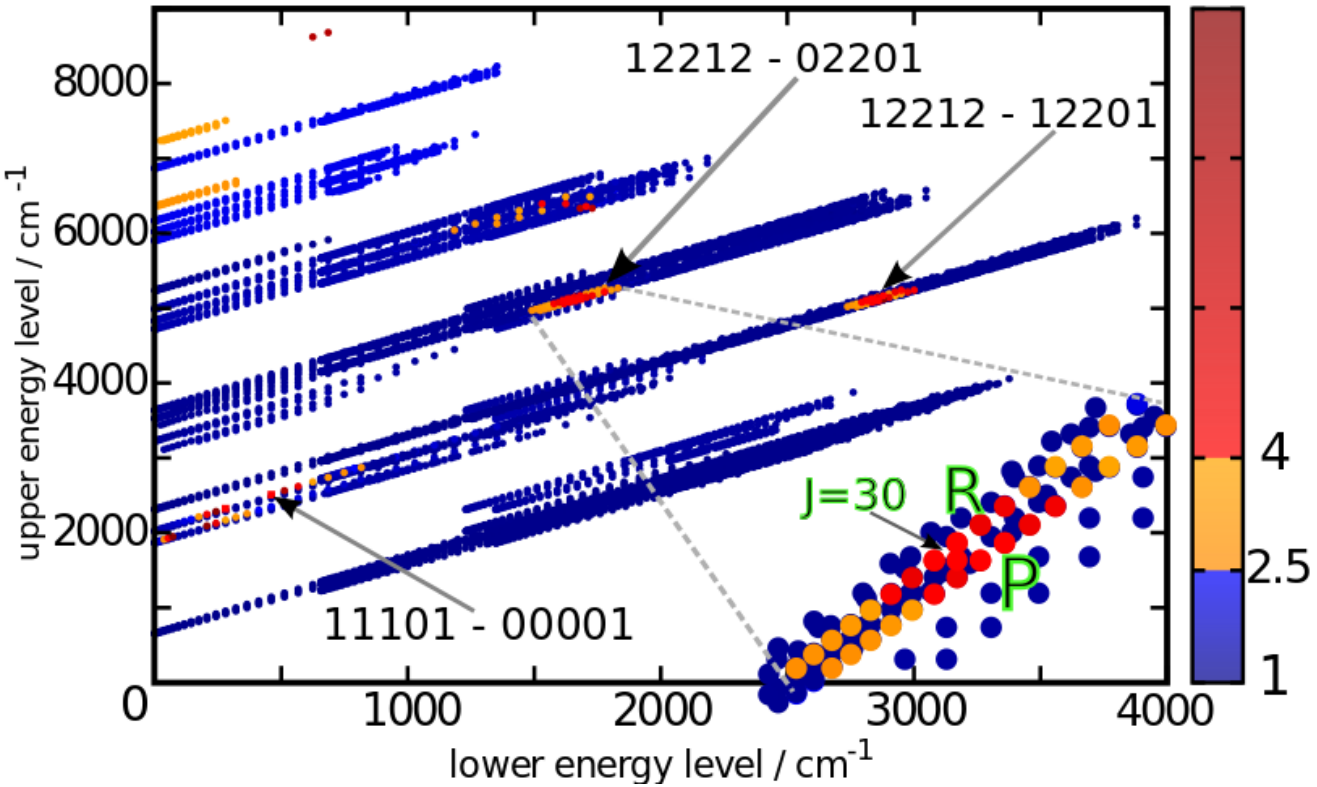


Figure: Scatter factor map for the 828 isotopologue [7]. Colour coding denotes respective classification of lines: blue stands for stable lines, orange for intermediate lines and red for unstable lines. Arrows indicate selected bands for which a J-localized peak in the scatter factor is observed. Zoomed inset in right bottom corner shows the peak region of the scatter factor for the 12212 – 02201 band. Both P and R branches are affected by the interaction around $J = 30$.

[7] Zak *et. al* JQSRT (submitted)

Example of a band perturbed by Coriolis interaction

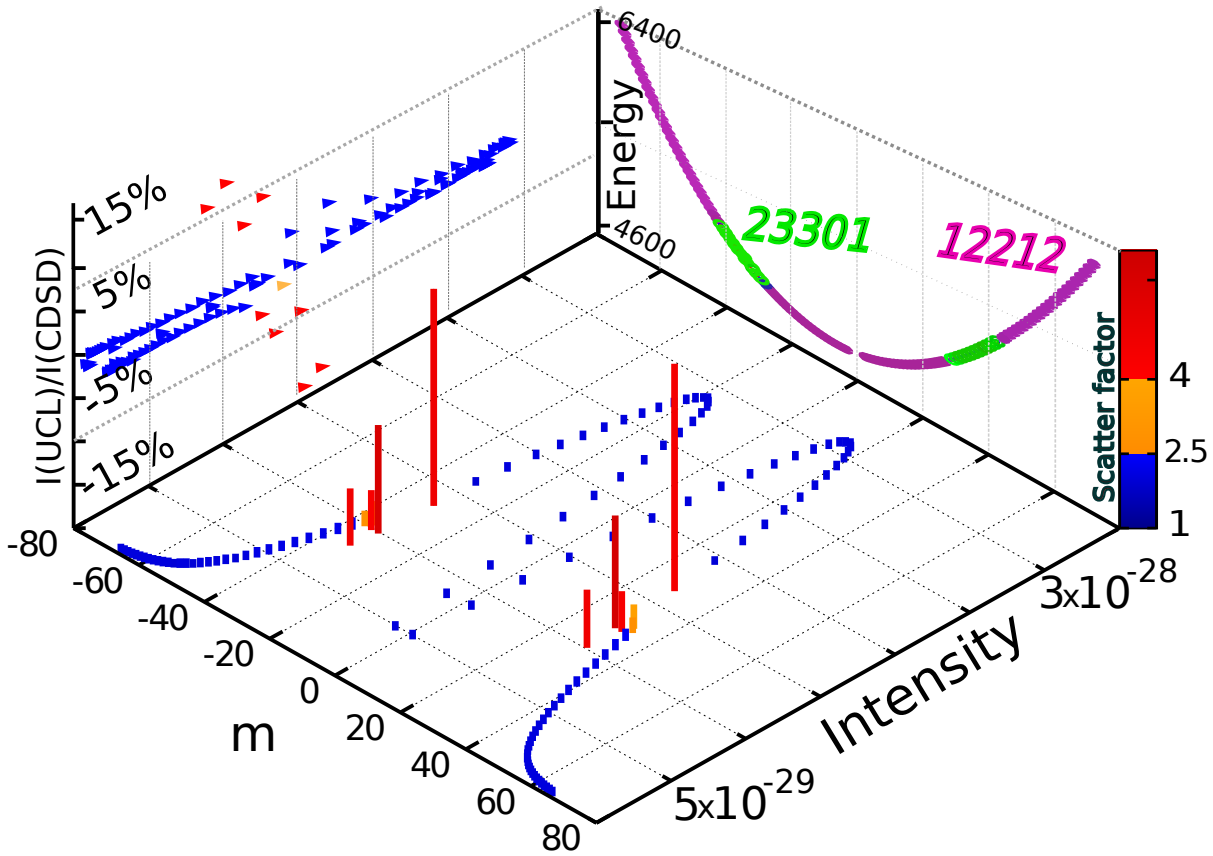


Figure: Multidimensional graph [8] characterising the 12212 – 02201 band of $^{12}C^{18}O_2$. The base plane depicts m dependence of line intensities with bar height and color code measuring the value of the scatter factor. The far right plane represents m dependence of energy levels of the perturbed state (12212) and perturber (23301), which nearly cross around $m = \pm 36$. Left plane gives intensity ratios of lines taken from the UCL-IAO line list and the CDSD-296 database.

[8] Zak *et. al* JQSRT (submitted)

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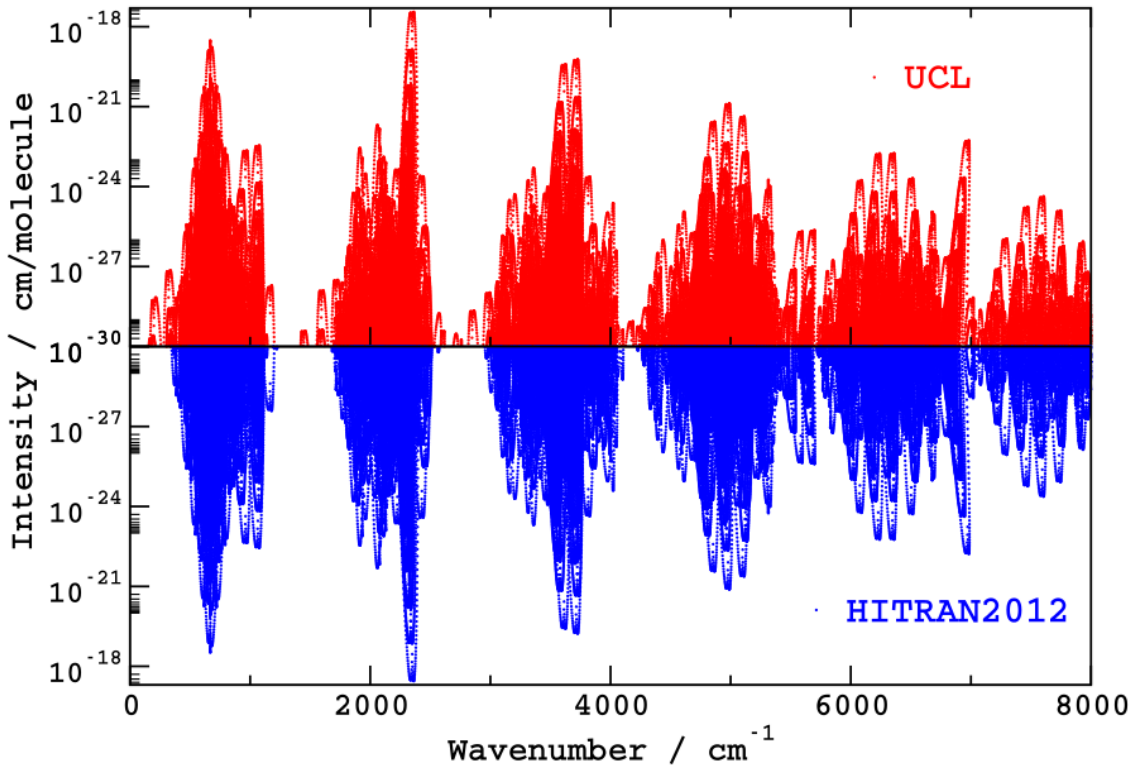
Spectral coverage vs. HITRAN2012



General overview of UCL line list and HITRAN2012 line list for $^{12}C^{16}O_2$.

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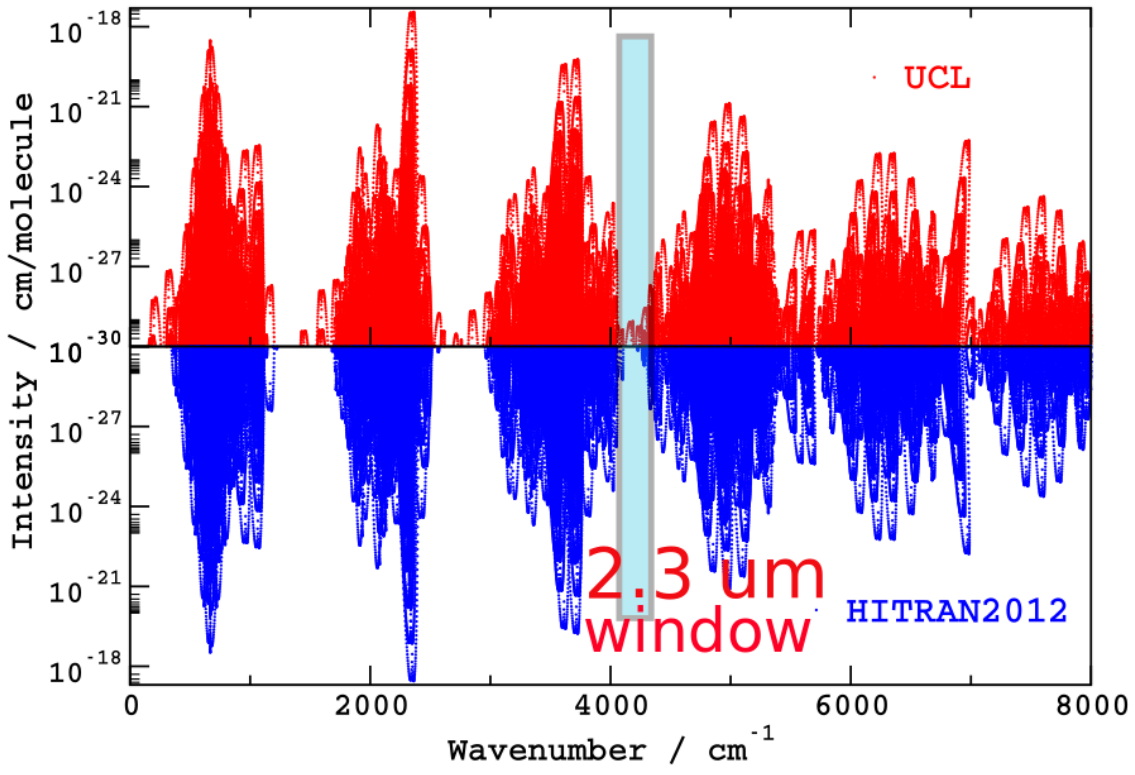

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[9] S. A. Tashkun, V. I. Perevalov, R. R. Gamache, J. Lamouroux, CDSD-296, high resolution carbon dioxide spectroscopic databank: Version for atmospheric applications, JQSRT 152 (2015) 45–73.

Line positions

- Ab initio PES (semi-empirical) : 1-2 cm^{-1} accuracy
- Ames-1 PES: 0.02 cm^{-1} accuracy - full spectral coverage for all isotopologues
- Effective Hamiltonian: 0.002 cm^{-1} accuracy - lack of data for less abundant isotopologues

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Line intensities: comparison to recent measurements ($^{12}C^{16}O_2$)

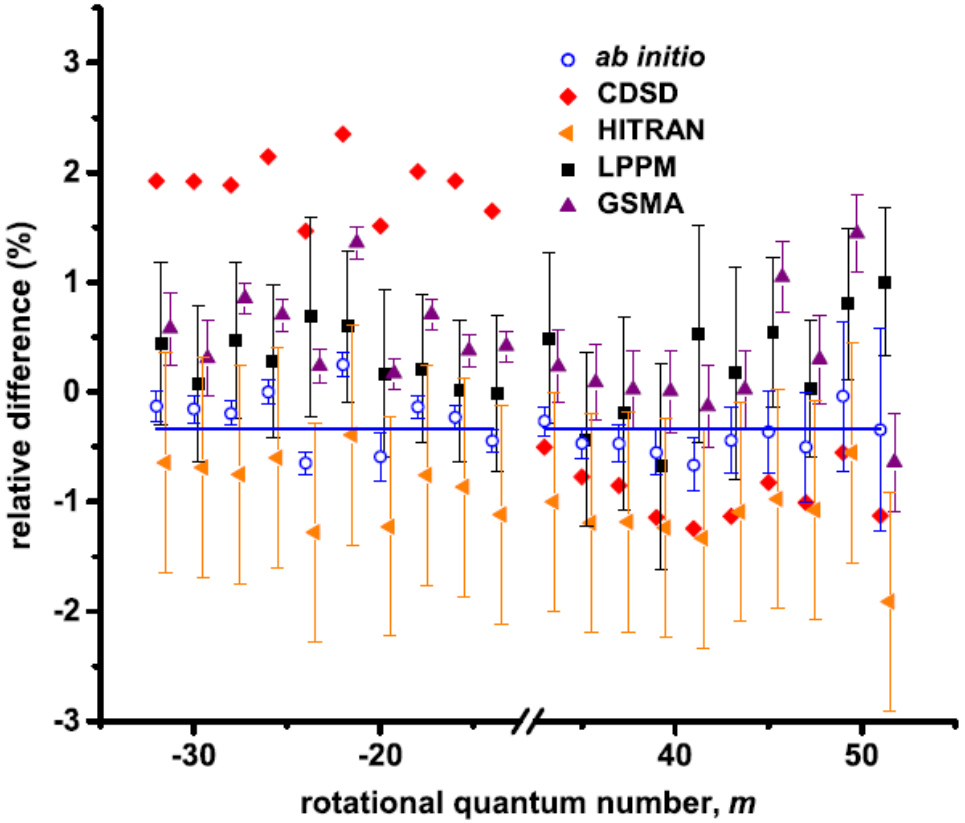

Figure: Comparison of experimental line intensities from ref. for the 30013 – 00001 band with present (UCL) [10], HITRAN2012, CDSD, LPPM[11] and GSMA values.

[10] Polyansky *et. al* PRL, 114, 243001 (2015).

[11] Boudjaadar *et. al* J. Mol. Spectrosc. 236, 158 (2006).

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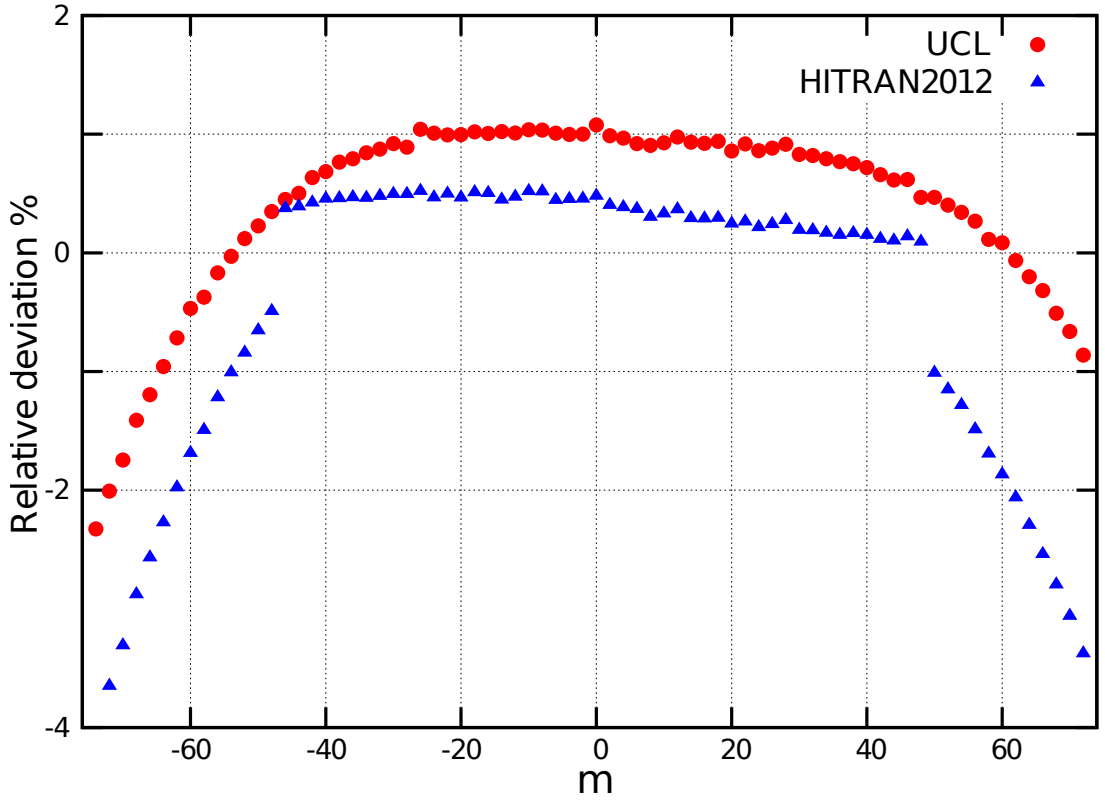

Comparison of experimental line intensities from Devi *et. al* [10] for the 30013 – 00001 band with present (UCL) [11] and HITRAN2012 values.

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4. Uncertainty of line intensities evaluated on a purely theoretical basis -NEW!
5. Ready for inclusion in databases

Acknowledgements

”The authors acknowledge the use of the UCL Legion High Performance Computing Facility (Legion@UCL), and associated support services, in the completion of this work.”

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