Anomalous Centrigugal Distorsion in HDO and Spectroscopic Data Bases

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Créteil, France

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Overview

[1] Rothman *et al.*, *J.Q.S.R.T.* **130** (2013) 4

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1. HDO used to study the earth atmosphere

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2. The main features of the HDO spectroscopy

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3. Line position analysis

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3. Line position analysis
4. Line strength analysis

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1. HDO used to study the earth atmosphere
2. The main features of the HDO spectroscopy
3. Line position analysis
4. Line strength analysis
5. Comparison with Hitran 2012[1]

[1] Rothman *et al.*, *J.Q.S.R.T.* **130** (2013) 4

HDO is used to study the earth atmosphere

[1] Herbin *et al.*, *Atmos. Chem. Phys.* **9** (2009) 9433

[2] $\delta\text{D} = 1000‰ \times (\frac{[\text{HDO}]/[\text{H}_2\text{O}]}{\text{SMOW}} - 1)$

[3] Schneider & Hase, *Atmos. Chem. Phys.* **11** (2011) 11207

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HDO is used to study the earth atmosphere

1. HDO allows us to study the water cycle in the earth atmosphere.[1]
2. It is used to derive tropospheric δD[2] IASI.[3]
3. HDO is much more convenient than the more abundant isotopic species $H_2{}^{18}O$ or $H_2{}^{17}O$ because the ν_2 bands of HDO and H_2O do not quite overlap.

[1] Herbin *et al.*, *Atmos. Chem. Phys.* **9** (2009) 9433

[2] $\delta D = 1000‰ \times (\frac{[HDO]/[H_2O]}{SMOW} - 1)$

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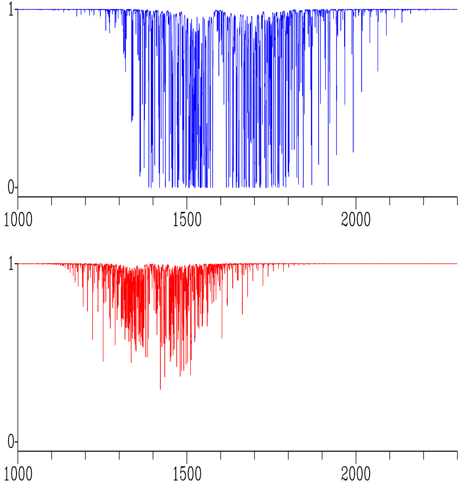
ν_2 band of HDO and H_2O



H_2O
0.05 Atm
$l = 20$ cm

HDO
0.05 Atm
$l = 100$ m

Anomalous centrifugal distortion effects

[1] De Lucia, Cook, & Gordy, *J. Chem. Phys.* **55** (1971) 5344

[2] Coudert, Martin-Drumel, & Pirali, *J. Mol. Spec.* **303** (2014) 36

Anomalous centrifugal distortion effects

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1. Anomalous centrifugal distortion effects in HDO were evidenced a long time ago.[1]
2. Distortion parameters in $\mathbf{J}^{10}$ had to be used to fit the microwave spectrum[1] in the ground state up to $J = 12$.
3. A modified version of the Bending-Rotation approach[2] will be used in the present analyses.

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The modified Bending-Rotation approach

Effective 4-dimensional Hamiltonian written using Radau[1] coordinates:

$$H_{\mathrm{Bend-Rot}} = B P_t (1 - t^2) P_t + B \left[\frac{J_x^2}{2(1-t)} + \frac{J_y^2}{4} + \frac{J_z^2}{2(1+t)} \right]$$

$$+ A \left[J_y \{ \sqrt{1-t^2}, P_t \} + \frac{\{J_x, J_z\}}{\sqrt{1-t^2}} \right] + V(t)$$

[1] Radau, *Ann. Sci. Ecole Normale Supérieure* **5** (1868) 311

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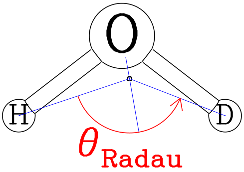
where

$$t = \cos \theta_{\mathrm{Radau}}$$



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The modified Bending-Rotation approach-*Continued*

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$$B = \frac{m_1 + m_2}{2m_1 m_2 {r_e}^2} = 28.153 \text{ cm}^{-1}$$

The modified Bending-Rotation approach-*Continued*

$$B = \frac{m_1 + m_2}{2m_1 m_2 {r_e}^2} = 28.153 \text{ cm}^{-1} \qquad A = \frac{m_1 - m_2}{4m_1 m_2 {r_e}^2} = 4.071 \text{ cm}^{-1}$$

The modified Bending-Rotation approach-*Continued*

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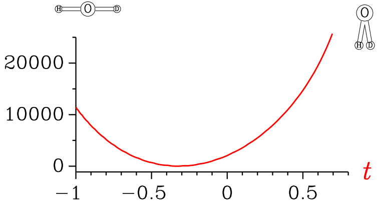
$V(t)/\text{cm}^{-1}$



$t_{\text{Min}} = -0.326$

$\theta_{\text{Radau}} = 109°$

Line position analysis: data set

Data type	Reference
Microwave data	De Lucia,[1] Messer,[2] & Baskakov[3]
Experimental levels	Toth[4]
IR transitions	Toth[4,5]
FIR transitions	Johns,[6] Paso,[7] & Parekunnel[8]

[1] De Lucia, Cook, Helminger, & Gordy, *J. Chem. Phys.* **55** (1971) 5334

[2] Messer, De Lucia, & Helminger, *J. Mol. Spec.* **105** (1984) 139

[3] Baskakov, Alekseev, Alekseev, & Pelevoi, *Opt. Spec.* **63** (1987) 1016

[4] Toth, *J. Mol. Spec.* **195** (1999) 73

[5] Toth, *J. Mol. Spec.* **162** (1993) 20

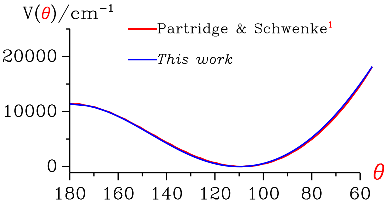
[6] Johns, *J. Opt. Soc. Am. B* **2** (1985) 1340

[7] Paso & Horneman, *J. Opt. Soc. Am. B* **12** (1995) 1813

[8] Parekunnel, Bernath, Zobov, Shirin, Polyansky, & Tennyson, *J. Mol. Spec.* **210** (2001) 28

Line position analysis: spectroscopic parameters

Parameter	Fitted	Calculated
B/cm^{-1}	27.870 322 9(2)	28.153
A/cm^{-1}	3.805 930 96(3)	4.071
59 distortion parameters		



[1] Partridge & Schwenke, *J. Chem. Phys.* **106** (1997) 4618

Line position analysis: results

Data type	Reference	N	K_a	RMS	χ^2
Levels (000)	Ref. [4]	218	10	0.3 mK	0.5
Levels (010)	Ref. [4]	203	10	0.4 mK	0.7
Microwave (000)	Ref. [1]	84	7	0.2 MHz	1.5
Microwave (010)	Ref. [2,3]	11	3	0.2 MHz	2.1
Rotational (000)	Refs. [4,6]	946	20	3.5 mK	1.1
Rotational (010)	Ref. [8]	252	20	9.7 mK	1.9
ν_2	Refs. [4,5,8]	2777	17	4.6 mK	1.1
All	Refs. [1–8]	4491	20	-	**1.1**

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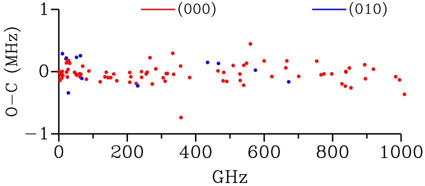
Line position analysis: O – C plot microwave transitions

This work
RMS = 0.16 MHz



[1] Tennyson *et al., J.Q.S.R.T.* **111** (2010) 2160

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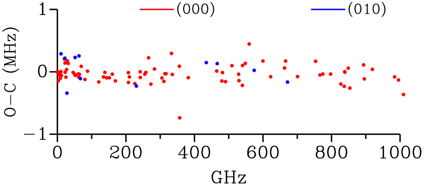
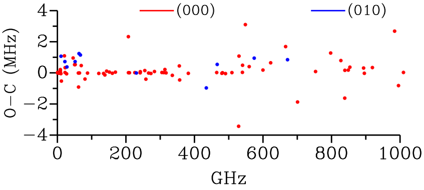


Tennyson *et al.*[1]
RMS = 2.9 MHz



[1] Tennyson *et al., J.Q.S.R.T.* **111** (2010) 2160

Line strength analysis: data set

Data type	Reference
FIR & IR transitions	Toth[1,2]

[1] Toth, *J. Mol. Spec.* **162** (1993) 20
[2] Toth, *J. Mol. Spec.* **195** (1999) 73

Line strength analysis: results

Data type	Reference	N	K_a	RMS	χ^2
Rot. (000), b-type	Ref. [2]	83	10	8.3%	1.6
ν_2, b-type	Ref. [1]	761	9	5.0%	1.0
ν_2, a-type	Refs. [1,2]	561	9	6.9%	1.0
All	Refs. [1,2]	1405	10	6.1%	**1.1**

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Expansion of $\mu_x(t)$ and $\mu_z(t)$ were determined[3]

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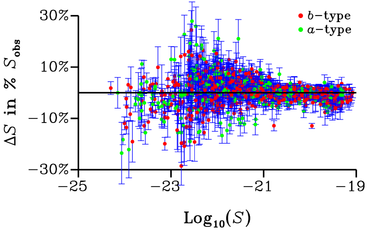
Line strength analysis: ΔS plots



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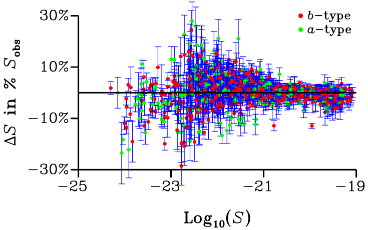

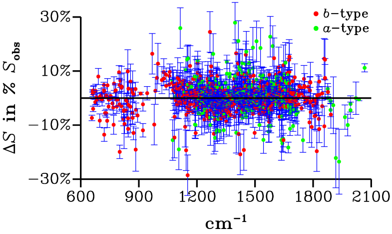

Building a Hitran-type database

[1] https://www.cfa.harvard.edu/hitran/molecules.html

[2] Rothman *et al.*, *J.Q.S.R.T.* **130** (2013) 4

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1. Transitions up to (010) and $J = 22$ were calculated in the 0–2000 cm^{-1} range.

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1. Transitions up to (010) and $J = 22$ were calculated in the 0–2000 cm^{-1} range.
2. An intensity cutoff of $10^{-28}\ \text{cm}^{-1}/(\text{molecule}\cdot\text{cm}^{-2})$ at 296 K was taken assuming assuming an isotopic abundance[1] of 3.107×10^{-4}.

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3. The new database contains 6142 transitions and was compared to Hitran 2012.[2]

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New data base vs. Hitran 2012: line positions

3063 lines out of 6142 found in Hitran 2012.[1]

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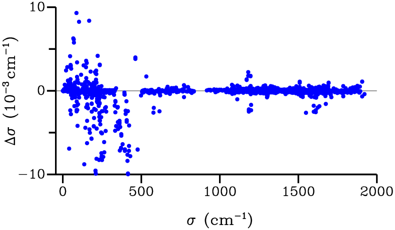

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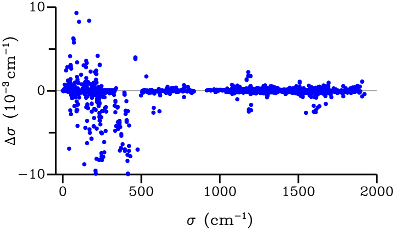

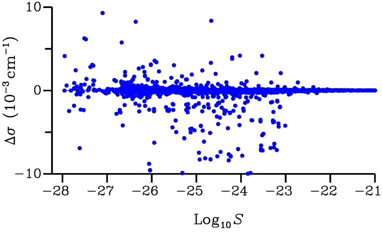

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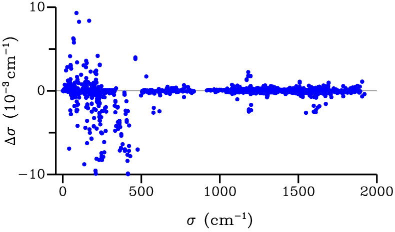

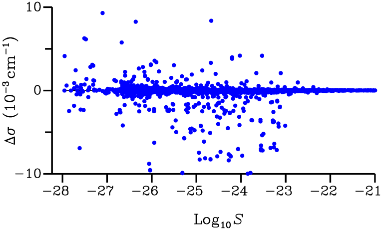

262 outliers with $10^{-28} \leq S \leq 10^{-21}$ $\text{cm}^{-1}/(\text{molecule}\cdot\text{cm}^{-2})$.

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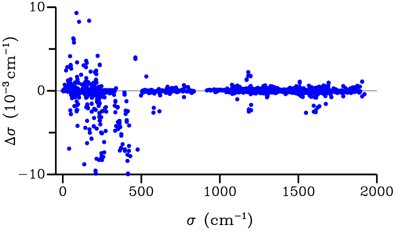

262 outliers with $10^{-28} \leq S \leq 10^{-21}$ cm^{-1}/(molecule $\cdot$ cm^{-2}).

$$12_{12,0} \leftarrow 11_{11,1}\ (000) \quad \text{at} \quad 488.8022\ \text{cm}^{-1} \quad \text{with} \quad \Delta\sigma = 1.5\ \text{cm}^{-1}$$
$$S = 1.8 \times 10^{-26}\ \text{cm}^{-1}/(\text{molecule} \cdot \text{cm}^{-2})$$

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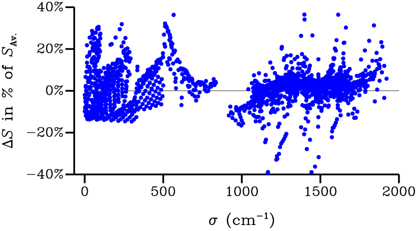
New data base vs. Hitran 2012: line strengths



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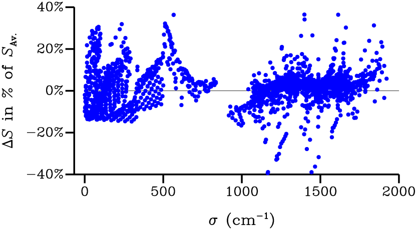

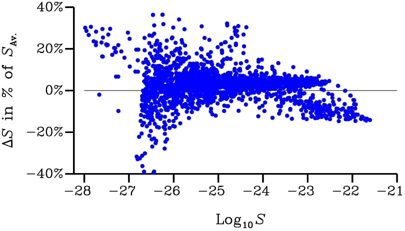

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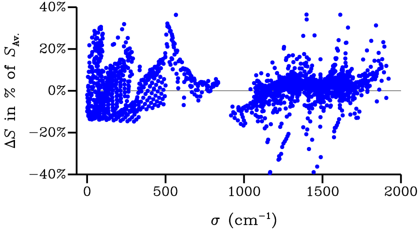
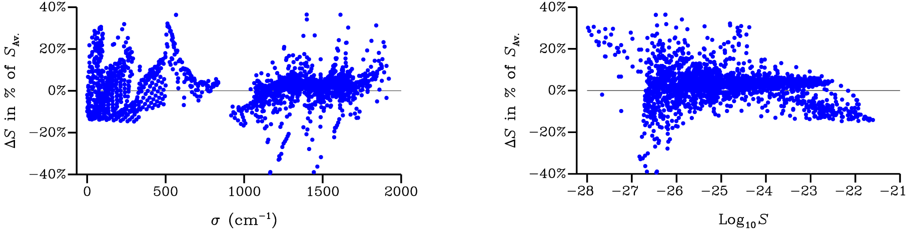


525 outliers with $10^{-28} \leq S \leq 10^{-21}$ $\text{cm}^{-1}/(\text{molecule} \cdot \text{cm}^{-2})$.

New data base vs. Hitran 2012: line strengths



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$$10_{4,7} \leftarrow 9_{2,8}\,(000) \quad \text{at} \quad 363.1669\ \text{cm}^{-1} \quad \text{with} \quad \Delta S = 190\%$$

$$S = 6.3 \times 10^{-24}\ \text{cm}^{-1}/(\text{molecule} \cdot \text{cm}^{-2})$$

Conclusion

[1] Rothman *et al.*, *J.Q.S.R.T.* **130** (2013) 4

Conclusion

1. For the ground and (010) vibrational states, there are large discrepancies between data base built in this work and Hitran 2012[1] for line positions as well as for line strengths.

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2. The results of this work should allow us to improve the Hitran database.

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2. The results of this work should allow us to improve the Hitran database.
3. Future work: including higher lying states in the data set.

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Thank You