Theoretical Rotational Spectra of Deuterated Benzene Isotopologues: Improvements on the Benzene' s quantification at Interstellar Medium

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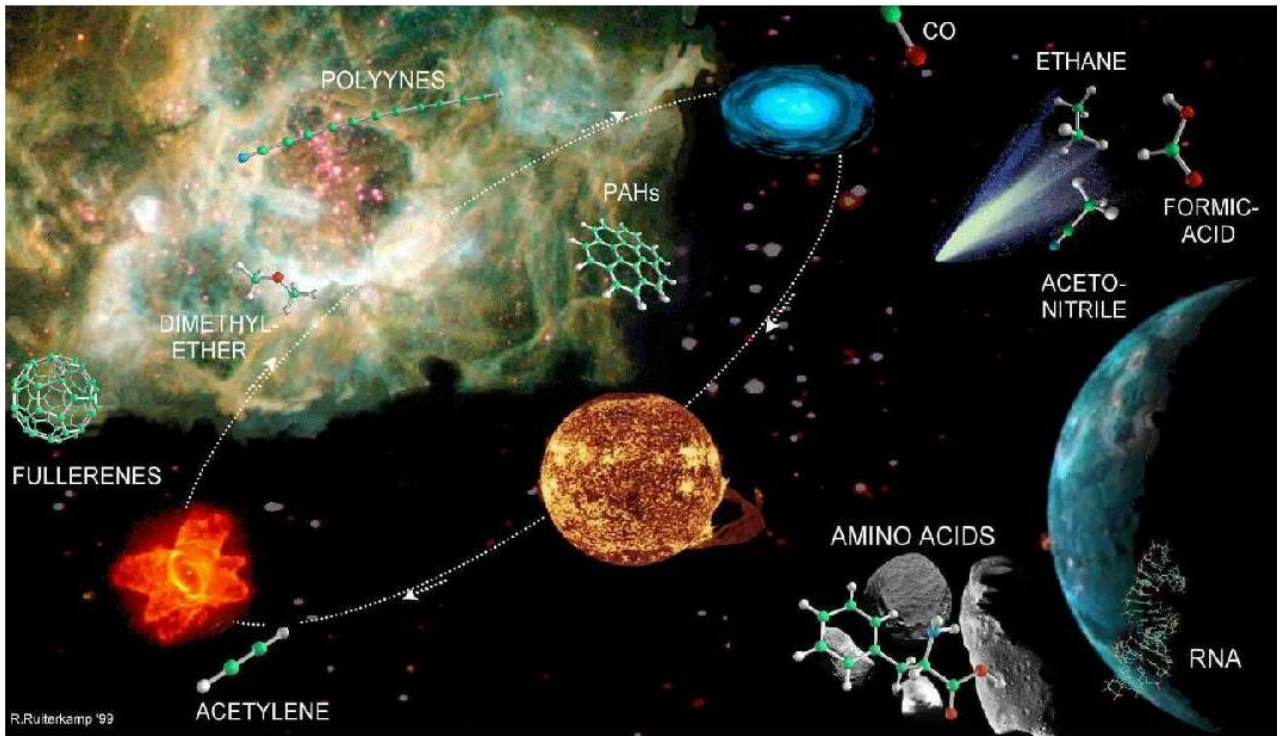
Molecules at ISM and CSS

About 195 molecules detecteds in the Interstelar (ISM) medium and Circumstellar Shells (CSS) (as of 06/2016)[2].

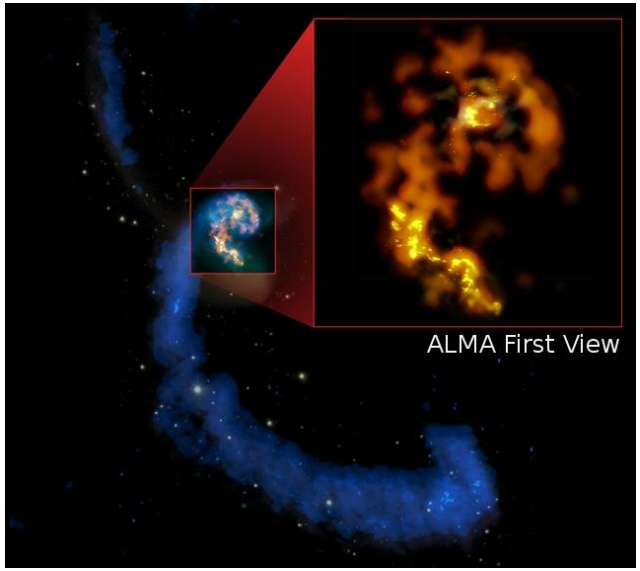


[2]The Cologne Database for Molecular Spectroscopy - CDMS, H. S. P. Muller et. al., J. Mol. Struct. 742, 215-227 (2005)

Molecules at ISM and CSS

Latest generation instrumentation to Radioastronomy.

(a) ALMA Radiotelescope



(b) NGC 4038 and 4039

ALMA - *Atacama Large Mm/Submm Array*
64 antennas at Chajnantor plateau - Chile (5058,7 m)
Front End: 10 bands between 31 - 950 GHz

Motivation: Deuterated isotopologues at ISM

- Deuterated Polycyclic Aromatic Hydrocarbons PAD in ISM[2].
- Key role of PAH in the astrochemical evolution of the ISM
- Formation of benzene in the ISM[3].

Proposal of Detection

The search for deuterated isotopologues of otherwise apolar molecules can be amplified using radio-telescopes if we have good synthetic spectra for these ones.

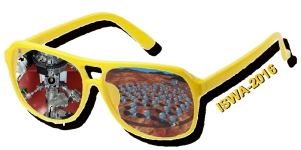
[2] Peeters et al., Astrophys. J., 604, 252 (2004)
[3] Jones et al., Proc. Nat. Ac. Soc., 108, 452 (2010)

Quantum Chemical Calculations

- Theoretical and computational approach for building highly accurate *ab initio* pure rotational spectra of deuterated isotopologues.
- Using these spectra to assist possible detections of polyatomic isotopologues of astrophysical interest.[4][5].

Simulating Pure Rotational Spectra

- Level of aproximation: our pure rotational spectra simulations needs dipole moments, rotational constants.
- We will not to consider centrifugal distortion constants, Hyperfine and/or Spin effects.

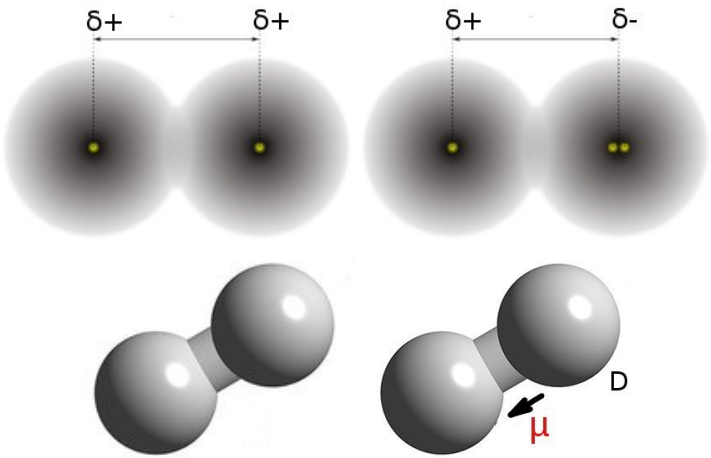


[4] R. Motiyenko, J. Phys. Chem. A, 2015, 119 (6),1048-1054
[5] C. Puzzarini, Phys. Chem. Chem. Phys., 2013,15, 6595-6607

The Isotopic Effect on Dipole Moments

Molecular Symmetry Breaking

e.g.: Hydrogen atoms (H) replaced by deuterium atoms (D)



Isotopic assymmetry on the electronic distribution

$$a_0 = \frac{4\pi\varepsilon\hbar^2}{me^2} \tag{1}$$

Consequence: dipole moment (DM) $\sim 10^{-3}$ debye to HD

Electronic Structure - Molecular Approximations

$$\hat{H}\psi(\vec{r},\vec{R}) = E\psi(\vec{r},\vec{R}) \tag{2}$$

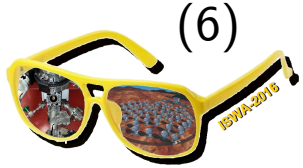
Adiabatic Model: Born-Oppenheimer Approximation(BOA)

$$\hat{H} = \hat{T}_{nuc} + \hat{H}_{BO} \tag{3}$$

$$\hat{H}_{BO} = -\sum_i \frac{\nabla_i^2}{2} + V \tag{4}$$

$$\hat{H}_{BO}\phi(\vec{r};\vec{R}) = E_{ele}\phi(\vec{r};\vec{R}) \tag{5}$$

$$E_{tot} = E_{ele} + \sum_{A=1}^{M}\sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}} \tag{6}$$



Potential Energy Surface - PES

Electronic Structure - Molecular Approximations

The BOA can't to predict the isotopic effect

↓

FNMC - Finite Nuclear Mass Correction

↓

The FNMC Model Hamiltonian FNMC[a]

[a] J.R. Mohallem, J. Phys. B: At. Mol. Opt. Phys. 32 (1999) 3805

$$\hat{H}_{FNMC} = \sum_{A}^{m}(-\sum_{i}^{n} P_A \frac{\nabla_i^2}{2M_A} P_A) + \hat{H}_{BO} \quad (7)$$

The computacional cost is identical to the BOA

Ab Initio Computational Packages Adapted to FNMC

- GAMESS/ISOTOPE - Gonçalves and Mohallem - 2003[6]
- deMon 2k - Mohallem et al - 2008[7]

DaltonFNMC - 2011[a]

[a] Arapiraca et al., J. Chem. Phys. 135, 244313 (2011)

- Dr. Dan Jonsson (CTCC, University of Tromsø- Norway)
- Dalton 2.0/2016: *Ab Initio* and *DFT* methods
- www.daltonprogram.org - Open Source Code

[6] C. P. Goncalves and J. R. Mohallem., J. Comp. Chem., 25, 1736, (2004)
[7] J. R. Mohallem et al, J. Phys. Chem. A, 118, 8896, (2008)

Vibrational Corrections on Molecular Properties

Theory X Experiment

Computing nuclear moviments of the molecular systems

ZPVC - Zero Point Vibrational Correction[a] [b]

[a] P-O. Astrand et al., J. Chem. Phys., 102, 3534, (1995).
[b] K. Ruud et al., J. Chem. Phys., 112, 2668, (2000).

- Dalton 2.0/2016 - HF/SCF, MCSCF (CAS/RAS) e DFT
- Variational expansion point - effective geometry (vibrationally averaged)
- 2^a order Perturbation Theory - feasible to polyatomics

Vibrationally Averaged Geometry and Dipole Moments

Effective Geometry

$$r_{ef} = \langle r_i \rangle = r_{e,i} - \frac{1}{4\omega_i} \sum_{j=1}^{3N-6} \frac{V_{ijj}^{(3)}}{\omega_j} \tag{8}$$

Perturbative expansion of the vibrational wavefunction $|\Psi\rangle_{vib}$

Vibrationally Averaged Dipole Moments

$$\langle \mu \rangle = \mu_{ef} + \frac{1}{4} \sum_i \frac{\mu_{ef,ii}^{(2)}}{4\eta\omega_{ef}} \tag{9}$$

η is the reduced mass of the system

FNMC/ZPVC Dipole Moments (Dalton 2016 Program)

FNMC/ZPVC predicts highly accurate dipole moments to

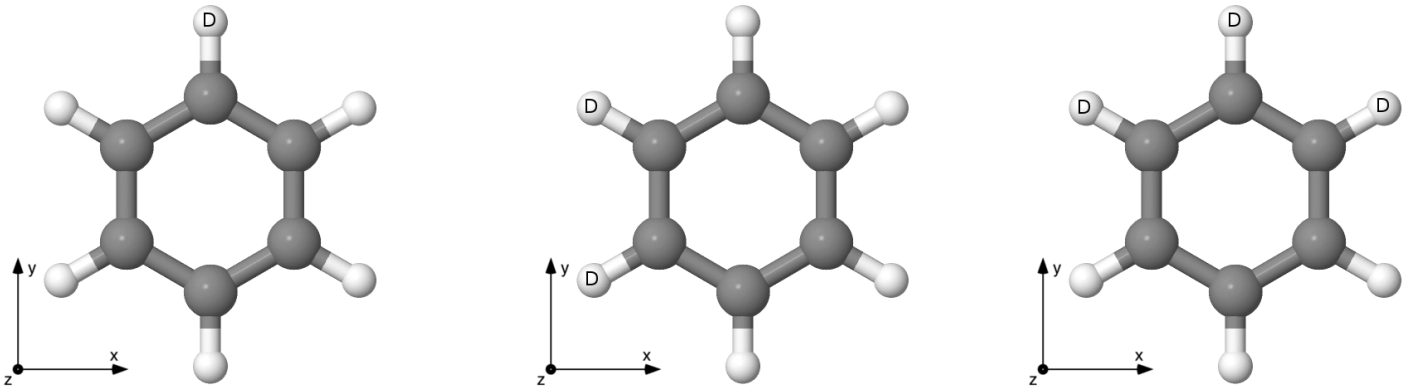
- HD, HT, CH_3CD_3, $^{13}CH_3CD_3$, $CH_3^{13}CD_3$, $CH_2CD2(asym.)$, $CHDCHD(cis)$ - Originally apolar systems. [8]
- C_3H_8, $CH_3CD_2CH_3$, $CD_3CH_2CD_3$, $CHD_2CH_2CHD_2$, CH_3CCH, CH_3CCD, CD_3CCH, CD_3CCD, H_2O, $[HDO]$, D_2O - Originally polar systems.[9]

Two importants findings

- The isotopic substitution trend.
- Accuracy relative to experimental data - Benchmark!.

[8] Arapiraca et al., J. Chem. Phys. 135, 244313 (2011)
[9] Arapiraca and Mohallem., Chem. Phys. Let., 609, 123 (2014)

FNMC/ZPVC Dipole Moments (Dalton 2016 Program)



B3LYP/FNMC/ZPVC/6-31G**	Dipole	Moments	
System	$\langle\mu\rangle_z$ [10]	Experiment [11]	Δ(%)
C_6H_5D	0.0078	0.0081[a]	3.7%
$C_6H_4D_2$	0.0134	-	-
$C_6H_3D_3$	0.0154	-	-

Vibrationally averaged isotopic dipole moments of benzene isotopologues in debye units at B3LYP/FNMC/ZPVC/6-31G** level

[10] Arapiraca et al., J. Chem. Phys. 144, 144301 (2016)

[11] M. Oldani and A. Bauder, Chem. Phys. Let., 108, 7 (1984)

ZPVC Rotational Constants (Gaussian 09 program)

	B3LYP/ZPVC/aug-cc-pVTZ	Experiment	Δ(%)
		C_6H_5D[12]	
A	5692.143	5689.144(6)	0.053%
B	5326.934	5323.934(6)	0.056%
C	2750.913	2749.674(6)	0.045%
		$C_6H_4D_2$[13]	
A	5501.102	5498.062	0.062%
B	5167.642	5164.242	0.066%
C	2663.735	2662.496	0.046%
		$C_6H_3D_3$	
A	5217.7295	-	-
B	5201.4588	-	-
C	2604.7907	-	-

Rotational constants of benzene isotopologues in *MHz* units.

[12] M. Oldani et al., J. Mol. Struc., 1909, 190 (1983)

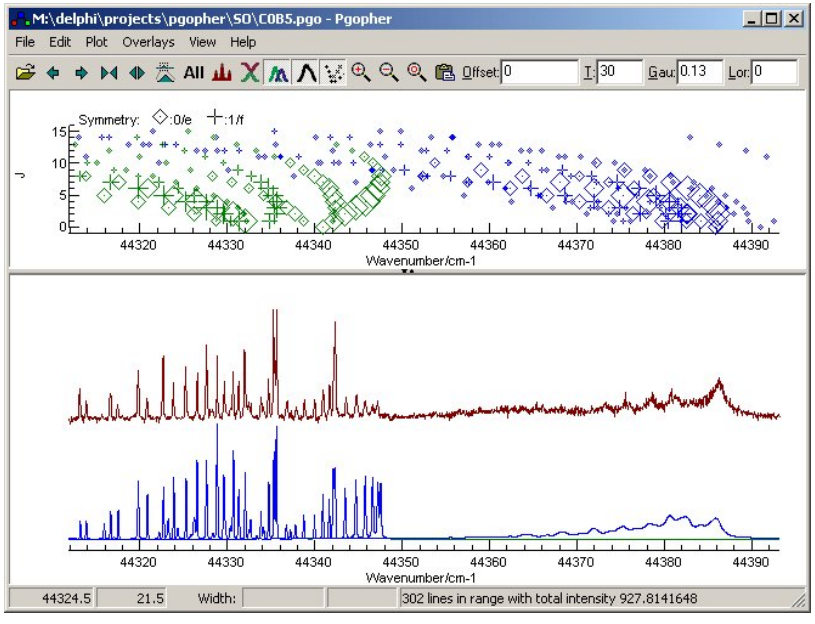
[13] M. Oldani and A. Bauder, Chem. Phys. Let., 108, 7 (1984)

Simulating Rotational Spectra (PGOPHER Program)

Programa PGOPHER

To resolve the molecular rotational structure[a]

[a]PGOPHER, a Program for Simulating Rotational Structure, C. M. Western, University of Bristol, http://pgopher.chm.bris.ac.uk



Simulating Rotational Spectra (PGOPHER Program)

Polyatomic Molecule - Asymmetric Top

Inertia moments and angular moment projections

$$I_A \leq I_B \leq I_C \tag{10}$$

$$A \leq B \leq C \tag{11}$$

$$\hat{H} = A\hat{J}_a^2 + B\hat{J}_b^2 + C\hat{J}_c^2 \tag{12}$$

$$\kappa = \frac{2B - A - C}{A - C} \tag{13}$$

Simulating Rotational Spectra (PGOPHER Program)

Einstein's Coefficients

Dipole moment approximation - Emission and Absorption

$$N_0 B_{1\leftarrow 0}\rho_\nu = A_{1\rightarrow 0}N_1 + B_{1\rightarrow 0}\rho_\nu N_1 \tag{14}$$

$$B_{1\leftarrow 0} = B_{1\rightarrow 0} \tag{15}$$

$$A_{1\rightarrow 0} = \frac{8\pi h\nu_{10}^3}{c^3} B_{1\leftarrow 0} \tag{16}$$

$$A_{1\rightarrow 0} = \frac{16\pi^3\nu^3}{3\varepsilon_0 hc^3}\mu_{10}^2 \tag{17}$$

Simulating Rotational Spectra (PGOPHER Program)

Computing state populations

Emission and Absorption Intensities

$$I(T)_{emiss} = \frac{64\pi^4}{3hc} \frac{\nu^3 S_g \mu_g^2 (e^{-E''/kT} - e^{-E'/kT})}{Q} \quad (14)$$

$$I(T)_{abs} = \frac{8\pi^3}{3hc} \frac{\nu S_g \mu_g^2 (e^{-E''/kT} - e^{-E'/kT})}{Q} \quad (15)$$

Multiplicative Mean Correction Factor - MCF

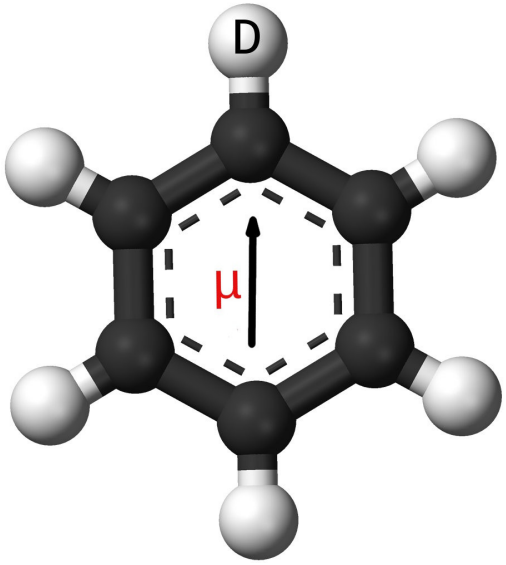
$$CF_i = \frac{V_i^{exp}}{V_i^{teo}} \tag{16}$$

$$MCF = \frac{1}{N} \sum_{i=1}^{N} FC_i \tag{17}$$

$$VC_i^{teo} = V_i^{teo} MCF \tag{18}$$

Benzene's Isotopologues Spectra

C_6H_5D



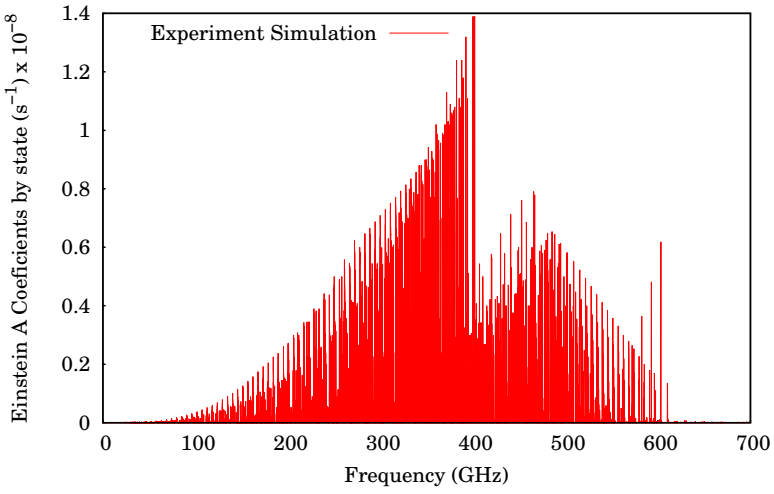
$C_{2v} - \kappa = 0.75$

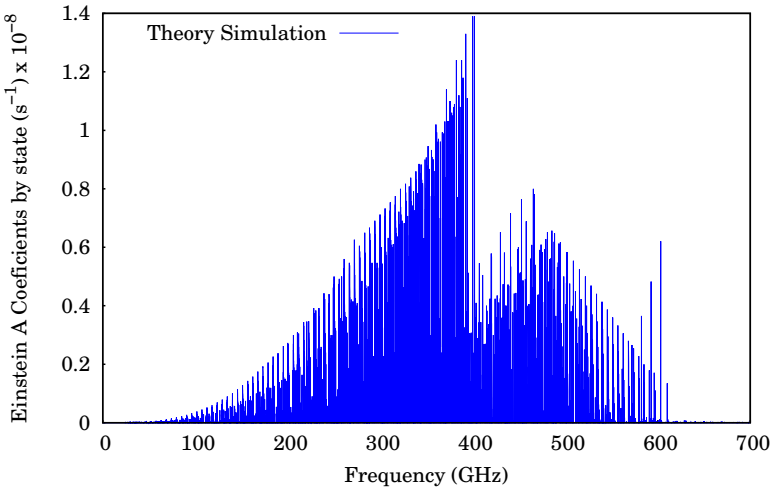
Watson Asymmetric Reduction III^r

Benzene's Isotopologues Spectra

C_6H_5D Spontaneous Emission Rates by State

29253 lines: $0 \leqslant J \leqslant 40 - 0 \leqslant K \leqslant 31$





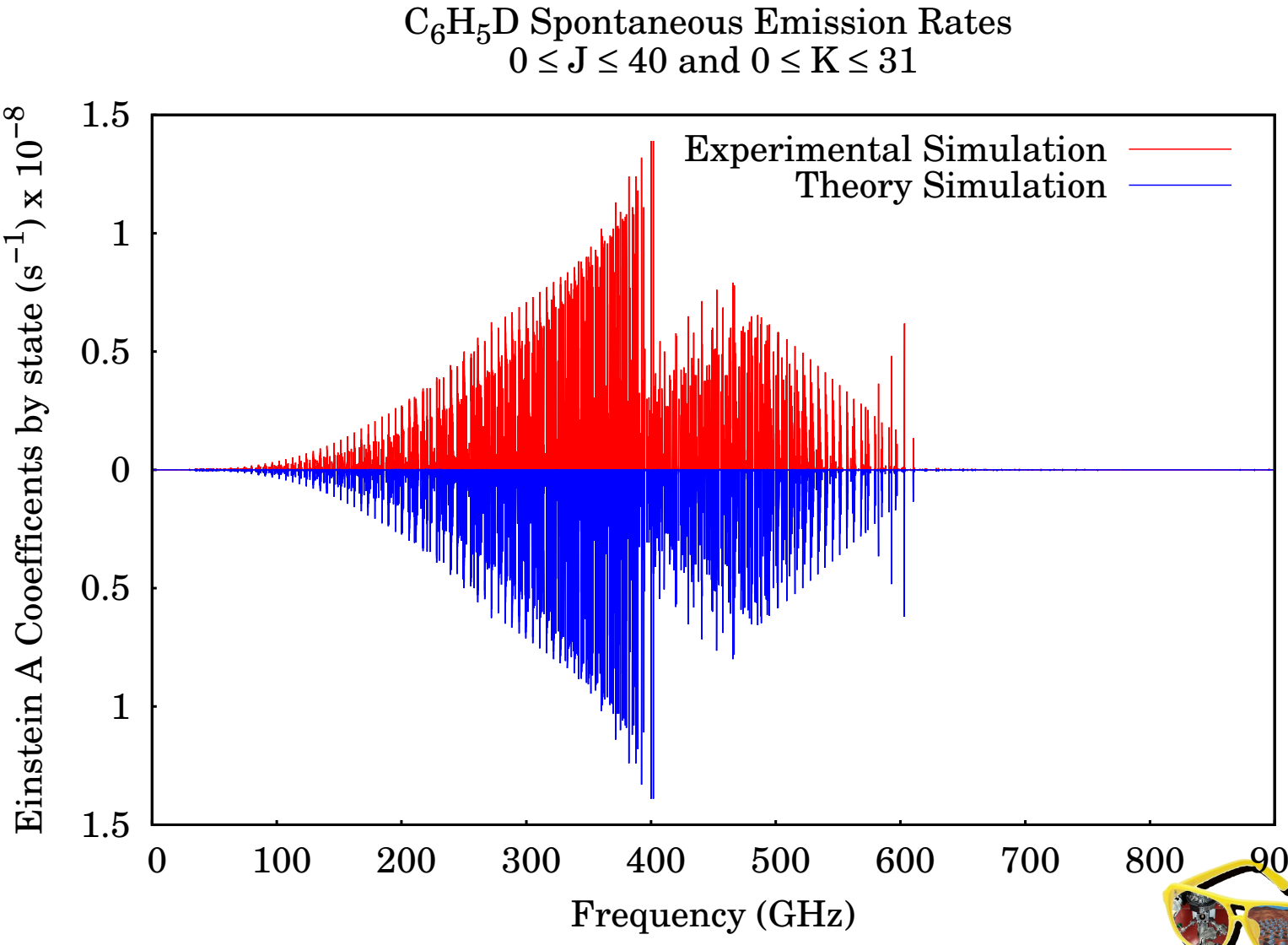
MAPE error without MCF correction

Frequency MAPE error: 0.08% - Intensity MAPE error: 7.51%

MAPE error with MCF correction

Frequency MAPE error: 0.03% - Intensity MAPE error: 0.44%

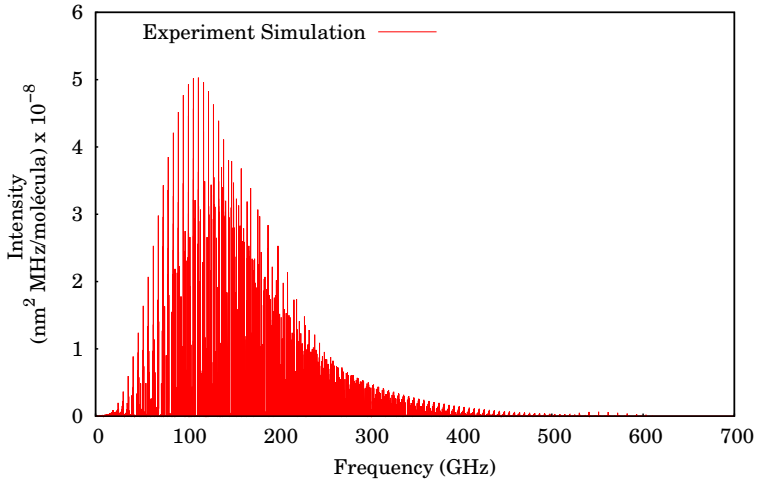
Benzene's Isotopologues Spectra

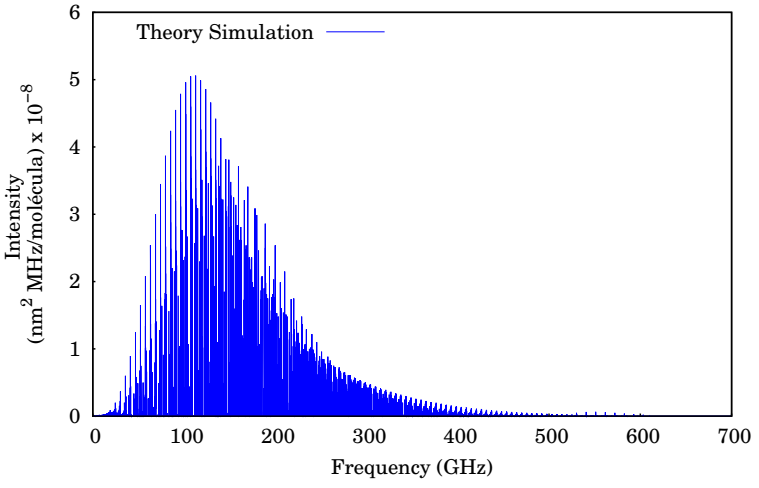


Benzene's Isotopologues Spectra

C_6H_5D Absorption Spectra at 35 K

29253 lines: $0 \leqslant J \leqslant 40 - 0 \leqslant K \leqslant 31$





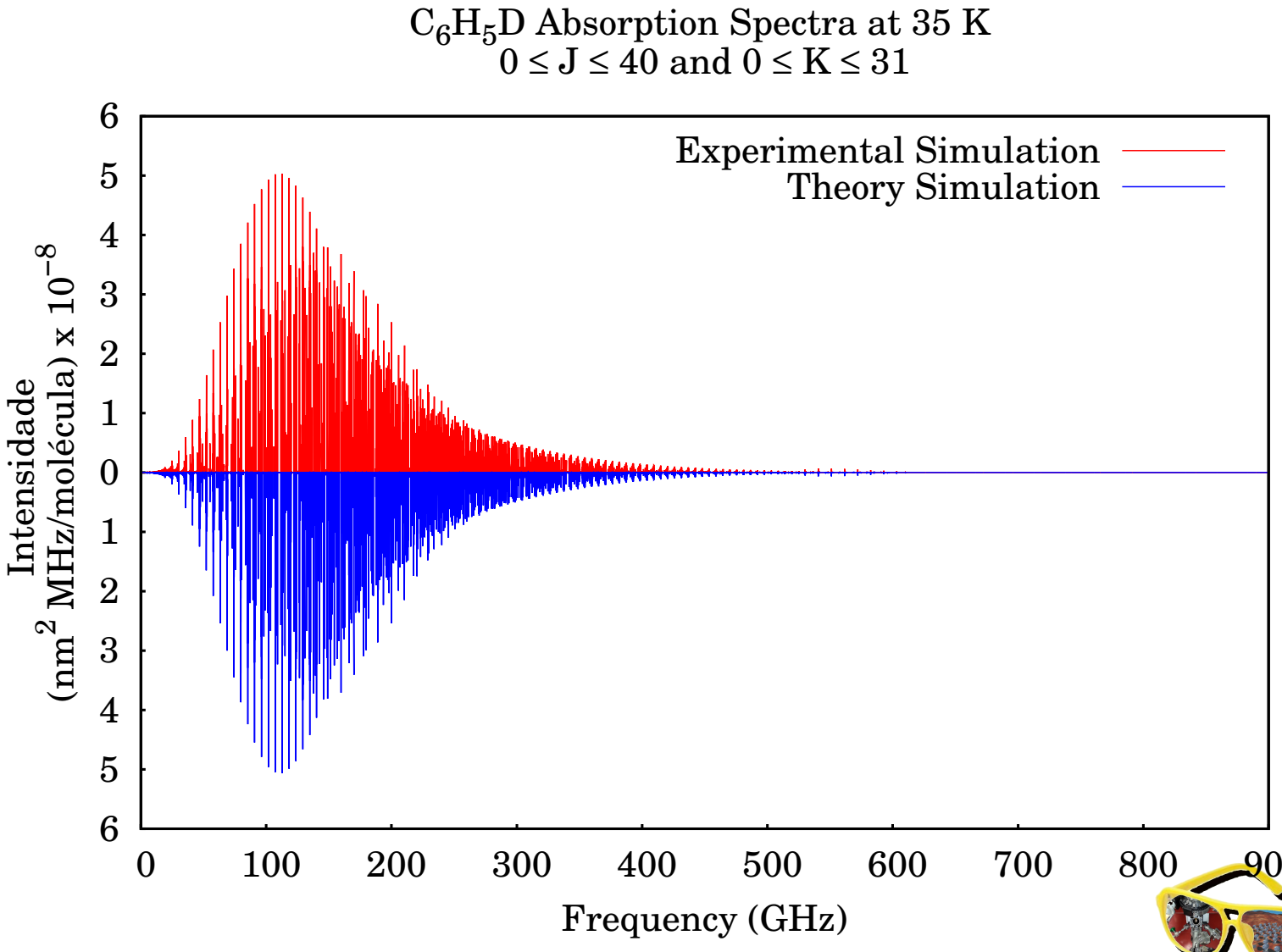
MAPE error without MCF correction

Intensity MAPE error: 7.78%

MAPE error with MCF correction

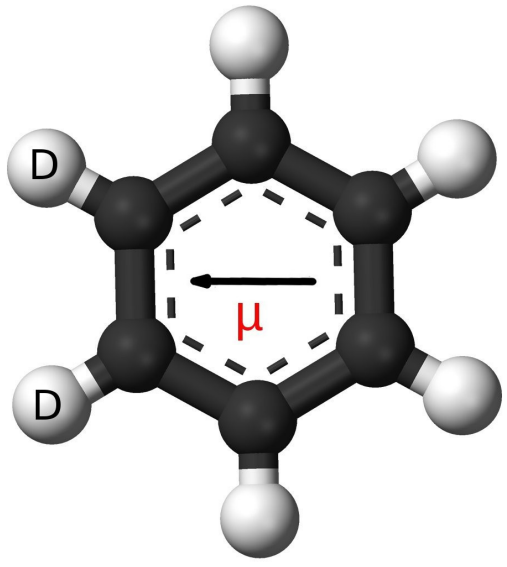
Intensity MAPE error: 0.45%

Benzene's Isotopologues Spectra



Benzene's Isotopologues Spectra

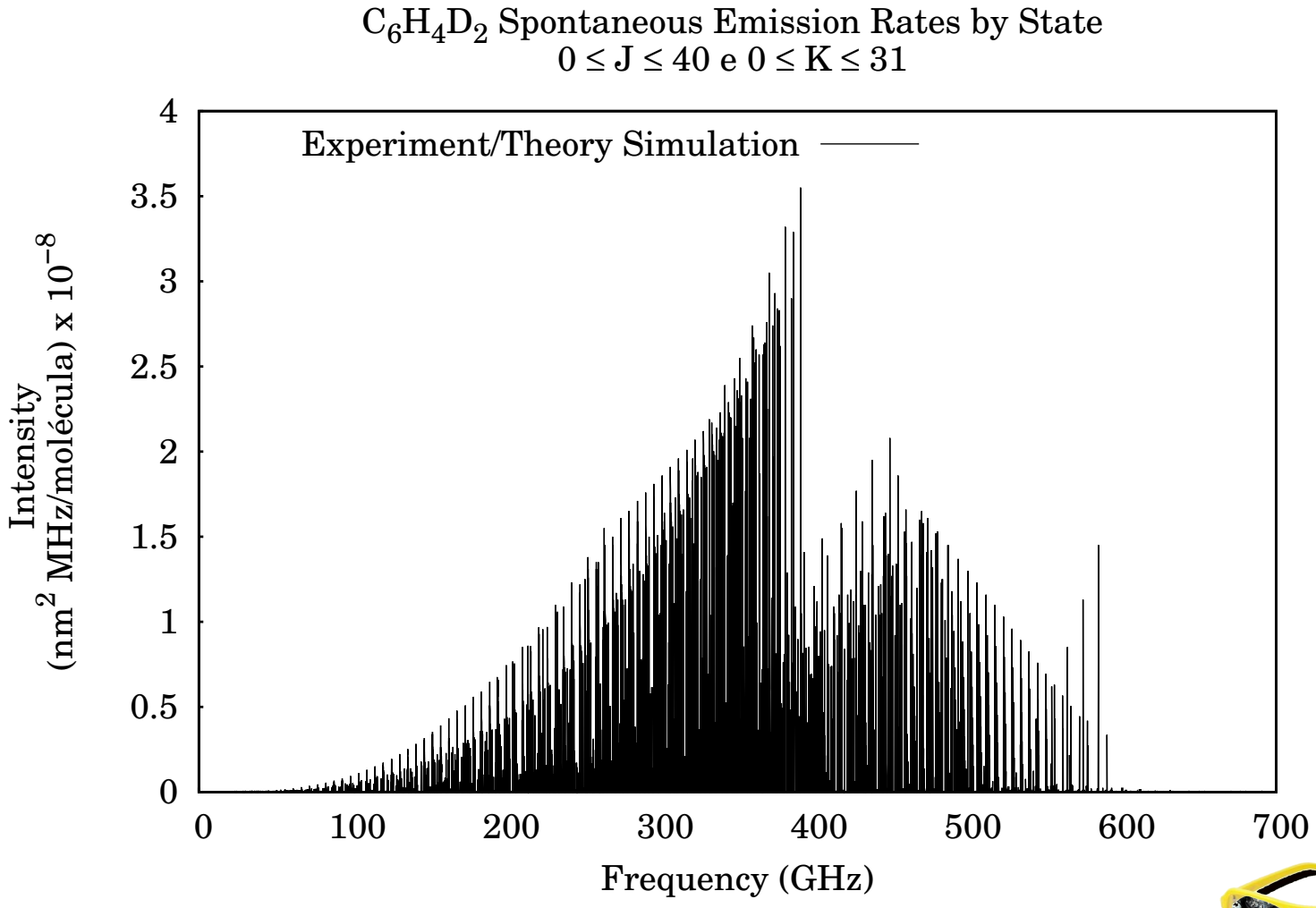
$C_6H_4D_2$



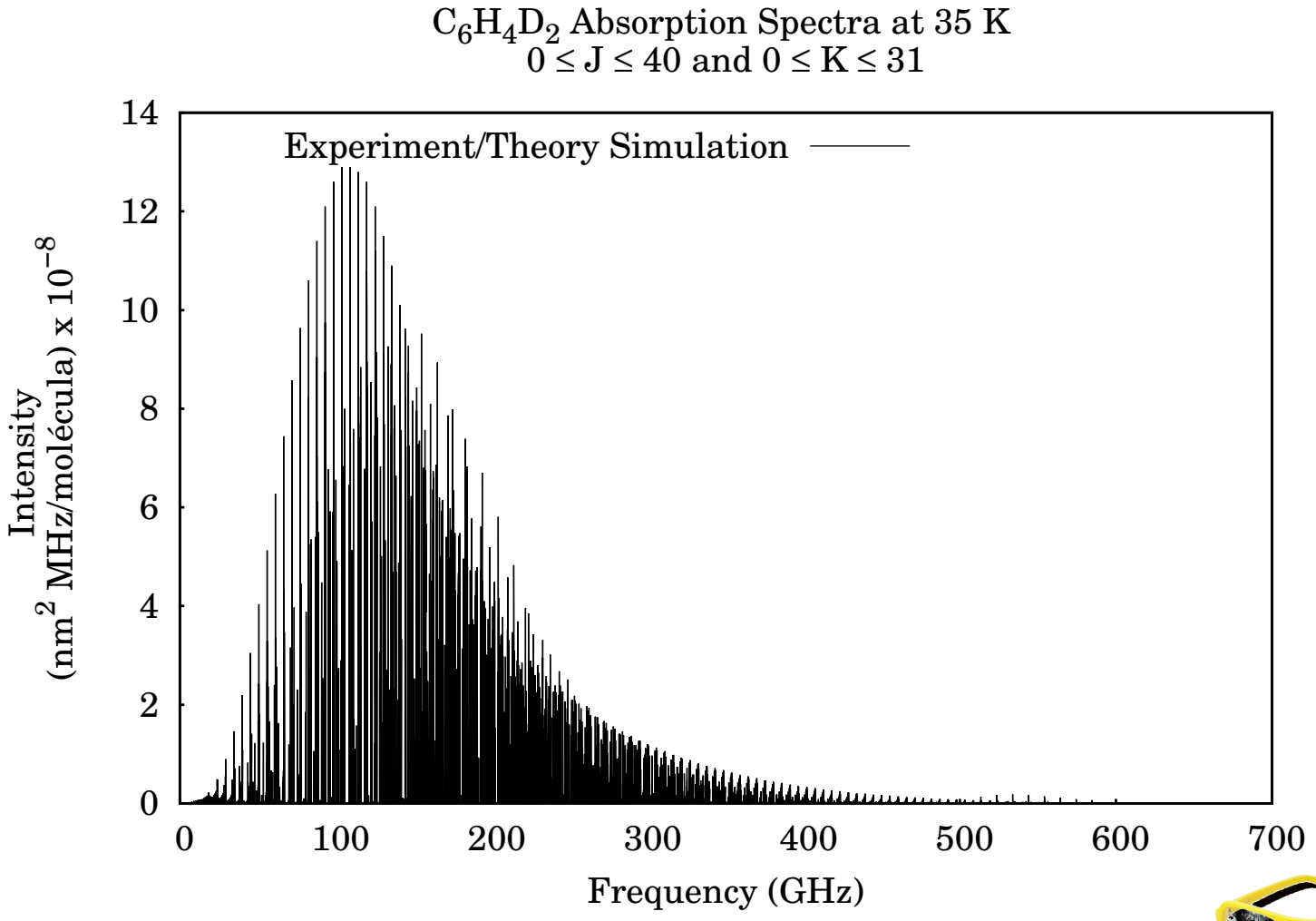
$C_{2v} - \kappa = 0.76$

Watson Asymmetric Reduction III^r

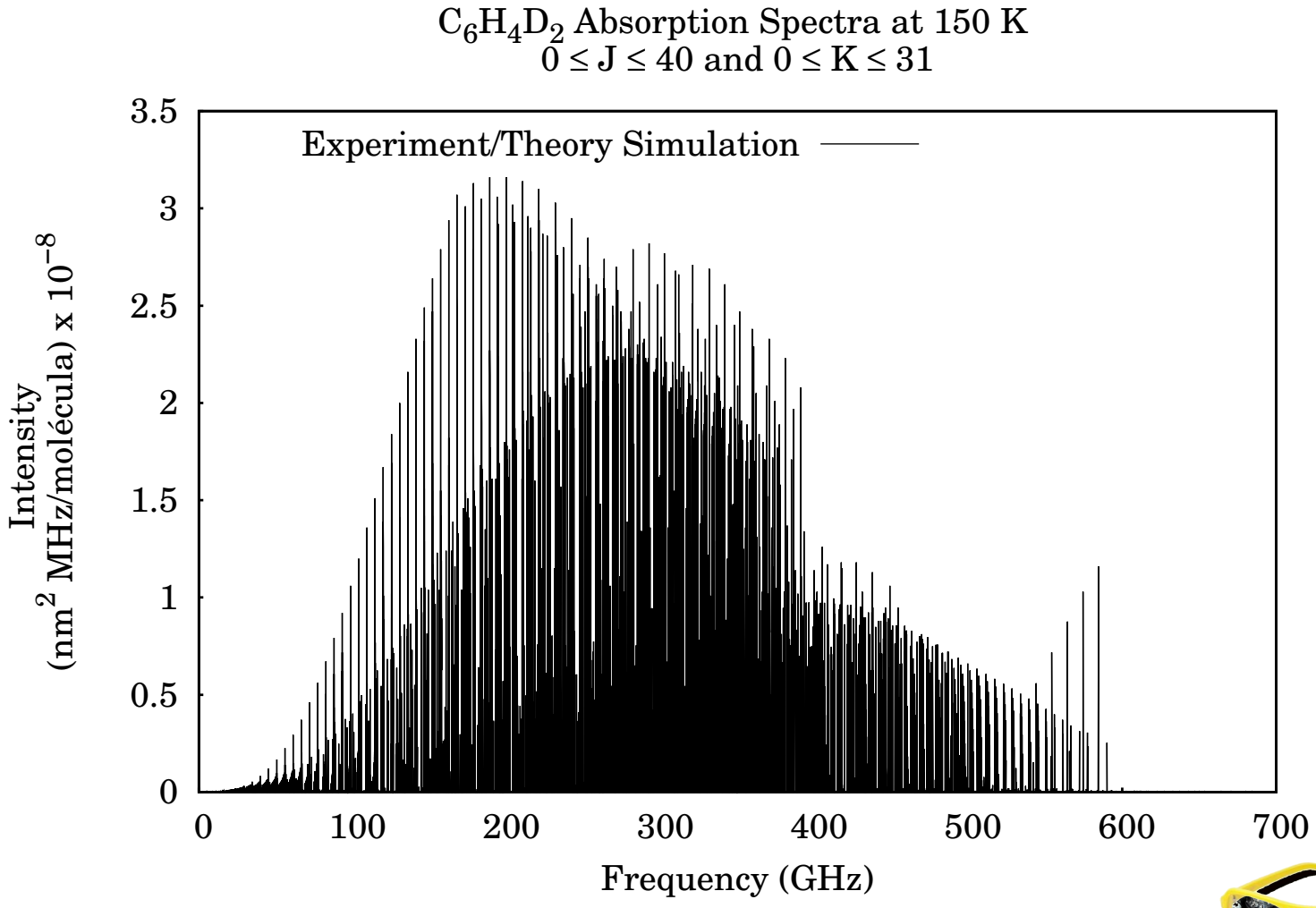
Benzene's Isotopologues Spectra



Benzene's Isotopologues Spectra

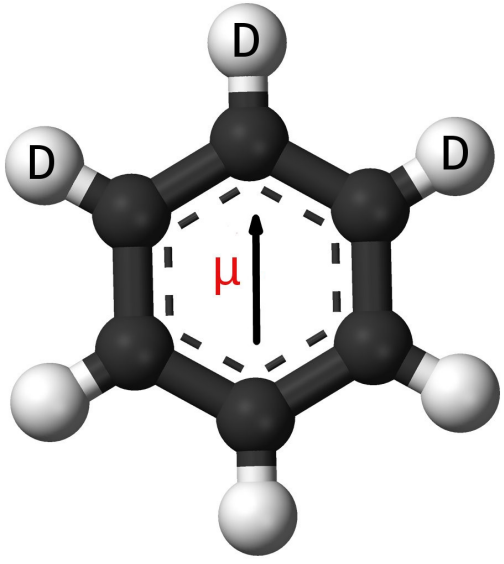


Benzene's Isotopologues Spectra



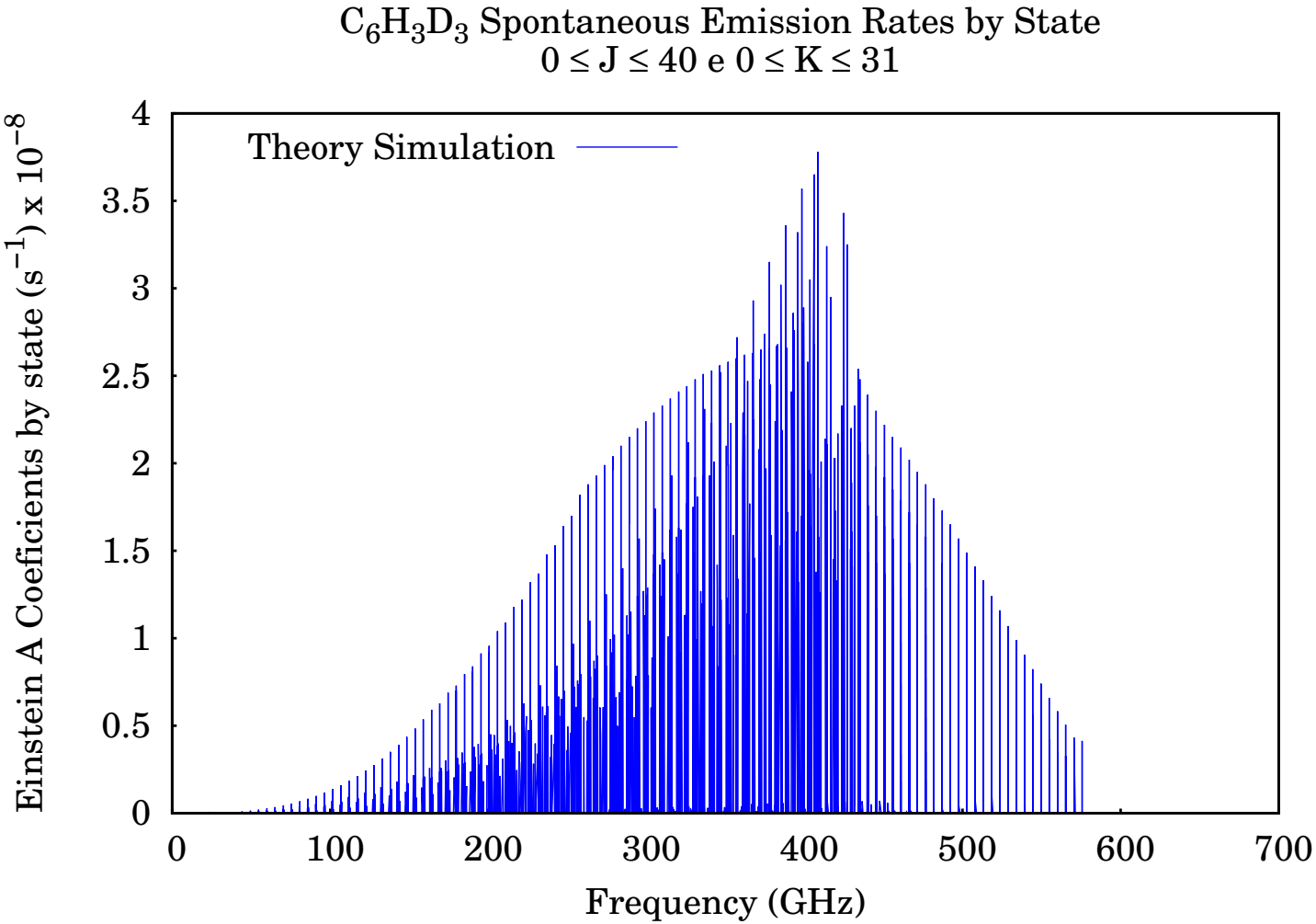
Benzene's Isotopologues Spectra

$C_6D_3H_3$

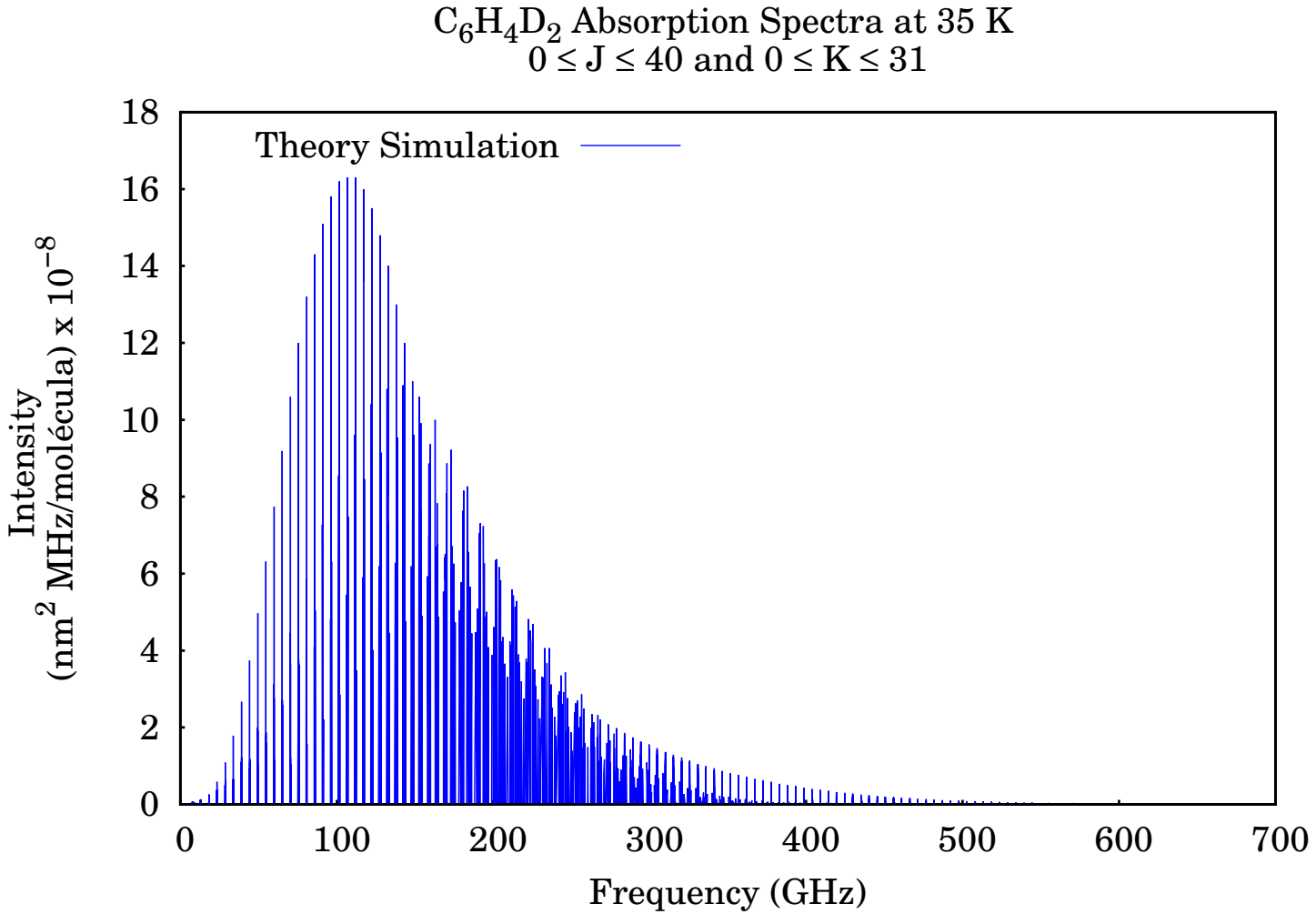


$C_{2v} - \kappa = 0.99$

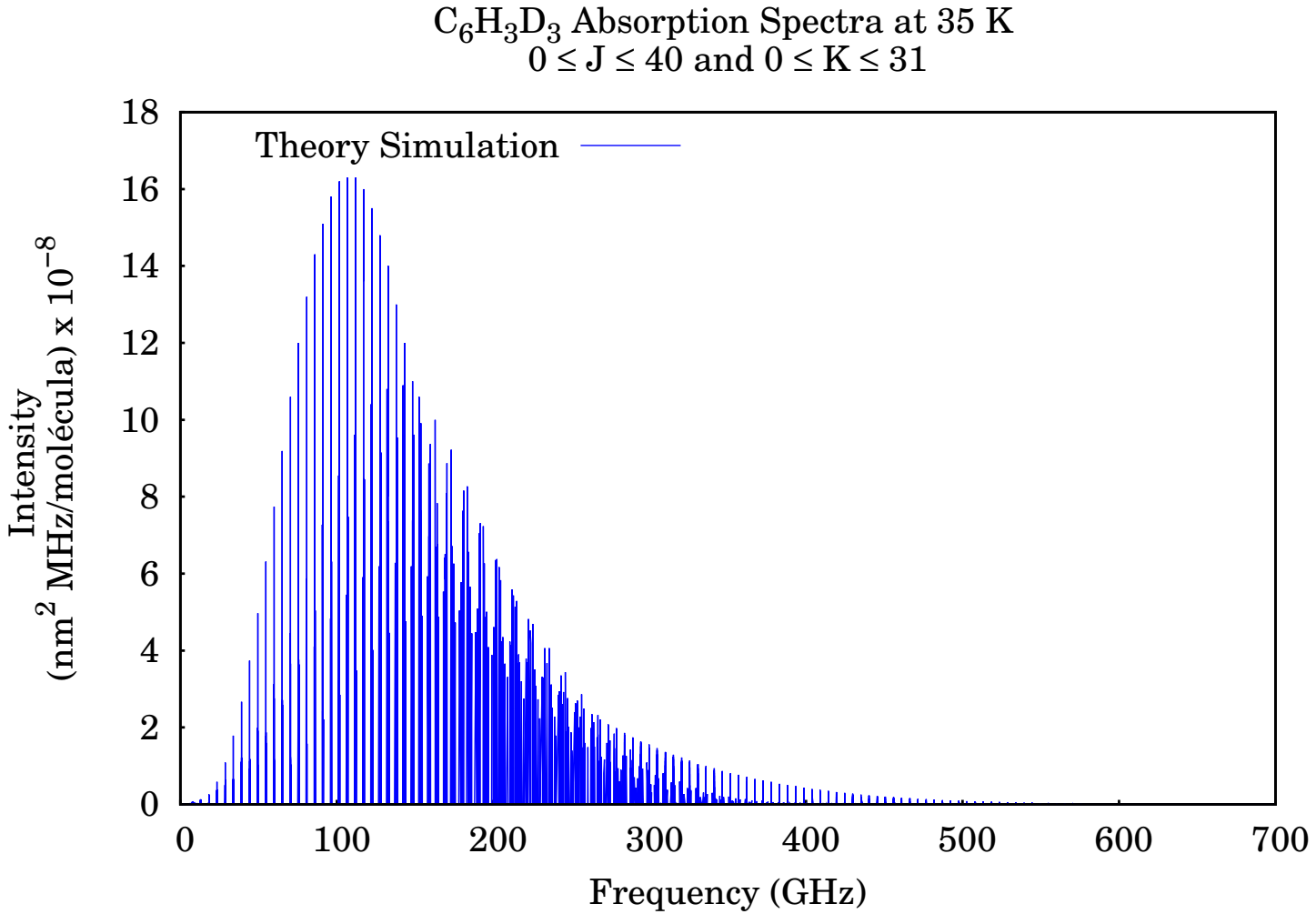
Watson Asymmetric Reduction III^r


$C_6H_3D_3$ Spontaneous Emission Rates by State
$0 \leq J \leq 40$ e $0 \leq K \leq 31$
Theory Simulation
Einstein A Coeficients by state (s^{-1}) x 10^{-8}
Frequency (GHz)
0
0.5
1
1.5
2
2.5
3
3.5
4
0
100
200
300
400
500
600
700


ISMA-2016


$C_6H_4D_2$ Absorption Spectra at 35 K
$0 \leq J \leq 40$ and $0 \leq K \leq 31$
Theory Simulation
Intensity
(nm^2 MHz/molécula) x 10^{-8}
0
2
4
6
8
10
12
14
16
18
0
100
200
300
400
500
600
700
Frequency (GHz)


ISMA-2016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0
2
4
6
8
10
12
14
16
18
0
100
200
300
400
500
600
700
Frequency (GHz)


ISMA-2016

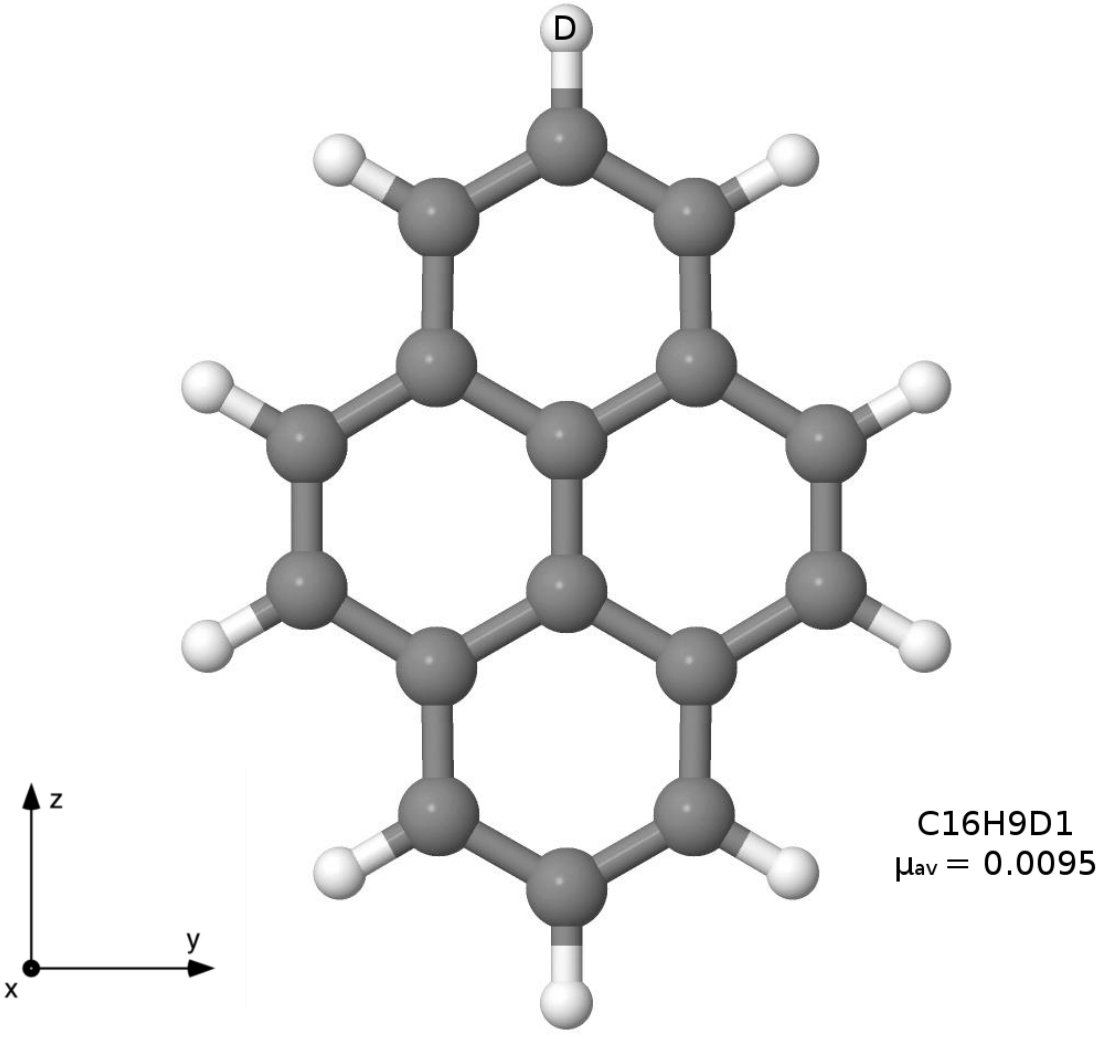
Conclusions

- Theoretical description of isotopic effects in molecules.
- Efficient Electronic and vibrational analysis.
- *Ab Initio* rotational spectra to deuterated molecules.
- Several proposals of experiments.

Perspectives

- Improving the error analysis.
- Theoretical support to detection of molecules.
- Line survey of SGR-B2 unidentified lines (Sergio Pilling).
- Column densities and abundances (RADEX...)(Edgar Mendoza).
- Deuterated benzene's formation process (João Bosco da Silva).
- PAH rotational spectra.

Coming Soon



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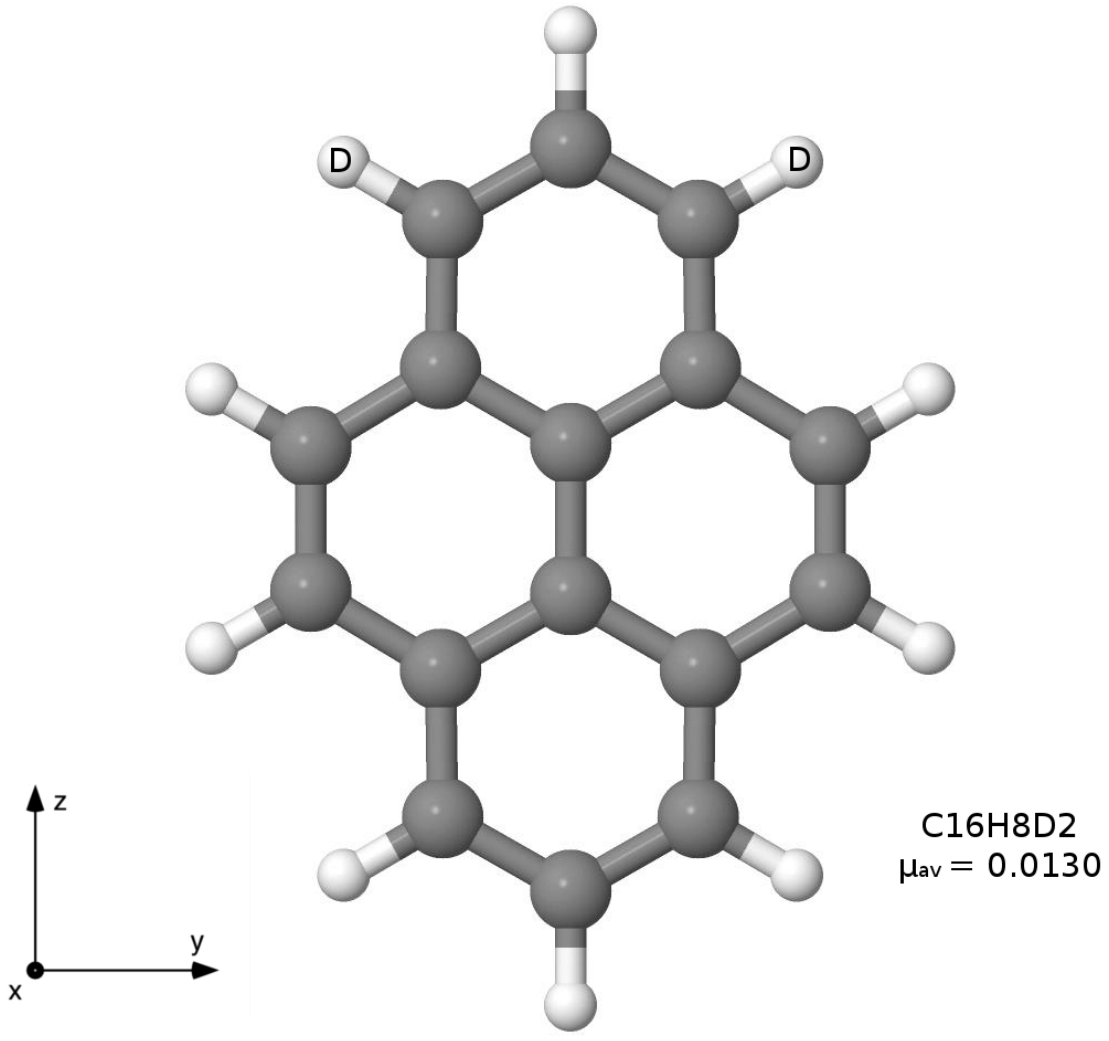

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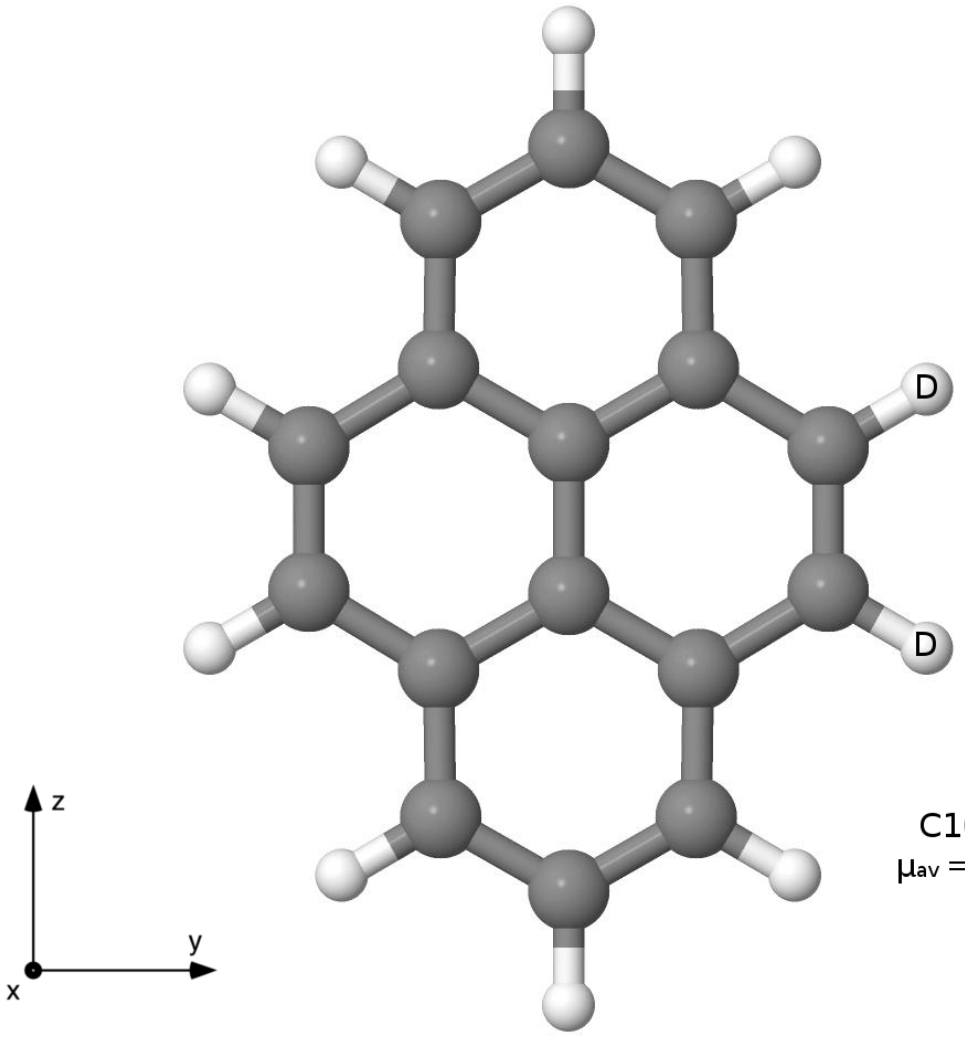

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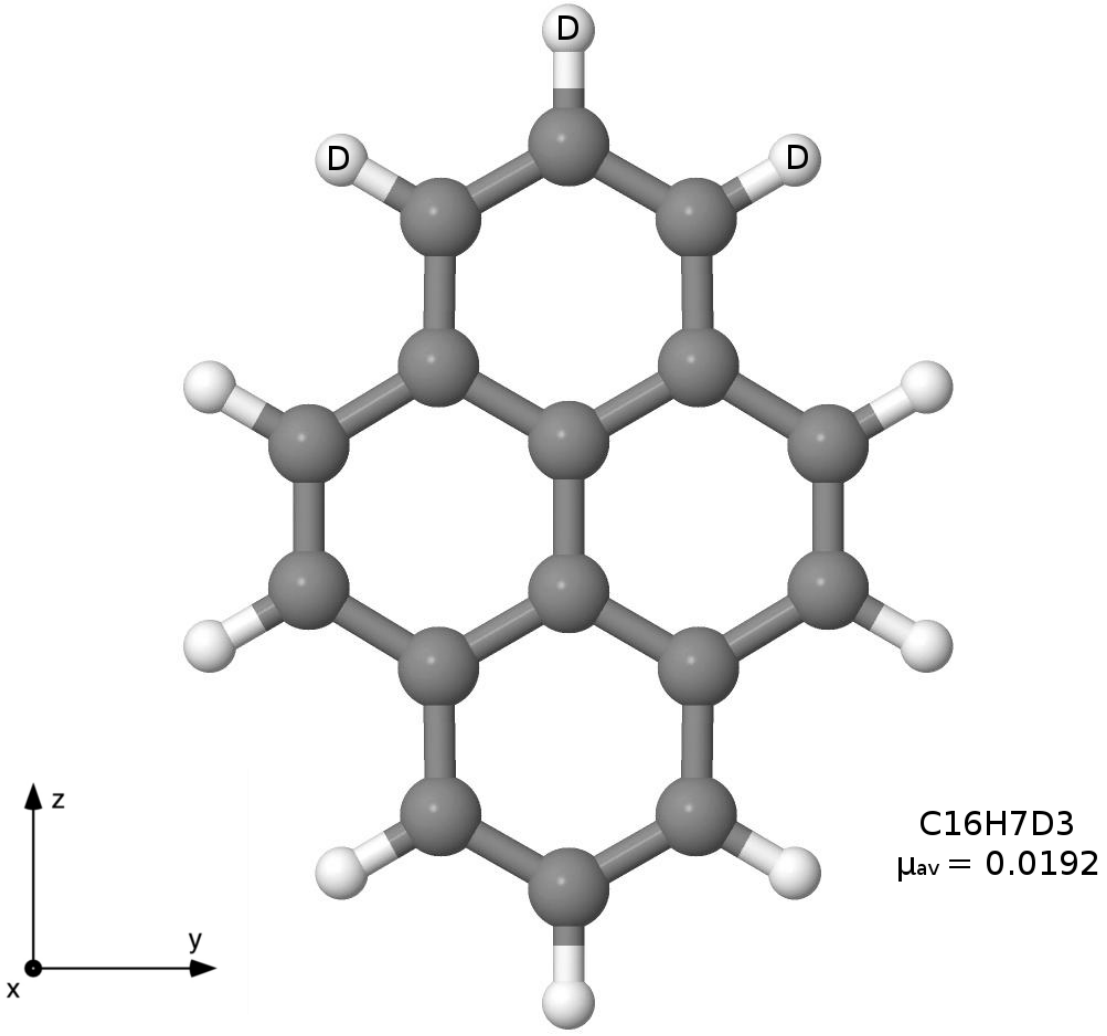

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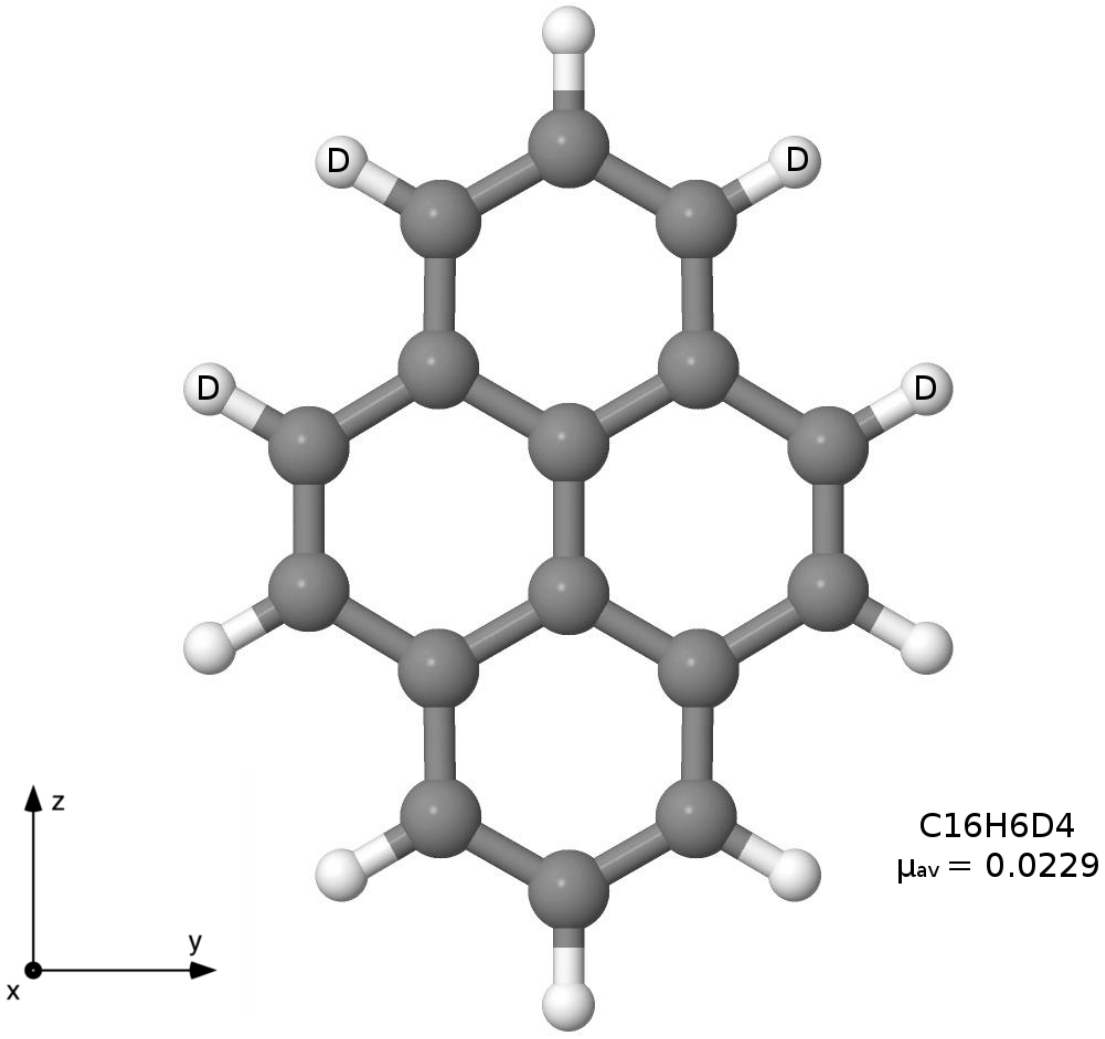

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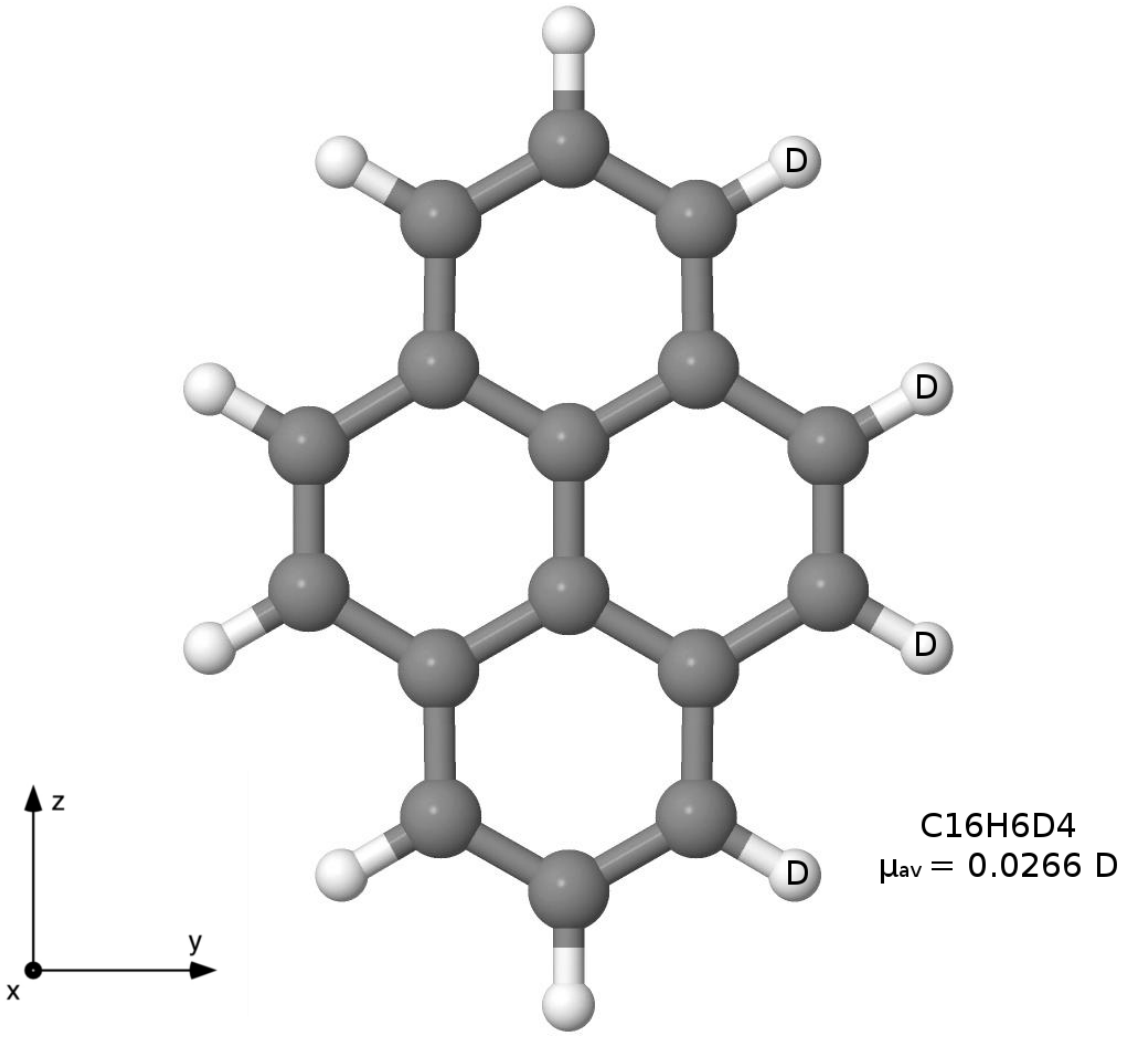

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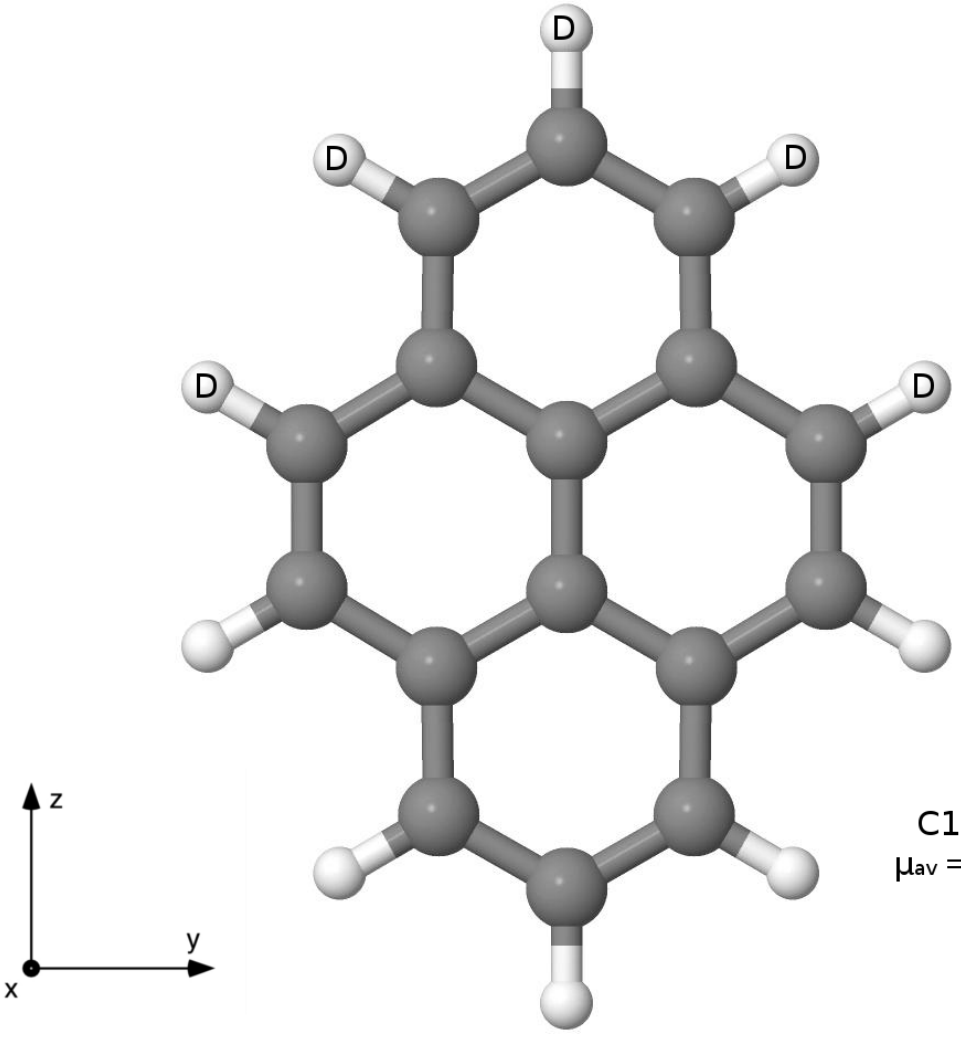

Acknowledgment

CNPq 60 ANOS
CAPES
FAPEMIG 25 ANOS
LCC - CENAPAD