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

Antônio F. C. Arapiraca*,†1
Sergio Pilling†
José Rachid Mohallem‡

*Centro Federal de Educação Tecnológica de Minas Gerais  
†Universidade do Vale do Paraíba  
‡Universidade Federal de Minas Gerais

July 8, 2016

1arapiraca@deii.cefetmg.br
About 195 molecules detected in the Interstellar (ISM) medium and Circumstellar Shells (CSS) (as of 06/2016).
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.

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.\(^4\)

**Simulating Pure Rotational Spectra**

- Level of approximation: 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
The Isotopic Effect on Dipole Moments

Molecular Symmetry Breaking

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

Isotopic assymetry on the electronic distribution

\[ a_0 = \frac{4\pi \varepsilon \hbar^2}{me^2} \]  (1)

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

\[ \hat{H}_\psi(\vec{r}, \vec{R}) = E_\psi(\vec{r}, \vec{R}) \]  

Adiabatic Model: Born-Oppenheimer Approximation (BOA)

\[ \hat{H} = \hat{T}_{\text{nuc}} + \hat{H}_{BO} \]  

\[ \hat{H}_{BO} = - \sum_i \frac{\nabla_i^2}{2} + V \]

\[ \hat{H}_{BO} \phi(\vec{r}, \vec{R}) = E_{\text{ele}} \phi(\vec{r}, \vec{R}) \]

\[ E_{\text{tot}} = E_{\text{ele}} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}} \]

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 $\hat{H}_{\text{FNMC}}$

\[ \hat{H}_{\text{FNMC}} = \sum_A^m (- \sum_i^n P_A \frac{\nabla^2_i}{2M_A} P_A) + \hat{H}_{\text{BO}} \]  


The computational cost is identical to the BOA
Ab Initio Computational Packages Adapted to FNMC

- **GAMESS/ISOTOPE** - Gonçalves and Mohallem - 2003
- **deMon 2k** - Mohallem et al - 2008

**DaltonFNMC - 2011**

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

---

Vibrational Corrections on Molecular Properties

Theory X Experiment
Computing nuclear movements of the molecular systems

ZPVC - Zero Point Vibrational Correction\textsuperscript{a} \textsuperscript{b}


- Dalton 2.0/2016 - HF/SCF, MCSCF (CAS/RAS) e DFT
- Variational expansion point - effective geometry (vibrationally averaged)
- 2\textsuperscript{a} order Perturbation Theory - feasible to polyatomics
Vibrationally Averaged Geometry and Dipole Moments

Effective Geometry

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

Perturbative expansion of the vibrational wavefunction \( |\psi\rangle_{vib} \)

Vibrationally Averaged Dipole Moments

\[ \langle \mu \rangle = \mu_{ef} + \frac{1}{4} \sum_i \frac{\mu_{ef,ii}^{(2)}}{4\eta\omega_{ef}} \]  \hspace{1cm} (9)

\( \eta \) is the reduced mass of the system
FNMC/ZPVC Dipole Moments (Dalton 2016 Program)

FNMC/ZPVC predicts highly accurate dipole moments to

- $HD$, $HT$, $CH_3CD_3$, $^{13}CH_3CD_3$, $CH_3^{13}CD_3$, $CH_2CD_2$ (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 important findings

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

\(^8\)Arapiraca et al., J. Chem. Phys. 135, 244313 (2011)
FNMC/ZPVC Dipole Moments (Dalton 2016 Program)

<table>
<thead>
<tr>
<th>System</th>
<th>Dipole $\langle \mu \rangle_z^{10}$</th>
<th>Experiment$^{11}$</th>
<th>$\Delta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_6H_5D$</td>
<td>0.0078</td>
<td>0.0081$^a$</td>
<td>3.7%</td>
</tr>
<tr>
<td>$C_6H_4D_2$</td>
<td>0.0134</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$C_6H_3D_3$</td>
<td>0.0154</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

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

### ZPVC Rotational Constants (Gaussian 09 program)

<table>
<thead>
<tr>
<th></th>
<th>B3LYP/ZPVC/aug-cc-pVTZ</th>
<th>Experiment</th>
<th>( \Delta(%) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_6H_5D^{12} )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>5692.143</td>
<td>5689.144(6)</td>
<td>0.053%</td>
</tr>
<tr>
<td>B</td>
<td>5326.934</td>
<td>5323.934(6)</td>
<td>0.056%</td>
</tr>
<tr>
<td>C</td>
<td>2750.913</td>
<td>2749.674(6)</td>
<td>0.045%</td>
</tr>
<tr>
<td>( C_6H_4D_2^{13} )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>5501.102</td>
<td>5498.062</td>
<td>0.062%</td>
</tr>
<tr>
<td>B</td>
<td>5167.642</td>
<td>5164.242</td>
<td>0.066%</td>
</tr>
<tr>
<td>C</td>
<td>2663.735</td>
<td>2662.496</td>
<td>0.046%</td>
</tr>
<tr>
<td>( C_6H_3D_3 )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>5217.7295</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>5201.4588</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>2604.7907</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Rotational constants of benzene isotopologues in MHz units.


Programa PGOPHER

To resolve the molecular rotational structure

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**

\[ I_A \leq I_B \leq I_C \]  
\[ A \leq B \leq C \]

\[ \hat{H} = A\hat{J}_a^2 + B\hat{J}_b^2 + C\hat{J}_c^2 \]

\[ \kappa = \frac{2B - A - C}{A - C} \]
Simulating Rotational Spectra (PGOPHER Program)

Einstein's Coefficients

Dipole moment approximation - Emission and Absorption

\[ N_0 B_{1\leftarrow 0} \rho_\nu = A_{1\rightarrow 0} N_1 + B_{1\rightarrow 0} \rho_\nu N_1 \] (14)

\[ B_{1\leftarrow 0} = B_{1\rightarrow 0} \] (15)

\[ A_{1\rightarrow 0} = \frac{8\pi h\nu_0^3}{c^3} B_{1\leftarrow 0} \] (16)

\[ A_{1\rightarrow 0} = \frac{16\pi^3 \nu^3}{3\varepsilon_0 hc^3} \mu_1^2 \] (17)
Simulating Rotational Spectra (PGOPHER Program)

Computing state populations

Emission and Absorption Intensities

\[
I(T)_{\text{emiss}} = \frac{64\pi^4}{3hc} \frac{\nu^3 S_g \mu_g^2 \left( e^{-E''/kT} - e^{-E'/kT} \right)}{Q} \tag{14}
\]

\[
I(T)_{\text{abs}} = \frac{8\pi^3}{3hc} \frac{\nu S_g \mu_g^2 \left( e^{-E''/kT} - e^{-E'/kT} \right)}{Q} \tag{15}
\]
Multiplicative Mean Correction Factor - MCF

\[ CF_i = \frac{V_i^{\text{exp}}}{V_i^{\text{teo}}} \]  \hspace{1cm} (16)

\[ MCF = \frac{1}{N} \sum_{i=1}^{N} FC_i \]  \hspace{1cm} (17)

\[ VC_i^{\text{teo}} = V_i^{\text{teo}} \cdot MCF \]  \hspace{1cm} (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: $0 \leq J \leq 40 - 0 \leq K \leq 31$

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

C$_6$H$_5$D Spontaneous Emission Rates
$0 \leq J \leq 40$ and $0 \leq K \leq 31$

Einstein A Coefficients by state ($s^{-1}$) x $10^{-8}$

Experimental Simulation
Theory Simulation
Benzene’s Isotopologues Spectra

$C_6H_5D$ Absorption Spectra at 35 K

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

MAPE error without MCF correction
Intensity MAPE error: 7.78%

MAPE error with MCF correction
Intensity MAPE error: 0.45%
Benzene’s Isotopologues Spectra

C$_6$H$_5$D Absorption Spectra at 35 K
$0 \leq J \leq 40$ and $0 \leq K \leq 31$

Experimental Simulation
Theory Simulation

Intensidade (nm$^2$ MHz/molécula) $\times 10^{-8}$

Frequency (GHz)
Benzene’s Isotopologues Spectra

\[ C_6H_4D_2 \]

\[ C_{2v} - \kappa = 0.76 \]

Watson Asymmetric Reduction \( III' \)
Benzene’s Isotopologues Spectra

C$_6$H$_4$D$_2$ Spontaneous Emission Rates by State

$0 \leq J \leq 40$ e $0 \leq K \leq 31$

Intensity (nm$^2$ MHz/molécula) $\times 10^{-8}$

Frequency (GHz)
Benzene’s Isotopologues Spectra

$C_6H_4D_2$ Absorption Spectra at 35 K
$0 \leq J \leq 40$ and $0 \leq K \leq 31$

Intensity
$(\text{nm}^2 \text{MHz/molécula}) \times 10^{-8}$
Frequency (GHz)

Experiment/Theory Simulation
Benzene’s Isotopologues Spectra

C$_6$H$_4$D$_2$ Absorption Spectra at 150 K

$0 \leq J \leq 40$ and $0 \leq K \leq 31$

Intensity (nm$^2$ MHz/molécula) $\times 10^{-8}$

Frequency (GHz)
Benzene’s Isotopologues Spectra

\[ C_6D_3H_3 \]

\[ C_{2v} - \kappa = 0.99 \]

Watson Asymmetric Reduction \( III' \)
C₆H₃D₃ Spontaneous Emission Rates by State

0 ≤ J ≤ 40 e 0 ≤ K ≤ 31

Einstein A Coefficients by state (s⁻¹) x 10⁻⁸
Frequency (GHz)
C$_6$H$_4$D$_2$ Absorption Spectra at 35 K

$0 \leq J \leq 40$ and $0 \leq K \leq 31$
C\textsubscript{6}H\textsubscript{3}D\textsubscript{3} Absorption Spectra at 35 K
0 \leq J \leq 40 and 0 \leq K \leq 31

Theory Simulation
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
Coming Soon
Coming Soon

C16H8D2
\( \mu_{av} = 0.0141 \)
Coming Soon
Coming Soon

C16H6D4
\( \mu_{av} = 0.0229 \)
Coming Soon
Coming Soon
Acknowledgment