AN EMPIRICAL APPROACH TO OBTAINING ACCURATE MOLECULAR ROTATIONAL CONSTANTS FOR ISOTOPICALLY-SUBSTITUTED SPECIES FROM *AB INITIO* CALCULATIONS

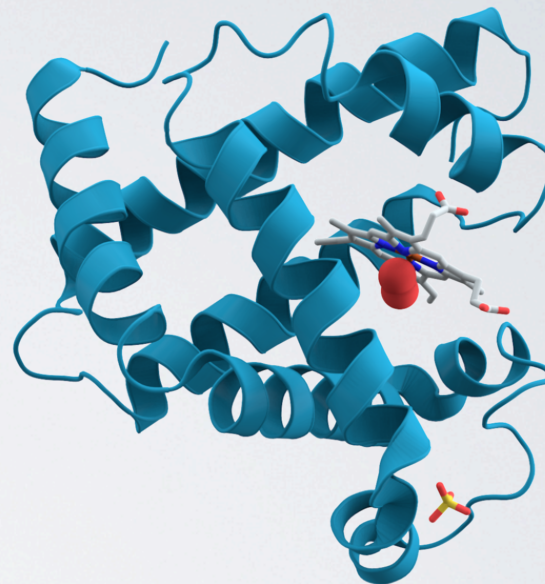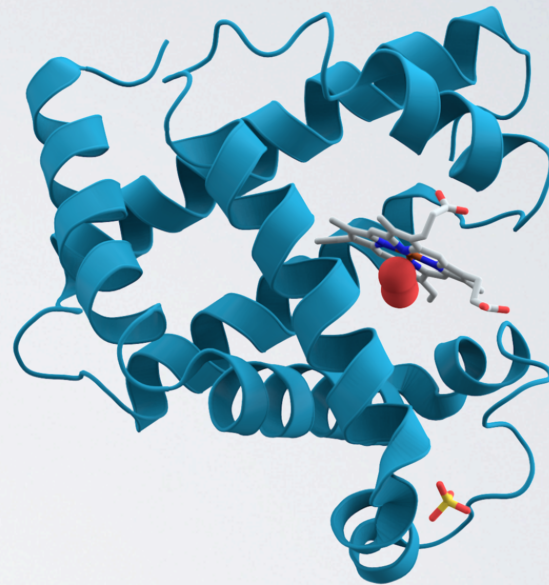Brett A. McGuire • P. Brandon Carroll • Steven T. Shipman • Geoffrey A. Blake

Why study isotopic substitution?

Zyankun, A. M., 2011, J Analytic. Chem., 66, 1243
Carroll, McGuire, Zaleski et al., 2013, J Mol Spec, 284-285, 21

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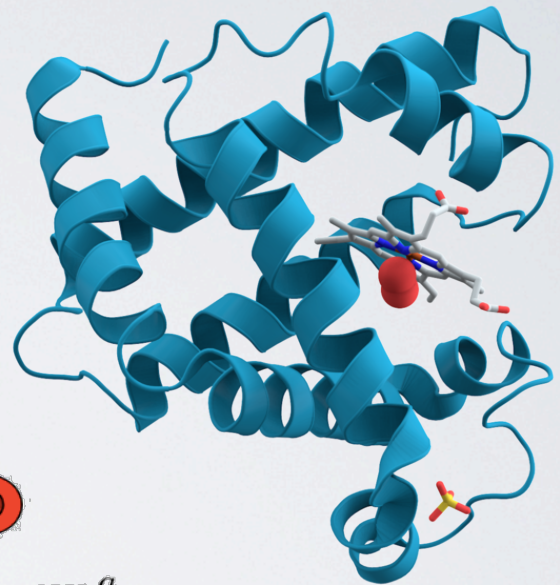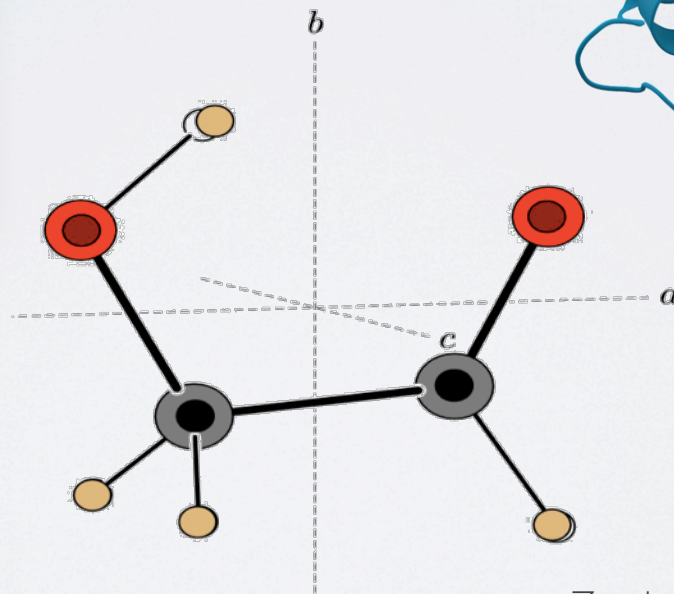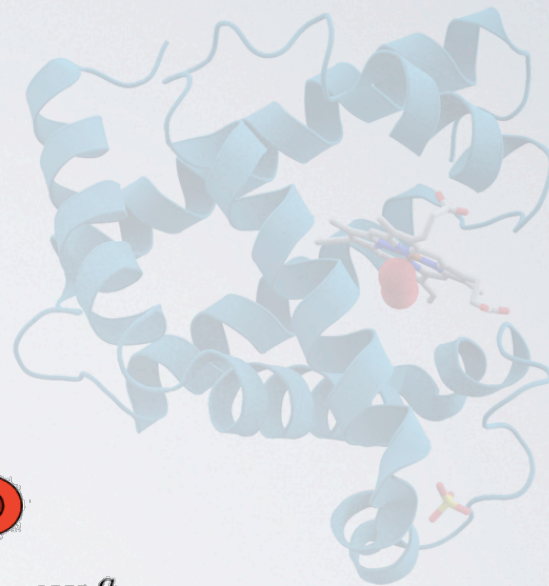
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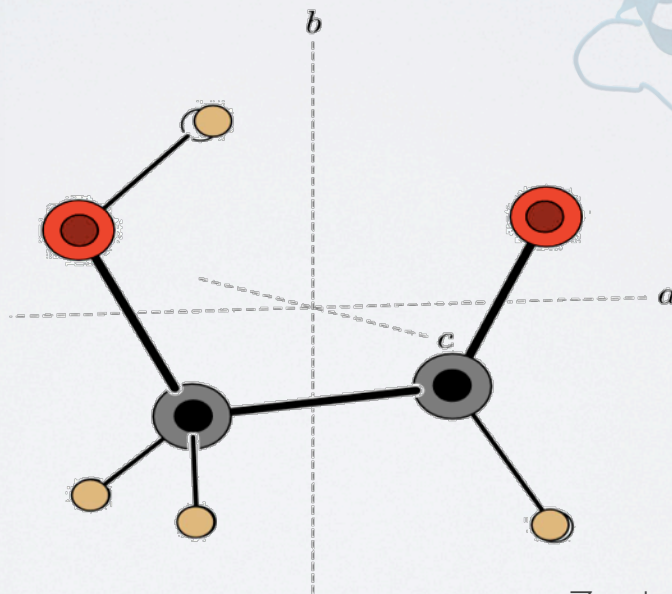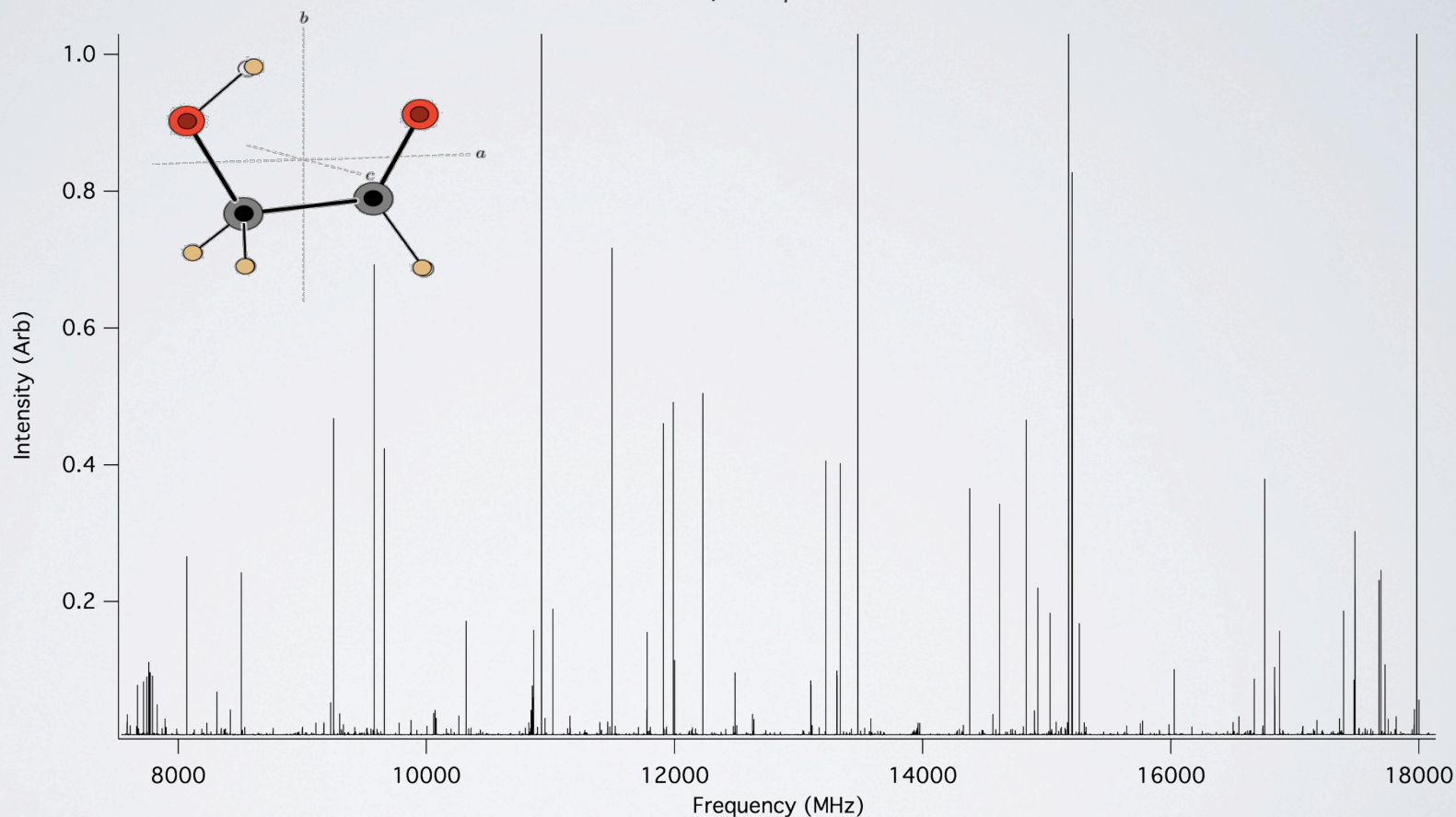Carroll, McGuire, Zaleski et al., 2013, J Mol Spec, 284-285, 21

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More accurate rotational constants result in better initial predictions of rotational transition frequencies

Carroll, McGuire, Zaleski et al., 2013, J Mol Spec, 284-285, 21

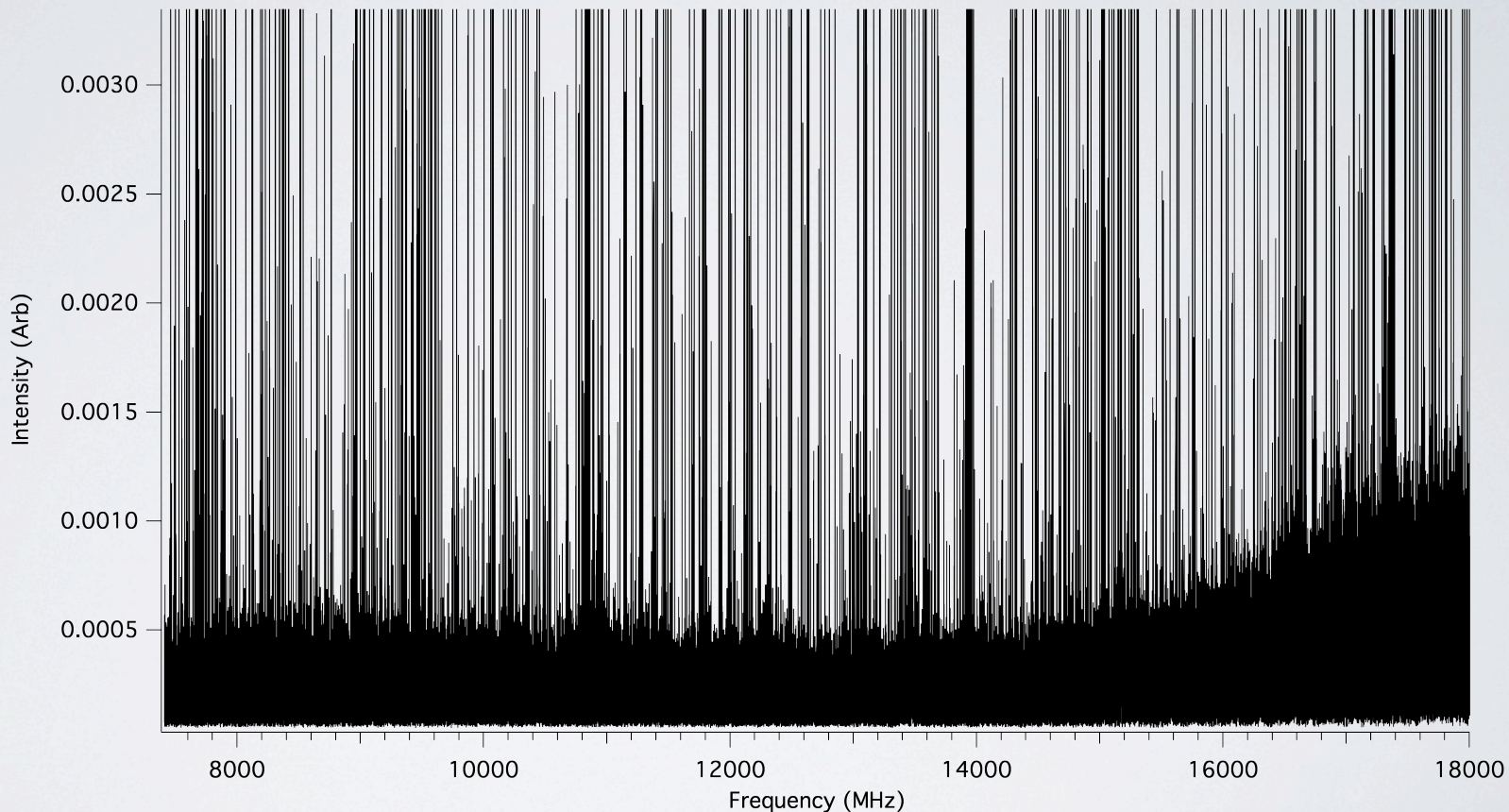*More accurate rotational constants result in better initial predictions of rotational transition frequencies*

WH16

6:00
1000 MP

Carroll, McGuire, Zaleski et al., 2013, J Mol Spec, 284-285, 21

What's wrong with what we have now?

- Basic computational methods return *equilibrium* (R_e) geometry

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- Basic computational methods return *equilibrium* (R_e) geometry

- R_0 geometry $\longrightarrow$ *much* more expensive

- Can do extremely well… for a price

Most accurate isotopologue structure with least computational expense (effort)

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- Combine to _quickly_ obtain useful predictions

1. Optimize structure at given Level of Theory/Basis Set

   • Calculate parent species rotational constants

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2. Assume no geometry change upon substitution

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3. Scale isotopologue rotational constants

$$B_{\text{scaled}} = \frac{B_{\text{exp}} \, (\text{parent})}{B_{\text{calc}} \, (\text{parent})} \times B_{\text{calc}}$$

Hold on, doesn't everyone do this already?

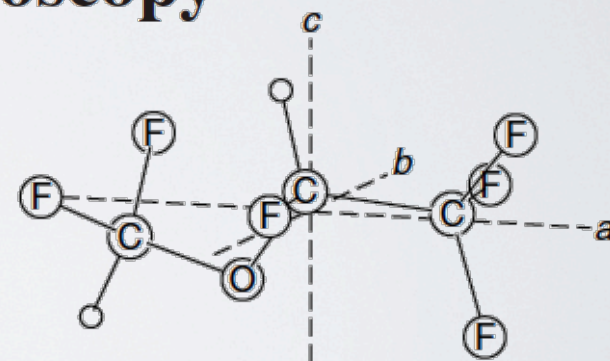*Hold on, doesn't everyone do this already?*

Probably?

The pure rotational spectrum of glycolaldehyde isotopologues observed in natural abundance

P. Brandon Carroll [a], Brett A. McGuire [a], Daniel P. Zaleski [b], Justin L. Neill [b], Brooks H. Pate [b,*], Susanna L. Widicus Weaver [a,*]

New Techniques in Microwave Spectroscopy

Steven T. Shipman and Brooks H. Pate
Department of Chemistry, University of Virginia, Charlottesville, VA, USA

Conformation I
0 cm^{-1}

Levels of theory

MP2 • B3LYP • M062X • CCSD

Basis sets

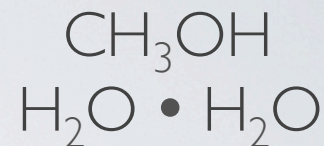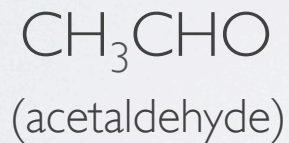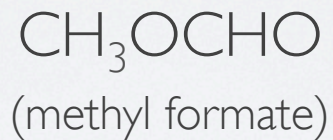6-31+G • 6-311++G(d,p) • cc-pVDZ • aug-cc-pVTZ

2

HCl

3

HCN
HNC
HCO^+

4

H_2CO
NH_3

6

CH_3OH
$H_2O \cdot H_2O$

7

CH_3CHO
(acetaldehyde)

8

CH_3OCHO
(methyl formate)

9

HC_7N
CH_3OCH_3
(dimethyl ether)

CH_3CH_2CN
(ethyl cyanide)
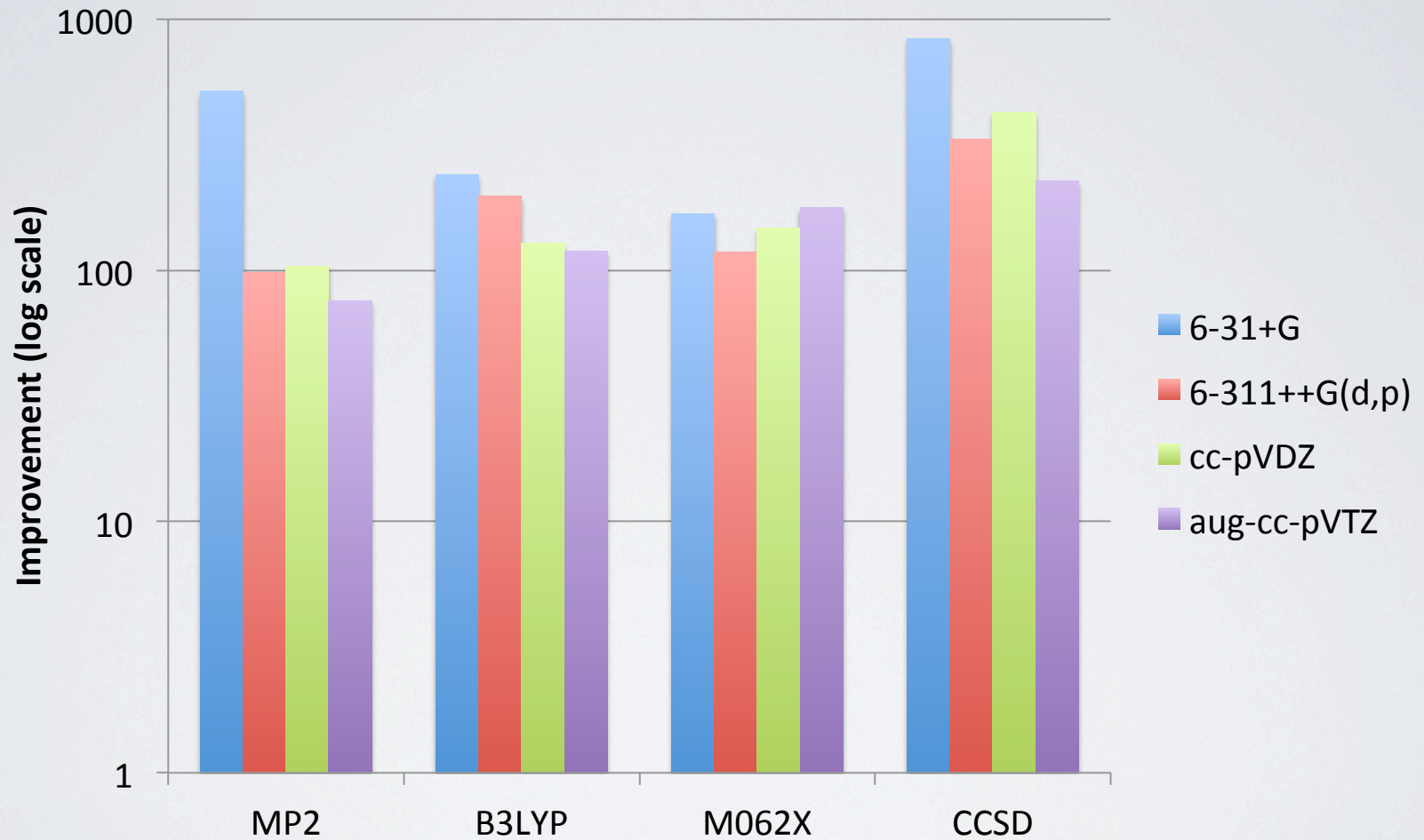
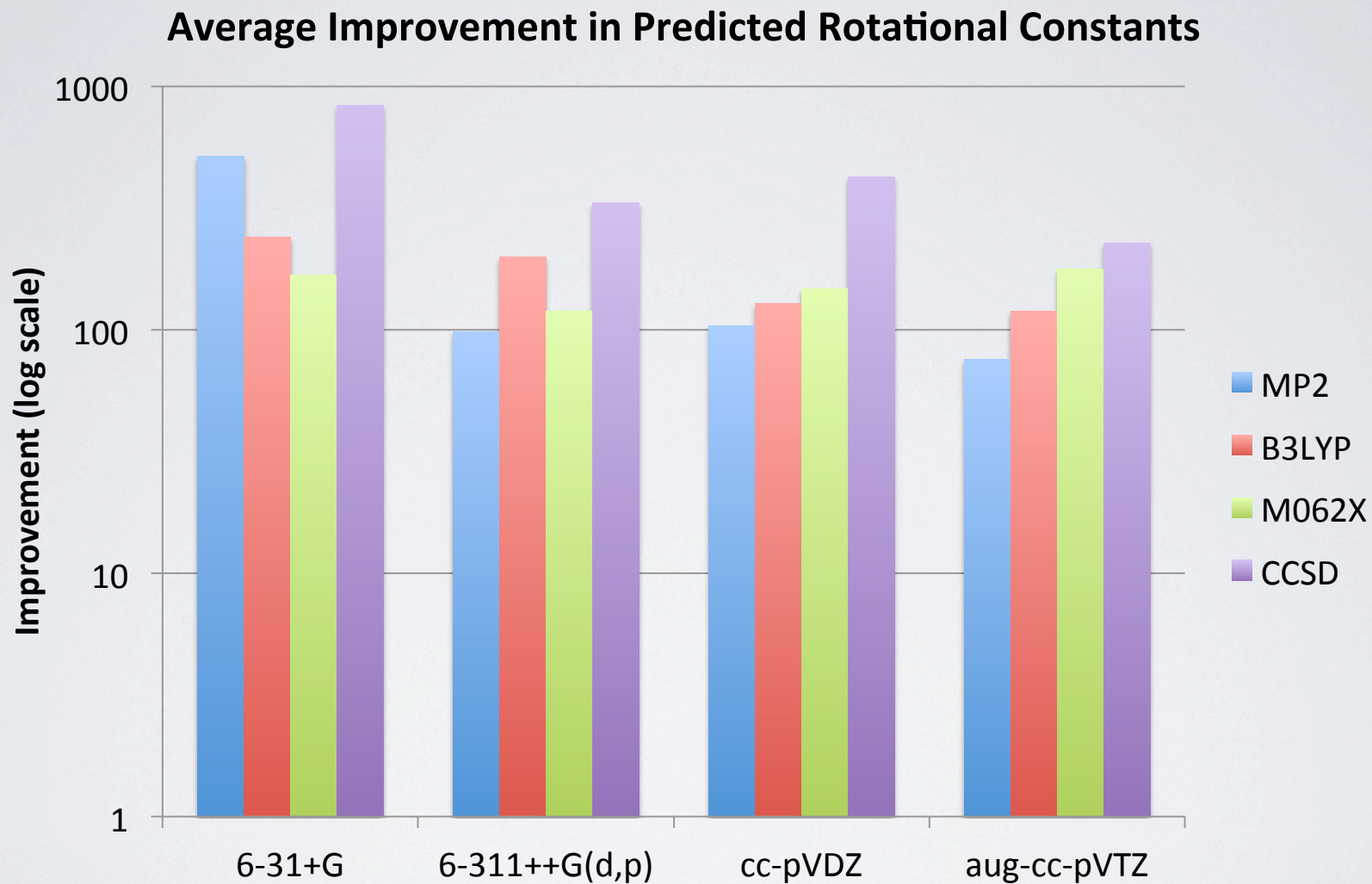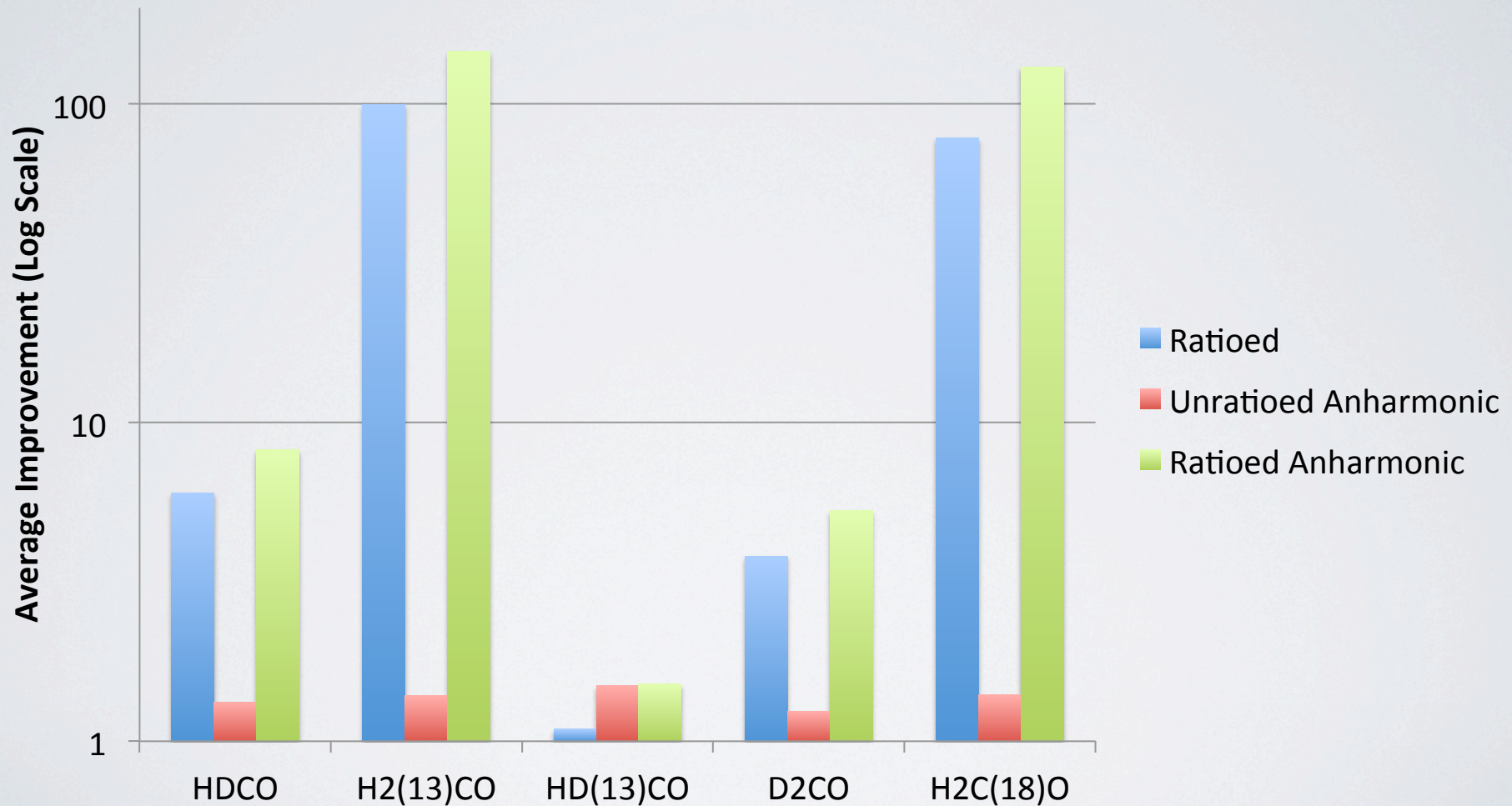Average Improvement in Predicted Rotational Constants

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Comparision of Effects of Including Anharmonic Ro-Vibrational Interactions

$H^{37}Cl$ - Dunham

Lit $= 312\ 519.12$ MHz

$$B\ (H^{37}Cl) = \frac{\mu\ (H^{35}Cl)}{\mu\ (H^{37}Cl)} \times B\ (H^{35}Cl) = 312\ 519.35\ \text{MHz}$$

(0.23 MHz)

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(0.23 MHz)

$H^{37}Cl$ - This work

$B\,(H^{37}Cl) = 312\,518.81\ \text{MHz}$

(0.31 MHz)

$H^{37}Cl$ - *Dunham*

Lit = 312 519.12 MHz

$$B\,(H^{37}Cl) = \frac{\mu\,(H^{35}Cl)}{\mu\,(H^{37}Cl)} \times B\,(H^{35}Cl) = 312\,519.35 \text{ MHz}$$
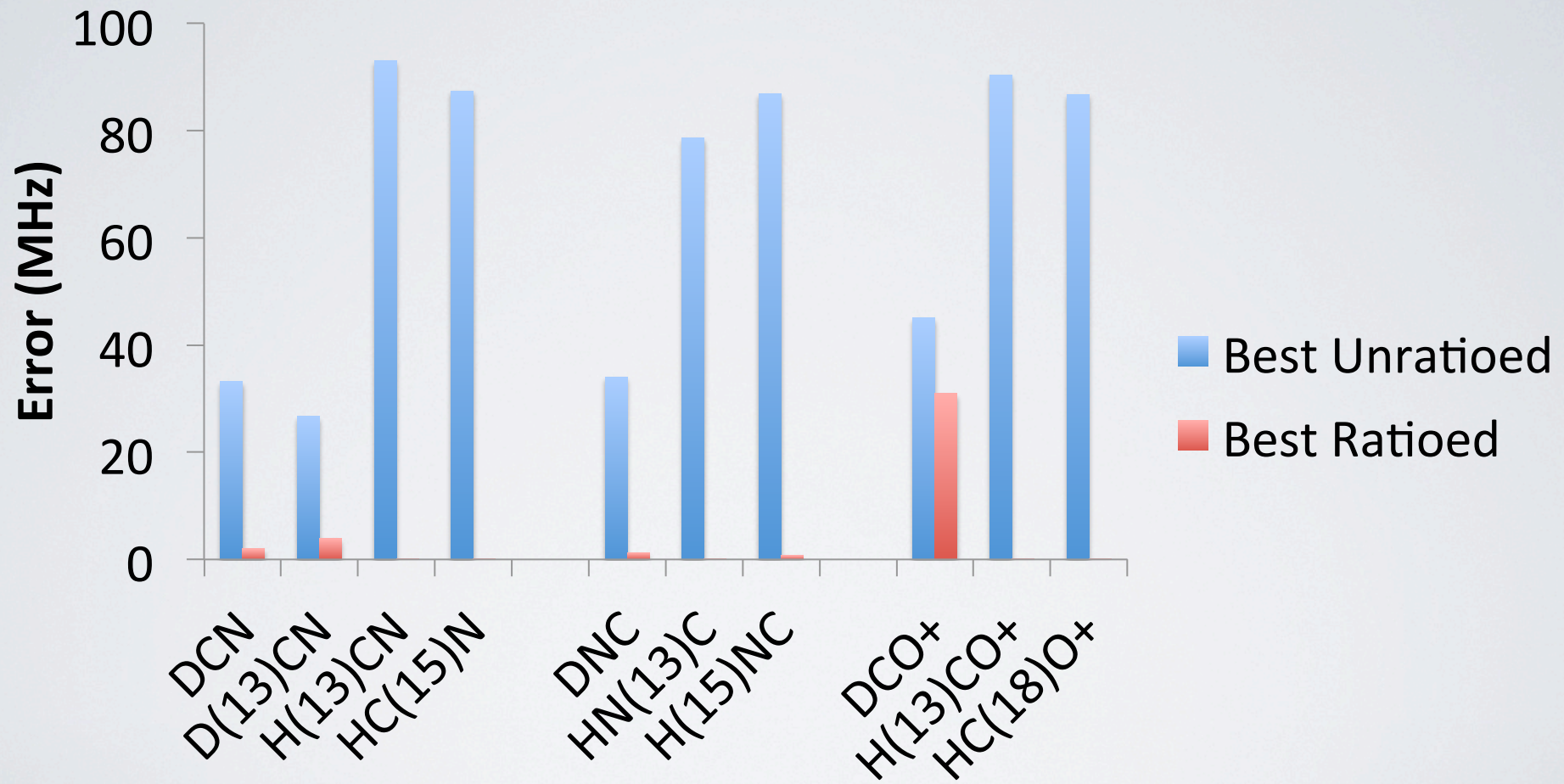
(0.23 MHz)

$H^{37}Cl$ - *This work*

$$B\,(H^{37}Cl) = 312\,518.81 \text{ MHz}$$
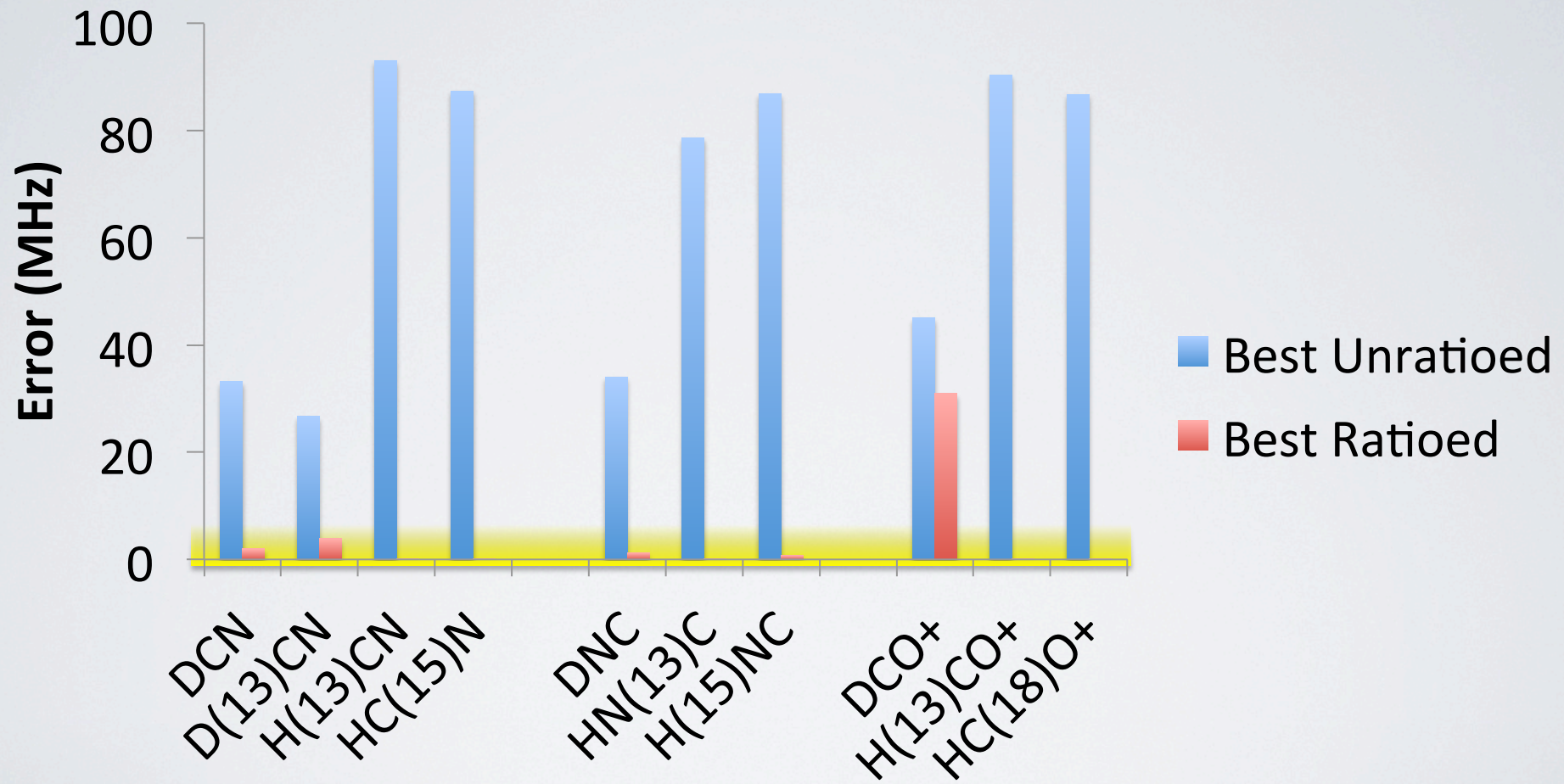
(0.31 MHz)

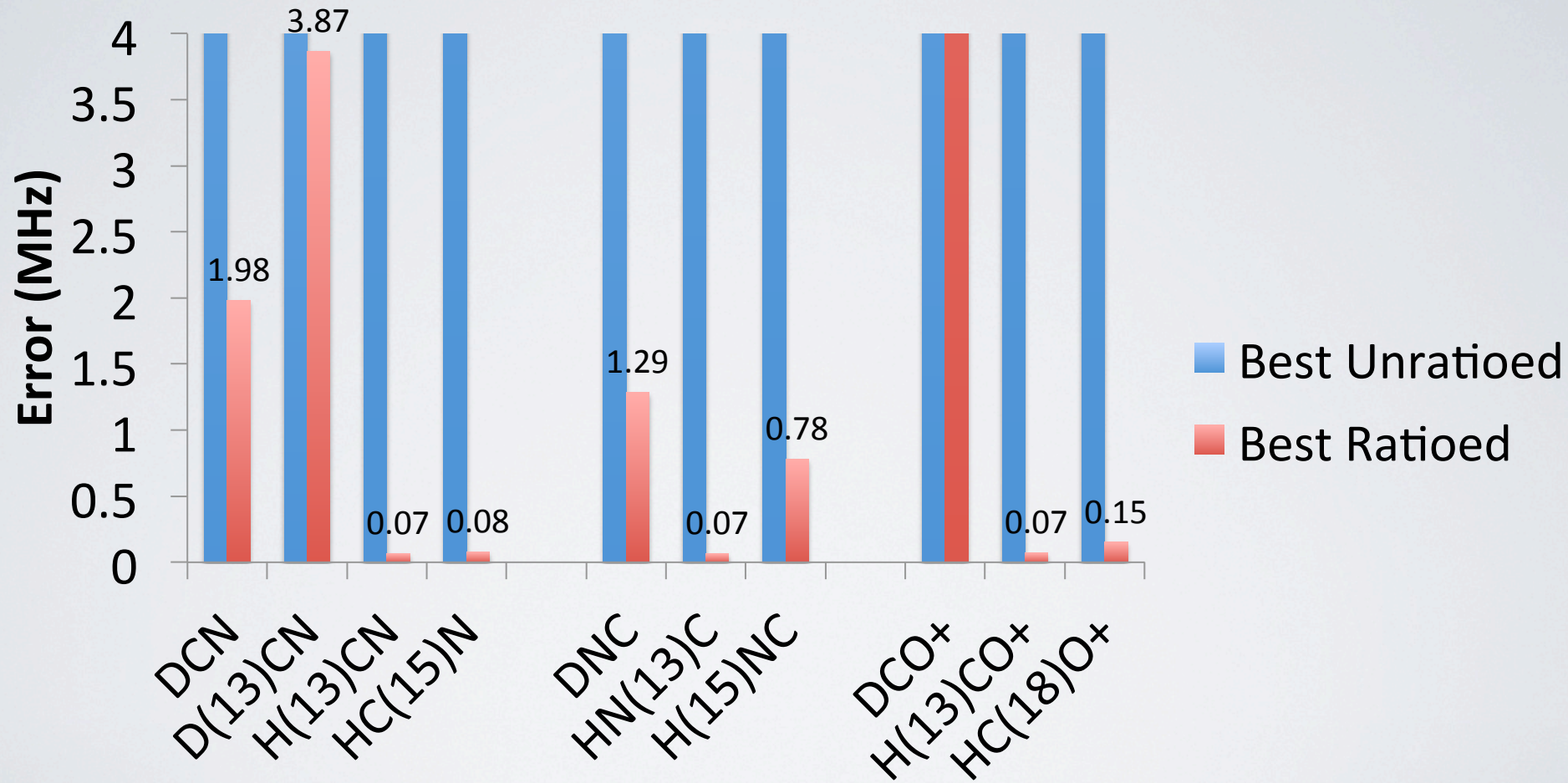Only this accurate at CCSD

Error in Predictions for Triatomics

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Takeaway key points

- **Be cautious with deuterium**

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- Most time efficient improvement
  MP2/6-311++G(d,p)

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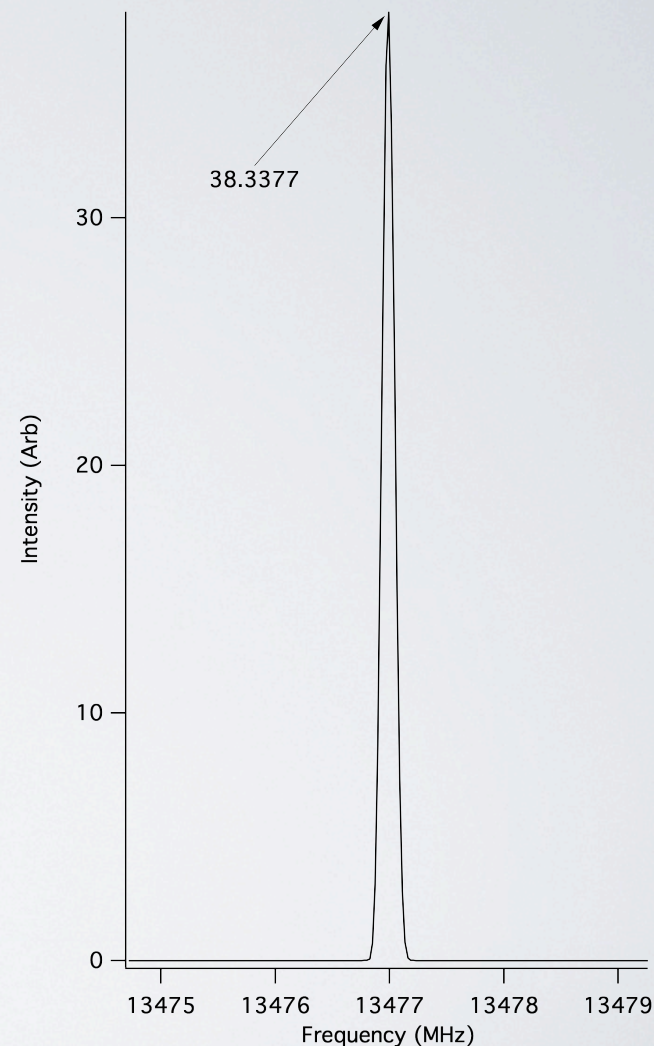- Most time efficient improvement
  B3LYP/6-31+G

Assigning $CH_3C(O)OD$

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Start with $1_{1,0}$ - $1_{0,1}$ transition

Scale by abundance: Intensity = 0.057

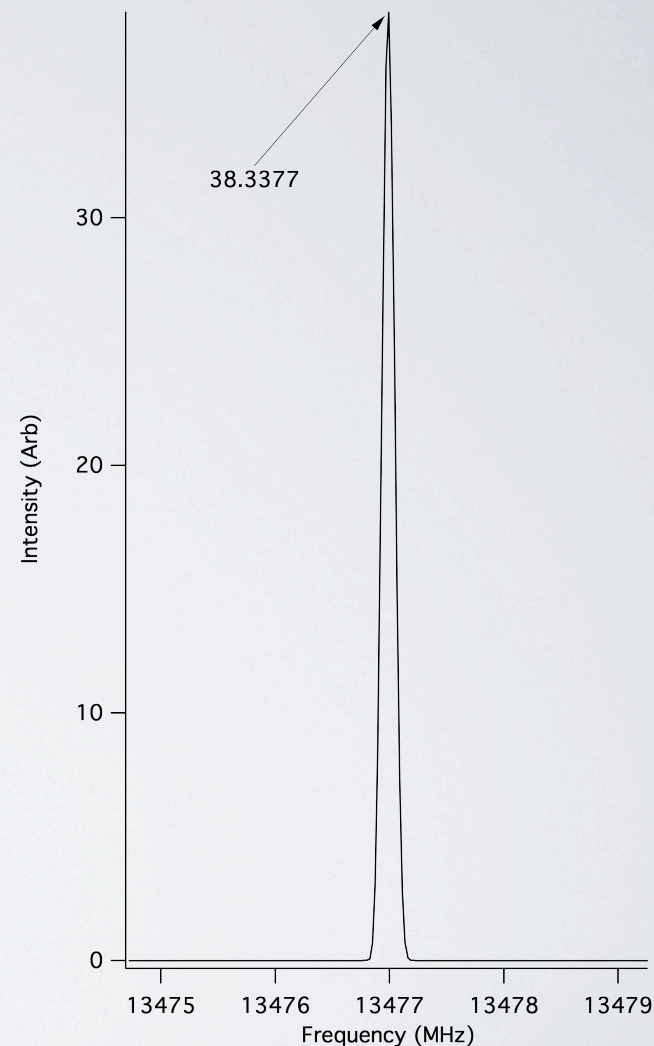## Assigning $CH_3C(O)OD$

Start with $1_{1,0}$ - $1_{0,1}$ transition

Scale by abundance: Intensity = 0.057

Lowest B-type: Freq = A - C

Error = Error (A) + Error (C)

38.3377

Carroll, McGuire, Zaleski et al., 2013, J Mol Spec, 284-285, 21

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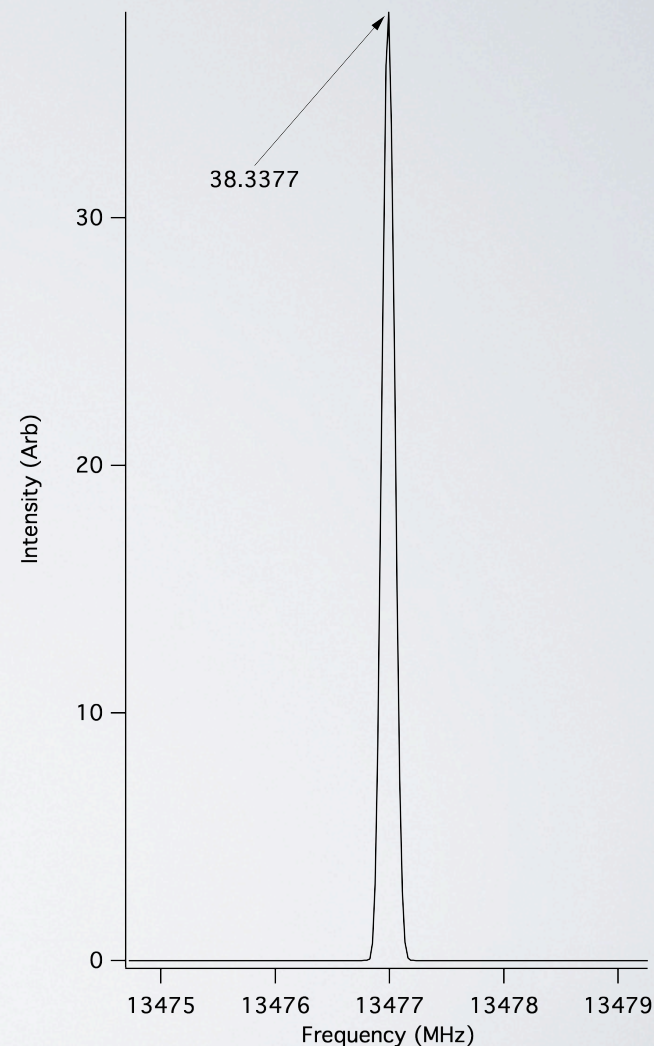Lowest B-type: Freq = A - C
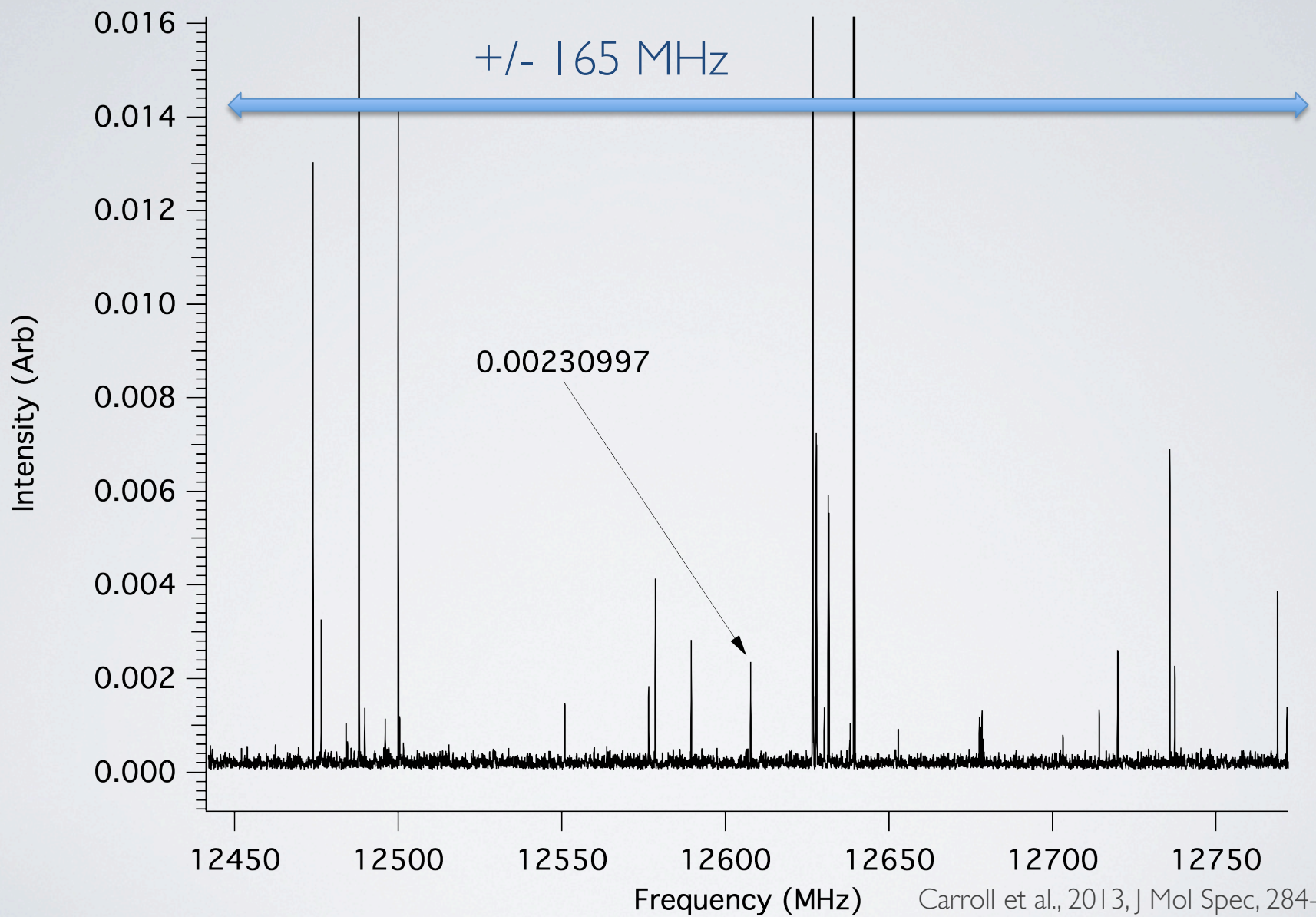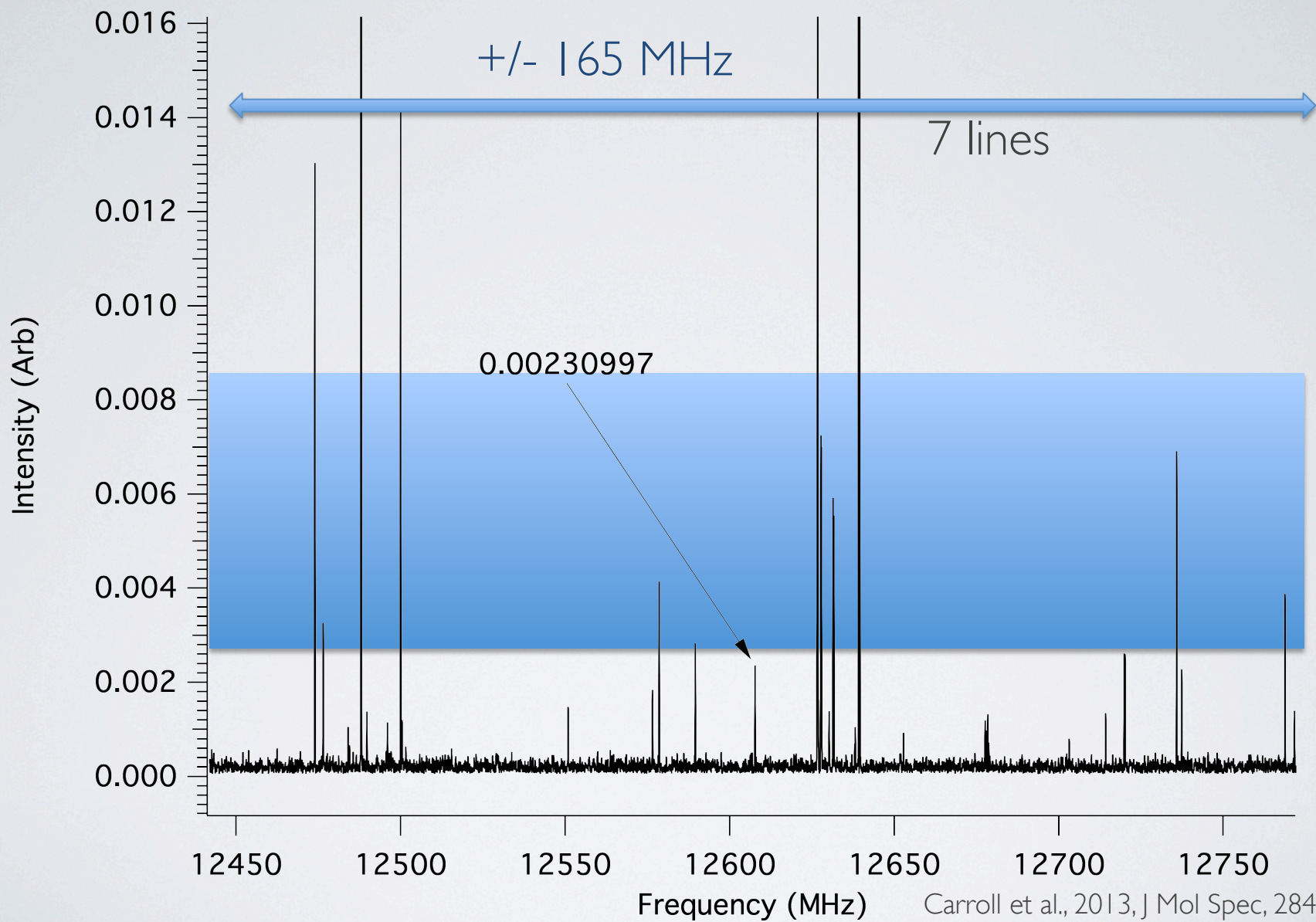
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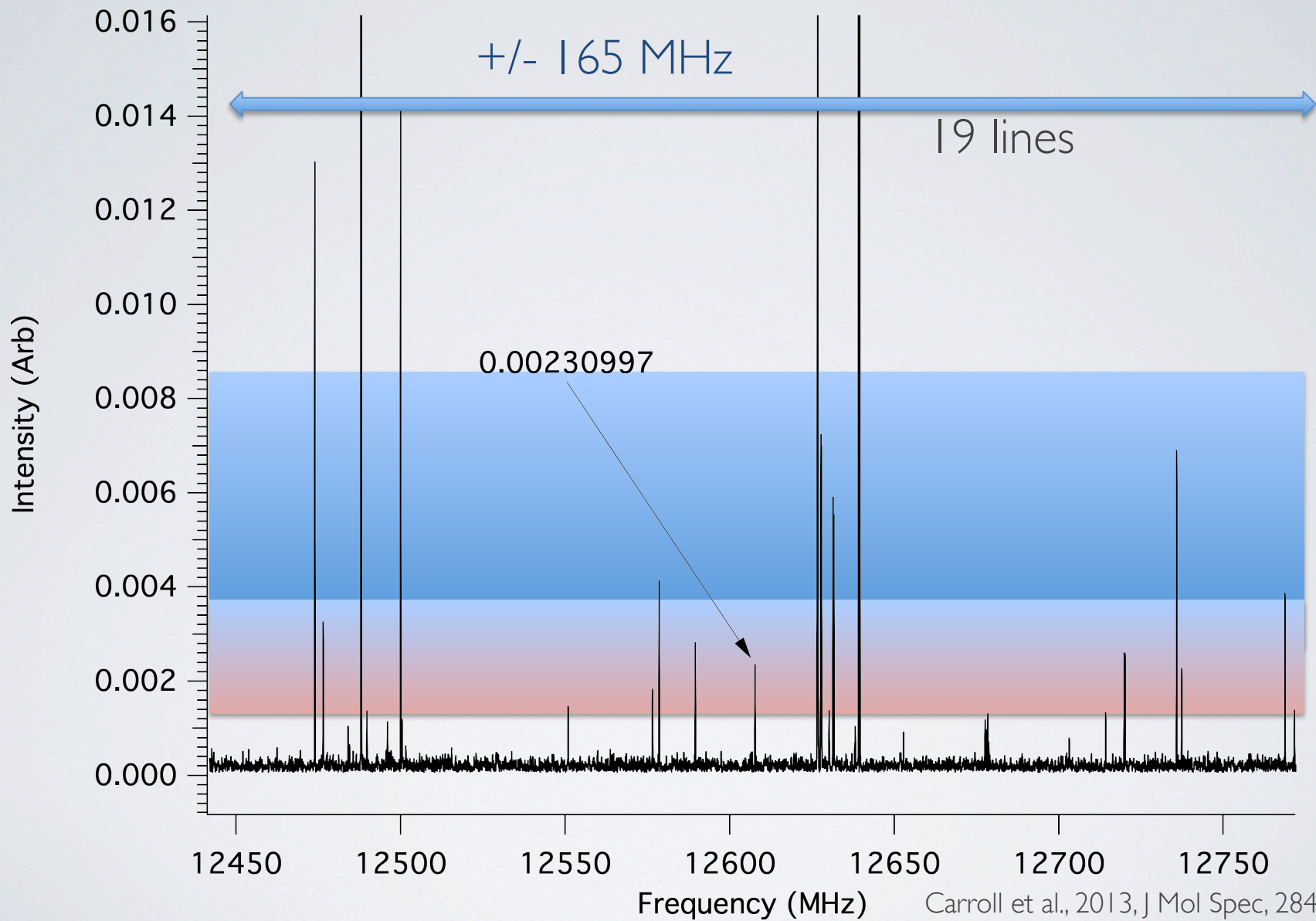| Error (Unratioed)	Error (Ratioed)
165 MHz	6 MHz

B3LYP/aug-cc-pVQZ

38.3377

Intensity (Arb)

30

20

10

0

13475   13476   13477   13478   13479

Frequency (MHz)

Carroll, McGuire, Zaleski et al., 2013, J Mol Spec, 284-285, 21

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+/- 6 MHz

1 line

0.00230997

Carroll et al., 2013, J Mol Spec, 284-285, 21

Carroll et al., 2013, J Mol Spec, 284-285, 21

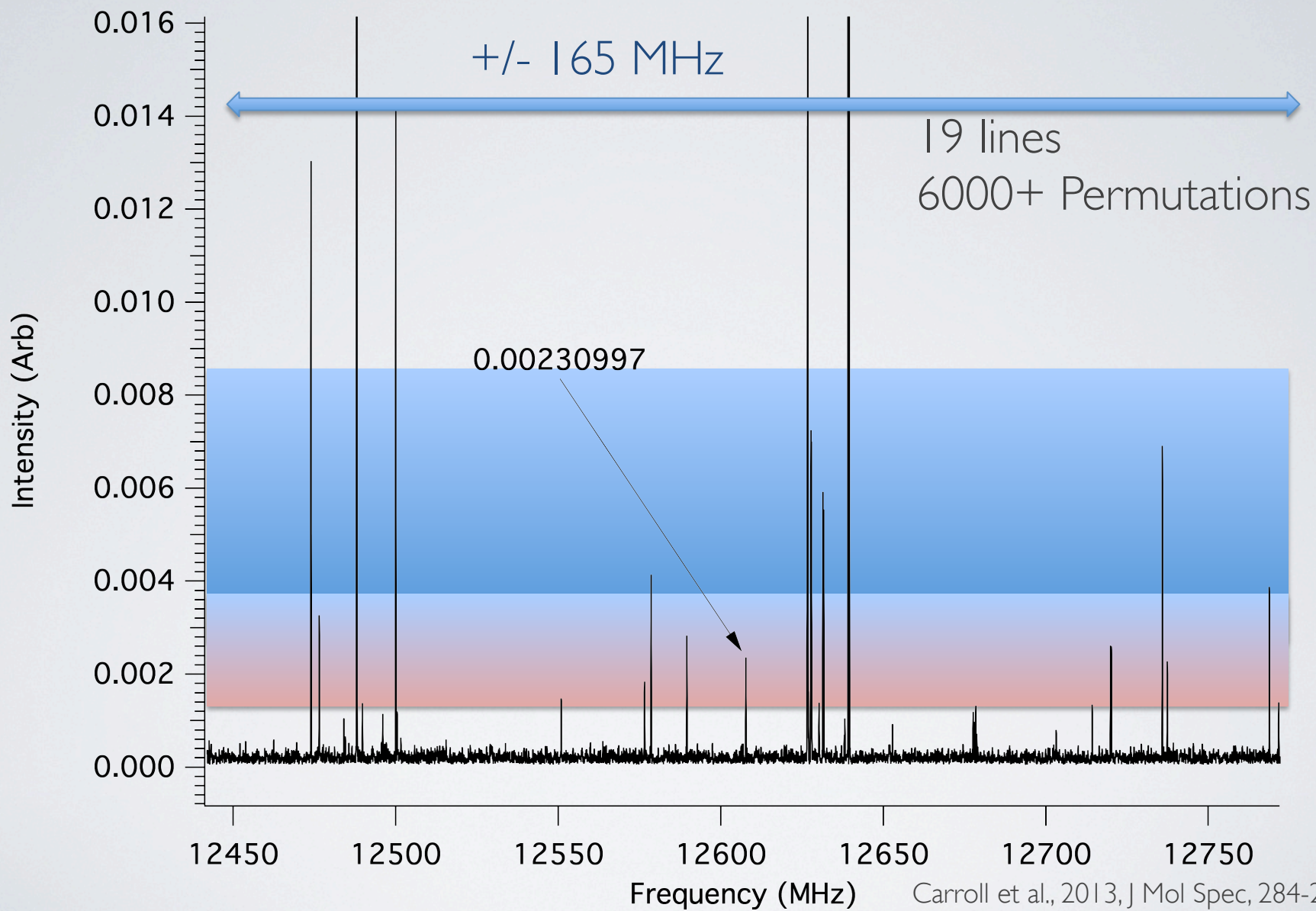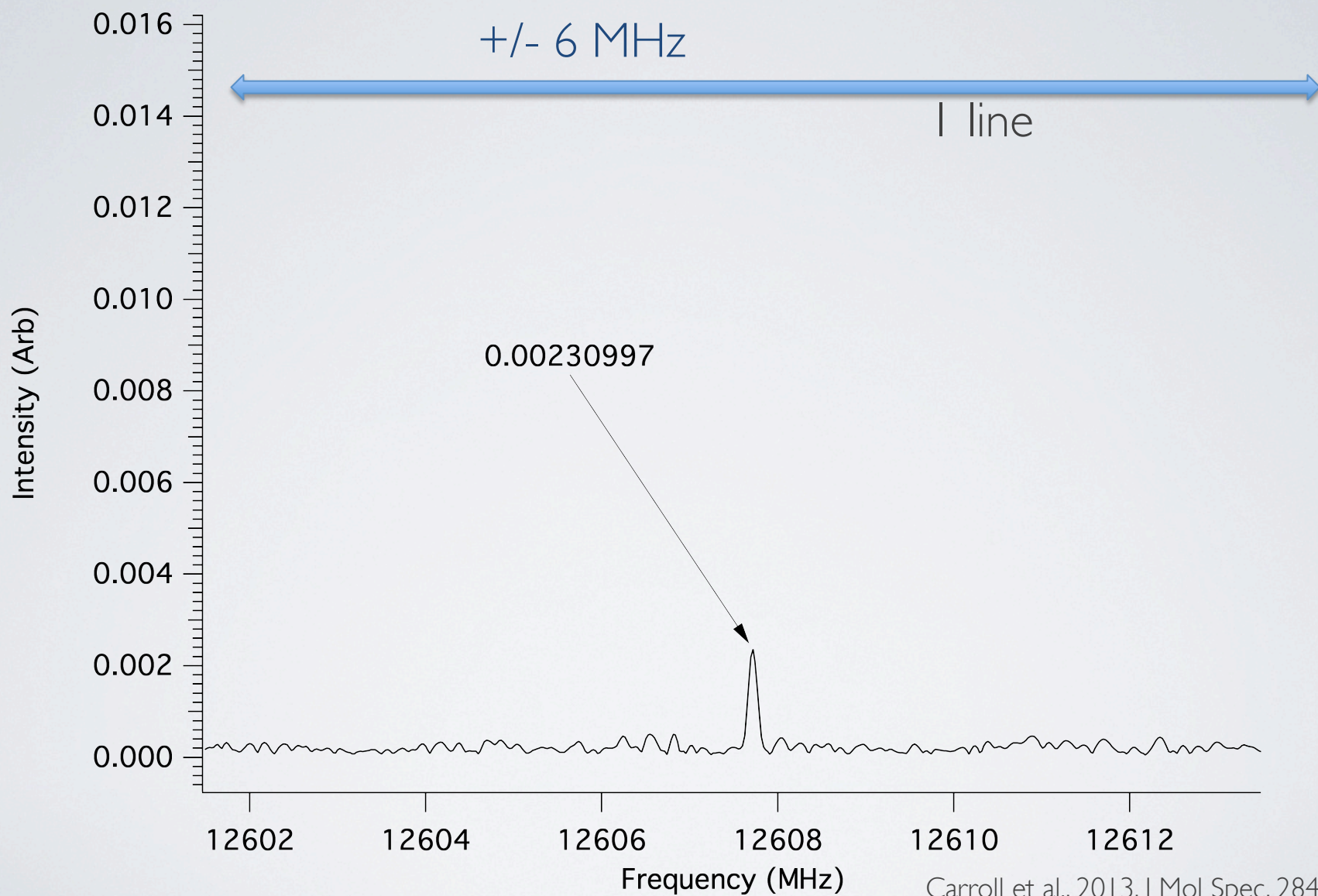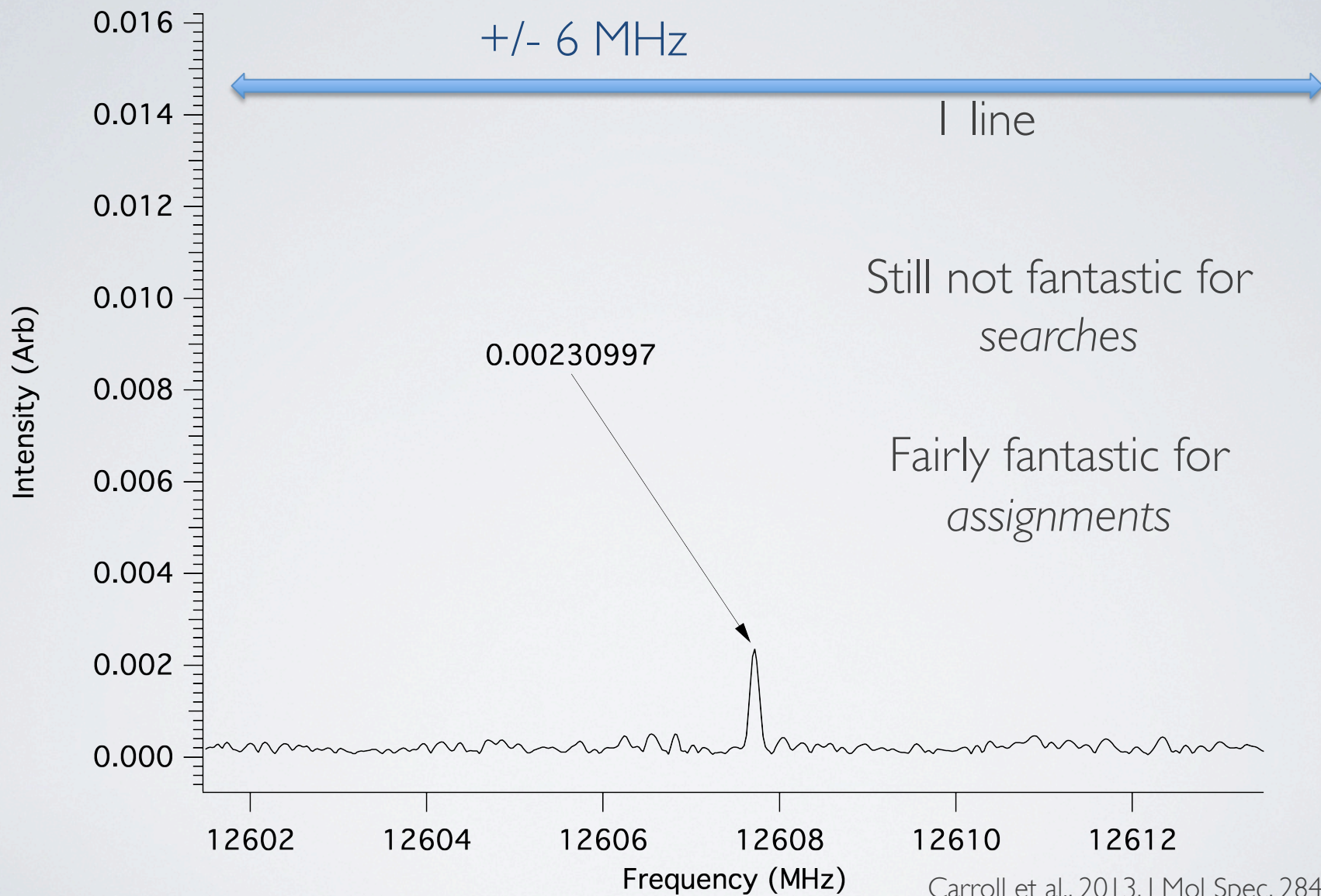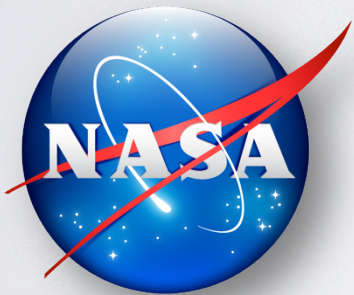## Special Thanks

Joel Bowman
Susanna Widicus Weaver
Thomas Miller

Funding

Take Home Message

We have presented a computationally inexpensive method for obtaining accurate rotational constants using mixture of experiment and theory

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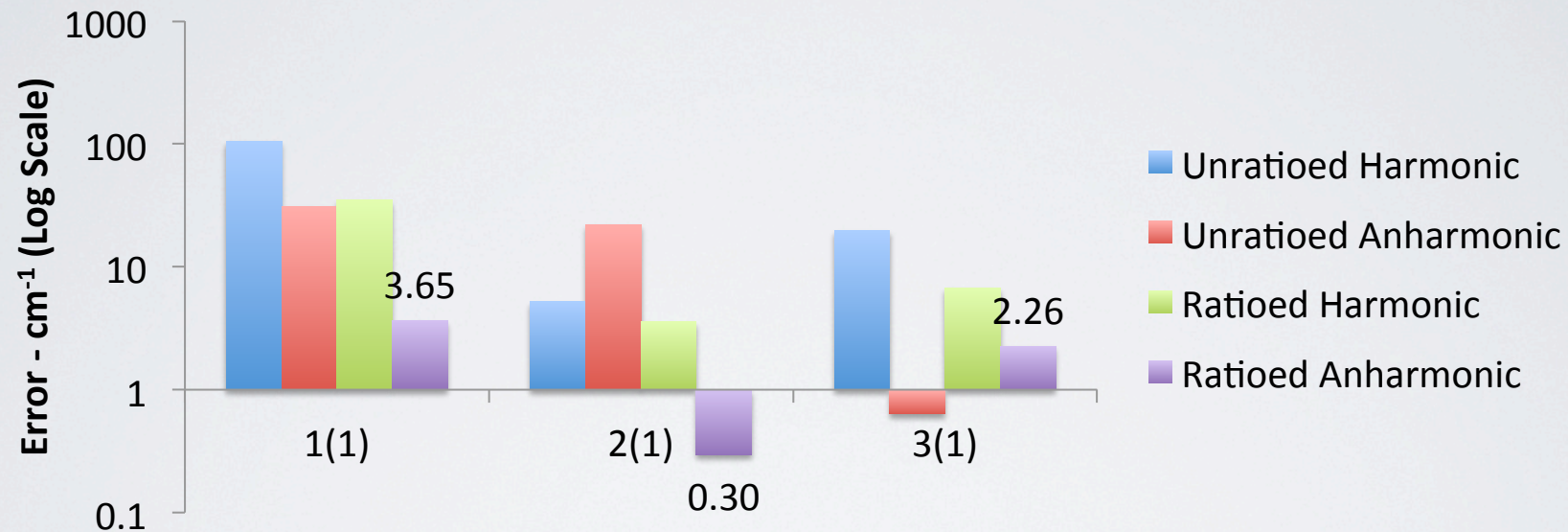Thomas Miller

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What happens if we apply the same methodology to calculated vibrational frequencies of H_2CO/D_2CO?

Error in Fundamental Vibrational Predictions for D_2CO

Requires identical symmetry!