Progress in the Rotational Analysis of the Ground and Low-Lying Vibrationally Excited States of Malonaldehyde

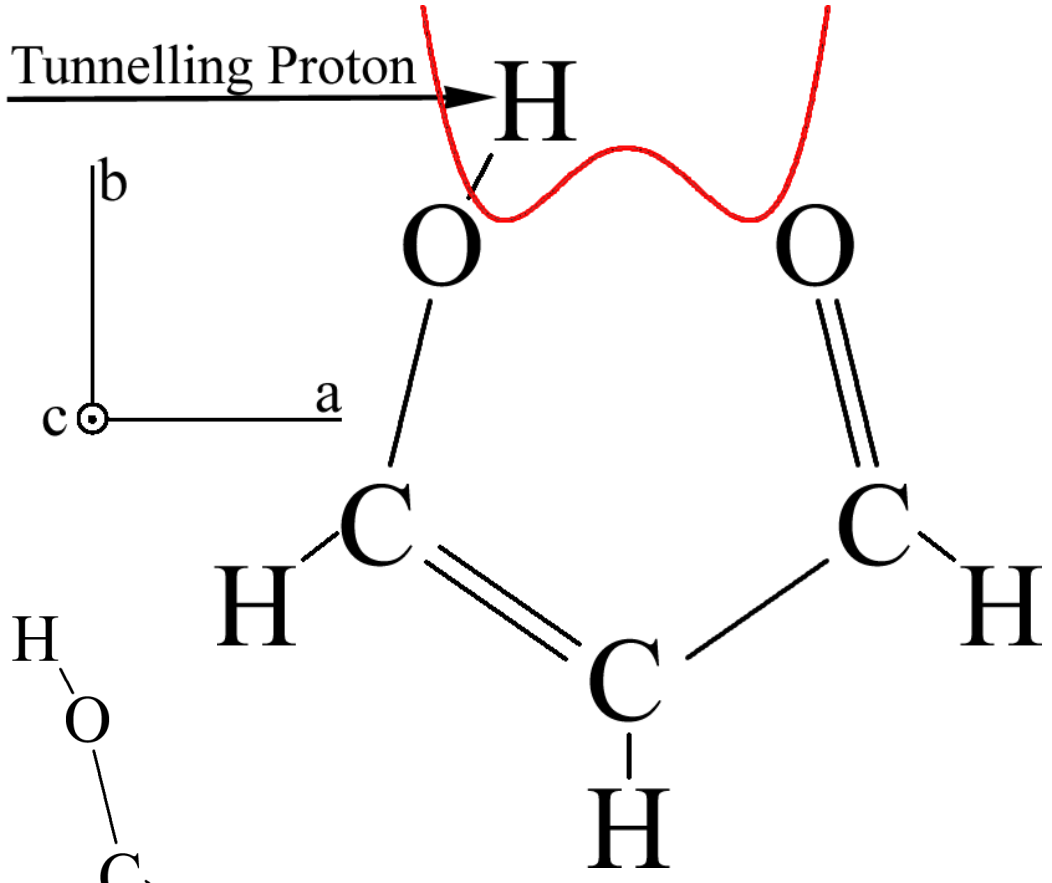
E. Scott Goudreau,
Dennis W. Tokaryk and Stephen C. Ross
Department of Physics
University of New Brunswick
Fredericton, New Brunswick, Canada

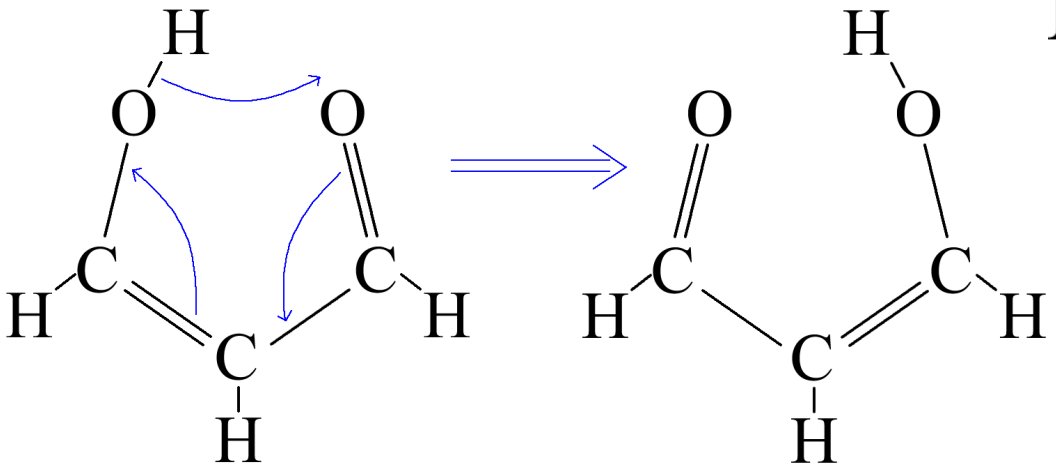
Brant E. Billinghurst
Canadian Light Source Inc.
Saskatoon, Saskatchewan, Canada

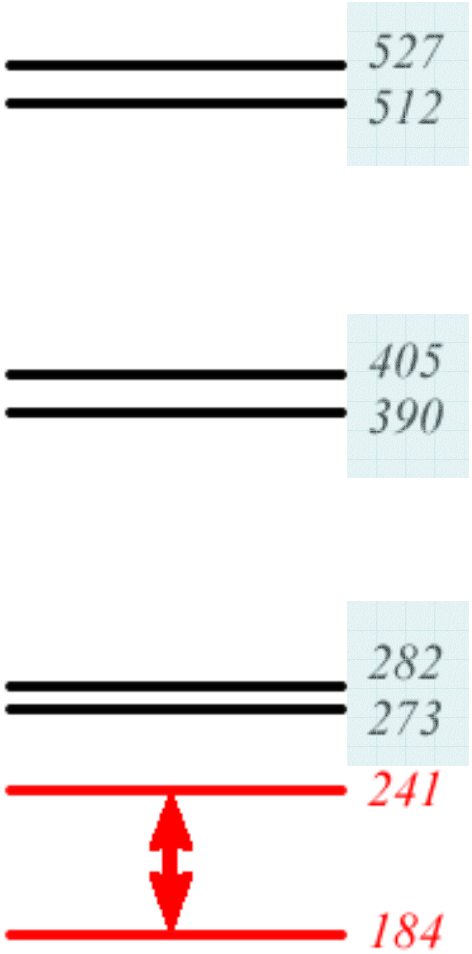
Malonaldehyde – An Intramolecular Tunnelling Prototype

- C_s symmetry with a C_{2v} transition state (MS group – G_4)

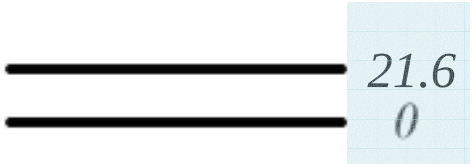
- Barrier height is about 1400 cm^{-1}
- from *ab initio* calculation
(Wang et al. 2008 and others)

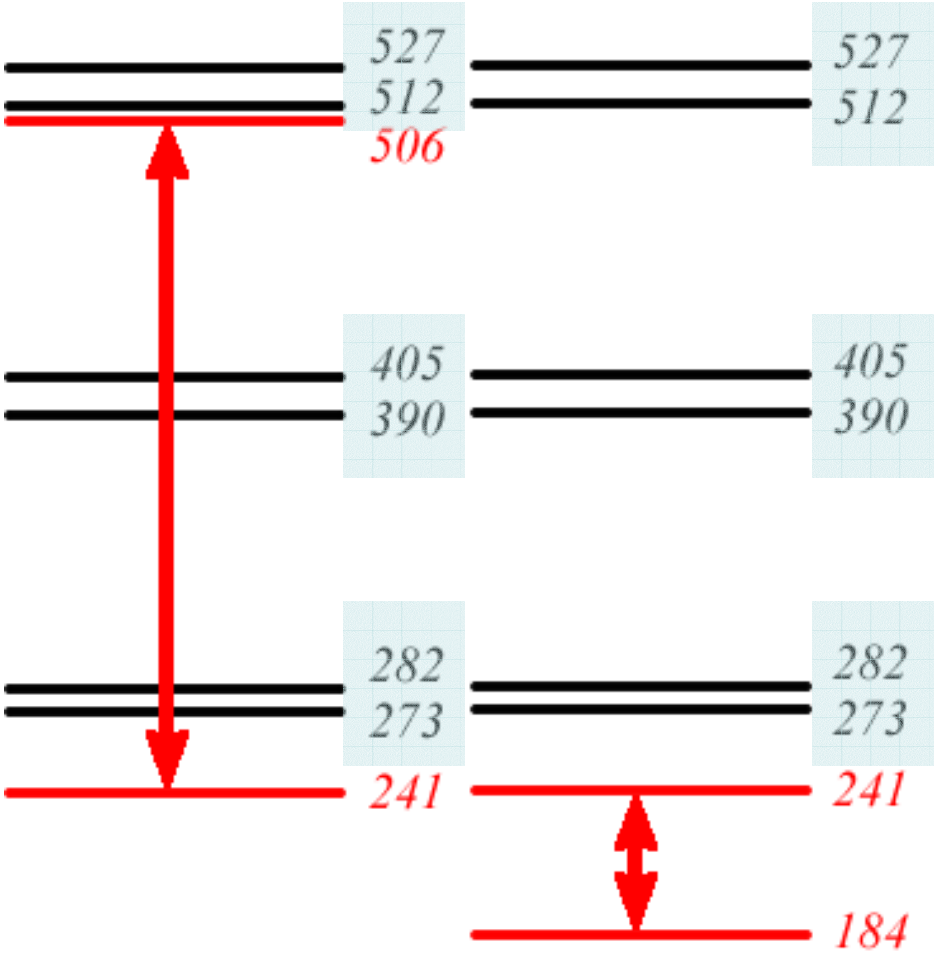






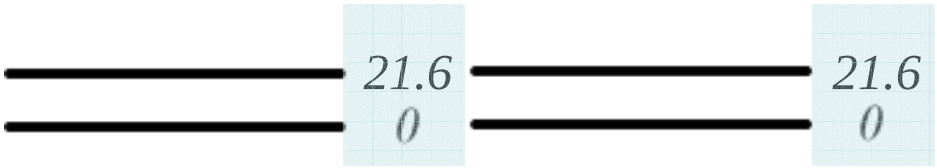
Lüttschwager et al.
(2013)
IR / Raman observations

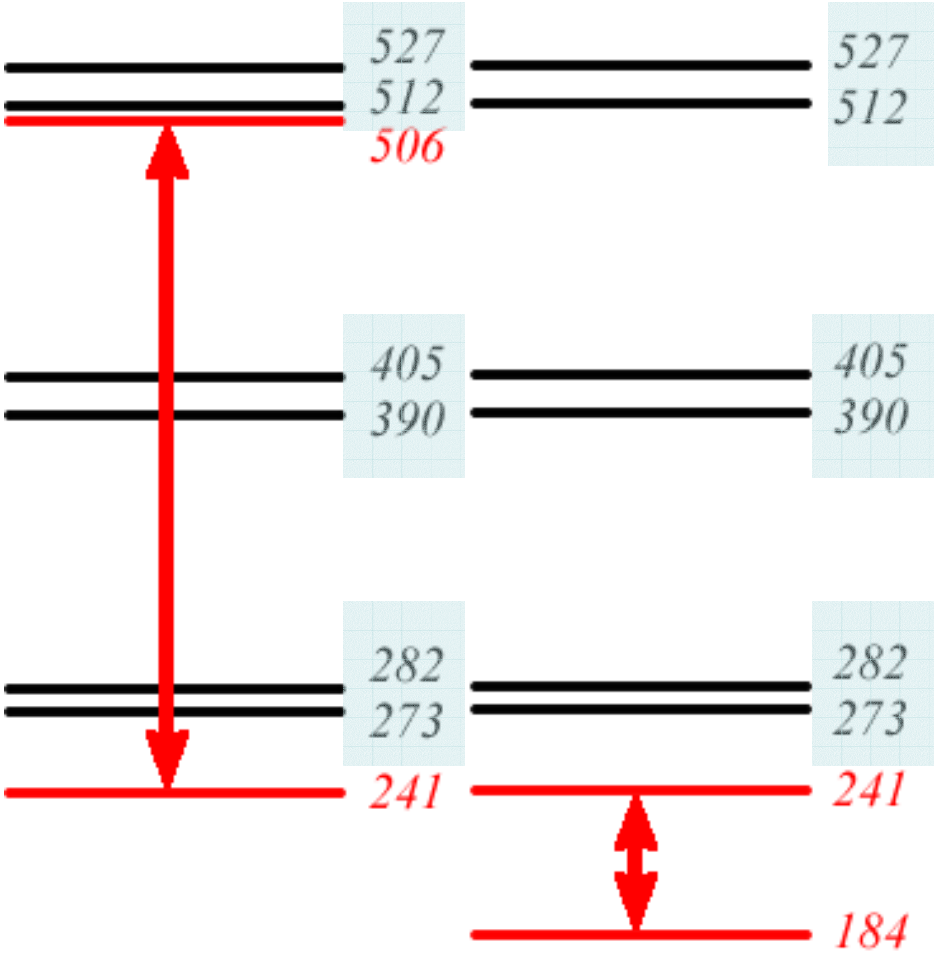




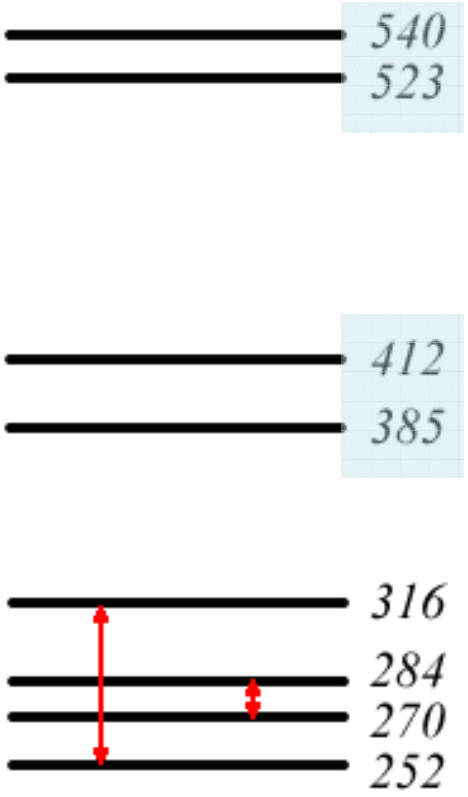
Lüttschwager et al. (2013)
IR / Raman observations

Assignment #1 **Assignment #2**



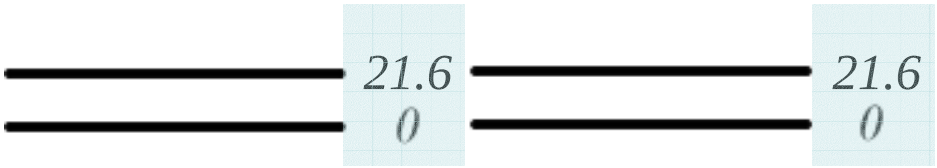


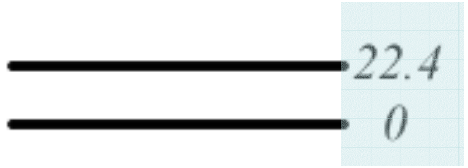
Lüttschwager et al. (2013)
IR / Raman observations

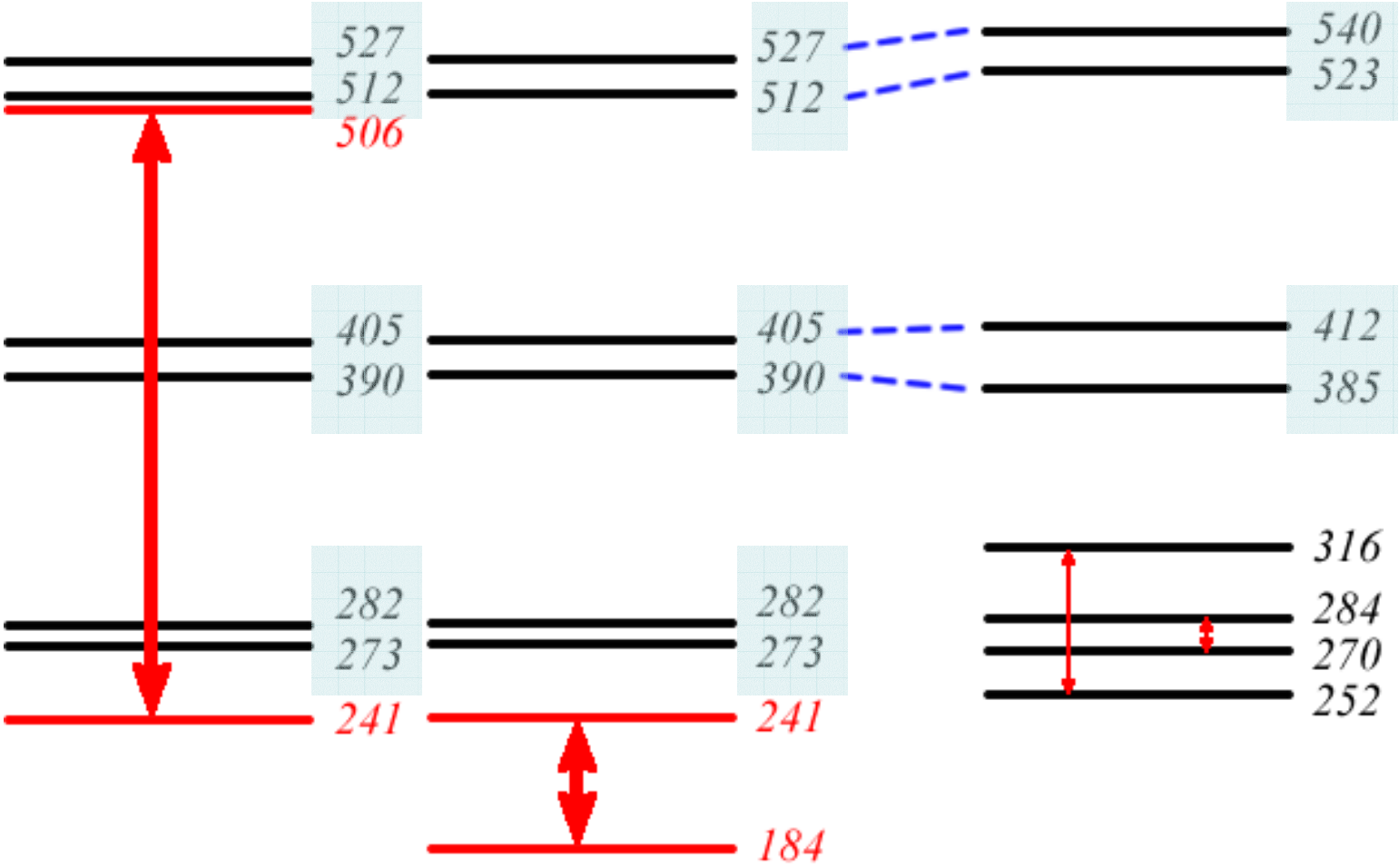


Schröder and Meyer (2014)
***ab initio* calculations**

Assignment #1 **Assignment #2**



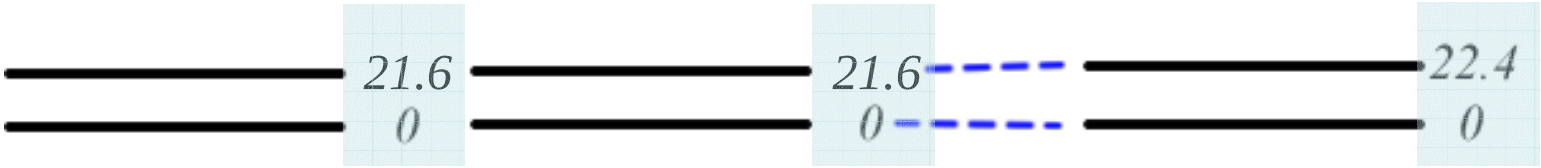


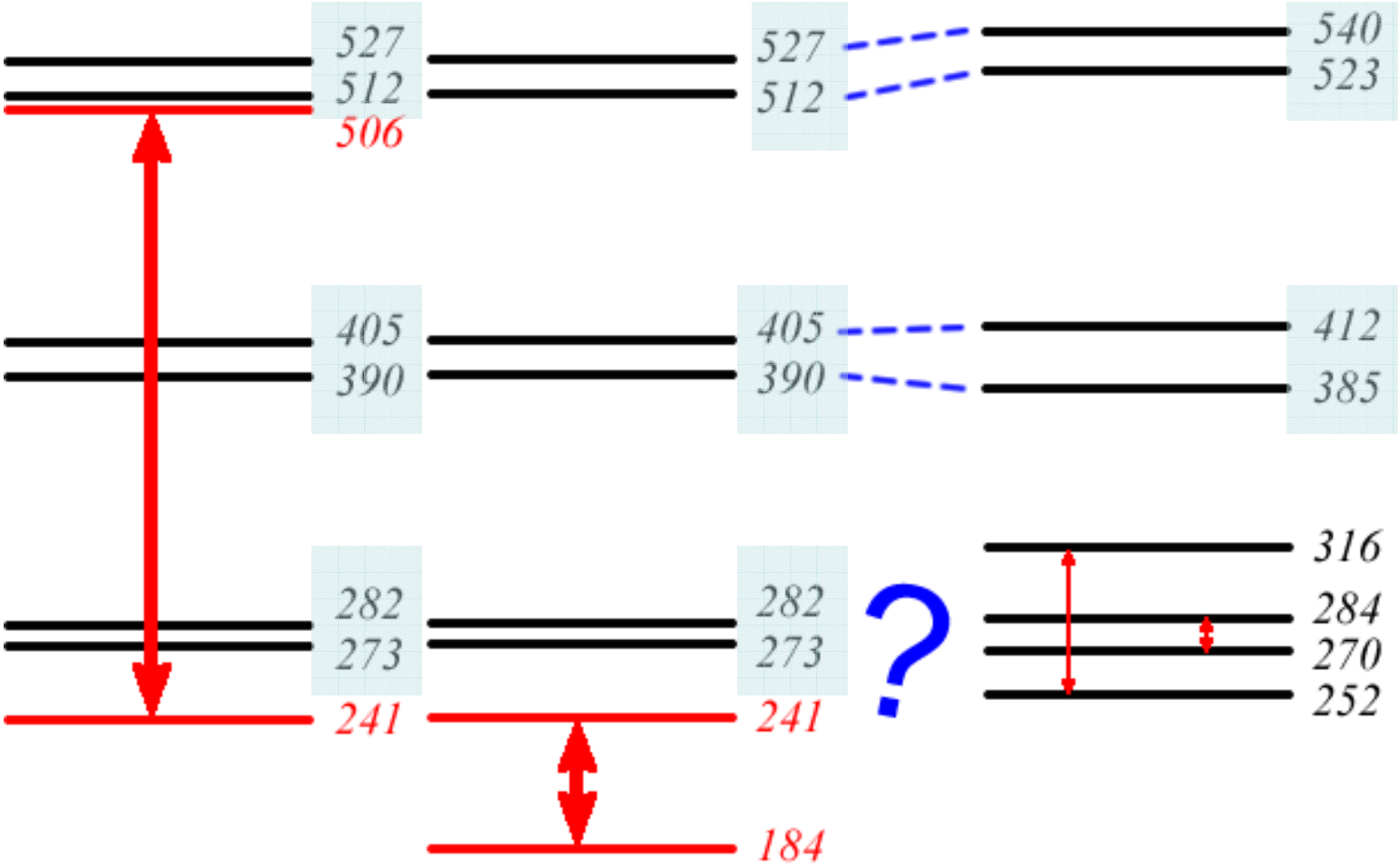


Lüttschwager et al. (2013)
IR / Raman observations

Assignment #1 **Assignment #2**

Schröder and Meyer (2014)
***ab initio* calculations**

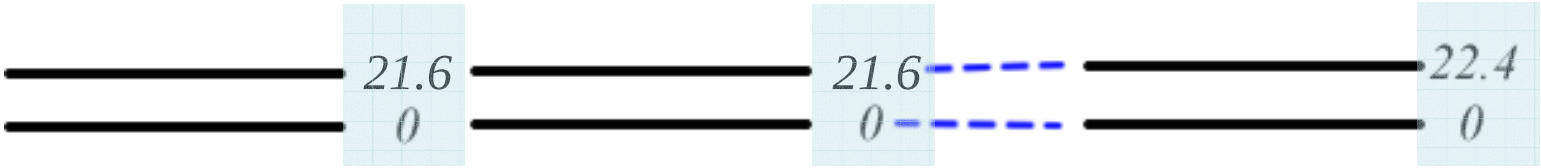


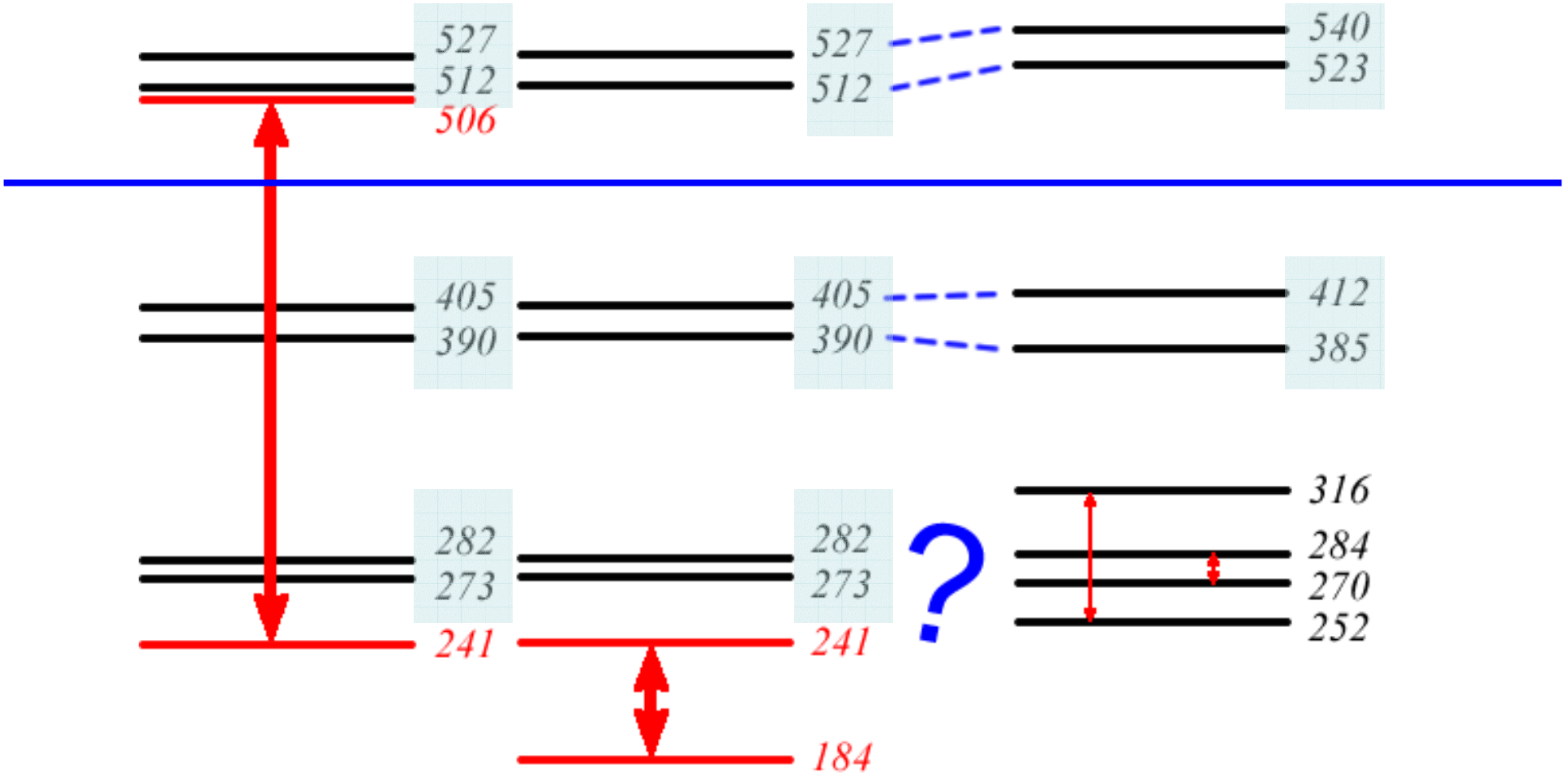


Lüttschwager et al. (2013)
IR / Raman observations

Assignment #1 **Assignment #2**

Schröder and Meyer (2014)
***ab initio* calculations**

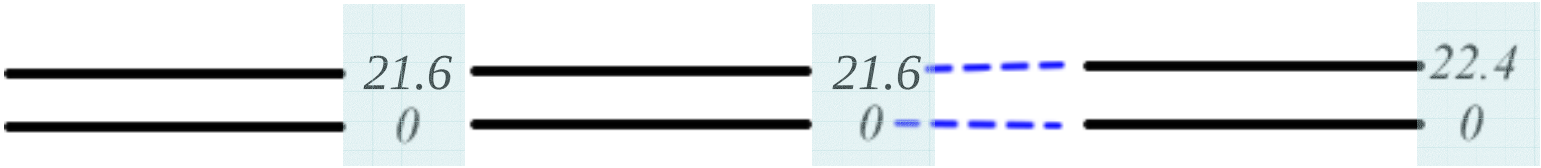




Lüttschwager et al. (2013)
IR / Raman observations

Assignment #1 **Assignment #2**

Schröder and Meyer (2014)
***ab initio* calculations**

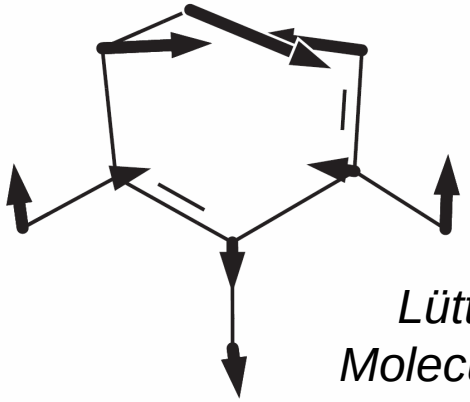


The Two Lowest-Frequency Modes

- ν O···O

In-plane ring opening/closing mode

- Increases tunnelling-splitting

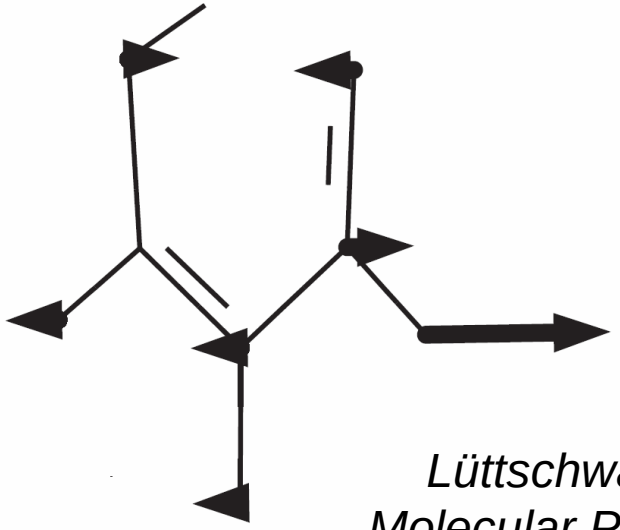


Lüttschwager et al. Molecular Physics, 2013

- γ C_cH

Out-of-plane bending mode

- Reduces tunnelling-splitting



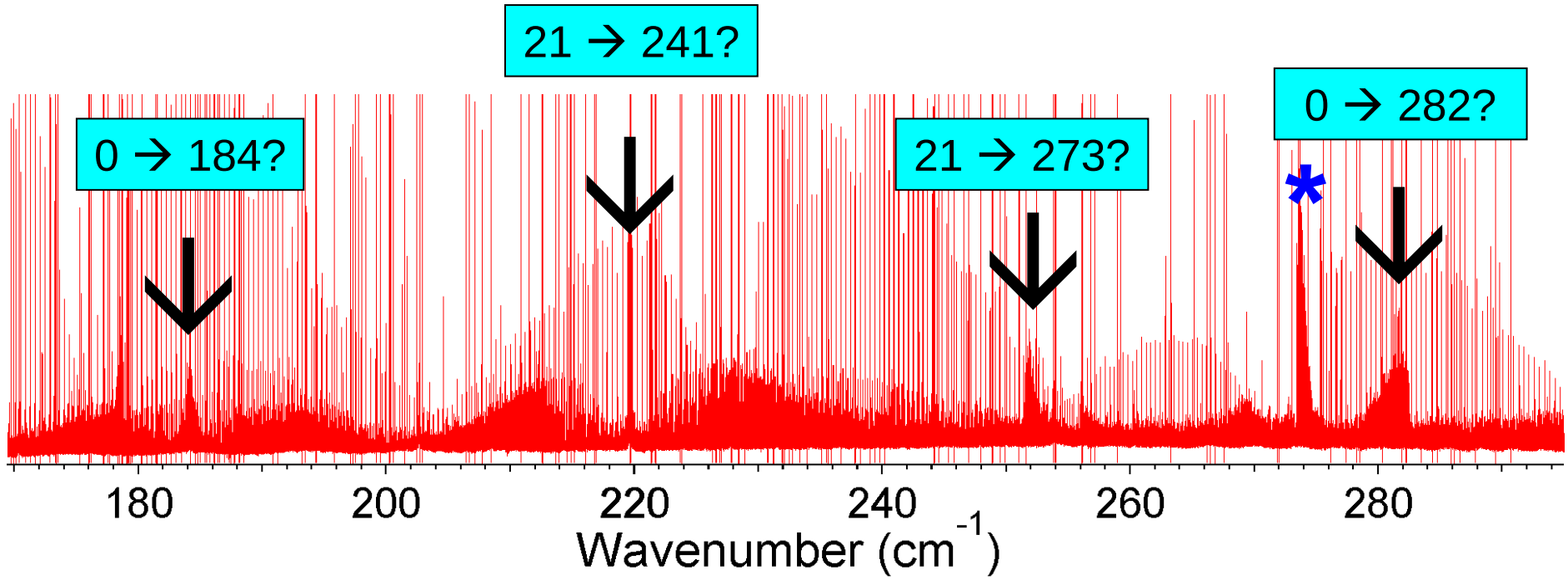
Lüttschwager et al. Molecular Physics, 2013

Canadian Light Source Synchrotron

[Image from: Winnewisser et al. Phys. Chem. Chem. Phys., 2014.]

Our CLS Malonaldehyde Spectrum

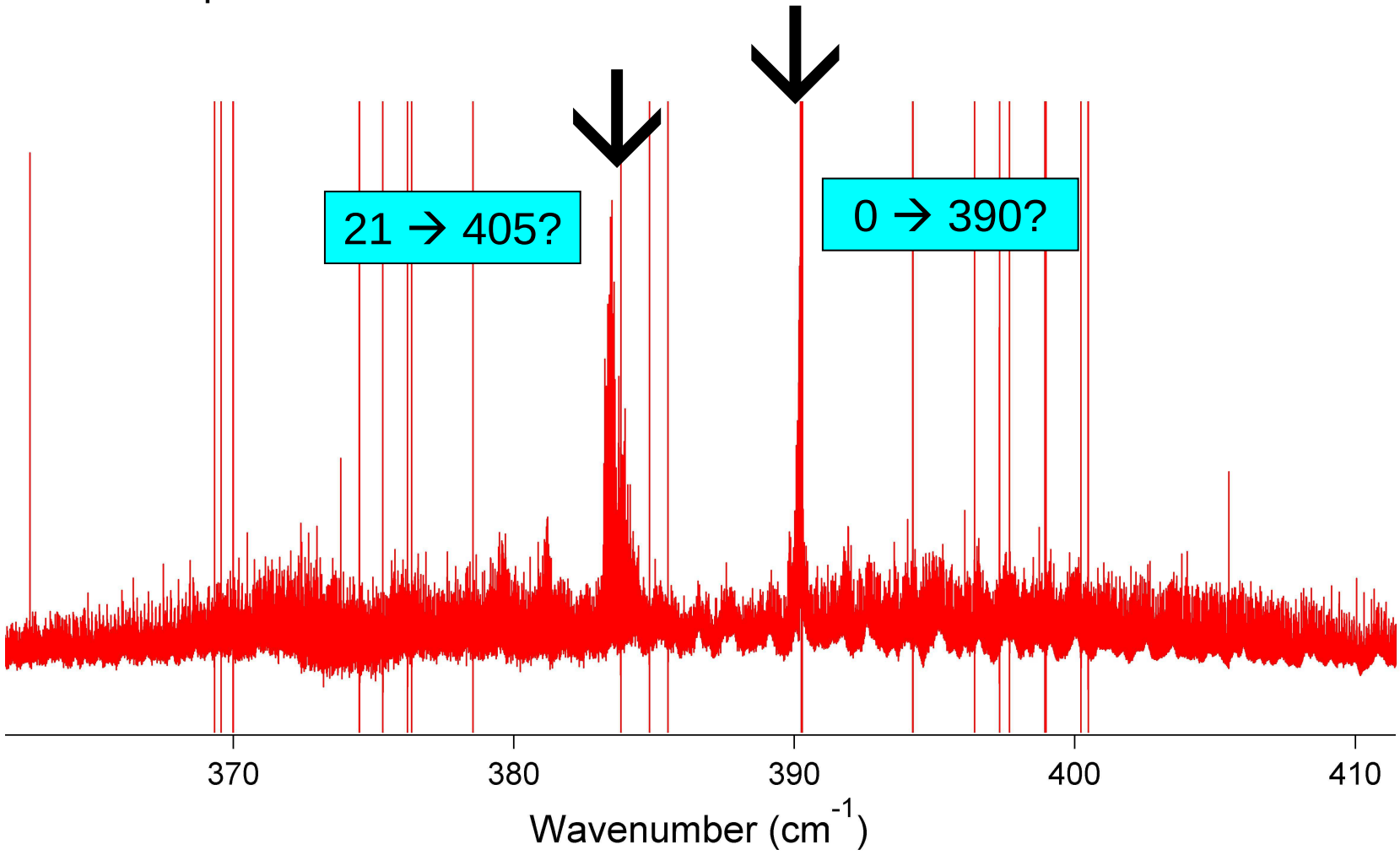
• Features corresponding to all of Lüttschwager's low-frequency assignments are present in the spectrum.



* = Impurity

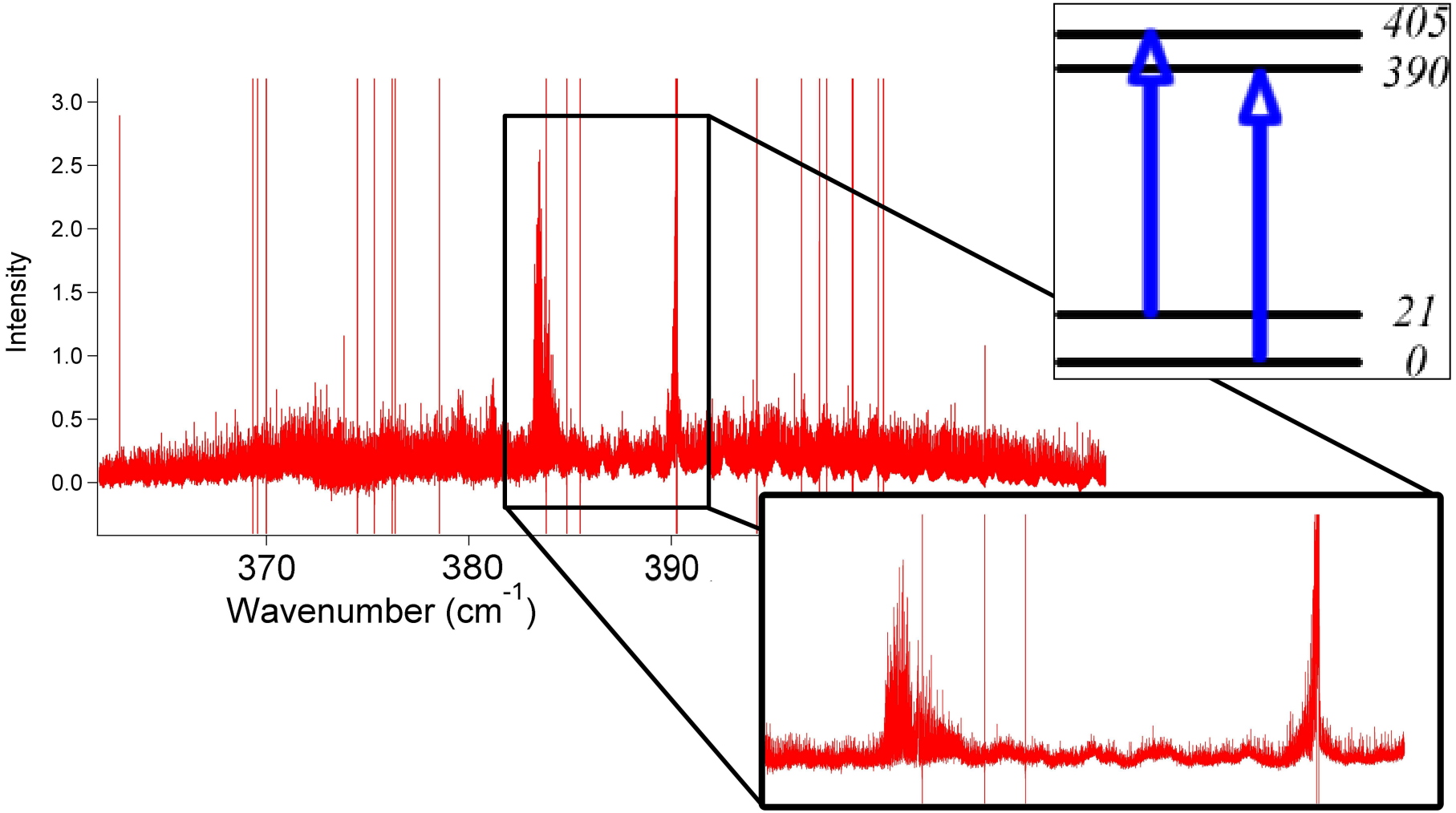
Our CLS Malonaldehyde Spectrum

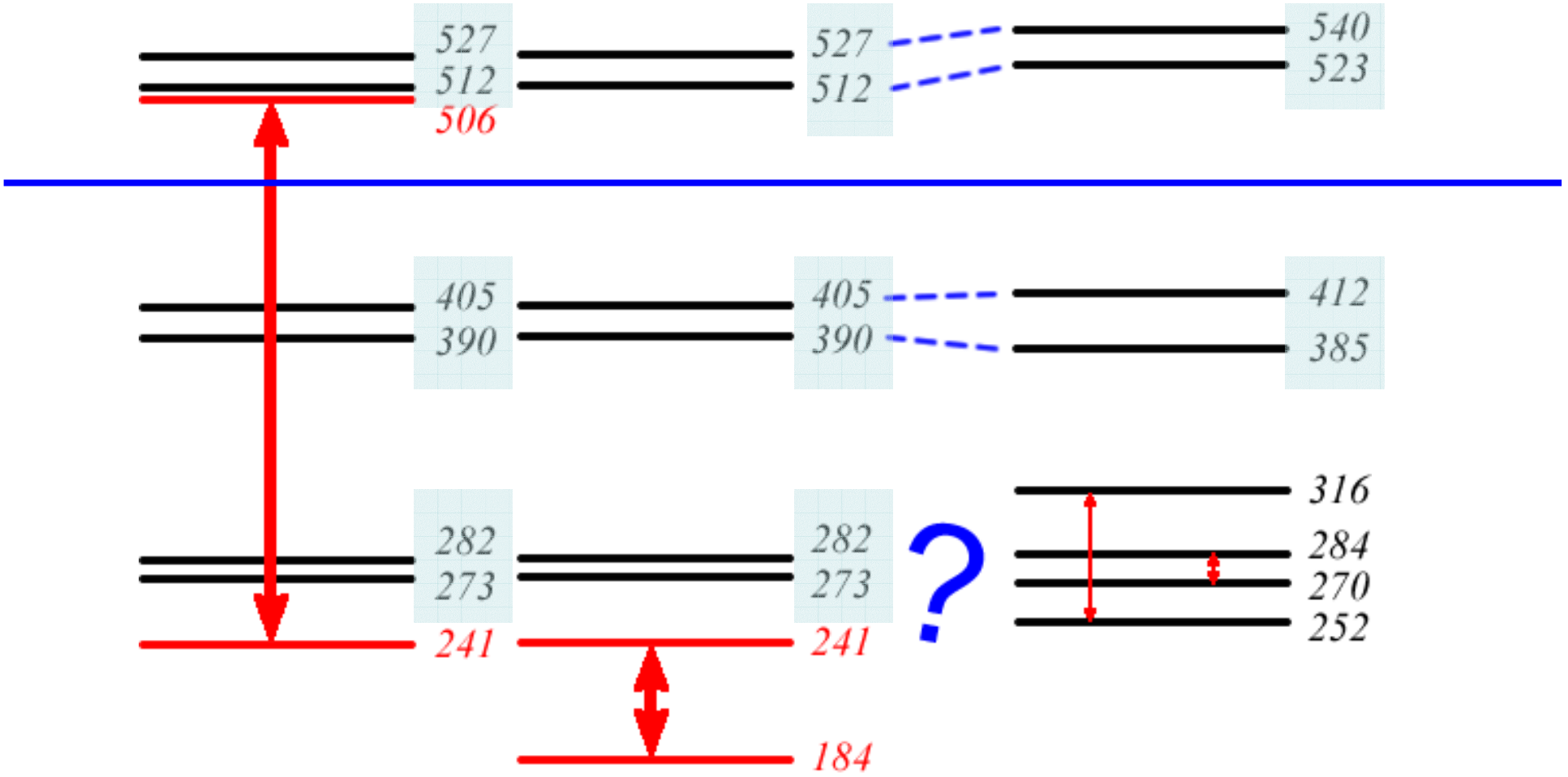
• Features corresponding to all of Lüttschwager's low-frequency assignments are present in the spectrum.



The 390/405 cm^{-1} Tunnelling Pair (out-of-plane)

c-type bands at 384/390 cm^{-1}

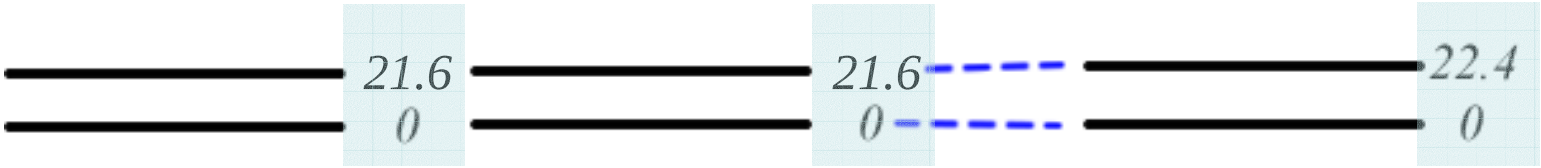


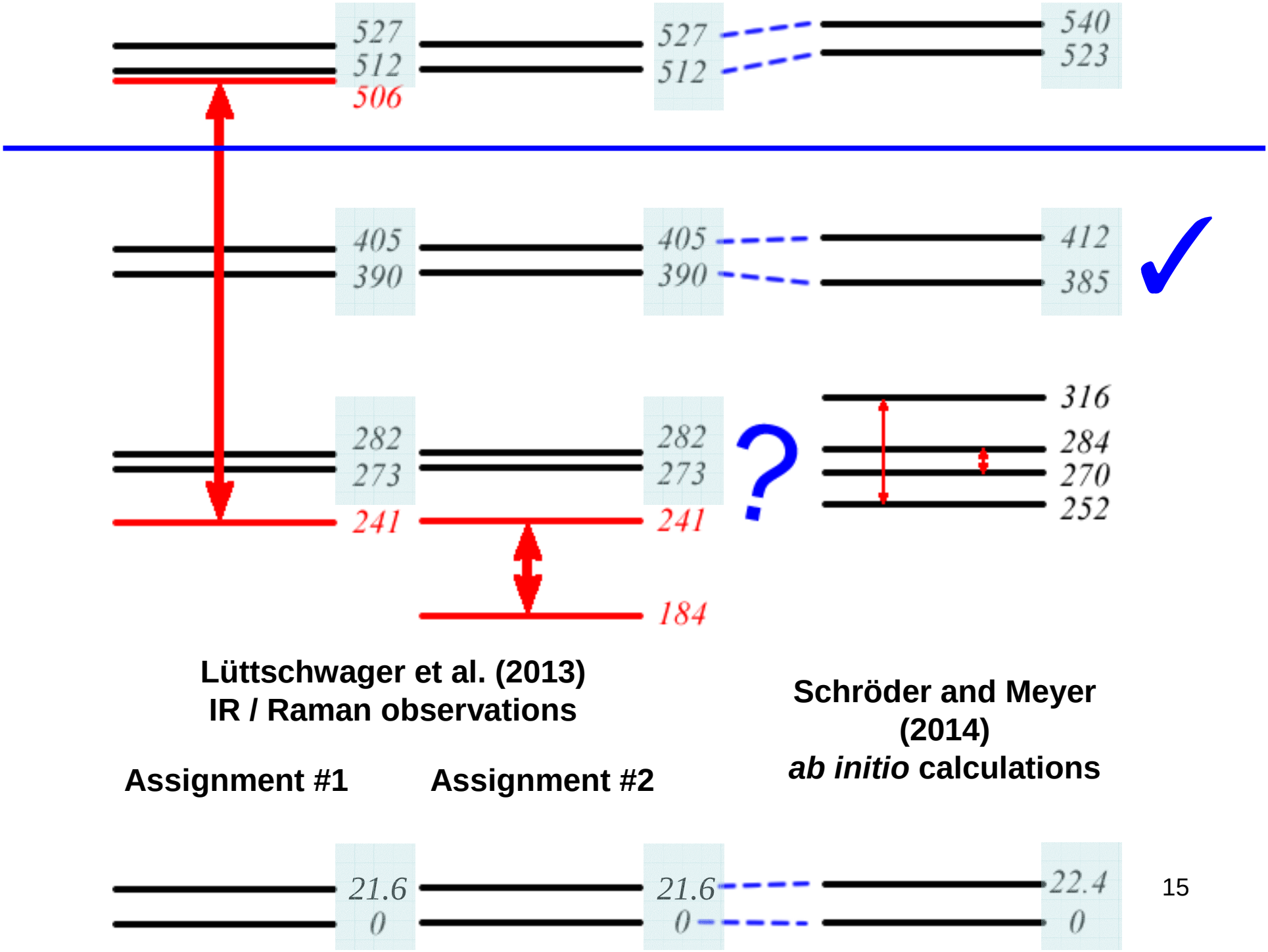


Lüttschwager et al. (2013)
IR / Raman observations

Assignment #1 **Assignment #2**

Schröder and Meyer (2014)
***ab initio* calculations**

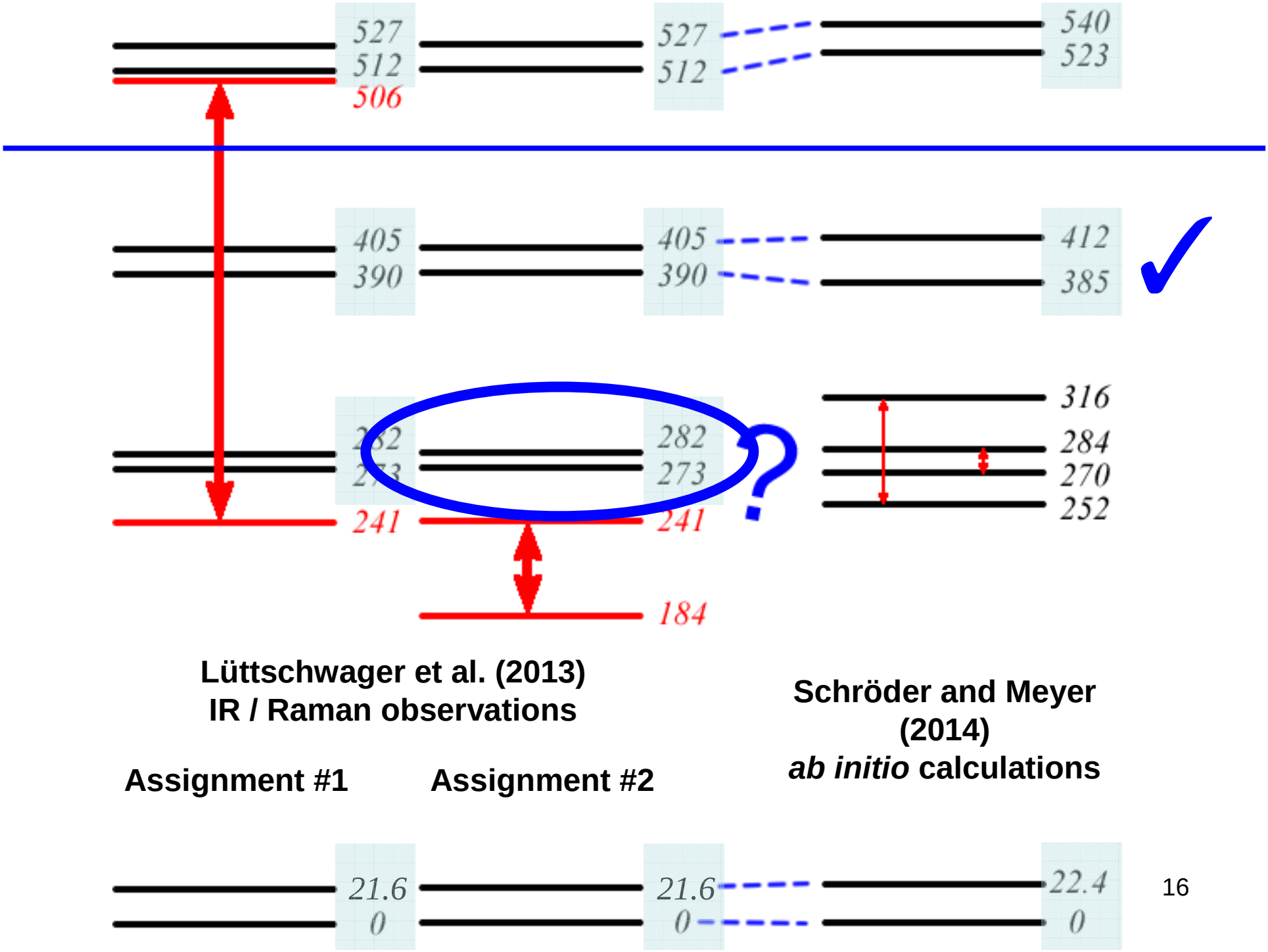




Lüttschwager et al. (2013)
IR / Raman observations

Assignment #1 **Assignment #2**

Schröder and Meyer (2014)
***ab initio* calculations**



Lüttschwager et al. (2013)
IR / Raman observations

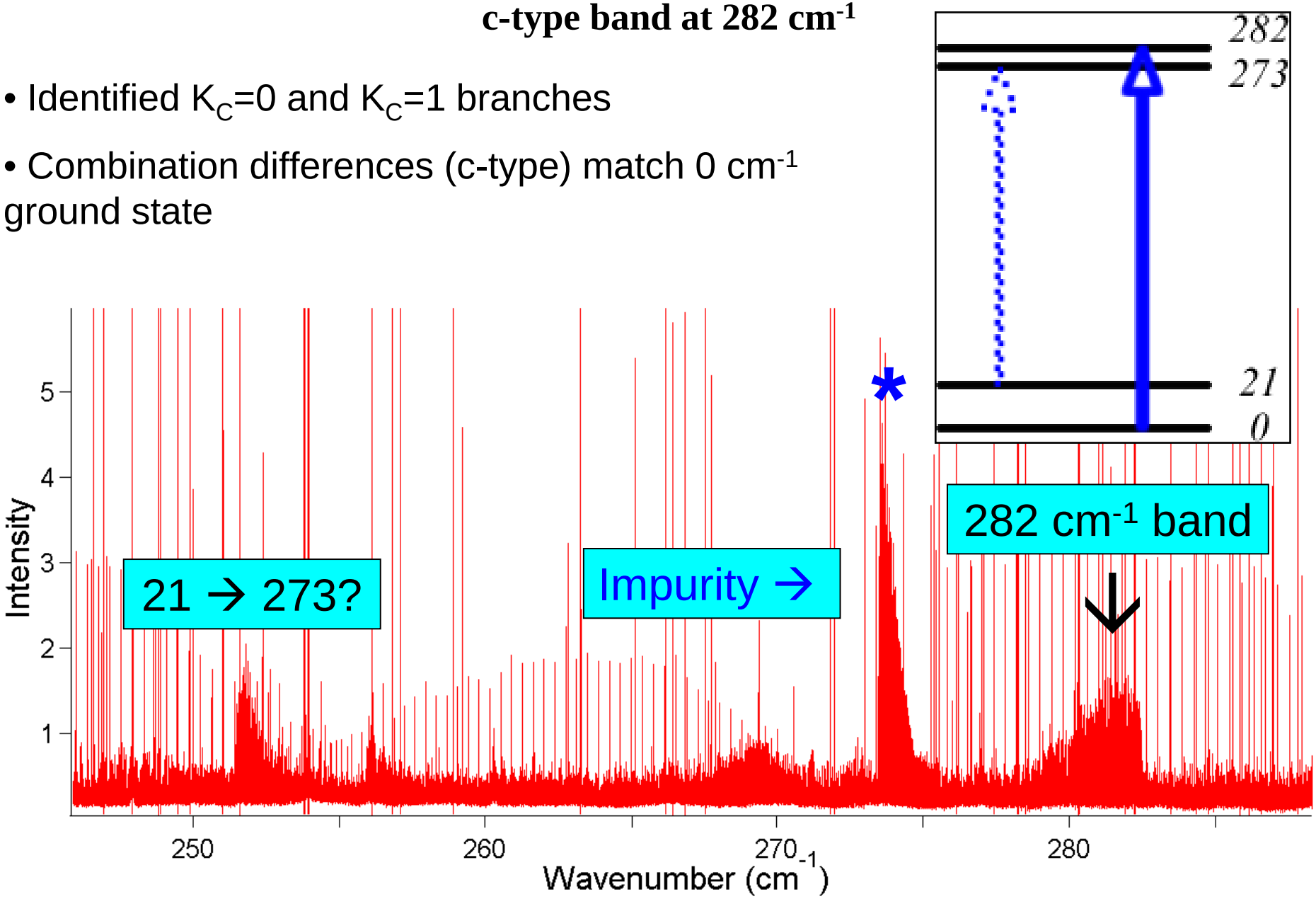
Assignment #1 **Assignment #2**

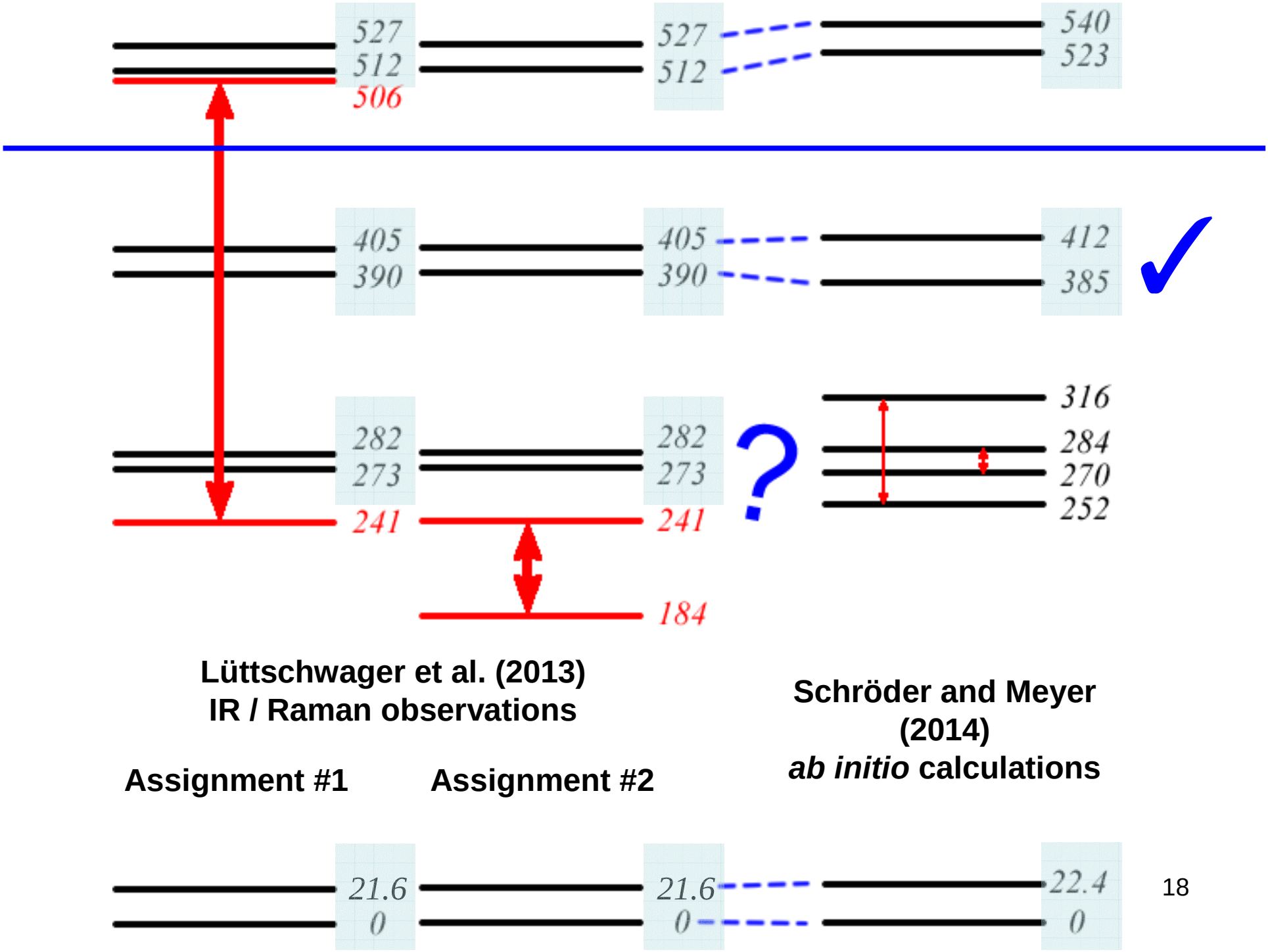
Schröder and Meyer (2014)
***ab initio* calculations**

The 282 cm^{-1} state (out-of-plane)

c-type band at 282 cm^{-1}

- Identified K_C=0 and K_C=1 branches
- Combination differences (c-type) match 0 cm^{-1} ground state

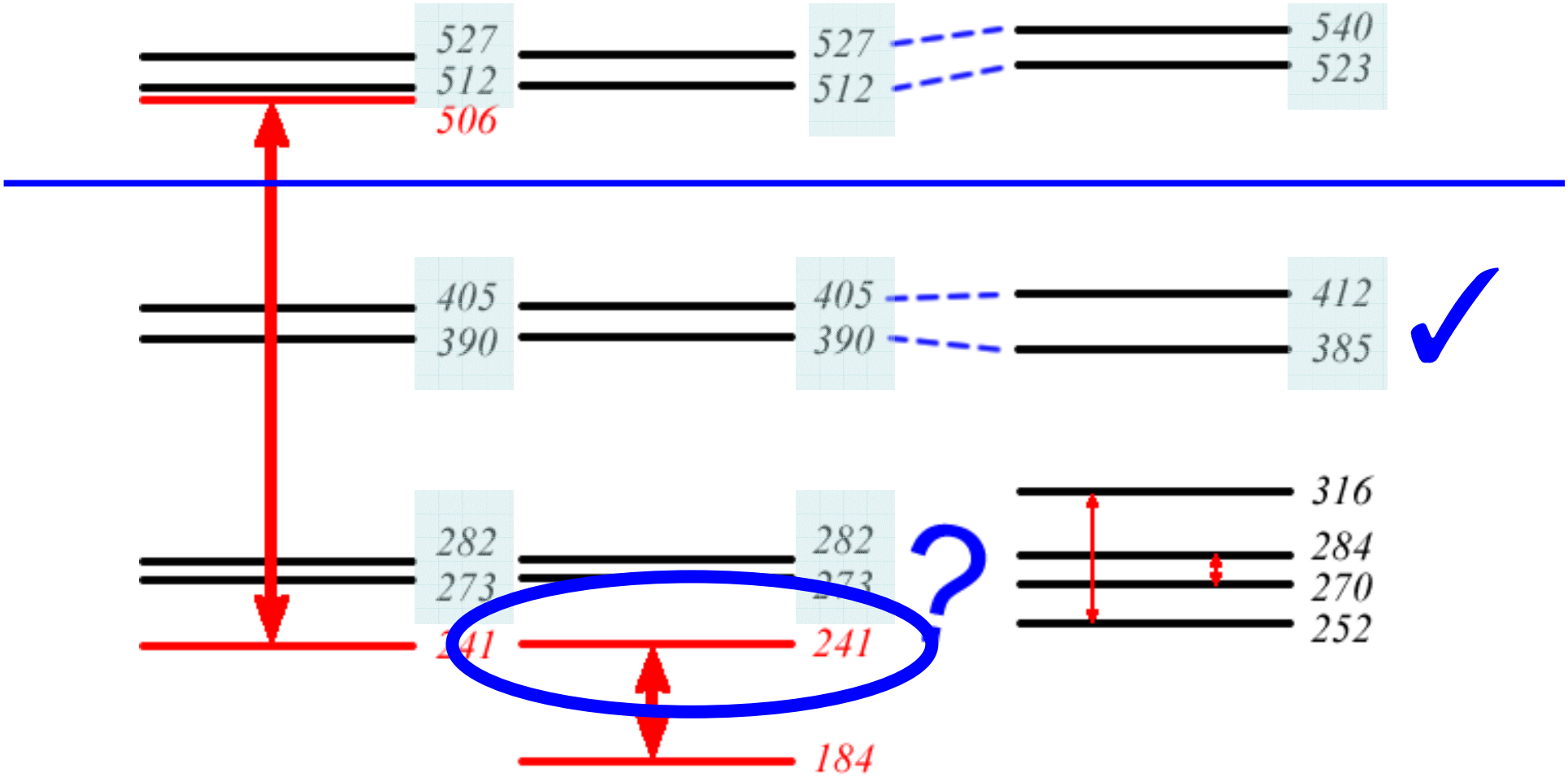




Lüttschwager et al. (2013)
IR / Raman observations

Assignment #1 **Assignment #2**

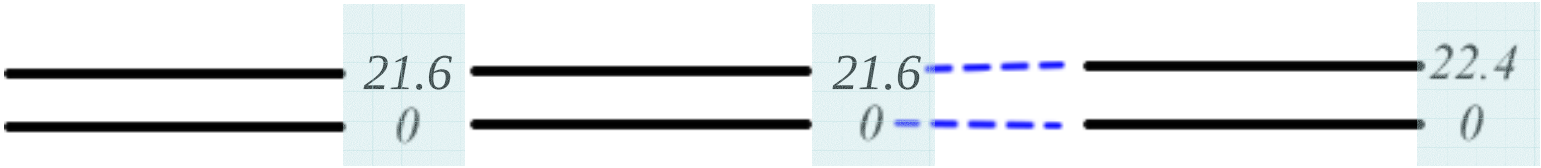
Schröder and Meyer (2014)
***ab initio* calculations**



Lüttschwager et al. (2013)
IR / Raman observations

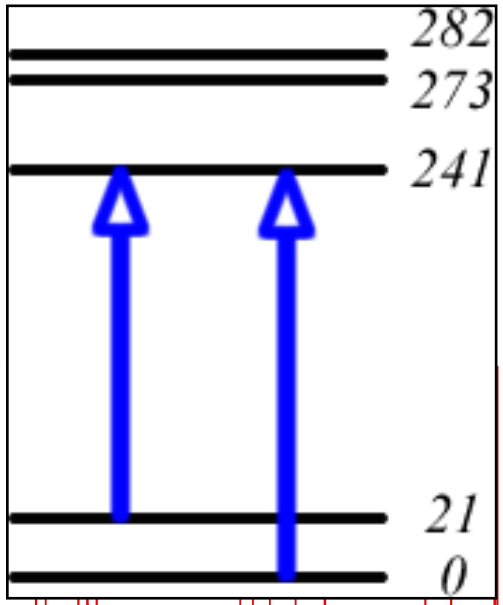
Assignment #1 **Assignment #2**

Schröder and Meyer (2014)
***ab initio* calculations**

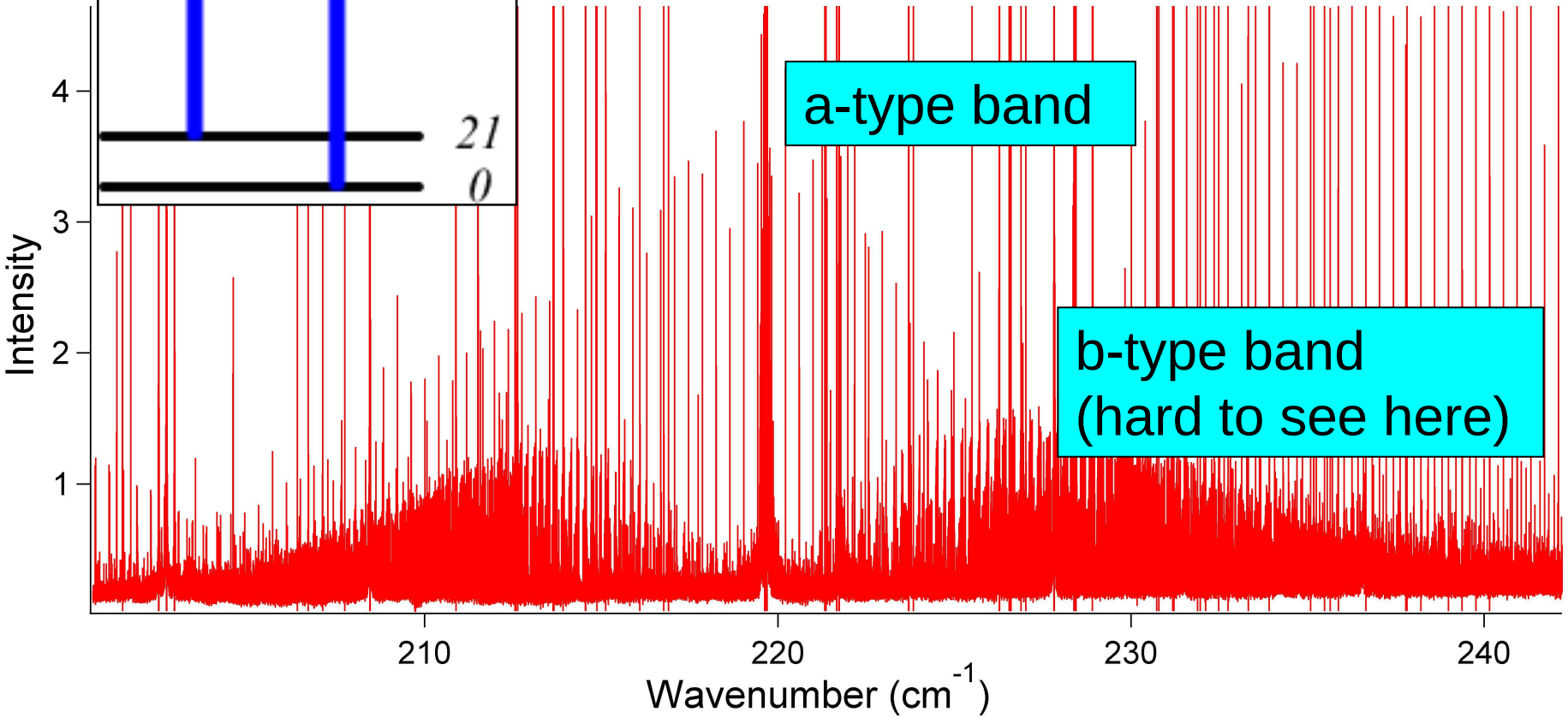


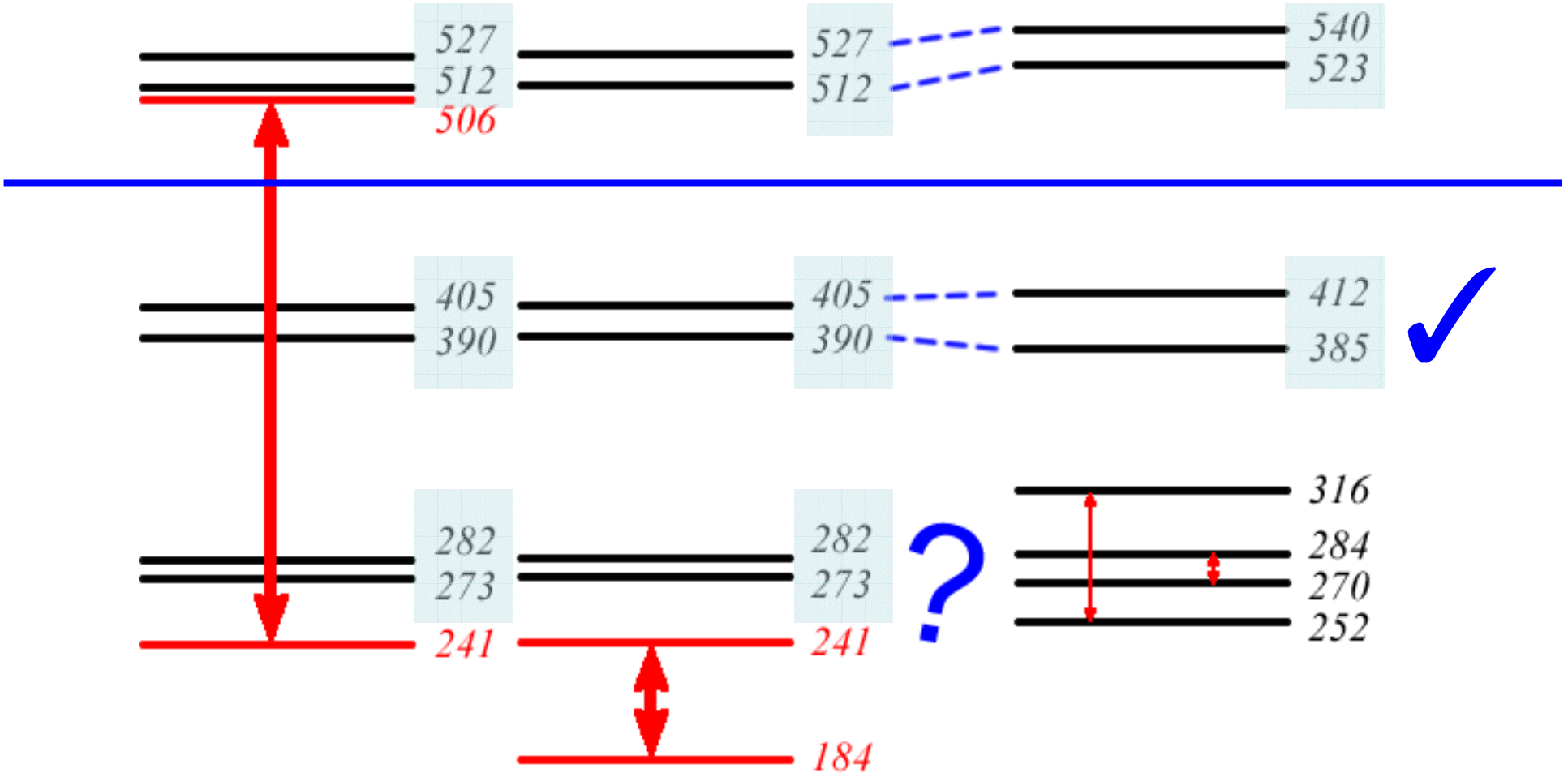
The 241 cm^{-1} state (in-plane)

a-type 220 cm^{-1} and b-type 241 cm^{-1} bands



- Both a- and b-type bands have a common upper state: confirmed by combination differences
- Lower states = ground state tunnelling pair
- Where is the other tunnelling component?

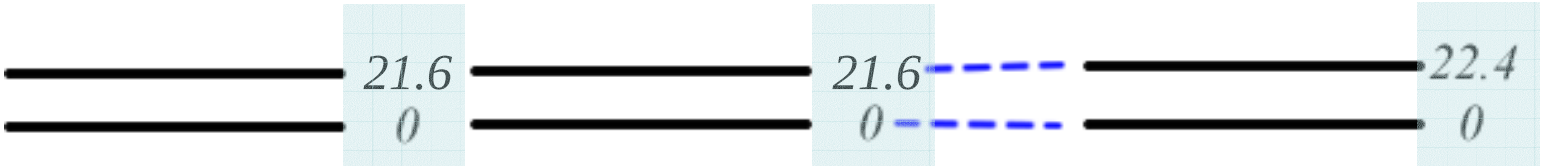


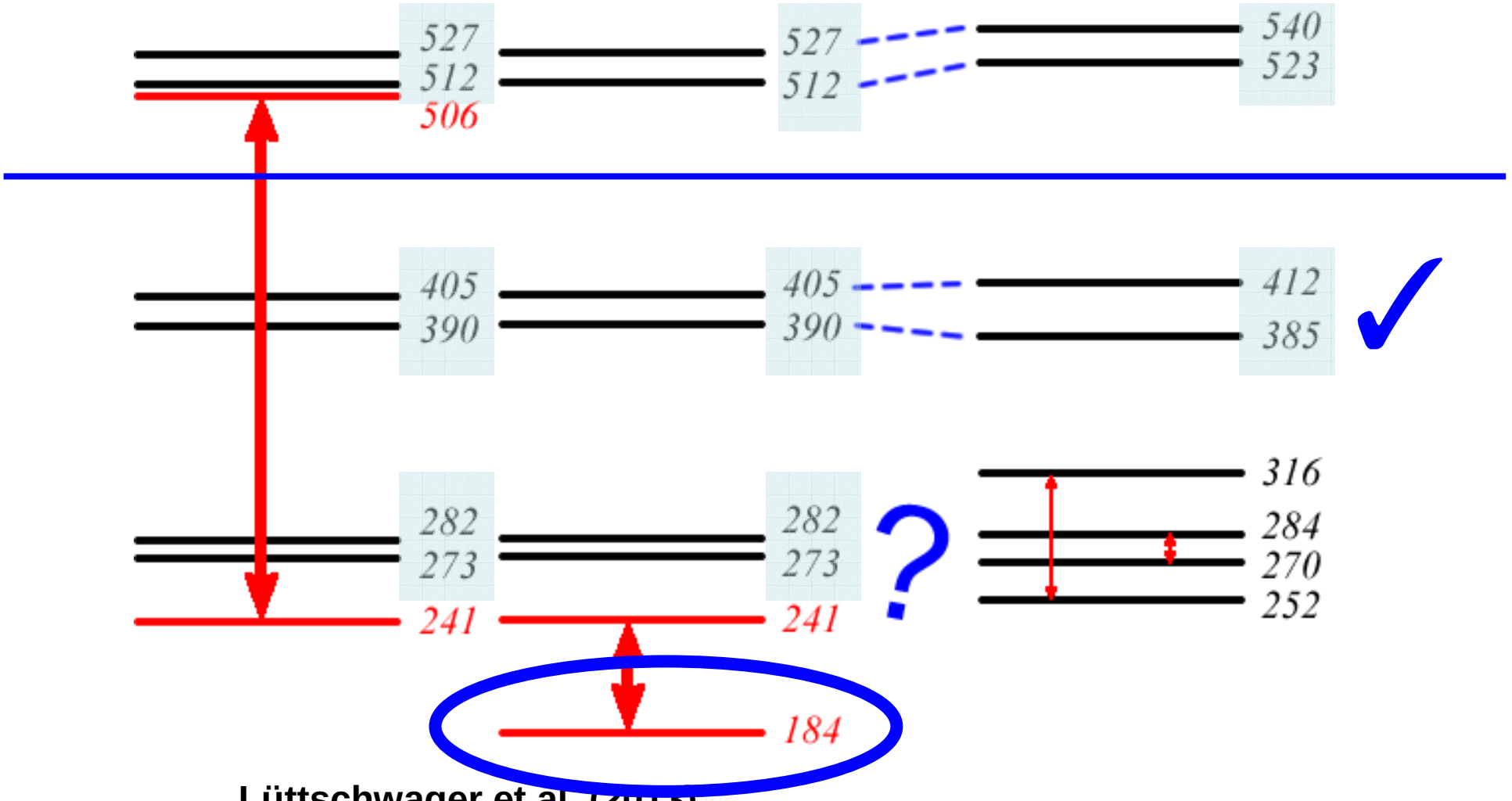


Lüttschwager et al. (2013)
IR / Raman observations

Assignment #1 **Assignment #2**

Schröder and Meyer (2014)
***ab initio* calculations**

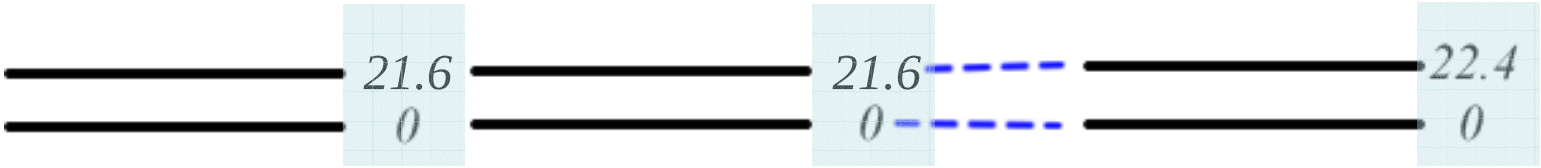




Lüttschwager et al. (2013)
IR / Raman observations

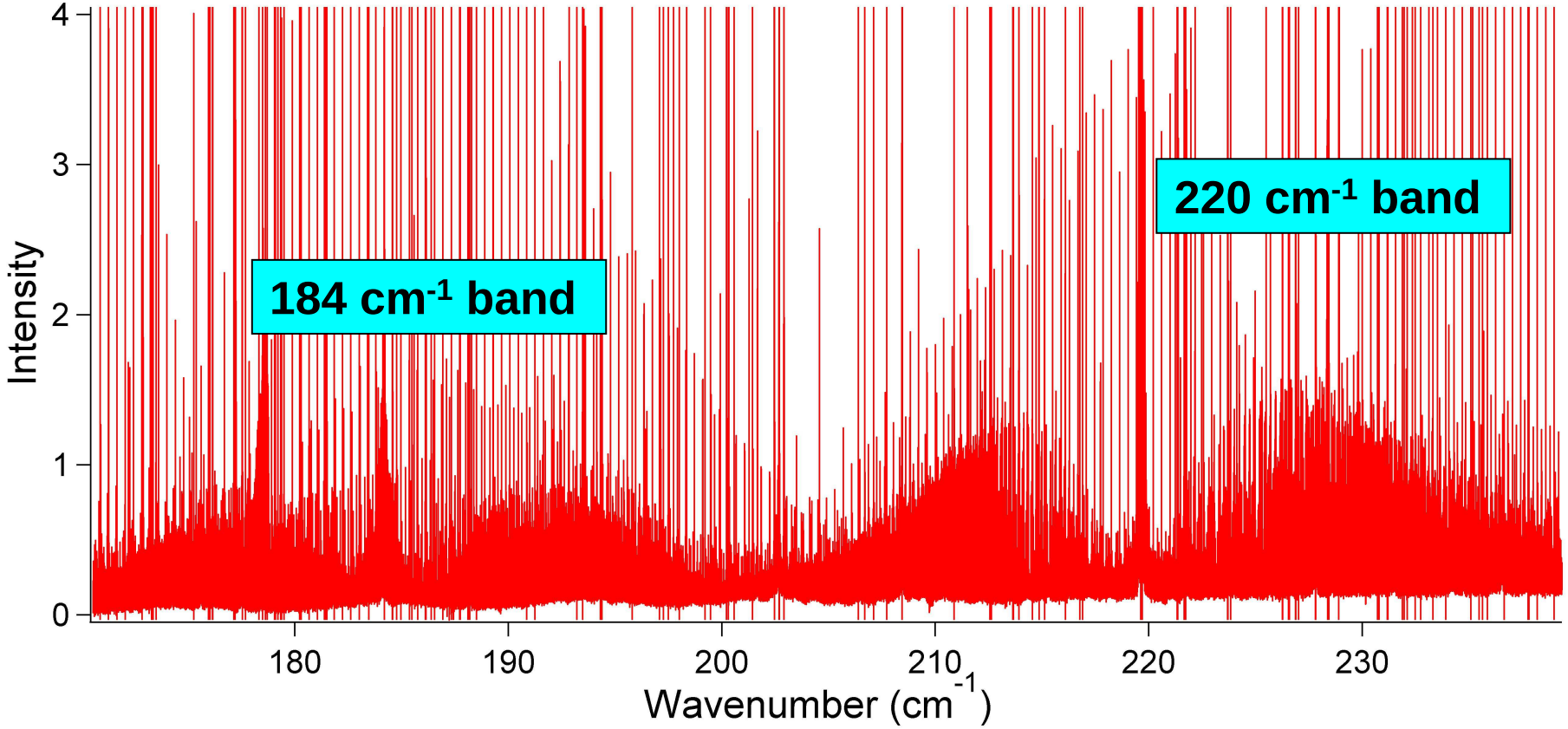
Assignment #1 **Assignment #2**

Schröder and Meyer (2014)
***ab initio* calculations**



The 184 cm^{-1} Band

- Several branches have been found
- However: *no matching combination differences*



The 1975 PhD Thesis of Walter Rowe

• Graduate student under E. Bright Wilson of Harvard University (co-author of “Molecular Vibrations”)

• Worked on the first major spectroscopic study of malonaldehyde (microwave)

• Reported a rotational analysis of 8 vibrational states including the ground state pair

• Rough vibrational frequencies using relative intensity

• Indication of mode symmetry (in-plane or out-of-plane) using inertial defect

Symmetry	Frequency (cm^{-1})
In-plane	**0**
In-plane	**16 ± 14**
In-plane	**277 ± 22**
In-plane	**293 ± 8**
Out-of-plane	**237 ± 20**
Out-of-plane	**282 ± 9**
Out-of-plane	**393 ± 59**
Out-of-plane	**390 ± 35**

The 1975 PhD Thesis of Walter Rowe

• Graduate student under E. Bright Wilson of Harvard University (co-author of “Molecular Vibrations”)

• Worked on the first major spectroscopic study of malonaldehyde (microwave)

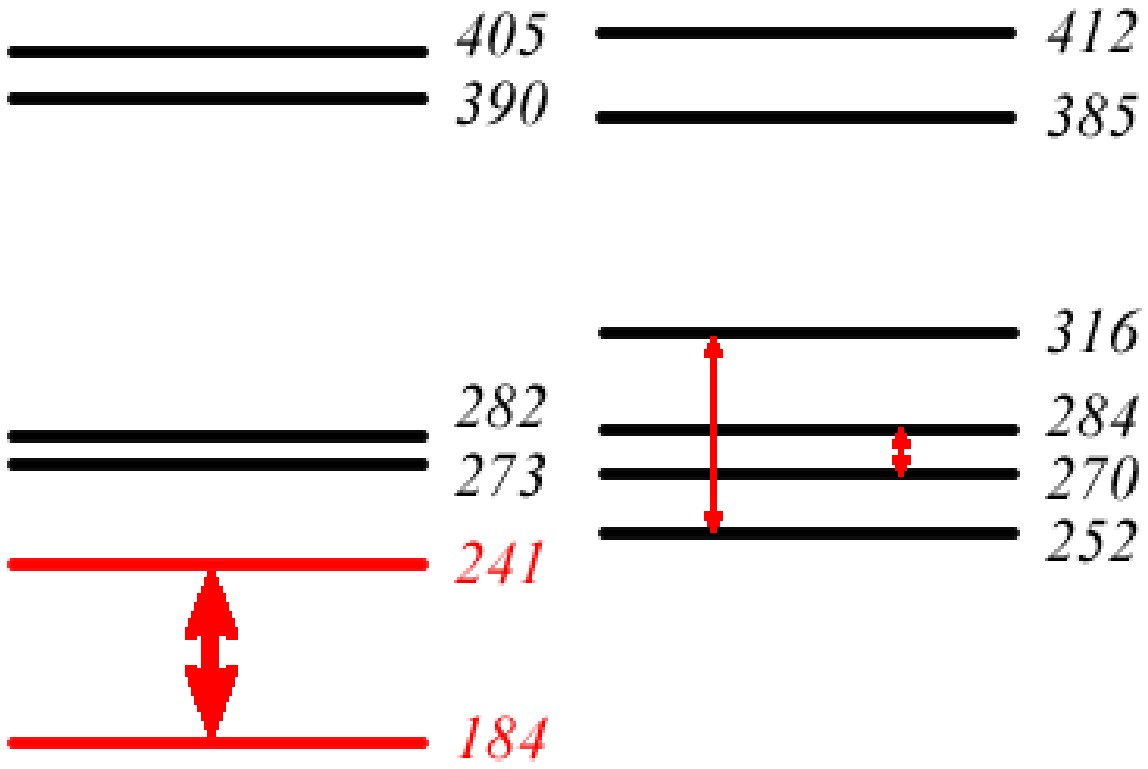
• Reported a rotational analysis of 8 vibrational states including the ground state pair

• Rough vibrational frequencies using relative intensity

• Indication of mode symmetry (in-plane or out-of-plane) using inertial defect

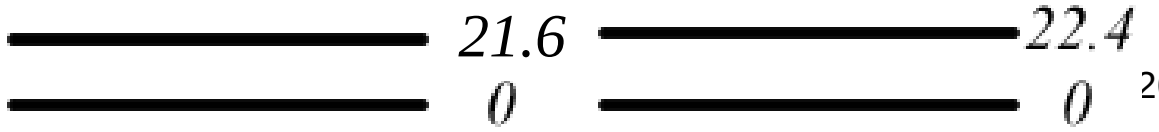
Symmetry	Frequency (cm^{-1})
In-plane	**0**
In-plane	**16 ± 14**
In-plane	**277 ± 22**
In-plane	**293 ± 8**
Out-of-plane	**237 ± 20**
Out-of-plane	**282 ± 9**
Out-of-plane	**393 ± 59**
Out-of-plane	**390 ± 35**

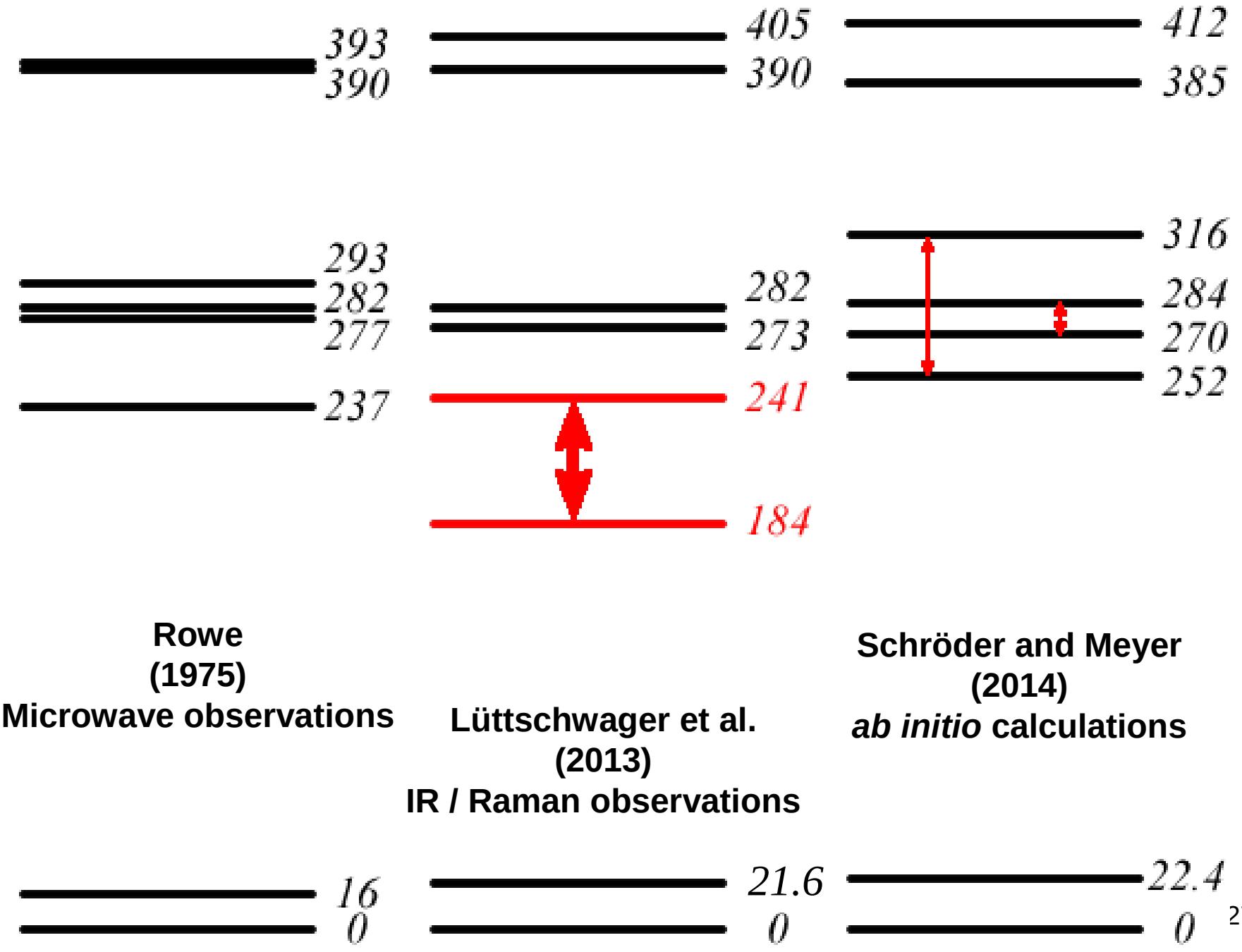
Rowe does not observe a state near 184 cm^{-1}



Lüttschwager et al. (2013)
IR / Raman observations

Schröder and Meyer (2014)
***ab initio* calculations**

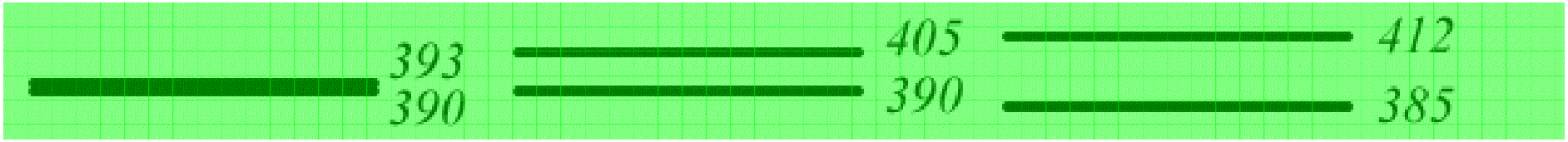


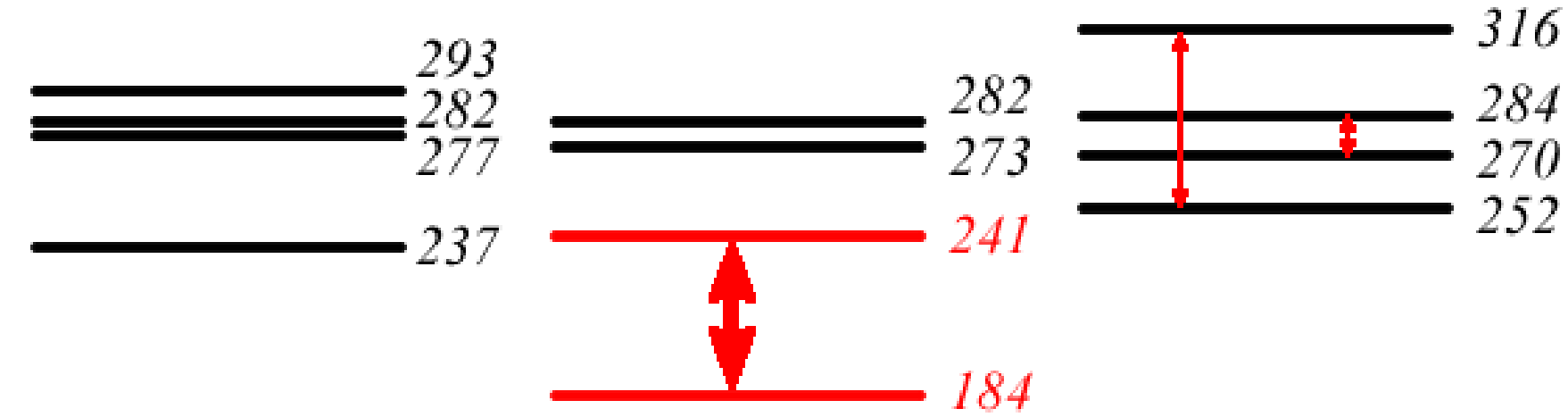


Rowe
(1975)
Microwave observations

Lüttschwager et al.
(2013)
IR / Raman observations

Schröder and Meyer
(2014)
***ab initio* calculations**





Rowe (1975) Microwave observations

Lüttschwager et al. (2013) IR / Raman observations

Schröder and Meyer (2014) *ab initio* calculations

The 390/405 cm^{-1} Tunnelling Pair (out-of-plane)

c-type bands at 384/390 cm^{-1}

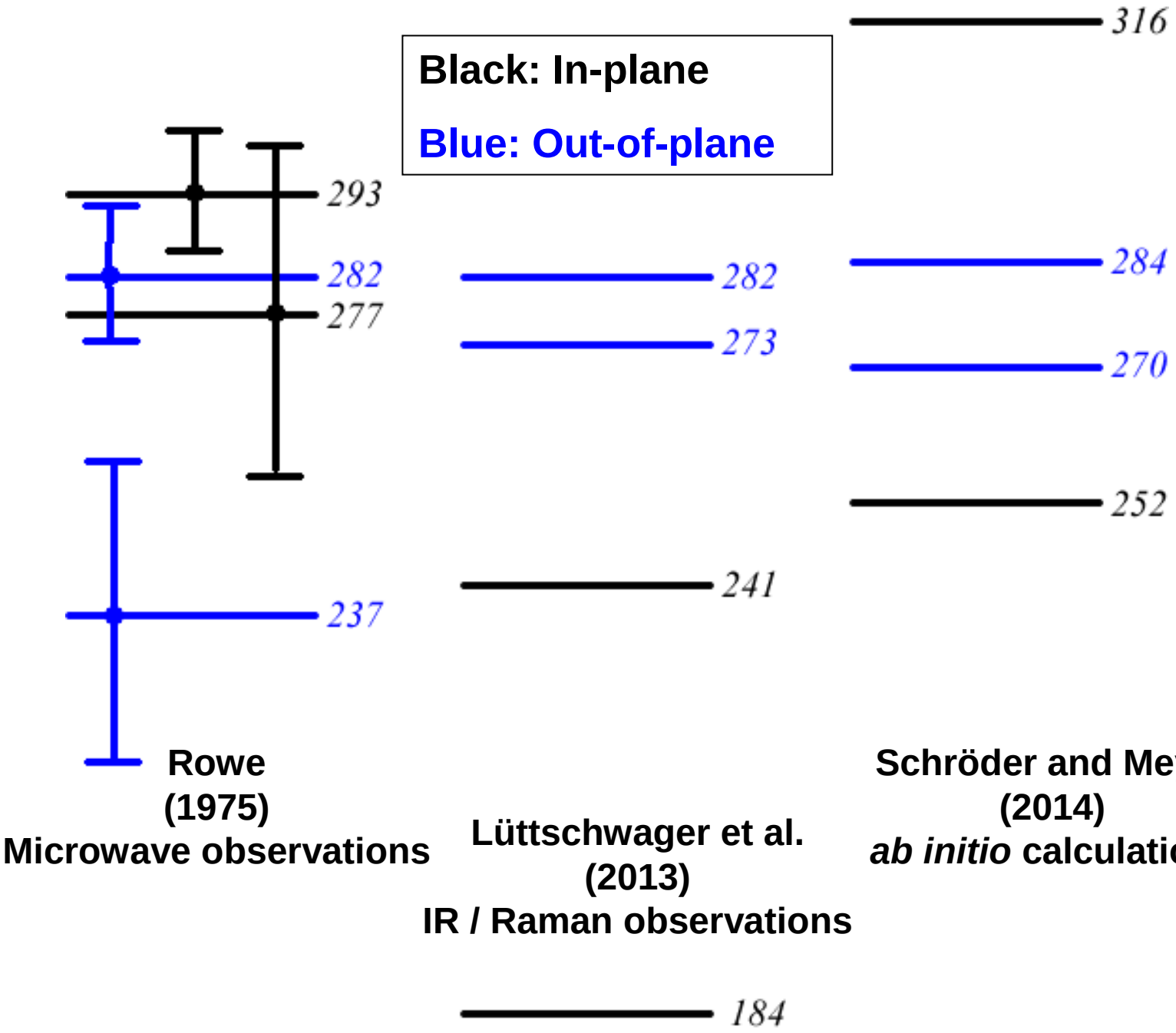
390 (Rowe Microwave) = 405 (IR)
393 (Rowe Microwave) = 390 (IR)

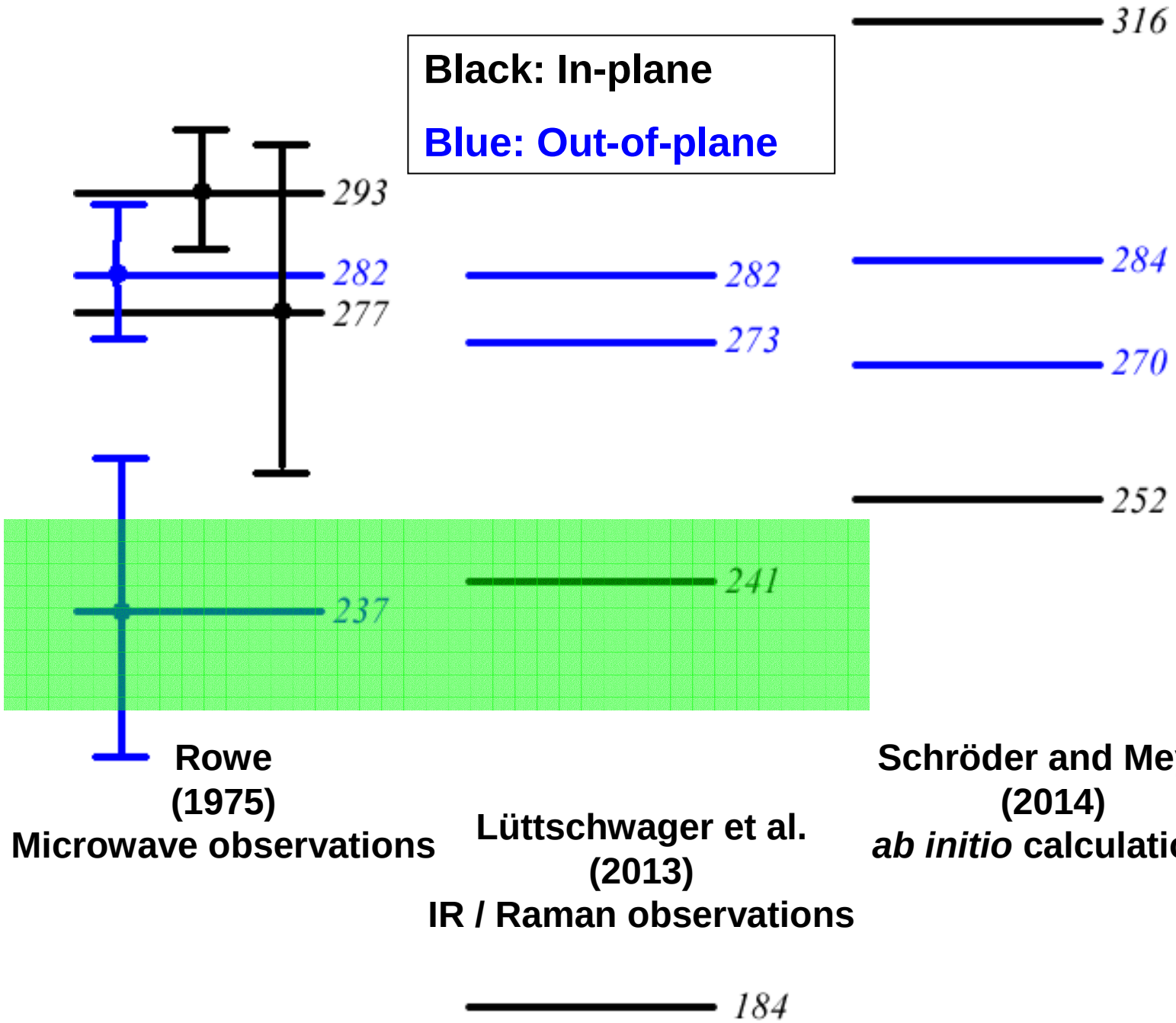
Confirmed by:

- Matching upper state combination differences
- Similarity of constants
- Able to fit 390 and 405 cm^{-1} states with IR and Rowe microwave data together

	Rowe 390 cm^{-1}	IR 405 cm^{-1}
A	9832.76 MHz	9832.79 MHz
B	5169.44 MHz	5169.27 MHz
C	3390.49 MHz	3390.36 MHz

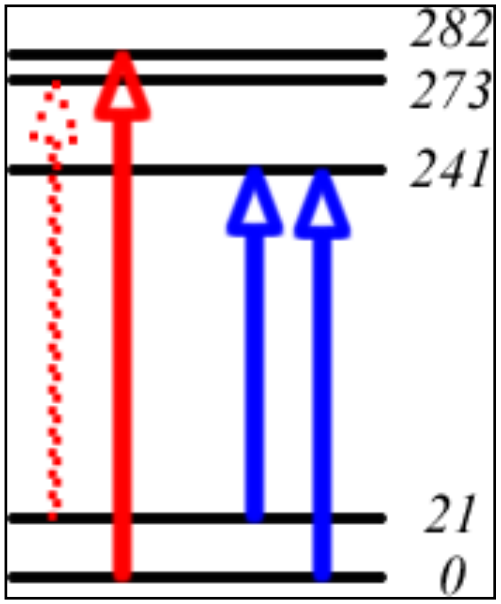
	Rowe 393 cm^{-1}	IR 390 cm^{-1}
A	9825.55 MHz	9825.66 MHz
B	5204.75 MHz	5205.46 MHz
C	3403.85 MHz	3402.97 MHz


Black: In-plane
Blue: Out-of-plane
316
293
282
277
284
282
273
270
252
241
237
184
Rowe
(1975)
Microwave observations
Lüttschwager et al.
(2013)
IR / Raman observations
Schröder and Meyer
(2014)
ab initio calculations


Black: In-plane
Blue: Out-of-plane
316
293
282
277
282
273
284
270
252
241
237
184
Rowe
(1975)
Microwave observations
Lüttschwager et al.
(2013)
IR / Raman observations
Schröder and Meyer
(2014)
ab initio calculations

The 241 cm^{-1} state (in-plane)

a-type 220 cm^{-1} and b-type 241 cm^{-1} bands

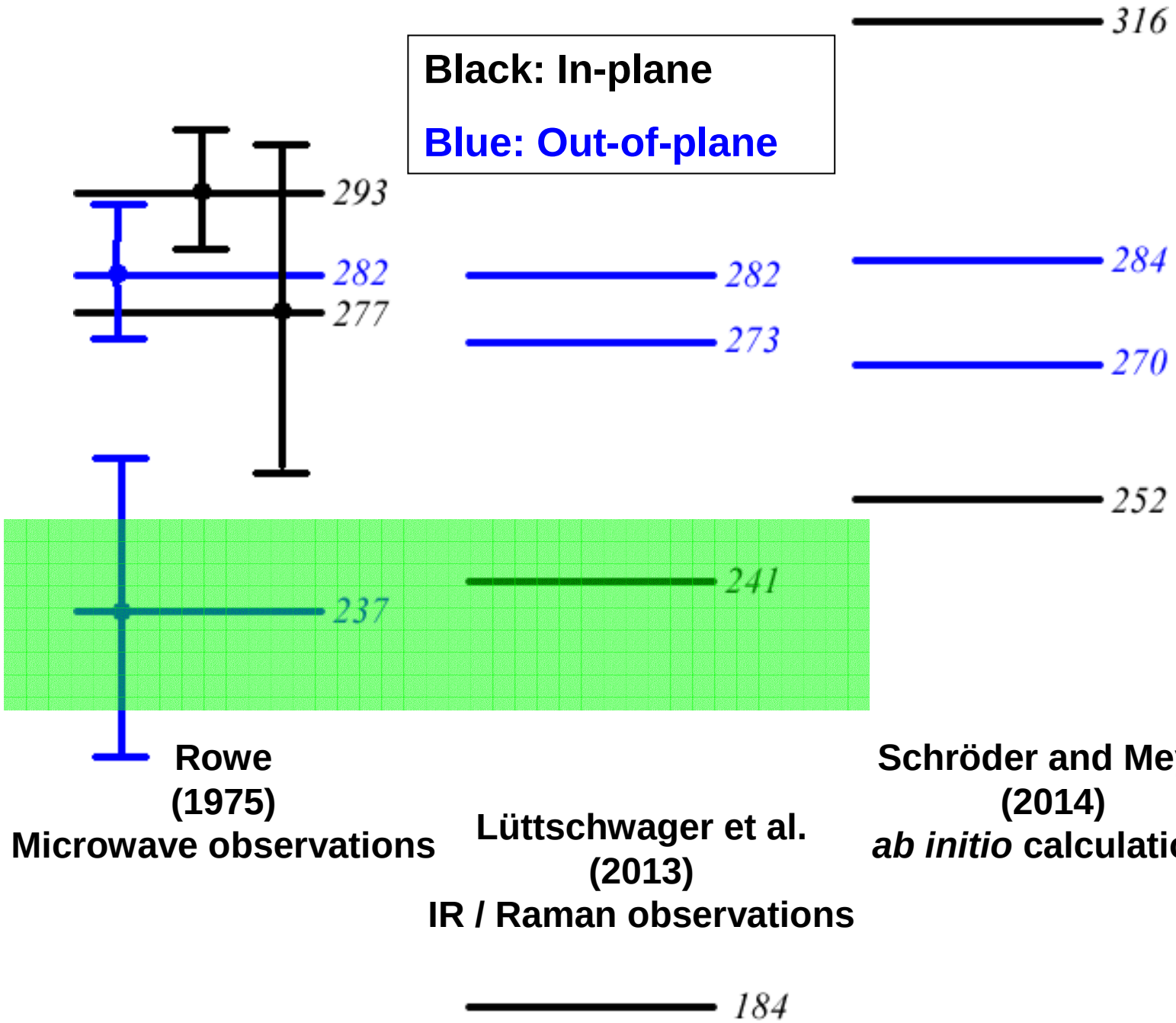


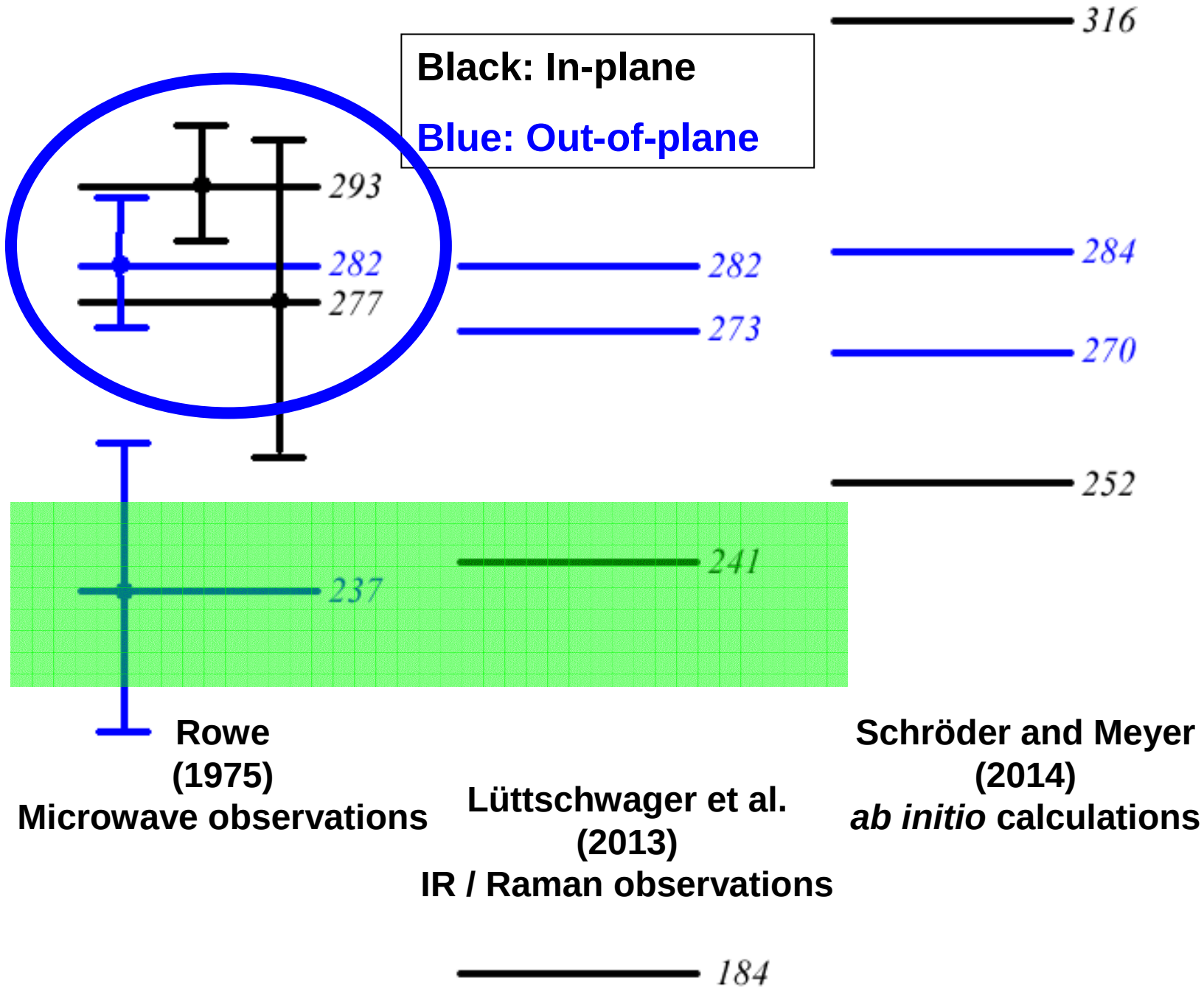
237 (Rowe Microwave) = 241 (IR)

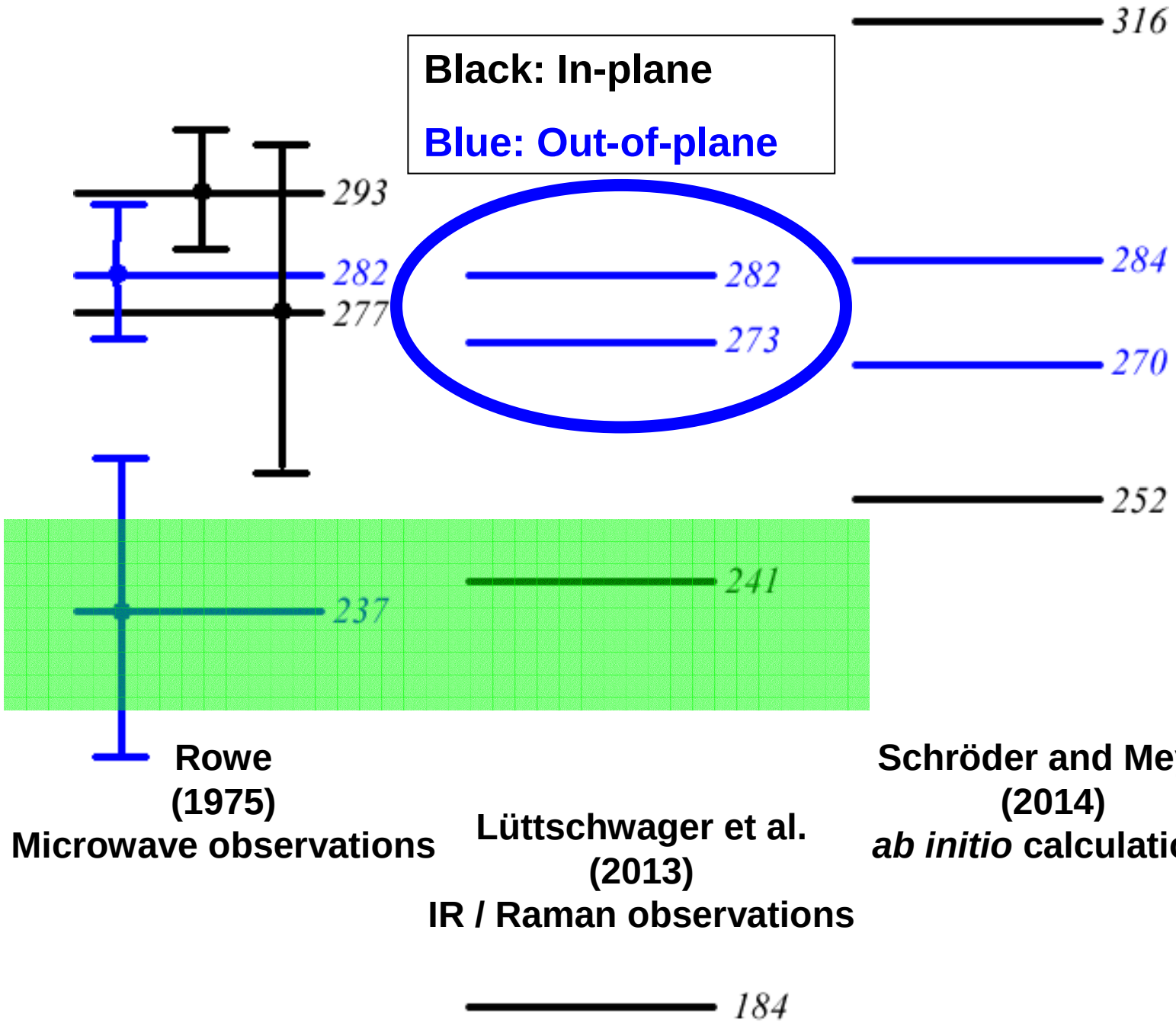
	Rowe 237 cm^{-1}	IR 241 cm^{-1}
A	9853.73 MHz	9853.76 MHz
B	5173.44 MHz	5173.45 MHz
C	3394.70 MHz	3394.75 MHz

Confirmed by:

- Matching upper state combination differences
- Similarity of constants
- Able to fit 241 cm^{-1} state with IR and Rowe microwave data together


Black: In-plane
Blue: Out-of-plane
316
293
282
277
282
273
284
270
252
241
237
184
Rowe
(1975)
Microwave observations
Lüttschwager et al.
(2013)
IR / Raman observations
Schröder and Meyer
(2014)
ab initio calculations

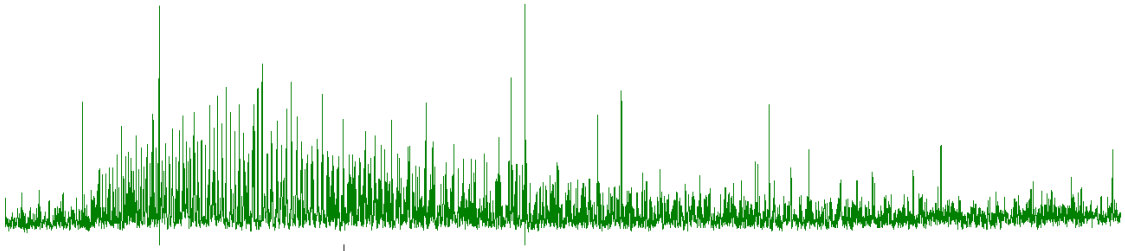

Black: In-plane
Blue: Out-of-plane
316
293
282
277
282
273
284
270
252
241
237
184
Rowe
(1975)
Microwave observations
Lüttschwager et al.
(2013)
IR / Raman observations
Schröder and Meyer
(2014)
ab initio calculations


Black: In-plane
Blue: Out-of-plane
316
293
282
277
282
273
284
270
252
241
237
184
Rowe
(1975)
Microwave observations
Lüttschwager et al.
(2013)
IR / Raman observations
Schröder and Meyer
(2014)
ab initio calculations

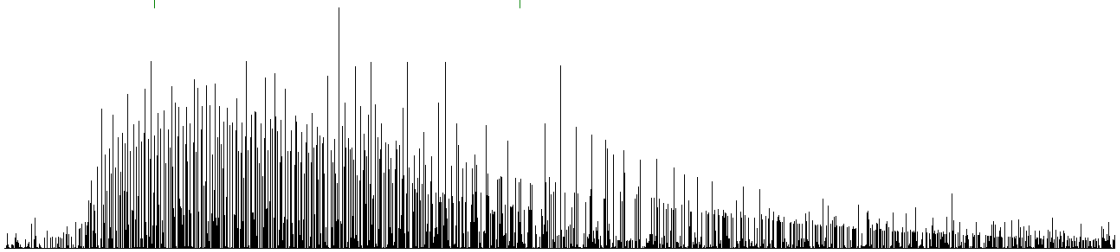
The 252 cm^{-1} band

Comparing to c-type simulated bands

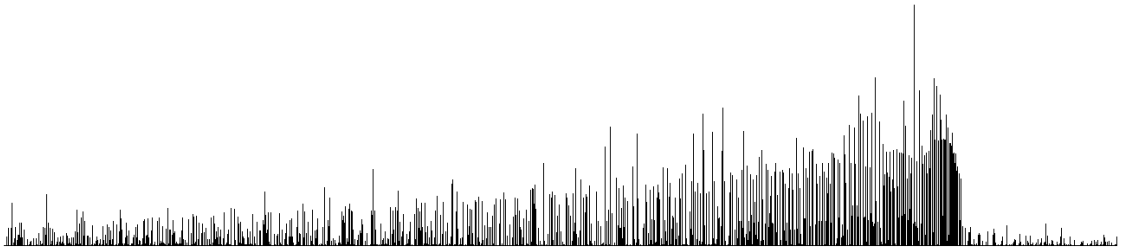
Q-branch of our experimental spectrum



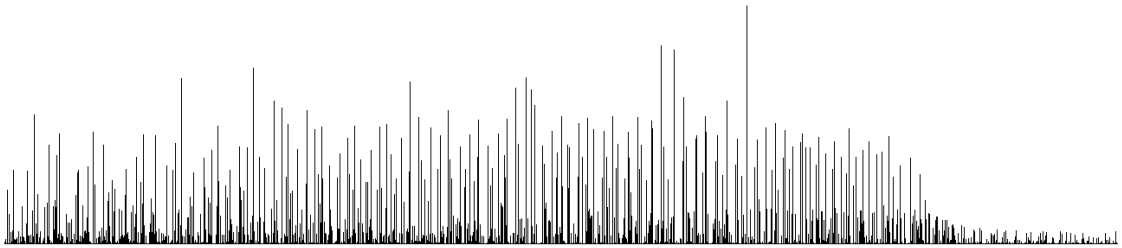
Simulated band from 21 cm^{-1} to Rowe's **277** cm^{-1} state



Simulated band from 21 cm^{-1} to Rowe's **282** cm^{-1} state



Simulated band from 21 cm^{-1} to Rowe's **293** cm^{-1} state



The 252 cm^{-1} band

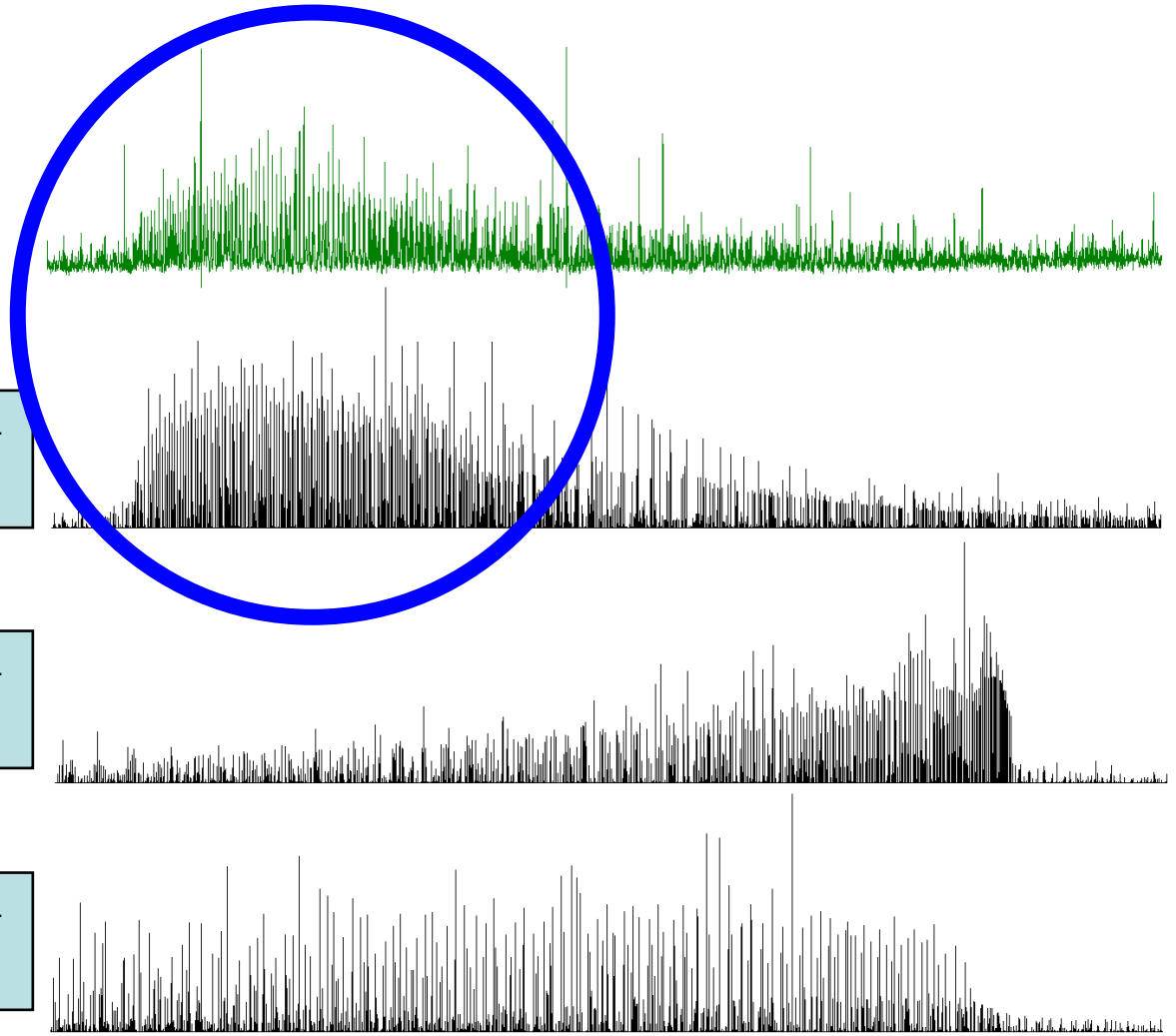
Comparing to c-type simulated bands

Q-branch of our experimental spectrum

Simulated band from 21 cm^{-1} to Rowe's **277** cm^{-1} state

Simulated band from 21 cm^{-1} to Rowe's **282** cm^{-1} state

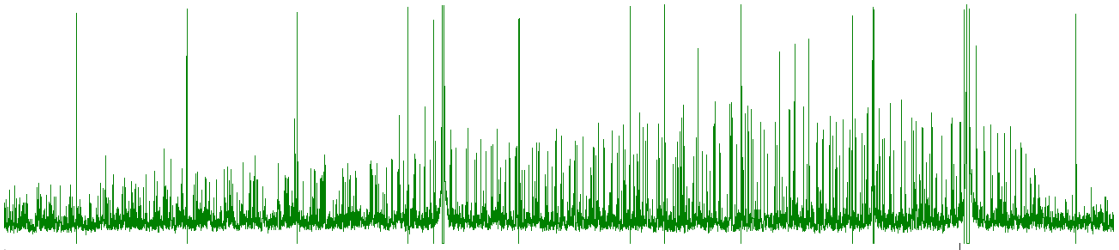
Simulated band from 21 cm^{-1} to Rowe's **293** cm^{-1} state



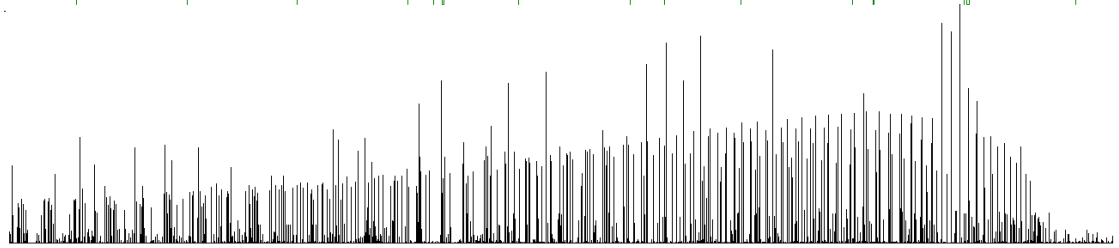
The 282 cm^{-1} state revisited

c-type band at 282 cm^{-1}

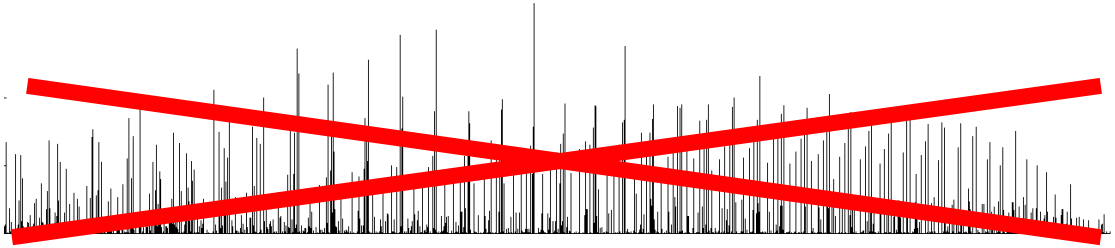
Q-branch of our experimental spectrum



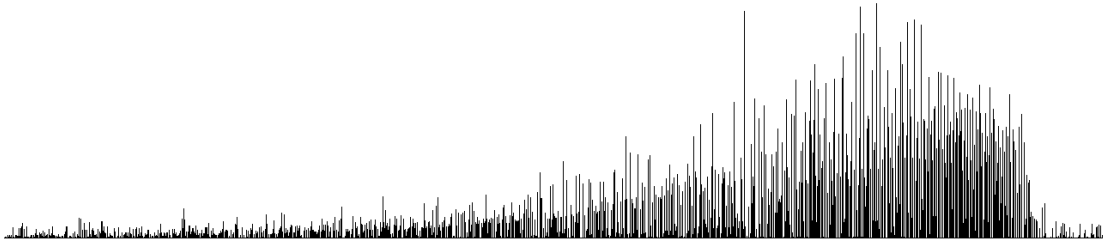
Simulated band from 0 cm^{-1} to Rowe's **282** cm^{-1} state



Simulated band from 0 cm^{-1} to Rowe's **277** cm^{-1} state



Simulated band from 0 cm^{-1} to Rowe's **293** cm^{-1} state



The 282 cm^{-1} state revisited

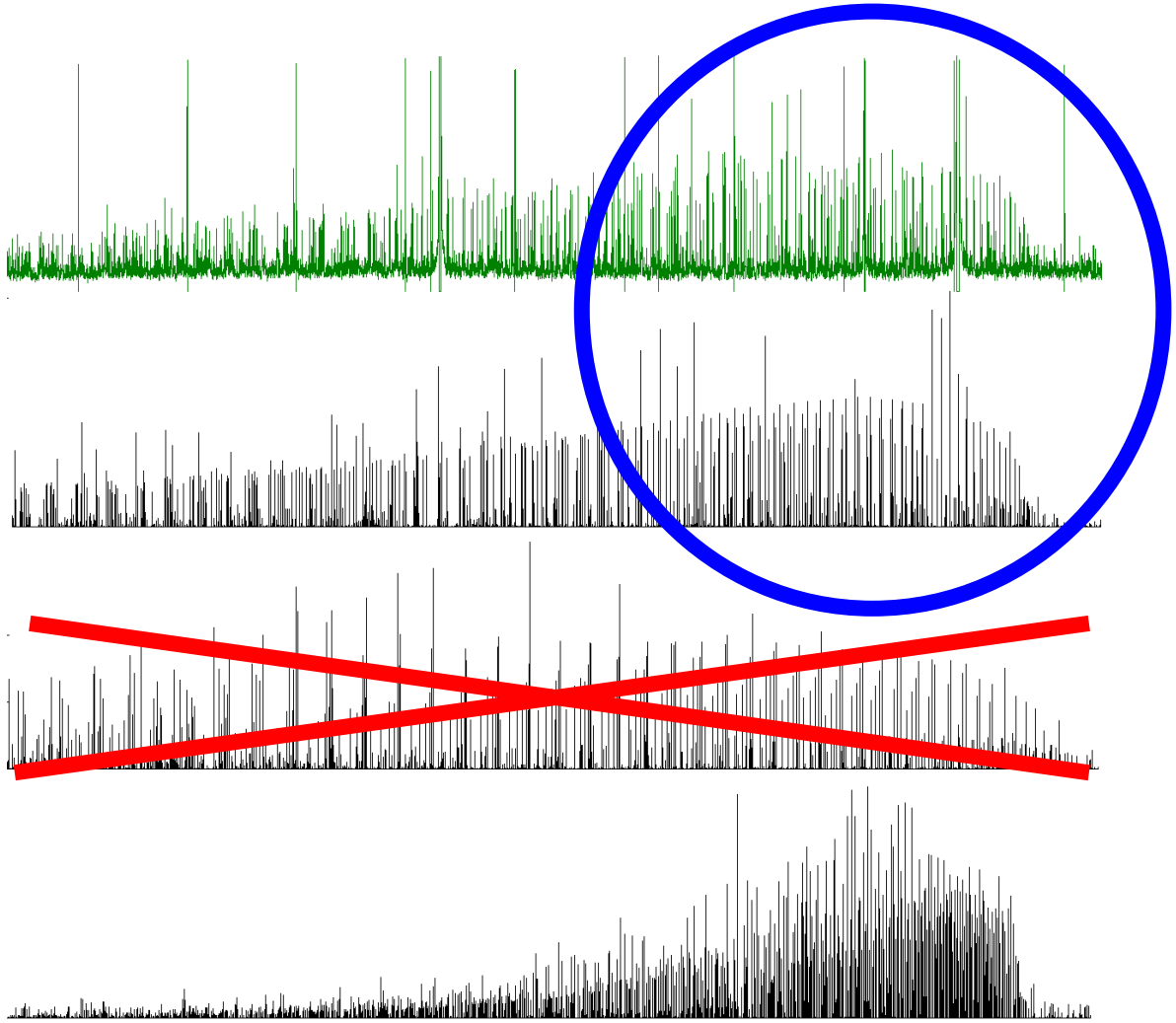
c-type band at 282 cm^{-1}

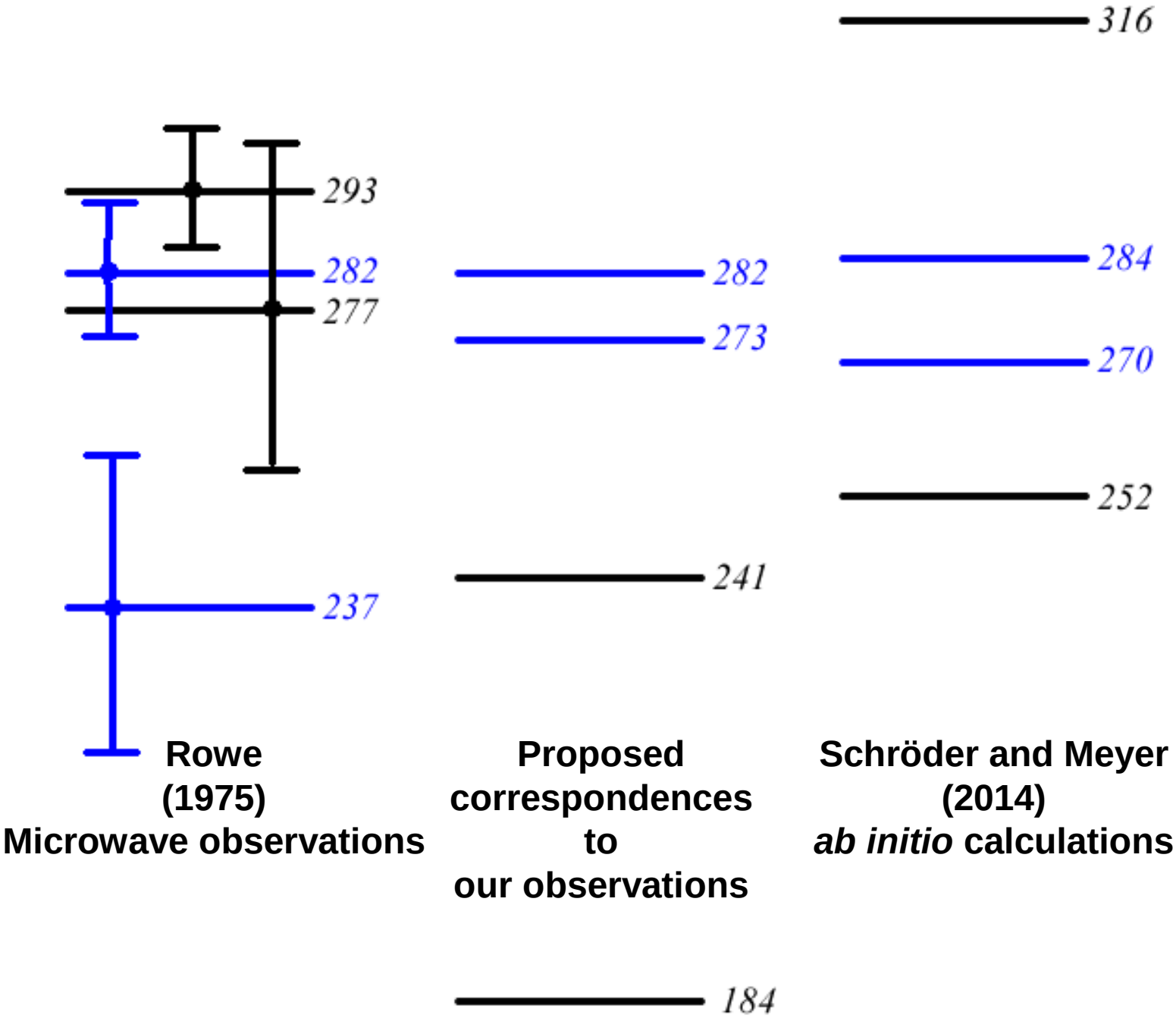
Q-branch of our experimental spectrum

Simulated band from 0 cm^{-1} to Rowe's **282** cm^{-1} state

Simulated band from 0 cm^{-1} to Rowe's **277** cm^{-1} state

Simulated band from 0 cm^{-1} to Rowe's **293** cm^{-1} state

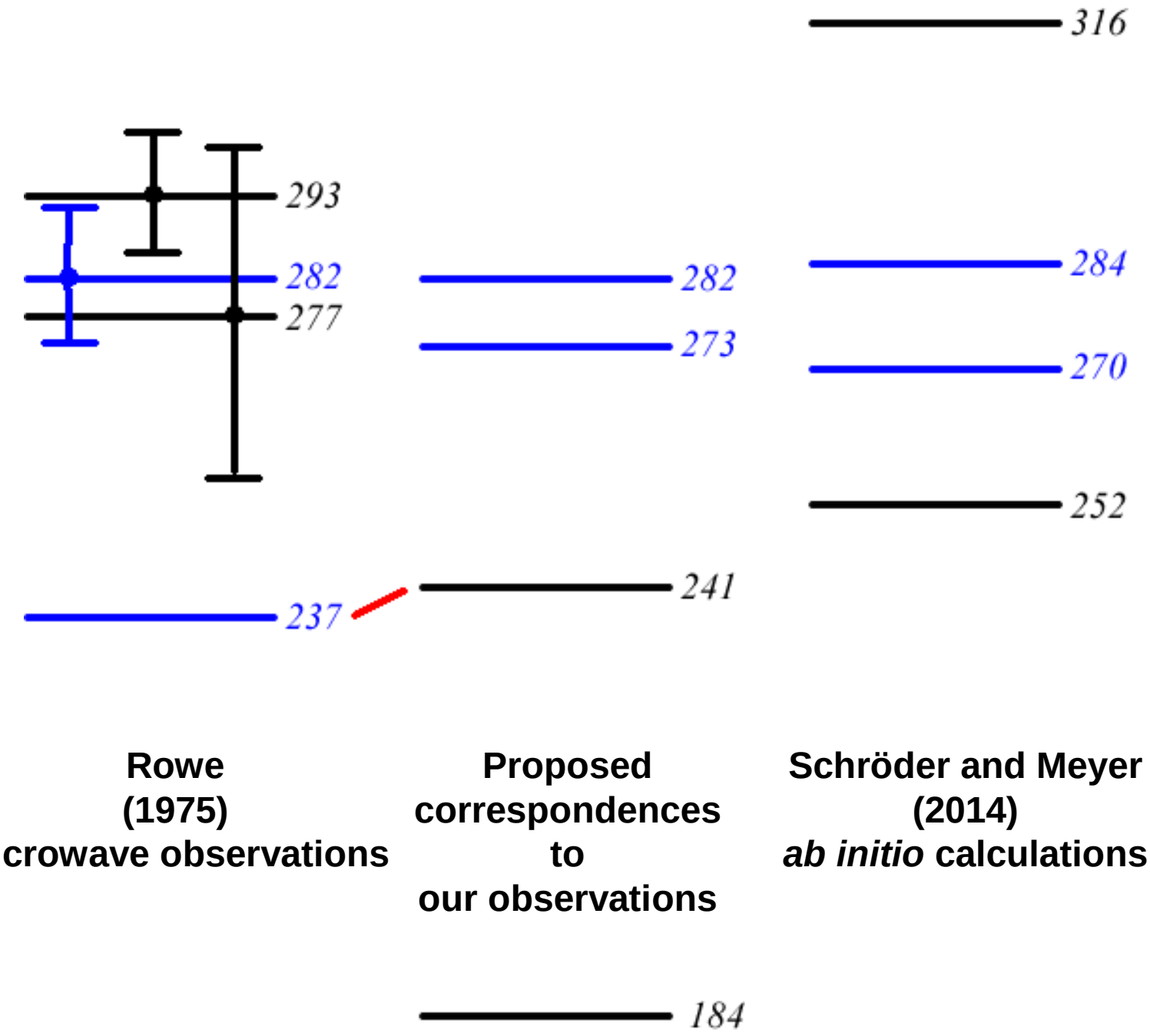




Rowe (1975) Microwave observations

Proposed correspondences to our observations

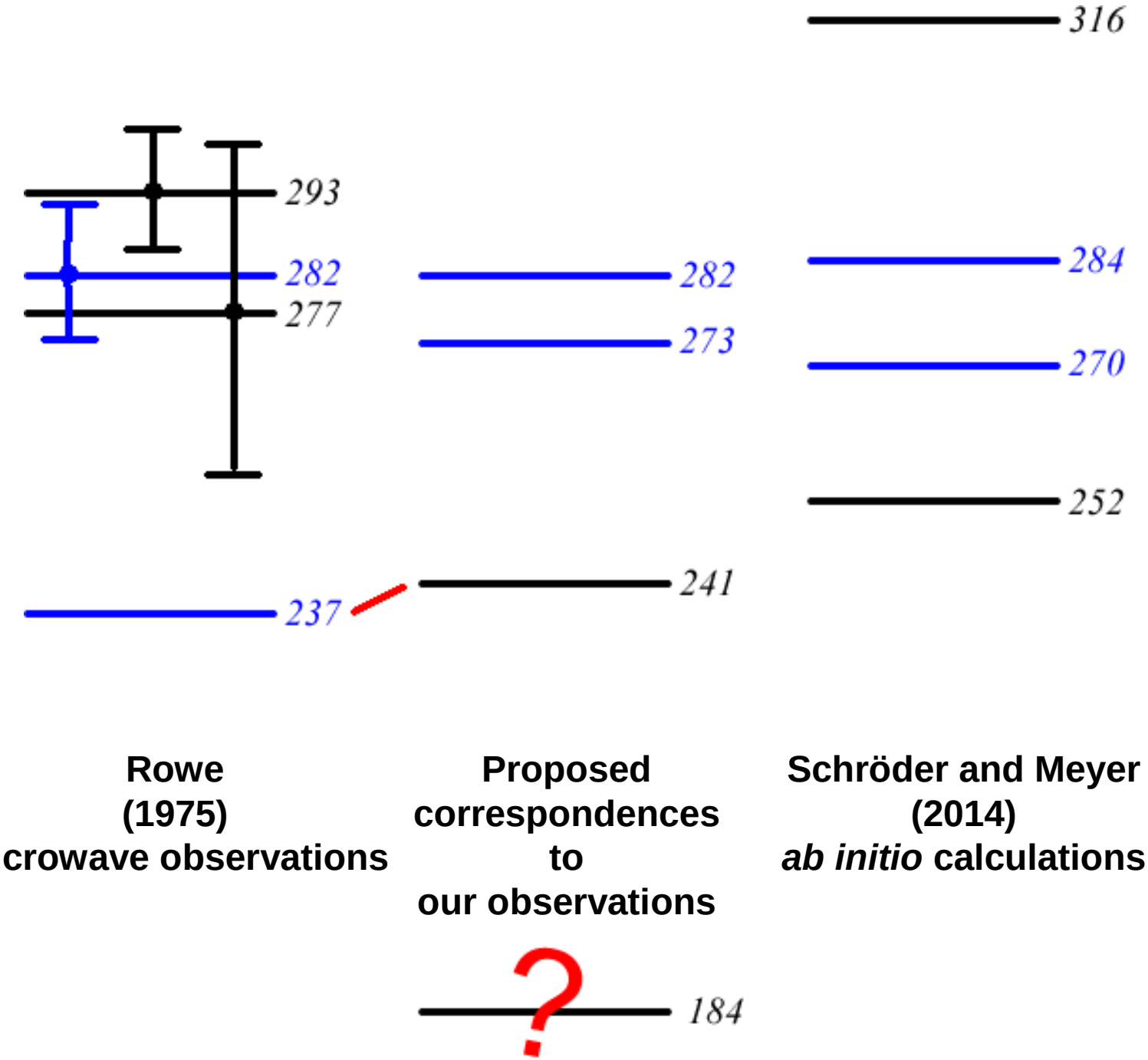
Schröder and Meyer (2014) *ab initio* calculations



Rowe (1975) Microwave observations

Proposed correspondences to our observations

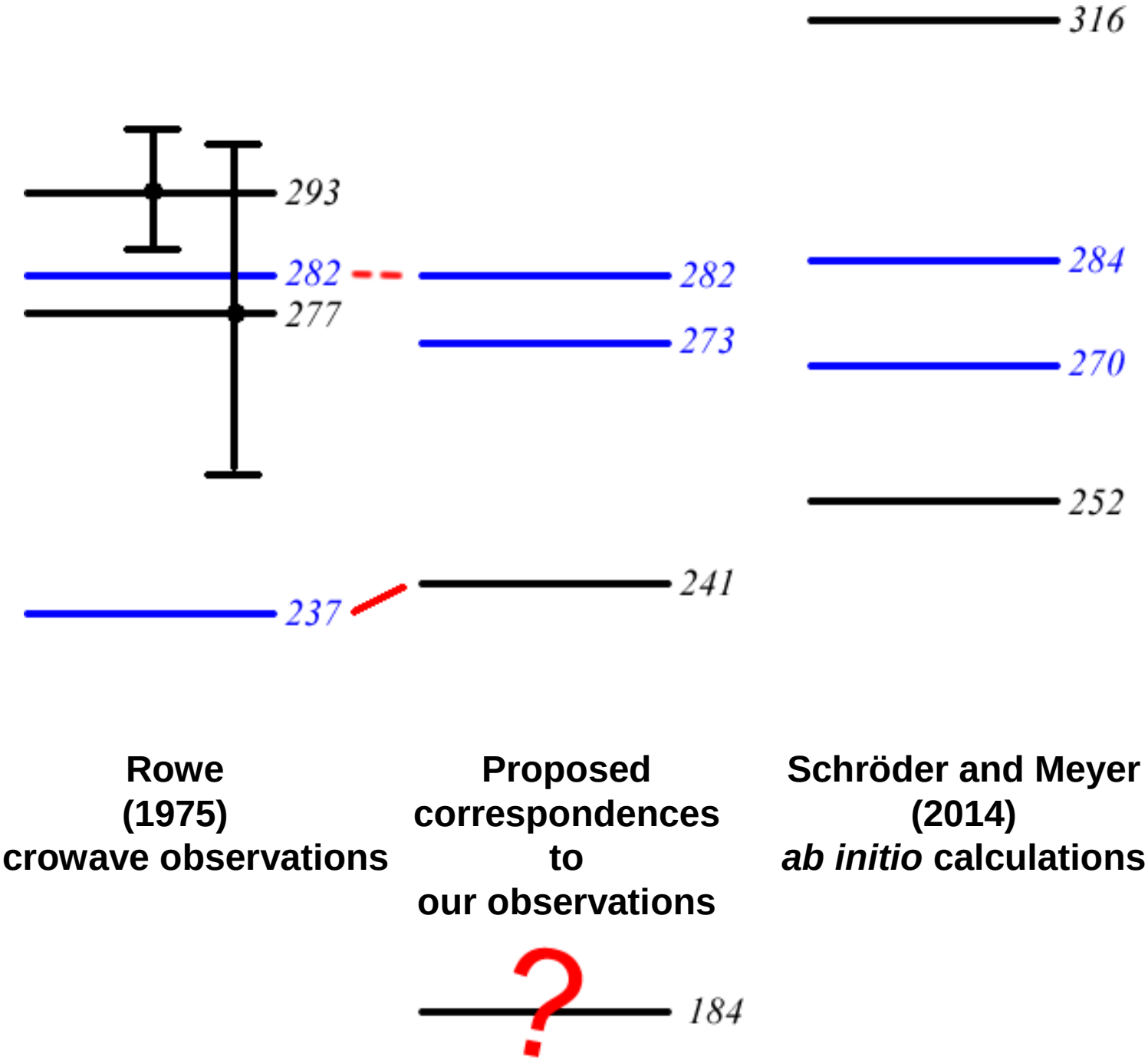
Schröder and Meyer (2014) *ab initio* calculations



Rowe (1975) Microwave observations

Proposed correspondences to our observations

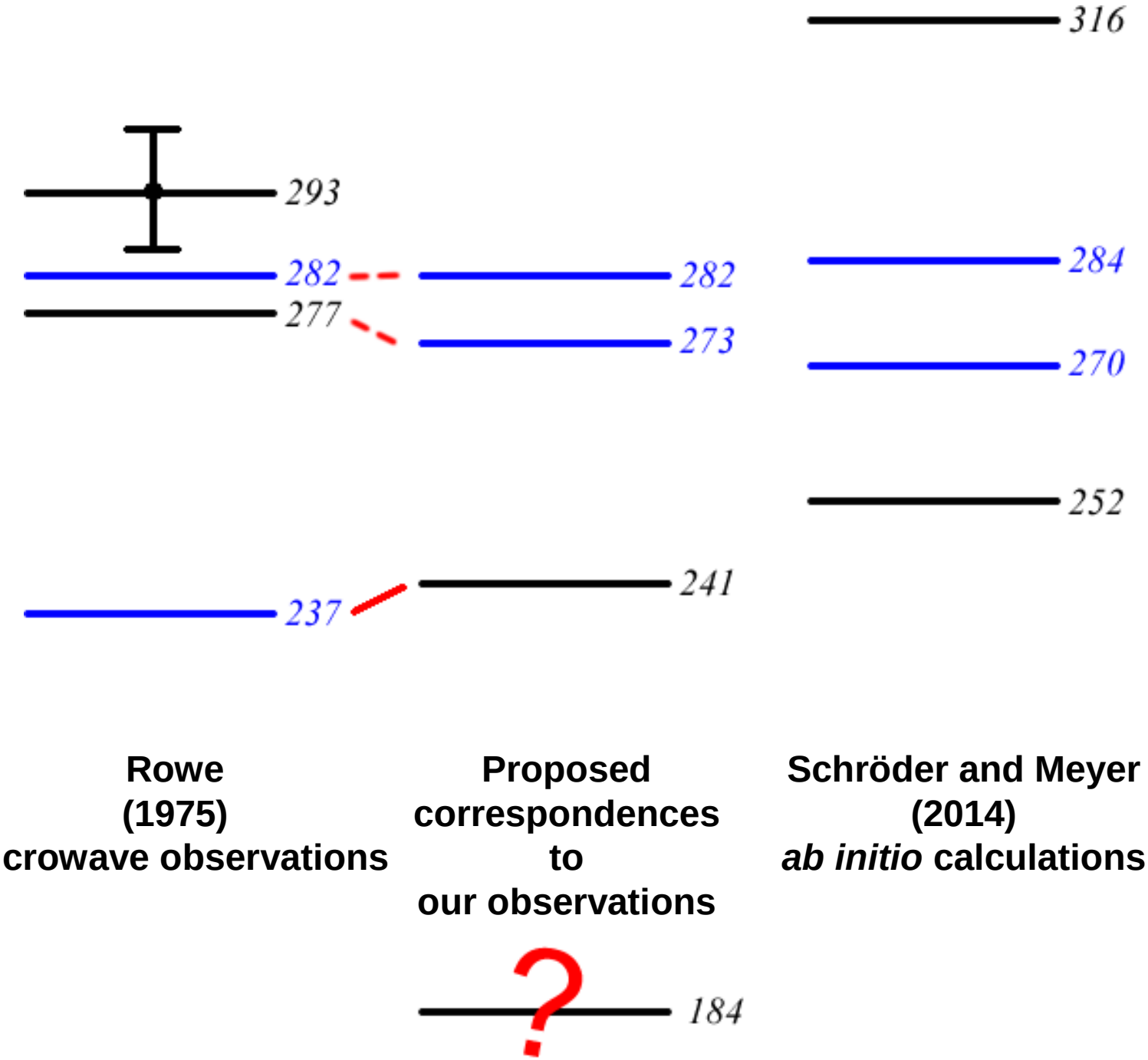
Schröder and Meyer (2014) *ab initio* calculations



Rowe (1975) Microwave observations

Proposed correspondences to our observations

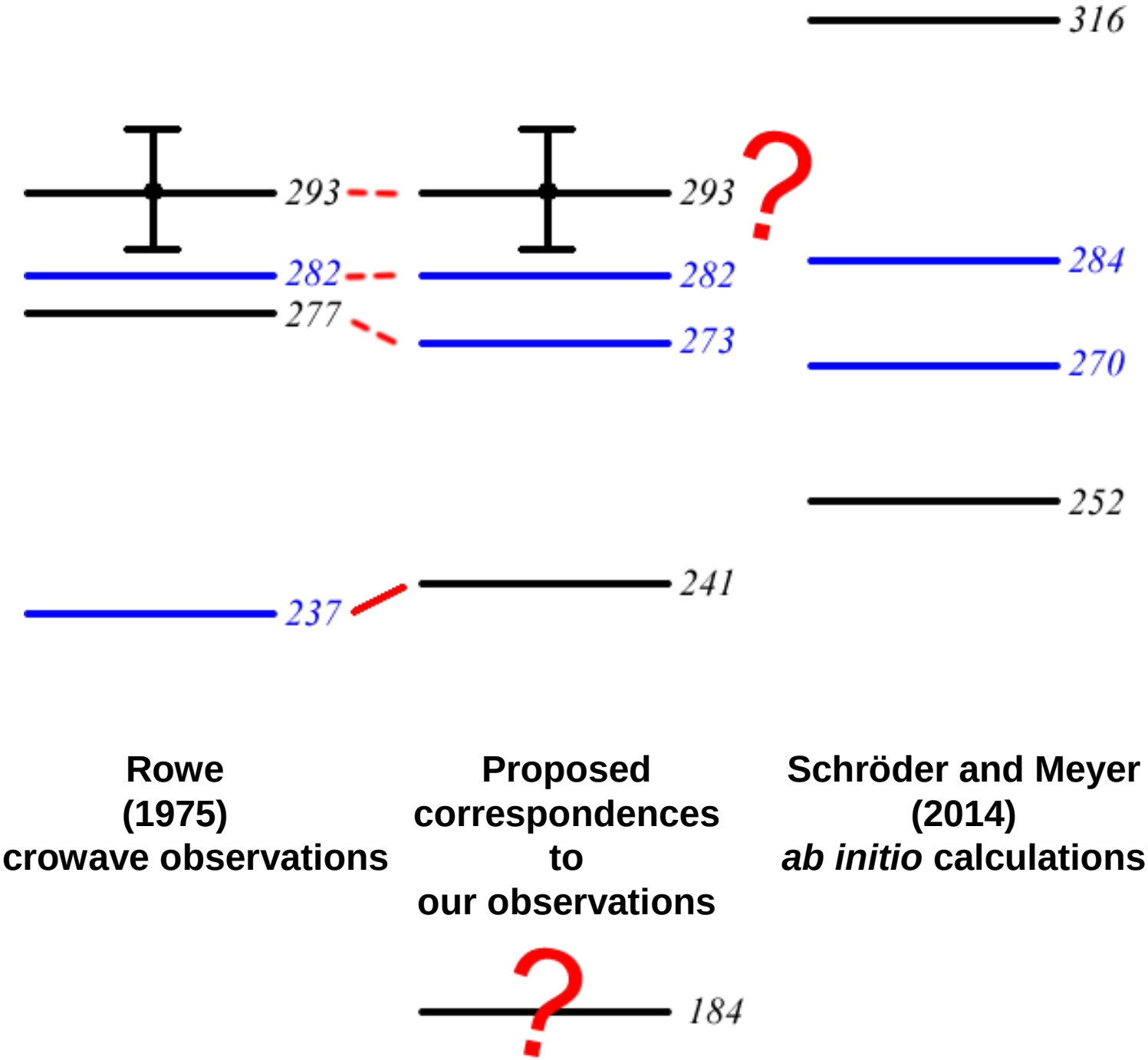
Schröder and Meyer (2014) *ab initio* calculations



Rowe (1975) Microwave observations

Proposed correspondences to our observations

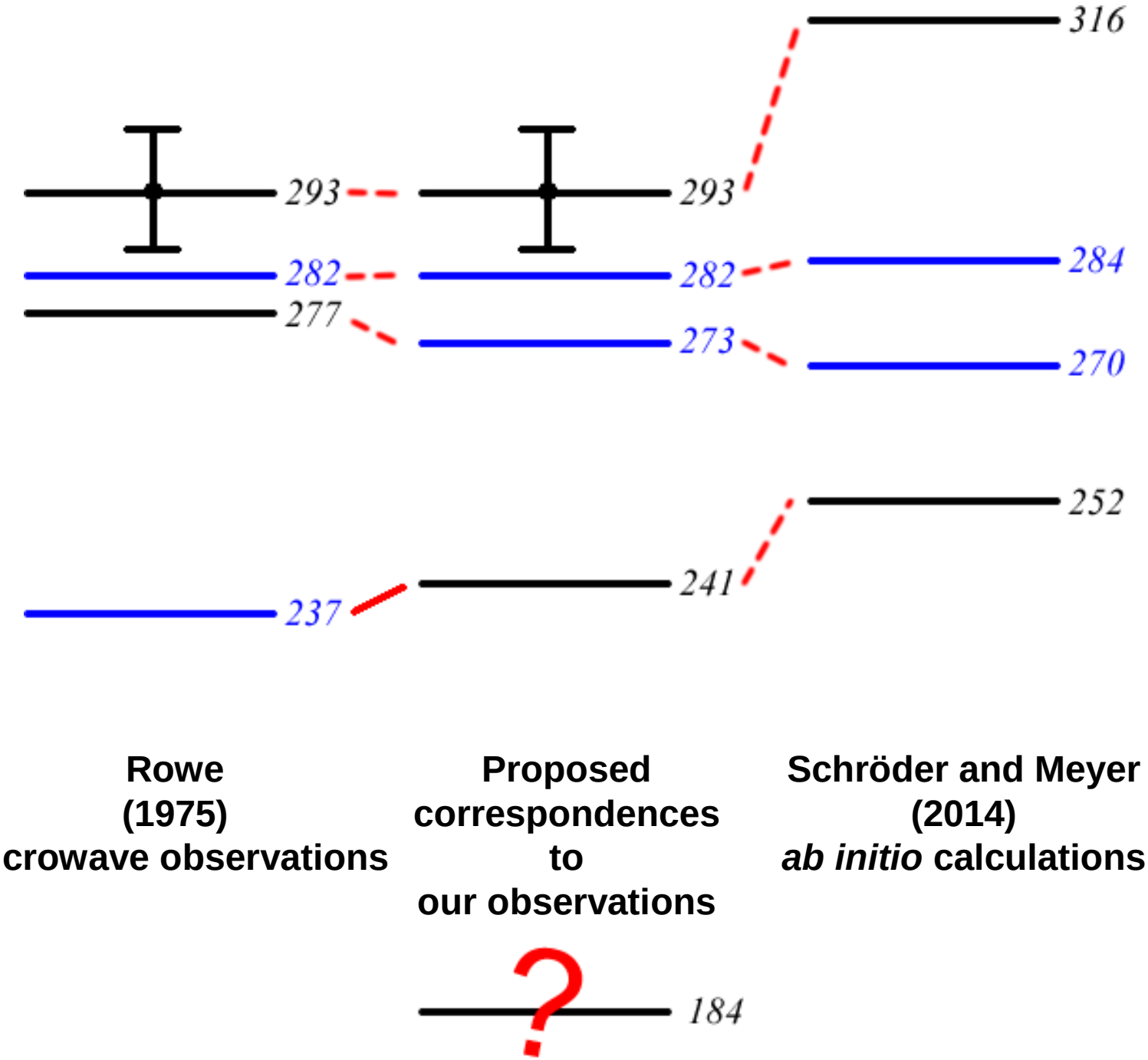
Schröder and Meyer (2014) *ab initio* calculations



Rowe (1975) Microwave observations

Proposed correspondences to our observations

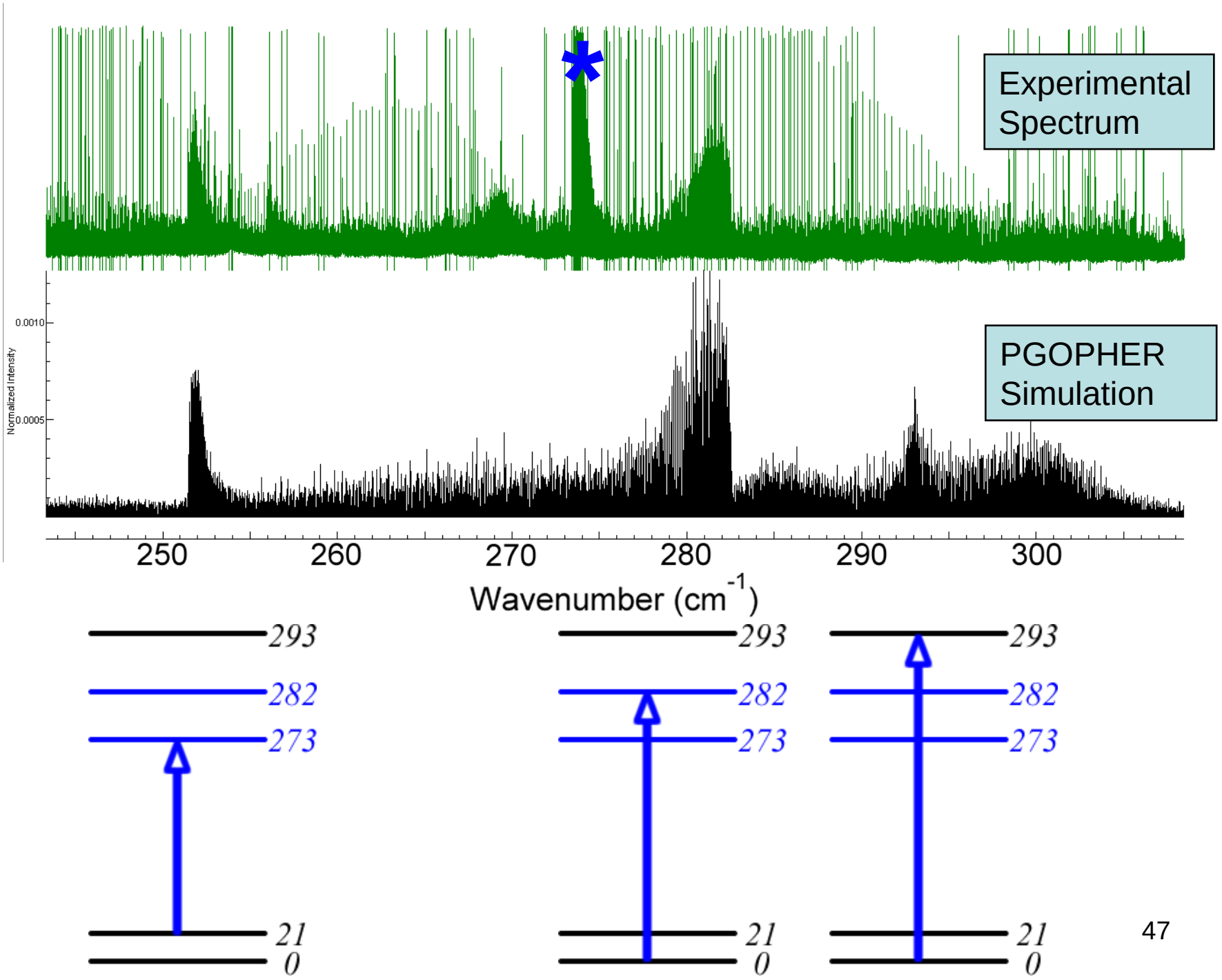
Schröder and Meyer (2014) *ab initio* calculations



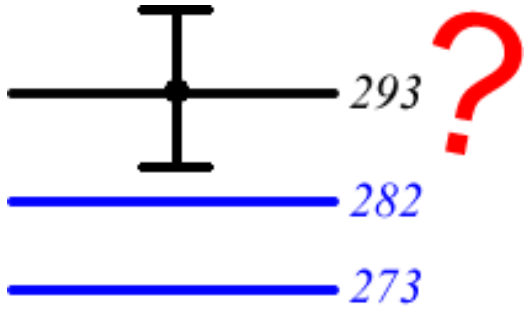
Rowe (1975) Microwave observations

Proposed correspondences to our observations

Schröder and Meyer (2014) *ab initio* calculations


Experimental Spectrum
PGOPHER Simulation
Normalized Intensity
0.0010
0.0005
250
260
270
280
290
300
Wavenumber (cm-1)
293
282
273
21
0
293
282
273
21
0
293
282
273
21
0

Conclusion



- Rowe's 40-year-old unpublished microwave observations from his 1975 thesis were extremely helpful in our analysis.

- Results:
  - vibrational assignments based on high-resolution synchrotron spectra (mostly) support Lüttschwager's assignments
  - rotational analysis of several bands
  - no evidence for a malonaldehyde fundamental at 184 cm^{-1}.

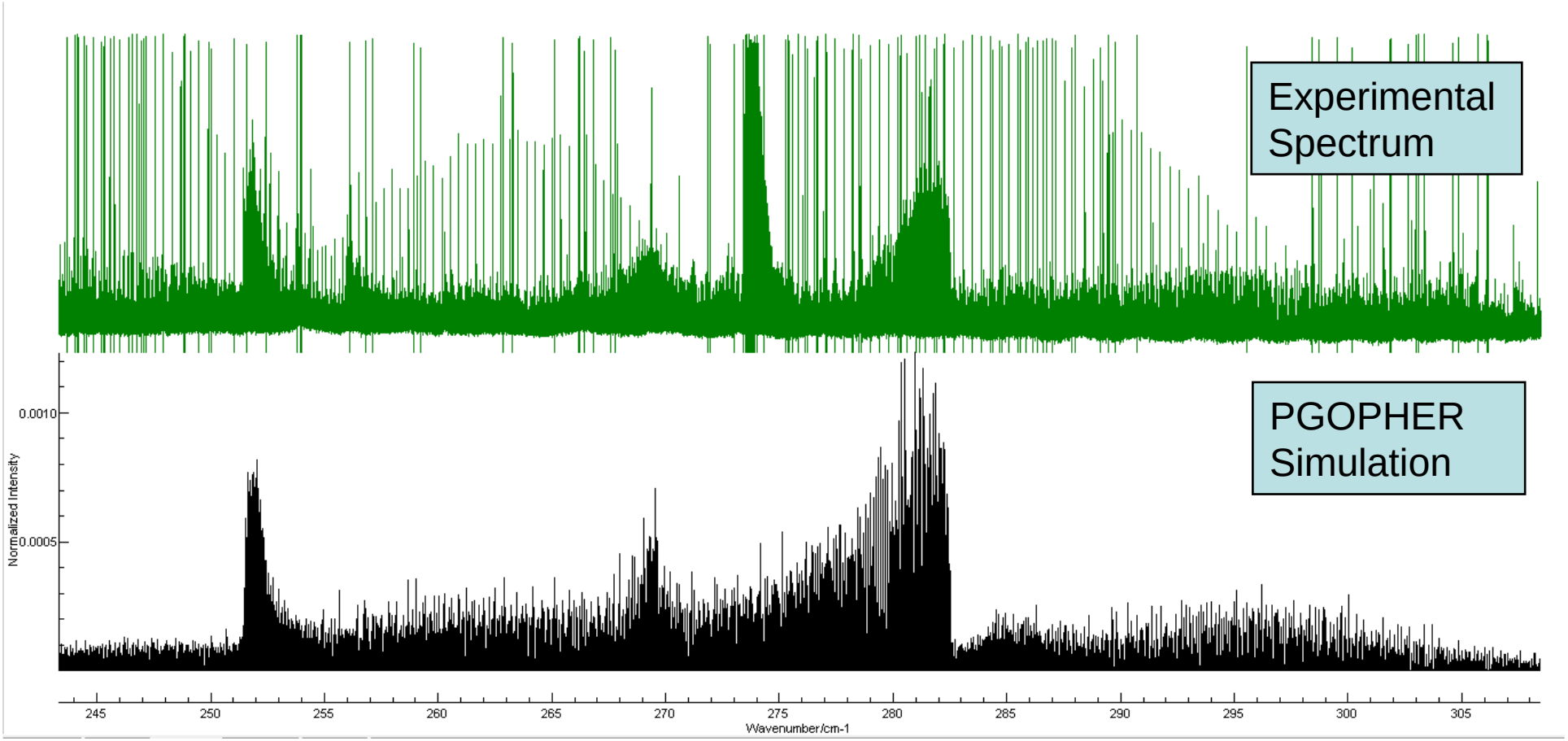
Acknowledgements

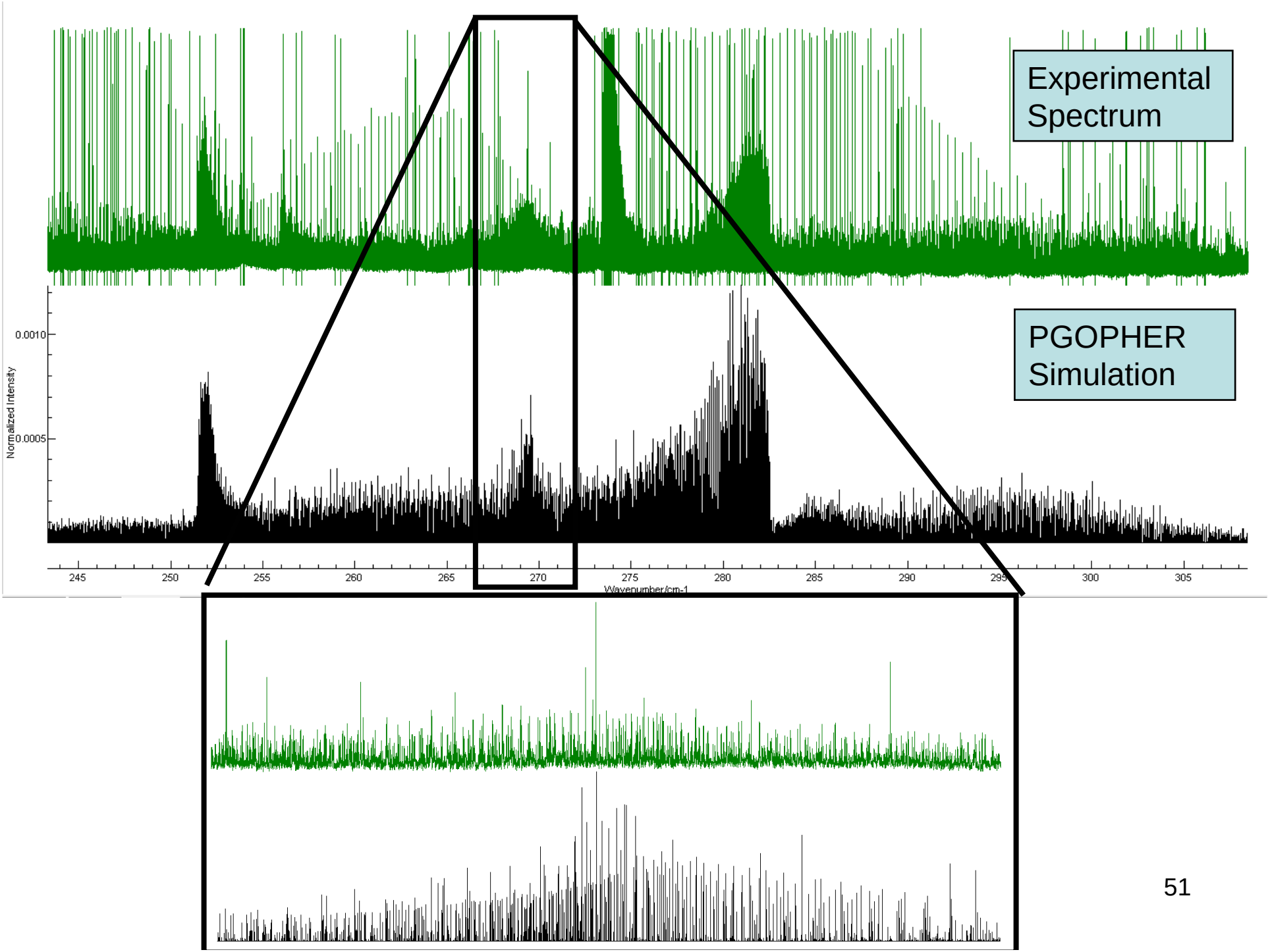
Dr. James Tait and Dr. David MaGee (UNB Chemistry)
– Malonaldehyde precursor synthesis

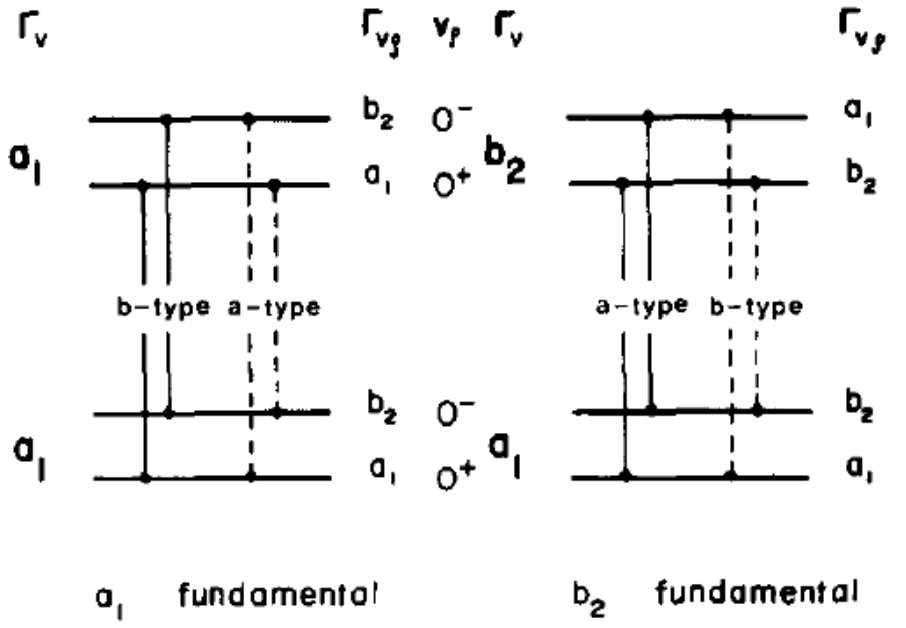
Dr. Colin Western (University of Bristol)
- PGOPHER program

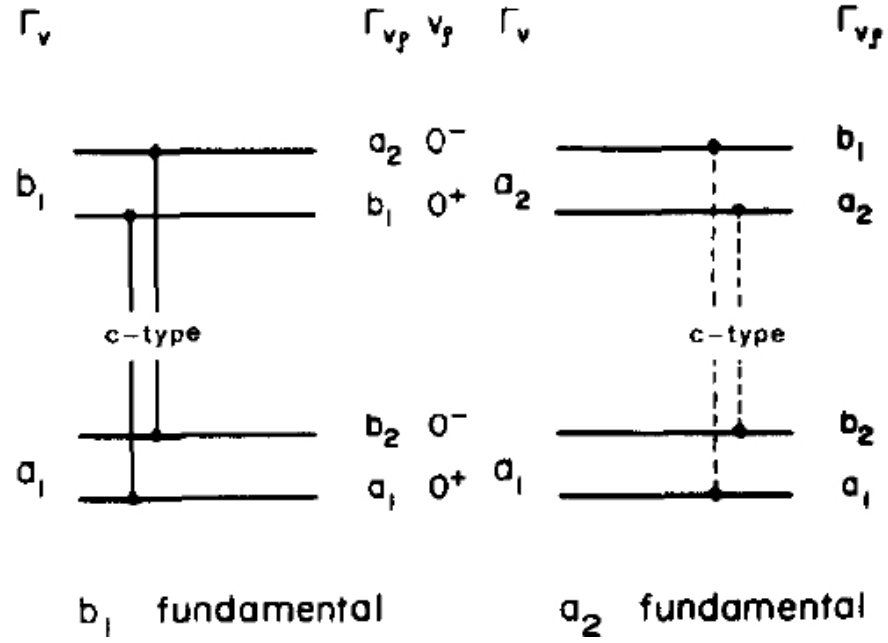
NSERC Discovery Grants (Tokaryk, Ross)

NSERC CGS-M award (Goudreau)


Experimental Spectrum
PGOPHER Simulation
Normalized Intensity
0.0010
0.0005
245
250
255
260
265
270
275
280
285
290
295
300
305
Wavenumber/cm-1


Experimental Spectrum
PGOPHER Simulation
Normalized Intensity
0.0010
0.0005
245
250
255
260
265
270
275
280
285
290
295
300
305
Wavenumber/cm-1





Seliskar and Hoffmann, J. Mol. Spectrosc., 1982