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

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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)
Lütt schwager et al. (2013)
IR / Raman observations
Lüttchschwager et al. (2013)
IR / Raman observations

Assignment #1  Assignment #2
Lüttschwager et al. (2013)  
IR / Raman observations  
Assignment #1  Assignment #2  
Schröder and Meyer (2014)  
*ab initio* calculations
Lüttchwager et al. (2013)
IR / Raman observations

Assignment #1

Assignment #2

Schröder and Meyer (2014)
*ab initio* calculations
Lüttswager et al. (2013)
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Assignment #1

Schröder and Meyer
(2014)

ab initio calculations

Assignment #2
Lüttswager et al. (2013)
IR / Raman observations

Assignment #1

Schröder and Meyer (2014)
\textit{ab initio} calculations

Assignment #2
The Two Lowest-Frequency Modes

• $\nu \text{O} \cdots \text{O}$
  In-plane ring opening/closing mode
  - Increases tunnelling-splitting

• $\gamma \text{C}_c\text{H}$
  Out-of-plane bending mode
  - Reduces tunnelling-splitting

Lüttschwager et al.
Molecular Physics, 2013
Canadian Light Source Synchrotron

Our CLS Malonaldehyde Spectrum

- Features corresponding to all of Lüttswager’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\(^{-1}\)
Lüttswager et al. (2013)  
IR / Raman observations

Assignment #1  Assignment #2

Schröder and Meyer  
(2014)  
*ab initio* calculations

21.6  21.6  22.4
Lüttswager 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
Lüttchwager et al. (2013)
IR / Raman observations

Assignment #1

Schröder and Meyer (2014)
ab initio calculations

Assignment #2
Lüttswager 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
Lütschwager et al. (2013)
IR / Raman observations

Schröder and Meyer (2014)
*ab initio* calculations

Assignment #1
Assignment #2
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

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Frequency (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-plane</td>
<td>0</td>
</tr>
<tr>
<td>In-plane</td>
<td>16 ± 14</td>
</tr>
<tr>
<td>In-plane</td>
<td>277 ± 22</td>
</tr>
<tr>
<td>In-plane</td>
<td>293 ± 8</td>
</tr>
<tr>
<td>Out-of-plane</td>
<td>237 ± 20</td>
</tr>
<tr>
<td>Out-of-plane</td>
<td>282 ± 9</td>
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<tr>
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Rowe does not observe a state near 184 cm⁻¹
Lüttswager et al. (2013) IR / Raman observations

Schröder and Meyer (2014) ab initio calculations
Rowe (1975) Microwave observations
Lüttswager et al. (2013) IR / Raman observations
Schröder and Meyer (2014) \textit{ab initio} calculations
Rowe (1975) 
Microwave observations

Lüttchwager et al. (2013) 
IR / Raman observations

Schröder and Meyer (2014) 
\textit{ab initio} calculations
The 390/405 cm\(^{-1}\) Tunnelling Pair (out-of-plane)
c-type bands at 384/390 cm\(^{-1}\)

\[
\begin{align*}
390 \text{ (Rowe Microwave)} &= 405 \text{ (IR)} \\
393 \text{ (Rowe Microwave)} &= 390 \text{ (IR)}
\end{align*}
\]

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

<table>
<thead>
<tr>
<th></th>
<th>Rowe 390 cm(^{-1})</th>
<th>IR 405 cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>9832.76 MHz</td>
<td>9832.79 MHz</td>
</tr>
<tr>
<td>B</td>
<td>5169.44 MHz</td>
<td>5169.27 MHz</td>
</tr>
<tr>
<td>C</td>
<td>3390.49 MHz</td>
<td>3390.36 MHz</td>
</tr>
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<th>IR 390 cm(^{-1})</th>
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<tbody>
<tr>
<td>A</td>
<td>9825.55 MHz</td>
<td>9825.66 MHz</td>
</tr>
<tr>
<td>B</td>
<td>5204.75 MHz</td>
<td>5205.46 MHz</td>
</tr>
<tr>
<td>C</td>
<td>3403.85 MHz</td>
<td>3402.97 MHz</td>
</tr>
</tbody>
</table>
ISMS 2016
Schröder and Meyer (2014)

*ab initio* calculations

Lüttschwager et al. (2013)

IR / Raman observations

Rowe (1975)
Microwave observations

Black: In-plane
Blue: Out-of-plane

316

293
282
277
237

30

282
273
252

284
270

184
Black: In-plane

Blue: Out-of-plane

Rowe (1975) Microwave observations
Lüttchwager et al. (2013) IR / Raman observations
Schröder and Meyer (2014) ab initio calculations

184

316

293

282

277

284

273

270

252

237

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

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

237 (Rowe Microwave) = 241 (IR)

<table>
<thead>
<tr>
<th></th>
<th>Rowe 237 cm(^{-1})</th>
<th>IR 241 cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>9853.73 MHz</td>
<td>9853.76 MHz</td>
</tr>
<tr>
<td>B</td>
<td>5173.44 MHz</td>
<td>5173.45 MHz</td>
</tr>
<tr>
<td>C</td>
<td>3394.70 MHz</td>
<td>3394.75 MHz</td>
</tr>
</tbody>
</table>

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

Rowe (1975) Microwave observations
Lütschwager et al. (2013) IR / Raman observations
Schröder and Meyer (2014) \textit{ab initio} calculations
Black: In-plane
Blue: Out-of-plane

Rowe (1975) Microwave observations
Lüttswager et al. (2013) IR / Raman observations
Schröder and Meyer (2014) ab initio calculations

293 282 277
237 241

316 284 270 252

184
ISMS 2016

Black: In-plane
Blue: Out-of-plane

Schröder and Meyer (2014) ab initio calculations
Lüttswager et al. (2013) IR / Raman observations
Rowe (1975) Microwave observations

IR / Raman observations
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 \textit{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
Proposed correspondences to our observations

Schröder and Meyer (2014) ab initio calculations

Rowe (1975) Microwave observations
Proposed correspondences to our observations

Rowe (1975) Microwave observations

Schröder and Meyer (2014) *ab initio* calculations
Proposed correspondences to our observations

Rowe (1975) Microwave observations

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Schröder and Meyer (2014) \textit{ab initio} calculations

Rowe (1975) Microwave observations
Proposed correspondences to our observations

? 184
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

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