Rotation-vibration spectra of malonaldehyde obtained with far-infrared synchrotron radiation

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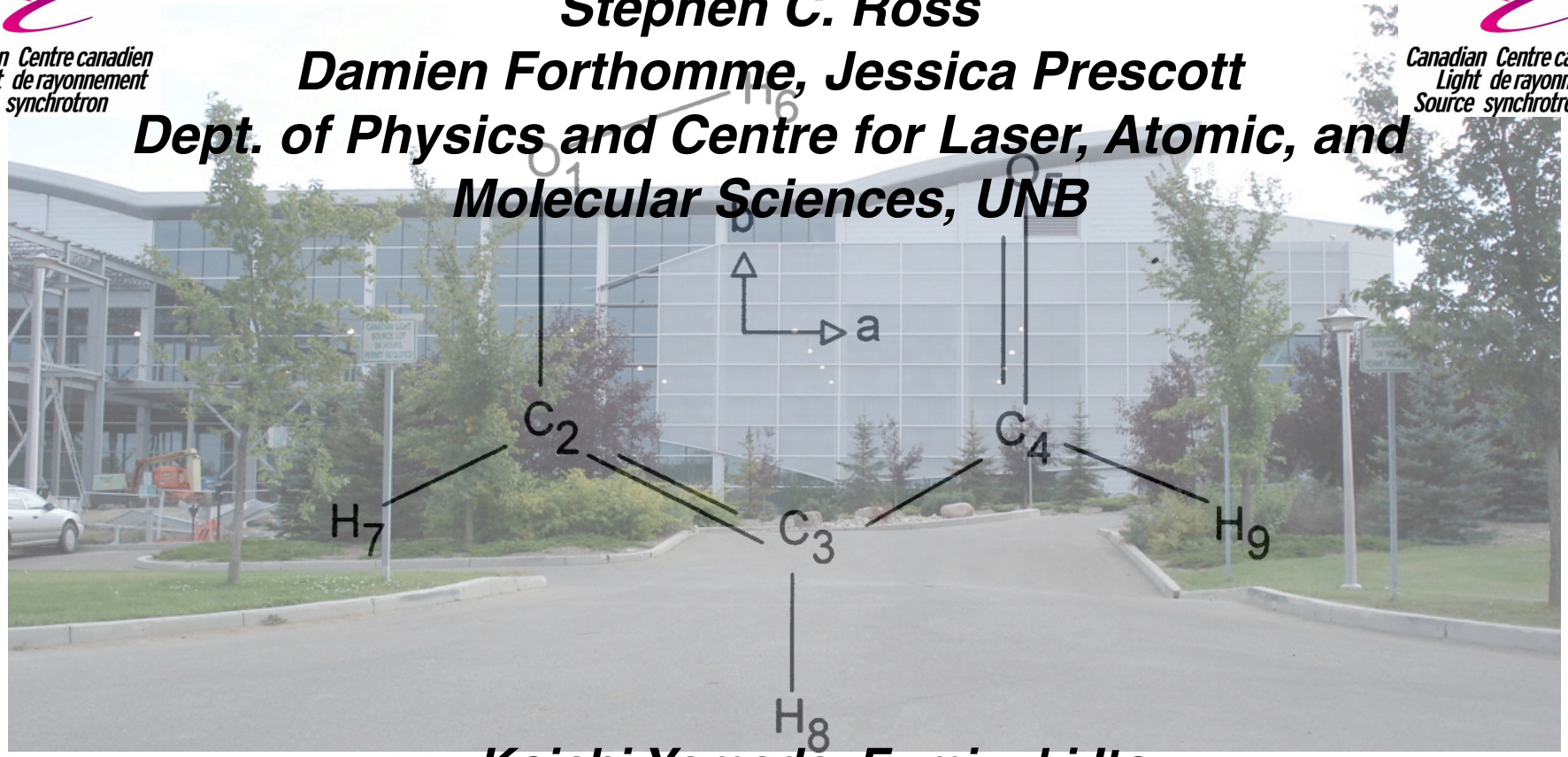
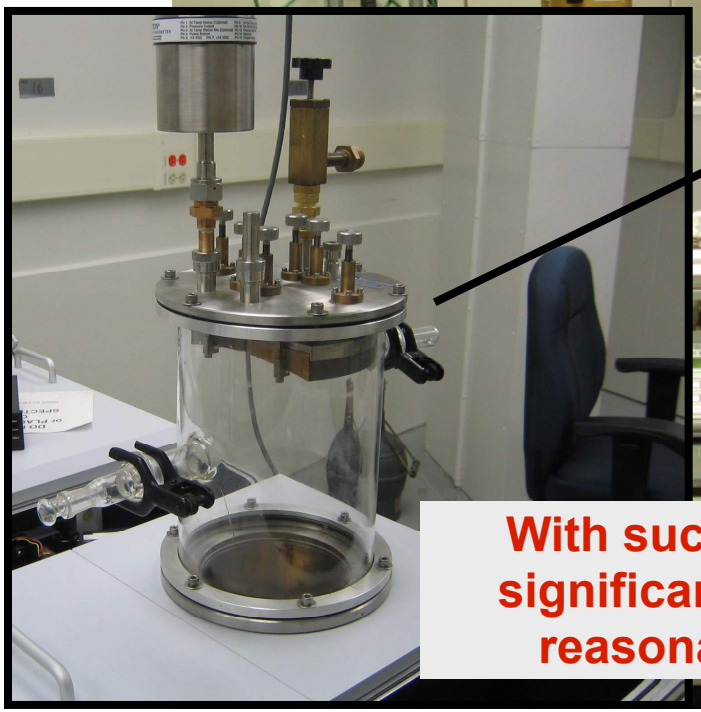


Koichi Yamada, Fumiyuki Ito

EMTech, Tsukuba, Japan

66th OSU International Symposium on Molecular Spectroscopy 2011

Bruker IFS 125HR high-resolution Fourier transform spectrometer
- 10 m path difference
- resolution of 0.001 cm^{-1}



With successive improvements, the synchrotron now has a significant advantage over the globar from 350 ~ 800 cm^{-1}, and reasonable advantage over the Hg lamp from 150-350 cm^{-1}.

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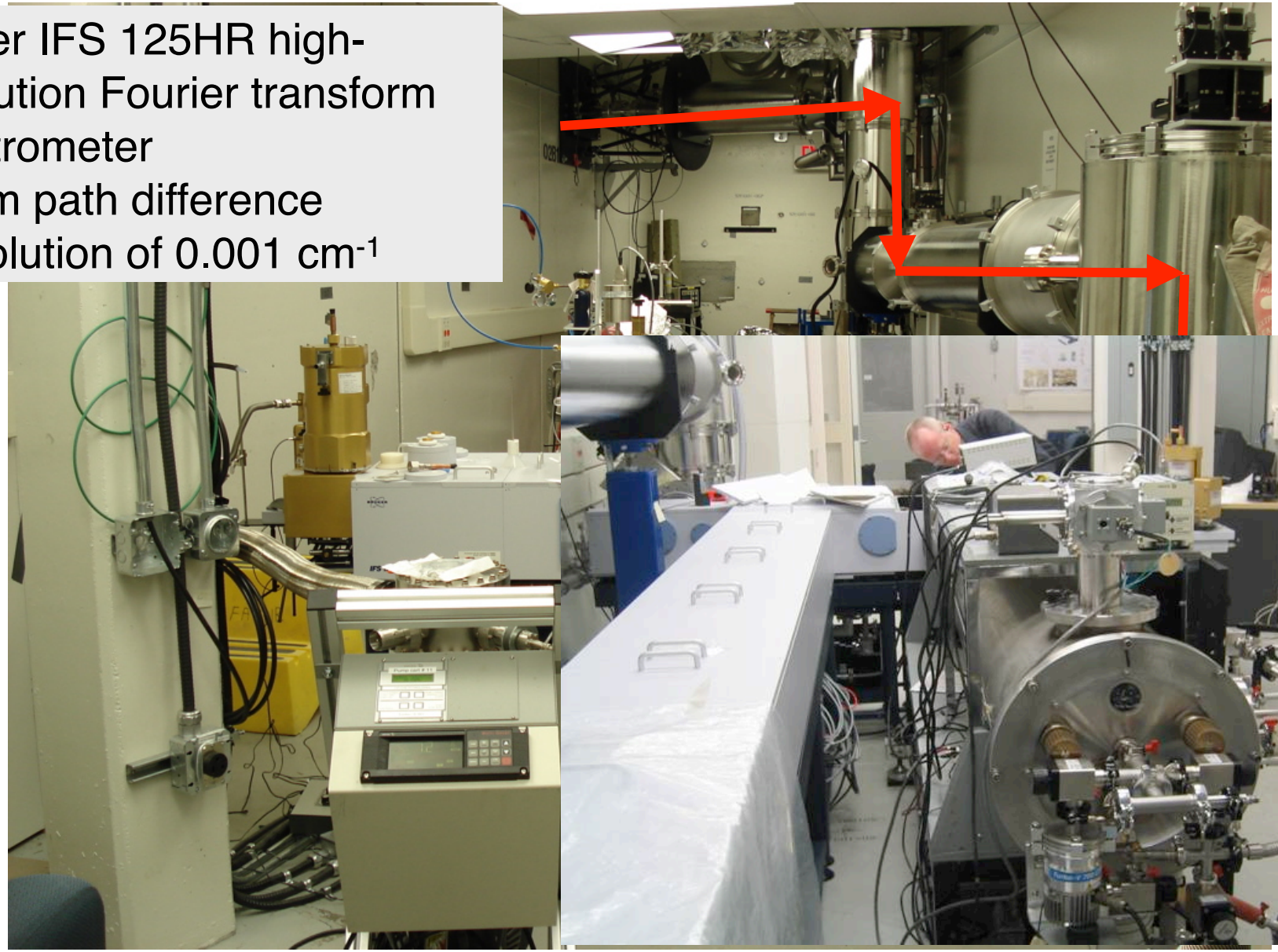
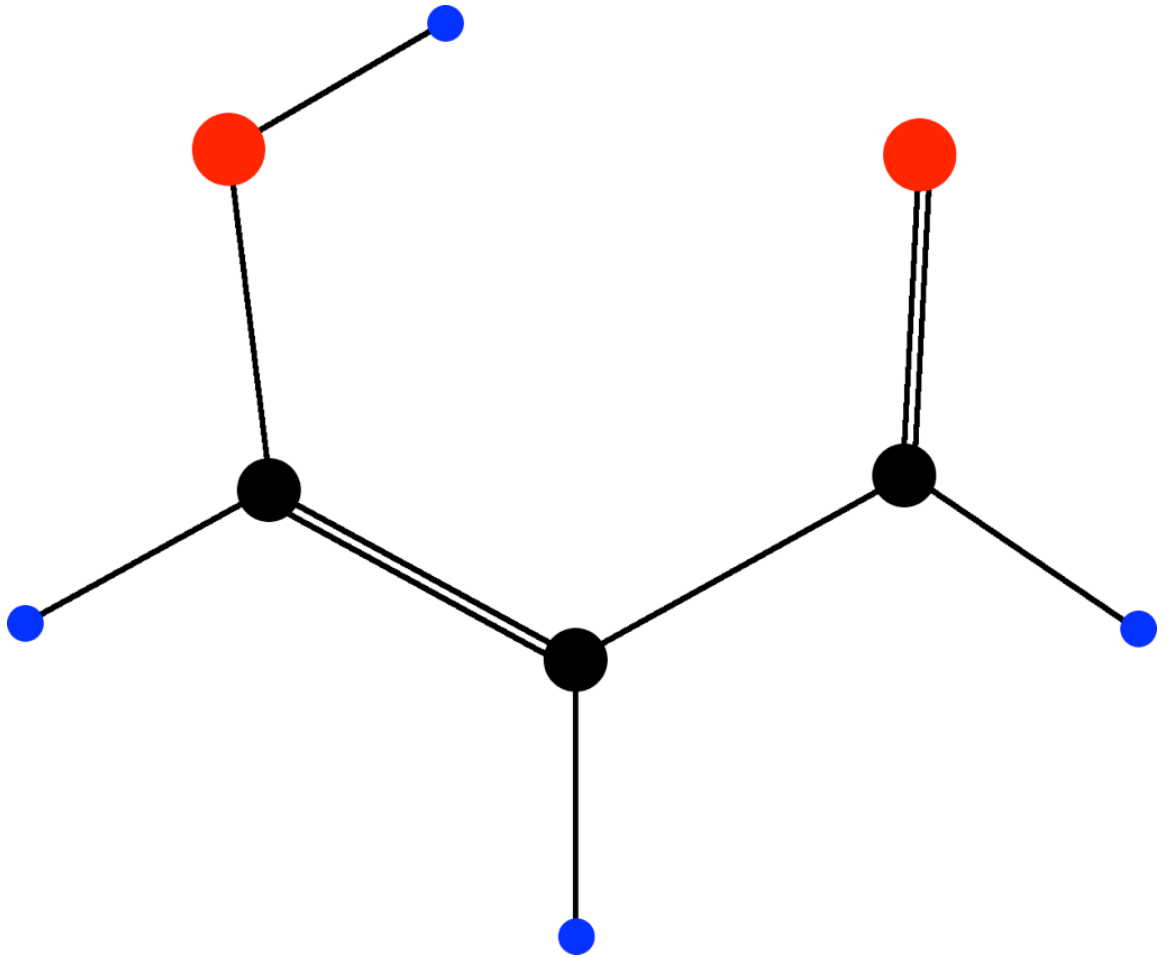
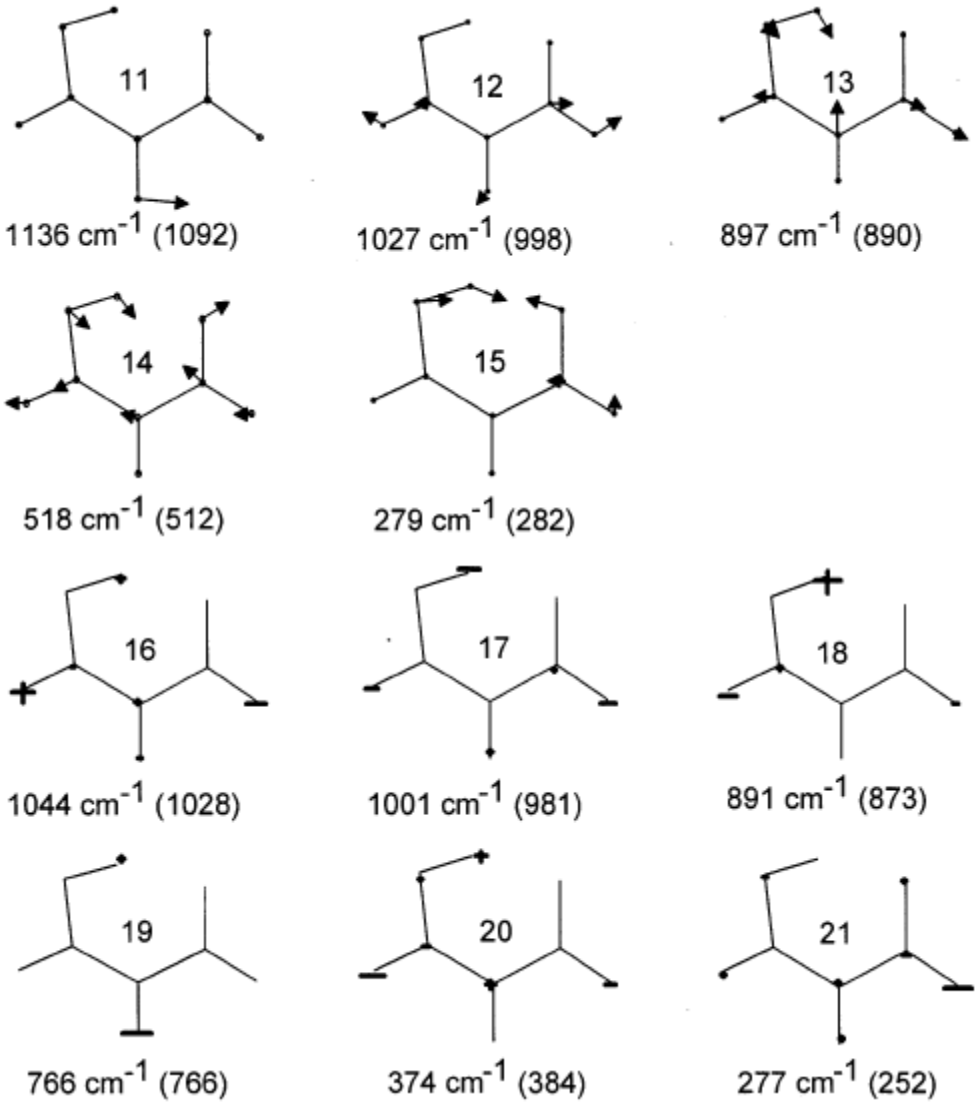


Malonaldehyde - a 5-membered 'open ring' molecule.



$C_3O_2H_4$

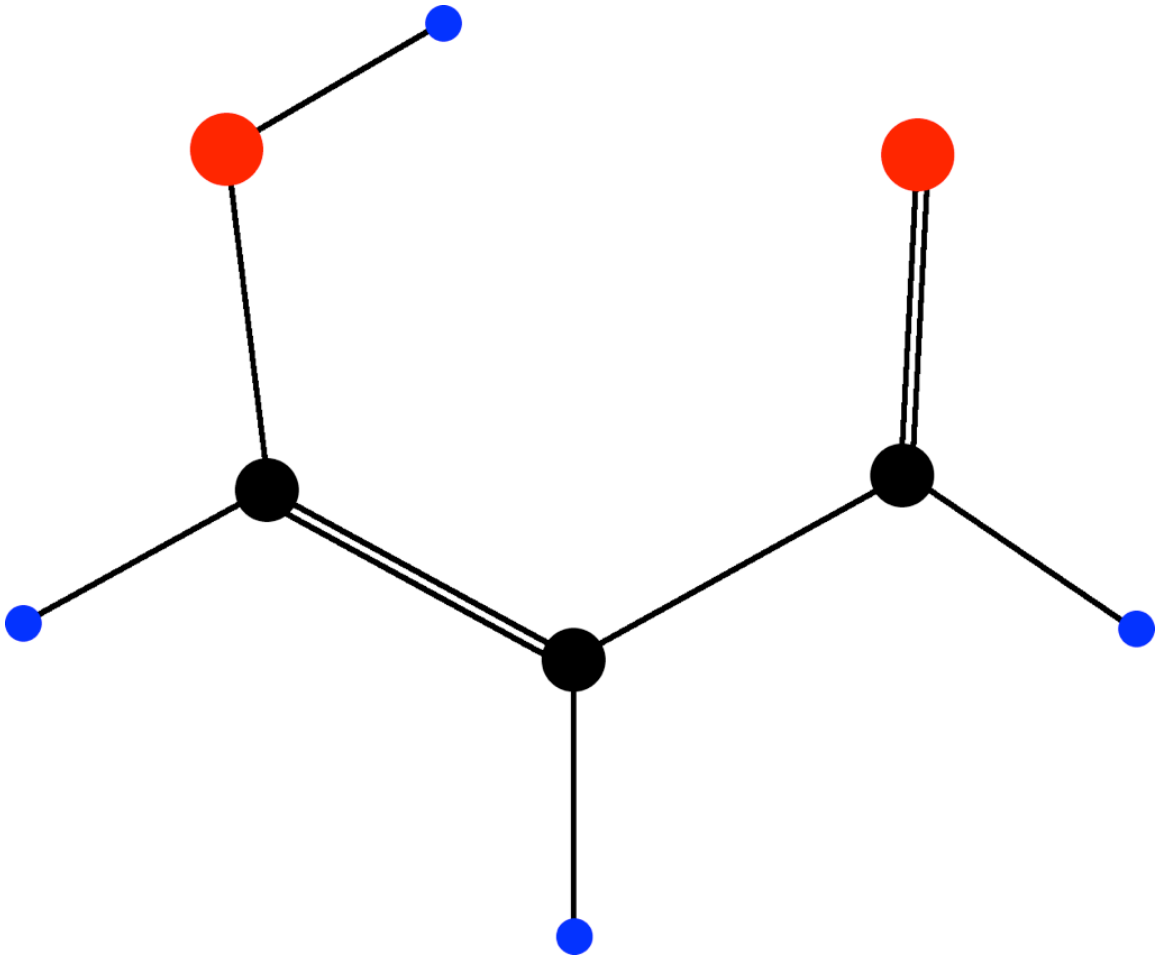


There are 21 normal modes of small-amplitude vibration (11 are shown).

However, the motion of the hydrogen nucleus attached to the oxygen is rather special...

Tayyari and Milani-Nejad
Spectrochimica Acta **54**, 255 (1998)

The topmost proton could associate with either oxygen atom.



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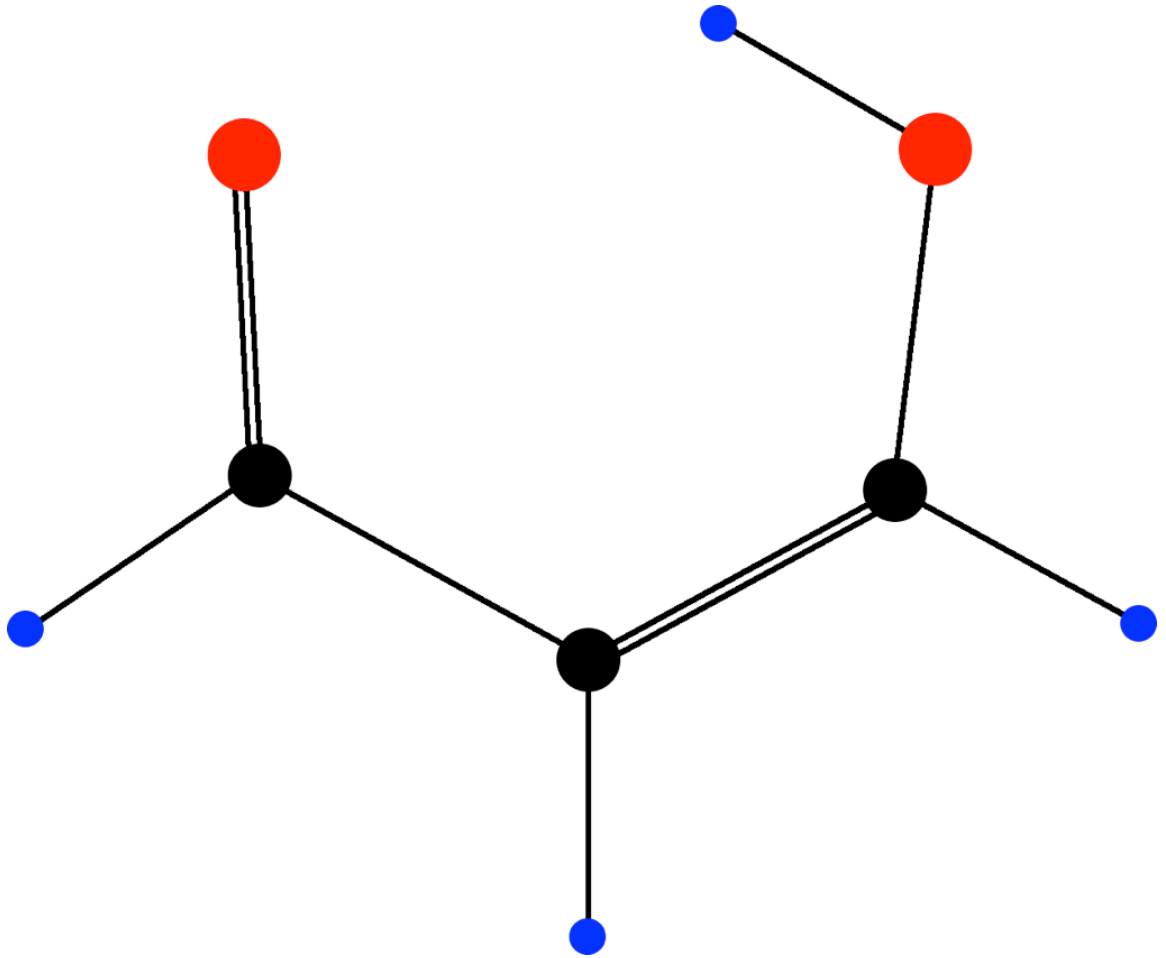
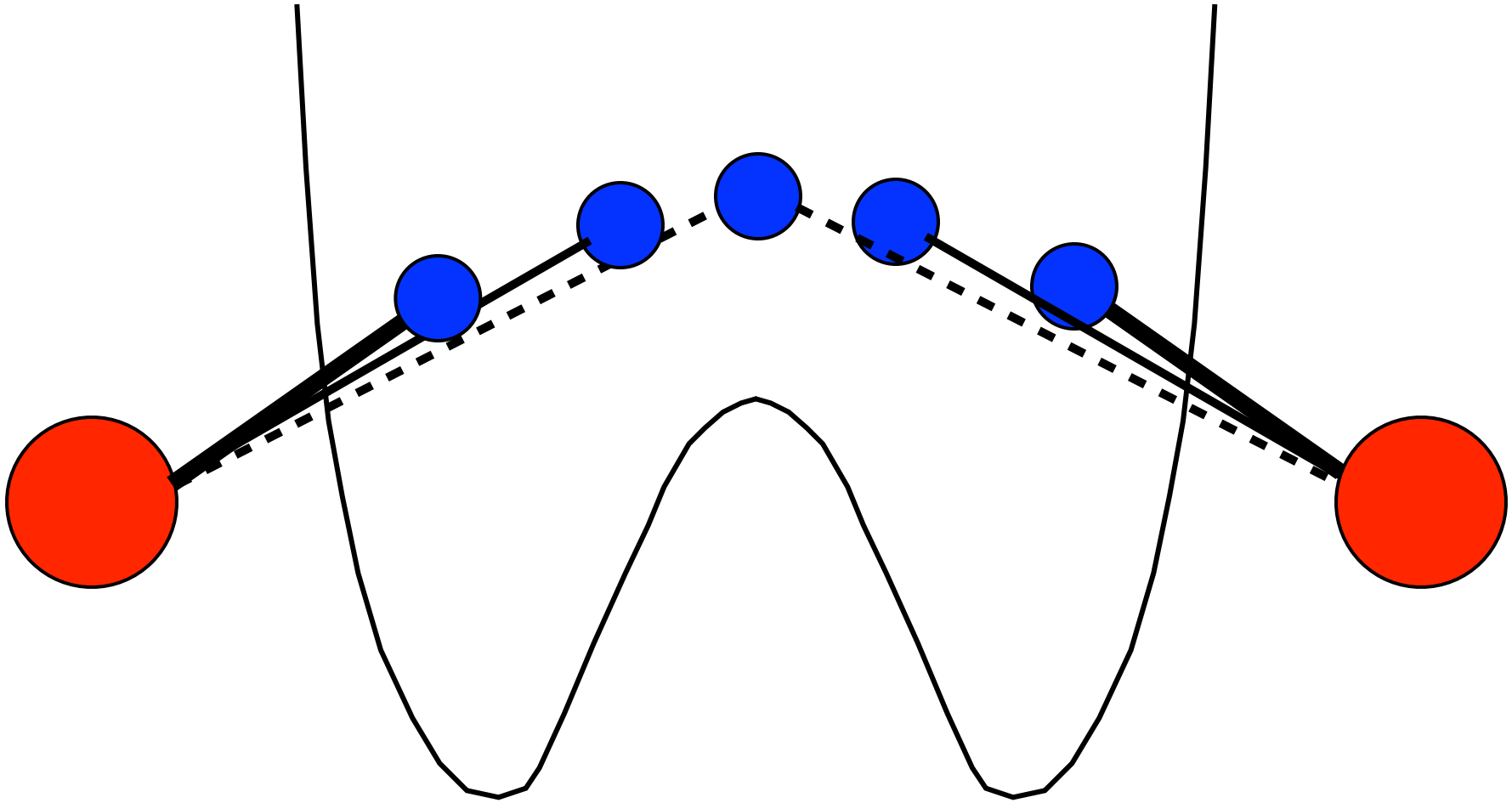
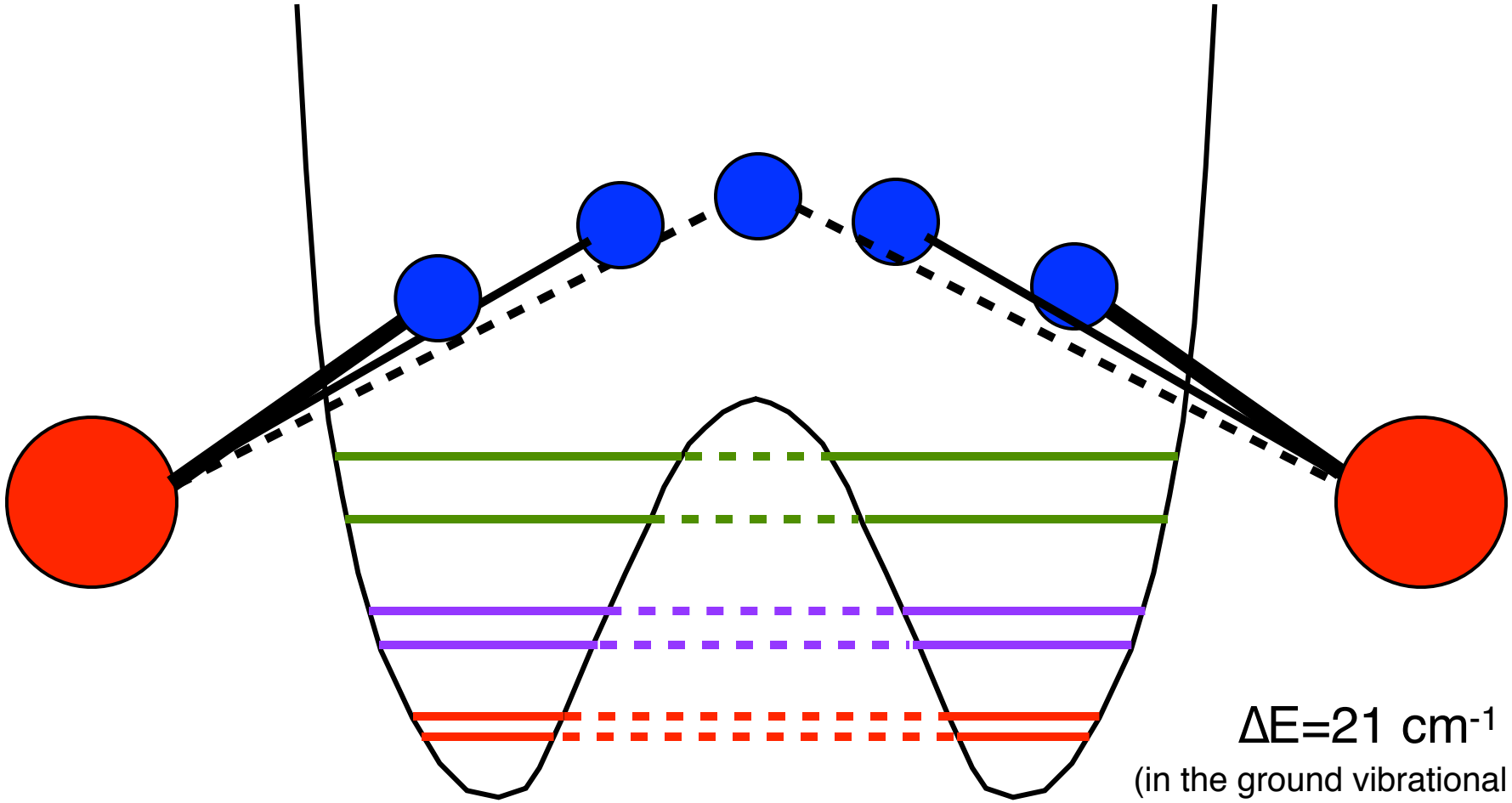


The proton associated with the oxygen atoms experiences a double-well potential



Excitation of the oxygen-hydrogen bond increases the tunnelling-splitting



$\Delta E = 21\ cm^{-1}$

(in the ground vibrational state)

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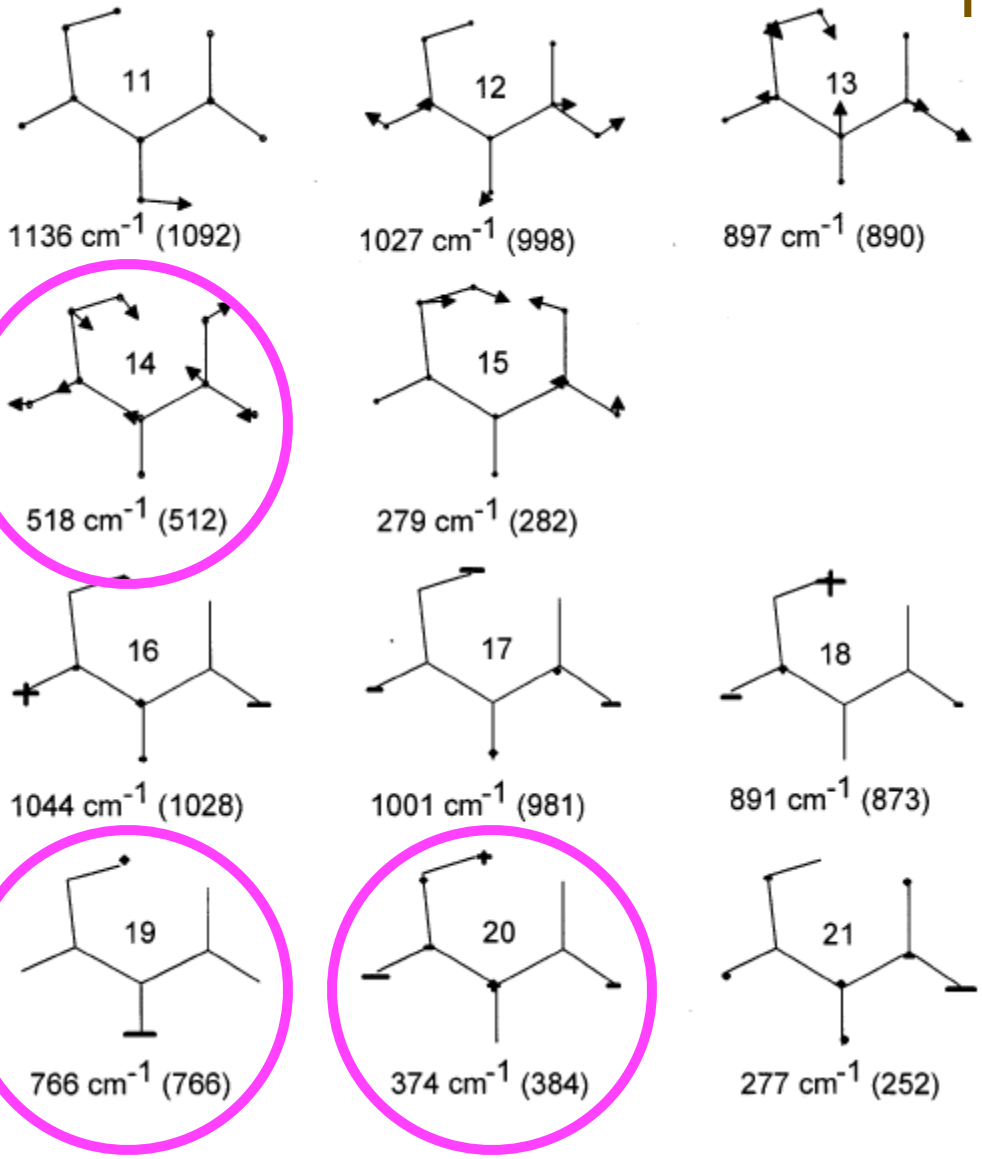
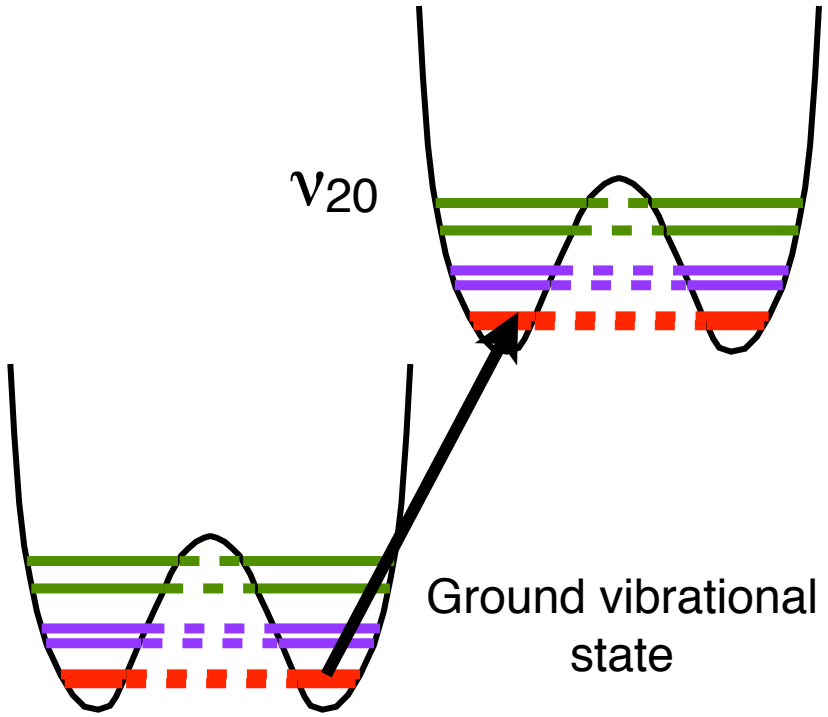
Rotation-vibration spectra of the fundamental vibrations will all show tunnelling-splitting, but the vibrational motion will modify it.





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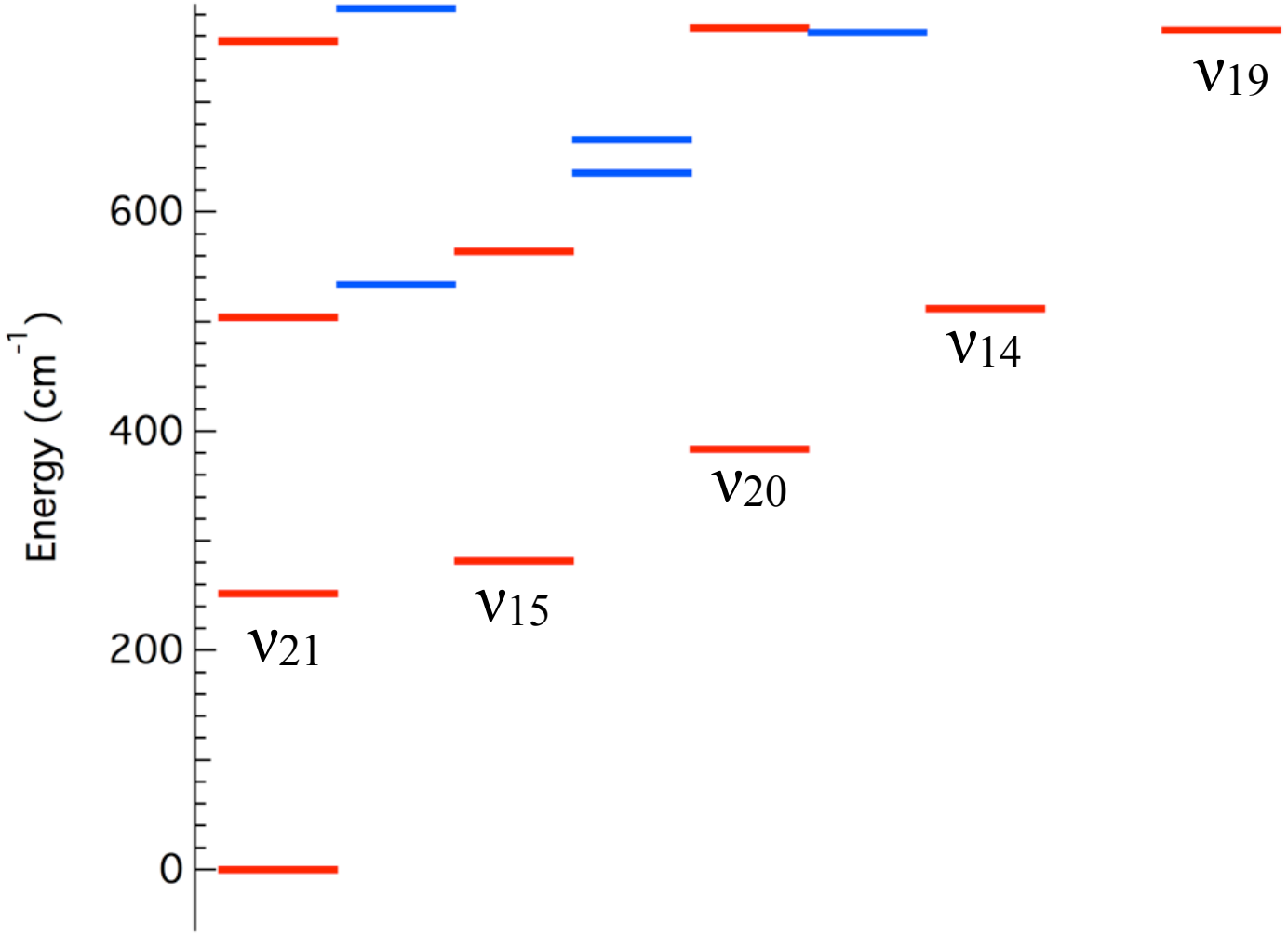
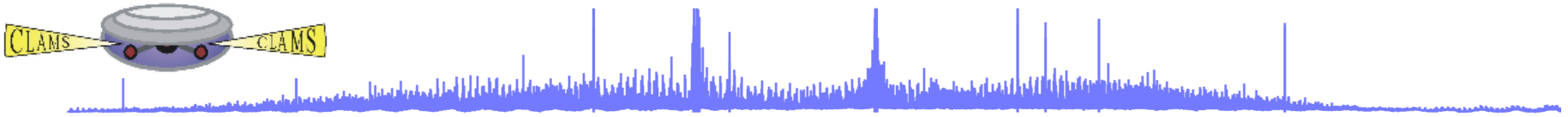
Energy level diagram for vibrations of malonaldehyde





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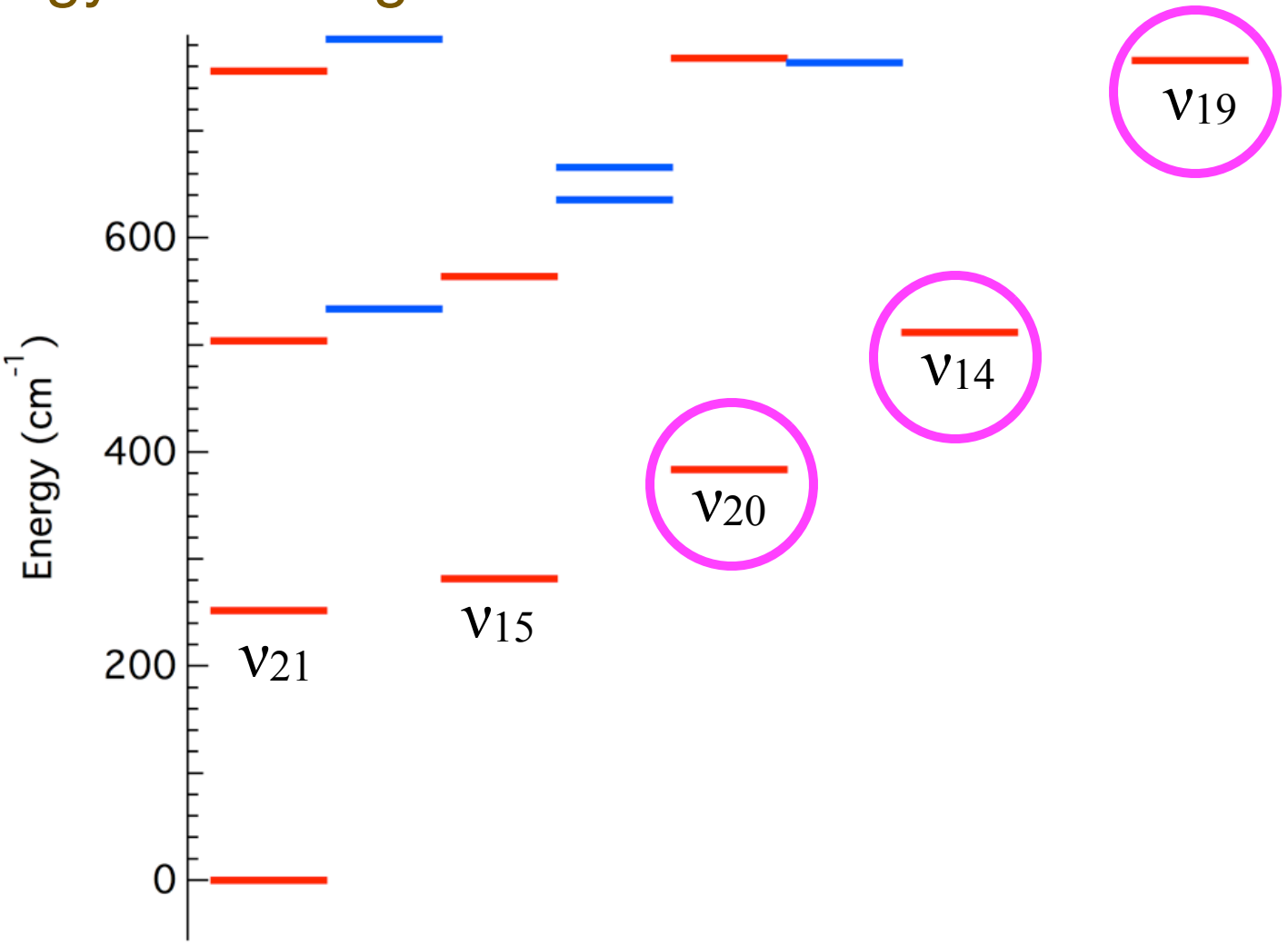
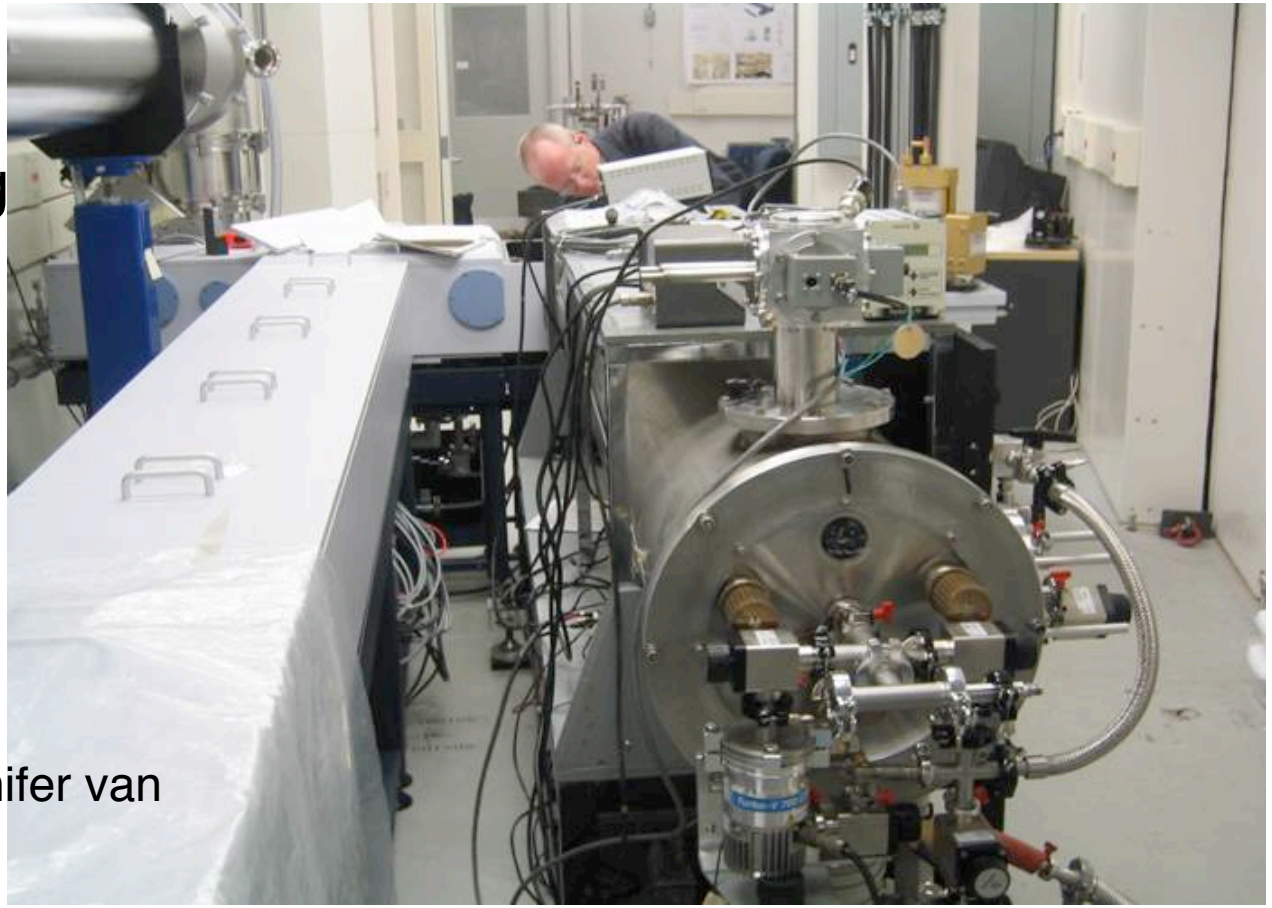


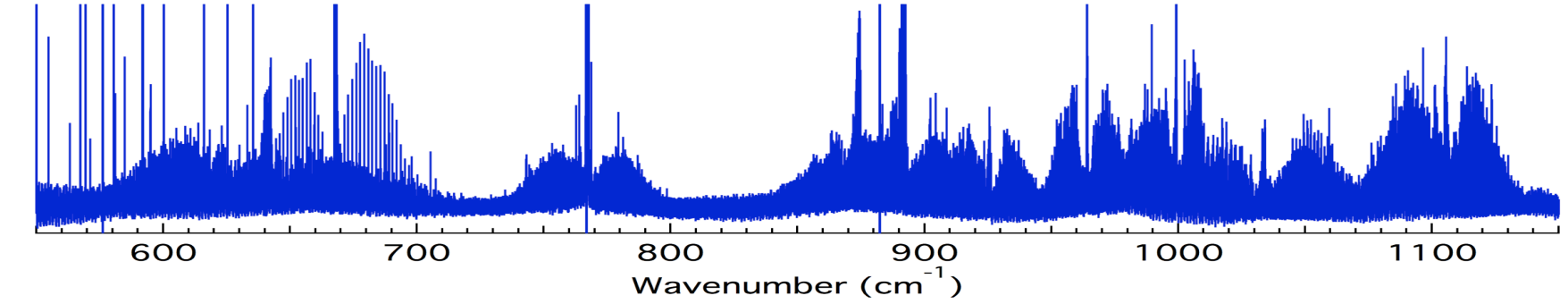
Sample preparation and handling!

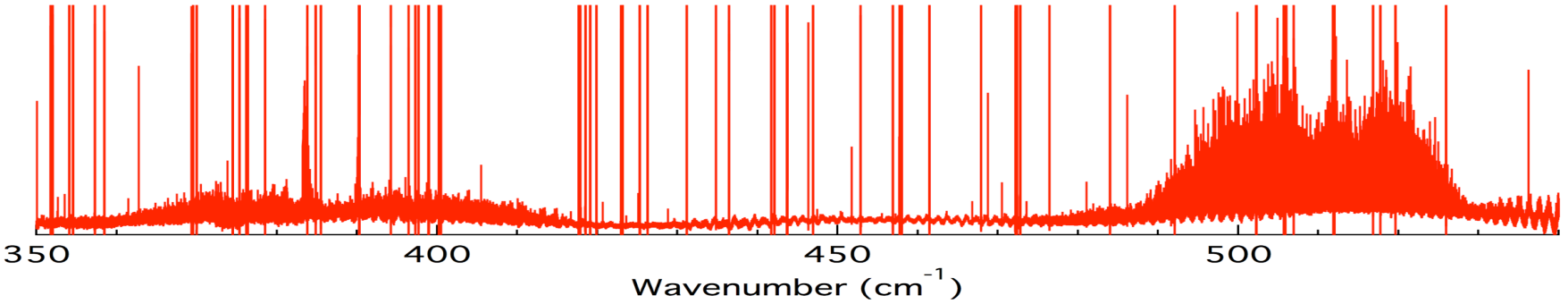
- Many thanks to David MaGee for producing the sodium-salt of malonaldehyde!
- Many thanks to Brant Billinghurst for helping with the conversion from the salt to malonaldehyde at the CLS

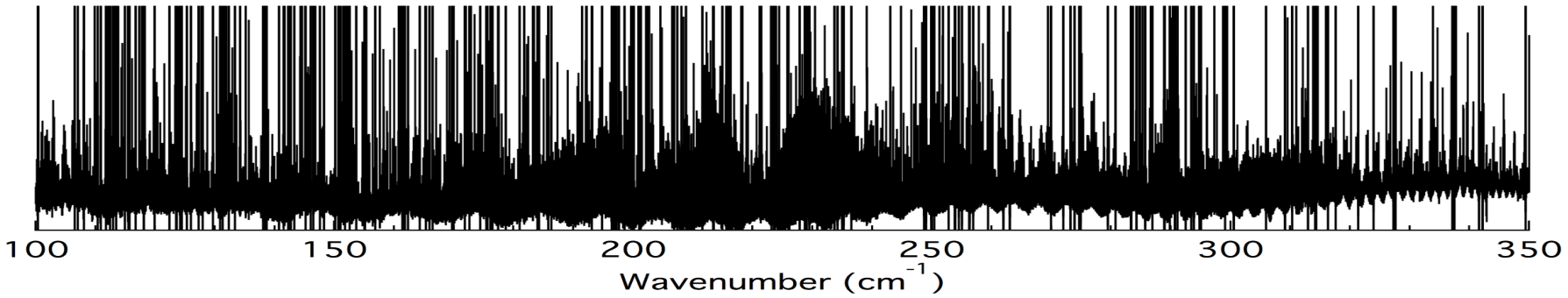


(Picture couresty of Jennifer van Wijngaarden)

Spectrum overview







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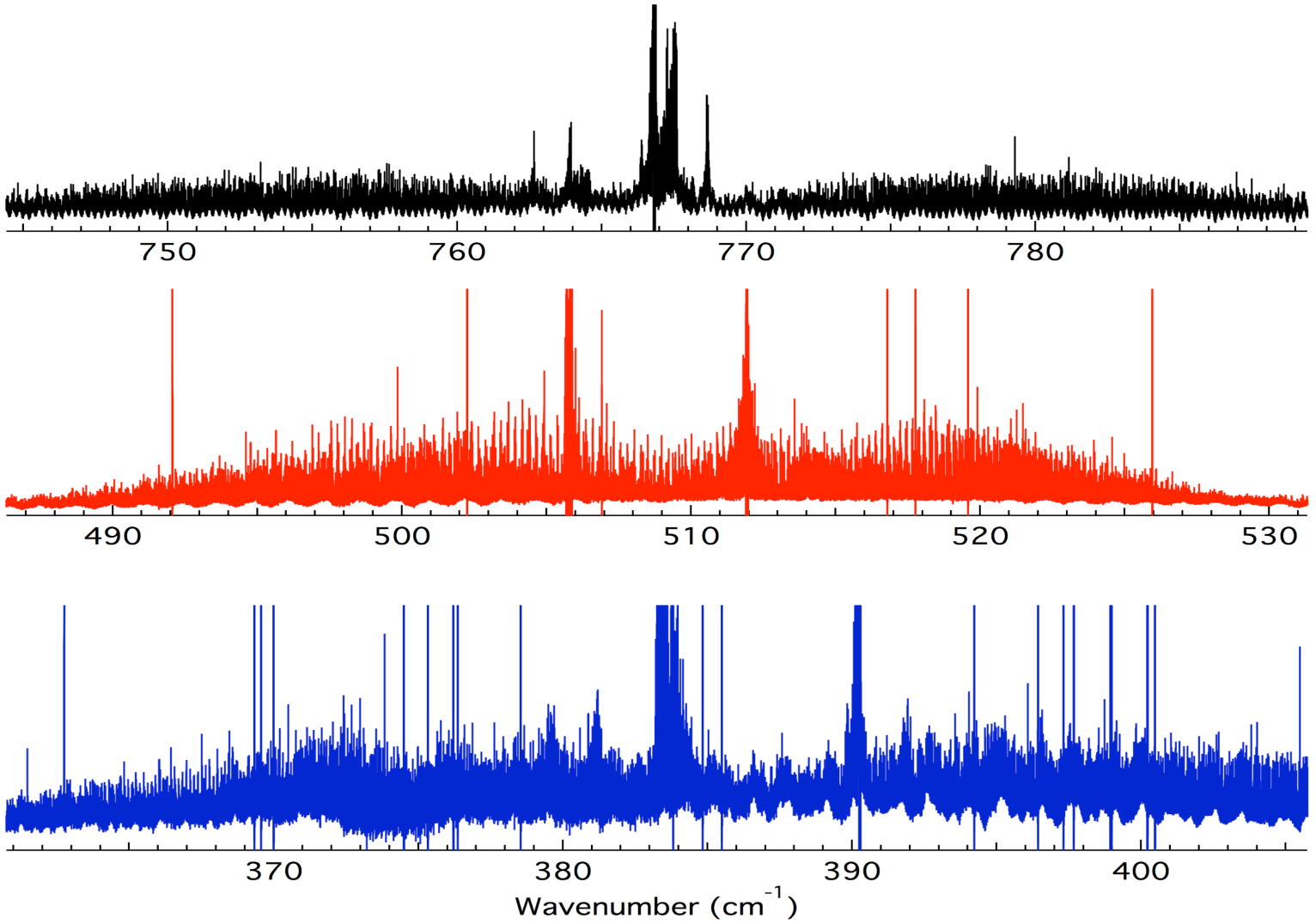
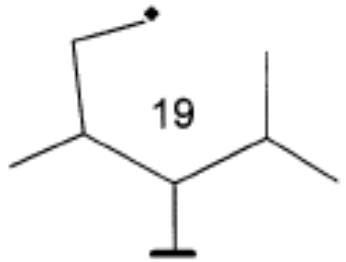
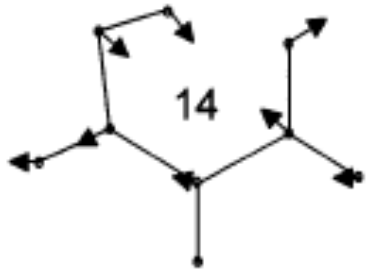
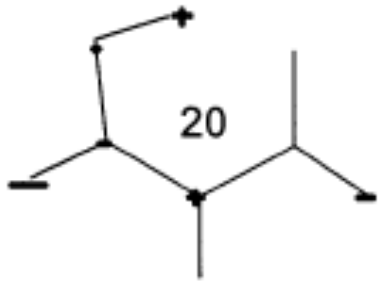
Three fundamental vibrational bands of malonaldehyde









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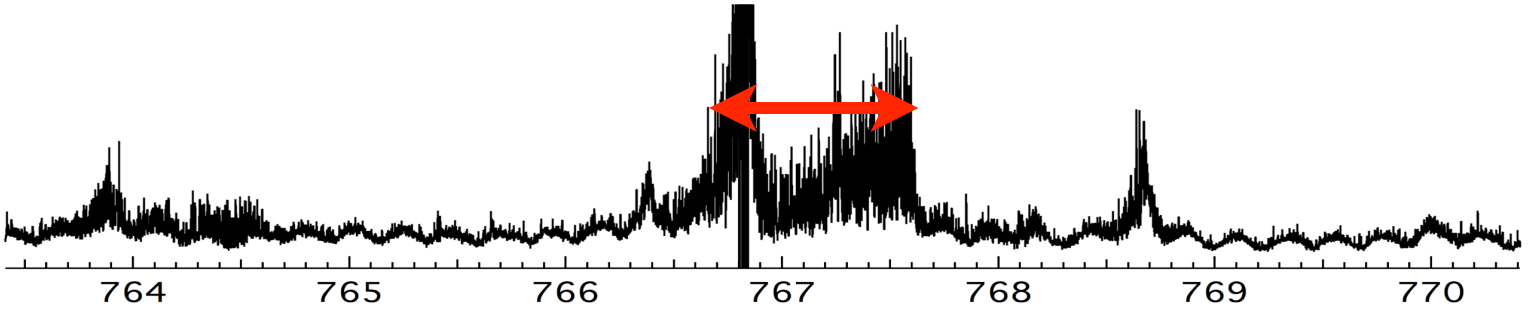
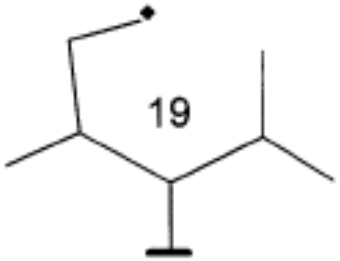
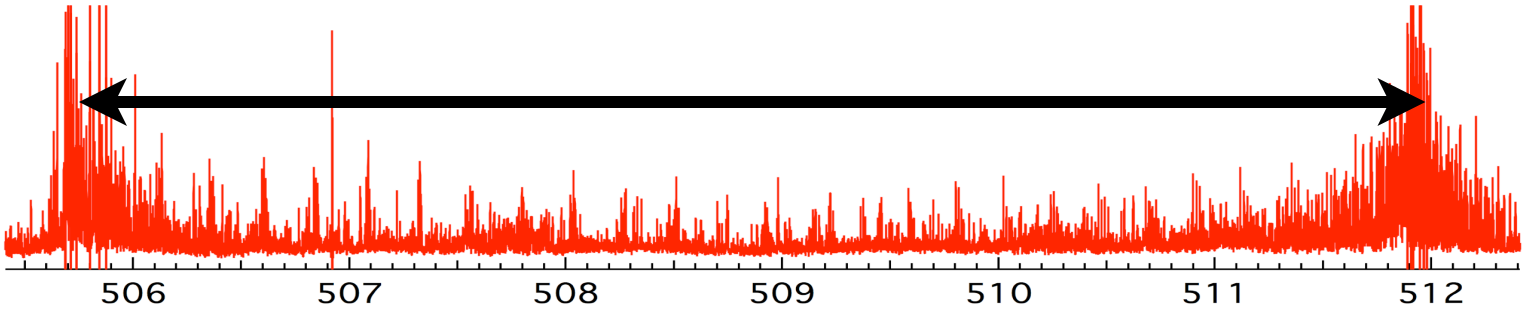
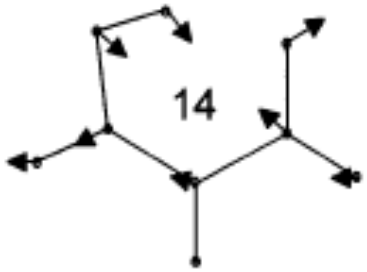
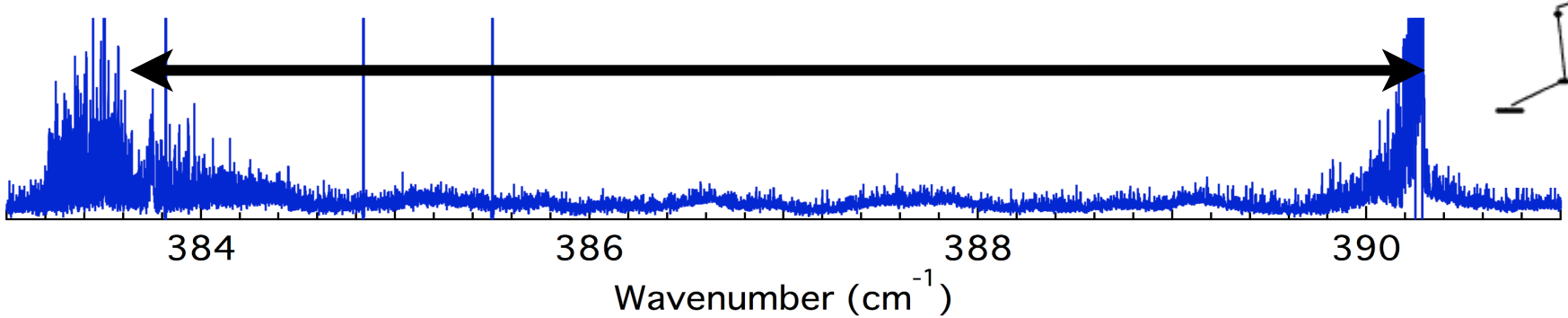
Relative tunnelling-splitting in three vibrational bands

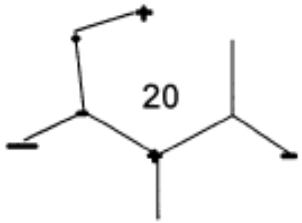


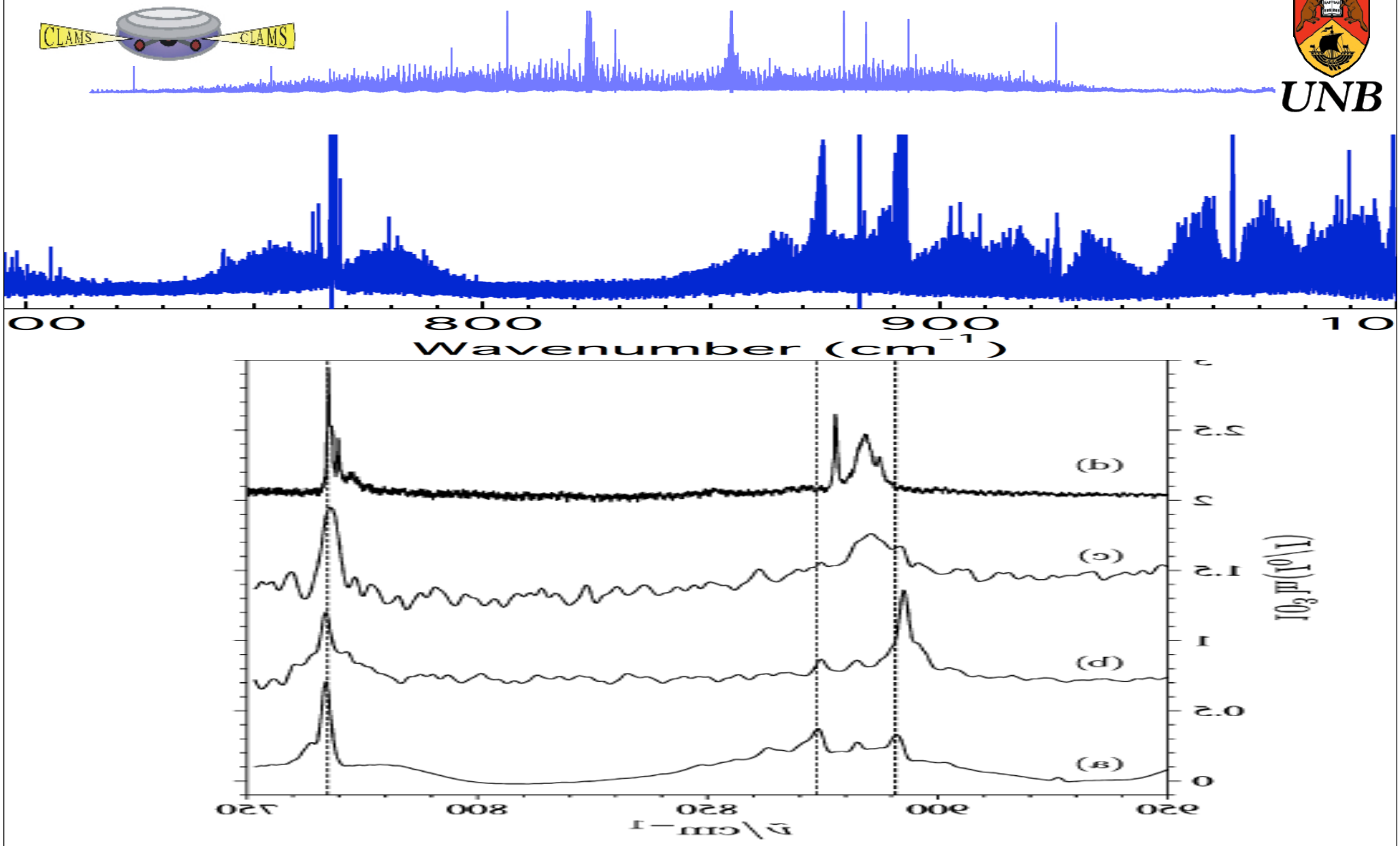












Wasserman et al, PCCP **8**, 2344 (2006)

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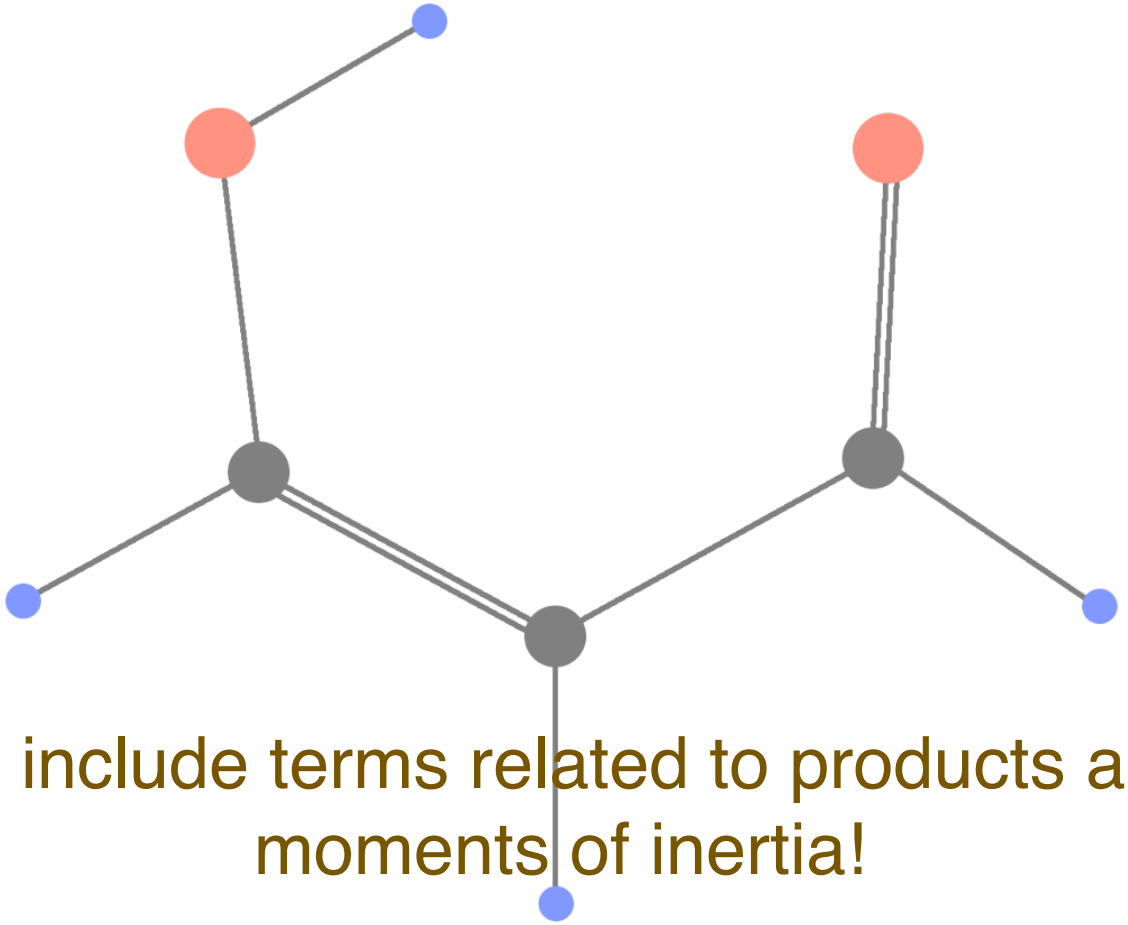
For a detailed determination of the splitting, we need to perform a rotational analysis of the bands



We must include terms related to products as well as moments of inertia!

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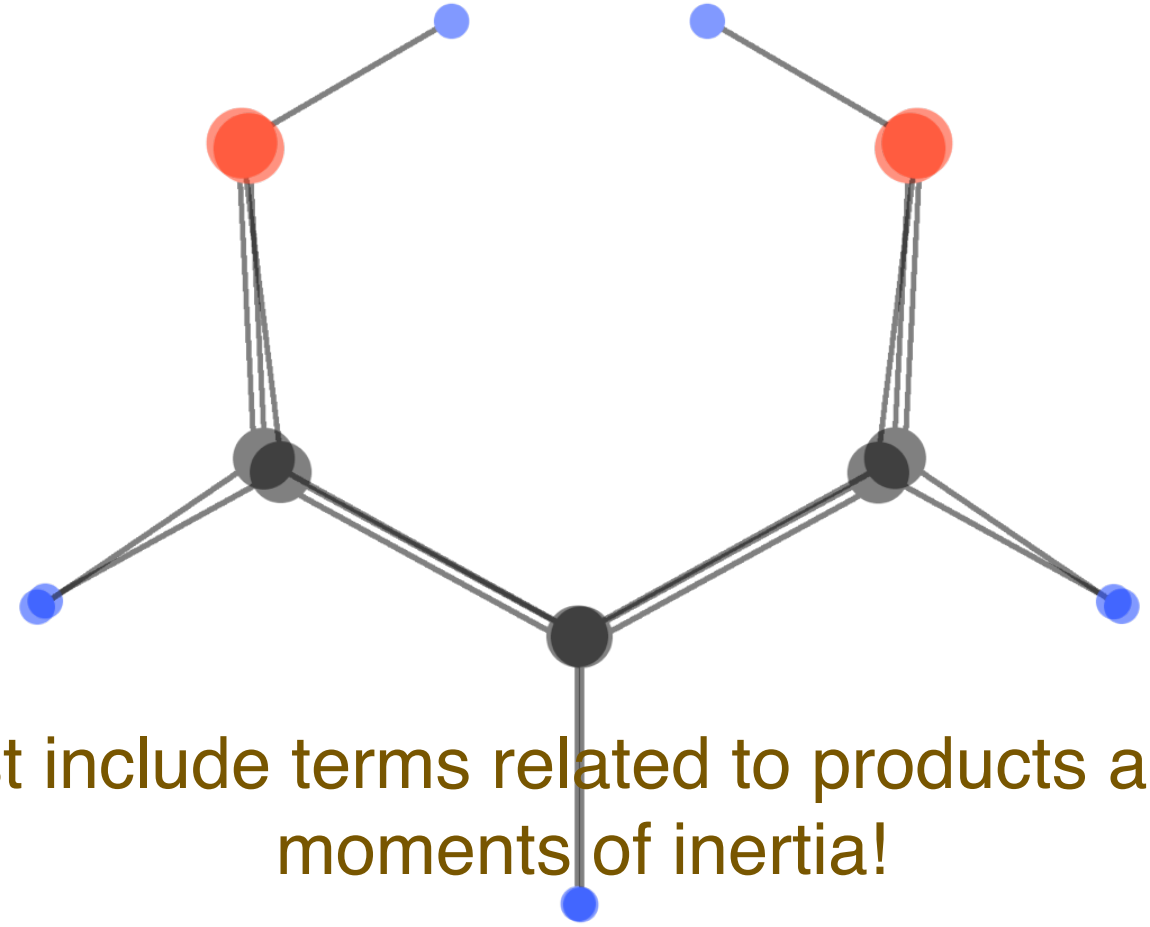

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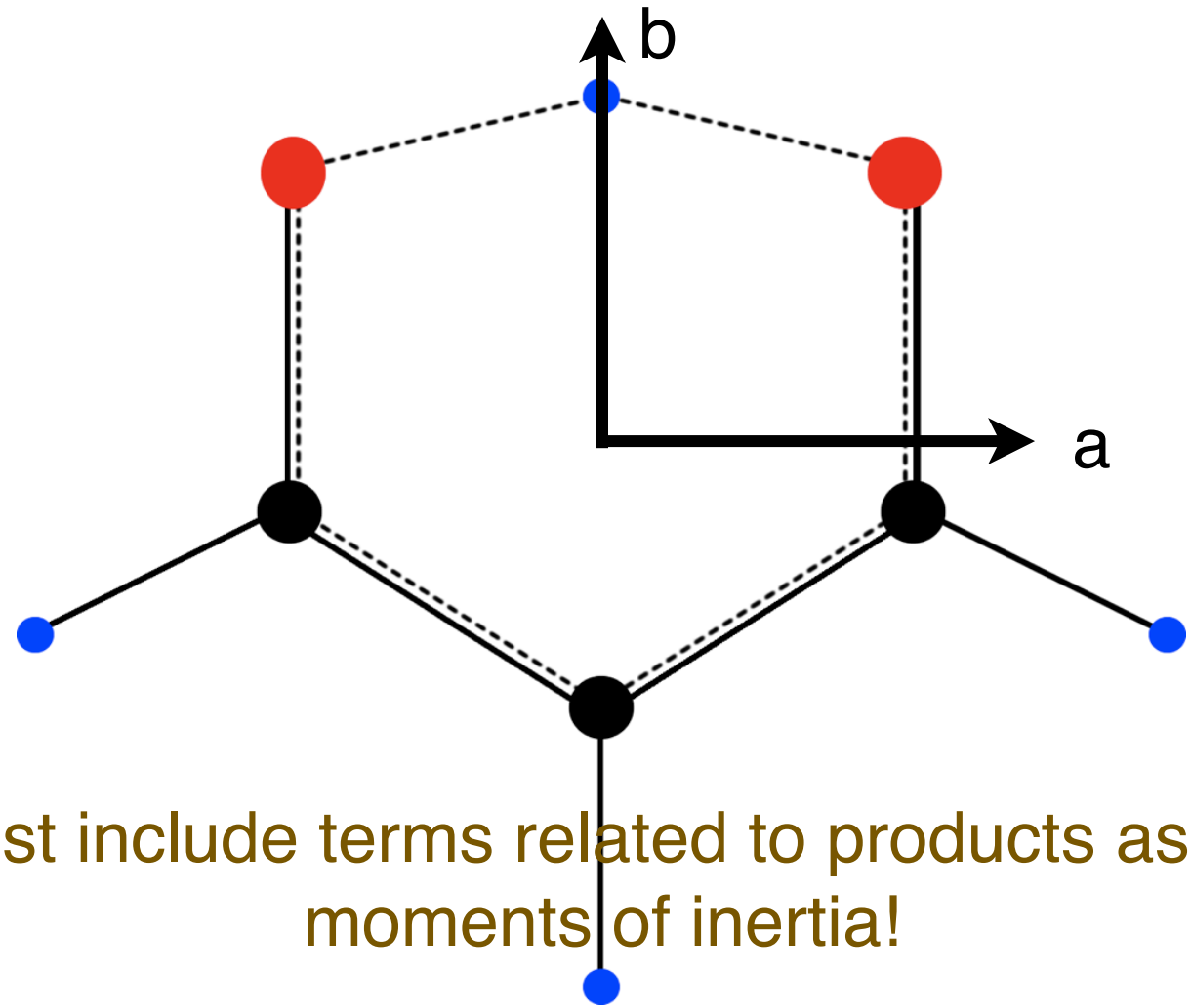

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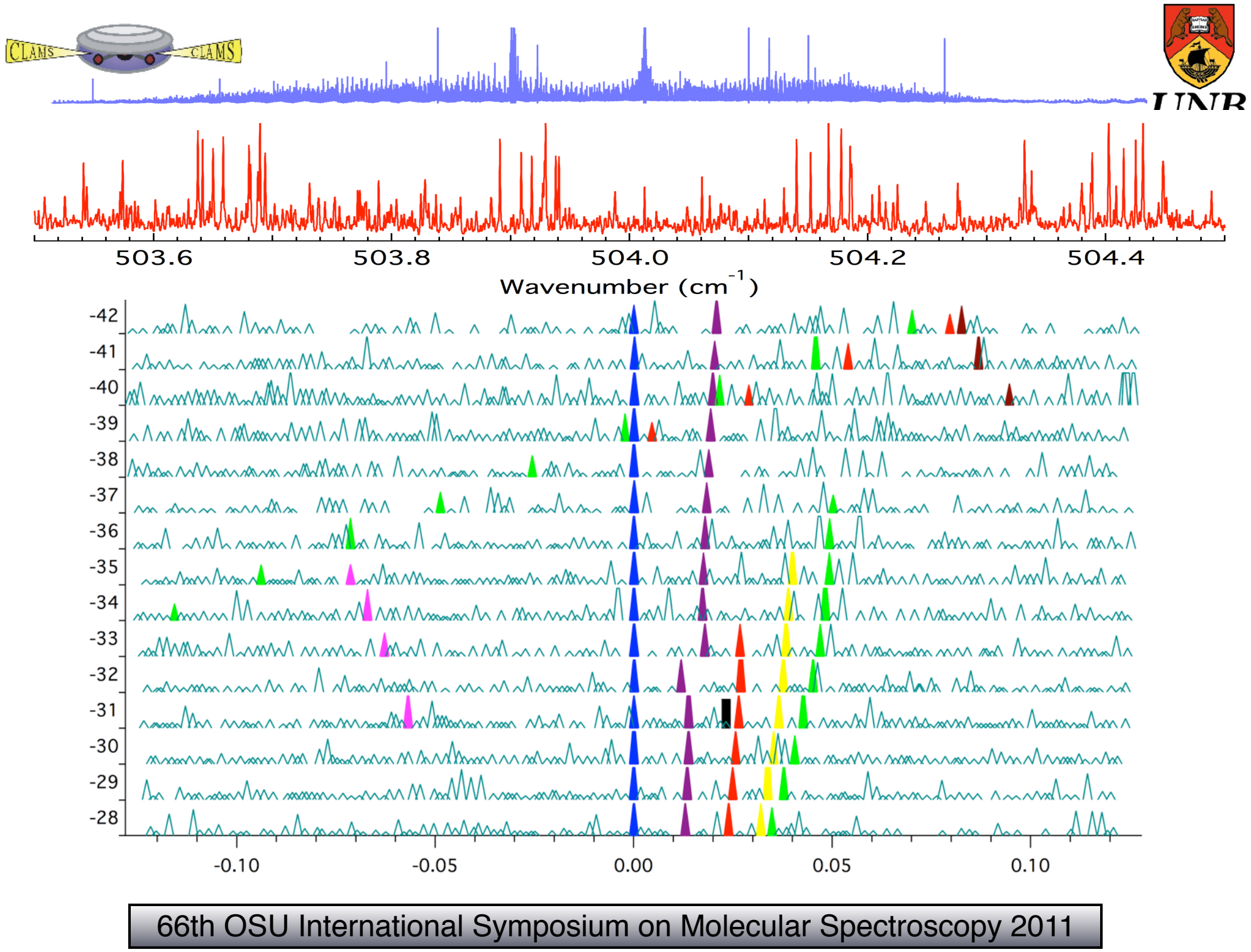

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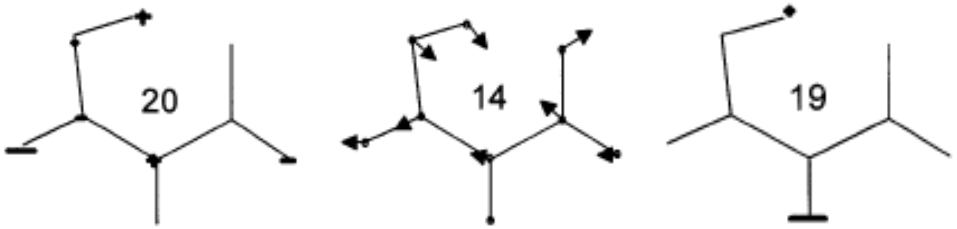
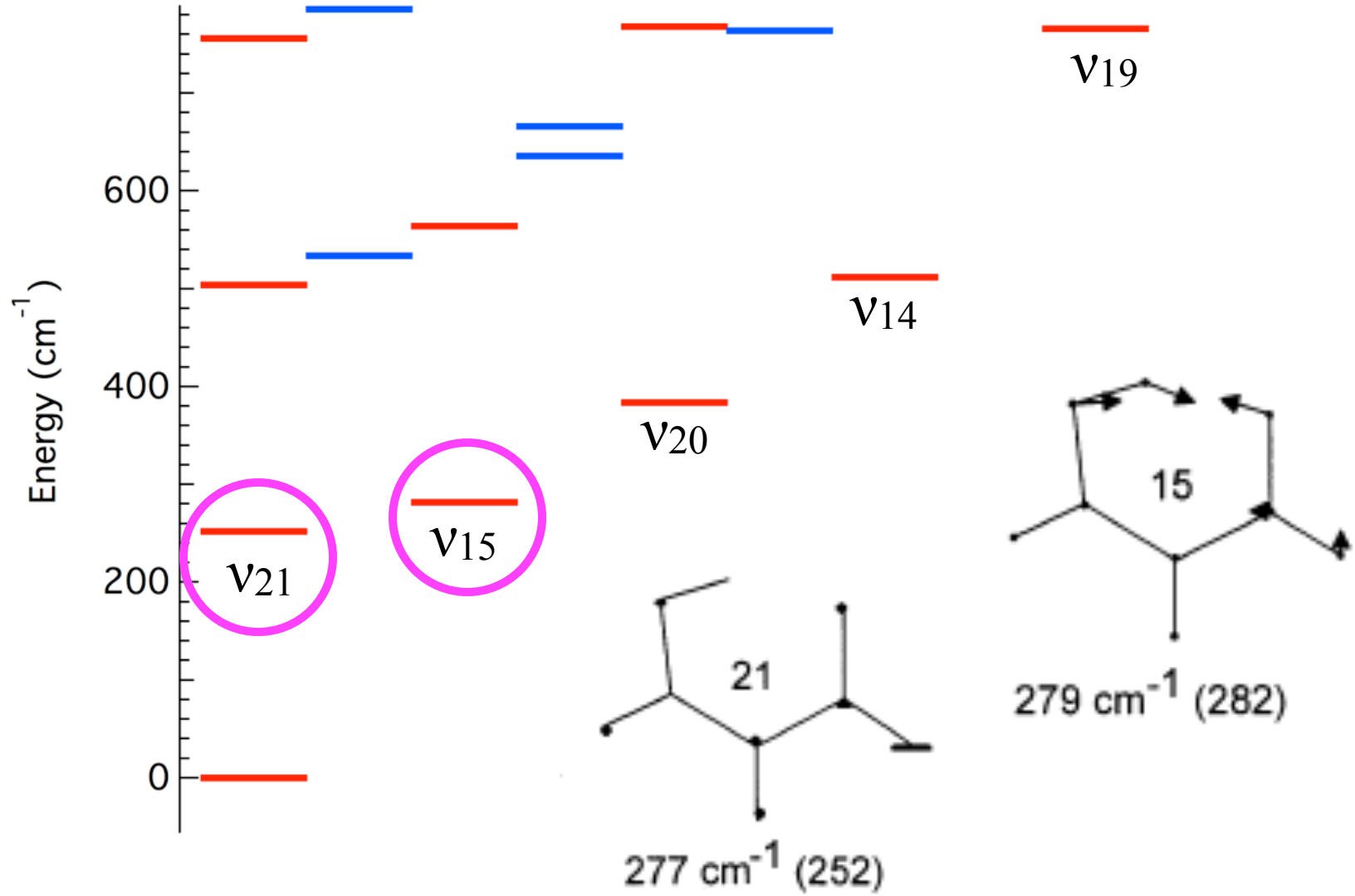
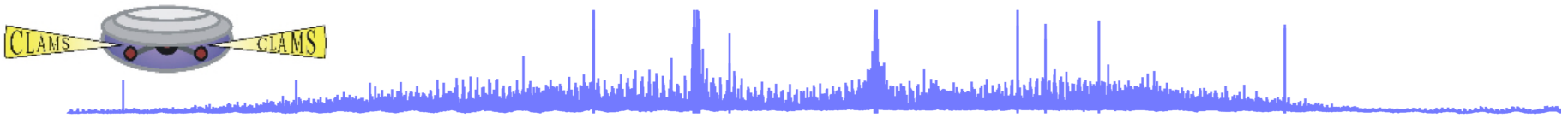
Preliminary results of fitting our three bands (in cm^{-1})



Parameter	Ground state	ν_{20}	ν_{14}	ν_{19}
T_0	0.0	386.744	508.775	767.2925
ΔE	21.58314	14.47	15.395	22.500
A	0.328021667	0.3277436	0.328987	0.3277305
B	0.173871472	0.1736465	0.1730581	0.1734395
C	0.113557783	0.1134916	0.1132003	0.11399315
(product of inertia)	0.00153094	0.0013609	0.00233617	0.0005851

Energy level diagram for vibrations of malonaldehyde





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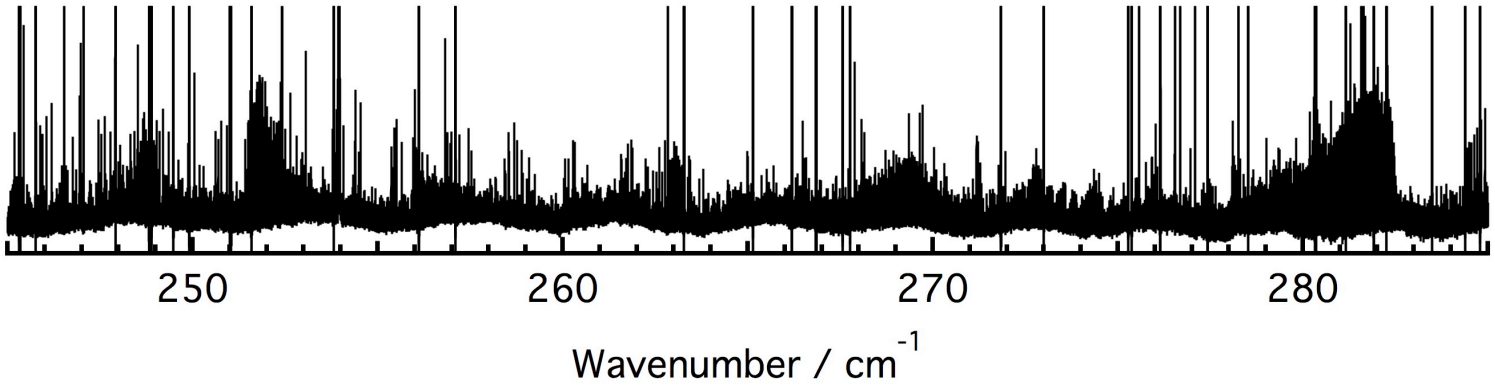
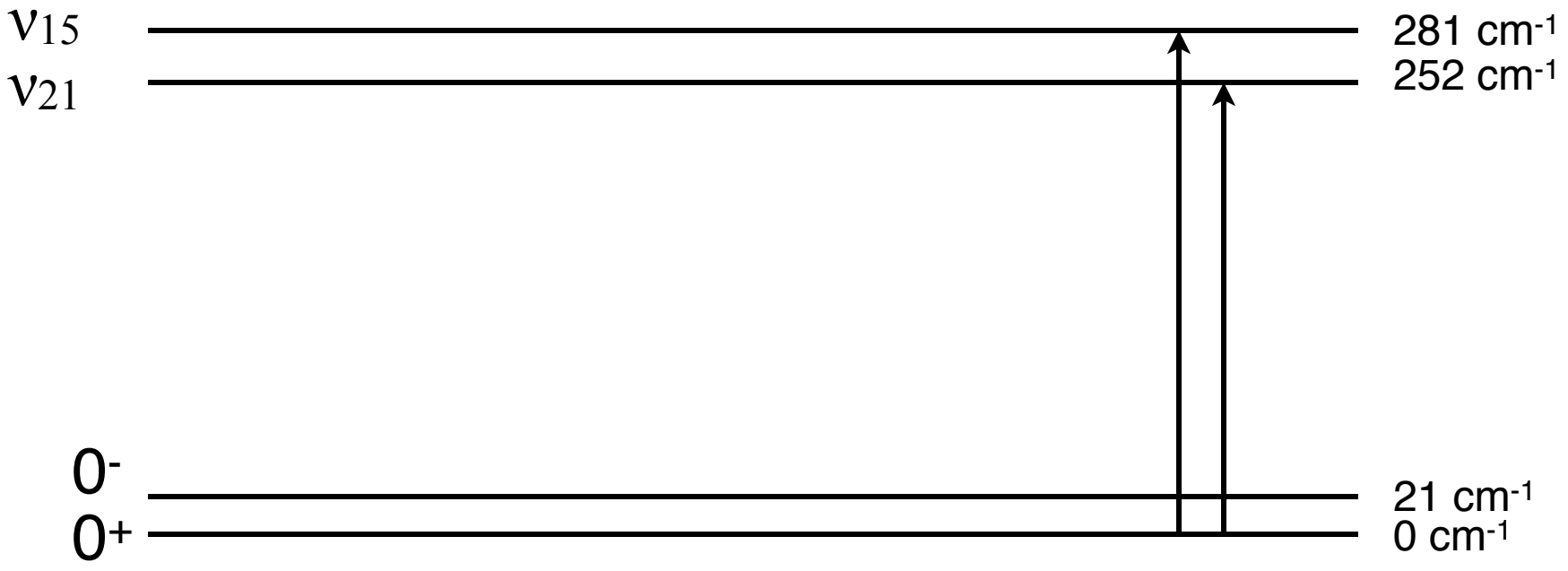
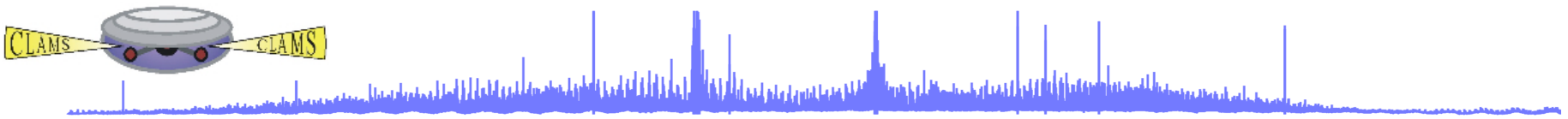
We can see features corresponding to heads assigned to the ν_{21} and ν_{15} bands...







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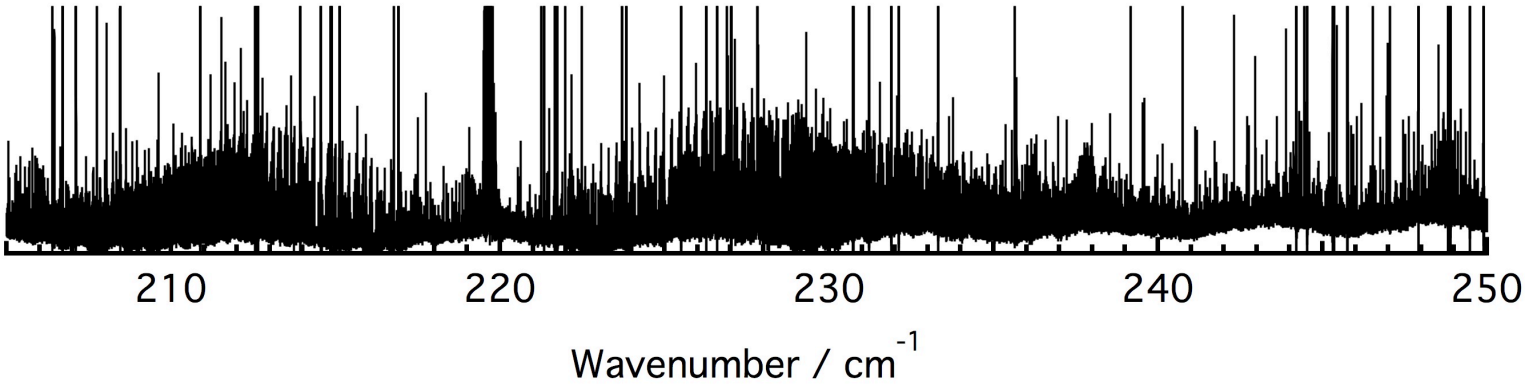
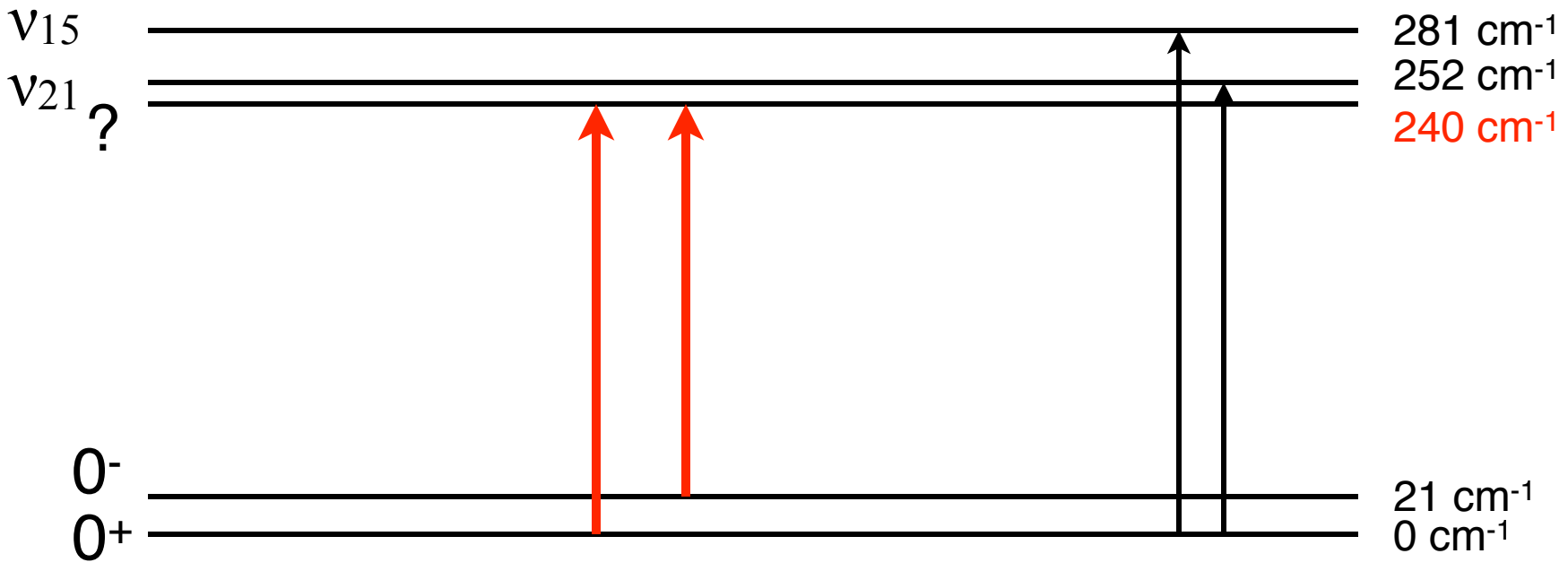
...so what are these two *a*-type bands, then??





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What we've learned so far...

- We can do this!! We know how to synthesize malonaldehyde, and how to take its rotation-vibration spectra at very high resolution at the CLS.
- The tunnelling-splitting in excited vibrational states can be determined with very high accuracy from our data, and we can see how it changes as different vibrational modes of the molecule are excited.
- We have found an intriguing new low-lying level that is not part of a conventional small-amplitude motion analysis of the vibrational structure.

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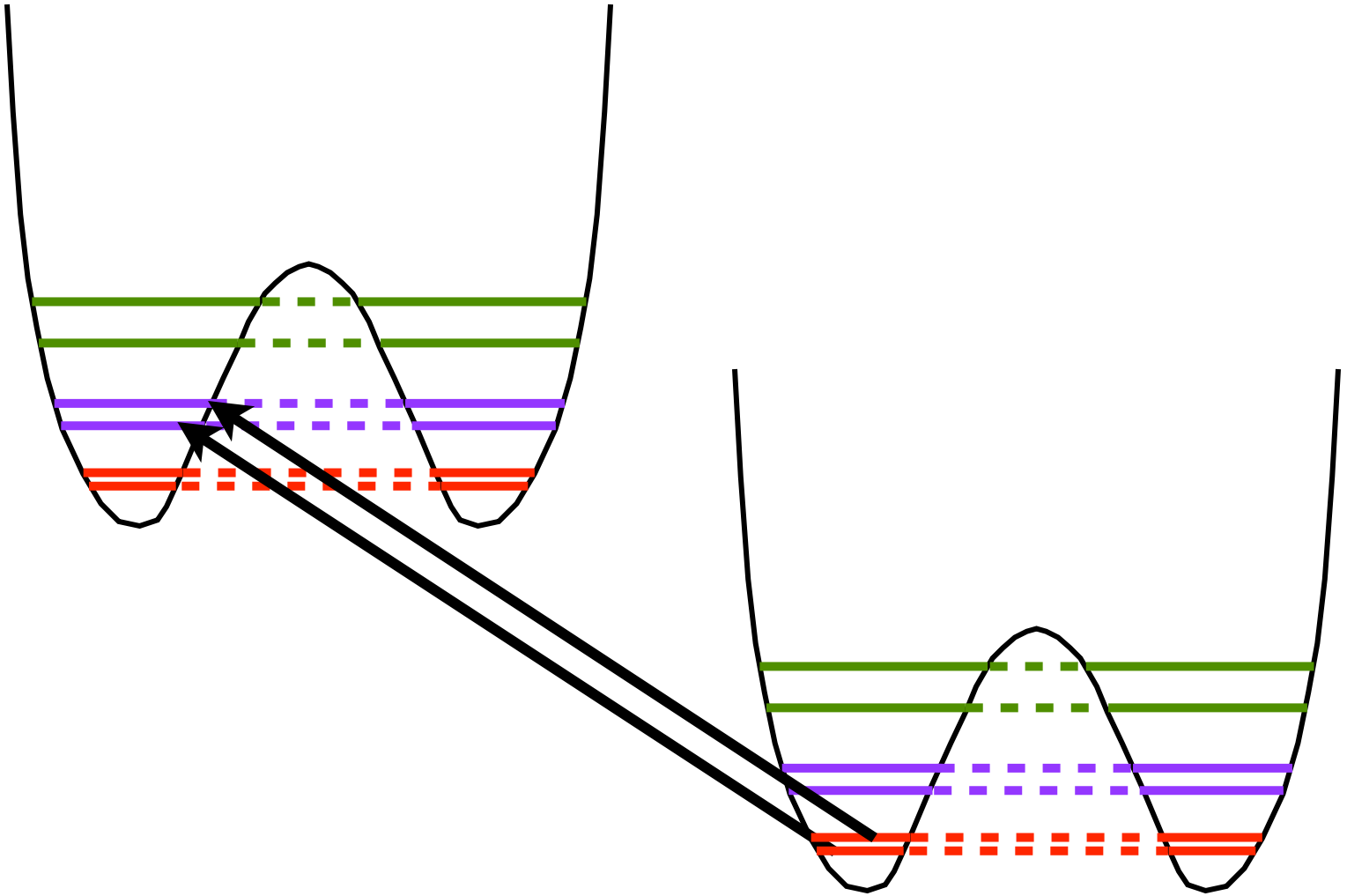
Fin du séminaire!

Special thanks to Dave MaGee (UNB Chemistry) and Brant Billinghurst (Canadian Light Source) for their help in synthesizing the malonaldehyde.

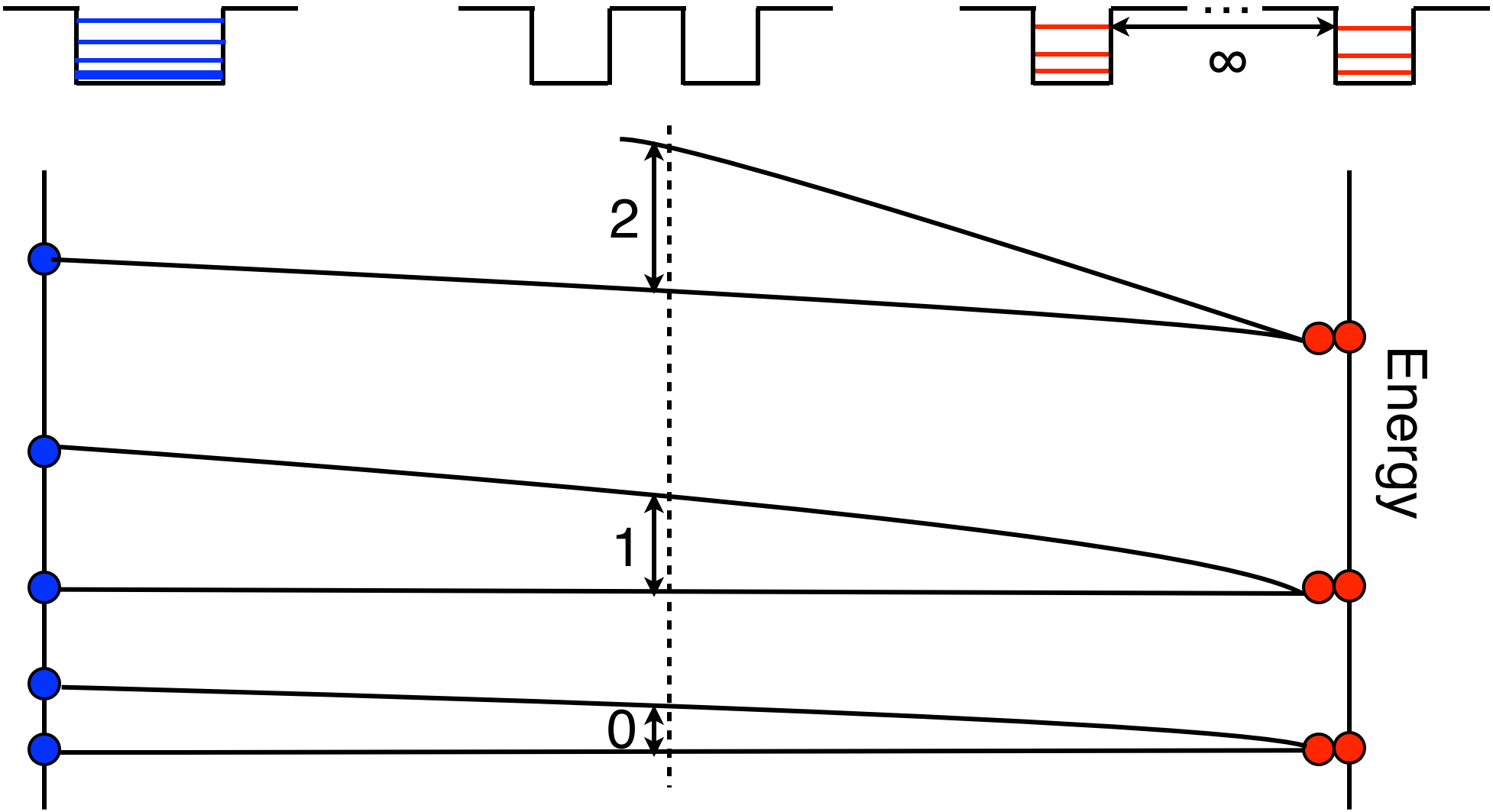
Thanks to NSERC, UNB, and the Canadian Light Source for funding and other forms of support.

Canadian Light Source
Centre canadien de rayonnement synchrotron

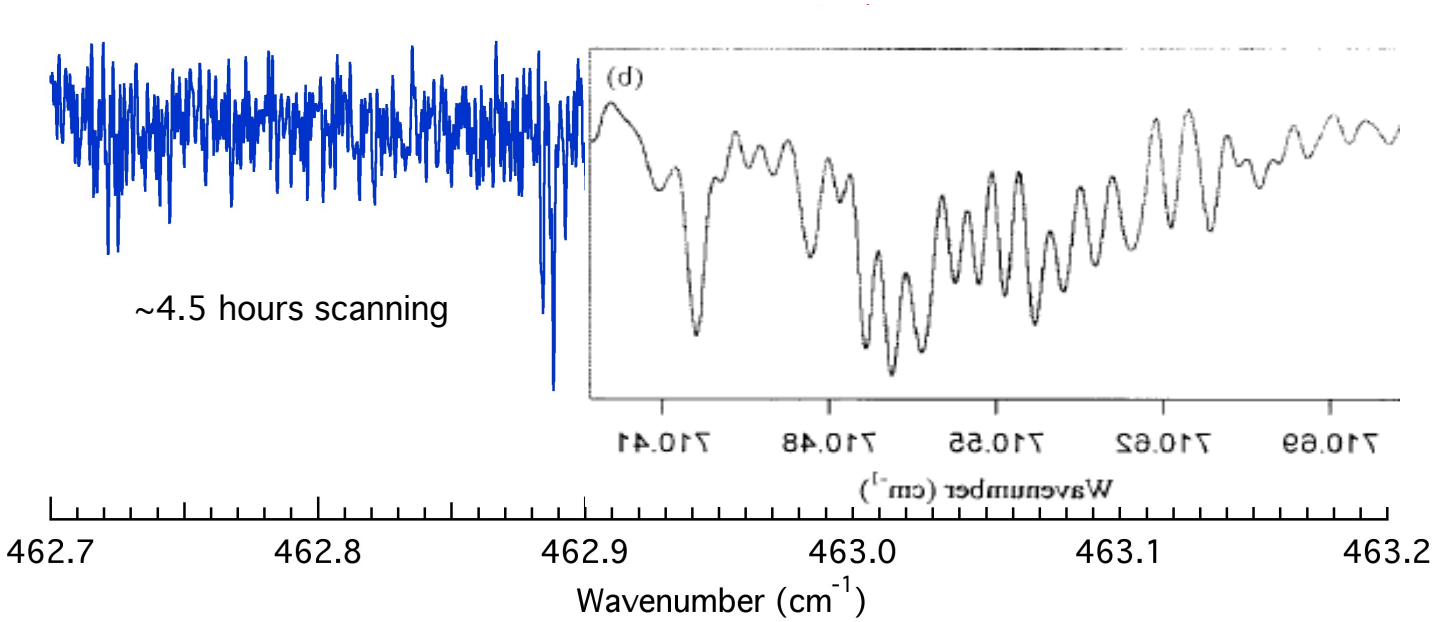
Excitations of the tunnelling potential function

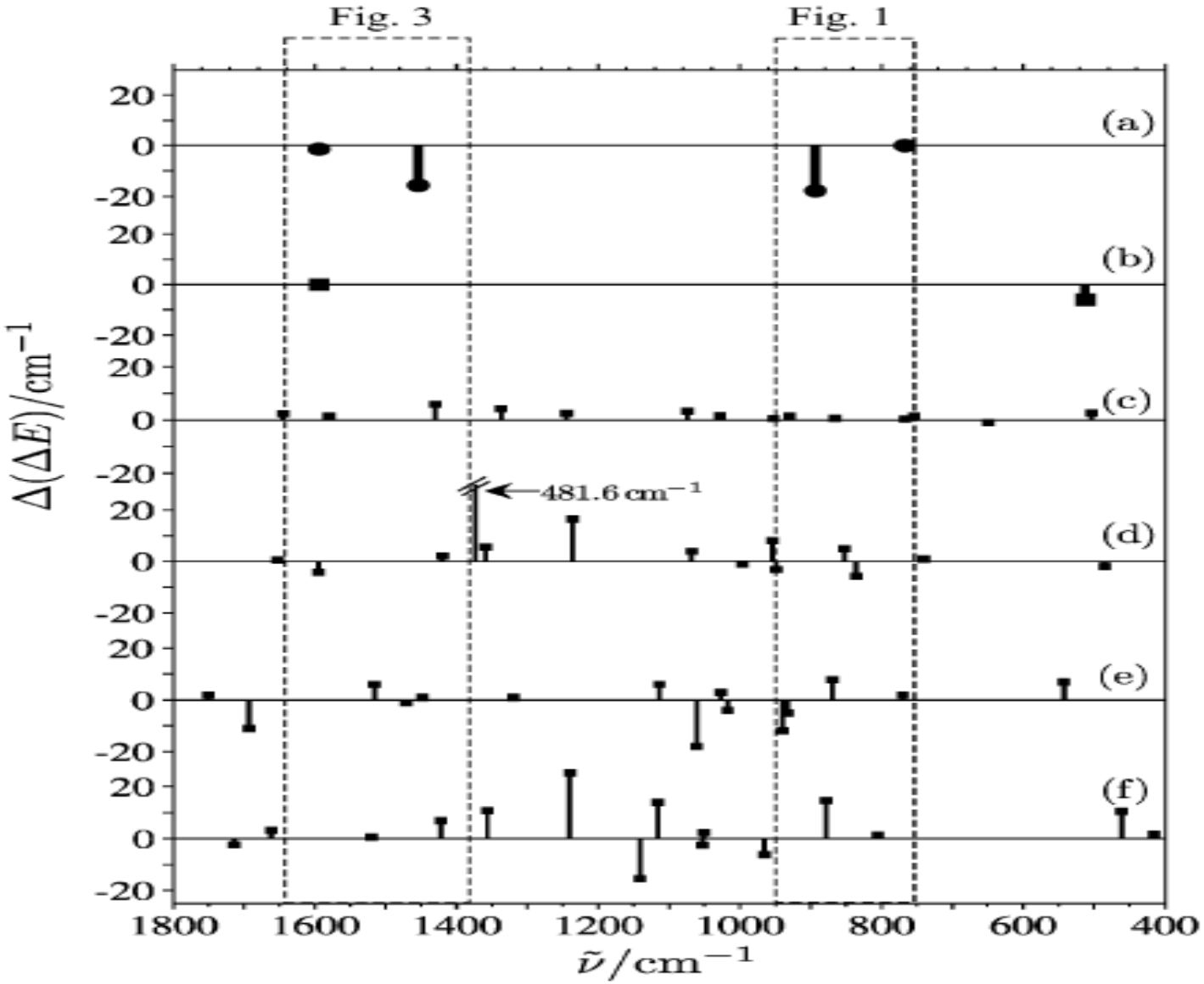


Consider a double square well potential



Comparison: synchrotron and globar spectra of pyrrole, 0.001 cm-1 resolution





Wasserman et al, PCCP **8**, 2344 (2006)