Far-infrared synchrotron-based spectroscopy of furan:
analysis of the ν_{14}-ν_{11} perturbation and the ν_{18} and ν_{19} levels

Dennis Tokaryk
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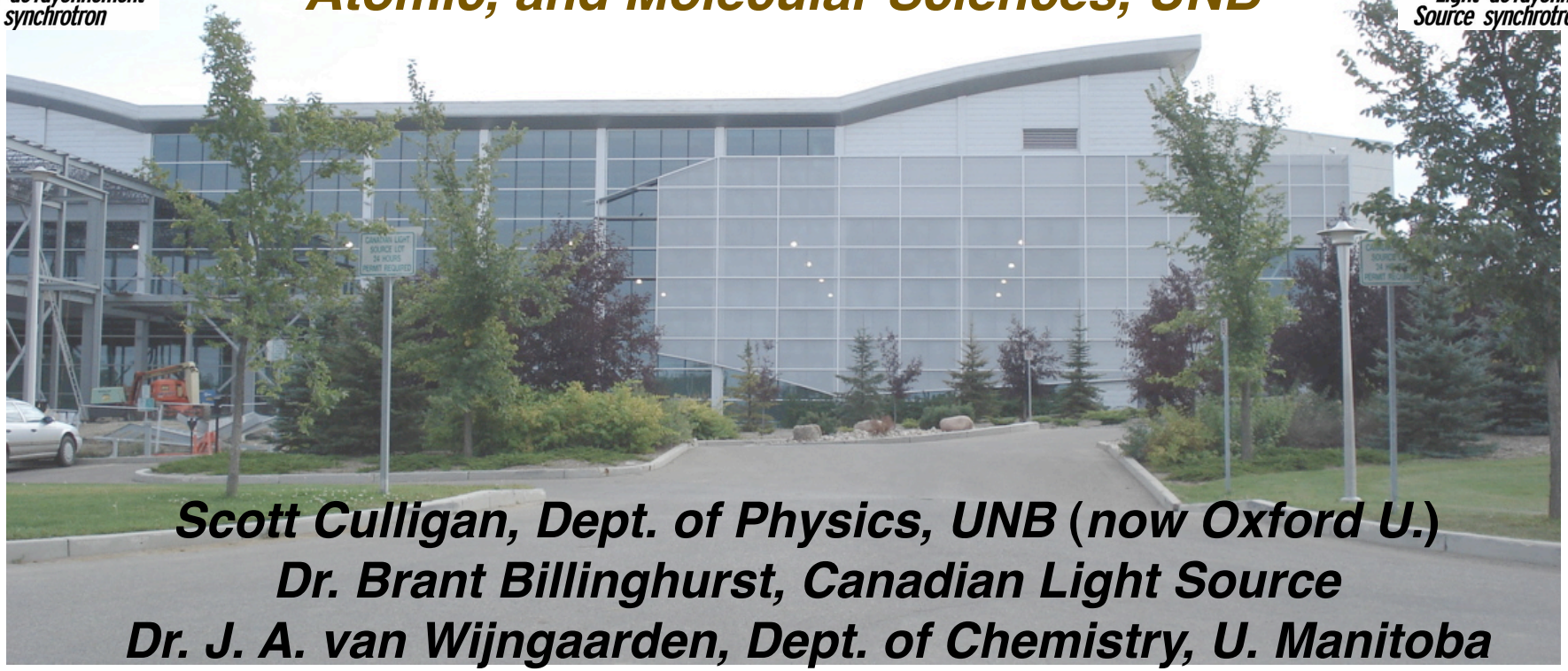

Scott Culligan, Dept. of Physics, UNB (now Oxford U.)
Dr. Brant Billinghurst, Canadian Light Source
Dr. J. A. van Wijngaarden, Dept. of Chemistry, U. Manitoba

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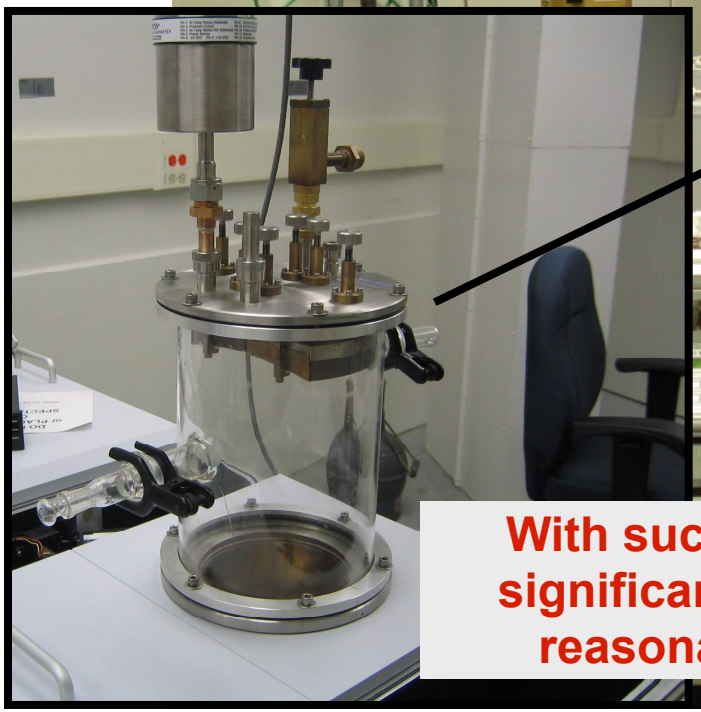
Bruker IFS 125HR high-resolution Fourier transform spectrometer
- 10 m path difference
- resolution of 0.001 cm^{-1}



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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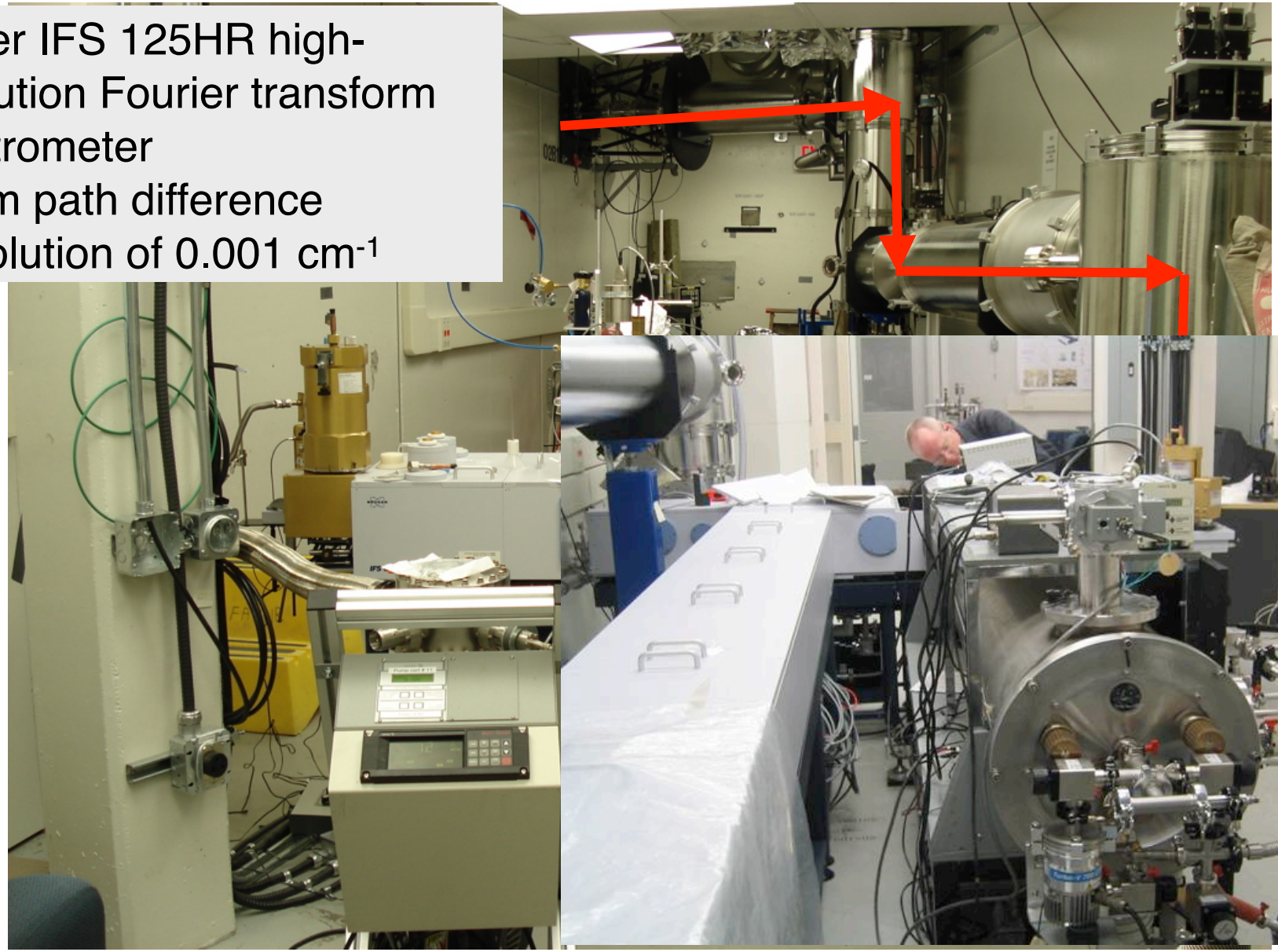
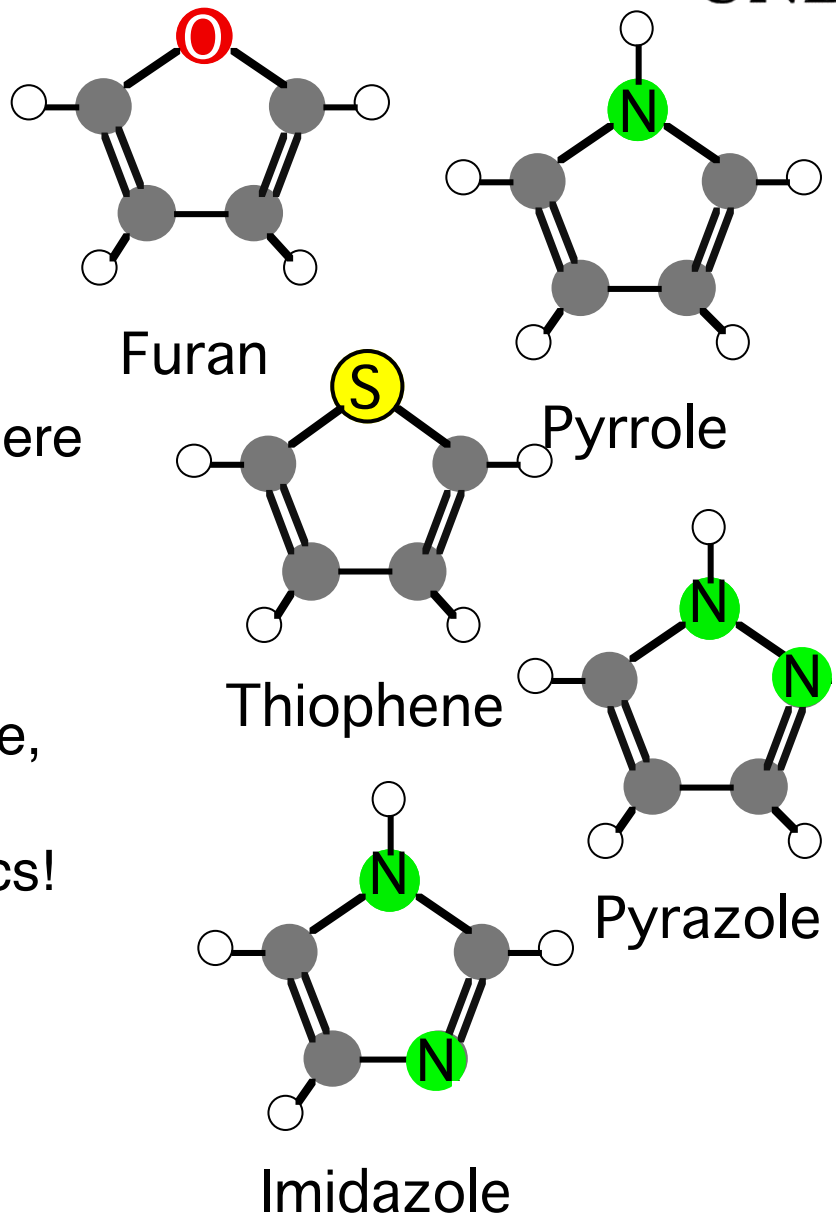
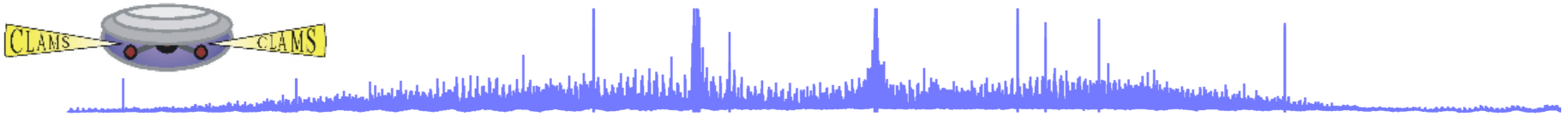


Simple 5-membered rings are large enough to have dense, complex spectra, but are easy to handle.

The molecules often absorb strongly just where we are seeing the greatest synchrotron advantage.

We have worked on pyrrole, furan, thiophene, pyrazole, and imidazole. They have been a great introduction to asymmetric rotor physics!





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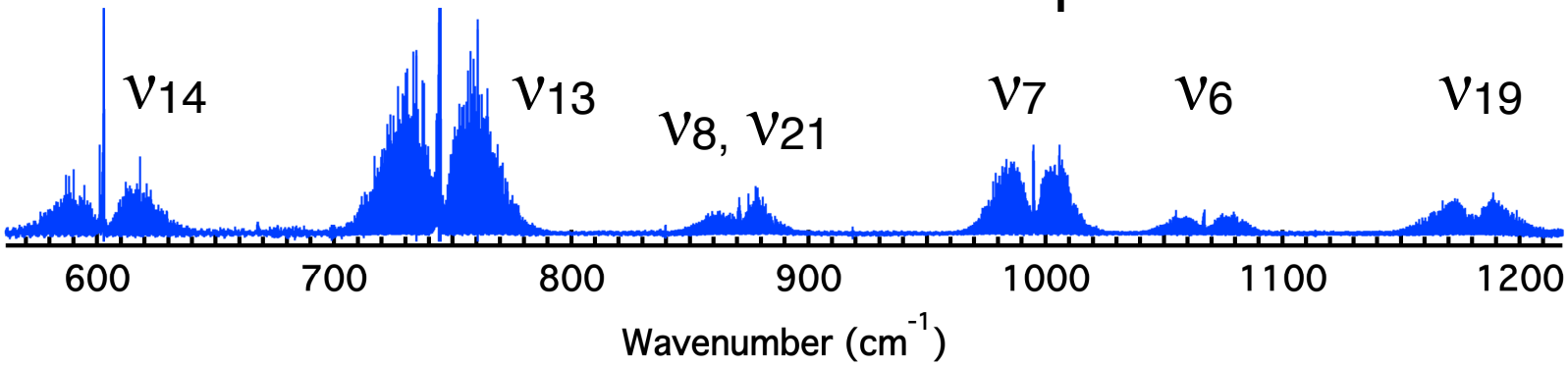
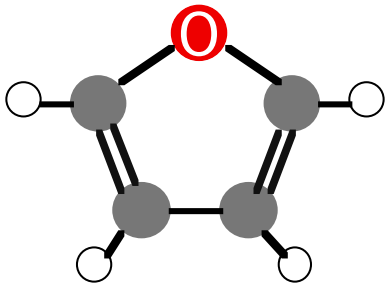
Furan: overview of our spectrum





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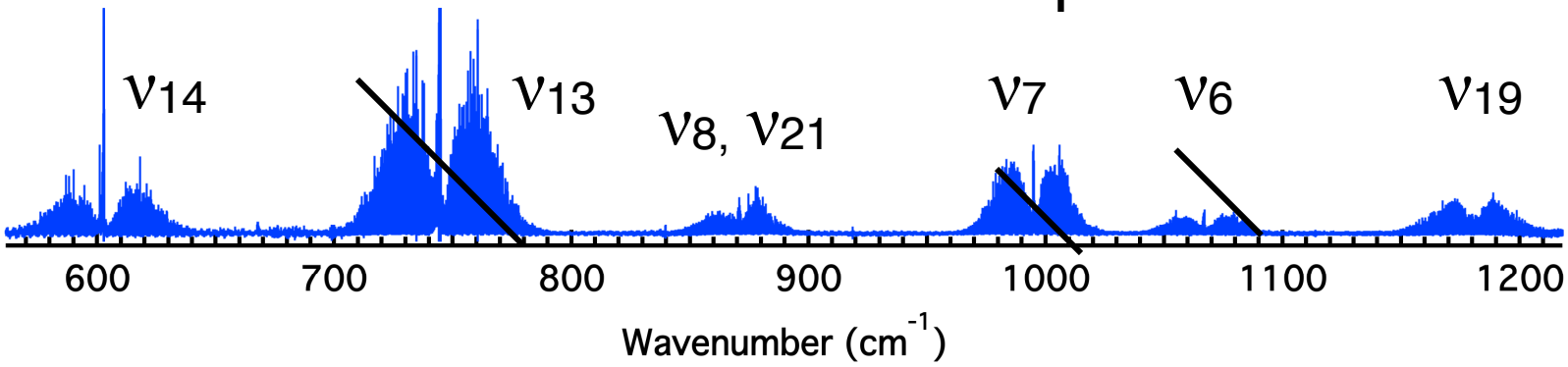

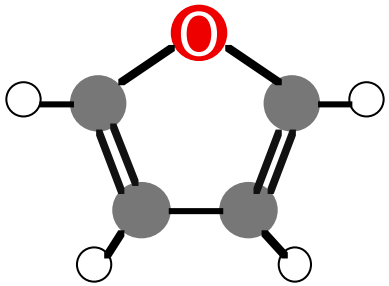

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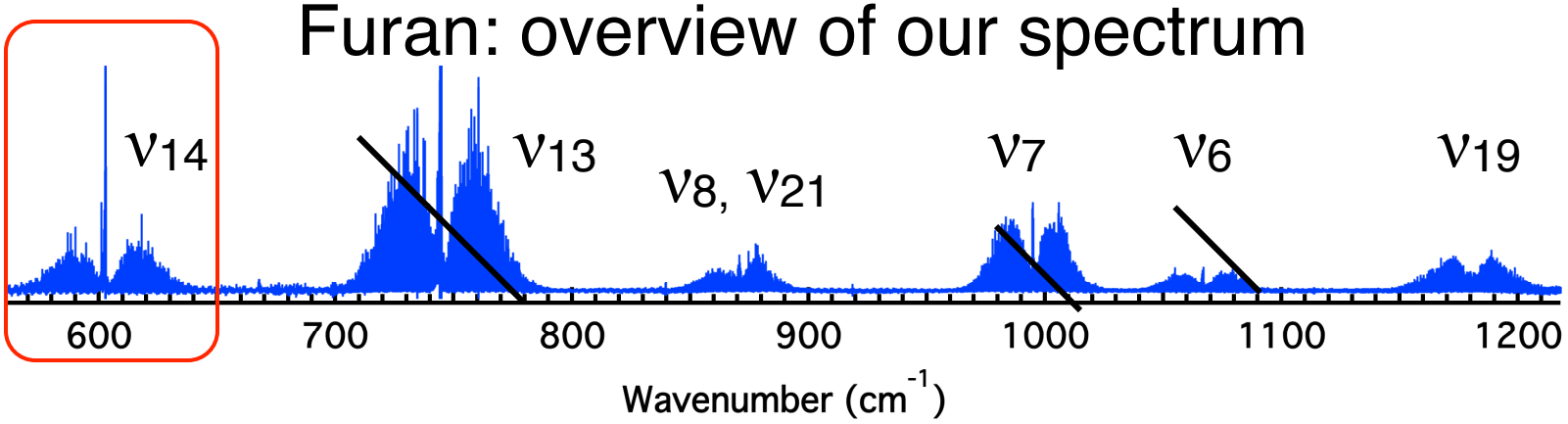

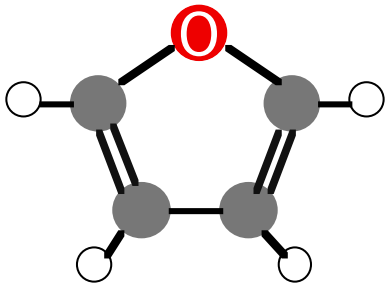

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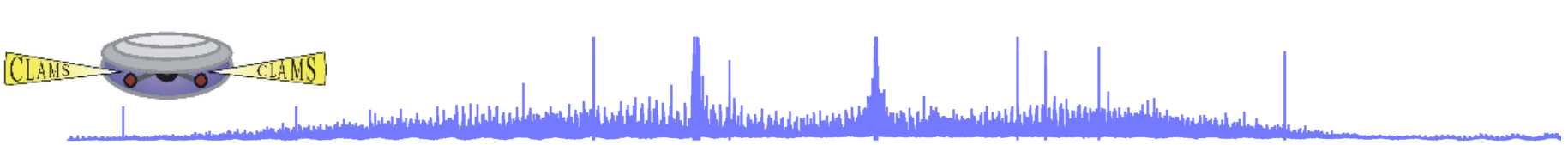

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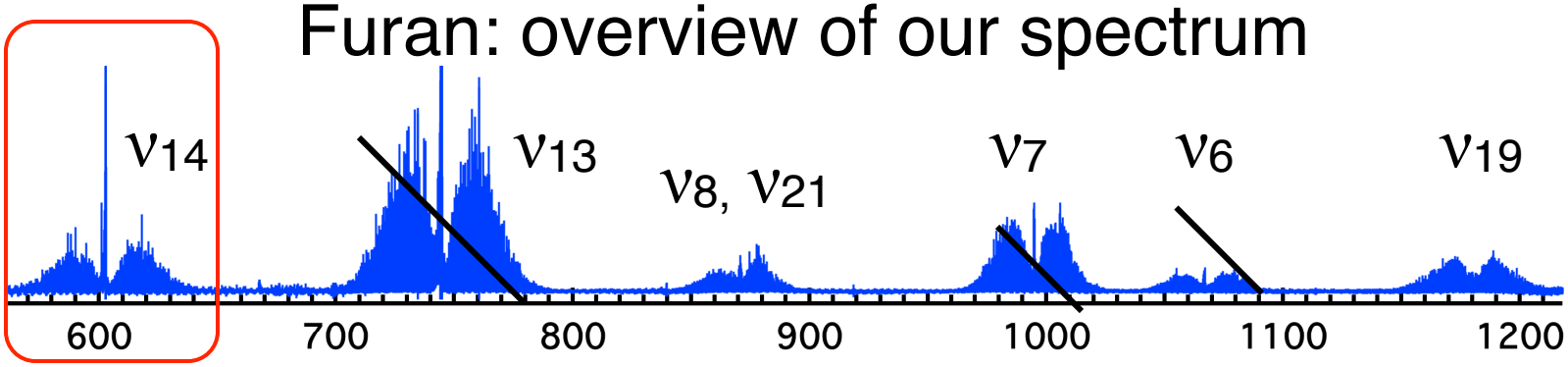

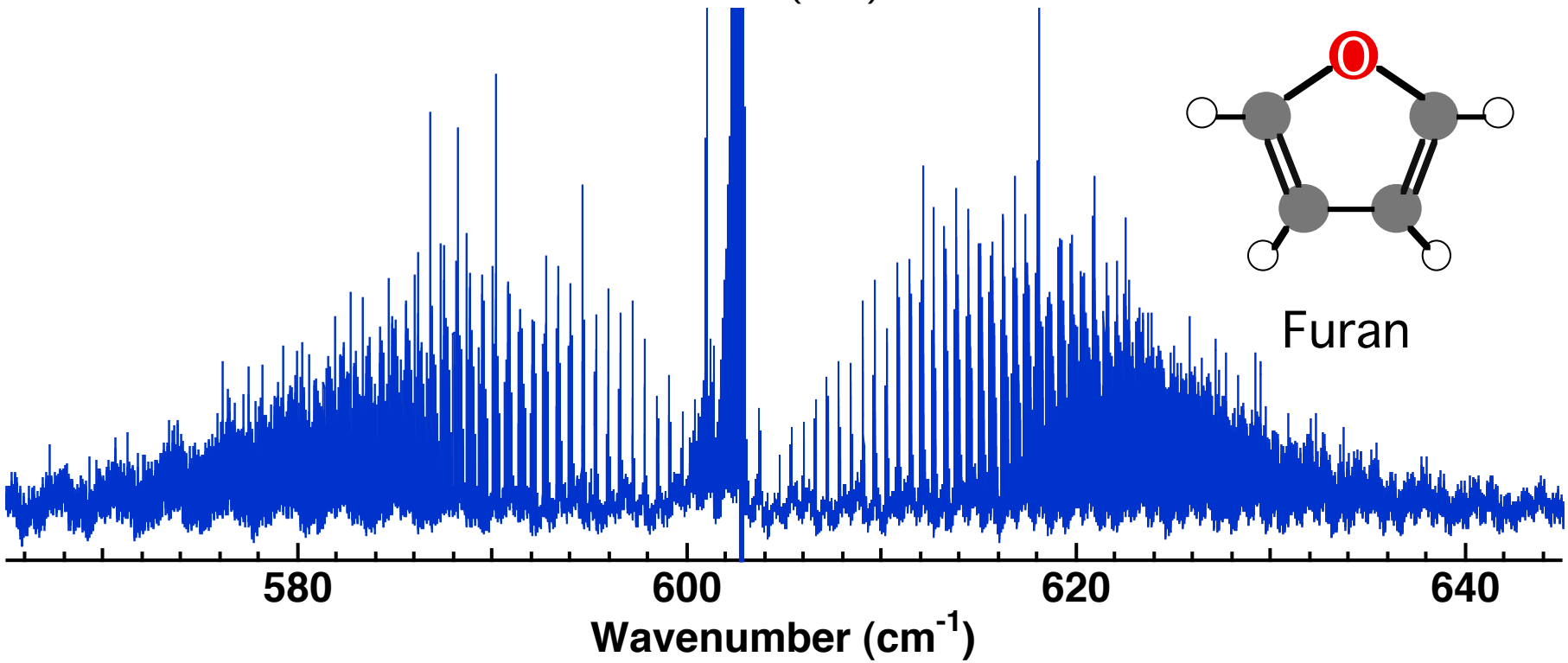

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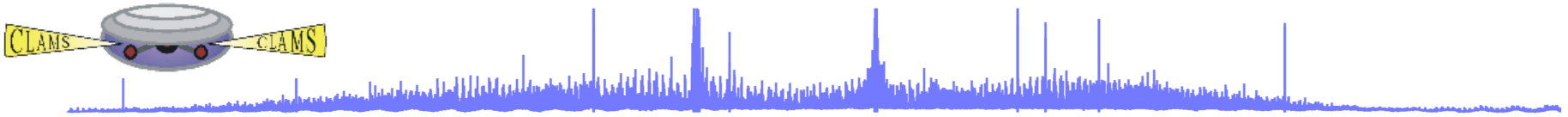

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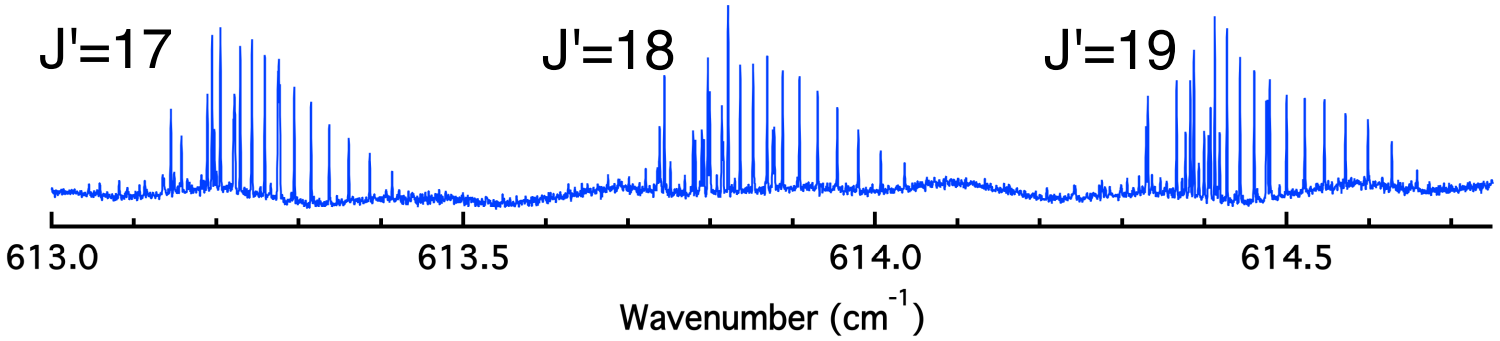

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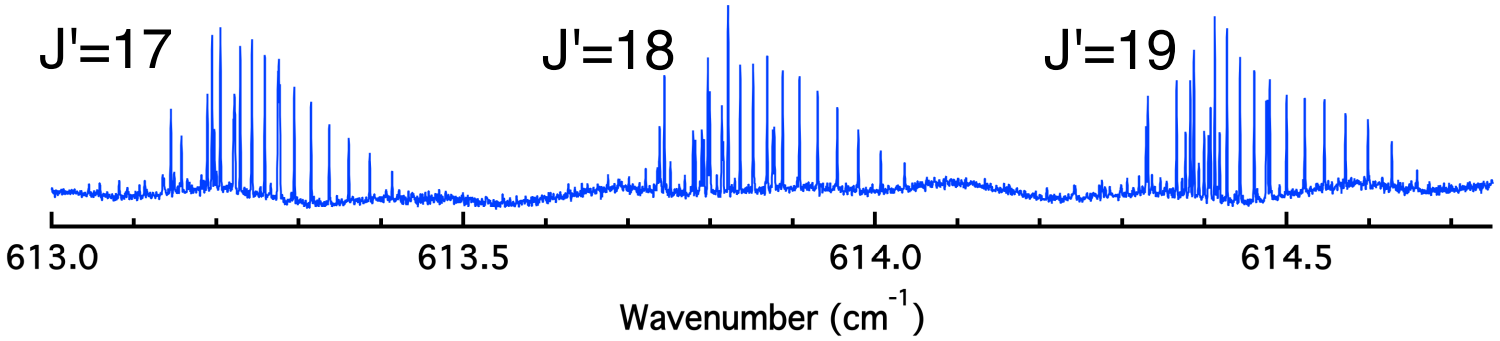

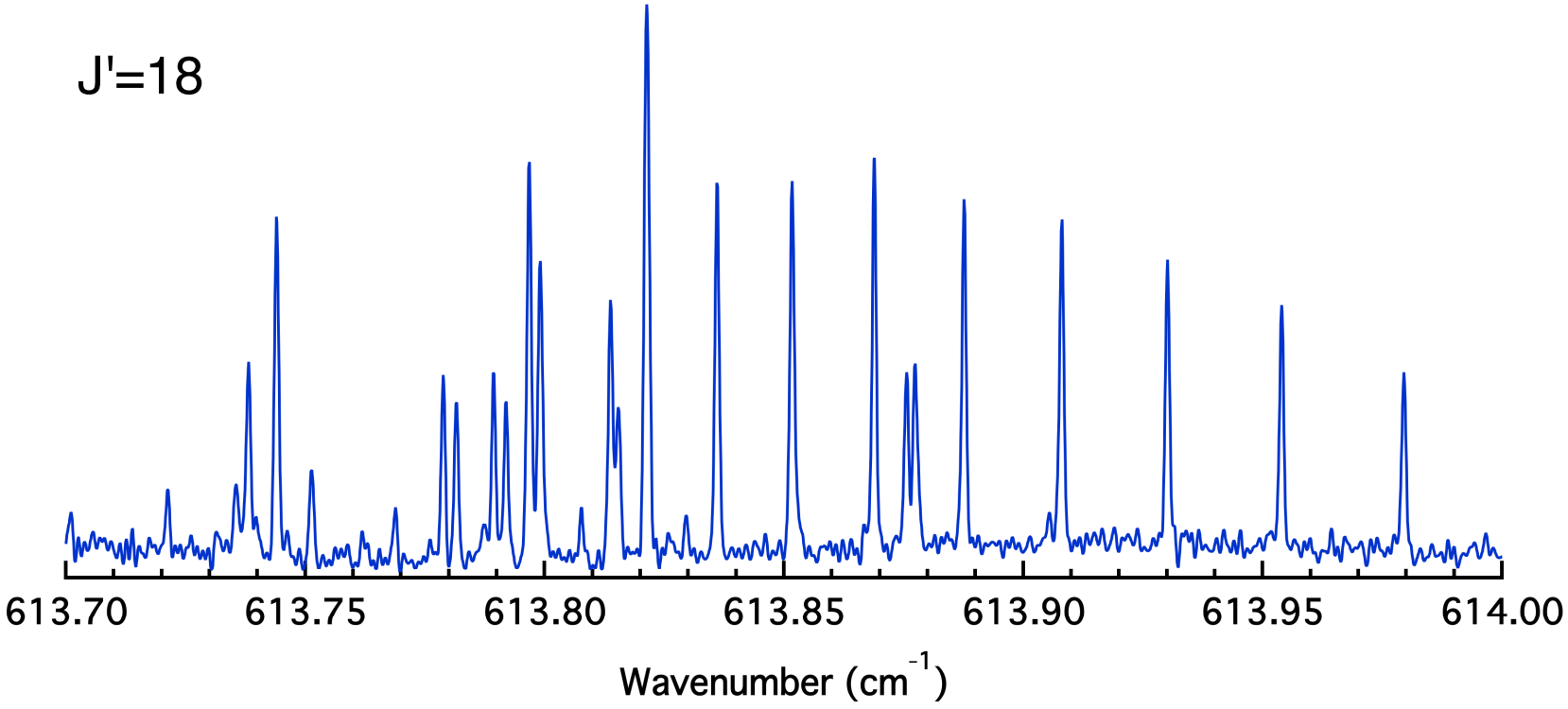

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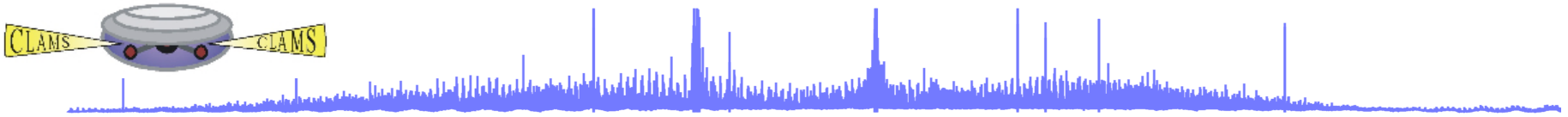
CLAMS
CLAMS

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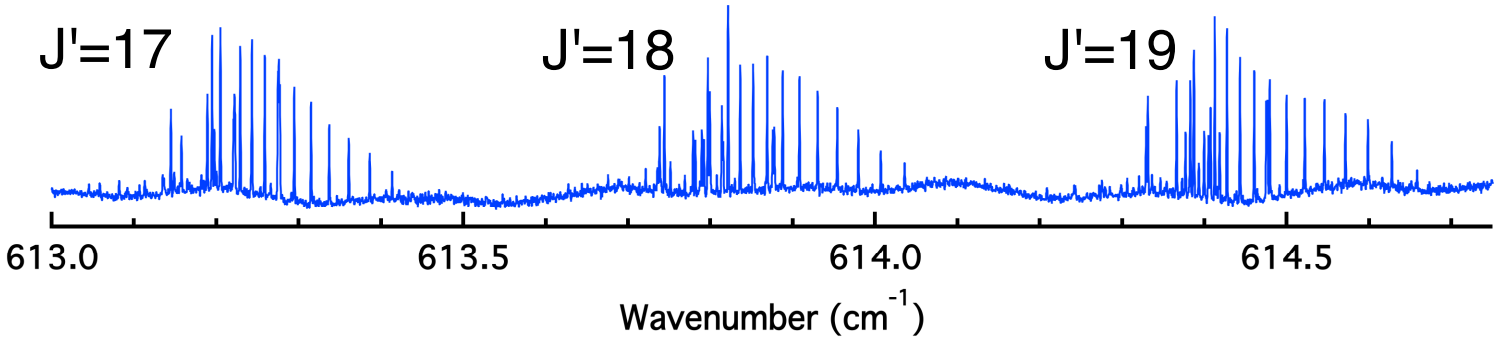
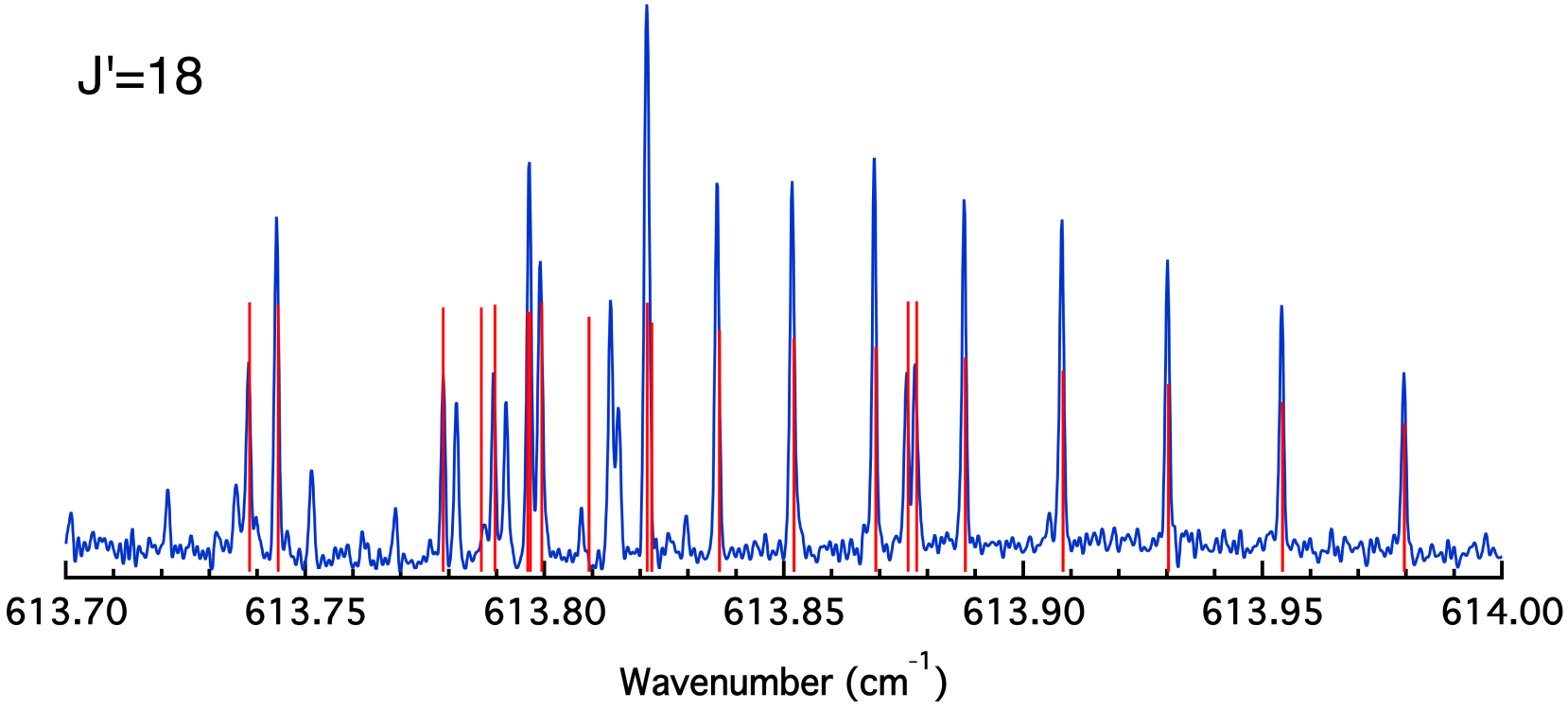
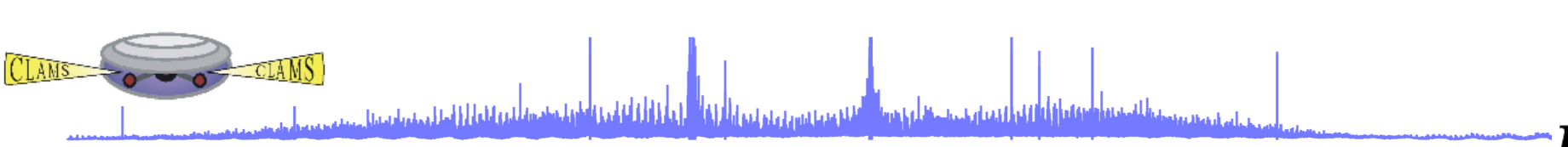

J'=17
J'=18
J'=19
613.0
613.5
614.0
614.5
Wavenumber (cm-1)


J'=18
613.70
613.75
613.80
613.85
613.90
613.95
614.00
Wavenumber (cm-1)



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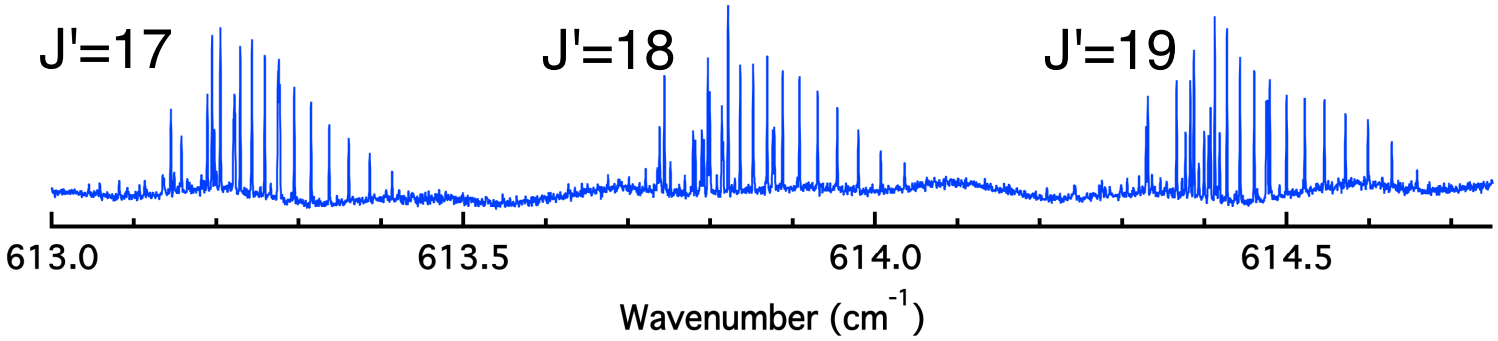

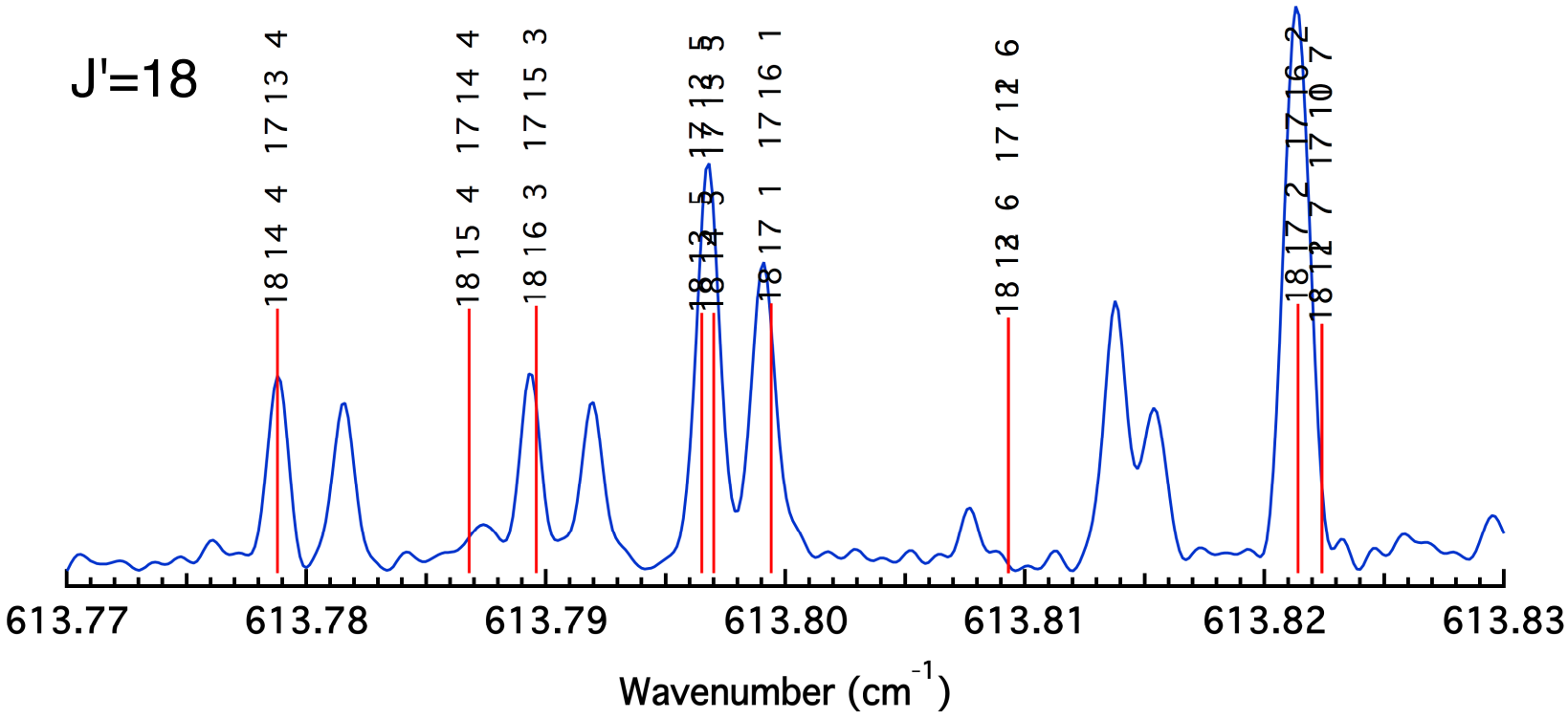

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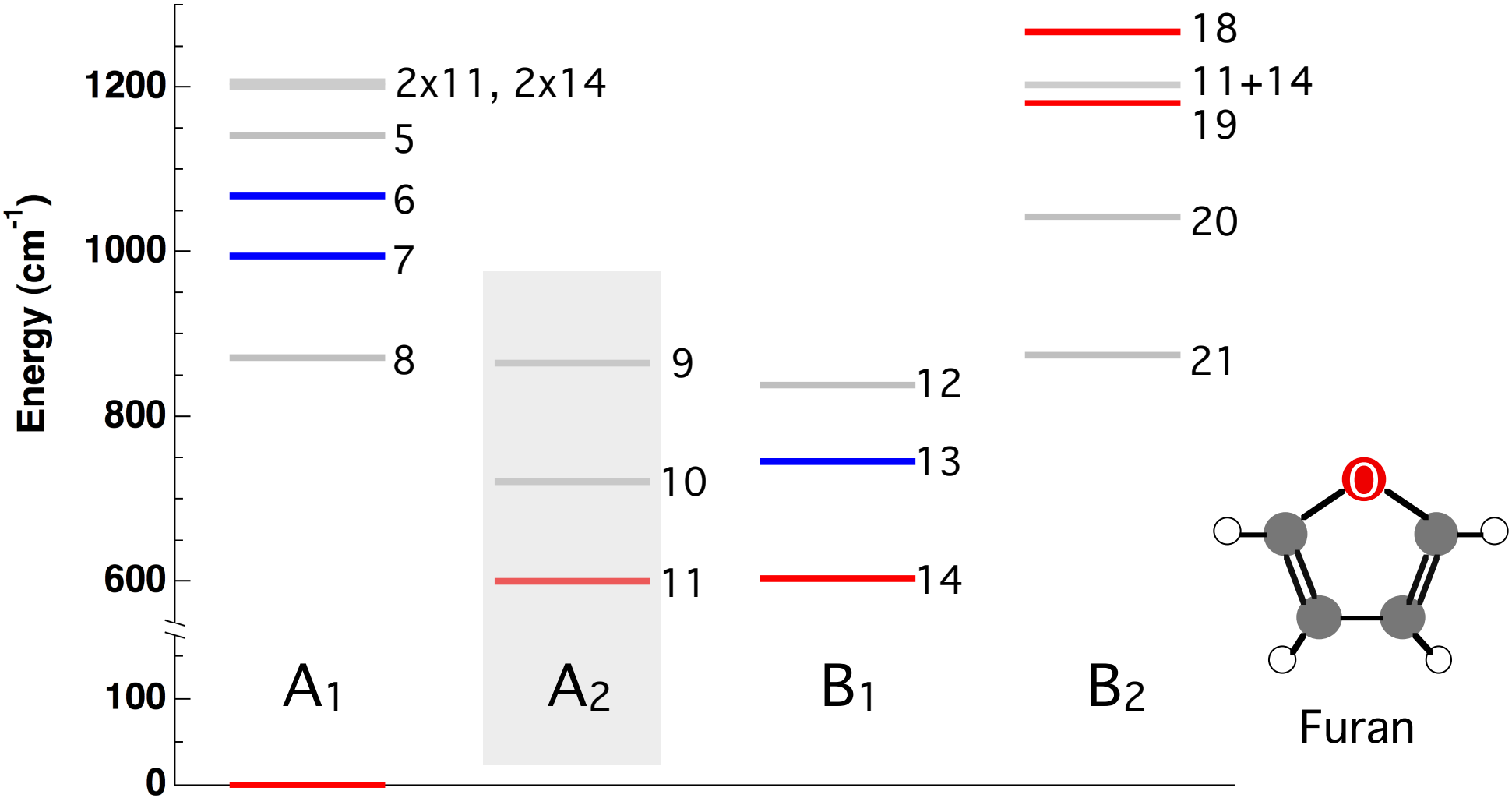
Furan: vibrational energy level structure



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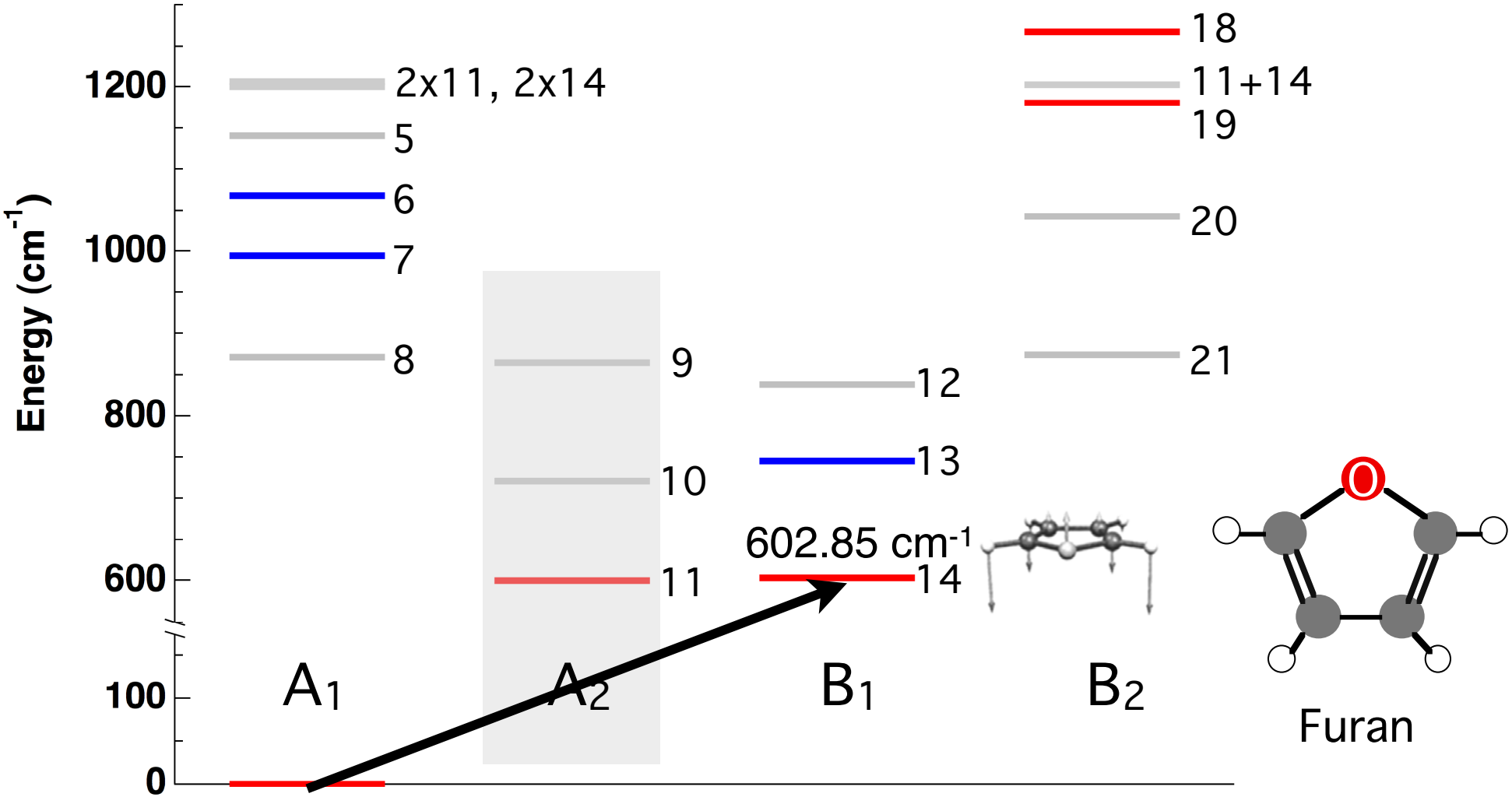

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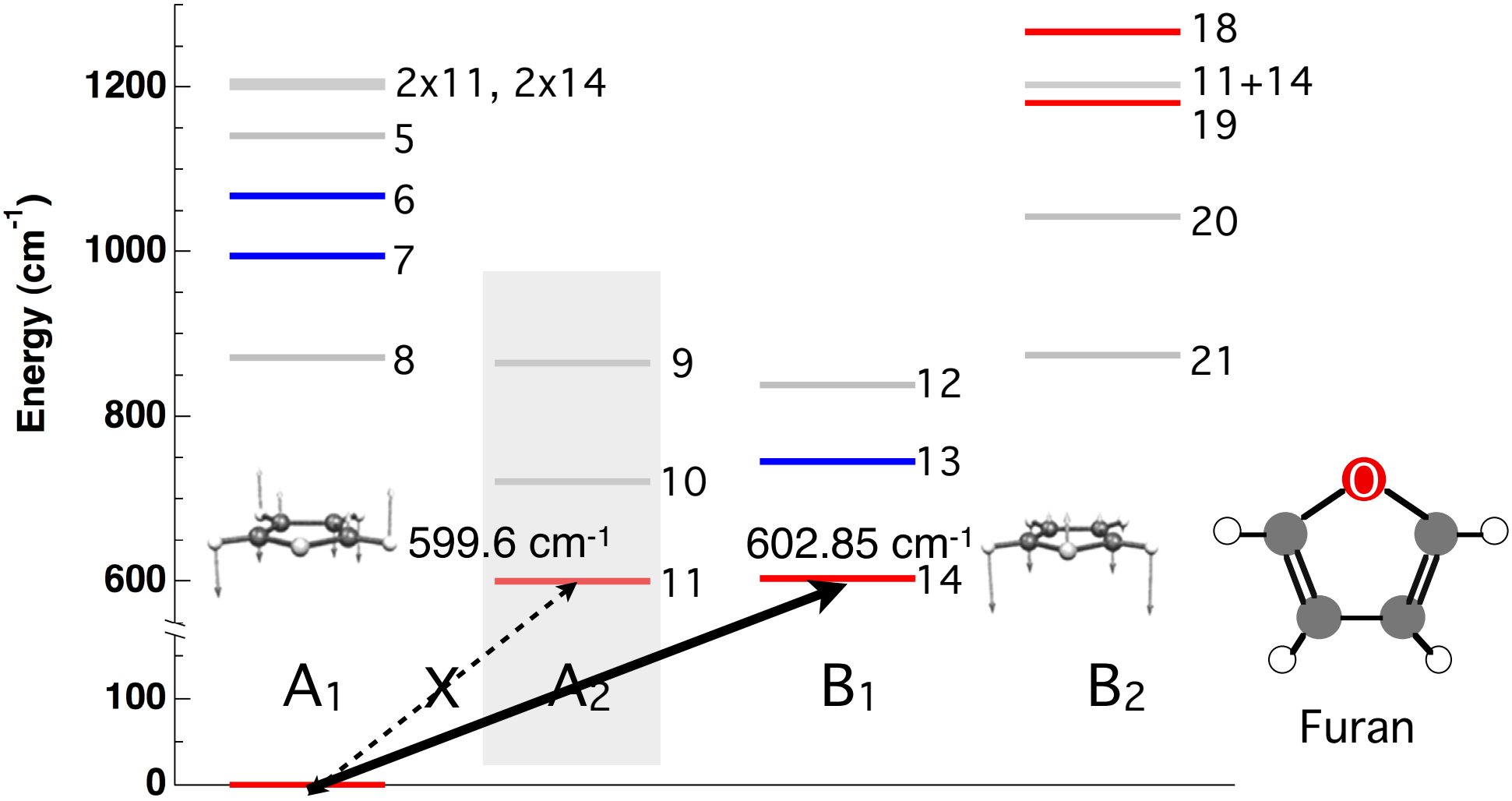

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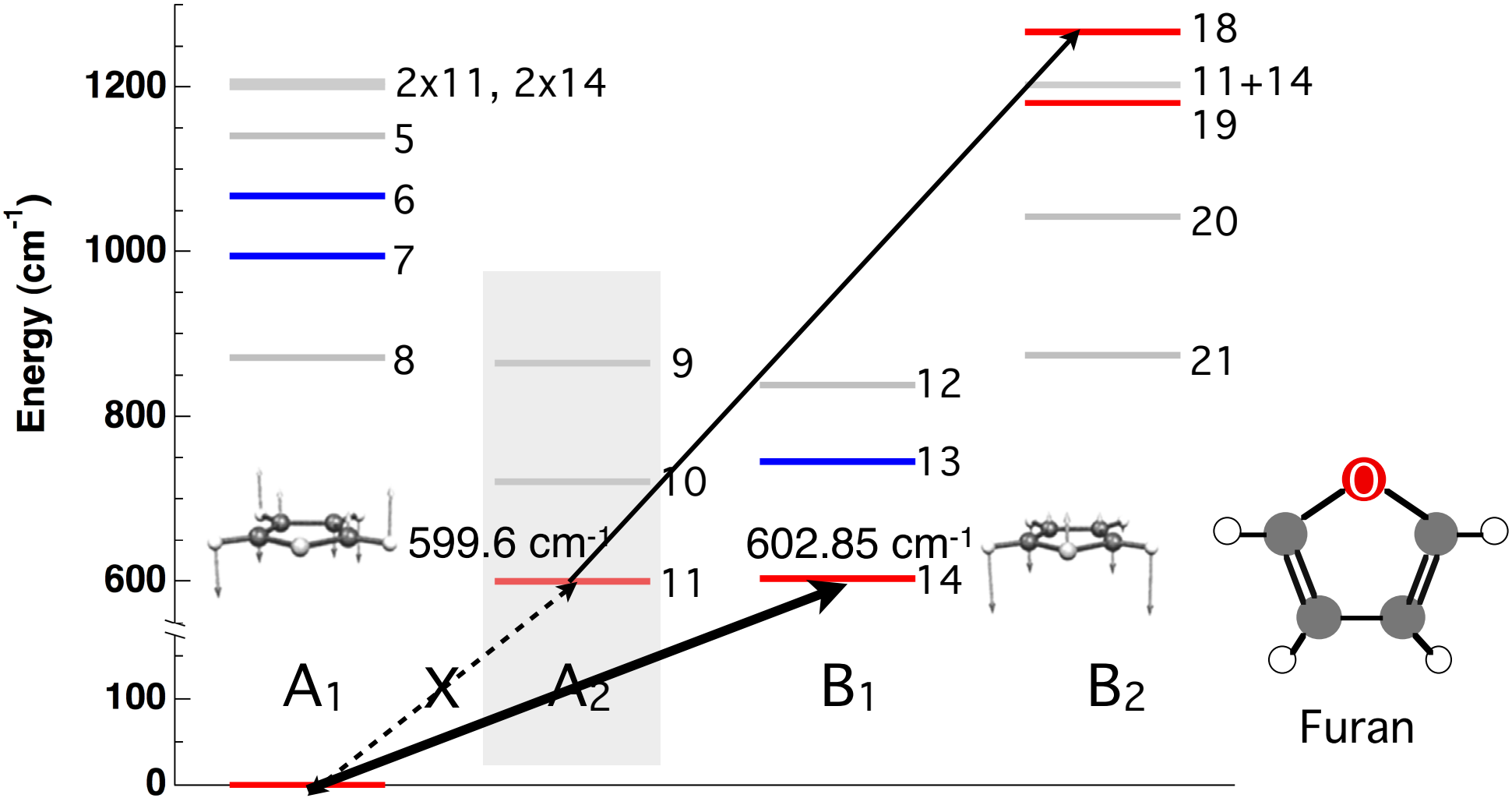

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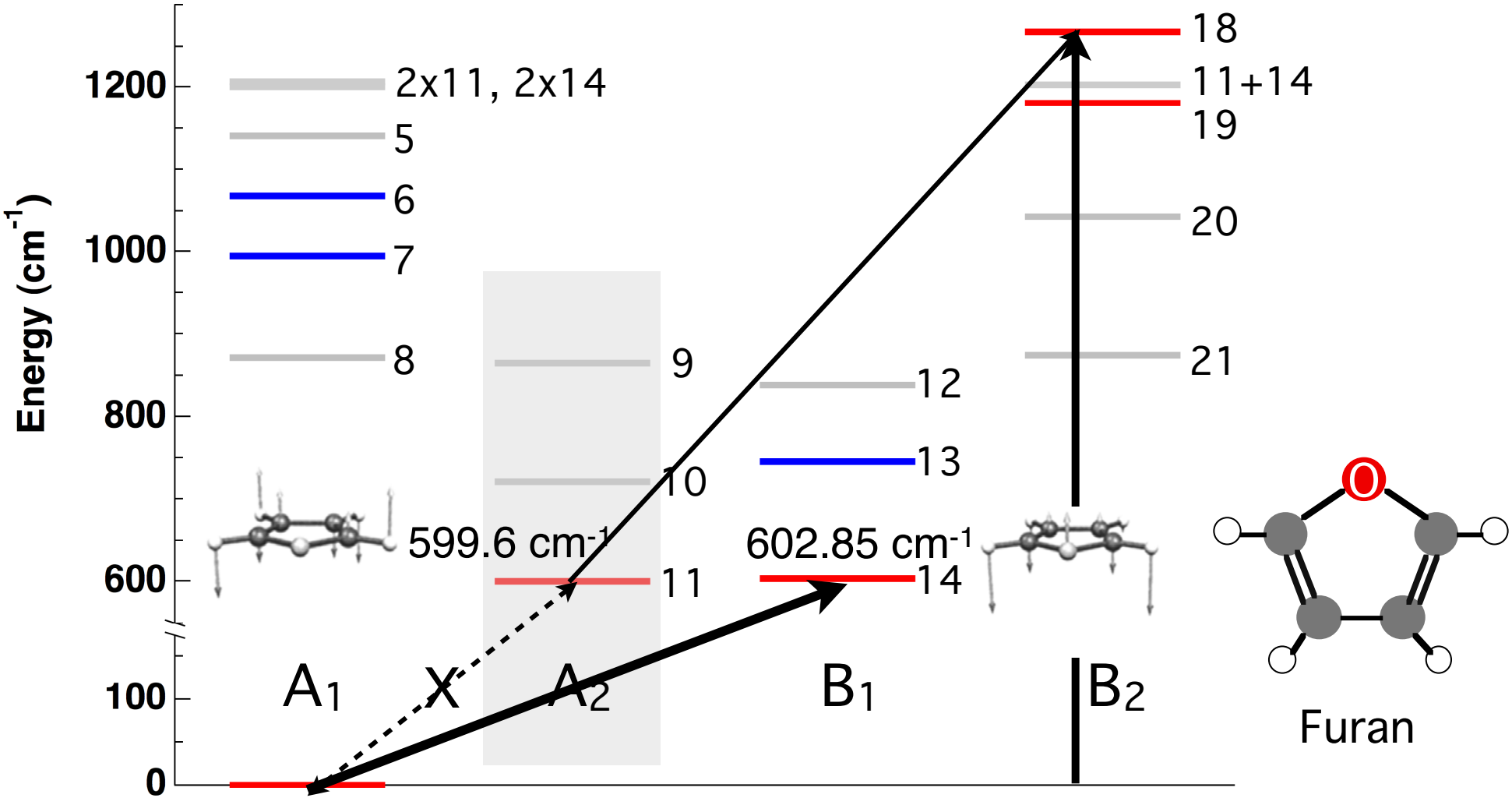

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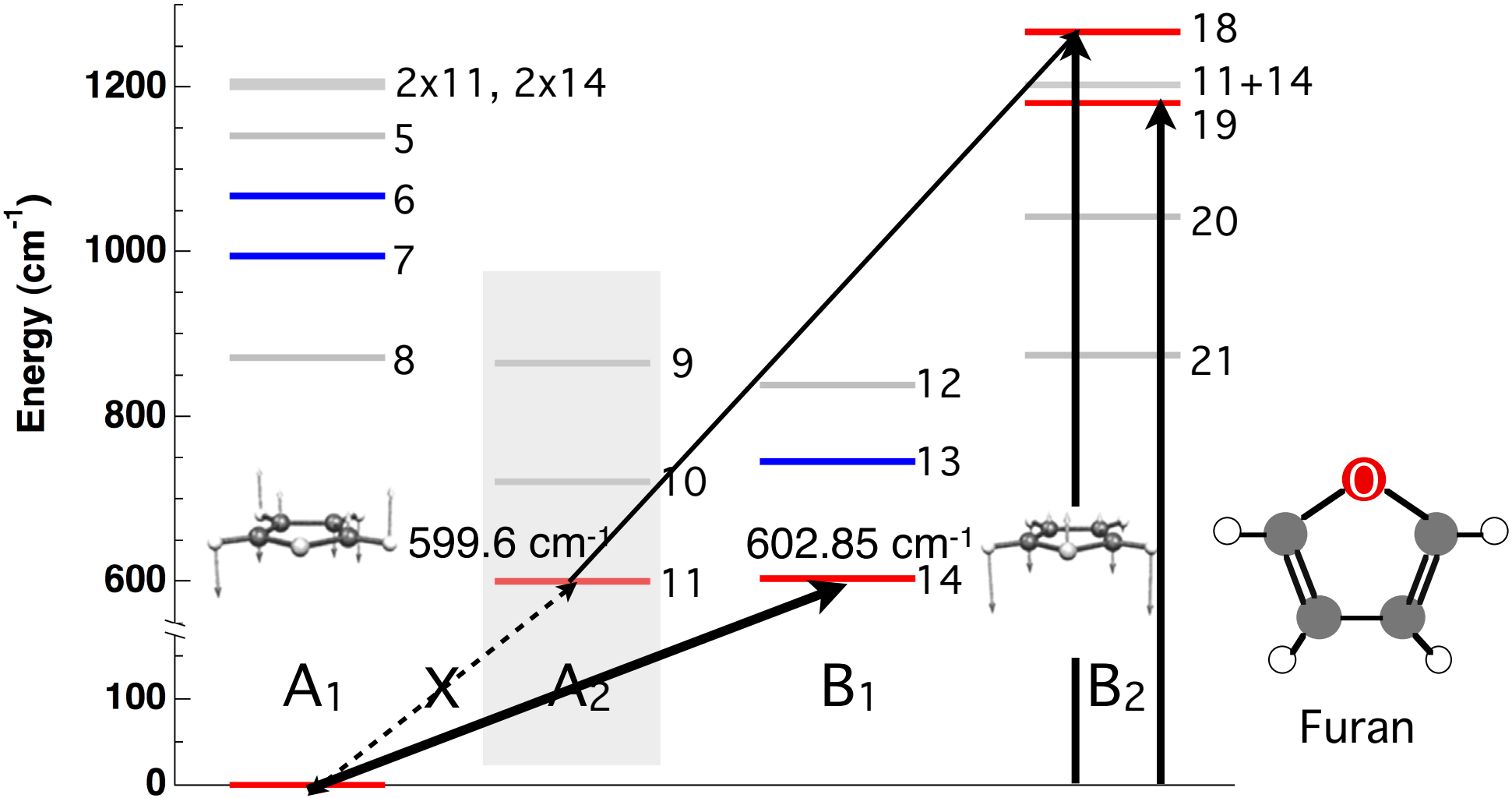

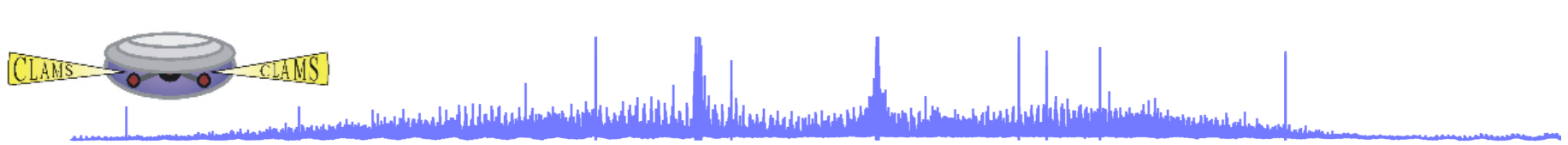

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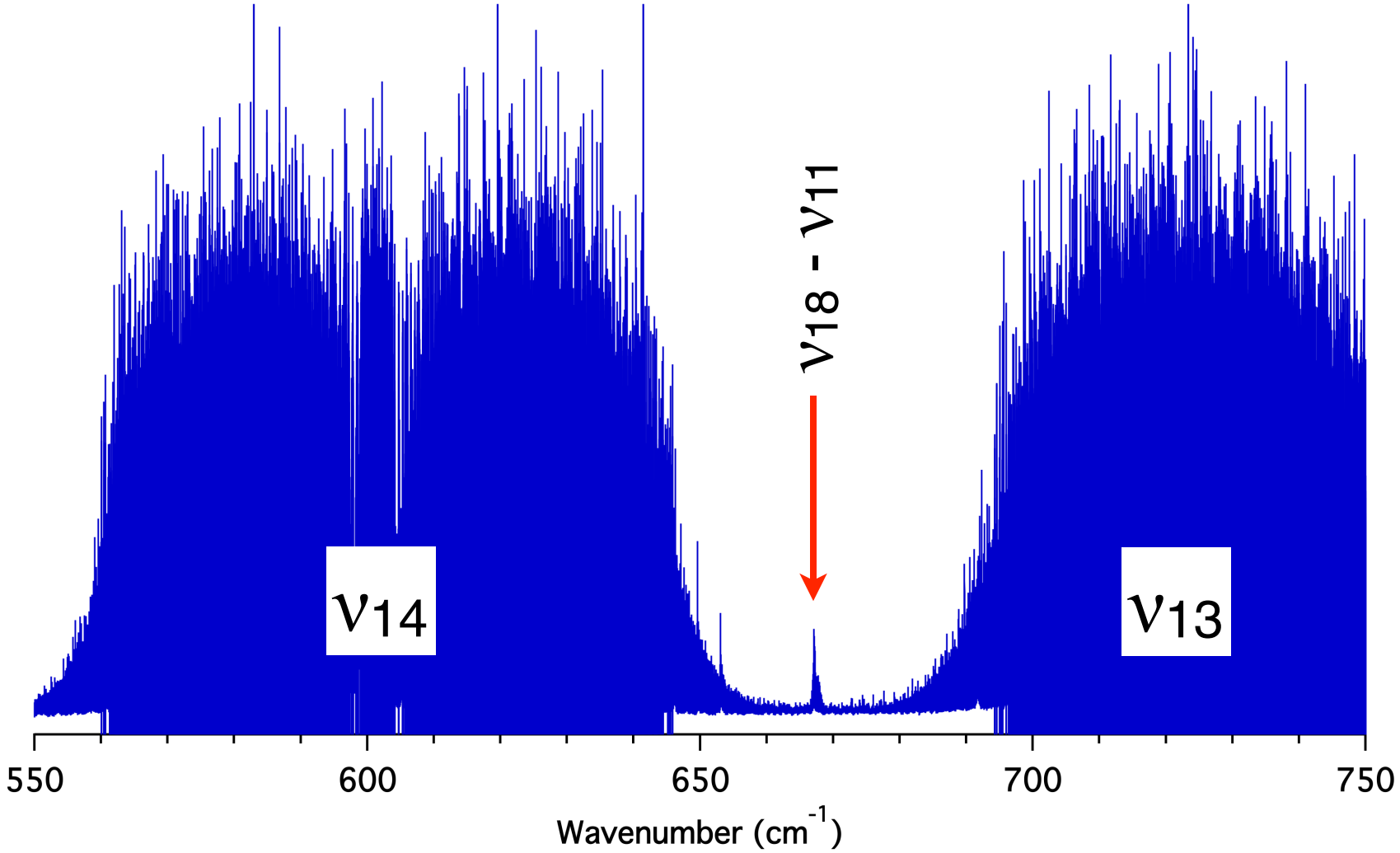
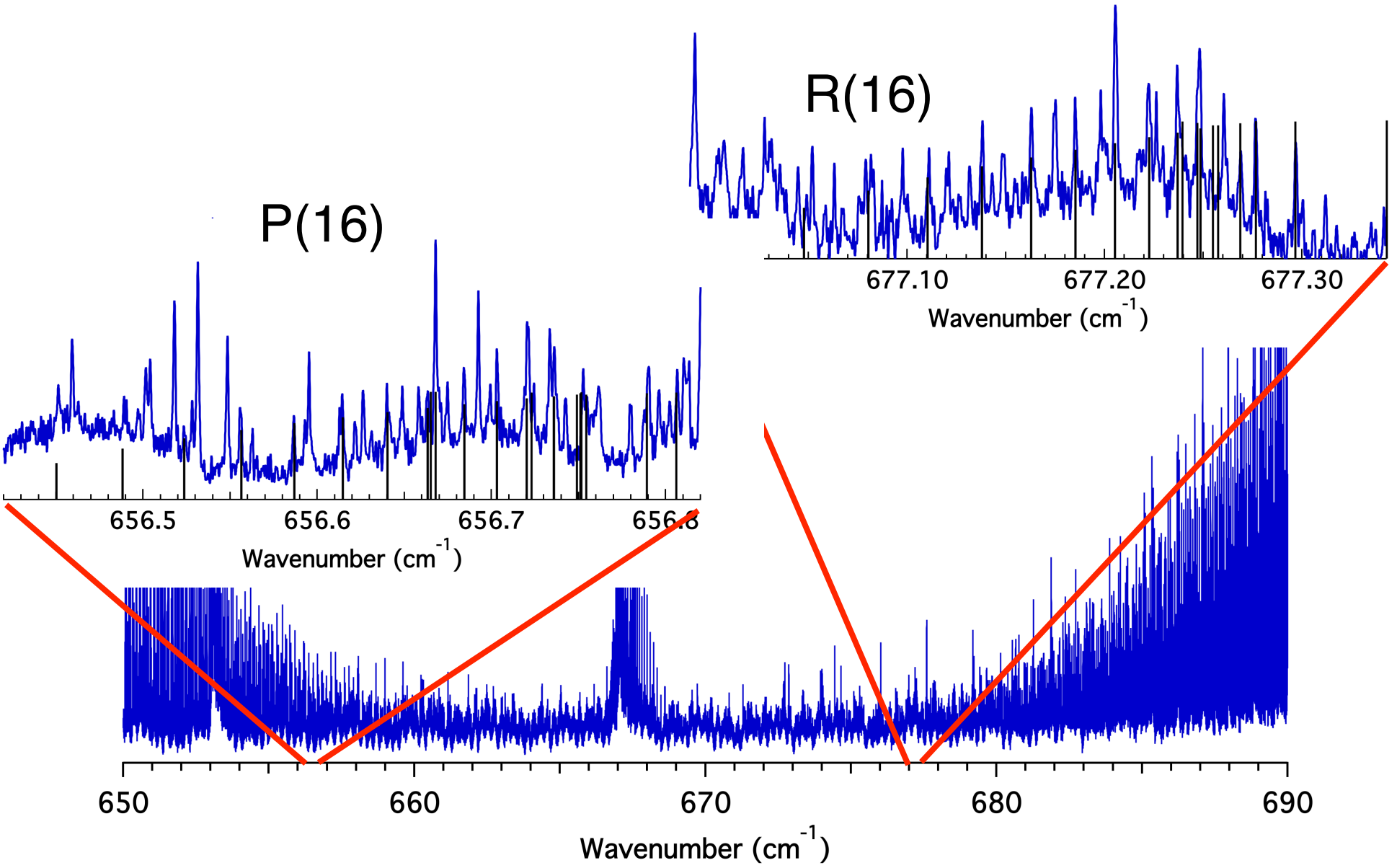
Furan: the ν_{18} - ν_{11} transition




R(16)
677.10
677.20
677.30
Wavenumber (cm-1)
P(16)
656.5
656.6
656.7
656.8
Wavenumber (cm-1)
650
660
670
680
690
Wavenumber (cm-1)

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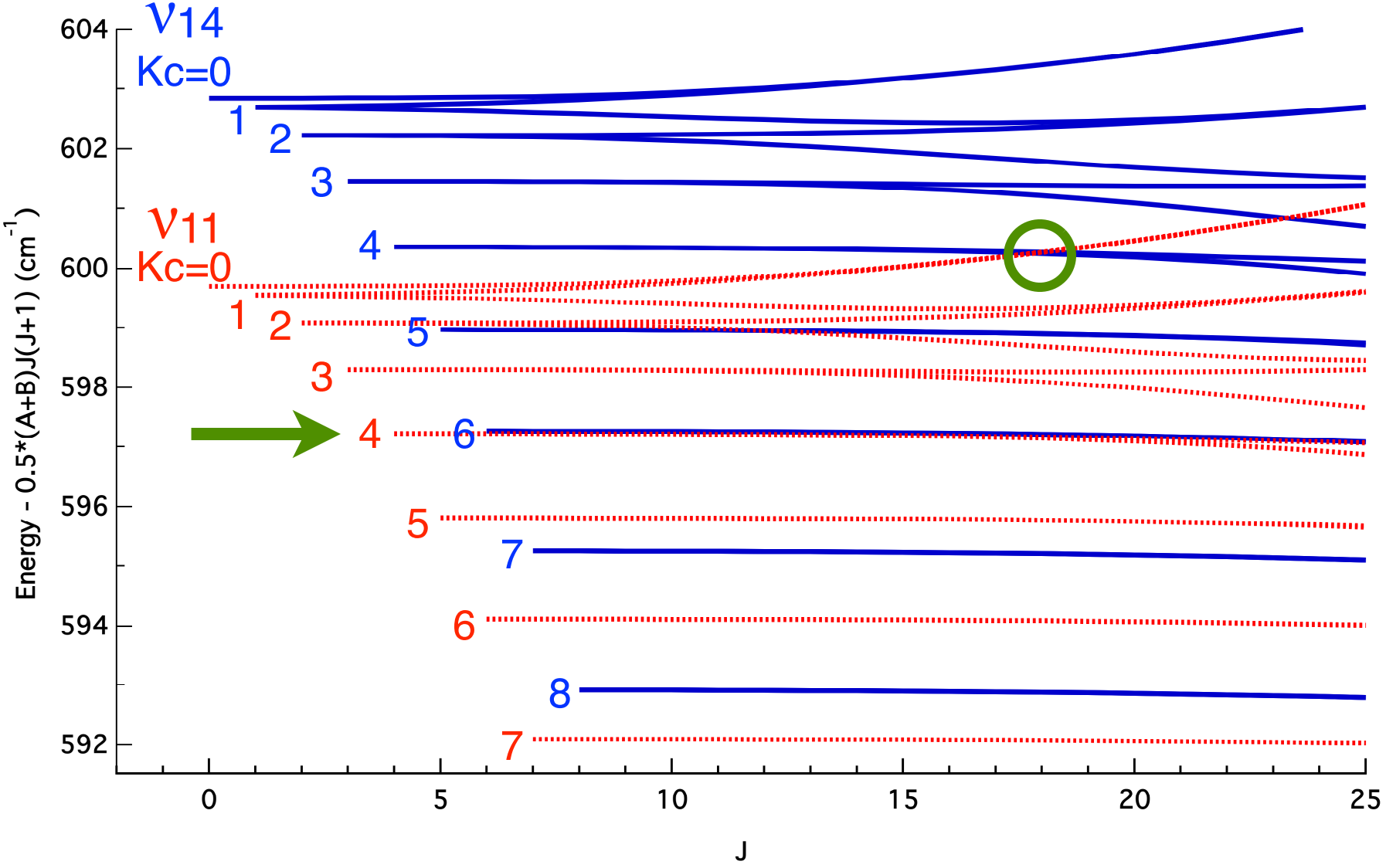
Furan: Reduced energies of the ν_{11} and ν_{14} levels



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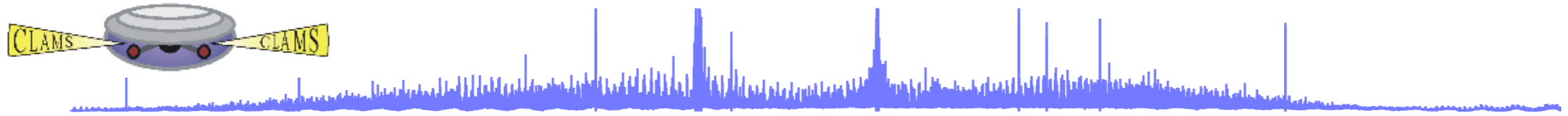
Fit to a Watsonian, *A*-reduction, III^r representation. All values in cm^{-1}.

	Ground state	ν_{14}	ν_{11}	ν_{18}	ν_{19}
T_0		602.8445069(94)	599.693665(26)	1266.750171(15)	1180.836732(13)
A	0.3151220975(74)	0.314310966(43)	0.31432994(30)	0.31529597(41)	0.31464163(24)
B	0.3084381338(75)	0.307602792(42)	0.30779360(29)	0.30884839(38)	0.30803831(19)
C	0.1558019445(69)	0.155846701(23)	0.155870786(60)	0.155686313(35)	0.155512886(30)
$D_J \times 10^8$	11.11682(66)	10.99943(92)	11.1629(40)	11.2596(44)	11.1412(31)
$D_{JK} \times 10^8$	-17.5584(11)	-17.0619(16)	-17.454(11)	-17.8158(84)	-17.6731(60)
$D_K \times 10^8$	7.6175(12)	7.2489(18)	7.4746(96)	7.7242(47)	7.6898(37)
$d_1 \times 10^8$	-0.17487(57)	-0.2147(11)	-0.5716(60)	-0.797(21)	-0.8608(76)
$d_2 \times 10^8$	0.1440(11)	0.1582(12)	0.1429(31)	0.1711(89)	0.1737(39)
$H_{JK} \times 10^{13}$	-1.738(46)				
$H_{KJ} \times 10^{13}$	1.746(60)				
$C_{Cor} \times 10^4$		1.15332(44)			

RMSE: 0.0001 cm^{-1}



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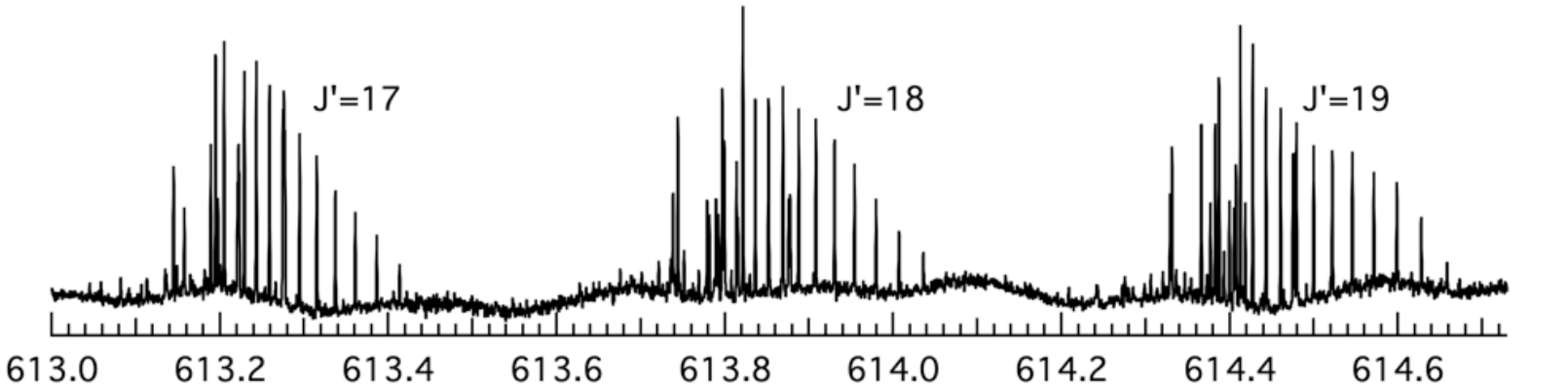

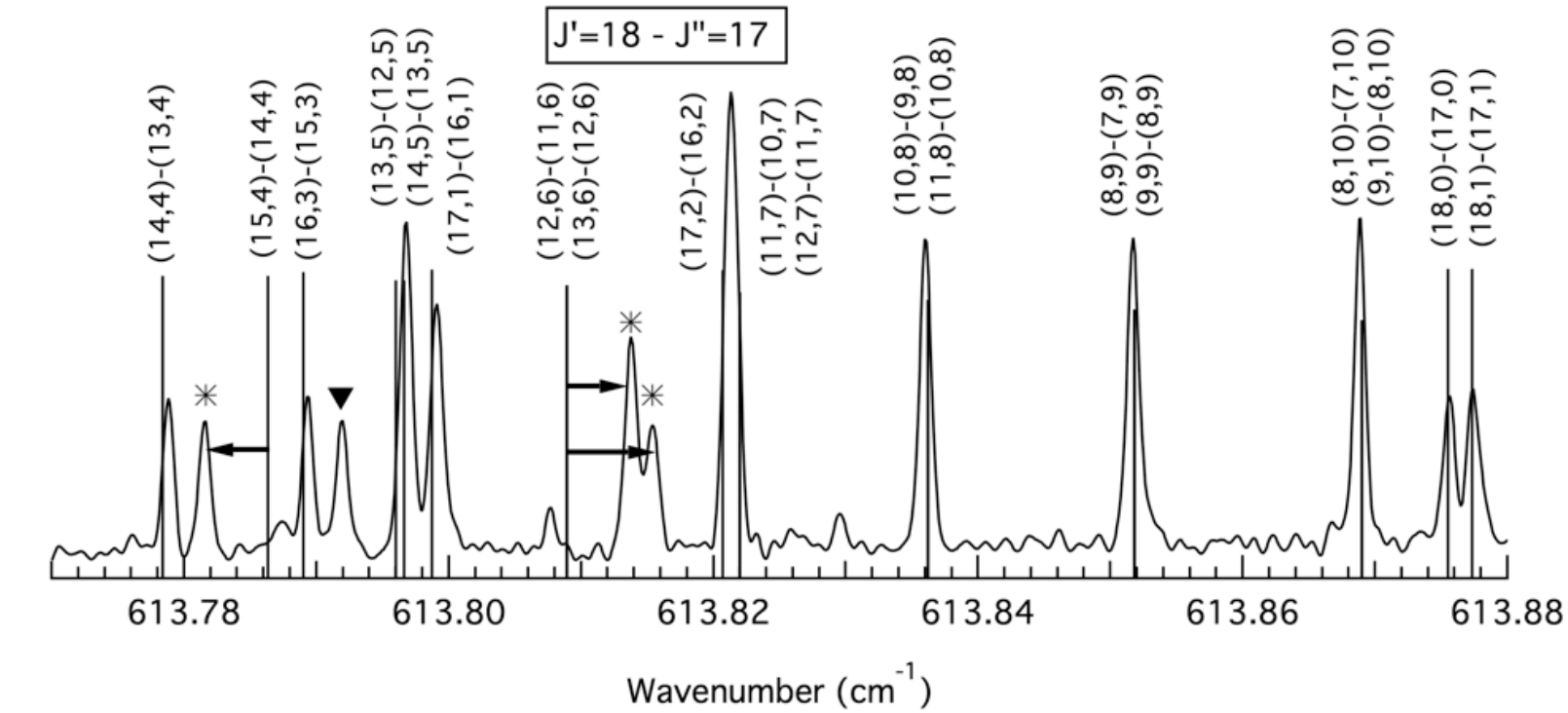

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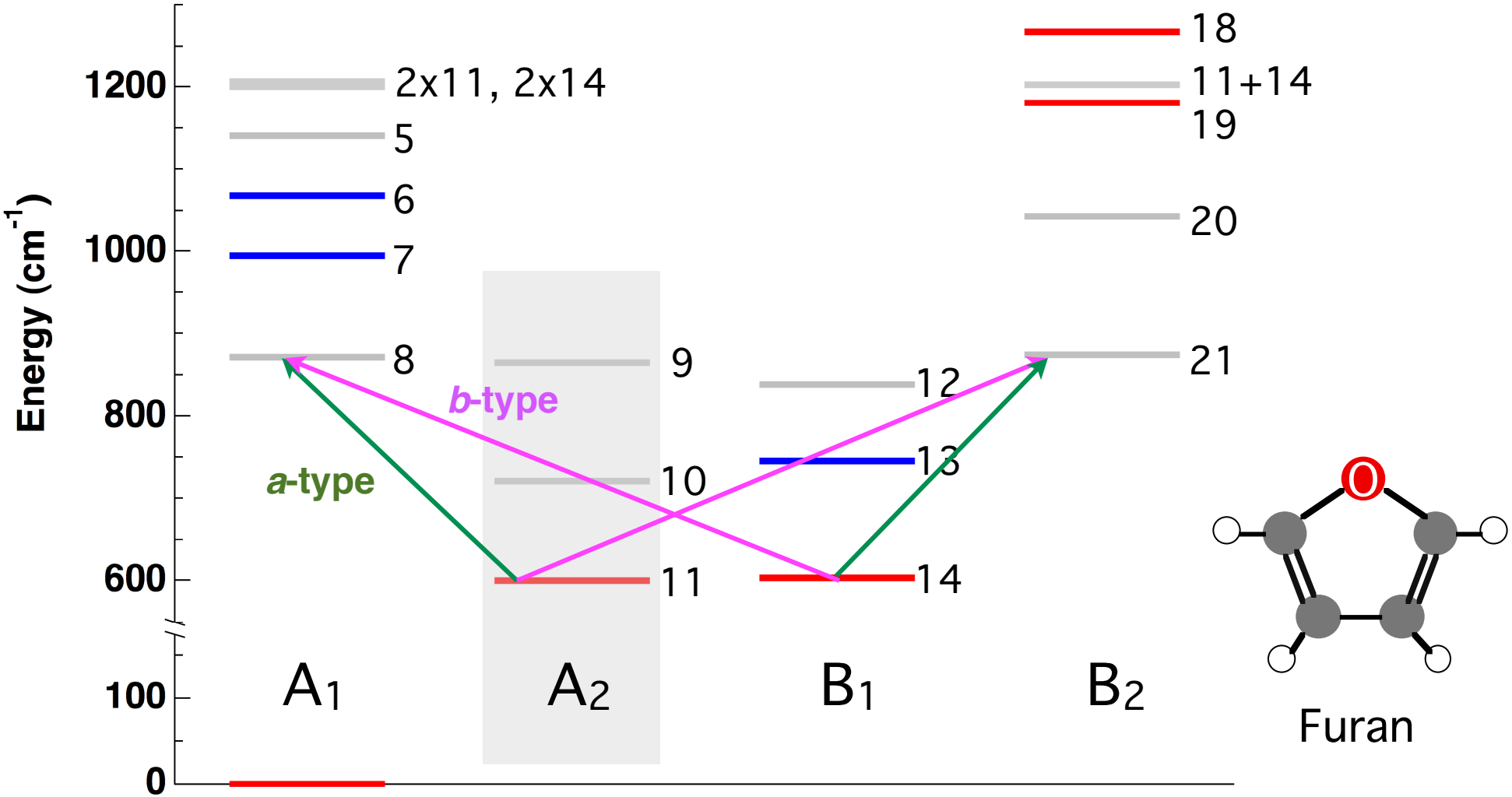
Possible cause of the second-order Corilois resonance?



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What we've learned so far...

- Perturbations in the ν_{11} and ν_{14} levels of furan are the result of a type-c Coriolis interaction.
- The second-order interaction with $\Delta K_c = \pm 2$ is the most obvious due to an accidental near-degeneracy of $K_c = 6$ lines in the ν_{14} state with $K_c = 4$ levels in the ν_{11} state.
- This analysis would have been extremely difficult without the advantage provided by far-IR synchrotron radiation coupled to a FT spectrometer run at very high resolution.

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

Synchrotron details:
- injections every 8 hours
- max. current of 250 mA, drops to ~150 mA before the next injection.

We run helium-cooled Cu:Ge and Si:bolometer detectors, as well as nitrogen-cooled MCTs

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}.