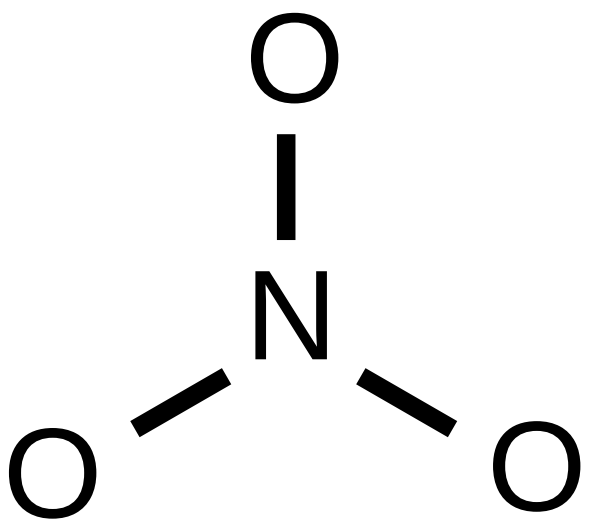
Two-Color Resonant Four-Wave Mixing Spectroscopy of Jet Cooled NO_3 (II)

Masaru Fukushima and Takashi Ishiwata

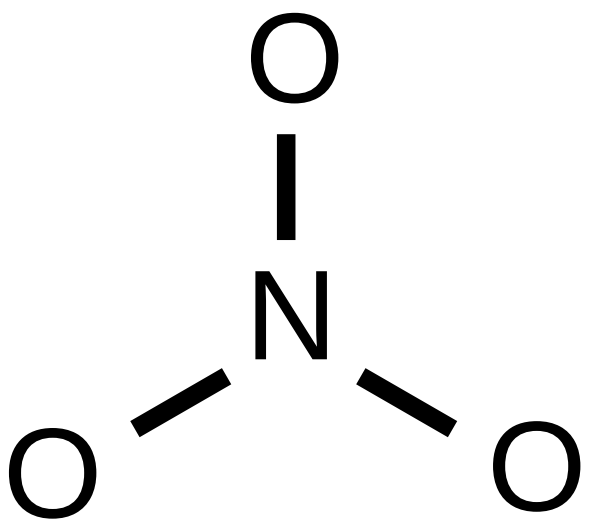
Graduate School of Information Sciences, Hiroshima City University,
Hiroshima 731-3194, Japan

What is NO_3 ?



D_{3h}

What is NO_3 ?



D_{3h}

BF_3

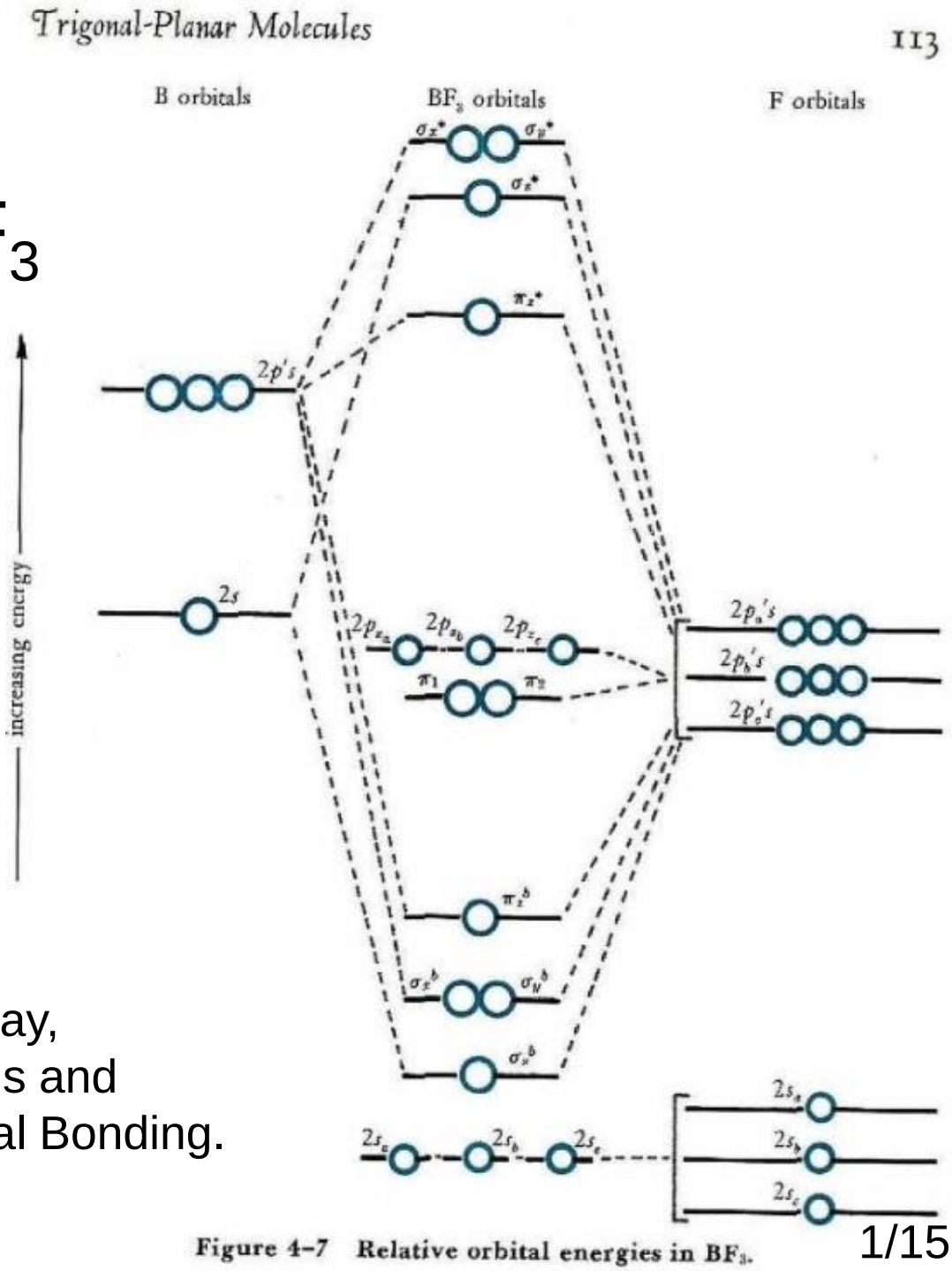


Figure 4-7 Relative orbital energies in BF_3.

H. B. Gray,
Electrons and
Chemical Bonding.

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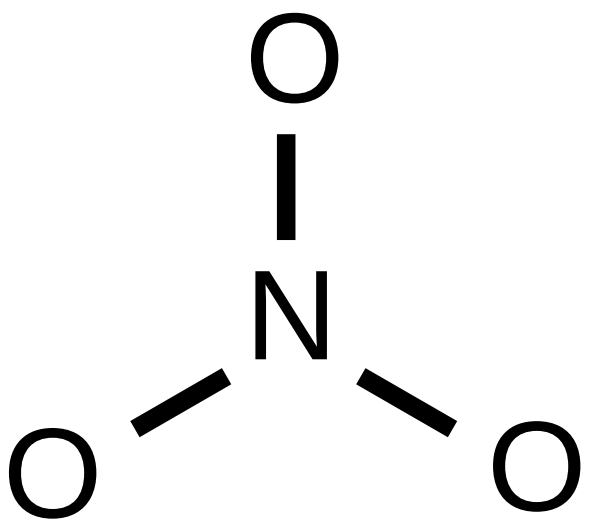
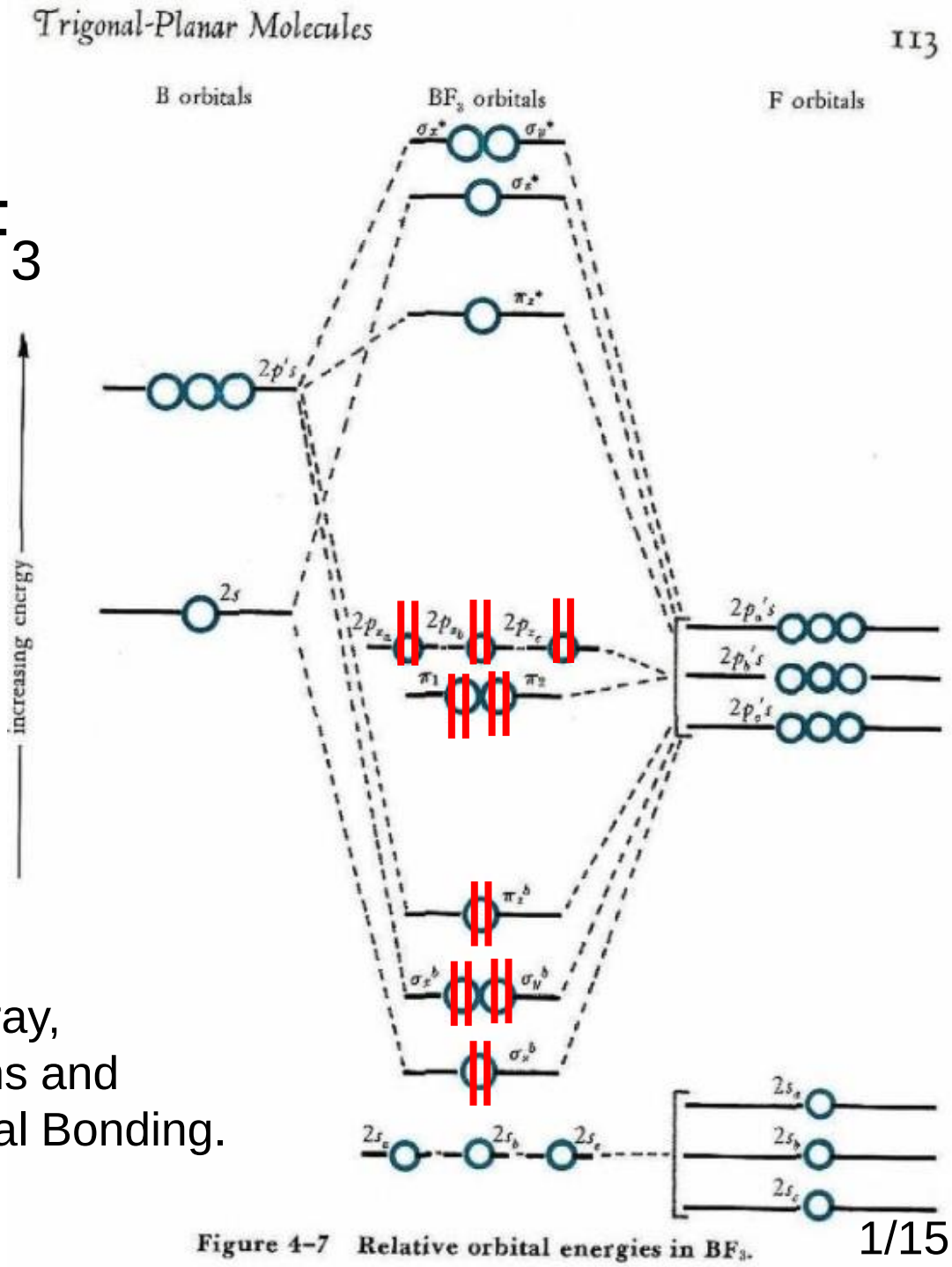


D_{3h}

BF_3



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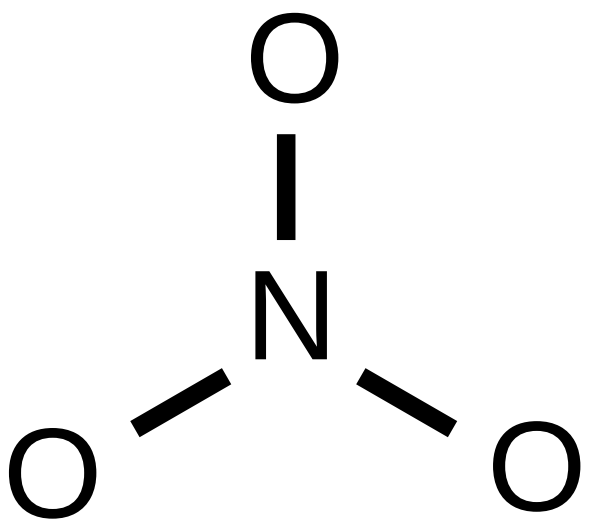


D_{3h}

NO_3

N orbitals

O orbitals

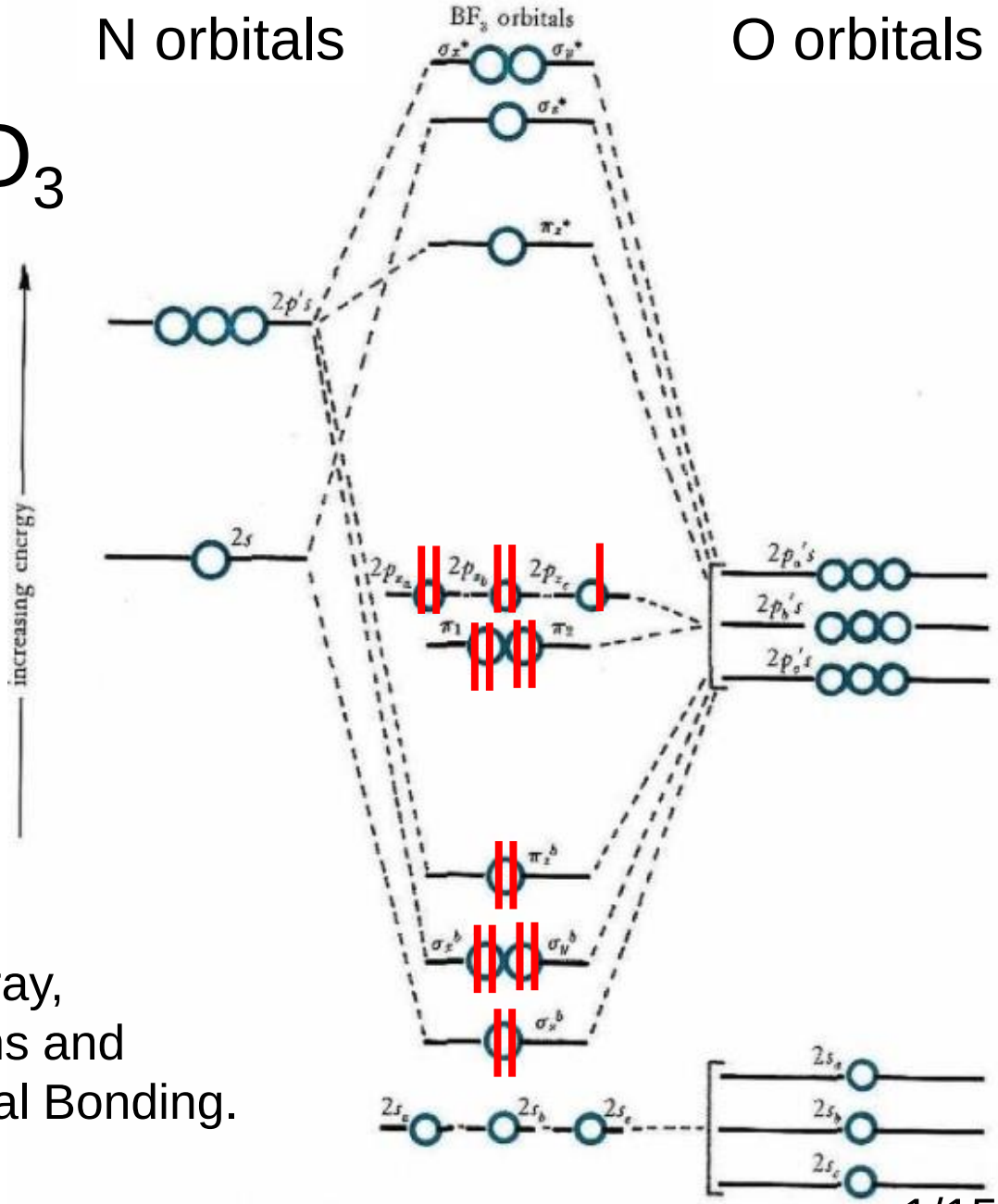
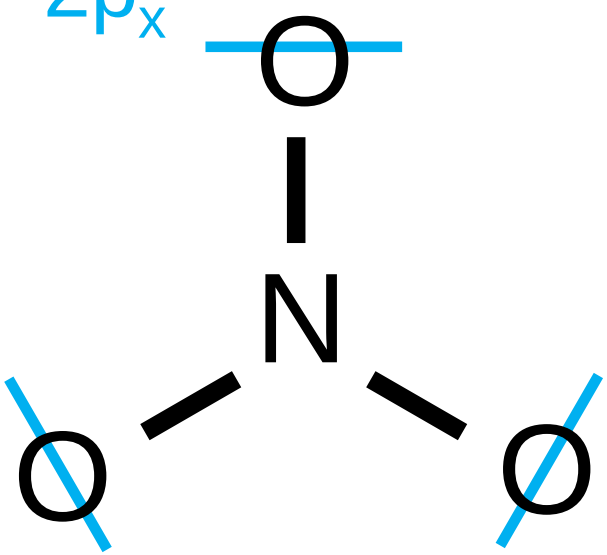


Figure 4–7 Relative orbital energies in BF_3.

H. B. Gray, Electrons and Chemical Bonding.

What is NO_3 ?

$2p_x$

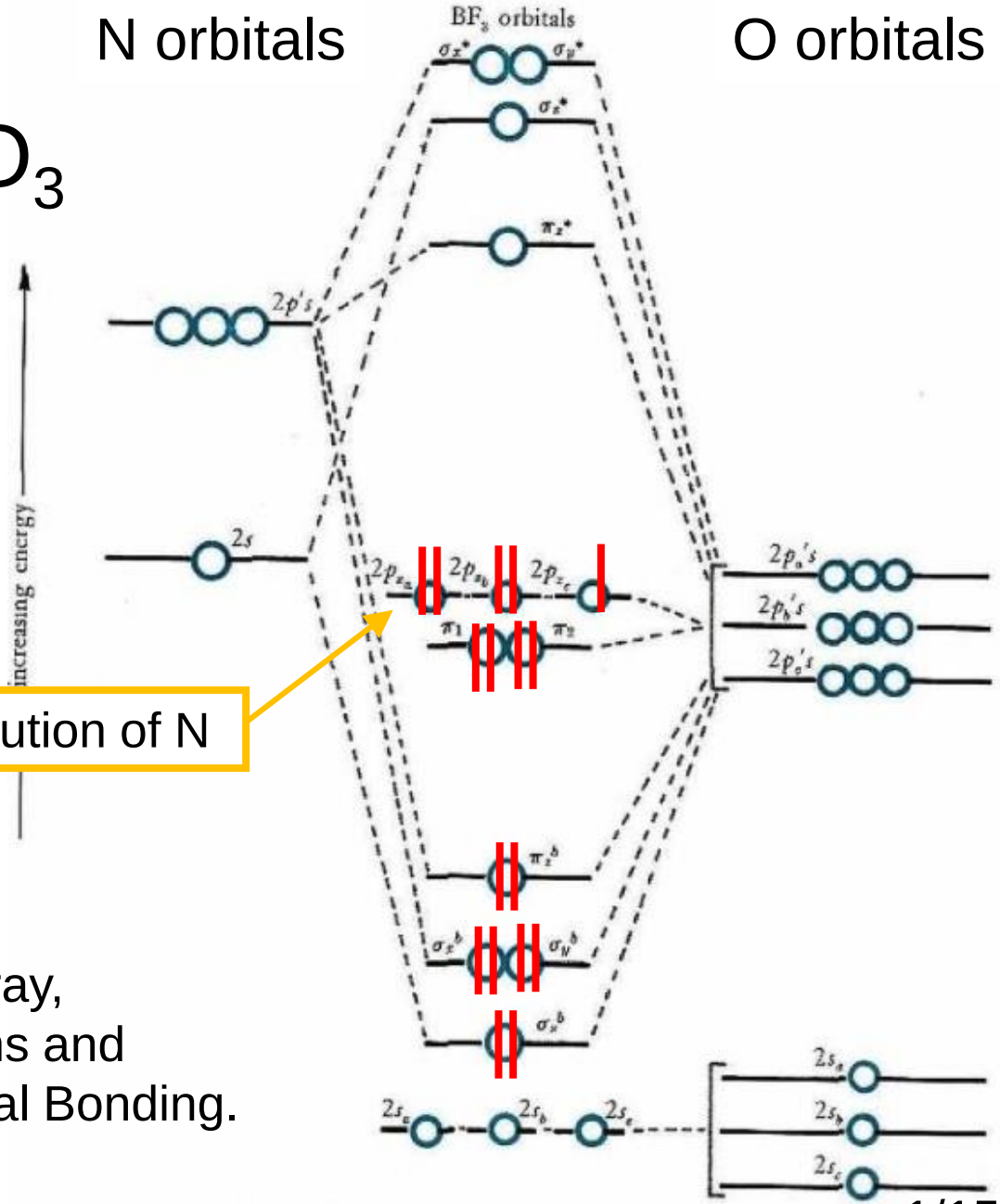


D_{3h}

NO_3

N orbitals

O orbitals



no contribution of N

H. B. Gray, Electrons and Chemical Bonding.

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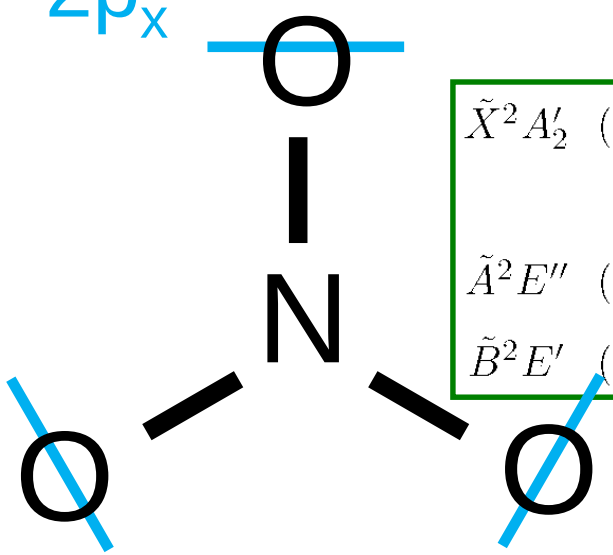
N orbitals

O orbitals

$2p_x$

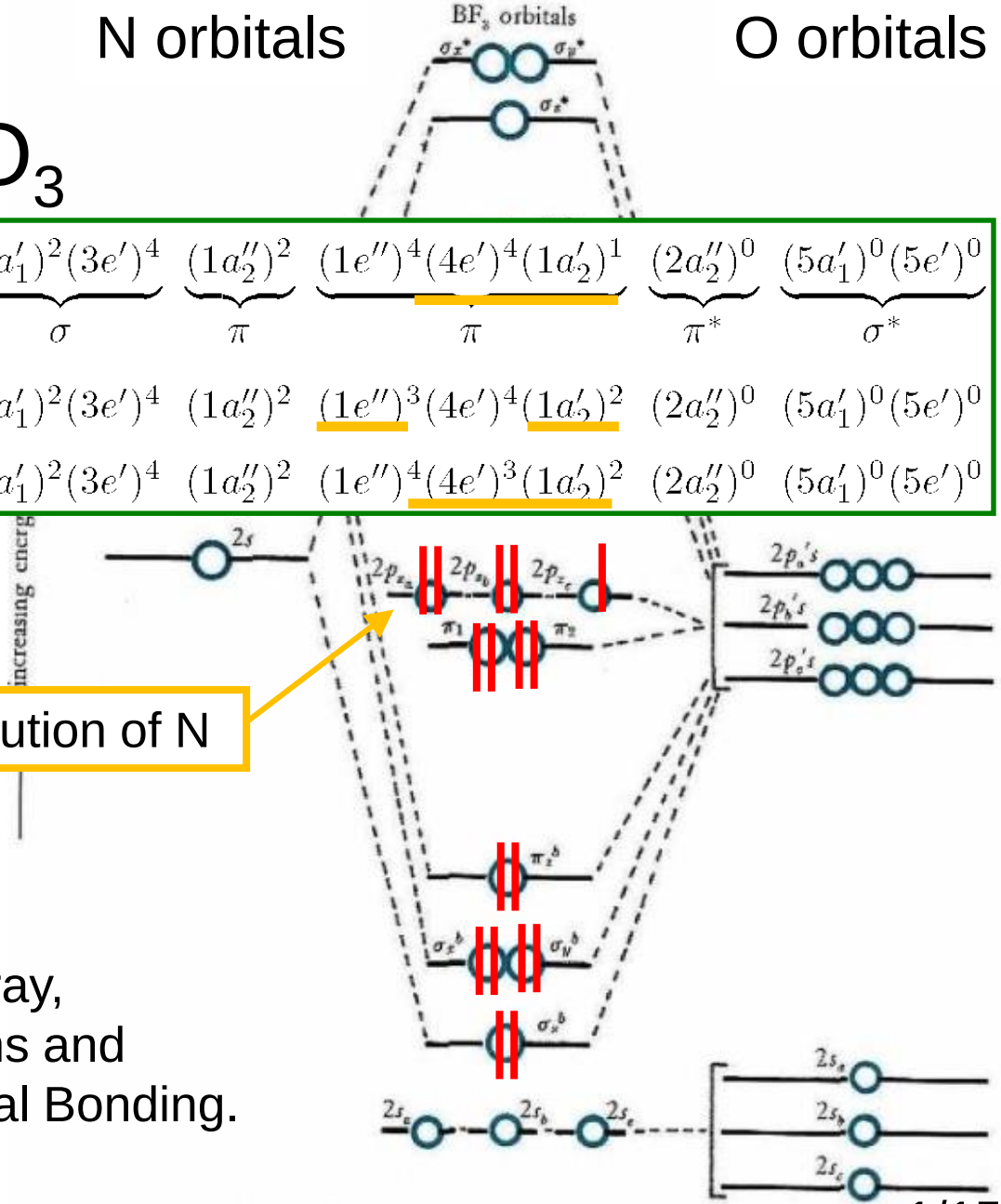


D_{3h}

NO_3

$\tilde{X}^2A_2'$	(core)	$\underbrace{(4a_1')^2(3e')^4}_{\sigma}$	$\underbrace{(1a_2'')^2}_{\pi}$	$\underbrace{(1e'')^4(4e')^4(1a_2')^1}_{\pi}$	$\underbrace{(2a_2'')^0}_{\pi^*}$	$\underbrace{(5a_1')^0(5e')^0}_{\sigma^*}$
$\tilde{A}^2E''$	(core)	$(4a_1')^2(3e')^4$	$(1a_2'')^2$	$(1e'')^3(4e')^4(1a_2')^2$	$(2a_2'')^0$	$(5a_1')^0(5e')^0$
$\tilde{B}^2E'$	(core)	$(4a_1')^2(3e')^4$	$(1a_2'')^2$	$(1e'')^4(4e')^3(1a_2')^2$	$(2a_2'')^0$	$(5a_1')^0(5e')^0$

no contribution of N



H. B. Gray,
Electrons and
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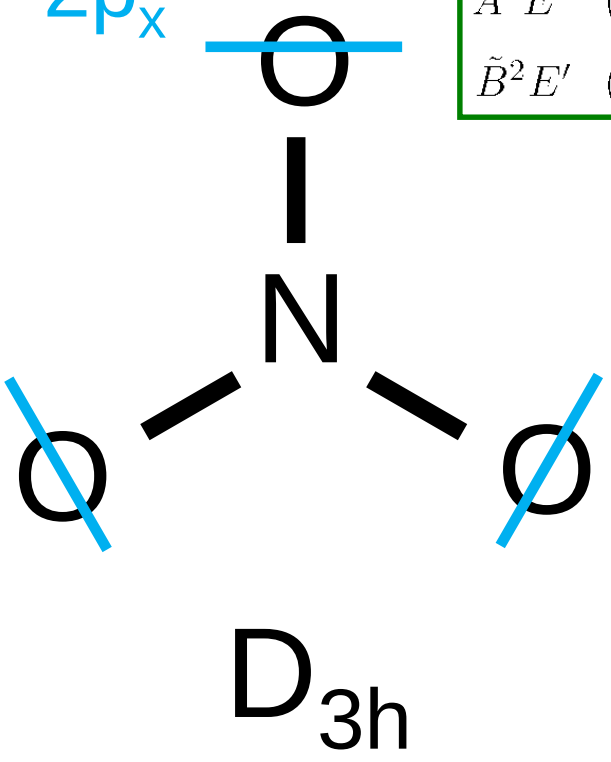
Figure 4-7 Relative orbital energies in BF_3.

What is NO_3 ?

$$
\begin{array}{llccccc}
\tilde{X}^2A_2' & (\text{core}) & \underbrace{(4a_1')^2(3e')^4} & \underbrace{(1a_2'')^2} & \underbrace{(1e'')^4(4e')^4(1a_2')^1} & \underbrace{(2a_2'')^0} & \underbrace{(5a_1')^0(5e')^0} \\
 & & \sigma & \pi & \pi & \pi^* & \sigma^* \\
\tilde{A}^2E'' & (\text{core}) & (4a_1')^2(3e')^4 & (1a_2'')^2 & (1e'')^3(4e')^4(1a_2')^2 & (2a_2'')^0 & (5a_1')^0(5e')^0 \\
\tilde{B}^2E' & (\text{core}) & (4a_1')^2(3e')^4 & (1a_2'')^2 & (1e'')^4(4e')^3(1a_2')^2 & (2a_2'')^0 & (5a_1')^0(5e')^0
\end{array}
$$



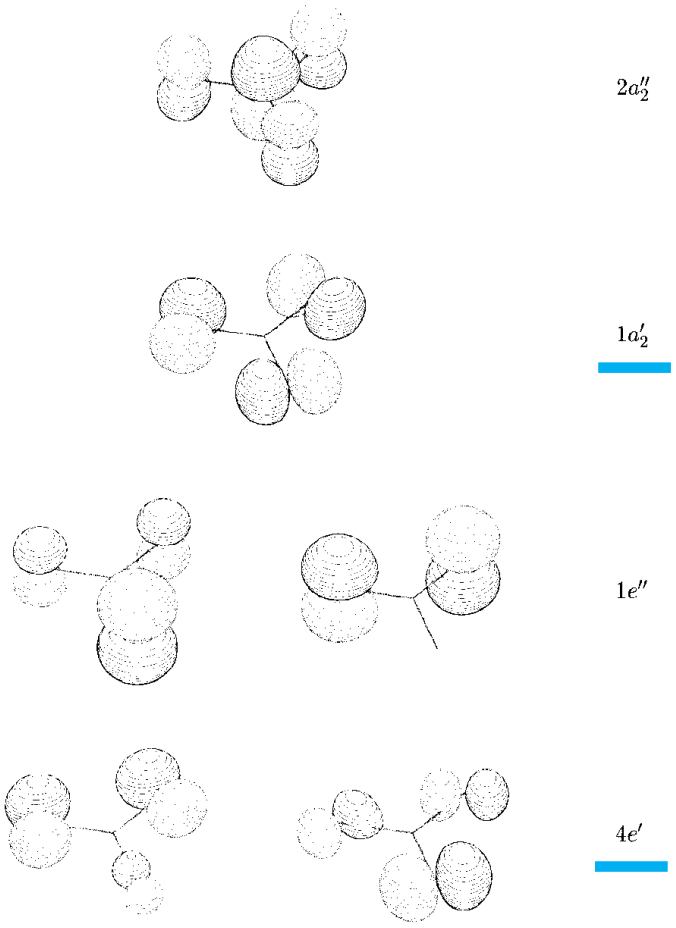


FIG. 1. Selected molecular orbitals of NO_3 as calculated by CASSCF at D_{3h} geometry with a N–O distance of 1.240 Å.

Eisfeld and Morokuma, J. Chem. Phys. 114, 9430 (2001).

What is NO_3 ?

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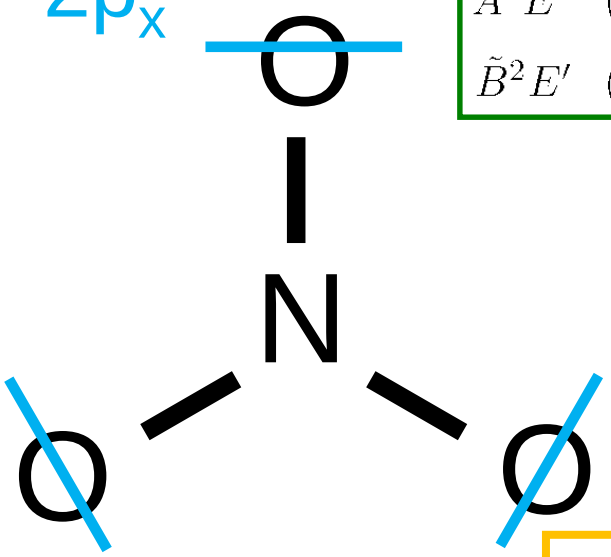
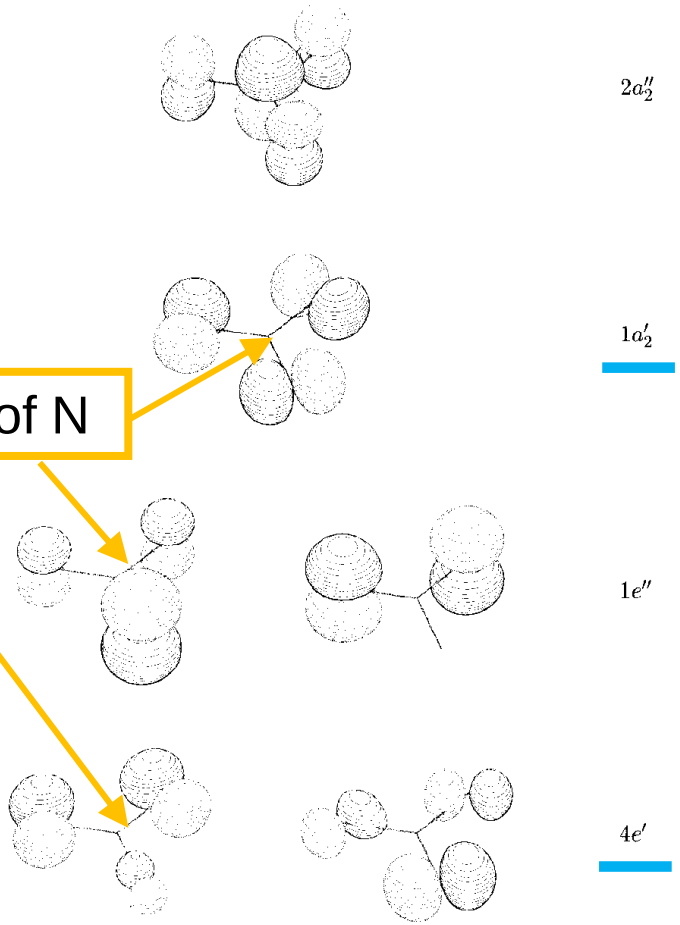
$2p_x$



D_{3h}

no contribution of N



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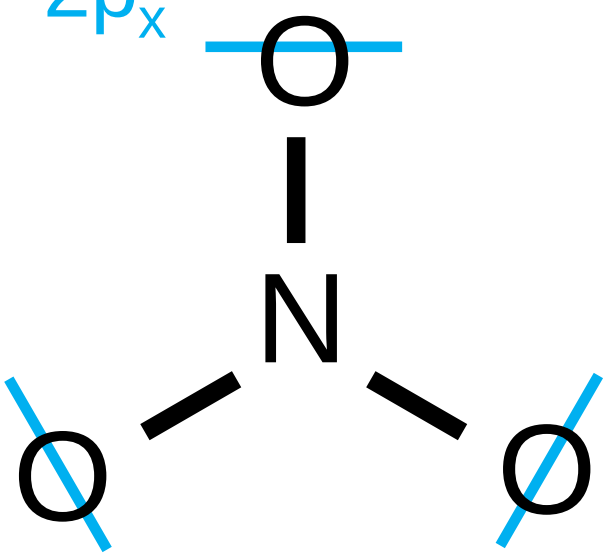

D_{3h}

NO_3

N orbitals

O orbitals

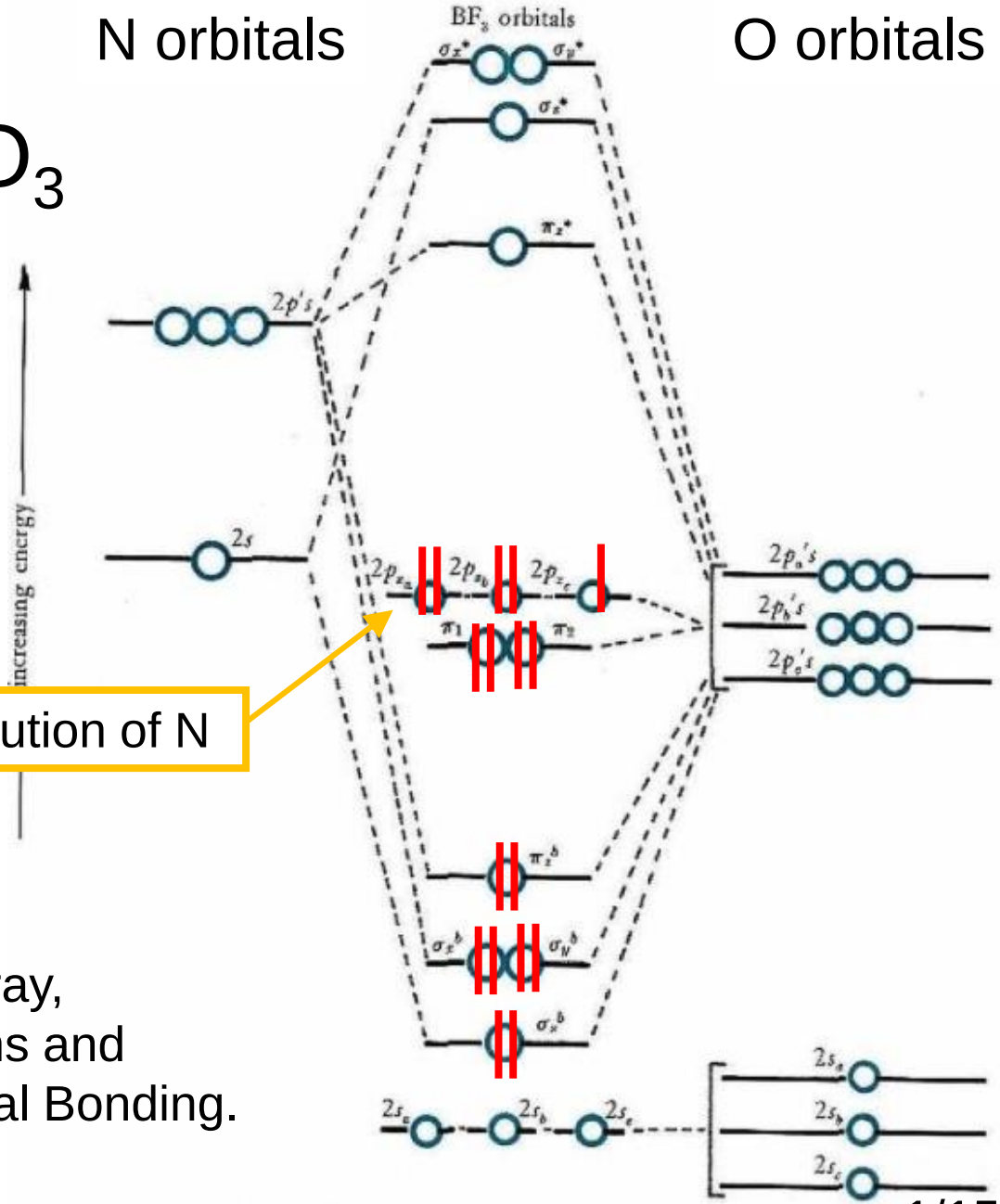

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Figure 4-7 Relative orbital energies in BF_3.

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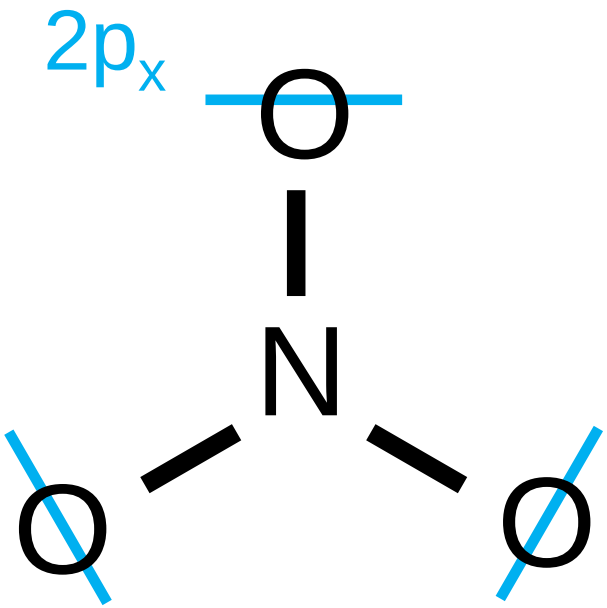
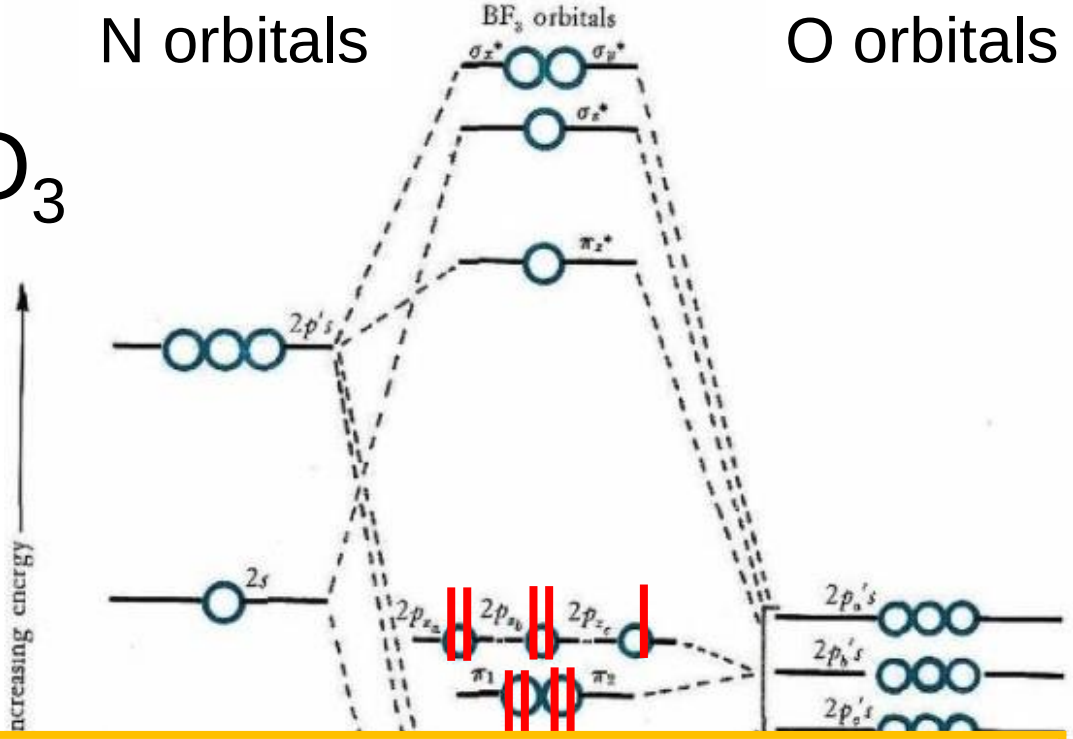


NO_3



1. SOMO's (singly occupied molecular orbital) have little contribution of N.
2. The un-paired electron is localized on O's.

⇒ SOMO just consists of 2p of O, and has no chemical bond.

⇒ The un-paired electron easily follows the motion of O's.

⇒ Vibronic couplings in the states are strong.

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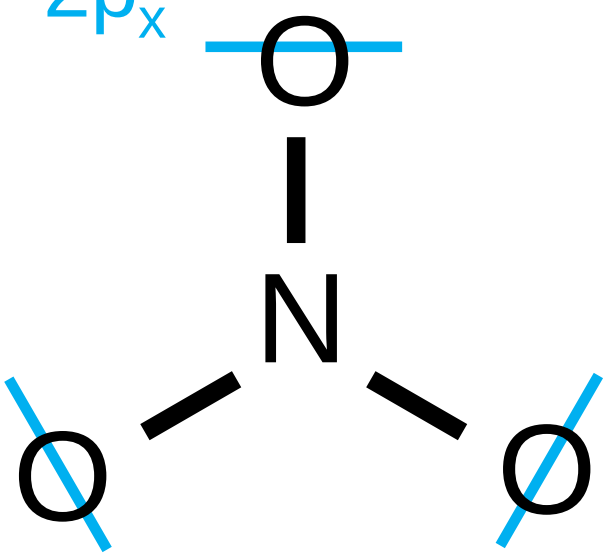
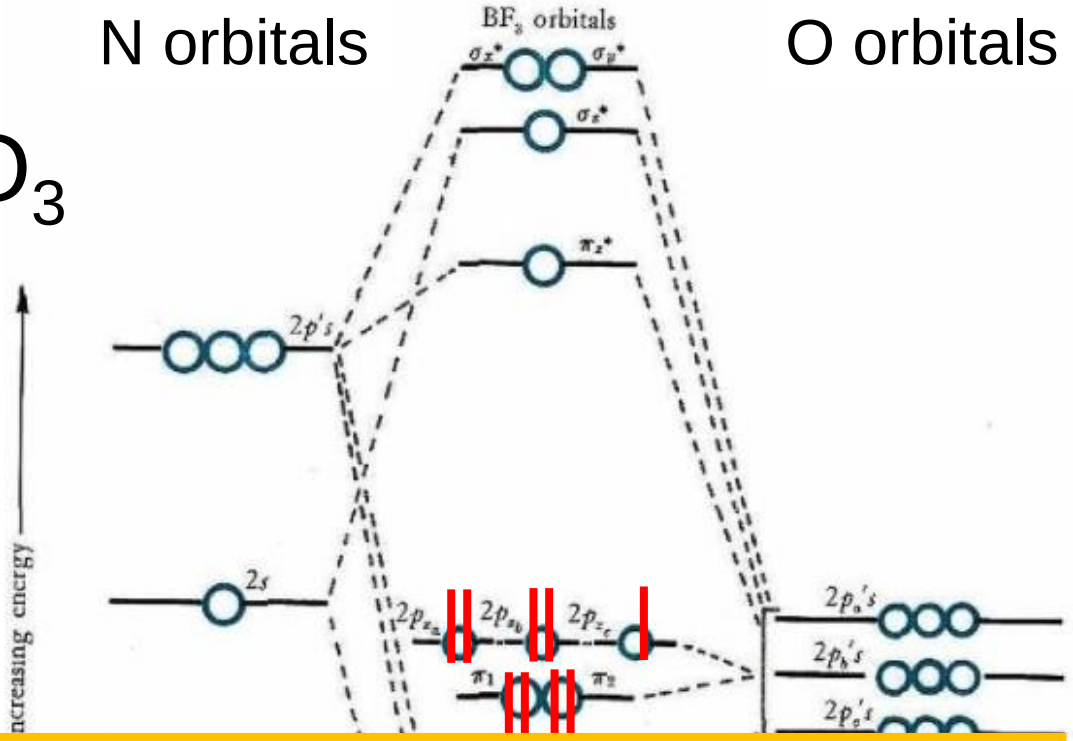
$2p_x$



NO_3

N orbitals

O orbitals



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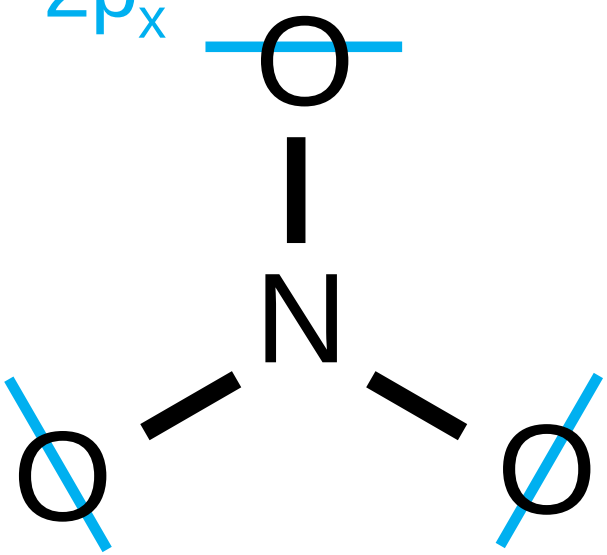

NO_3

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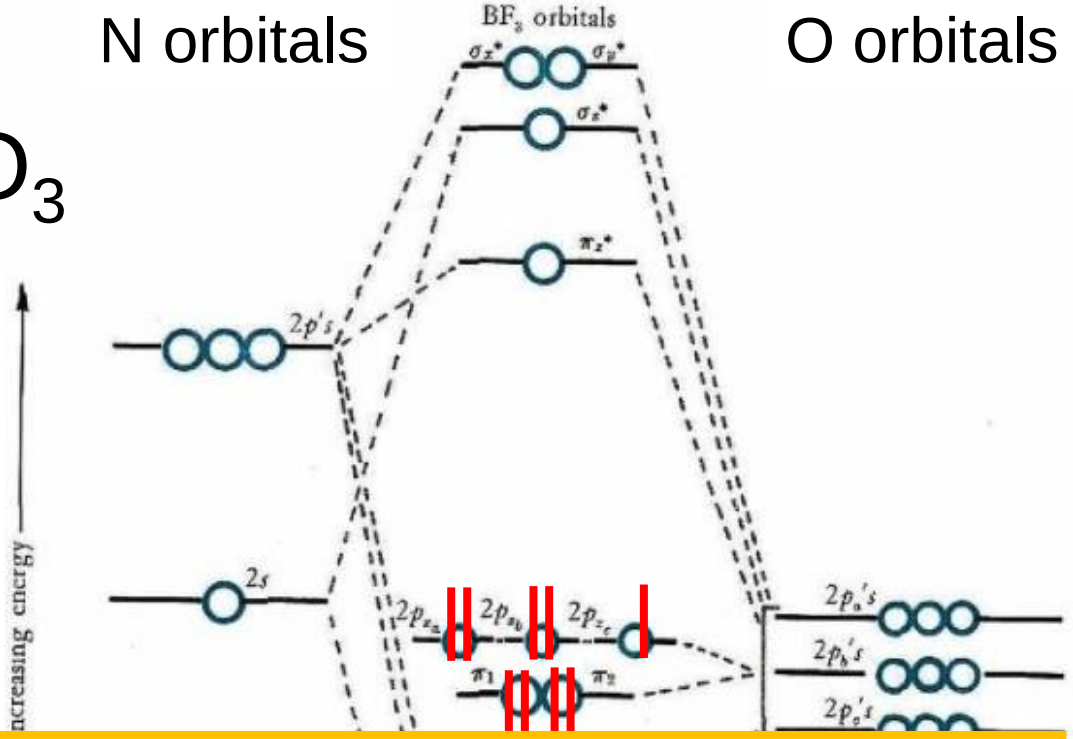

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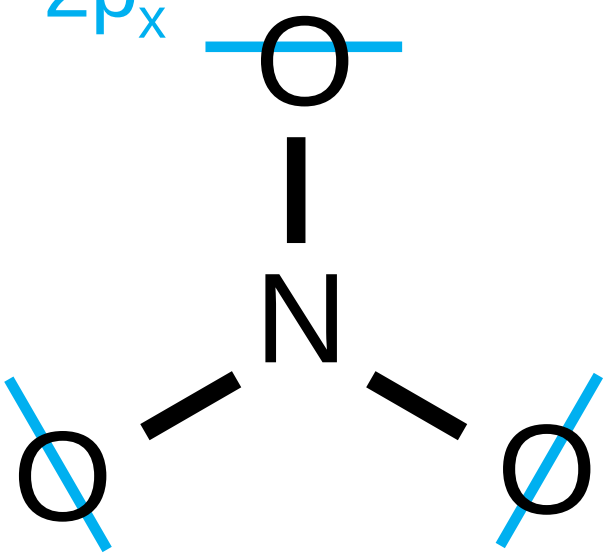
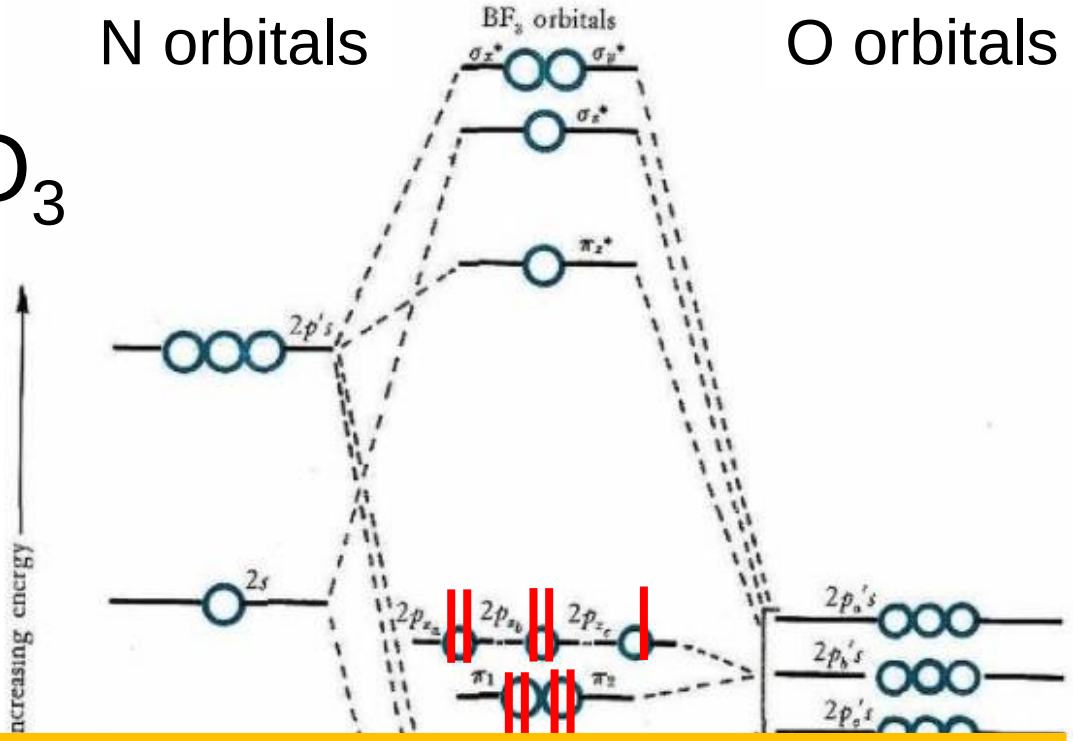


NO_3

N orbitals

O orbitals



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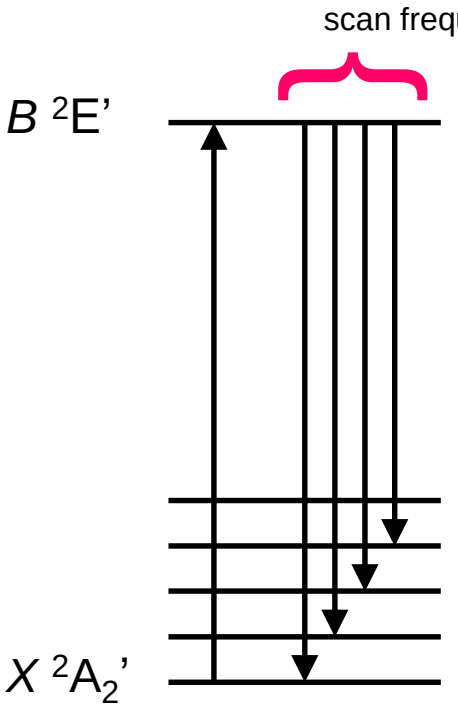
Why 4WM ?

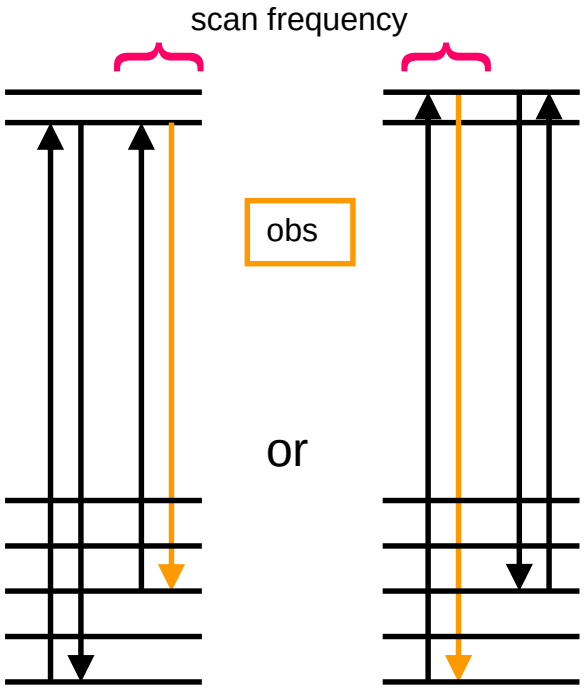
Spectral resolution

Dispersed fluorescence spec.



resolution : monochromator
(vibrationally resolved)

Four-wave mixing spec.
(4WM spec.)

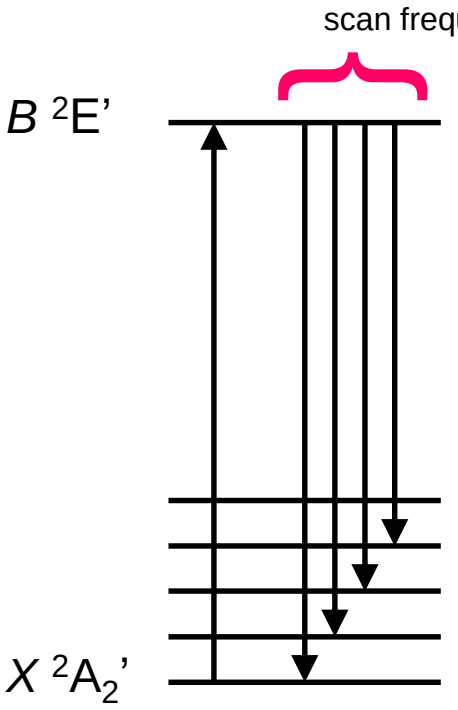


resolution : excitation laser
(rotationally resolved)

Why 4WM ?

We use 4WM to measure rotationally resolved DF spectra.

Dispersed fluorescence spec.



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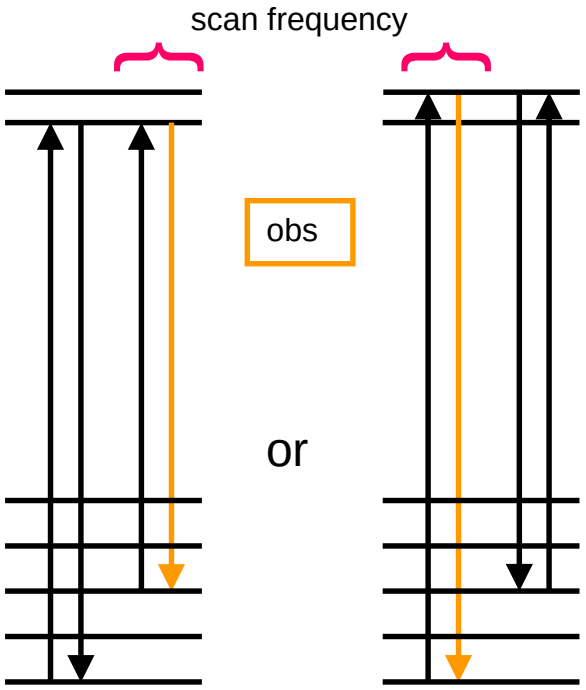

resolution : excitation laser
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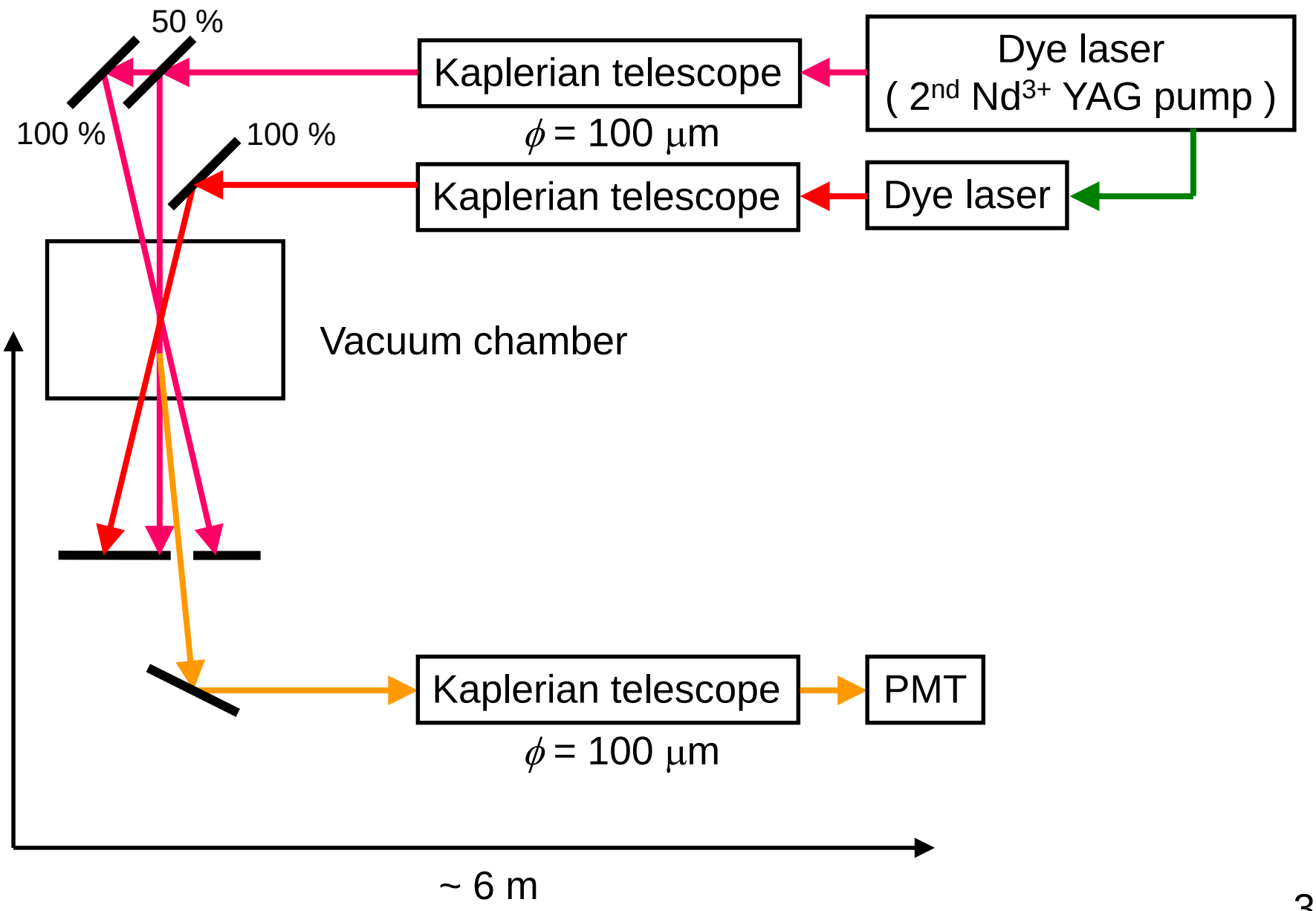
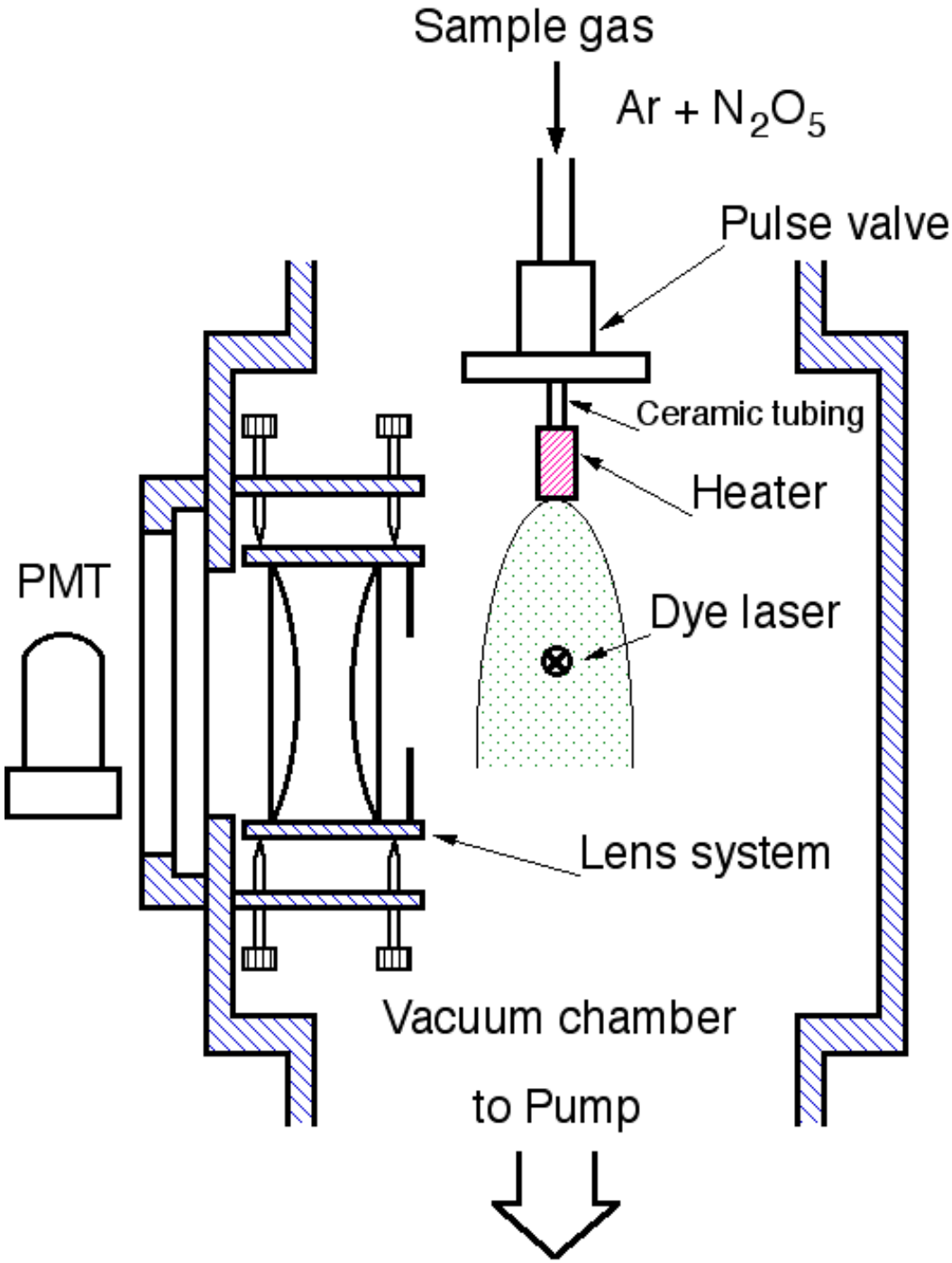
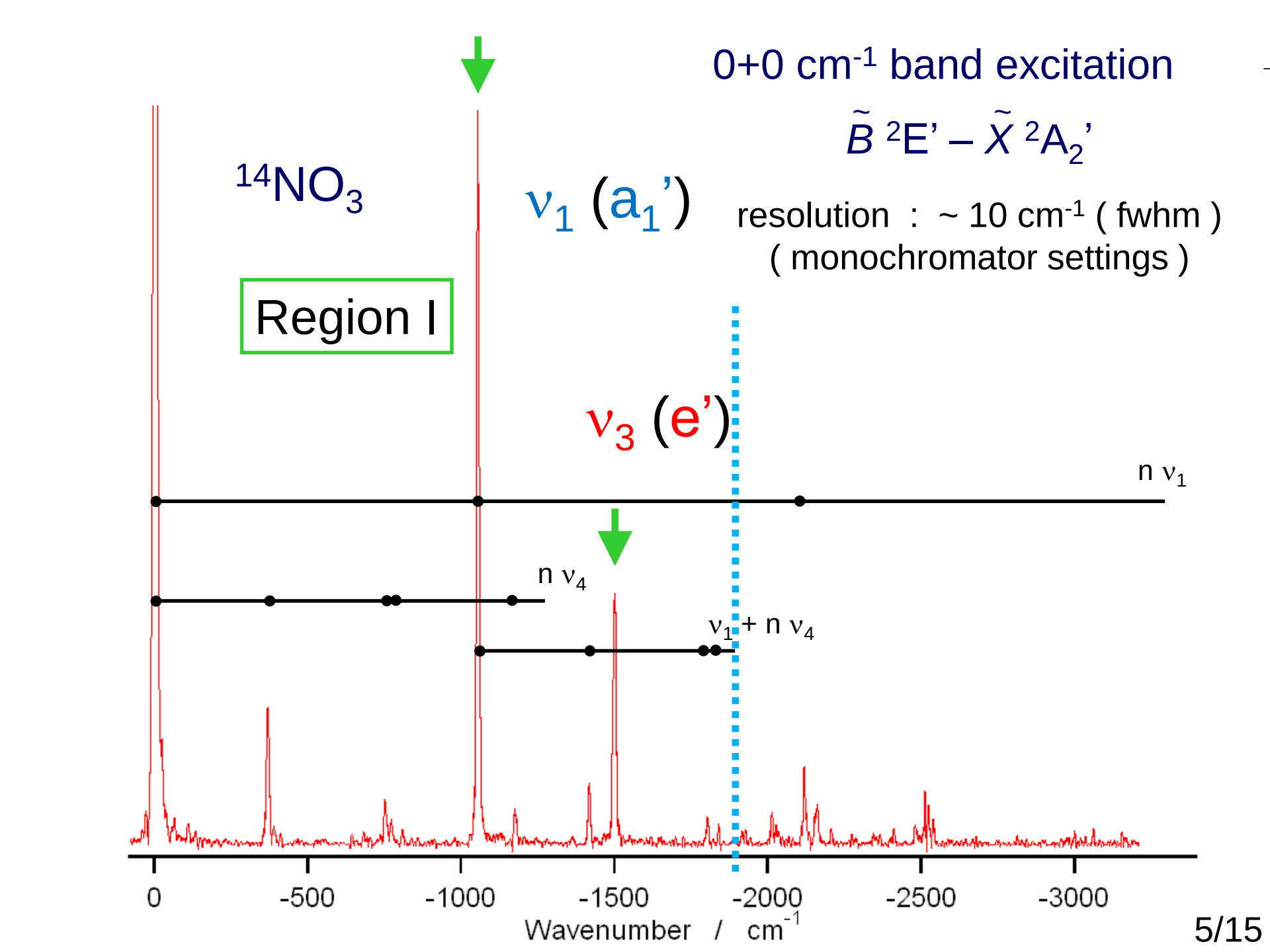
Experiment

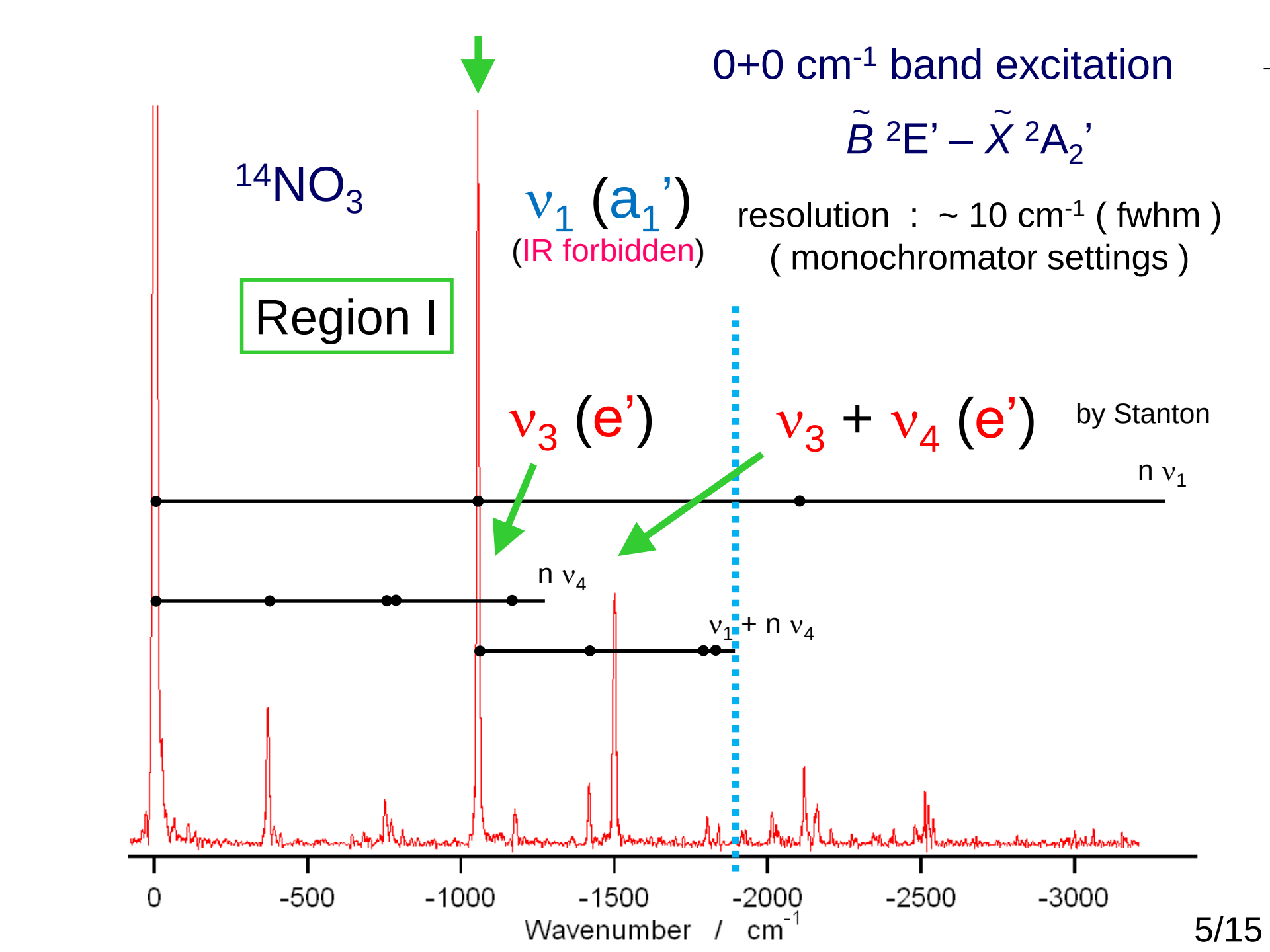
for 2C-R4WM



Experiment


Sample gas
Ar + N_2O_5
Pulse valve
Ceramic tubing
Heater
PMT
Dye laser
Lens system
Vacuum chamber
to Pump


0+0 cm-1 band excitation
$\tilde{B}\ ^2E' - \tilde{X}\ ^2A_2'$
$^{14}NO_3$
ν_1 (a_1')
resolution : ~ 10 cm-1 (fwhm)
(monochromator settings)
Region I
ν_3 (e')
n ν_1
n ν_4
ν_1 + n ν_4
0
-500
-1000
-1500
-2000
-2500
-3000
Wavenumber / cm-1


0+0 cm-1 band excitation
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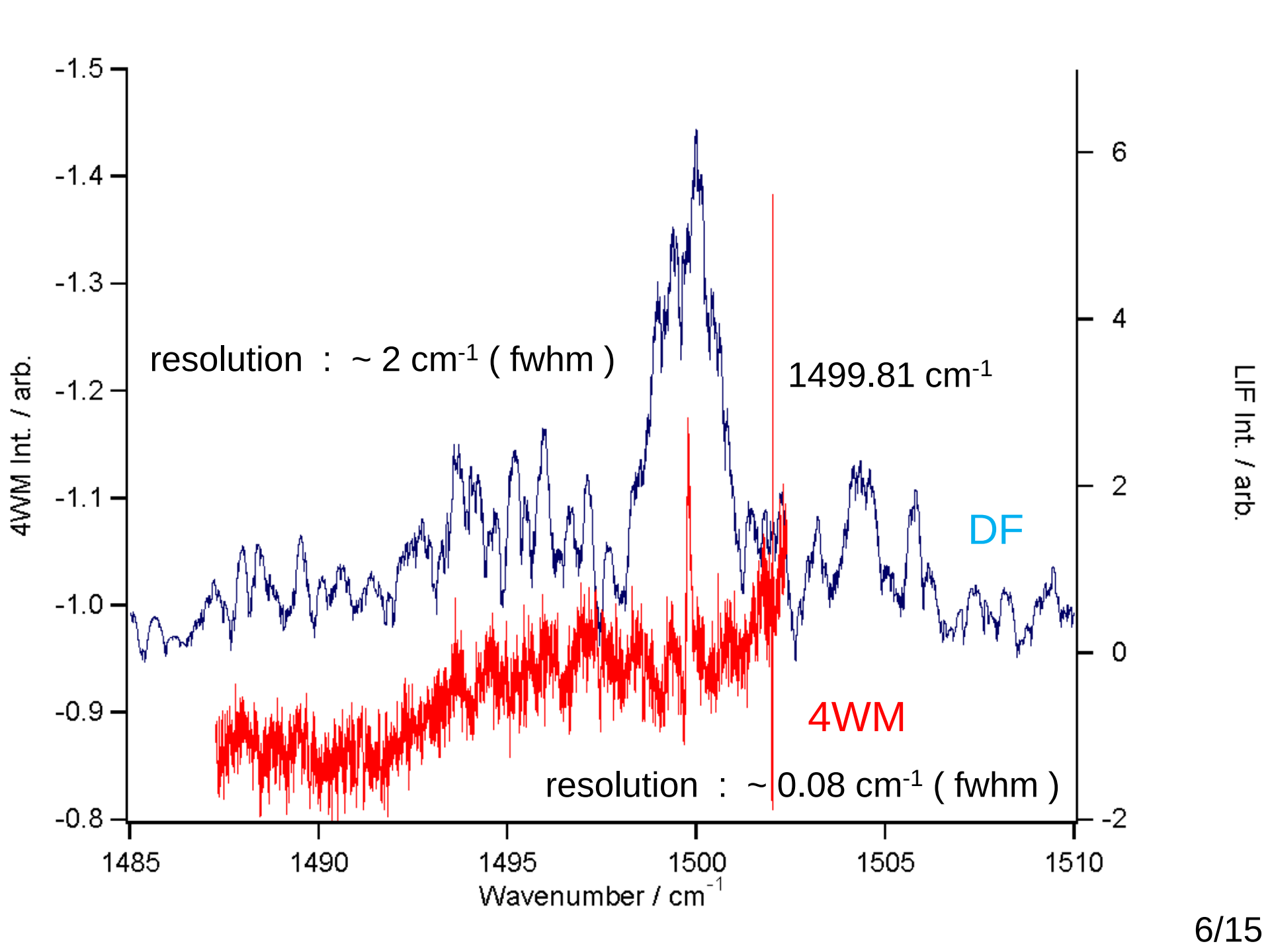
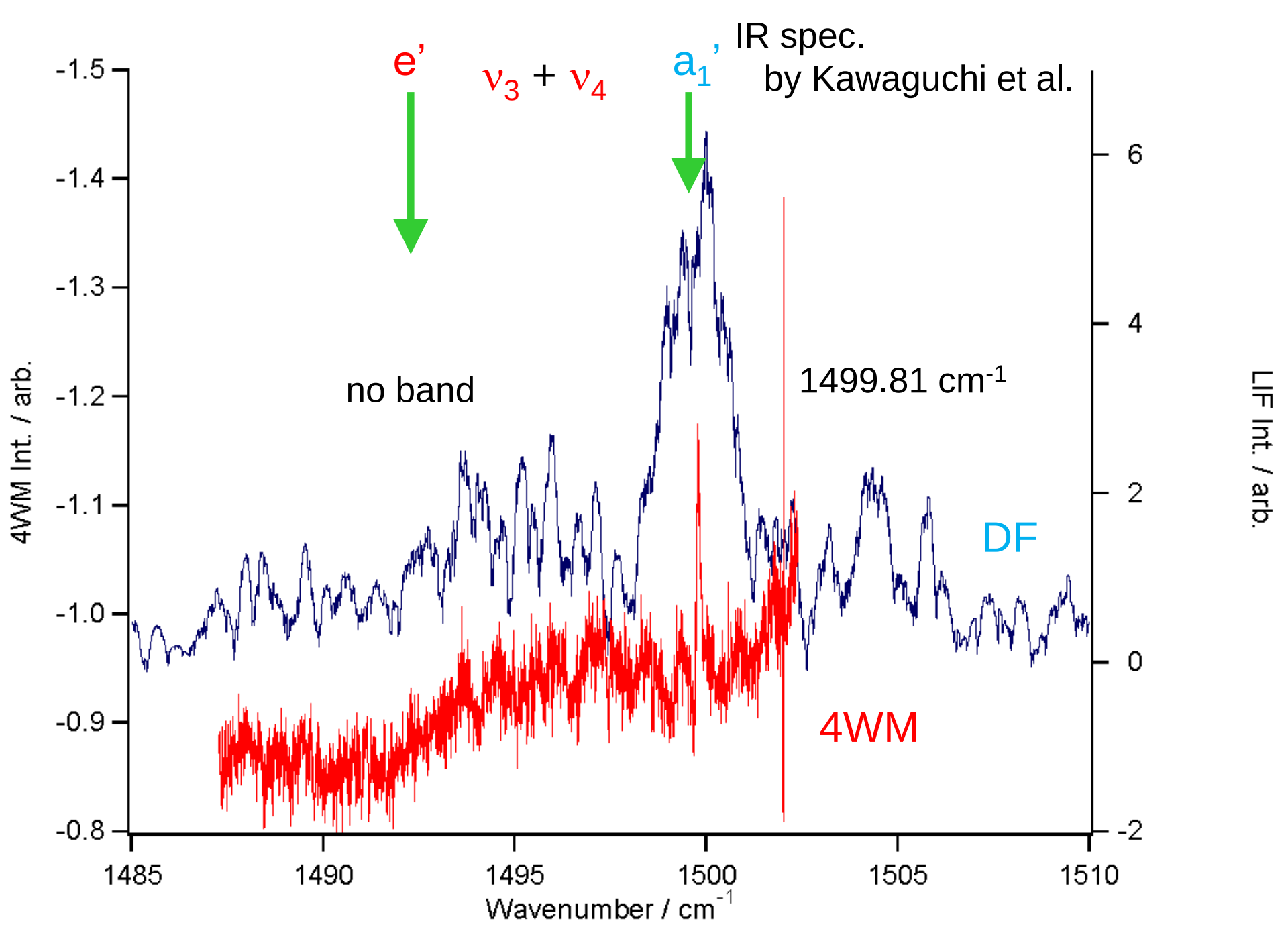
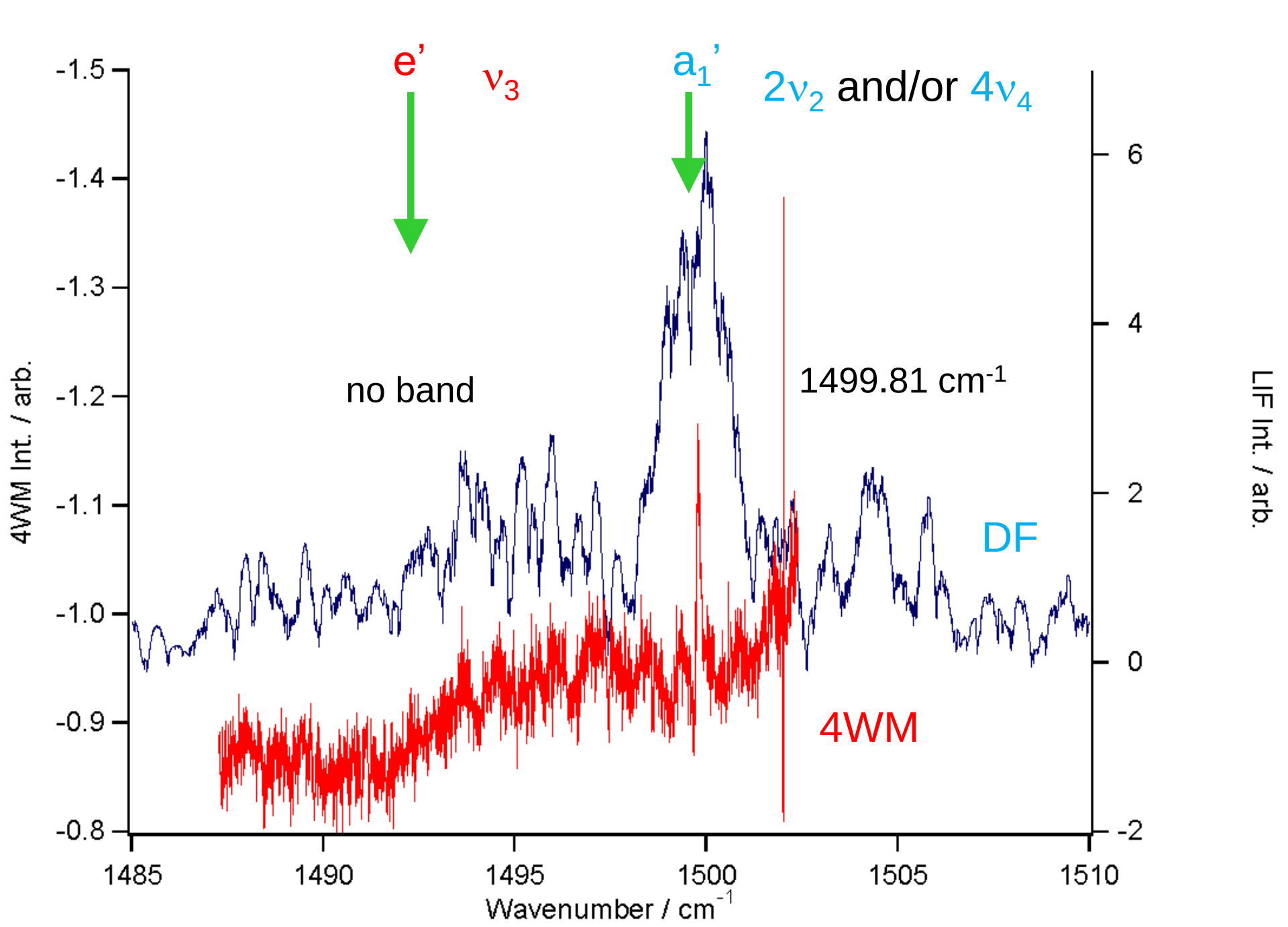
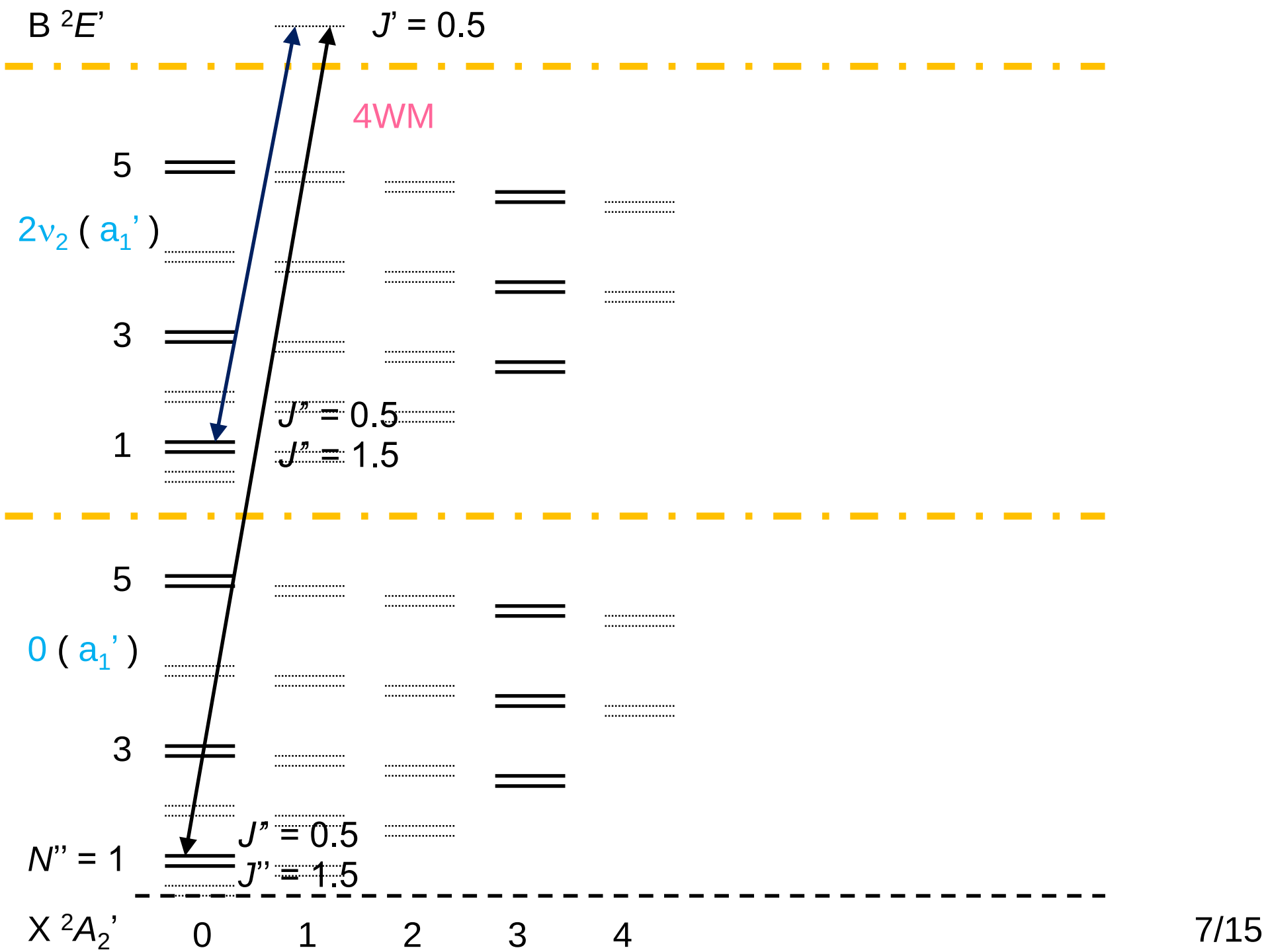
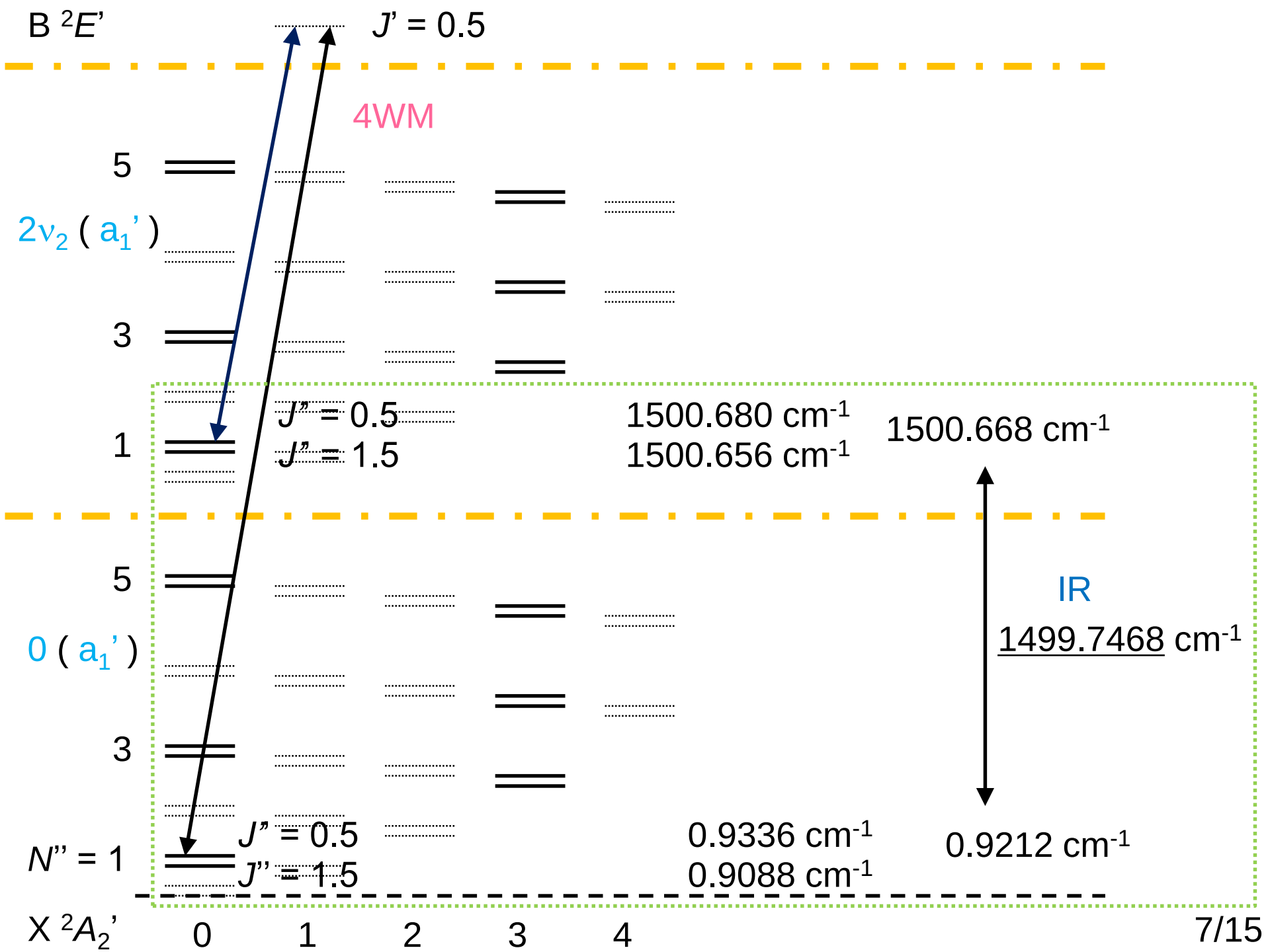
$^{14}NO_3$
ν_1 (a_1')
(IR forbidden)
resolution : ~ 10 cm-1 (fwhm)
(monochromator settings)
Region I
ν_3 (e')
$\nu_3 + \nu_4$ (e')
by Stanton
n ν_1
n ν_4
ν_1 + n ν_4
0
-500
-1000
-1500
-2000
-2500
-3000
Wavenumber / cm-1

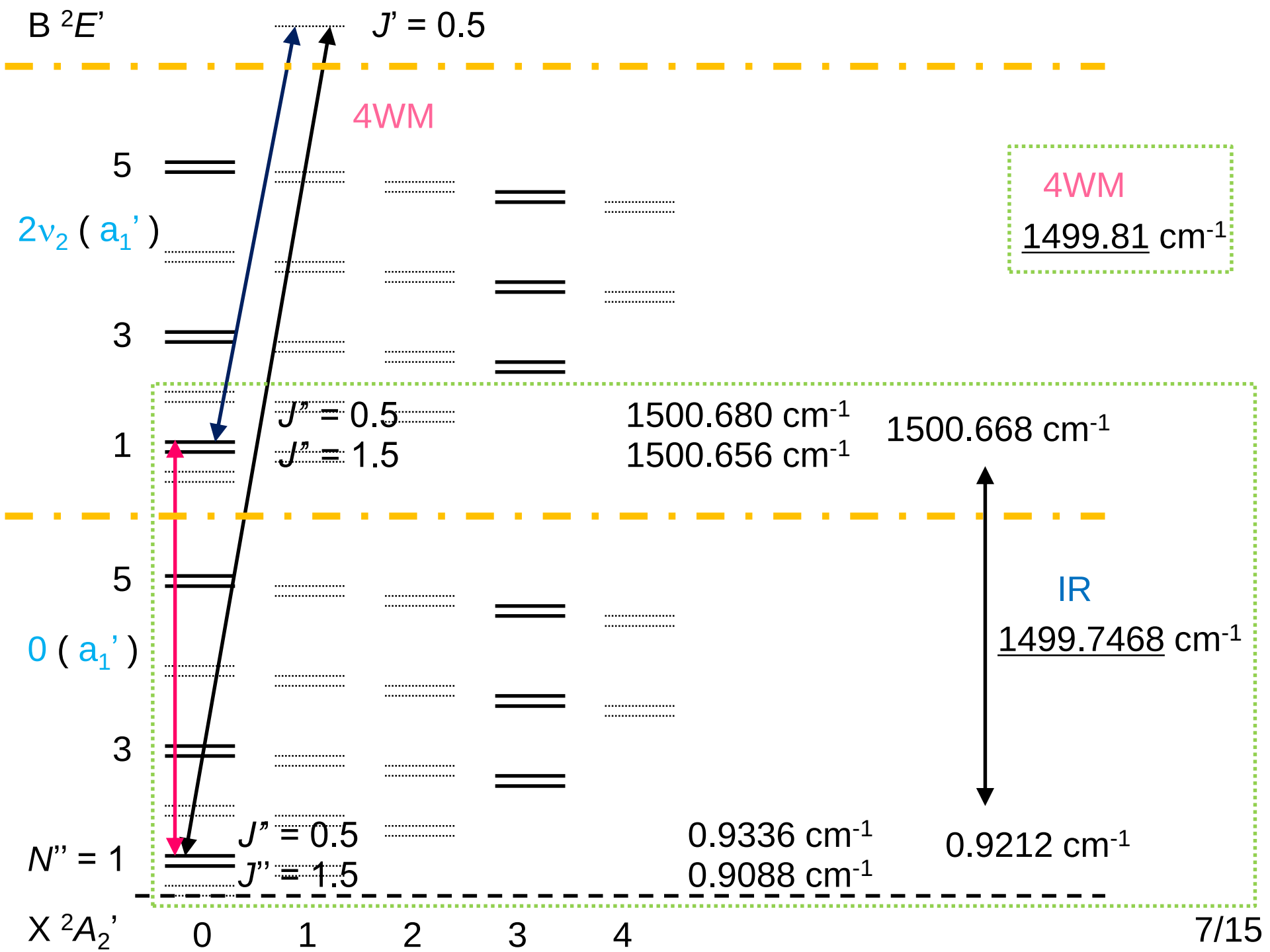

-1.5
-1.4
-1.3
-1.2
-1.1
-1.0
-0.9
-0.8
4WM Int. / arb.
6
4
2
0
-2
LIF Int. / arb.
resolution : ~ 2 cm-1 (fwhm)
1499.81 cm-1
DF
4WM
resolution : ~ 0.08 cm-1 (fwhm)
1485
1490
1495
1500
1505
1510
Wavenumber / cm-1

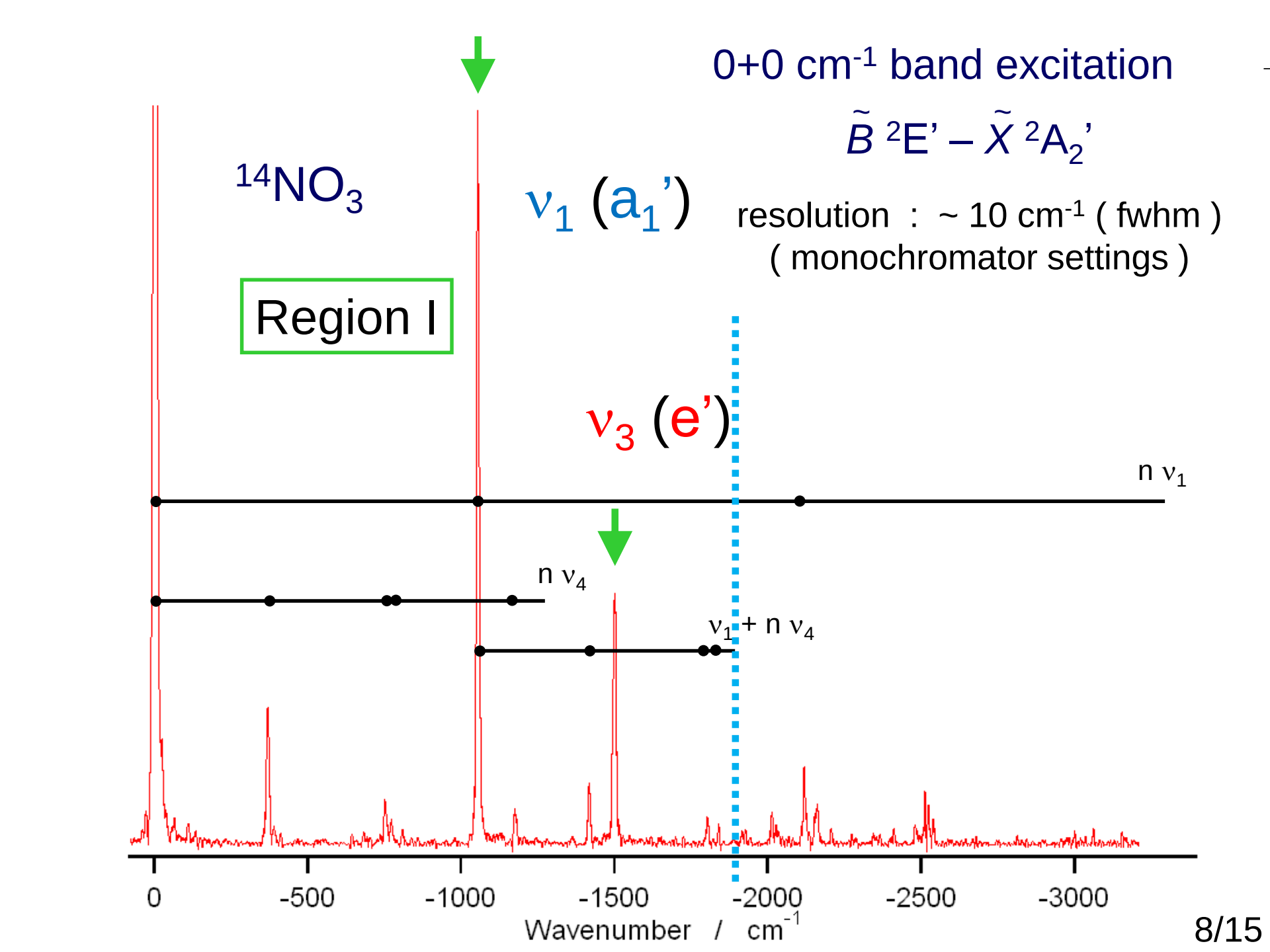

e'
$\nu_3 + \nu_4$
a_1'
IR spec.
by Kawaguchi et al.
no band
1499.81 cm^{-1}
DF
4WM
4WM Int. / arb.
LIF Int. / arb.
-1.5
-1.4
-1.3
-1.2
-1.1
-1.0
-0.9
-0.8
6
4
2
0
-2
1485
1490
1495
1500
1505
1510
Wavenumber / cm^{-1}

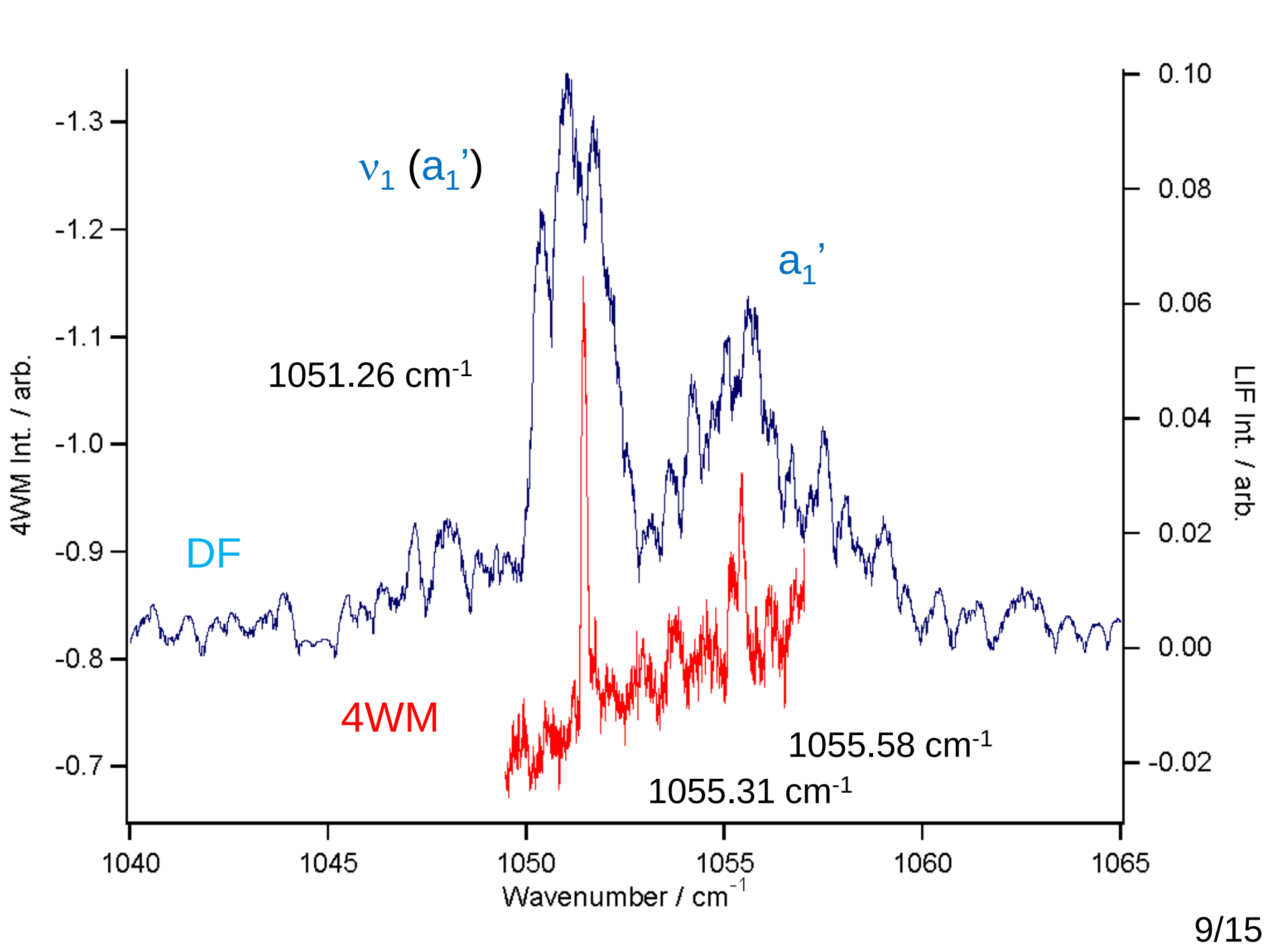

e'
ν_3
a_1'
$2\nu_2$ and/or $4\nu_4$
no band
1499.81 cm^{-1}
DF
4WM
4WM Int. / arb.
LIF Int. / arb.
Wavenumber / cm^{-1}
-1.5
-1.4
-1.3
-1.2
-1.1
-1.0
-0.9
-0.8
6
4
2
0
-2
1485
1490
1495
1500
1505
1510

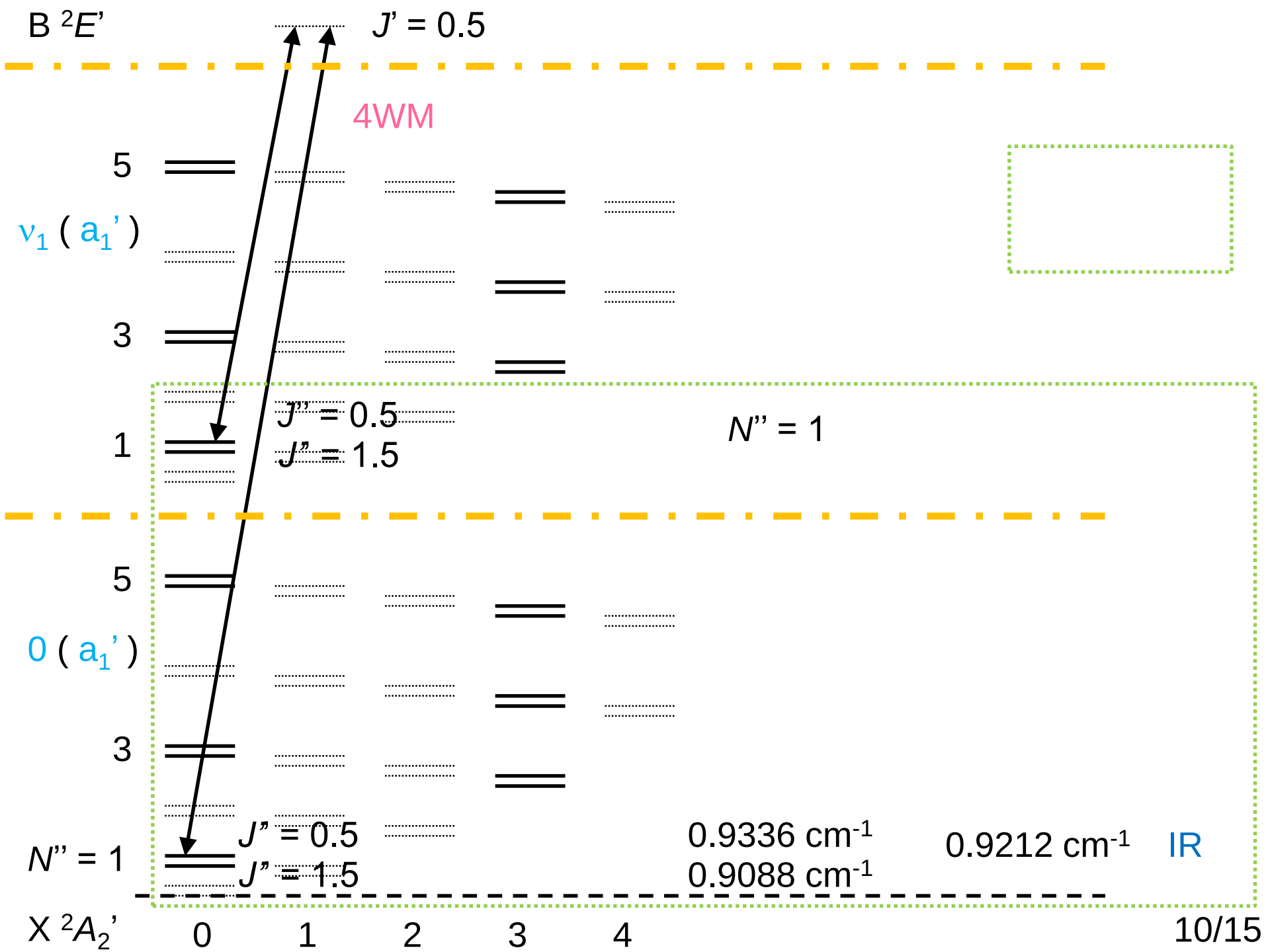

B $^2E'$
J' = 0.5
4WM
5
$2\nu_2$ (a_1')
3
J'' = 0.5
1
J'' = 1.5
5
0 (a_1')
3
J'' = 0.5
N'' = 1
J'' = 1.5
X $^2A_2'$
0
1
2
3
4

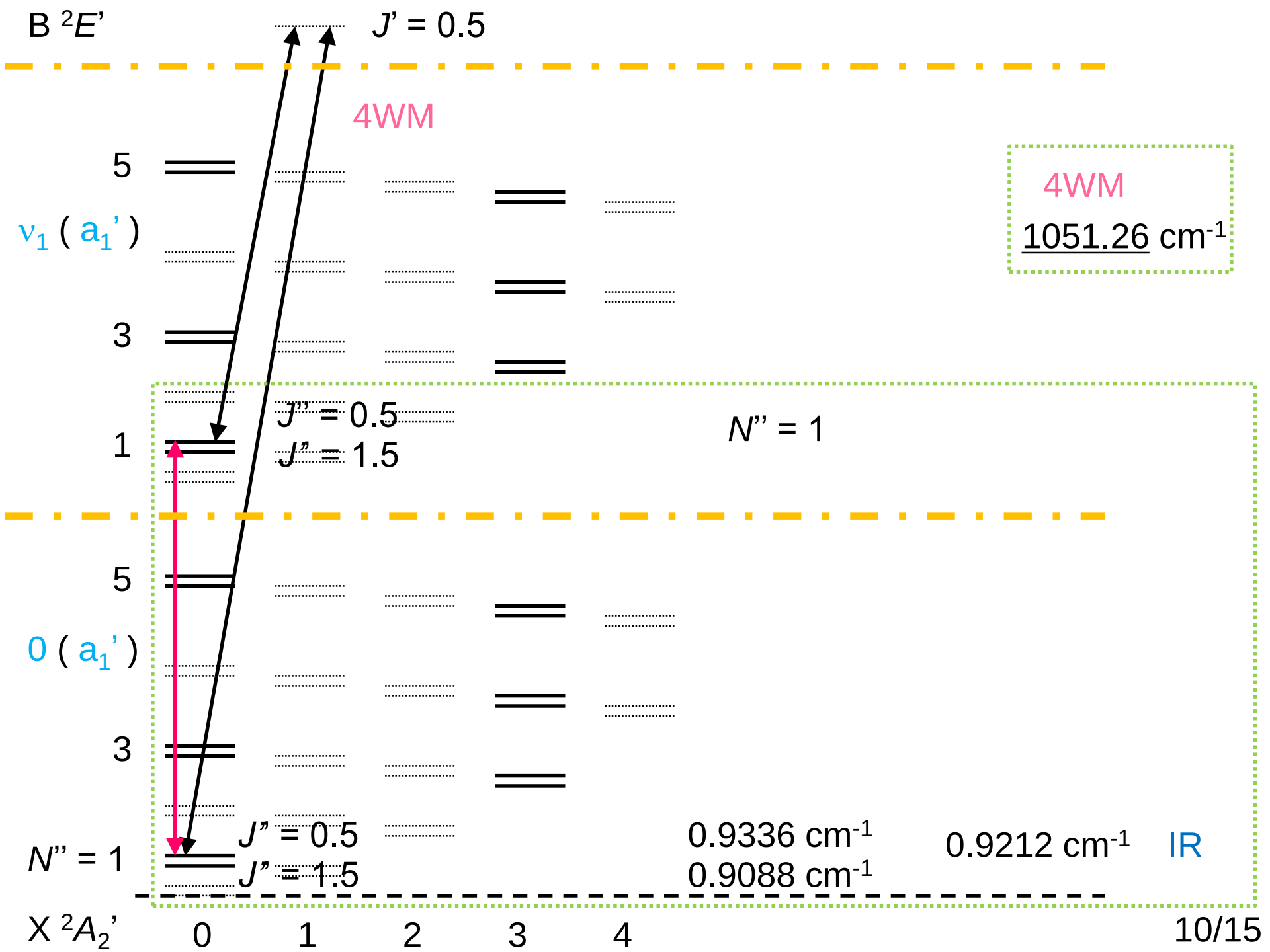

B $^2E'$
J' = 0.5
4WM
5
$2\nu_2$ (a_1')
3
1
J'' = 0.5
J'' = 1.5
1500.680 cm^{-1}
1500.656 cm^{-1}
1500.668 cm^{-1}
IR
1499.7468 cm^{-1}
5
0 (a_1')
3
N'' = 1
J'' = 0.5
J'' = 1.5
0.9336 cm^{-1}
0.9088 cm^{-1}
0.9212 cm^{-1}
X $^2A_2'$
0
1
2
3
4

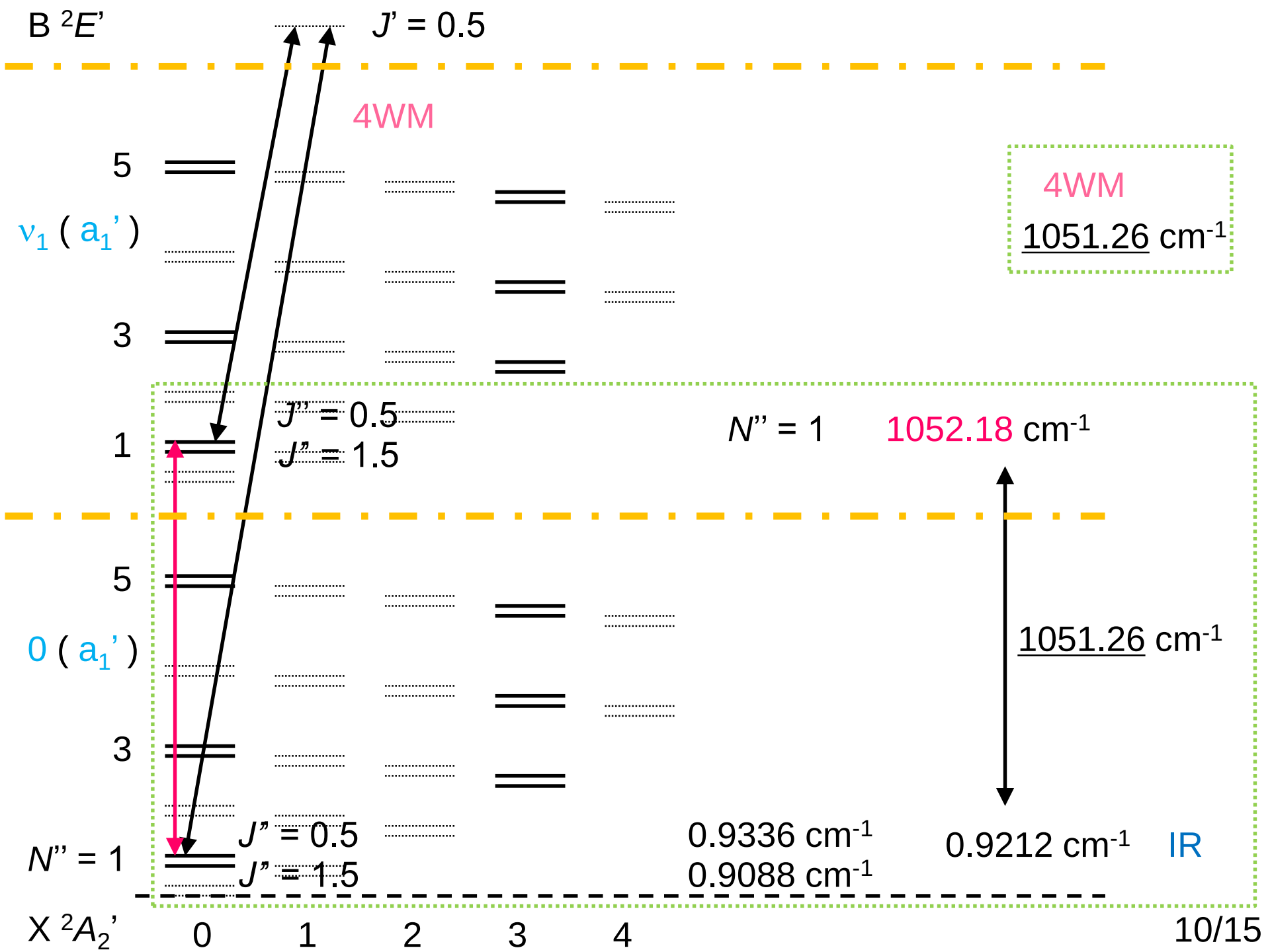

B $^2E'$
J' = 0.5
4WM
5
$2\nu_2$ (a_1')
3
1
J'' = 0.5
J'' = 1.5
1500.680 cm^{-1}
1500.656 cm^{-1}
4WM
1499.81 cm^{-1}
1500.668 cm^{-1}
IR
1499.7468 cm^{-1}
0.9212 cm^{-1}
5
0 (a_1')
3
N'' = 1
J'' = 0.5
J'' = 1.5
0.9336 cm^{-1}
0.9088 cm^{-1}
X $^2A_2'$
0
1
2
3
4

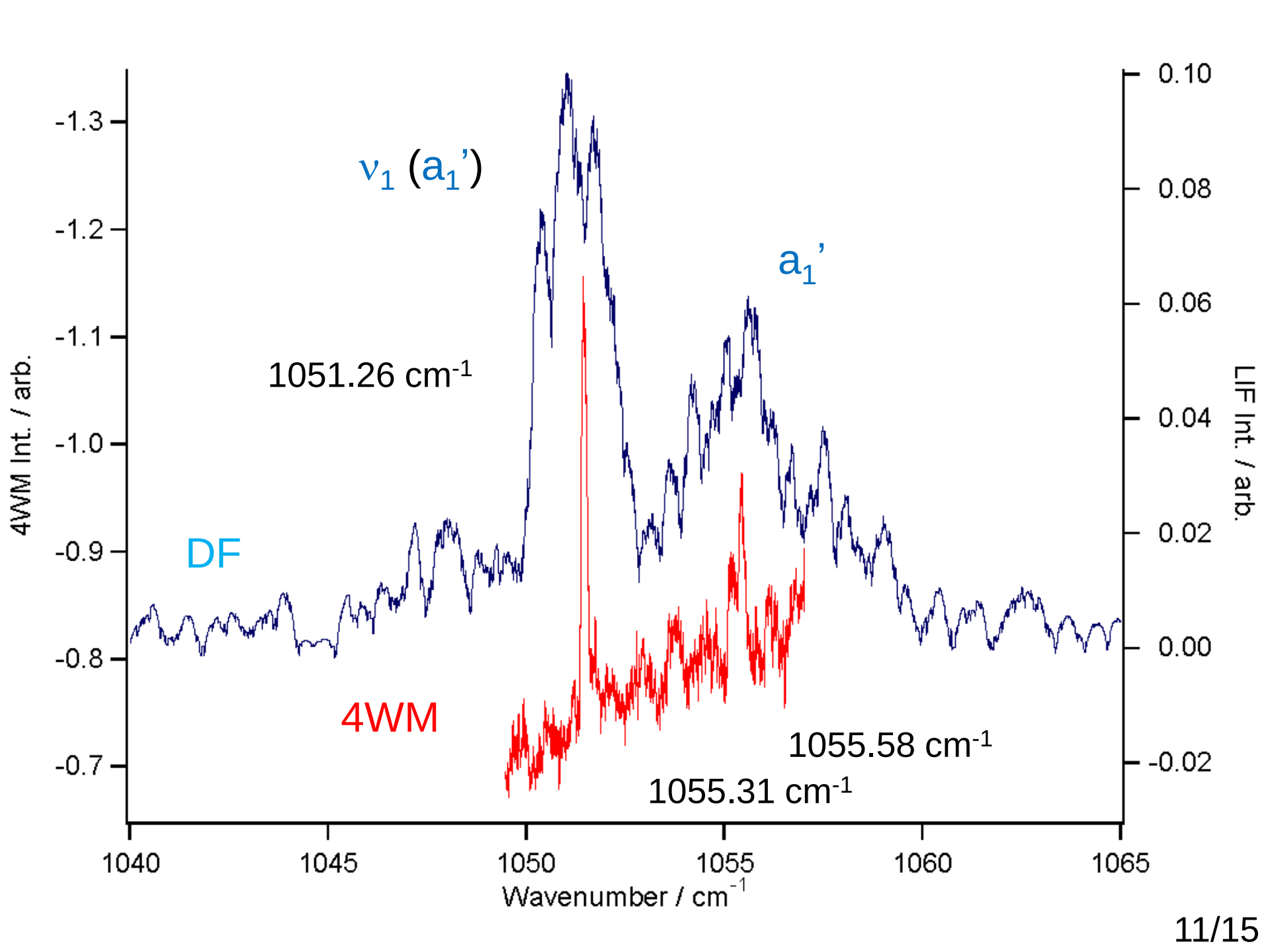

0+0 cm-1 band excitation
$\tilde{B}\ ^2E' - \tilde{X}\ ^2A_2'$
$^{14}NO_3$
ν_1 (a_1')
resolution : ~ 10 cm-1 (fwhm)
(monochromator settings)
Region I
ν_3 (e')
n ν_1
n ν_4
ν_1 + n ν_4
0
-500
-1000
-1500
-2000
-2500
-3000
Wavenumber / cm-1

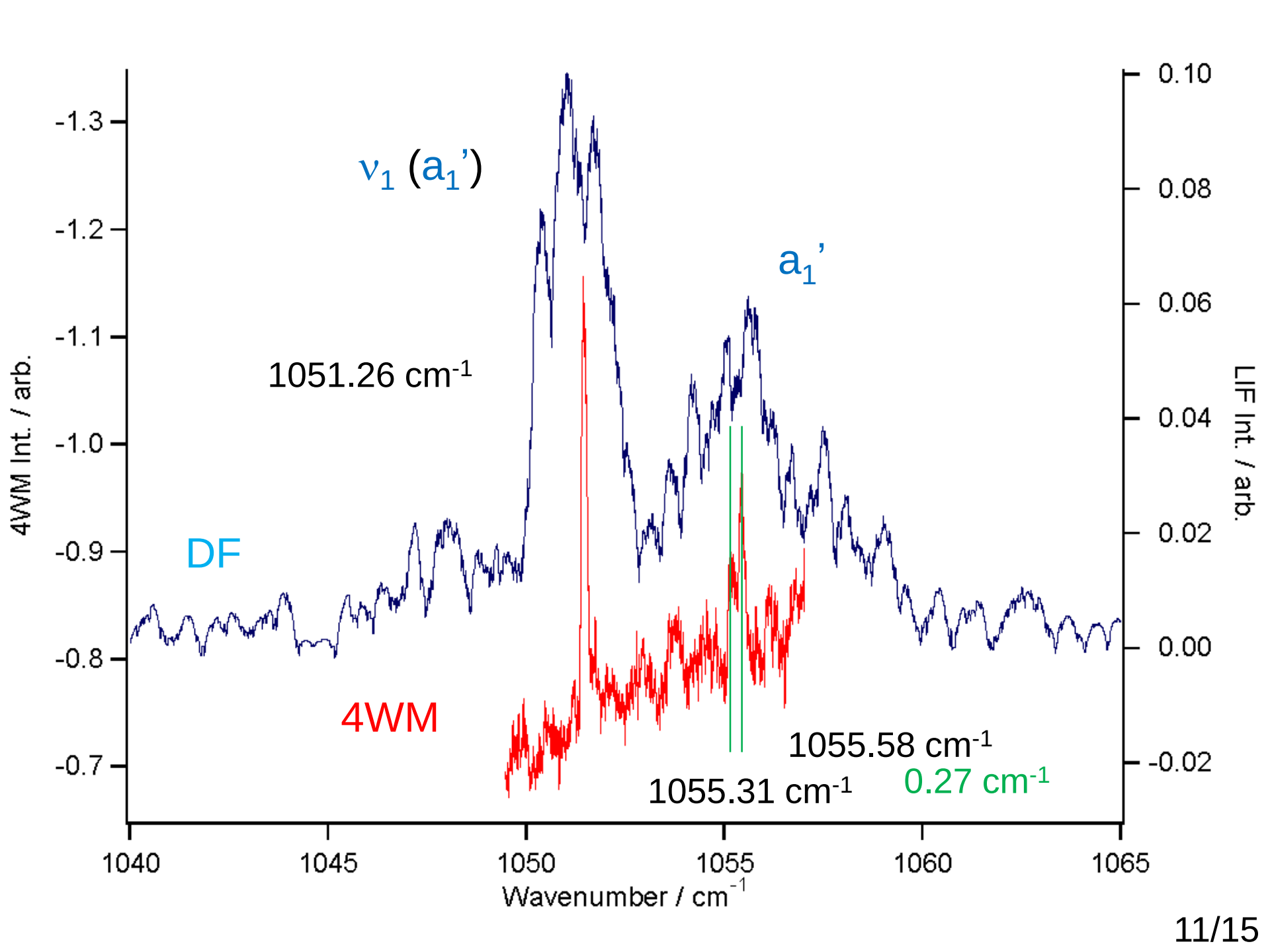

ν1 (a1')
a1'
1051.26 cm-1
DF
4WM
1055.58 cm-1
1055.31 cm-1
4WM Int. / arb.
LIF Int. / arb.
Wavenumber / cm-1
-1.3
-1.2
-1.1
-1.0
-0.9
-0.8
-0.7
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
1040
1045
1050
1055
1060
1065

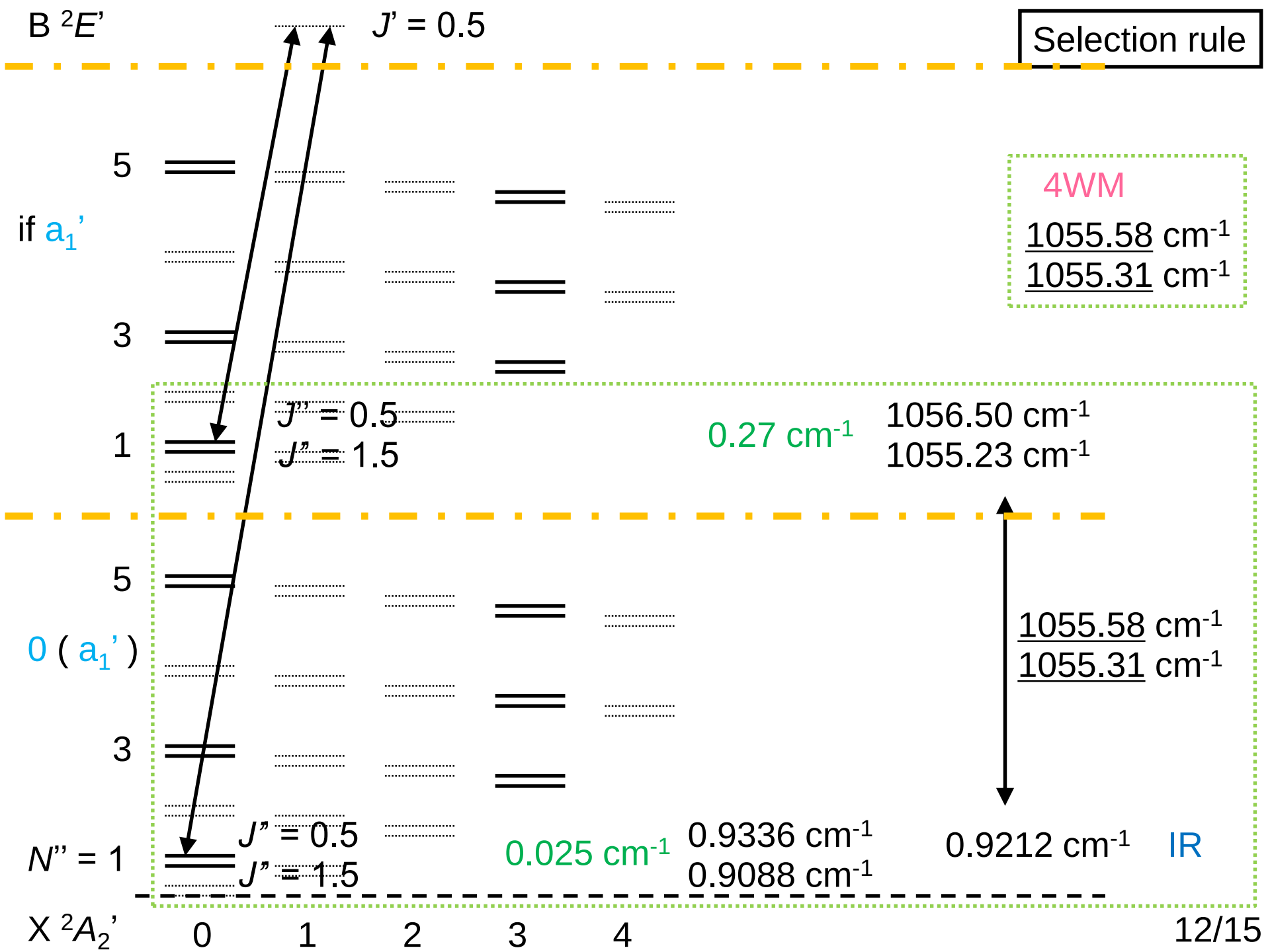

B $^2E'$
$J' = 0.5$
4WM
5
ν_1 (a_1')
3
1
$J'' = 0.5$
$J'' = 1.5$
$N'' = 1$
5
0 (a_1')
3
$N'' = 1$
$J'' = 0.5$
$J'' = 1.5$
0.9336 cm^{-1}
0.9088 cm^{-1}
0.9212 cm^{-1}
IR
X $^2A_2'$
0
1
2
3
4

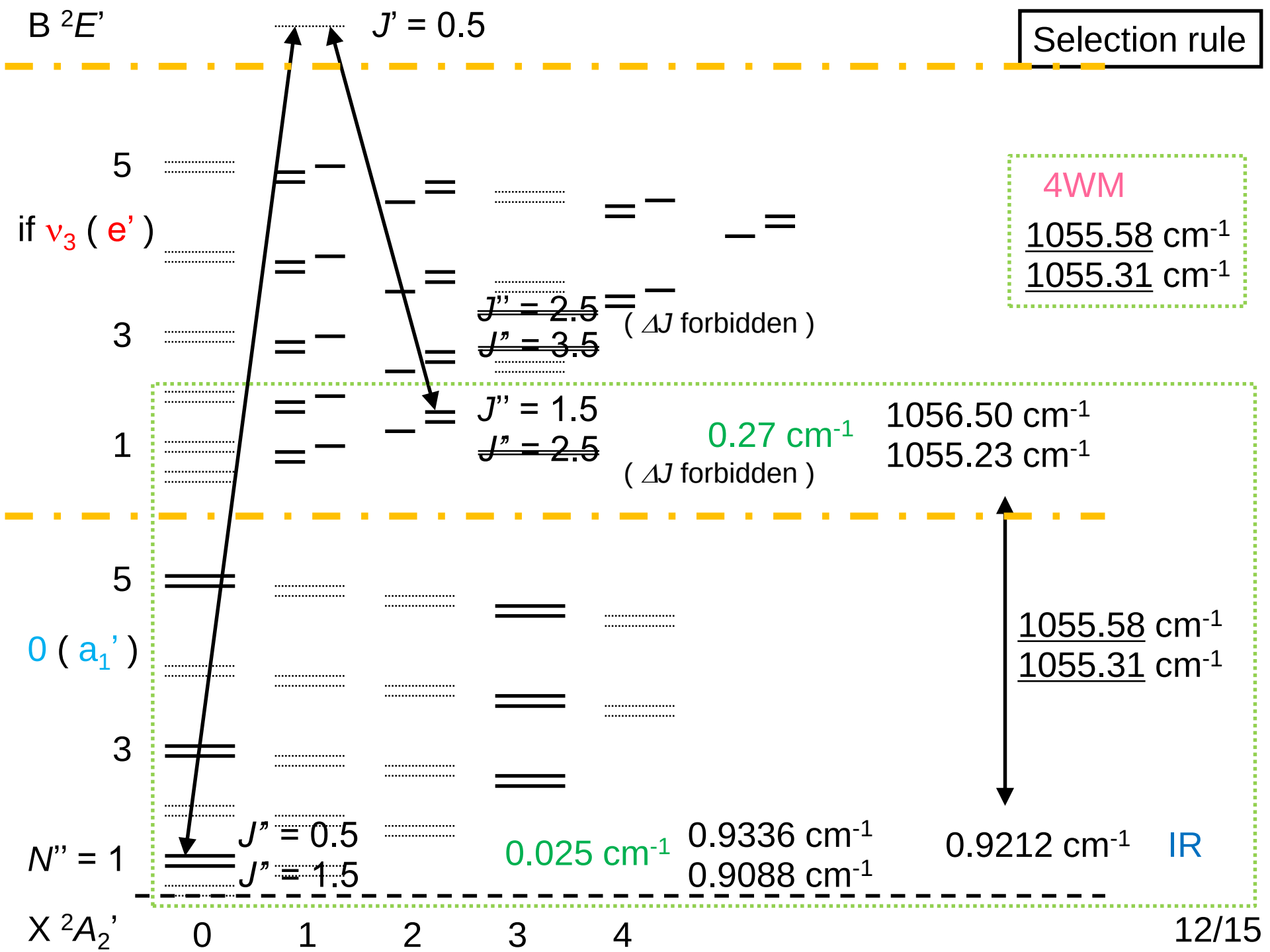

B $^2E'$
$J' = 0.5$
4WM
5
ν_1 (a_1')
3
1
$J'' = 0.5$
$J'' = 1.5$
$N'' = 1$
4WM
1051.26 cm^{-1}
5
0 (a_1')
3
$N'' = 1$
$J'' = 0.5$
$J'' = 1.5$
0.9336 cm^{-1}
0.9088 cm^{-1}
0.9212 cm^{-1}
IR
X $^2A_2'$
0
1
2
3
4

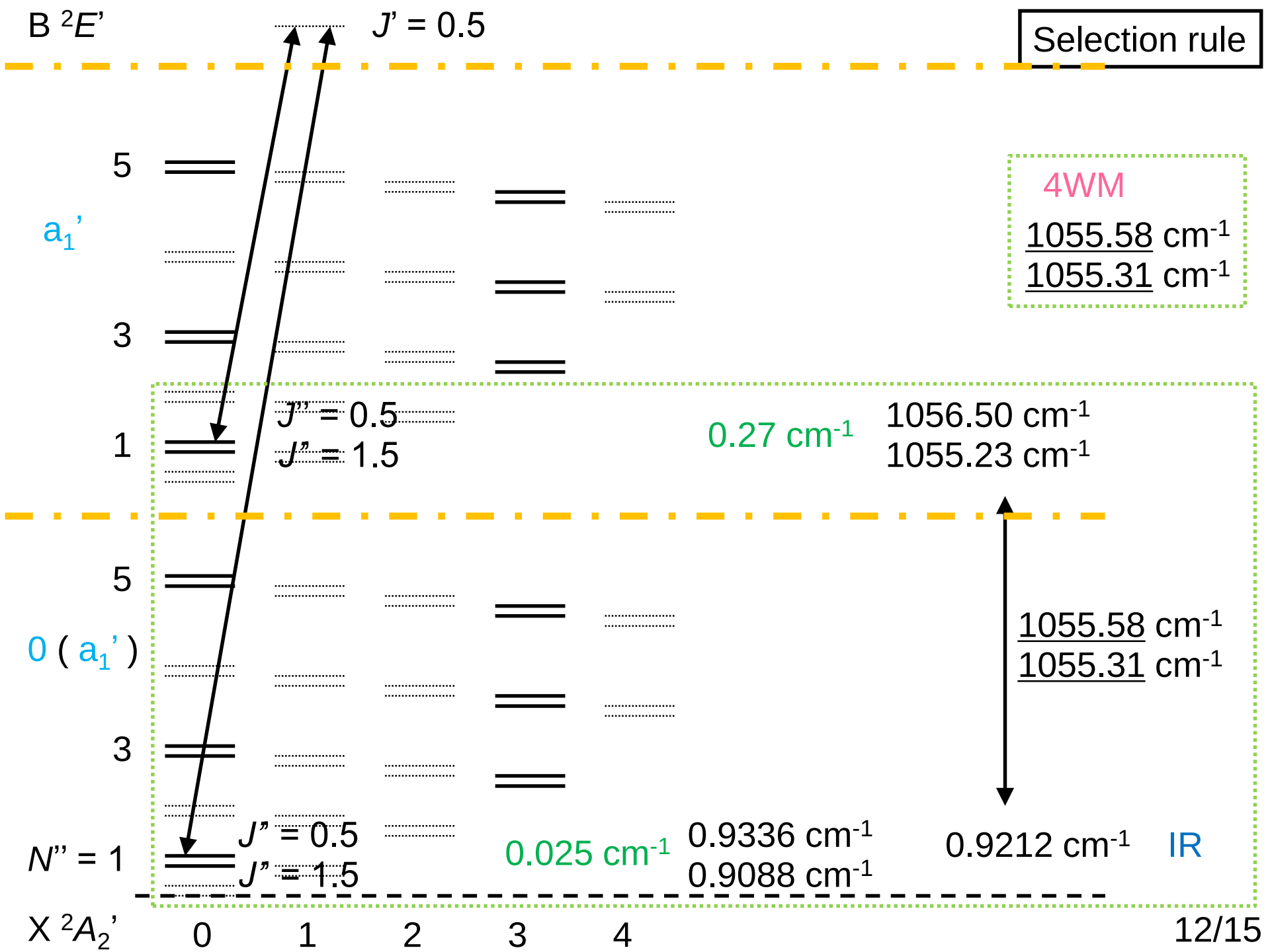

B $^2E'$
J' = 0.5
4WM
5
ν_1 (a_1')
3
1
J'' = 0.5
J'' = 1.5
N'' = 1
1052.18 cm^{-1}
4WM
1051.26 cm^{-1}
5
0 (a_1')
3
1051.26 cm^{-1}
J'' = 0.5
J'' = 1.5
N'' = 1
0.9336 cm^{-1}
0.9088 cm^{-1}
0.9212 cm^{-1}
IR
X $^2A_2'$
0
1
2
3
4


ν1 (a1')
a1'
1051.26 cm-1
DF
4WM
1055.58 cm-1
1055.31 cm-1
4WM Int. / arb.
LIF Int. / arb.
Wavenumber / cm-1
-1.3
-1.2
-1.1
-1.0
-0.9
-0.8
-0.7
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
1040
1045
1050
1055
1060
1065


ν1 (a1')
a1'
1051.26 cm-1
DF
4WM
1055.58 cm-1
1055.31 cm-1
0.27 cm-1
4WM Int. / arb.
LIF Int. / arb.
Wavenumber / cm-1
-1.3
-1.2
-1.1
-1.0
-0.9
-0.8
-0.7
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
1040
1045
1050
1055
1060
1065


B $^2E'$
J' = 0.5
Selection rule
5
if a_1'
3
1
J'' = 0.5
J'' = 1.5
4WM
1055.58 cm^{-1}
1055.31 cm^{-1}
0.27 cm^{-1}
1056.50 cm^{-1}
1055.23 cm^{-1}
5
0 (a_1')
3
N'' = 1
J'' = 0.5
J'' = 1.5
0.025 cm^{-1}
0.9336 cm^{-1}
0.9088 cm^{-1}
1055.58 cm^{-1}
1055.31 cm^{-1}
0.9212 cm^{-1}
IR
X $^2A_2'$
0
1
2
3
4
12/15


B $^2E'$
$J' = 0.5$
Selection rule
5
if ν_3 (e')
3
1
$J'' = 2.5$
$J' = 3.5$
(ΔJ forbidden)
$J'' = 1.5$
$J' = 2.5$
0.27 cm^{-1}
(ΔJ forbidden)
4WM
1055.58 cm^{-1}
1055.31 cm^{-1}
1056.50 cm^{-1}
1055.23 cm^{-1}
5
0 (a_1')
3
1055.58 cm^{-1}
1055.31 cm^{-1}
$N'' = 1$
$J'' = 0.5$
$J'' = 1.5$
0.025 cm^{-1}
0.9336 cm^{-1}
0.9088 cm^{-1}
0.9212 cm^{-1}
IR
X $^2A_2'$
0
1
2
3
4


B $^2E'$
$J' = 0.5$
Selection rule
5
a_1'
3
1
4WM
1055.58 cm^{-1}
1055.31 cm^{-1}
$J'' = 0.5$
$J'' = 1.5$
0.27 cm^{-1}
1056.50 cm^{-1}
1055.23 cm^{-1}
5
0 (a_1')
3
1055.58 cm^{-1}
1055.31 cm^{-1}
$N'' = 1$
$J'' = 0.5$
$J'' = 1.5$
0.025 cm^{-1}
0.9336 cm^{-1}
0.9088 cm^{-1}
0.9212 cm^{-1}
IR
X $^2A_2'$
0
1
2
3
4

The splitting, 0.27 cm^{-1}, at N = 1 of the new a_1' vibronic level.

We think the new a_1' level is assigned to 3 ν_4 (a_1').

We consider two limiting cases;

(1) l and Σ are independent;

$$|v_4, l, \Sigma\rangle = |\, v_4, l \,\rangle\, |\, \Sigma \,\rangle$$

(2) l and Σ are coupled;

$$|v_4, l, \Sigma, P\rangle \neq |\, v_4, l \,\rangle\, |\, \Sigma \,\rangle$$

$$(P = l + \Sigma)$$

The splitting, 0.27 cm^{-1}, at N = 1 of the new a_1' vibronic level.

a_1' (l = 0) vibronic levels
(zero-vibrational, ν_1 fundamental)

$$|v_4, l, \Sigma\rangle = |v_4, l\rangle |\Sigma\rangle$$

N = 1 $\quad J$ = 0.5 $\quad |0, 0\rangle |-\frac{1}{2}\rangle$

J' = 1.5 $\quad |0, 0\rangle |+\frac{1}{2}\rangle$

K = 1

splitting : spin-rotation (0.025 cm^{-1})

a_1' ($l = \pm 3$) vibronic levels
3 ν_4 (a_1')

$$|v_4, l, \Sigma\rangle = |v_4, l\rangle |\Sigma\rangle$$

N = 1 $\quad J$ = 0.5 $\quad |3, 0; a_1'\rangle |-\frac{1}{2}\rangle$

J = 1.5 $\quad |3, 0; a_1'\rangle |+\frac{1}{2}\rangle$

K = 1

$$a_1' : |3, +3\rangle + |3, -3\rangle : |3, 0; a_1'\rangle$$

$$a_2' : |3, +3\rangle - |3, -3\rangle : |3, 0; a_2'\rangle$$

The splitting, 0.27 cm^{-1}, at N = 1 of the new a_1' vibronic level.

a_1' (l = 0) vibronic levels
(zero-vibrational, ν_1 fundamental)

$$|v_4, l, \Sigma\rangle = |v_4, l\rangle |\Sigma\rangle$$

N = 1 $\quad J$ = 0.5 $\quad |0, 0\rangle |-\frac{1}{2}\rangle$

$\quad\quad\quad\quad J'$ = 1.5 $\quad |0, 0\rangle |+\frac{1}{2}\rangle$

K = 1

splitting : spin-rotation (0.025 cm^{-1})

a_1' ($l = \pm 3$) vibronic levels
3 ν_4 (a_1')

$$|v_4, l, \Sigma\rangle = |v_4, l\rangle |\Sigma\rangle$$

N = 1 $\quad J$ = 0.5 $\quad |3, 0; a_1'\rangle |-\frac{1}{2}\rangle$

$\quad\quad\quad\quad J$ = 1.5 $\quad |3, 0; a_1'\rangle |+\frac{1}{2}\rangle$

K = 1

$$|v_4, l, \Sigma, P\rangle \neq |v_4, l\rangle |\Sigma\rangle$$
($P = l + \Sigma$)

N = 1 $\quad J$ = 0.5 $\quad |0, 0, -\frac{1}{2}, -\frac{1}{2}\rangle$

$\quad\quad\quad\quad J$ = 1.5 $\quad |0, 0, +\frac{1}{2}, +\frac{1}{2}\rangle$

K = 1

$$|v_4, l, \Sigma, P\rangle \neq |v_4, l\rangle |\Sigma\rangle$$
($P = l + \Sigma$)

N = 1 $\quad J$ = 0.5 $\quad |3, 0, \mp\frac{1}{2}, \mp\frac{1}{2}\rangle$

$\quad\quad\quad\quad J$ = 1.5 $\quad |3, 0, \pm\frac{1}{2}, \pm\frac{1}{2}\rangle$

K = 1

$$a_1' : |3, 0, \pm\tfrac{1}{2}, \pm\tfrac{1}{2}\rangle = |3, +3, +\tfrac{1}{2}, +\tfrac{7}{2}\rangle + |3, -3, -\tfrac{1}{2}, -\tfrac{7}{2}\rangle$$

$$a_1' : |3, 0, \mp\tfrac{1}{2}, \mp\tfrac{1}{2}\rangle = |3, +3, -\tfrac{1}{2}, +\tfrac{5}{2}\rangle + |3, -3, +\tfrac{1}{2}, -\tfrac{5}{2}\rangle$$

The splitting, 0.27 cm^{-1}, at N = 1 of the new a_1' vibronic level.

a_1' (l = 0) vibronic levels
(zero-vibrational, ν_1 fundamental)

$$|v_4, l, \Sigma\rangle \;=\; |\, v_4, l \,\rangle \,|\, \Sigma \,\rangle$$

N = 1, K = 1:
- J = 0.5 : $|\, 0, 0 \,\rangle \,|\, -\tfrac{1}{2} \rangle$
- J' = 1.5 : $|\, 0, 0 \,\rangle \,|\, +\tfrac{1}{2} \rangle$

splitting : spin-rotation (0.025 cm^{-1})

$$|v_4, l, \Sigma, P\rangle \;\neq\; |\, v_4, l \,\rangle \,|\, \Sigma \,\rangle$$

($P = l + \Sigma$)

N = 1, K = 1:
- J = 0.5 : $|\, 0, 0, -\tfrac{1}{2}, -\tfrac{1}{2}\rangle$
- J = 1.5 : $|\, 0, 0, +\tfrac{1}{2}, +\tfrac{1}{2}\rangle$

a_1' (l = $\pm$3) vibronic levels
3 ν_4 (a_1')

$$|v_4, l, \Sigma\rangle \;=\; |\, v_4, l \,\rangle \,|\, \Sigma \,\rangle$$

N = 1, K = 1:
- J = 0.5 : $|\, 3, 0; a_1{}' \,\rangle \,|\, -\tfrac{1}{2} \rangle$
- J = 1.5 : $|\, 3, 0; a_1{}' \,\rangle \,|\, +\tfrac{1}{2} \rangle$

Different splitting is expected.
(***S***-uncoupling among the P bases ?)

$$|v_4, l, \Sigma, P\rangle \;\neq\; |\, v_4, l \,\rangle \,|\, \Sigma \,\rangle$$

($P = l + \Sigma$)

N = 1, K = 1:
- J = 0.5 : $|\, 3, 0, \mp\tfrac{1}{2}, \mp\tfrac{1}{2}\rangle$
- J = 1.5 : $|\, 3, 0, \pm\tfrac{1}{2}, \pm\tfrac{1}{2}\rangle$

$$a_1{}' \;:\; |3, 0, \pm\tfrac{1}{2}, \pm\tfrac{1}{2}\rangle \;=\; |3, +3, +\tfrac{1}{2}, +\tfrac{7}{2}\rangle + |3, -3, -\tfrac{1}{2}, -\tfrac{7}{2}\rangle$$

$$a_1{}' \;:\; |3, 0, \mp\tfrac{1}{2}, \mp\tfrac{1}{2}\rangle \;=\; |3, +3, -\tfrac{1}{2}, +\tfrac{5}{2}\rangle + |3, -3, +\tfrac{1}{2}, -\tfrac{5}{2}\rangle$$

Conclusions

LIF DF (higher resolution) and 2C-R4WM spectra have been measured for vibronic bands at the 1050 and 1500 cm^{-1} regions, and three a_1' bands, ν_1, $2\nu_2$, and $3\nu_4$, give the 2C-R4WM signals.

- The $2\nu_2$ (a_1') spectrum confirms that 2C-R4WM can be applied to characterize vibrational levels.
- The term value of ν_1 has been determined, though the spin splitting is not resolved.
- 2C-R4WM spectrum of the new 1055 cm^{-1} band shows larger spin splitting at $K = 1$ and $N = 1$, and this indicates this is an a_1' band, and this agrees with our $3\nu_4$ (a_1') assignment of this band.

Acknowledgement

Dr. Peter Radi, Paul Scherrer Inst., Villigen, Szwitterland and
Prof. Pat Vaccaro, Yale Univ., New Heaven, Connecticut
for their valuable suggestions and comments on this 4WM experiment.

Problems of computational results

1000 cm^{-1} (near ν_1) region

- The ν_3 fundamental, which predicted to be at ~ 1000 cm^{-1} (near ν_1), has not been observed yet by IR spectroscopy.

Stanton (2007) : The ν_3 fundamental is too week.
Viel & Eisfeld (2018) : It should be observed.

1500 cm^{-1} (near "traditional" ν_3) region

- The a_2' level, which assigned to be the $\nu_3+\nu_4$ combination, has not been observed yet by IR spectroscopy.

Stanton (2007) : The a_3' level should be observed.
Viel & Eisfeld (2018) : It should be observed.

Symmetric molecules, like NO_3, have strong ν_3 fundamental, as "traditional" ν_3 assignment for NO_3.