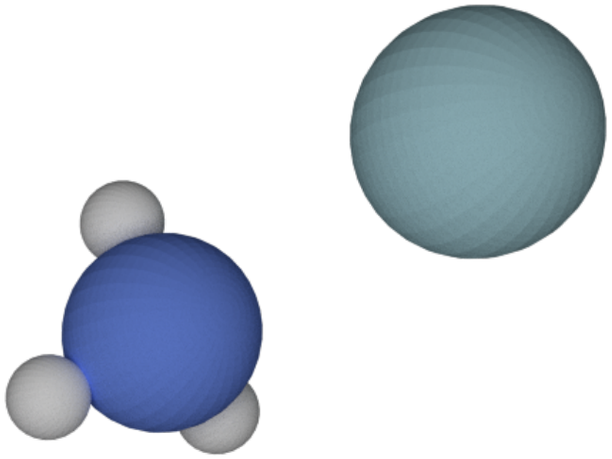
2OH overtone spectroscopy of water-containing van der Waals species

THOMAS VANFLETEREN

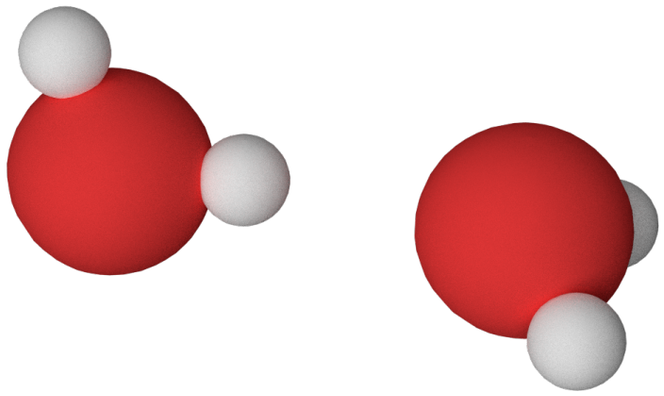
photo credit: Jenny Mottar

Investigated molecules

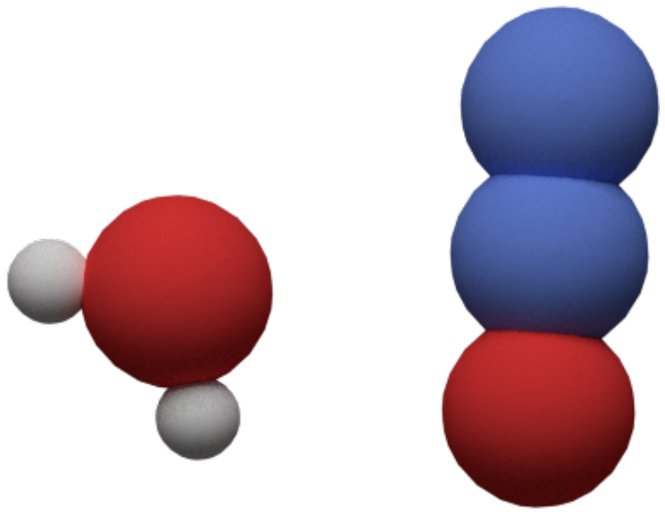
$^{14,15}NH_3$-Ar/Kr



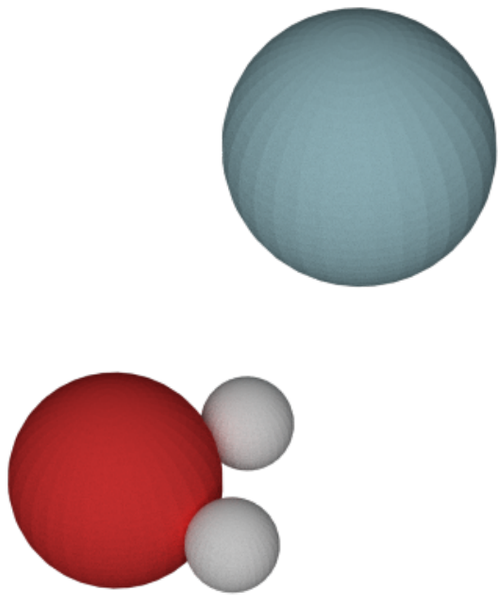
$(H_2O)_2$



HDO-N_2O



H_2O-Ar/Kr



Investigated molecules

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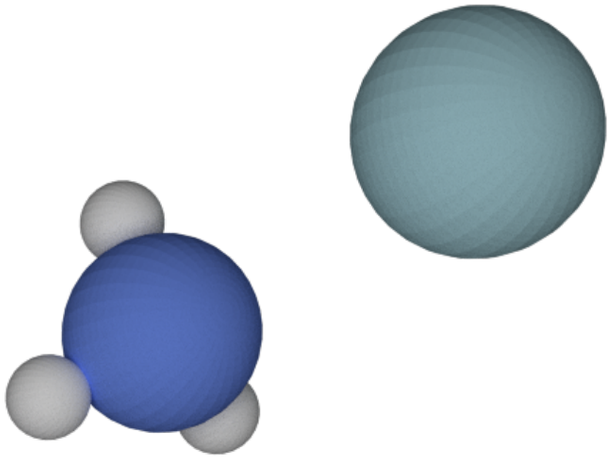

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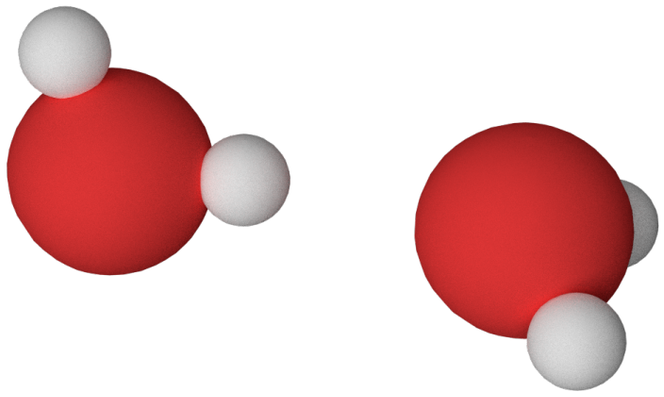
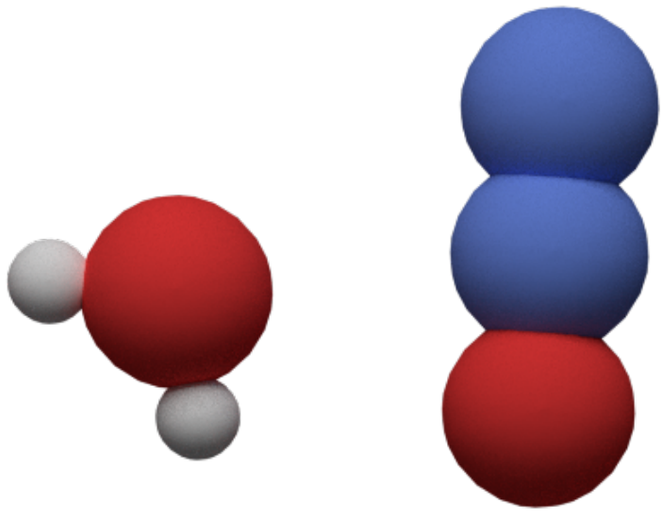
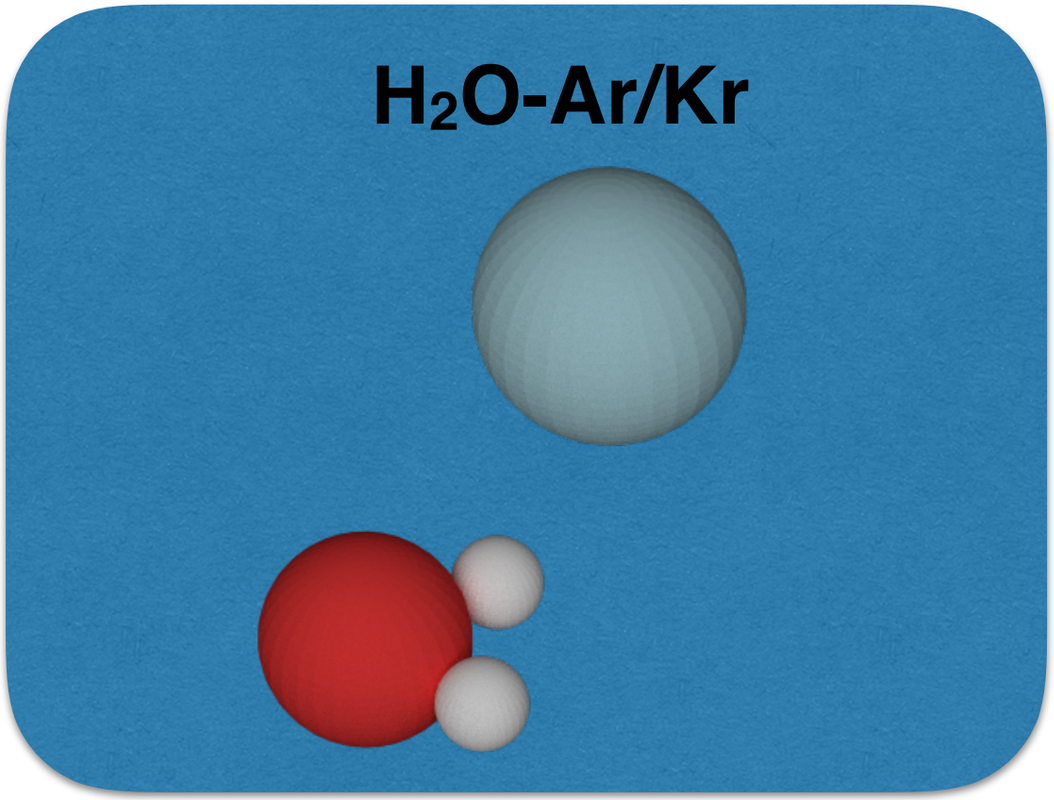


HDO-N_2O

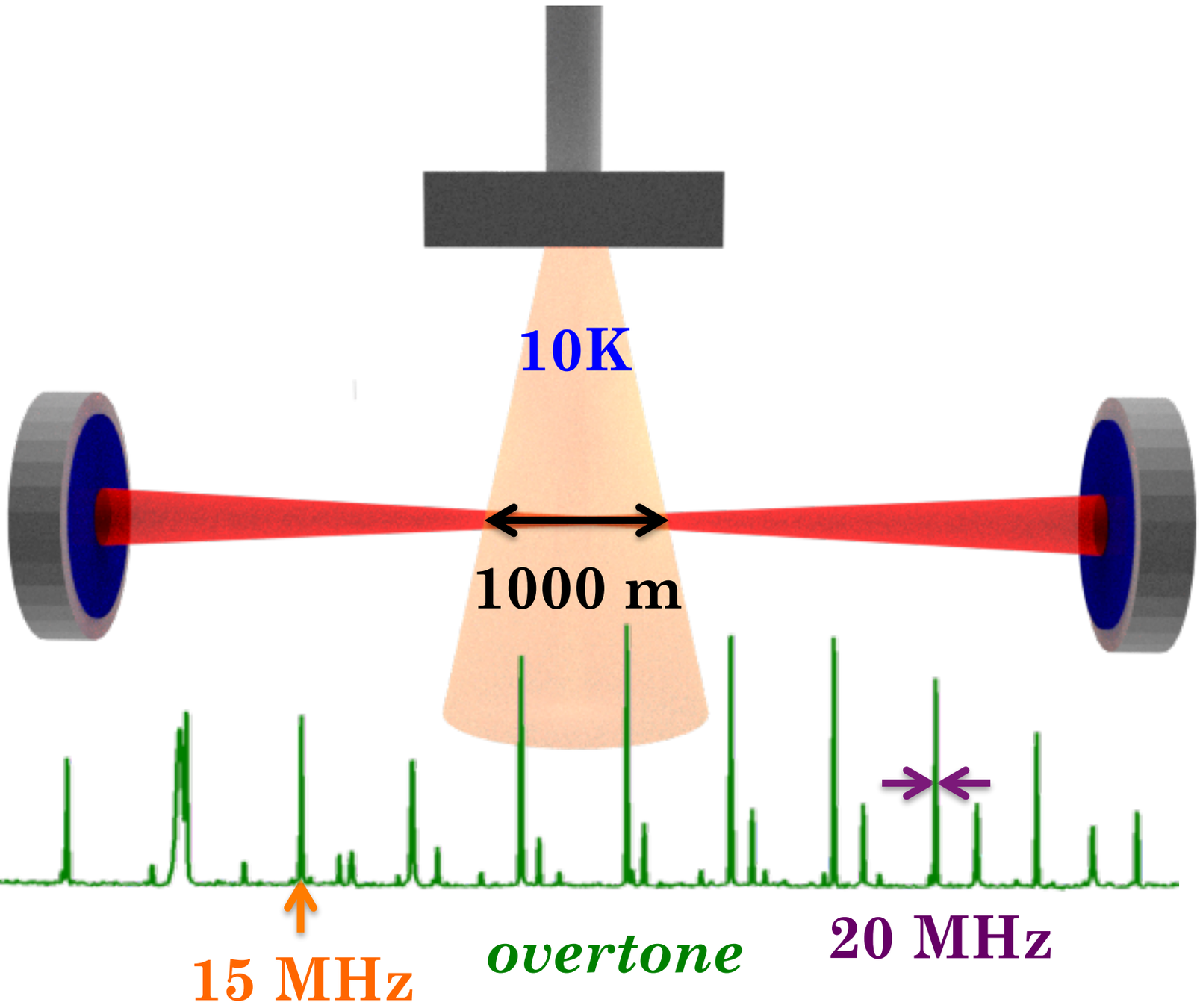


H_2O-Ar/Kr



Experimental set-up

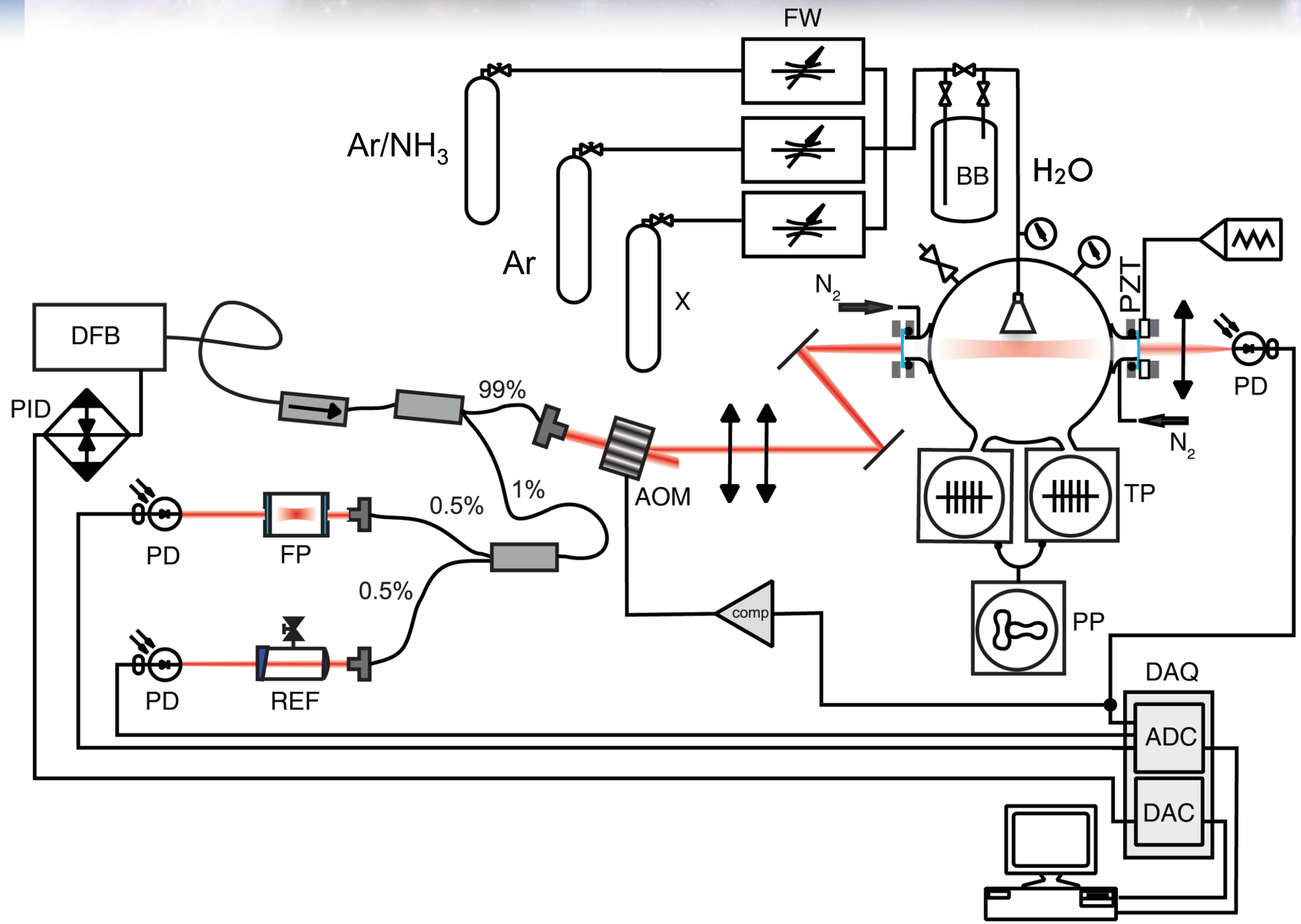
Supersonic jet



Mirrors reflectivity: 99.999 %

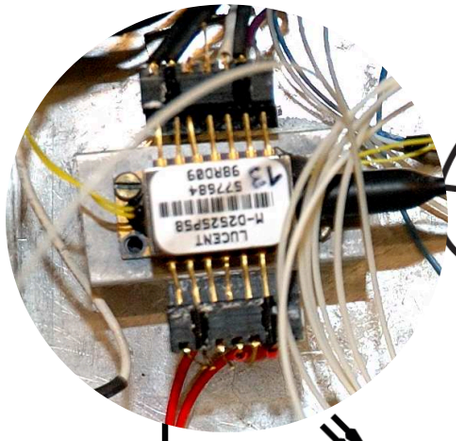
Cavity Ring Down Spectroscopy

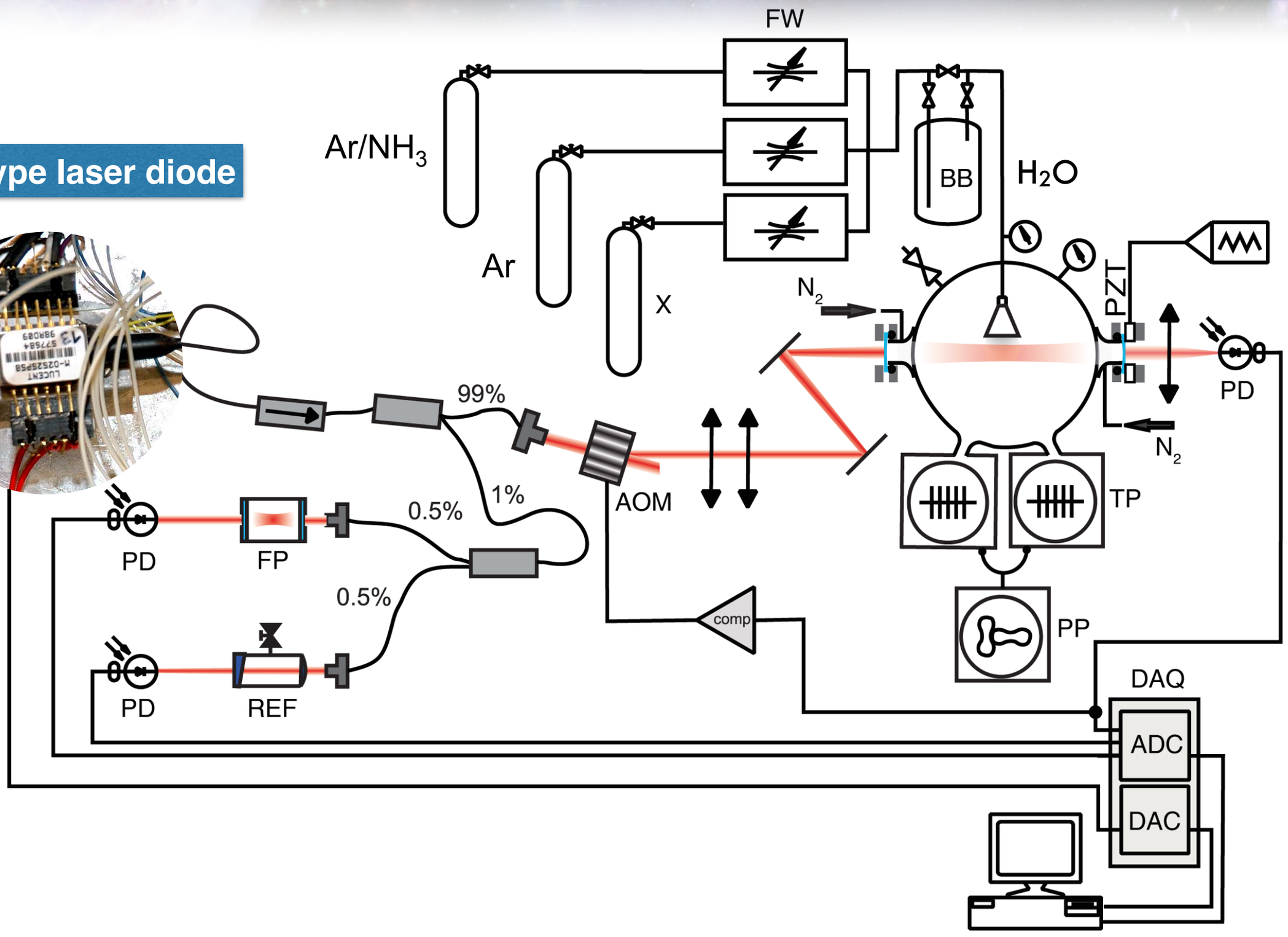
Experimental set-up



Experimental set-up

DFB-type laser diode





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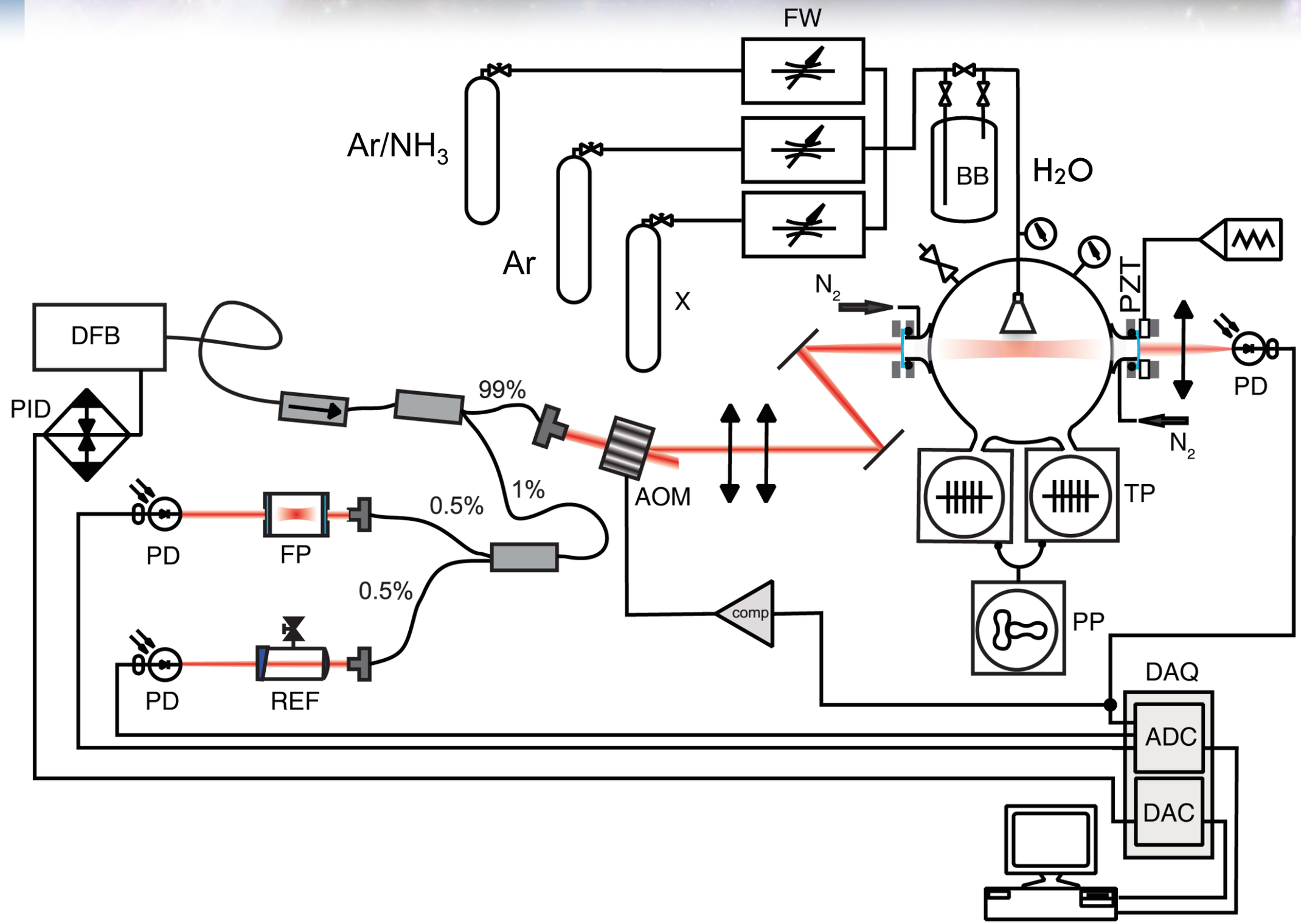

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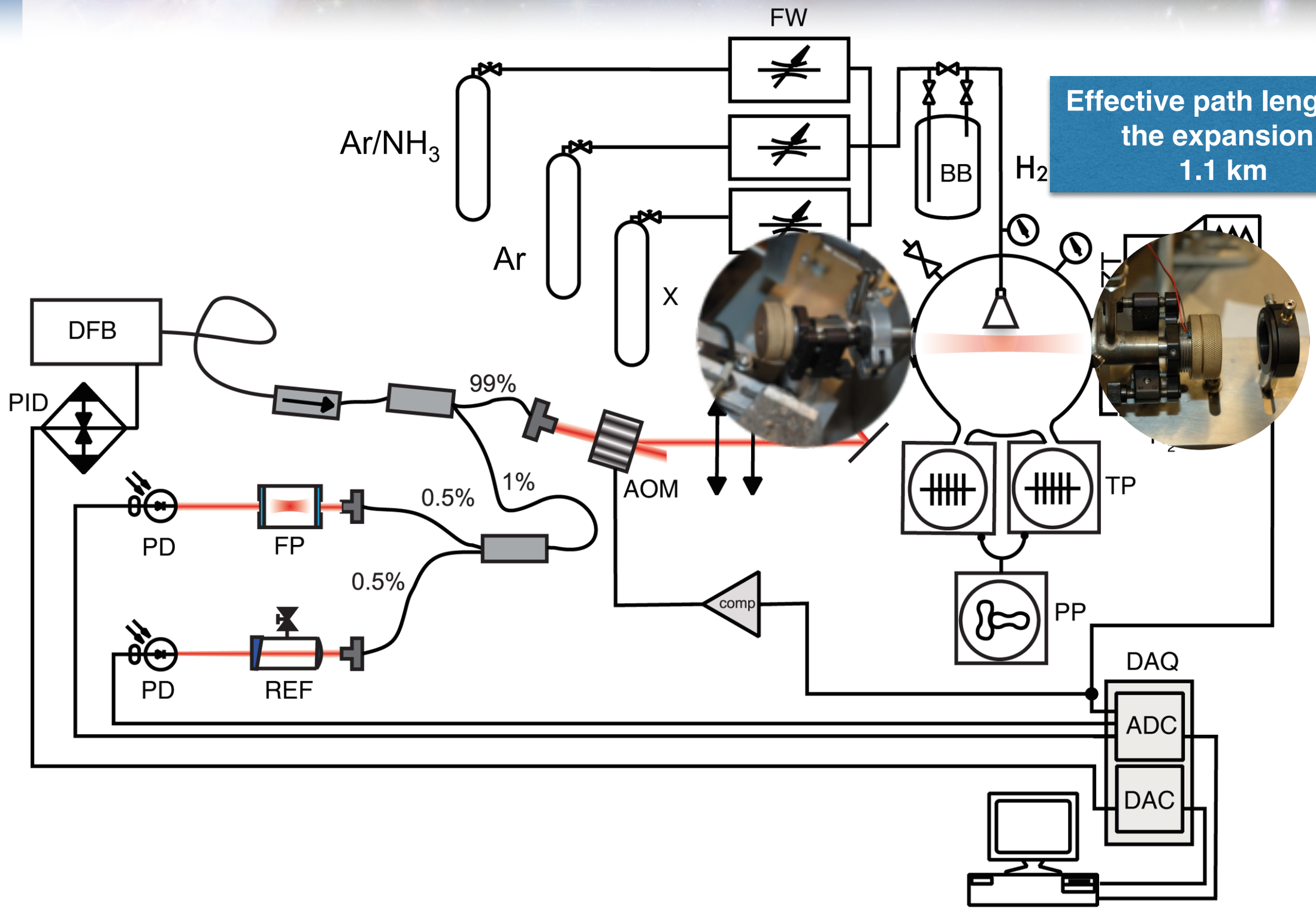
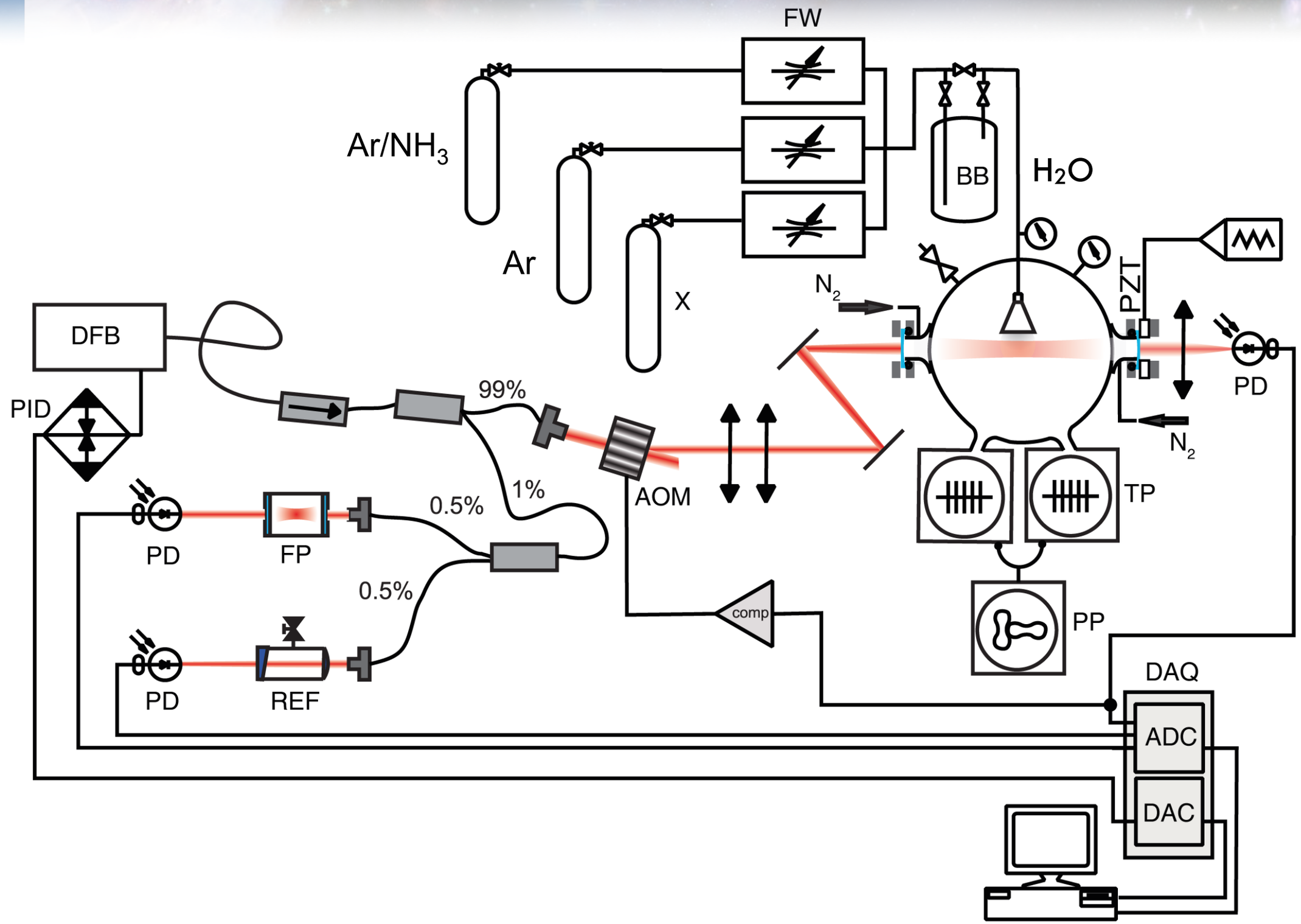
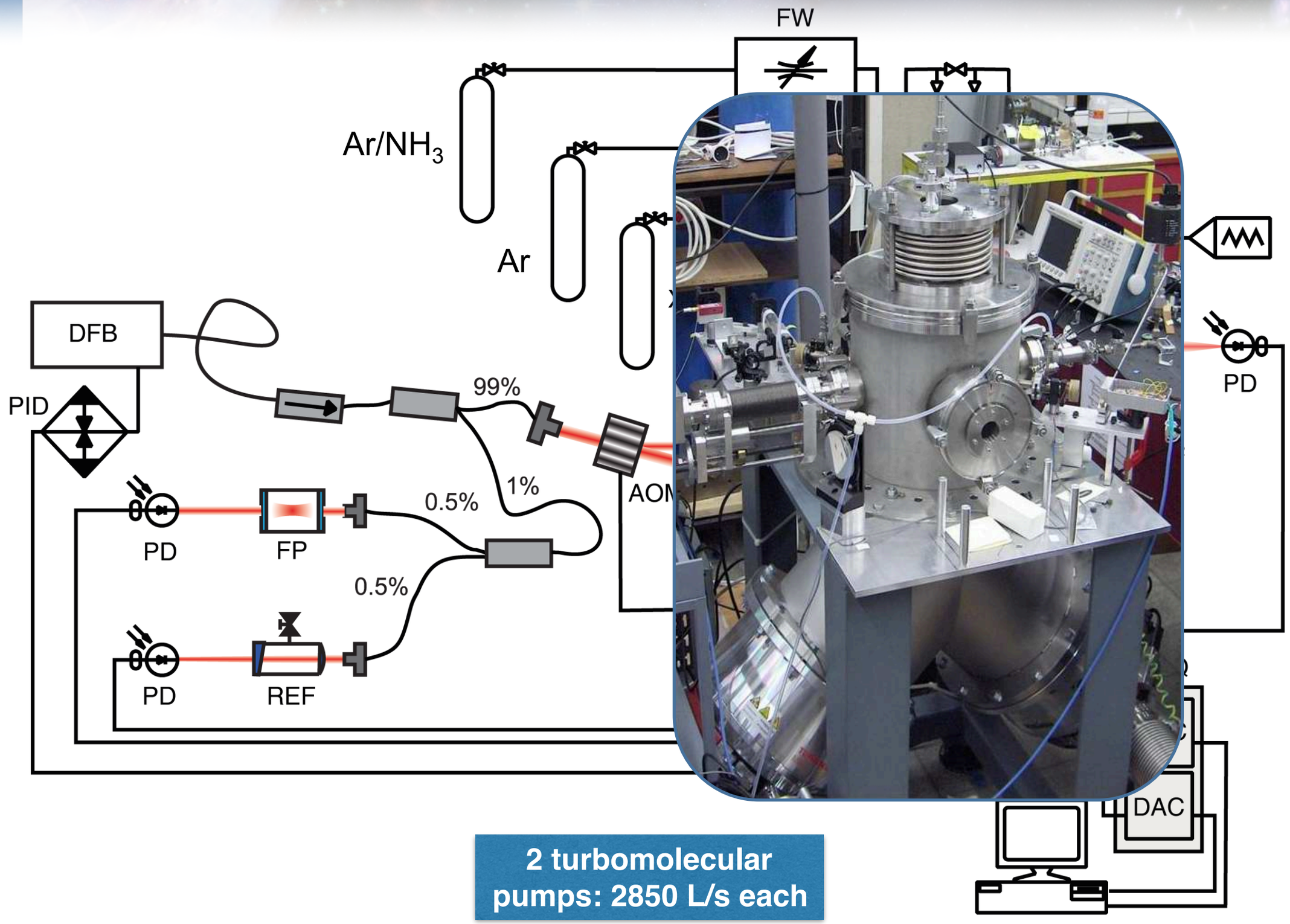


Effective path length in the expansion: 1.1 km

Experimental set-up



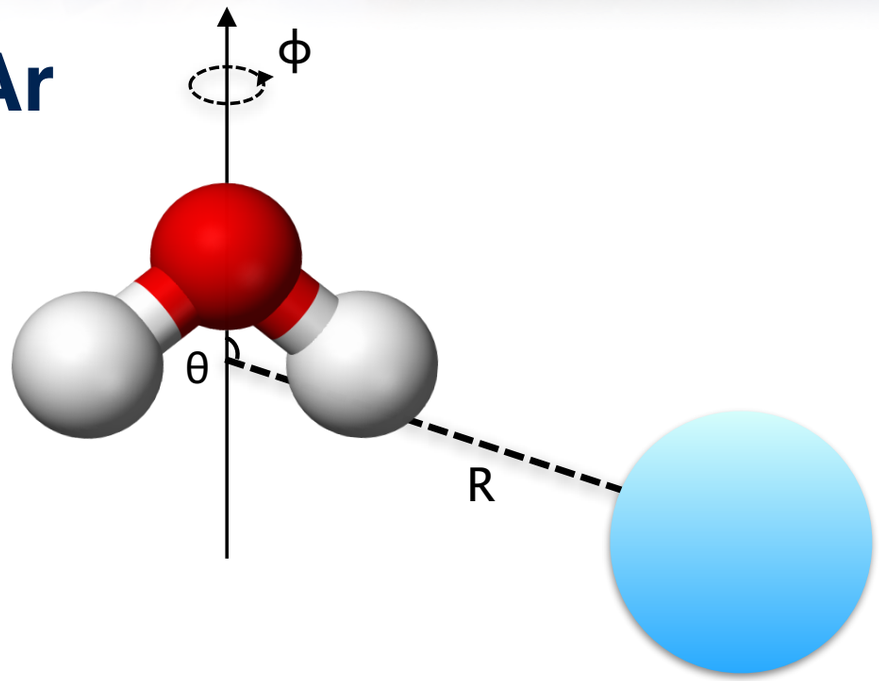
Experimental set-up



2 turbomolecular pumps: 2850 L/s each

Energy levels labelling

H_2O-Ar

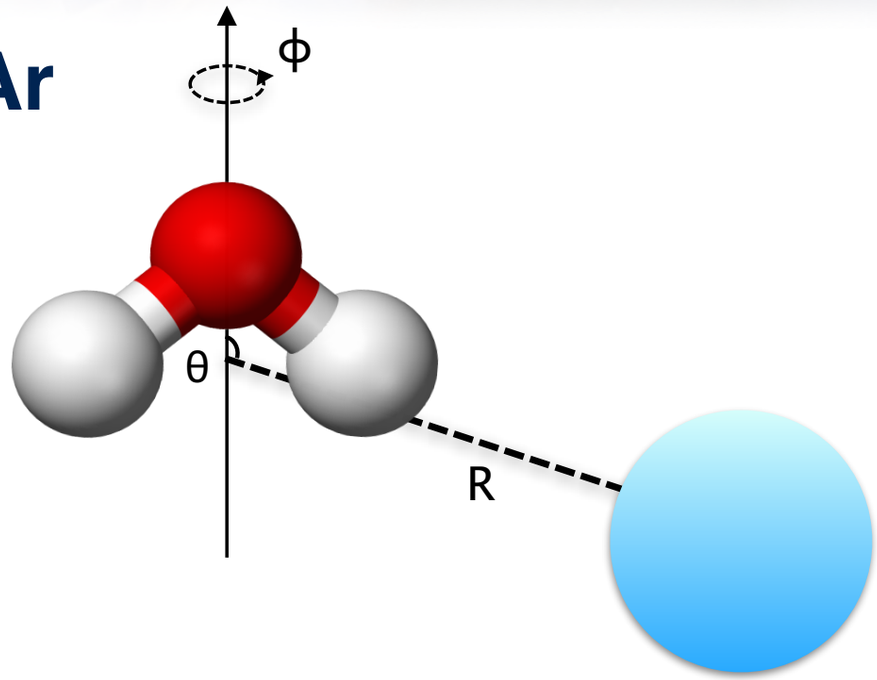


H_2O-Ar [a]
θ = 100.5°
ϕ = 0° (planar)
R = 3.630 Å
D_0 = 139.53 cm^{-1}

[a] D. Hou *et al.*, J. Chem. Phys. 144, 014301 (2016)

Energy levels labelling

H_2O-Ar



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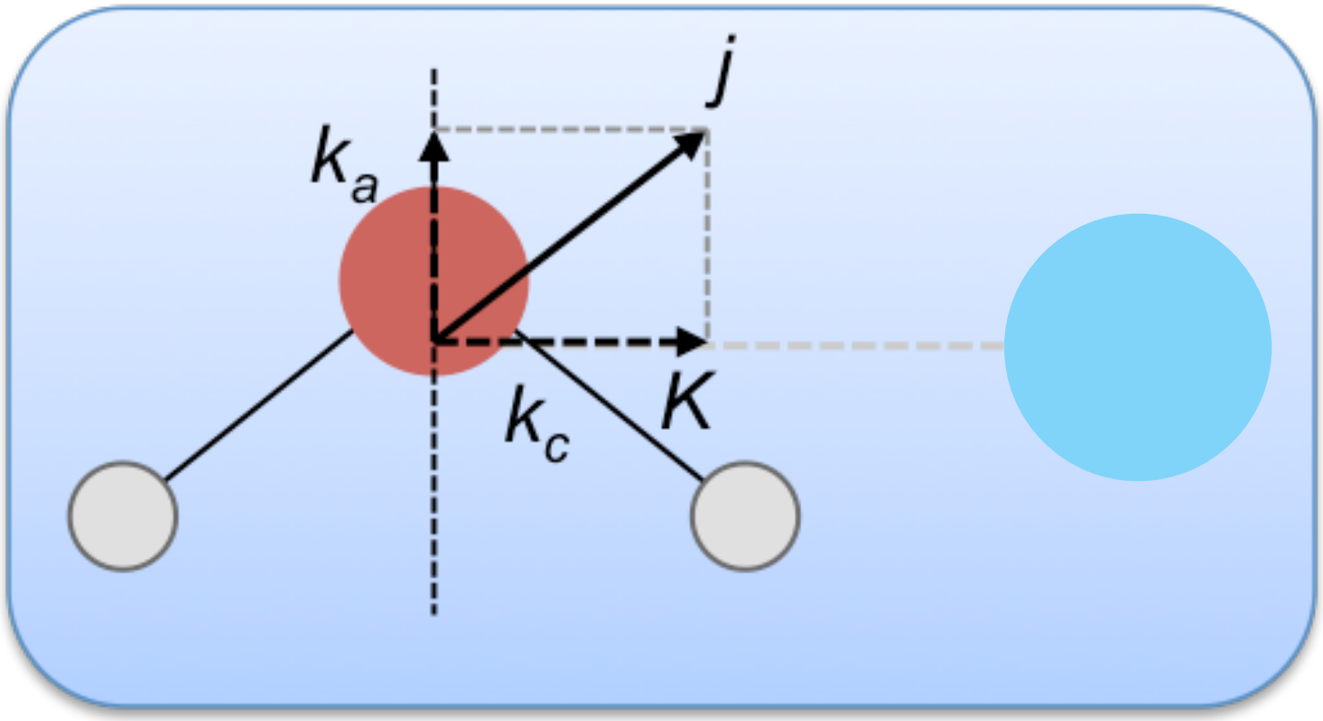

Linear species approximation

$$K = 0, 1, 2, \ldots$$
$$\downarrow \quad \downarrow \quad \downarrow$$
$$\Sigma, \Pi, \Delta, \ldots$$

[a] D. Hou *et al.*, J. Chem. Phys. 144, 014301 (2016)

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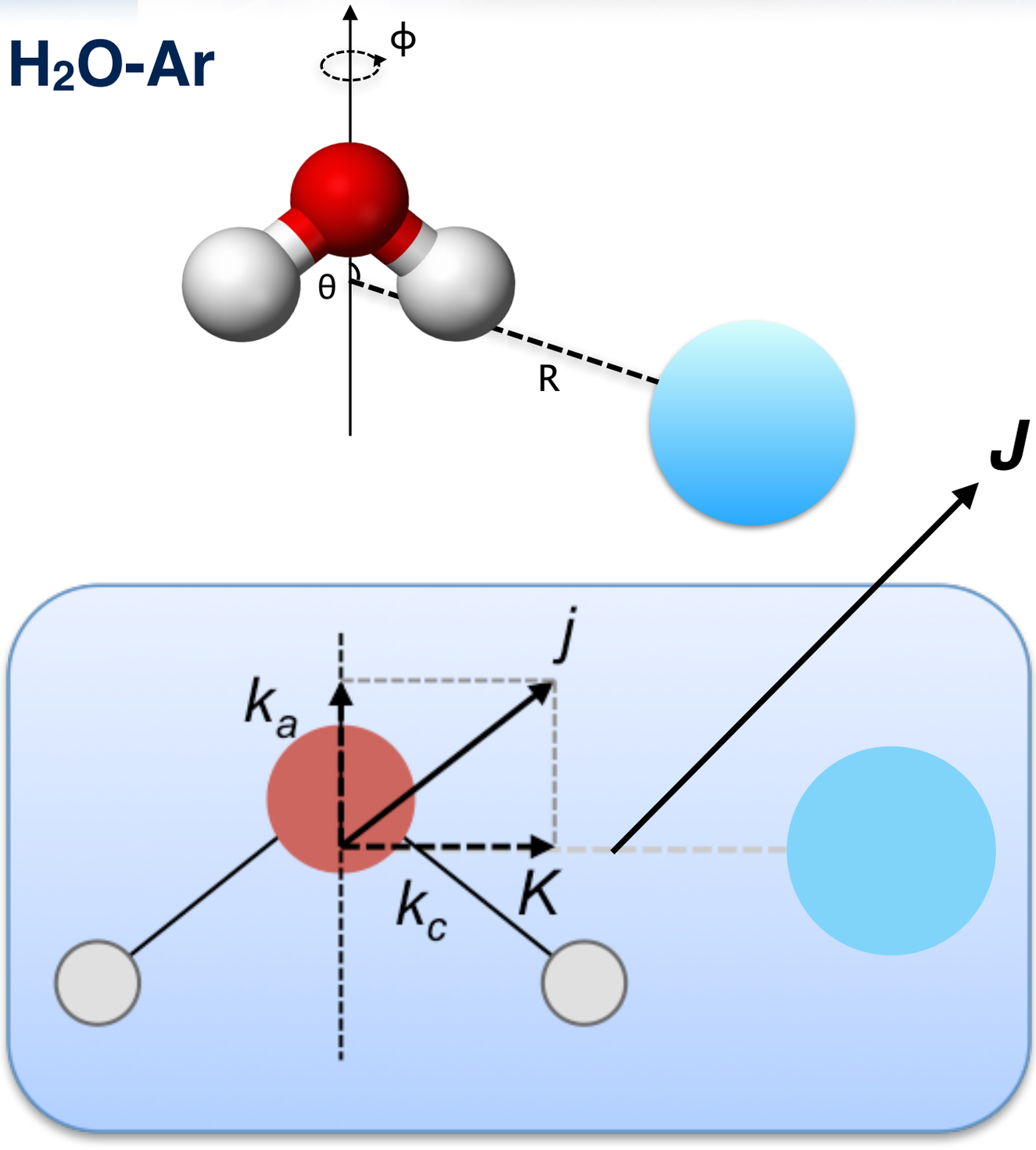

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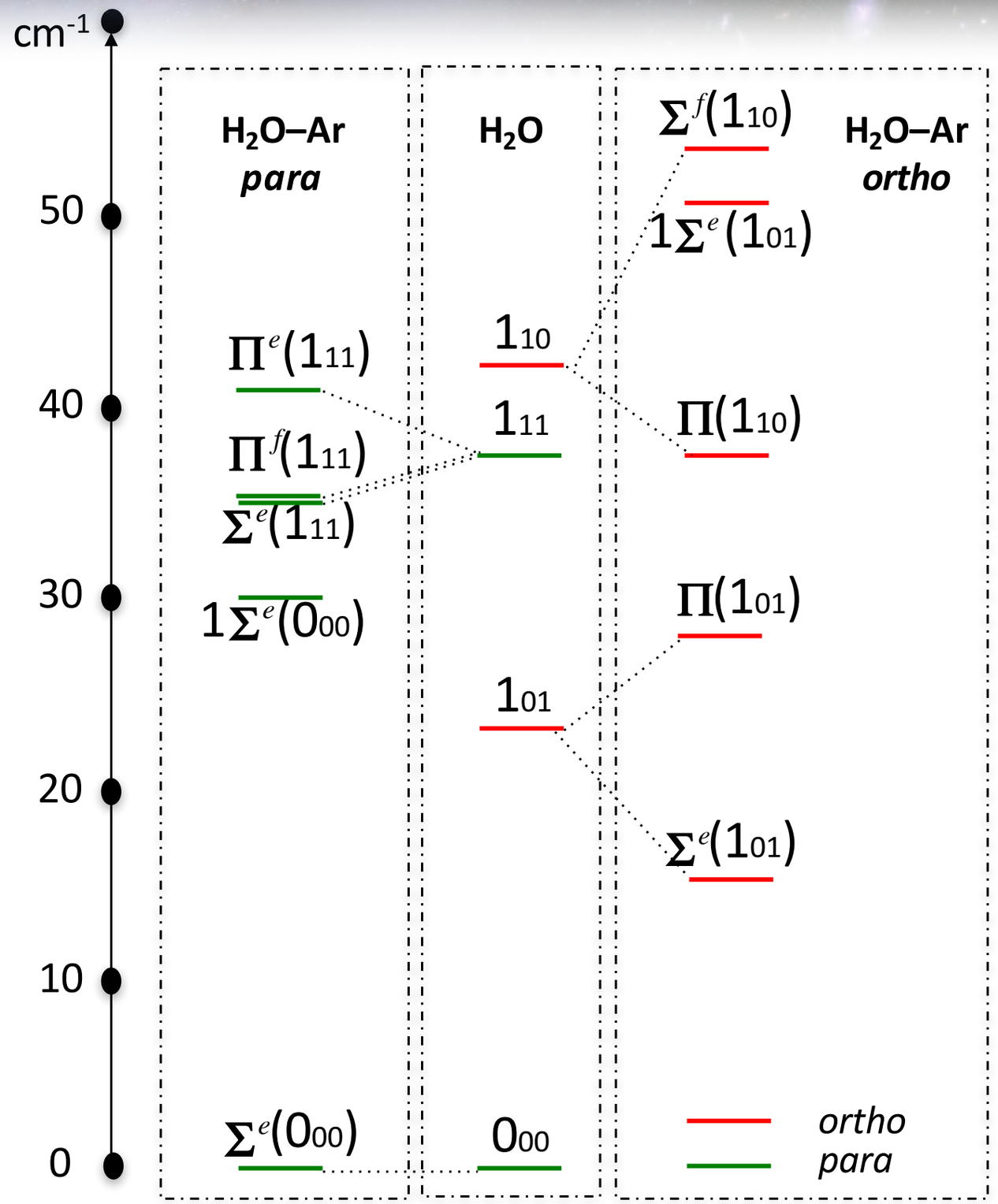
Ground state energy levels

MW and FIR investigations:

G. T. Fraser et al., *J. Mol. Spectrosc.*, 144, 97 (1990)

…

L. Zou and S. L. W. Weaver, *J. Mol. Spectrosc.*, 324, 12 (2016)



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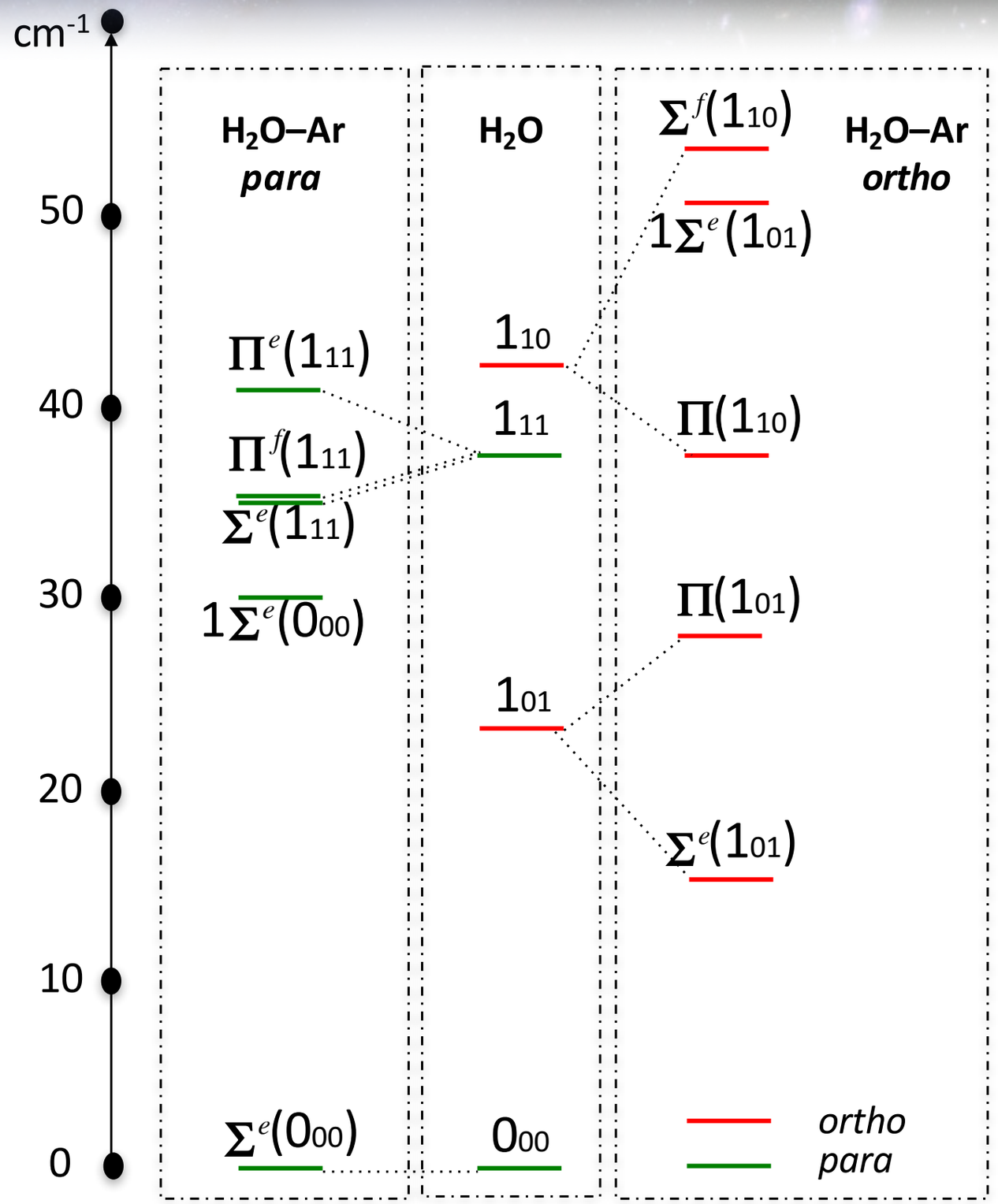
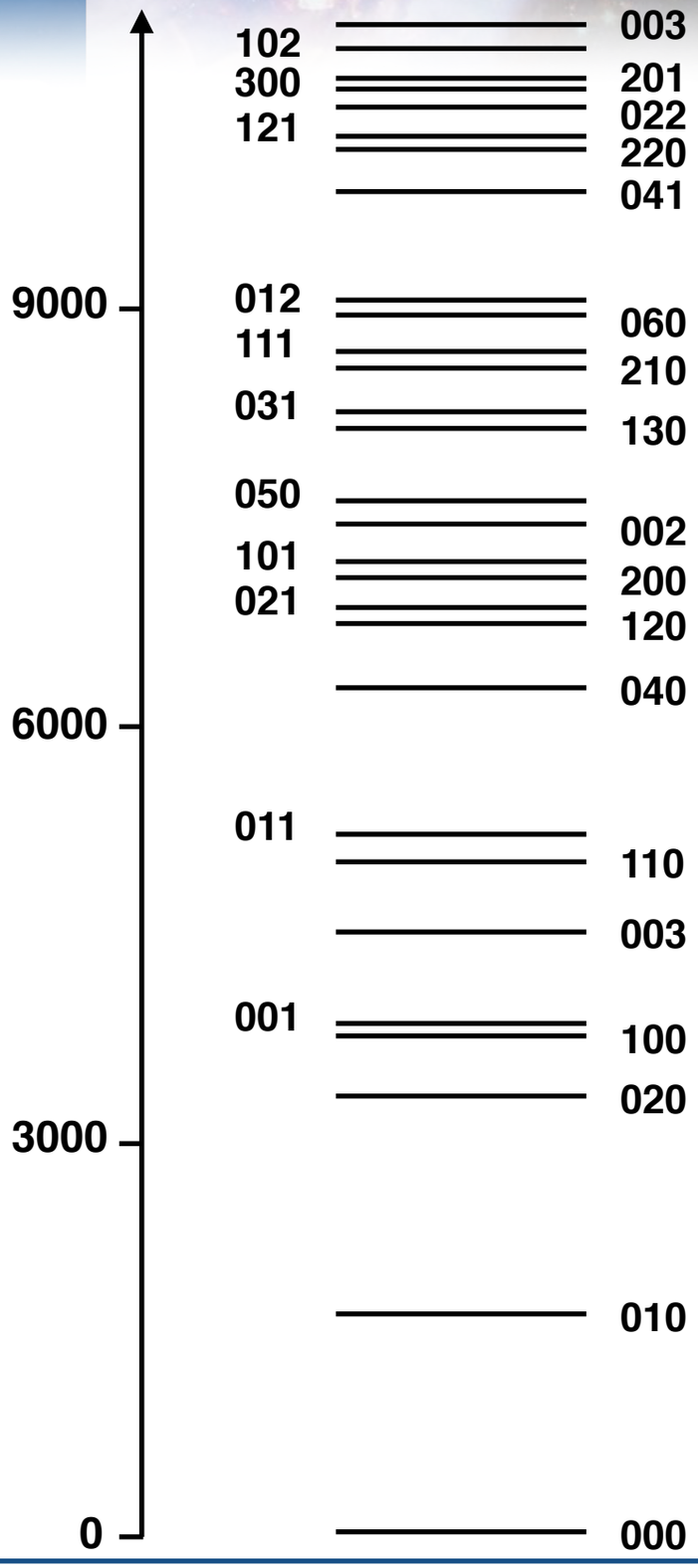
Inversion of *ortho/para* when the vibration is asymmetric



H_2O vibrational modes

IR investigations:



H_2O vibrational modes

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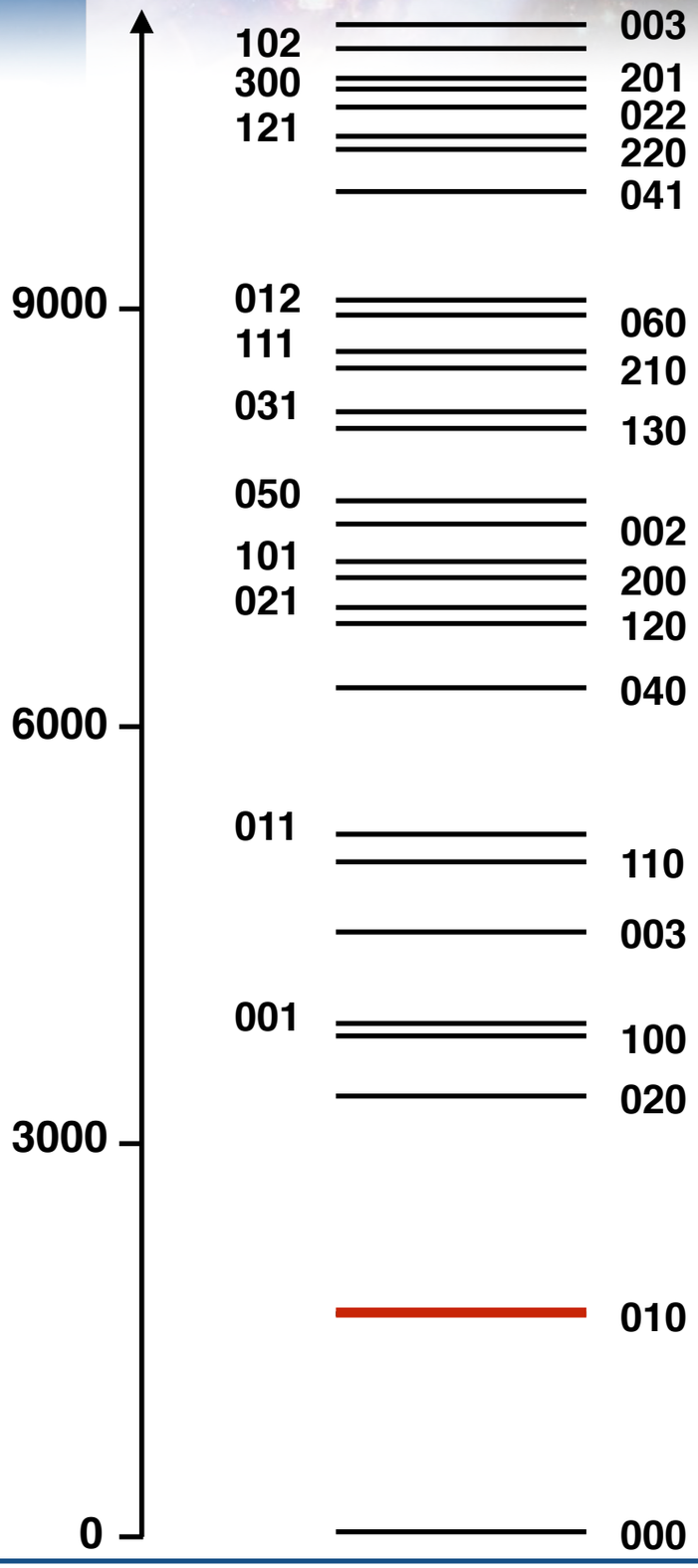

M. J. Weida and D. J. Nesbitt, *J. Chem. Phys.*, 206, 3078 (1997)
X. Liu and Y. Xu, *J. Mol. Spectrosc.*, 301, 1 (2014)

H_2O-Ar

H_2O vibrational modes

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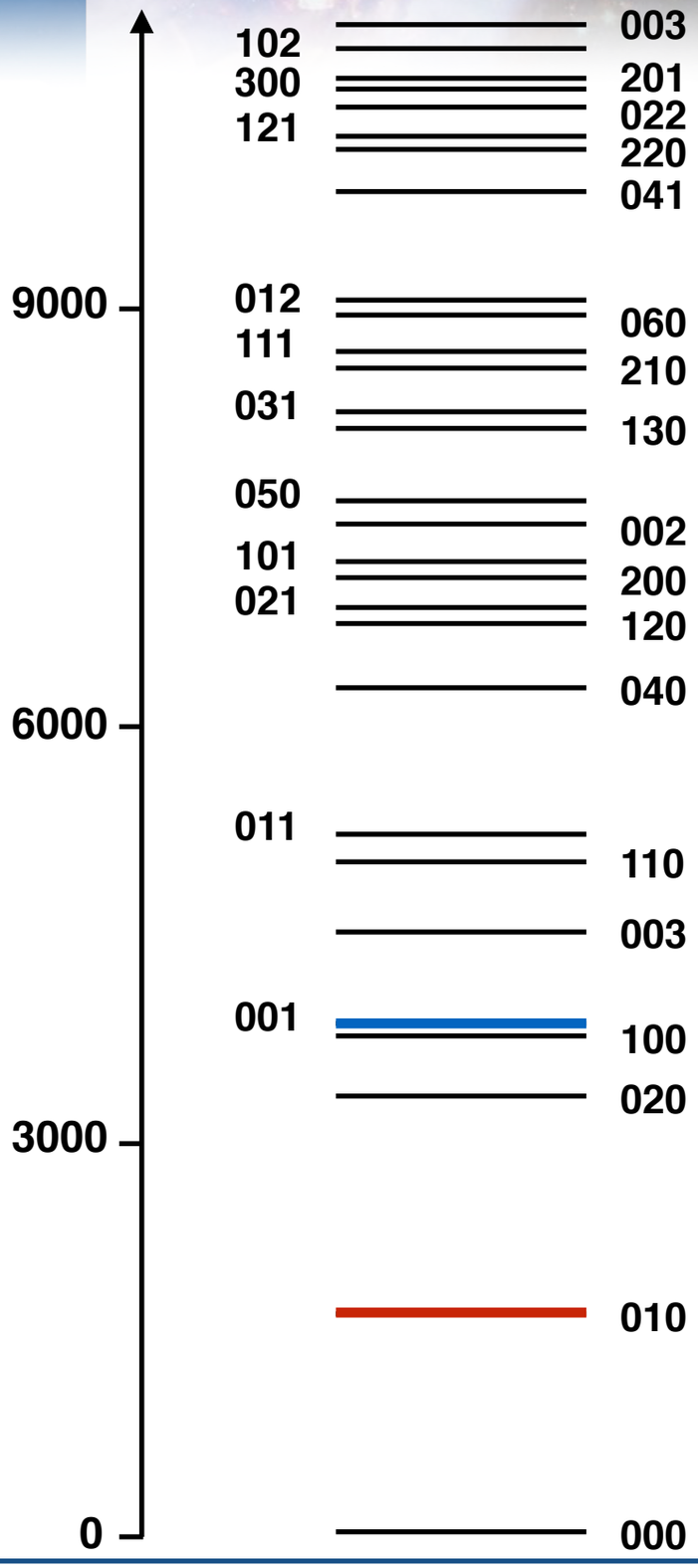

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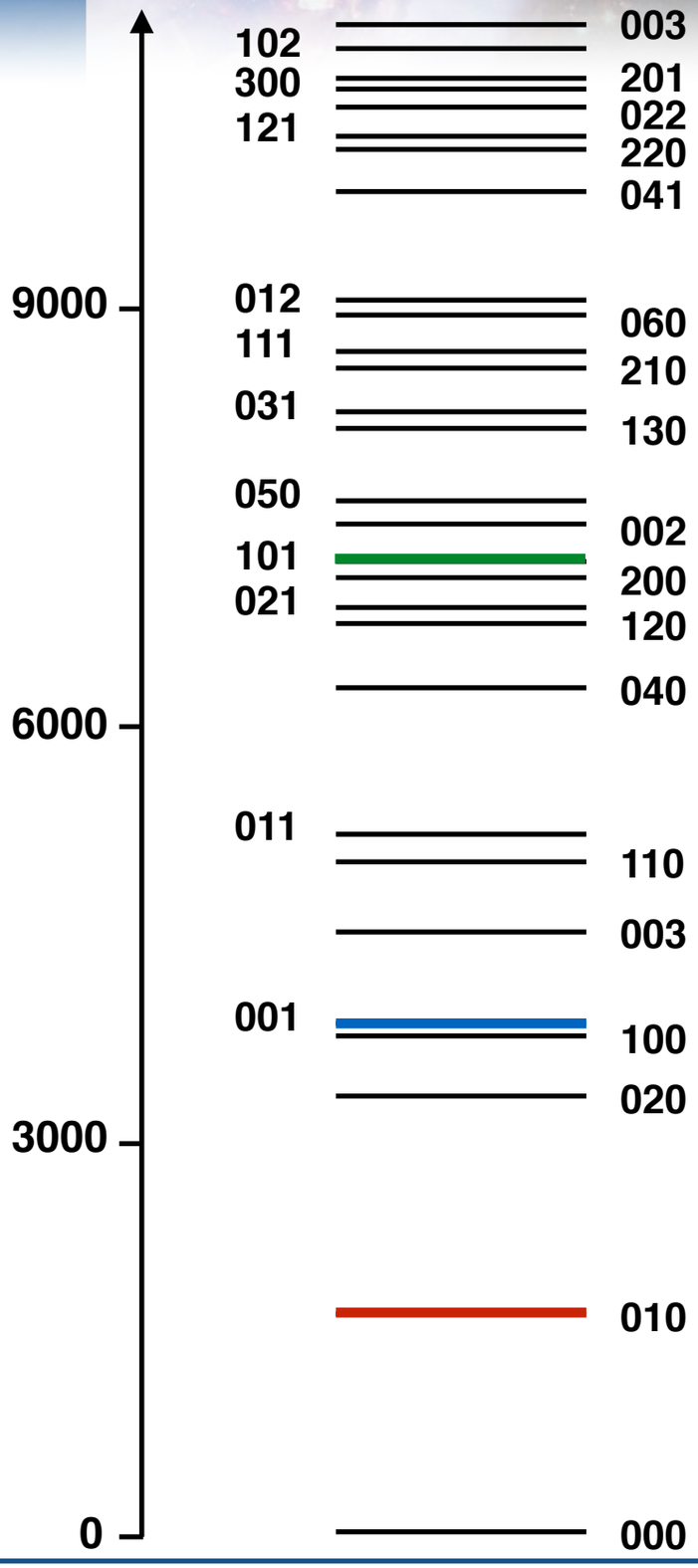

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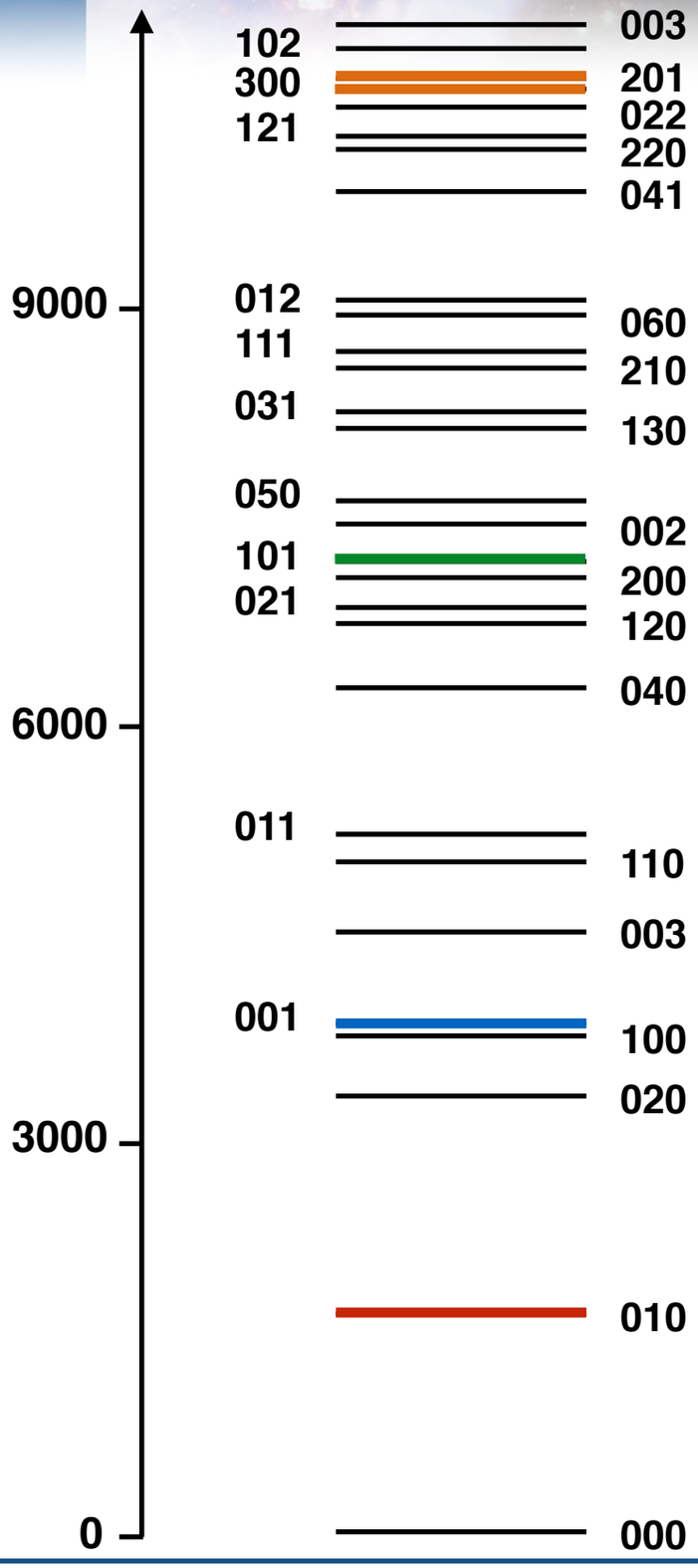

O. Votava, S. R. Mackenzie, and D. J. Nesbitt, *J. Chem. Phys.*, 120, 8443 (2004)

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H_2O-Ar

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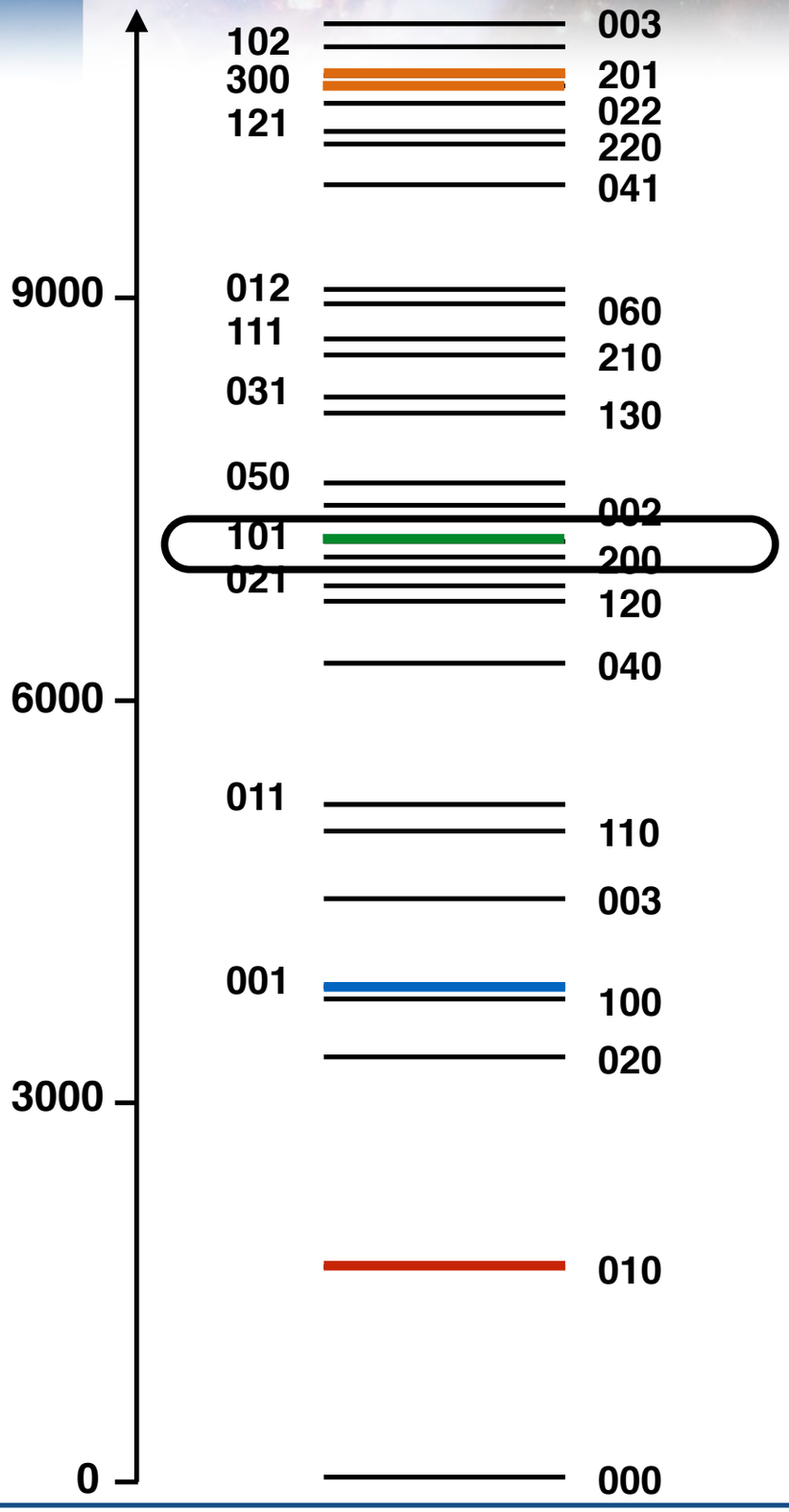

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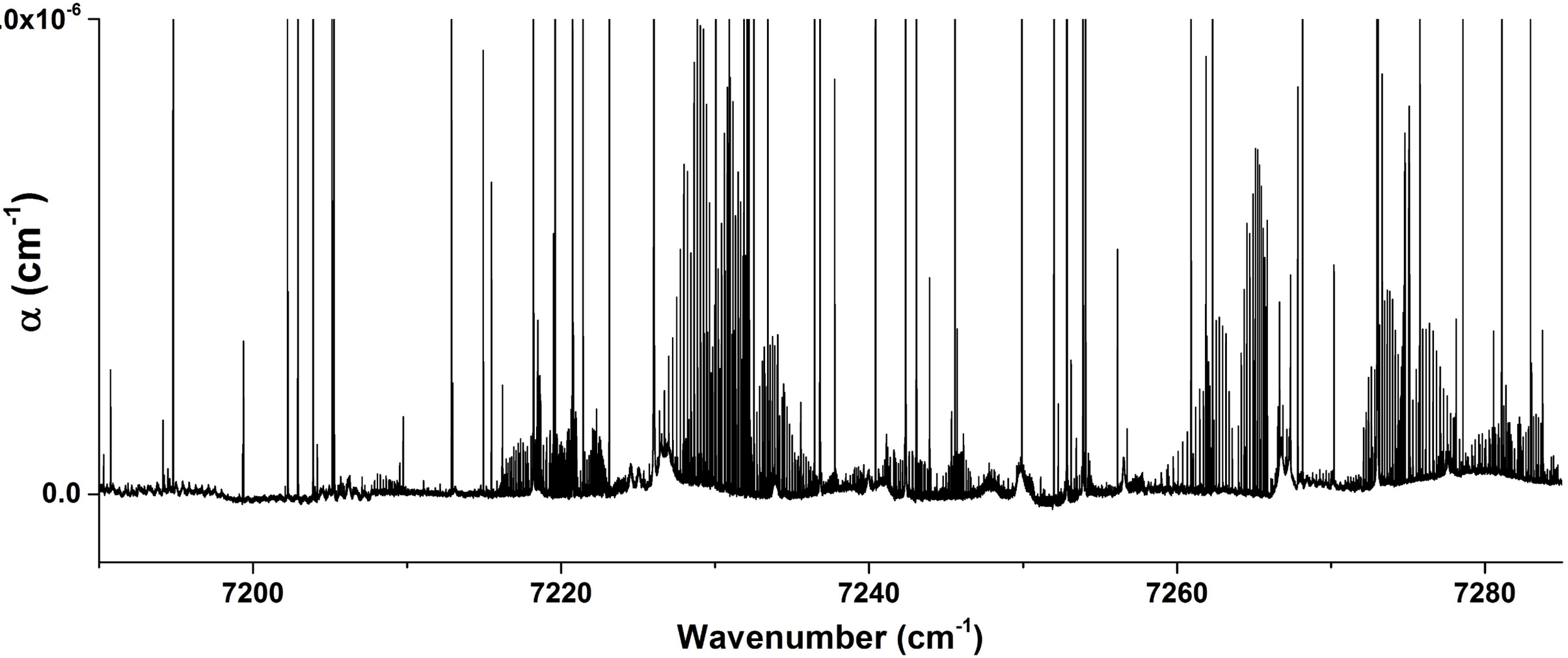
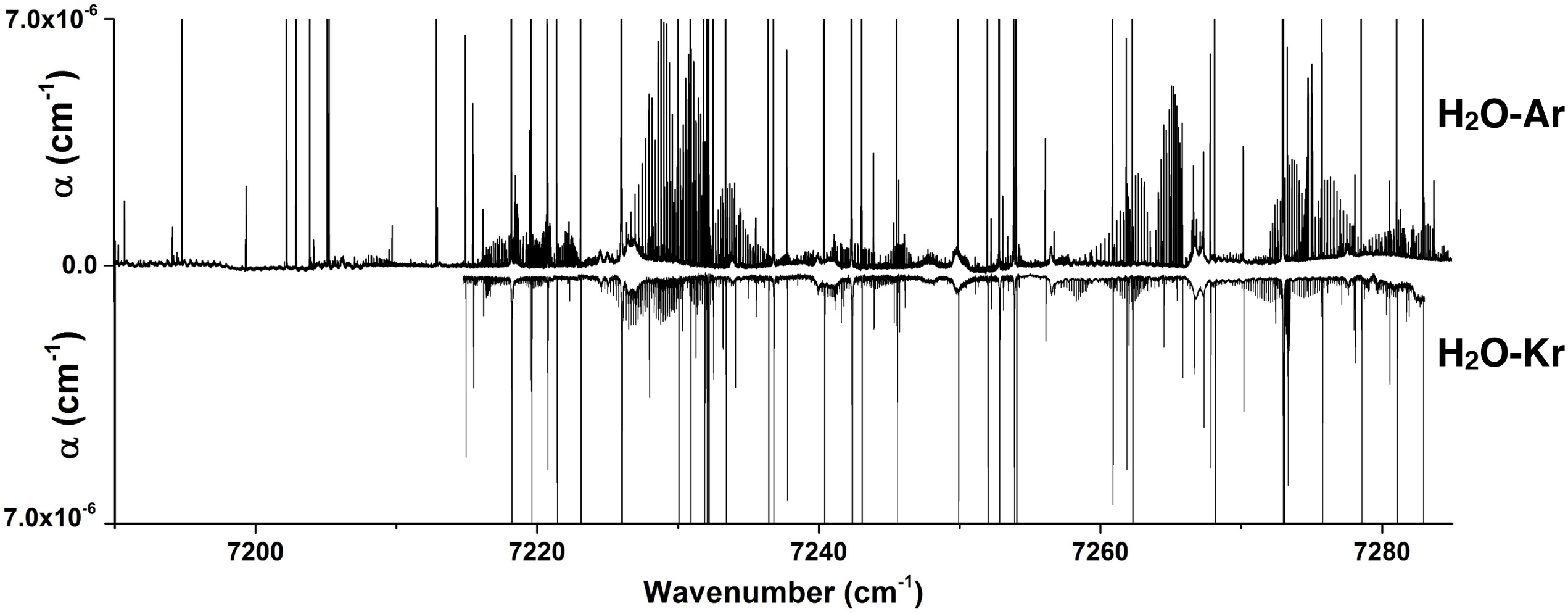
H_2O-Ar

H_2O-Ar spectrum



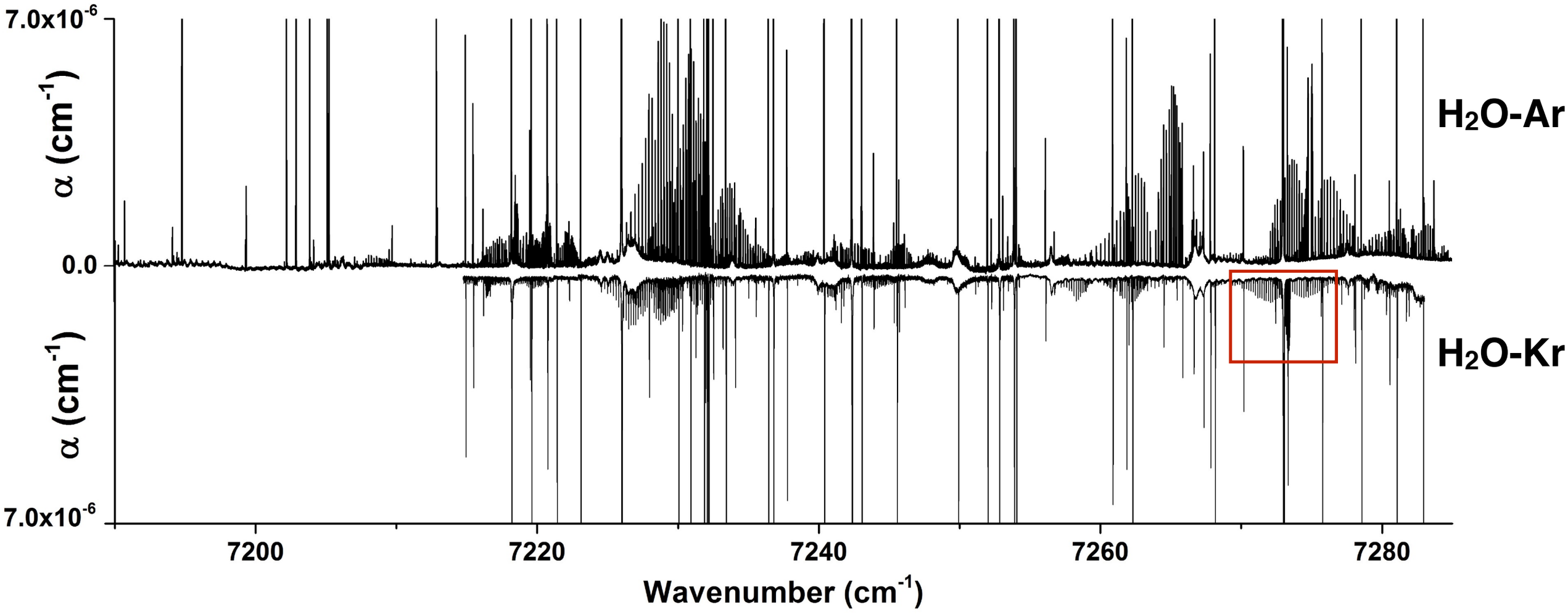
- 100 cm^{-1} spectral range
- S/N ratio > 300
- more than 20 rovibrational bands

H_2O-Ar/Kr spectrum



Same injection conditions

H_2O-Ar/Kr spectrum

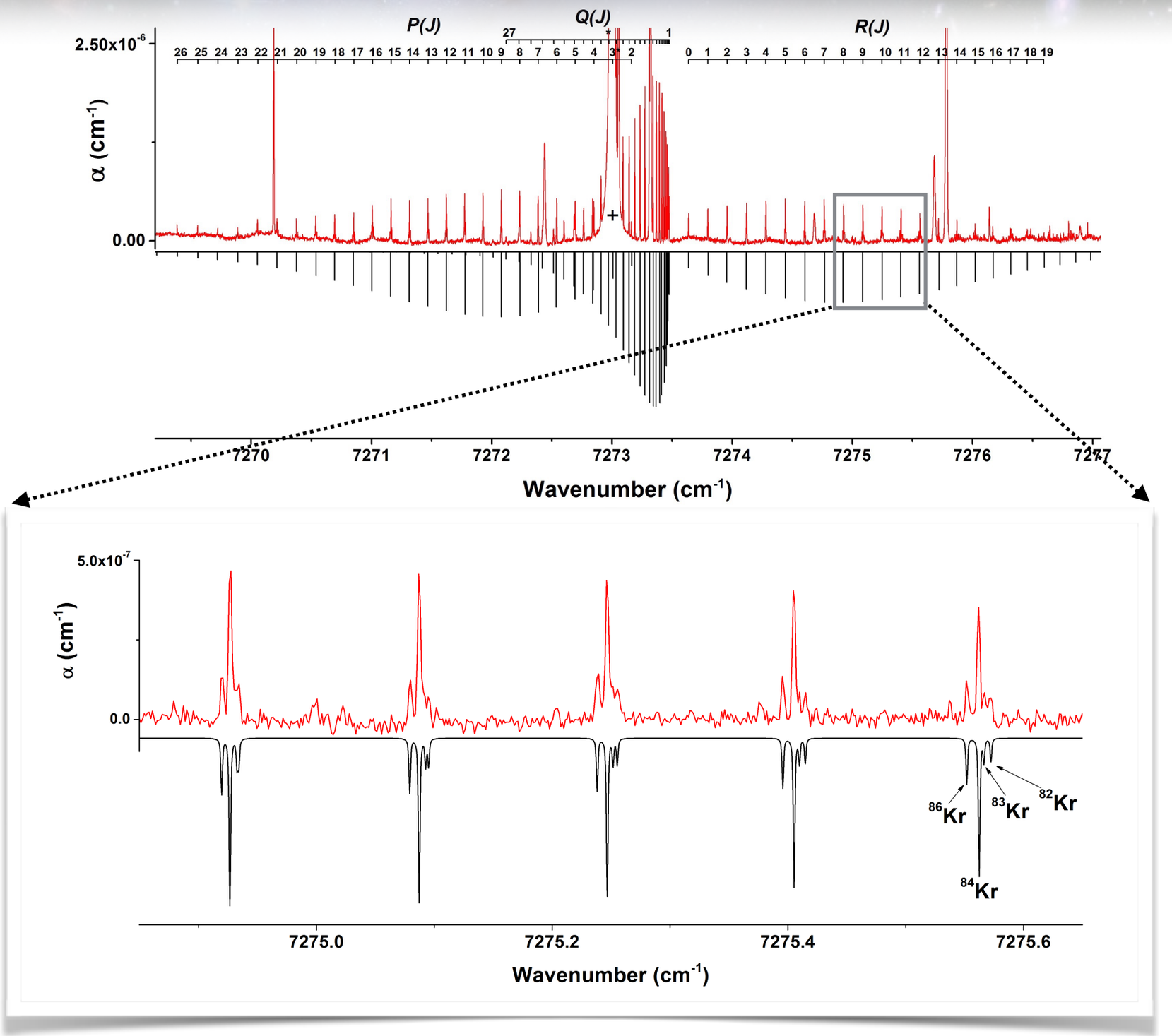


Same injection conditions

H_2O-Kr spectrum

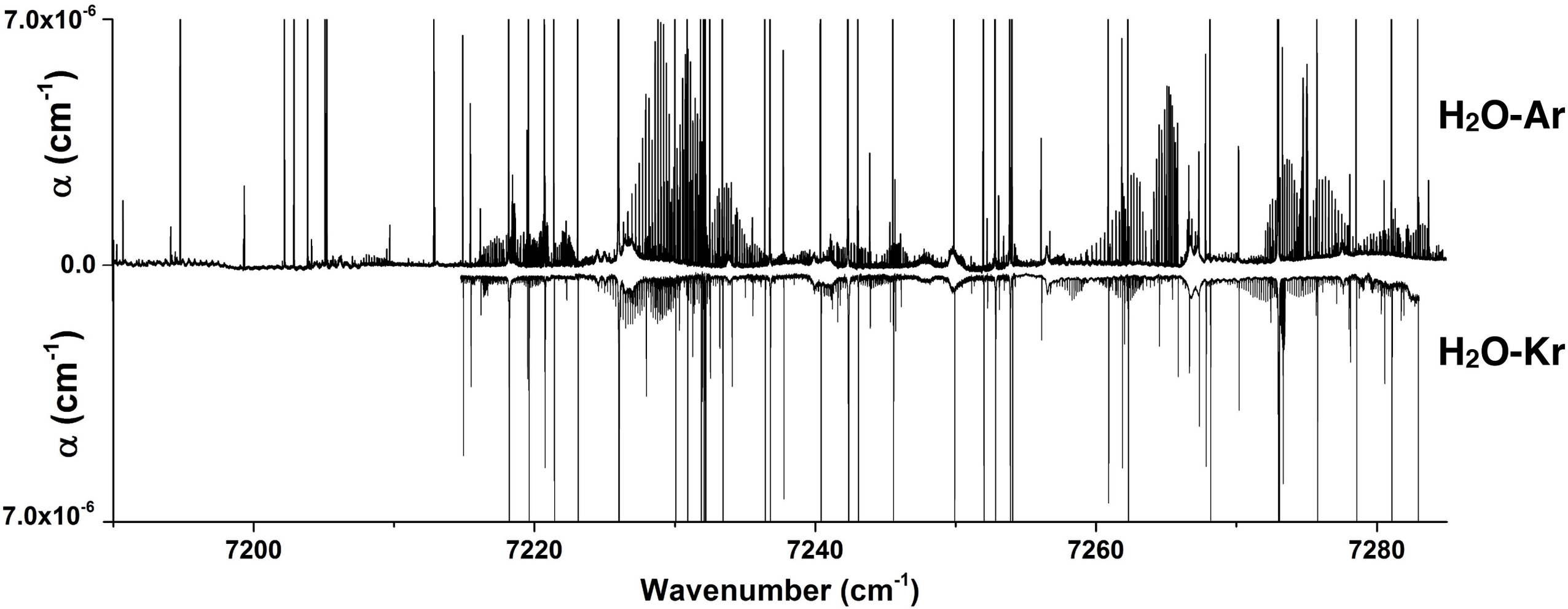
H_2O-Kr

Isotope	Natural abundance
^{82}Kr	11.6 %
^{83}Kr	11.5 %
^{84}Kr	57 %
^{86}Kr	17.3 %

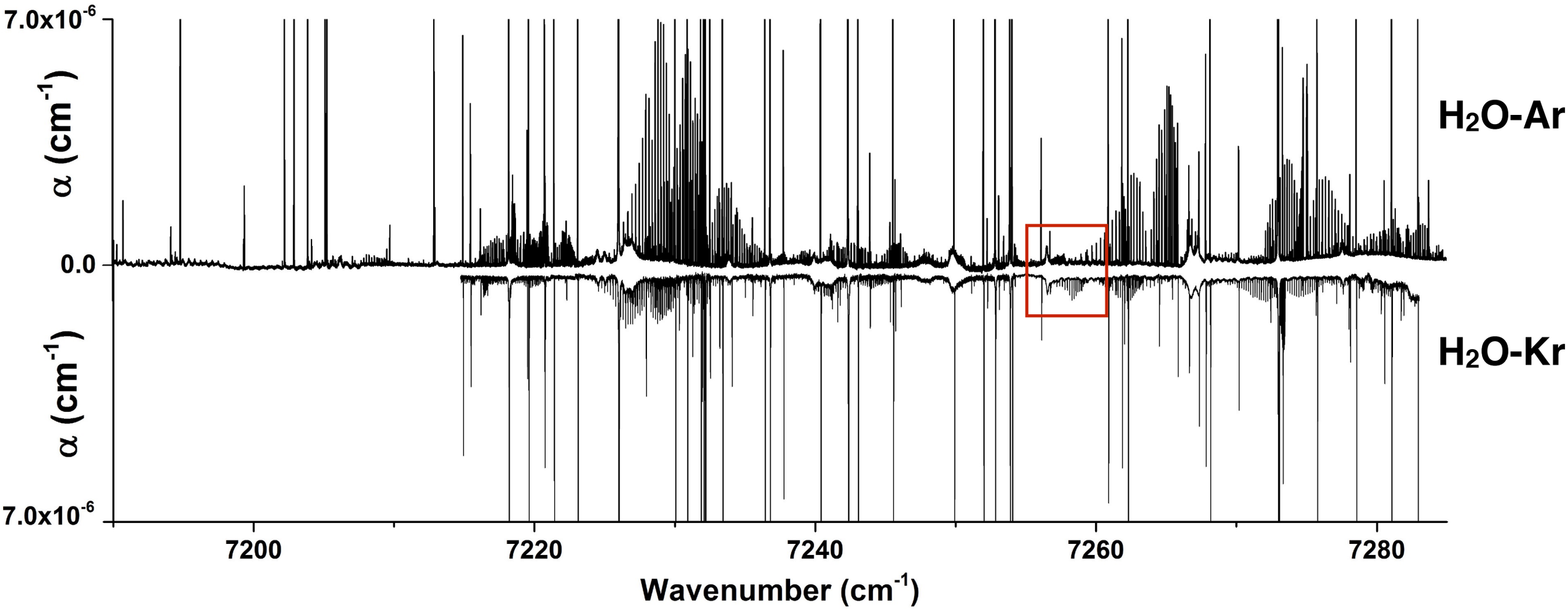


T. Vanfleteren, T. Földes, J. Vander Auwera, and M. Herman, *Chem. Phys. Lett.*, 618, 119 (2015)

$(H_2O)_2$ spectrum



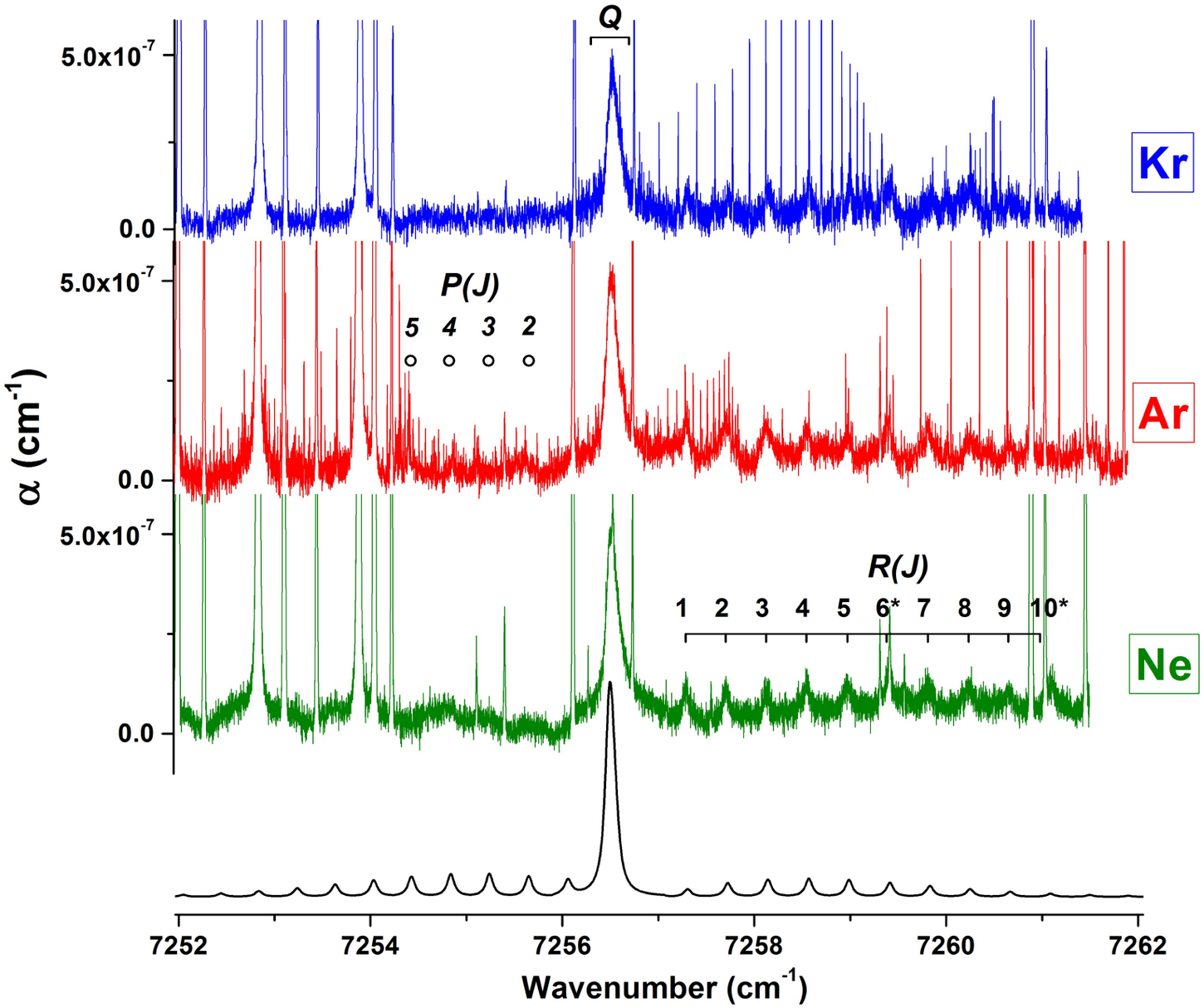
$(H_2O)_2$ spectrum



$(H_2O)_2$ spectrum

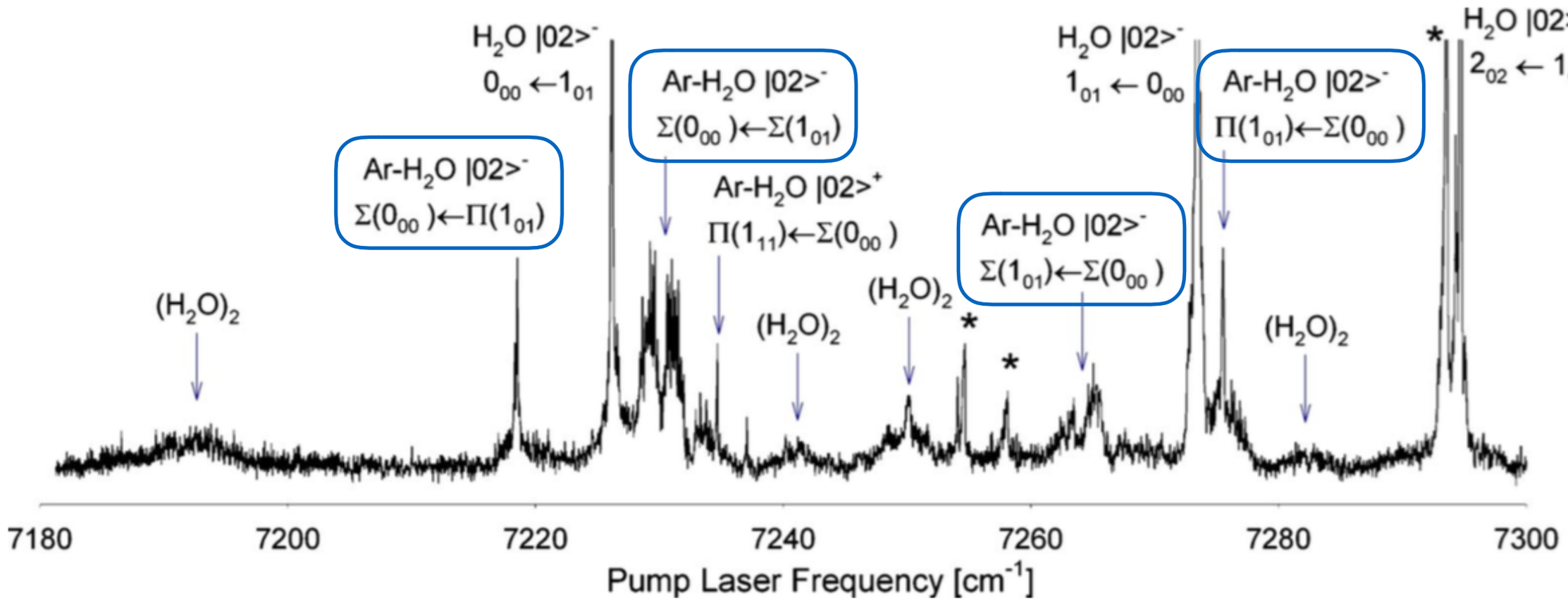
$(H_2O)_2$

- Rotationally resolved band
- Fitted with MW data
- Broad lines



T. Földes, T. Vanfleteren, and M. Herman, *J. Chem. Phys.*, 141, 111103 (2014)
T. Vanfleteren, N. Suas-David, T. Földes, S. Kassi, R. Georges, and M. Herman, *J. Phys. Chem. A*, 119, 10022 (2015)

H_2O-Ar spectrum



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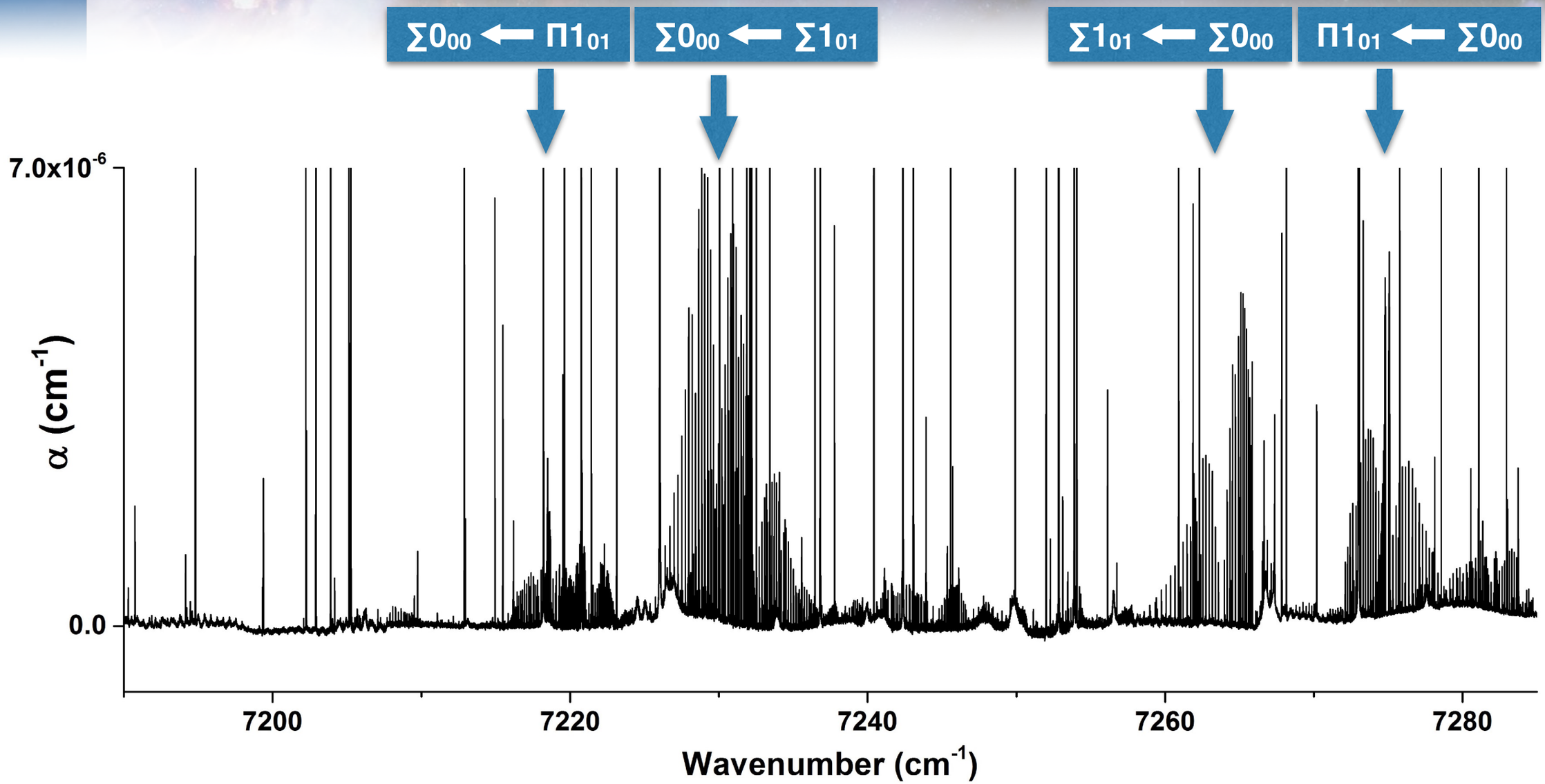

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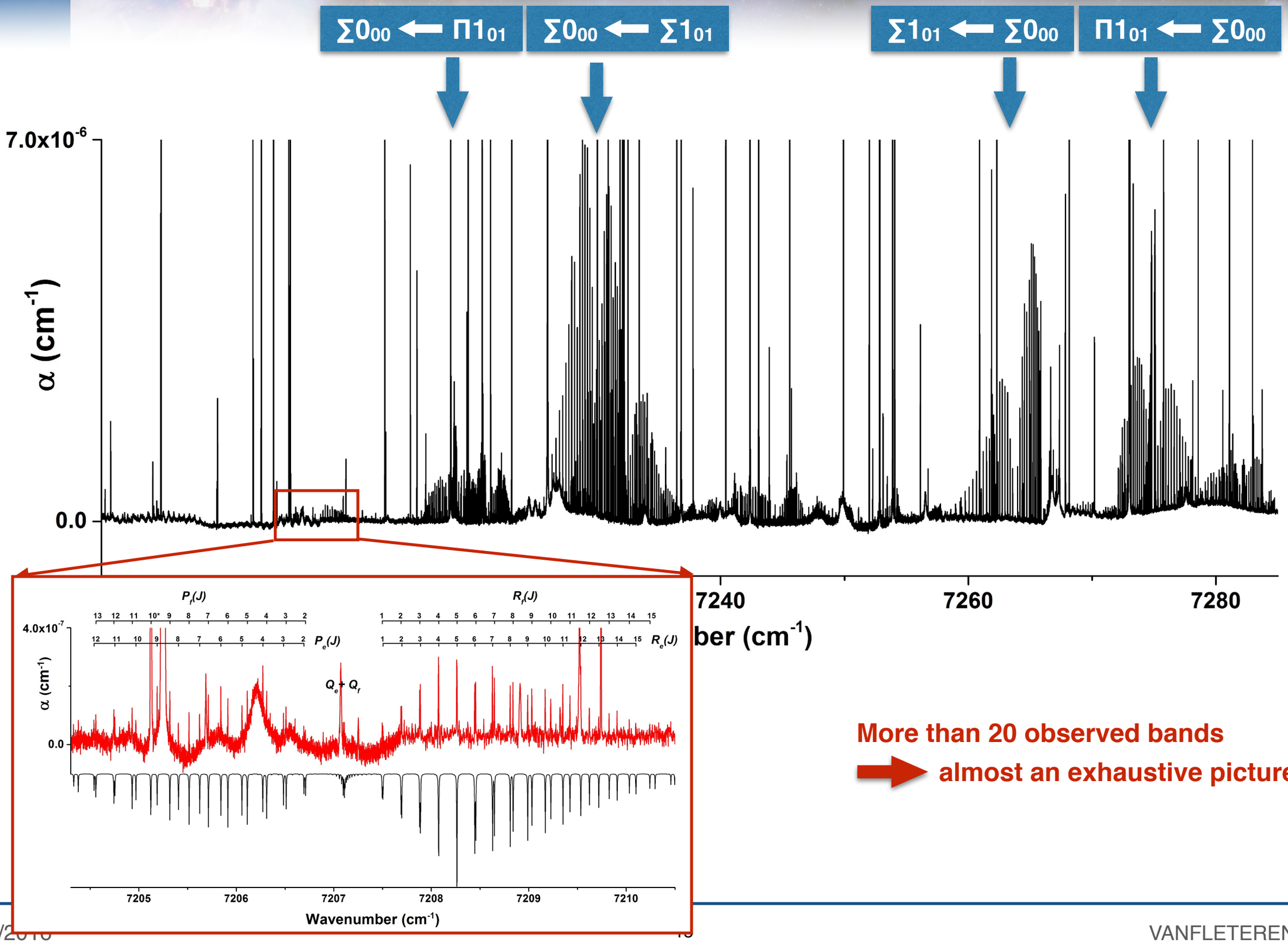
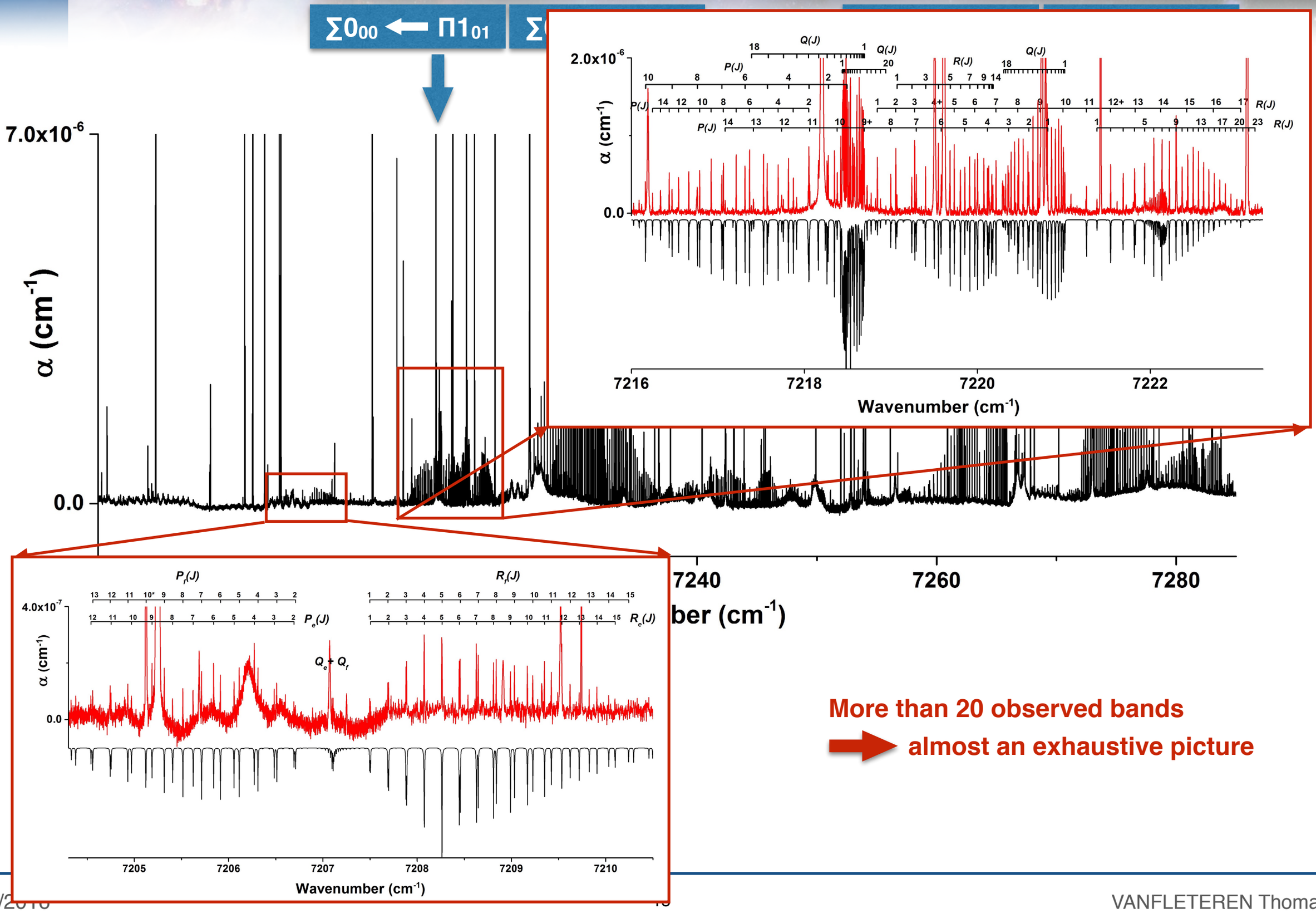


More than 20 observed bands

→ almost an exhaustive picture

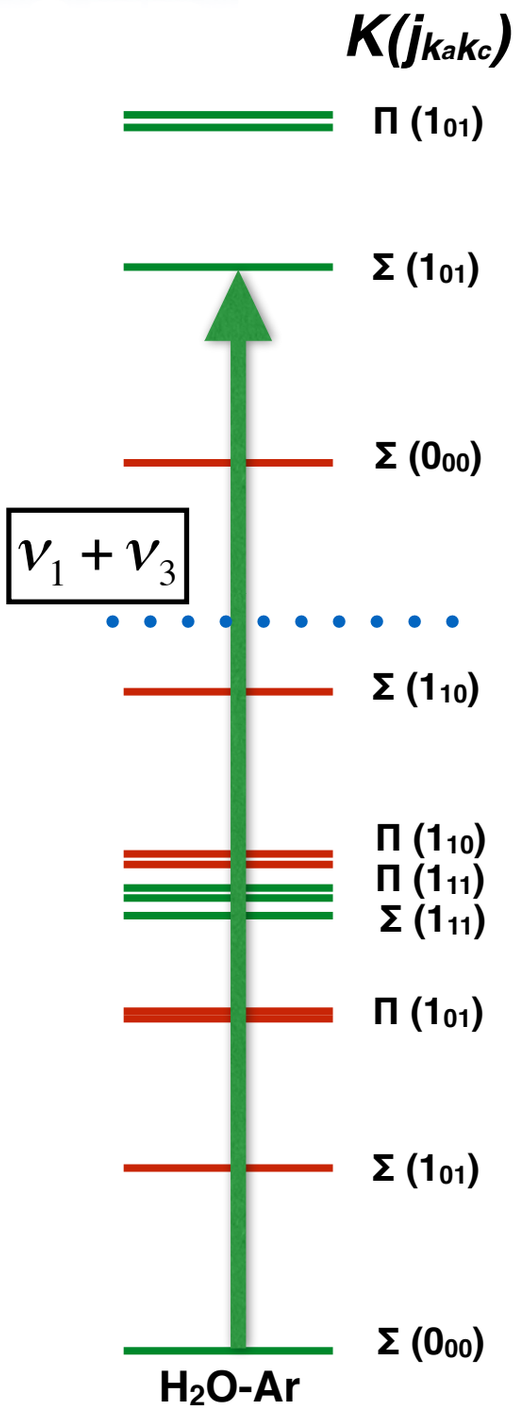
H_2O-Ar spectrum



More than 20 observed bands

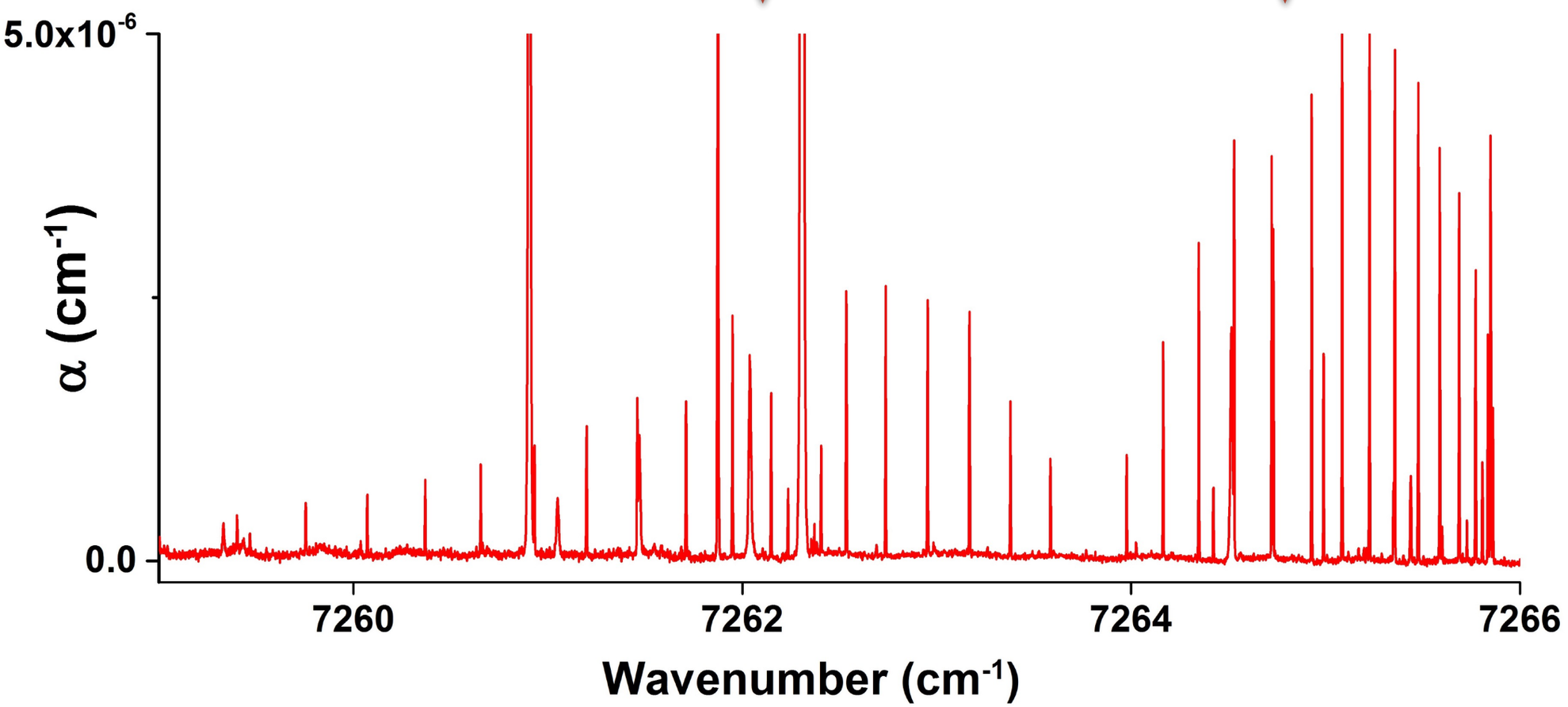
→ almost an exhaustive picture

Bands assignment

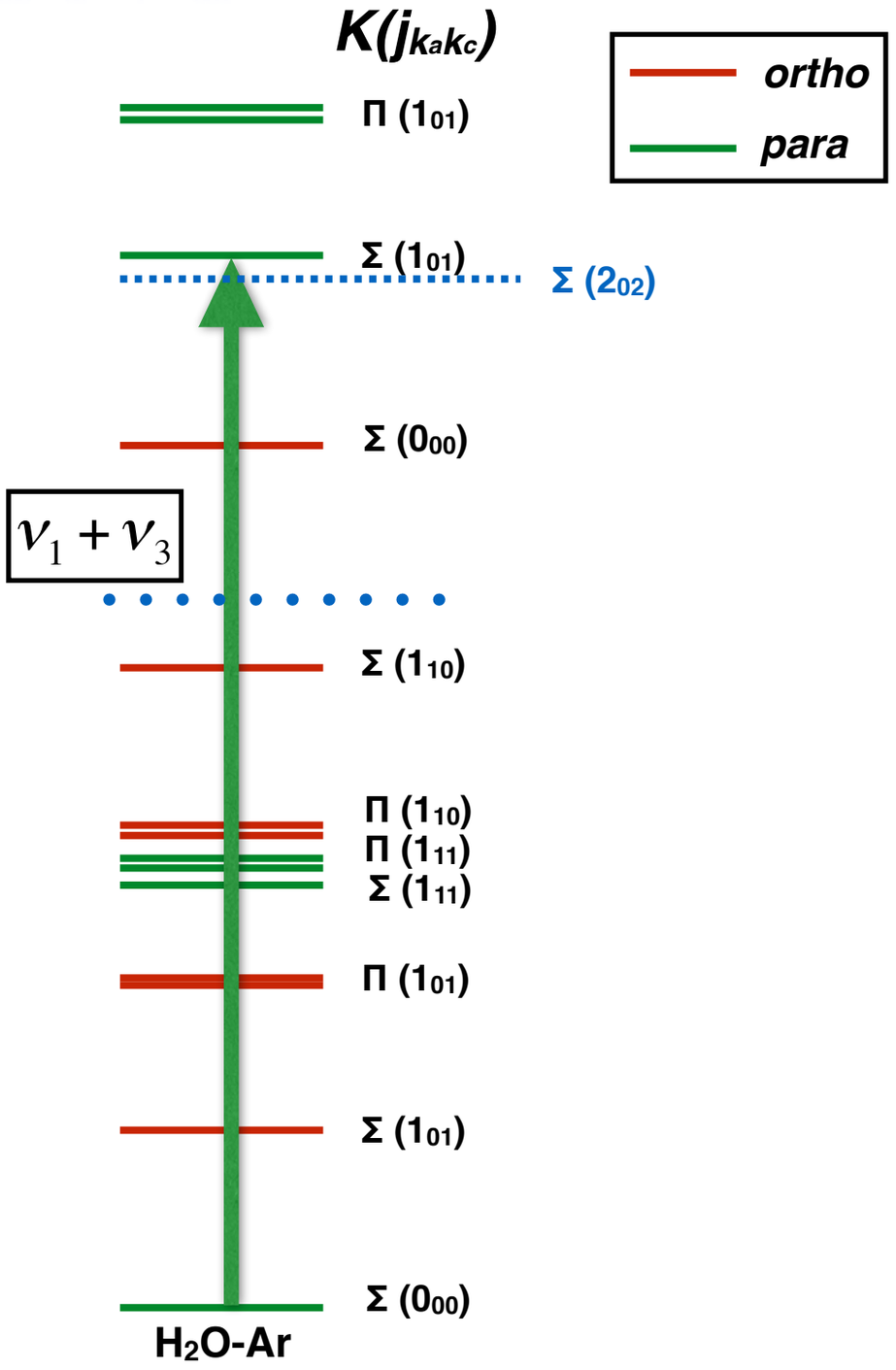


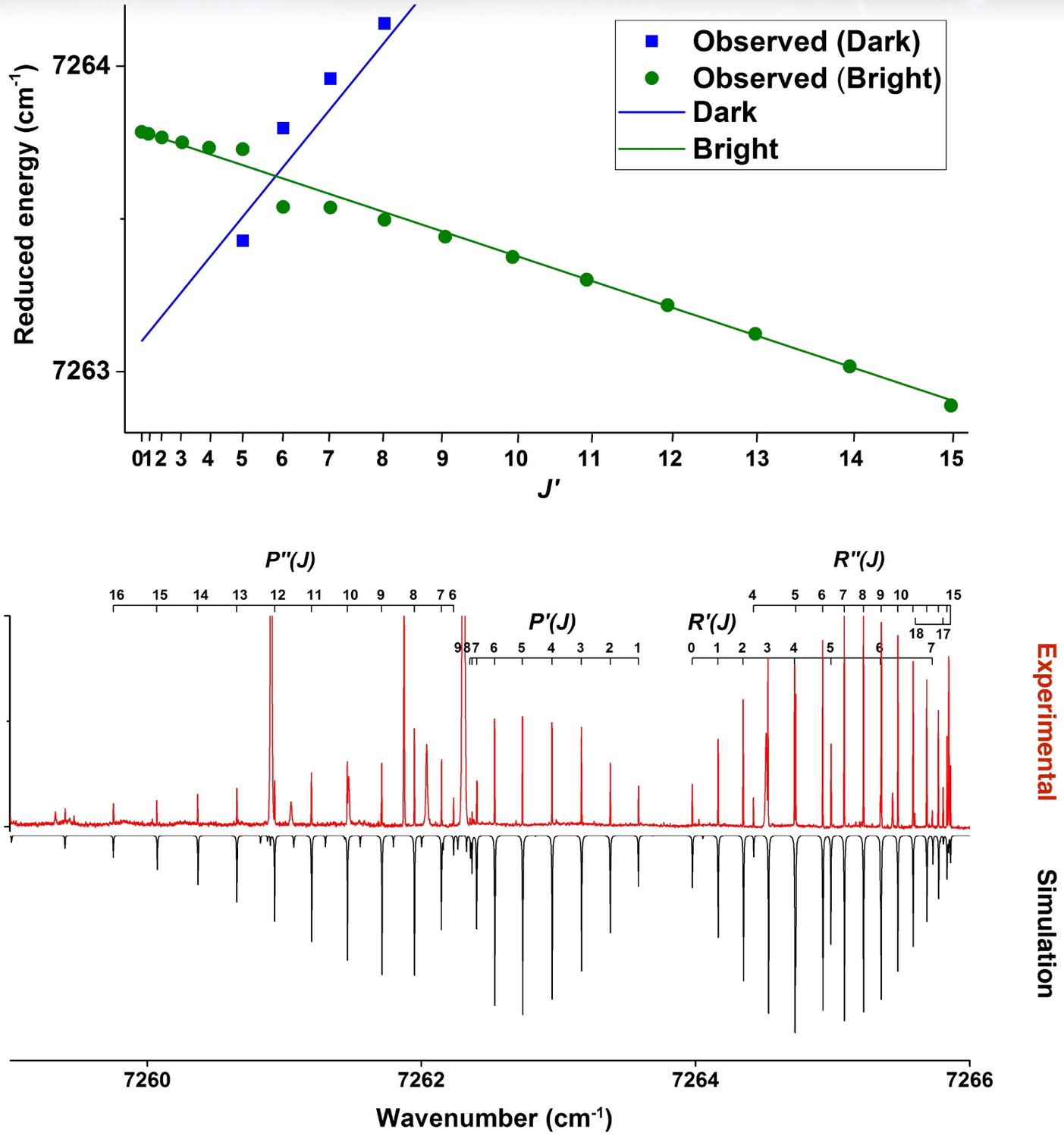
Σ101 ← Σ000

Signs of perturbation



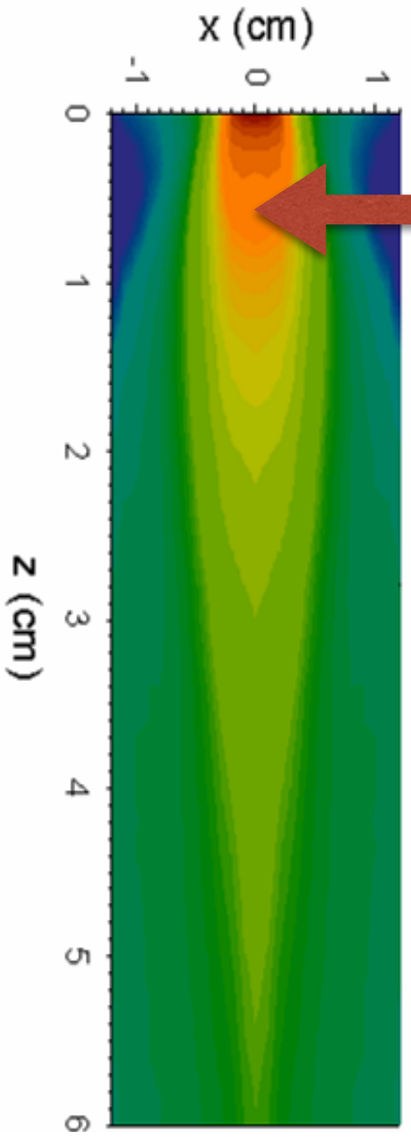
Perturbation analysis





Ab initio **calculations from J. Liévin, J. Loreau and L. H. Coudert**

Line profile analysis

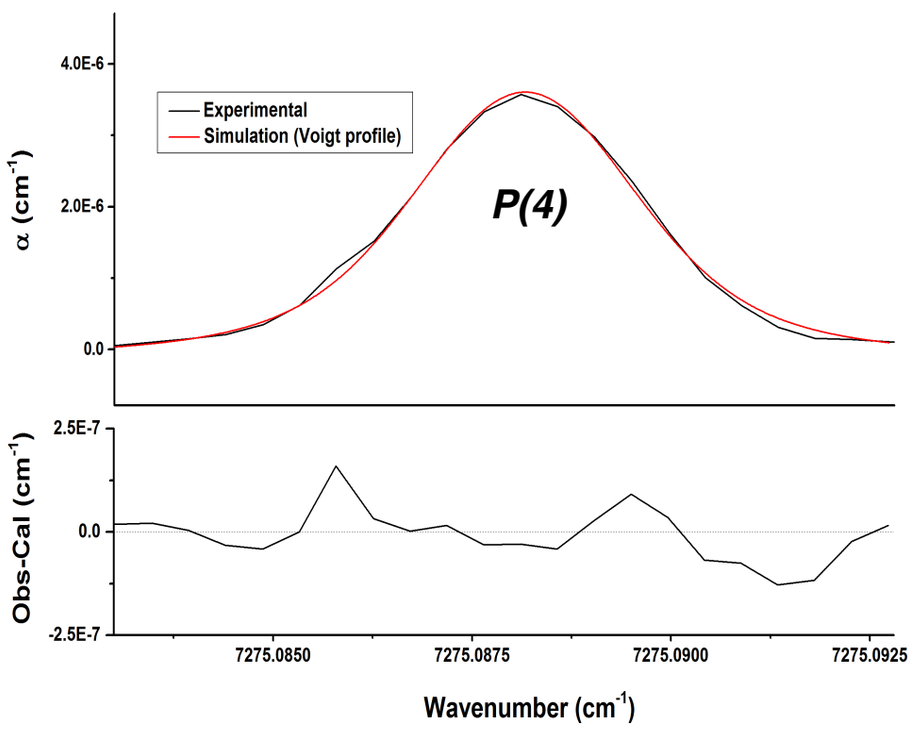


Laser beam

Silence zone → **no pressure broadening**

+ very low temperature → **small Doppler effect**

H_2O-Ar Voigt profile

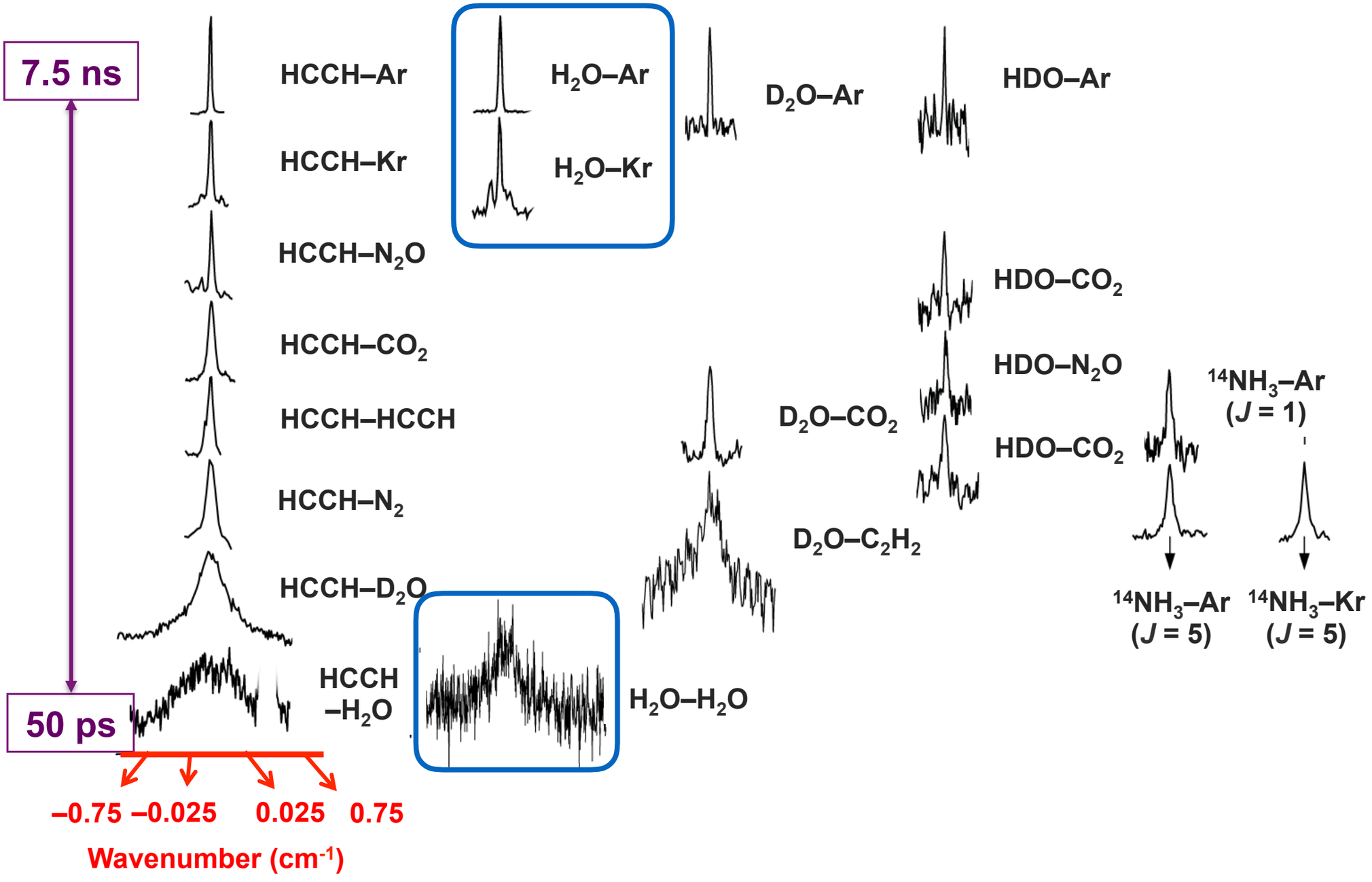


Linewidth: natural width related to the predissociation lifetime

$$\Delta\tilde{\nu}^{L}_{1/2} = \frac{1}{2\pi c}\frac{1}{\tau_1}$$

$$\tau_1 = \frac{1}{2\pi c\ \Delta\tilde{\nu}^{L}_{1/2}}$$

Predissociation lifetimes



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Overtone spectroscopy of molecular complexes containing small polyatomic molecules

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More on this in this very recent review!

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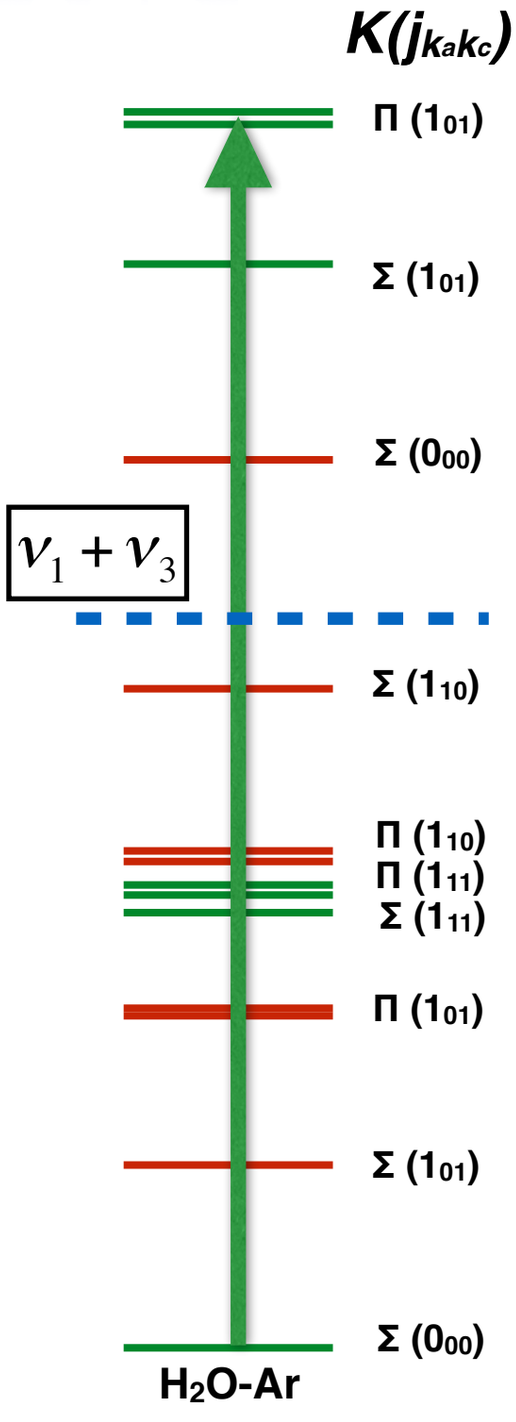
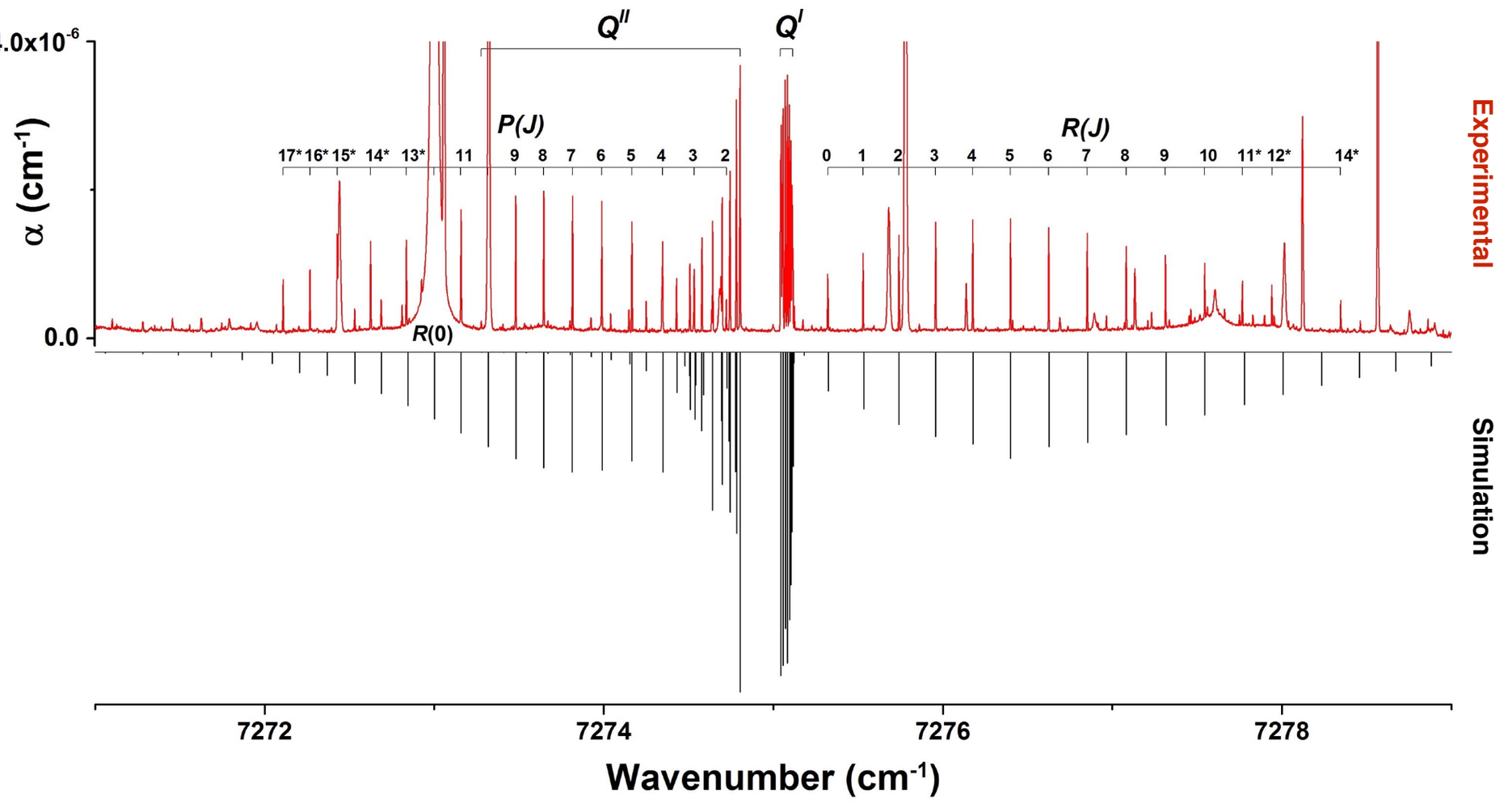
2OH overtone spectroscopy of water-containing van der Waals species

THOMAS VANFLETEREN

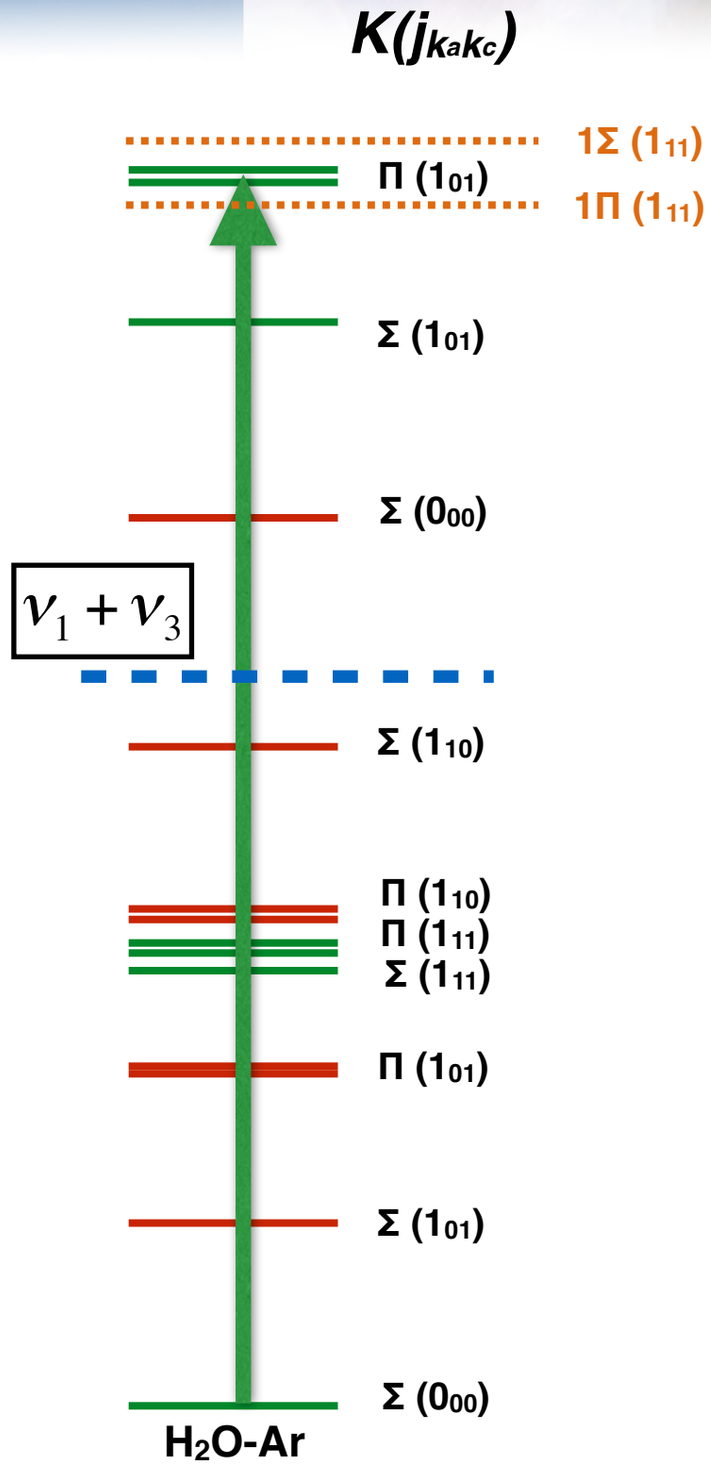
photo credit: Jenny Mottar

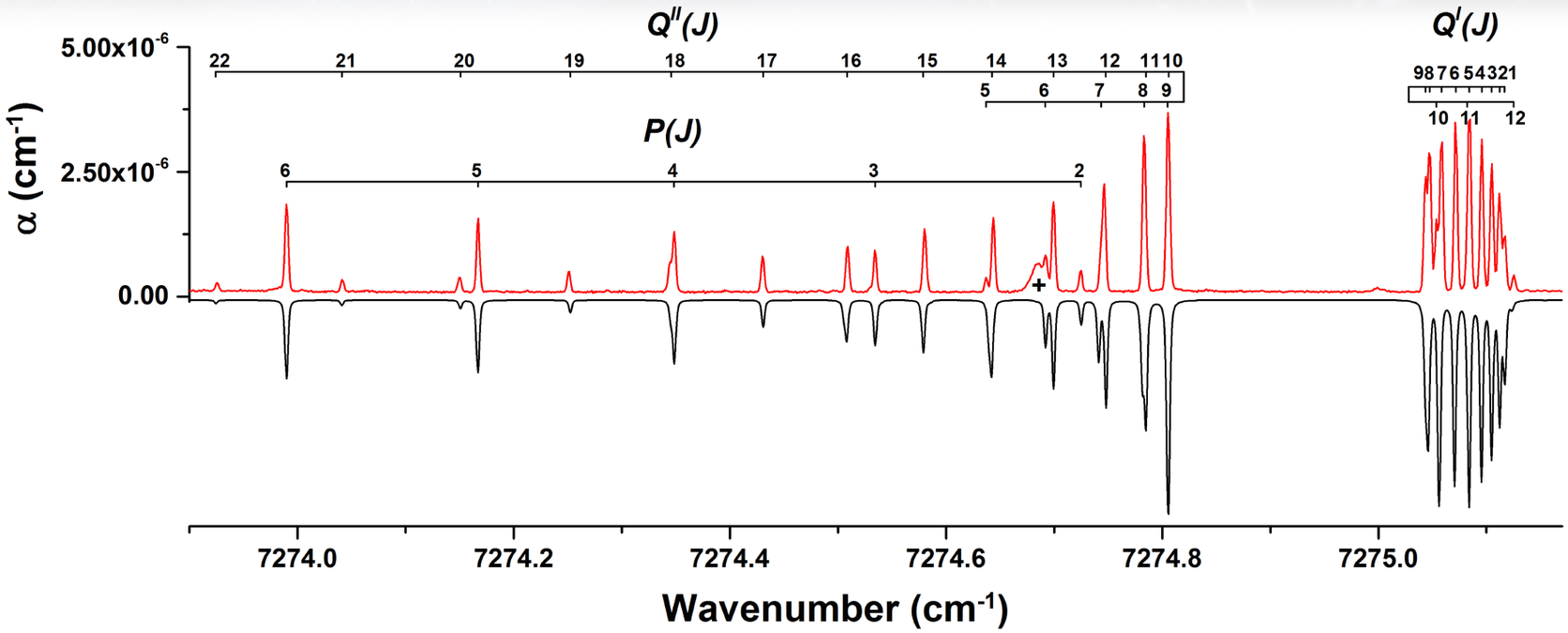
Bands assignment

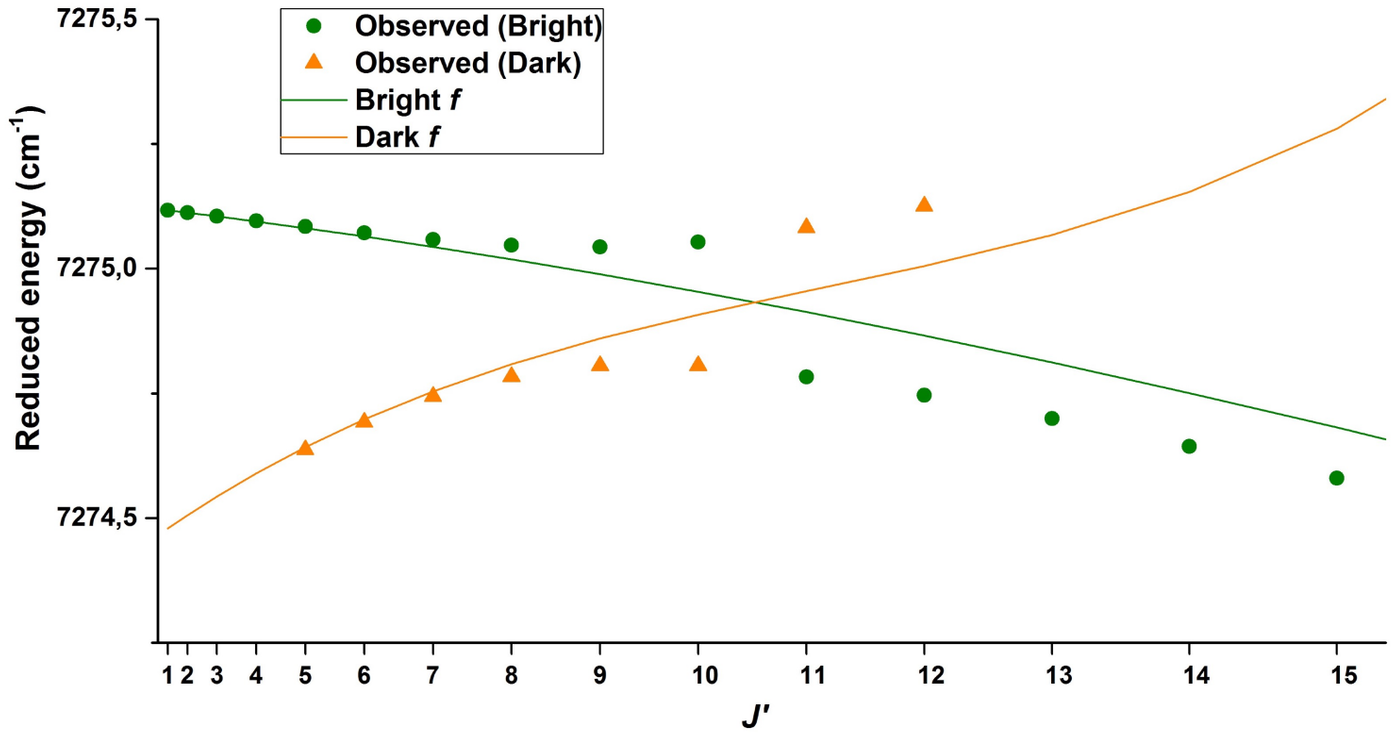




Perturbation analysis







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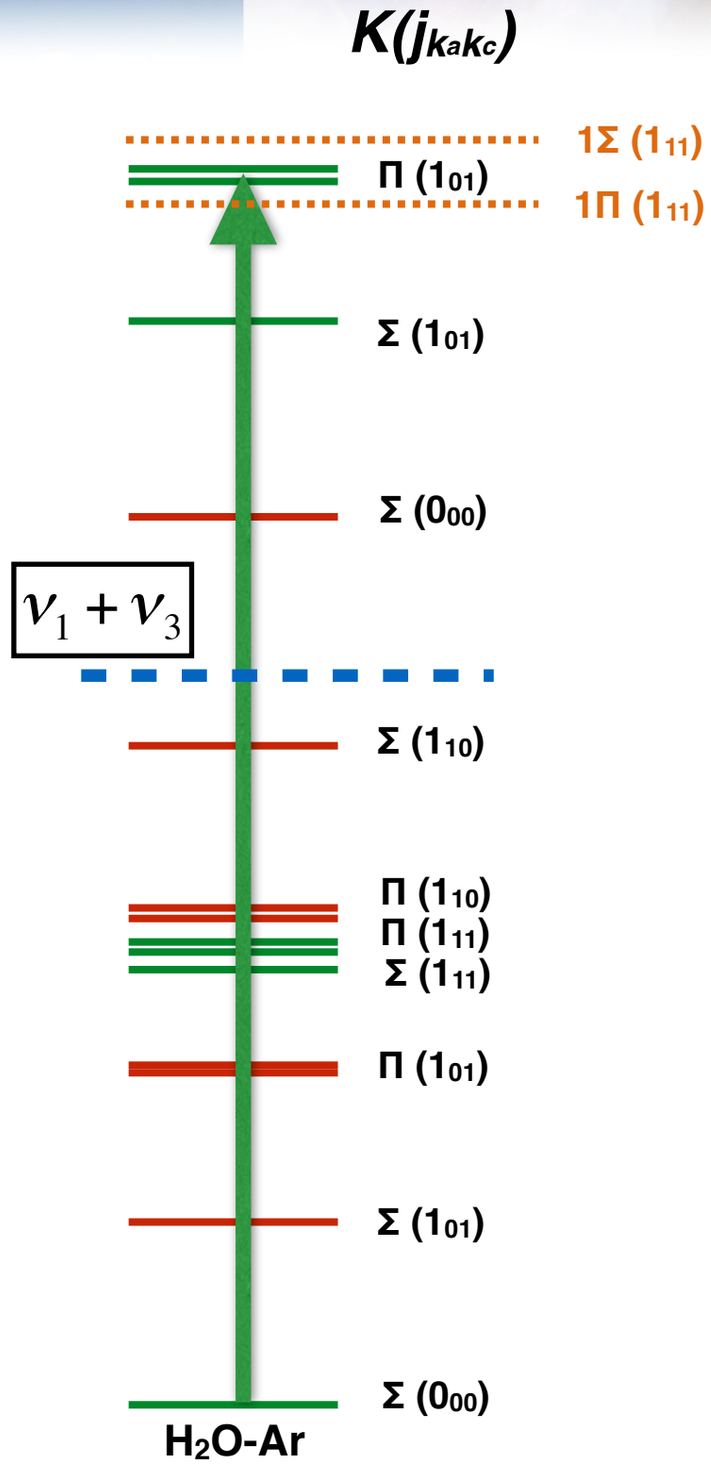
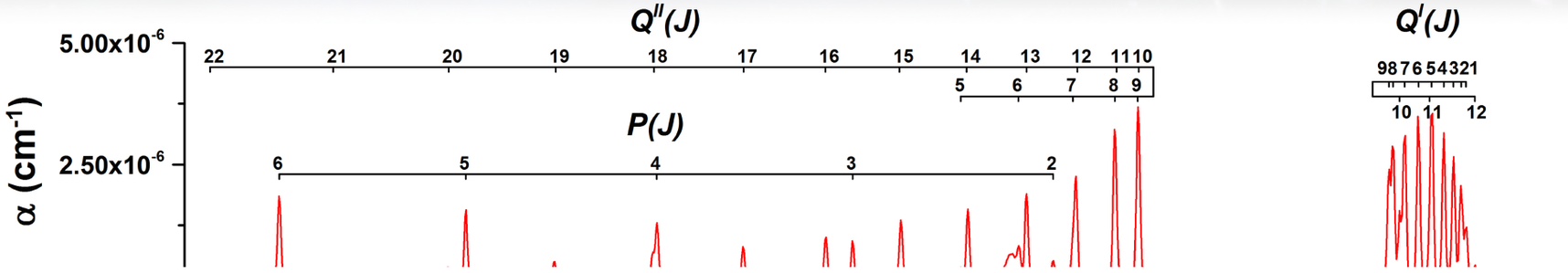
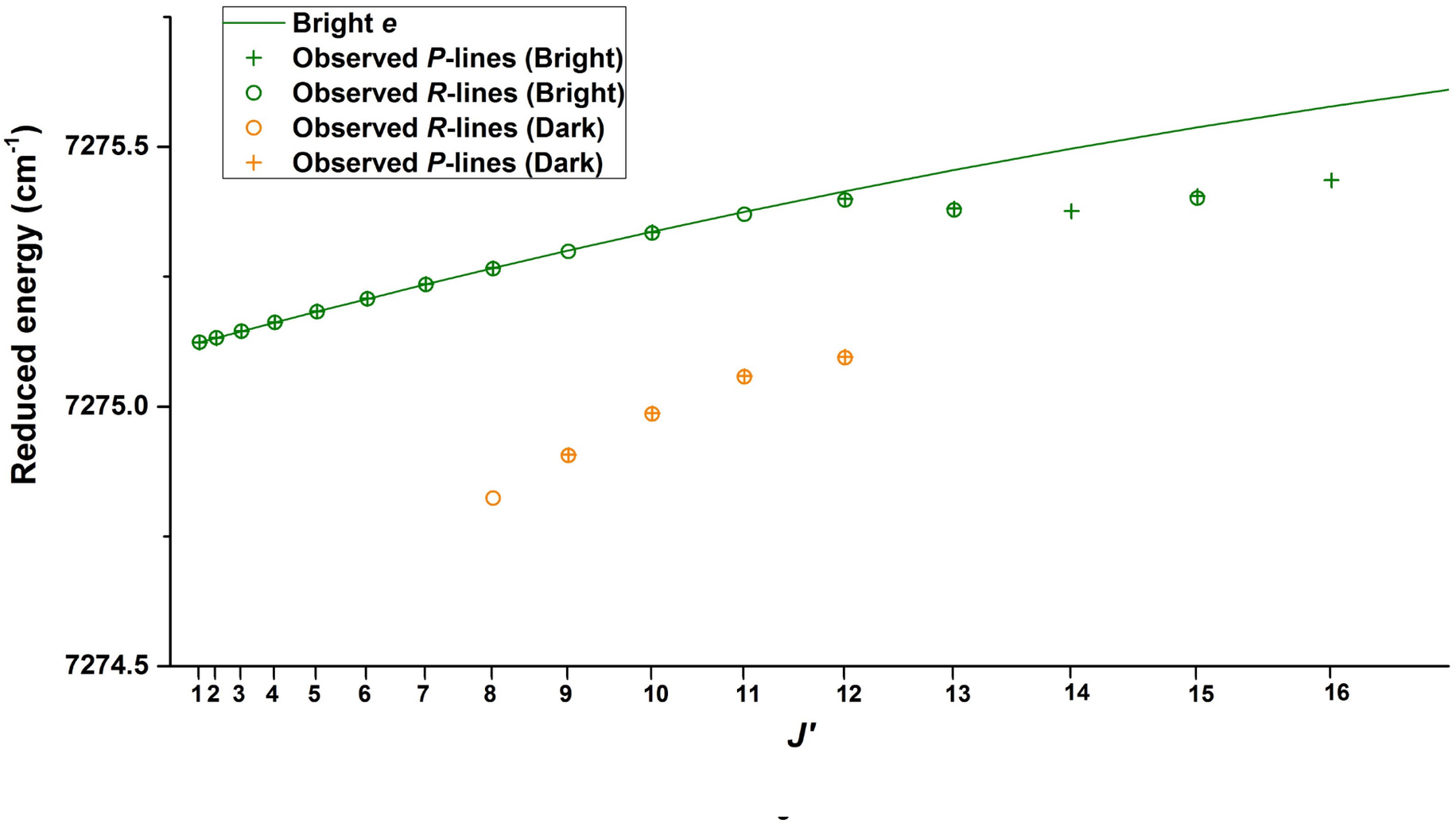
Perturbation analysis







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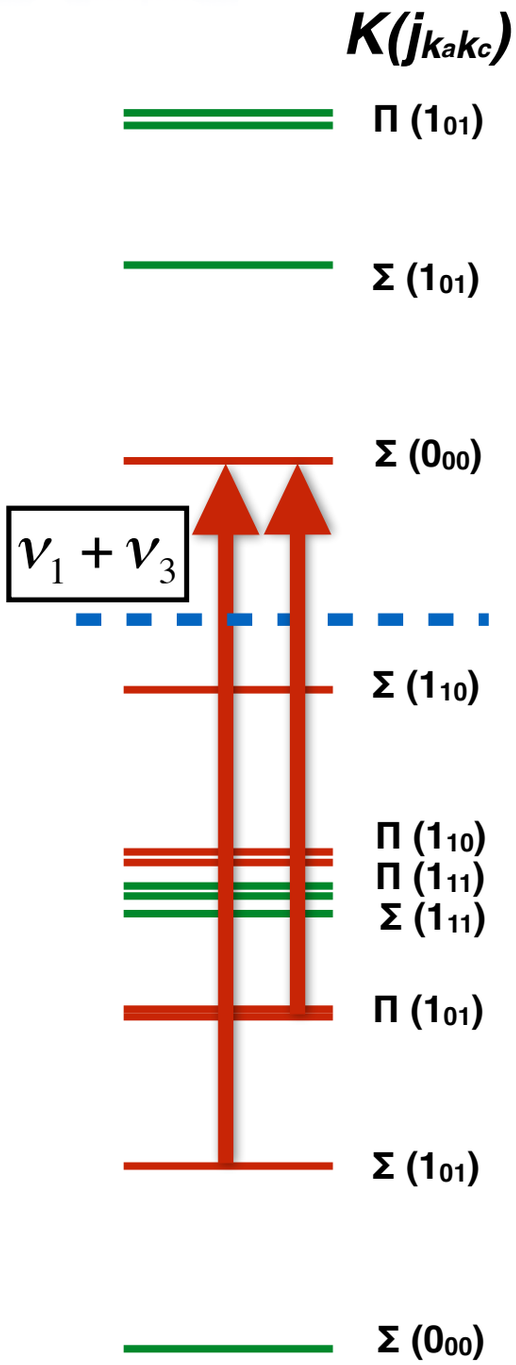

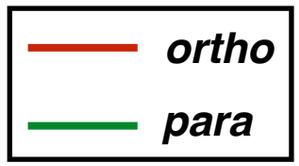

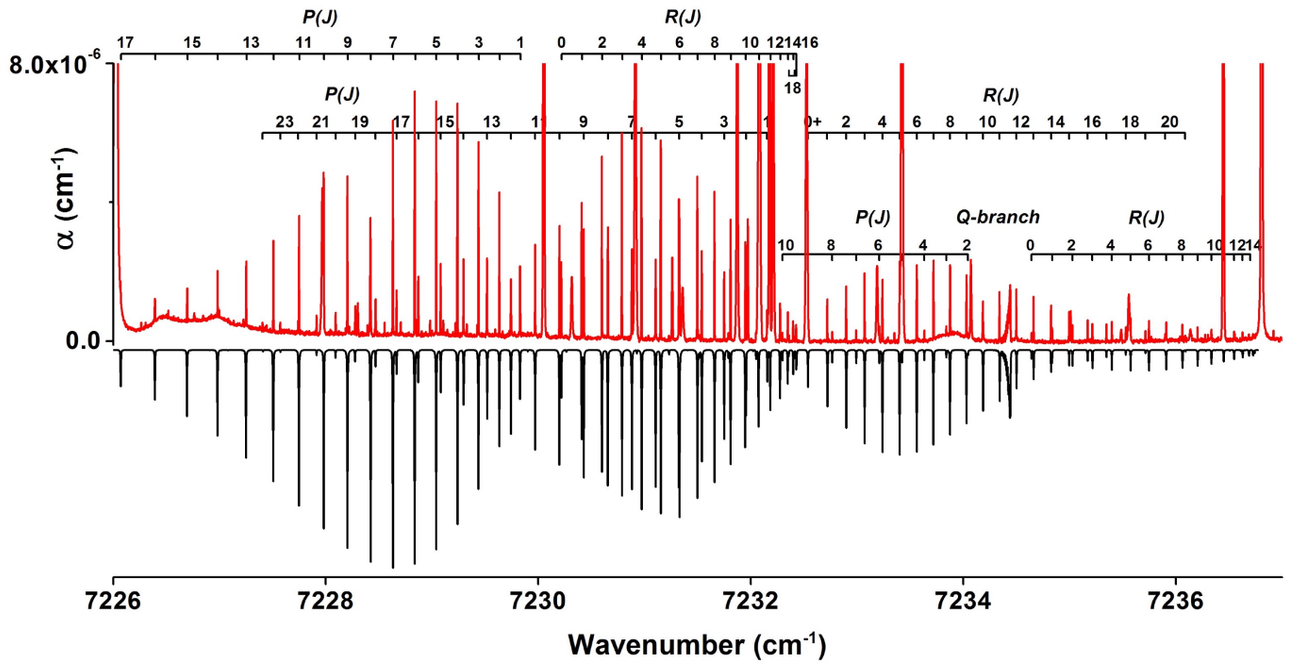

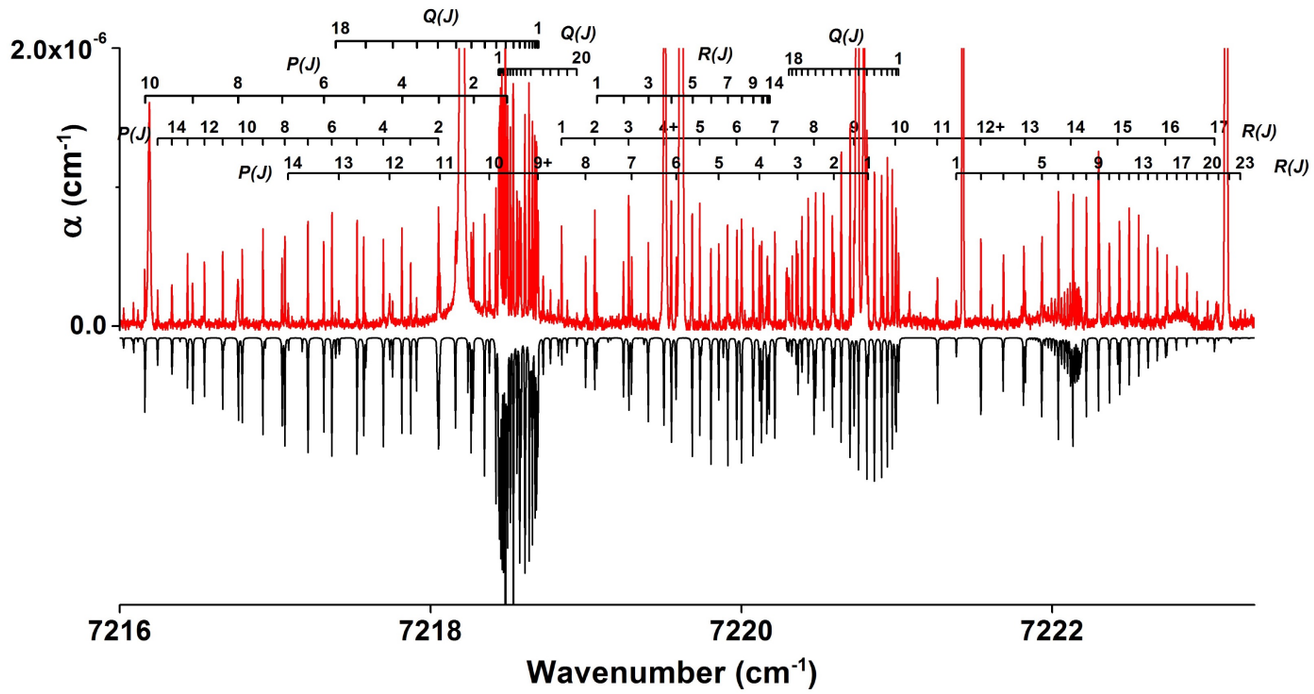

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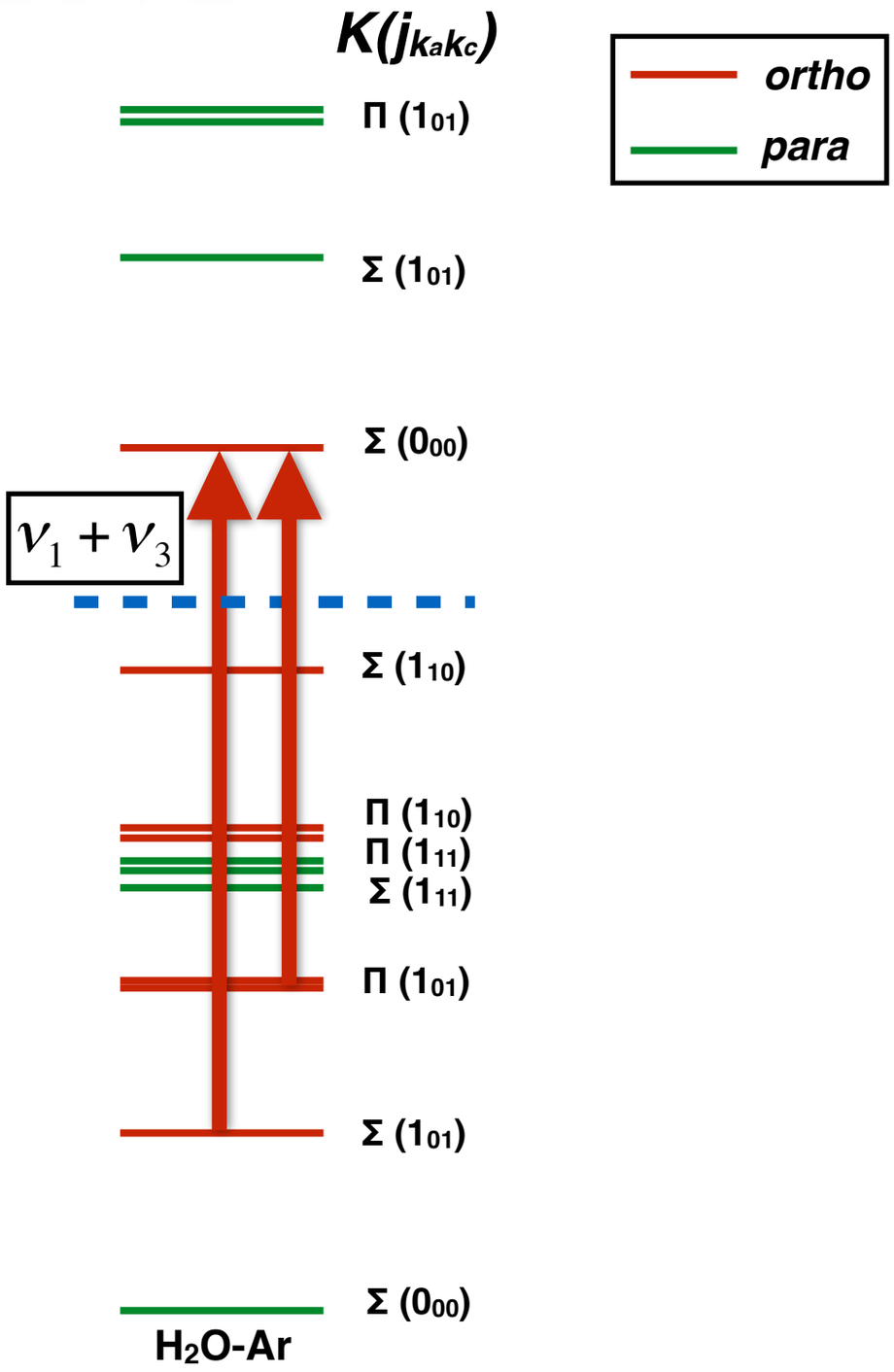
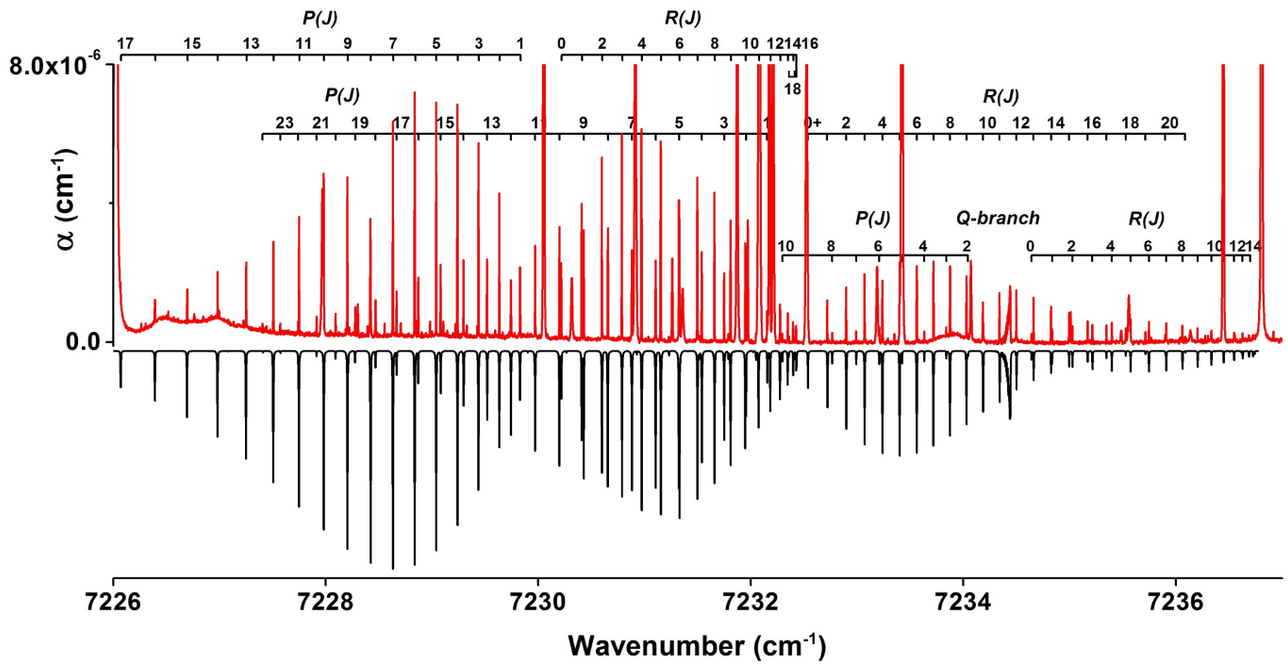
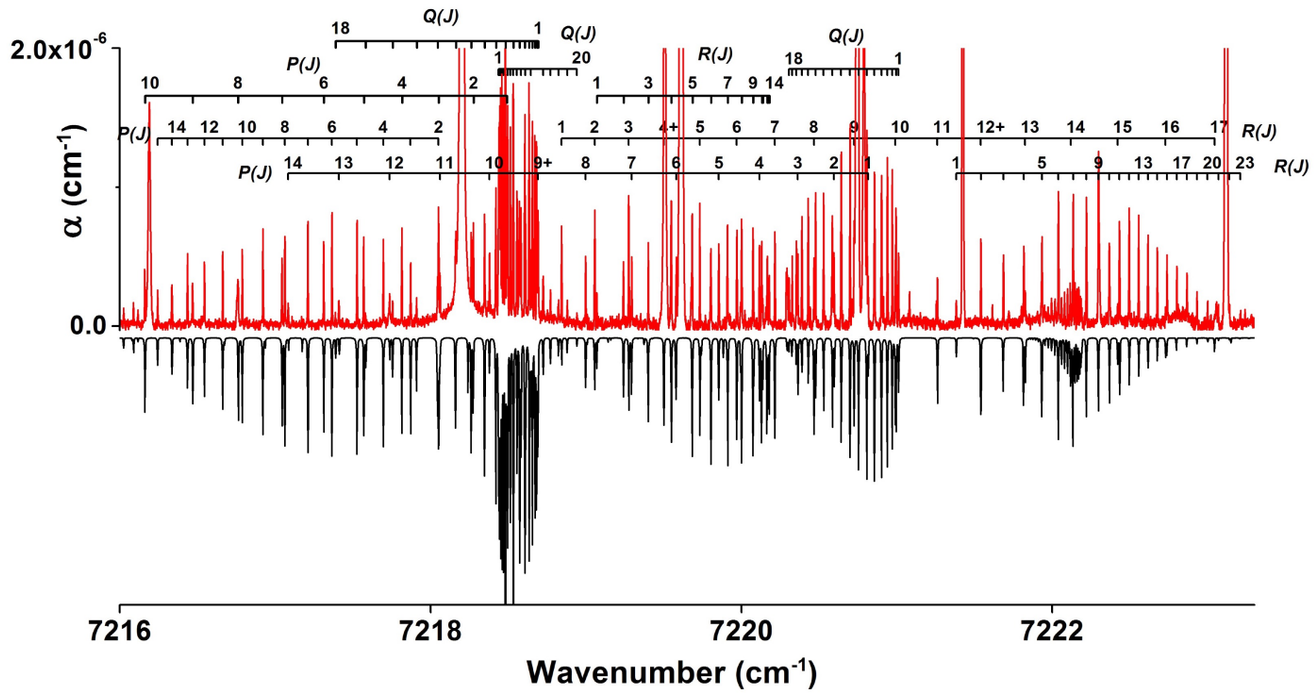
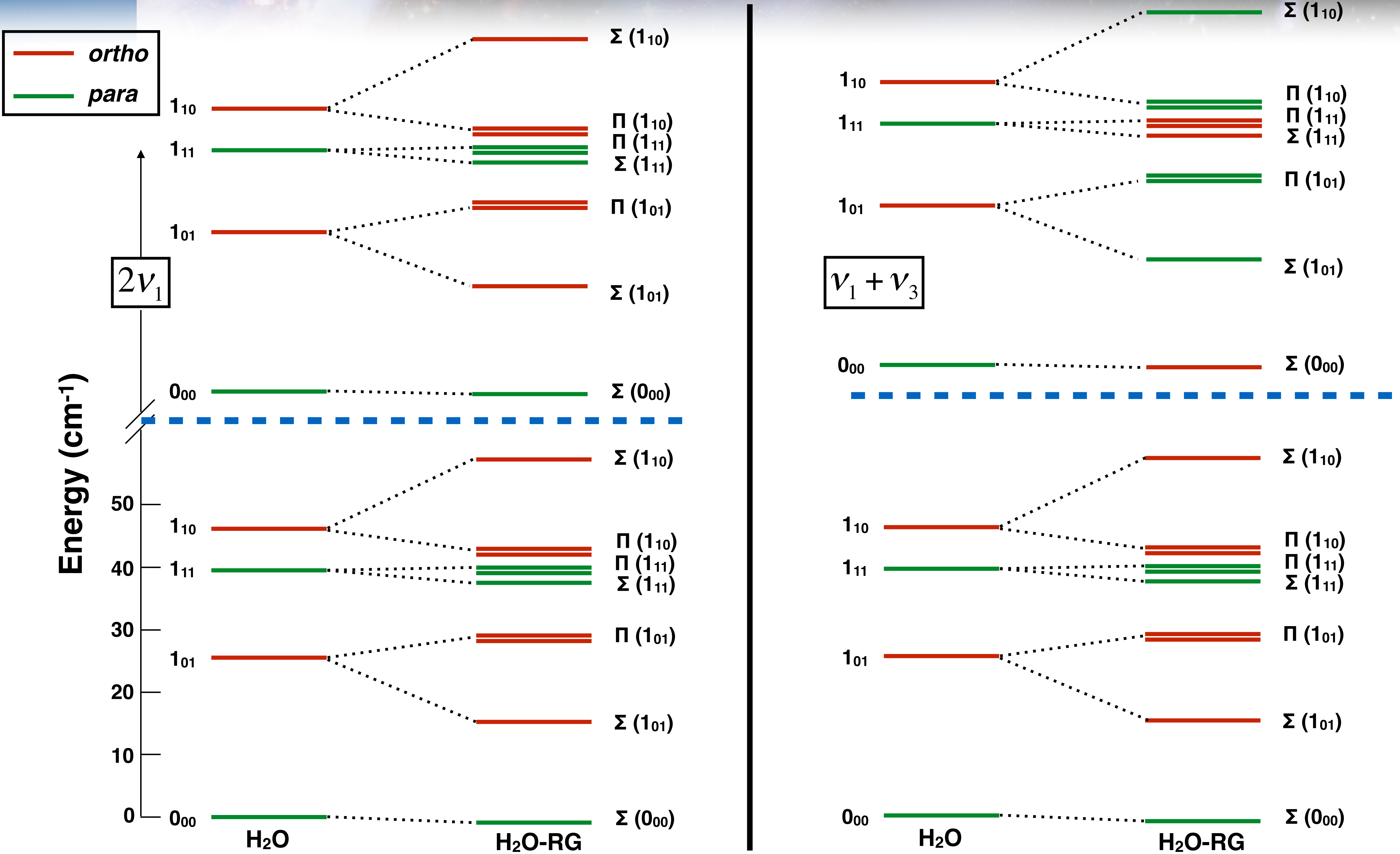






H_2O-Ar


ortho
para
$2\nu_1$
$\nu_1 + \nu_3$
Energy (cm-1)
0
10
20
30
40
50
1_{10}
1_{11}
1_{01}
0_{00}
Σ (1_{10})
Π (1_{10})
Π (1_{11})
Σ (1_{11})
Π (1_{01})
Σ (1_{01})
Σ (0_{00})
H_2O
H_2O-RG

	$^{82}Kr-H_2O$	$^{83}Kr-H_2O$	$^{84}Kr-H_2O$	$^{86}Kr-H_2O$
Ground state ($\Sigma 0_{00}$)				
B	0.0794967932(26)	0.07932665(13)	0.0791610866(13)	0.0788407869(25)
D_J	1.647888(375) E-6	1.6425(67) E-6	1.632704(162) E-6	1.619068(344) E-6
H	-2.32(127) E-11	-	-4.973(519) E-11	-3.88(115) E-11
Upper state: 2OH ($\Pi 1_{01}$)				
B	0.0799041(109)	0.0795695(112)	0.07862704(180)	0.07923191(760)
q	-	-	1.8637(23) E-3	-
D_J	2.7800(449) E-6	2.286(16) E-6	2.54750(677) E-6	2.7567(396) E-6
qD	-	-	-4.358(104) E-7	-
H	4.199(551) E-10	-	3.4995(947) E-10	4.520(621) E-10
qH	-	-	1.147(117) E-10	-
$\tilde{\nu}_0$	7273.479965(768)	7273.4954(18)	7273.47959(11)	7273.47919(41)
# lines	19	16	69	25
σ	0.40	0.97	0.35	0.32

All values are in cm^{-1}