

# Frequency Comb Assisted IR Measurements of $\text{H}_3^+$ , $\text{H}_2\text{D}^+$ and $\text{D}_2\text{H}^+$ Transitions

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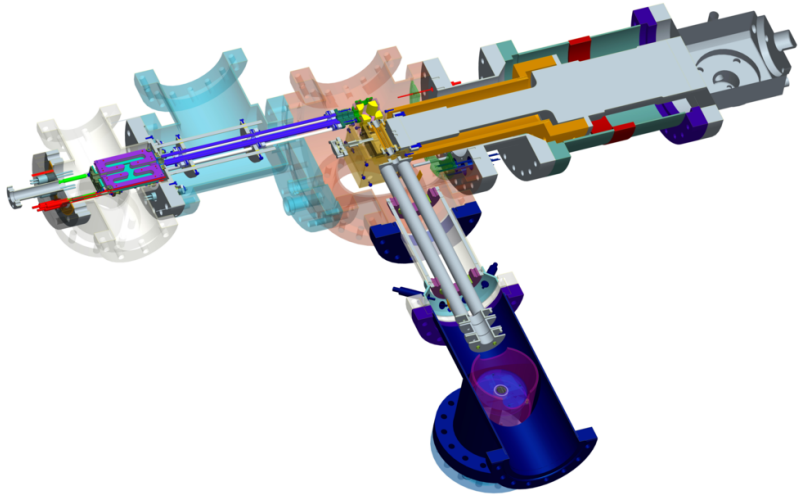
# COLTRAP and FELion (and photoshop)



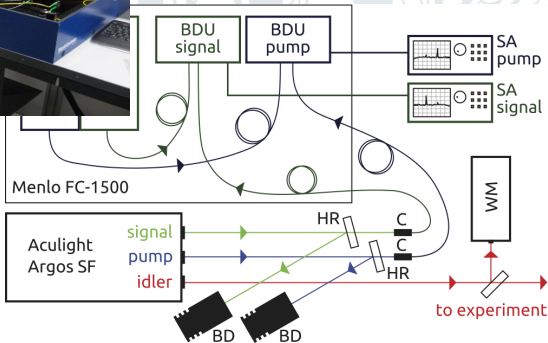
## Outline

- COLTRAP in Cologne
- ro-vibrational spectroscopy
- rotational spectroscopy

# COLTRAP



# Frequency Comb and 22-pole Trap



Asvany Rev. Sci. Instrum 83, 093110 (2012)

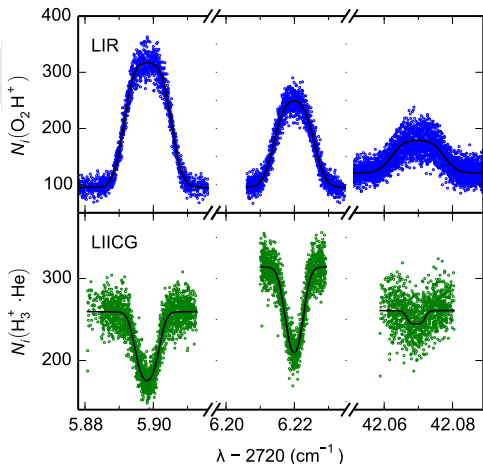
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# LIR and LIICG of $\text{H}_3^+$

Suitable reaction:

- $\text{H}_3^+ + \text{O}_2 \rightarrow \text{O}_2\text{H}^+ + \text{H}_2$
- $T_a \approx 170 \text{ K}$
- $T_i \approx 20 \text{ K}$
  
- $T_i \ll 20 \text{ K}$

Spectrum  $\nu_2$  band:



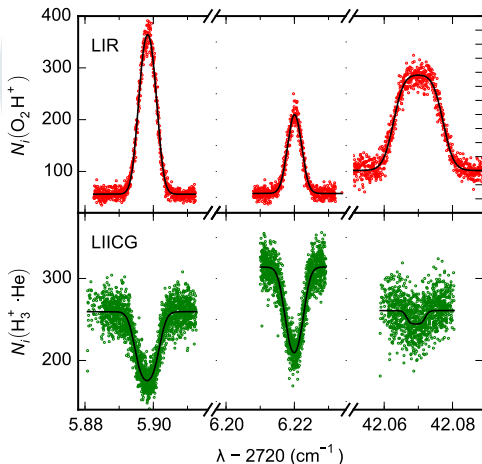
LIICG: Chakrabarty JPCL 4, 4051 (2013)

# LIR and LIICG of $\text{H}_3^+$ Revised

Suitable reaction:

- $\text{H}_3^+ + \text{O}_2 \rightarrow \text{O}_2\text{H}^+ + \text{H}_2$
- $T_a \approx 170 \text{ K}$
- $T_i \approx 20 \text{ K}$
  
- $T_i \ll 20 \text{ K}$

Spectrum  $\nu_2$  band:



LIICG: Chakrabarty JPCL 4, 4051 (2013)  
 $\text{H}_3^+$ : Jusko J.Mol.Spec 319, 55 (2016)

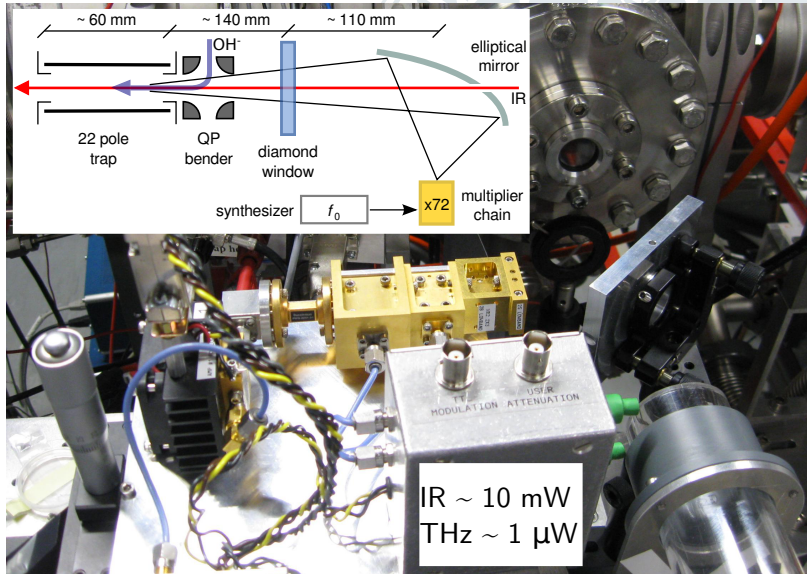
# LIR and LIICG of $H_3^+$

Different results between different groups:

MHz	R(1,0)	R(1, 1) <sup>u</sup>	R(2, 2) <sup>l</sup>
Hodges JCP, (2013)	81720377.29	81730020.44	82804769.99
Shy (2013)	81720371.55	81730028.33	82804761.12
This work 2013	81720376.57	81730019.99	82804770.08

MHz	R(1,0)	R(1, 1) <sup>u</sup>	R(2, 2) <sup>l</sup>
Hodges JCP, (2013)	81720377.29(23)	81730020.44(38)	82804769.99(31)
Shy (priv.)	81720376.14(18)	81730019.95(28)	82804769.75(33)
This work 2016	81720376.62(11)	81730019.82(20)	82804769.99(65)

# Two Photon Process (IR + THz Photon)





# Two Photon Process: $\text{OH}^- J = 1 \leftarrow 0$ Transition

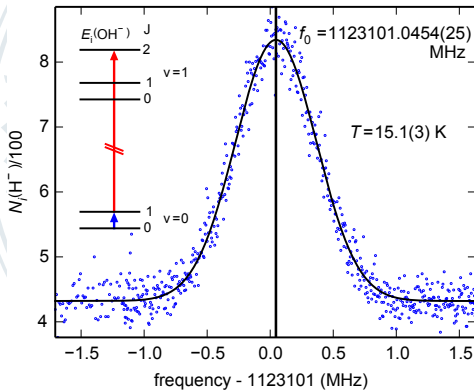
Sequence:

- $\text{OH}^- (\nu = 0, J = 0) + h\nu_1 \rightarrow \text{OH}^- (\nu = 0, J = 1)$
- $\text{OH}^- (\nu = 0, J = 1) + h\nu_2 \rightarrow \text{OH}^- (\nu = 1, J = 1)$
- $\text{OH}^- (\nu = 1, J = 1) + \text{H}_2 \rightarrow \text{H}^- + \text{H}_2\text{O}$

$h\nu_1$  – THz photon

$h\nu_2$  – NIR photon

Jusko PRL 112, 253005 (2014)  
Matshushima JMS 235, 261 (2006)



this work      1123101.0410(14) MHz  
prev. work    1123100.985(324) MHz

# Combination Differences – Prediction of Pure Rotational Transitions

$\text{H}_2\text{D}^+$ :

Type	Transition	MHz	Ref.
prediction	$2_{12} \leftarrow 1_{11}$	2363241.71(70)	
measurement		2363242.82(69)	Yonezu JMS 256 2009
prediction	$2_{02} \leftarrow 1_{01}$	2576756.5(16)	
measurement		2576756.6(10)	Amano PTRS A 364 2006
prediction	$2_{11} \leftarrow 1_{10}$	3102324.2(35)	
measurement		3102329.28(56)	Yonezu JMS 256 2009

$\text{D}_2\text{H}^+$ :

Type	Transition	MHz	Ref.
prediction	$2_{02} \leftarrow 1_{11}$	1572823.78(76)	
prediction	$2_{12} \leftarrow 1_{01}$	2258688.28(80)	

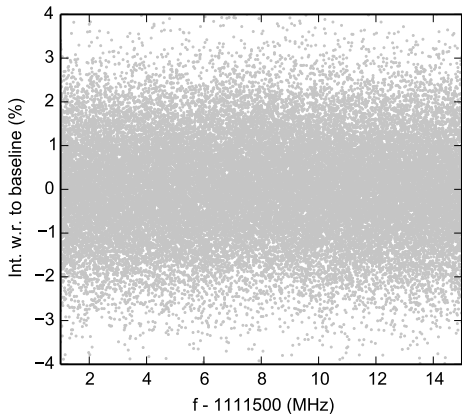
# Two Photon Process:

## Sequence:

1.  $\text{H}_2\text{D}^+ (2_{12}) + h\nu_1 \rightarrow \text{H}_2\text{D}^+ (2_{11})$
2.  $\text{H}_2\text{D}^+ (\nu = 0, 2_{11}) + h\nu_2 \rightarrow \text{H}_2\text{D}^+ (\nu = 1, 1_{10})$
3.  $\text{H}_2\text{D}^+ (\nu = 1, 1_{10}) + \text{H}_2 \rightarrow \text{H}_3^+ + \text{HD}$

$h\nu_1$  – THz photon

$h\nu_2$  – NIR photon



Prediction (CDMS)

1111509.2 MHz

# Two Photon Process: $\text{H}_2\text{D}^+$ $2_{11} \leftarrow 2_{12}$

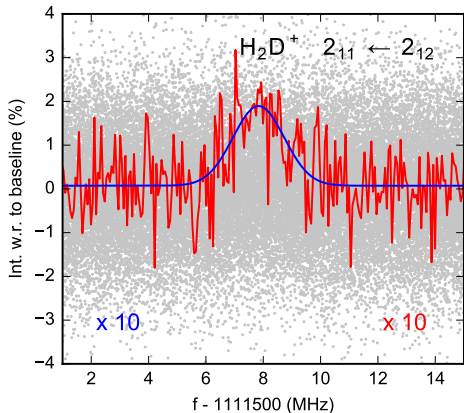
Sequence:

1.  $\text{H}_2\text{D}^+ (2_{12}) + h\nu_1 \rightarrow \text{H}_2\text{D}^+ (2_{11})$
2.  $\text{H}_2\text{D}^+ (\nu = 0, 2_{11}) + h\nu_2 \rightarrow \text{H}_2\text{D}^+ (\nu = 1, 1_{10})$
3.  $\text{H}_2\text{D}^+ (\nu = 1, 1_{10}) + \text{H}_2 \rightarrow \text{H}_3^+ + \text{HD}$

$h\nu_1$  – THz photon

$h\nu_2$  – NIR photon

Center position  $\pm 100$  kHz



Prediction (CDMS)

1111509.2 MHz

# Cologne Group



\$\$\$:  
DFG,  
SFB 965,  
Alexander von  
Humboldt

Thanks:  
Cologne  
workshop

The seal of the University of Cologne is a large, circular emblem in the background. It features a central scene with three figures: a standing figure on the left holding a staff, a central figure pointing upwards, and a seated figure on the right holding a child. Above them is a star. The seal is surrounded by Latin text and a decorative border.

Thank You for Your Attention