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LaserLaB AMSTERDAM

Determination of the dissociation energy of para-H_2

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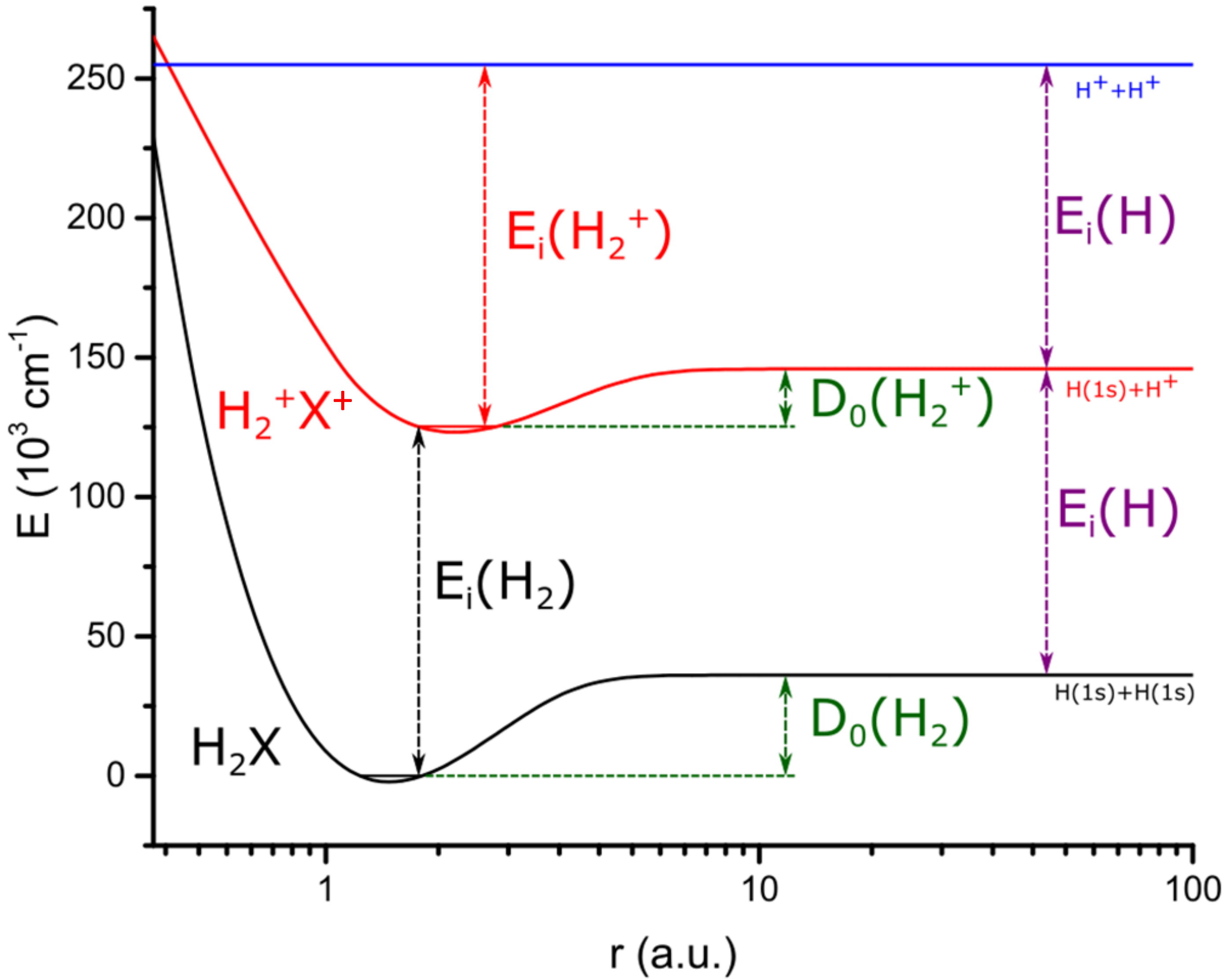
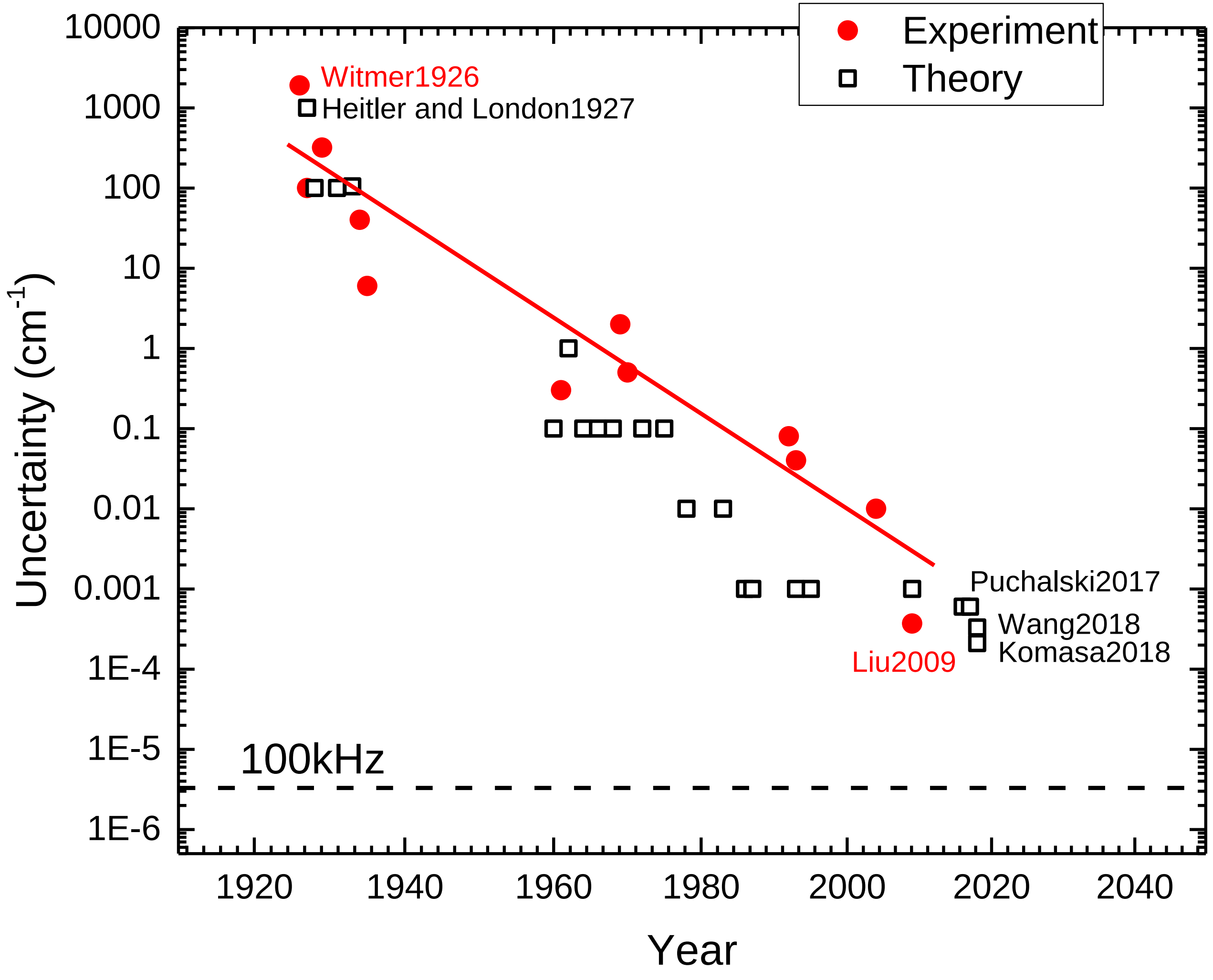
[c] Department of Chemical Physics, University of Science and Technology of China

[d] Laboratoire Aimé Cotton, CNRS, Orsay

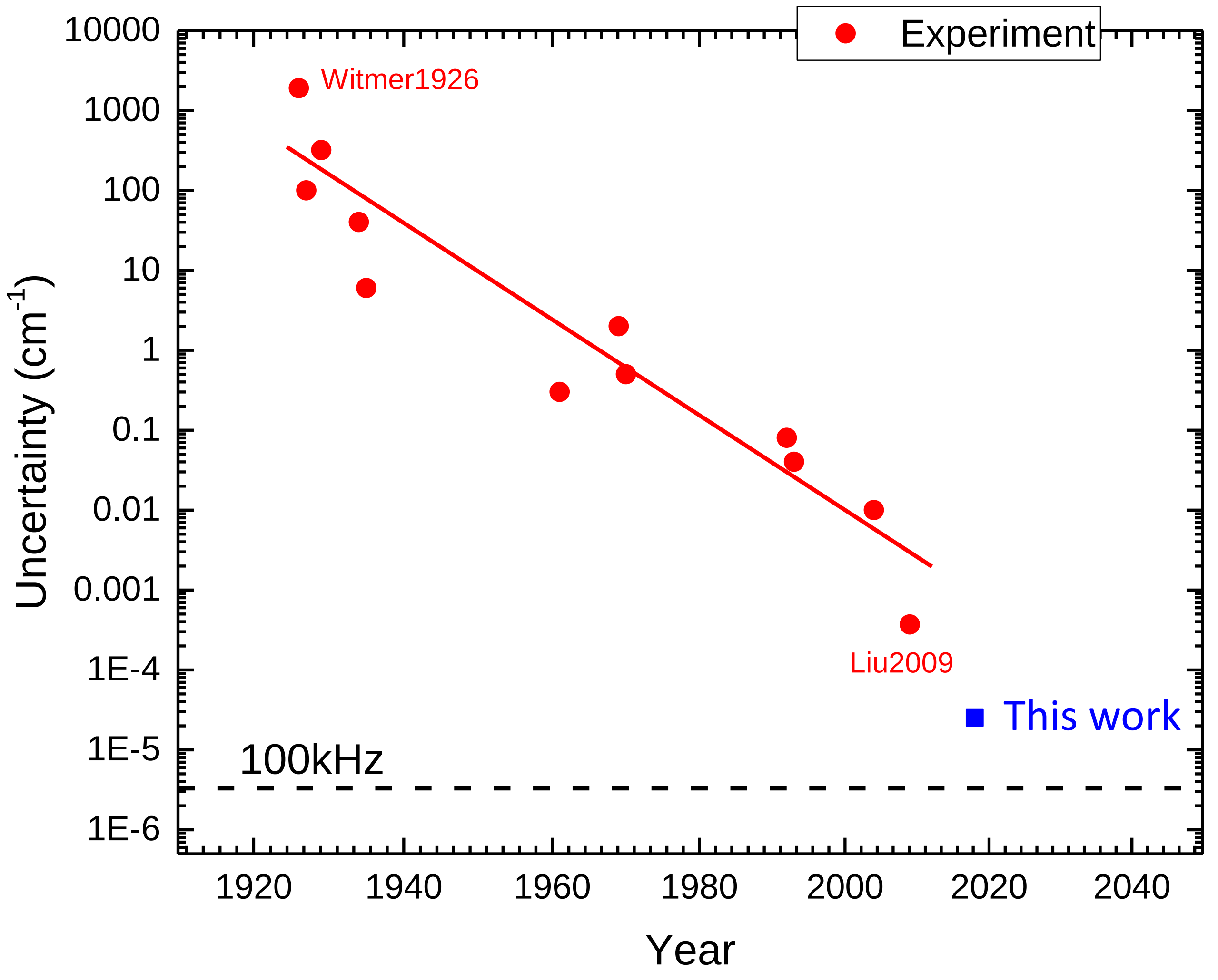
Determining D_0



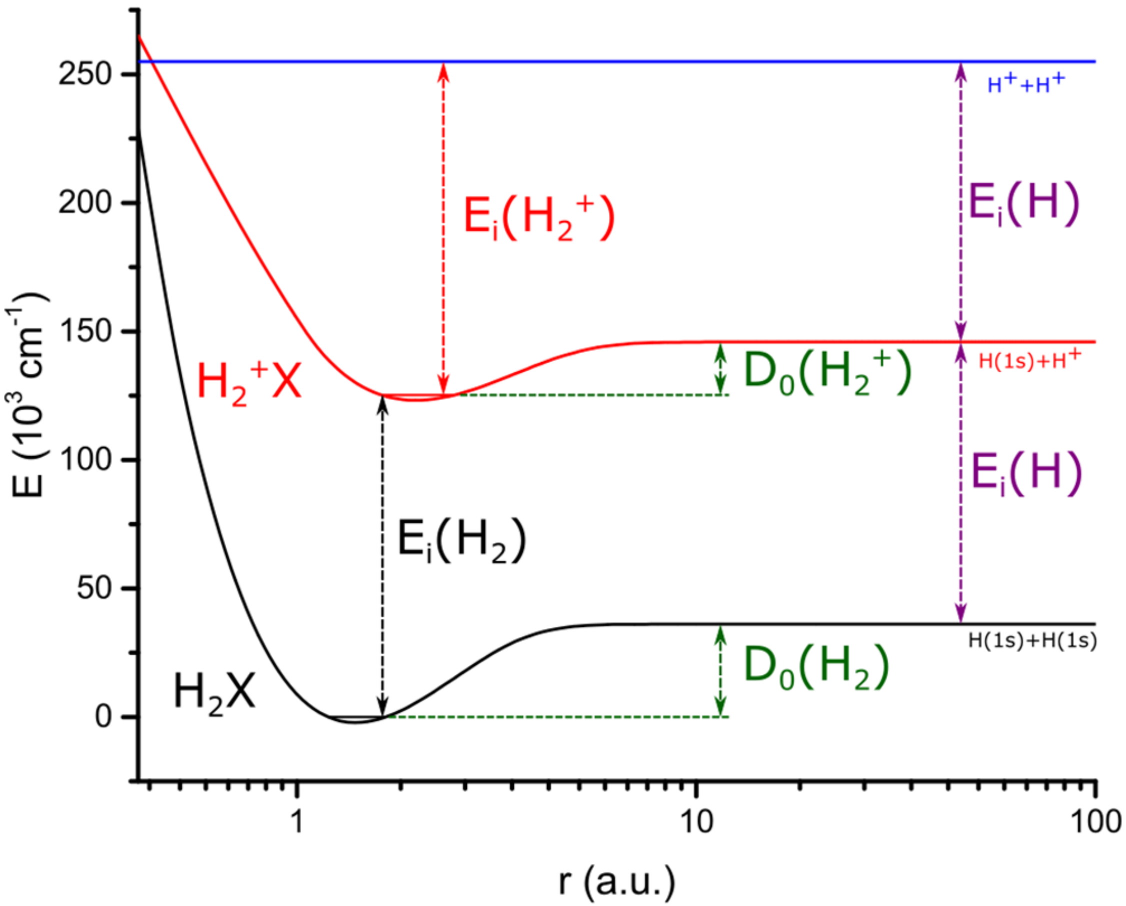
Test of molecular theory with D_0



Test of molecular theory with D_0



Determining D_0(Ortho-H_2)



$D_0(H_2) = E_i(H_2) + E_i(H_2^+) - 2E_i(H)$

E_i(H) =109678.77174307(10) cm-1
~3 kHz

E_i(H_2+) =131058.1219937(6) cm-1
~18 kHz

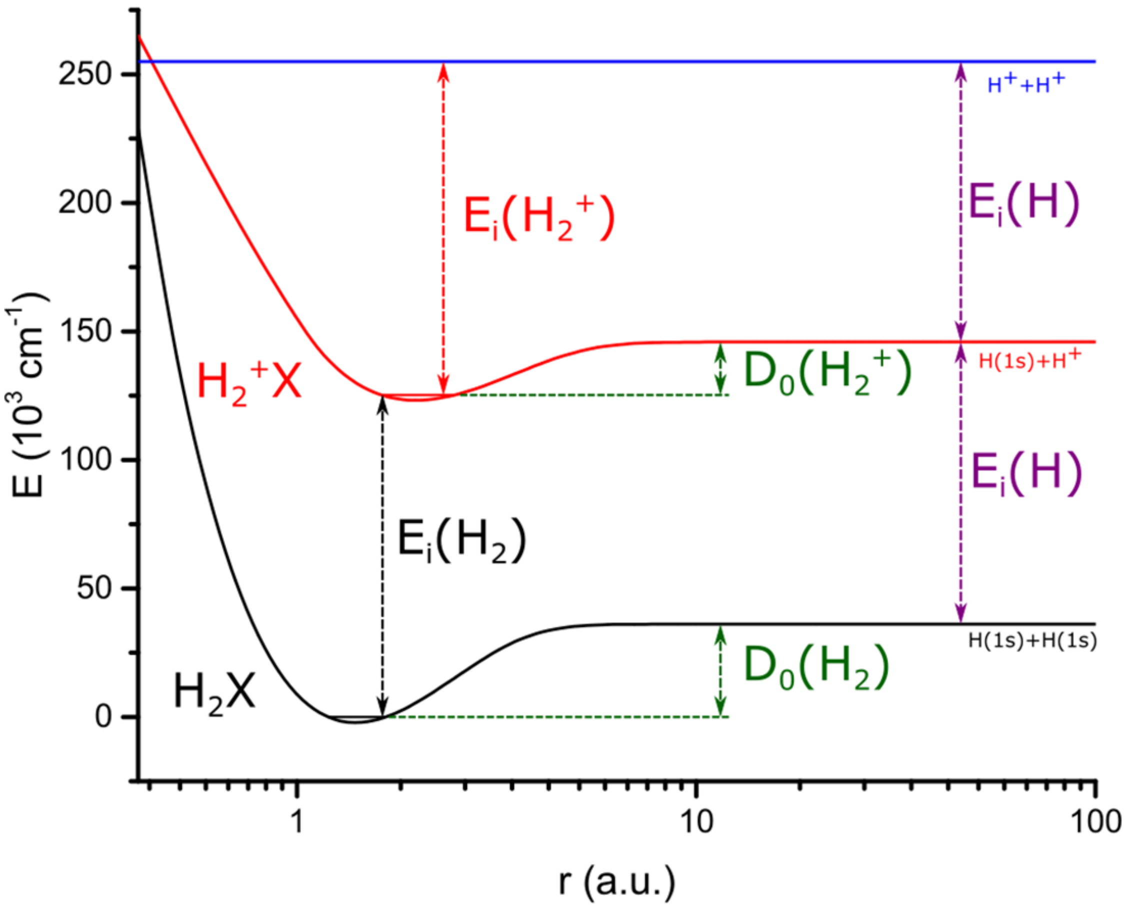
E_i(H_2) =124417.49113(37) cm-1
~11 MHz

D_0(H_2) = 36118.0696(4) cm-1
~11MHz

Korobov, PRL 2017
Mohr, RMP 2016
Liu, JCP 2009

Determining D_0(Ortho-H_2)

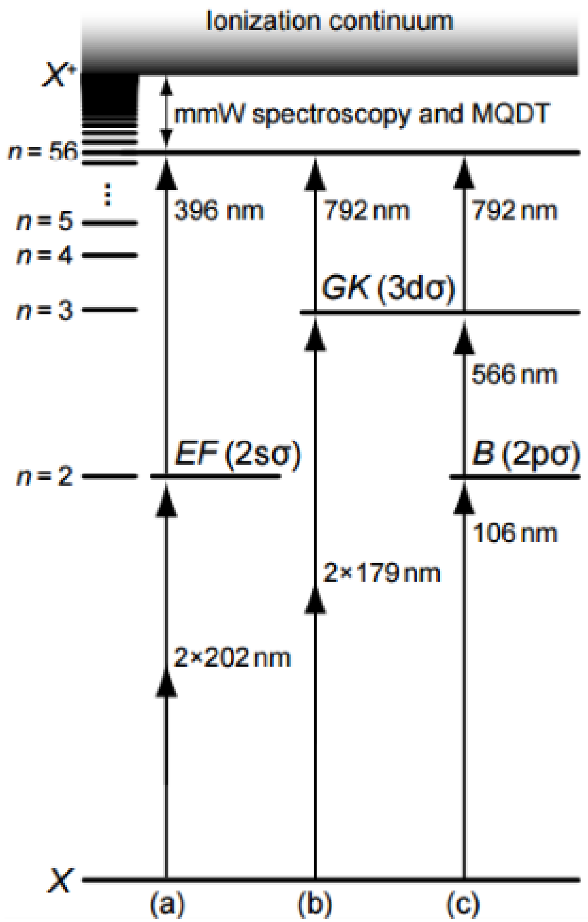
$$D_0(H_2) = E_i(H_2) + E_i(H_2^+) - 2E_i(H)$$



Value	Uncertainty
$E_i(H)$	3 kHz
$E_i(H_2^+)$	18 kHz
$E_i(H_2)$	11 MHz
$D_0(H_2)$	11 MHz

Korobov, PRL 2017
Mohr, RMP 2016
Liu, JCP 2009

The ionization energy

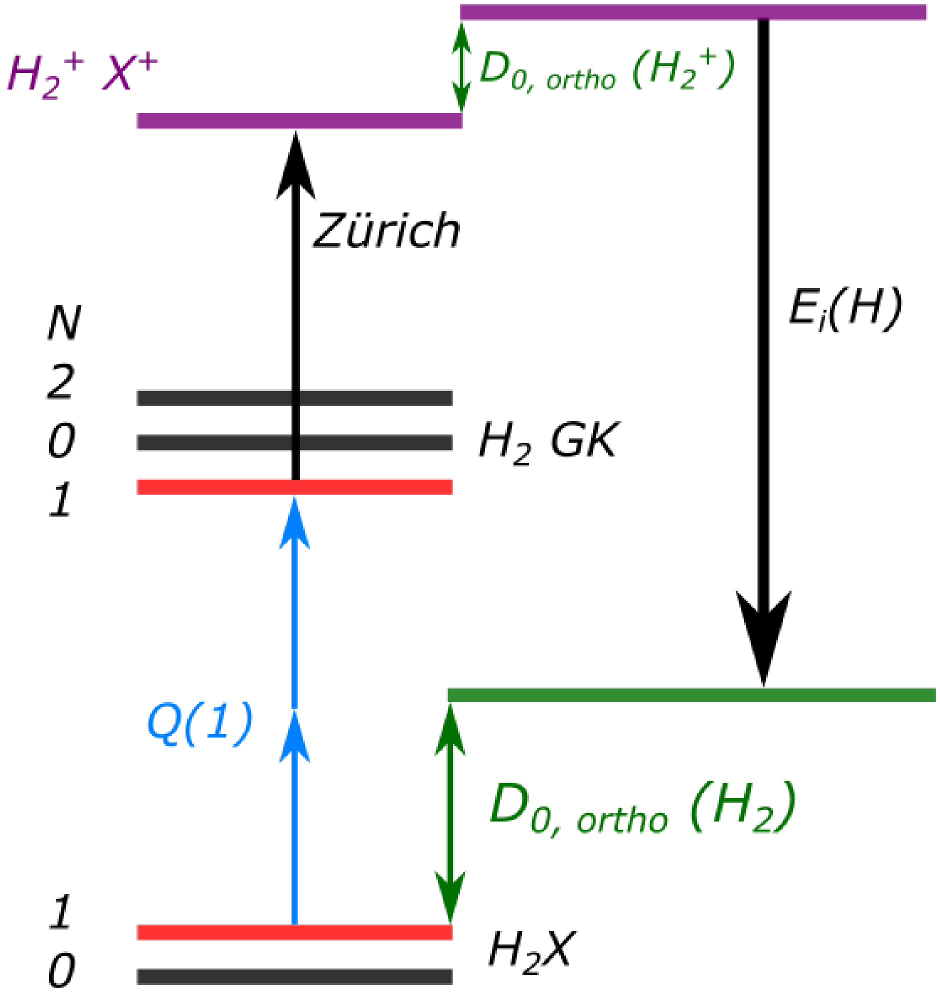


D. Sprecher et al. Faraday Discuss. Chem. Soc. 150, 51 (2011)

Ortho- and Para-Hydrogen

Ortho:

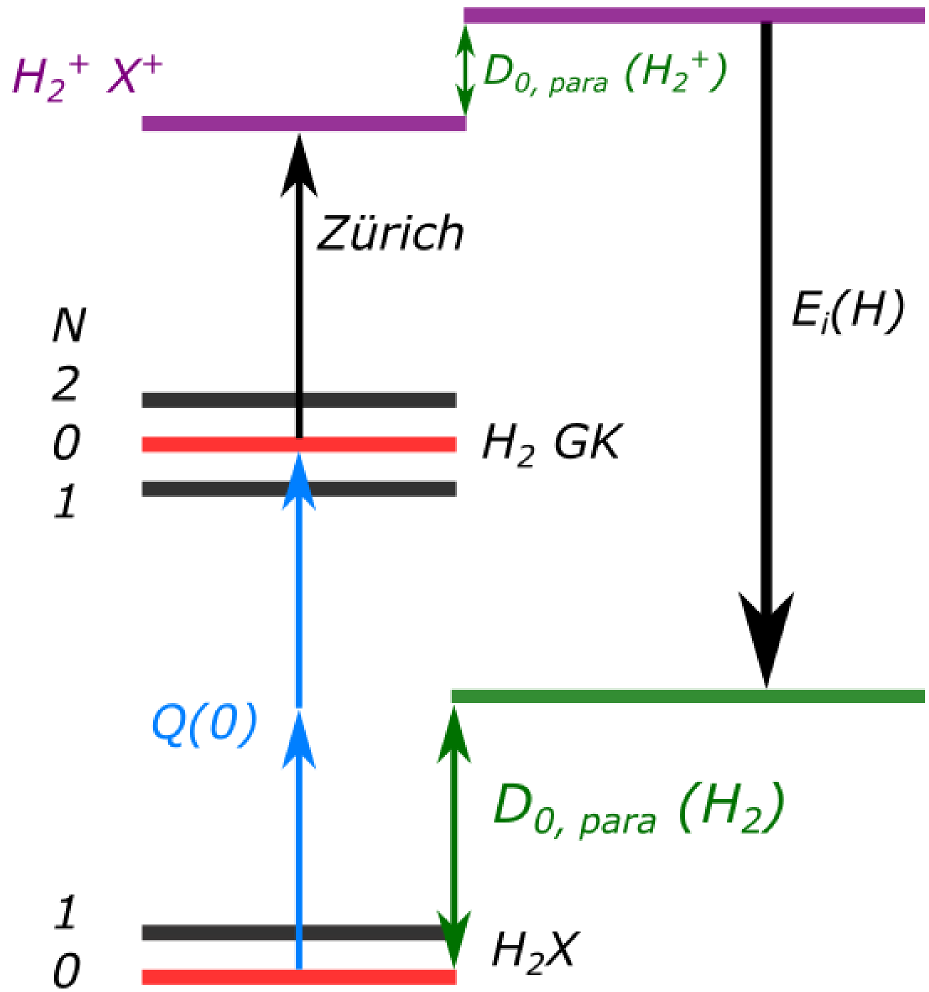
- Nuclear spins parallel
- More signal
- Previous measurements



Ortho- and Para-Hydrogen

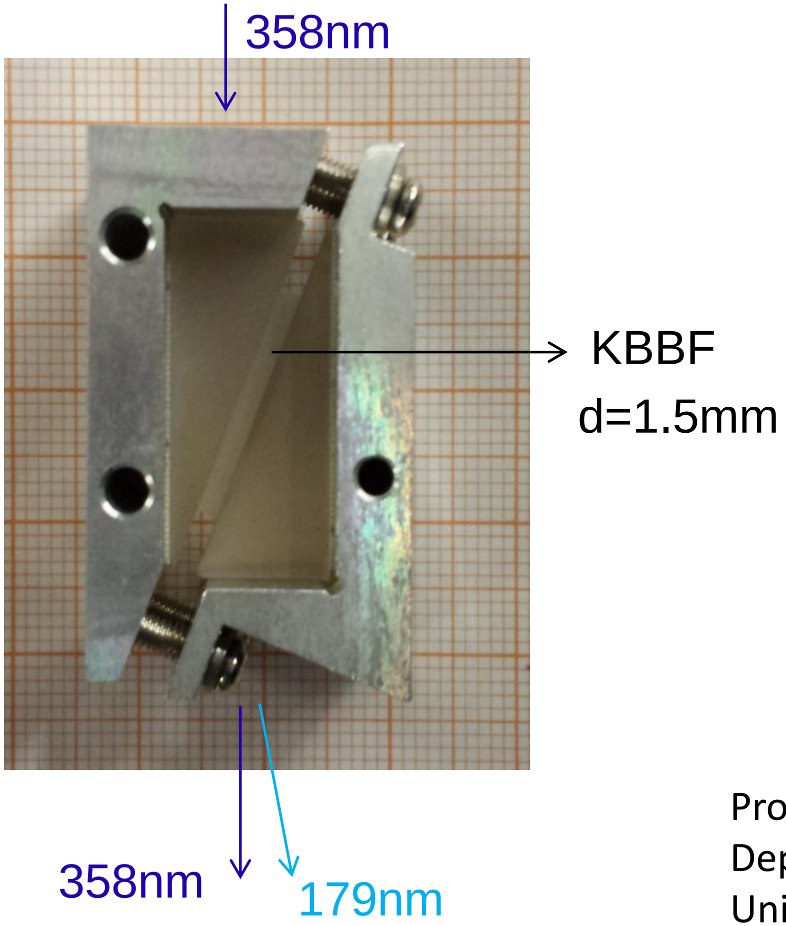
Para:

- Nuclear spins antiparallel
- No hyperfine structure
- “Real” Dissociation Energy



VUV generation: KBBF

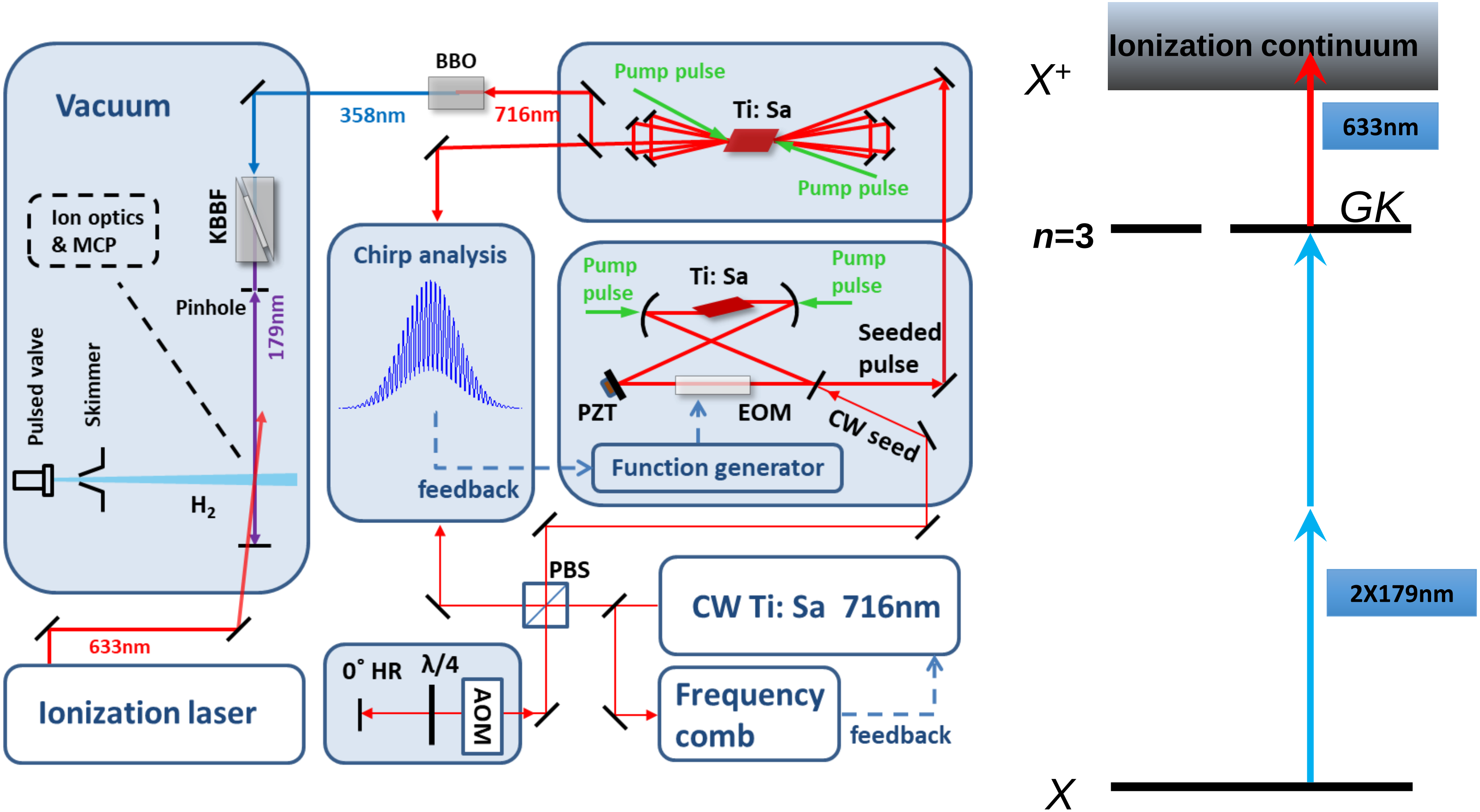
2nd harmonic from 716 nm laser



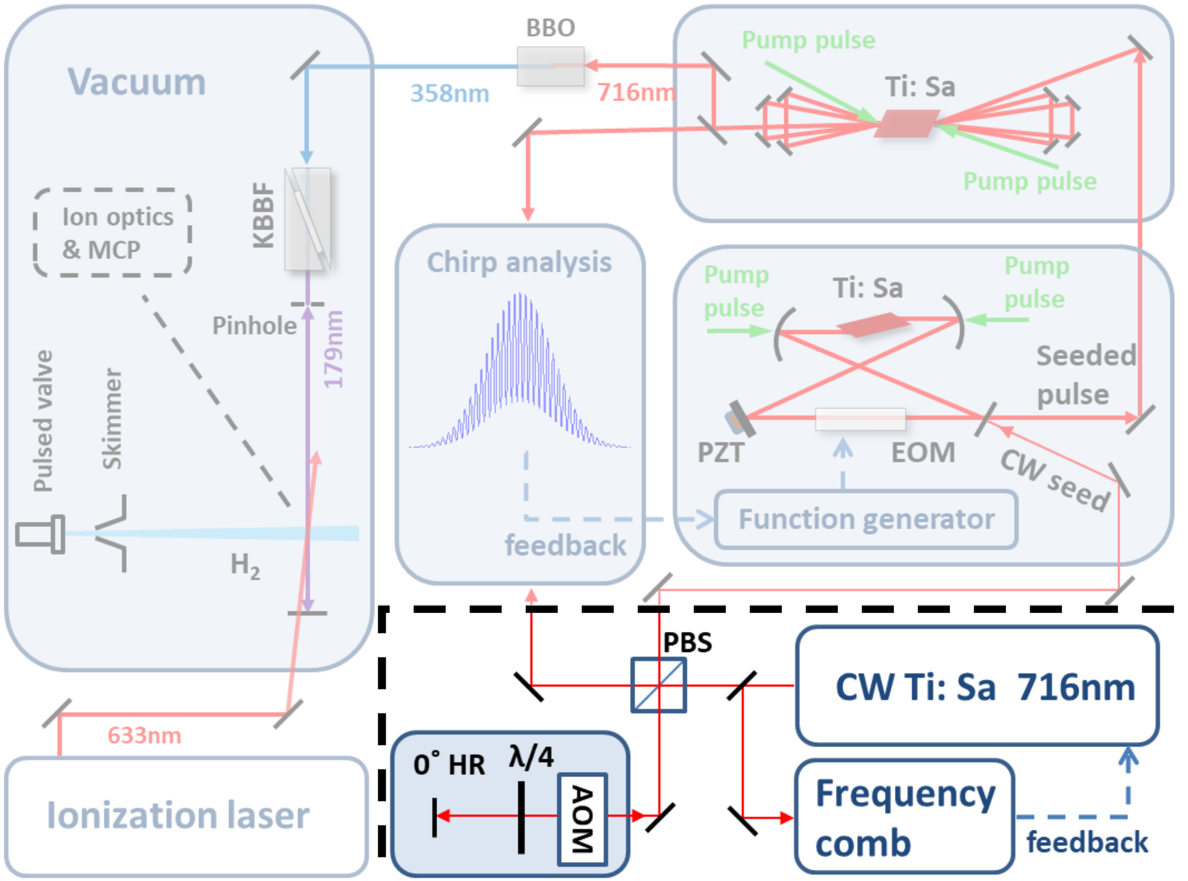
- $KBe_2BO_3F_2$
- Used in Vacuum
- Low efficiency (0.01% to 0.1%)
- Low damage threshold

Provided by prof. dr. S. Hu,
Department of Chemical Physics,
University of Science and Technology of China

Experimental setup



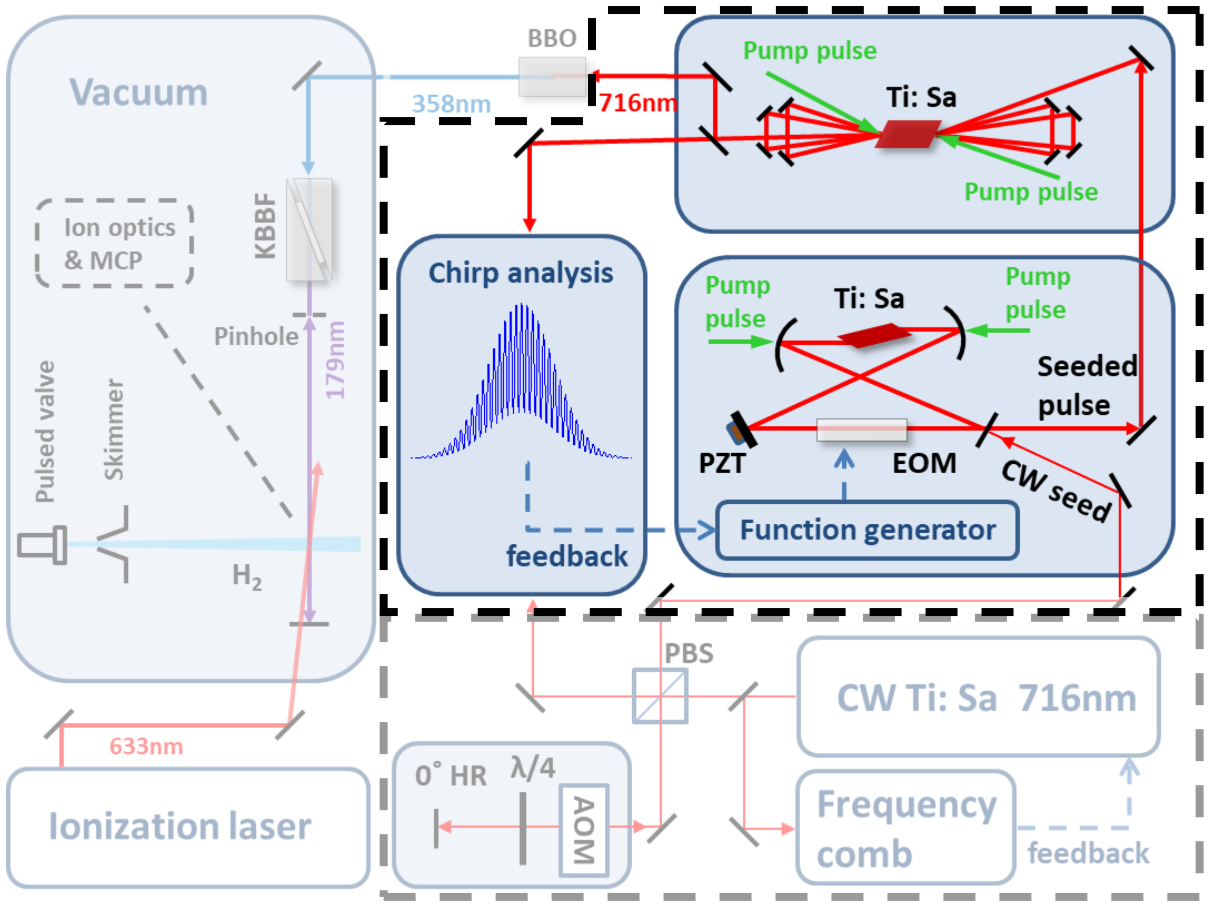
Experimental setup



Frequency accuracy < 10^{-12}

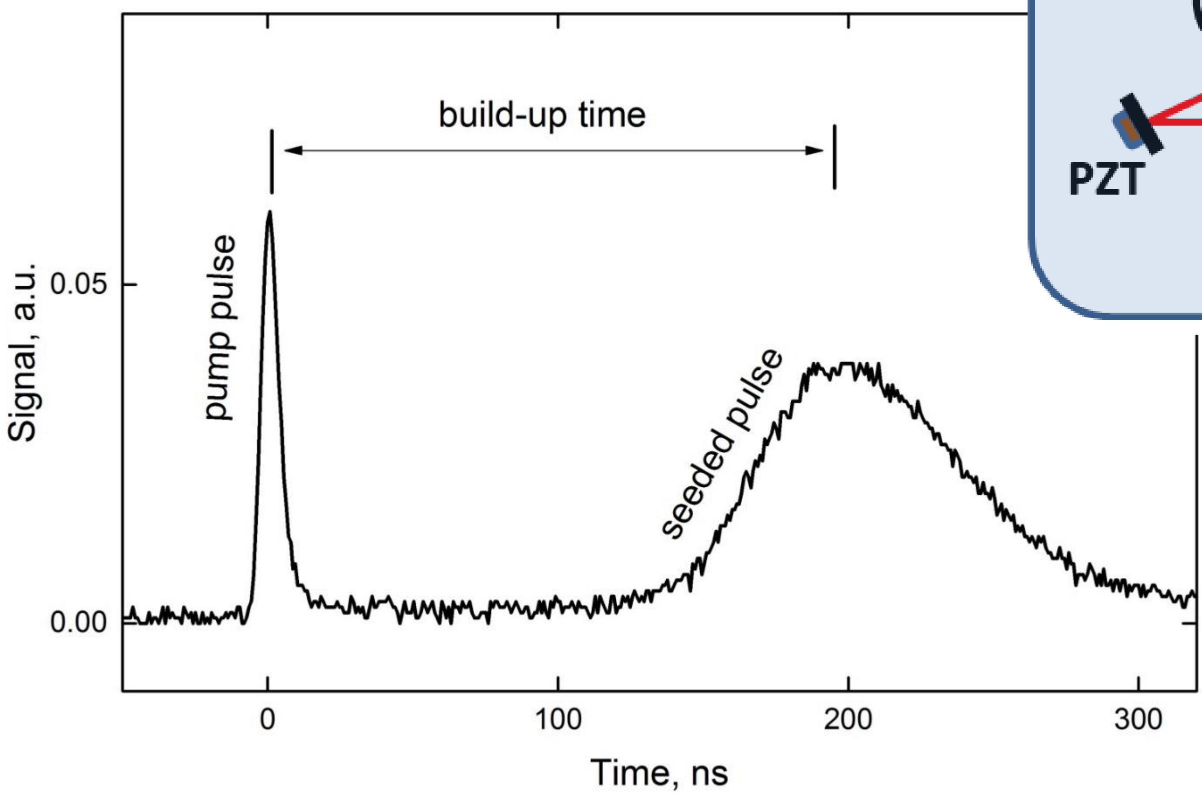
Experimental setup

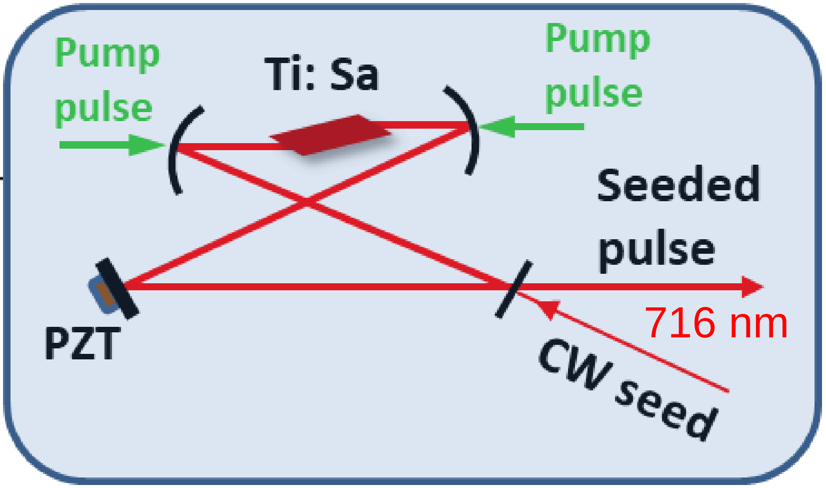
High power, high accuracy



Frequency accuracy < 10^{-12}

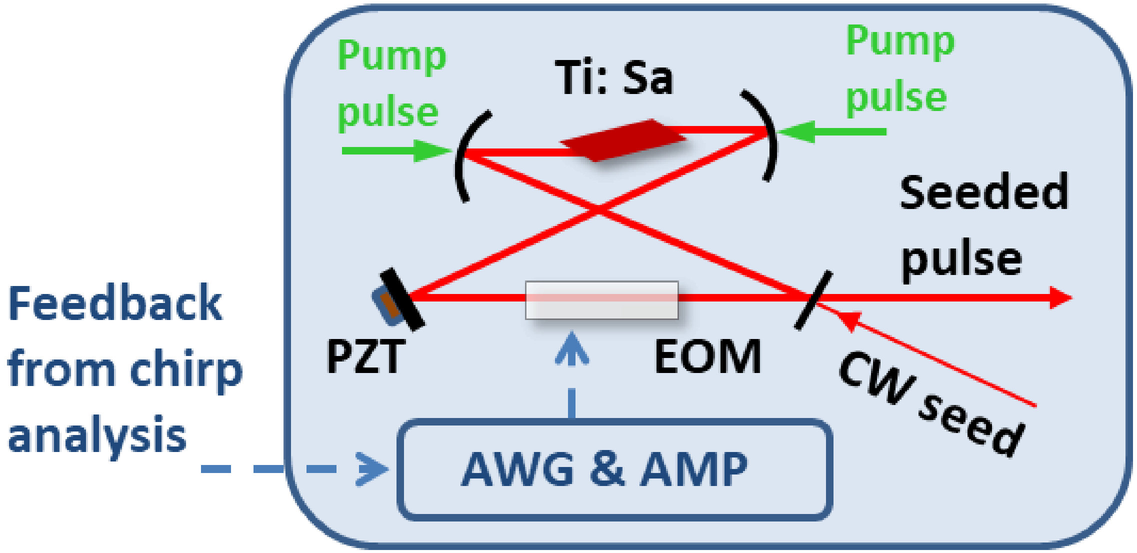
Chirp





- ➢ Cavity Pulling
- ➢ Frequency chirp

Anti-chirp

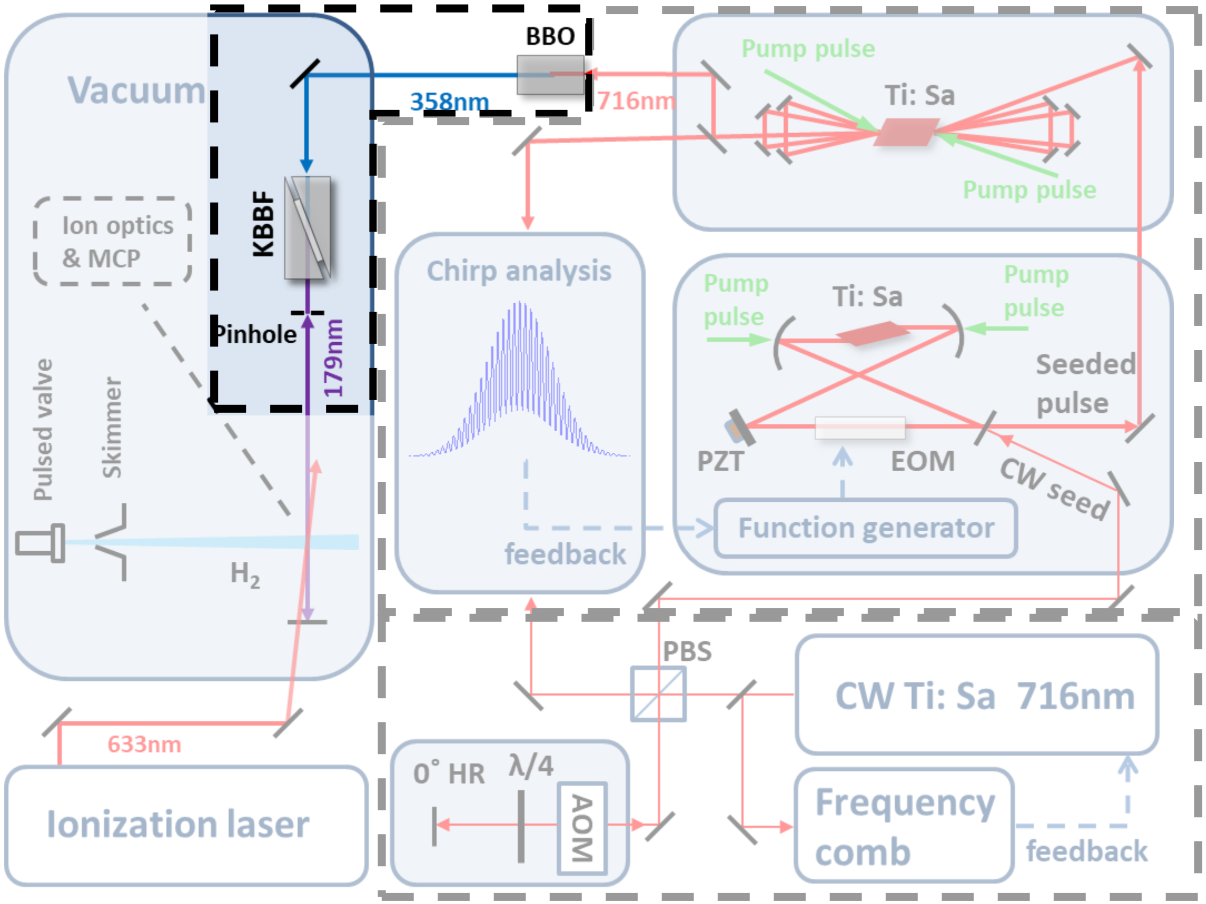


- Sensitive to temperature and stress
- Arbitary function generator to drive
- Amplified to max 150V

Experimental setup

VUV generation

High power, high accuracy

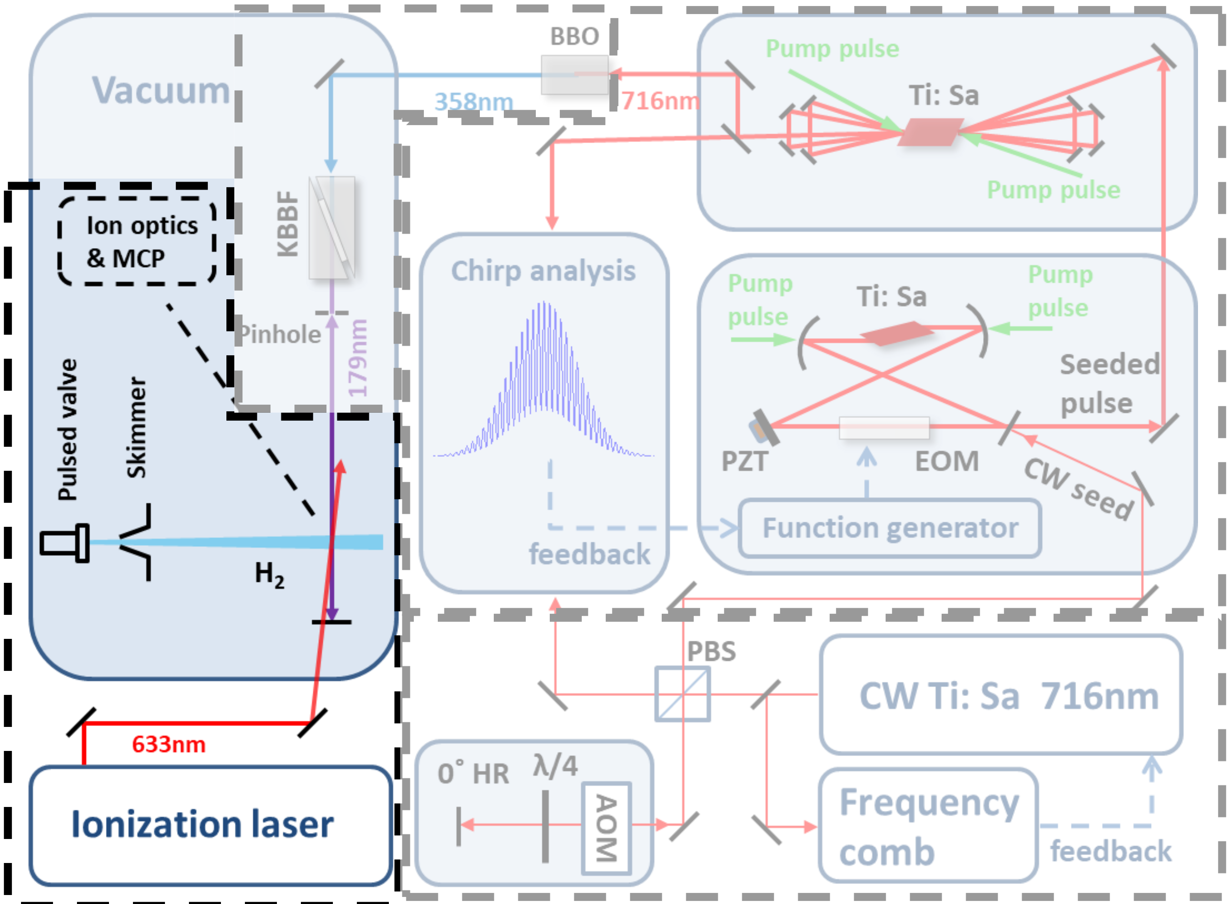


Frequency accuracy < 10^{-12}

Experimental setup

VUV generation

High power, high accuracy

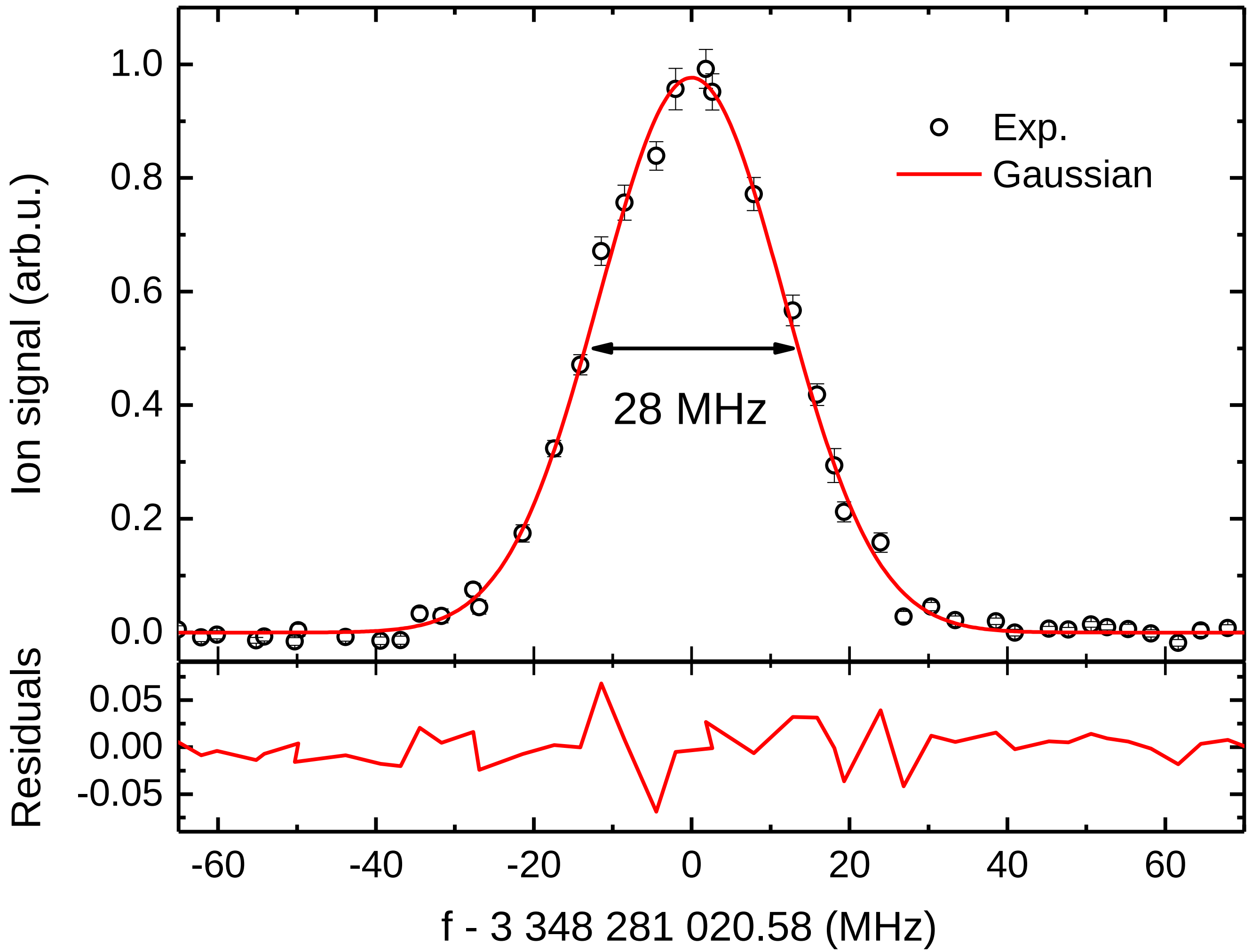


Ionize and detect

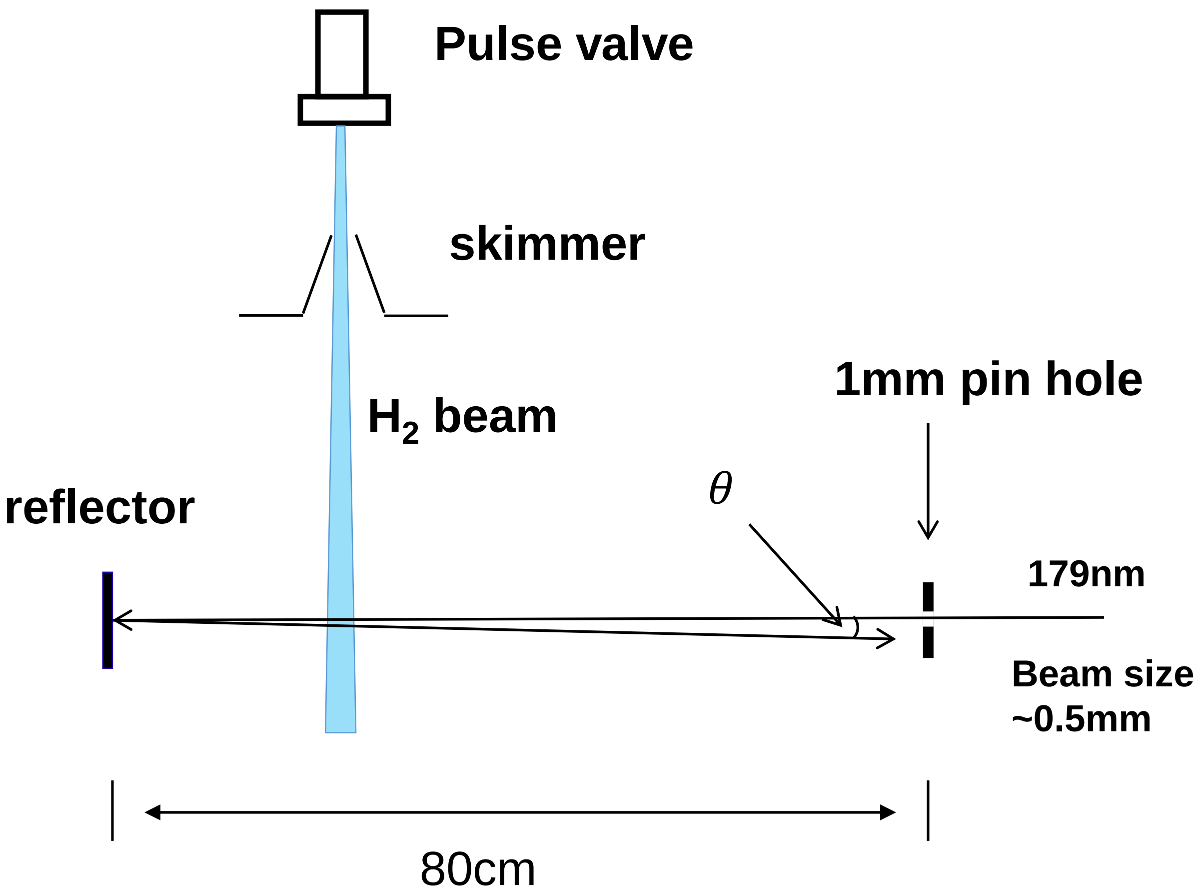
Frequency accuracy < 10^{-12}

Scan of GK-X Q(1) in H_2

GK(v=1, N=1) - X(v=0, N=1), chirp compensated shot-by-shot.



Systematic check: Residual Doppler

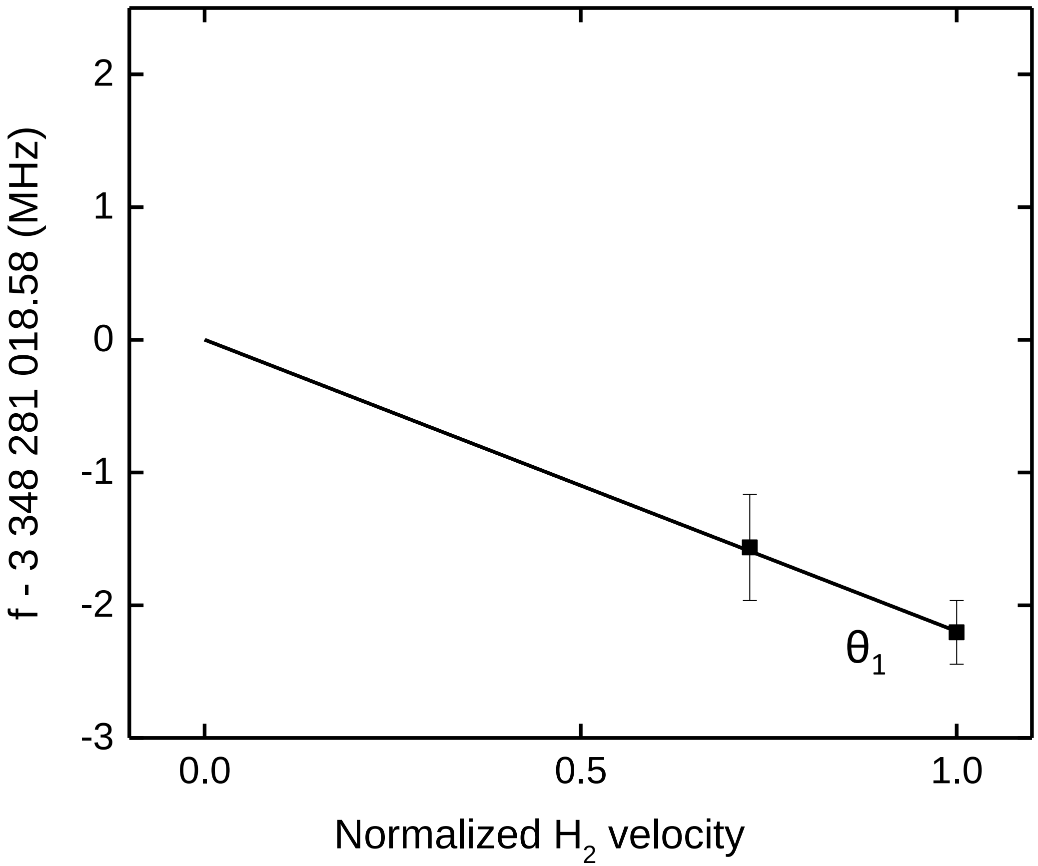


$$\frac{\delta f}{f} = \frac{v}{c}\sin\frac{\theta}{2}$$

v = 2900(300) m/s
θ < 0.3mrad
→ δf < 3MHz

Systematic check: Residual Doppler

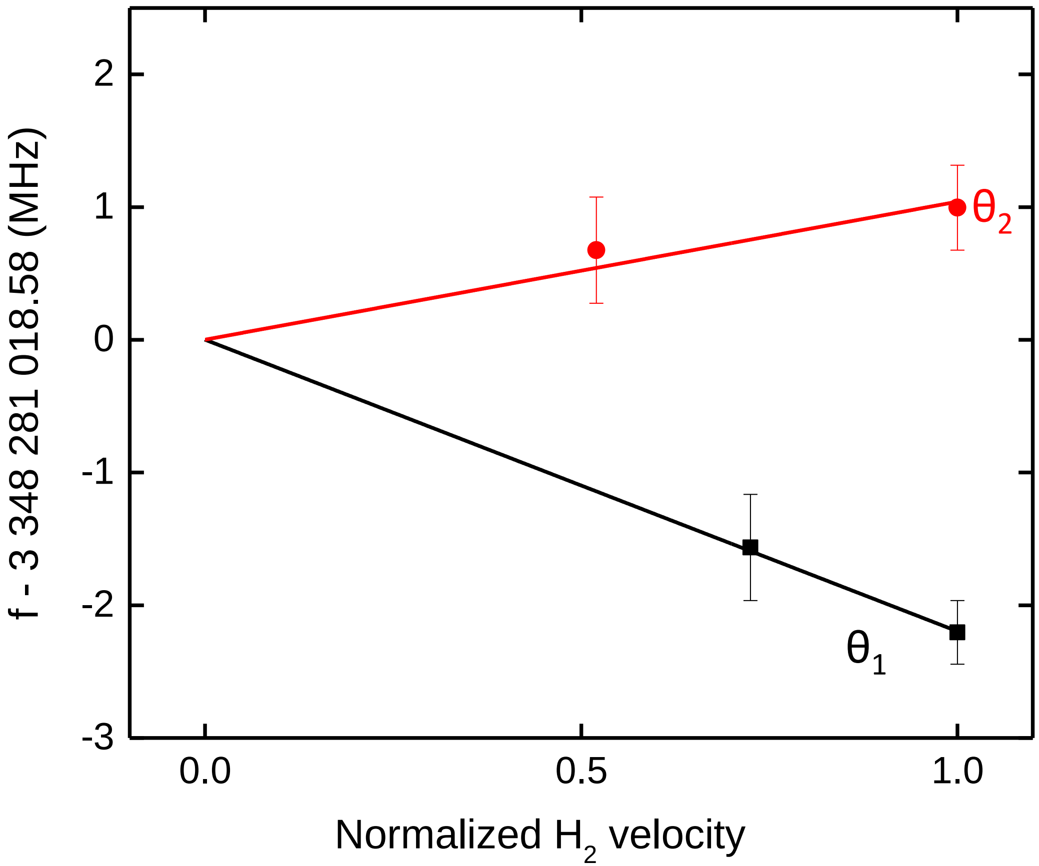
$$v_{norm} = \frac{v_{mix}}{v_{pure}} = \sqrt{\frac{m_{H_2}}{n_{H_2} \cdot m_{H_2} + n_{Ne} \cdot m_{Ne}}}$$



Systematic check: Residual Doppler

$$v_{norm} = \frac{v_{mix}}{v_{pure}} = \sqrt{\frac{m_{H_2}}{n_{H_2} \cdot m_{H_2} + n_{Ne} \cdot m_{Ne}}}$$

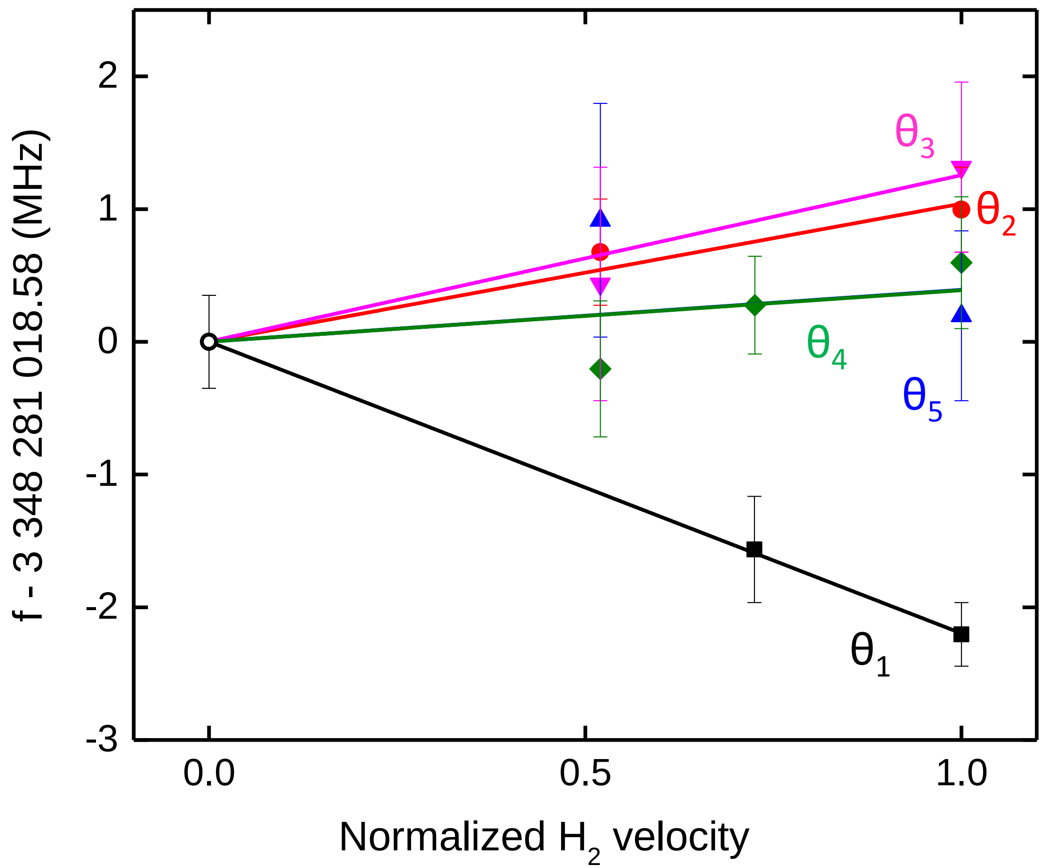
Changing θ



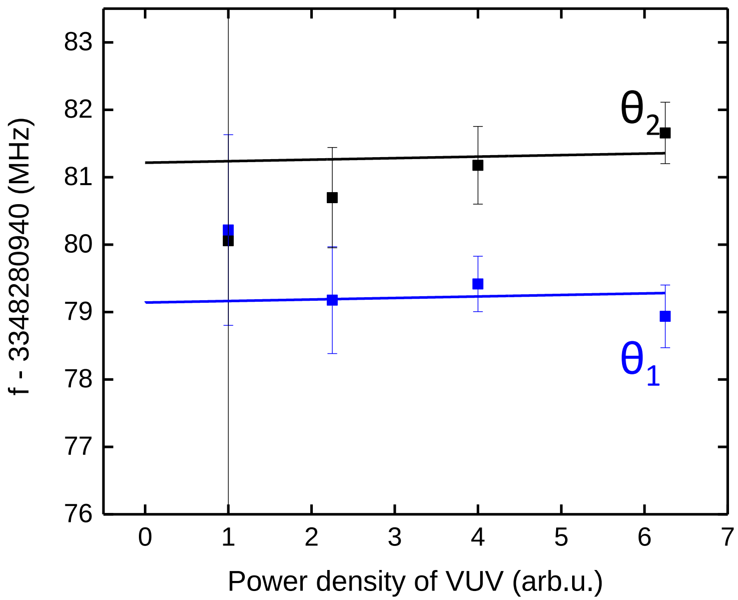
Systematic check: Residual Doppler

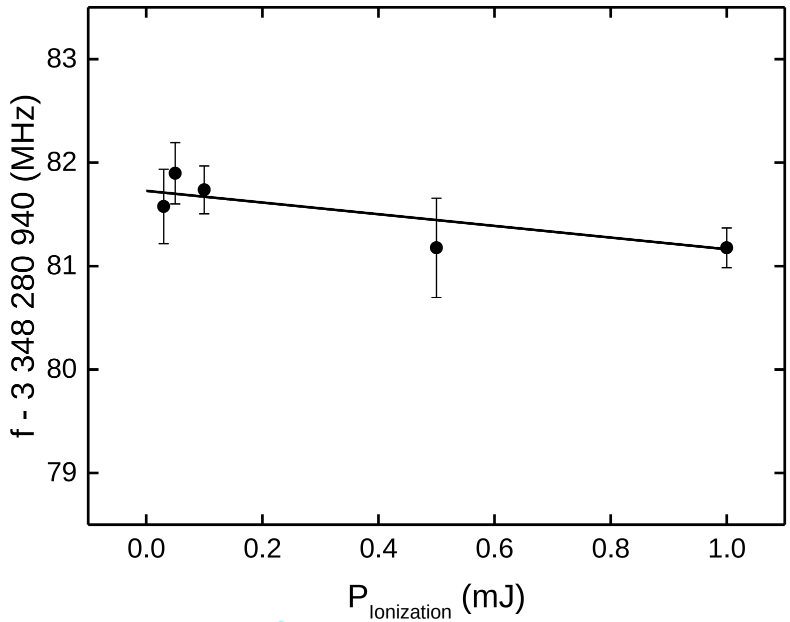
$$v_{norm} = \frac{v_{mix}}{v_{pure}} = \sqrt{\frac{m_{H_2}}{n_{H_2} \cdot m_{H_2} + n_{Ne} \cdot m_{Ne}}}$$

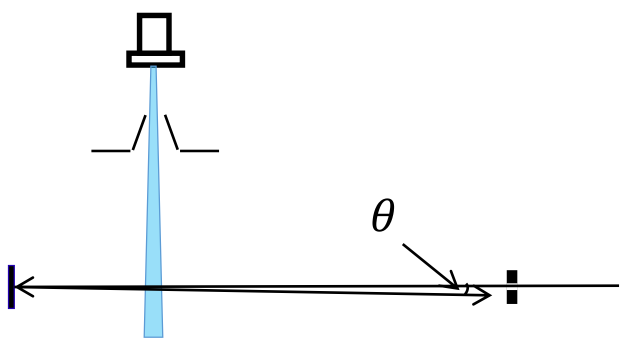
Changing θ

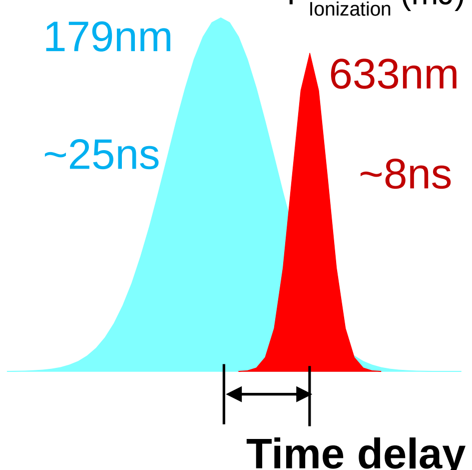


Systematic check: AC Stark

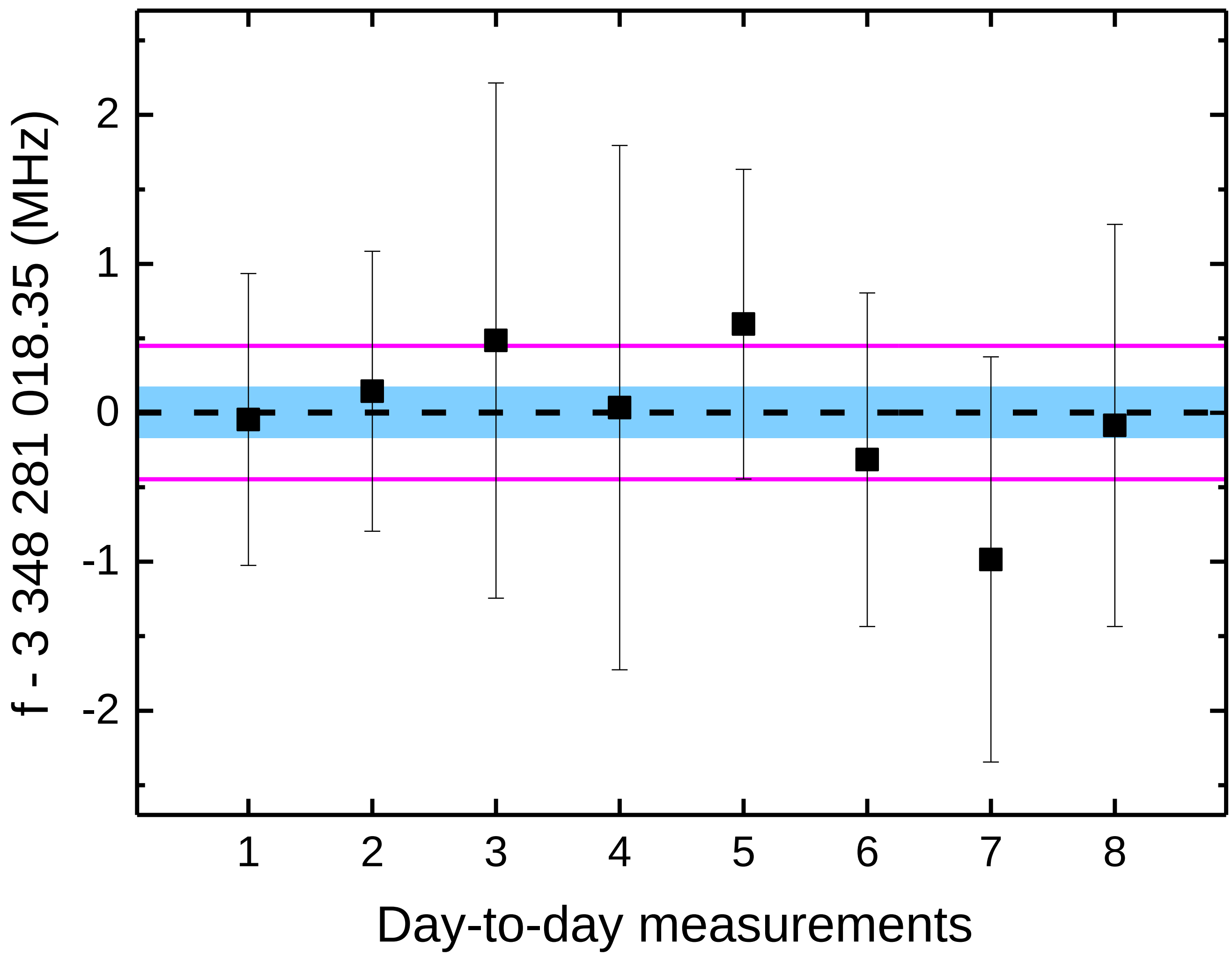








Statistical uncertainty



Error budget ortho-hydrogen

For GK(v=1, N=1) - X(v=0, N=1) (ortho-H_2)

Measured frequency	3348281018.58(49) MHz	
Effect	Correction	Uncertainty
Chirp		$(<490kHz)_{stat}$
Residual 1st order Doppler		350kHz
2nd order Doppler		<30kHz
AC Stark red	-40kHz	90kHz
AC Stark VUV	-190kHz	200kHz
Hyperfine structure		<100kHz
Total systematic uncertainty		426kHz
Final frequency	$3348281018.35(49)_{stat}(43)_{sys}$ MHz	

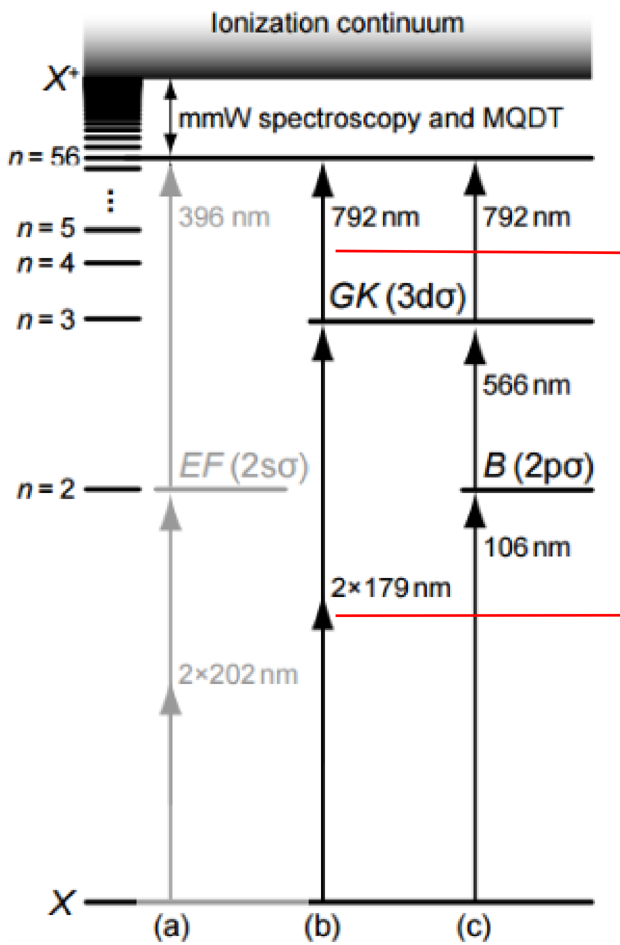
Error budget ortho-hydrogen

For GK(v=1, N=1) - X(v=0, N=1) (ortho-H_2)

Measured frequency	3348281018.58(49) MHz	
Effect	Correction	Uncertainty
Chirp		(<490kHz)
Total systematic uncertainty		426kHz
Final frequency	$3348281018.35(49)_{stat}(43)_{sys}$ MHz	

Total accuracy is 650 kHz: $2\text{x}10^{-10}$ for GK-X

Ionization energy of H_2 at 750 kHz



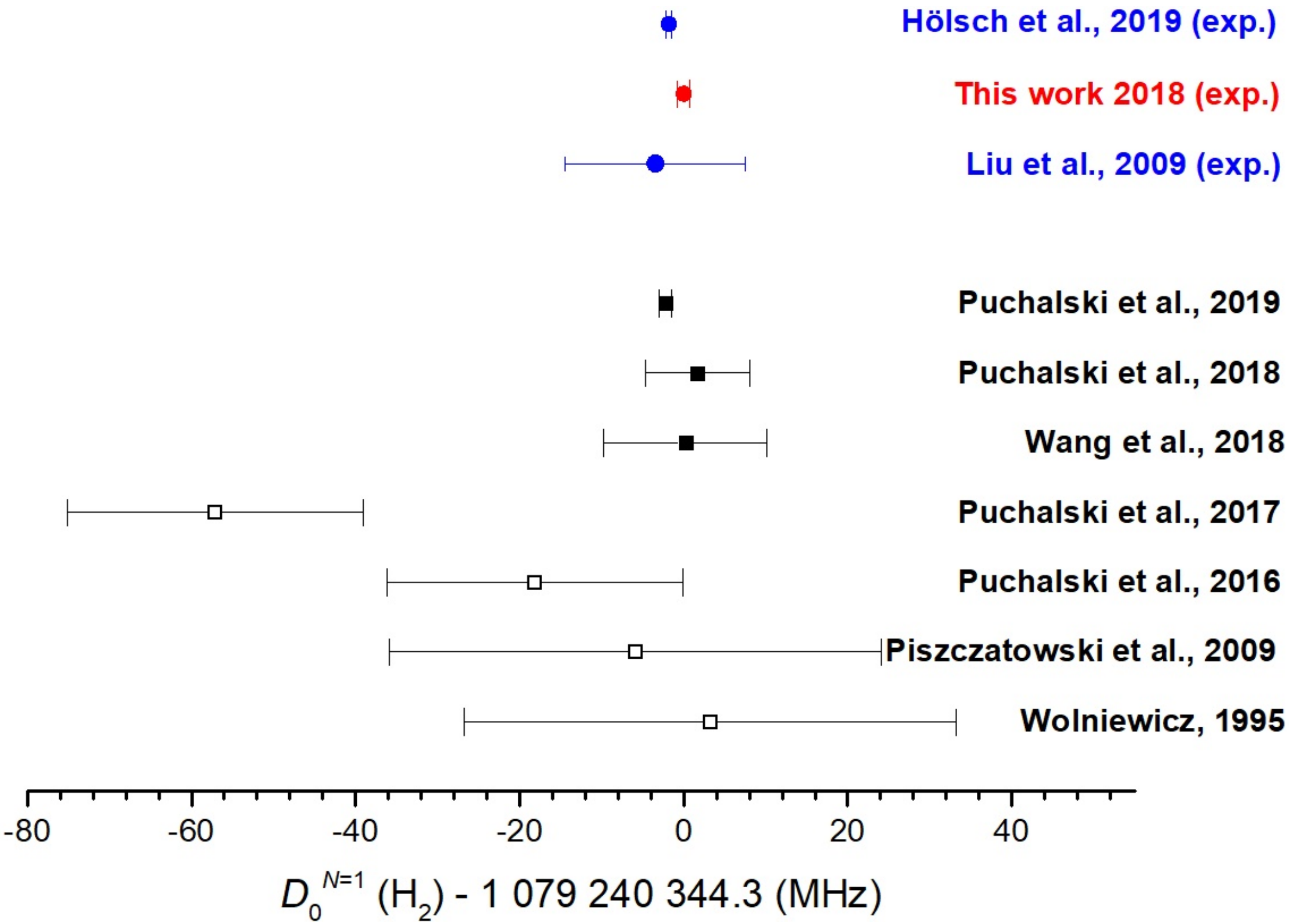
Δf = 100 kHz

Δf = 360kHz

M. Beyer, N. Hölsch, J. A. Agner, F. Merkt, ETH Zürich.

Δf = 650 kHz

Dissociation Energy of ortho-H_2

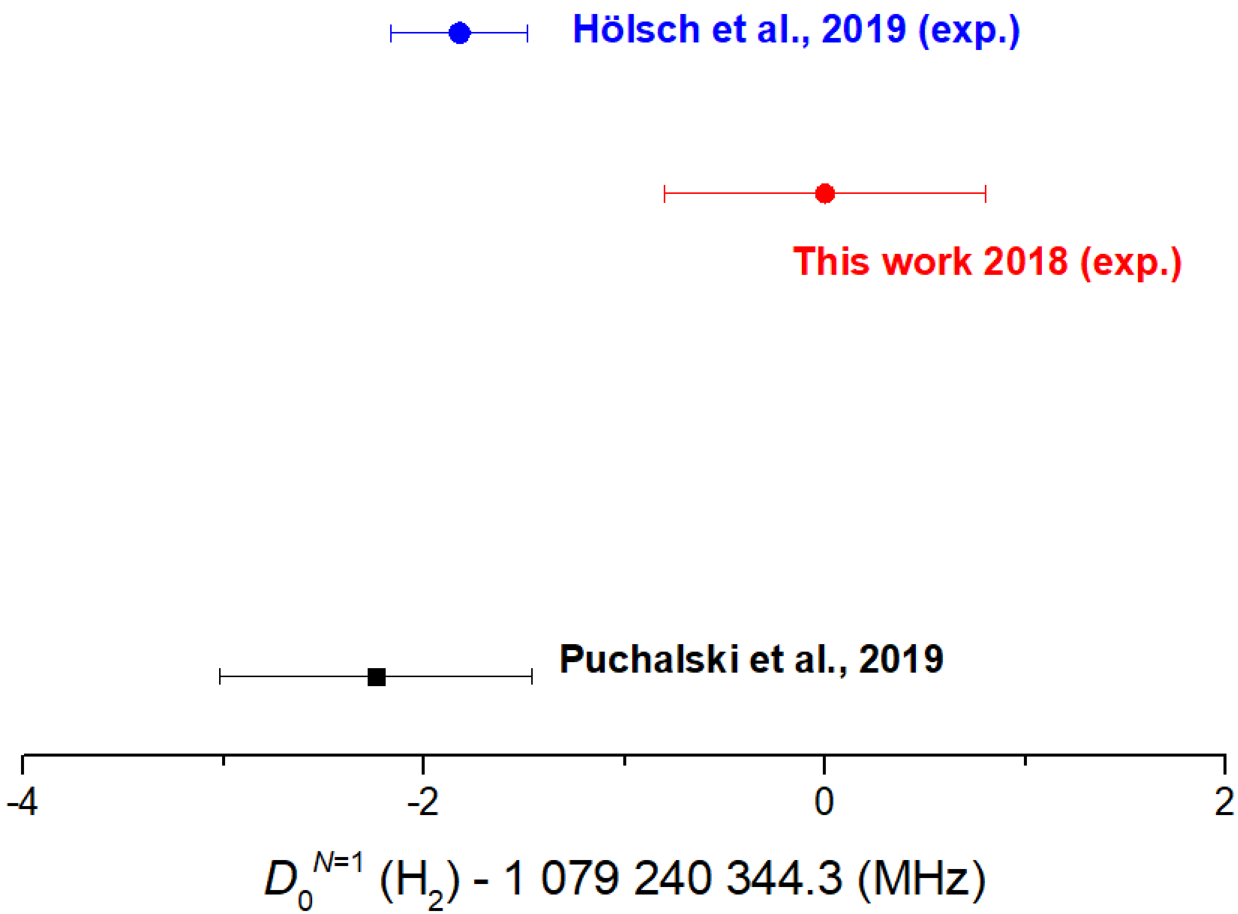


This work:

"Dissociation energy of the hydrogen molecule at 10^{-9} accuracy"

C. Cheng, J. Hussels, et al. *Phys. Rev. Lett.* 121.013001 (2018)

Dissociation Energy of ortho-H_2



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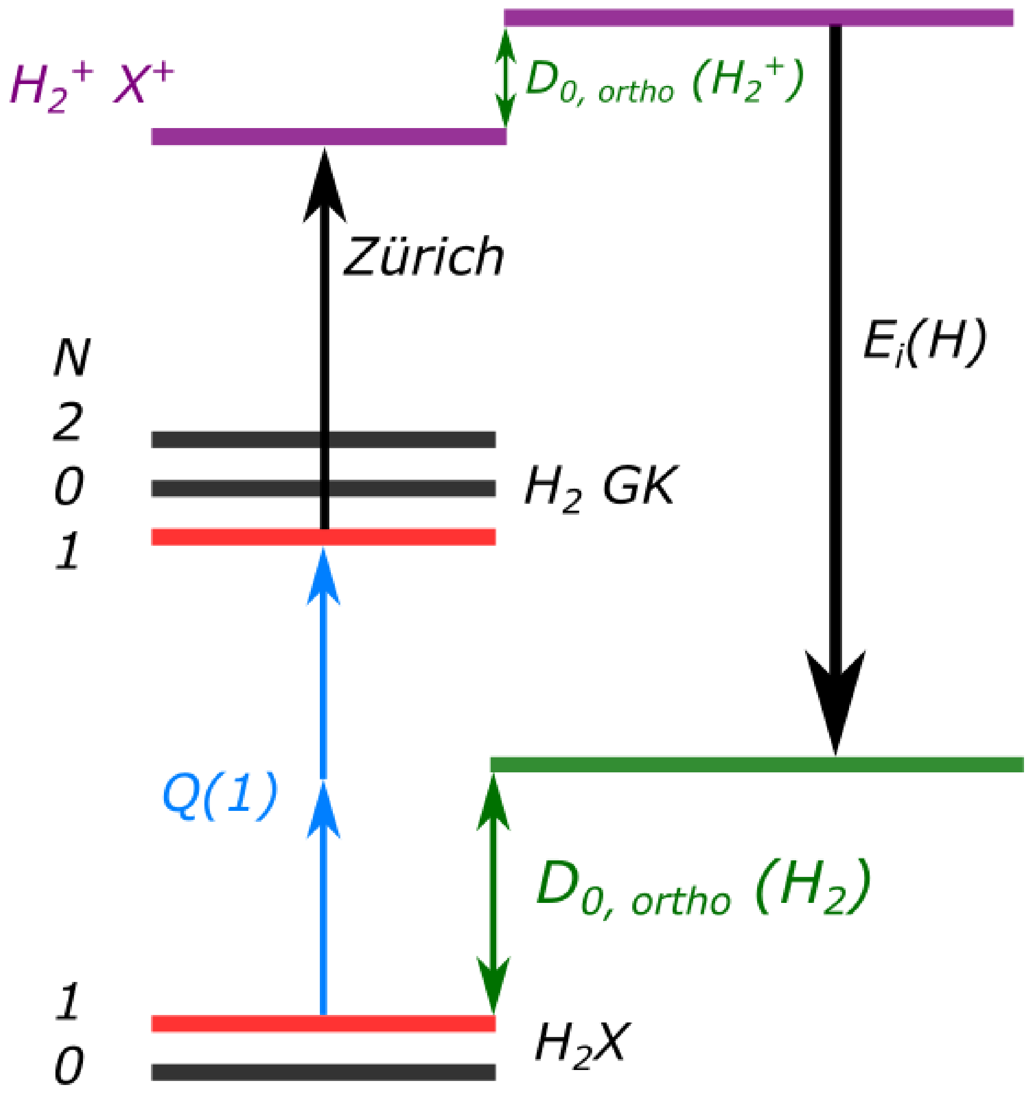
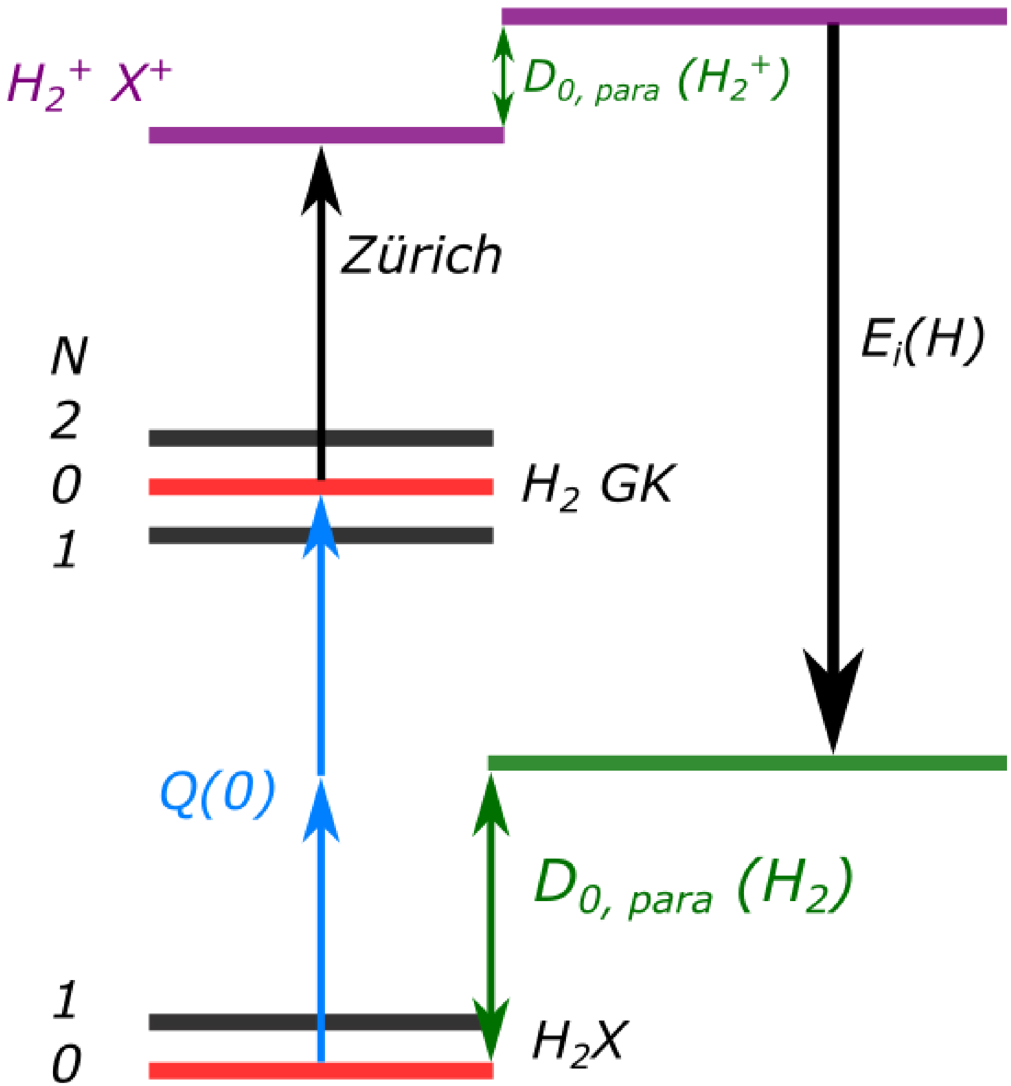
C. Cheng, J. Hussels, et al. *Phys. Rev. Lett.* 121.013001 (2018)

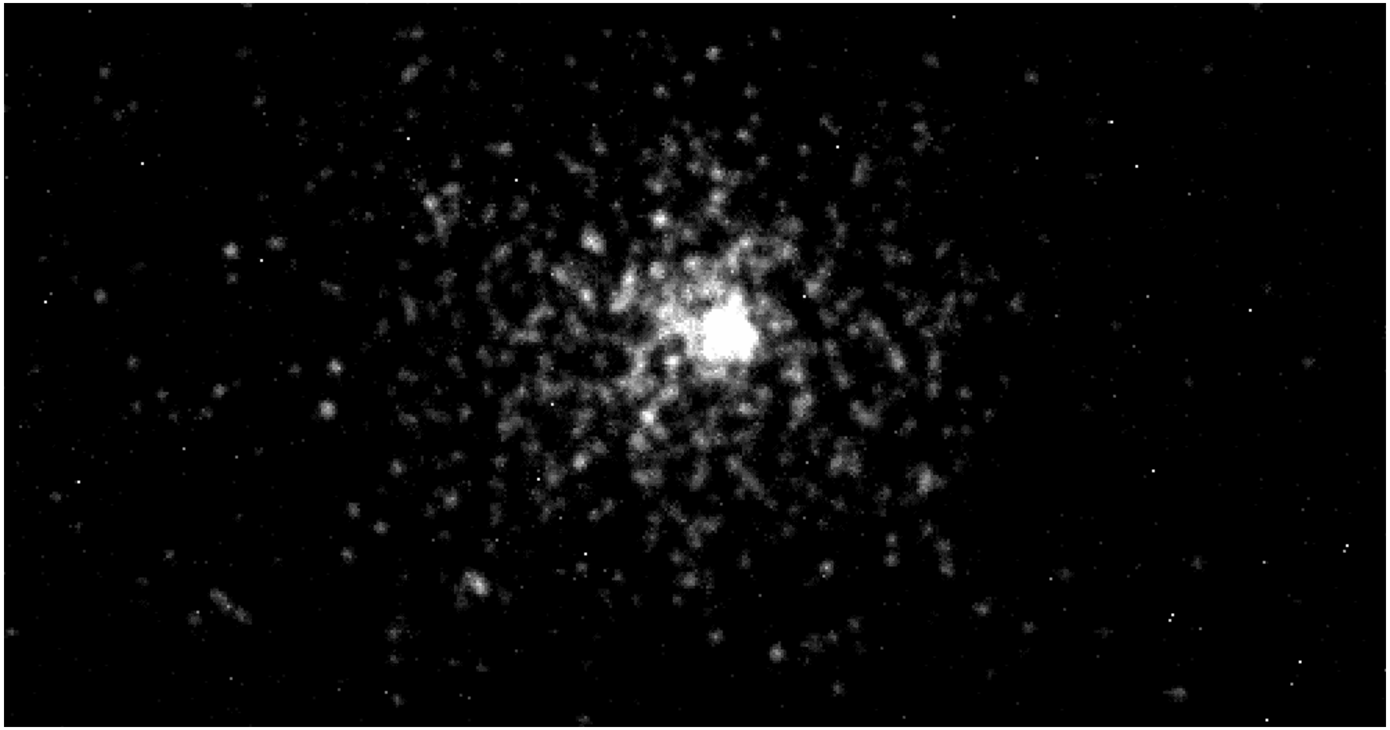
Ortho Hydrogen



Para Hydrogen

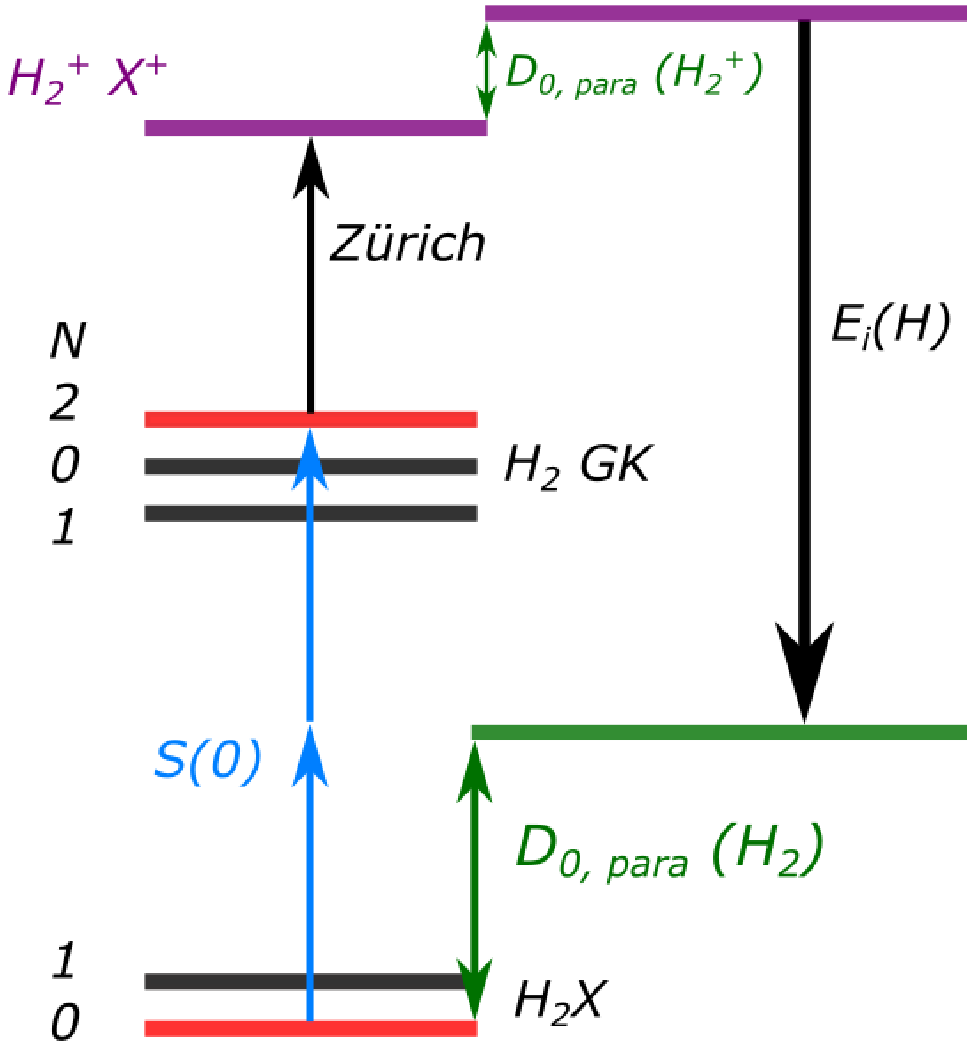


The search for Q(0)....

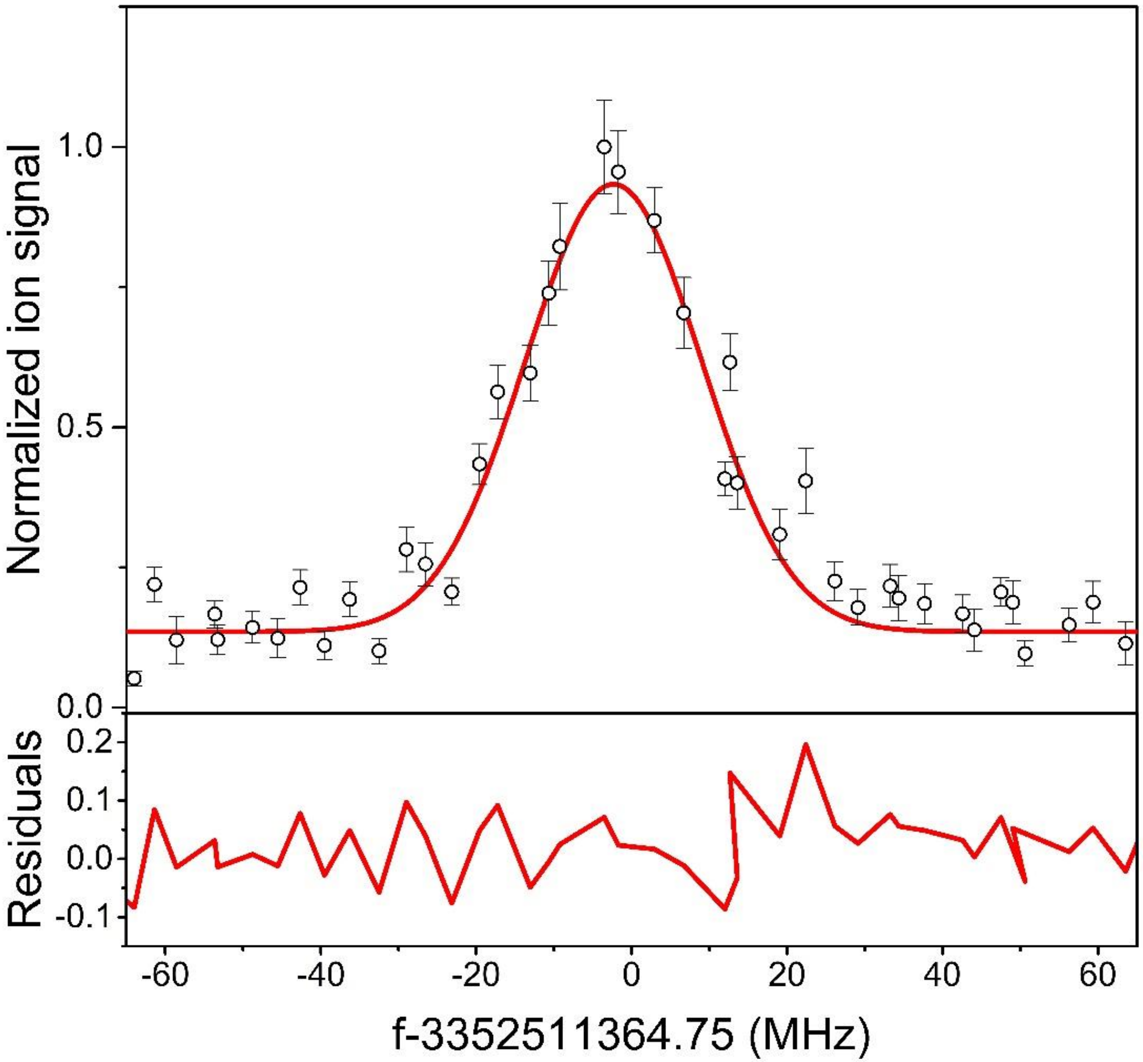


Signal after 60 seconds averaging with VMI
More than 100 times smaller compared to Q(1)?!?

S(0)



S(0)



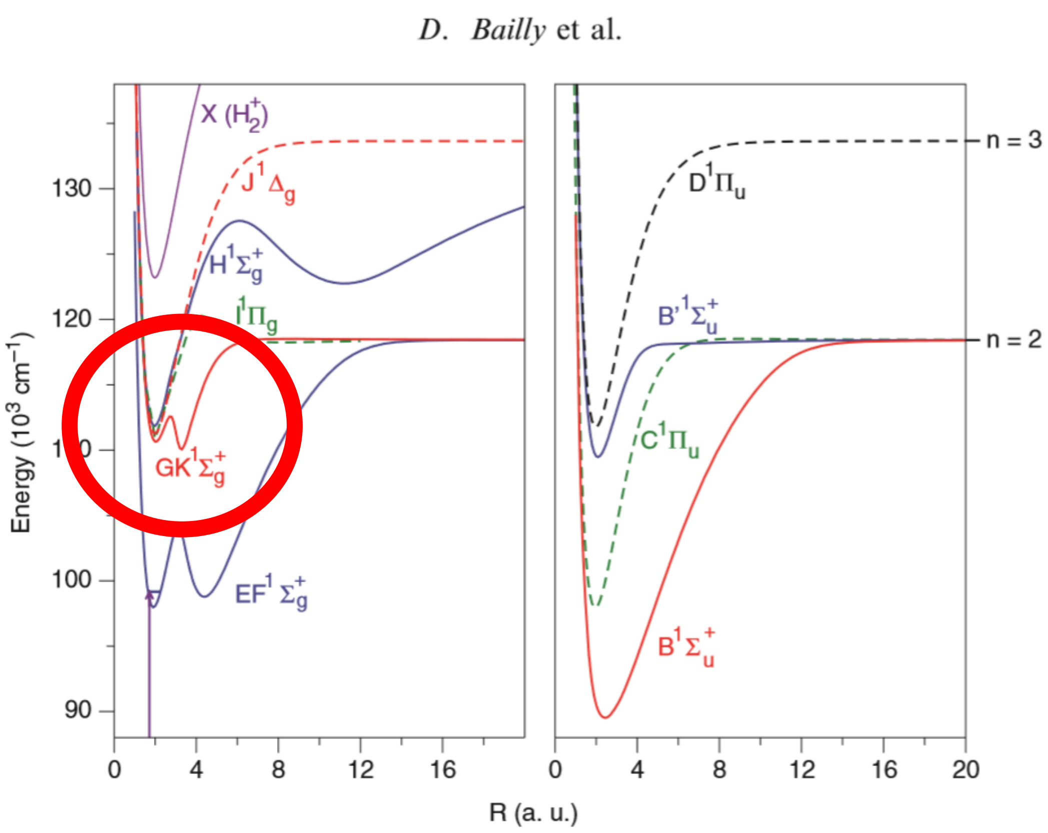
Normalized ion signal
1.0
0.5
0.0
Residuals
0.2
0.1
0.0
-0.1
-60
-40
-20
0
20
40
60
f-3352511364.75 (MHz)

S(0)

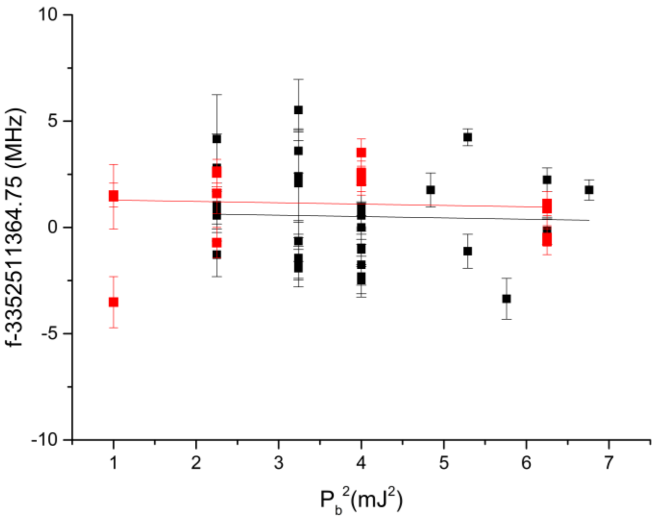
Π-state mixing?

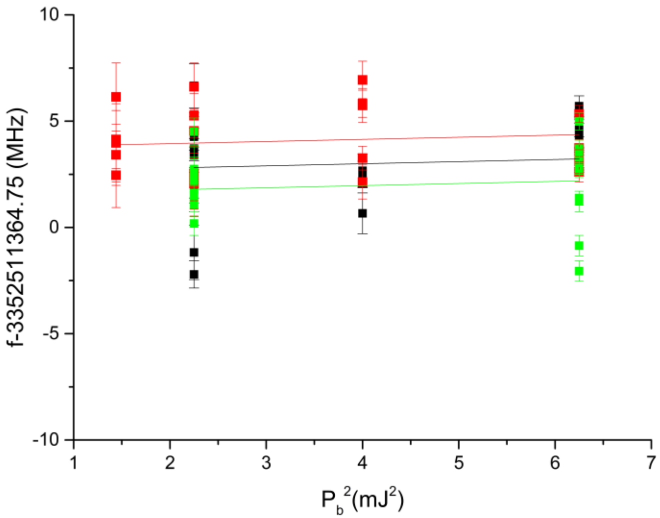
GK(v=1, N)	P(GK)	P(I)
N=0	0.96291	0
N=1	0.78205	0.16964
N=2	0.67133	0.25516

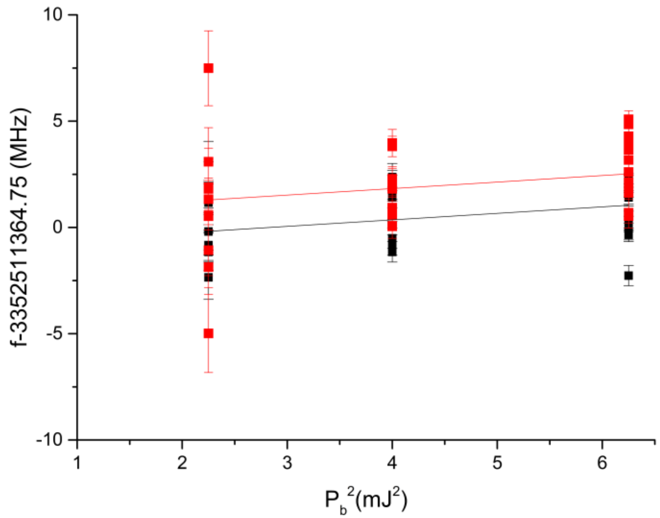
S. Yu and K. Dressler (1994)



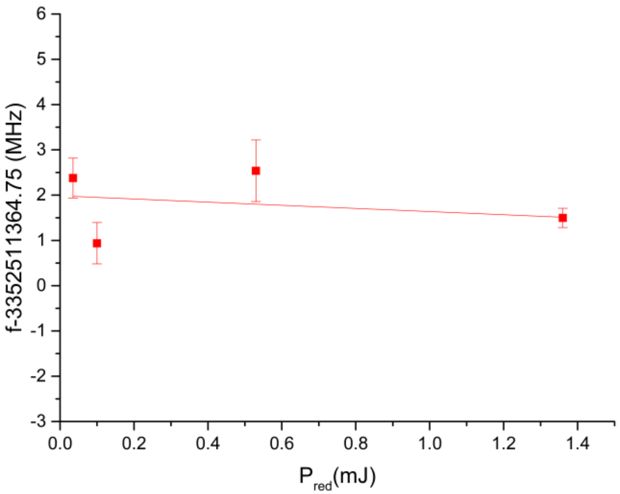
S(0): 3 rounds of Stark VUV

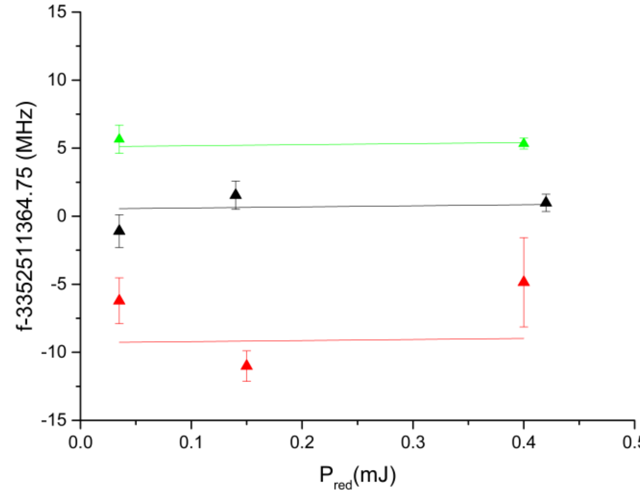


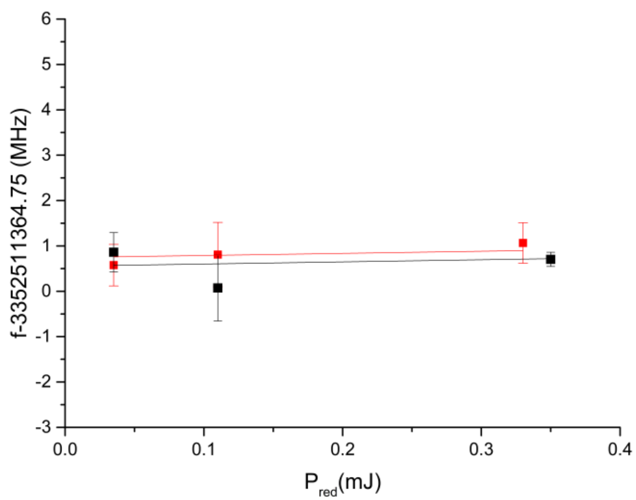




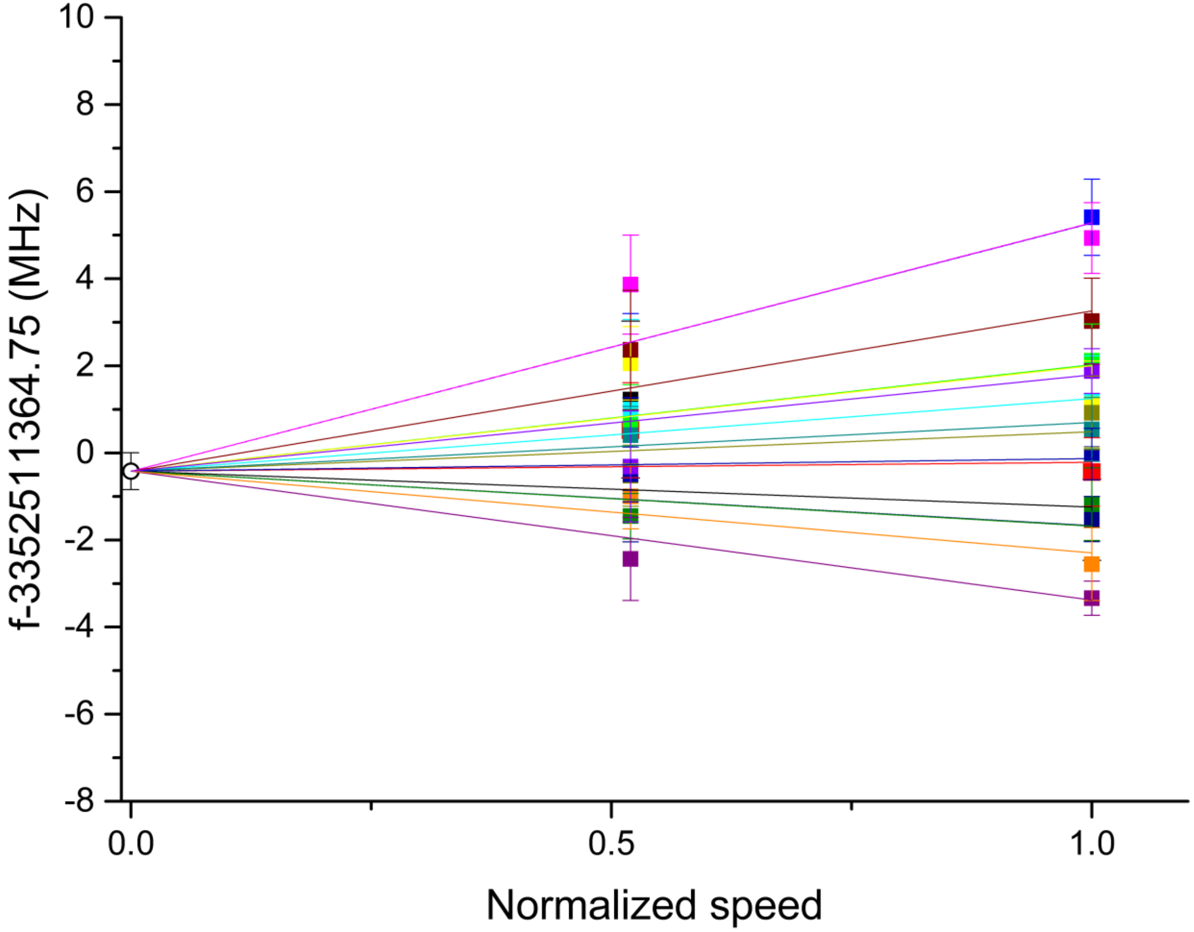
S(0): 3 rounds of Stark ionization



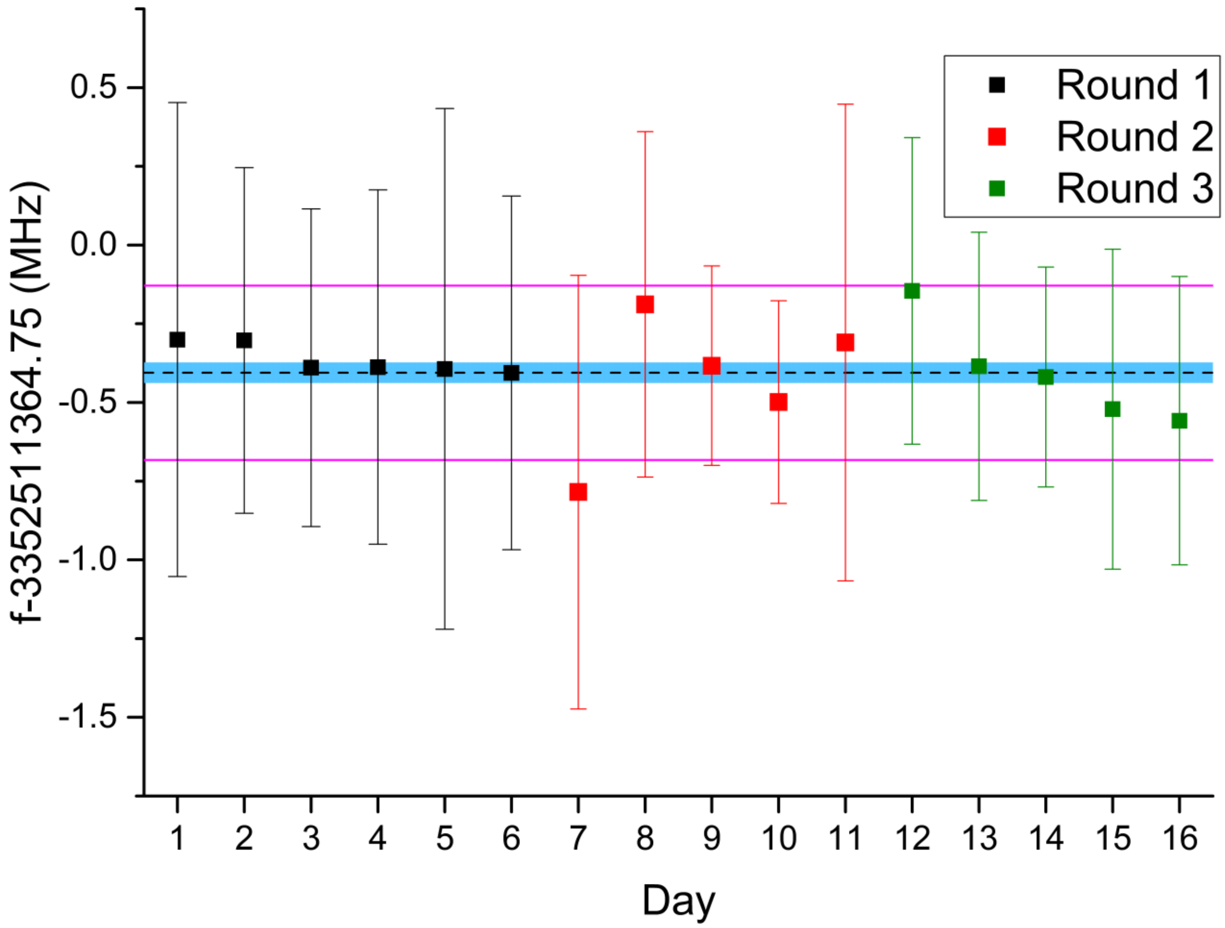




S(0): 3 rounds Doppler analysis



S(0): 3 rounds statisitcal analysis



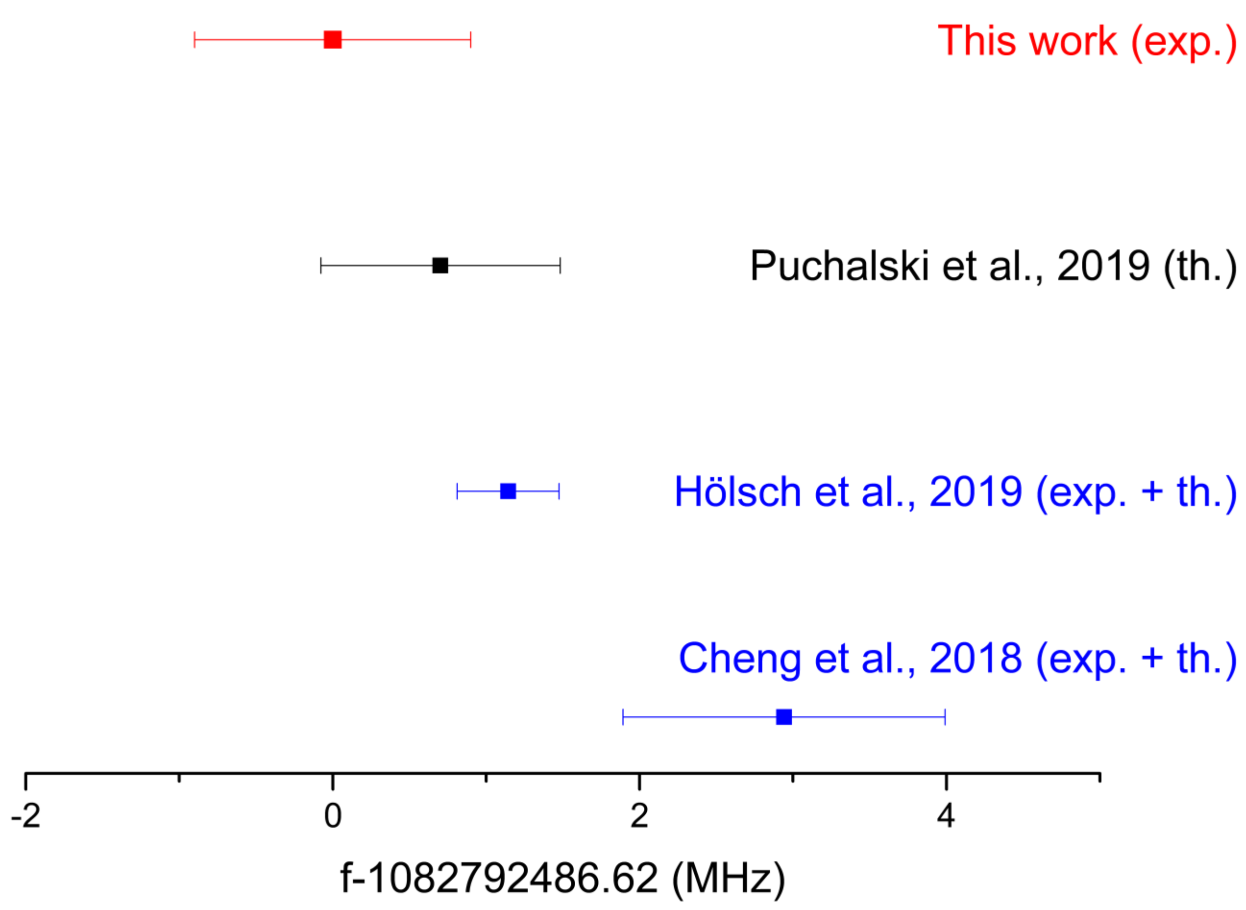
Error budget

For GK(v=1, N=2) - X(v=0, N=0) (para-H_2)

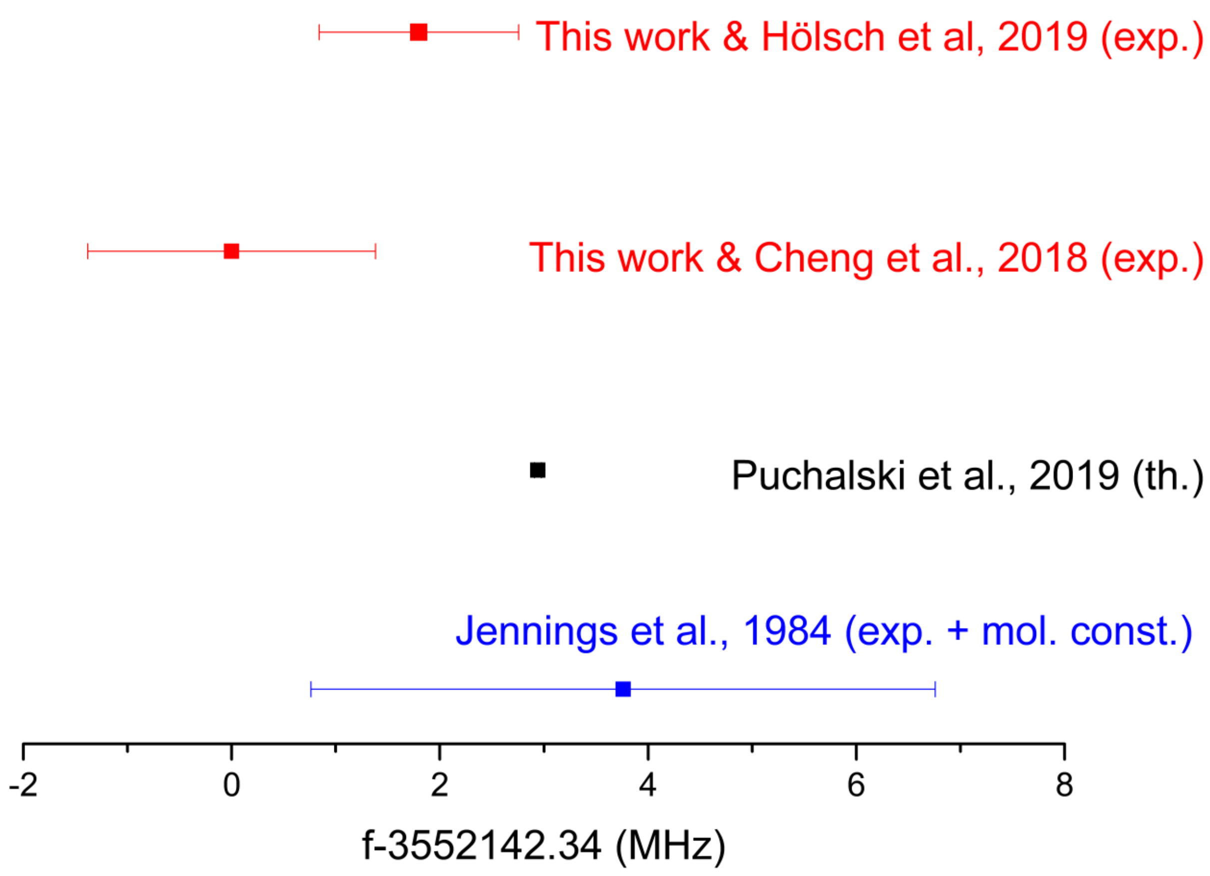
Measured frequency	3 352 511 364.34(3) MHz
Effect	Uncertainty
Chirp	$(<32kHz)_{stat}$
Residual 1^{st} order Doppler	425kHz
2^{nd} order Doppler	<16kHz
AC Stark red	120kHz
AC Stark VUV	452kHz
Hyperfine structure	-
Total systematic uncertainty	632kHz
Final frequency	$3\ 352\ 511\ 364.34(3)_{stat}(63)_{sys}$ MHz

Total accuracy is 640kHz

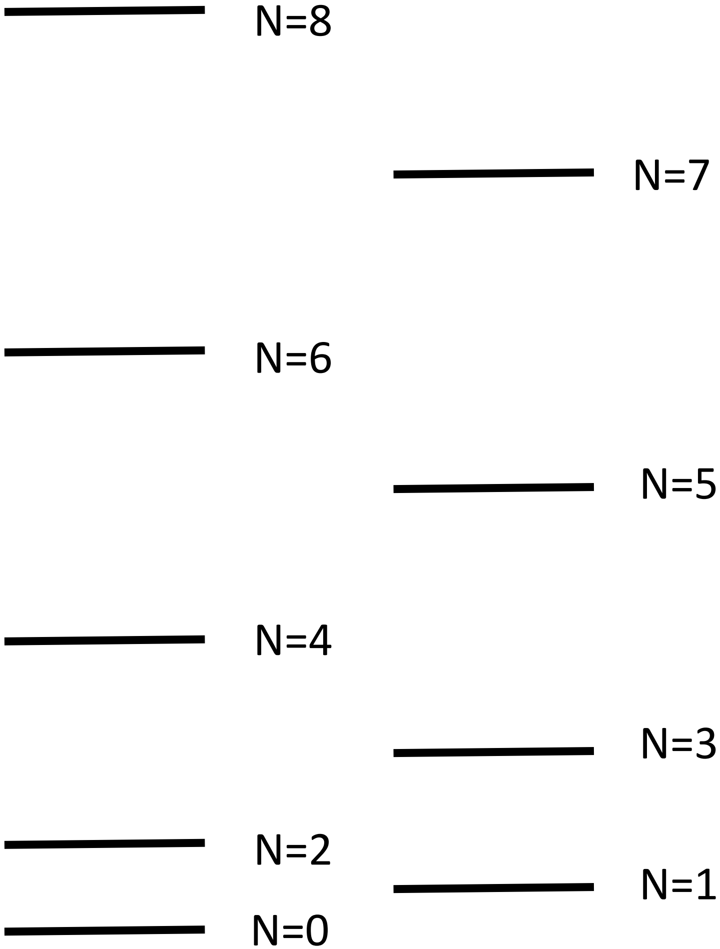
Dissociation Energy of para-H_2



Ortho-para splitting



Ortho-para splitting

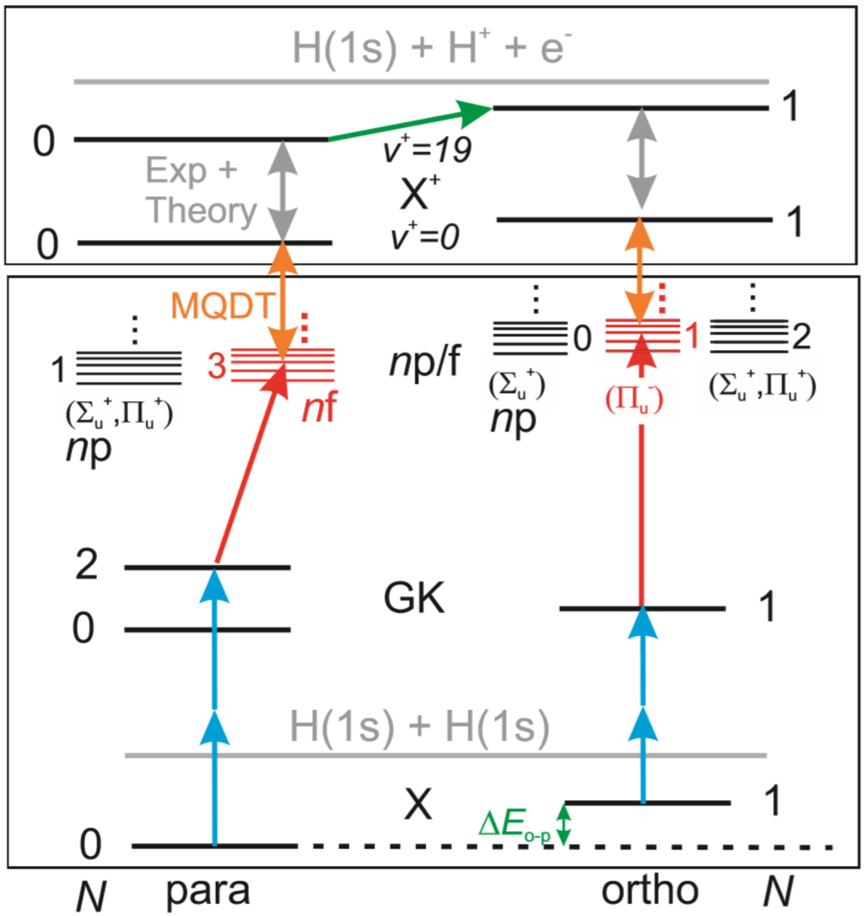


Assuming

$E(N)=B*N(N+1)-D*N^2(N+1)^2+...$

(Jennings et al., 1984)

Ortho-para splitting



First ortho-para interaction in H_2^+:
Critchley et al., PRL 86, 1725 (2001)

Now possible to connect to H_2

Conclusion & Outlook

- GK (v=1, N=1) – X(v=0, N=1) and GK (v=1, N=2) – X(v=0, N=2) have been measured directly for the first time. An accuracy of 0.65 MHz and 0.64 MHz was achieved.
- D_0(ortho-H_2) determination has been improved by an order of magnitude to 0.75 MHz.
- D_0(para-H_2) determination has been improved to 0.78 MHz.

Conclusion & Outlook

- GK (v=1, N=1) – X(v=0, N=1) and GK (v=1, N=2) – X(v=0, N=2) have been measured directly for the first time. An accuracy of 0.65 MHz and 0.64 MHz was achieved.
- D_0(ortho-H_2) determination has been improved by an order of magnitude to 0.75 MHz.
- D_0(para-H_2) determination has been improved to 0.78 MHz.
- The splitting between ortho- and para-H_2 could be derived with an accuracy of 0.99 MHz.
- Ortho- and para levels in H_2 can be linked for the first time

- Future: Similar measurements for HD and D_2

Thanks to:

LaserLaB, VU Amsterdam:

Dr. Cunfeng Cheng
Dr. Ming Li Niu
Dr. Edcel Salumbides
Dr. Hendrick Bethlem
Prof. dr. Kjeld Eikema
Prof. dr. Wim Ubachs

Rob Kortekaas (Technician)

ETH, Zürich:

Maximilian Beyer
Nicolas Hölsch
Josef Agner
Prof. dr. Frédéric Merkt

CNRS, Orsay:

Prof. dr. Christian Jungen

USTC, Hefei:

Lei-Gang Tao
Prof. dr. Shui-Ming Hu

European Research Council

LaserLaB Amsterdam

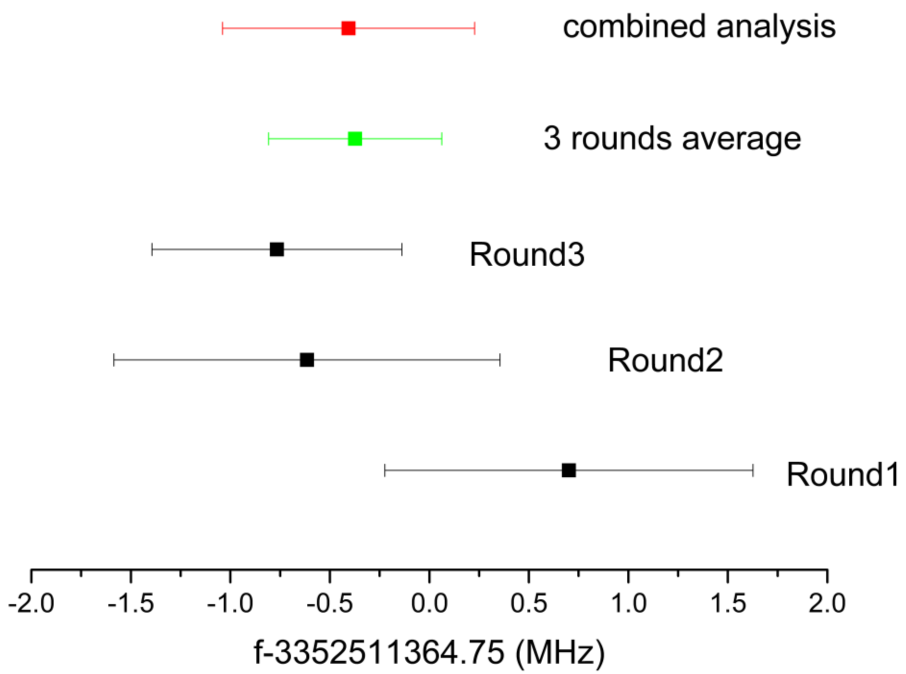
VU Vrije Universiteit Amsterdam

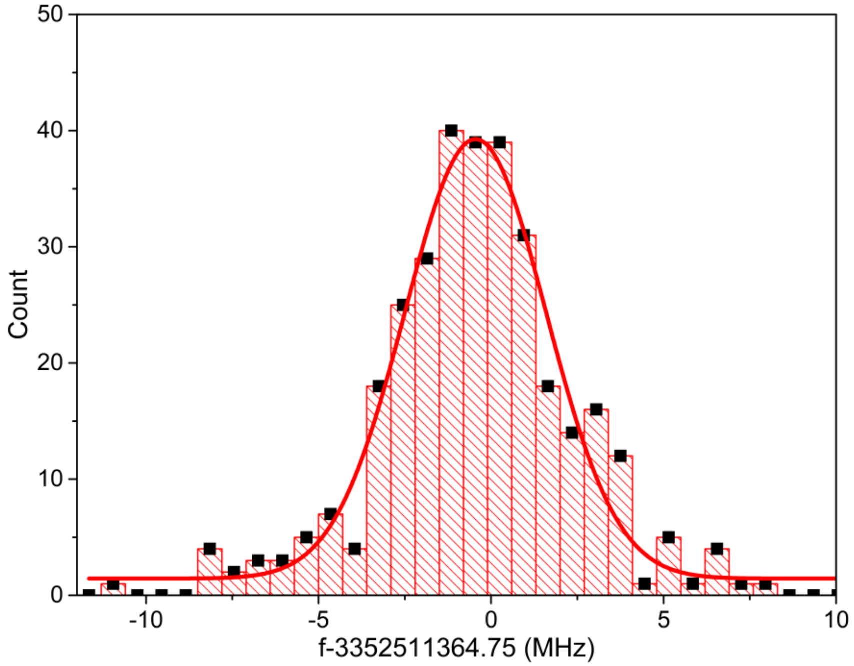
NWO

ETH zürich

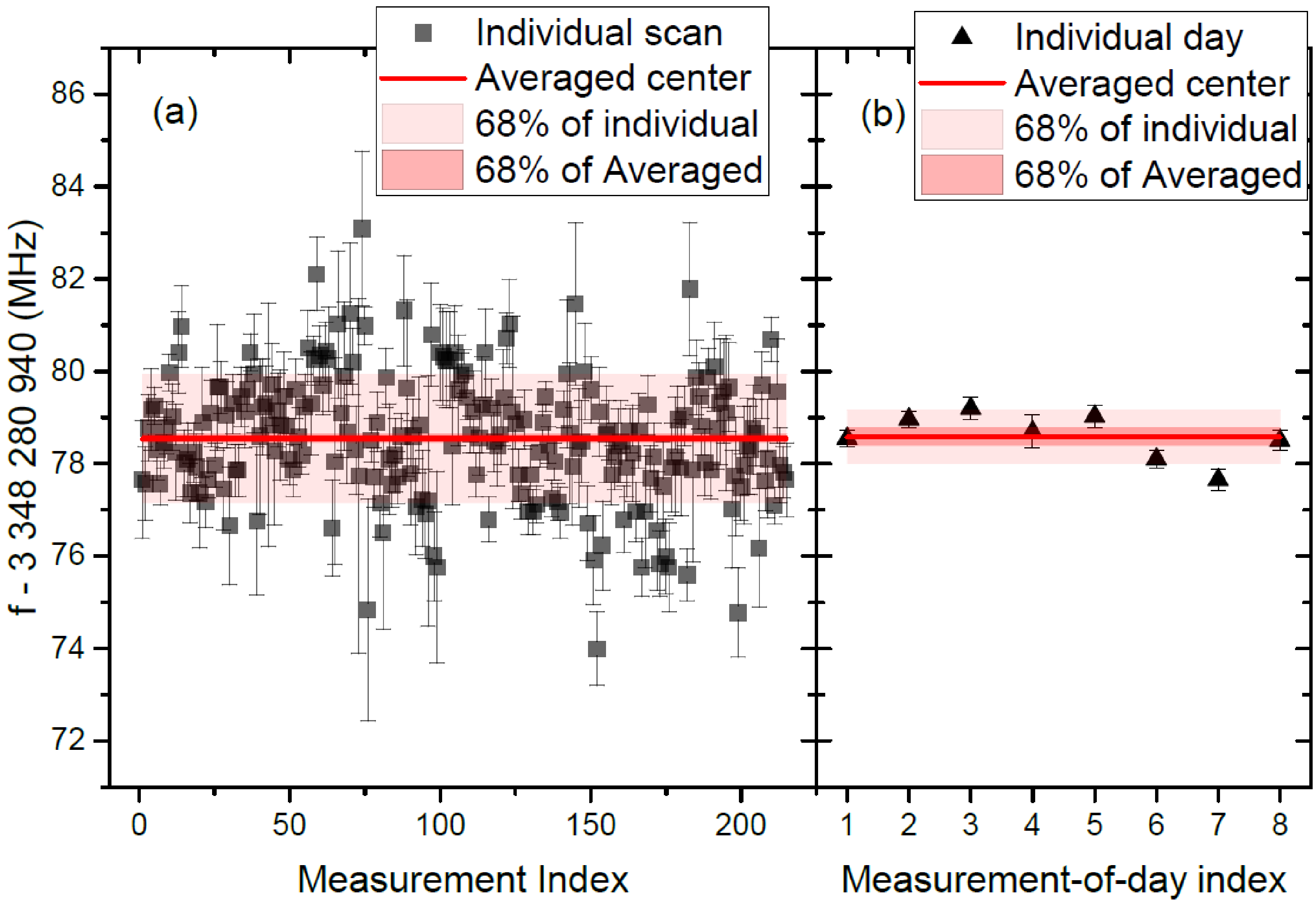
中國科学院 CHINESE ACADEMY OF SCIENCES

S(0): 3 rounds statisitcal analysis

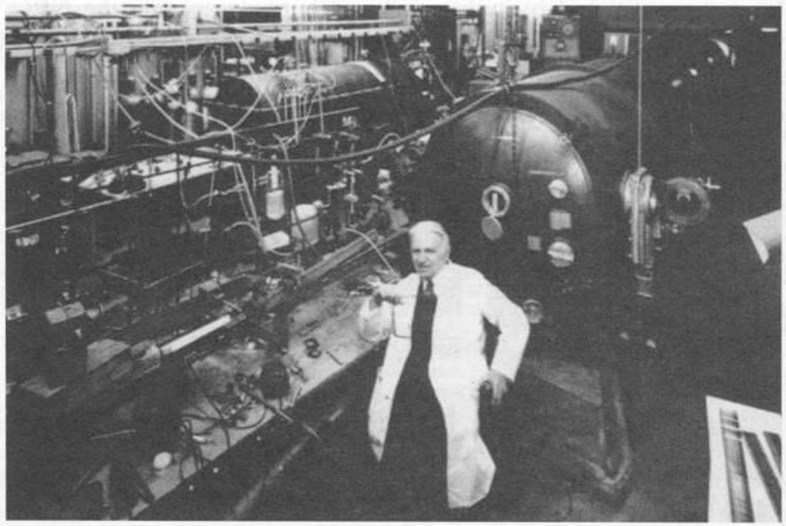




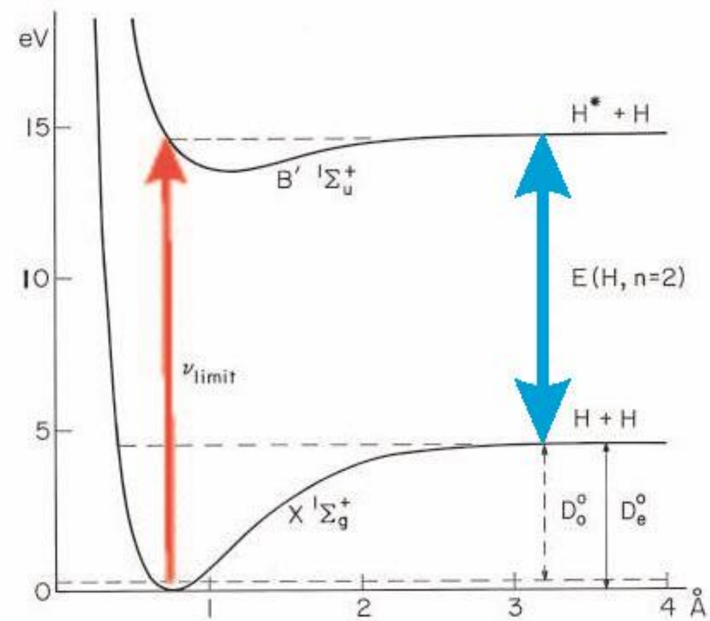
Residual systematical and statistical Q(1)

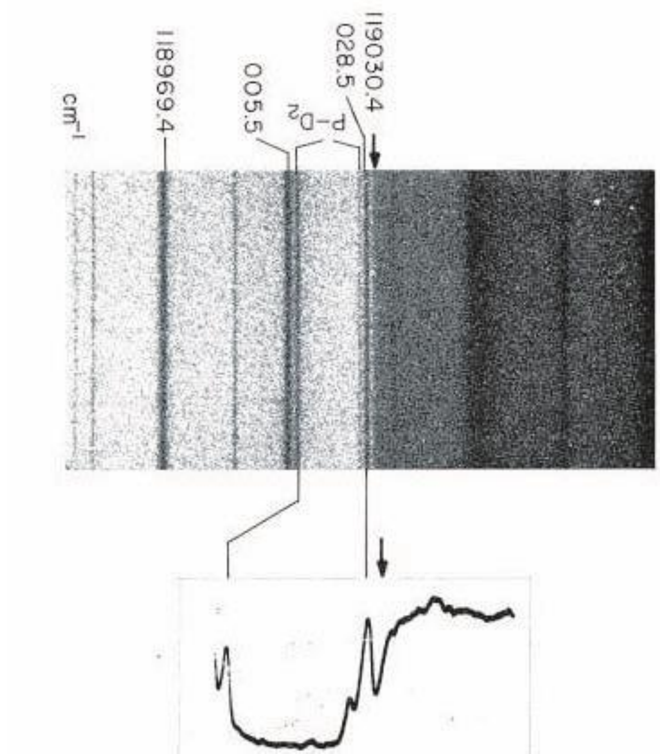


H_2 Dissociation energy; benchmark

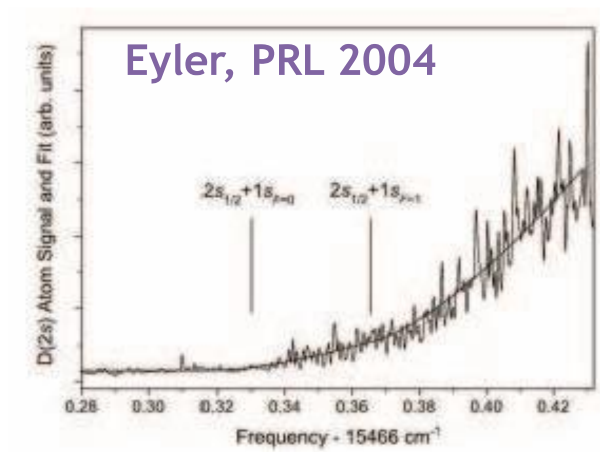


Herzberg in his laboratory.



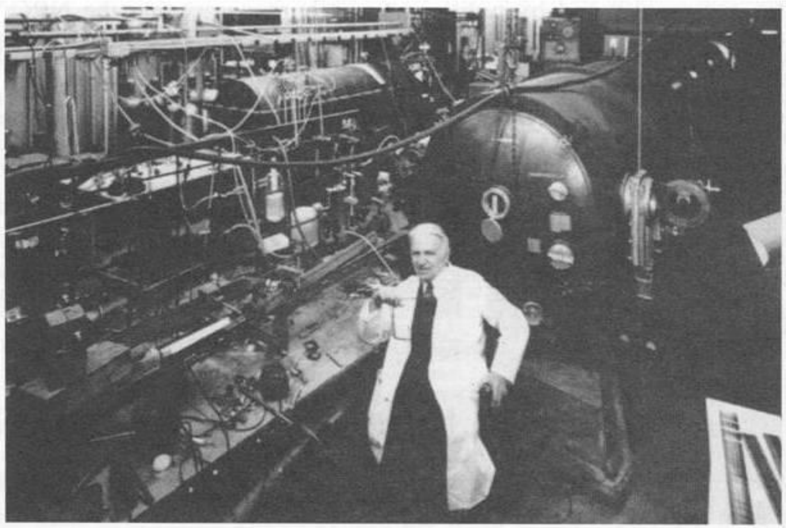


Herzberg Nobel Lecture

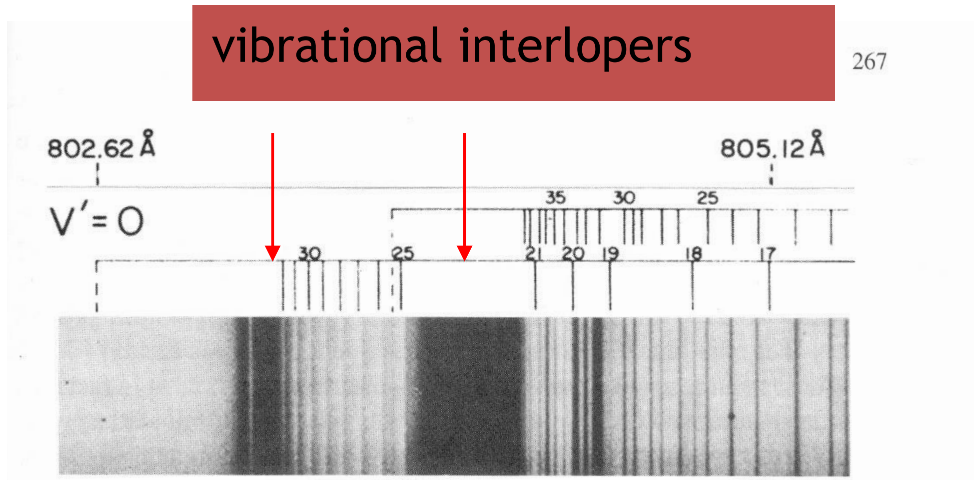


Eyler, PRL 2004

H_2 Dissociation energy; measurement of IP

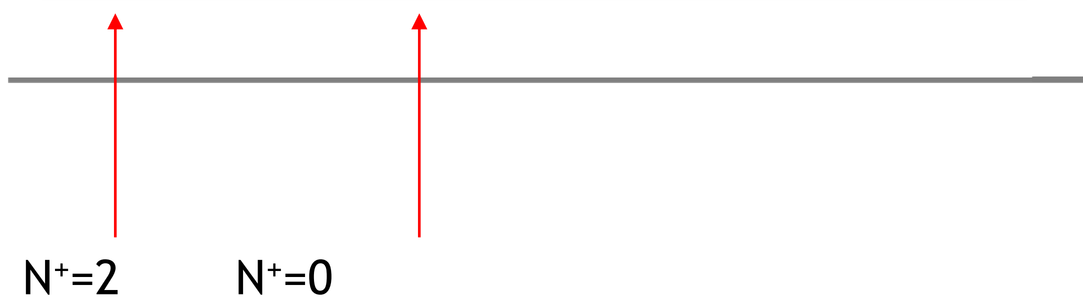


Herzberg in his laboratory.



Absorption spectrum of para-H_2 showing two Rydberg series, going to two different limits, after Herzberg and Jungen, 1972.

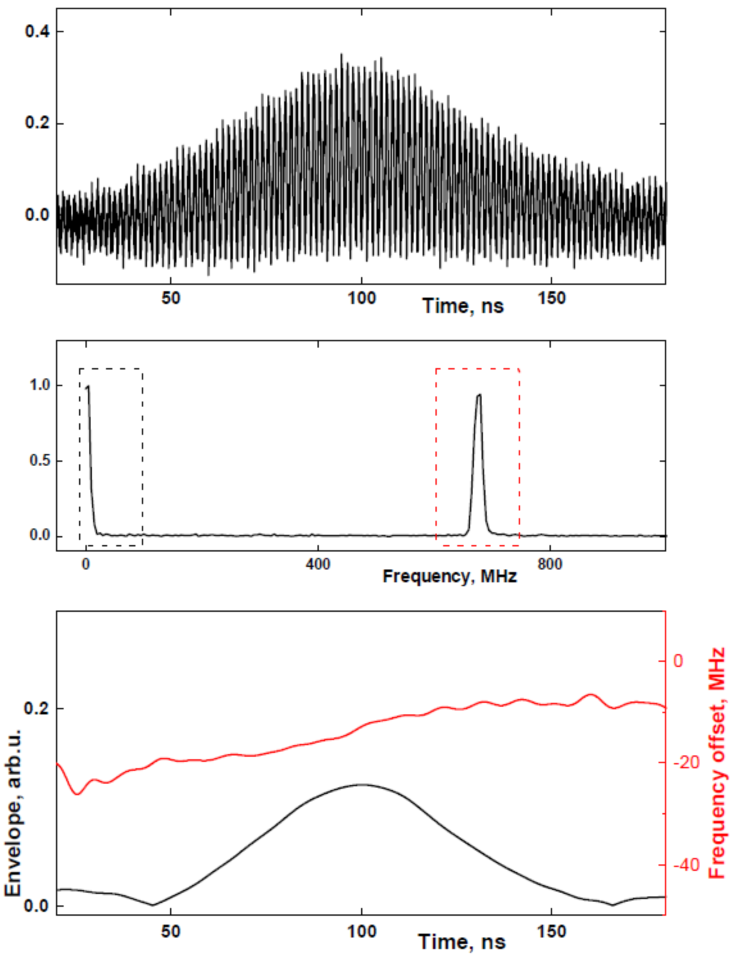
Christian Jungen



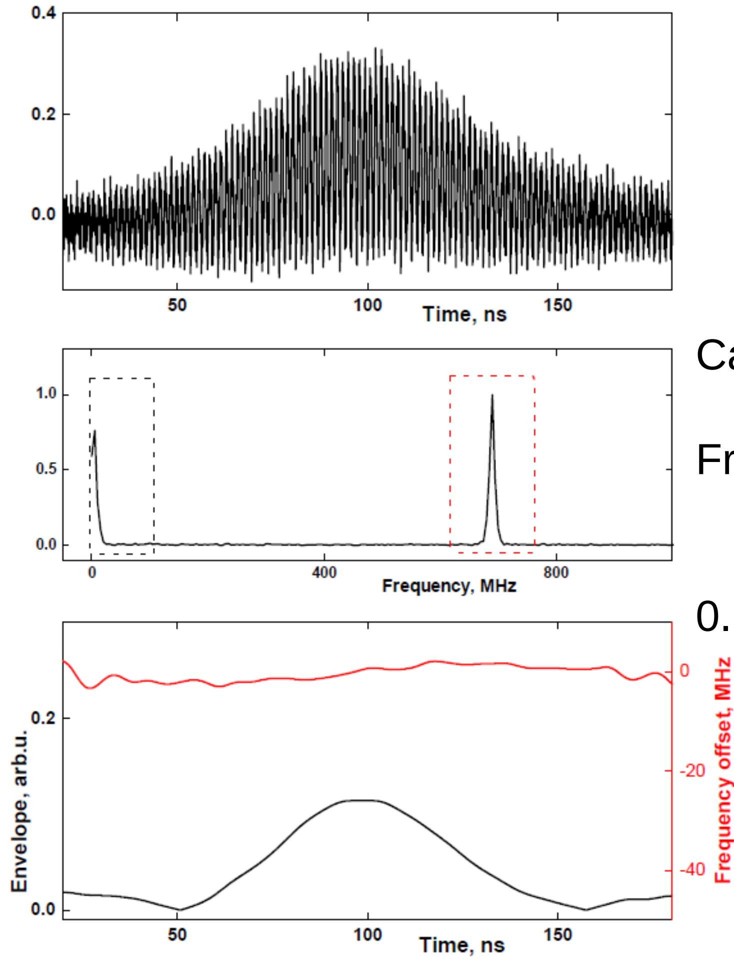
Herzberg and Jungen 1972
MQDT of molecules

Chirp measurement

w/o anti-chirp



with anti-chirp



Cavity pulling:

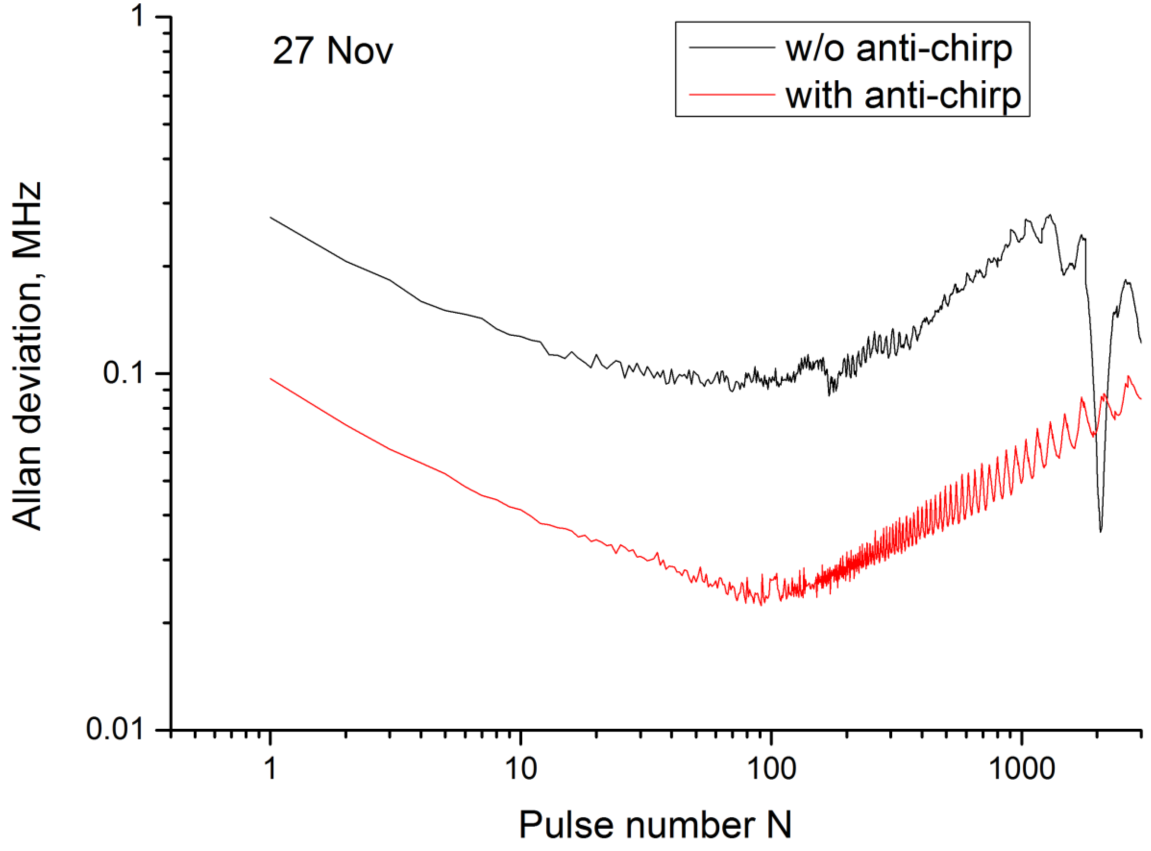
~ 0 MHz

Freq chirp:

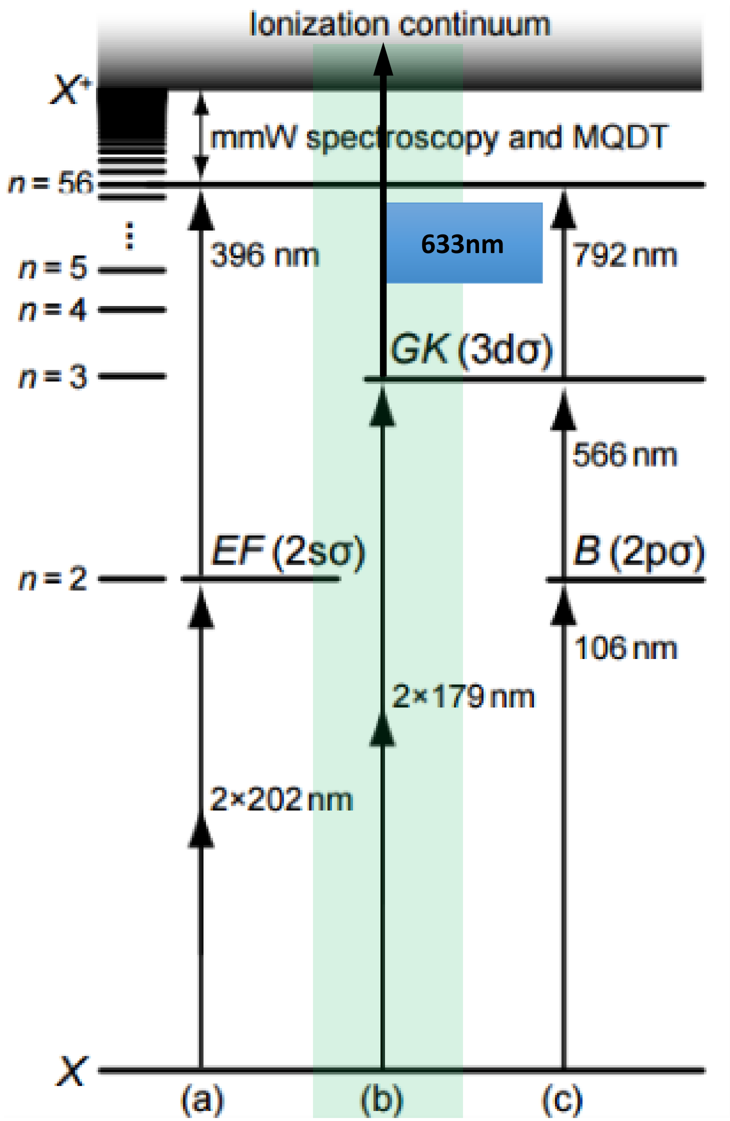
< 1.5 MHz/50 ns

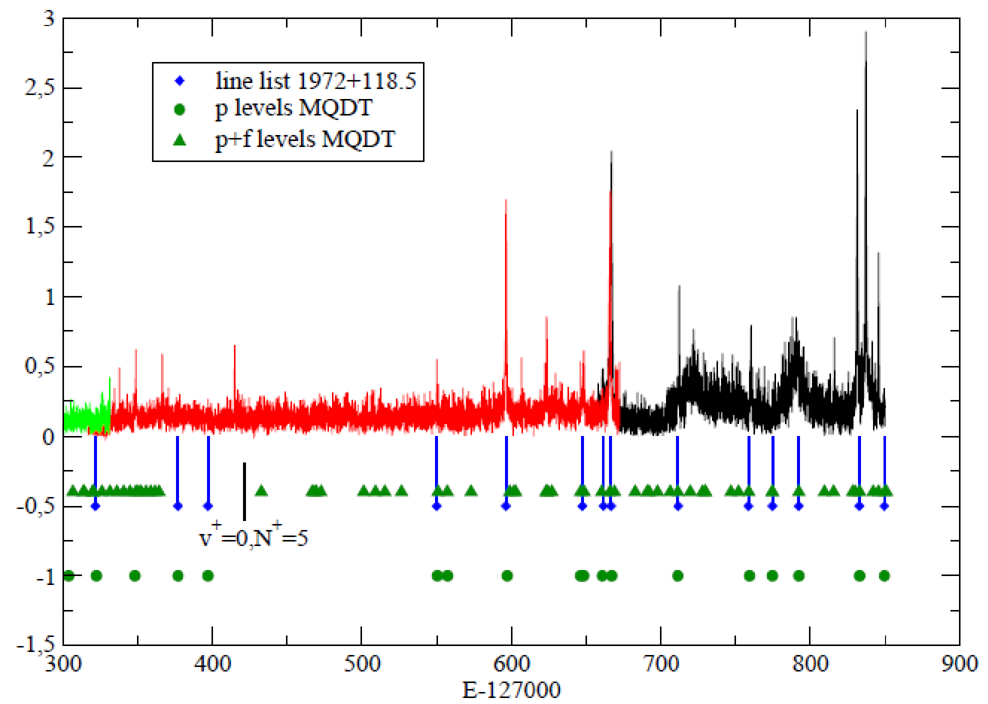
0.1 MHz uncertainty

Development of anti-chirp

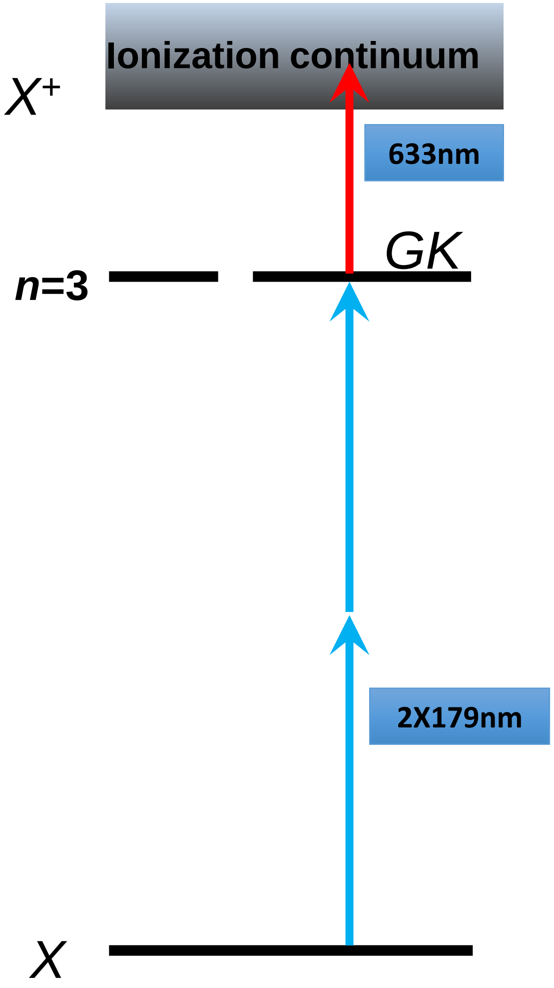


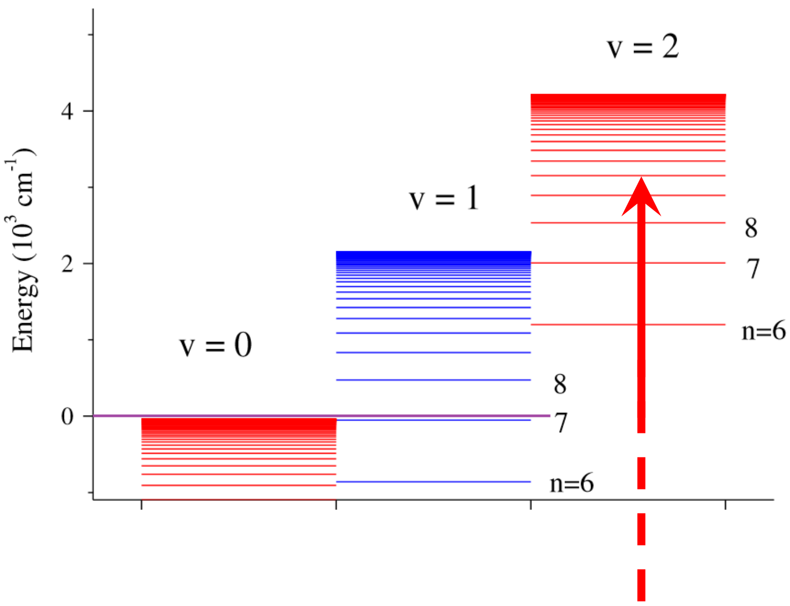
Auto-ionization



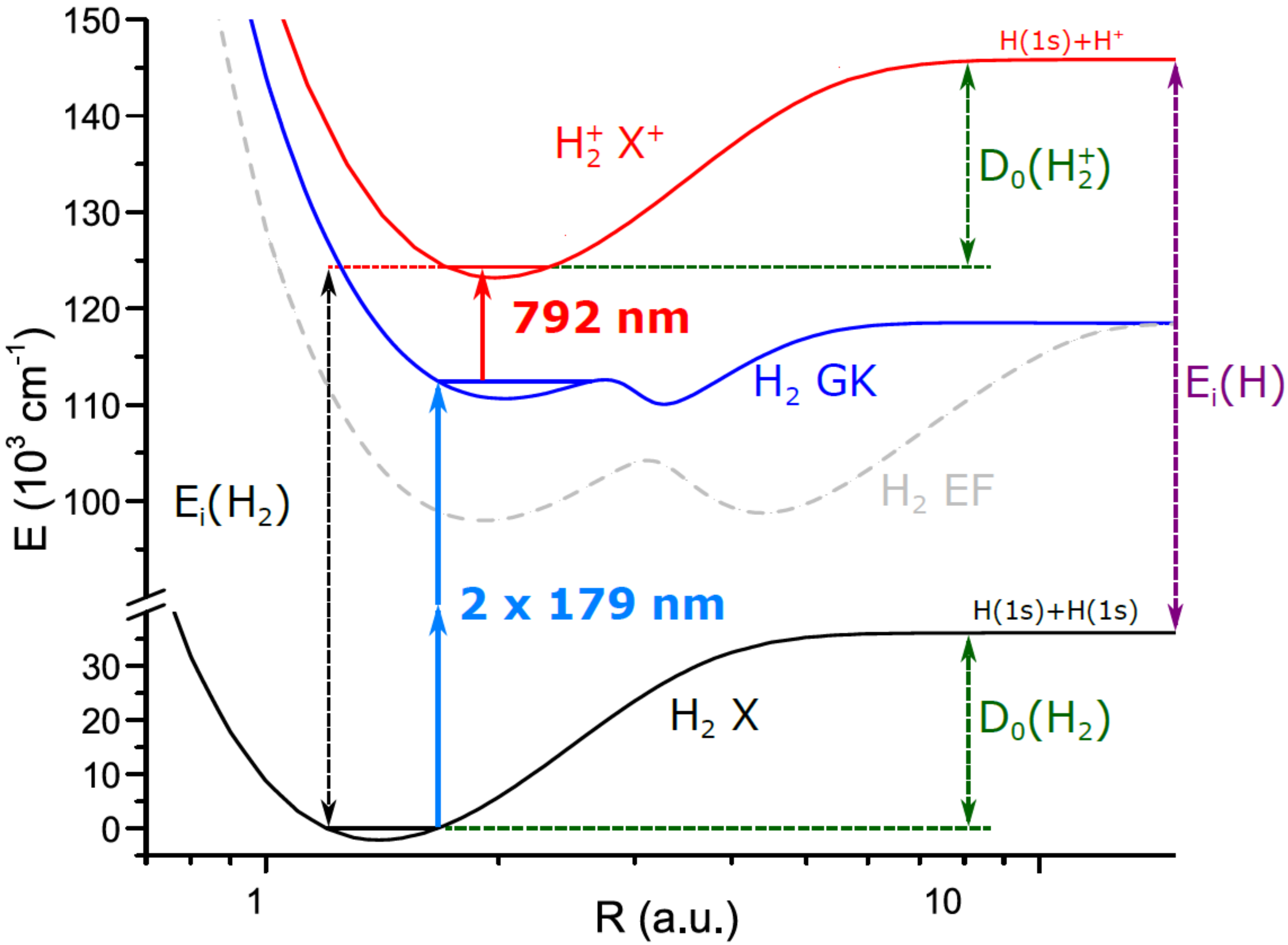


Measurement of GK-X

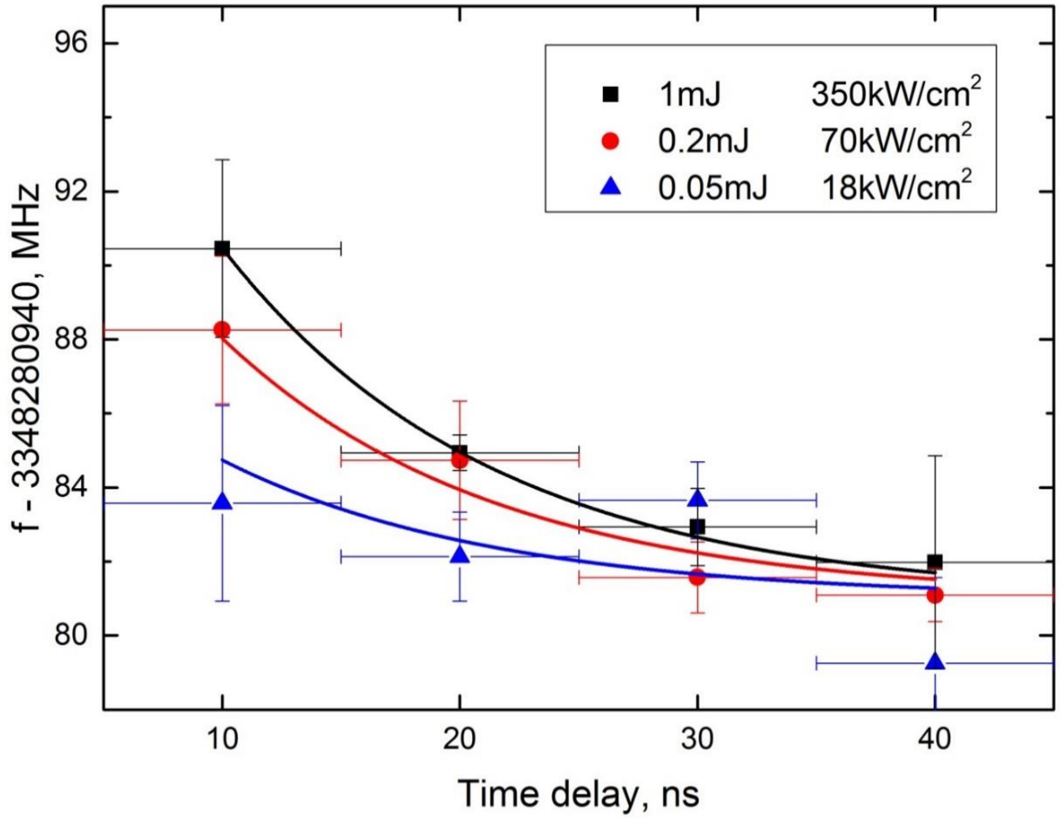


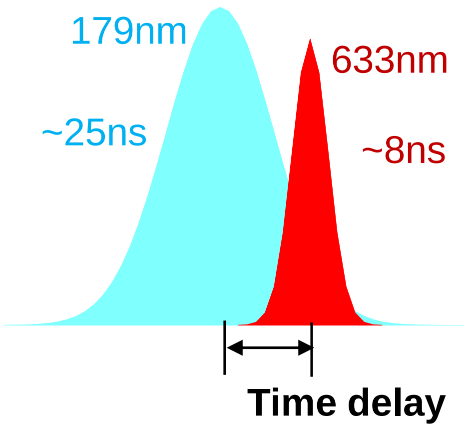


H_2 Potentials



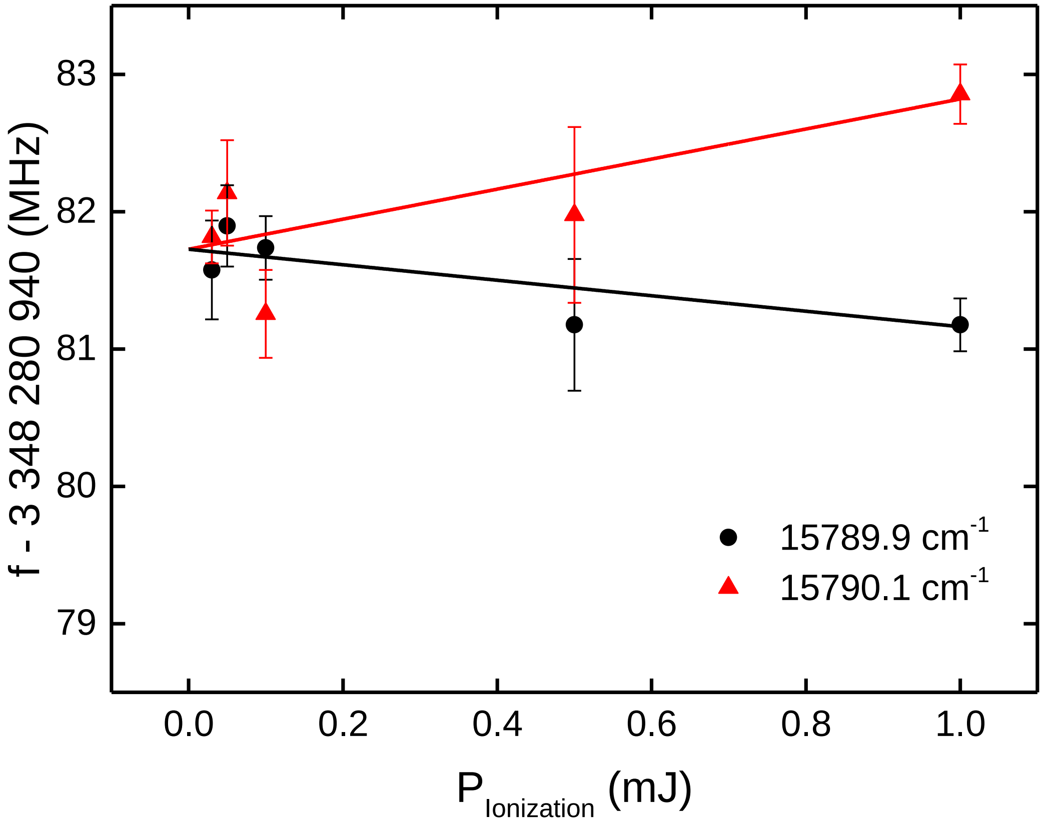
Systematic check: AC-stark of ionization light

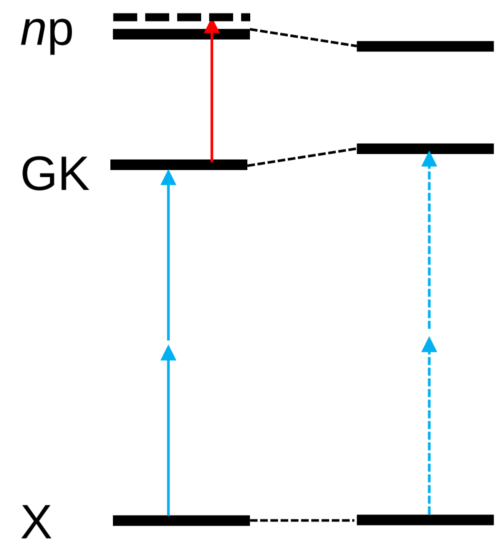




Systematic check: AC-stark of ionization light

The time delay: 30ns





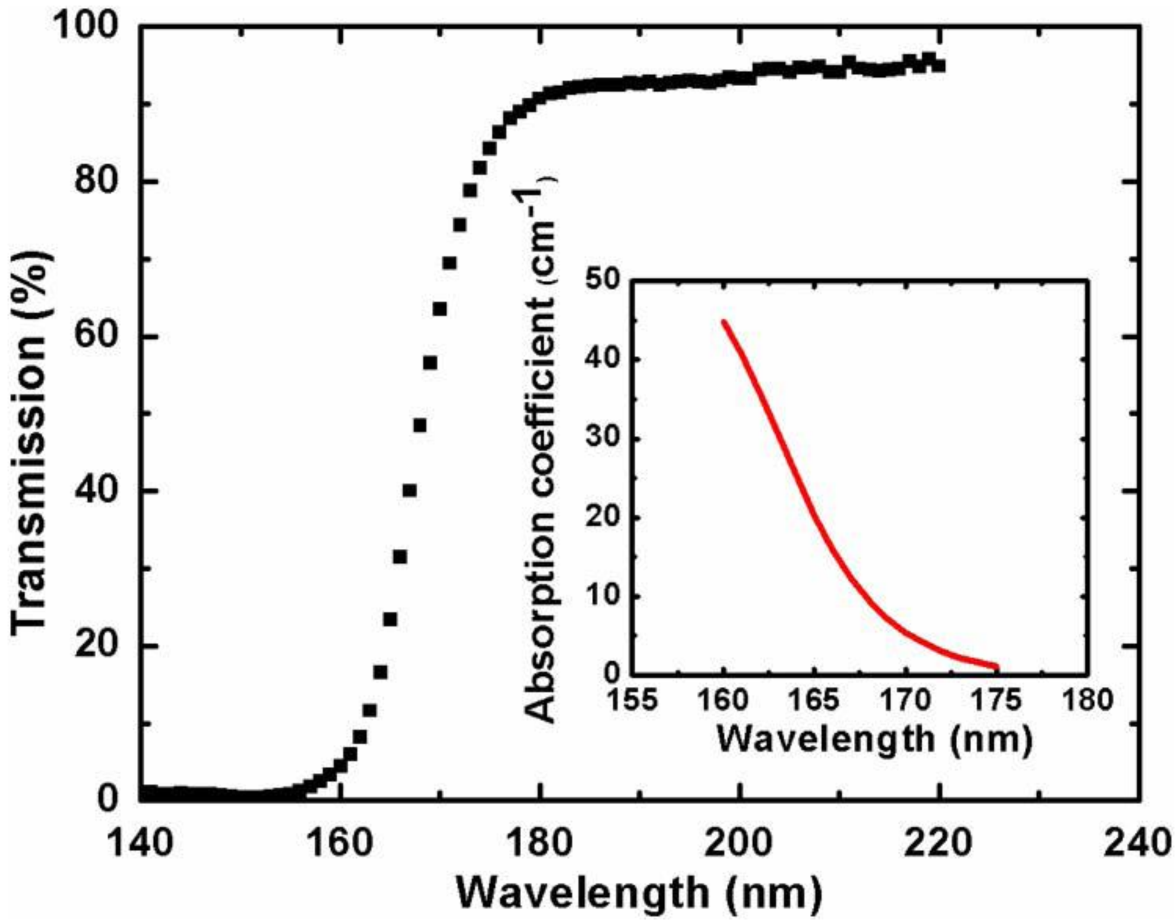
Power range:

0.05 – 1.0mJ (633nm)

About

18 – 350 kW/cm^2

KBBF



100
80
60
40
20
0
Transmission (%)
140
160
180
200
220
240
Wavelength (nm)
50
40
30
20
10
0
Absorption coefficient (cm-1)
155
160
165
170
175
180
Wavelength (nm)

Test QED in H_2 system

Ground state $E_{level} = E_{BO} + E_{AD} + E_{NAD} + E_{REL} + E_{QED}$

Non- Relativistic

Relativistic

Born-Oppenheimer
$E_{BO} = E_{ELE} + (E_{VIB} + E_{ROT})$

Electron's self energy & vacuum field
~ 10^{-5} of BO

Adiabatic
finite nuclear mass correction
~ 10^{-4} of BO

Relativistic corrections for orbiting electron
~ 10^{-5} of BO

Non-Adiabatic
Couples electronic and nuclear motion
~10^{-4}-10^{-5} of BO

1cm^{-1}~30GHz

- Current calculation accuracy 3~30MHz, including QED
- Proton size kicks in when accuracy reaches 0.01~0.1MHz

Jacek Komasa, Krzysztof Pachucki, *et.al.*
J. Chem. Theory Comput. 7, 3105–3115 (2011)

Systematic check: AC Stark VUV

Power range:

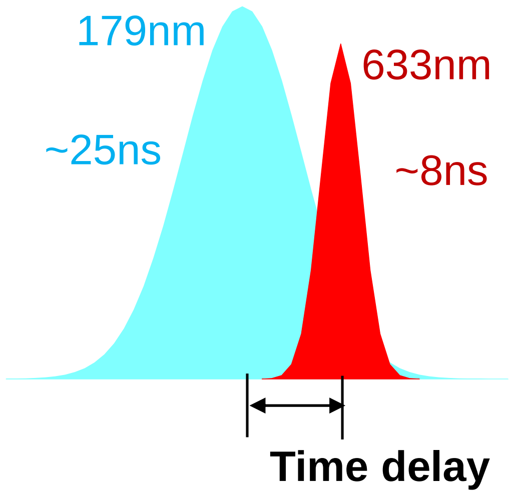
1 – 2.5mJ (358nm)

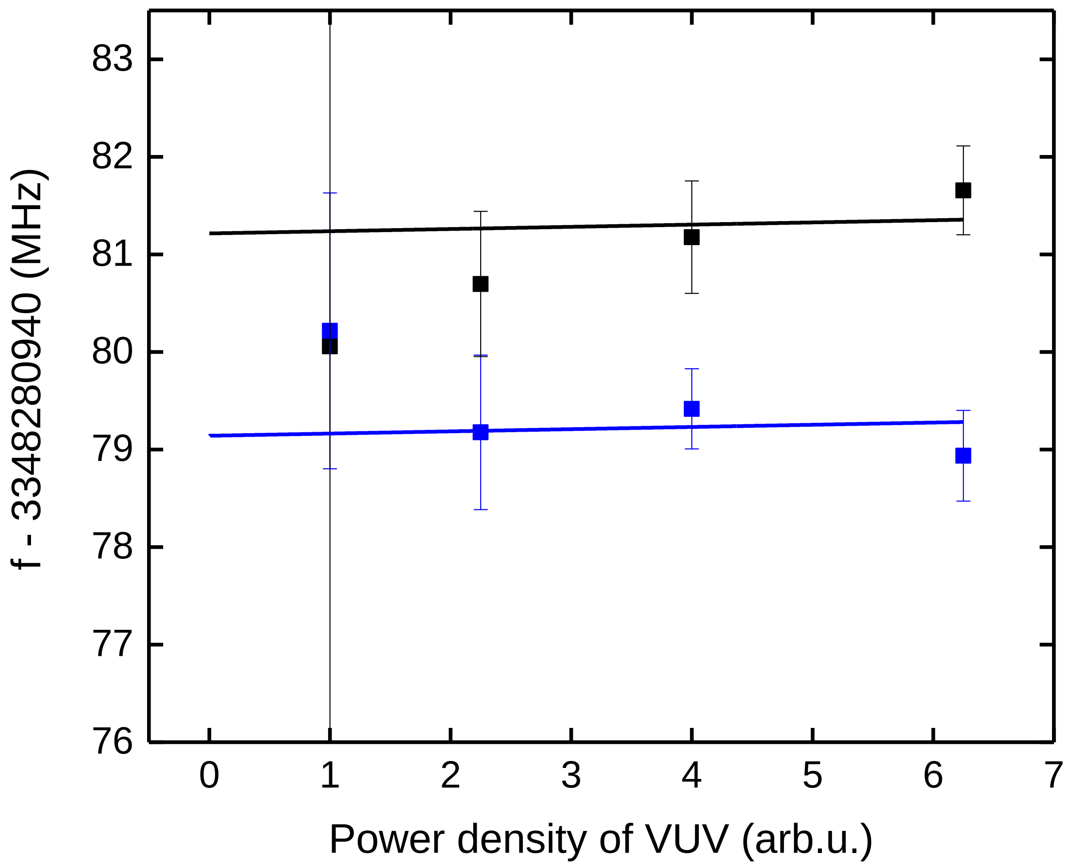
About

1 – 10uJ (179nm)

4 – 40 kW/cm^2

Two different “Doppler” alignments





Systematic check: AC Stark ionization

Power range:

0.05 – 1.0mJ (633nm)

About

18 – 350 kW/cm^2