

# Improvement of the Dissociation Energy of the Hydrogen Molecule (Part II)

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# Principle of Earlier Measurements of the Dissociation Energy

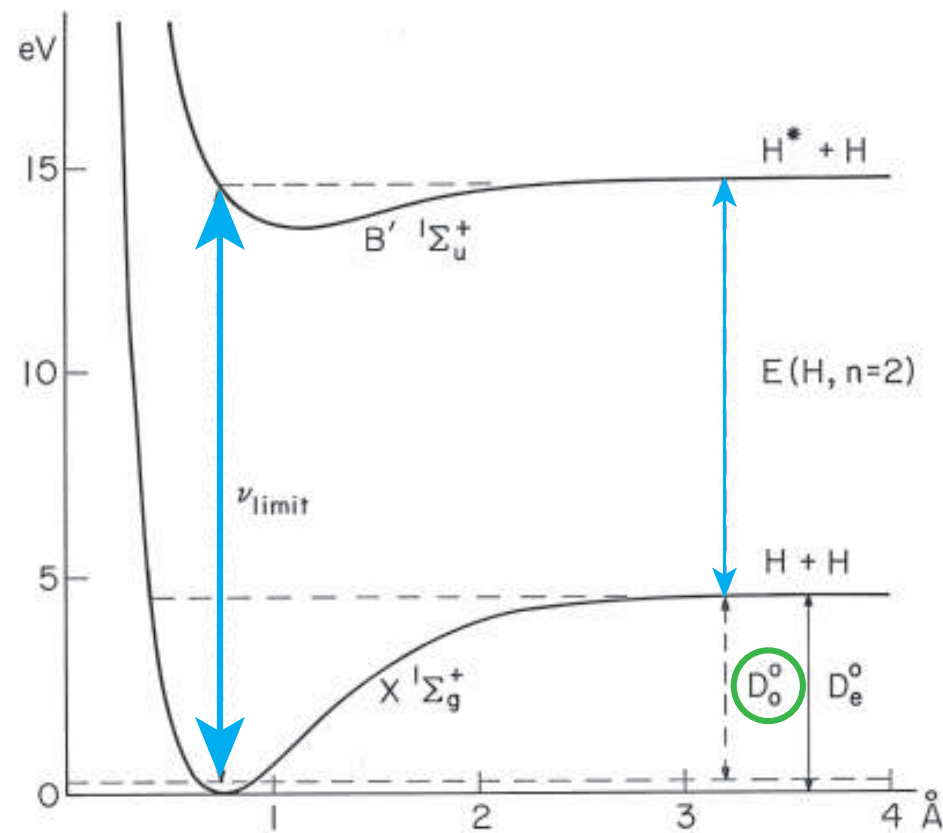
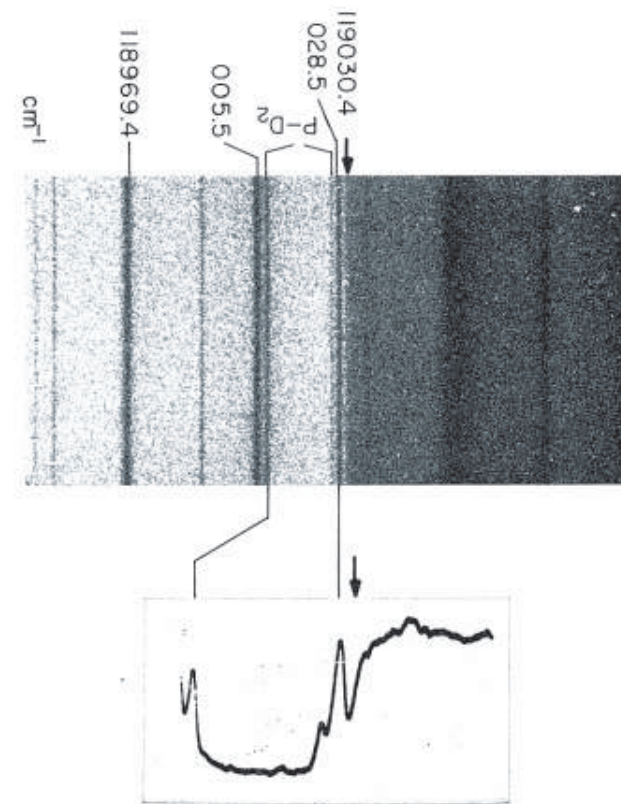
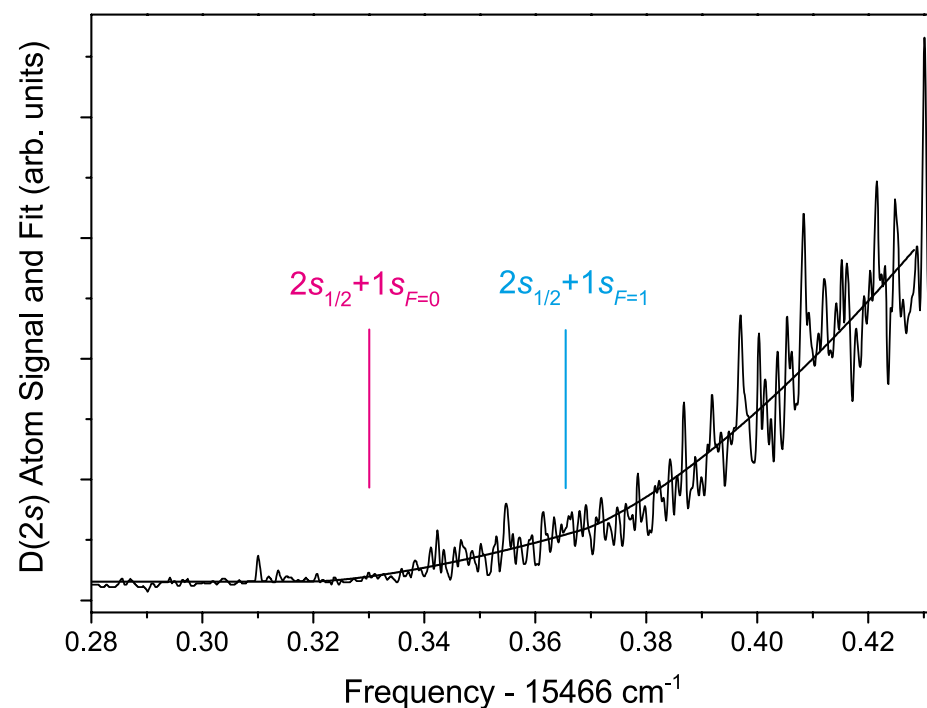


Fig. 2.  
Potential functions of the ground state ( $X^1\Sigma_g^+$ ) and the second excited state ( $B'^1\Sigma_u^+$ ) of  $\text{H}_2$  showing the relation between the absorption limit and the dissociation energy in the ground state:  $D_0^0 = \nu_{\text{limit}} - E(\text{H}, n = 2)$ .

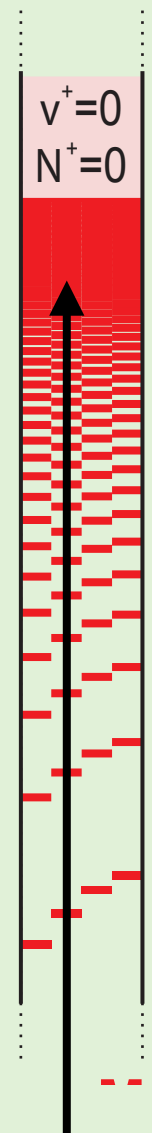


G. Herzberg, Nobel lecture 1971



Eyler and coworkers,  
*PRL* **92**, 203003 (2004)

This work:  
Measurement of  
ionization energy



# Measurement Principle

$$D_0(\text{H}_2) = E_{\text{I}}(\text{H}_2) + D_0(\text{H}_2^+) - E_{\text{I}}(\text{H})$$

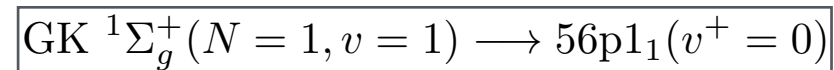
## One-electron problems

CODATA value

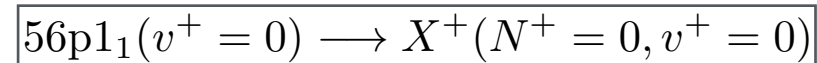
ab initio calculations from  
Korobov, *Mol. Phys.* **116**, 93-98 (2018)

## "Zürich Part":

1. cw excitation of high- $np$  Rydberg states from the intermediate GK state

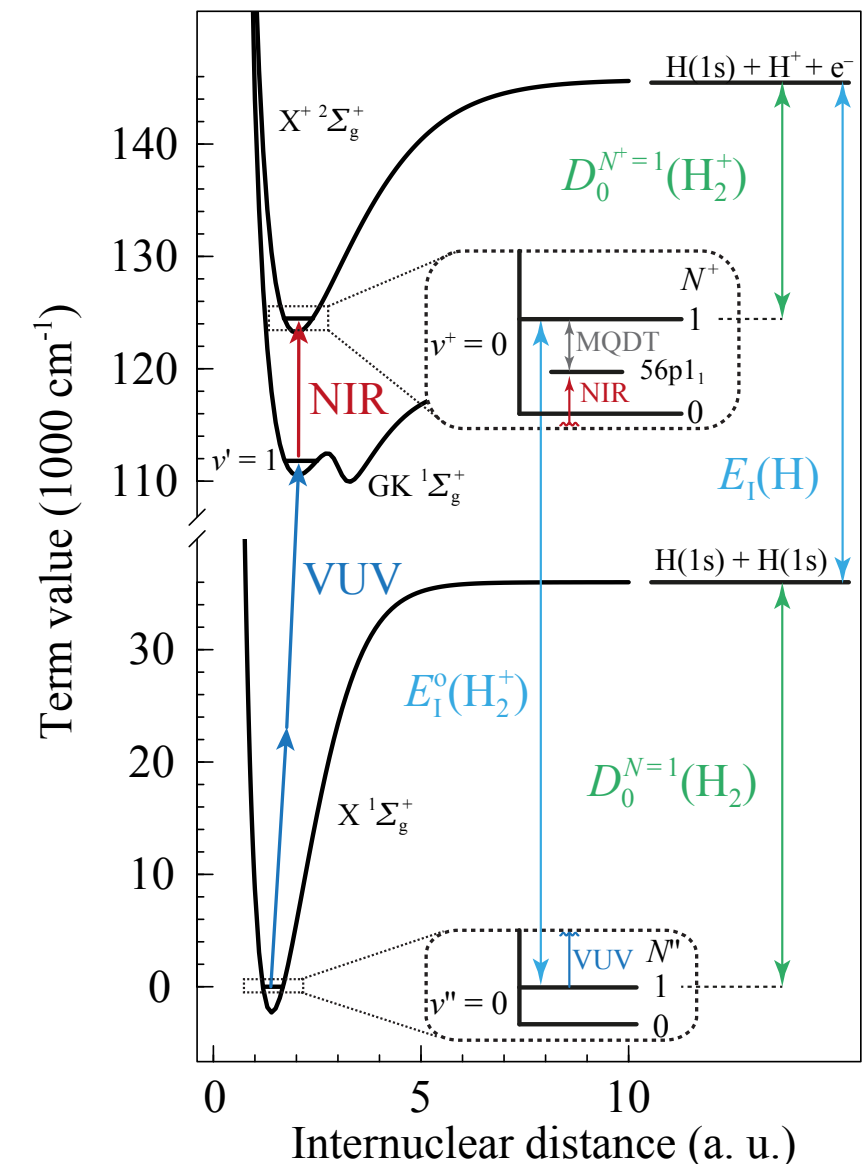
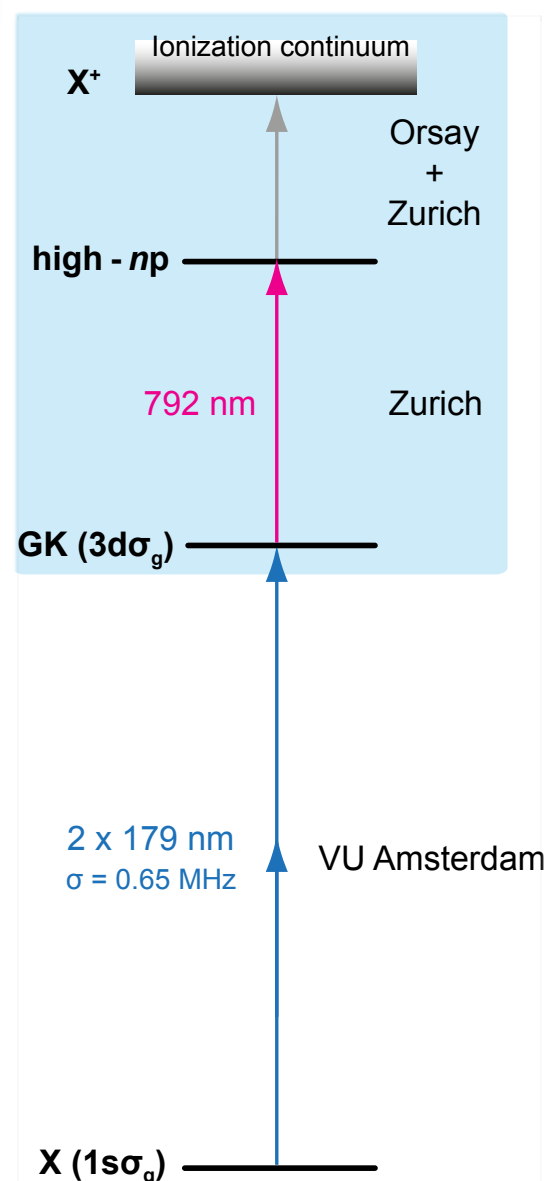


2. MQDT-assisted extrapolation to the ground state of ortho- $\text{H}_2^+$



MQDT-extrapolation performed previously in Sprecher et al., *J. Chem. Phys.* **140**, 104303 (2014) yielded:

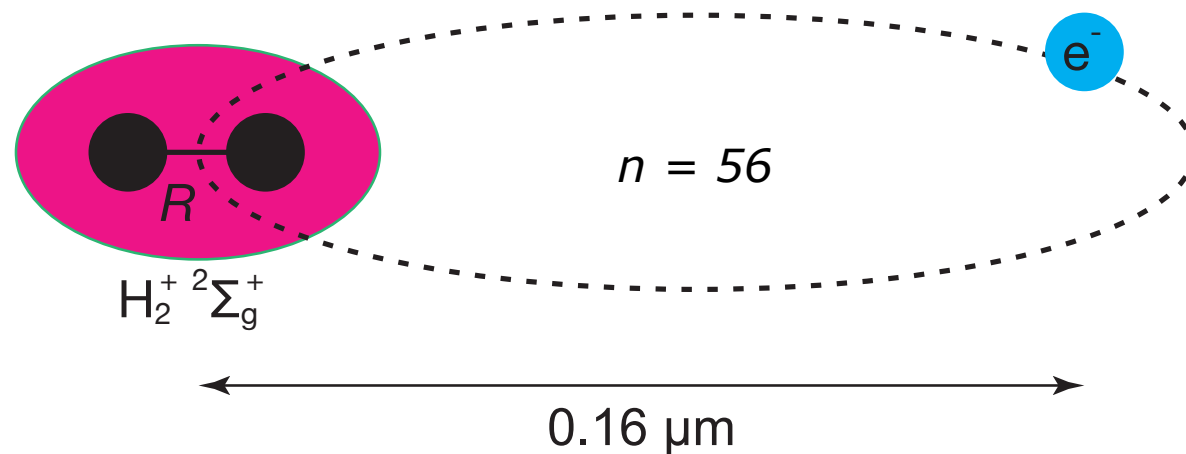
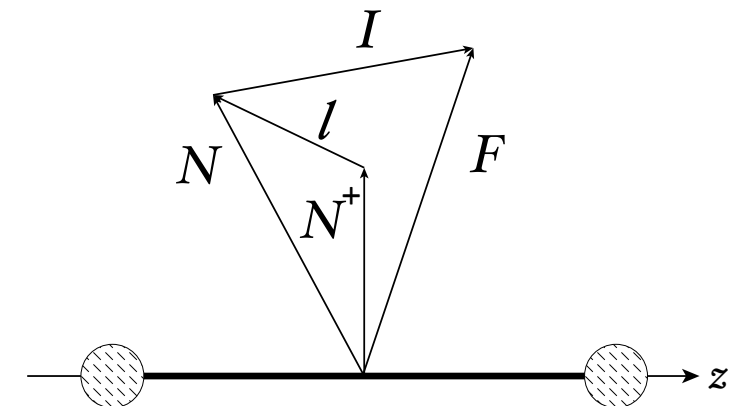
$$\Rightarrow E_{\text{bind}}(56p1_1) = 34.881112(5)\text{cm}^{-1}$$



# Molecular Rydberg States

## Description in Hund's case (d):

$$n l N_N^+ (v^+ = 0, S = 0, \vec{F} = \vec{N} + \vec{I})$$



## Important Properties & related effects:

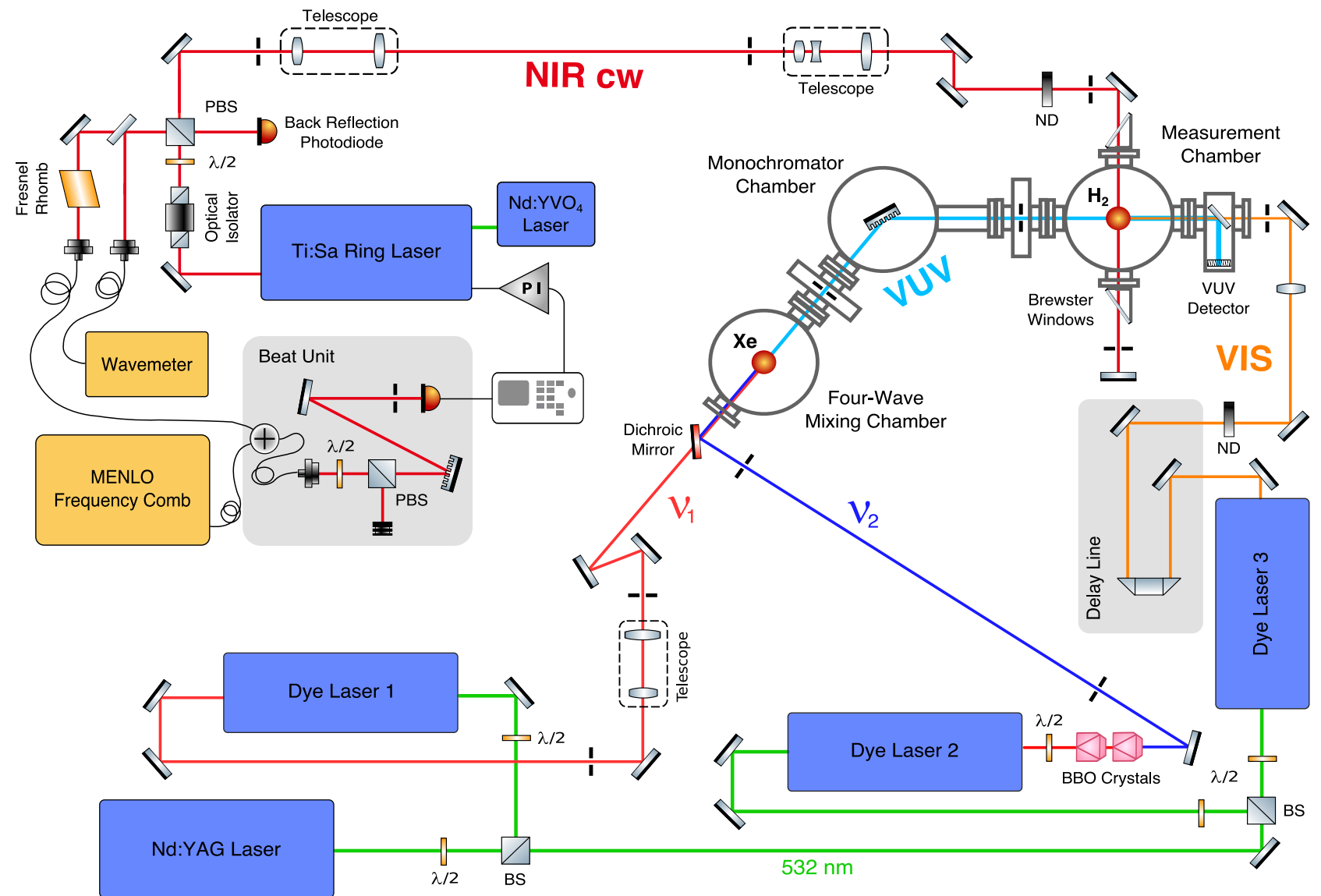
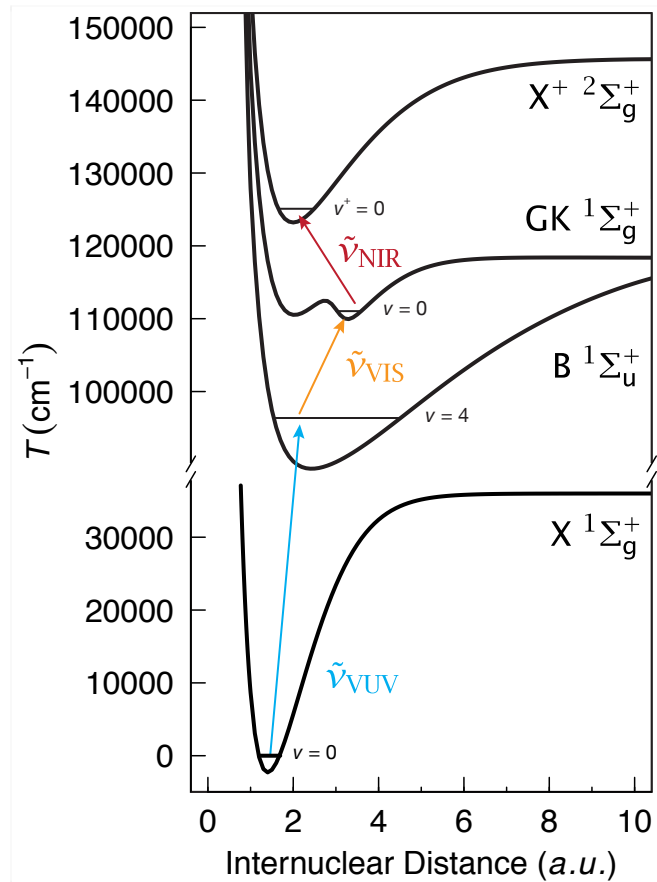
transition moment	$n^{-3}$	-
polarizability	$n^7$	dc-Stark shift
dynamical polarizability	-	ponderomotive shift
lifetime	$n^3$	natural broadening
orbit size	$n^2$	pressure shift

electric field compensation

single-photon cw excitation  
(difficult for molecular Rydberg states)

low densities in the molecular beam

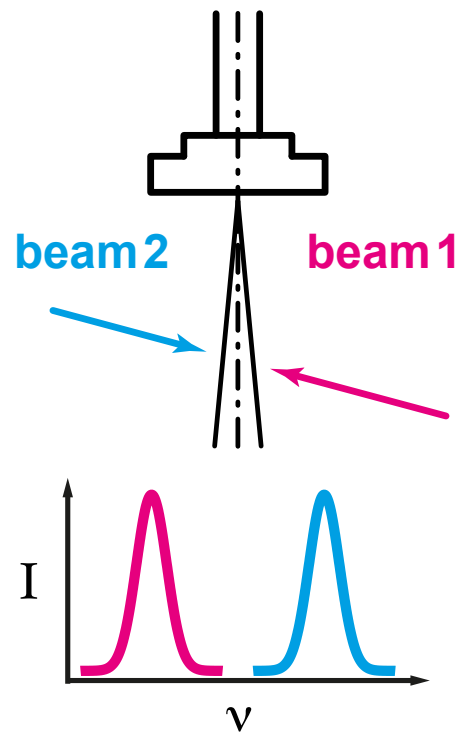
# Experimental Setup



- VUV generation by four-wave mixing
- pulsed dye lasers to reach GK intermediate states
- final transition by cw-NIR laser locked to frequency comb

# The Doppler Effect

## 1) Doppler Shift

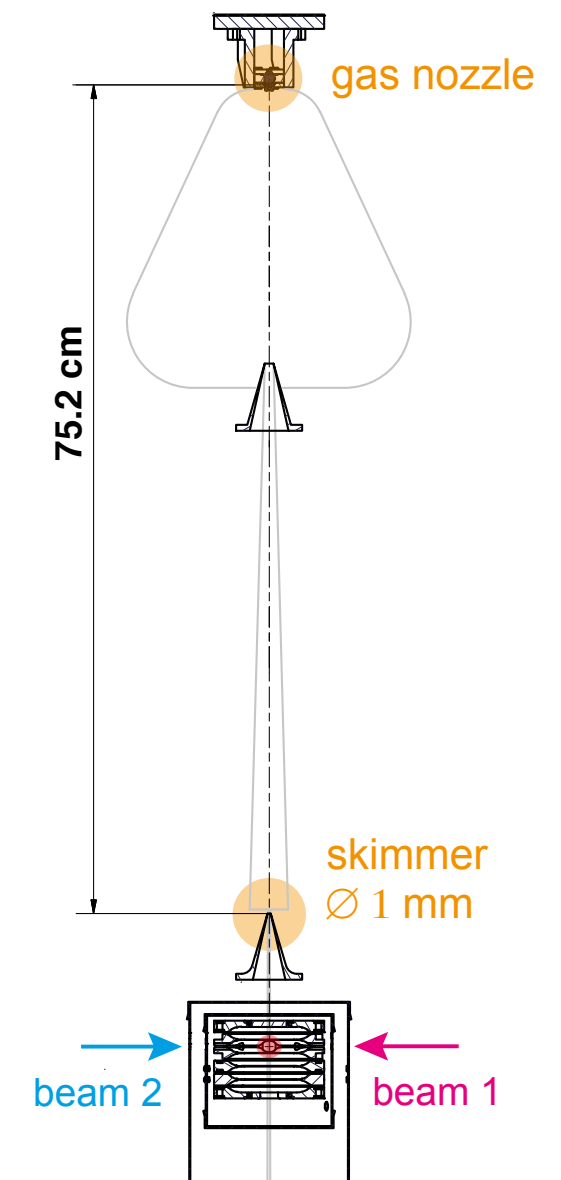
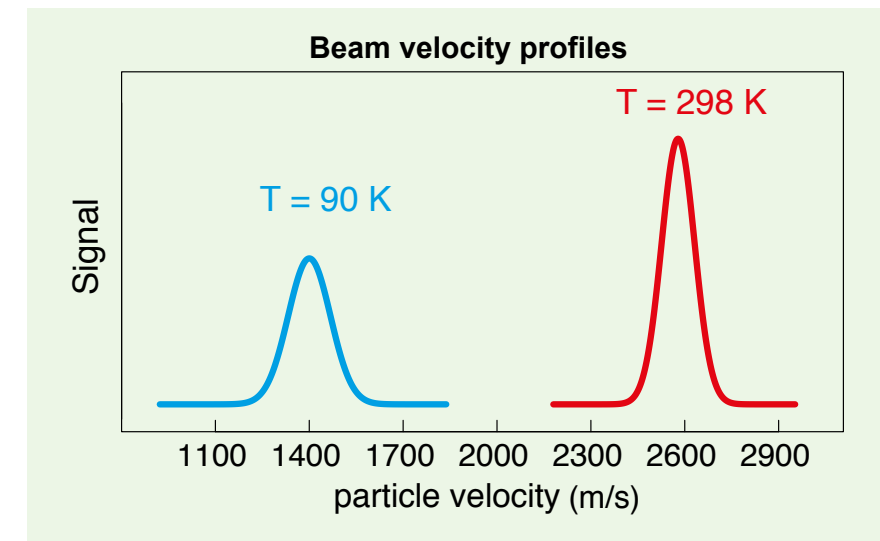
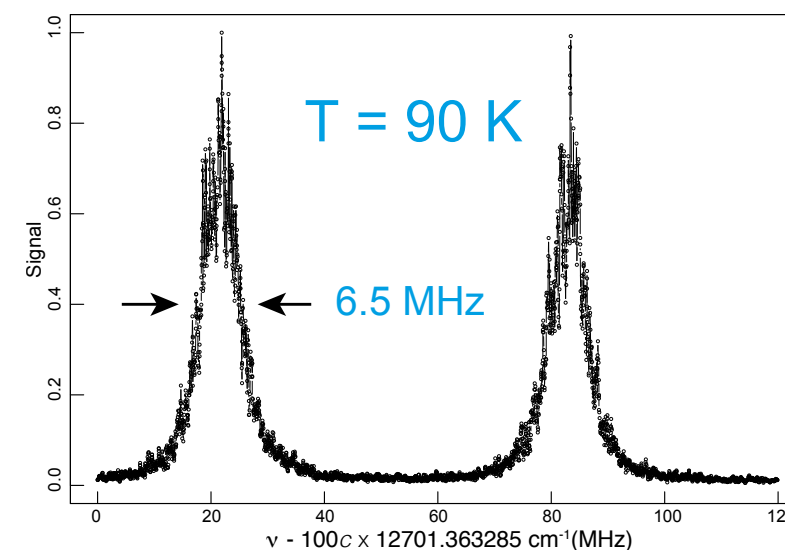
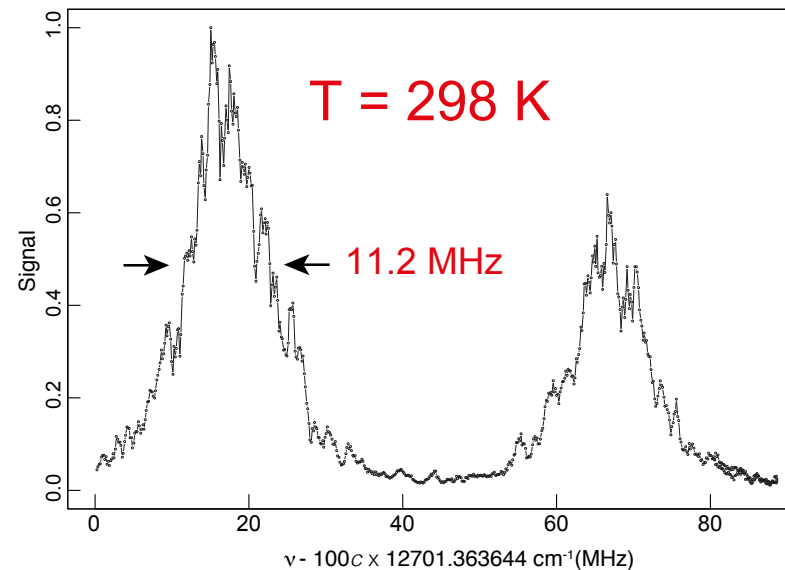


Beam angle controlled by overlapping the back reflection on a photodiode over a distance of 10 m

→ statistical error  $\Delta\nu < 120$  kHz

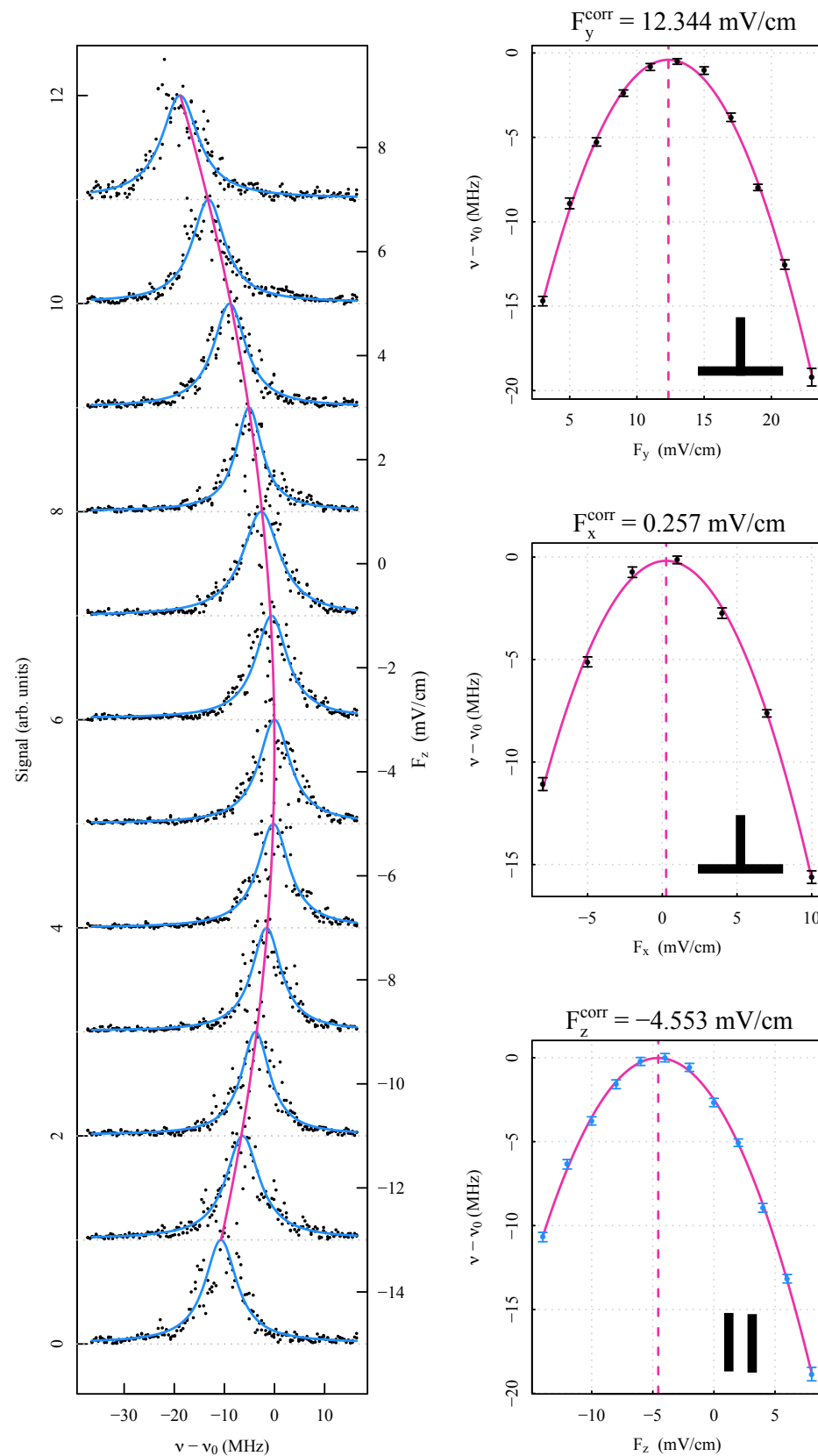
## 2) Doppler Broadening

GK(0,2) - 70f0<sub>3</sub> (para-H<sub>2</sub>):



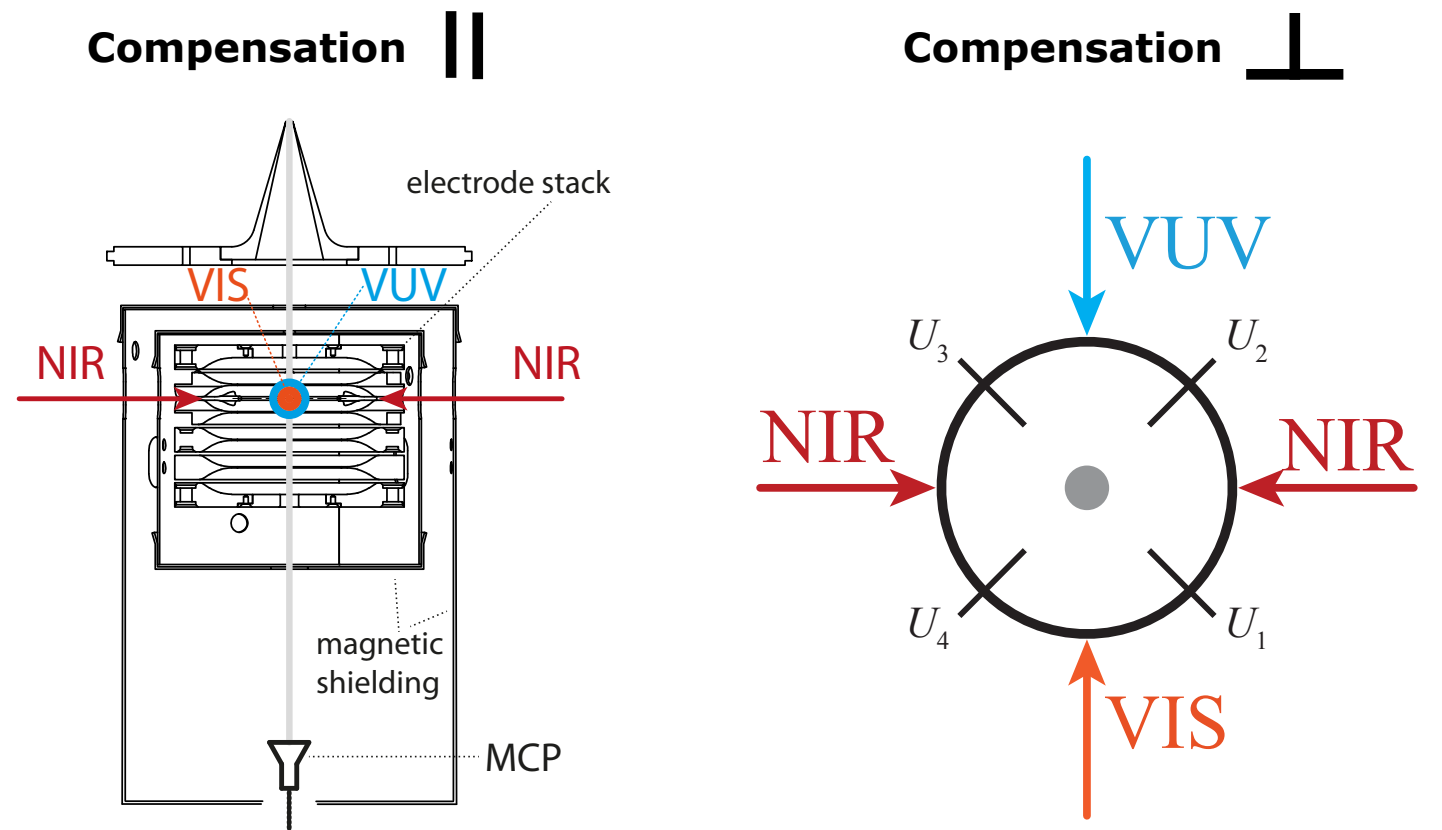
# Electric Field Compensation & Magnetic Shielding

extrapolation of quadratic Stark shift:



## 3D Field Compensation:

- remaining stray fields: **< 0.1 mV/cm (10 kHz)**



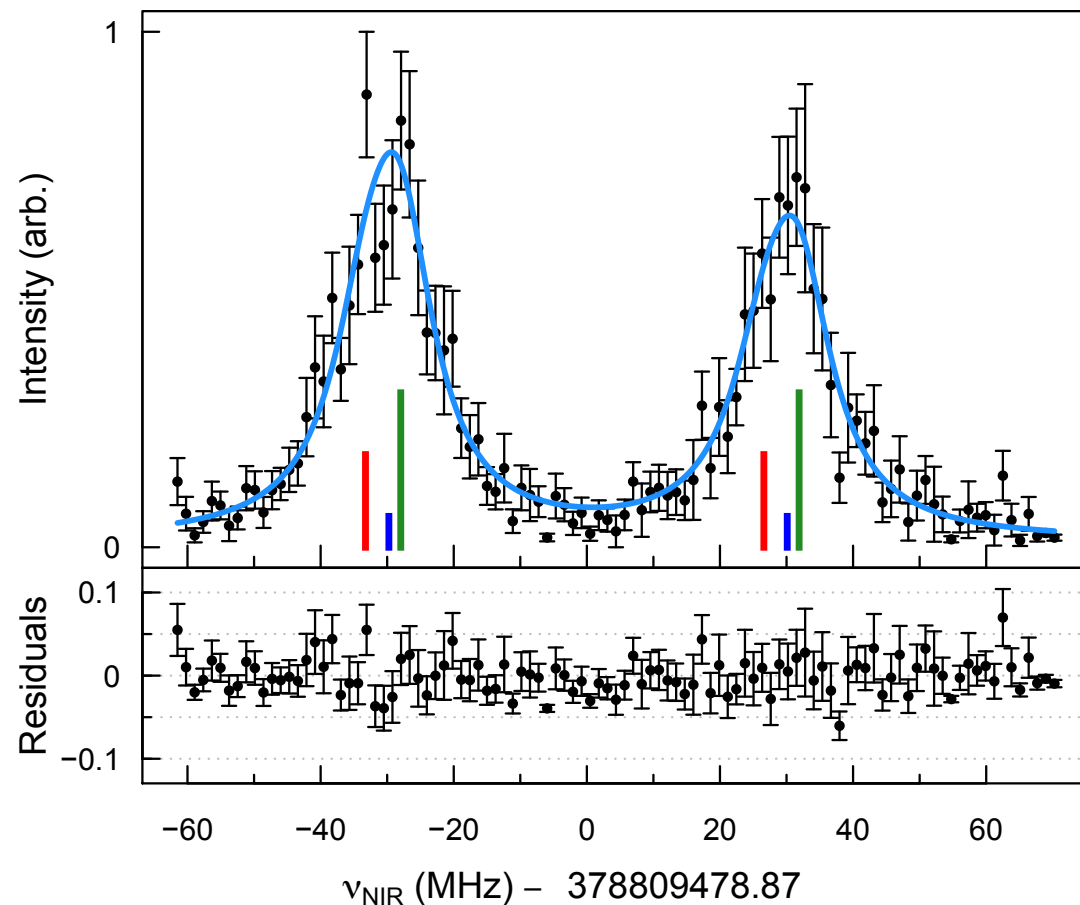
## Magnetic Shielding:

- double-layer mumetal encasing
- magnetic field in extraction region: **< 10 mG (10 kHz)**



# Determination of Transition Frequency

**Hyperfine structure of ortho-H<sub>2</sub> (total nuclear spin I=1):**  
56p1<sub>1</sub> (F=0,1,2) components

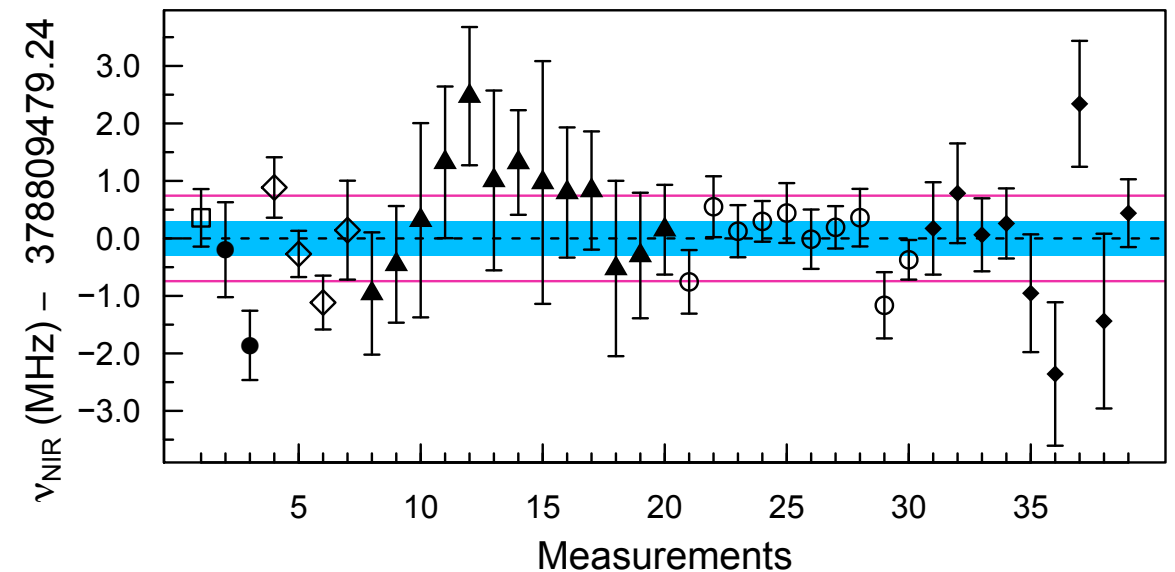


**Weighted fit with Lorentzian lineshape model:**

- Hyperfine structure known  
[Osterwalder et. al, *J. Chem. Phys.* **121**, 11810 (2004)]
- Statistical populations 2F+1 assumed

Transition recorded on six different days

➔ standard deviation of the mean:  $\bar{\sigma} = \sigma/\sqrt{N}$



**Corrections to the transition frequency:**

$$\omega_{ik} = \omega_0 + \vec{k} \cdot \vec{v} - \omega_0 \frac{v^2}{2c^2} + \omega_0^2 \frac{\hbar}{2Mc^2} + \dots$$

Measured frequency 378 809 479.24(30) MHz

Second-order Doppler shift +0.0041 MHz

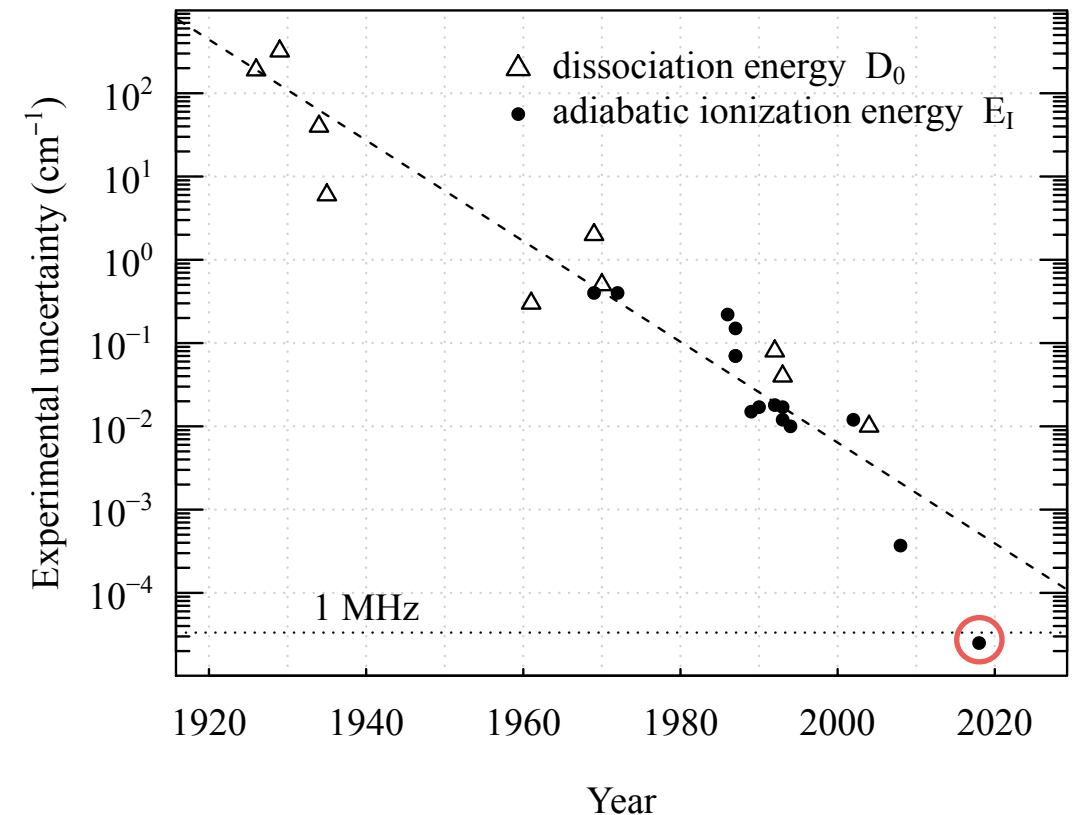
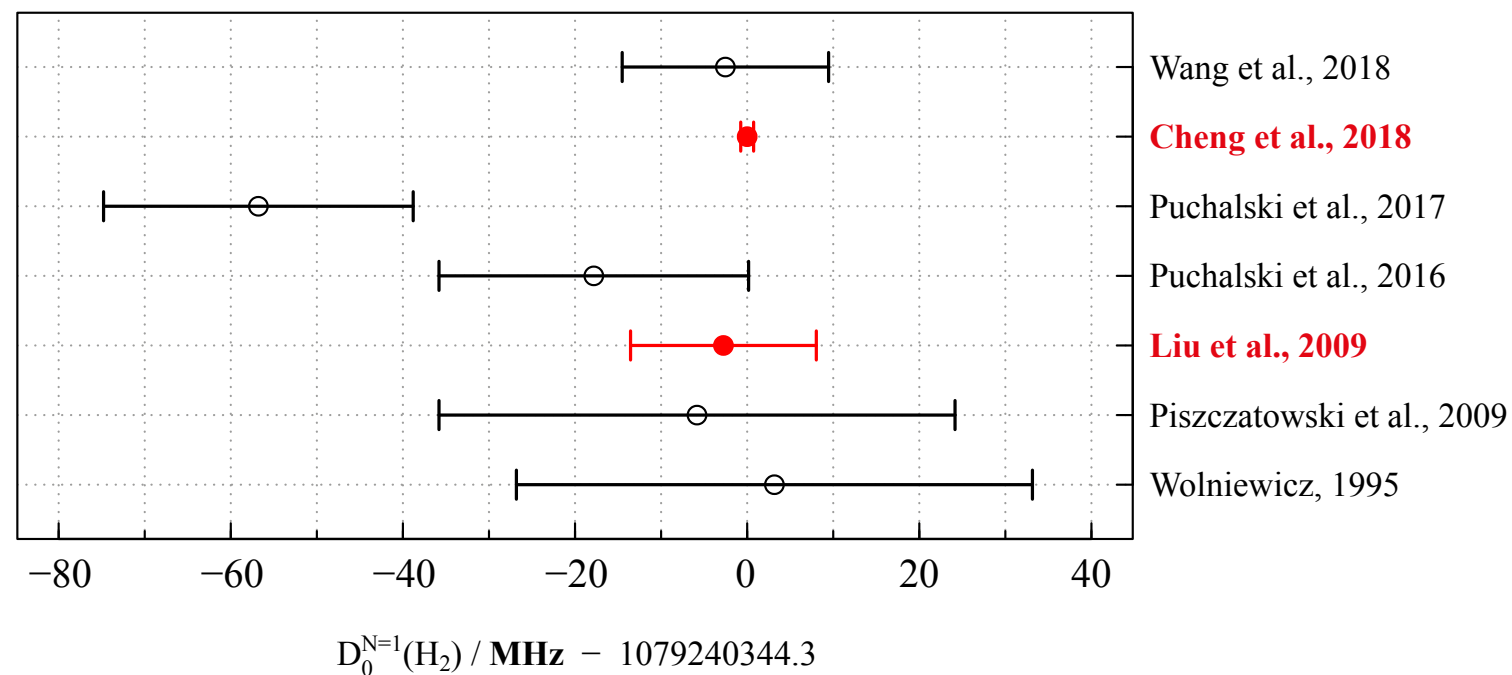
Photon-recoil-shift correction -0.16 MHz

$(\Delta E_{GK(1,1)-56p1_1})/h$  378 809 479.08(30)<sub>stat</sub>(22)<sub>sys</sub> MHz



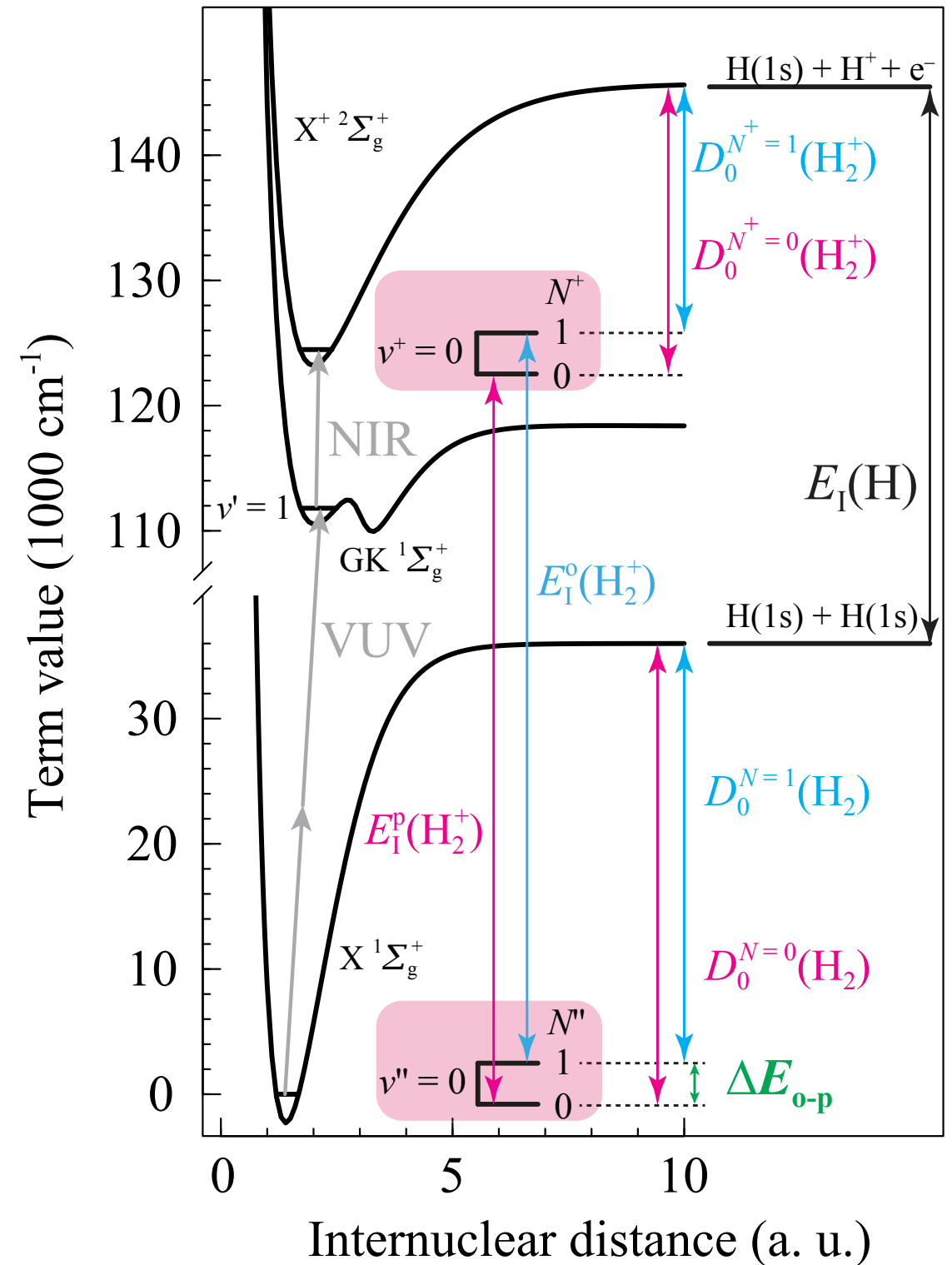
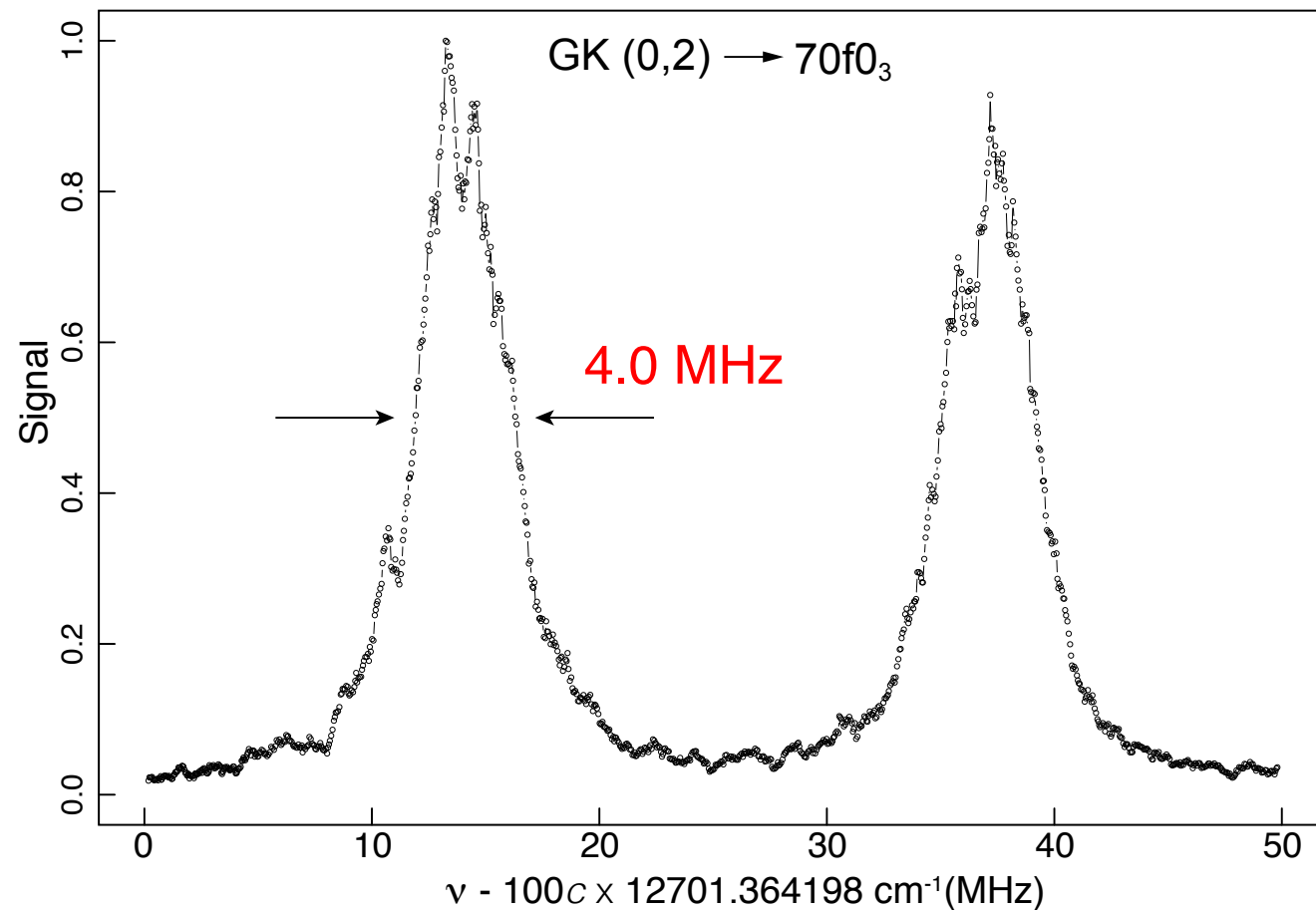
# Final Results

Energy level interval		Value
(1)	$\text{GK}(v = 1, N = 1) - \text{X}(v = 0, N = 1)$	111 686.632 836(22)
(2)	$56\text{p}1_1(v^+ = 0, S = 0, \text{center}) - \text{GK}(v = 1, N = 1)$	12 635.724 114(12)
(3)	$\text{X}^+(v^+ = 0, N^+ = 1, \text{center}) - 56\text{p}1_1(v^+ = 0, S = 0, \text{center})$	34.881 112(5)
(4)	$D_0^{N^+=1}(\text{H}_2^+)$	21 321.116 575 5(6)
(5)	$E_{\text{I}}(\text{H})$	109 678.771 743 07(10)
(6)	$E_{\text{I}}^{\circ}(\text{H}_2) = (1)+(2)+(3)$	124 357.238 062(25)
(7)	$D_0^{N=1}(\text{H}_2) = (1)+(2)+(3)+(4)-(5)$	35 999.582 894(25)



# Outlook: Dissociation Energy of para-H<sub>2</sub>

- direct link of ortho and para level structure in H<sub>2</sub>
- no complications from hyperfine structure  
(largest uncertainty in present work)  
➔ more accurate determination of line centers



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