Testing Quantum Calculations with Measurements on Radioactive Molecular Hydrogen Isotopologues

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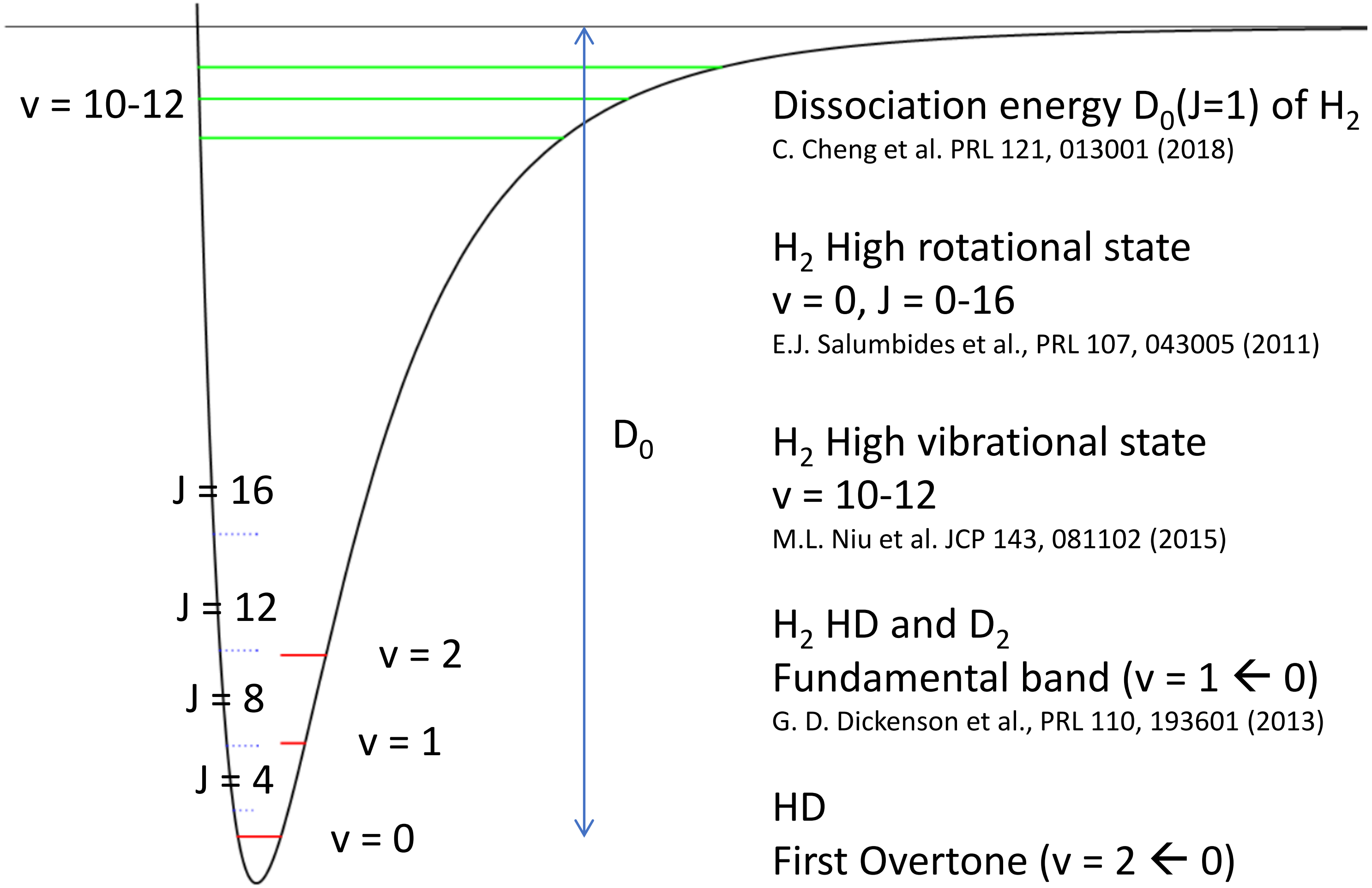
H_2 and Isotopologues as Benchmark Molecule

- Simplest neutral molecule
- Internal nuclear motion
  - Numerous transition available to test calculation



Dissociation energy $D_0(J=1)$ of H_2
C. Cheng et al. PRL 121, 013001 (2018)

H_2 High rotational state
v = 0, J = 0-16
E.J. Salumbides et al., PRL 107, 043005 (2011)

H_2 High vibrational state
v = 10-12
M.L. Niu et al. JCP 143, 081102 (2015)

H_2 HD and D_2
Fundamental band ($v = 1 \leftarrow 0$)
G. D. Dickenson et al., PRL 110, 193601 (2013)

HD
First Overtone ($v = 2 \leftarrow 0$)
F.M.J. Cozijn et al., PRL 120, 153002 (2018)

$$E_{level} = \alpha^2 E^{(2)} + \alpha^4 E^{(4)} + \alpha^5 E^{(5)} + \cdots$$

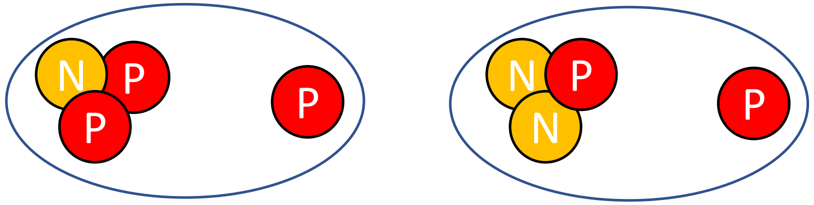
Heavier Tritiated Species

$$E^{(2)} = E^{(2,0)} + E^{(2,1)} + E^{(2,2)}$$

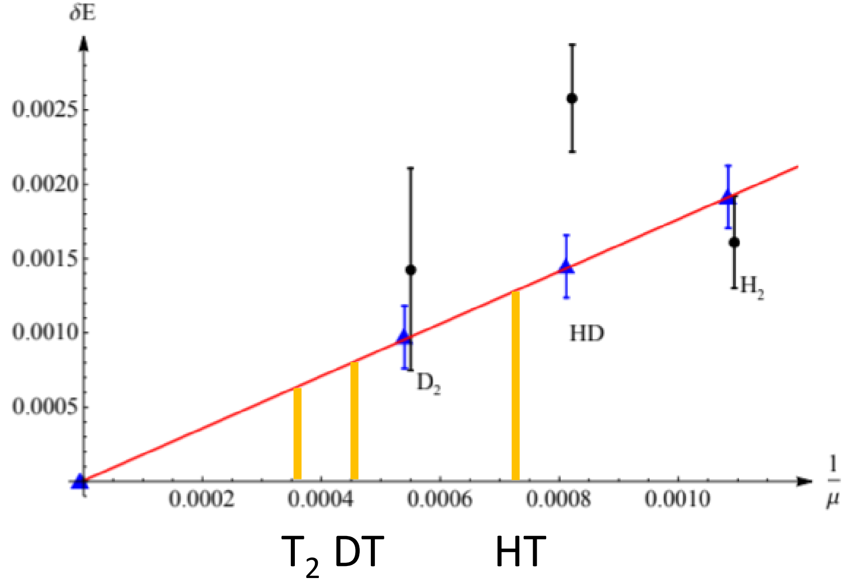
- $E^{(2,0)}$ → BO energy
- $E^{(2,1)}$ → Adiabatic correction $\left(\frac{m_e}{\mu}\right)$
- $E^{(2,2)}$ → Non-adiabatic correction $\left(\frac{m_e}{\mu}\right)^2$

- Studies on heavier tritium-containing isotopologues doubles the no. candidates
- Non-adiabatic contribution is smaller with larger reduced mass
- Investigate g-u mixing contribution in HT and DT

H^3He^+ vs HT



Non-adiabatic correction to $E^{(4)}$



M. Puchalski et al., PRL 121, 073001 (2018)

Calculation on tritiated species

NAPT calculation by P. Czachorowski

TABLE II. Calculated contributions to the Q(1) transition energy in the fundamental band of tritium-bearing molecular hydrogen. E_{FS} is the finite nuclear size correction with $r_p = 0.840\,87(39)$ fm [49], $r_d = 2.127\,71(22)$ fm [50], and $r_t = 1.759(36)$ fm [51], for the proton-, deuteron-, and triton sizes, respectively. Values are given in cm^{-1}.

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Total	2 463.348 358(62)	2 741.732 09(11)	3 431.575 50(44)

Uncertainty fundamental band v = 1 ← 0
~**10^{-4}** cm^{-1} for DT and HT
6 x 10^{-5} cm^{-1} for T_2

100-fold improvement to C. Schwartz et al. (1987)

"Recent" experiment on tritiated species

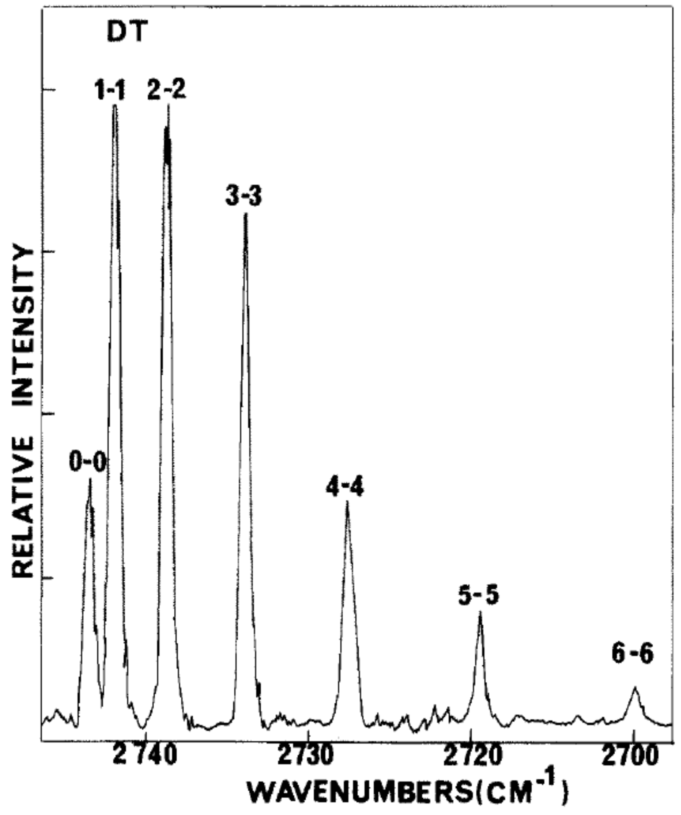


FIG. 1. The Q branch of the 1–0 Raman band of DT. p = 473 Torr. Slit width was 0.5 cm⁻¹.

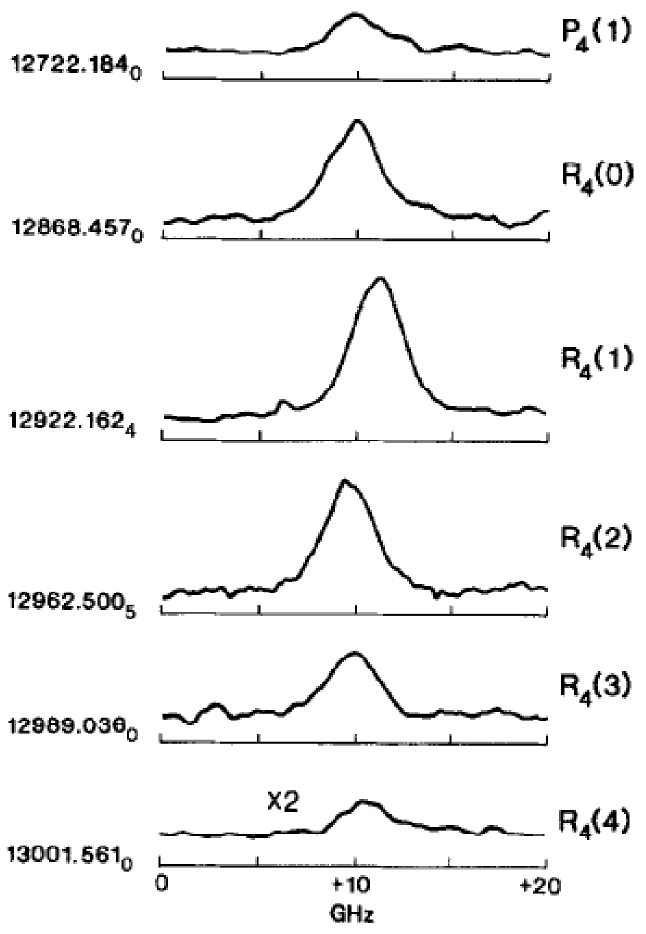
J.E. Barefield et al. J. Mol. Spectosc. 80, 233-236 (1980)

Uncertainty of old measurement on vibrational transition

T_2 and DT
> **5 x 10^{-2}** cm^{-1}

HT
> **5 x 10^{-3}** cm^{-1}

Latest calculation uncertainty
< **10^{-4}** cm^{-1}



M.C. Chuang et al. J. Mol. Spectosc. 121, 380-400 (1987)

Experimental challenge

Beta decay of tritium
Half-life : 12.3 years

$$\mathrm{T} \rightarrow {}^{3}\mathrm{He}^{+} + \mathrm{e}^{-} + \overline{\nu}_{\mathrm{e}}$$

Tritium sample from Tritium laboratory in KIT

Legal limit: <1 GBq radioactivity

~ 2.5 mbar T_2, or

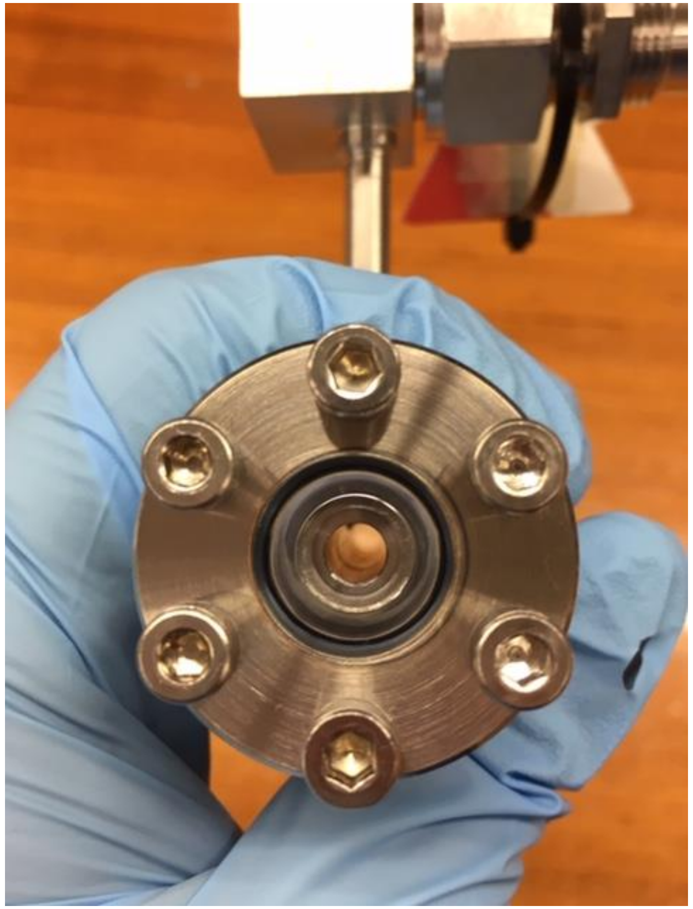
~ 4 mbar DT,

(HT is preparing)

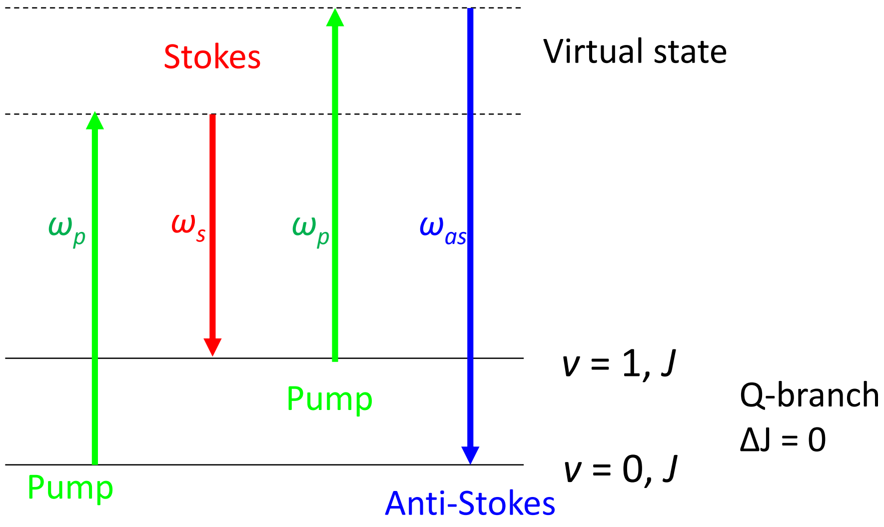
in 4 cm^3 well-sealed gas cell

Limited methods for measurement

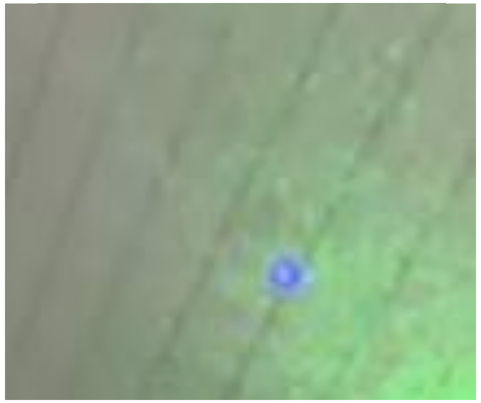
Not feasible for molecular beam experiment



Coherent Anti-Stokes Raman Scattering



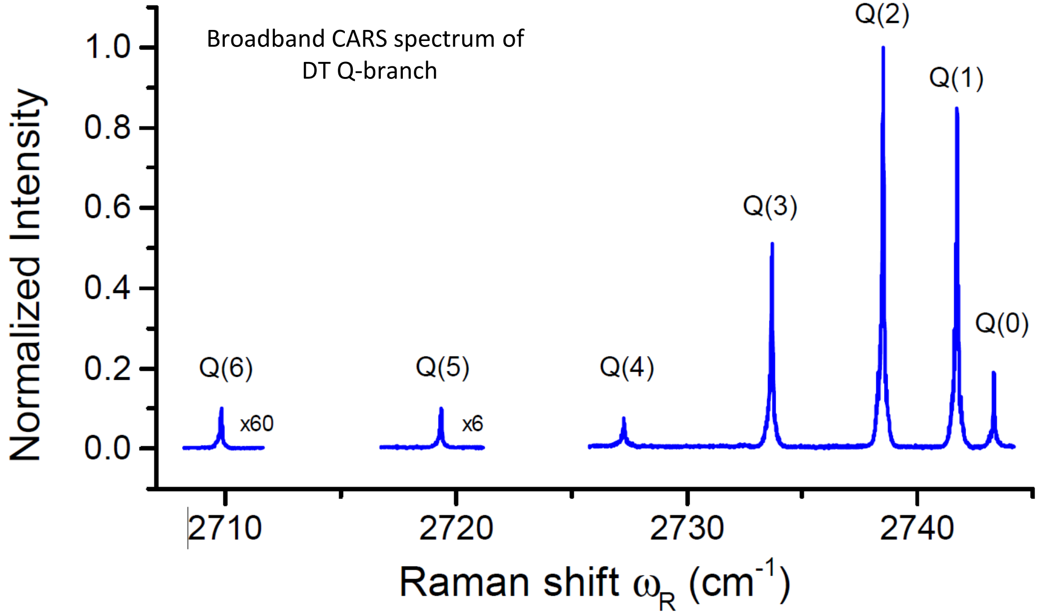
$$\omega_{as} = 2\omega_p - \omega_s$$
$$\omega_R = \omega_p - \omega_s$$



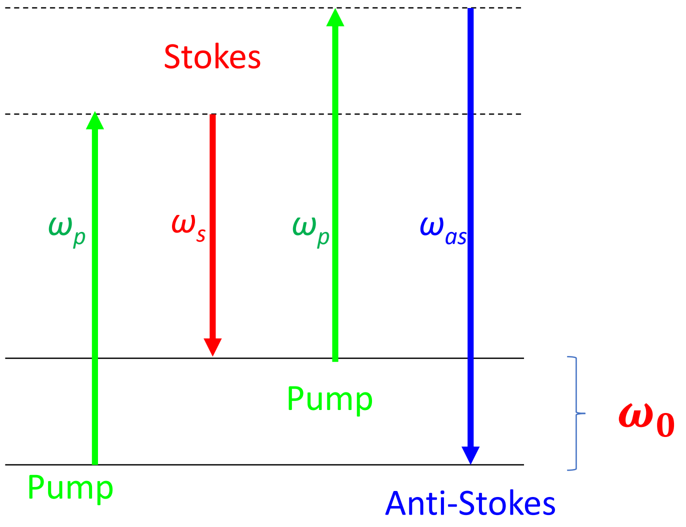
Visible blue light of Q(1) transition from 1 bar D_2

Advantage

- Non-destructive and sensitive method
- Anti-Stokes signal can be easily separated



Doppler-limited measurement

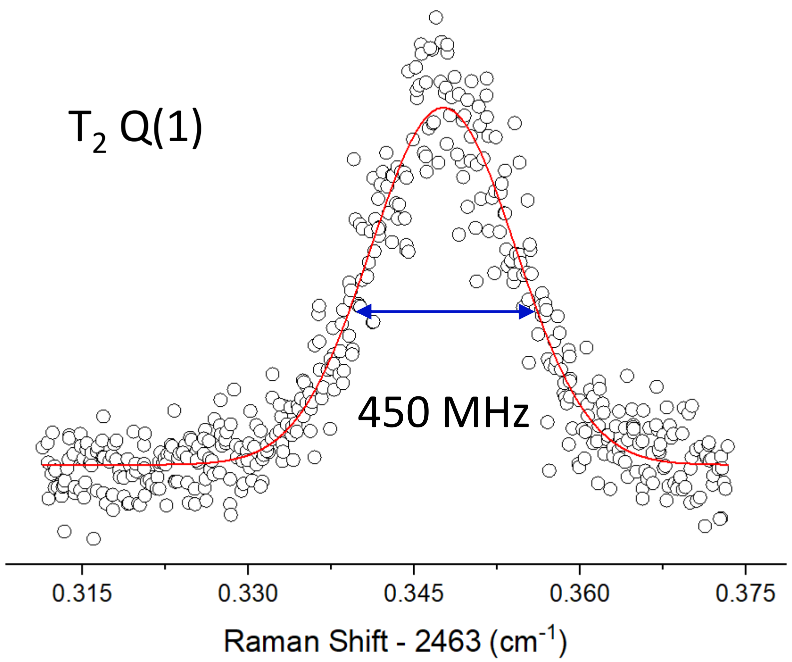


$$\omega_{as} = 2\omega_p - \omega_s$$
$$\omega_R = \omega_p - \omega_s$$

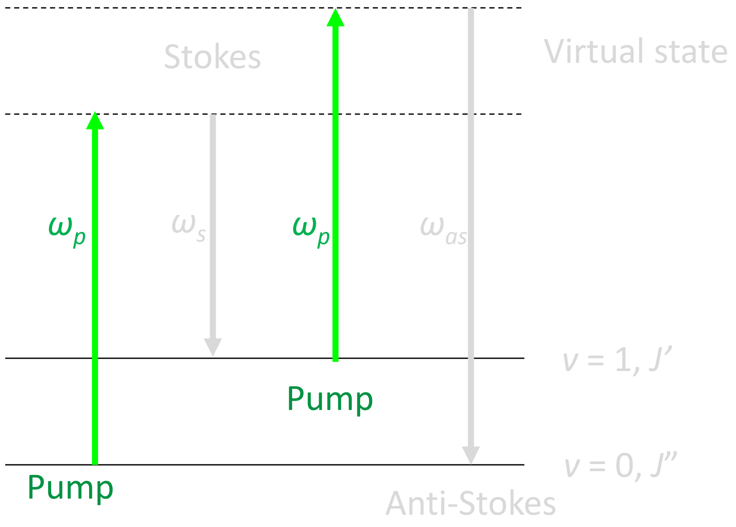
Doppler-limited spectrum

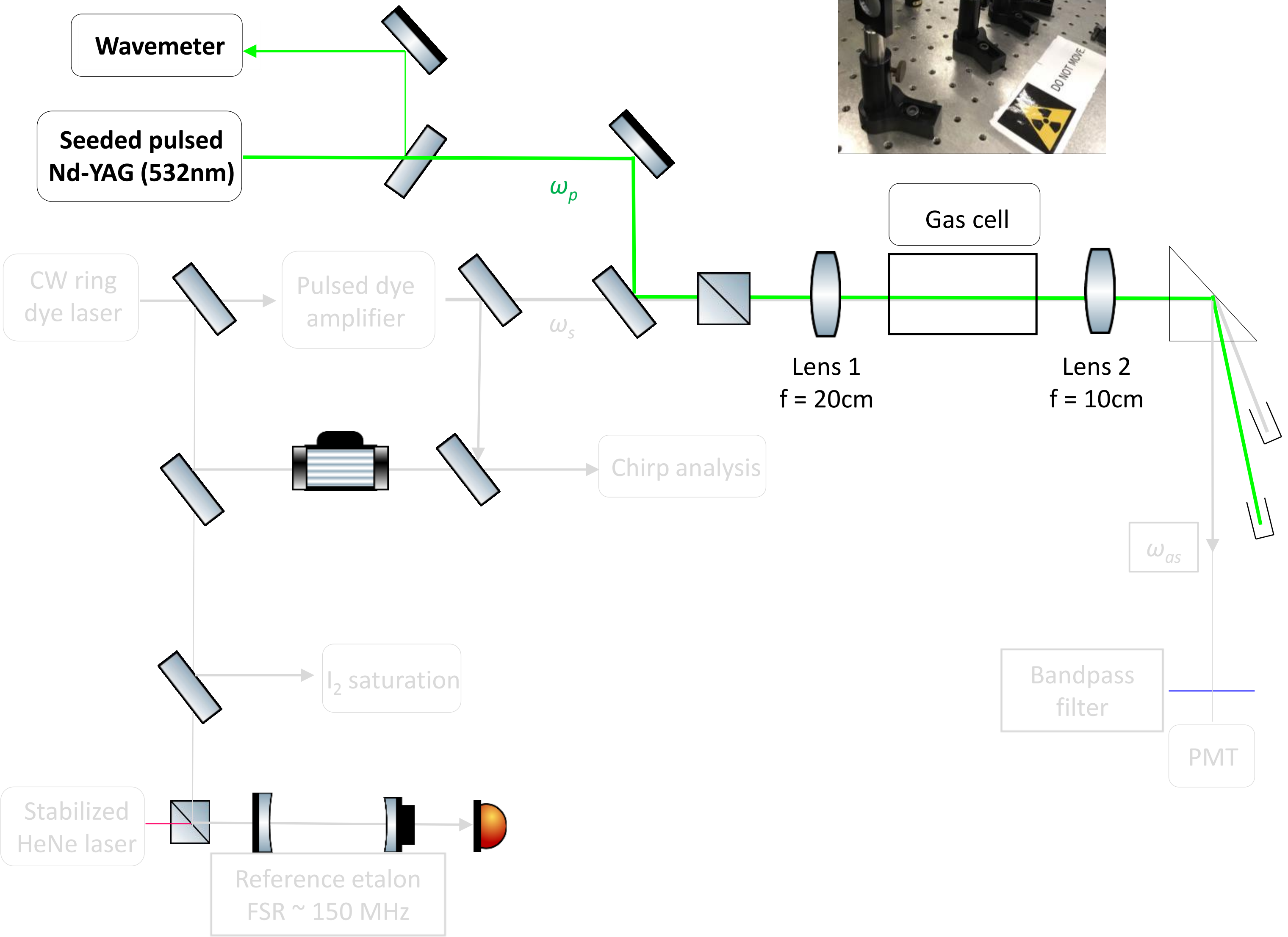
$$\text{FWHM} \sim \frac{2\omega_0}{c}\sqrt{\frac{2kT\ln 2}{M}}$$

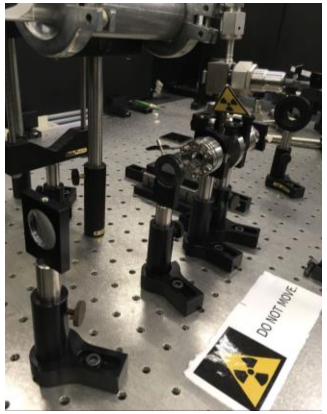
	Q-branch Doppler Width @ Room temp
D_2	550 MHz
HT	630 MHz
DT	450 MHz
T_2	370 MHz



Experimental Setup

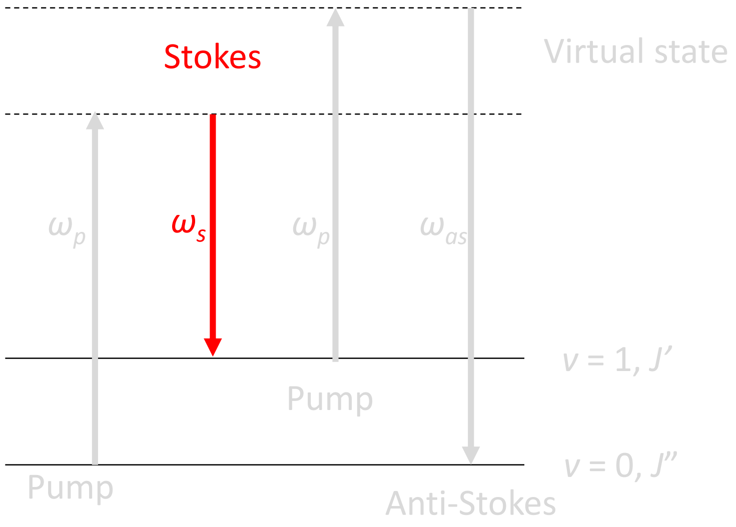


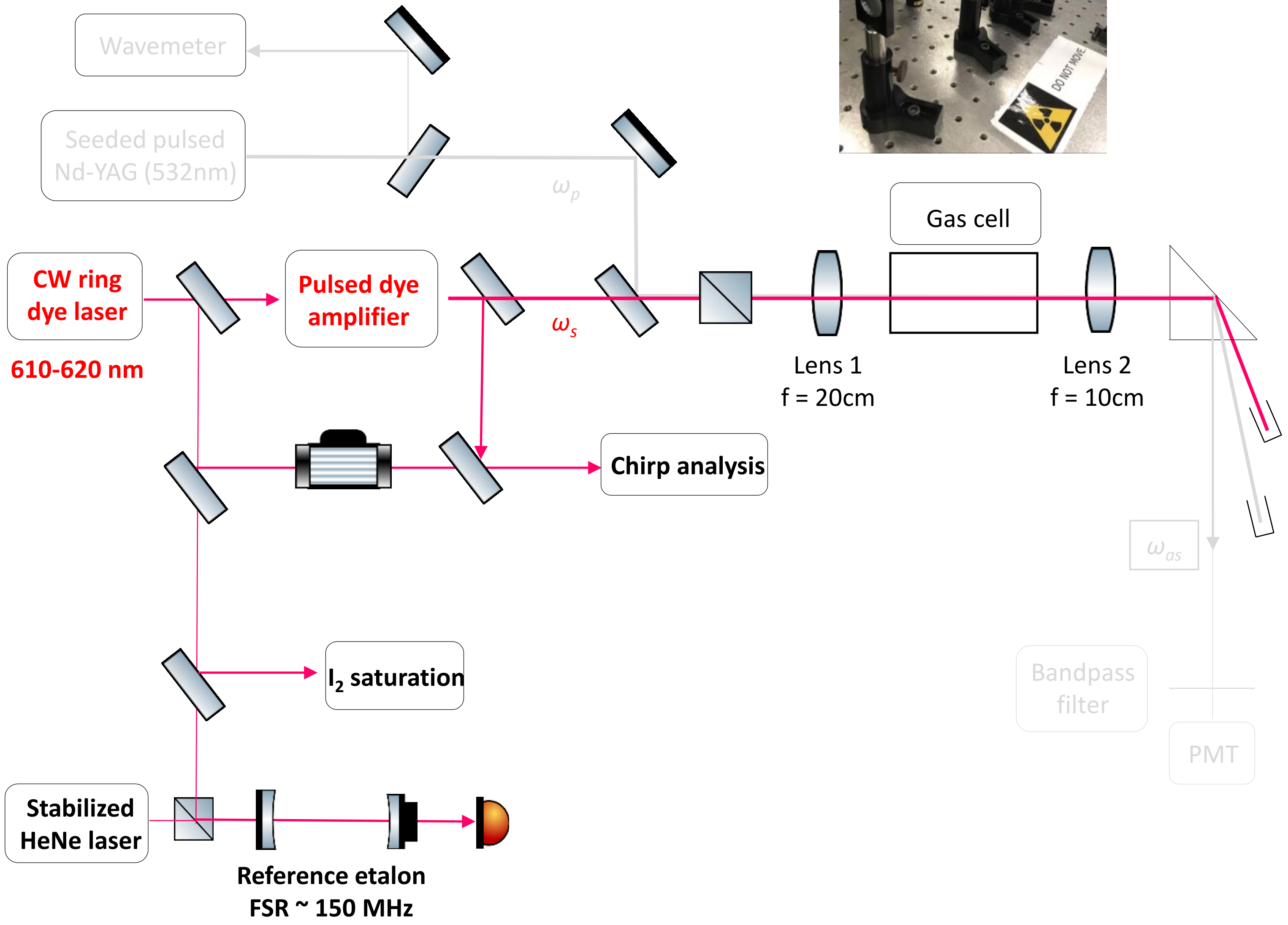


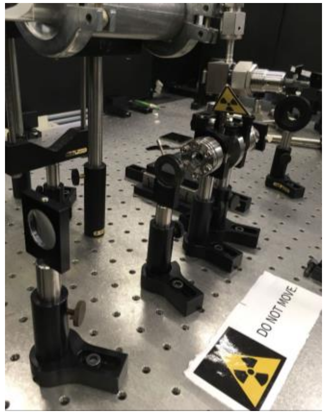


Freq. uncertainty:
6 MHz

Experimental Setup





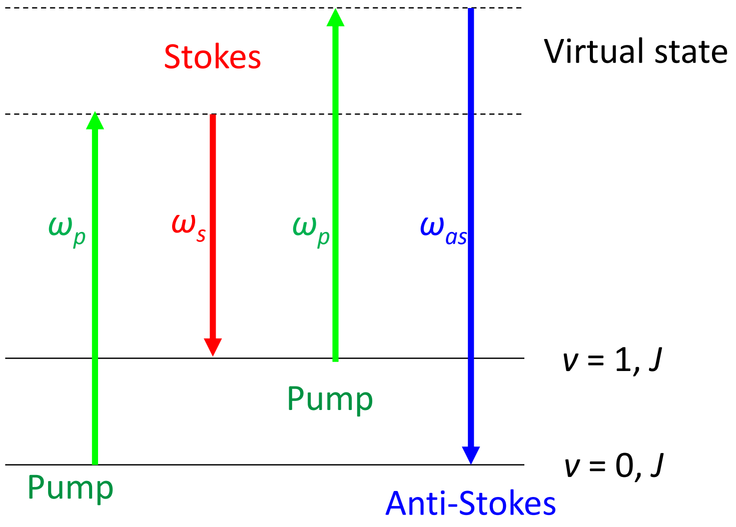


cw light freq. uncertainty:
1 MHz

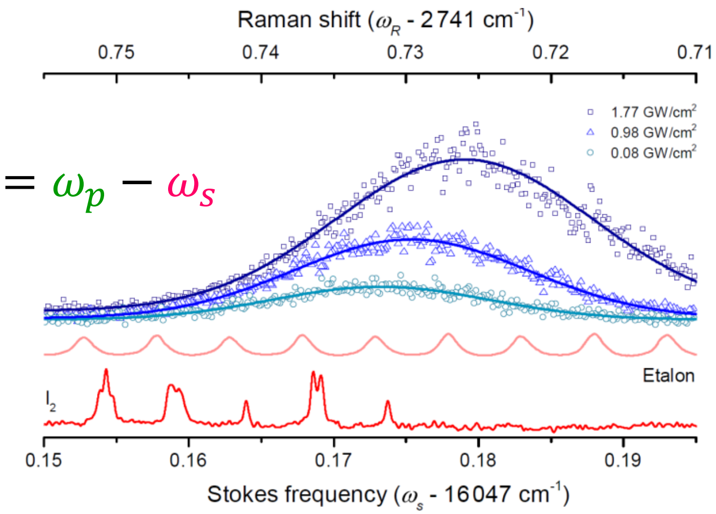
Stokes cw-pulse freq. offset

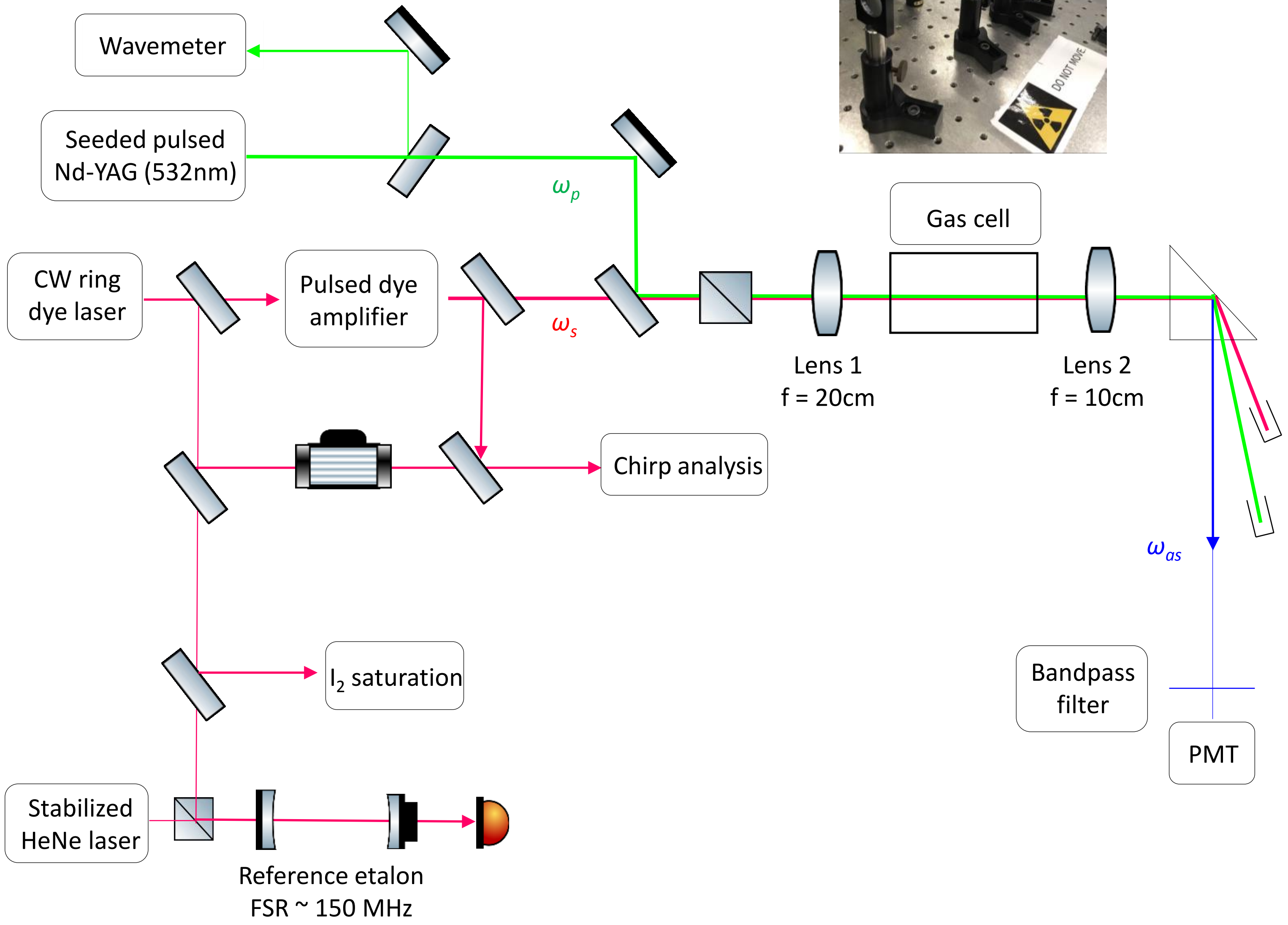
~ 20 (5) MHz for DCM dye
~ -30 (5) MHz for Rh. 101 dye

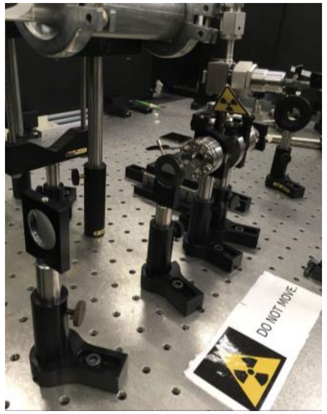
Experimental Setup



$$\omega_R = \omega_p - \omega_s$$







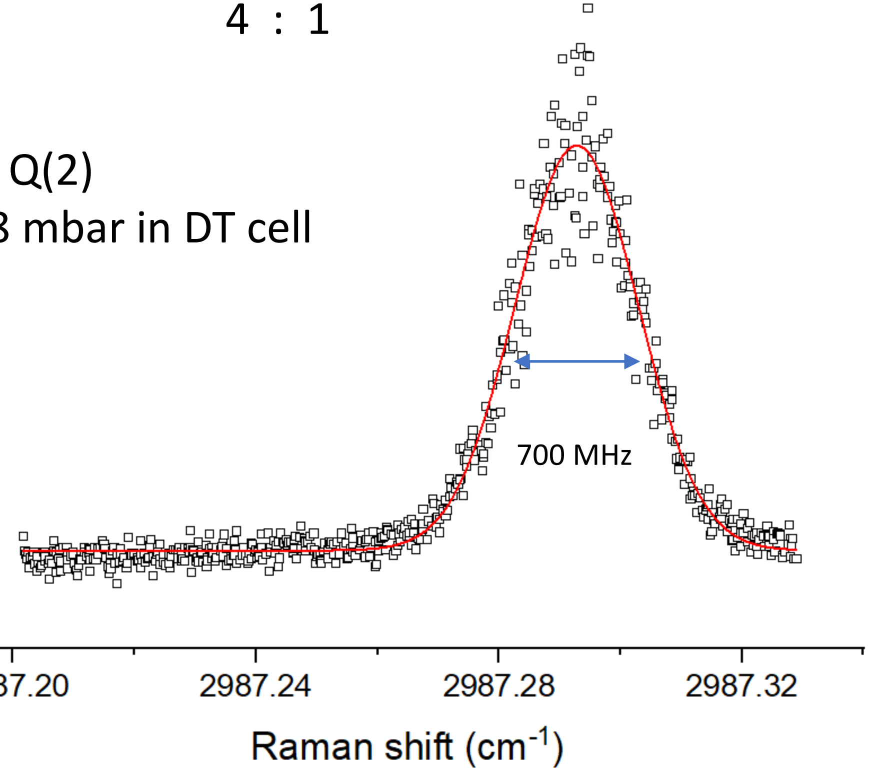
Benchmark: D_2 Q-branch

Preparation of DT

$D_2 + T_2 \rightarrow D_2 + DT + T_2$

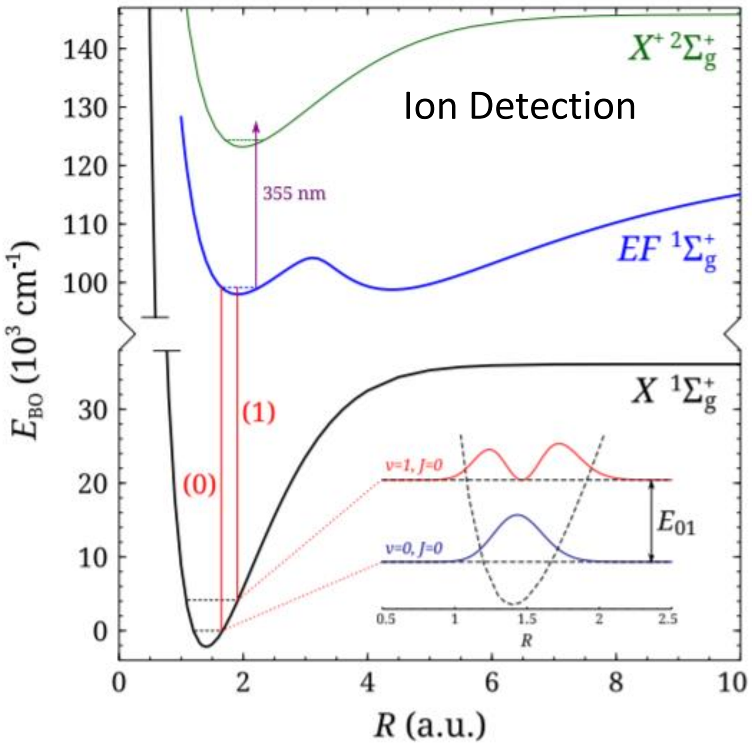
4 : 1

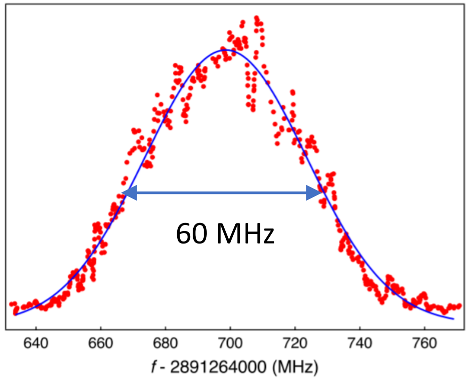
D_2 Q(2)
~ 8 mbar in DT cell



Fundamental band (v = 1 ← 0) with molecular beam setup

G. D. Dickenson et al., PRL 110, 193601 (2013)





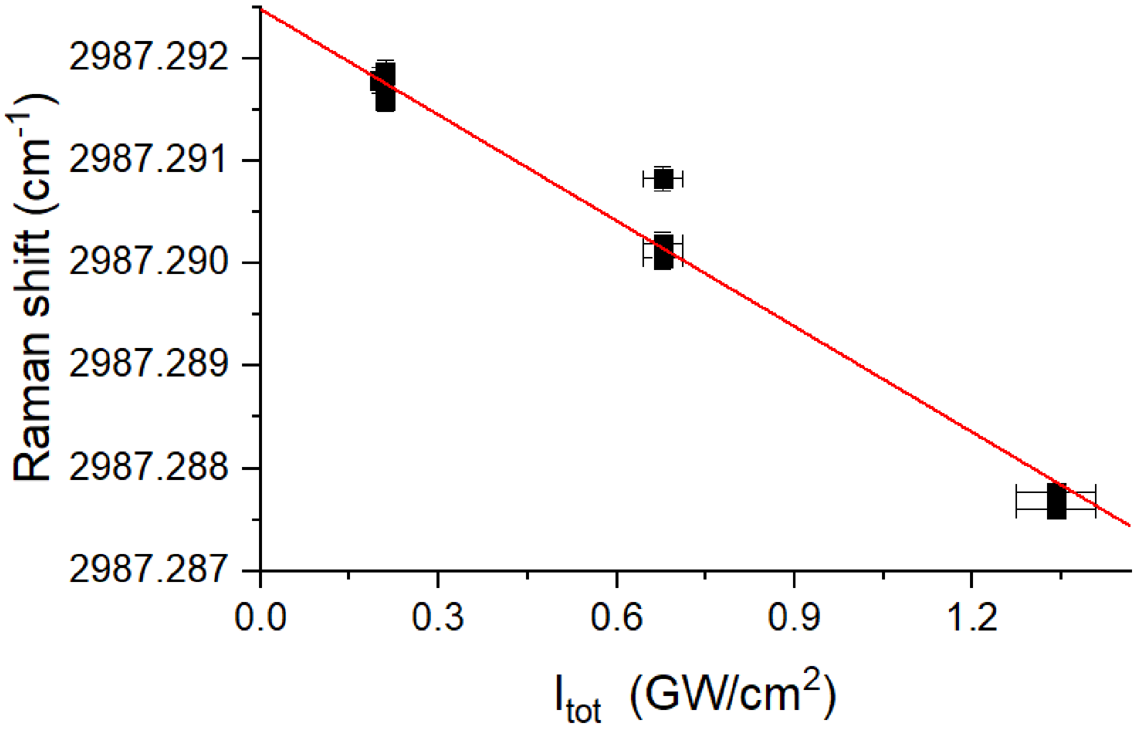
Uncertainty D_2 Q-branch

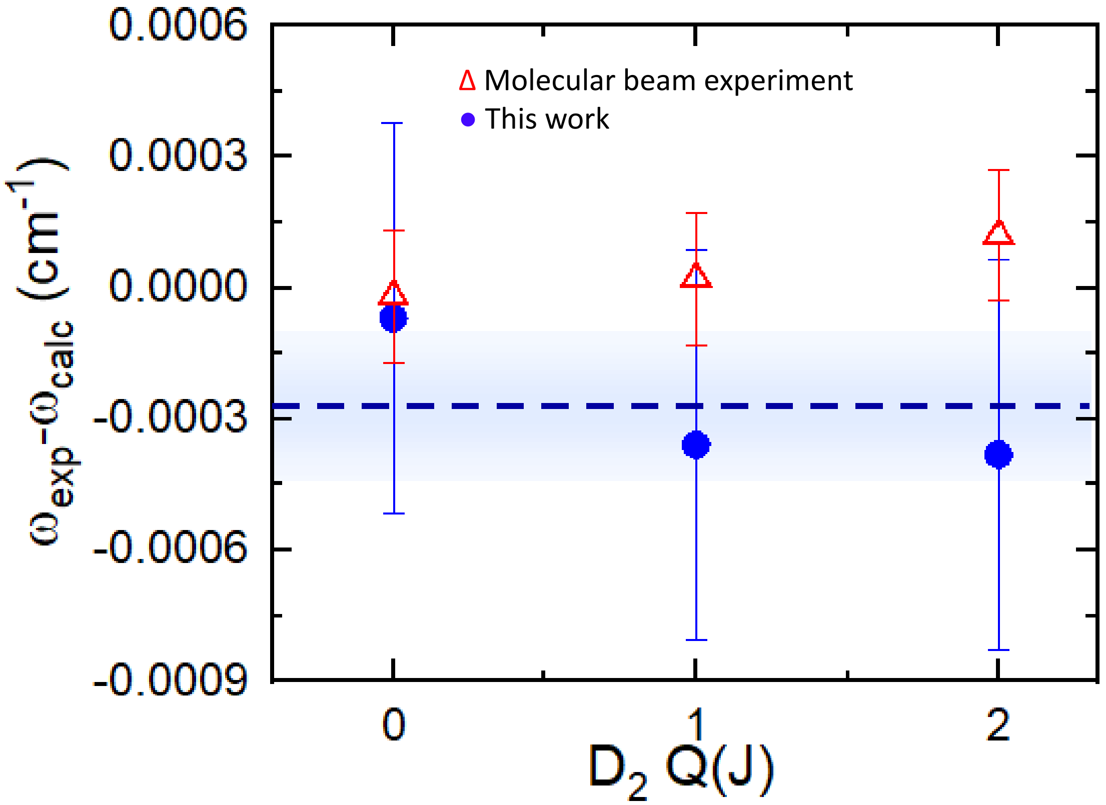
4.5 MHz / 1.5 x 10^{-4} cm^{-1}

Benchmark: D_2 Q-branch

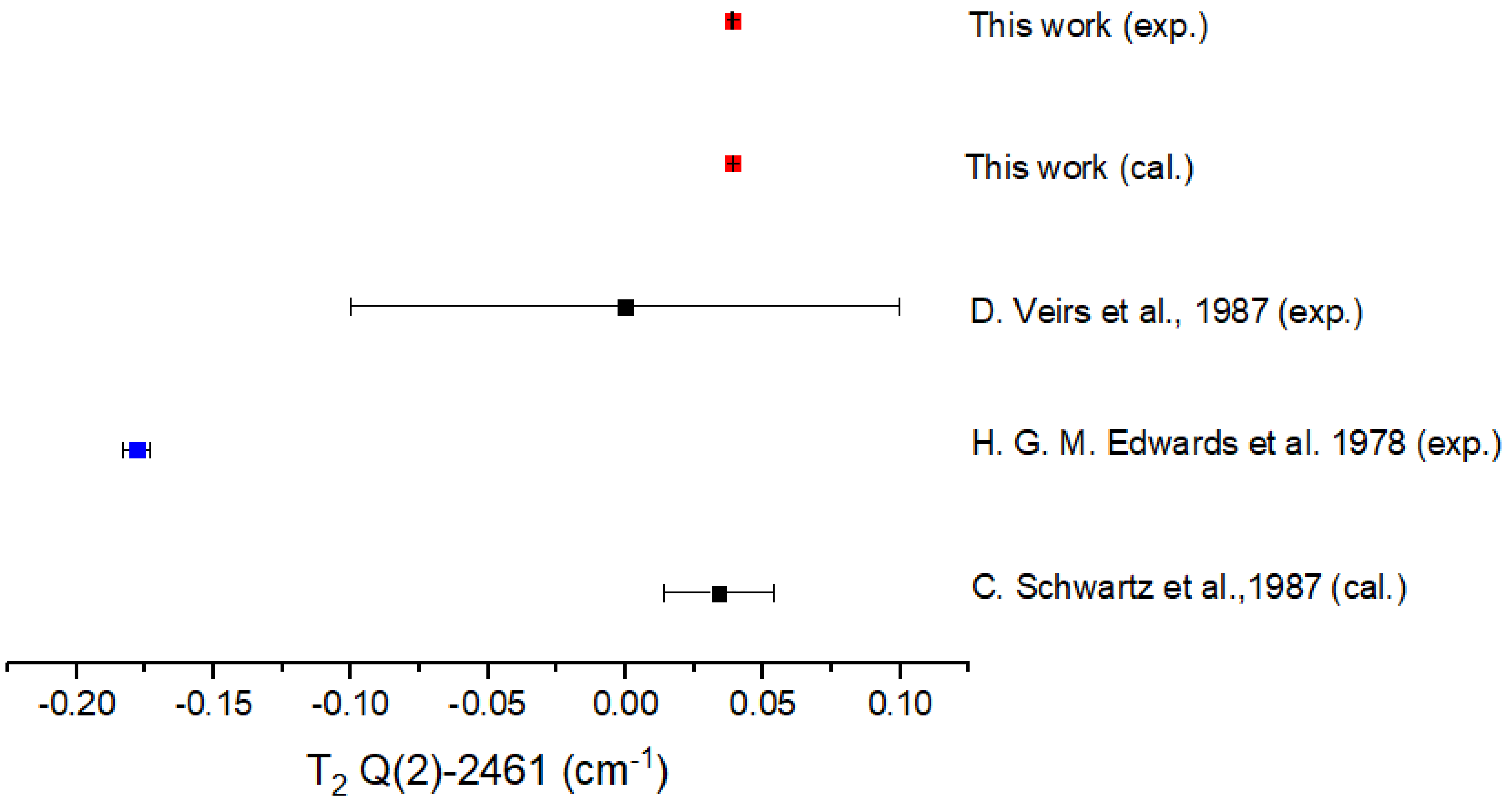
Uncertainty contribution (MHz)	
Pump (ω_P) calibration	6
Stokes (ω_S) cw calibration	2
Stokes cw–pulse chirp correction	5
AC-Stark analysis	6
Collisional shift	1
Statistics	7
Combined (1σ)	12

D_2 Q(2) ac-Stark analysis

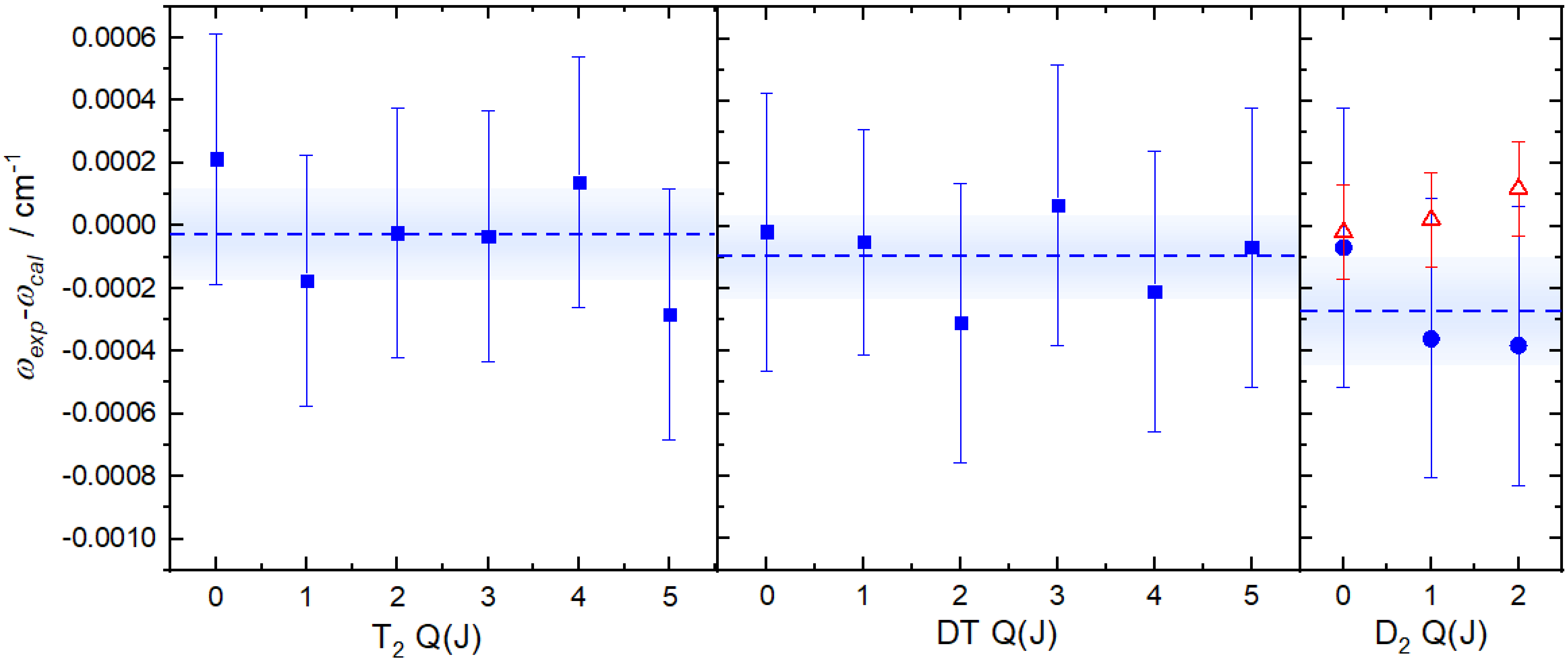




Comparison with old results



Comparison with calculation



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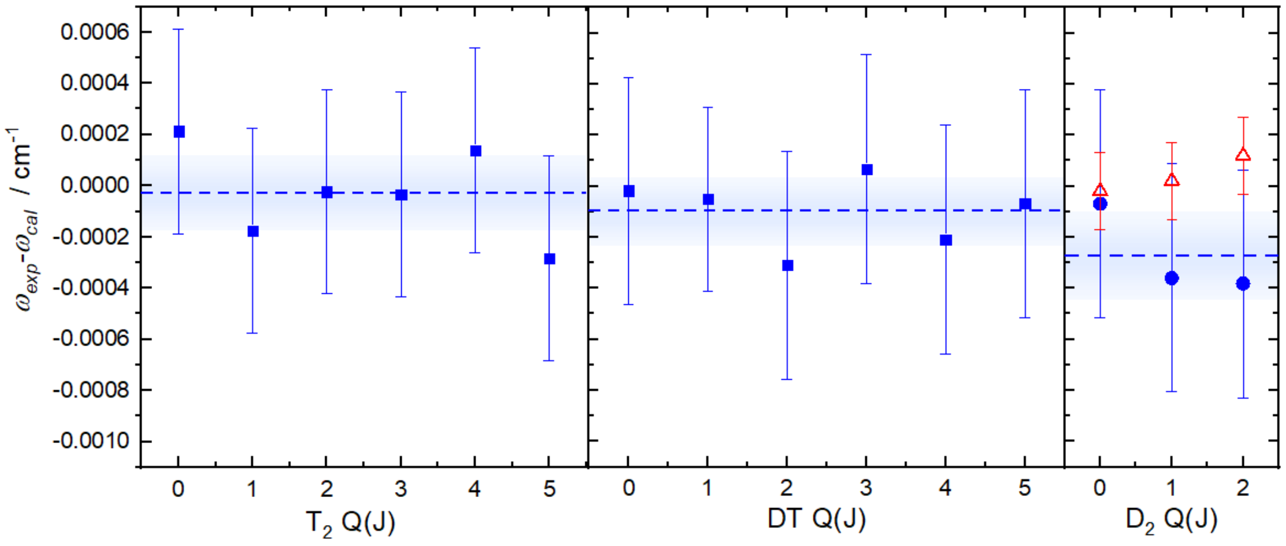

Mainly dominated non-adiabatic contribution of $E^{(2)}$

Possible to do full calculation on $E^{(2)}$
With uncertainty ~ 10^{-8} cm^{-1}

T_2 Q(1) uncertainty < 10^{-5} cm^{-1}
> **10-times** less than our measurement uncertainty

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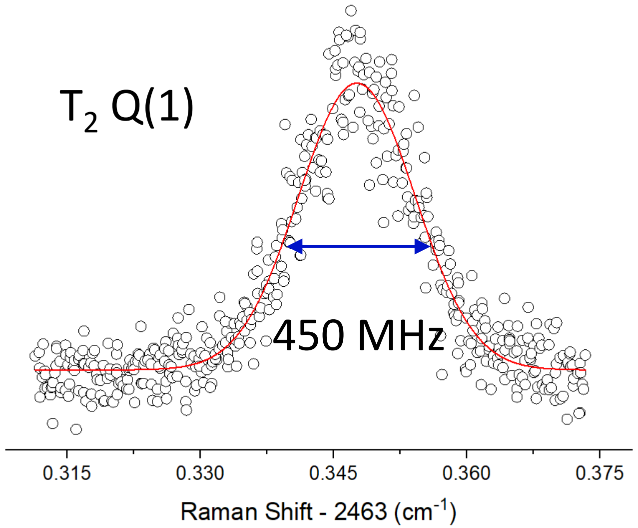
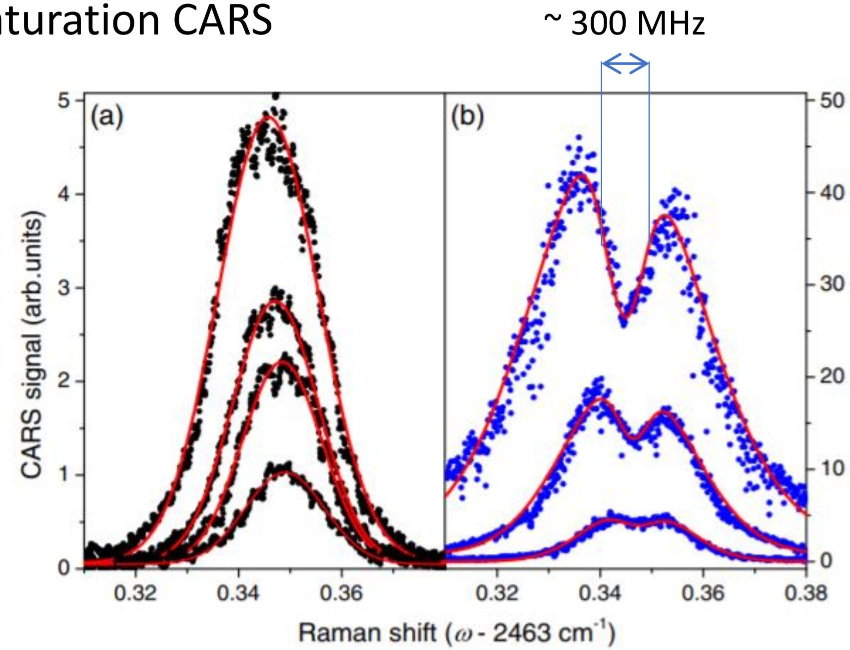


- Molecular beam CARS (not for tritiated species)
  ~100 MHz (laser bandwidth of current setup)

- Cooling sample cell with pre-cooled air
  300 K → ~ 100 K
  450 MHz → ~250 MHz

$$\text{FWHM} \sim \frac{2\omega_0}{c}\sqrt{\frac{2k\boldsymbol{T}\ln 2}{M}}$$

- Saturation CARS



Saturation of CARS profile

R. P. Lucht and R. L. Farrow

Vol. 6, No. 12/December 1989/J. Opt. Soc. Am. B 2313

Saturation effects in coherent anti-Stokes Raman scattering spectroscopy of hydrogen

Robert P. Lucht and Roger L. Farrow

Combustion Research Facility, Sandia National Laboratories, Livermore, California 94551

Received May 2, 1989; accepted August 28, 1989

Saturation of coherent anti-Stokes Raman scattering (CARS) spectra of the $Q(1)$ line of the hydrogen (1, 0) vibrational transition was investigated experimentally by using high-resolution lasers and theoretically by solving the time-dependent density matrix equations. The saturation behavior of hydrogen is complicated by the large Doppler width of the resonance and the high rate of velocity-changing collisions relative to dephasing collisions. Experimentally, CARS line shapes and saturation curves were measured in pure hydrogen at pressures of 100 and 3050 Torr. Surprisingly, the measured saturation intensity was found to be less at 3050 Torr than at 100 Torr. The

1. Saturation in upper level
2. Interference coherence (Q_i) by different velocity classes

$$I_a \sim \left| \sum_i N \left(\frac{\partial \alpha}{\partial q} \right) A_p \boldsymbol{Q_i} \right|^2$$

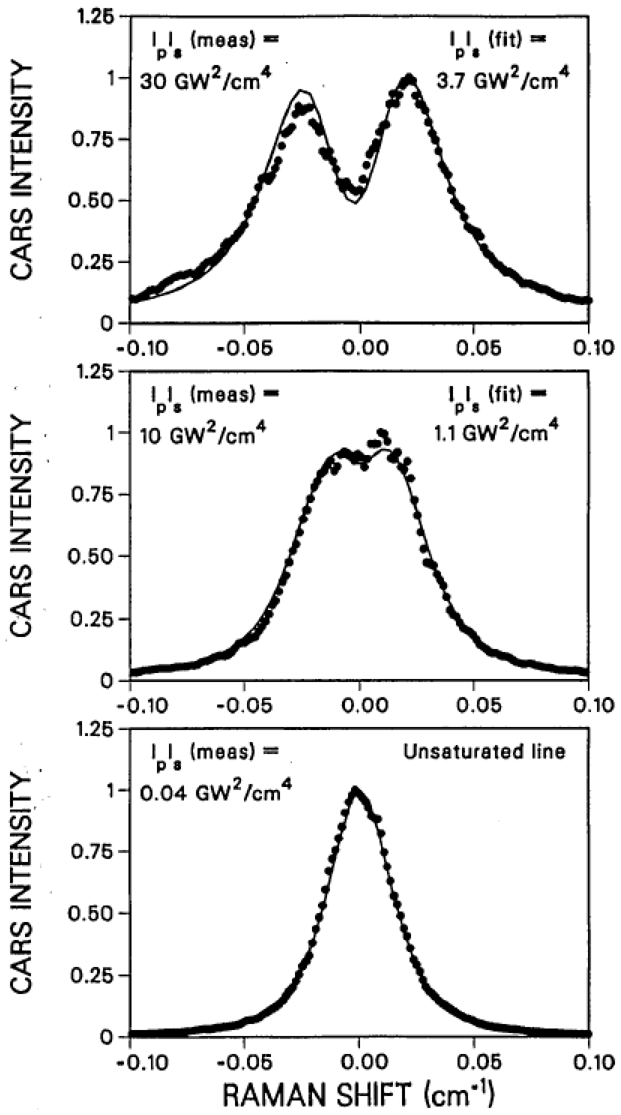
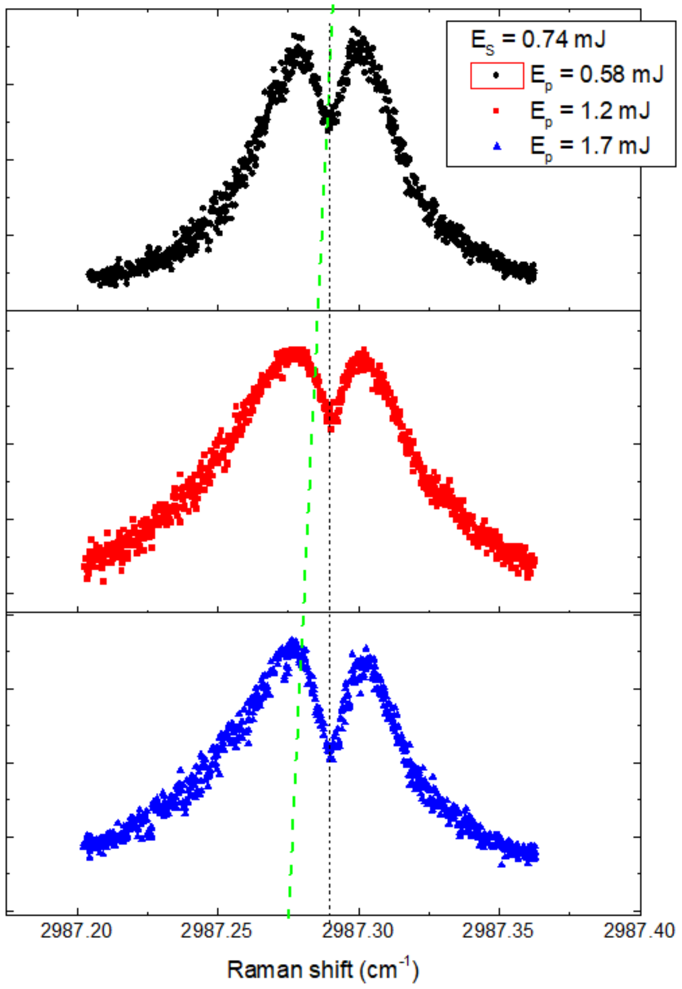


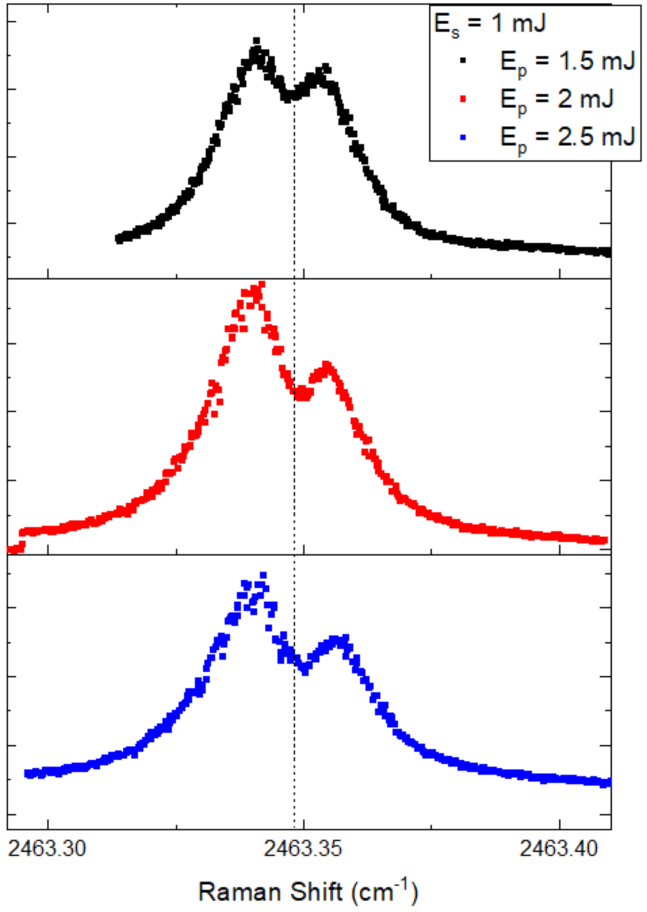
Fig. 2. Comparison of experimental and theoretical line shapes for the $Q(1)$ line of hydrogen at 100 Torr at three different laser intensities.

Saturation of CARS profile

D_2 Q(2)

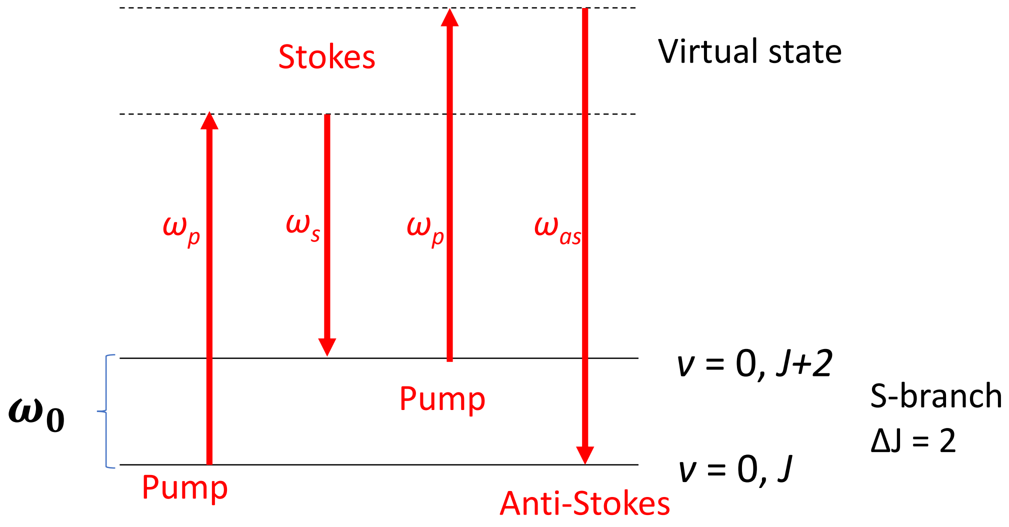


T_2 Q(1)



- Unexpected ac-stark shift
- Doppler profile getting more asymmetric at high energy
- Position of saturation dip is not centered at Doppler profile
- Need full understanding about the saturated profile

Pure Rotational Transition



$$\omega_{as} = 2\omega_p - \omega_s$$

	S(0) Doppler Width @ room temp	Expected linewidth
D_2	33 MHz	<100 MHz (depending on laser bandwidth)
HT	44 MHz	
DT	27 MHz	
T_2	22 MHz	

T_2 S(0) ω_0 ~ 120 cm^{-1}

Requiring **2** laser sources working at **similar freq.**
+
Separate anti-Stokes for detection

H.G.M. Edwards et al. J. Chem. Sot. Faraday Trans. II 74, 1203-1207 (1978).

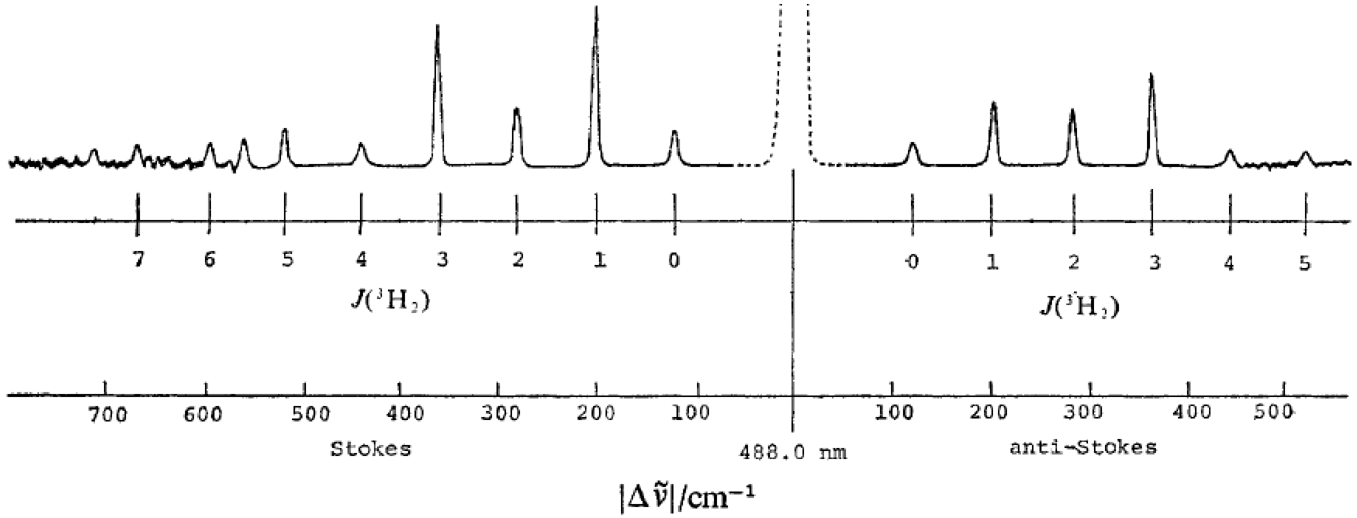


FIG. 1.—Microdensitometer traces (combined) of the photographically-recorded Stokes and anti-Stokes regions of the pure rotational Raman spectrum of $^3H_2$.

Conclusion & Outlook

- D_2 Q(0)-Q(2) show good agreement with molecular beam experiment
- T_2 and DT Q(0)-Q(5) have been measured with **12 MHz uncertainty**
- All of them have good agreement with latest calculated value

- Move on to last isotopologue HT

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