



vrije Universiteit amsterdam



Carbon Chain Spectroscopy

Some results from the VU-CRDS experiment

Wim Ubachs

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Dongfeng Zhao, Harold Linnartz

DAN-II meeting 28 nov 2018

Work connected to DIBs

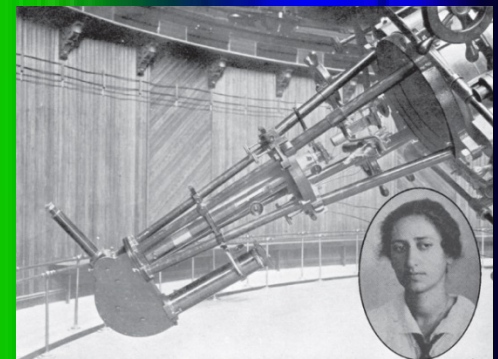
- Small carbon chains
- Nonlinear carbon chains

Building blocks of:

- PAHs
- Fullerenes

Observations

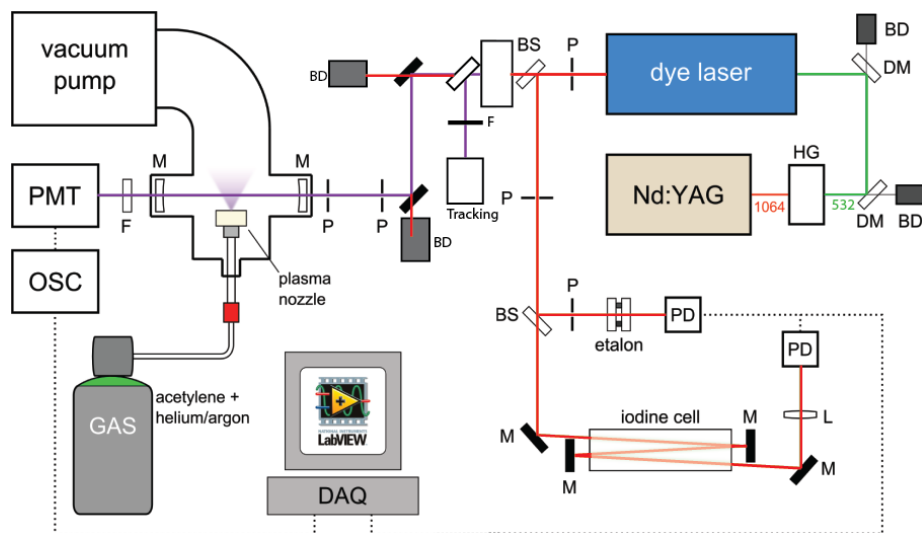
- diffuse vs. dense clouds
- radio astronomy vs optical



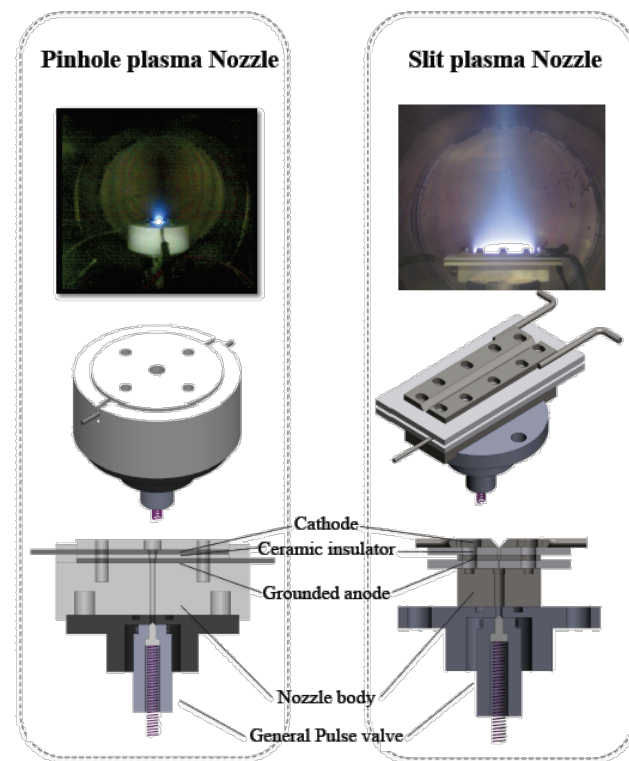
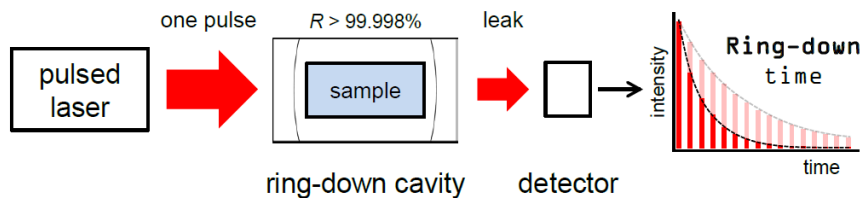
Mary Lea Heger - 1919

Cavity Ring Down Spectroscopy in plasma jet expansion

Setup

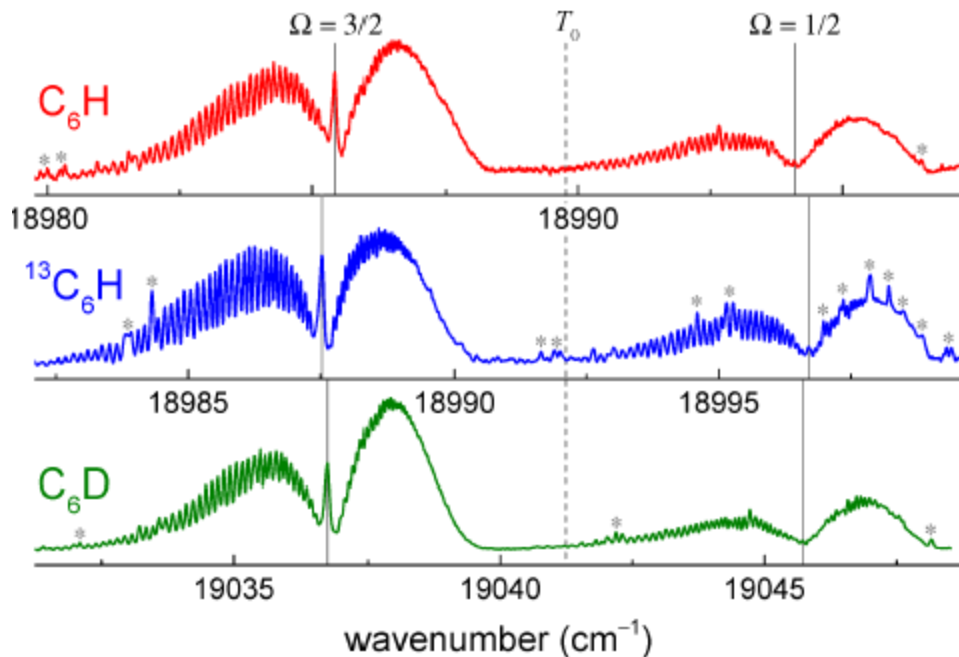


CRD



CRD is limited – combine with
 + REMPI-TOF studies
 + Matrix studies
 + DFT calculations
 + Isotope substitution (^{13}C , D)

Linear molecules: C_6H – 1. Origin band in high-resolution

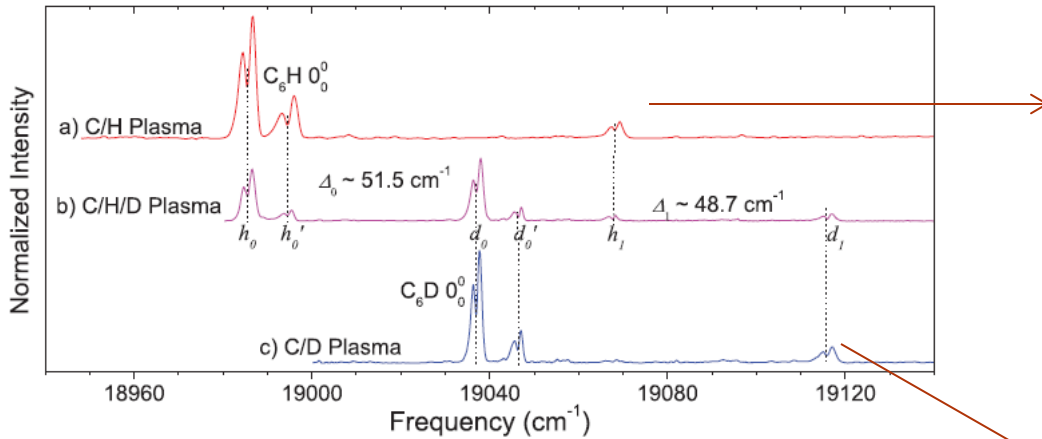


Identification:

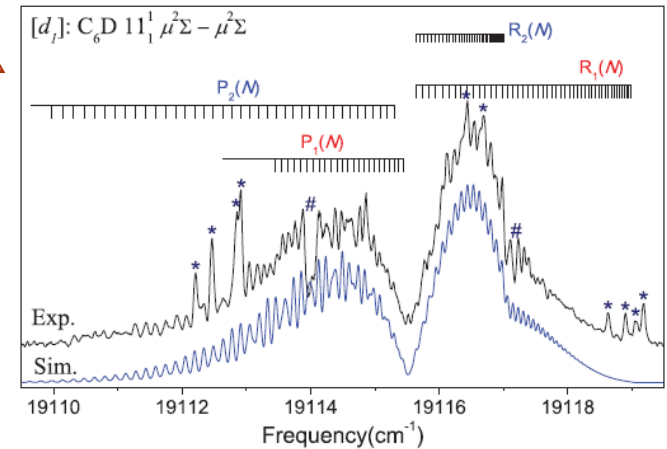
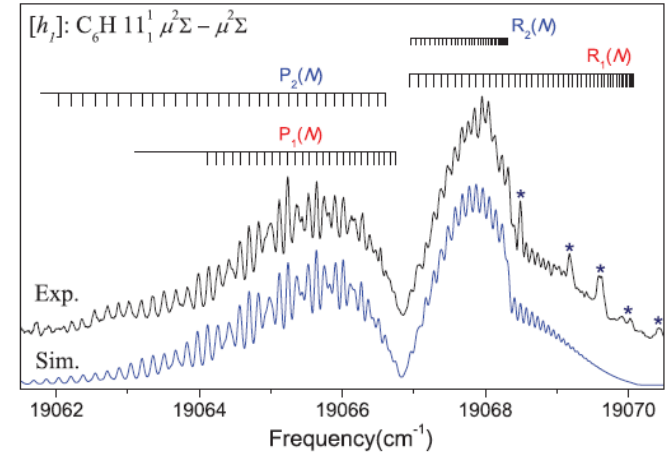
- Matrix mass-deposit spectra
- Microwave ground state
- Rotational constants
- Isotopic substitution

The $B^2\Pi_{\Omega} - X^2\Pi_{\Omega} (0,0)$ Origin Band

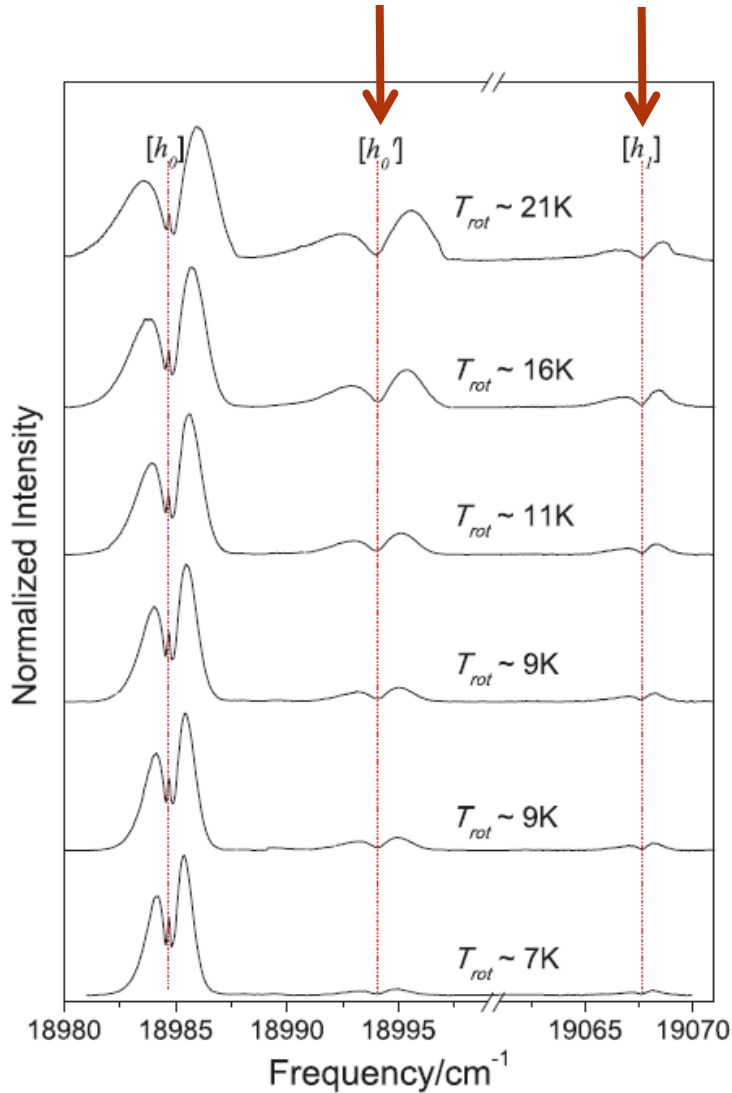
Linear molecules: C₆H – 2. Renner-Teller ground state



$\Sigma-\Sigma$ character –
bending modes

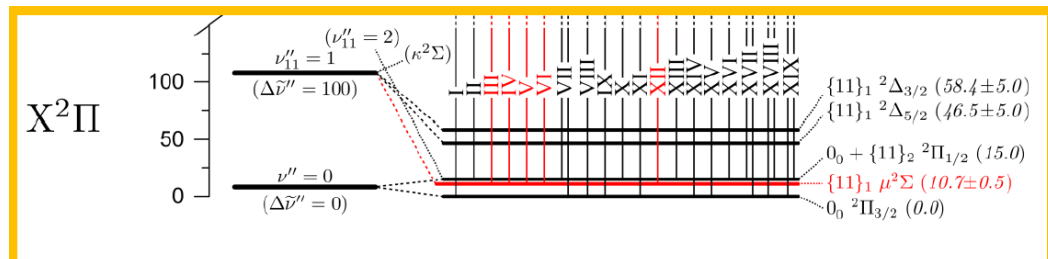
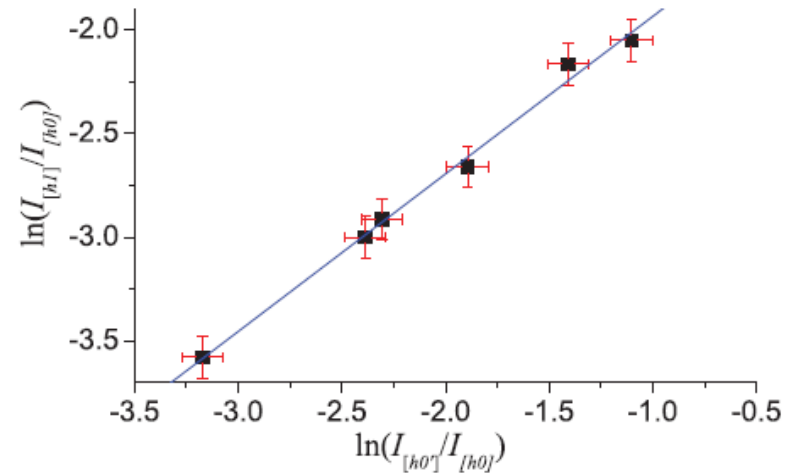


Linear molecules: C₆H – 2. Energy of the bending mode



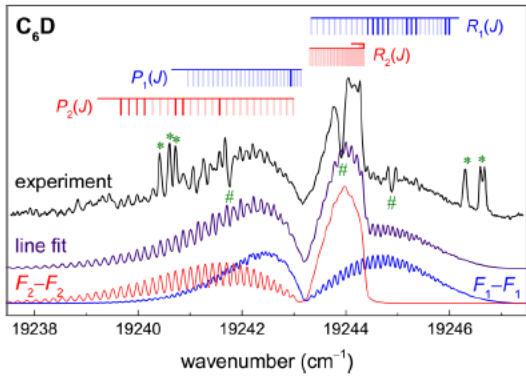
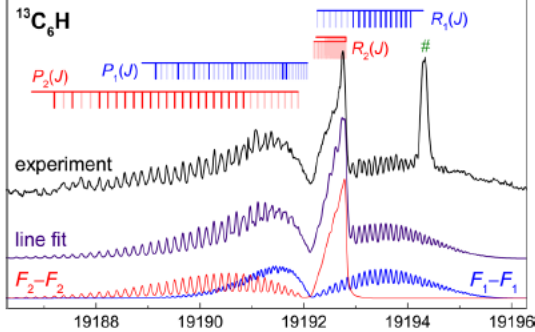
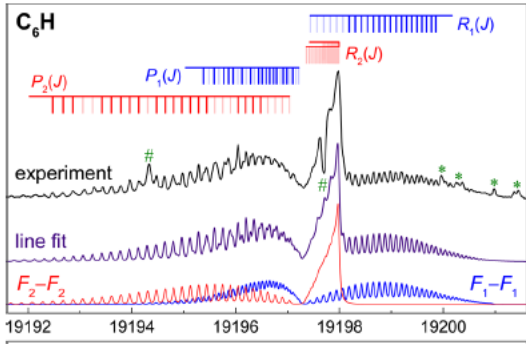
From Boltzmann temperature

$$\ln\left(\frac{I_{[h_1]}}{I_{[h_0]}}\right) = \frac{E(11_1 \mu^2 \Sigma)}{|A_0|} * \ln\left(\frac{I_{[h_0']}}{I_{[h_0]}}\right) + C$$

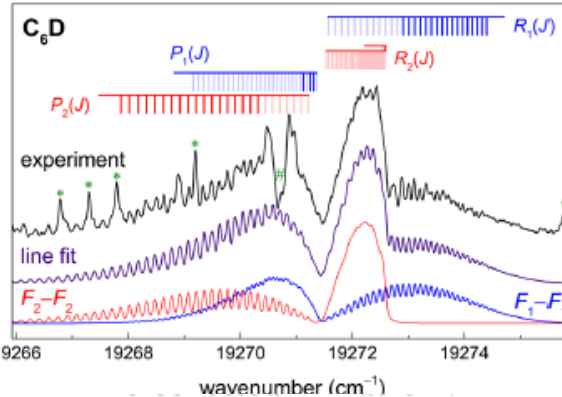
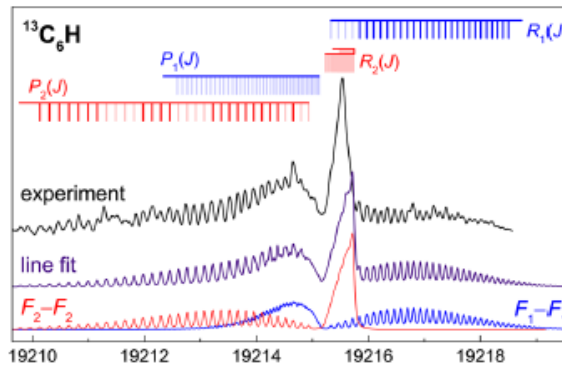
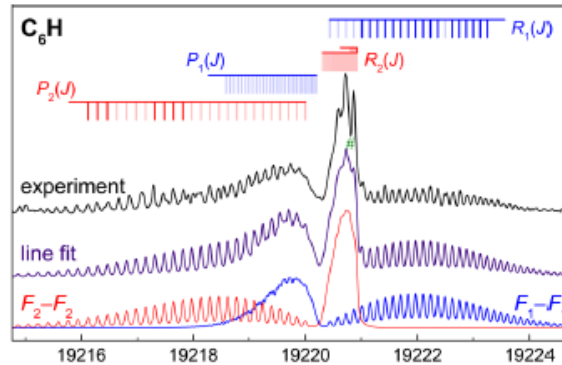


Microwave: Gottlieb, McCarthy, Thaddeus

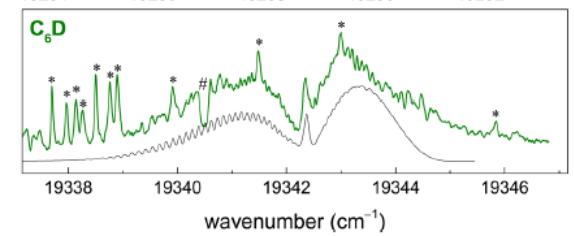
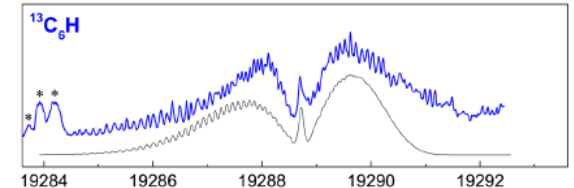
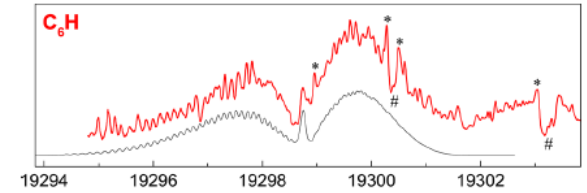
Linear molecules: C₆H – 3. Vibronic structure



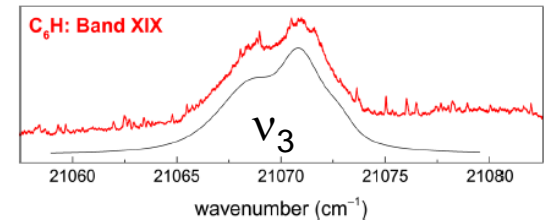
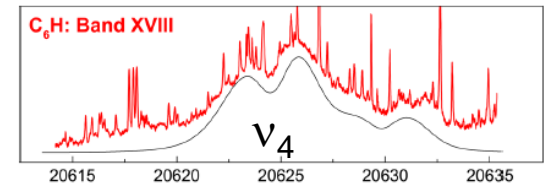
Band IV: {10}¹{11}₁
 $\mu^2\Sigma-\mu^2\Sigma$ Vibronic Band.



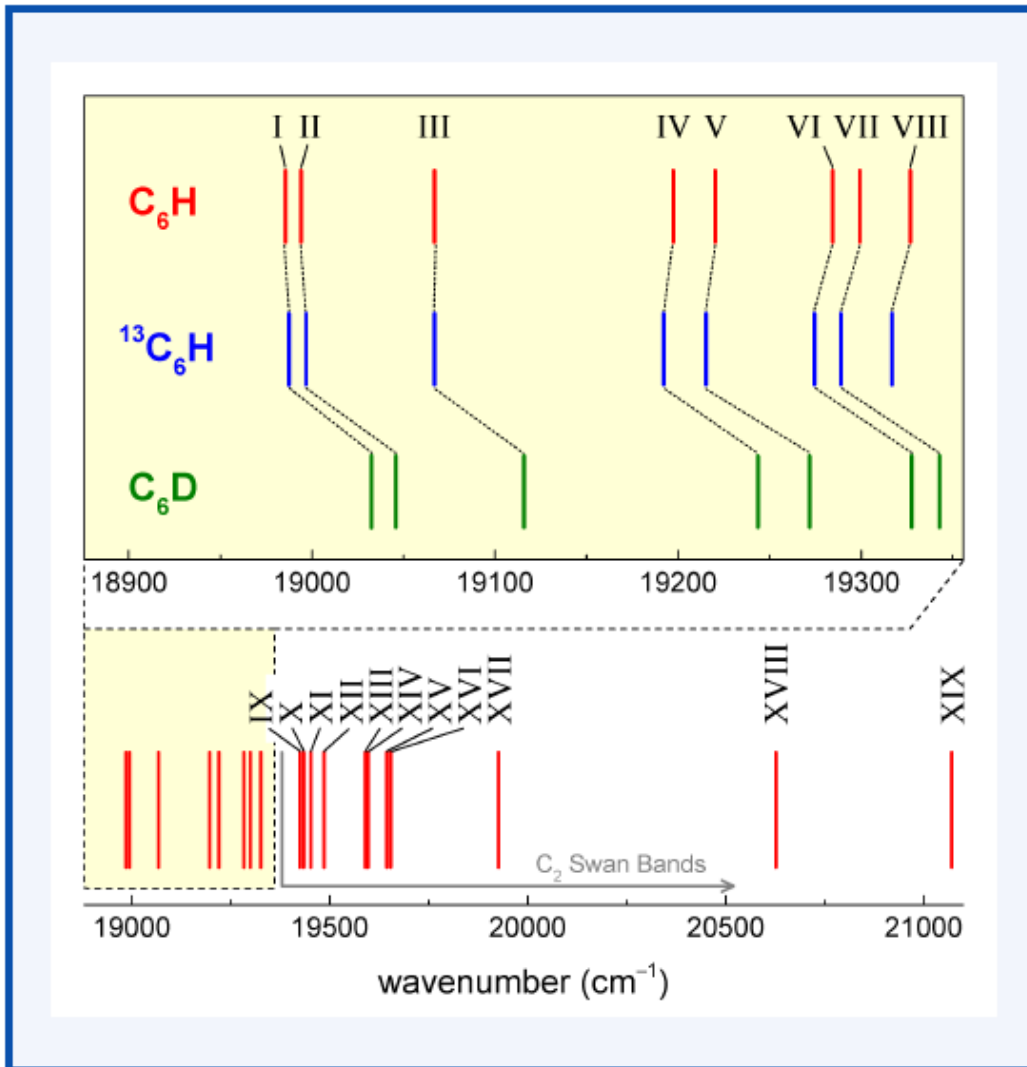
Band V: {10}¹{11}₁
 $\kappa^2\Sigma-\mu^2\Sigma$ Vibronic Band.



Band VII: B²Π_Ω-X²Π_Ω
 Cannot be non-degenerate



Linear molecules: C_6H – 3. Vibronic structure



$B^2\Pi - X^2\Pi$

Knowledge:

$\Pi-\Pi$ transitions (stretch)

$\Sigma-\Sigma$ transitions (bending)

+ ab initio modes (ground)

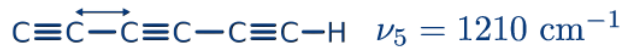
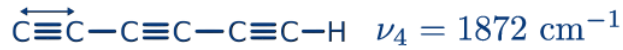
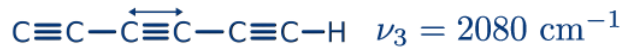
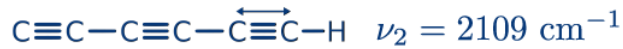
→ Assignment

Overview spectrum (473-527 nm)

Linear molecules: C₆H – 3. Vibronic structure

Ab initio calculations
(ground state)

Six stretching modes



Five doubly degenerate
bending modes

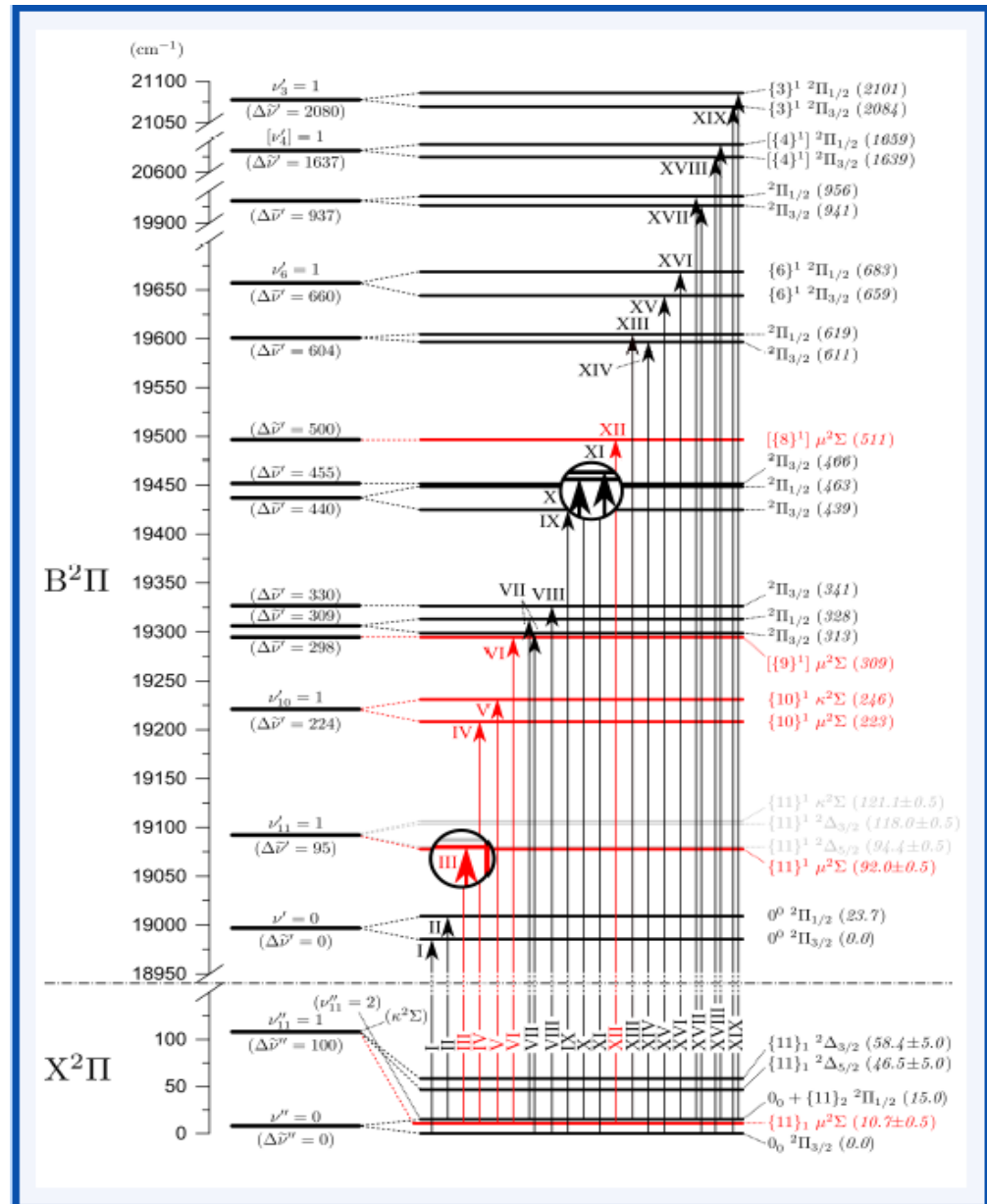
$$\nu_7 = 561 - 679 \text{ cm}^{-1}$$

$$\nu_8 = 519 - 553 \text{ cm}^{-1}$$

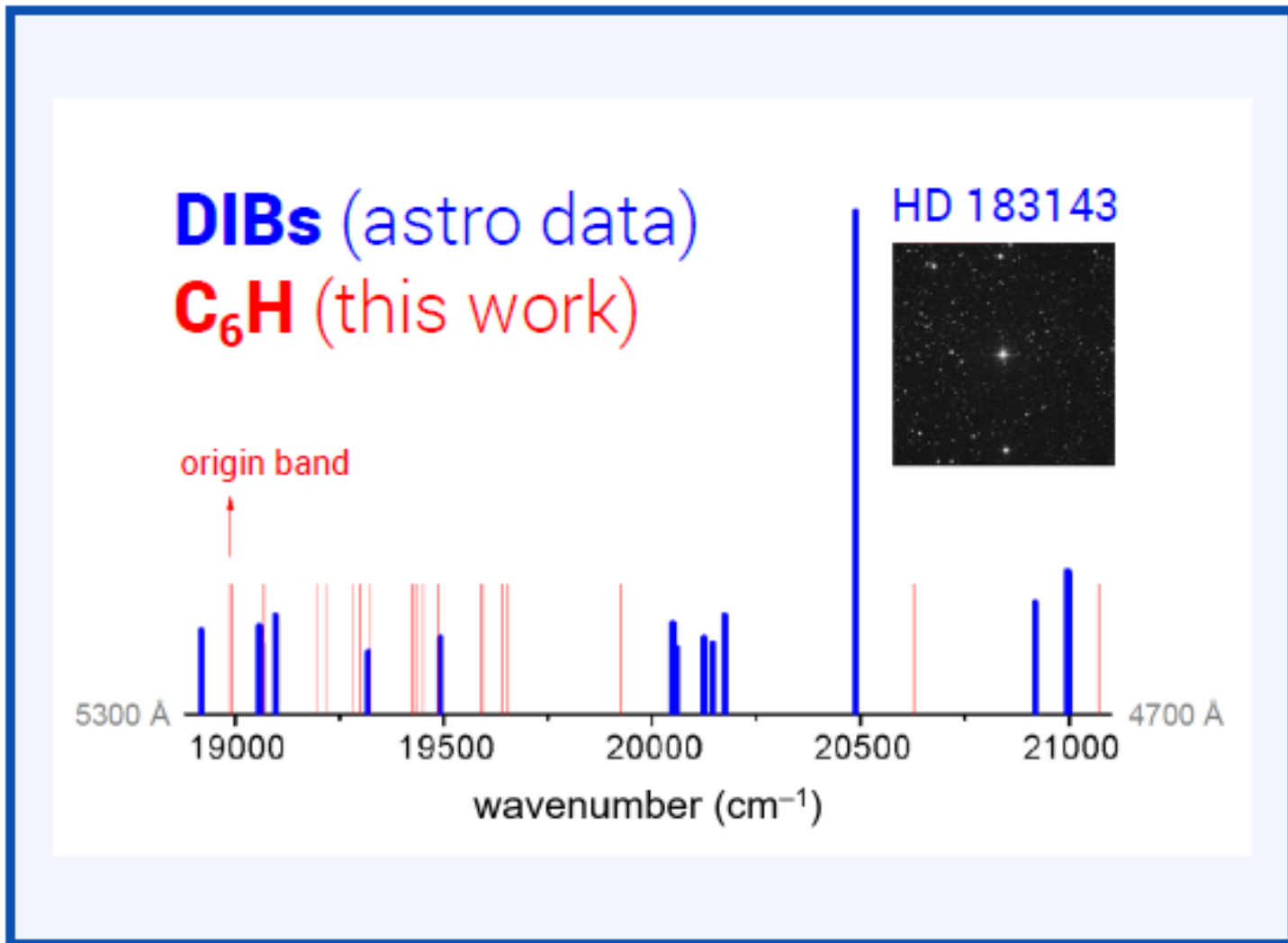
$$\nu_9 = 396 - 445 \text{ cm}^{-1}$$

$$\nu_{10} = 214 - 255 \text{ cm}^{-1}$$

$$\nu_{11} = 110 - 120 \text{ cm}^{-1}$$

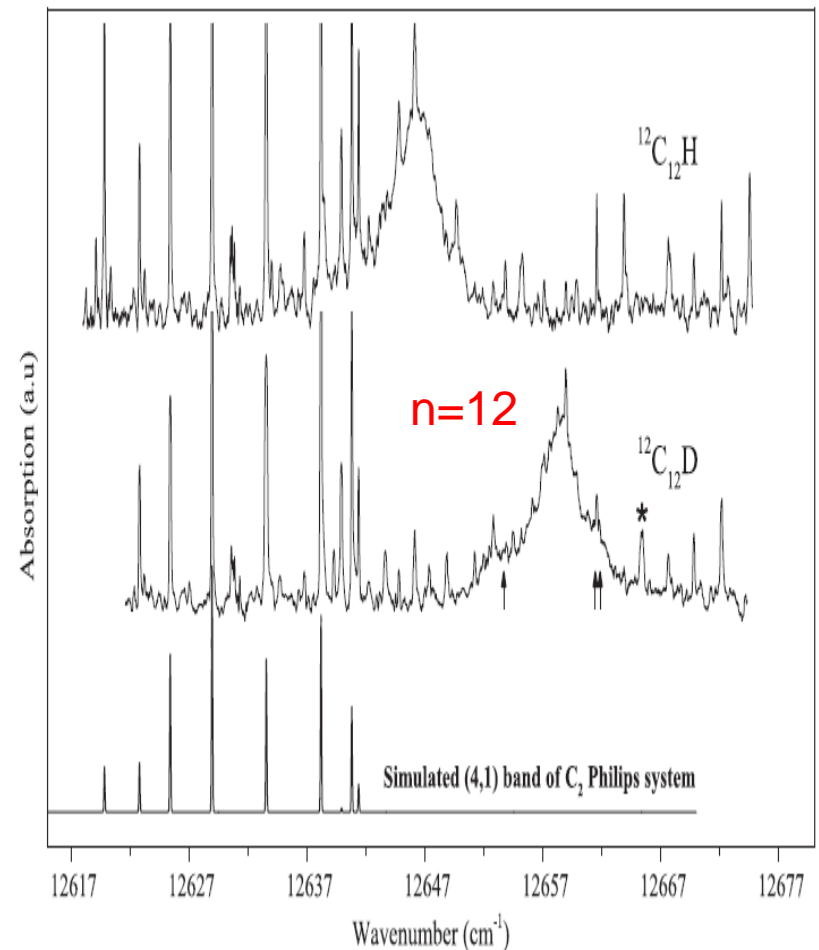
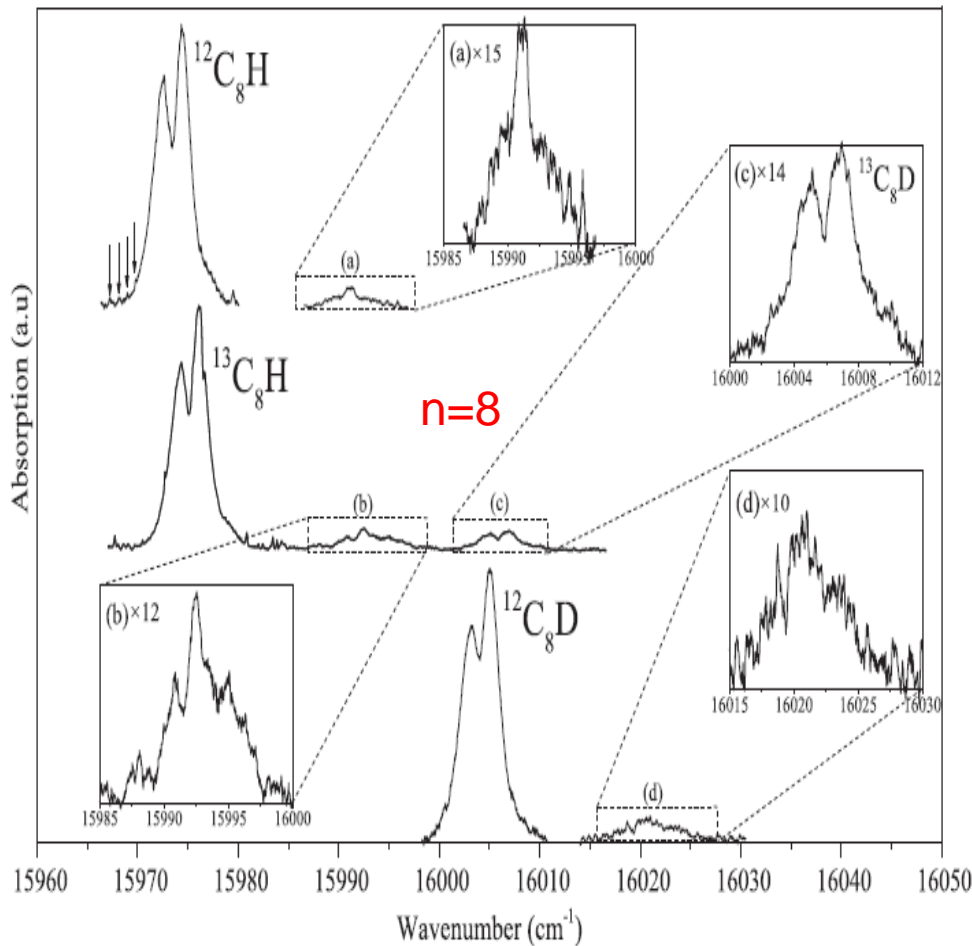


Linear molecules: C_6H – DIBs

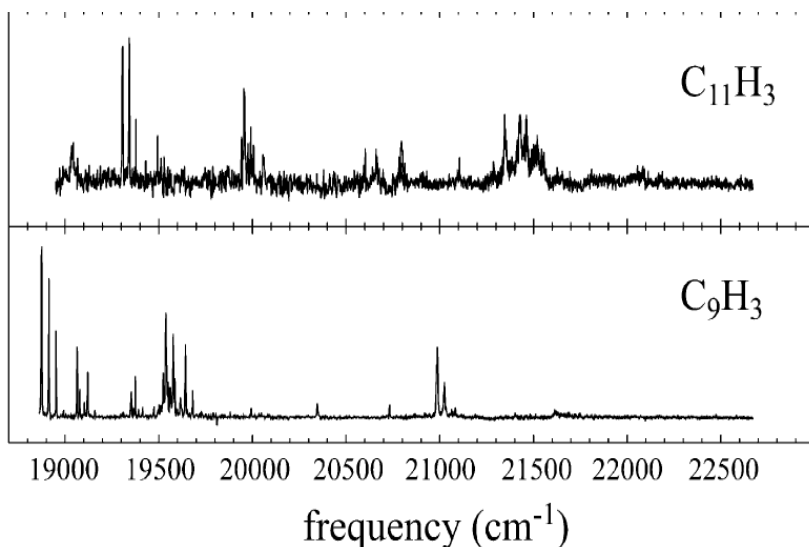


Linear long-chain molecules: C_8H , $C_{10}H$, $C_{12}H$ (^{13}C , D)

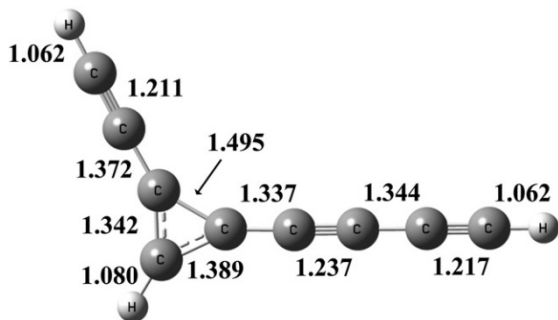
- Redshifted: particle-in-box
- Life-time broadening for longer chains; Internal conversion
- $\Gamma(n=8) = 0.8 \text{ cm}^{-1}$; $\Gamma(n=10) = 3.8 \text{ cm}^{-1}$; $\Gamma(n=12) = 4.8 \text{ cm}^{-1}$



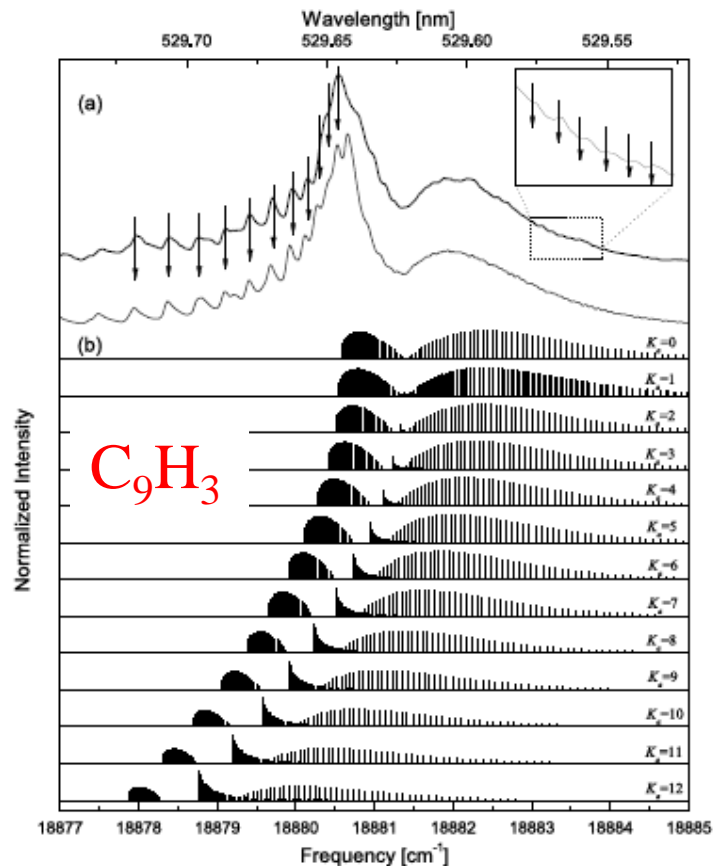
Bent geometry from spectroscopy



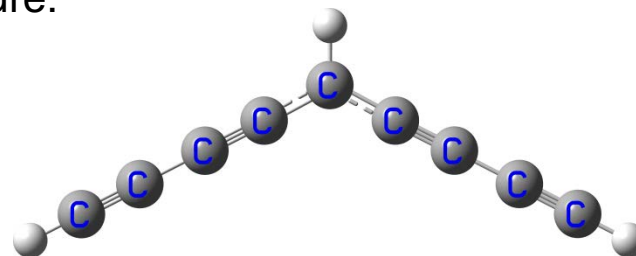
Mass-selective REMPI:
Structure determination not available.
(Schmidt et al., *Int. J. Mass Spectr.*, **2003**, 107, 6550)



(Zhang, *J. Chem. Phys.*, **2004**, 121, 8212)



High-resolution CRDS:
K-stack structure and partially resolved rotational structure, suggesting the likely C_9H_3 structure:



(*Chem. Phys. Lett.*, **2011**, 501, 232)

Spectra of C_nH_3 with

pure H

pure D

50-50% H/D

Molecular symmetry (three positions for H)

- C_s or C_1 : Three H atoms are NON-interchangeable

Eight isotopologues are expected with **equal** production

probability: HHH, HHD, HDH, DHH, HDD, DHD, DDH, DDD

- C_{2v} or C_2 : Two H atoms are interchangeable (e.g., H^I and H^{III})

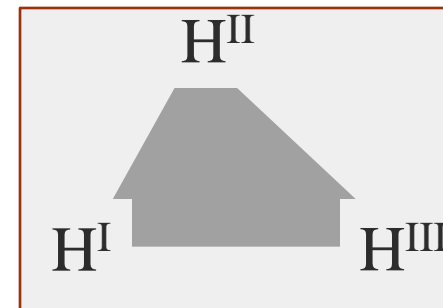
Six isotopologues are expected: HHH, **HHD=DHH**, HDH, **HDD=DDH**, DHD, DDD,

where **HHD and HDD** have **two times** the production probability than other four;

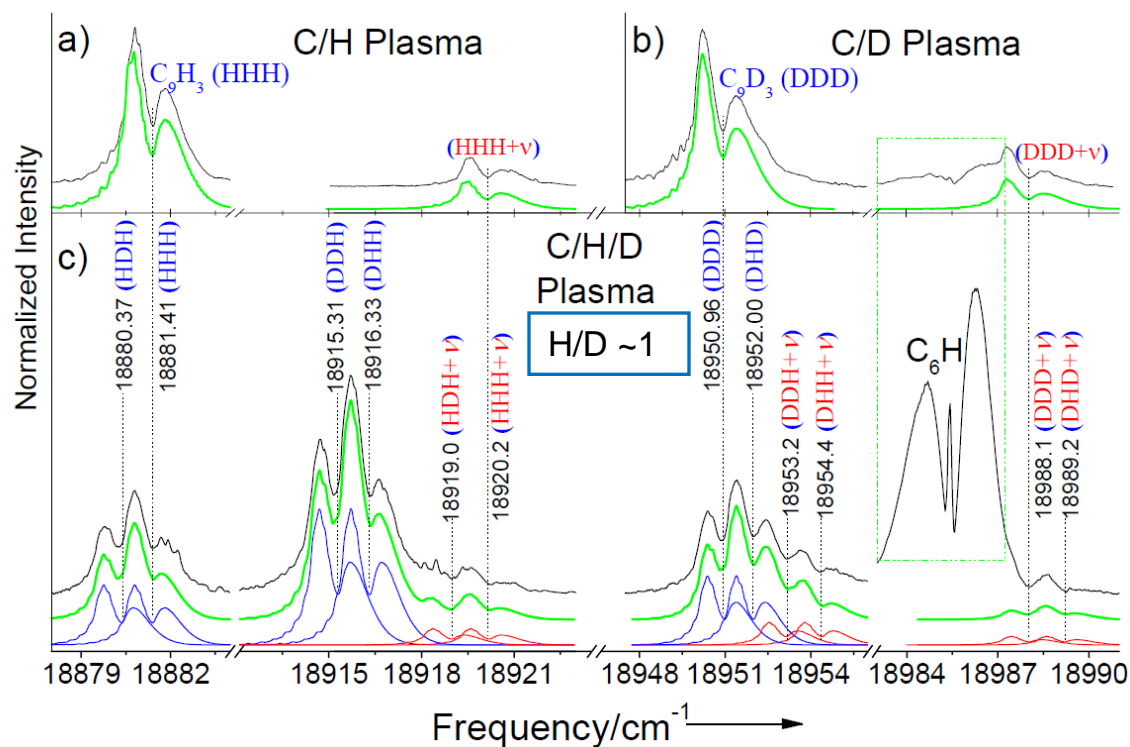
- C_{3v} or D_{3h} : All three H atoms are interchangeable

Four isotopologues are expected: HHH, **HHD=HDH=DHH**, **HDD=DHD=DDH**, DDD,

where **H_2D and HD_2** have **three times** the production probability wrt H_3 and D_3 .



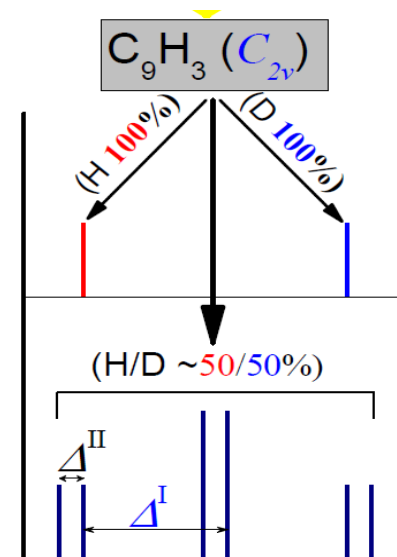
C₉H₃: C_{2v} case



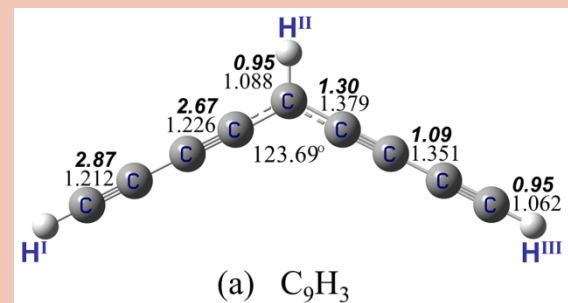
For both origin and bending vibronic band transitions

$$\Delta_{\text{H/D}}^{\text{I}} = +34.90 \text{ cm}^{-1}$$

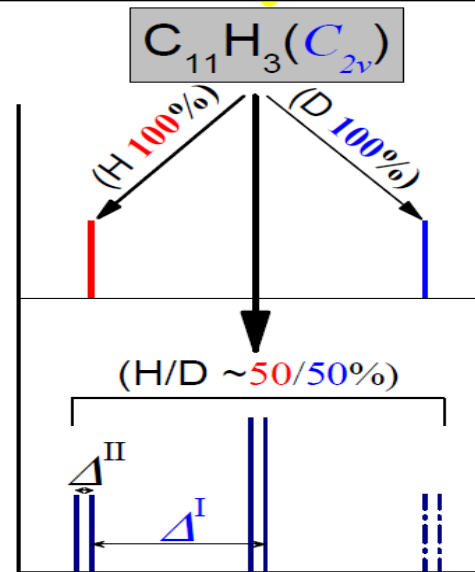
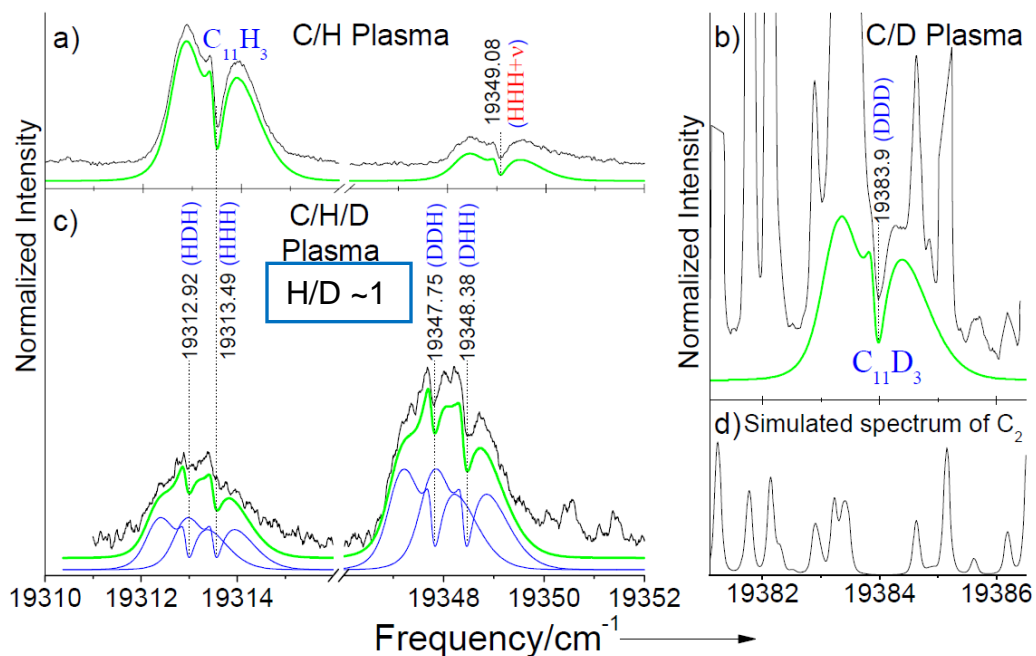
$$\Delta_{\text{H/D}}^{\text{II}} = -1.04 \text{ cm}^{-1}$$



Combined with DFT-B3LYP calculations on rotational constants(A, B, C), electronic transition energy, and low-lying bending vibration, molecular structure is determined as:

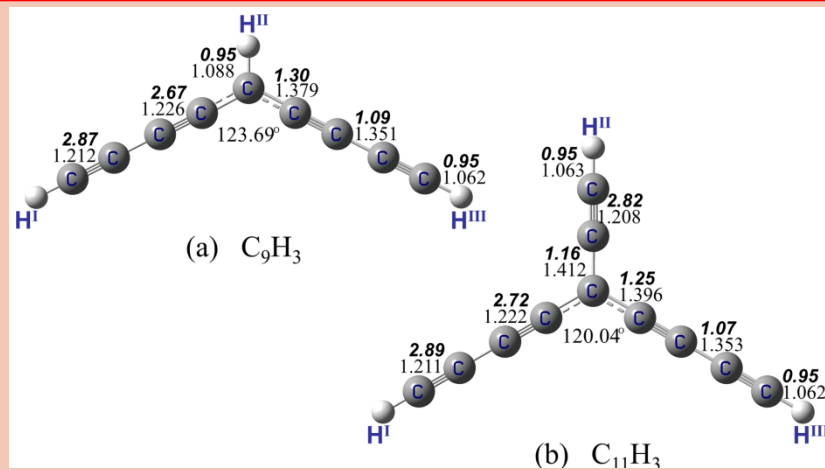


$C_{11}H_3: C_{2v}$ case

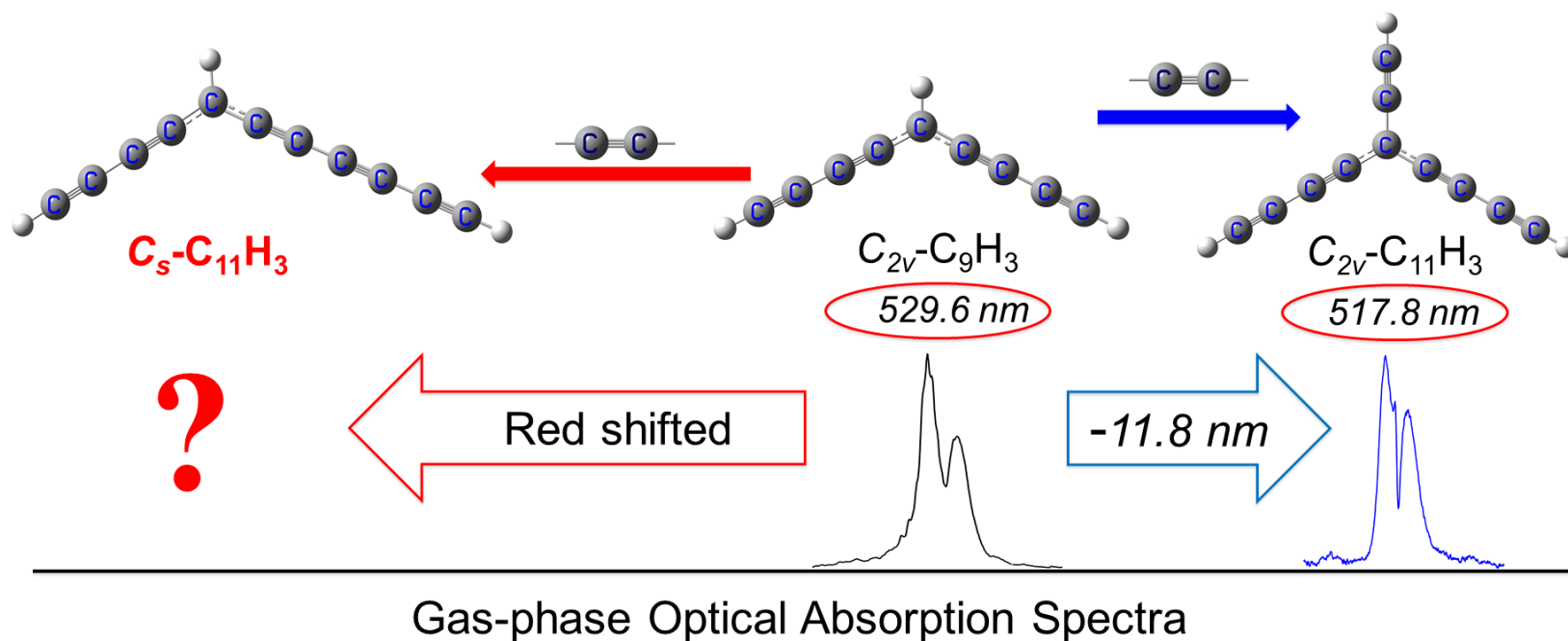


$\Delta_{H/D}^I = +34.9 \text{ cm}^{-1}$
 (**identical to C_9H_3**)
 $\Delta_{H/D}^{II} = -0.6 \text{ cm}^{-1}$
 (**half of $\Delta (C_9H_3)$**)

- Isotope shifts → structure similarities and differences
- DFT-B3LYP calculations



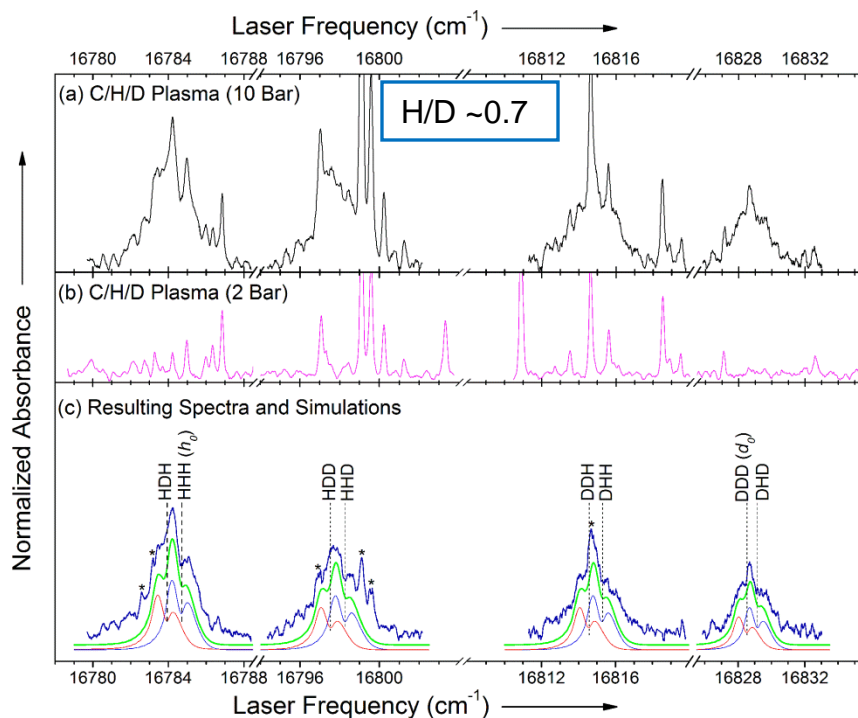
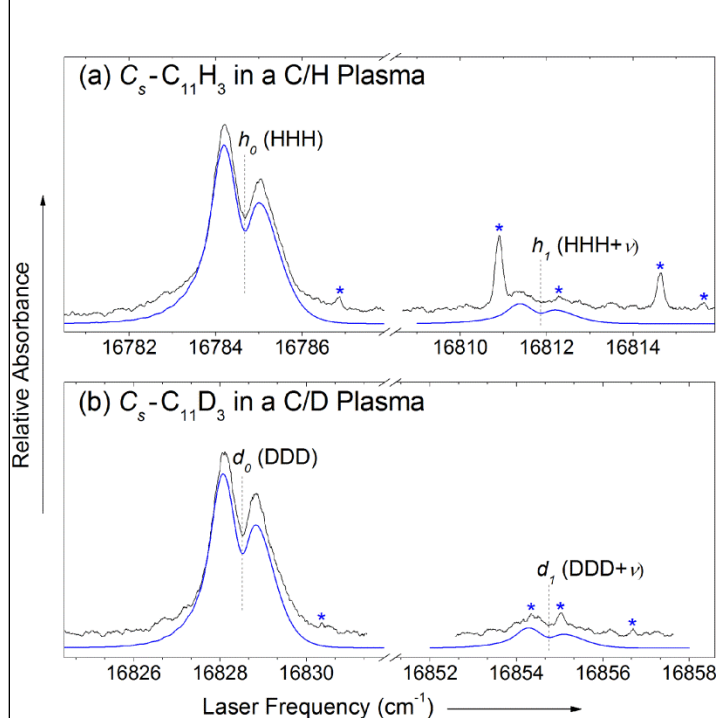
$C_{11}H_3$: C_s case ?



A red shift of ~ 70 nm is expected for C_s - $C_{11}H_3$ with respect to C_{2v} - C_9H_3 , due to the 'particle-in-a-box' behavior that has been found for linear carbon chains previously, and also DFT calculations.



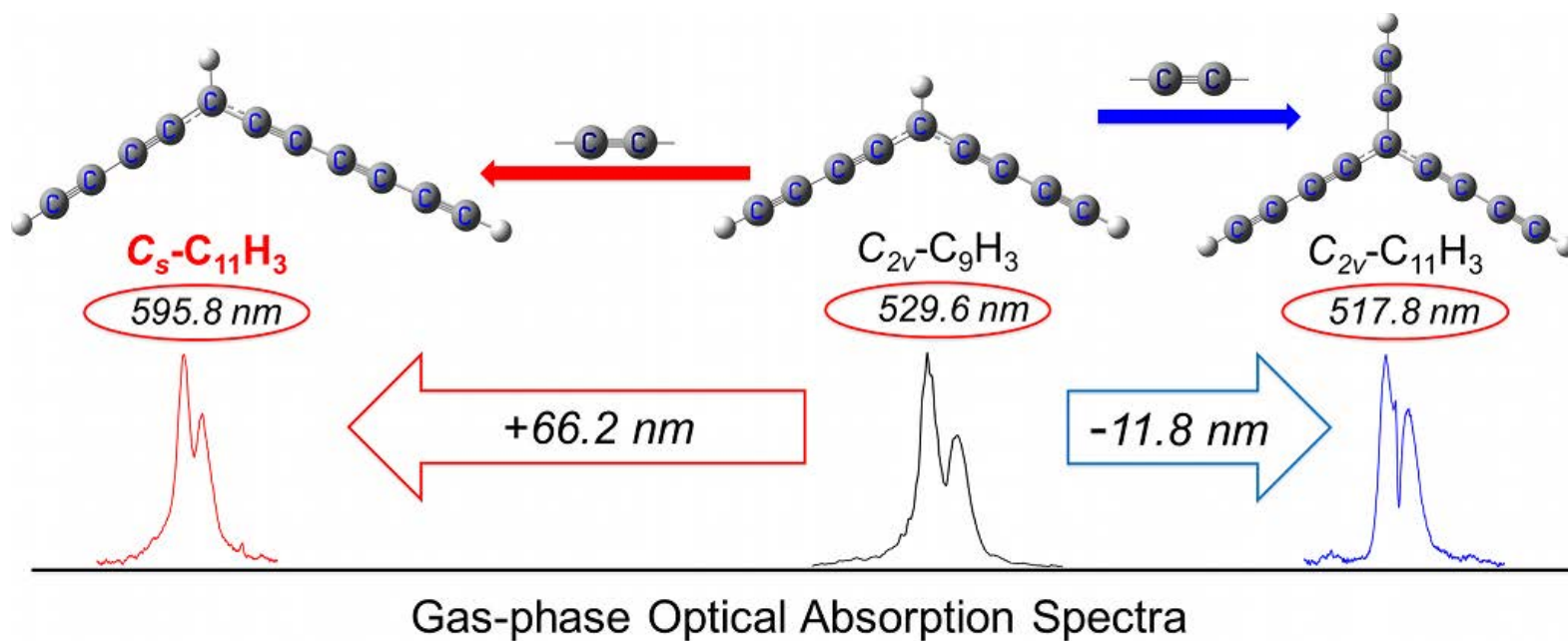
- No mass selective spectroscopic information reported;
- Searched in the expected wavelength region.



Large carbon chains
not favored

- Red shift with respect to $\text{C}_{2v}\text{-C}_9\text{H}_3$: ~ 66.2 nm
- Isotopic shift:
 $\Delta^{\text{I}} = +30.6$ cm^{-1} , $\Delta^{\text{II}} = -0.7$ cm^{-1} (close to values for C_9H_3)
 $\Delta^{\text{III}} = +13.6$ cm^{-1}
- Rotational constants, low-lying bending vibration, and band position consistent with DFT-B3LYP calculations on $\text{C}_s\text{-C}_{11}\text{H}_3$

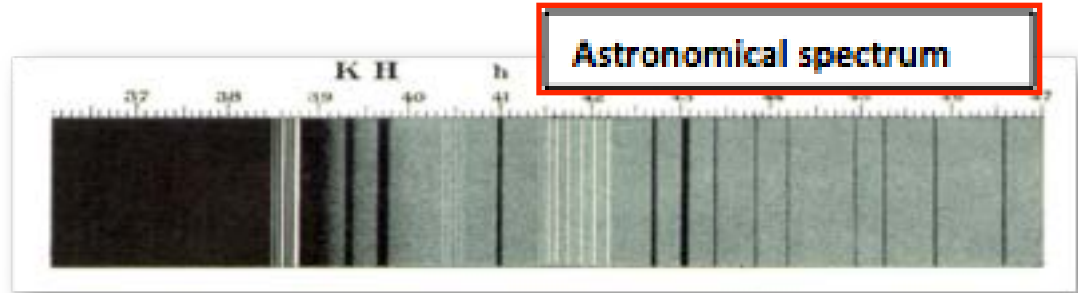
Conclusion: unraveling of the puzzle



(see Zhao et al., *J. Chem. Phys.*, **2012**, 136, 054307)

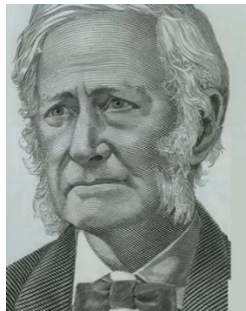
The 4051 Å comet band (C_3)

The Great Comet of 1861



I. "Preliminary Note on the Photographic Spectrum of Comet δ 1881. By WILLIAM HUGGINS, D.C.L., LL.D., F.R.S. Received June 27, 1881.

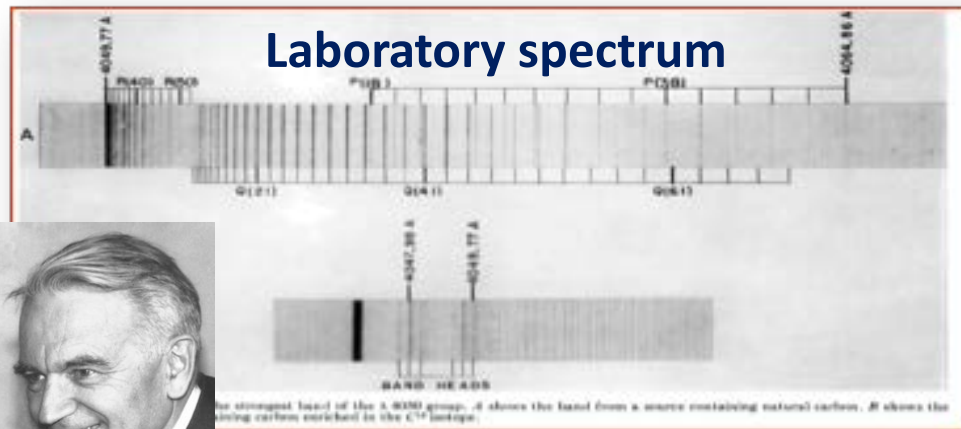
REVUEUE 1 JUNE 27 1881



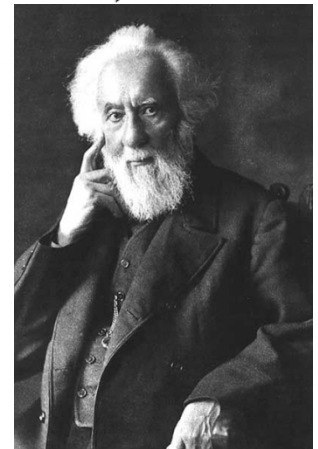
John Tebbutt



Laboratory spectrum

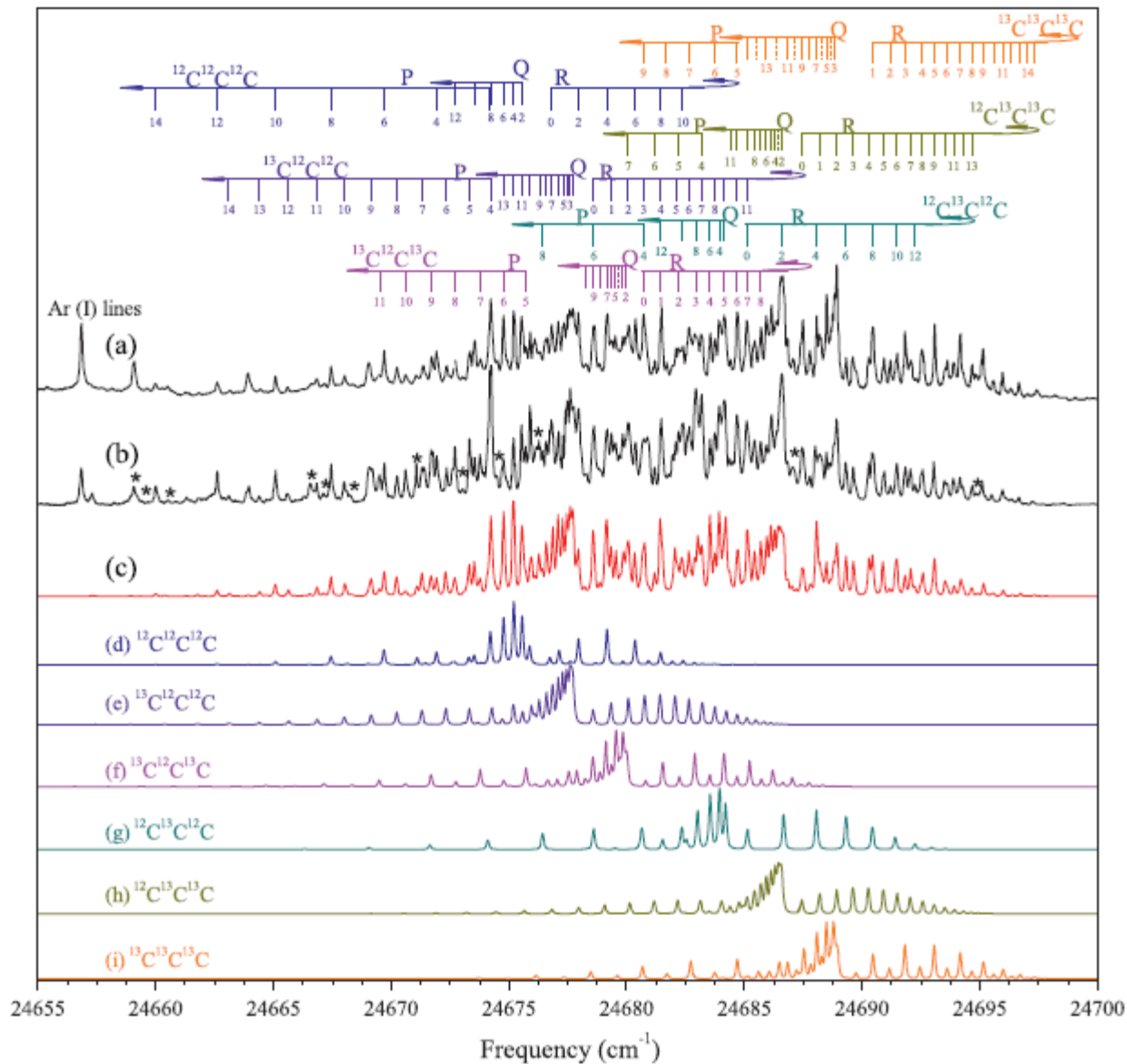


Gerhard Herzberg; assignment to C_3 by Alec Douglas



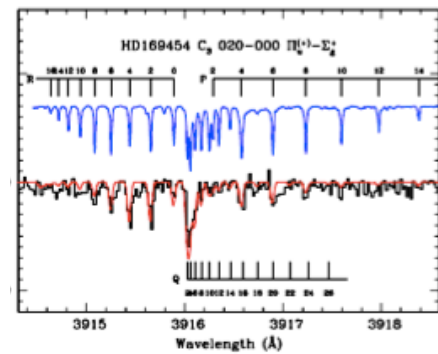
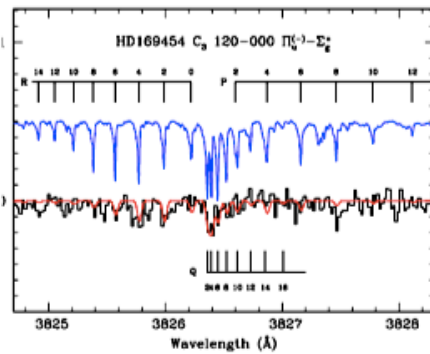
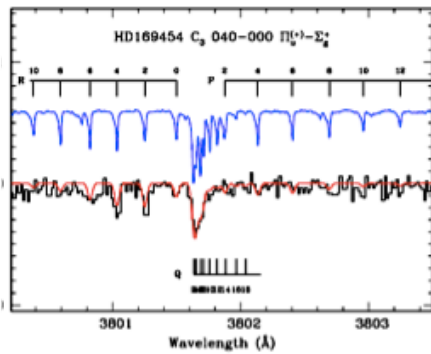
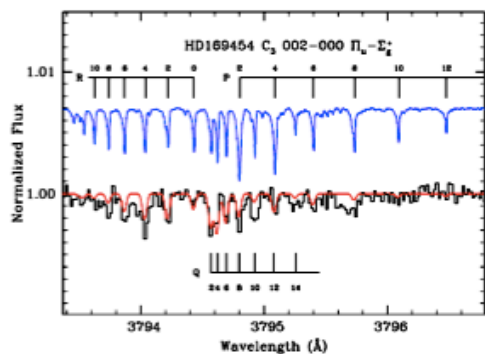
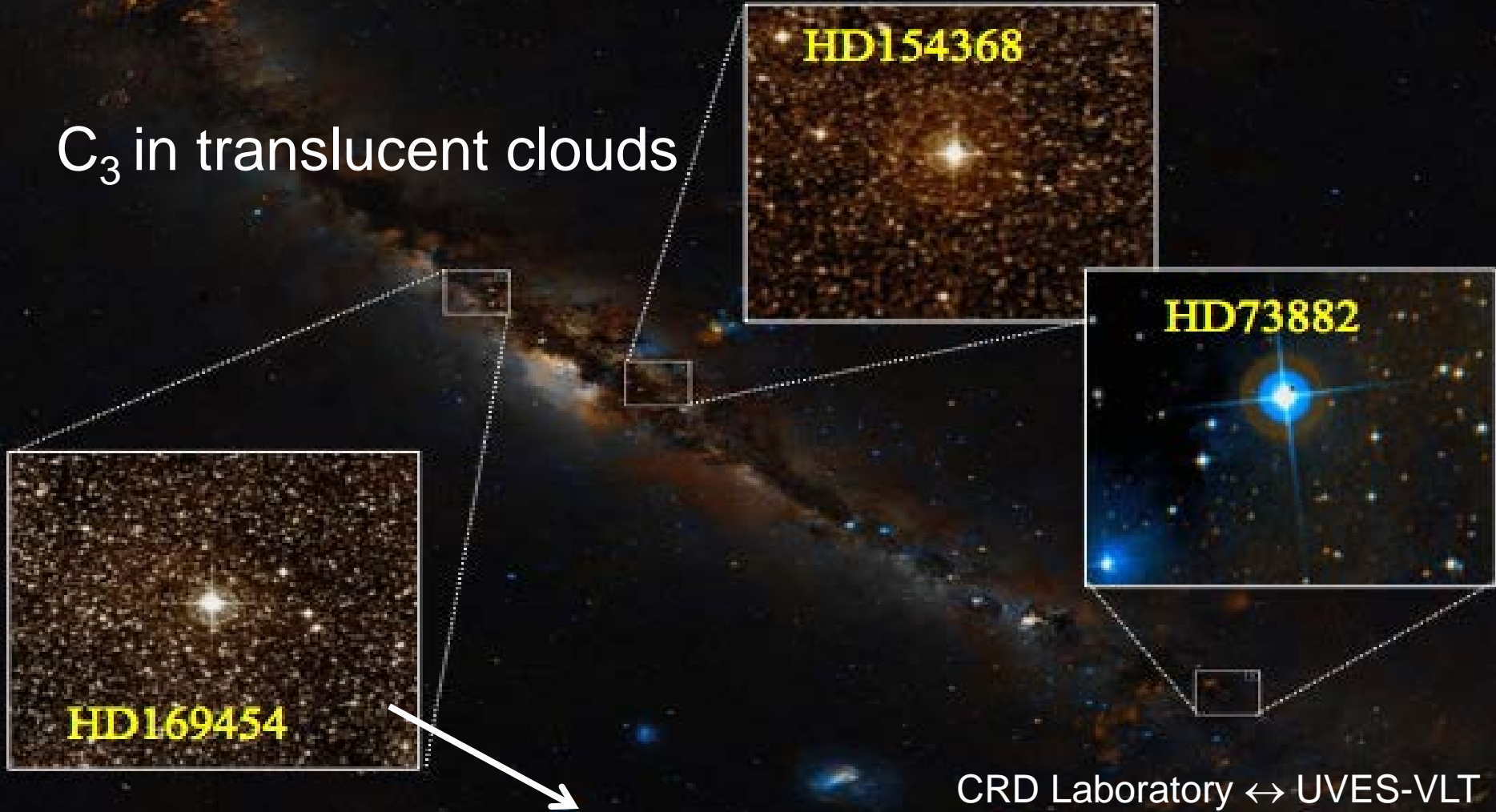
William Huggins

Six isotopologues of C₃



Seven vibronic bands of C₃

C₃ in translucent clouds



HD154368

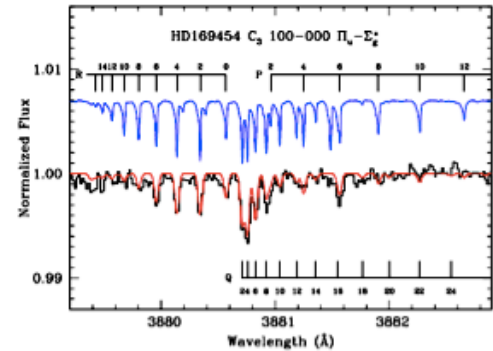
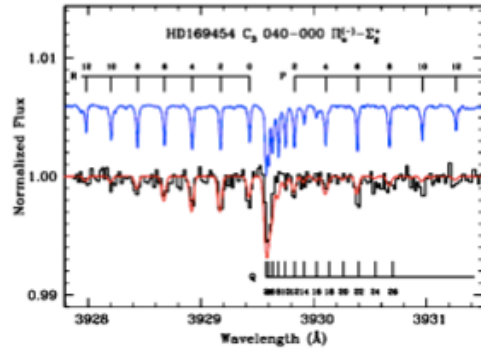
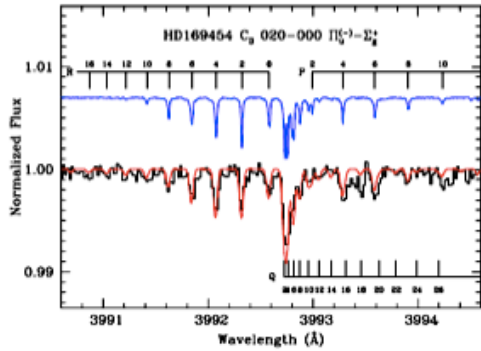
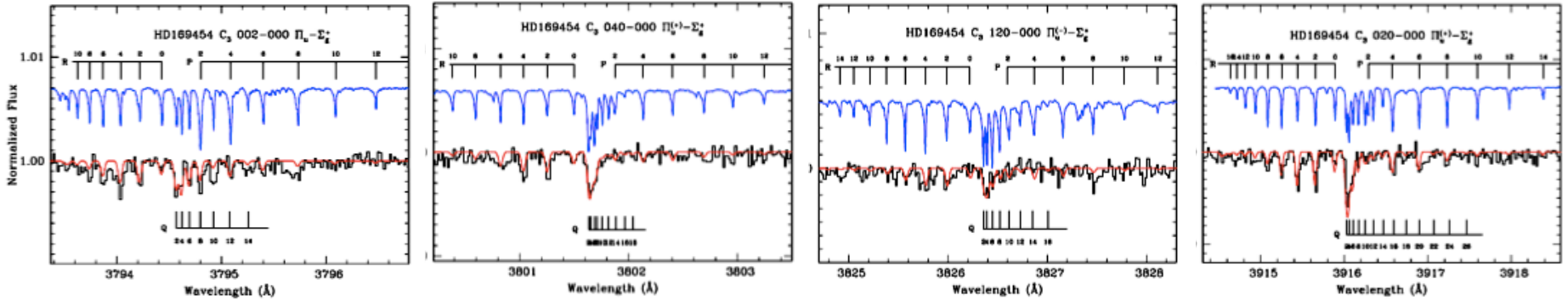


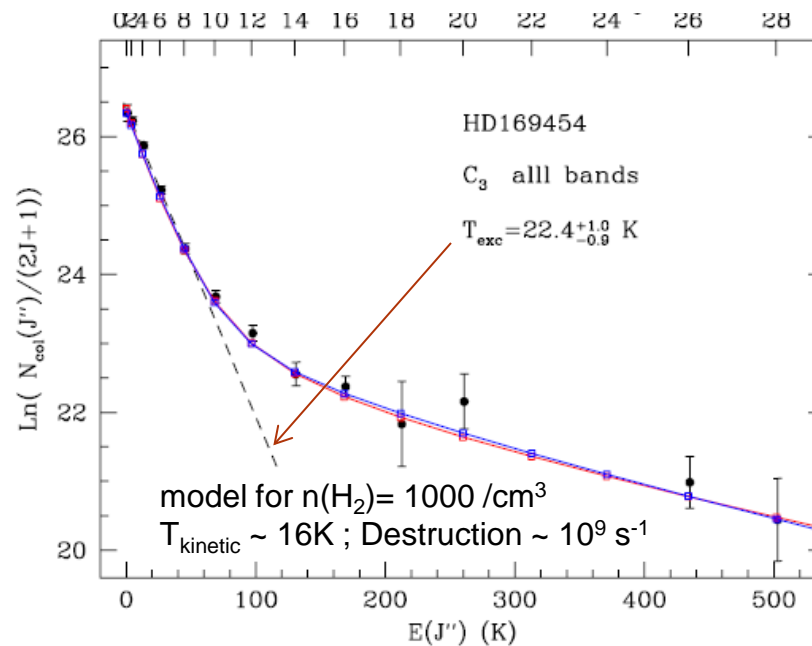
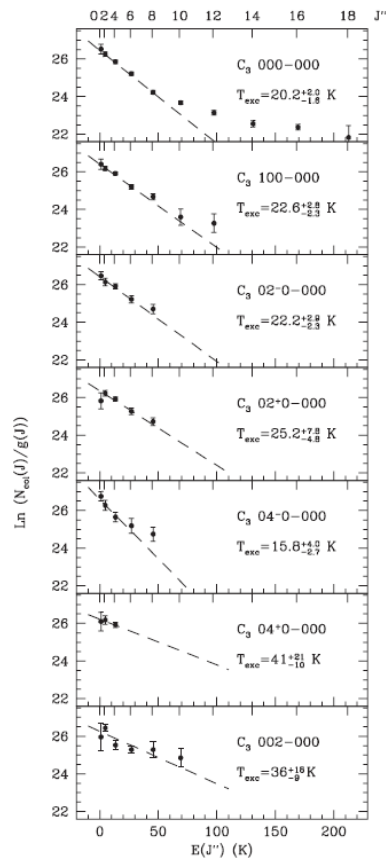
Figure 4. Spectrum in sideline to HD 169454 (black) and laboratory experimental spectrum (blue line) for the C₂ 020-000 Π_u⁺-Σ_u⁺ system.

Figure 5. Spectrum in sideline to HD 169454 (black) and laboratory experimental spectrum (blue line) for the C₂ 040-000 Π_u⁺-Σ_u⁺ system.

Figure 6. Laboratory experimental spectrum (blue line) and spectrum in sideline to HD 169454 (black) for the C₂ 100-000 Π_u-Σ_u⁺ system.

Detection of vibronic bands of C₃ in a translucent cloud towards HD 169454

M. R. Schmidt,¹★ J. Krelowski,² G. A. Galazutdinov,^{3,4} D. Zhao,⁵ M. A. Haddad,⁶ W. Ubachs⁶ and H. Linnartz⁵



Excitation PDR-model Roueff et al. (2002)

First time: multiple bands of C₃

Destruction/photolysis-formation of C₃ ; (higher)

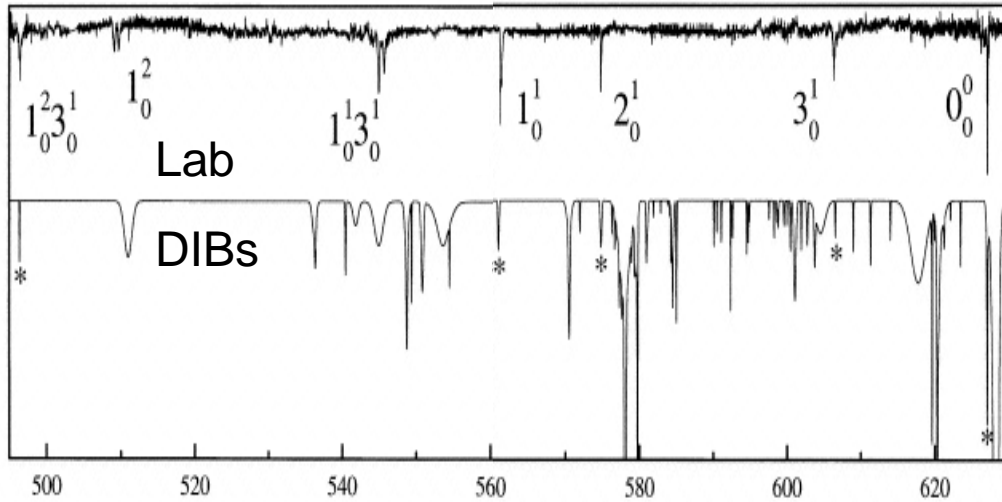
Collisional rates RADEX –Van der Tak (2007)

$N_{\text{col}}(\text{C}_3) = 6.61 (19) \times 10^{12} / \text{cm}^2$

Conclusion

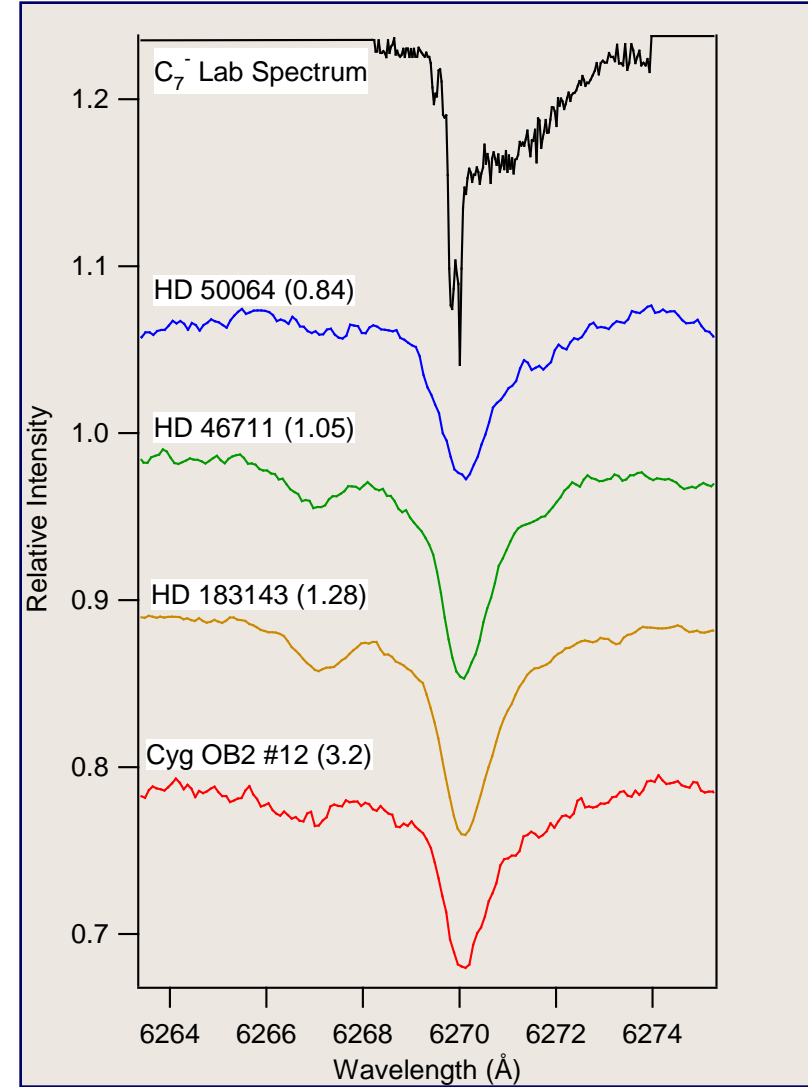
Thanks

The C₇⁻ DIB story



M. Tulej et al., *Astrophys. J.* 506, L69 (1998)

C₇⁻ origin band



McCall, Oka