# Molecular Astrophysics

## Interstellar chemistry

Brief history, astrophysical context

## Translucent molecular clouds: unresolved problems

$CH^+$: Non-Maxwellian velocity distributions, XDRs, PDRs

$H_3^+$: X-ray driven chemistry, ionisation rate

DIBs: change of ionisation balance

## VLT/UVES Observations: Molecules in Magellanic Clouds

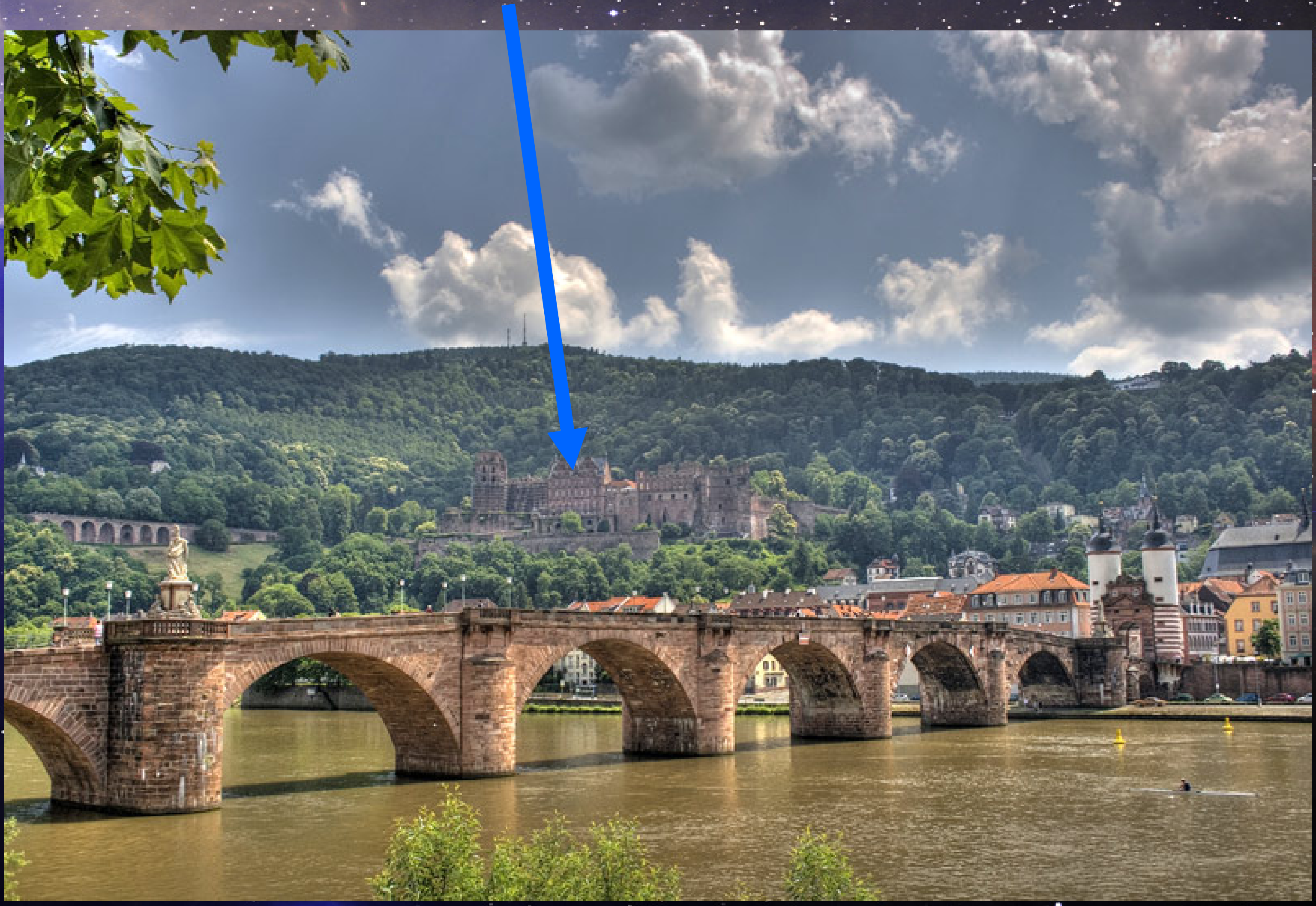
first optical detection of CH, $CH^+$, CN beyond Galaxy

## HST & FUSE observations of CO and $H_2$ in the Galaxy

N(CO) vs. N($H_2$)

Complemented by High R CH, CH+, CN (ESO CES & McDonald)

- Y. Sheffer, S. Federman, D. Lambert, D. Welty
- Roland Gredel, MPIA Heidelberg



# Interstellar molecules

## I. Brief History

- 1922 — 5780, 5797 stationary features (Heger 1922)
- 1926 — Eddington, molecules cannot survive ISRF
- 1934 — Merrill, several strong DIBs detected
- 1937-39 — CH, $CH^+$, CN: stationary optical absorption lines
- 1951 — Bates & Spitzer, first models (Kramers & ter Haar 1946)
- 1963 — Radio astronomy, OH, $NH_3$
- 1970 — $H_2$ Copernicus satellite, UV absorption lines
- 1973 — Herbst & Klemperer, ion-molecule reactions
- 1975 — X-ogen ($HCO^+$)
- 2005 — some 125 gas-phase molecules confirmed

# Interstellar Medium

- **Phase transitions: $H^+ \rightarrow H \rightarrow H_2$**
  - Hot ionised HII: $5\ 10^5$ K, $5\ 10^{-3}$ $cm^{-3}$
  - Warm HI/HII: 8000 K, 0.3 $cm^{-3}$
  - Cool atomic: 80 K, 30 $cm^{-3}$
  - Cold molecular: 10-100 K, 100 - $10^3$ $cm^{-3}$
    - Diffuse → giant molecular clouds
    - Pressure equilibrium: nT = const

# Interstellar Dust

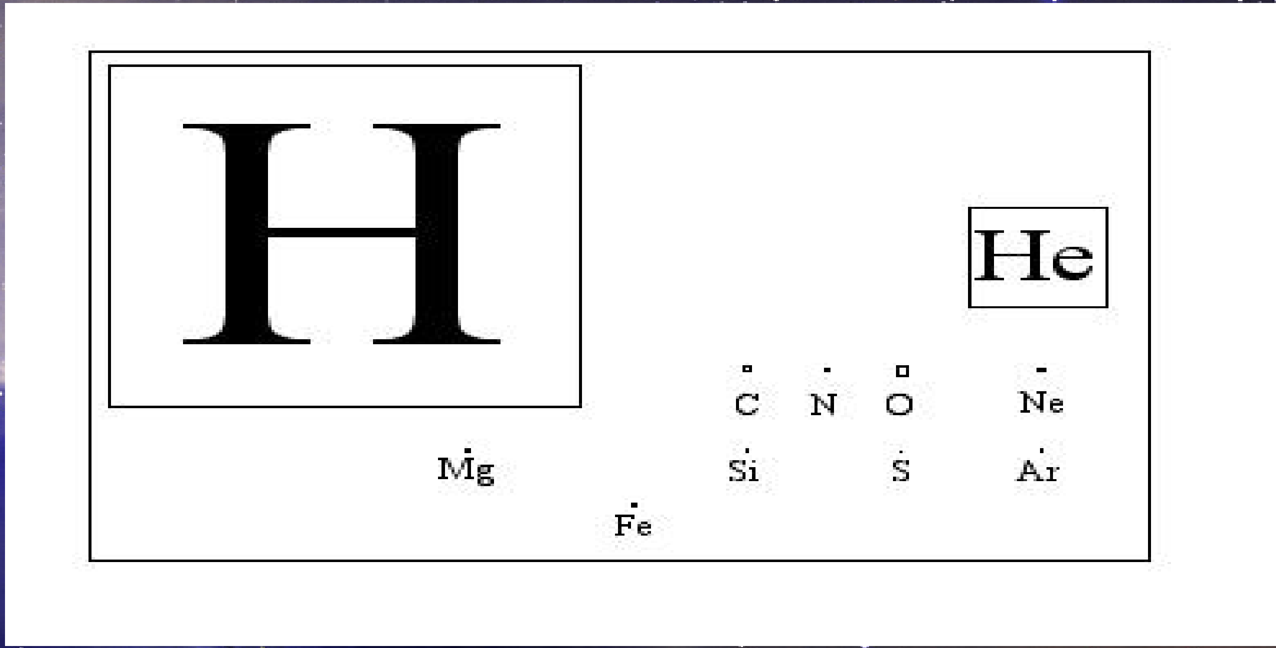
- **Absorption & polarisation of starlight**
  - Variation with wavelength: reddening $E_{B-V}$
  - Visual extinction $A_V = -2.5 \log F_V/F_0$
    - » Absorption law: $F_V/F_0 = \exp(-k\,x)$
  - $A_V/E_{B-V} = 3.1$
    depends on dust properties
  - Gas/Dust ratio: 0.01

# Molecular clouds

- **Diffuse clouds and translucent clouds**
  - Optical detections of molecules, DIBs
- Giant molecular clouds and isolated globules
  - **Rich chemistry, large and complex organic molecules**
- Hot cores, UCHII regions, PDRs


The Horsehead Nebula — Barnard 33
HUBBLESITE.org

# Interstellar chemistry




- ion-molecule reactions
  - **Ionising source: photons (diffuse clouds), X-rays, cosmic rays (dense clouds)**
- Dissociative & radiative recombination
  - **free electrons required**
- Neutral-neutral reactions
- Initiation of gas phase chemistry: $H_2$ required

# Interstellar chemistry

I. H → $H_2$

- by radiative association, H(1s) + H(1s) → $H_2$ + hv
  - Very slow, forbidden in first order for homonuclear molecules
- on grain surface, H + H:gr → $H_2$ + gr

II. $H_2$ → $H_3^+$

$H_2$ + CR → $H_2^+$

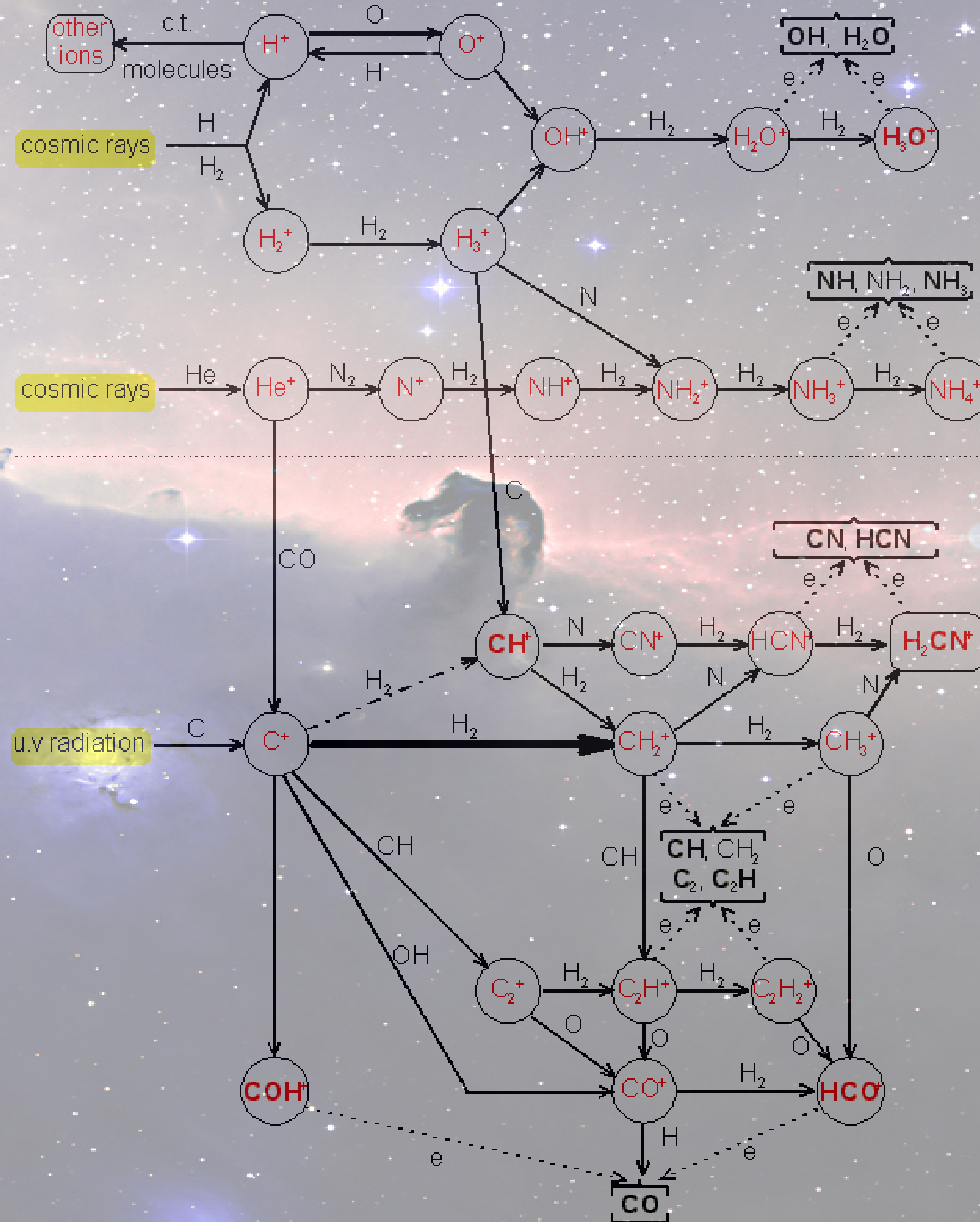
$H_2^+ + H_2 \rightarrow H_3^+$

- $H_3^+$ + e → $H_2$ + H
  - dissociative recombination rate

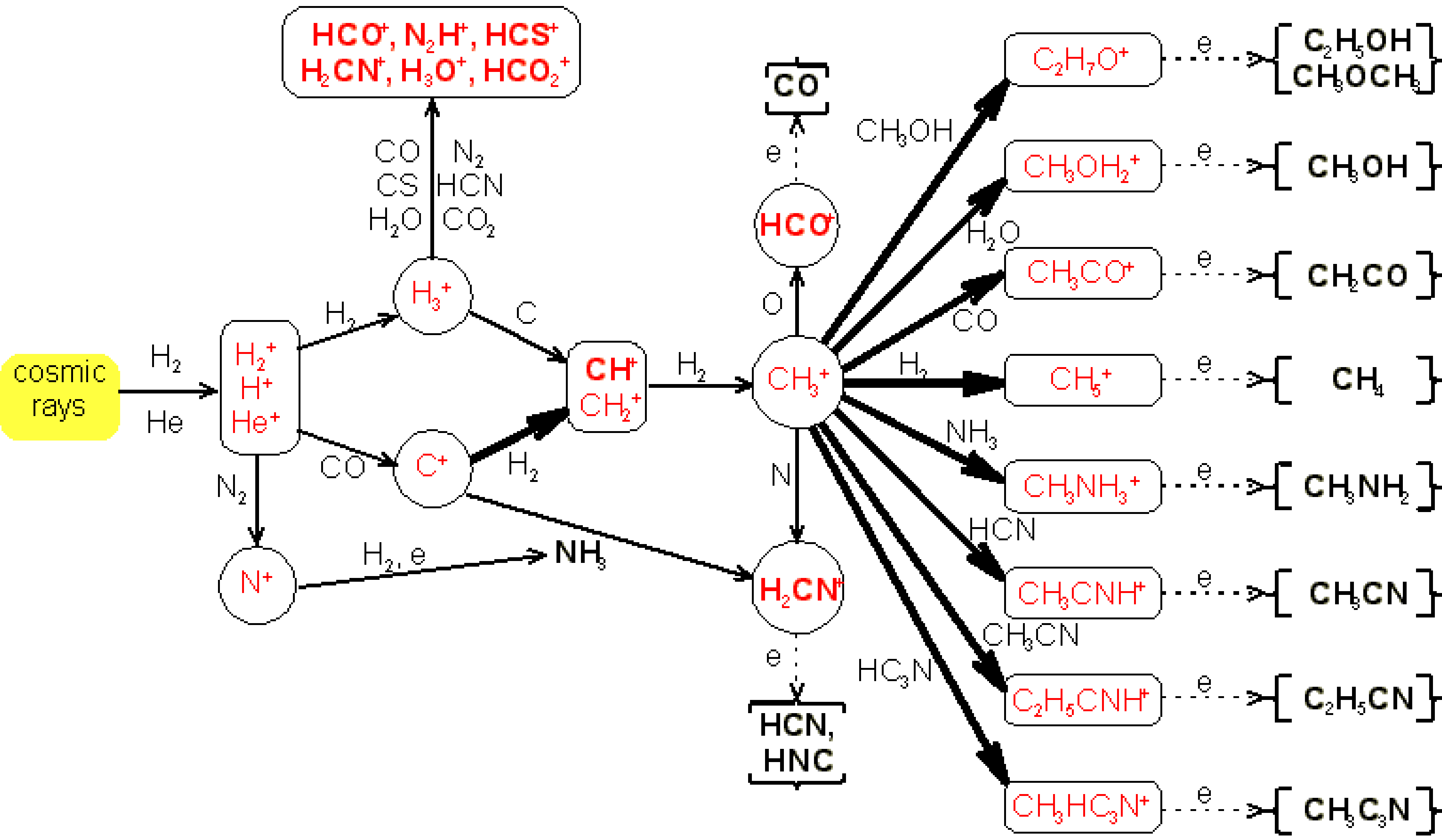
Fast (Amano 1988, Larsson 2000)

Slow (Plasil et al. 2003) minority view

# The ion chemistry of diffuse interstellar clouds



# The initial reactions and radiative association in dense interstellar clouds



# Interstellar chemistry

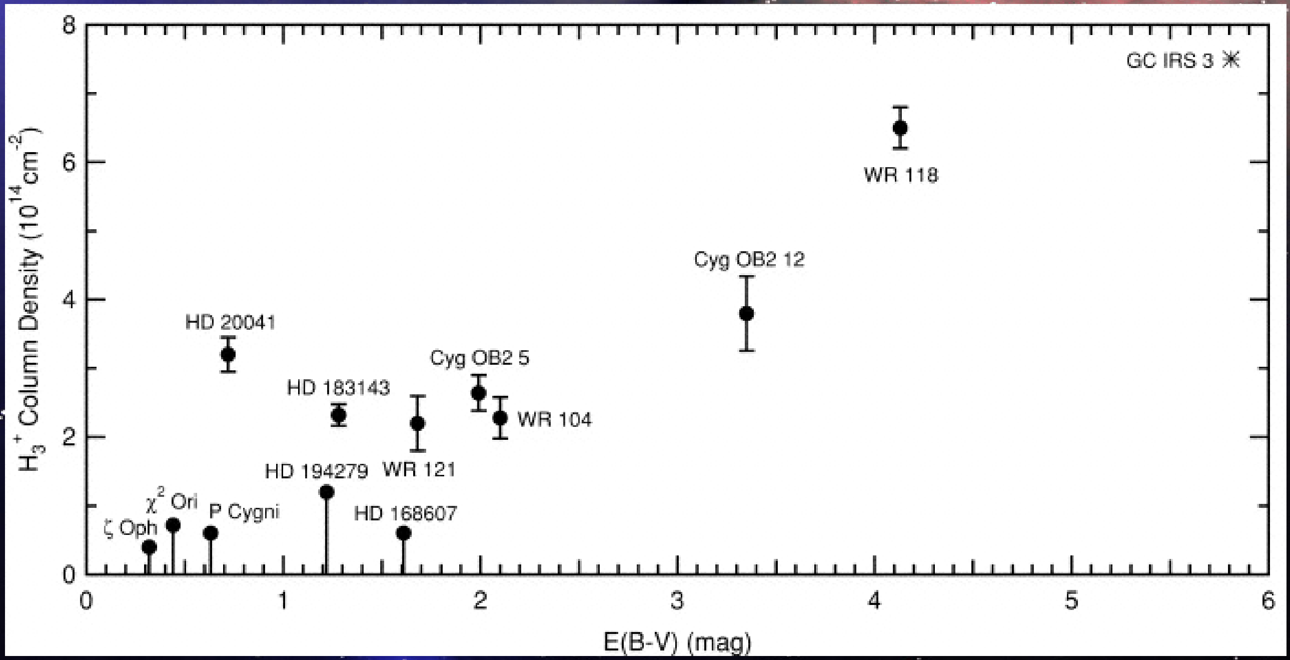
- New Standard Model
  - Bettens 1995, 3785 reactions, 409 species
  - $\zeta = 10^{-17}\ s^{-1}$

- Famous problems remain: DIBs, $H_3^+$, $CH^+$
  I. Carriers of Diffuse Interstellar Bands
  II. DIBs and $H_3^+$: impact on ionisation rates
  III. $CH^+$ formation scenarios not understood

# $H_3^+$

Geballe & Oka 1996; McCall et al. 2002

- Very important detection
- Abundances too high if dissociative recombination is fast
- General correlation $N(H_3^+) \sim E_{B-V}$

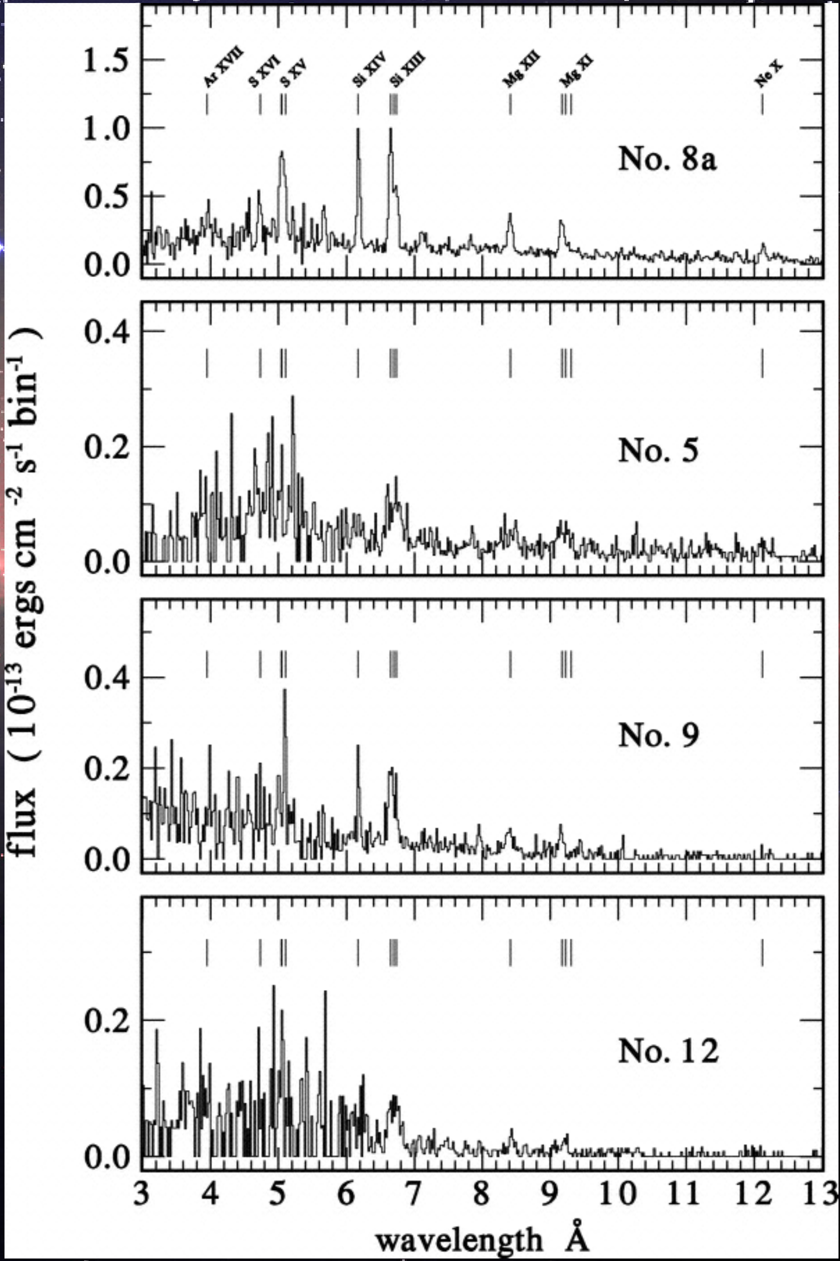


# $H_3^+$ in Cyg OB2 No. 12

- McCall et al. 1998
  - Formation in diffuse material, very long pathways
  - $L = 400 - 1200$ pc, $n = 10$ $cm^{-3}$
- Cecchi-Pestellini & Dalgarno 2000
  - Dense clumps of gas embedded in diffuse material
  - $C_2$ formation at $n = 7000$ $cm^{-3}$
- Gredel, Black & Yan 2001
  - $T_{kin} = 35K$, $n = 600$ $cm^{-3}$
  - increased radiation field from OB stars
  - X-ray induced chemistry

$$\zeta = 0.6 - 3\ 10^{-15}\ s^{-1}$$

# Cyg OB2




## X-rays from Cyg OB2

- **Chandra observations Waldron et al. 2004**
- **Rapidly exanding stellar winds, shocks → X-ray emission**

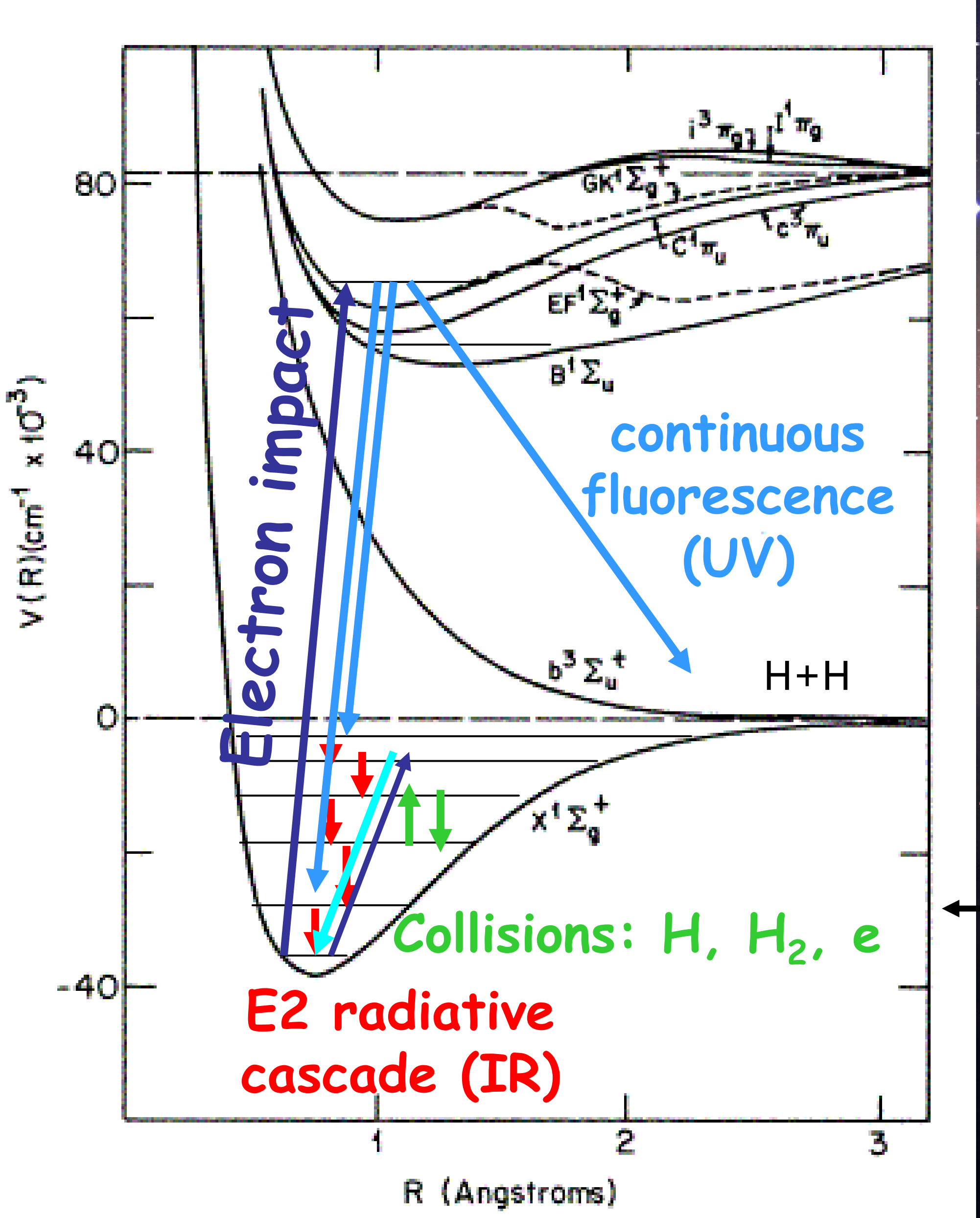
# X-ray induced chemistry

- Cool molecular clouds subjected to X-rays
  Gredel, Lepp, Dalgarno, Black, Yan; various papers

- **M + Xray → $M^{++}$ + 2e**
  - $C^{++} + H_2 \rightarrow CH^+ + H^+$

- Energy deposition by fast secondary electrons
  - Coulomb losses to thermal electrons
  - Ionisation and excitation of H and $H_2$
  - He, n→ 2, 3 singlet and triplet S and P states and to $4^1P$

# $H_2$ X-ray excitation




- Different selection rules
- UV: Lyman & Werner bands, continuous
- NIR $H_2$ emission
- Optical emission: high $\Delta v$
- $T_{gas}$, $n$, $I_{UV}$, $v_s$, $x_e$

# X-ray induced chemistry

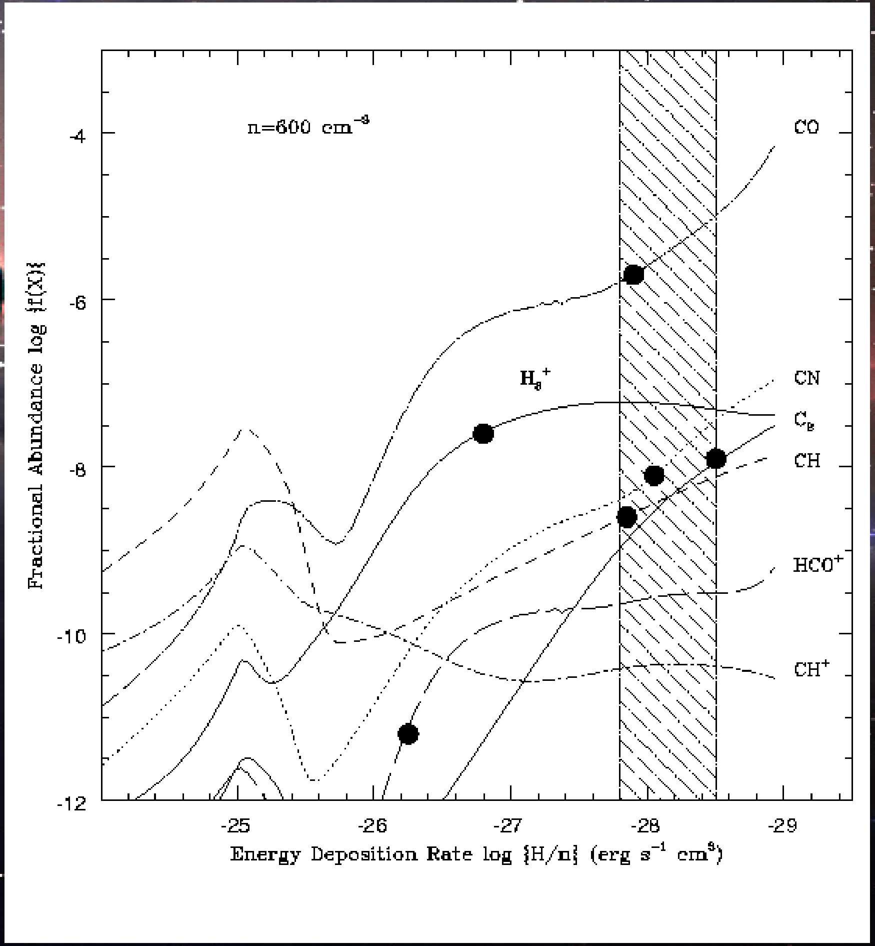
- Radiation field in dense molecular clouds
  - Energetic, secondary electrons from X-ray ionisation
  - $H_2$ + e → $H_2$*
  - $H_2$ → $H_2$(vJ) + UV-photons (Lyman and Werner bands)
  - $H_2$ (vJ) → $H_2$ + NIR-photons (E2 cascade)
- Increased photoionisation and photodissociation rates
  - Explains C/CO ratio in dense clouds

# Cyg OB2 No. 12

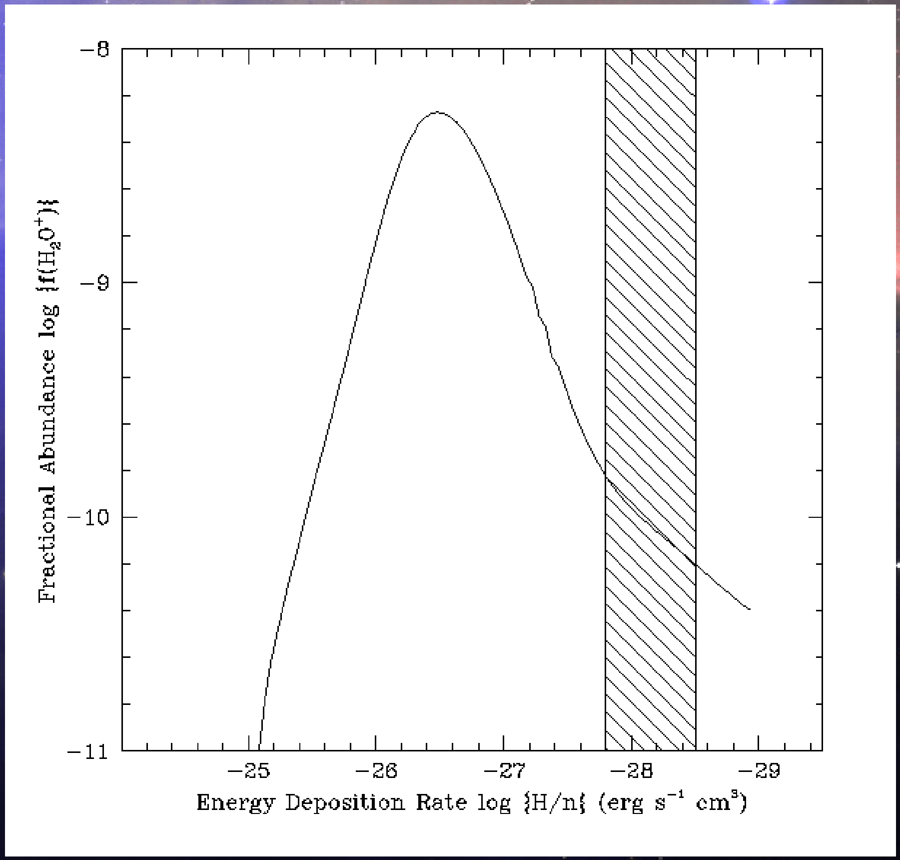
Detailed chemical model
including X-ray ionisations

**T, $n_H$, $n_e$ constrained by observations**
**Cool gas with T = 35 K, n = 600 $cm^{-3}$**

$\zeta = 0.6 - 3\ 10^{-15}\ s^{-1}$



# Cyg OB2 No. 12




Model prediction:

- Observable amounts of $H_2O^+$ in absorption
- S/N > 1000 spectrum of Cyg OB2 no. 12

# $H_3^+$ in the diffuse ISM

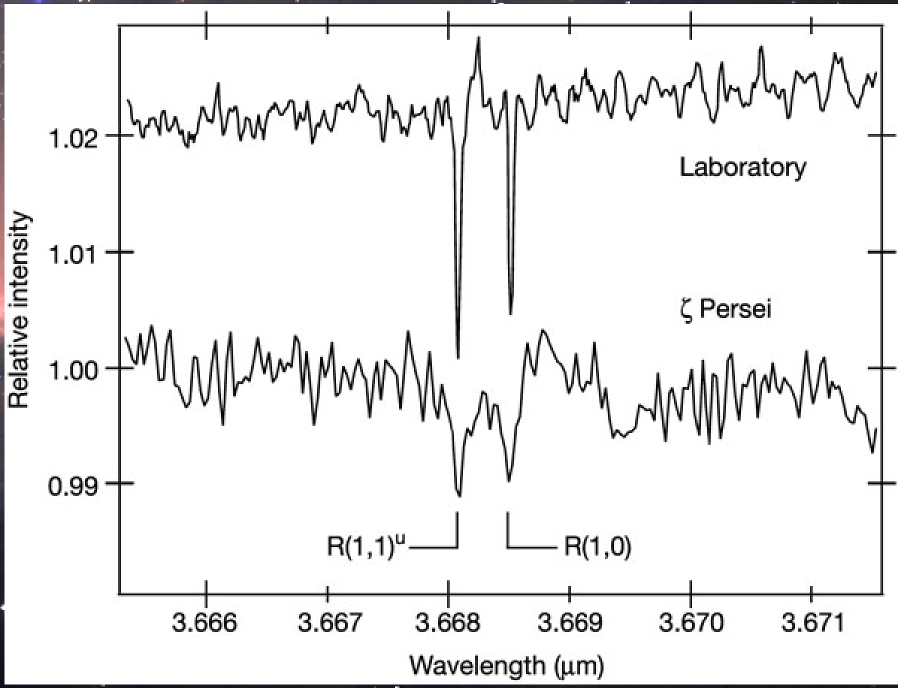
McCall et al. 2003

Large abundance towards ζ Per

High cosmic ray ionisation rate

$\zeta = 1.2\ 10^{-15}\ s^{-1}$

General solution !?



# The ironic twists in $H_3^+$

I. Lepp et al. 1988, large molecules

- **Chemical models including photoelectric heating of LM: large, observable abundance of $H_3^+$**

  Wrong. slow recombination rate used

- **Model predictions did not stimulate observations to detect $H_3^+$**

II. New laboratory measurements: $H_3^+$ + e very fast

- **Models: $H_3^+$ abundance too low to be detected**
- **Stimulated huge observational efforts to detect $H_3^+$**

III. 2003: large abundance of $H_3^+$ detected in diffuse ISM

**Ionisation rate to be increased?**

# The $CH^+$ problem

- $N_{obs}/N_{model}$ = 1000
  - $C^+ + H_2 \rightarrow CH^+ + H$ $\Delta E = 0.4$ eV
- Thermal formation scenarios
  - Elitzur & Watson 1978, 1980: J-type shocks
  - Pineau des Forets et al. 1986: C-type shocks
  - Falgarone, dissipation of interstellar turbulence, boundary layers

**$CH^+$ formation in hot gas, T = 1000 – 4000 K**

# The $CH^{+}$ problem

I. CH – $CH^{+}$ velocity difference

- Detailed shock model towards z Oph (Draine 1986)
- Model result: v(CH) – v($CH^{+}$) = 3.4 km $s^{-1}$
- Very high R observations: Dv < 0.5 km $s^{-1}$

MHD SHOCKS IN DIFFUSE CLOUDS. III. 409

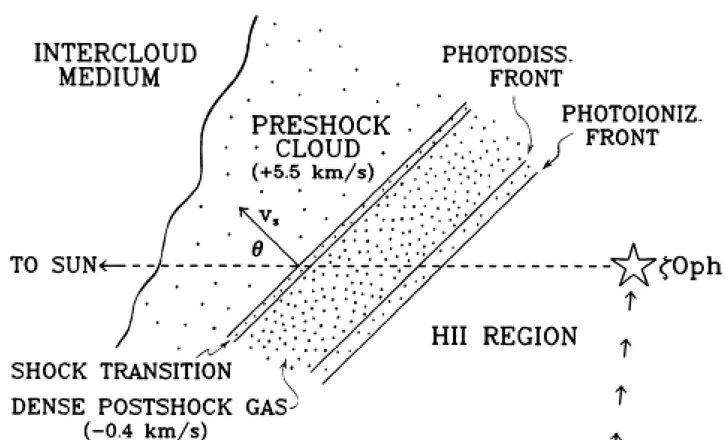
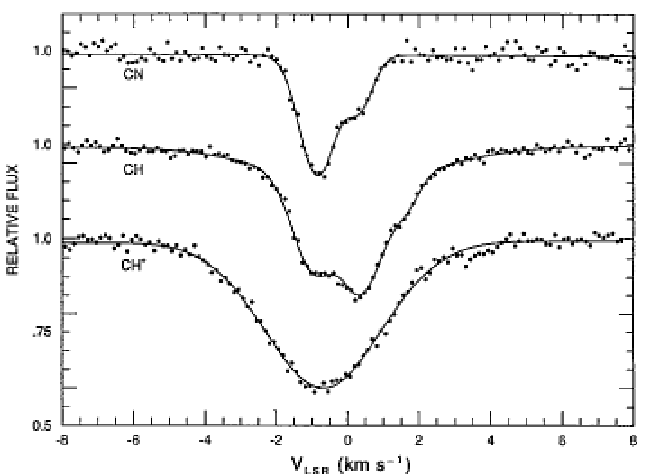



FIG. 1.—Proposed geometry of the preshock material, shock transition zone, and postshock material on the line of sight to ζ Oph (see text)

L20 LAMBERT, SHEF



# The $CH^+$ problem

- Spatially related stars: $N(CH^+) \sim E_{B-V}$
  - Tight correlation in single translucent clouds (Gredel et al. 2003; 2004)
- Radial velocities agree within errors
  - Earlier results with $v(CH) - v(CH^+) > 4$ km $s^{-1}$ cannot be reproduced: upper limit to shock velocities
- $C_2$ observations → n, T
  - $CH^+$ formation sites in cool gas

# Interstellar $CH^+$

- Thermal models

  **Multiple shocks, model for dissipation of IS turbulence**

  - Gredel, Pineau des Forets & Federman 2002
  - Model for dissipation of IS turbulence
  - Criss-crossing, low-velocity shocks

- Non-thermal models

  **Non-Maxwellian velocity distributions**

  - Gredel van Dishoeck & Black 1993, 1997
  - 'broad' lines: $CH^+$ highly reactive, no thermal profiles
  - Super-thermal $C^+$
  - $b(CH^+) = b(CH) = 1 - 2$ km $s^{-1}$

# The $CH^+$ problem

Special case: Pleiades

- White 1984: very large $CH^+$ abundances at low optical depths
- ISM very close to stars
- Very high UV ionisation rates
- $CH^+$ produced in PDR

# LMC & SMC observations

- Kueyen/UVES & archival data

7 SMC & 13 LMC sightlines, V = 11 – 14 mag

Selected from Tumlinson (2002) FUSE $H_2 > 10^{19}$ $cm^{-2}$

Reanalysis of FUSE →

- $T_{01}$ = 45 – 90 K
- $I_{UV}$ = 3 – 10 (30 – 900 near 30 Dor and SW SMC)
- $n_H$ = 100 – 600 $cm^{-3}$

LMC: $E_{B-V}$ = 0.08 – 0.51 mag

SMC: $E_{B-V}$ = 0.07 – 0.34 mag

Galactic foreground absorption 0.02 – 0.06 mag

# Interstellar Molecules in the Magellanic Clouds

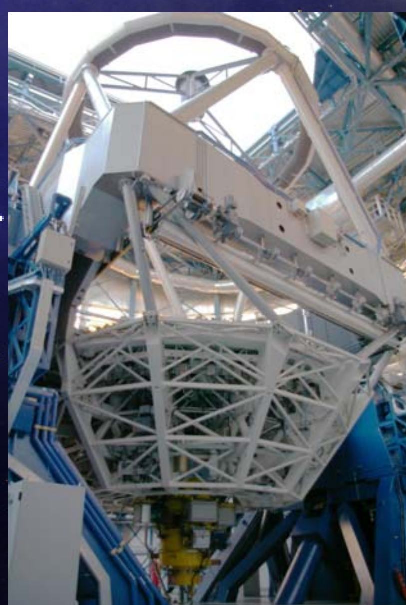
- Why Magellanic Clouds?

- Increased radiation fields, factors of ~ 5
- Lower metallicities, factors of 2 (LMC) to 4-5 (SMC)
- Lower gas-to-dust ratios, factors of 3 (LMC) to 8 (SMC)

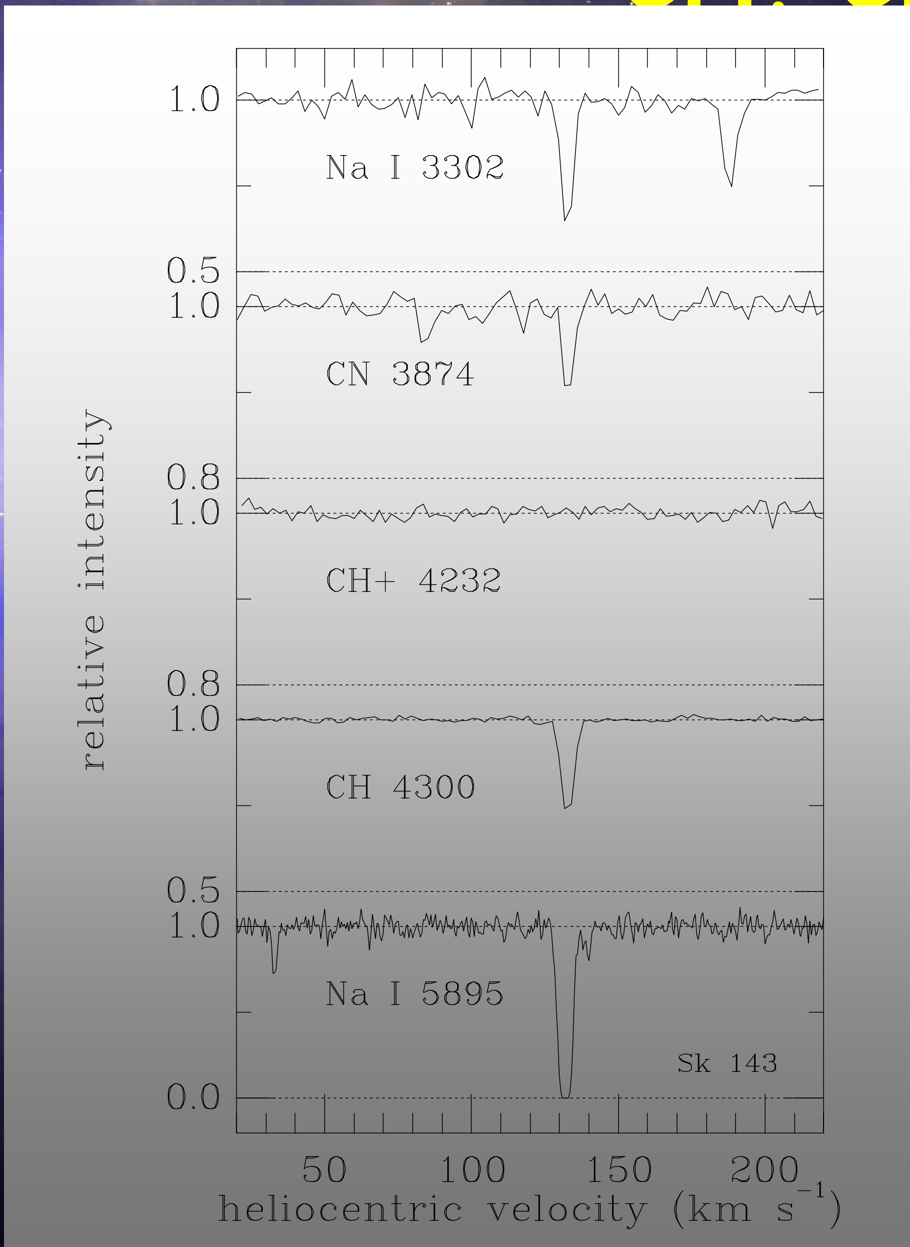
→ Test models & expectations in different physical & chemical environment

# Observing technique

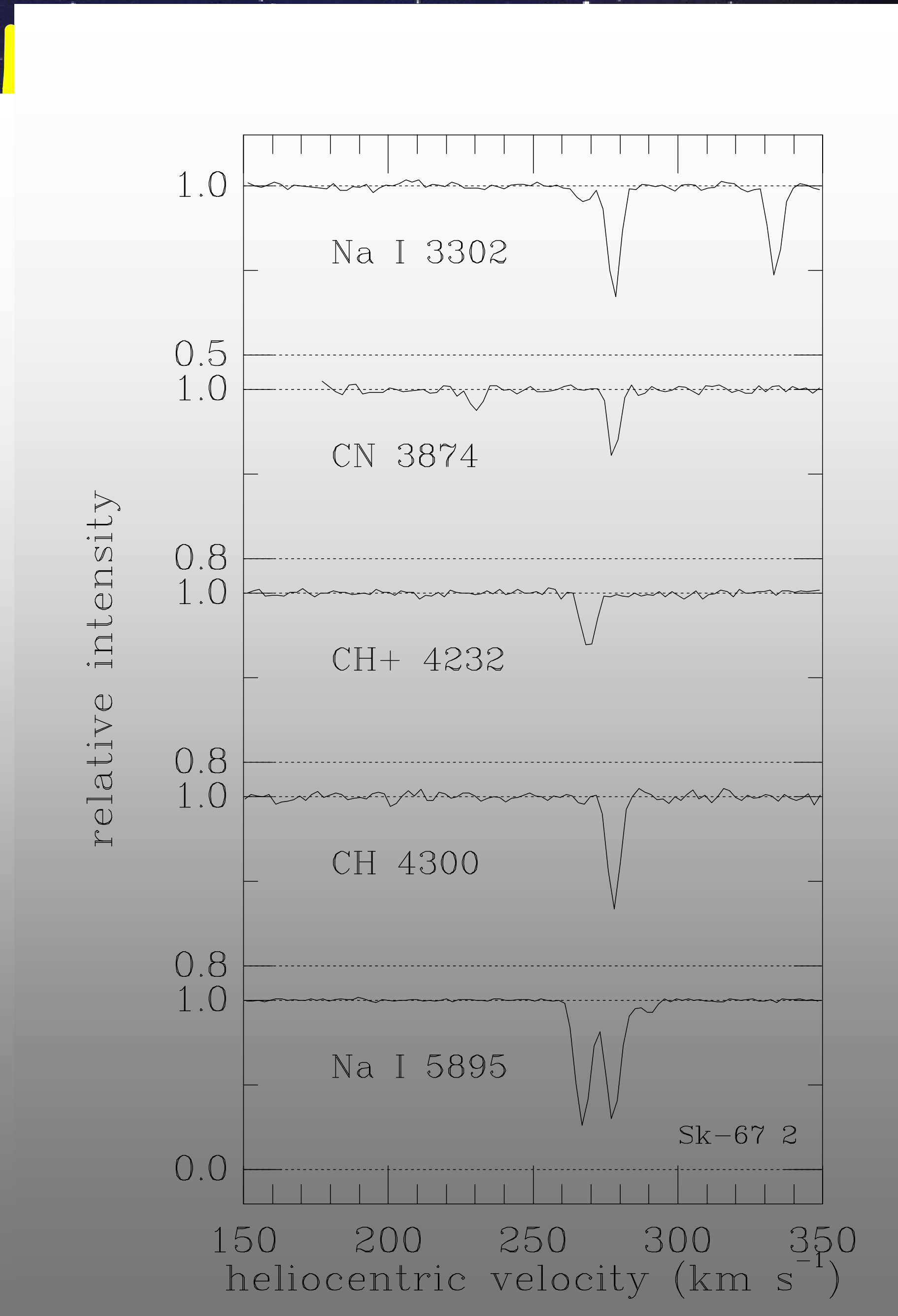
Interstellar absorption lines
→ bright, featureless continua



# CH, C

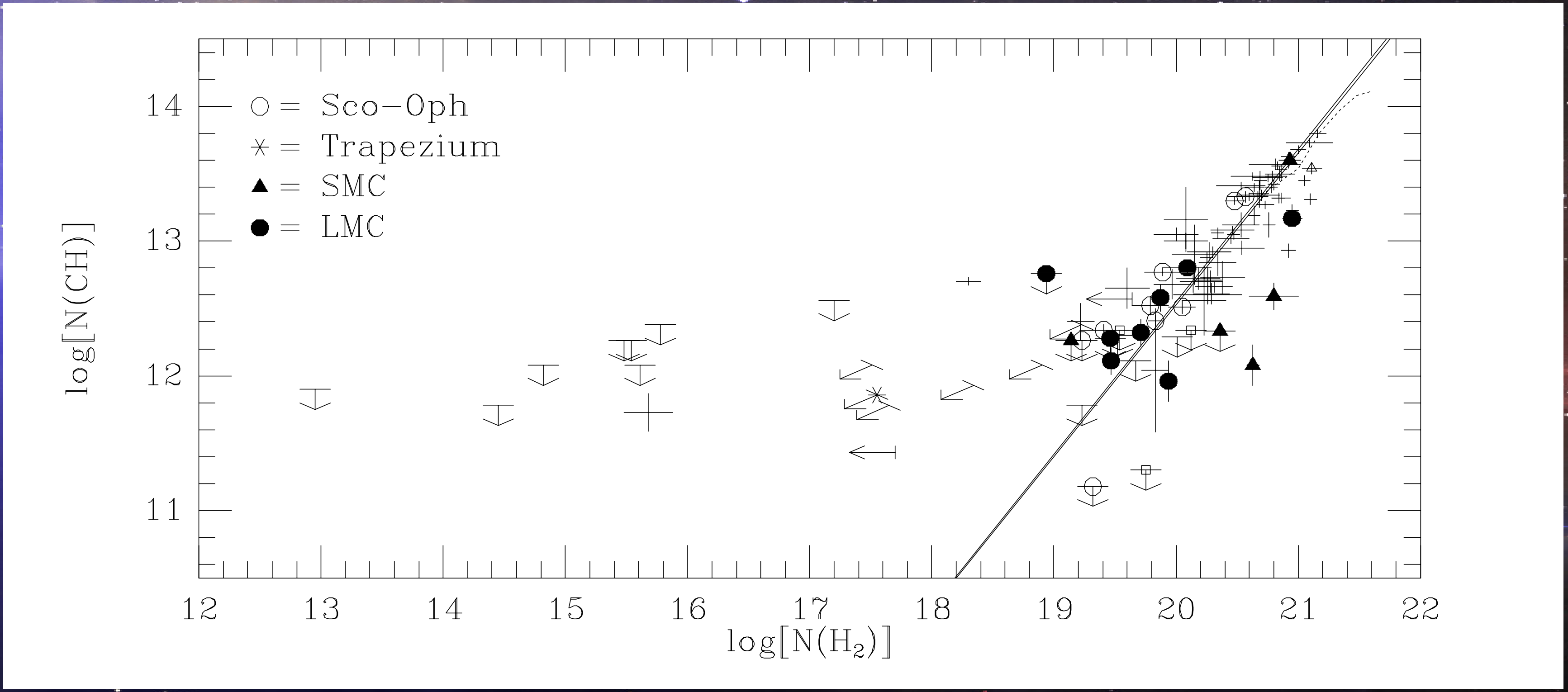


1.0
Na I 3302
0.5
1.0
CN 3874
0.8
1.0
CH+ 4232
0.8
1.0
CH 4300
0.5
1.0
Na I 5895
Sk 143
0.0
relative intensity
50
100
150
200
heliocentric velocity (km s$^{-1}$)

1.0
Na I 3302
0.5
1.0
CN 3874
0.8
1.0
CH+ 4232
0.8
1.0
CH 4300
0.8
1.0
Na I 5895
Sk−67 2
0.0
relative intensity
150
200
250
300
350
heliocentric velocity (km s$^{-1}$)

# N(CH) - N($H_2$) relation




## Galaxy: N(CH) ~ N($H_2$)

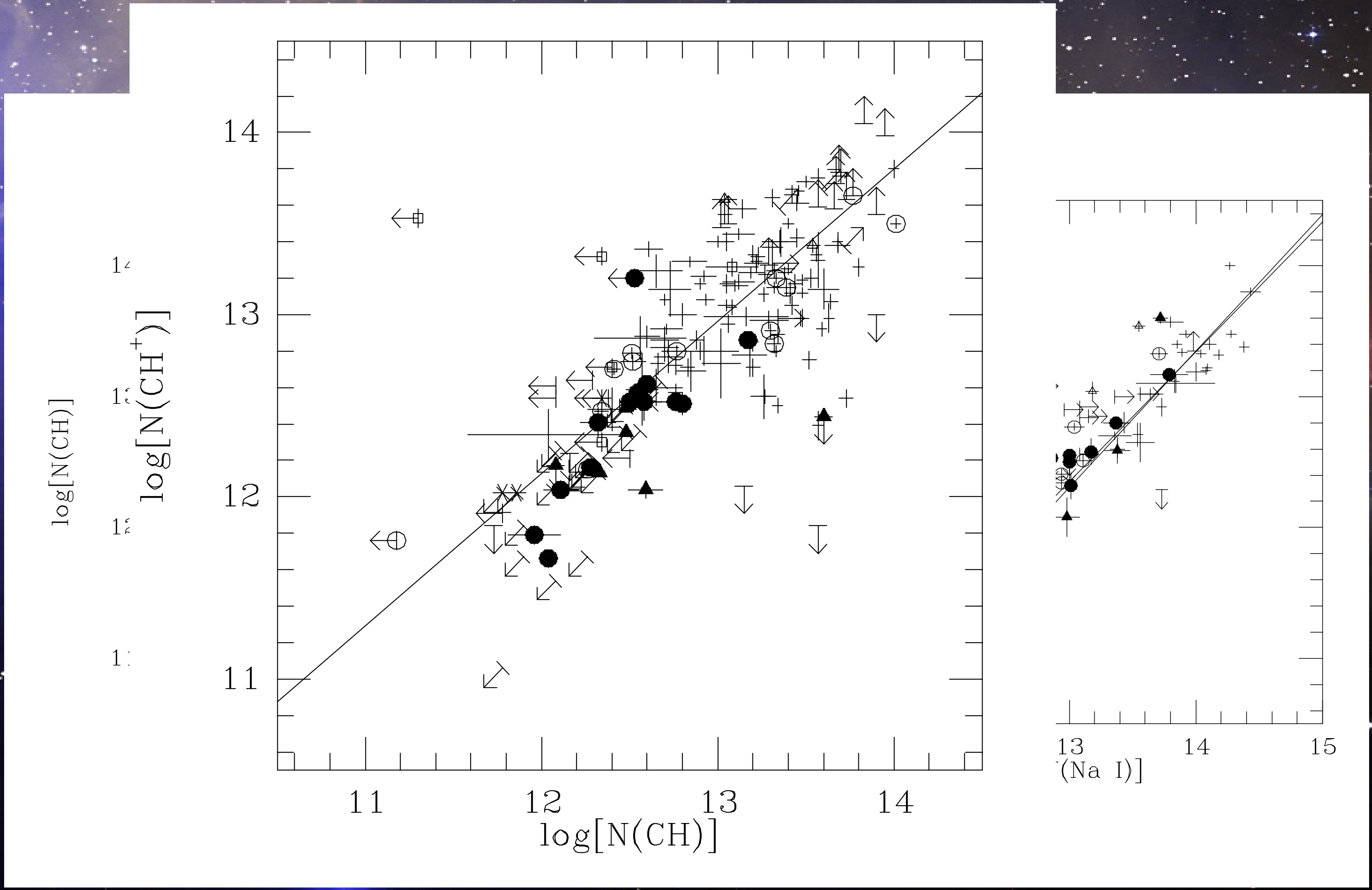
- Danks, Federman & Lambert (1984), Mattila (1986), Rachford et al. (2002)
- van Dishoeck & Black (1989), $n_H$ = 500 - 1000 $cm^{-3}$

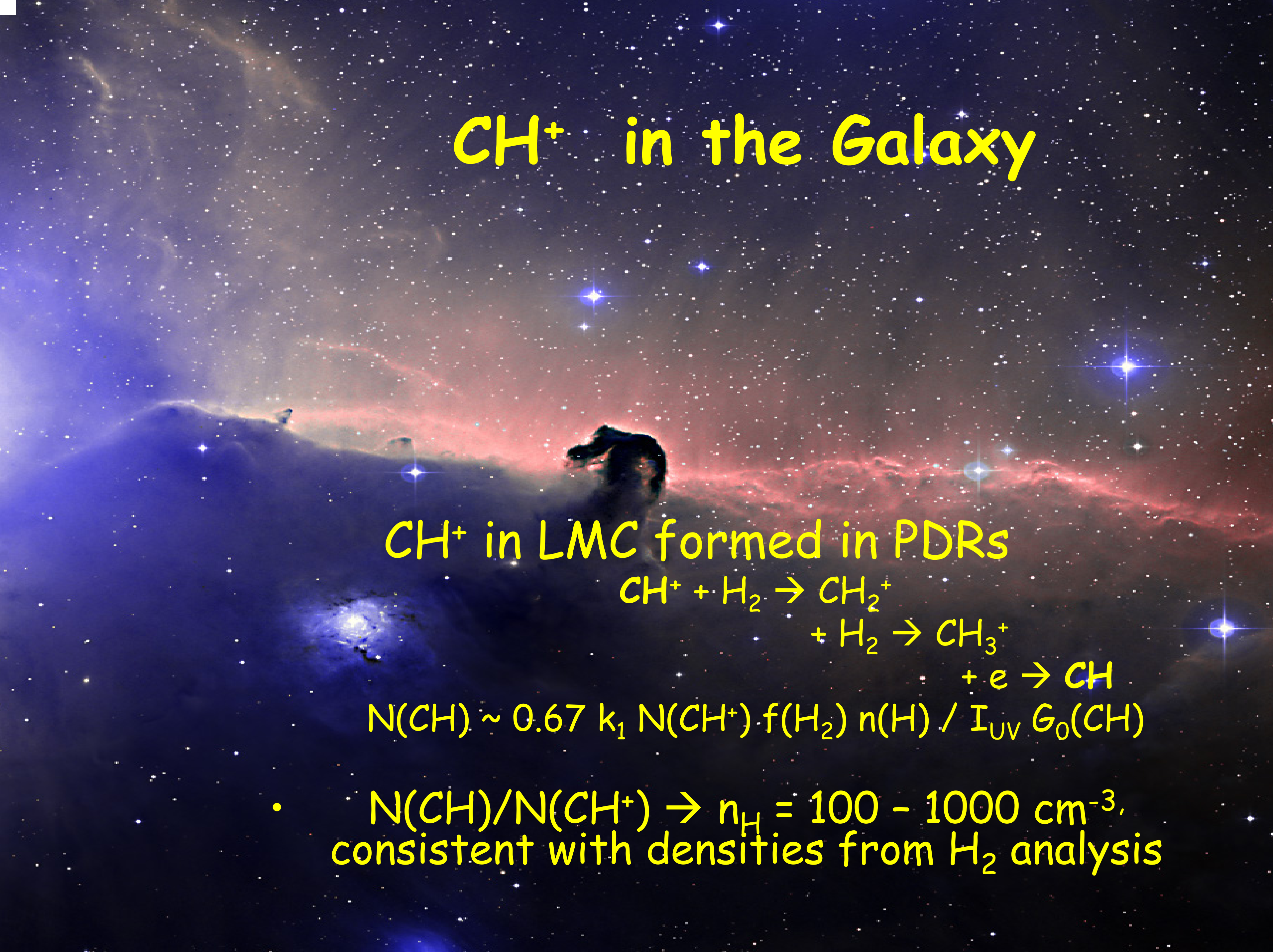
## LMC, LMC: same regression

# Interstellar CH

- Very abundant in LMC and SMC
- Equilibrium gas-phase chemistry in quiescent gas
  - $C^+ + H_2 \rightarrow CH_2^+ \rightarrow$ **CH**
    $\rightarrow$ $CH/H_2$ correlation expected
  - removed by photodissociation
    $N(CH) \sim 0.67\ k_1\ x(C^+)\ N(H_2)\ n(H)/\{I_{UV}\ G_0(CH)\ ...\}$
    $\rightarrow$ Galaxy: $CH/H_2$ reproduced by $(I_{UV} = 1)$ $n_H = 500\ cm^{-3}$
  - LMC/SMC: $x(C^+)$, $I_{UV}$ $\rightarrow$ $n_H = 1200 - 2900\ I_{UV}$
  - **Inconsistent with densities inferred from $H_2$**

# CH ~ KI, NaI
# $CH^+$ ~ CH





CH+ in the Galaxy
CH+ in LMC formed in PDRs
CH+ + H2 → CH2+
+ H2 → CH3+
+ e → CH
N(CH) ~ 0.67 k1 N(CH+) f(H2) n(H) / IUV G0(CH)
• N(CH)/N(CH+) → nH = 100 – 1000 cm-3,
consistent with densities from H2 analysis

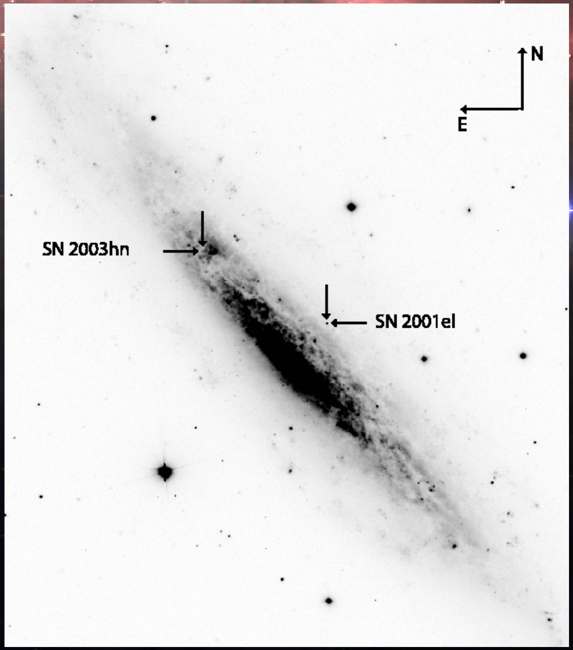
# The diffuse interstellar bands

- 226 DIBs confirmed, maybe up to 400
  - **BD+63º1964 (Tuairisg et al. 2000)**
  - **Confusion limit, >1 carrier responsible for a given feature**
- Carriers
  - **Large C-bearing molecules in gas phase**
  - **PAH and fullerene cations**
  - **Lyα induced 2-photon absorption by $H_2$**
- Needed:
  - **Use CH, $CH^+$, CN, $C_2$, CaI, CaII, NaI to determine variations in physical parameters**

# The diffuse interstellar bands

- Ehrenfreund et al. 2002
  - **DIBs in the MCs**
  - **Not too different from Galactic clouds despite low metallicity**
- Sollerman et al. 2005
  - **DIBs towards SNIa in NGC 1448**
  - **Correlations with CaII and NaI**

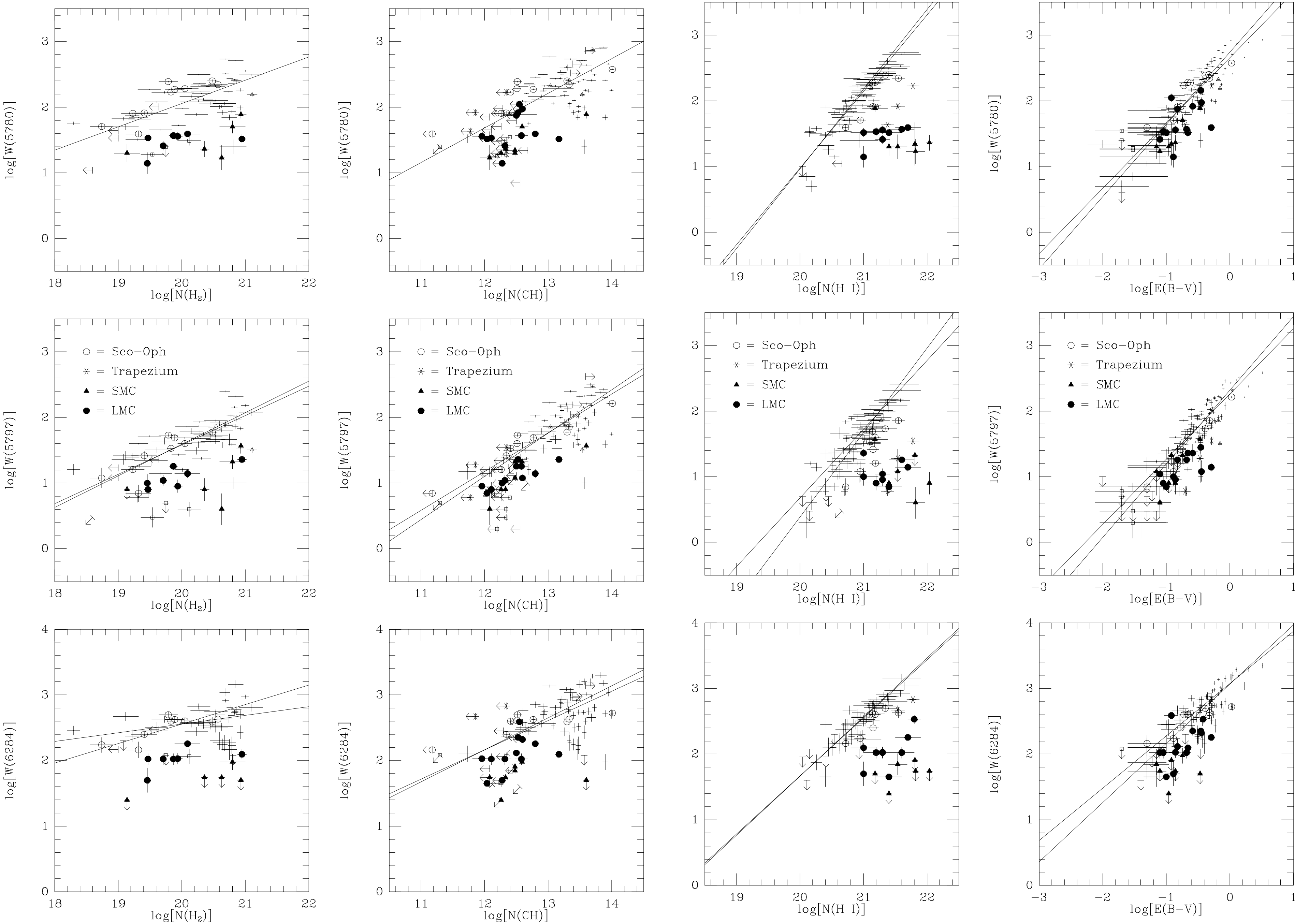
Local conditions affect DIB strength, in particular IUV
SN absorptions: DIBs are readily formed and survive different physical & chemical environments
→ **universal carbon chemistry**



# DIB carriers

- Large Molecules → fundamental role in ionisation balance
  - Liszt 2003 PAH grain neutralisations
    - Heating balance: radiative and dielectronic recombination of charged ions
    - $PAH^- + H^+$ → PAH + H rapid destruction of protons

Ionisation rate must be significantly increased



log[W(5780)]
log[W(5797)]
log[W(6284)]
log[N(H₂)]
log[N(CH)]
log[N(H I)]
log[E(B−V)]
○ = Sco−Oph
✳ = Trapezium
▲ = SMC
● = LMC

# Diffuse Interstellar Bands in MCs

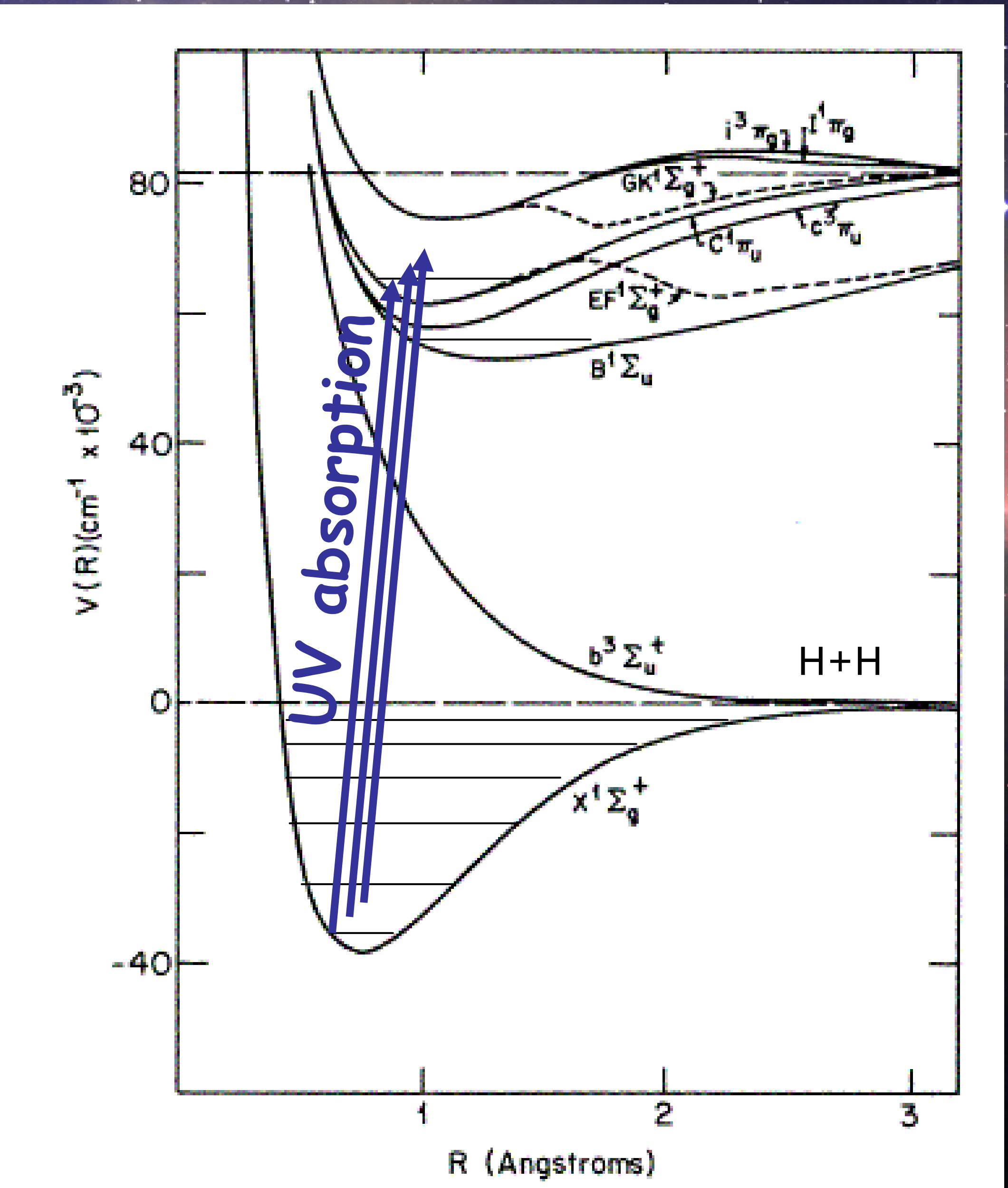
- Several detections
  - No obvious correlation with N(HI) as in Galaxy
  - Good correlation with $E_{B-V}$
  - On average weaker 5780, 5797, 6284 DIBs
    by factors of 10 in LMC, 20 in SMC, relative to HI
    by factors of 2 relative to $E_{B-V}$
  - W(6284)/N(HI)  factors 30-70 below Galaxy
  - $C_2$-DIBs as strong as in Galaxy

  - **No uniform scaling relations**

# FUV $H_2$ & CO absorption lines

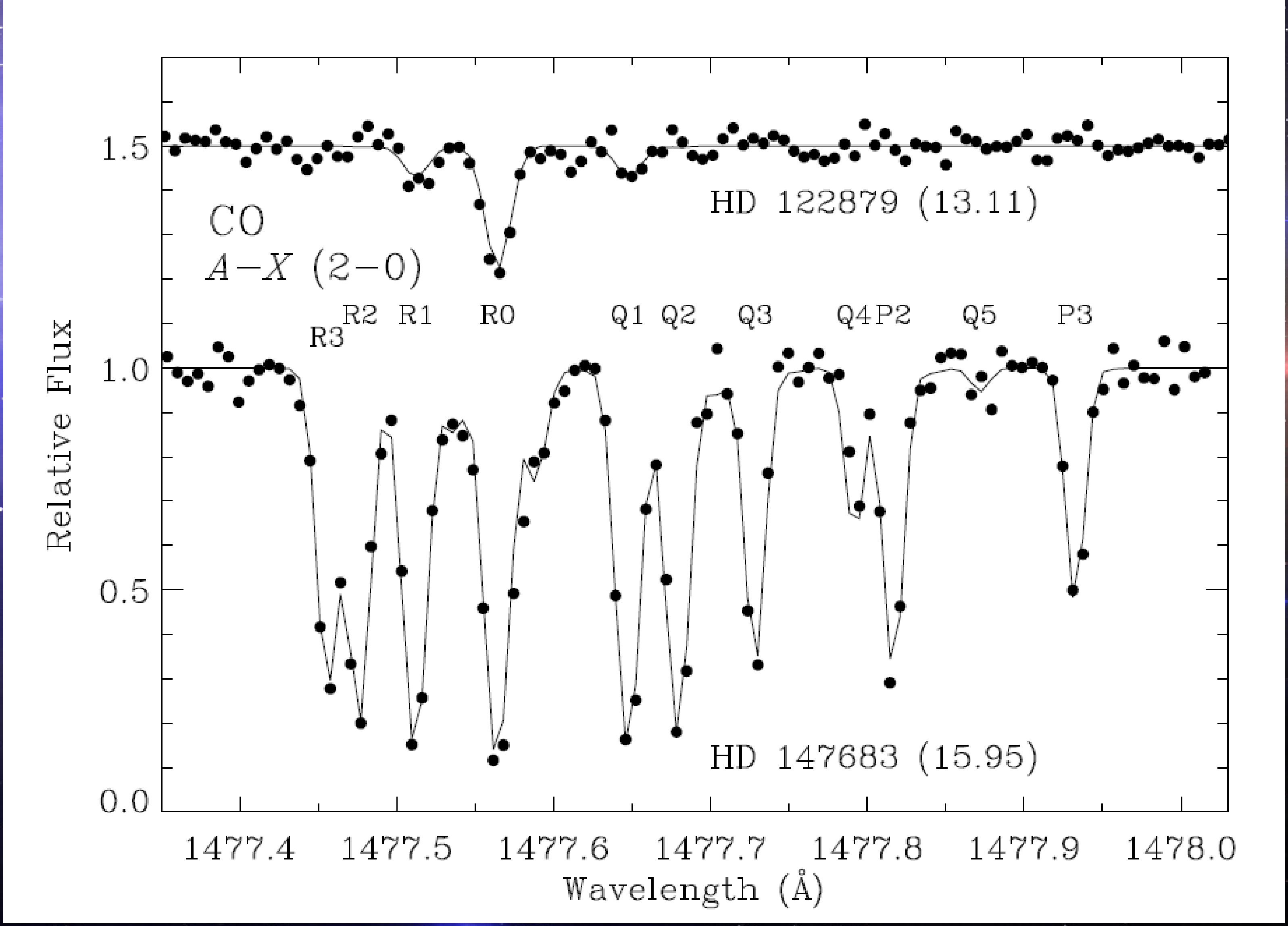
- HST: CO A-X band, 1229 – 1544 a
  - 66 sightlines, 43 new results
- FUSE: $H_2$ (2,0), (3,0), (4,0) Lyman bands
  - 58 sightlines, 33 new results
- Saturation → profile fitting
  - cloud structure confined by CH
  - → accurate N($H_2$), N(CO)
- ESO & McDonald data
  - CH, CH+, CN
  - R = 170,000 – 220,000

# FUV absorption lines of $H_2$

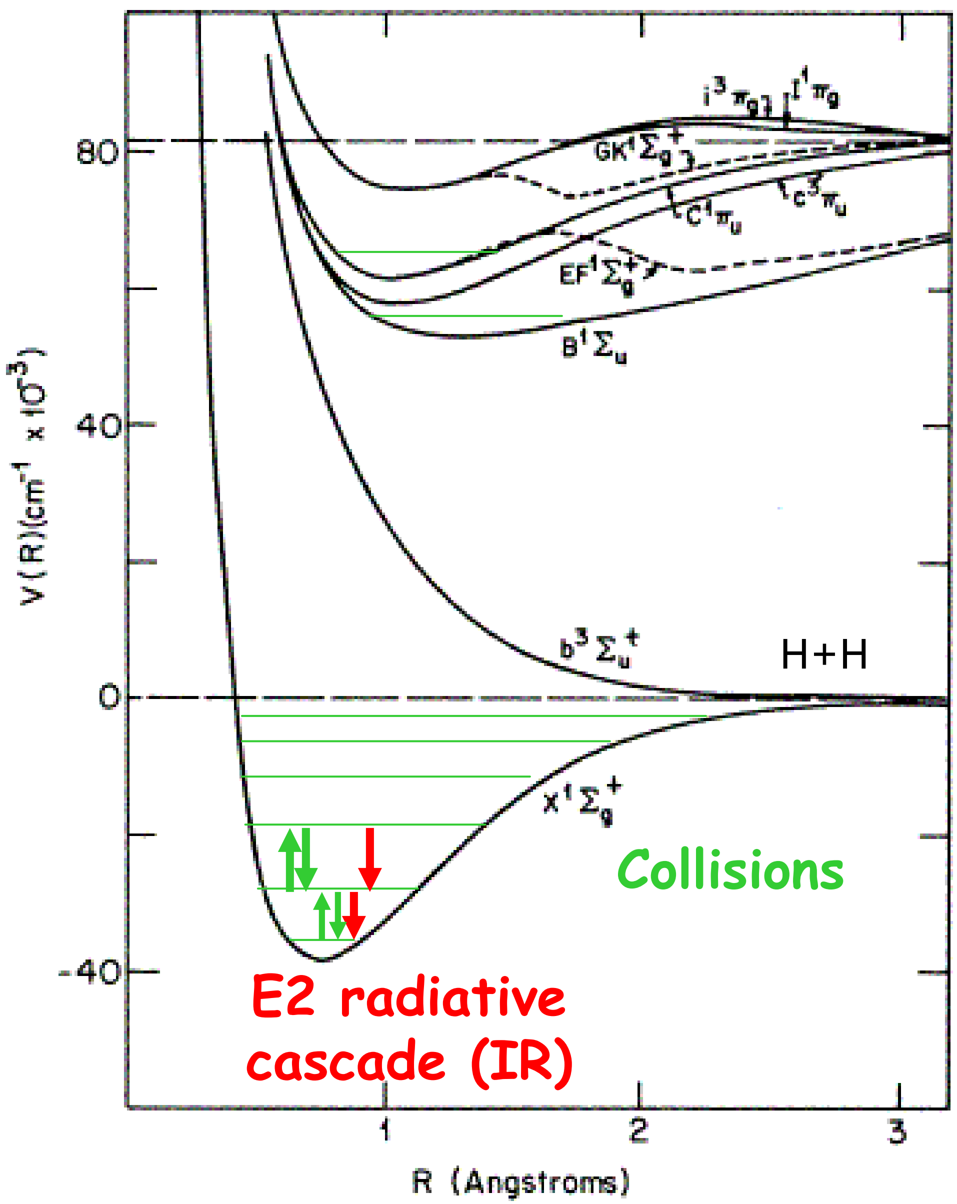



- UV: Lyman & Werner bands
- $T_{rot}$, $n_H$, $I_{UV}$

# FUV $H_2$ & CO absorption lines

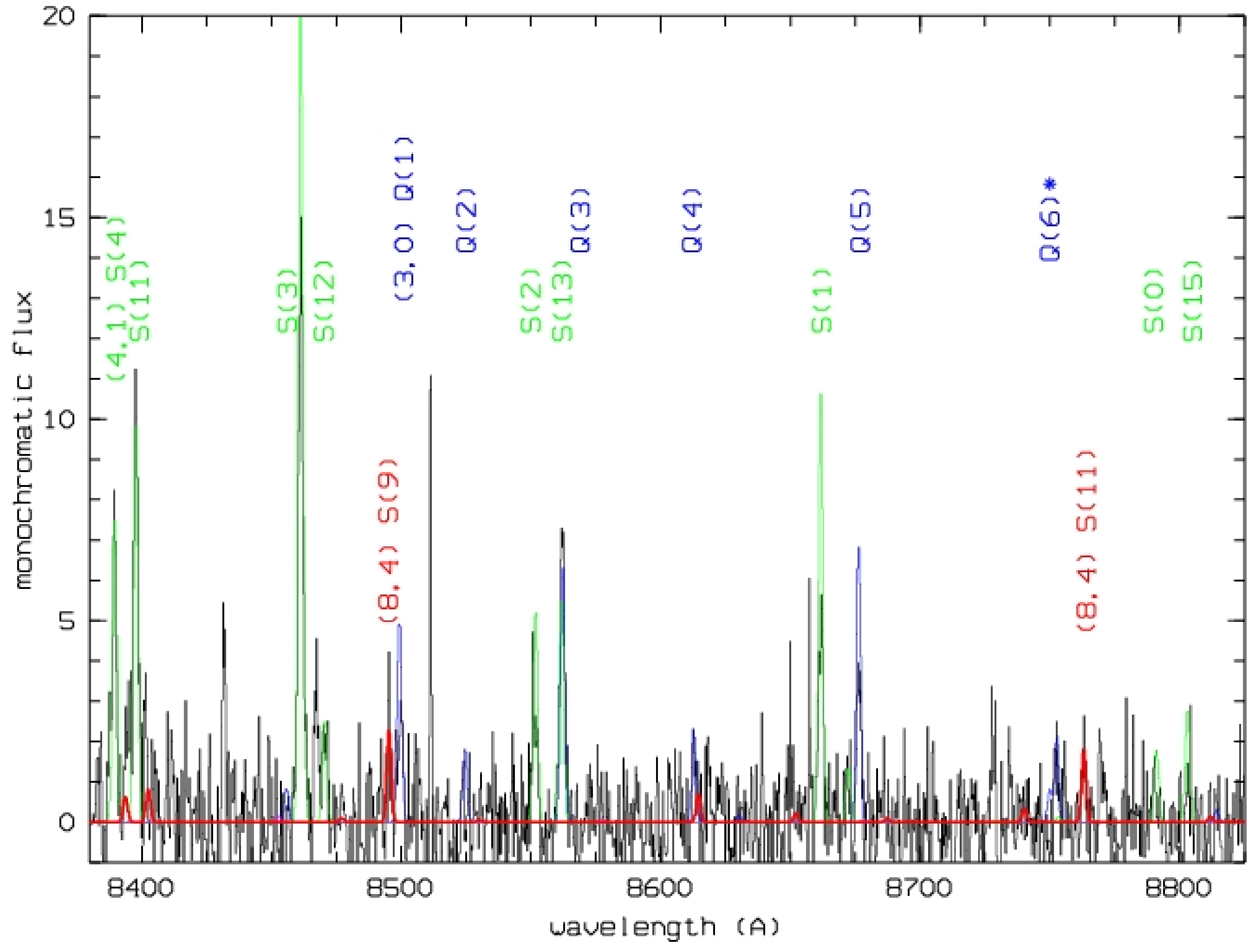


# $H_2$ thermal excitation in shocks

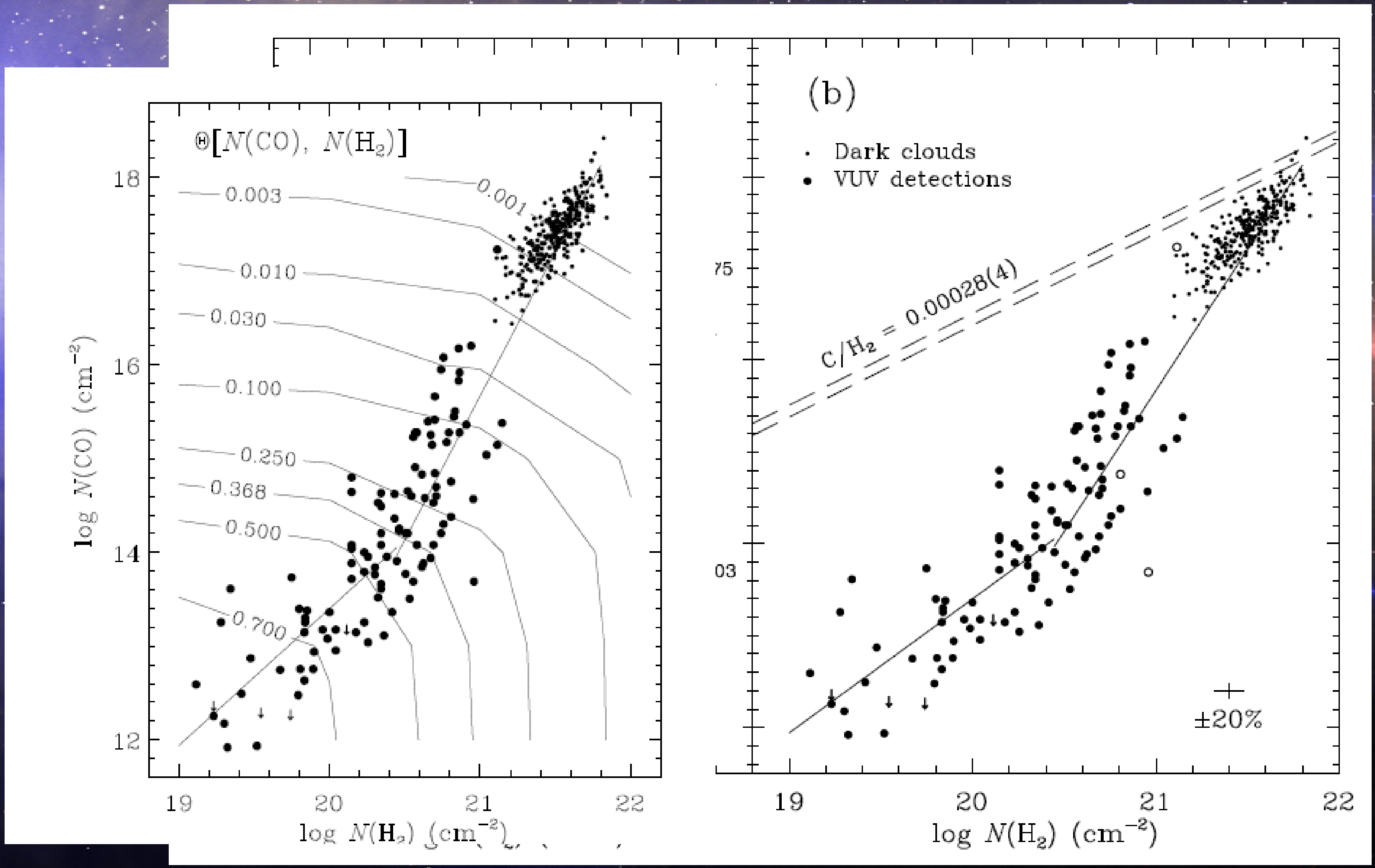



- $X\ ^1\Sigma_g^+$ v'J' collisional excitation by H, H2, He
- Boltzmann distribution up to v'J'
- **NIR $H_2$ emission**
- **v'J' → v''J'' E2**
- C-type vs. J-type → evolutionqry state
- L($H_2$) ~ L(YSO)
- **T, n, ($v_s$)**

# $H_2$ in interstellar shocks



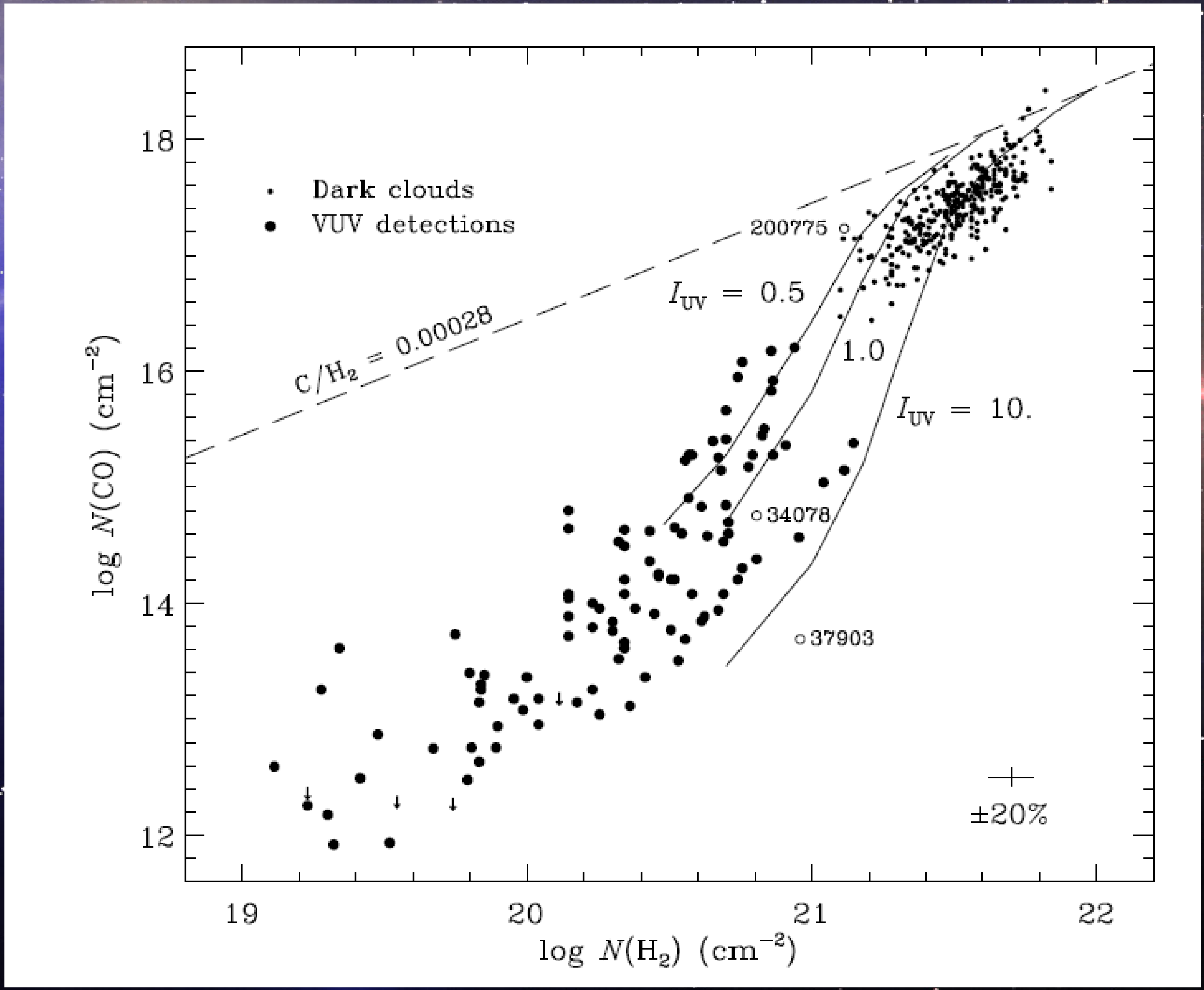
# N(CO) vs. N($H_2$)


Θ[N(CO), N(H2)]
0.001
0.003
0.010
0.030
0.100
0.250
0.368
0.500
0.700
log N(CO) (cm−2)
log N(H2) (cm−2)
(b)
Dark clouds
VUV detections
C/H2 = 0.00028(4)
±20%
12
14
16
18
19
20
21
22

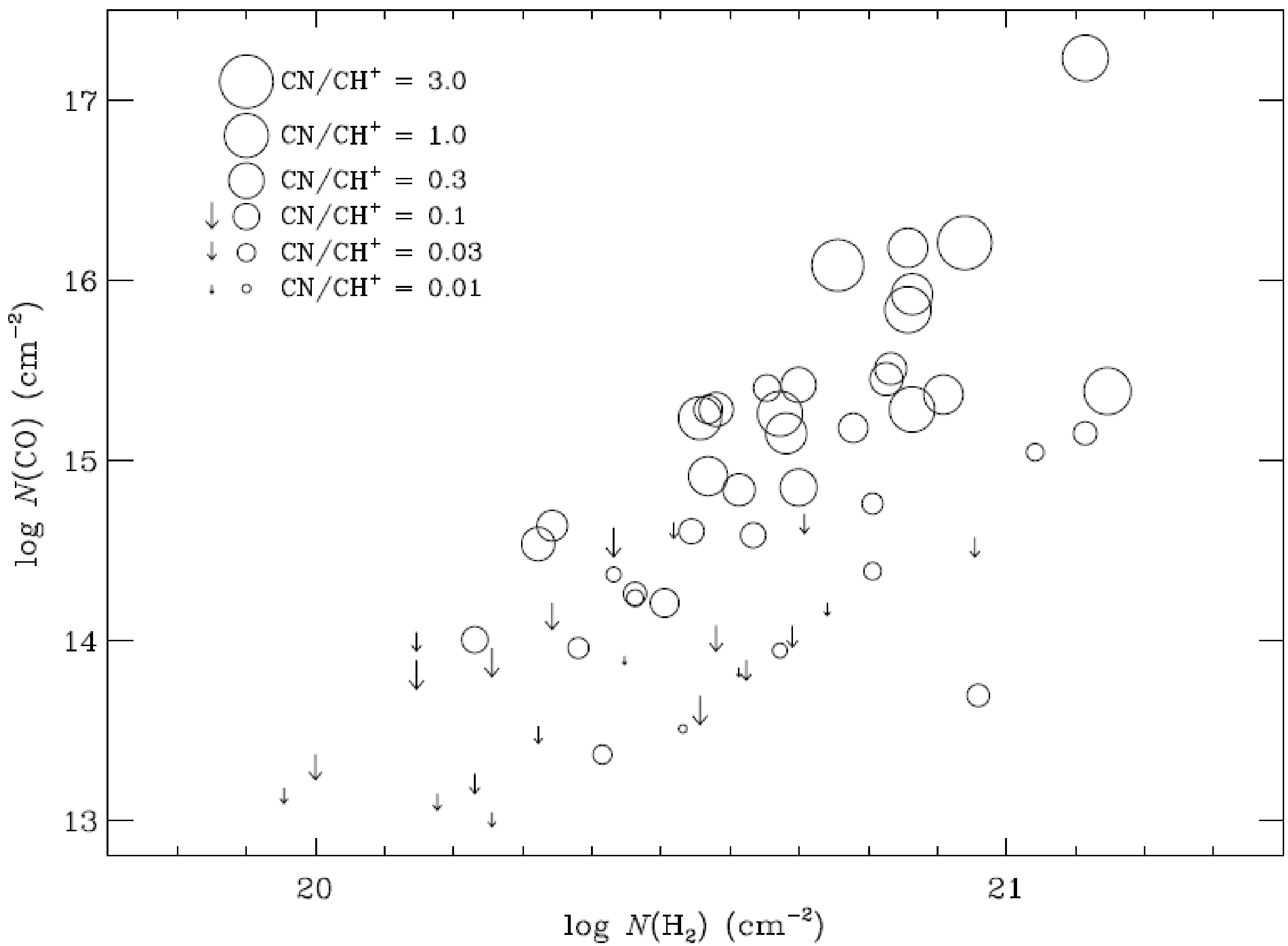
# N(CO) vs. N($H_2$)

- Break in quadratic relation
  - log N(H2) ~ 1.5 log N(CO) $< 10^{14}$ cm$^{-2}$
  - log N(H2) ~ 3.1 log N(CO) $< 10^{14}$ cm$^{-2}$
  - good connection to dark cloud values (CO from $W_{CO}$; N($H_2$) inferred from $A_V$
  - CO shielding parameter
    - Break caused by change in CO photochemistry
    - Initiation of CO UV shielding
    - confirmation of vD&B1988 shielding function
  - Break: Low density vs. high density chemistry

# N(CO) vs. N($H_2$)

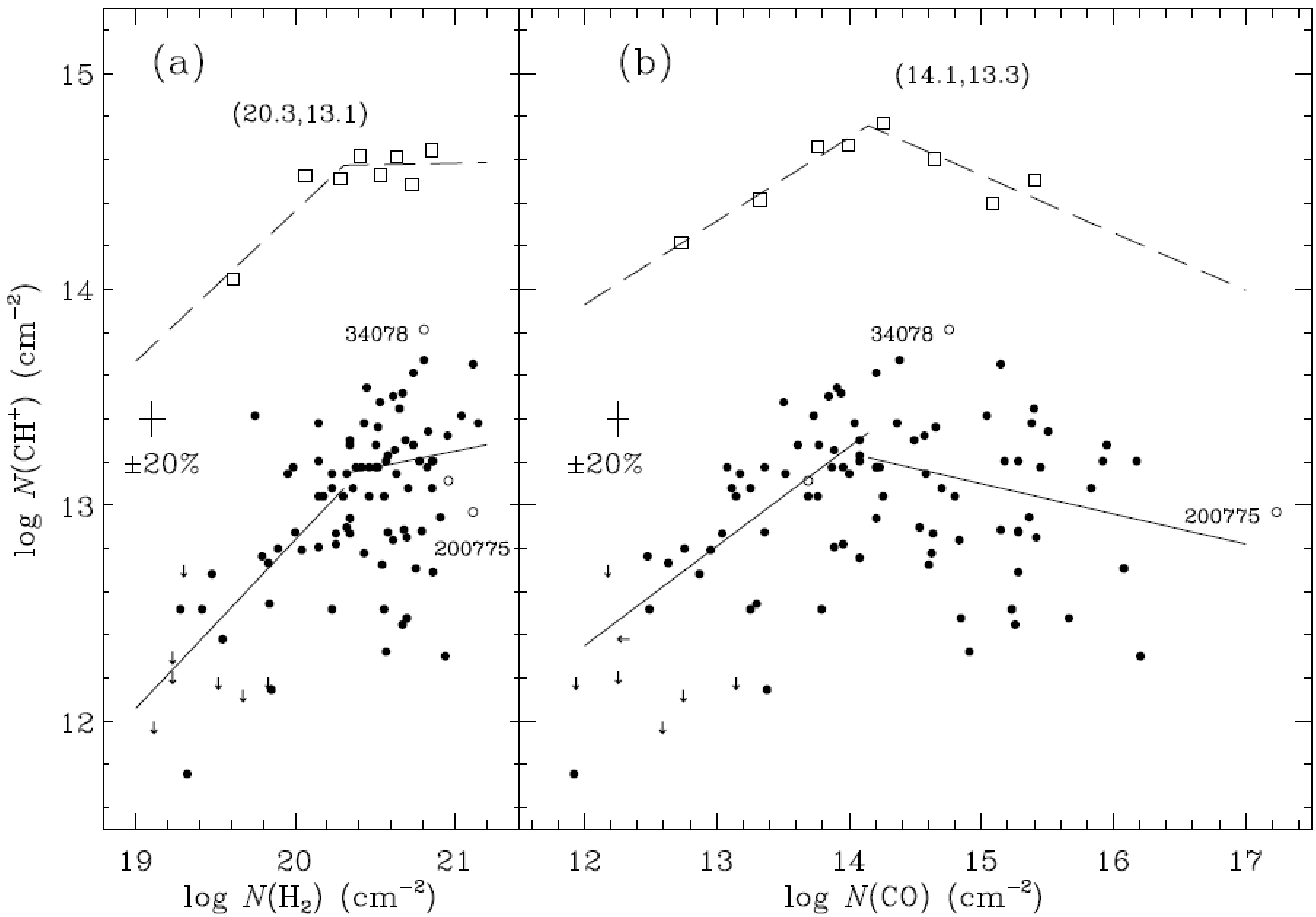


Dark clouds
VUV detections
C/H2 = 0.00028
200775
IUV = 0.5
1.0
IUV = 10.
34078
37903
±20%
log N(CO) (cm−2)
log N(H2) (cm−2)
18
16
14
12
19
20
21
22

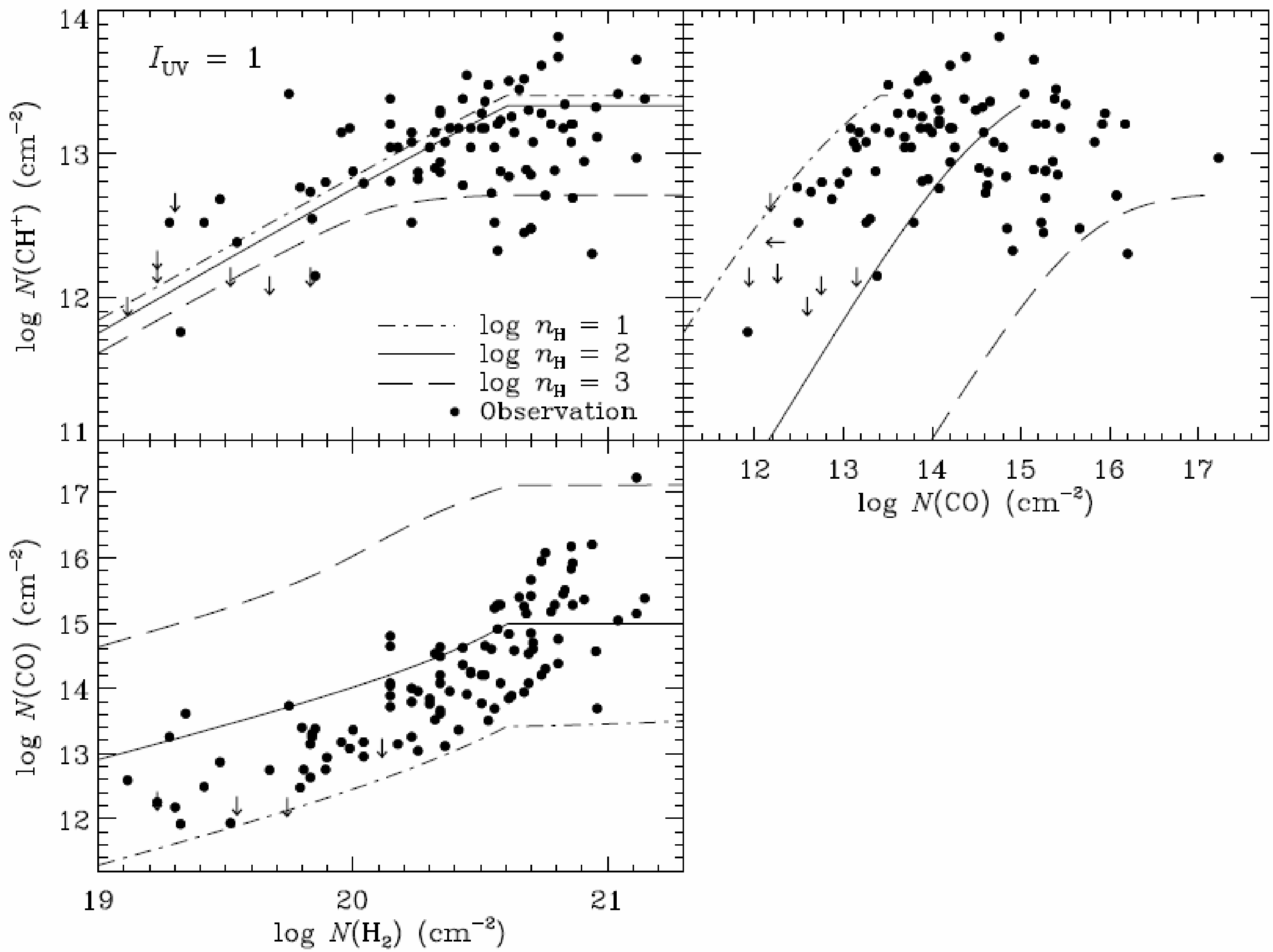


CN/CH+ = 3.0
CN/CH+ = 1.0
CN/CH+ = 0.3
CN/CH+ = 0.1
CN/CH+ = 0.03
CN/CH+ = 0.01
17
16
15
14
13
log N(CO) (cm−2)
20
21
log N(H2) (cm−2)

# CH vs. $H_2$, $CH^+$ vs. CO, $H_2$



# CH vs. $H_2$, $CH^+$ vs. CO, $H_2$



# Summary

## I. Diatomic molecules

- First detection of CH, $CH^+$ (SN1987A) & CN
- **CH production in extensive PDRs together with $CH^+$**
- Dense gas (CN-like CH) towards Sk 143 & Sk –67°2

## II. Diffuse Interstellar Bands

- 5780, 5797, 6284 weaker by 10 (LMC) – 20 (SMC) relative to HI, weaker by 2 – 6 relative to $E_{B-V}$ ← $I_{UV}$, metallicity
- $C_2$-DIBs towards Sk143 and Sk-67°2, similar strengths as in Galaxy

  → **no uniform scaling relations**

# Summary

- Direct determination of $X = N(H_2)/N(CO)$
- $N(CO) \sim N(H_2)$
  - Importance of CO UV shielding
  - Importance of CO production via $CH^+$
  - LePetit 2006, Sonnentrucker 2007
  - Reproduction of observed $CH^+$ levels in non-Maxwellian velocity fields

# Outlook

- DIBs: Jena, D. Huisken → UV spectra of potential carriers