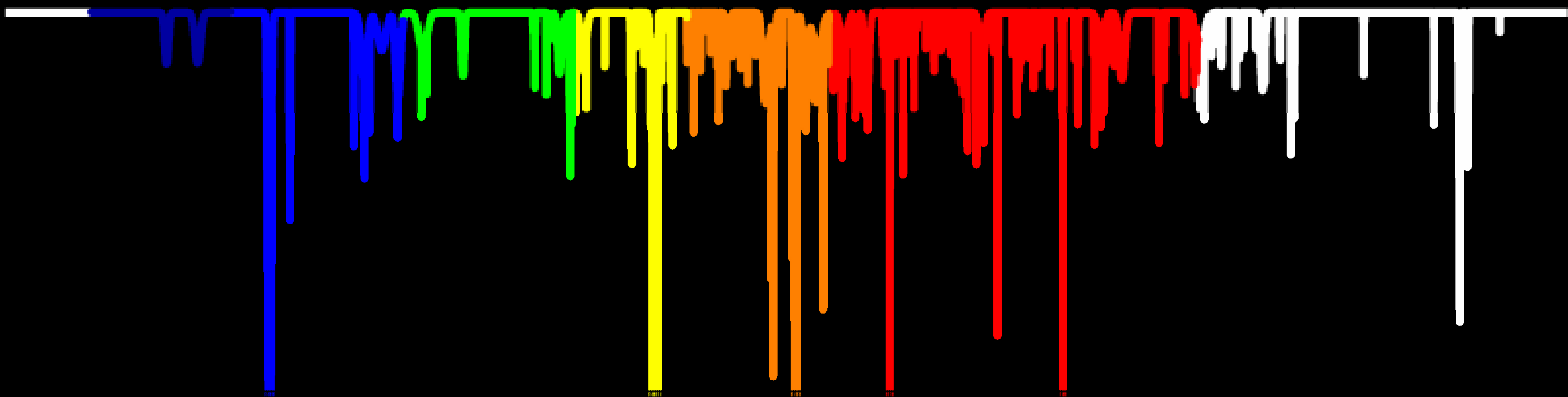


Electronic Transition Spectra of Thiophenoxy and Phenoxy Radicals in Hollow cathode discharges

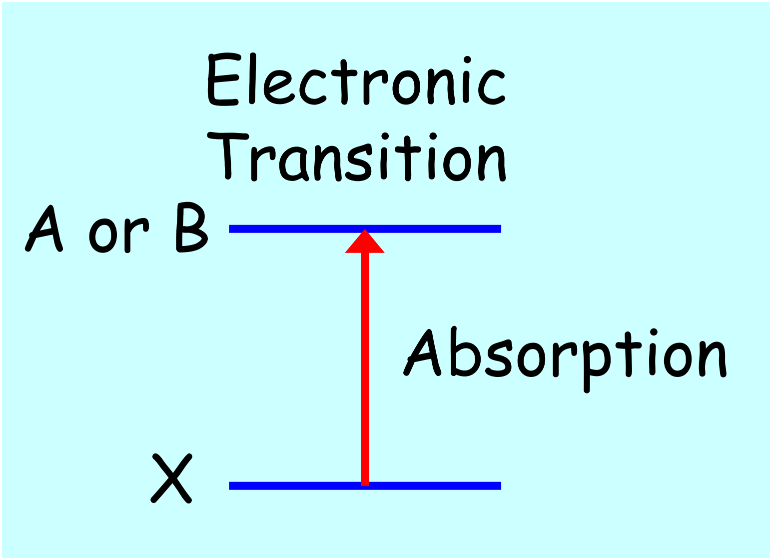
Tokyo Univ. Science

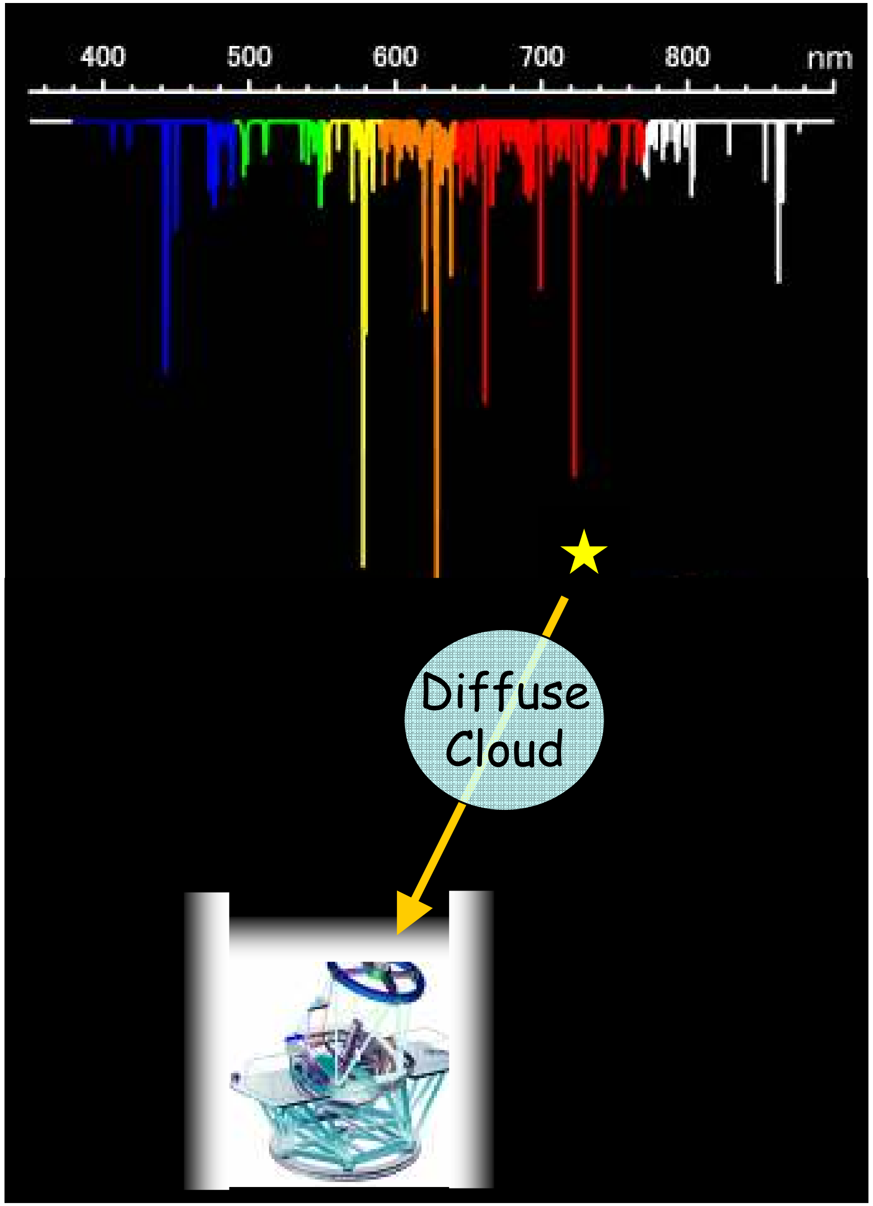
Mitsunori ARAKI, Hiromichi WAKO,

Kei NIWAYAMA and Koichi TSUKIYAMA○

2014/06/16

Diffuse Interstellar Bands





- Optical absorption lines by molecule in diffuse cloud
- Near infrared ~ optical (line width: 0.5-50Å)
- First report: 1922
- ~600 lines

What are origins of DIBs ?

Optical Transition

⇩

Ion and/or radical

Large Molecule

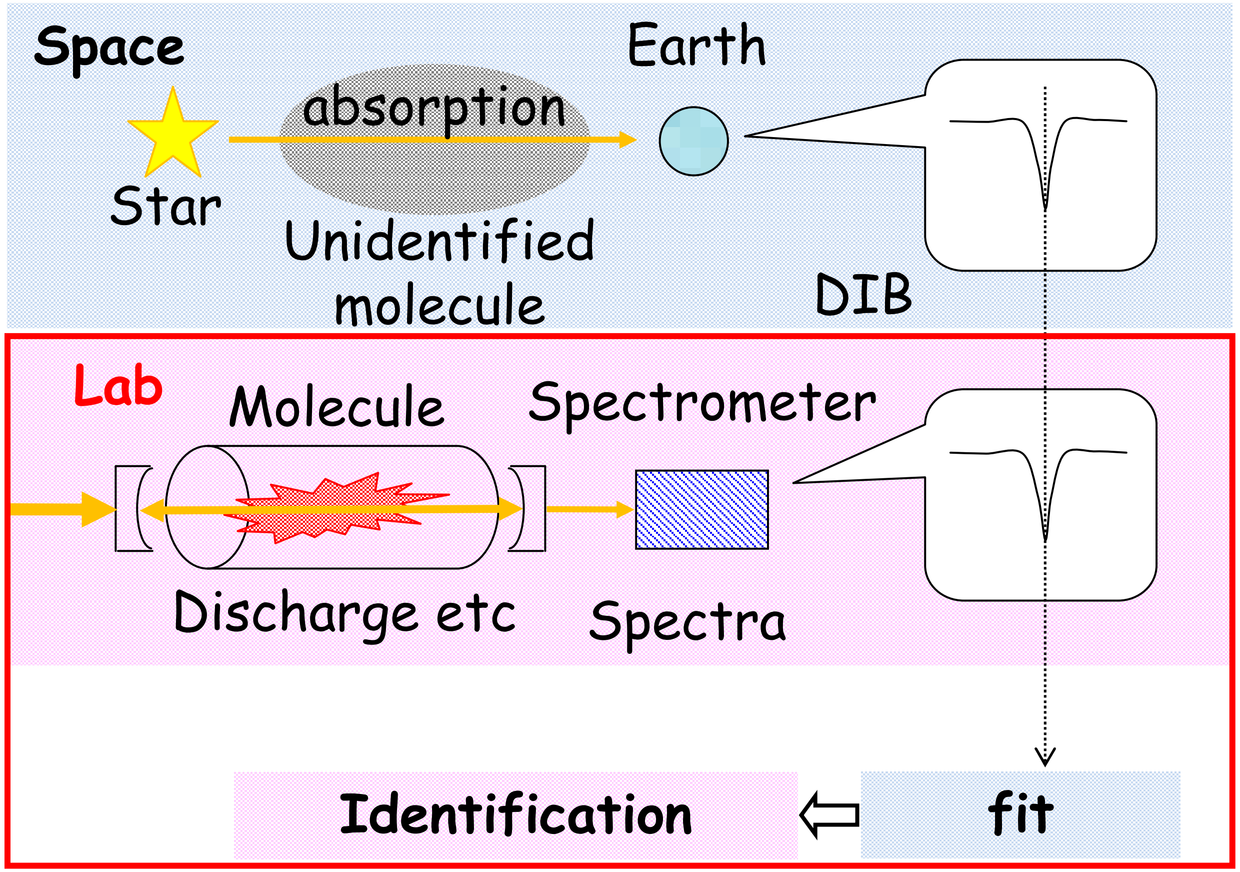
⇩

Not Identified yet

Identification of DIBs
by Laboratory Spectroscopy

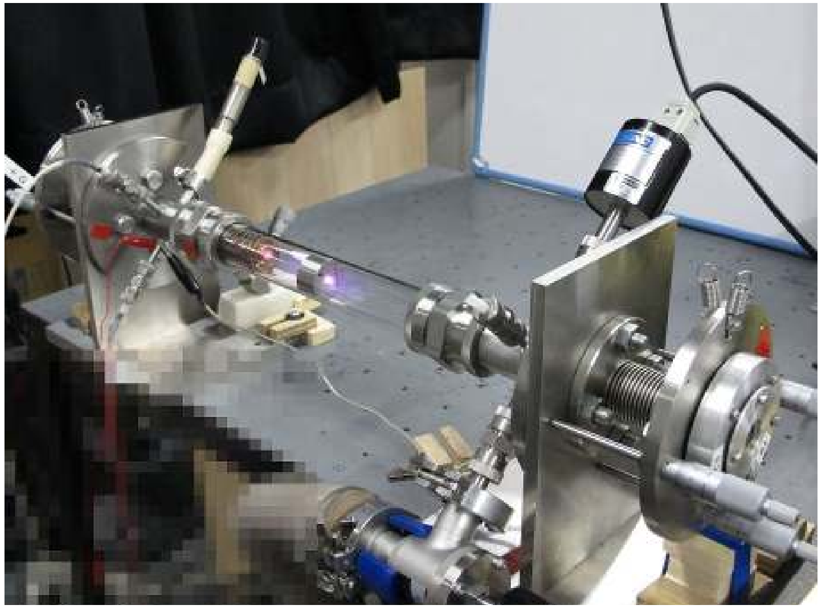
How to identify DIBs ?

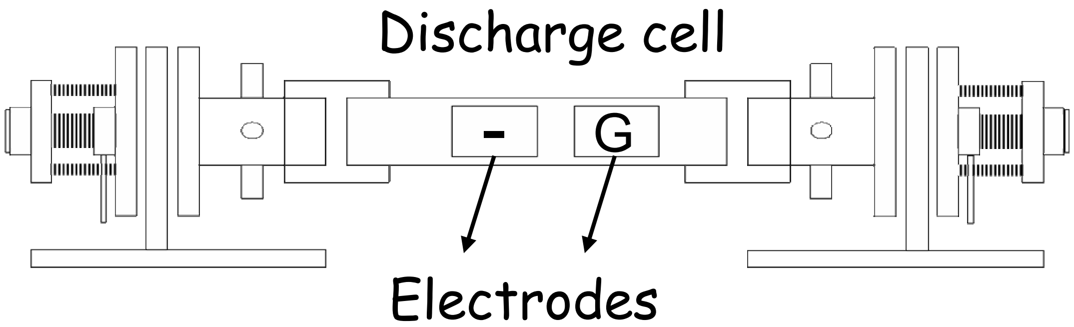
Optical Electronic Transition



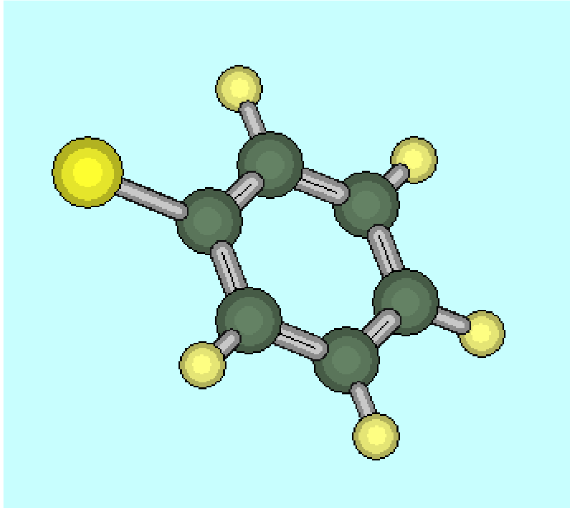
Cavity Ring Down Spectrometer

Pulsed dye laser, 10 Hz, $\Delta\nu$ = 0.1 cm^{-1}





Thiophenoxy Radical C_6H_5S



Rotational Profile
Model molecule to discuss
Non-Boltzmann Distribution
in diffuse cloud

- Radical: Optical Transition
- 10% of interstellar molecules -> Sulfide
- Simple PAH
- **Good candidate of DIB**

Dose it fit to DIBs?

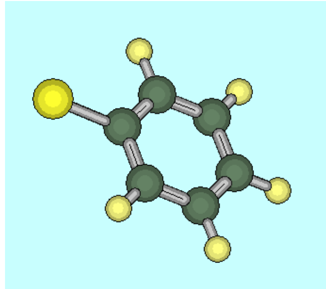
Reported Laboratory Spectrum

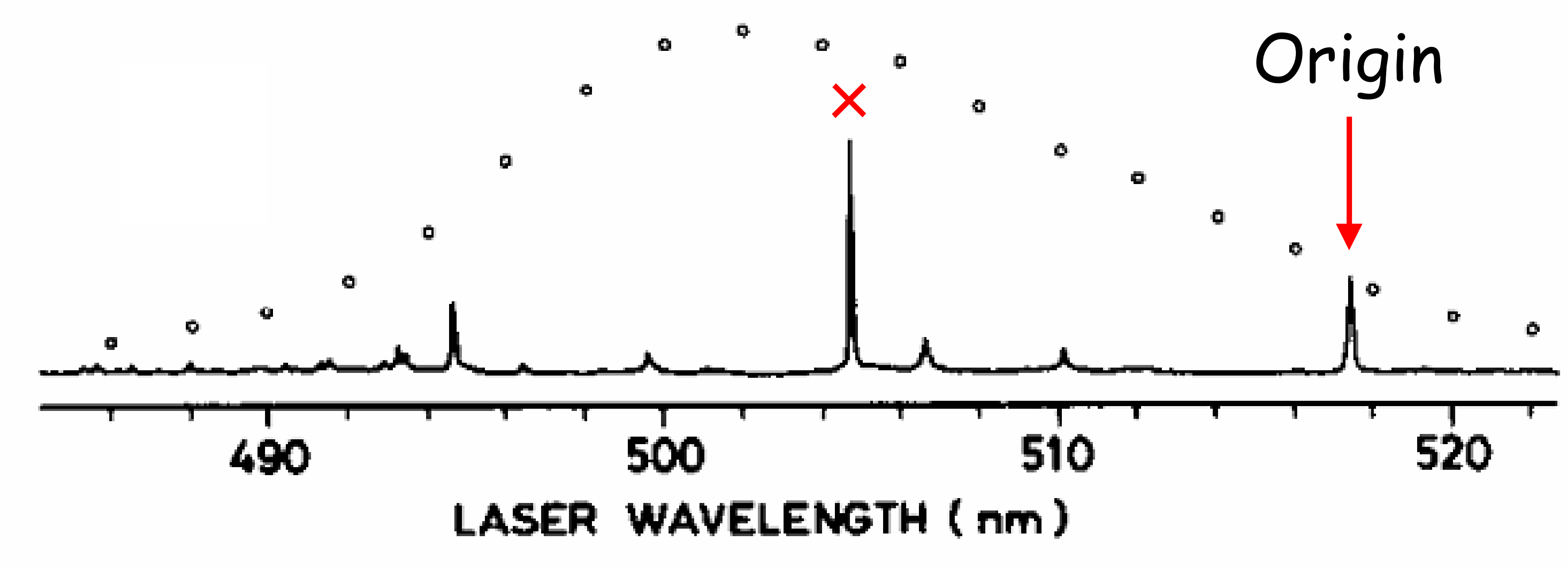
Electronic Transition

$^2A_2$ <- X^2B_1

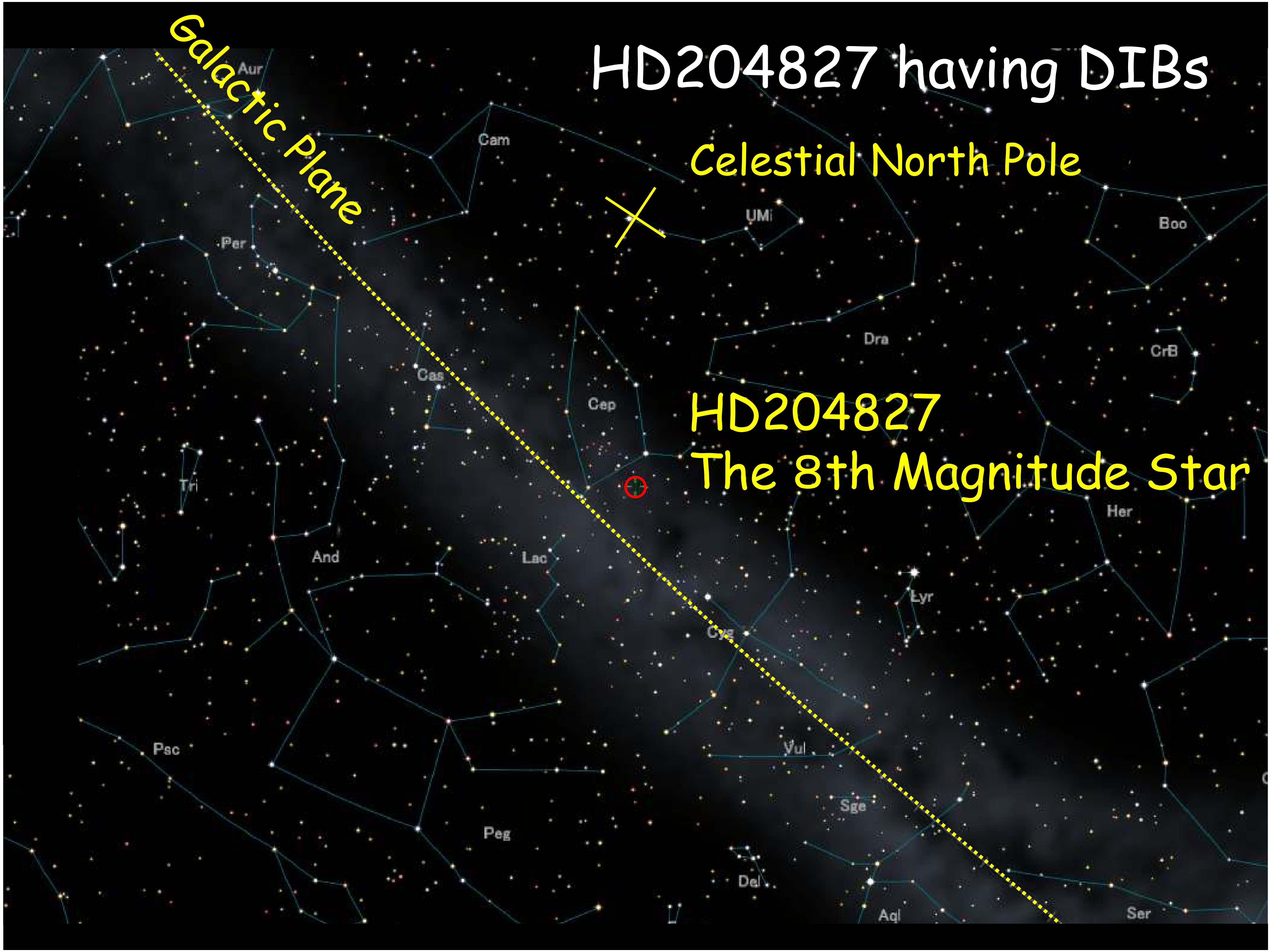
LIF

DIBs
Disturbed

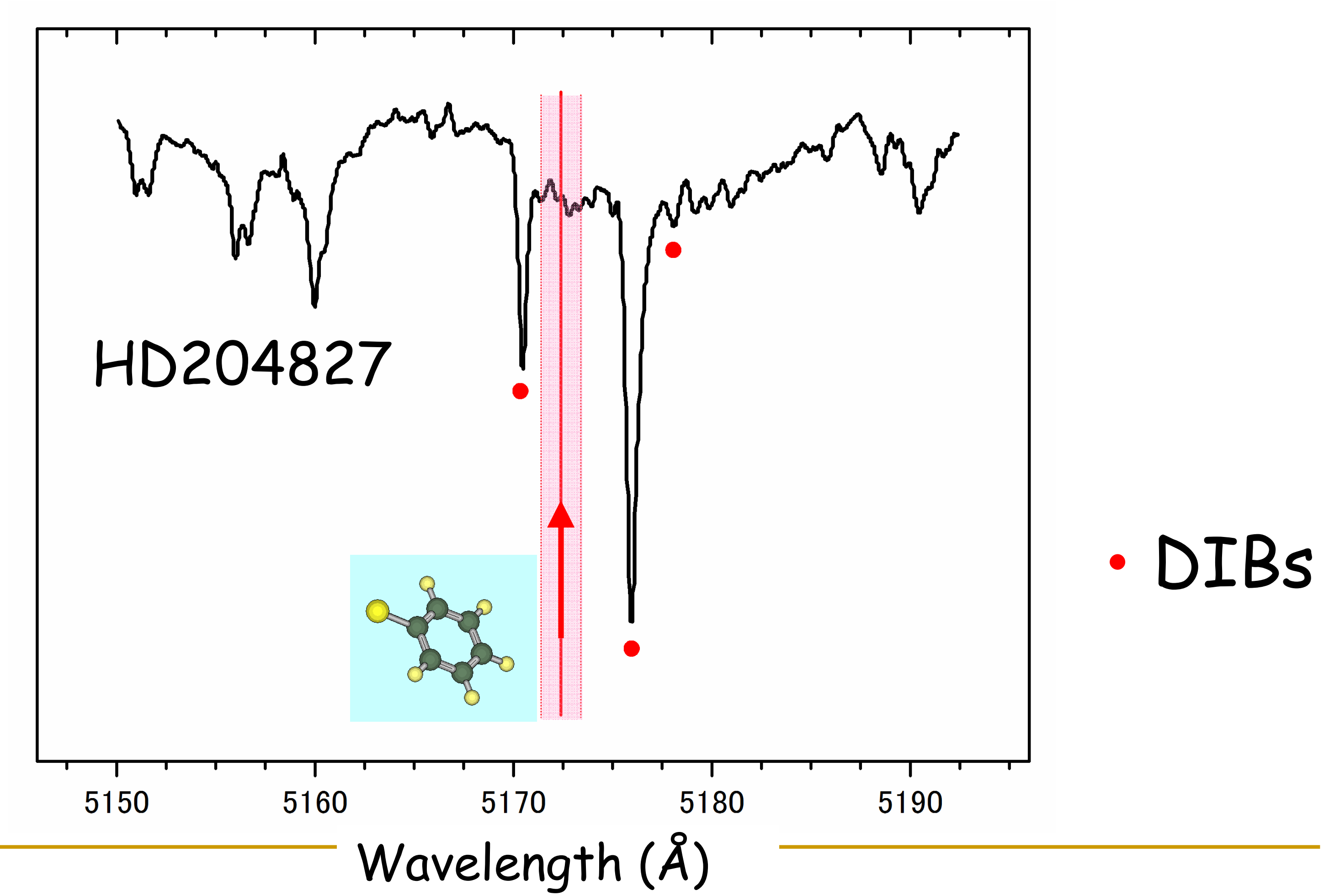




Shibuya et al., *Chemical Physics*, **121**, 237-244, 1988

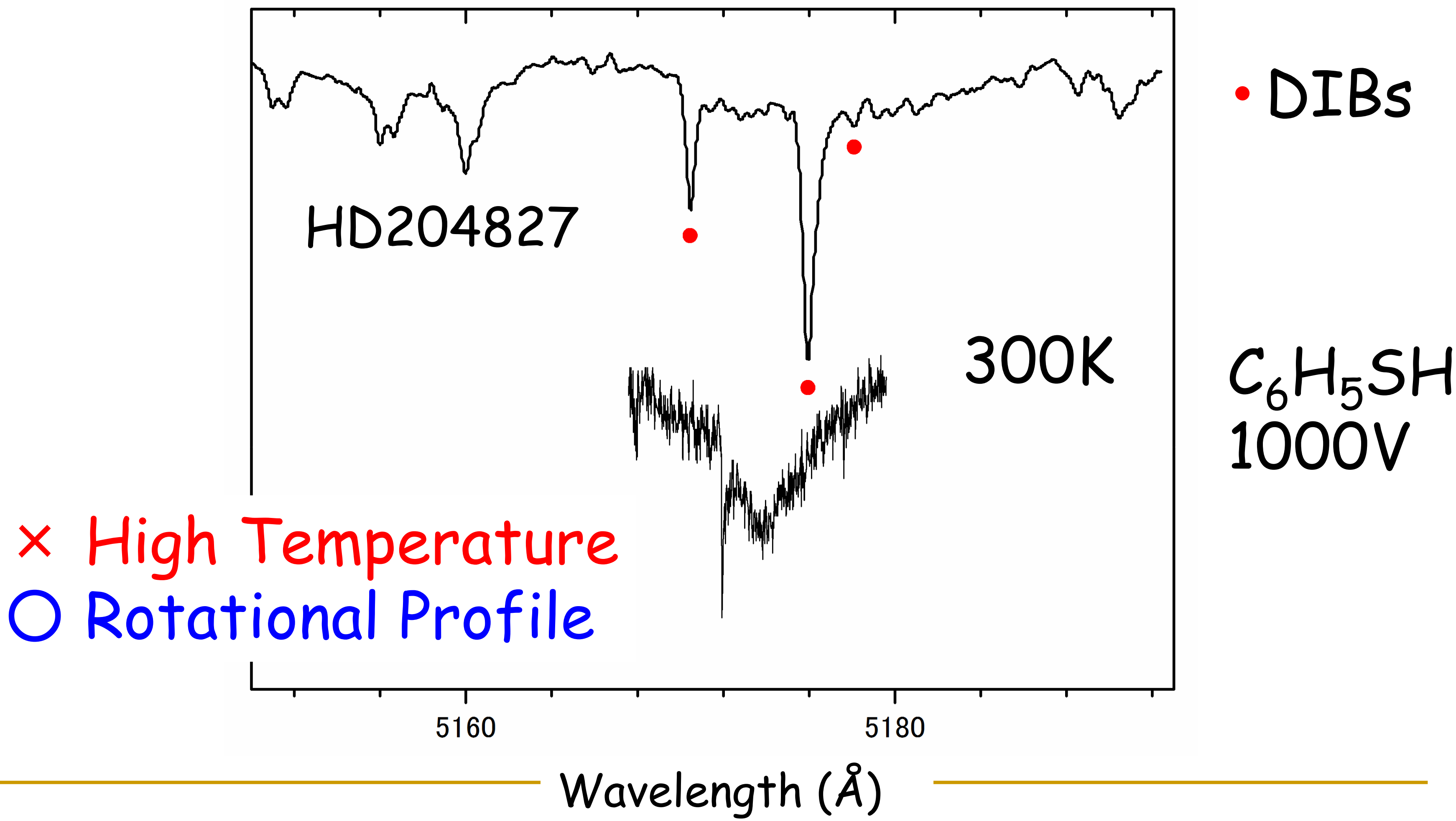

HD204827 having DIBs
Galactic Plane
Celestial North Pole
HD204827
The 8th Magnitude Star
Aur
Cam
UMi
Boo
Per
Dra
CrB
Cas
Cep
Tri
Her
And
Lac
Lyr
Cyg
Psc
Vul
Sge
Peg
Del
Aql
Ser

DIBs and
Reported Laboratory Spectrum



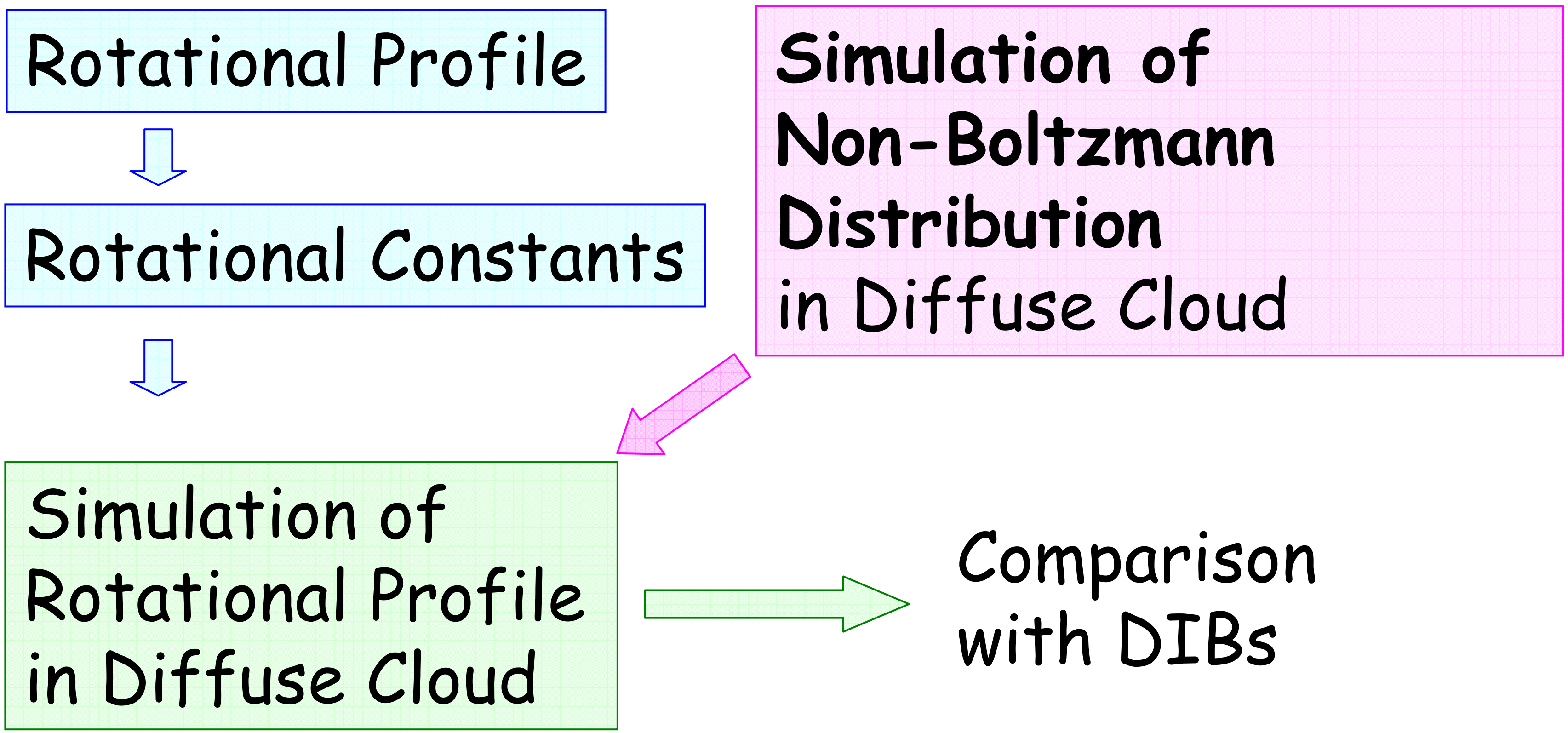
Hobbs *et al.*, *ApJ*, **680**, 1256 (2008)

DIBs and Present Laboratory Spectrum by CRD

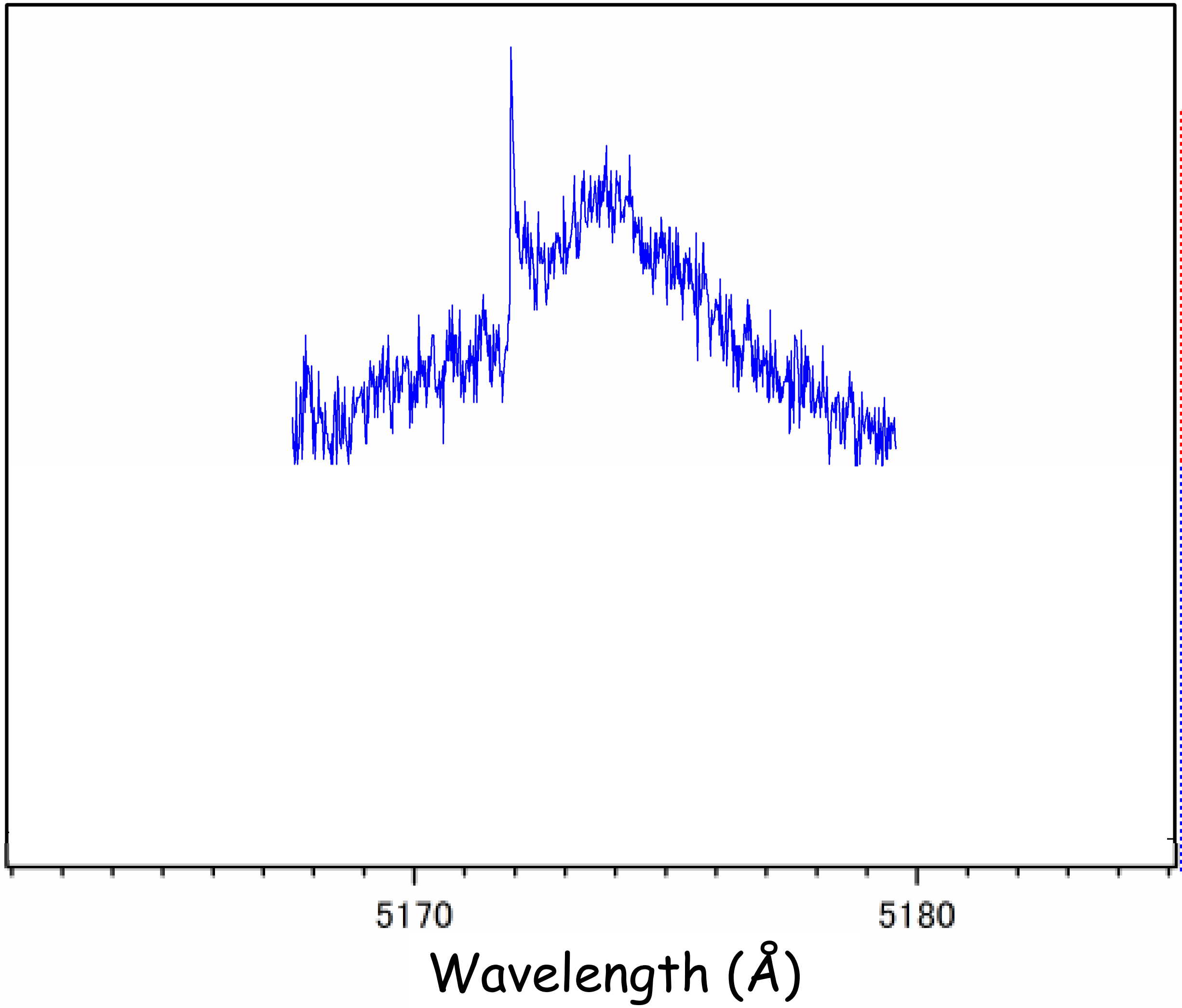


Hobbs *et al.*, *ApJ*, **680**, 1256 (2008)

Analysis of C_6H_5S



Rotational Constants from Rotational Profile



(cm^{-1})

B3LYP/cc-pVTZ

$A'' = 0.1893$

$B'' = 0.0546$

$C'' = 0.0424$

$\Delta A = 0.0073(5)$

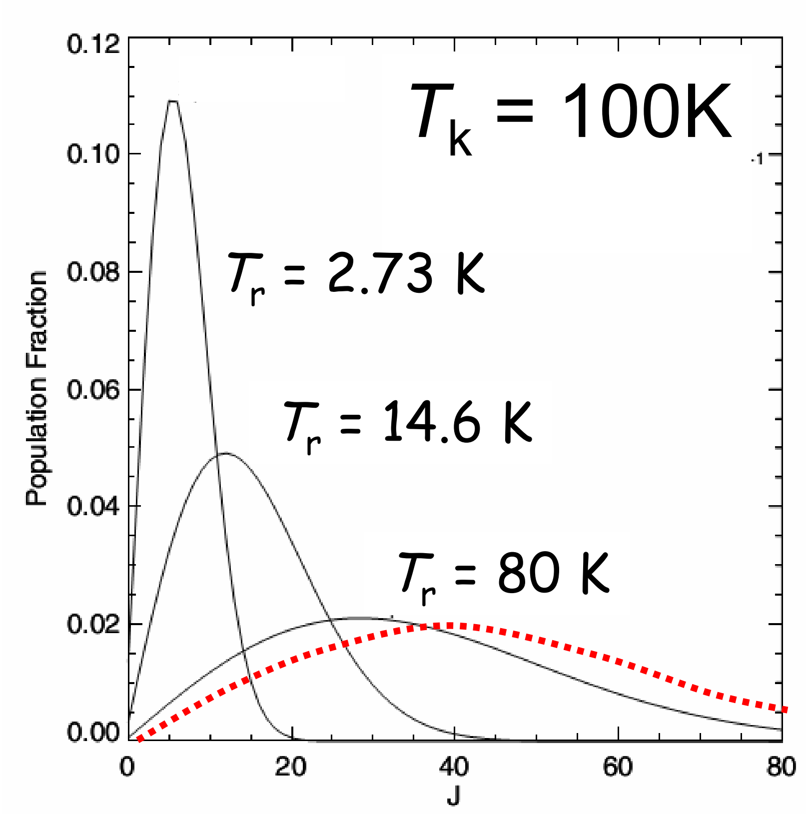
$$\Delta\left(\frac{B+C}{2}\right) = -0.0017(1)$$

$T_{00} = 19327.7(3)$

Pgopher

Non-Boltzmann Distribution in Diffuse Cloud

- Dark Clouds — Collision >> Radiation
- Diffuse Clouds — Less Collision + Radiation



Linear Molecule

Oka *et al.*, 2013, ApJ, 773, 42O

Non-Boltzmann Distribution in Diffuse Cloud

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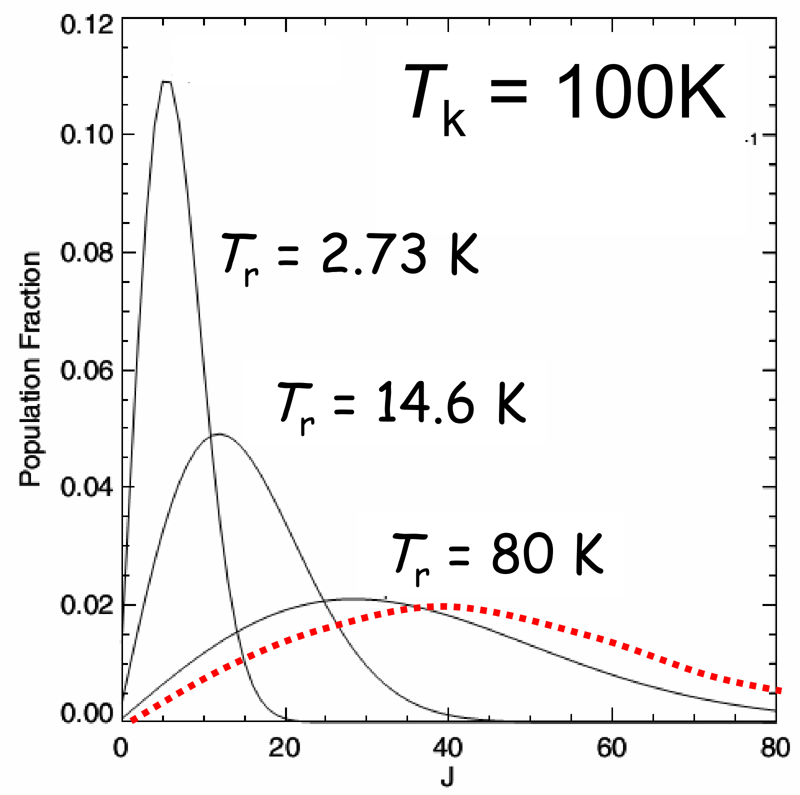


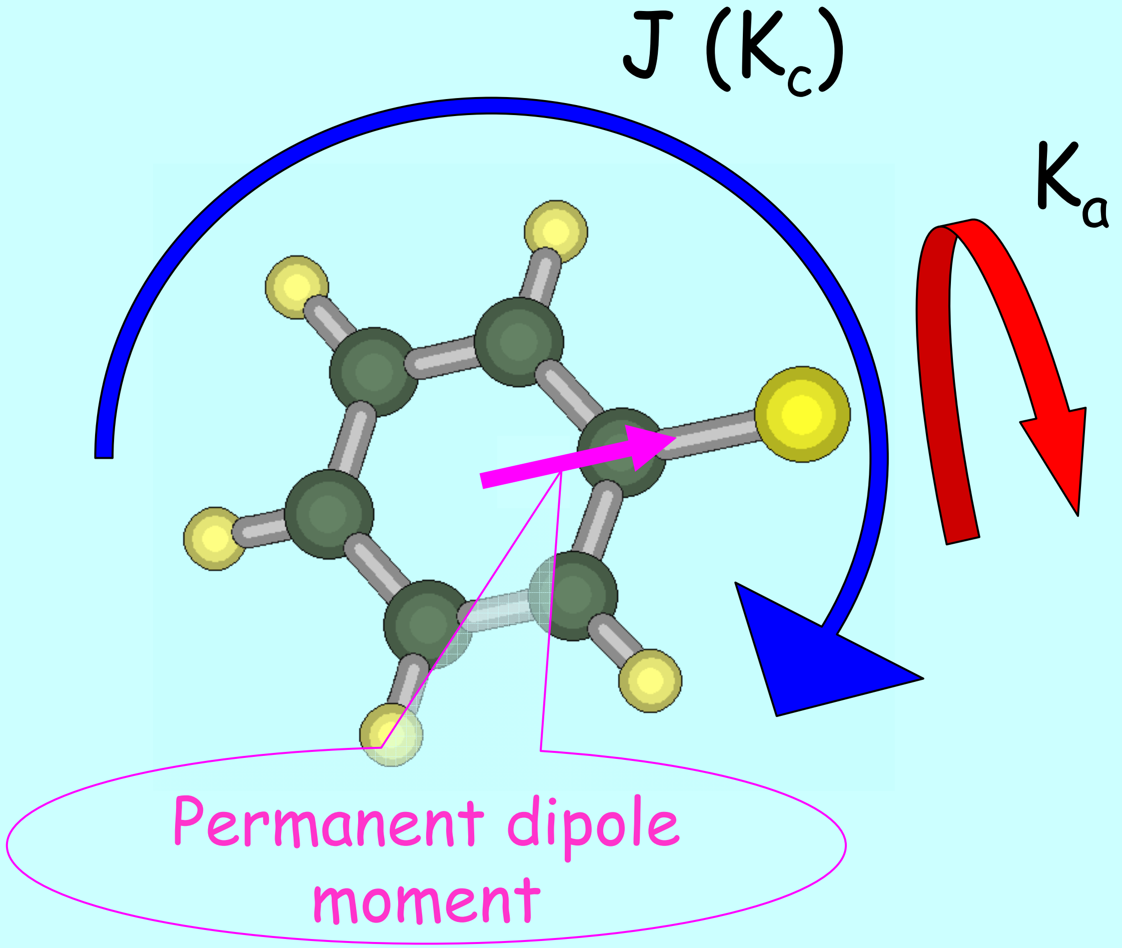
Linear Molecule

Oka *et al.*, 2013, ApJ, 773, 42O

C_{2v} Asymmetric Top

Singlet

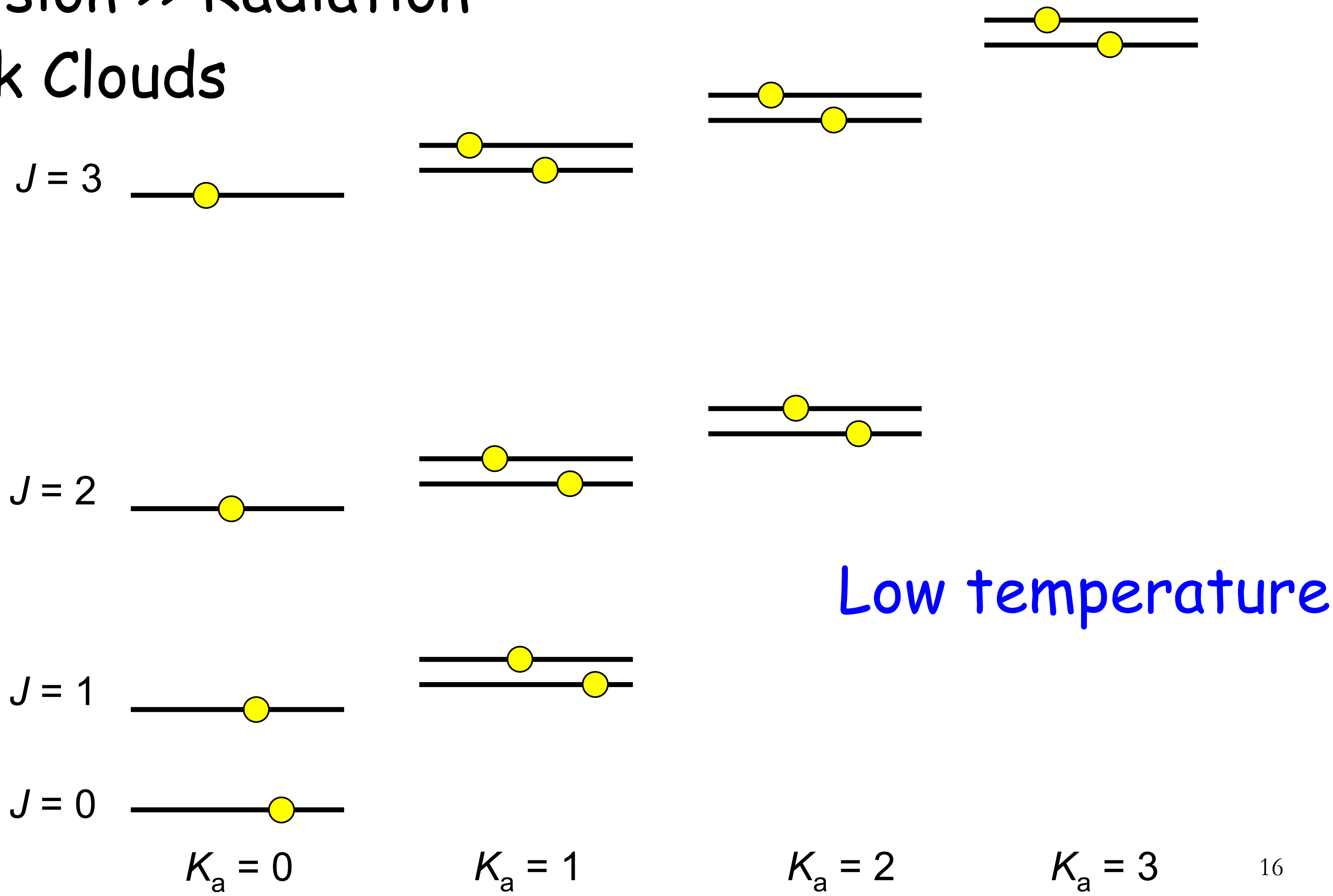
Rotation of C_{2v} Asymmetric Top



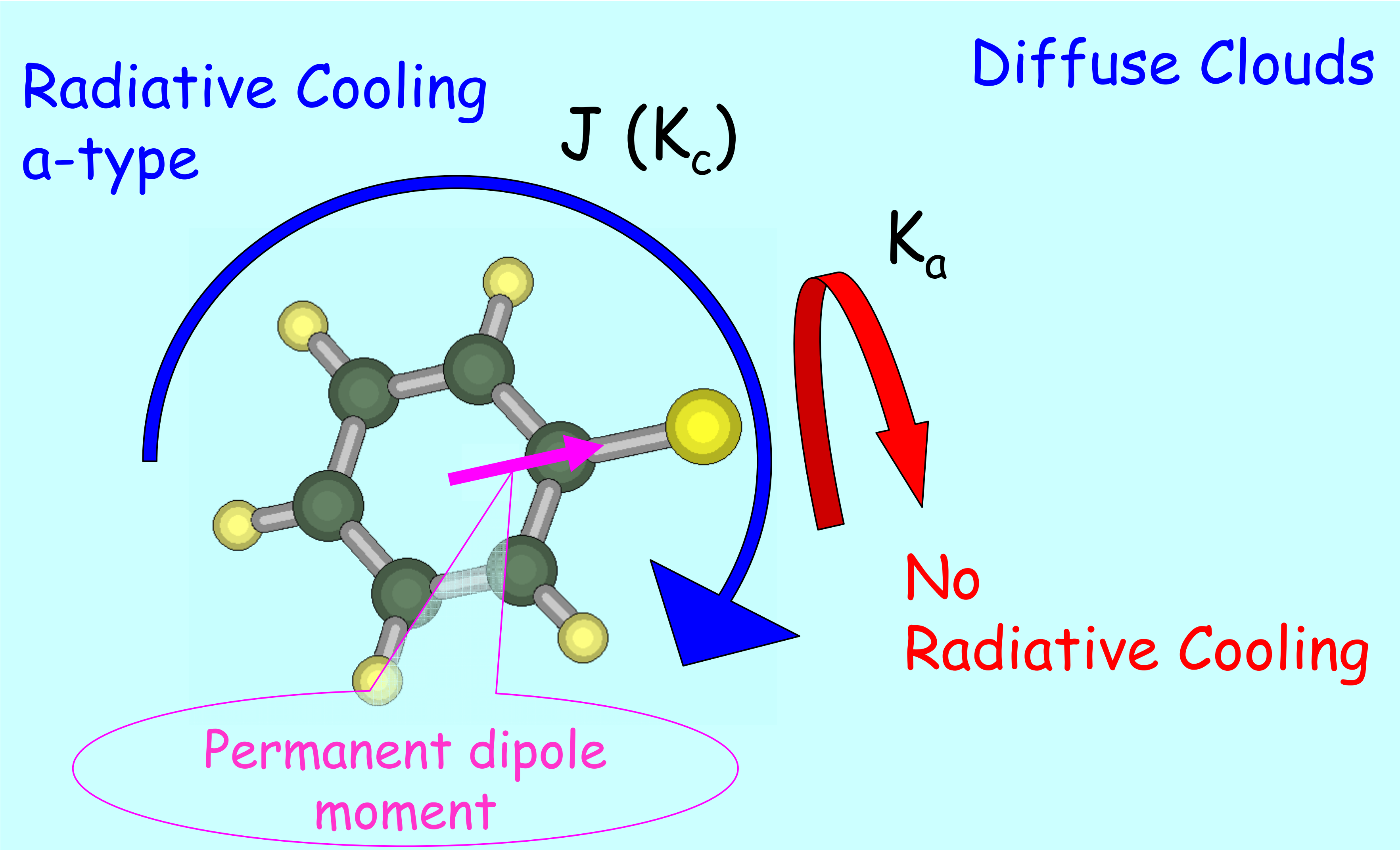
Boltzmann Distribution

Collision >> Radiation

Dark Clouds



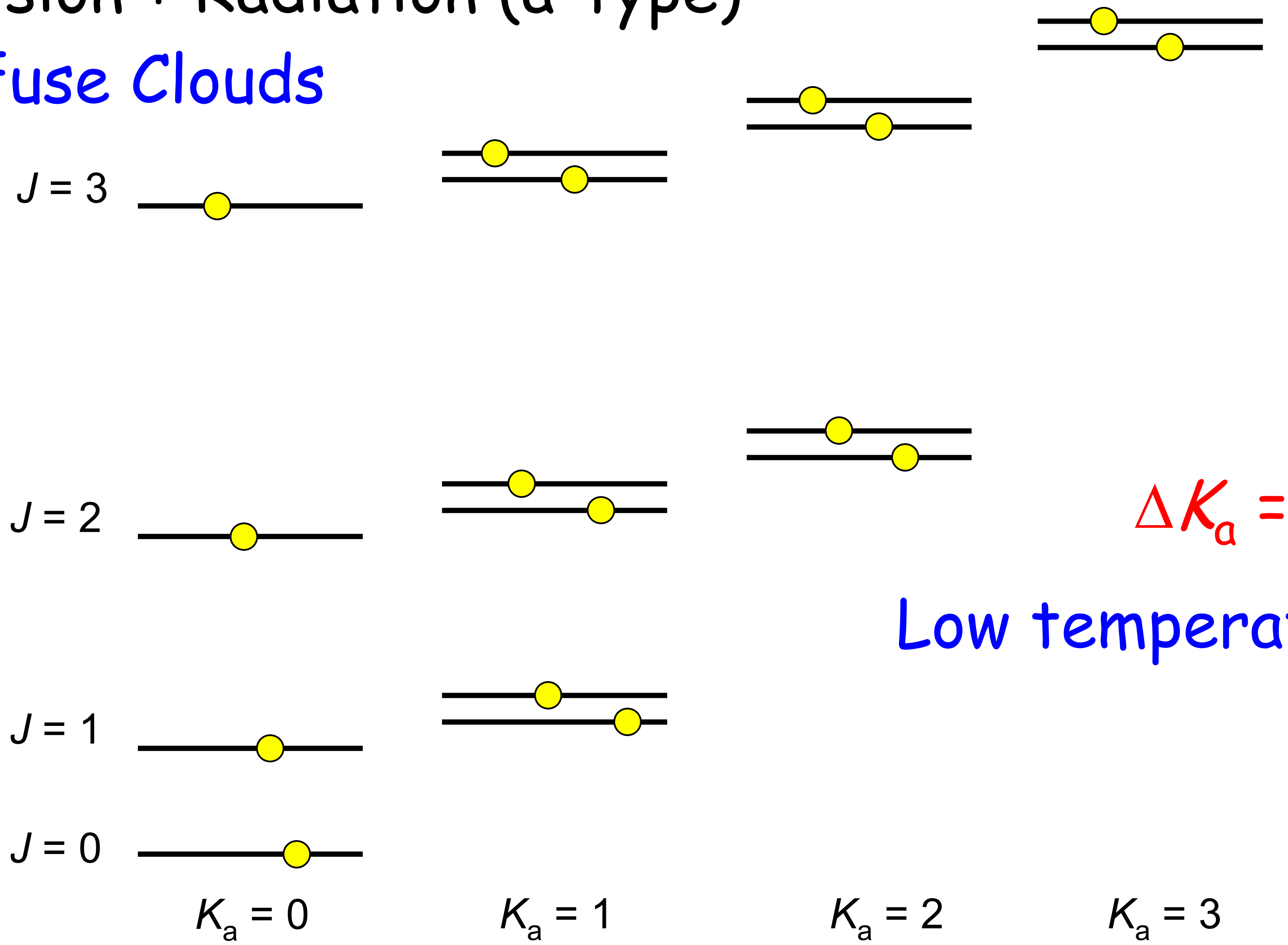
Rotation of C_{2v} Asymmetric Top



Distribution in Diffuse Cloud

Collision + Radiation (a-type)

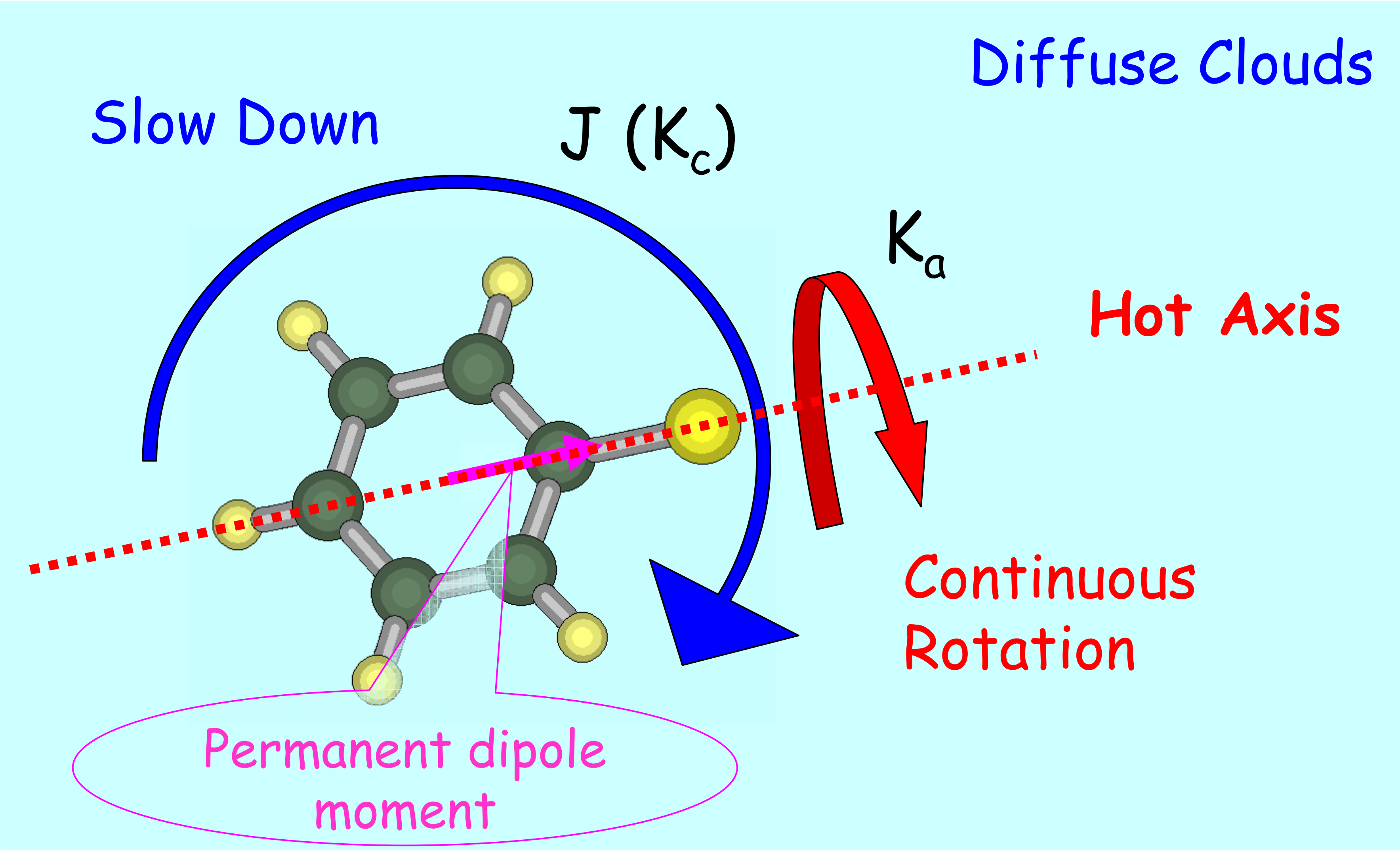
Diffuse Clouds



$\Delta K_a = 0$

Low temperature

Rotation of C_{2v} Asymmetric Top



Analysis of C_6H_5S

Rotational Profile

⇩

Rotational Constants

⇩

Simulation of Non-Boltzmann Distribution in Diffuse Cloud

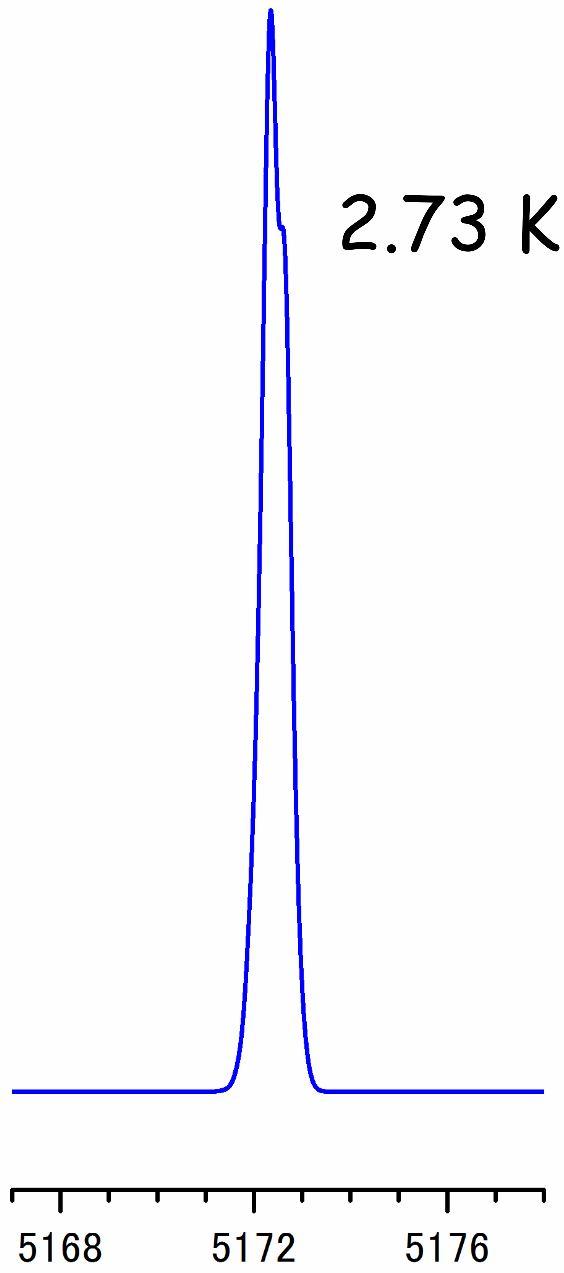
Simulation of Rotational Profile in Diffuse Cloud

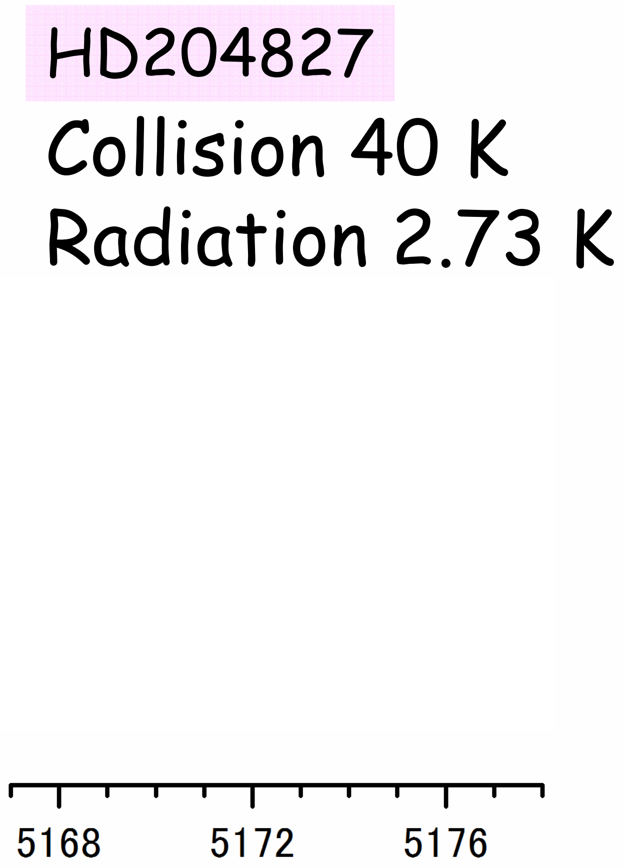
Pgopher

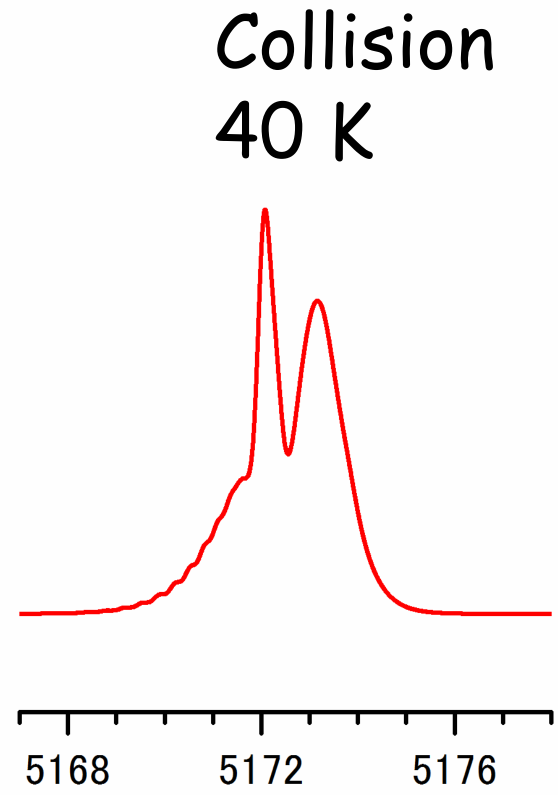
⇨ Comparison with DIBs

Rotational Profile in diffuse cloud

Non-Boltzmann distribution is important in diffuse clouds.





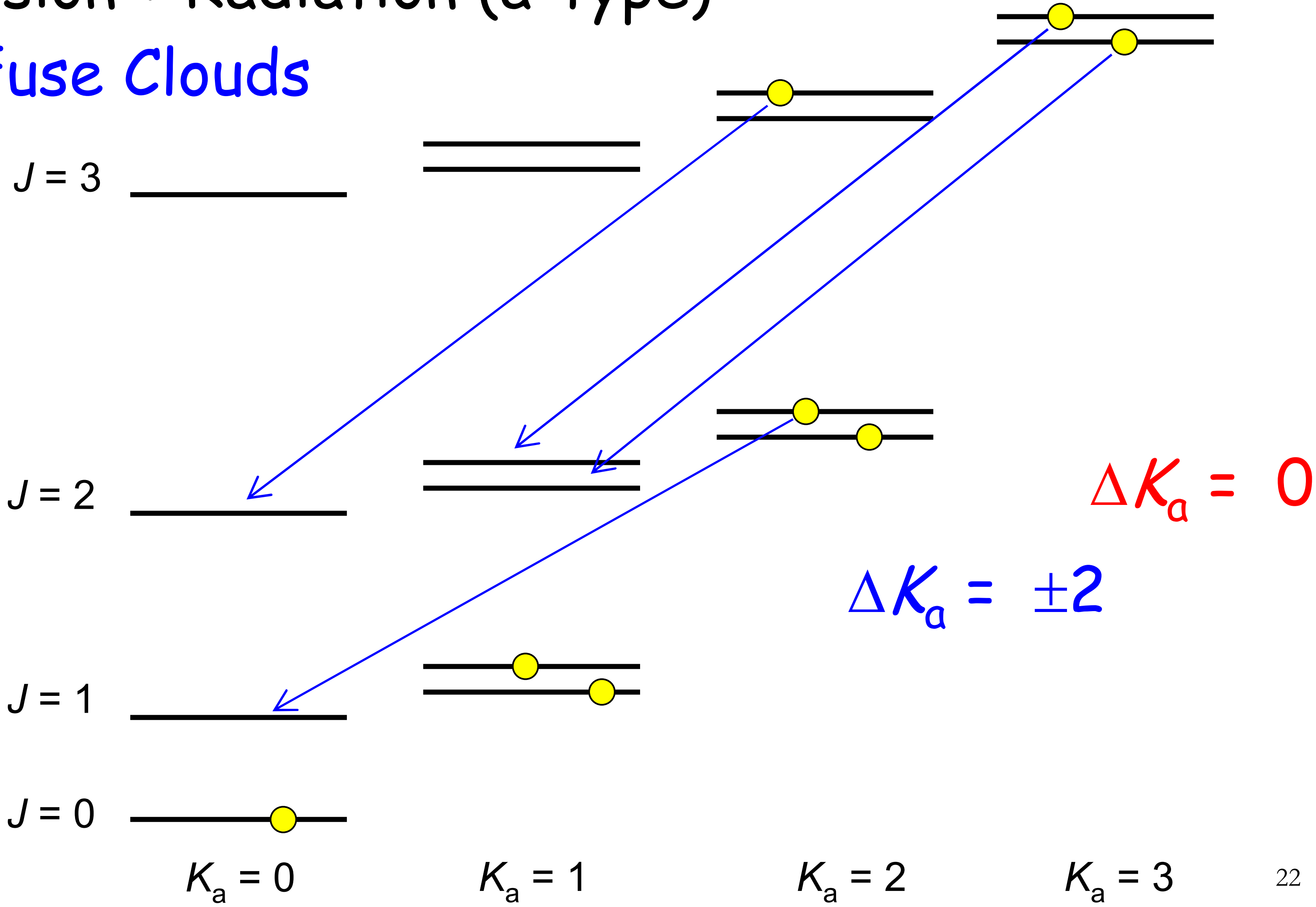


Wavelength /Å

Distribution in Diffuse Cloud

Collision + Radiation (a-type)

Diffuse Clouds



Distribution in Diffuse Cloud

Collision + Radiation (a-type)

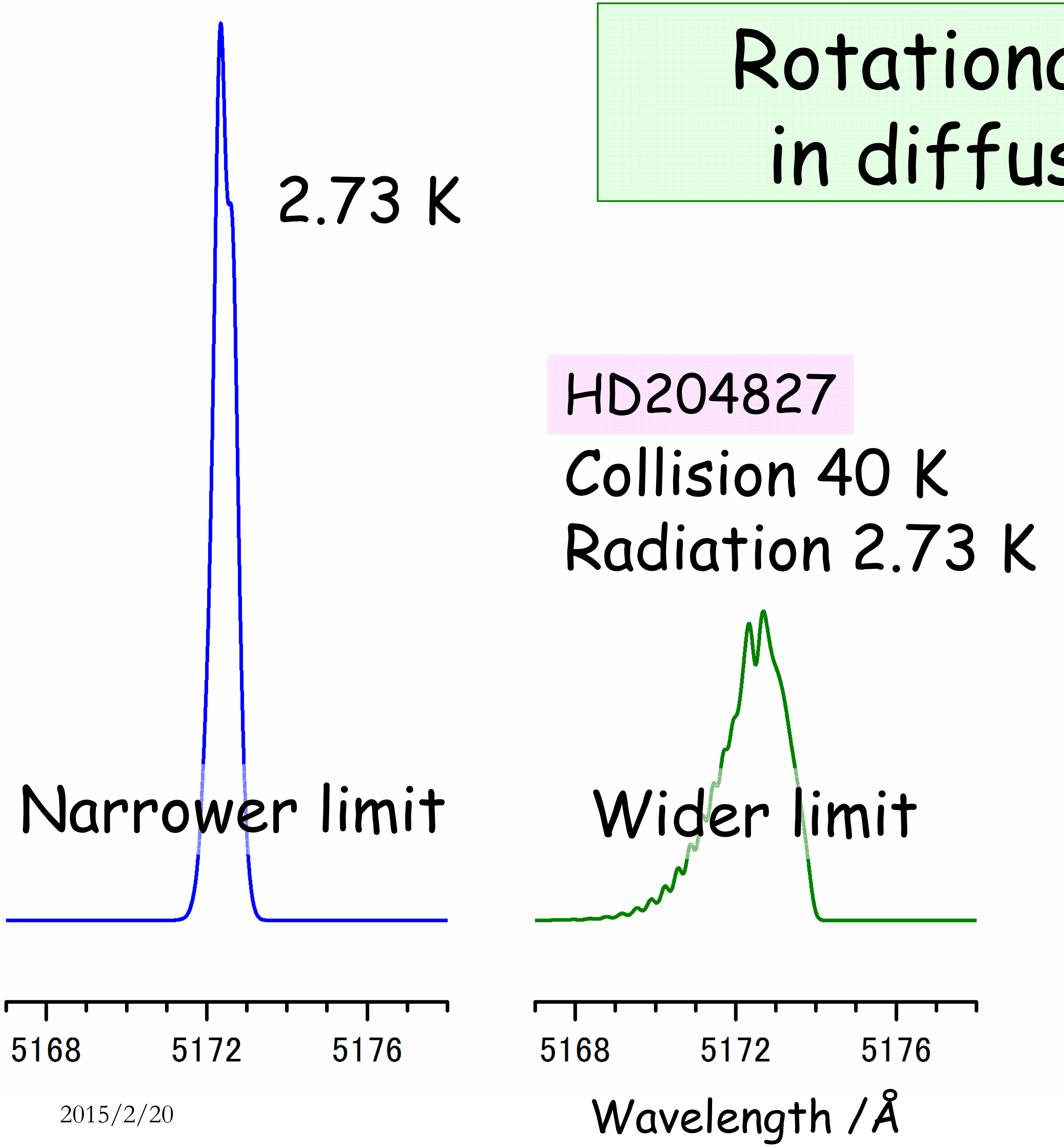
Diffuse Clouds

$$A(\Delta K_a = 0) > \underline{A(\Delta K_a = \pm 2) \sim \text{Collision}}$$

⇧

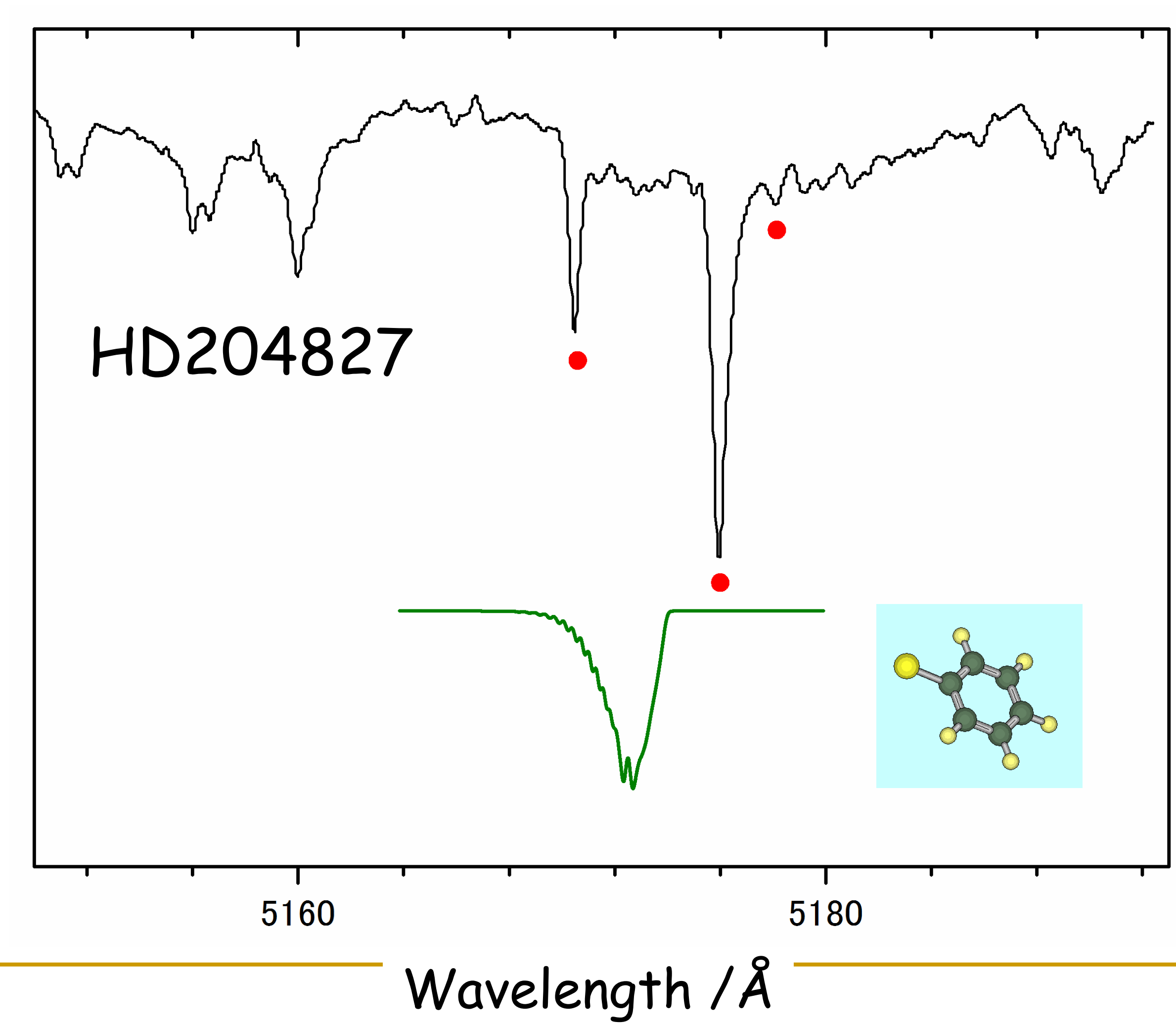
- The profile can depend on <u>this competition.</u>

Rotational Profile in diffuse cloud



Comparison with DIBs

No fit
No detection



Upper Limit of Column Density

- Simulation of Rotational Profile

  Band Width of C_6H_5S: 2Å

- Theoretical Calculation (TD-B3LYP / cc-pVTZ)

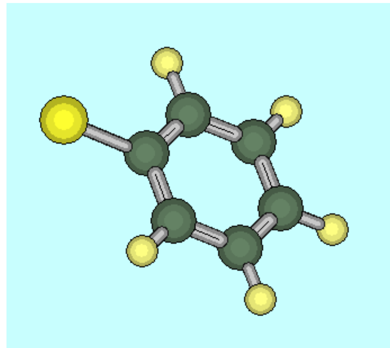
  Oscillator Strength: $f = 0.003$

- HD204827, Hobbs et al., ApJ, 680, 1256 (2008)
- Detection threshold: S/N = 5

- Upper limit of column density 2×10^{13} cm^{-2}

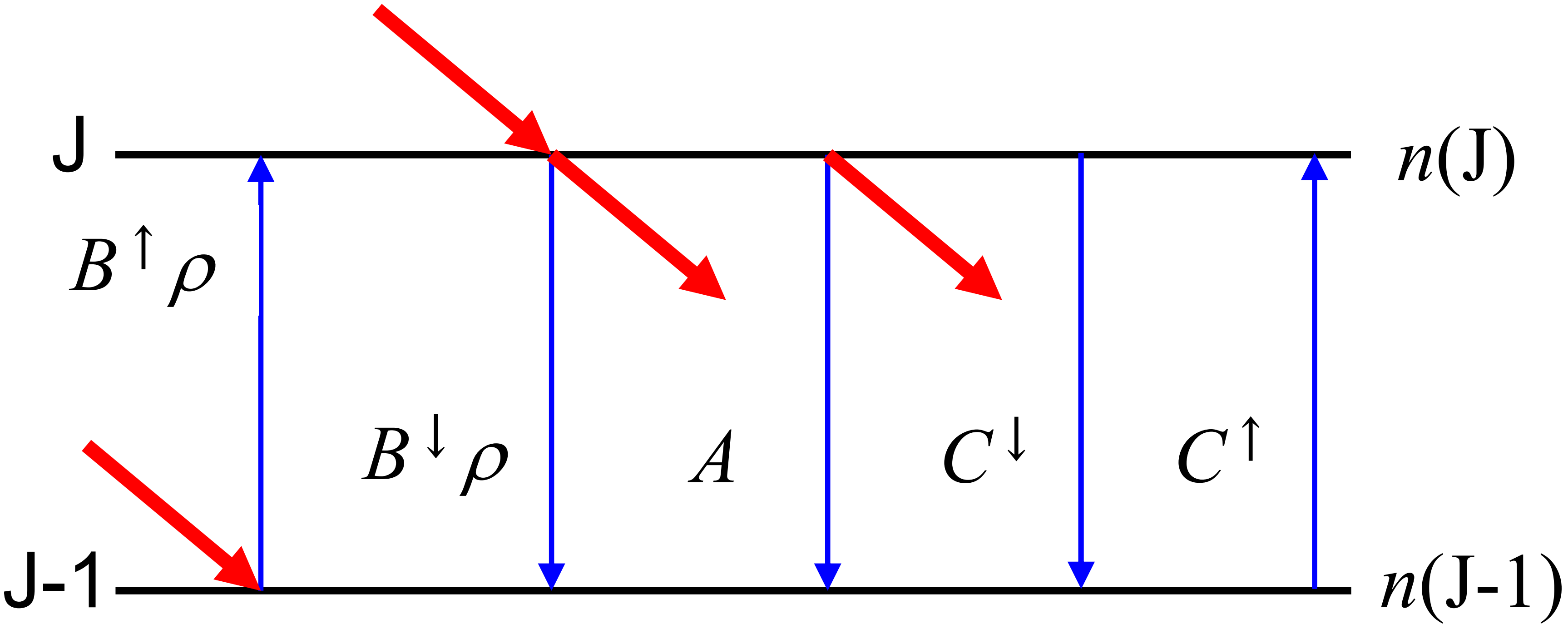
Summary

Electronic Spectrum of Thiophenoxy Radical C_6H_5S



- By Cavity Ring Down Spectroscopy
- Simulation of Rotational Profile in Diffuse Cloud
  - Upper limit of column density 2×10^{13} cm^{-2}
  - Non-Boltzmann distribution is important in diffuse cloud.

Einstein Coefficients and Oka Coefficient (1973)



$$n(J)\left(A^J + B^{\downarrow}_{J-1}\rho + C^{\downarrow}_{J-1}\right) = n(J-1)\left(B^{\uparrow}_{J-1}\rho + C^{\uparrow}_{J-1}\right)$$

Rotational Distribution

Linear

$$n(J)=n(0)\prod_{m=1}^{J}\left[\frac{\alpha B^3\mu^2\frac{m^4}{2m-1}\frac{1}{\exp(2hBm/kT_r)-1}+C\sqrt{\frac{2m+1}{2m-1}}\exp(-hBm/kT_k)}{\alpha B^3\mu^2\frac{m^4}{2m+1}\left(1+\frac{1}{\exp(2hBm/kT_r)-1}\right)+C\sqrt{\frac{2m-1}{2m+1}}\exp(hBm/kT_k)}\right]$$

Asym top

$$n(J)=n(0)\prod_{m=K_a+1}^{J}\left[\frac{\alpha \overline{B}^3\mu^2\frac{m^3S}{2m-1}\frac{1}{\exp(2h\overline{B}m/kT_r)-1}+C\sqrt{\frac{2m+1}{2m-1}}\exp(-h\overline{B}m/kT_k)}{\alpha \overline{B}^3\mu^2\frac{m^3S}{2m+1}\left(1+\frac{1}{\exp(2h\overline{B}m/kT_r)-1}\right)+C\sqrt{\frac{2m-1}{2m+1}}\exp(h\overline{B}m/kT_k)}\right]$$

Radiation temp. (dust)	T_r = 40 K
Kinetic (collisional) temp. (H_2)	T_k = 2.73 K
Oka's Collisional Coefficient	C = 10E-7
Rotational Constant	B = 1454 MHz
Permanent Dipole Moment	μ = 3.1 D

What parameters are determining the rotational profile?

- With a hot axis or not.
- With a permanent dipole moment or not.
  - Radiation temperature T_r
  - Kinetic temperature T_k
  - C constant
  - Permanent dipole moment
  - Rotational constants
  - Rotational constants difference
  - Lifetime