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

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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

\[ \downarrow \]

Ion and/or radical

Large Molecule

\[ \downarrow \]

Not Identified yet

Identification of DIBs by Laboratory Spectroscopy
How to identify DIBs?

Optical Electronic Transition

Space  
Star  
absorption  
Unidentified molecule  
Earth  
DIB

Lab  
Molecule  
Discharge etc  
Spectrometer  
Spectra

Identification  
fit
Cavity Ring Down Spectrometer

Pulsed dye laser, 10 Hz, $\Delta \nu = 0.1 \text{ cm}^{-1}$
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
$^2A_2 \leftarrow X^2B_1$

LIF

DIBs Disturbed

Origin

Shibuya et al., *Chemical Physics*, **121**, 237-244, 1988
HD204827 having DIBs

Celestial North Pole

HD204827

The 8th Magnitude Star

Galactic Plane
DIBs and Reported Laboratory Spectrum

DIBs and Present Laboratory Spectrum by CRD

Analysis of $\text{C}_6\text{H}_5\text{S}$

- Rotational Profile
- Rotational Constants
- Simulation of Non-Boltzmann Distribution in Diffuse Cloud
- Simulation of Rotational Profile in Diffuse Cloud
- Comparison with DIBs
Rotational Constants from Rotational Profile

\[
\begin{align*}
A'' &= 0.1893 \\
B'' &= 0.0546 \\
C'' &= 0.0424 \\
\Delta A &= 0.0073(5) \\
\Delta \left( \frac{B + C}{2} \right) &= -0.0017(1) \\
T_{00} &= 19327.7(3)
\end{align*}
\]

B3LYP/cc-pVTZ
Non-Boltzmann Distribution in Diffuse Cloud

- Dark Clouds: Collision $\gg$ Radiation
- Diffuse Clouds: Less Collision + Radiation

Linear Molecule
Non-Boltzmann Distribution in Diffuse Cloud

- Dark Clouds  Collision $\gg$ Radiation
- Diffuse Clouds  Less Collision + Radiation

$T_k = 100 \text{K}$
$T_r = 2.73 \text{K}$
$T_r = 14.6 \text{K}$
$T_r = 80 \text{K}$

Linear Molecule

$C_{2v}$ Asymmetric Top
Singlet
Rotation of $C_{2v}$ Asymmetric Top

J ($K_c$)

$K_a$

Permanent dipole moment
Boltzmann Distribution

Collision >> Radiation

Dark Clouds

\[ J = 3 \]

\[ J = 2 \]

\[ J = 1 \]

\[ J = 0 \]

\[ K_a = 0 \]
\[ K_a = 1 \]
\[ K_a = 2 \]
\[ K_a = 3 \]

High temperature

Low temperature

2015/2/20
Rotation of $C_{2v}$ Asymmetric Top

Radiative Cooling
a-type

J ($K_c$)

K_a

No Radiative Cooling

Permanent dipole moment

Diffuse Clouds
Distribution in Diffuse Cloud

Collision + Radiation (a-type)

Diffuse Clouds

$J = 3$

$J = 2$

$J = 1$

$J = 0$

$K_a = 0$

$K_a = 1$

$K_a = 2$

$K_a = 3$

$\Delta K_a = 0$

Low temperature
Rotation of $C_{2v}$ Asymmetric Top

Slow Down $J \ (K_c)$

Diffuse Clouds

Permanent dipole moment

Hot Axis

Continuous Rotation

2015/2/20
Analysis of $C_6H_5S$

Rotational Profile

Rotational Constants

Simulation of Non-Boltzmann Distribution in Diffuse Cloud

Simulation of Rotational Profile in Diffuse Cloud

Comparison with DIBs

Pgopher
Non-Boltzmann distribution is important in diffuse clouds.

HD204827
Collision 40 K
Radiation 2.73 K

Collision 40 K
Distribution in Diffuse Cloud

Collision + Radiation (a-type)

Diffuse Clouds

\[ J = 3 \]

\[ J = 2 \]

\[ J = 1 \]

\[ J = 0 \]

\[ K_a = 0 \quad K_a = 1 \quad K_a = 2 \quad K_a = 3 \]

\[ \Delta K_a = 0 \]

\[ \Delta K_a = \pm 2 \]
Distribution in Diffuse Cloud

Collision + Radiation (a-type)

Diffuse Clouds

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

☐ The profile can depend on this competition.
Rotational Profile in diffuse cloud

HD204827
Collision 40 K
Radiation 2.73 K

Narrower limit

Wider limit

Wavelength /Å

2.73 K

2015/2/20
Comparison with DIBs

No fit
No detection

Wavelength /Å

HD204827
Upper Limit of Column Density

- Simulation of Rotational Profile
  Band Width of $\text{C}_6\text{H}_5\text{S}$: 2Å

- Theoretical Calculation (TD-B3LYP / cc-pVTZ)
  Oscillator Strength: $f = 0.003$

- Detection threshold: $\text{S/N} = 5$

- Upper limit of column density $2 \times 10^{13}$ 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 $2 \times 10^{13}$ 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

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

Asym top

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

Radiation temp. (dust) \( T_r = 40 \text{ K} \)
Kinetic (collisional) temp. (H\(_2\)) \( T_k = 2.73 \text{ K} \)
Oka’s Collisional Coefficient \( C = 10\text{E-7} \)
Rotational Constant \( B = 1454 \text{ MHz} \)
Permanent Dipole Moment \( \mu = 3.1 \text{ D} \)
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