Laboratory Spectroscopy of 1,2,3-butatriene cation H$_2$CCCCH$_2^+$ as a Candidate for a Diffuse Interstellar Band Carrier

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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
Material Cycle in Space

Optical Observation

Diffuse Cloud

Dark Cloud

Radio Observation

Late Type Star

Star

Planetary Forming Region

Molecular Cloud

Star Comet
History of DIBs Carrier Candidates

Interstellar Matter
Detected
Reported

Hypothesizes are suggested.

Carbon Chain Mol.
PAH
H$_2$

Molecular Hypothesis
Small Mol.
Large Mol.

Dust Hypothesis

AD (+1900)
19 34 37 70 77 80 85 95 106

2015/2/20
How to identify DIBs?

Optical electronic transition

Interstellar space

Star (Light Source)

Unknown absorption

The Earth

DIBs

Laboratory

Mol.

Production

Spectrometer

Lab. Spectrum

Identification ↔ Agreement
Rejected Carbon-Chains DIBs Candidates

\[ C_n, \ C_nH, \ HC_{2n}H, \ H_2CCC, \ HC_{2n}H^+ \]

\[ H_2C_{2n}H_2^+ \] is fundamental but not checked yet.

\[ H_2CCCH_2^+ \]

1,2,3-butatriene cation
Experimental
Laboratory Spectrometer to Identify Diffuse Interstellar Bands

- **Spectrometer**
  - \(\rightarrow\) Discharge Emission Spectrometer
  - \(\rightarrow\) Cavity Ring Down Spectrometer (P17)

- **Production of Ion**
  - \(\rightarrow\) Follow Cathode Discharge
  - \(\rightarrow\) Extended Negative Glow Discharge
Discharge Emission Spectrometer

Voltage: ~ 500 V
Current: 50 mA

Pulse Freq.: 400 Hz

A/DC → PC

Lock-in Amp. → PMT → Spectrometer

20 kΩ → Gas

Lens

Cathode → Anode (G)

Pump
Laboratory Spectrometer to Diffuse Interstellar Bands

- Spectrometer
  - Discharge Emission Spectrometer
  - Cavity Ring Down Spectrometer

- Production of Ion
  - Follow Cathode Discharge
  - Extended Negative Glow Discharge
Hollow Cathode Discharge
Discharge Emission Spectrometer

A/DC

PC LabVIEW

PMT Spectrometer

Lock-in Amp.

Pulse Generator

Voltage: ~ 500 V
Current: 50 mA

Lens

Cathode
Anode (G)

Gas

Pulse Freq.: 400 Hz

Pump

20 kΩ
Production of Ion by Hollow Cathode Discharge

$[\text{Ar ion}] \sim [\text{Neutral Ar}]$
Results and Discussion
HCCCH\(^+\)

\[ \text{Wavelength (nm)} \]

540 530 520 510 500 490 480

[Graph showing wavelength in nm with peaks labeled HCCCH\(^+\) and \(\text{C}_2\)]

\[ \text{Wavenumber (cm}^{-1}\text{)} \]

18500 19000 19500 20000 20500 21000

4905 Å

[Graph showing wavenumber with peaks labeled \(\text{H}^+\) and \(\text{H}^0\)]

2015/2/20
Photo-Electron Spectrum of Neutral $\text{H}_2\text{CCCCH}_2$

Photo-Electron Spectrum

\[ 2.55 \pm 0.04 \text{ eV} = 20570 \pm 320 \text{ cm}^{-1} \]

Emission: \(20381 \text{ cm}^{-1} (4905 \text{ Å})\)

\[ \text{H}_2\text{CCCCH}_2^+ \rightarrow \text{X}^2\text{B}_3 \]

\[ \text{H}_2\text{CCCCH}_2 \rightarrow \text{X} \]
Photo-Electron Spectrum: $20570 \pm 320 \text{ cm}^{-1}$
Emission Spectrum: No Rotational Structure

Confirmation of Assignment

- **Chemical Tests**
  - Temperature Dependence
  - Sample Gas Dependence
  - Oxygen and Nitrogen Tests

- **Physical Tests**
  - Extended Negative Glow Discharge
  - Electrode Switching
  - Vibrational Analysis
Photo-Electron Spectrum: 20570±320 cm$^{-1}$
Emission Spectrum: No Rotational Structure

Confirmation of Assignment

- **Chemical Tests**
  - Temperature Dependence
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  - Extended Negative Glow Discharge
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  - Vibrational Analysis
Temperature Dependence

- Molecule produced by Growth in Discharge → Increasing by Cooling
- Decreasing: This band can be by Fragmentation.

4905 Å
Photo-Electron Spectrum: $20570 \pm 320 \text{ cm}^{-1}$
Emission Spectrum: No Rotational Structure

Confirmation of Assignment

- **Chemical Tests**
  - Temperature Dependence
  - **Sample Gas Dependence**
  - Oxygen and Nitrogen Tests

- **Physical Tests**
  - Extended Negative Glow Discharge
  - Electrode Switching
  - Vibrational Analysis
Sample Gas Dependence

Butatriene Cation
$H_2CCCCH_2^+$

2-butyne

(4905 Å)
Photo-Electron Spectrum: $20570 \pm 320 \text{ cm}^{-1}$
Emission Spectrum: No Rotational Structure

**Confirmation of Assignment**

- **Chemical Tests**
  - Temperature Dependence
  - Sample Gas Dependence
  - Oxygen and Nitrogen Tests

- **Physical Tests**
  - Extended Negative Glow Discharge
  - Electrode Switching
  - Vibrational Analysis
Is air leak working?

- 2-butyne (0.2 torr) $\bigcirc$
- 2-butyne (0.2 torr) + N$_2$ (0.2 torr) $\bigtriangleup$
- 2-butyne (0.2 torr) + O$_2$ (0.2 torr) $\bigtriangleup$

No Increasing $\rightarrow$ Air leak may not be working.
Same Origin?

4905 Å
Photo-Electron Spectrum: $20570 \pm 320 \text{ cm}^{-1}$
Emission Spectrum: No Rotational Structure

Confirmation of Assignment

- **Chemical Tests**
  - Temperature Dependence
  - Sample Gas Dependence
  - Oxygen and Nitrogen Tests

- **Physical Tests**
  - Extended Negative Glow Discharge
  - Electrode Switching
  - Vibrational Analysis
Extended Negative Glow Discharge

Sample gas

Pump

Coil

Cathode

Anode (Ground)

Solenoid Power Supply

Cathode

Anode
Extended Negative Glow Discharge
Extended Negative Glow Discharge

Sample gas: 2-butyne
Pressure: 0.2 Torr
Voltage: 1500V
Pulse freq.: 400Hz

2015/2/20
Extended Negative Glow Discharge

0 G

HCCCCCH⁺

H₂CCCCH₂⁺

500 G

HCCCCCH⁺

H₂CCCCH₂⁺

4905 Å

Same Origin

Wavenumber (cm⁻¹)
Photo-Electron Spectrum: $20570 \pm 320 \text{ cm}^{-1}$
Emission Spectrum: No Rotational Structure

**Confirmation of Assignment**

- **Chemical Tests**
  - Temperature Dependence
  - Sample Gas Dependence
  - Oxygen and Nitrogen Tests

- **Physical Tests**
  - Extended Negative Glow Discharge
  - Electrode Switching
  - Vibrational Analysis
Electrode Switching

Is the 4905 Å band cation?
Electrode Switching

The 4905 Å band is cation.

\[
\frac{I_{HCCCCH^+}^i}{I_{C_2}^i} = 0.8 \pm 0.1
\]

\[
\frac{I_{H_2CCCCH_2^+}^i}{I_{C_2}^i} = 0.7 \pm 0.1
\]
Photo-Electron Spectrum: 20570 ± 320 cm$^{-1}$
Emission Spectrum: No Rotational Structure

Confirmation of Assignment

- **Chemical Tests**
  - Temperature Dependence
  - Sample Gas Dependence
  - Oxygen and Nitrogen Tests

- **Physical Tests**
  - Extended Negative Glow Discharge
  - Electrode Switching
  - Vibrational Analysis
Is the 4905Å band the origin band ($\nu = 0-0$)?

DIB candidate
### Molecular Structure

**Torsional Structure**

<table>
<thead>
<tr>
<th></th>
<th>$R_{CC1}$</th>
<th>$R_{CC2}$</th>
<th>$R_{CH}$</th>
<th>$\angle HCC$</th>
<th>$\tau$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{2}B_{3u}$</td>
<td>1.397</td>
<td>1.250</td>
<td>1.072</td>
<td>119.33</td>
<td>41.73</td>
</tr>
<tr>
<td>$X^{2}B_{2g}$</td>
<td>1.342</td>
<td>1.230</td>
<td>1.075</td>
<td>120.24</td>
<td>33.34</td>
</tr>
</tbody>
</table>

**ab initio CASSCF(5,4)/cc-pVTZ**

554 cm$^{-1}$

**Torsional Vib.**

2015/2/20
[the 4905Å band] - [no band] = ?
[the 4905Å band] - [no band]
How to Analyze?

Torsional potential

Simplification

Double Minimum Torsional Potential

front view
Torsional potential

Strongly Twisted

Intermediate

Planer

\[ C_4 \]

\[ C_4 \]

\[ C_4 \]
Qualitative Analysis

\[ \ ^2B_{3u} \]

\[ \chi^2 B_{2g} \]

Selection Rule

\[ + \leftrightarrow - \]

4905 Å
Our Model

If DIB

4905 Å

Our Model

If DIB

4905 Å

Our Model

If DIB

4905 Å

Our Model

If DIB

4905 Å

Our Model

If DIB

4905 Å

Our Model

If DIB

4905 Å

Our Model

If DIB

4905 Å

Our Model

If DIB

4905 Å

Our Model

If DIB

4905 Å

Our Model

If DIB

4905 Å
Double Minimum Torsional Mode

\[ V(\theta) = 2k\theta^2 + \varepsilon \left\{ \exp\left\{-4\alpha\theta^2\right\} - 1 \right\} \]

\[ \theta = \tau / 2 \]

\[ H(\theta) = -A^+ \frac{d^2}{d\theta^2} + 2k\theta^2 + \varepsilon \left\{ \exp\left\{-4\alpha\theta^2\right\} - 1 \right\} \]

\( A^+ \): rotational constants
Simple Quantitative Analysis

83.7 cm⁻¹ fix (C₂H₄⁺)

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<tr>
<th>Vib.</th>
<th>Energy Level in $^2B_{2g}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Obs.</td>
</tr>
<tr>
<td></td>
<td>cm⁻¹</td>
</tr>
<tr>
<td>3</td>
<td>1291</td>
</tr>
<tr>
<td>2</td>
<td>708</td>
</tr>
<tr>
<td>1</td>
<td>107</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

4905 Å
Simple Quantitative Analysis

Theoretical Value: 624 cm$^{-1}$

Obtained Torsional Potential

<table>
<thead>
<tr>
<th>Vib.</th>
<th>Energy Level in $^2B_{2g}$</th>
<th>Obs. cm$^{-1}$</th>
<th>Calc. cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1291</td>
<td>1267</td>
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<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
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</tbody>
</table>

Good Agreement
Our Model

If DIB

4905 Å

Our Model

OK

Potential Energy

Relative Frequency / cm⁻¹

Torsional angle / degree

2B3u

2B2g
Torsional Analysis

- The 4905 Å band is the origin band (0-0).

DIB candidate
Comparison with DIBs


HD183143

4905 Å
Comparison with DIBs

Upper limit $10^{13}$ cm$^{-2}$

Summary

- The 4905 Å band was observed by using an emission spectrometer.
- The chemical and physical behaviors of the band was tested.
- The band was surely assigned to $\text{H}_2\text{CCCCH}_2^+$. 

This cation does not correspond to the currently-known DIBs, even though this is one of the basic unsaturated carbon chain molecules.


Related Poster: #17

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List of Interstellar molecule: URL & QR code → Posters #15 & #17.