# TDDFT studies of PAHs: the case of PAHs with five membered rings

M. Hammonds[1], **A. Pathak[2]**, P. J. Sarre[1] and S. Rastogi[3]

1. School of Chemistry, University of Nottingham
**2. Physics Department, Tezpur University, INDIA**
3. Physics Department, DDU Gorakhpur Univeristy INDIA


India
भारत
State or Union Territory
National Capital
State or Union Territory Capital
0 200 400 Kilometers
0 200 400 Miles
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Turkmenistan
Uzbek.
Tajikistan
Afghanistan
Kabul
Islamabad
Pakistani line of control
Chinese line of control
Jammu & Kashmir
Srinagar
Jammu
China
Himachal Pradesh
Shimla
Punjab
Chandigarh
Dehra Dun
Uttaranchal
Pakistan
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New Delhi
Delhi
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Tibet
Sikkim
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Dispur
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Meghalaya
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Tripura
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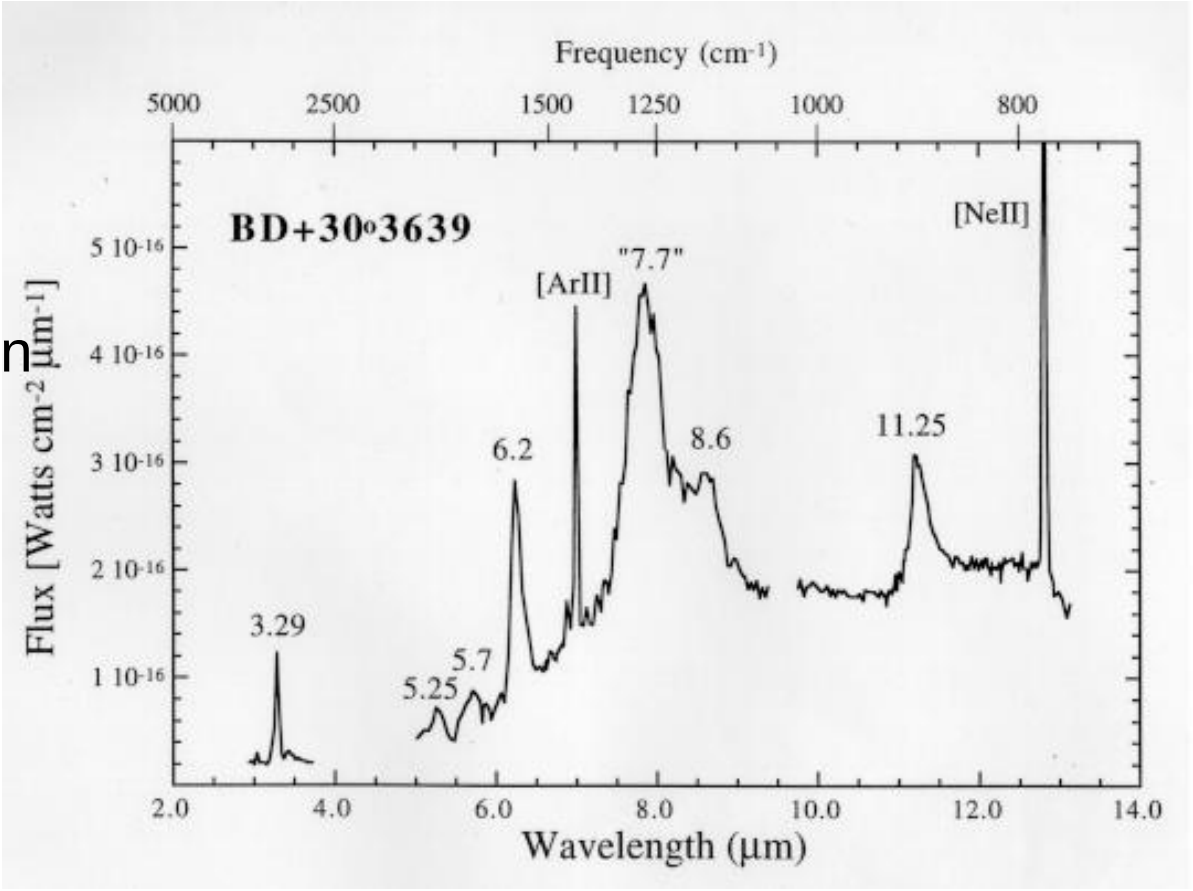
Myanmar
Gandhinagar
Gujarat
Bhopal
Madhya Pradesh
Chhattis-garh
Raipur
Orissa
Bhubaneswar
Daman
Diu
Dadra & Nagar Haveli
Silvassa
Maharashtra
Mumbai (Bombay)
Rangoon
Hyderabad
Arabian Sea
Pondicherry
Bay of Bengal
Panaji
Goa
Andhra Pradesh
Karnataka
Andaman Islands
Port Blair
Chennai (Madras)
Bangalore
Pondicherry
Tamil Nadu
Andaman and Nicobar Islands
Andaman Sea
Kavaratti
Lakshadweep
Kerala
Thiruvananthapuram
Nicobar Islands
Sri Lanka
Colombo
Laccadive Sea
Maldives
Indian Ocean

# Tezpur University Campus



# Motivation for studying PAHs

- Aromatic Infrared Bands
- UV bump at 217.5 $nm$.
- The Extended Red Emission (PAHs clusters).
- Diffuse Interstellar Bands.



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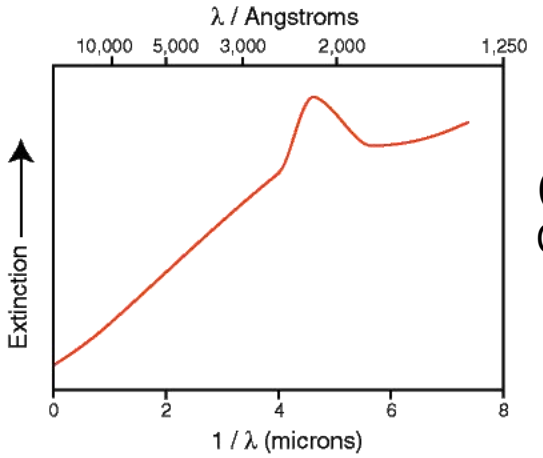
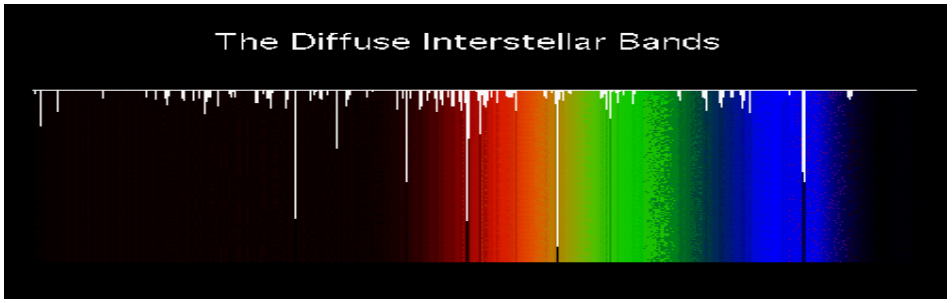
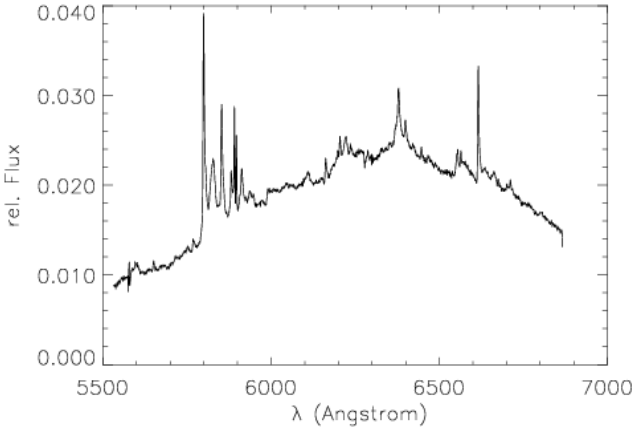



(Joblin 1992 & Clayton 2004)



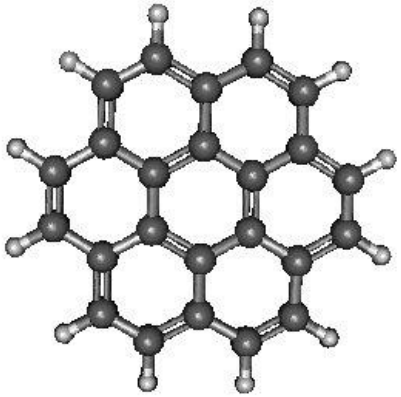

(Salama et al., Ap. J. 1999, 526 : 265)




(Witt et al., Ap. J. 2006)

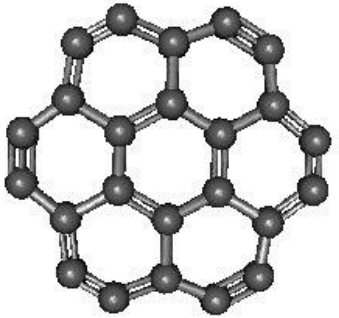
# Formation of $C_{60}$ in space

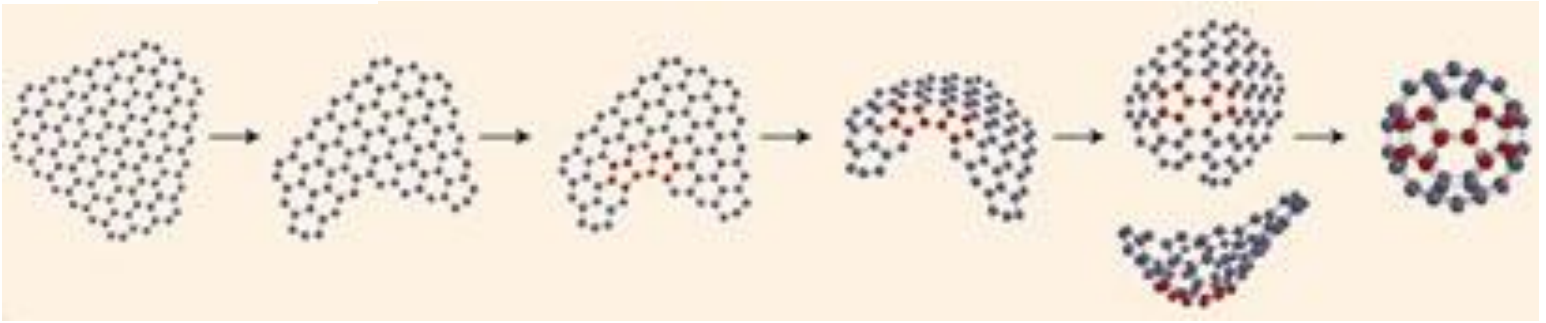
The formation path of $C_{60}$ is build-up from atomic carbon, carbon clusters or rings. In the ISM, such processes are efficient in the hot (1500 K) and dense ($n_H > 10^{11}$ $cm^{-3}$) envelopes of evolved stars.



In less dense environments

Dehydrogenation of PAHs





Carbon loss followed by pentagon formation initiates the curling of the molecule.
The graphene sheet curls up, then forms a bowl-like structure, and forms a ball.

Chuvilin et al., Nature Chemistry 2010, 2, 450-453

Berne & Tielens, 2011, PNAS

# Reactivity Trends

**Reaction rate coefficients**

Snow group, Ap. J. Lett., 2006

| PAHs | H | O | N |
|---|---|---|---|
| $C_6H_6^{+\cdot}$ | $2.2 \times 10^{-10}$ | $1.0 \times 10^{-10}$ | $1.2 \times 10^{-10}$ |
| $C_{10}H_8^{+\cdot}$ | $1.9 \times 10^{-10}$ | $1.0 \times 10^{-10}$ | $2.3 \times 10^{-11}$ |
| $C_{16}H_{10}^{+\cdot}$ | $1.4 \times 10^{-10}$ | $1.0 \times 10^{-10}$ | $1.5 \times 10^{-12}$ |
| $C_{24}H_{12}^{+\cdot}$ | $1.4 \times 10^{-10}$ | $1.3 \times 10^{-10}$ | no reaction |

**Reaction with H leads to the formation of protonated PAHs**

**High proton affinities of PAHs helps in formation of protonated PAHs**

# TDDFT Calculations

TDDFT is a widely applied method for the calculation of excited electronic states of medium-sized and large molecules.

It provides a valuable indication of the general region in which electronic transitions are expected to fall and guidance for laboratory experiments.

The present results on neutral and protonated PAHs were obtained using the Q-Chem and GAMESS quantum chemistry suite of programs.

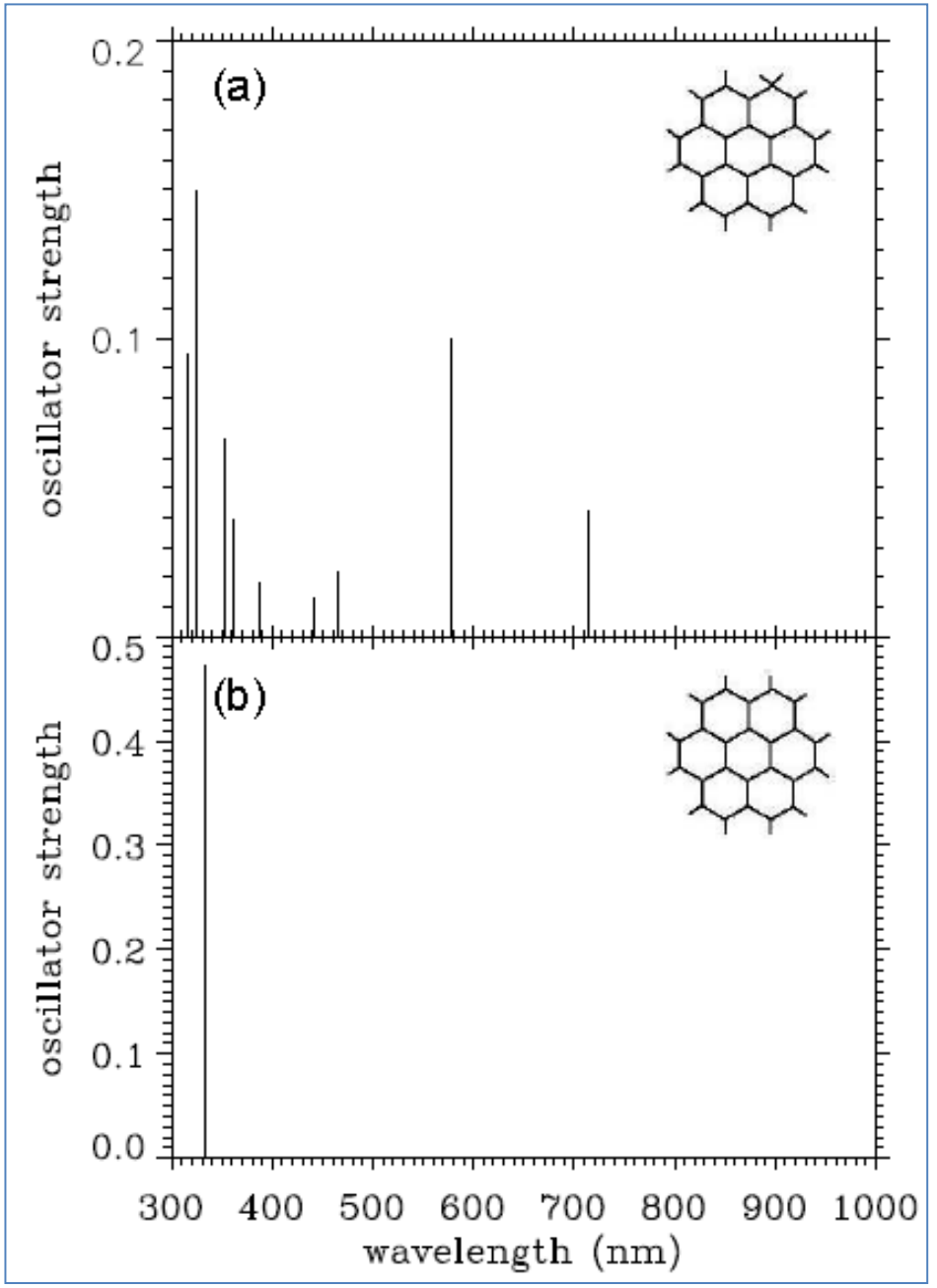
Ground state geometries optimized using DFT with a B3LYP/6-311G** basis.

Vertical electronic excitation energies and oscillator strengths were obtained using TDDFT with BLYP and the 6-311G** basis.

Halasinski et al. 2003; Hirata et al. 2003; Weisman, Lee & Head-Gordon 2001
Weisman et al. 2003; Hirata, Lee & Head-Gordon 1999

# Protonated PAHs

- Coronene spectrum shows a pair of transitions near 330 $nm$ but none in the visible region.
- For protonated coronene the most striking difference is the appearance of strong features in the visible region.
- This shift of the spectrum to longer wavelengths appears to be a general feature on protonation of neutral PAHs.




Pathak & Sarre, MNRAS Lett 2008

# Protonated PAHs

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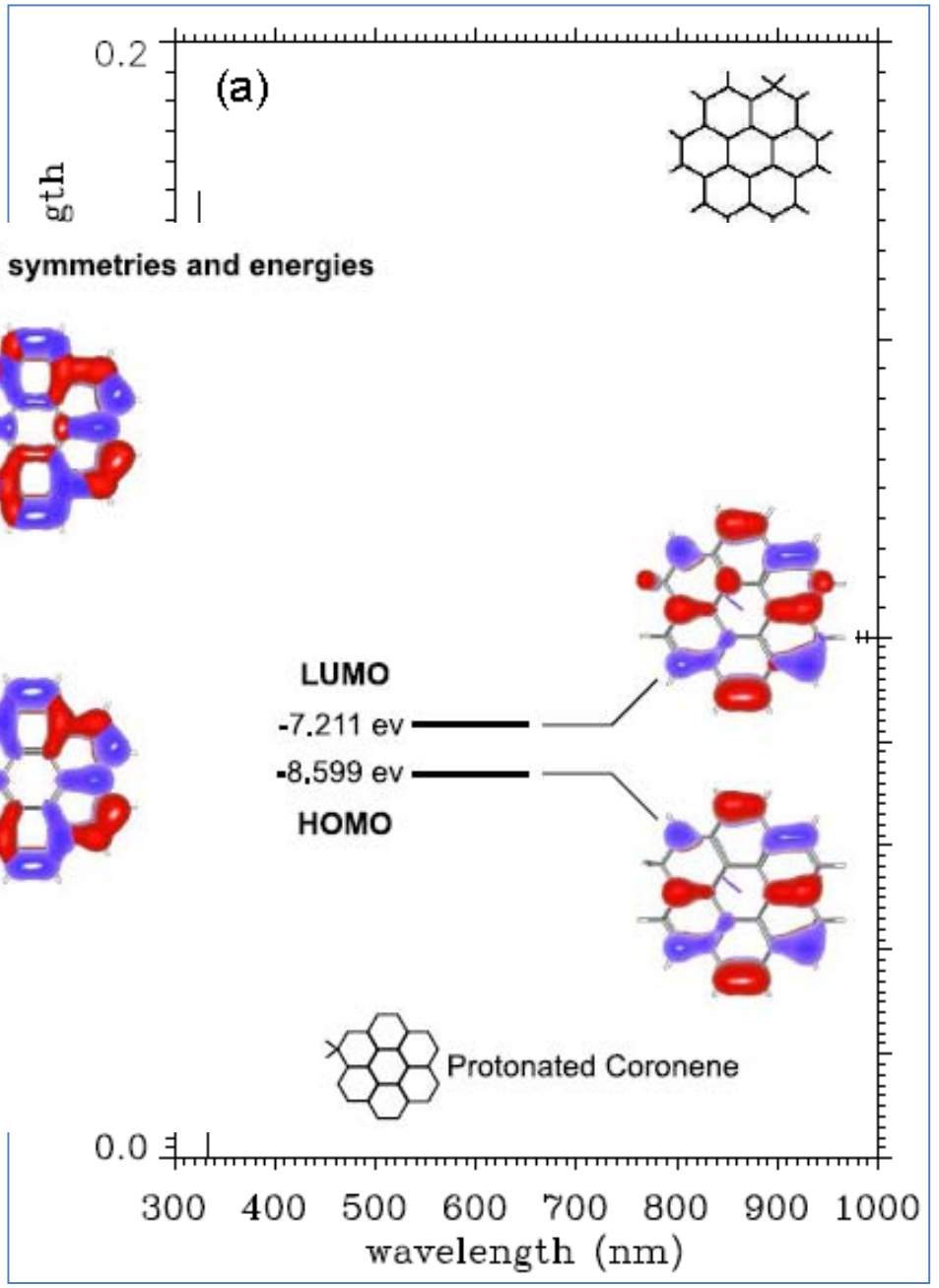
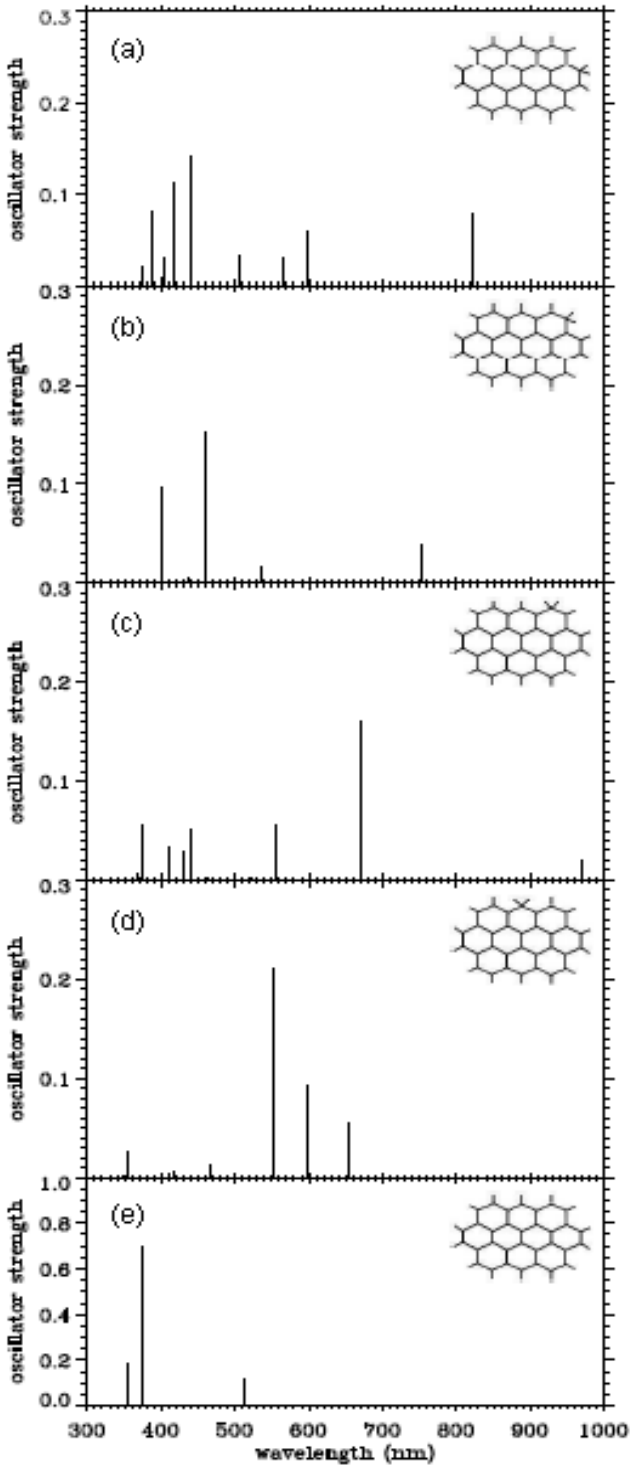



Pathak & Sarre, MNRAS Lett 2008

# Ovalene

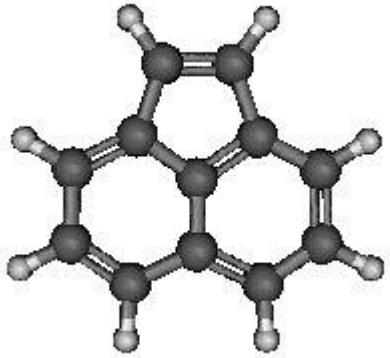
- Ovalene has four unique sites for protonation; all having different spectrum.
- This feature may help in complying with available Carbon budget.



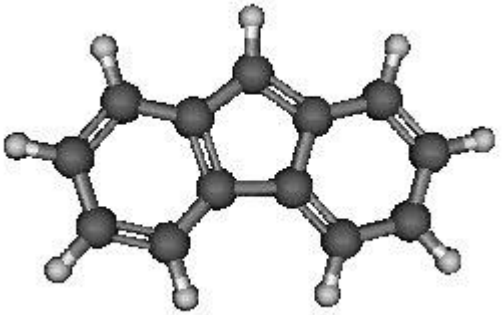

Pathak & Sarre, MNRAS Lett 2008

# TDDFT for PAHs with five-member rings

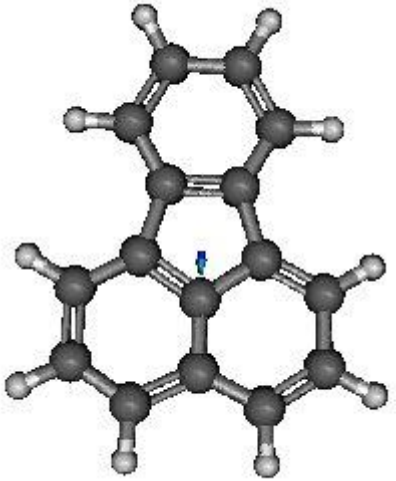
**The Sample**



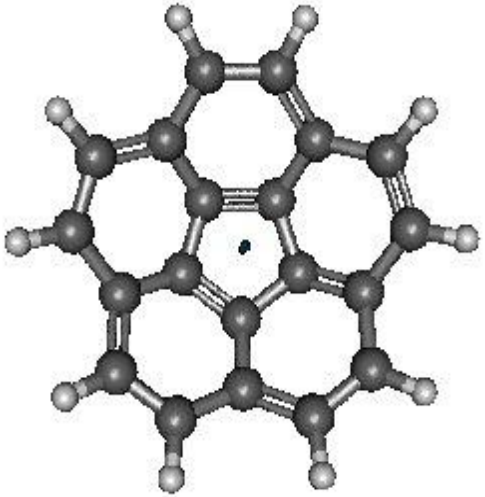
Acenaphthylene



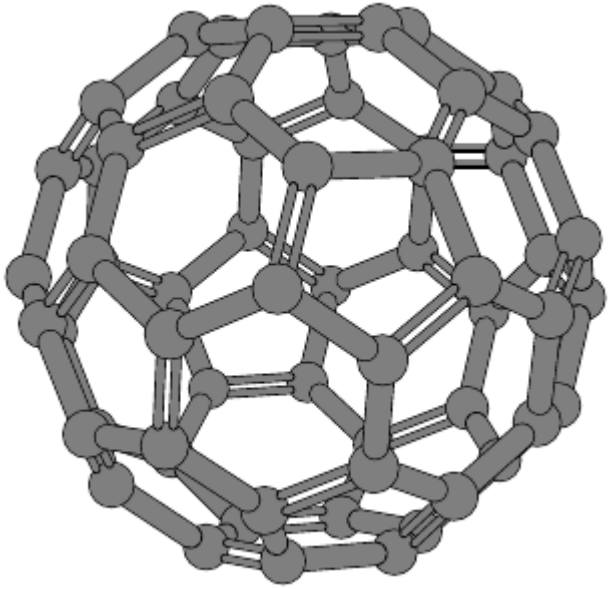
Fluorene



Fluoranthene

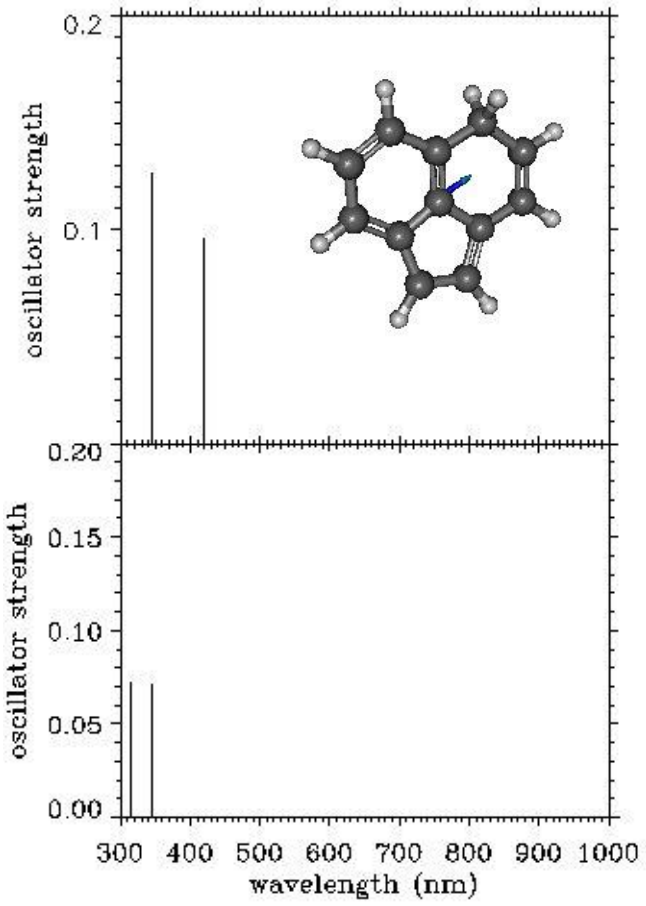


Corannulene

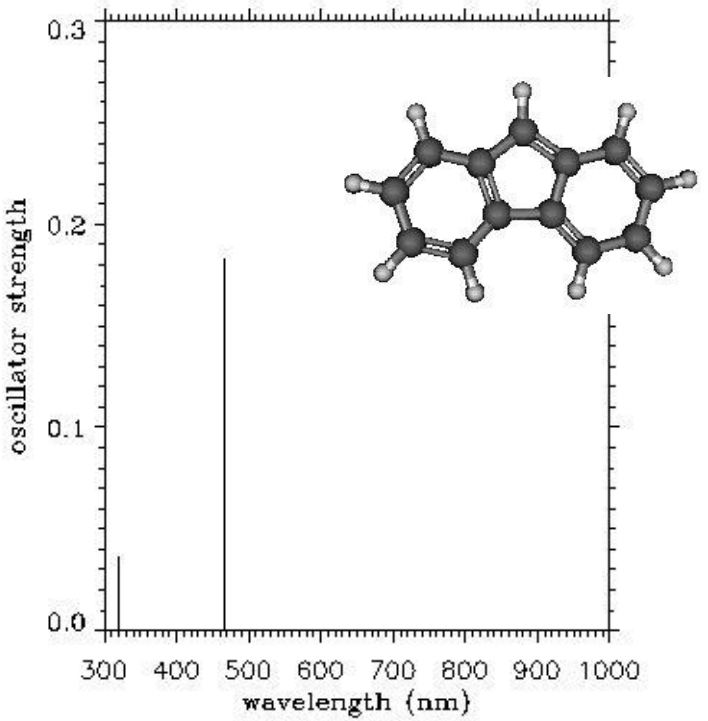


Buckminster-Fullerene $C_{60}$

# Some Results

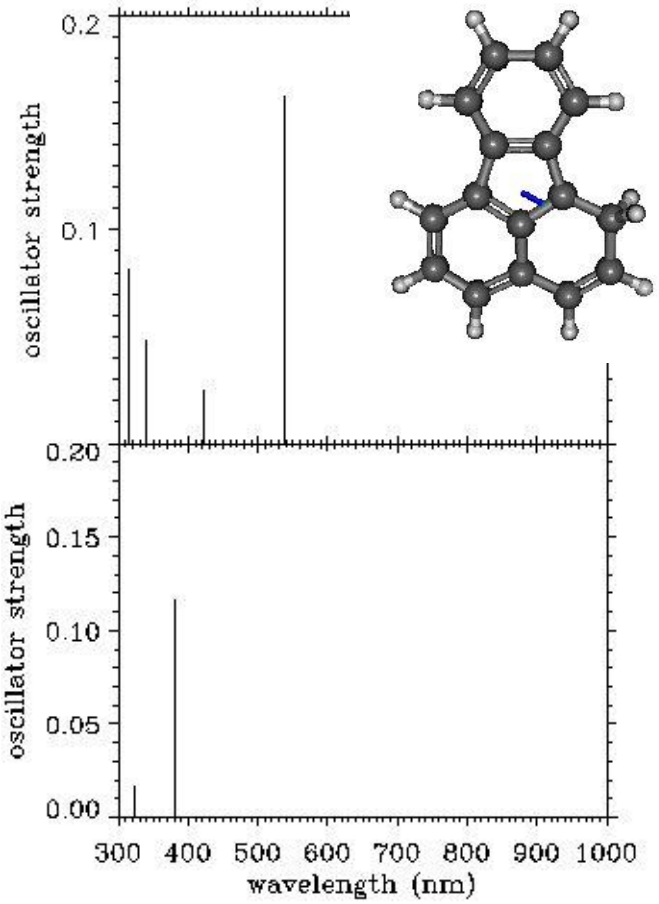



Acenaphthylene
neutral and protonated



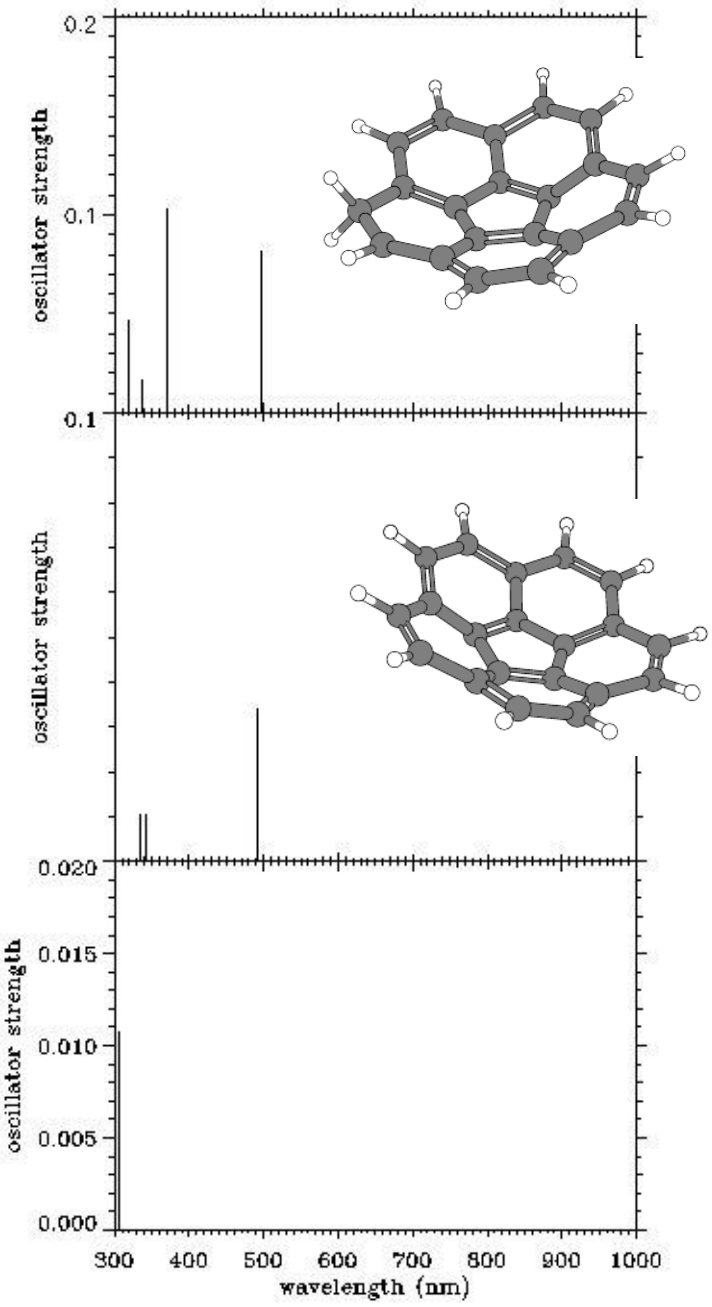

Fluorene cation
Protonated Fluorene is open shell and hydrogenated Fluorene has transitions in the UV

# Results contd.

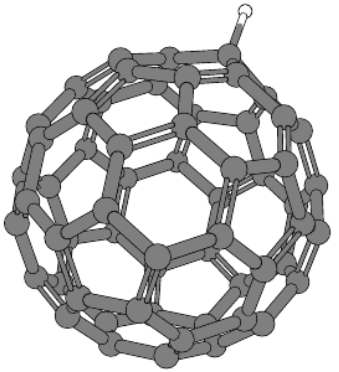


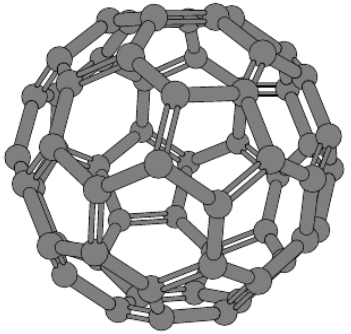

Fluoranthene
neutral and protonated

Corannulene
neutral, cation
and
protonated

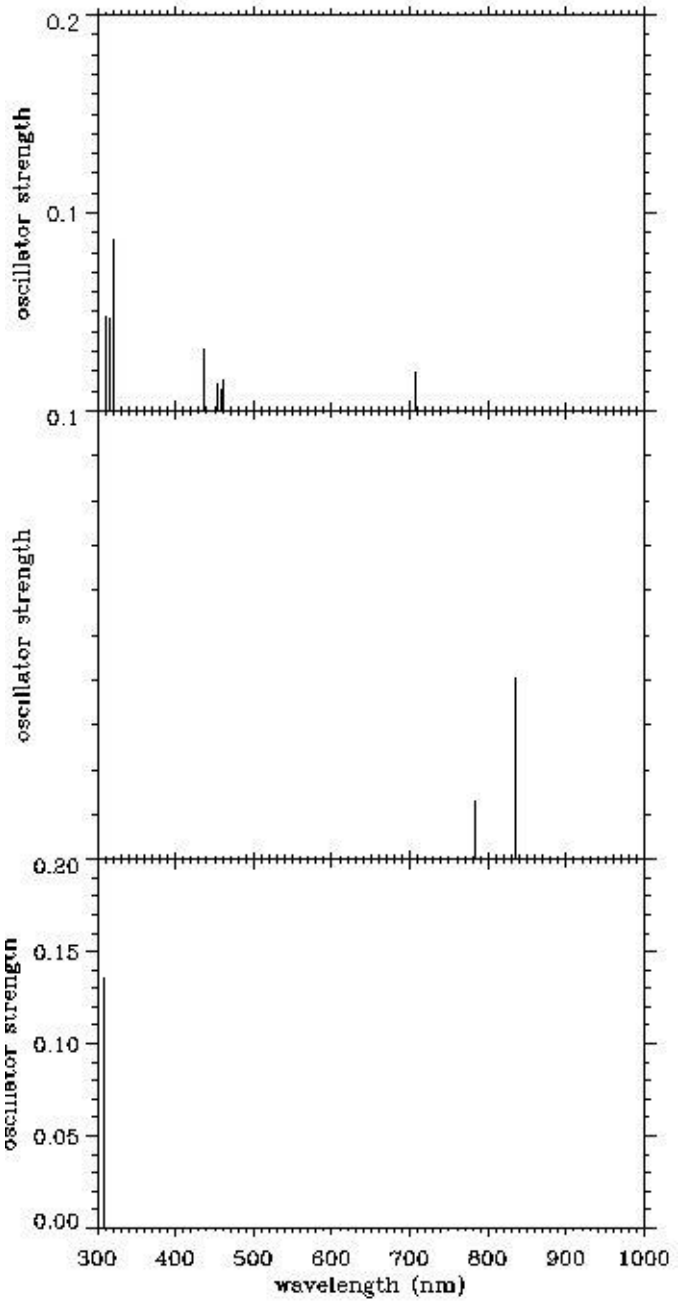


# Results contd.





$C_{60}$ neutral, cation and protonated



# Summary

- TDDFT calculations act as pointers to select candidate PAHs for laboratory studies.
- PAHs with five-membered rings show similar transitions as regular PAHs.
- Upon protonations, several transitions occur in the visible region.
- Several unique protonation sites on a single PAH result in different spectrum for each site.
- This feature may help in complying with the available interstellar Carbon budget.
- Protonated PAHs have permanent dipole moment – detection in the microwave.