UNRAVELLING SPECTRAL SIGNATURES AND PHOTOCHEMICAL PROCESSES OF PAHs

Annemieke Petrignani
University of Amsterdam

The Physics and Chemistry of the Interstellar Medium
Celebrating the first 40 years of Xander Tielens’ contribution to Science
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OUTLINE

• The physics and chemistry of the ISM IS PAHs
• Electronic signatures of IS PAHs
• Photochemistry of PAHs as driver for D storage
THE PHYSICS AND CHEMISTRY OF IS PAHs

Cosmic Inventory?

Cosmic Chemistry?
The Physics of IS PAHs

How to identify IS PAHs?

- Limited correlation
- Fortitude of possible isomers
- Individual abundances too low?
- No match found (yet)
- But… lack of accurate validated predictions and accurate experiments under IS conditions

Diffuse Interstellar Bands

PAHs as carriers?

Cami et al.
HIGH-RESOLUTION ACTION SPECTROSCOPY UNDER INTERSTELLAR CONDITIONS

- Sample vapor and expansion gas
- Seeded supersonic expansion
- Mass selection
- Ionization chamber isomer selection
- TOF spectrometer
- Resonant Enhanced MultiPhoton Ionisation (REMPI)

IE ionization energy
S<sub>0</sub> excitation
S<sub>1</sub> excitation
Gas-Phase Electronic Spectra

Dibenzo[a,c]anthracene

$S_1$

27,438 cm$^{-1}$

Dibenzo[a,h]anthracene

$S_1$

Benzo(ghi)perylene

$S_1$

Anthanthrene

$S_1$

Roeterdink et al., *in preparation*

More results on poster of Hernán Velásquez Navarro
GAS-PHASE ELECTRONIC SPECTRA

Roeterdink et al., in preparation
Gas-Phase Electronic Spectra

Measured 23.879 cm⁻¹

TD DFT 21.320 cm⁻¹

TD DFT 25.312 cm⁻¹

~11% deviation of \( S_0 \rightarrow S_1 \) transitions

Roeterdink et al., *in preparation*
VALIDATE AND IMPROVE PREDICTIONS

• Cold high-resolution laboratory data of isolated PAHs
• TD DFT <15%

Roeterdink et al., *in preparation* (2)
VALIDATE AND IMPROVE PREDICTIONS

- Cold high-resolution laboratory data of isolated PAHs
- TD DFT <15%
- Predictions ~1%!

Roeterdink et al., *in preparation* (2)
**The Photochemistry of IS PAHs**

**PAHs as Sink for Deuterium**

- D/H ratio: Primordial ~26 ppm
  ISM ~7 to 22 ppm
- Predictions & observations
- Experimental data lacking
- Mechanism?

Could PAHs form a sink
Does photochemistry play a role

Buragohain et al. 2016
PHOTOLYSIS OF D⁺-ANTHRACENE IONS

- D-PAH⁺ yields H loss only
- H-PAD⁺ yields D loss mostly

UV

Wiersma et al. *in preparation*
PHOTO-INDUCED SCRAMBLING

Wiersma et al. *in preparation*

Castellanos et al. 2018

4.8 (4.9) eV

2.6 (2.7) eV
Photochemistry of IS PAHs
• Photolysis induces scrambling in D-PAH
• Driver for D storage
• Structure and size dependency?
• Re-interpretation of C-D band observations?

Electronic Signatures of IS PAHs
• Laboratory data under interstellar conditions
• Validated predictions within 1% accuracy
• Measuring DIB candidates in the lab!
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Thank you Xander

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VENI Grant
VALIDATE AND IMPROVE PREDICTIONS

- Cold high-resolution laboratory data of isolated PAHs
- TD DFT <15%
- Predictions <1%!
- Structure!

Roeterdink et al., *in preparation* (2)
Photolysis of D\textsuperscript{+}-Anthracene Ions

- D-PAH\textsuperscript{+} yields H loss only
- H-PAD\textsuperscript{+} yields D loss mostly
- IRMPD follows UV fragmentation

Wiersma et al. *in preparation*
PHOTOLYSIS OF ANTHRACENE

\[ [H-C_{14}H_{10}]^+ \]

\[ [D-C_{14}H_{10}]^+ \]

\[ [H-C_{14}D_{10}]^+ \]