



Charge resonance effects in PAHs clusters cations

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Relevance of charge resonance for the physical chemistry of interstellar medium

Context: PAH clusters, as recently proposed from observational data (Berné *et al* A&A 469, 575–586 (2007); NGC7023, blind signal separation method).

Role of cations: Due to the unique stability of PAH dimer cations, the UV InterStellar Radiations Field can enhance the photocatalysed formation of cationic PAH clusters.
PAH- -PAH + hv → (PAH)₂⁺ + e⁻ through an excitonic intermediate

What is Charge Resonance? Pauli principle and in the PAH dimers ?

$$\Psi_{+/-} = \Psi_1^+ \Psi_2 \pm \Psi_1 \Psi_2^+$$

Information comes from Lab work:

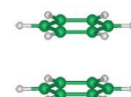
- Starting from neutrals: PES/PES spectroscopy
- Starting from cations: Optical spectroscopy

CR bands are caused by the interaction between the π electrons of the aromatic rings in the dimer cations, giving rise to a **dipole-allowed** transition (intrinsically broad).

Inokuchi Y. *et al*, 1995, 1996, 2001

Rapacioli M. *et al*, J. Chem. Theory Comput. 2011, 7, 44–55 - DFTB-VBCI method

Stacked Sandwich Bz dimer cation (D_{6h})



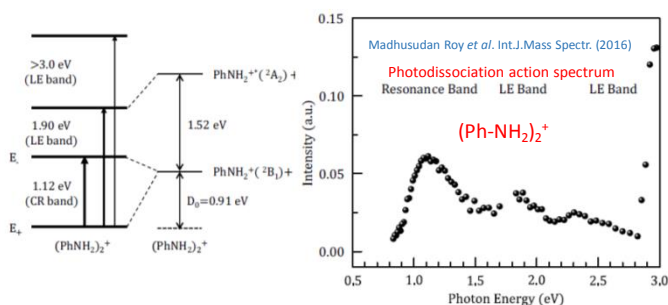
Some small PAH homodimers and polymers

Homodimer cations

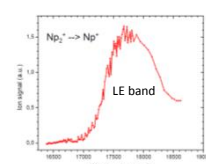
$$(h\nu_{D2})_{dim} = (h\nu_{D2})_{mono} + CR + (D_{gr} - D_{ex})$$

(Np)₂⁺ 0.23 eV $\Delta D = D_{gr} - D_{ex}$ 0.22 eV (Np-CH₃)₂⁺
0.57 eV CR (charge resonance) 0.55 eV

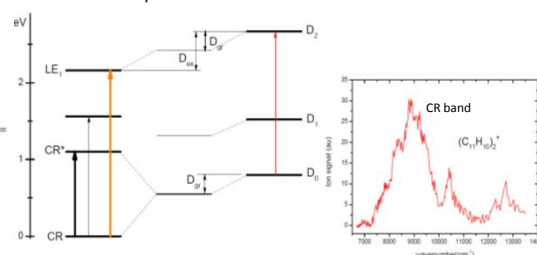
Aniline dimer Roy, Kim, Nam, Song, Park Int. J. Mass Spectr. 402, 66 (2016)



A « head to tail » type stacked CR structure



LE: Locally excited state



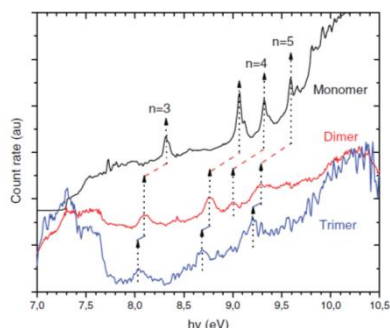
CR: Charge resonance interaction

Friha *et al*, in EAS Publications Series, 58 (2012) 373–378, ECLA, C. Stehlé, C. Joblin & L. d'Hendecourt (eds)

Most of the experimental studies show that cationic (PAH)_n⁺ clusters with size n>2 contain a strongly bound dimer core

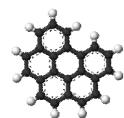
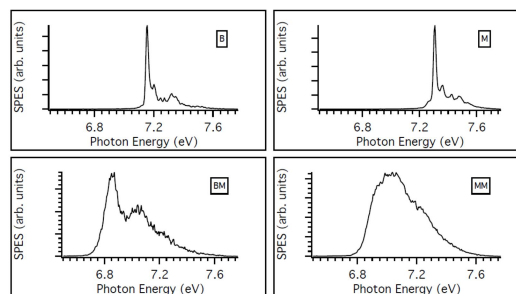
Coronene clusters, through TPES spectra

Homo/hetero dimer cations



Comparison of partial ion yield spectra of coronene monomer, dimer, and trimer with electron KE resolution $\epsilon = 0.8$ eV. Scaling factors (5 for dimer, 50 for trimer) and vertical translations were used for better clarity. The cluster spectral shifts are emphasized: red segments from monomer to dimer and blue segments from dimer to trimer.

A set of Rydberg states converging towards the excited electronic state of the monomer cation lying at $PI=10.2$ eV, seen in the dimer and trimer, shows the strength of the dimer stabilization due to charge resonance (CR), even in neutral states having ion-like wavefunctions.



Benzo(ghi)coronene

ionization energy	Coronene	BenzoPerylene	
n=1	7.31	7.16	
n=2	Coro+Coro	BzPer+Coro	
threshold	6.8	6.7	
Energy redshift (threshold)	0.51	0.46	
Peak values	7.0	6.85	0.31 excitation of BzPer shifted by Coro
	broad	7.05	0.26 excitation of Coro shifted by BzPer

CONCLUSION:

- optical spectroscopy offers higher resolution (while time-consuming), but it is often limited to allowed transitions, or by oscillator strength;
 - photoelectron spectroscopy has limited resolution but explore all the states in the experimental spectral window, which often exhibit high spectral congestion.
- Consequence : the two kinds of techniques can fruitfully complement each other.

Directions: in the case of dimers or larger clusters, the study of the charge delocalization is a key point; it requires theoretical input. Modeling such processes in **interstellar conditions** remain to be explored.