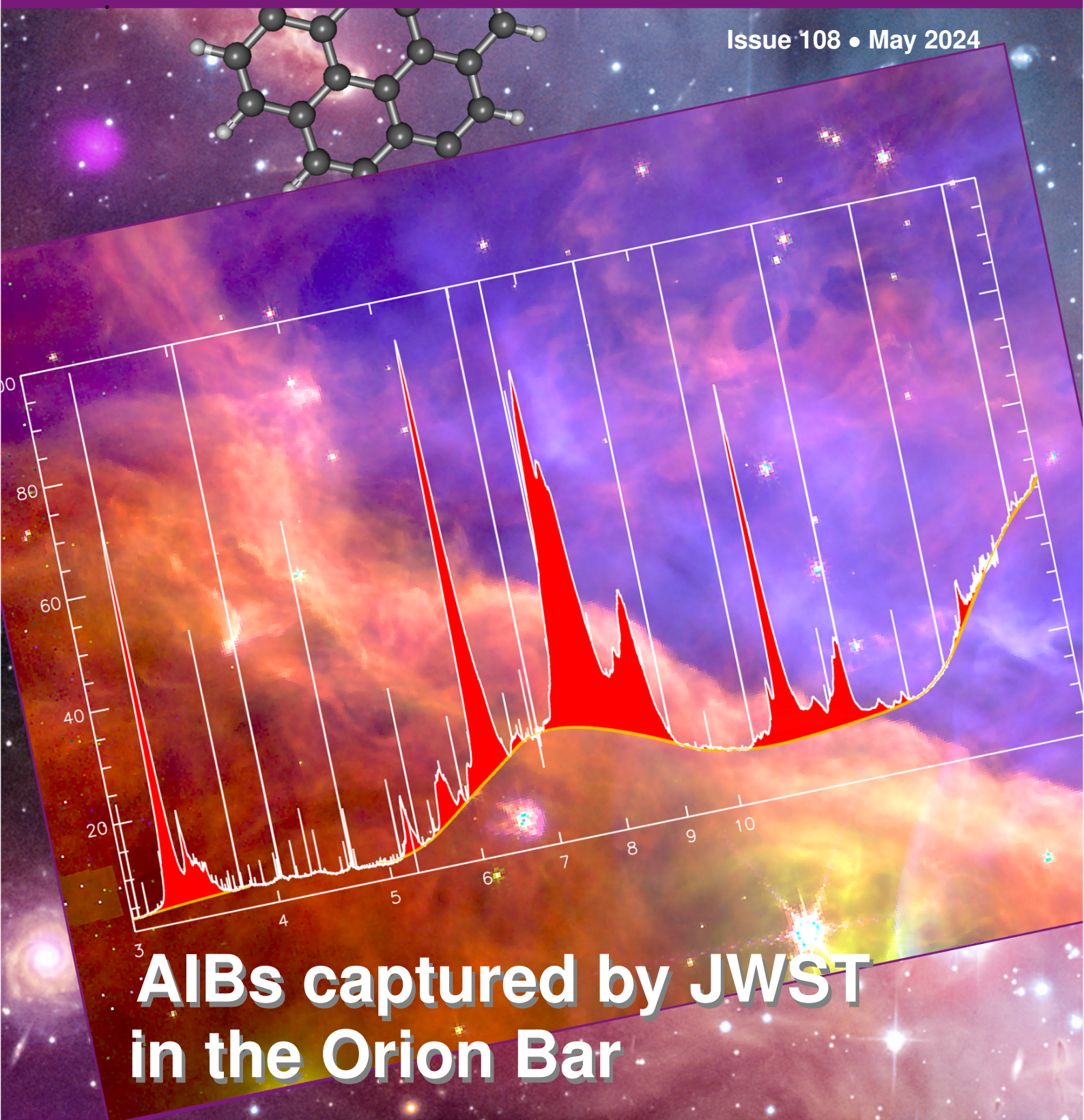


AstropAH

A Newsletter on Astronomical PAHs

Issue 108 • May 2024



**AIBs captured by JWST
in the Orion Bar**



Editorial

Dear Colleagues,

Welcome to our new AstroPAH volume no. 108! We hope all of you are healthy and doing well, as we are already nearing the end of May!

The Orion Bar has been given a new look with James Webb's most sensitive and highest resolution IR spectral image ever taken of the famous PDR. Our Picture of the Month, featured on the cover, shows the spectrum of the Aromatic IR Bands (AIBs) captured by these observations, that was recently published by Chown et al. in *Astronomy & Astrophysics*.

Our In Focus this month features an interview with one of our editors, Sandra Wiersma, who is starting a new job. Congratulations, Sandra!

We thank you as always for all your contributions and submissions. This month, we share new papers about nitrile stretch spectroscopy of cyano-PAHs, C_{59} anion stability, infrared bands of carbon clusters, C_{60}^+ electronic structure and ground-state symmetry, and the AIBs found in the Orion Bar.

If you are on Instagram, be sure to check out our next [PAH of the Month!](#)

We hope you enjoy reading our newsletter, and we thank you for your dedication and interest in AstroPAH! Please continue sending us your contributions, and if you wish to contact us for a future In Focus or other ideas, feel free to use our [email](#).

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Next issue: 20 June 2024.
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PAH Picture of the Month

The most sensitive, highest resolution view of the aromatic infrared bands has been captured by the JWST in the prototypical PDR, the Orion Bar.

Credits: The image of the Orion Bar and the AIB spectrum used to generate the PoM were provided by Christiaan Boersma and Els Peeters, respectively. [R. Chown et al. 2024](#) and references therein.

An interview with Sandra Wiersma

Dr. Sandra Wiersma was a postdoctoral researcher at the Institut de Recherche en Astrophysique et Planétologie in Toulouse, France. There, she studied the formation of PAHs in laser-ablated and magnetron-sputtered stardust analogues, with a special interest in the potentially catalytic effects of silicon and iron. She obtained her PhD in 2021 from University of Amsterdam, working with the FELIX free-electron laser to study the (far)-infrared spectra of cationic PAHs. At present, she started a new job outside of academia as a certification engineer in the heat pump lab of the Dutch company Kiwa.



What inspired you to become a scientist?

I spent too much time in front of the TV as a kid, but National Geographic and the Discovery Channel got the same amount of attention as the Cartoon Network. I had really broad interests, and I saw connections everywhere I looked. One side of me was a creative little day-dreamer, and one an annoying kid that couldn't stop asking "why". At a certain point, my dad told me that I wouldn't be able to make a living as an artist, so the only logical thing for me was to dream of becoming a scientist.

How did you get into astrochemistry research??

When I was a physics student, I was a member of a small committee that organized monthly lunch colloquia for bachelor students, given by visiting researchers. One these researchers was the late and great Prof. Harold Linnartz. His talk really lit a little fire in me, that allowed me to dream of a field in which I could combine my interests in both physics, chemistry and astronomy.

What did it mean for you to be a part of the AstroPAH editorial team? What aspect did you like best?

It meant the world to me. I moved to France during the lockdown phase of the pandemic, by myself, while I was also trying to finish up my PhD. It was rough, but AstroPAH helped me

to still feel connected to a bigger community, and gave me a sense of accomplishment when I needed it the most.

What is your next adventure going to be?

I'm a pretty extroverted person, and I thrive in teams where I see other people on a daily basis, and it's easy to receive and give feedback. I loved this about my PhD work at a large facility like FELIX. Considering that I started my postdoc during lockdown, and that I did most of my experiments in a different building from the rest of the team, I didn't end up having fun until the last year of my three-and-a-half year stay. It confronted me with how insular being a scientist can be, and it also made it very clear to me that I crave connection and some sense of stability. So I decided to leave academia, and go home. That way I'd have a much better shot at a permanent position, and I'd have a bigger support system available to me.

One thing that made this decision easier, is when I found out that I could also use my scientific skills to make the world a better place. I specifically applied for jobs somewhere in the sustainability sphere, which is how I ended up where I am now. In my current position, I'll be helping companies that develop heat pumps bring their new products onto the market in a way that helps consumers make educated, sustainable choices. A really nice perk is that I will be operating huge climate cells with shiny, well-calibrated equipment.

How do you balance your professional and personal life?

With the exception of things like pressing deadlines and writing a PhD thesis, I've tried to keep my weekends work free, and at least make sure I ate healthy meals and exercised. I loved doing science, but I never wanted it to completely consume me.

What do you do outside of work?

I love to cook, and I especially love to cook for my friends. The fact that we get to befriend people from all of the world is one of the things I loved the most about being a scientist, and getting to know all of their cuisines is almost as awesome. I would never have gotten to know the richness of all of the different regional cuisines India has to offer if I hadn't met lots of different, wonderful Indians, and I wouldn't have learnt how to make the perfect hummus if it weren't for my Lebanese bestie.

Running is the only thing I'm equally crazy about. It has kept me sane through many a tough phase in my life, because it's meditation with added endorphins. It's also allowed me to explore the many cities I have visited on conferences during the wee hours of the morning. My favorite memory is having climbed up to the white castle of Belgrade at 6:30, before the morning commute had really started, basking in the morning sun while slightly hungover.

What was the most important advice somebody gave you? What advice would you give a grad student who wants a career in academia?

A friend from high school gave me a self-help book a long time ago, titled "Daring Greatly", by Brené Brown, a US researcher on the topic of vulnerability and courage. One of the

biggest takeaways for me was that there is no creativity without vulnerability. If you feel like you can't make mistakes, how can you move forward, try something new? Especially in a field where we *aren't supposed* to have all of the answers? So, to any grad students who are looking for their first position, I'd like to encourage them to find collaborators who will encourage you to try things, learn and grow. Your new supervisor can be the smartest person in their field, but they're only a good supervisor if they don't make you feel stupid while you work with them.



Abstracts

CN stretches around 4.4 microns dominate the IR absorption spectra of cyano-polycyclic aromatic hydrocarbons

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Anharmonic quantum chemical computations reveal a strong, narrow (width = 0.075 μm) band in the 4.3 - 4.5 μm region of the absorption spectra of the cyano-substituted polycyclic aromatic hydrocarbons (CN-PAHs) cyanonaphthalene, cyanoanthracene, cyanophenanthrene, and cyanopyrene. This narrow window with intense IR lines implies that CN-PAHs of various shapes and sizes offer little variation in both wavelength and intensity in this region. Subsequently, this band can be used as a tracer for CN-PAHs. The distinct features making up the band are assigned to mixed vibrational states consisting of the CN stretch fundamental and various combination bands, including in-plane CH bends, CC skeletal bends, and CC skeletal breathing motions. The extraordinarily large intrinsic intensity of the fundamental CN stretch is redistributed to nearby states via anharmonic coupling, which is readily captured when using second order vibrational perturbation theory with resonance polyad matrices. This redistribution of intensity leads to a complex spectrum. The intense bands in this wavelength region may contribute to the baseline continuum and undulating macroscopic structure seen in recent JWST NIRSpec observations.

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Stability of C₅₉ Knockout Fragments from Femtoseconds to Infinity

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We have studied the stability of C₅₉ anions as a function of time, from their formation on femtosecond timescales to their stabilization on second timescales and beyond, using a combination of theory and experiments. The C₅₉⁻ fragments were produced in collisions between C₆₀ fullerene anions and neutral helium gas at a velocity of 90 km/s (corresponding to a collision energy of 166 eV in the center-of-mass frame). The fragments were then stored in a cryogenic ion-beam storage ring at the DESIREE facility where they were followed for up to one minute. Classical molecular dynamics simulations were used to determine the reaction cross section and the excitation energy distributions of the products formed in these collisions. We found that about 15 percent of the C₅₉⁻ ions initially stored in the ring are intact after about 100 ms, and that this population then remains intact indefinitely. This means that C₆₀ fullerenes exposed to energetic atoms and ions, such as stellar winds and shock waves, will produce stable, highly reactive products, like C₅₉, that are fed into interstellar chemical reaction networks.

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Infrared bands of neutral gas-phase carbon clusters in a broad spectral range

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The identification of species in the interstellar medium requires precise and molecule-specific spectroscopic information in the laboratory framework, in broad spectral ranges and under conditions relevant to interstellar environments. In this work, we measure the gas-phase infrared spectra of neutral carbon clusters, C_N ($N = 6 - 11$), in a molecular beam. The CN distribution is formed by photofragmentation of C_{60} molecules, concurrently showing a top-down formation mechanism. A broad spectral range in the infrared between $500 - 3200 \text{ cm}^{-1}$ ($20 - 3.125 \text{ }\mu\text{m}$) is investigated. We observe strong bands between 5 and $6 \text{ }\mu\text{m}$, in conjunction with novel features in the $3 \text{ }\mu\text{m}$ region. Density functional theory calculations reveal that these short wavelength modes correspond to combinations bands with significant infrared intensity. Moreover, we identify the $N \leq 10$ clusters as linear, while C_{11} adopts a ring configuration, placing the linear-to-ring transition at $N = 11$ under our molecular beam conditions. The linearity of C_{10} is discussed based on the formation pathway from larger clusters in energetic conditions. Given the vast and very precise infrared information already been released from the James Webb Space Telescope mission, this infrared spectroscopic data set in conjunction with information on formation mechanisms is of major relevance for identifying neutral carbon clusters in astronomical environments.

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<https://pubs.rsc.org/en/content/articlehtml/2024/cp/d3cp05756a>

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Probing the electronic structure and ground state symmetry of gas phase C_{60}^+ via VUV photoionization and comparison with theory

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Recently, some of us reviewed and studied the photoionization dynamics of C_{60} that are of great interest to the astrochemical community as four of the diffuse interstellar bands (DIBs) have been assigned to electronic transitions in the C_{60}^+ cation. Our previous analysis of the threshold photoelectron spectrum (TPES) of C_{60} [Hrodmarsson *et al.*, *Phys. Chem. Chem. Phys.* **22**, 13880–13892 (2020)] appeared to give indication of D_{3d} ground state symmetry, in contrast to theoretical predictions of D_{5d} symmetry. Here, we revisit our original measurements taking account of a previous theoretical spectrum presented in the work of Manini *et al.*, *Phys. Rev. Lett.* **91**(19), 196402 (2003), obtained within a vibronic model parametrized on density functional theory/local-density approximation electronic structure involving all h_g Jahn–Teller active modes, which couple to the 2H_u components of the ground state of the C_{60}^+ cation. By reanalyzing our measured TPES of the ground state of the C_{60} Buckminsterfullerene, we find a striking resemblance to the theoretical spectrum calculated in the work of Manini *et al.*, *Phys. Rev. Lett.* **91**(19), 196402 (2003), and we provide assignments for many of the h_g modes. In order to obtain deeper insights into the temperature effects and possible anharmonicity effects, we provide complementary modeling of the photoelectron spectrum via classical molecular dynamics (MD) involving density functional based tight binding (DFTB) computations of the electronic structure for both C_{60} and C_{60}^+ . The validity of the DFTB modeling is first checked vs the IR spectra of both species which are well established from IR spectroscopic studies. To aid the interpretation of our measured TPES and the comparisons to the ab initio spectrum we showcase the complementarity of utilizing MD calculations to predict the PES evolution at high temperatures expected in our experiment. The comparison with the theoretical spectrum presented in the work of Manini *et al.*, *Phys. Rev. Lett.* **91**(19), 196402 (2003), furthermore, provides further evidence for a D_{5d} symmetric ground state of the C_{60}^+ cation in the gas phase, in complement to IR spectroscopy in frozen noble gas matrices. This not only allows us to assign the first adiabatic ionization transition and thus determine the ionization energy of C_{60} with greater accuracy than has been achieved at 7.598 ± 0.005 eV, but we also assign the two lowest excited states (${}^2E_{1u}$ and ${}^2E_{2u}$) which are visible in our TPES. Finally, we discuss the energetics of additional DIBs that could be assigned to C_{60}^+ in the future.

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IV. An embarrassment of riches: Aromatic infrared bands in the Orion Bar

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Context. Mid-infrared observations of photodissociation regions (PDRs) are dominated by strong emission features called aromatic infrared bands (AIBs). The most prominent AIBs are found at 3.3, 6.2, 7.7, 8.6, and 11.2 μm . The most sensitive, highest-resolution infrared spectral imaging data ever taken of the prototypical PDR, the Orion Bar, have been captured by JWST. These high-quality data allow for an unprecedentedly detailed view of AIBs.

Aims. We provide an inventory of the AIBs found in the Orion Bar, along with mid-IR template spectra from five distinct regions in the Bar: the molecular PDR (i.e. the three H_2 dissociation fronts), the atomic PDR, and the H II region.

Methods. We used JWST NIRSpec IFU and MIRI MRS observations of the Orion Bar from the JWST Early Release Science Program, PDRs4All (ID: 1288). We extracted five template spectra to represent the morphology and environment of the Orion Bar PDR. We investigated and characterised the AIBs in these template spectra. We describe the variations among them here.

Results. The superb sensitivity and the spectral and spatial resolution of these JWST observations reveal many details of the AIB emission and enable an improved characterization of their detailed profile shapes and sub-components. The Orion Bar spectra are dominated by the well-known AIBs at 3.3, 6.2, 7.7, 8.6, 11.2, and 12.7 μm with well-defined profiles. In addition, the spectra display a wealth of weaker features and sub-components. The widths of many AIBs show clear and systematic variations, being narrowest in the atomic PDR template, but showing a clear broadening in the H II region template while the broadest bands are found in the three dissociation front templates. In addition, the relative strengths of AIB (sub-)components vary among the template spectra as well. All AIB profiles are characteristic of class A sources as designated by Peeters (2022, AA, 390, 1089), except for the 11.2 μm AIB profile deep in the molecular zone, which belongs to class B11.2. Furthermore, the observations show that the sub-components that contribute to the 5.75, 7.7, and 11.2 μm AIBs become much weaker in the PDR surface layers. We attribute this to the presence of small, more labile carriers in the deeper PDR layers that are photolysed away in the harsh radiation field near the surface. The 3.3/11.2 AIB intensity ratio decreases by about 40% between the dissociation fronts and the H II region, indicating a shift in the polycyclic aromatic hydrocarbon (PAH) size distribution to larger PAHs in the PDR surface layers, also likely due to the effects of photochemistry. The observed broadening of the bands in the molecular PDR is consistent with an enhanced importance of smaller PAHs since smaller PAHs attain a higher internal excitation energy at a fixed photon energy.

Conclusions. Spectral-imaging observations of the Orion Bar using JWST yield key insights into the photochemical evolution of PAHs, such as the evolution responsible for the shift of 11.2 μm AIB emission from class B11.2 in the molecular PDR to class A11.2 in the PDR surface layers. This photochemical evolution is driven by the increased importance of FUV

processing in the PDR surface layers, resulting in a “weeding out” of the weakest links of the PAH family in these layers. For now, these JWST observations are consistent with a model in which the underlying PAH family is composed of a few species: the so-called ‘grandPAHs’.

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