The discovery of cosmic fullerenes

In 2010, the Spitzer Space Telescope detected evidence of a complex form of carbon that had never been seen in extraterrestrial environments. Jan Cami recounts the discovery of buckminsterfullerene in space.

■ **How did you first develop a fascination with complex carbonaceous molecules?**
My dad was my final year high school physics and chemistry teacher, and when I was a kid, he got a subscription to *EOS*, a popular science magazine that first appeared in 1983 and that could quench my thirst for science knowledge. Later on, it was in *EOS* that I would first read about and be intrigued by buckyballs (the colloquial name given to buckminsterfullerene), those weird carbonaceous particles shaped like a soccer ball. The article featured a picture of chemist Harry Kroto juggling with buckyball models, and a quote by his colleague Richard Smalley stating that these newly discovered molecules would turn out to be important in space. As part of the discovery of this species, they realized that they would be widespread and abundant in space[1].

After I completed my undergraduate degree in physics at the KU Leuven in Belgium, I enrolled in a European master's programme in astronomy and astrophysics that took me to the Leiden Observatory to work with Pascale Ehrenfreund on the diffuse interstellar bands (DIBs), and that's when I got hooked on mysterious molecules in space. The DIBs are a set of about 600 absorption bands that are routinely measured in the optical and near-infrared (IR) spectra of objects that we observe through interstellar clouds. We know that the bands originate in interstellar clouds, and there are many good reasons to suspect that they are caused by large carbonaceous molecules. In my master's thesis, I used a few DIB line profiles to determine the size of their carrier molecules, and one DIB in particular represented a size of about 60 carbon atoms — like buckyballs! Targeted astronomical searches for the spectral features of neutral C_{60} did not result in a detection[2–4], but Pascale and colleague Bernard Foing realized that in the interstellar medium, fullerenes could well be ionized, and we should thus be searching for C_{60}^+. The biggest challenge here was to figure out at what wavelengths we should expect to see the spectral features of C_{60}^+. Bernard and Pascale used laboratory data to predict that they would occur in a wavelength range in the near-IR that most astronomers shy away from, because it is heavily contaminated by spectral lines due

to the Earth's atmosphere. But they pushed through and their perseverance paid off: their dedicated observational search resulted in two DIB-like absorption bands very close to the wavelengths they had predicted and with other characteristics that were consistent with C_{60}^+ (refs. [5,6]). During my MSc time, I was thus exposed to first-hand research accounts and discussions about C_{60} and C_{60}^+ in space.

■ **Were there any attempts to find cosmic C_{60} in the mid-IR back then?**
In November 1995 came an astronomical milestone: the launch of the Infrared Space Observatory (ISO)[7]. The ISO was the first space observatory that offered astronomers the opportunity to study the mid-IR sky in great detail. For my PhD, I switched fields and would primarily use the Short Wavelength Spectrometer (SWS)[8], an instrument that could provide spectra from 2.3 to 45 μm. With ISO/SWS, I studied the circumstellar gas and dust around evolved stars[9], sharing the excitement of working with brand-new, literally never-seen-before data with a large contingent of other PhD students in the Netherlands.

There were several efforts to detect the mid-IR vibrational modes of fullerenes. Clayton et al.[10] realized that R Cor Bor stars would be good environments to produce C_{60}, but a search for the 19 μm band in Infrared Astronomical Satellite spectra of several objects did not turn up any evidence, and they did not see the C_{60} band they expected at 8.6 μm in observations with NASA's InfraRed Telescope Facility, either. Kwok, Volk and Hrivnak[11] presented the ISO spectra of several evolved objects, and reported features at 17.85, 18.90 and 19.15 μm on top of a broad 21 μm feature. They note that C_{60} has features at 17.54 and 18.90 μm, but do not find an 8.5 μm band or an evident 7.0 μm band.

While working on my PhD, I also kept DIB work going with Pascale and Bernard, and we put in a proposal to use ISO/SWS to search for the strongest vibrational band of C_{60}, expected at about 19 μm, in the reflection nebula NGC 7023. No band was detected though[12]. A few years later, I got suddenly very excited, because several of my evolved stars showed a new dust feature around 19 μm and my first thought was of

course this might be C_{60} — which would have been very surprising since the stars I was studying were oxygen-rich rather than carbon-rich, and C-rich molecules were thus not expected. Further scrutiny quickly eroded away my original excitement: the feature was really at 19.5 μm, it was much too broad to be C_{60} and there were no other bands that could be attributed to C_{60} either. It was a good exercise in scientific rigour. It would not be the last time that early excitement about observations would turn out to be incorrect. Ironically, it turns out that during my PhD work, I did in fact see a C_{60} band but didn't realize it. Indeed, the 17.4 μm C_{60} band is present in the ISO/SWS observations of the enigmatic post-asymptotic-giant-branch (AGB) star HR 4049, an object whose IR spectrum resulted in two papers[13,14] and correspondingly two chapters in my PhD thesis[9]. I definitely remember that I was annoyed by that bump while I was studying CO_2 lines in that spectrum, but I thought it was perhaps an instrumental feature rather than something exciting. Later, the Spitzer spectrum of HR 4049 showed all molecular bands in much greater detail owing to a much better signal-to-noise ratio, and especially after subtracting a model for CO_2 and H_2O emission, the C_{60} bands at 17.4 μm and 19 μm become quite clear[15] (also see ref. [16]). It was my own graduate student Sarah Malek who pointed out that I had in fact been staring C_{60} in the face without realizing it.

To add to the irony, I recall my judgement back then about the Spitzer Space Telescope that was launched in 2003. I had experienced many new discoveries with ISO that essentially relied on high spectral resolution and large wavelength coverage. The Spitzer Space Telescope had less wavelength coverage (especially at the shortest wavelengths) and much lower resolution than ISO/SWS, so I thought that Spitzer would not yield many new discoveries. Boy, was I wrong; I will never underestimate the role of high sensitivity for the rest of my career!

■ **How did the Spitzer Space Telescope contribute to the campaign?**
It should be clear by now that the discovery of C_{60} in space was not unexpected and

that the IR was a good wavelength range to search for it. In spite of much earlier efforts, it would take the Spitzer Space Telescope to clearly establish its presence. Werner et al.[17] found several new emission features in NGC 7023, including a feature at 19.0 μm. NGC 7023 is rich in polycyclic aromatic hydrocarbon (PAH) emission, and we know now that the PAH bands overlap with the C_{60} bands, which caused confusion. Importantly, they note that the 16.4 μm PAH feature and the newly detected 19.0 μm feature are spatially anti-correlated and speculate that these newly detected features could be other aromatic hydrocarbons or nanoparticles of unknown mineralogy. A note added in proof reveals that Mike Jura suggested to the authors that the 17.4 and 19.0 μm features could be due to C_{60}. Peeters et al.[18] investigated this range in more detail and compared the spectra of a few different sources. They conclude that the 19 μm feature (and to some extent the 15–20 μm plateau) could arise from changes in the PAH charge distribution, or alternatively the 19 μm feature originates from a non-carbonaceous carrier. Later, Boersma et al.[19] also studied this range and suggest the 19 μm band originates from a species that is more stable than other PAHs.

One of the key observational innovations about the Spitzer Space Telescope was the possibility to make spectral maps of extended sources and study how spectral features change with their environment. Sellgren et al.[20] used this powerful technique to study the spatial variations of the features in NGC 7023 in great detail. They confirmed the earlier result by Werner et al.[17] concerning the different spatial distributions for some of these features. Indeed, the 16.4 μm PAH feature peaks near the photodissociation region front where also the other PAH features peak, while the 18.9 μm feature peaks near the central star of the nebula. They consider a wide range of possible carriers for the 18.9 μm feature, and include a detailed discussion about the possibility that it is due to C_{60}. They note that C_{60} would exhibit a feature at 17.4 μm as well, but that the observed 17.4 band does not spatially correlate very well with the 18.9 μm feature. This, they argue, could be due to having two components to the 17.4 μm feature — one due to C_{60}, and another due to PAHs. As a future test, they propose to search for the two C_{60} features at shorter wavelengths to confirm their hypothesis.

When presenting the literature like this, with perfect hindsight, the path towards discovering C_{60} seems very clear at this point already, and it would just be a matter of time before somebody would provide

Credit: Frank Neufeld, Western University

convincing evidence for C_{60}. However, there was some scepticism in the community because there were no clearly accepted identifications, and that was not for a lack of searching in the right places. I certainly didn't expect to find it — I was mostly focused on model spectra of much smaller molecules at that time, and thus I was blissfully unaware of these previous results, including much of the

work that my PhD colleague, and partner, Els Peeters did.

■ **How did the discovery of cosmic fullerenes come about?**

In the winter of 2006, we moved to the University of Western Ontario and I became an assistant professor — a completely new and very different life. With responsibilities in teaching and service, and a desire to

do well in those aspects, there was simply not much time left for research and, consequently, I did not publish much. As part of my New Year's resolutions in January 2010, I decided I would do something about that. By the end of January, I finished one paper[21], which greatly motivated me and cleared my mind to work on something else.

The third week of February is an oasis of calm in the hectic winter term. It's called reading week, and it's essentially a week without teaching. While going through a stack of unread papers, I got a phone call from Els who had received an e-mail from our friend Jeronimo Bernard-Salas, another PhD colleague. Earlier that year, Jeronimo (in collaboration with Els and myself) had published a paper on an interesting object that showed the strongest ever benzene absorption bands, and a whole host of other carbonaceous molecules[22]; this thus appeared to represent the key phase where the complex chemistry occurs that leads to the formation of large aromatics (or PAHs). Excited by this discovery, Jero was searching the Spitzer archive for similar objects, and Stuart Pottasch suggested he looked at Tc 1, which he did. During his literature study, he came across a paper about Spitzer observations of PNe[23], and noticed a very unusual spectrum in their set. It was the IR spectrum of Tc 1 observed with the Infrared Spectrograph[24] on board the Spitzer Space Telescope[25]. The authors noted that this unusual spectrum showed hydrogenated PAHs, and that this would be discussed in a forthcoming paper. Jeronimo recognized the importance of this unusual spectrum, and since Els is one of the world's experts on PAHs, he asked her whether she thought this spectrum indeed was due to PAHs. She did not, but did not have a clear idea of how to explain the observations either. While she was on the phone, she sent the spectrum over e-mail, and as soon as I saw the spectrum, I saw a strong peak at 19 µm that looked similar in appearance to PAH features. And I said "Oh wow, yes, I think I know what that is — that's C_{60}!" I just knew immediately and instinctively we were looking at C_{60}. It definitely was some sort of cosmic coincidence and luck, but as they say, luck favours the prepared mind, and I was ready for this. What I didn't know was how nerve-wrecking, exhausting and stressful the next few weeks of my life would turn out to be. Els pointed out that other teams had been looking for C_{60} and if we could find and recognize it in the spectrum of Tc 1 in the literature, so could others, so we would have to act fast.

What followed was an exemplary team effort. We divided up the different tasks that needed to be done. Jero worked on
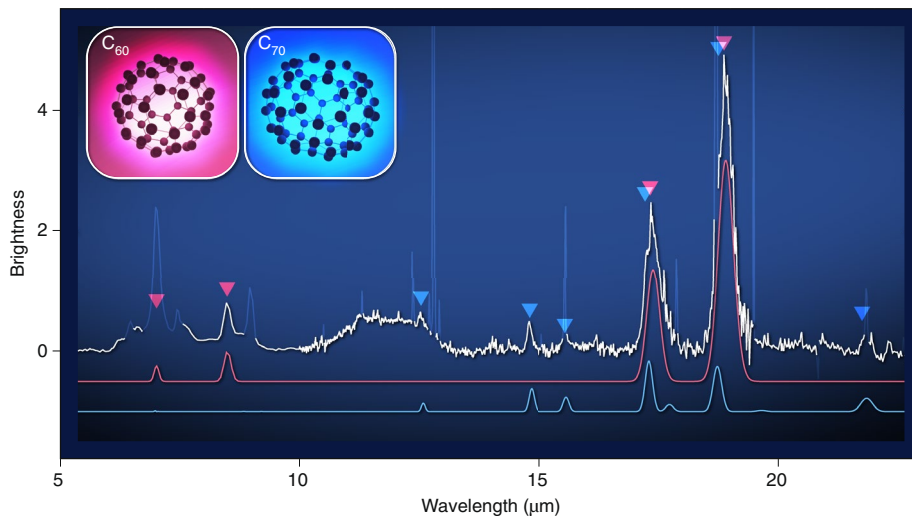
Credit: NASA/JPL-Caltech/J. Cami (Univ. of Western Ontario/ SETI Institute

the data reduction and researched the properties of Tc 1, Els searched for more sources that could show C_{60} and I delved into the literature to study the properties of C_{60} in more detail. I tasked my graduate student Sarah Malek with figuring out some of the details of the expected profiles. We discussed our progress and exchanged ideas on a daily basis. It only took us a short while to realize that the beautiful spectrum of Tc 1 showed all four expected C_{60} features: strong emission bands at 7.0, 8.5, 17.4 and 18.9 µm. The case for C_{60} in Tc 1 was particularly clear because there was virtually no contamination by PAH bands. There were weaker bands in the spectrum at 15.56, 14.79 and 12.51 µm (642, 676, 799 cm^{-1}) and these were reported in laboratory spectra as well[26]. It was not immediately clear whether these were C_{60} combination bands or rather bands of C_{70}. Within a few days of hard work and in-depth discussions, we could convince ourselves that the weaker bands were indeed compatible with C_{70}, and thus we had what we thought were sound identifications for both C_{60} and C_{70}, which made the case much more convincing and appealing.

To really seal the deal, it would be great if we could also somehow match the expected emission band strengths. From my work with Christiaan Boersma in the context of the NASA Ames PAH database[27], I had a PAH fluorescence code ready, and when putting in the numbers for C_{60}, the model produced a decent (but not perfect) fit to the observations, and reproduced especially the intensity of the strong band at 7 µm quite well. However, that was problematic: the emission line we observed at 7.0 µm is a blend of C_{60} and a forbidden [Ar II] line originating from the ionized gas in the

nebula. State-of-the-art models for the Tc 1 nebula at that time predicted that at least 85% of the flux we measured at 7 µm must be due to this [Ar II] line. I therefore looked at it from a different perspective. From the three uncontaminated C_{60} emission bands (at 8.5, 17.45 and 18.9 µm), I calculated how many C_{60} molecules we needed in each of the vibrationally excited states to reproduce the bands we saw. When I plotted these three numbers as a function of the energy of the excited states, it showed a straight line, with a prediction for much less emission in the 7 µm band than the fluorescence model predicted. A straight line was definitely not what we expected — it is a result that would be expected when the C_{60} molecules would all be in thermal equilibrium, but it would be hard to argue how C_{60} could be in thermal equilibrium in a planetary nebula! When I did the same exercise for the four weaker, isolated bands of C_{70}, they also showed a straight line.

The appealing bit about this analysis was that with just two parameters (the C_{60} and C_{70} temperatures), I could reproduce all the relative strengths of the fullerene bands given what we knew about the nebula at that point. But I had no good justification for using a thermal model. A conversation with Xander Tielens gave me some ideas, and in our discovery paper, we argued that the only way this could work was that somehow, the fullerenes were attached to dust grains, and hence assumed the dust temperature. The last question to address was what was so special about Tc 1 that it created copious amounts of fullerene emission whereas most other, similar PNe do not. Jero's research into the properties

of Tc 1 pointed out the problem with Tc 1: there is nothing particularly unusual about it. It is bland. Apart from the C_{60} emission. The literature describing laboratory experiments essentially offered only two possible formation pathways at that time: fullerenes could either form at very high temperatures[28], or they could form in H-poor conditions[29]. The high temperatures seemed unlikely for the location where we saw the C_{60} emission, and so we concluded that H-poor conditions were more likely. The absence of PAHs was appealing in that sense as well — since combustion experiments in a C/H mixture at 'normal' temperatures always produce PAHs.

Within a week with very little sleep, we had a solid identification of C_{60} and C_{70}, a species astronomers had been searching for for 25 years. We also had a plausible explanation for the thermal-appearing emission and a hypothesis about their formation in this environment. For the first time in my life, I was convinced that we had a major discovery in our hands that was going to be relevant for other scientific disciplines as well, and thus a good shot at getting a high-impact paper published. On 23 February 2010, I first contacted *Nature* to gauge interest. It was not a yes and not a no to begin with, and what followed were six weeks of revisions and additions that ultimately did not convince the editor. After some advice from my mentors, we rewrote the manuscript one last time, and submitted it to *Science* on 10 May. The experience was entirely different this time: the editors promptly sent the paper to reviewers. The reviewers returned their reports by 11 June, we sent a revised version by 2 July and the paper was accepted 7 July.

■ **Did you expect this discovery to appeal so much to the general public?**
I thought so, yes: the resemblance of C_{60} to a soccer ball and the fact that scientists had been searching for this species for 25 years would resonate with the general public, and so it was a great outreach opportunity that I passionately pursued in collaboration with the Spitzer media team at the Jet Propulsion Laboratory (JPL). While preparing a press release, I had an idea for an artist's illustration based on the incredible free kicks of the Brazilian soccer player Roberto Carlos. I had stumbled upon an article describing some of the physics behind the Magnus effect that so nicely curves his free kicks. The connection with C_{60} was clear. So I produced a quick sketch of a planetary nebula with a series of C_{60} renderings that followed a Roberto Carlos-like trajectory coming from behind the object to the foreground.
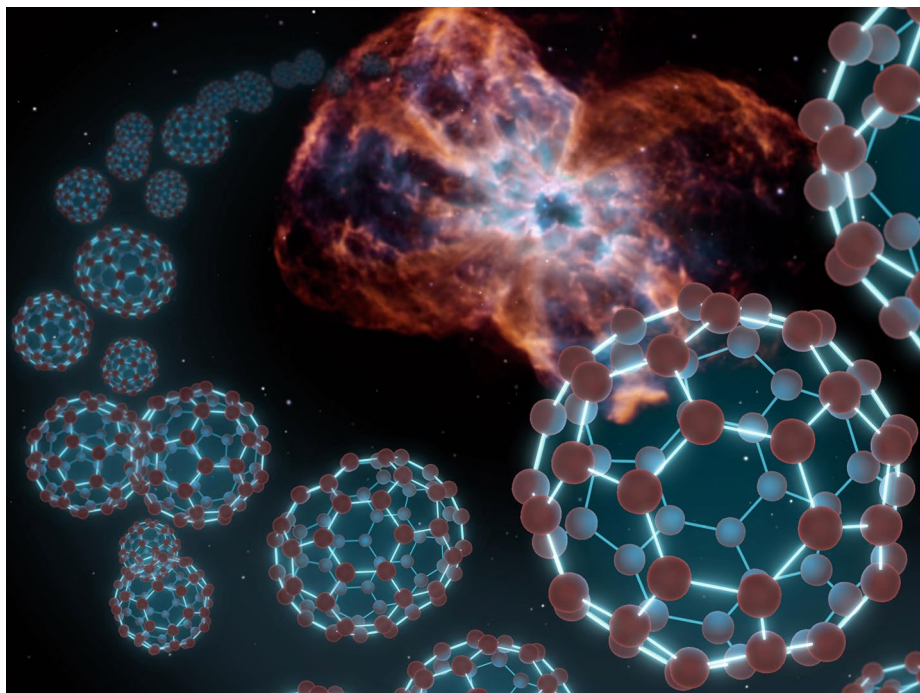
Credit: NASA, ESA and K. Noll (STScI)

We also asked Sir Harry Kroto to comment on our work for the press release. I suspected he would be excited to hear about this detection — and I was not wrong about that. It was a week of hard work to get everything right, but the team at JPL was very professional and an enormous pleasure to work with. In the meantime, we had heard from *Science* that our paper would be released online as a rapid-release paper, meaning it would appear online already on Thursday 22 July.

With the press release and the graphics done and submitted to NASA HQ, we could in principle sit back and relax. But I had another idea. If this story was going to be on NASA's website, shouldn't we aim for the state of the art? At that time, animations on web sites were not very common, and especially so in the context of science. If we could animate the C_{60} vibrational modes that we had detected, that would be a great way to show people how this part of the science works. Robert Hurt and Tim Pyle on JPL's media team were excited about this as well, and they animated the vibrations. In addition, they created a morph from a rotating soccer ball on a green pitch to a visualization of a rotating C_{60} molecule in space. It was brilliant! In the meantime, Jeff Renaud from Western Media Relations recorded a video interview in my office. It took many hours on Tuesday evening (20 July) to upload that footage, and, incredibly, by Thursday morning, JPL's

team had combined the interview with the animations to create a short video clip about our results in time for the official publication, and that video became quite popular!

■ **And how about the media response?**
While I thought that we had an appealing story to the public, I was not quite sure whether it would be picked up by news and media outlets. You just never know, and it depends on the other news of the day. I definitely hoped on some recognition — that would probably help my case for getting tenure. Even in my wildest dreams, I could not have predicted the attention that would follow. On Thursday at 2:00 pm, NASA's main web site showed our artist's illustration with the title 'NASA telescope finds elusive buckyballs in space for first time', and we also featured on such well-known outlets as the BBC, National Geographic, the Discovery Channel and a large slew of others — but mostly in North America. A colleague talked to somebody from a Belgian press agency, and on hearing this discovery was made by a Belgian astronomer they issued their own press release — including my name, age and origin from Belgium. That press release blew up all over Europe and well beyond. The Belgian radio news wanted to have an interview with me, and given the time difference, this meant that I needed to be up and on the phone before 5:00 am on Friday. It was the first (and probably the last)

ever radio interview I did in my pyjamas. A clip of the interview was played on the 1:00 pm news in Belgium, and this was the point where my parents also realized that this discovery was a big thing, as my mom heard me on the national news while she was in the car. There were websites and news articles about buckyballs in space all over the world! The day after, a newspaper in Belgium turned our discovery into a full-page ad for a beer that was associated with the national soccer league. I was perhaps prouder of the success in public outreach than of the identification itself! Connecting to people has always been important to me, and this worked out well!

■ How was the discovery received by your colleagues and peers?

The euphoria over the success in the media would not last long, and would soon be replaced by stress, anxiety and doubts in what became a competitive research field. While working on our manuscript and preparing for our media campaign, we realized that we needed to work on our follow-up. We had found C_{60} bands also in IC 418, a similarly low-excitation object, and in several more planetary nebulae in the Magellanic Clouds. We decided to focus on one of the Magellanic Cloud detections, with Jero as the lead on that paper. Over the summer, we made good progress, and by mid-September, we had a letter for the *Astrophysical Journal* more or less ready — all that was left was a few minor edits to make the paper a bit shorter. However, the day we organized a Skype call to finalize the manuscript, there was an article on astro-ph (on arXiv) that claimed the detection of fullerenes in the Small Magellanic Cloud — in precisely the source that we had written a manuscript about[30]. Very little remained in our paper to warrant publication. Putting all the work in a paper to then being scooped like that is an awful feeling, and, unfortunately, it wasn't the first time this happened to me, and it wouldn't be the last time either.

The tone of that paper sounded quite harsh to our ears, and focused on the fact that — according to the authors — we had incorrectly identified Tc 1 as an H-poor environment and thus that our suggestion about efficient formation in H-poor environments was completely wrong. While I certainly did not enjoy reading this paper, I did not object to the authors pointing out the flaws in our paper. That is how science works, and moreover, in my mind, there was still lots of room for subtleties that could reconcile the presence of H in the star and the nebula with a H-poor C_{60} formation scenario.

The García-Hernández et al.[30] paper was not the first C_{60} paper that appeared after our *Science* paper. Earlier in September, Kris Sellgren had posted her now accepted paper on astro-ph, discussing C_{60} in the reflection nebulae NGC 7023 and NGC 2023[31]. While the contamination by PAHs made a secure identification of C_{60} in NGC 7023 perhaps more challenging, it had of course always been there as these authors had suspected earlier on[20]. They had essentially done everything right: they had listed C_{60} as one of the potential carriers, predicted that if true, they should find the remaining bands at shorter wavelengths, and with additional Spitzer data, they did indeed find those short-wavelength bands. We just happened to stumble upon a cleaner source that allowed a more convincing identification. In the Sellgren et al.[31] paper too, the authors point out a problem in our *Science* paper: the excitation mechanism. They argue that in circumstellar and interstellar environments, large aromatic molecules cannot be in thermal equilibrium, and therefore they should emit through fluorescence rather than through thermal emission. They carried out model calculations for such a fluorescence model, and concluded that such a model can indeed explain the observed C_{60} emission in their objects. I was surprised to read this, because we had started out with a fluorescence model, and essentially had to abandon it because it didn't work well. On closer inspection of their paper, however, I concluded that their fluorescence model didn't work for all their detections. In particular for NGC 2023, their models greatly over-predict the observed emission at 7.0 μm, unless one adopts unrealistic model parameters.

And so, within a few weeks of publication of our *Science* paper, the tone was set for what would turn out to be a competitive decade.

■ What have been some of the key recent developments in our understanding of cosmic buckyballs?

Finding C_{60} in space rallied up laboratory researchers as well. Since Foing and Ehrenfreund[5], several laboratory groups had aimed to measure the gas-phase electronic spectrum of cold C_{60}^+ but the problem turned out to be much harder than one would think. In 2015, John Maier's group in Basel came up with a solution. They built a 22-pole ion trap that could confine C_{60}^+ molecules, and then cooled them with cold He. Under these conditions, the researchers could synthesize C_{60}^+–He complexes. With a tunable laser, they then fired photons at these complexes. At resonance frequencies, the excitation would result in the loss of

the He atom, which they measured with a time of flight spectrometer. The result is technically the spectrum of the C_{60}^+–He complex, but the effect of the He atom is small, and has in the meantime been well characterized. Their measurements showed a good comparison with the observational data, and furthermore revealed two weaker bands that were subsequently detected in astronomical spectra as well[32]. This was a major result in my mind — the first identification of DIBs! However, the DIB field can also be competitive at times, and this was the case here as well. Very quickly, doubt was cast over this identification[33] and a lively debate ensued in the literature and at conferences and other professional meetings. I tried to put things in perspective: sure, there were some details that warranted a closer look (the precise wavelengths and relative band strengths in the lab, the method for performing a telluric correction on astronomical data), but all in all I found this a much stronger identification than the one from the IR bands confirming the neutral C_{60}. Of course, in science, some competition is good, and after several years, a combination of independent laboratory measurements[34,35], ground-based observations[36–38], spectra unaffected by the Earth's atmosphere obtained with the Hubble Space Telescope[39,40] and theoretical calculations about the electronic structure of C_{60}^+ (ref. [41]) have confirmed beyond any reasonable doubt that these DIBs are indeed due to C_{60}^+.

Owing to the identification of the C_{60}^+–DIBs and the diverse IR detections of neutral C_{60}, the past ten years have then led to the realization that fullerenes are indeed widespread and abundant in space, in spite of the fact that they are perhaps not frequently seen. Indeed, fullerenes have been detected in a wide variety of astrophysical sources. The majority of detections are in various types of evolved stars (PNe, but also post-AGB stars, proto-PNe, R Cor Bor stars and others[16,30,42–50]), showing that evolved stars are the birthplace of fullerenes. But fullerenes have also been found in very different environments, corresponding to other phases of the cosmic recycling process. Neutral C_{60} has been detected in the diffuse interstellar medium[51], and of course numerous interstellar sightlines contain the C_{60}^+ DIBs. Fullerenes are also incorporated in the material from which stars and planets form, and indeed, they show up in young stellar objects and protoplanetary disks[52], as well as in the photon-dominated regions surrounding massive hot stars (see, for example, refs. [31,53–55]). In some of these objects, we can determine the fullerene abundance, and with some caveats, it

appears that fullerenes could be representing perhaps of the order of 1% of the cosmic carbon in the interstellar medium[56], which is a lot for a single species! This widespread nature and high abundance of fullerenes and their high stability is at odds with the fact that fullerenes are not frequently seen. In a study of PNe, for instance, it was found that less than 3% of the PNe showed the C_{60} bands[44]. The PNe that show the C_{60} bands are all young objects, and as these objects evolve, we would expect the fullerenes to survive; yet there is not a single more mature PN that contains C_{60}. It is possible that C_{60} itself evolves into other species that we have not yet characterized or that are much harder to detect (such as, for example, $C_{60}H^+$; see ref. [57]). Laboratory experiments have also shown that fullerenes readily react with other carbonaceous materials to form carbonaceous dust grains[58]. The picture that is emerging is thus that the fullerenes we see are only the tip of the iceberg so to speak — there must be much more fullerenic material than we currently recognize as such.

In the past ten years, the research community has also put a great effort into understanding the physical processes — at the molecular level — that lead to the formation of fullerenes, their evolution and destruction, and their excitation. A very cool result in this context showed that in principle, PAHs can be turned into fullerenes. Based on astronomical observations, Berné and Tielens[59] suggested that ultraviolet photons could strip large PAHs of their H atoms, and once fully dehydrogenated, the bare carbon clusters would turn into cages that then shrink to C_{60}. To test this idea, researchers in the Sackler laboratory at the Leiden Observatory built a dedicated experimental setup that indeed confirmed this idea[60]. In the process, they realized that this offered researchers a technique to study graphene flakes of arbitrary size! Whether this mechanism can work efficiently in space however is not quite clear.

In spite of all observational, theoretical and experimental efforts from the past ten years, however, it is clear that our understanding of these processes is far from complete. We do not yet have a consistent model that can explain why we see fullerenes in some objects but not in others that otherwise look similar. For the sources where we know the location of the C_{60} emission (see, for example, ref. [61]), we do not have a model that can explain why the fullerenes are emitting precisely there. And finally, we cannot yet reproduce the details of the observed IR C_{60} emission bands nor the absorption profiles of the C_{60}^+ DIBs or their relative band strengths either.

One may be forgiven for thinking that this is not a big deal — after all, we are only talking about a single species. However, our ignorance here is not about the species, but about the physical processes that determine their appearance in astrophysical environments. The very same physical processes will affect the entire population of aromatic carbonaceous molecules and dust grains, including PAHs that are much more abundant in space and play key roles in large-scale processes such as star formation and galactic evolution[62]. A good understanding of these molecular processes thus has ramifications for many different research fields in astrophysics. Arguably the most important development in the past ten years is that cosmic fullerenes have shown us that there is much about the formation, evolution, excitation and destruction of carbonaceous molecules and dust grains that we do not fully understand. Perhaps somewhat paradoxically, they may well be the key to resolve these same issues since C_{60}, C_{60}^+ and C_{70} are the only identified large aromatics and thus the only real species that we can use to improve and test our understanding.

■ What is next for this new branch of astrochemistry?

As mentioned above, there are most probably a lot more fullerene compounds in space than those we can currently detect or recognize, and I expect that in the next years, there will be studies about other forms of fullerenes or related materials (for example, nanotubes) that could exist in these environments (some work has already been done in that context — see, for example, refs. [57,63]). At the same time, a large effort will go into improving our understanding of the physical processes that influence the formation, excitation and evolution of fullerenes and the chemical pathways that are the result. This will come first and foremost from developing a detailed, spatially resolved quantitative characterization of the environments where we see the fullerenes. The upcoming James Webb Space Telescope will play a big role in this part of the exercise with its unprecedented sensitivity and spatial resolution. Once the physical conditions in these environments are mapped, we can use laboratory measurements to evaluate which physical processes and chemical reactions will occur depending on the local conditions, and build a comprehensive model that predicts where we should see fullerenes and in what form. Comparing those predictions to observations will then reveal where the shortcomings are in our understanding. In this process, we

will need to evaluate several processes at the molecular level in detail as well. For example, isomerization may be a crucial process that can lead to different pathways depending on the available timescales. We need to do this exercise in the different environments where we see the fullerenes, since different environments may represent different formation routes. For instance, it is conceivable that interstellar dust grains contain fullerenic material created in evolved star environments, and that all that is needed in reflection nebulae is to expose these fullerenes to make them visible. That is quite different from the evolved star environments where at least at the onset, we start from a hot atomic gas and need to build up molecules and dust in a bottom-up way. The next decade thus looks at least as exciting and innovative as the previous decade!

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