Cosmic Fullerenes

Orsay, Sep 19–21, 2018

Scientific Program & Abstract Book

ISMO
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Physique : Atomes Lumière Matière

Scientific Program

Wednesday, Sep 19

9:30–10:00		Welcome; Coffee & Tea
10:30–11:30	**Jan Cami**	*Astronomical Observations of Cosmic Fullerenes*
11:30–12:00	**Jacek Krełowski**	*Abundances of simple carbon molecules and strengths of suspected C_{60} cation features*
12:00–12:30	**Julianna Palotas**	*Infrared spectroscopy of protonated fullerenes*
12:30–14:00		**Lunch Break**
14:00–14:45	**Michael Gatchell**	*Probing the influence of He on the spectroscopy of C_{60} and corannulene ions*
14:45–15:30	**Dieter Gerlich**	*Hydrocarbons and fullerenes in cryogenic ion traps*
15:30–16:00		**Coffee Break**
16:00–16:30	**Dmitry Strelnikov**	*Matrix isolation spectroscopy of strongly absorbing fullerene fragments.*
16:30–17:00	**Gazinur Galazutdinov**	*Near-infrared diffuse bands attributed to C_{60}^+ vs. other interstellar features*
17:00–17:30	**Christine Joblin**	*Testing the formation of cosmic large carbonaceous molecules: the Nanocosmos project*
17:30–19:00		**Lab Visit, Poster Session & Welcome Cocktail**
20:00–		**Dinner at restaurant (informal)**

Thursday, Sep 20

9:00–10:00	**Patrick Fowler**	TBD
10:00–10:30	**Cyril Falvo**	*Simulating the structural diversity of astrophysical carbon clusters C_{24}, C_{42}, and C_{60}.*
10:30–11:00		**Coffee Break**

11:00–11:30	**Fernando Martin**	*The unusual stability of charged, endohedral and exohedral fullerenes*
11:30–12:00	**Clément Dubosq**	*Spectroscopic characterization of amorphous carbonaceous clusters*
12:00–12:30	**Alessandra Candian**	*Exploring the astronomical cage world: Stability and vibrational spectra of* C_{44}*,* C_{50}*,* C_{56}*,* C_{62}*,* C_{64}*,* C_{66} *and* C_{68} *isomers*
12:30–14:00		**Lunch Break**
14:00–15:00	**Chris Ewels**	*Mechanisms of Fullerene growth*
15:00–15:30	**Denis Sabirov**	*Theoretical studies of fullerenes in the aspect of their interstellar chemistry*
15:30–16:00		**Coffee Break**
16:00–16:30	**Franco Cataldo**	*Fullerenes, fulleranes and other derivatives of astrochemical interest*
16:30–18:00		**Discussion & Poster Session**
19:30–		**Conference Dinner @"Le Gramophone"**

Friday, Sep 21

9:00–10:00	**Henning Zettergren**	*Dynamics of fullerenes*
10:00–10:30	**Nora Berrah**	*Time-Resolved Photoionization and Fragmentation Dynamics of Fullerenes Studied with X-Ray Free Electron Laser*
10:30–11:00		**Coffee Break**
11:00–11:30	**Marin Chabot**	*PAH destruction by heavy cosmic rays carbon chains, production rates*
11:30–12:00	**Emmanuel Dartois**	*Experimental simulation of cosmic ray ion irradiations of interstellar carbonaceous dust analogues : release of small to large molecules*
12:00–12:30	**Olivier Berné**	*Astrophysical studies of the chemical evolution of carbonaceous species and fullerenes in space*
12:30–14:00		**Lunch Break**
14:00–16:00		**Discussion & Wrap-Up**

Abstracts: Oral Presentations

Astronomical Observations of Cosmic Fullerenes

Jan Cami[1,2]

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In recent years, fullerenes have been detected in a variety of astrophysical environments, from the circumstellar carbon-rich surroundings of evolved stars to diffuse clouds, interstellar reflection nebulae and young stellar objects. Most detections involve emission through the infrared vibrational transitions of neutral C_{60}, or absorption due to the cation C_{60}^{+} that is responsible for several diffuse interstellar bands (DIBs).

In this review talk, I will give an overview of the environments where we have detected fullerenes. I will summarize the key observational properties as well as what we have learned from these detections. More importantly, I will highlight some of the remaining issues we face in understanding these observations and coming up with a coherent picture for the life cycle of fullerenes and related carbonaceous species in space.

Abundances of simple carbon molecules and strengths of suspected C_{60} cation features

Jacek Krełowski
Center for Astronomy, Nicolaus Copernicus University, Toruń, Poland

Two evident interstellar spectral features, near 9577 and 9633 Å are believed to be carried by the C_{60} cation. It seems reasonable that abundances of complex carbon molecules should be related in a way to the simplest ones. I checked thus whether the strengths (abundances) of the C_2 and C_3 known interstellar molecules do correlate with the suspected C_{60} cation features. The result is negative: the 9577 feature can be strong when C_2 and C_3 bands are barely seen and weak when the latter are strong. While it may not be considered as an evident proof that the infrared bands are not carried by the C_{60} cation, it should be taken into account while modelling the interstellar clouds' chemistry.

Infrared spectroscopy of protonated fullerenes

Julianna Palotas, G. Berden, J. Martens and J. Oomens
FELIX Laboratory, Faculty of Science, Radboud University, Nijmegen, the Netherlands

We investigate protonated fullerenes in an ion trap mass spectrometer with IR multiple photon dissociation (IRMPD) spectroscopy using the wide wavelength tunability and high pulse energies of the FELIX free electron laser. For ionization, we use an atmospheric pressure chemical ionization (APCI) source which is efficient for less polar molecules. With this measurement, we present the first gaseous IR spectra of $C_{60}H^+$ and $C_{70}H^+$. When one proton attaches to the highly symmetrical neutral fullerene, their symmetry is significantly reduced causing many bands that were inactive in the unprotonated system to become IR-active, resulting in a rich vibrational spectrum. The spectra of the protonated species are therefore entirely different in appearance from those of the neutral C_{60} and C_{70}. Experimental data are supported by results from quantum-chemical calculations at the DFT level.

This work is supported by the European MCSA ITN network EUROPAH and the Dutch Astrochemistry Network (DAN-II).

Probing the influence of He on the spectroscopy of C_{60} and corannulene ions

Michael Gatchell, Paul Martini, Alexander Kaiser and Paul Scheier

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Action spectroscopy using He atoms as messengers has proven itself to be a powerful tool in obtaining the gas phase absorption spectra of complex molecular ions. This was demonstrated particularly well with the identification of C_{60}^+ as the carrier of several diffuse interstellar bands (DIBs) in 2015 [1].

In Innsbruck we have been studying C_{60}^+ and corannulene ($C_{20}H_{10}^+$) ions produced in superfluid He nanodroplets. By ionizing neutral droplets doped with these molecules we obtain the fullerene and PAH ions decorated with anything from a single He atom to many tens of atoms. Using mass spectrometric and action spectroscopy techniques we are able to deduce the size-dependent influence of the He solvation on the decorated ions, such as the formation of solvation layers and spectral shifts. With this technique we have shown that the first 32 He atoms around a C_{60}^+ induce a redshift that increases linearly with the number of He atoms [2], in good agreement with the results by Campbell et al. [3].

At the meeting I will present a study of how line profiles of C_{60}^+ systematically vary as a function of the number of solvating He atoms [4]. I will also present results from recent spectroscopic measurements on corannulene cations, which show much richer variation in the redshifts induced by surrounding He atoms compared to C_{60}^+ [5], and discuss the implications this has on studies of molecules other than the highly symmetric fullerenes.

This work is supported by the Austrian Science Fund FWF (projects P26635 and P31149), and the Swedish Research Council (Contract No. 2016-06625).

References

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Hydrocarbons and fullerenes in cryogenic ion traps

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In the last 25 years, He buffer gas cooling of trapped ions became a very efficient method for studying their structure and reactivity. Various applications in ion spectroscopy became possible by in situ synthesis of He–M^+ complexes from mass selected M^+ ions. In the introduction of my talk, I will briefly summarize the long way from the first idea to use He tagging to its routine use in analytical chemistry. The method will be illustrated presenting spectra of various ions. An important technical aspect is the use of a linear RF quadrupole trap instead of a higher order multipole. Photo-dissociation of CH^+ will demonstrate advantages and limitations.

In the last years, special attention has been paid to NIR spectra of C_{60}^+ measured in the Basel ion trap. These results have been complemented by IR-spectra of HeC_{60}^{n+} (n=1–3) ions measured between 1100 and 1600 cm^{-1} using the instrument ISORI (Jana Roithova, now Radboud University). The broad lines, caused by fast internal conversion, rule out high-resolution measurements. Reproducible sidebands with distances between 5 and 20 cm^{-1} enrich the spectra. Comparison of the HeC_{60}^+ spectrum with that of $N_2C_{60}^+$ reveals shifts up to 6 cm^{-1} while the IR spectra of HeC_{60}^{3+} and $He_{32}C_{60}^{3+}$ are very similar.

A subject of current interest is the influence of the tags on the position and the shape of the lines. An alternative is to use the method of Laser Induced Inhibition of Complex Growth for getting spectra of the naked ions. All this requires to understand both the kinetics of He-attachment and the structure of the (meta-)stable complexes. A related result is the decay of thermalized $He_{32}C_{60}^{3+}$ complexes after excitation with a single 1329 cm^{-1} photon.

Matrix isolation spectroscopy of strongly absorbing fullerene fragments.

Dmitry Strelnikov and Manfred M. Kappes
Karlsruhe Institue of Technology, Germany

Mass-selected cationic fullerene fragments C_n^+ ($n < 25$) produced in an electron impact ionization source have been deposited in a Ne matrix. The deposited C_n^+ species along with C_n and C_n^- have been studied by optical absorption spectroscopy from UV to IR. At least part of these fragments are linear carbon chains. Astrophysical relevance of our new observations is discussed.

Near-infrared diffuse bands attributed to C_{60}^{+} vs. other interstellar features

Gazinur Galazutdinov

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Measurements of diffuse interstellar bands attributed to C_{60}^{+} is a challenge. Indeed, there are at least two issues that need to be addressed: (I) the wavelength range of interest is severely polluted by strong water-vapour lines of the telluric origin; (II) some diffuse bands are blended with stellar lines in spectra of hot stars affected by non-LTE effects; We present the most recent results concerning the relations between interstellar features and the intensity of the near-infrared diffuse bands, measured with all the precautions mentioned above.

Testing the formation of cosmic large carbonaceous molecules: the Nanocosmos project

Christine Joblin, J.A. Martin Gago, J. Cernicharo and the Nanocosmos[1] team
IRAP, Univ. Toulouse, CNRS / ICMM, CSIC, Madrid / IFF, CSIC, Madrid

The Nanocosmos ERC synergy project aims at better understanding the formation of cosmic dust in particular in the environments of evolved stars. To address this question, the project carries a strong laboratory astrophysics activity involving several experimental setups, which bring complementary data.

In particular, the Stardust machine [1], has been specifically built to simulate dust formation in the atmosphere of evolved stars. Cold plasma reactors and a laser vaporisation source are also used to study the chemical paths that can lead to the growth of carbonaceous molecules including fullerenes and polycyclic aromatic hydrocarbons, as well as the formation of carbon dust particles. In addition of standard analytical tools, diagnosis setups have been developed to probe the chemistry, in particular the gas cell that makes use of broadband rotational spectroscopy [2] and the molecular analyser AROMA [3]. The on-going experiments tackle the influence of the carbon/hydrocarbon precursors on the chemistry, as well as the role of oxygen, hydrogen and metals. The objective of this talk is to describe the different setups and the methodology that is used to address this topic. First results will be shown.

References

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[1] `https://nanocosmos.iff.csic.es/`

Fullerenes: simple chemical models and systematics

Patrick Fowler
University of Sheffield, UK

Some surprisingly simple models based on graph theory are useful for understanding general features of the fullerene family, such as isomer counts, geometric and electronic structure, spectral signatures, growth and isomerisation. This talk will survey the types of information available from these models and suggest some extensions that may be relevant to characterisation of fullerenes in space.

Simulating the structural diversity of astrophysical carbon clusters C_{24}, C_{42}, and C_{60}.

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[2]*Laboratoire Interdisciplinaire de Physique, Université Grenoble Alpes*

From a few atoms to bulk matter, carbon clusters show a significant ability to hybridize in sp, sp^2 or sp^3 chemical bonds, reflecting at finite size the wide allotropy of bulk carbon matter. In the interstellar medium (ISM), only the smallest molecules C_2, C_3, C_5 and the fullerenes C_{60} and C_{70} have been observed so far [1,2]. The detection of C_{60} in space was made possible from its peculiar spectral features originating from the high (icosahedral) symmetry that gives rise to only four infrared active bands. In order to obtain a better understanding of the formation mechanism of cosmic fullerenes and to identify other possible forms of carbon clusters in the ISM, it is essential to characterize the possible structural diversity of carbon clusters and map these structures onto their spectroscopic signature.

During this presentation, I will present atomistic simulations of the structural diversity of the carbon clusters C_{24}, C_{42}, and C_{60}. A few realistic potentials of interaction are available for carbon, which correctly account for bond breaking and formation and the various hybridization environments displayed by carbon. Here we have performed simulations using the reactive empirical bond-order potential (REBO) from Brenner [3] and the adaptive intermolecular reactive empirical bond-order potential (AIREBO) of Stuart and coworkers [4]. In order to obtain a representative database of structures we have performed Replica Exchange Molecular Dynamics (REMD) simulations over a wide range of temperatures followed by quenching to identify local minima. All the minima were sorted in energy and analyzed using various order parameters to monitor the evolution of their structural and chemical properties. The structural diversity measured by the fluctuations in these various indicators is found to increase significantly with energy, the number of carbon rings, especially 6-membered, exhibiting a monotonic decrease in favor of low-coordinated chains and branched structures.

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The unusual stability of charged, endohedral and exohedral fullerenes

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Fullerene anions and cations, as well as endohedral and exohedral fullerenes, have unique structural, electronic, and chemical properties that make them substantially different from pristine neutral fullerenes. In fast collisions with ions, electrons and photons or in arc-discharge experiments where they are produced, the theoretical prediction of the most stable structures is a very challenging task due to the large number of isomeric forms accessible in such hot environments (e.g., more than 20 billion isomers for $C_{60}X_8$). Here we present a simple model [1-3], exclusively based on topological arguments, that allows one to predict the relative stability of these fullerene species without the need for electronic structure calculations or geometry optimizations. We show that the subtle interplay between π delocalization, cage strain, and steric hindrance is responsible for, e.g., (i) the formation of non IPR (isolated pentagon rule) cage structures in contrast with their pristine fullerene counterparts, (ii) the appearance of more pentagon-pentagon adjacencies than predicted by the PAPR (pentagon- adjacency penalty rule), and (iii) the variations in fullerene cage stability with the progressive addition of chemical species. The predicted most stable structures are in good agreement with those found in experiments. The model has been recently implemented in the FullFun code for a widespread use by the fullerene community [4,5].

Molecular Dynamics (MD) simulations have also been used to understand the interaction of charged fullerenes with He atoms in a He nanodroplet environment. Combination of these results with a simple model that describes the polarizability induced by the He atoms on the fullerene cage allows us to interpret the absorption line shifts as a function of the number of He atoms observed in recent experiments [6].

References

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Spectroscopic characterization of amorphous carbonaceous clusters

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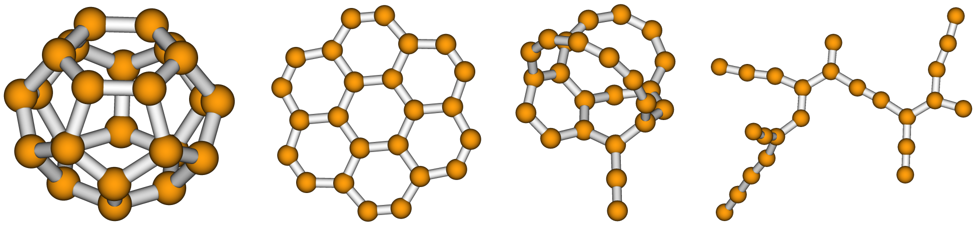
The interstellar medium (ISM) is a carbon-rich medium with an active carbon chemistry. Given our currents knowledge on interstellar matter, carbon can be found under different forms from polycyclic aromatic hydrocarbons (PAHs) to carbonaceous grains, that can be characterized by their spectroscopic signatures. In particular, a set of mid-infrared emission bands, the so-called AIBs (for Aromatic Infrared Bands) has been assigned to a PAH population [1]. However, despite a longstanding synergy between observations, experiments and theoretical studies, a specific carrier for these AIBs has not been clearly identified. In particular the presence of polycyclic aromatic aliphatic mixed hydrocarbons (PAAMHs) or amorphous carbon grains has not been ruled out.

In the context of the PACHYNO [2] project (Probing the diversity of Astrophysically relevant Carbon and Hydrogen NaNO particles), in collaboration with ISMO and LiPHY, we determine the characteristics of amorphous carbonaceous and hydrocarbonaceous structures. We perform our analysis using the Self-Consistent Charge Density Functional Tight Binding (SCC-DFTB) electronic structure method, which can be viewed as an approximate DFT scheme. The goal of the project is to establish correlation between structural and spectroscopic features, and to consider their possible contributions to the AIBs.

Our contribution to this project consists in extensive SCC-DFTB calculations to determine the minimal energy structures and to simulate the IR absorption spectra of a diversity of carbon and hydrogenated carbon clusters structures of sizes ranging from 24 to 60 carbon atoms. We used as starting point the structures obtained by Falvo et al. with their parametrized REBO potential. In this presentation, I will show the evolution of the harmonic absorption infrared spectra as a function of energy. Finally, I will compare our computed spectra to astronomical spectra.



0.0 eV | +0.3 eV | +9.0 eV | +19.1 eV

Figure 1: Examples of relaxed isomer of C_{24} optimized at the SCC-DFTB level.

References

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Exploring the astronomical cage world: Stability and vibrational spectra of C_{44}, C_{50}, C_{56}, C_{62}, C_{64}, C_{66} and C_{68} isomers

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The discovery of the buckminsterfullerene molecule (C_{60})[1] in space has opened a new fascinating window of the Carbonaceous Universe, that will be explored in detail thanks to the incredible spatial and spectral resolution of the James Webb Space Telescope (JWST), to be launched in 2021. To be able to fully exploit the JWST data, dedicated experimental and theoretical studies are needed to put the properties of fullerene and cage like carbonaceous molecules into astrophysical perspective.

In this study, we use Density Functional Theory (B3LYP/6-31G*) to investigate two sets of cage C_n isomers: 1) the ones corresponding to the so-called magic numbers [2], with n=44, 50 and 56; 2) the ones between C_{60} and C_{70}, (n=62, 64, 66 and 68). The isomers were chosen to have lower number of isolate pentagons within their structure (Isolate Pentagon Rule [3]). For each n, we evaluated the thermodynamical and kinetic stability for both neutral and singly charged species, comparing with previous results. Moreover we calculated the vibrational spectra of the different isomers and compared them to astronomical spectra of 3 planetary nebulae (1 in the Milky Way and 2 in the Magellanic Clouds) known to display C_{60} vibrational bands.

Our findings suggest that the results of laboratory studies on the stability of charged cages can be applied to neutral species as well, and C_{44}, C_{50} and C_{56} can be considered magic numbers also for neutral cages. Moreover, two almost isoenergetic C_{64} isomers show higher C_2 dissociation energies and HOMO-LUMO band gaps than their $n+2$ and $n-2$ neighbors, suggesting this also can be considered a magic number. The calculated vibrational spectra show that individual isomers can be identified in astronomical spectra only if they are abundant and their structure is highly symmetric, with C_{50} being a promising candidate. Nevertheless, populations of fullerenes can give rise to broad, plateau-like features, are detected in astronomical spectra in conjunction with C_{60} [4].

References

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Mechanisms of Fullerene growth

Chris Ewels

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Understanding the growth of fullerene molecules is a complex area, since conditions required for growth such as high temperature and gas phase carbon are not easily accessible for experimental characterisation. As a result there have been many competing proposed mechanisms, often relying heavily on computational modelling. In this review talk I will briefly introduce fullerenes, common synthesis methods, and then discuss key aspects of the thermodynamics and kinetics of their growth, the various growth models proposed in the literature, and key atomic-scale processes in their growth and structural transformation. Particular emphasis will be made on available computational modelling studies.

Theoretical studies of fullerenes in the aspect of their interstellar chemistry

Denis Sh. Sabirov

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Fullerenes are intriguing molecular species detected in interstellar and circumstellar environments. They have the largest molecular size among the other interstellar molecules and there is a gap between the sizes of C_{60}/C_{70} and typical interstellar organic molecules (having up to 13 atoms). Currently, diverse approaches try to rationalize their formation mechanism under natural and laboratory conditions [1–3].

The present report summarizes our theoretical studies on fullerenes and their compounds and provides a comparison with the previous relevant works. We briefly discuss Irle-Morokuma molecular mechanics simulation on the self-assembly of the giant fullerenes (C_{300}) from the C_2 molecules [4]. Though this work is an undoubted advance in the field, it is not able to explain the predominant yields of C_{60} and C_{70} [5]. To reconcile theory and observations, we have deeply analyzed thermodynamic and structural parameters of more than 2000 fullerenes C_n [6, 7]. Thus, the DFT-based phenomenological model of the dependence of the standard formation enthalpy on the size of the selected fullerenes shows that C_{60}, C_{70}, C_{180}, and C_{1500} hold a prominent position among the hypothetical and experimentally discovered fullerenes as follows from the statistical analysis of the regression equations $\Delta H_f^\circ = f(n)$ [6].

We have used information entropy h, a structural descriptor quantifying the complexity of molecular structure (within this approach, more symmetric molecules are less complex and having lower h values), to sort 2079 fullerene structures from *An Atlas of Fullerenes* by P. W. Fowler and D. E. Manolopoulos. We have found that the h values of only 14 fullerenes ($< 1\%$ of the studied structures) lie between the values of C_{60} and C_{70}, the two most abundant fullerenes. Interestingly, buckminsterfullerene is the only fullerene with zero information entropy, i.e. an exclusive compound of the fullerene family [7]. Furthermore, the experimental ratios of the yields of $He@C_{60/70}$ and $He_2@C_{60/70}$ (and related endofullerenes $Ne_n@C_{70}$, $(H_2)_n@C_{70}$, and $NHe@C_{60/70}$) may be qualitatively described in terms of the information entropy approach using the respective changes in information entropy upon the formation of singly and doubly filled endofullerenes [8]. This approach stresses the probabilistic nature of the formation processes of fullerenes and endofullerenes.

Another unusual and noteworthy result deals with the direct correlation between the volume and stability of the isomeric fullerene molecules [9]. We have found here that larger C_{84} cages reveal higher stability. Commonly, inner space of the fullerene cages is considered as a factor of their instability. We have further discovered that larger volume allows achieving more spherical shape of the fullerene molecules. This proposition has been confirmed with numerical estimates of sphericity and topological roundness of the C_{84} isomers.

Polarizability plays an important role in physical chemistry of fullerenes [10]. This facilely computable molecular quantity may be relevant to the interaction of the interstellar molecules with diverse radiation fields. We have analyzed possible detectability of fullerene hydrides

$C_{60}H_x$ (x = 2–36) under interstellar conditions using the DFT estimates of their polarizability [11]. Previously, minimum-energy principle (MEP) was successfully applied to understanding of the ratios of interstellar isomeric species [12, 13]. For this purpose, we additionally recommend the minimum-polarizability principle, MPP (less polarizable isomer should be more abundant). MEP and MPP generally provide the consistent results and MPP works in the case when MEP fails. Our theoretical estimates of polarizability of the isomeric compounds are compared with available observational data on their interstellar abundances [11].

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Fullerenes, fulleranes and other derivatives of astrochemical interest

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C_{60} fullerene was expected to be present in space since the time of its discovery [1], but only in 2010 it was detected through its infrared spectral signature in a young planetary nebula [2]. Later, C_{60} was found in other astrophysical environments including the interstellar medium [3,4]. Recently, C_{60} as radical cation was recognized as contributor to the DIBs in the gas phase [5]. The stability of C_{60} toward high energy radiation was demonstrated suggesting an high permanence of this molecule in the harsh space conditions [6]. More recently using neutrons bombardment of C_{60} and C_{70} fullerenes it was found the former more stable than the latter [7]. In laboratory the infrared spectra of C60 and C_{70} fullerenes were recorded in a wide range of temperatures [8]. The position of certain infrared bands of fullerenes are sensitive to temperature and undergo a shift as function of temperature [8]. These properties are useful for searching and recognizing fullerenes in space as well as the determination of the absorption cross section of each absorption band which is a useful property for the determination of column density in space [8]. When dissolved in fuming sulfuric acid, C_{60} and C_{70} are ionized to radical cations [9,10]. Because of the strong high dielectric constant ($\epsilon \approx 110$) of the solution medium and its high acidity the fullerene radical cation electronic transitions undergo a solvatochromic shift, and were found blue shifted and broadened [8,9] with respect to the radical cation band position in the gas phase [4].

C_{60} and C_{70} fullerenes are readily reactive with atomic hydrogen yielding fulleranes the hydrogenated fullerenes [11]. The fullerenes are so avid of hydrogen that the hydrogenation in the laboratory conditions leads directly to $C_{60}H_{18}$ and $C_{60}H_{36}$ [11,12]. Thus, it is completely reasonable to think that hydrogenated fullerenes may be present in space [11]. Indeed, a tentative detection of hydrogenated fullerenes was made by Kwok et al in the PPNe IRAS 01005+7910 [13]. Other fulleranes searches were made in fullerene-containing planetary nebulae [14]. Hydrogenated fullerenes are releasing molecular hydrogen when irradiated with UV light playing a role in the conversion of atomic hydrogen to molecular hydrogen in space [11,15]. Furthermore, $C_{60}H_{36}$ presents a unique absorption band at 217 nm resembling the UV bump absorption observed in the interstellar light extinction curve [11,13]. When irradiated with UV light $C_{60}H_{36}$ loses hydrogen and the maximum of absorption is gradually shifted towards longer wavelengths [11,13]. Thermal treatment of fulleranes causes the release of hydrogen and the restoration of the pristine C_{60} although the yield is not quantitative and also carbon soot as by-product is obtained [16].

Fullerenes were found in various space environments, sometime mixed with other complex molecules like PAHs or metals. Therefore it was thought that also fullerene adducts should be searched in space [17]. Indeed, it is well known that fullerenes form adducts, for example with PAHs through the Diels-Alder reaction. The synthesis of all the adducts series of C_{60} and acenes (anthracene, tetracene and pentacene) was performed and the infrared spectra were recorded together with the electronic absorption spectra [18-20]. The acenes adducts with C_{70} were studied as well [21]. Theoretical approaches involving chemical thermodynamics and adducts polarizability calculations were also considered to establish the formation conditions and the stability of the acene adducts [22,23]. When C_{60} and C_{70} fullerenes were irradiated with visible light in presence of iron pentacarbonyl they yield the respective iron tetracarbonyl adducts [24]. Iron is one of the most abundant metal in the universe and CO is ubiquitous. Fe and CO can react in mild conditions to produce $Fe(CO)_5$ which is a highly volatile iron compound. When irradiated with C_{60} or C_{70} the iron carbonylcompound forms interesting adducts. The fullerene-iron carbonyl adduct presents a moderate thermal stability but very characteristic infrared spectra [24]. Fullerenes form also weak molecular complexes called also charge-transfer complexes with arenes and alkylnaphthalenes [25,26].

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Dynamics of fullerenes

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In this talk I will highlight advances in our understanding of the dynamics of isolated fullerenes and their clusters following electron, photon, or ion/atom impact. I will discuss the intricate balance between different statistical relaxation processes (electron emission, radiative cooling and fragmentation) occurring on picosecond timescales or longer, and give examples of non-statistical fragmentation dynamics occurring on sub-picosecond timescales. Furthermore, I will discuss how a surrounding (cluster) environment affects such processes and give a brief overview of studies of atom capture dynamics - i.e. endohedral formation in fullerene-atom collisions.

Time-Resolved Photoionization and Fragmentation Dynamics of Fullerenes Studied with X-Ray Free Electron Laser

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Time-resolved photo-induced responses of fullerenes subject to femtosecond free electron laser (FEL) X-ray ionization provide critical understanding of the fundamental mechanisms that drive the conversion of photons into chemical and kinetic energy on ultrafast timescales [1]. We have measured and predicted the critical change in the behavior of C_{60} ionization using photons at 640 eV energy with 20 fs pulse duration. The experiment used the LCLS fresh slice X-ray pump and X-ray probe technique. The time-resolved experiment is interpreted with Molecular Dynamics Modeling to expose, from a fundamental point of view, the physical and chemical processes and their time evolution involved in the formation of a nanoplasma as well as information on the radiation damage relevant to bio-molecules. Our work indicates that at the current XFEL fluence, electron redistribution during ionization is very important to the molecular dynamic. Our work further extends the model to ultra-high X-ray intensity, predicting the critical molecular ionization behavior change to be 50 fs with the new XFELs in Europe and Asia. This work, which improves the existing models of the response of carbon-containing materials to FEL X-ray radiation, is necessary for developing the FEL-based diffraction-before-destruction techniques with the new, more intense XFELs, and for studying materials of relevance for life sciences. We will also present, time permitting, measurements on encapsulated fullerenes, $Ho_3N@C_{80}$ and $Sc_3N@C_{80}$ using strong field infra-red lasers [2,3], FEL [4] and synchrotron radiation [5].

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PAH destruction by heavy cosmic rays carbon chains, production rates

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The ISM contains both cosmic rays (CR) and PAHs. The frontal impact of a single heavy CR with one PAH, strips out many electrons. The highly charged species then relax by multifragmentation, potentially feeding the interstellar medium with hydrocarbon chains. I will present results of calculations for this process. The IAE model was used for collisional purposes while a new microcanonical model was used for fragmentation. Both models agree with experiments. The production rate of low hydrogenated hydrocarbon chains (Nc = 5–15) is found to be within 0.1 to 1 ζ depending on the size and morphology of the PAH, and on the adopted content of heavy particles in the impinging CR flux.

Experimental simulation of cosmic ray ion irradiations of interstellar carbonaceous dust analogues : release of small to large molecules

T. Pino, M. Chabot, K. Beroff, M. Godard, F. Fernandez-Villoria, K.C. Le, L. Breuer, M. Herder, A. Wucher, M. Bender, D. Sverin, C. Trautmann and **Emmanuel Dartois**

Top-down chemistry is suspected to be at work for the formation of the large molecular compounds such as the polycyclic aromatic hydrocarbons-like molecules and the fullerenes observed in the interstellar medium. The release of these large molecules from the parent grains remains an issue. The exposure of carbonaceous dust analogues to cosmic rays is simulated in the laboratory by irradiating interstellar analogues with energetic ions. Sputtering in the electronic regime of the stopping power, as for cosmic rays, or desorption of molecules, could contribute to the enrichment of the large molecular component.

The carbonaceous dust analogues were produced using a flame and the resulting soot nanoparticles were generated in well-defined conditions. These deposited soots were irradiated by swift heavy ions and mass spectra of the ionic and neutral molecular fragments emitted shortly after the impact were monitored. The experiments performed show that large molecular fragments are formed and released into the gas phase.

In this presentation, we will show that these include neutral and ionic polycyclic aromatic hydrocarbons containing up to several tens of carbon atoms. Ionic fullerenes were also detected. Although the absolute efficiencies were not obtained, these experiments provide a clear proof of principles of top-down scenario involving energetic processing of interstellar dust to produce the large molecular compounds observed in space.

Astrophysical studies of the chemical evolution of carbonaceous species and fullerenes in space

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On one side, there are the aromatic infrared bands (AIBs), observed in emission in the infrared (IR) throughout the universe, and, on the other, the diffuse interstellar bands (DIBs) seen in absorption ubiquitously. Understanding the origin of these fingerprints has been one of the greatest challenges of astrochemistry for several decades. The consensus is that both signatures are due to large species made up of carbon, and the recent attribution of some IR emission features and DIBs to the same species, i.e. C_{60}^{+} has brought strong support to this proposal.

The goal of this contribution is to illustrate how spatially resolved spectroscopic observations of the IR features in UV irradiated regions we have performed recently, from star forming regions to the diffuse ISM, can be used to rationalize the chemical evolution of cabonaceous species (including fullerenes) in space, with the help of astrophysical models. For instance, this approach lead to idea that fullerenes can form top-down from PAHs in the interstellar medium. These astrophysical studies can provide guidelines to identify which are the key species and/or processes that must be studied theoretically and/or experimentally. This approach will be particularly interesting in the context of the upcoming JWST mission, which will give access to the features of fullerenes and other carbonaceous species, in emission and in absorption.

Abstracts: Poster Presentations

Nano carbon dust emission in proto-planetary discs: the aliphatic-aromatic components

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In the interstellar medium, the carbon (nano-)grains are a major component of interstellar dust. This solid phase is more vulnerable to processing/destruction than its silicate counterpart. It exhibits a complex, size-dependent evolution due to interactions within different radiative environments, which provides a modeling challenge. To probe the composition and evolution of carbon nano-grains at the surface of proto-planetary discs around Herbig stars, we present spatially resolved mid infrared emission spectra obtained with NAOS CONICA at the VLT in the 3–4μm range, which includes aromatic, olefinic and aliphatic bands. We apply a gaussian fitting to analyse the observed spectral signatures. Finally, we propose an interpretation in the framework of the THEMIS dust model. We show the presence of features spatially extended, related to aromatic and aliphatic materials in discs around Herbig stars. The correlation and constant intensity ratios between aliphatic and aromatic CH stretching bands suggest a common nature of carriers that seems continuously replenished at the disc surfaces.

Infrared signatures and characteristics of carbonaceous clusters.

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The question of the carrier of aromatic infrared bands (AIBs) is still open despite numerous experimental and theoretical studies. It is supposed that these bands are carried by a population of polycyclic aromatic hydrocarbons (PAHs). Nevertheless, some carbonaceous species have been identified as the C_{60} fullerene [1,2] and the C_{70} fullerene [2] . We want to determine the impact of amorphous carbon clusters on the infrared spectra and its possible connection to the AIBs. By amorphous carbon clusters, we mean species far from usual and well formed PAHs. These structures will include aromatic cycles as aliphatic chains, and are supposed to overlap species as fullerenes and usual PAHs. In the framework of the PACHYNO project (PACHYNO for Probing the diversity of Astrophysically relevant Carbon and Hydrogen NaNO particules) [3] which involves the collaboration between ISMO, LiPHY and LCPQ laboratory, we perform infrared analysis on a wide range of isomer for C_{24} , C_{42} and C60 at Self-Consistent Charge Density Functional Tight Binding (SCC-DFTB) level using the deMonNano code [4]. These sets of geometries include a large diversity of structures going through fullerene to amorphous isomers. In this poster, I will show you some results of the analysis that I performed on these species and the infrared signature that appears depending on their stability.

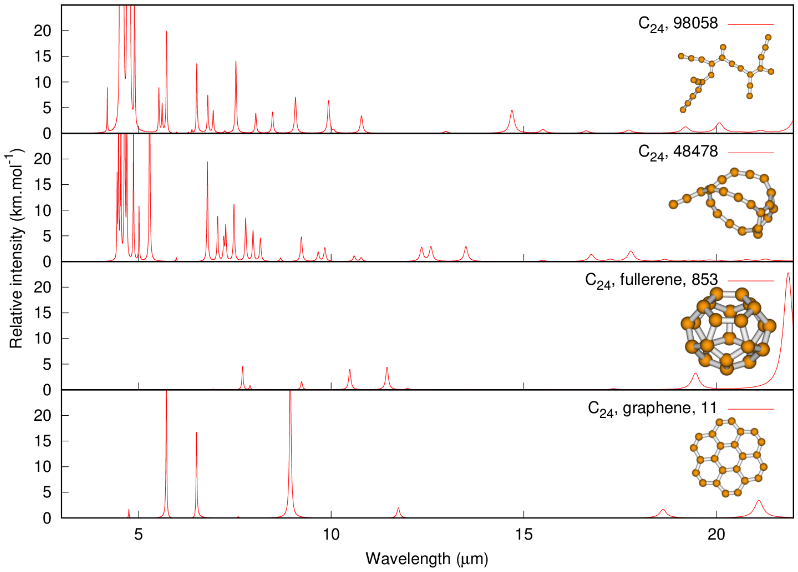

Figure 1: Examples of absorption IR spectra for optimized isomers of C_{24} at the SCC-DFTB level. A scaling of 0.84 on the vibrational energy is applied for wavelengths above 6 μm.

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Photofragmentation of Fullerene and Corannulene cations solvated in helium droplets

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The special properties of superfluid helium nano droplets (HND) [1] can be used to reproduce the harsh conditions of the interstellar medium (ISM), which makes this cryogenic matrix a perfect laboratory for the investigation of potential carriers of diffuse interstellar bands (DIB) like C_{60}^{+} [2] or many other polycyclic aromatic hydrocarbons.

The HND are produced via supersonic expansion and doped by individual pick-up with Fullerenes or Corannulene molecules. Inside the HND $(C_{60})He_n^-$ or $(C_{20}H_{10})He_n$ complexes are formed and covered with many helium atoms. Subsequently, the clusters are ionized via electron bombardment and analyzed by a high resolution time-of-flight mass spectrometer (TOF-MS) where spectra were recorded with respect to the m/q ratio [3].

Combining this with an action spectroscopy method, we were able reproduce the results obtained by Campbell et al. [4] and observe a size-dependent influence of the helium solvation on the decorated ions. Like our previous results [5], where the C_{60}^{+} Hen complexes show a spectral redshift, which shifts linearly up to 32 He atoms, we observed a similar behavior for the $(C_{20}H_{10})^{+}He_n$ clusters.

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This work was supported by the FWF (Project numbers P26635, P31149 and W1259), and the European Commission (ELEVATE, Horizon 2020 research and innovation program under grant agreement No. 692335)

Vibrational partition functions for cold large carbon molecules, possibility for observing cold gas phase IR absorption spectra.

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Laboratory infrared spectra are known for neutral fullerenes and a number of PAH molecules in the solid phase. A limited number of works on the IR emission from hot gas phase neutral C_{60} and C_{70} molecules are also available [1,2]. For cosmic fullerene spectroscopy it would be important to know the IR gas phase spectra of such large carbon molecules at very low temperatures. Previous attempts using molecular beams were not successful in obtaining such spectra, due to inefficient vibrational cooling, thus low population of the vibrational ground state [3], while no IR cold gas phase spectra have been published due partially to the unavailability of strong enough tunable IR lasers [4].

The thermal population of vibrational levels is directly indicated by vibrational partition functions (vpf). It seemed important to calculate such quantities for cold fullerenes and some representative PAH molecule. In this work we report the temperature dependence of vpf for C_{60}, C_{70} and coronene. The partition functions were calculated initially by the original Beyer-Swinehart algorithm using direct vibrational level counting in the harmonic approximation , and later by the modified Beyer-Swinehart algorithms (Multimode/ Densum code [5]). These calculations show that up to about 100 K for all these large molecules essentially only the ground state level is populated. Thus absorption spectroscopy should be possible.

We present a so far unpublished HENDI spectrum for C_{60} [6] that clearly shows the two lowest IR active vibrational modes in absorption. The vibrational band frequencies (and widths) are obtained as 529 ± 2 cm^{-1} (4.57 cm^{-1}) and 577 ± 2 cm^{-1} (3.82 cm^{-1}) using a Gaussian line fit. In a previous work [2] band center frequencies were extrapolated to 0 K as 531.22 and 574.37 cm-1 for C_{60}. This approximate agreement shows that the vibrational bands observed were indeed due to C_{60}.

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Topology-based simple model for prediction of selectivity on Diels-Alder reactions on fullerenes

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DielsAlder (DA) cycloadditions are a powerful tool for the introduction of a six-membered ring to a fullerene cage which have enabled the preparation of many derivatives with applications in material and biological sciences [1,2]. Furthermore, it is possible that fullerenes and PAHs, if coexist in interstellar medium, lead to fullerene/PAH adducts formed via DA reaction [3].

Due to the existence of different types of CC bonds on a fullerene cage, regioselectivity is commonly exhibited. Taking C_{60} as an example, the DA addition prefers to take place on the [6,6] bonds (junctions of two hexagon rings) over the [5,6] ones (junctions of an hexagon and a pentagon ring), as revealed by experiments and computations [4]. For larger and less symmetrical cages, a great number of possible regioadducts may be formed. Due to the existence of many possible isomers, it is not straightforward to predict the most stable structures. Thus, it is necessary to establish simple models and rules that allow making reliable predictions.

Our topology-based simple model, that incorporates the effects of π delocalization energy, σ strain and steric repulsion, has been used to predict the most stable fullerene structures for charged [5] and neutral exohedral fullerenes [6]. In this work [7], it has been used to predict the preferential addition site of DA reactions to empty fullerenes. We show that DA cycloadditions to empty fullerenes occur preferentially at a few simple bond patterns, which can be used as a visual guide for approximate prediction of the DA reactive sites. Moreover, we suggest two quantitative descriptors that have a direct chemical interpretation in terms of bond forming and breaking ability and in terms of local aromaticity.

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Dissociation of PAHs at high energy: MD/DFTB simulations vs. collision experiments

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The energetic processing of polycyclic aromatic hydrocarbons (PAHs) in the interstellar medium (ISM) has sustained a lot of interest lately, motivated in particular by the need to understand the link between PAHs and other detected molecules (fullerenes, small molecules such as H_2 and C_2H_2) in space. At the vicinity of a star or in shock wave regions, PAHs are likely to undergo high energy collisions. We aim at reproducing these conditions and understanding the underlying physical and chemical processes via a synergistic approach between theory and experiment. In this poster, we present theoretical results obtained for the dissociation of pyrene $C_{16}H_{10}$ at high energy obtained with molecular dynamics (MD) using a self-consistent-charge density functional based tight binding potential (SCC-DFTB) [1]. The theoretical results are compared to collision experiments (1 keV protons). The good agreement between theoretical and experimental mass spectra (Fig. 1) -(i)- validates the SCC-DFTB potential, -(ii)- confirms the main assumption used for the modeling, ie the fast internal conversion, and -(iii)- validates the energy transfer model. Insights into the structures of the fragments (Fig. 2) and fragmentation kinetics are also provided [2].

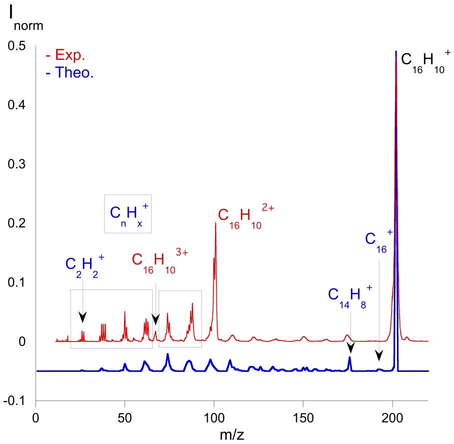

Fig. 1

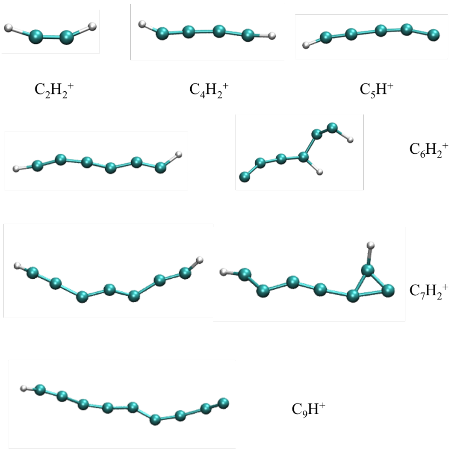

Fig. 2

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Fullerenes and Polyynes formed from Laser Ablation of Graphite

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Fullerenes are formed by condensation of carbon vapor molecules in laser vaporization [1], resistive heating [2], arc discharge [3], and laser ablation of graphite in a furnace [3]. An important factor which is not dismissed for fullerene-formation efficiency is the high temperature condition. Temperature dependent yields of fullerene C_{60} and C_{70} as well as of higher fullerenes, C_{2n} ($2n$ = 76, 78, 82, and 84), were investigated by systematic control of furnace temperature in laser ablation [4], where annealing of precursory carbon clusters, such as linear chains, monocyclic rings, and cages is crucial.

Recently, polyynes, i.e. hydrogen-capped linear carbon chain molecules, were formed by laser ablation of carbon particles in liquid organic solvents [5], and characterized by Raman [6] and NMR spectroscopy [7]. Under the rich abundance of hydrogen in space, nascent linear carbon clusters are subjected to competing processes of termination into polyynes or growth into fullerenes. In this presentation, conditions and products upon laser ablation of graphite are discussed.

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Unexpected Molecules in Planetary Nebula: Implications for C_{60} and C_{60}^{+} in Diffuse Clouds

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The origin of C_{60} and C_{60}^{+} in diffuse clouds remains a mystery. Because of the low densities found in such objects, it is difficult to explain the presence of these fullerenes by in situ gas-phase formation, although a top-down scheme involving the degradation of hydrogenated amorphous carbon (HACs) is possible. An alternative explanation is that these species were created in a different environment and injected into diffuse gas.

About 85% of the material in the interstellar medium comes from mass loss from Asymptotic Giant Branch (AGB) stars, which pass through the Planetary Nebula (PN) phase. AGB stars are well-known to contain envelopes that are abundant in gas-phase molecules and dust, particularly those which are carbon-rich. As AGB stars evolve into PNe, the star sheds most of its mass and becomes a white dwarf. The remnant AGB envelope becomes highly-ionized due to the ultraviolet (UV) radiation emitted from this white dwarf. It has always been thought that the relic gas-phase molecules from the AGB phase would be destroyed by this UV radiation over the short lifetime of the PN phase, about 10,000 years. Recent observations, however, have shown this not to be the case. Millimeter observations of over 20 PNe spanning the age range $\sim$500 to 12,000 years have demonstrated that CO, HCN, HNC, CCH, CS, CN and HCO^+ remain abundant throughout the nebular lifetime. Among the objects studied include NGC 6720 (Ring), NGC 7293 (Helix), NGC 6537, K4-47, K3-58, K3-17, M3-28, K3-15, M2-48, and M4-14 [1–7]. Other molecules detected include SiO, H_2CO, SO, SO_2, N_2H^+, c-C_3H_2, HC_3N, and HCCN. Perhaps the most striking result is that the molecular abundances do not vary significantly with nebular age, such that, even in the oldest nebula such as the Helix and K3-58 (age ¿ 10,000 years), species such as CCH, c-C_3H_2, H_2CO, HCN, and HNC have significant abundances, typically $f \sim 10^{-8}$–10^{-6}, relative to H_2. The molecules appear to be contained in dense ($\sim 10^5$–10^6 cm^{-3}) and cool (T$\sim$20–50 K) clumps, mixed with shielding dust. These data imply that PN ejecta are in part molecular in nature, and therefore diffuse clouds are seeded with chemical compounds that had an origin in the AGB/post-AGB phase. Diffuse clouds contain all the chemical species observed in the late PNe stage, but with reduced abundances consistent with the notion of clump injection and dissipation with time.

In analogy to these simpler species, C_{60} also may be part of PN ejecta. C_{60} was likely formed in the AGB/post-AGB phase, as observations suggest, survived in the molecular clumps into the late PN stages, and was injected into diffuse clouds, along with other smaller molecules.

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