

Invited contributions

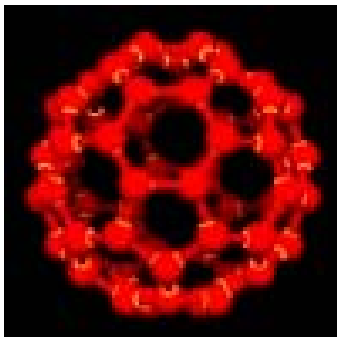


Some spectroscopic issues in astrophysical chemistry

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Since the discovery of the long chain cyanopolyynes in the mid 70's there have been numerous papers discussing the role of large carbon molecules in interstellar space. Indeed it was a quest for the origin of the carbon chain species in the ISM as well as their possible relationship with the DIBs that led to the detection of the C₆₀ Buckminsterfullerene molecule in the laboratory. The properties of carbon in the vapour phase has been known to be a fascinating and complex problem for a long time and



The soccer ball molecule C₆₀

the detection of the fullerenes added a new and exciting layer. The discovery also stimulated new technical approaches to the study of carbon vapour which has turned out to be even more complicated than expected.

Most of the original astrophysical questions however still remain unanswered though there have been many conjectures - many of which have focused on bio-emotive issues such as the significance of large carbonaceous species on the origin of life on the planet. In this presentation a survey of various aspects of carbon chemistry which appear to be germane to the astrophysical questions are discussed. Some spectroscopic data which have been assigned to large carbonaceous species will also be discussed.

Harold W. Kroto was one of the co-recipients of the 1996 Nobel Prize in Chemistry. This Nobel Prize was based on the discovery of buckminsterfullerene, a form of pure carbon better known as "bucky-balls." The extraordinary molecule consists of 60 carbon atoms arranged as a spheroid, in a pattern exactly matching the stitching on soccer balls. The configuration reminded Kroto of the geodesic domes designed by the late inventor/architect Buckminster Fuller, hence the name "buckminsterfullerines."



Harry Kroto. After teaching for 37 years at the University of Sussex in England, Kroto joined the Florida State University, USA as a Francis Eppes Professor in the Department of Chemistry and Biochemistry in 2004. He said his move will allow him to not only open up some new research avenues but also maintain the considerable momentum that his research has built up over the past 10 years in his international educational outreach work.

Metastable H_3^+ near the Galactic center: Interplay between radiative and collisional interactions

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H_3^+ , the simplest polyatomic molecule, is ubiquitous both in dense and diffuse clouds and acts as the universal proton donor (acid) to initiate chains of chemical reactions. Here I discuss a subtle interplay of its spontaneous emission and reactive collisions which makes H_3^+ a powerful and unique probe for studying the 200 pc radius Central Molecular Zone

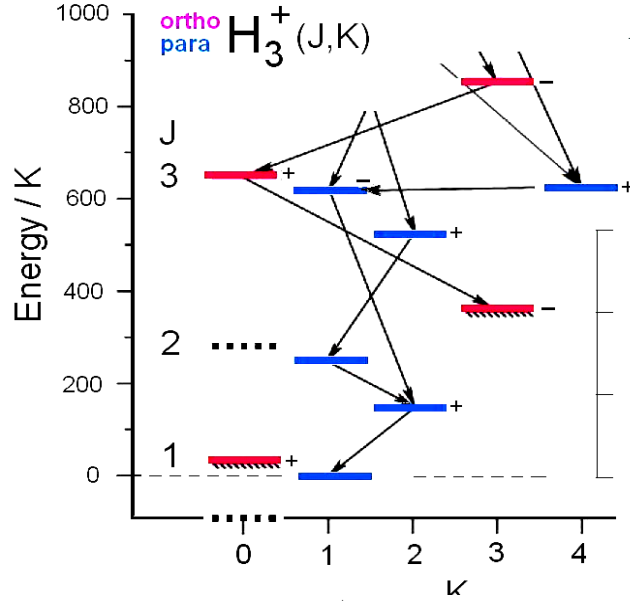


Fig. 1: Rotational energy levels of H_3^+ in the ground vibrational state.¹

(CMZ) of the Galaxy which is full of highly energetic and mysterious phenomena.

We have observed high column densities ($\sim 10^{15} \text{ cm}^{-3}$) of H_3^+ in the $(J, K) = (3, 3)$ rotational level toward several infrared stars in the CMZ. H_3^+ in the $(2, 2)$ level which is much lower in energy, however, is

hardly observable. This remarkable non-thermal rotational distribution is a result of metastability of the (3, 3) level from which a spontaneous emission is rigorously forbidden by the dipole selection rule, and instability of the (2, 2) level from which a spontaneous emission to the ground (1, 1) level is allowed due to breakdown of the C_3 symmetry by centrifugal distortion. Using three spectral lines starting from the three qualitatively different rotational levels, that is, the metastable (3, 3) level, the unstable (2, 2) level, and the ground (1, 1) level we can obtain definitive information on temperature and density of molecular clouds. A model calculation on the H_3^+ thermalization has been published.¹

Using our observational data at the Gemini South Observatory, the United Kingdom Infrared Telescope, and the Subaru Telescope, together with the model calculation, we have discovered a vast amount of high temperature (~ 250 K) and low density (~ 100 cm⁻³) gas in the CMZ. For the sightline of the brightest Quintuplet object GCS 3-2, about half of the gas has the huge negative velocity of -100 km s⁻¹, indicating that it is associated with the 180 pc radius Expanding Molecular Ring which approximately forms outer boundary of the CMZ. The other half, with velocities of about -50 km s⁻¹ and 0 km s⁻¹, is probably closer to the center. Metastable H_3^+ is not observable in the Galactic disk indicating that the hot and diffuse gas is unique to the CMZ.²

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Absorption spectra of dark interstellar clouds

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The first absorption spectral features - the CaII doublet, known since the era of Fraunhofer as H and K lines - originating in the interstellar space, were discovered by Hartmann in 1904. Both lines proved to be of very narrow profiles; moreover they did not participate in the Doppler shifts observed in stellar lines of spectroscopic binaries. Since that discovery many interstellar atomic lines have already been discovered - most of them using extraterrestrial instrumentation.

Moreover, since 1921, one can observe the still unidentified diffuse interstellar bands. Currently more than 300 of such unidentified features have been listed; an extension of this list seems to be only a matter of time and growing S/N ratio of the spectra. In the 1930-ties several spectral features, originating in simple molecular species have been discovered. Until now the list of molecules, revealed thanks to absorption spectra, exceeds 10 entries. However, the observations of radio microwave emission features, extended the list of known molecular species to about 140. Thus it seems to be proved beyond a doubt that the interstellar clouds are, in fact, large chemical factories, containing a lot of more or less complex molecules. In fact the diffuse interstellar bands are commonly believed to be originated in some complex species as well. Their identification seems to require a comparison between laboratory gas-phase spectra of some molecules with the astrophysical observations. The latter may try to establish the physical conditions inside the clouds using intensities and profiles of atomic and molecular features.

Seemingly two possible ways of performing the task of DIB identification can be proposed. One of them requires very high S/N ratio spectra in a very broad range of wavelengths to match the wavelengths and relative intensities of a set of selected features having a counterpart in laboratory spectra of some species. The second one requires ultra high resolution profiles of individual features. Such profiles of many DIBs contain substructures, resembling those of known molecular bands with unresolved rotational structure. The substructure pattern may be characteristic for a given molecular spectrum and if it matches the observed profile it may be a sufficient argument connecting a DIB with the chosen molecular species. It is emphasized that a criterion of identification must

meet the requirements of both: experimentalists and observers.

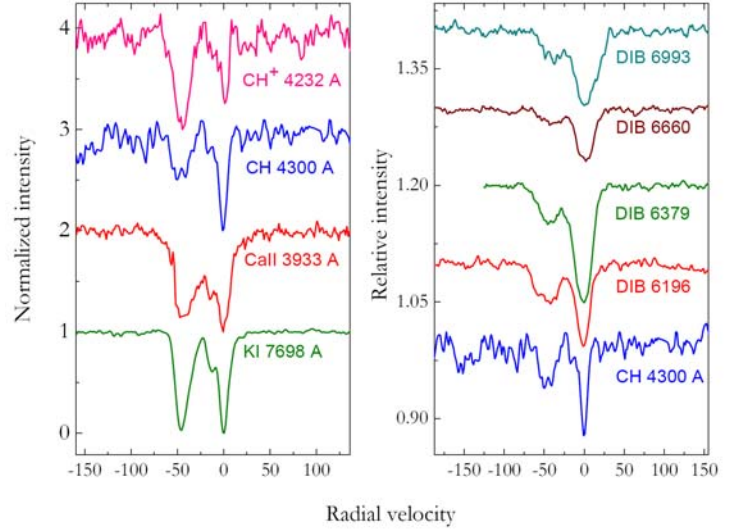


Fig. 1: Doppler splitting of interstellar absorption features seen in the spectrum of BD +58° 2580. Narrow diffuse bands, depicted in the right frame clearly resemble the CH 4300 Å feature while the components of other identified features are of evidently different strength ratios.

This paper describes the astrophysical spectra obtained using several different instruments which allows to estimate the precision of the measurements. Possible relations between different spectral features are briefly discussed.

Gas phase laboratory studies of electronic spectra of carbon containing molecules of relevance to astrophysics

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The gas-phase electronic absorption spectra of several new carbon molecular systems could be observed in the laboratory allowing a direct comparison with astronomical DIB data. These include the non-linear carbon chains, $C_nH_4^+$ $n = 4, 6, 8$, C_5H_5 isomers which absorb near the 4429 DIB, and large cyclic systems such as C_{18} , C_{22} , all with absorptions in the visible. The implication of these and earlier studies on the smaller carbon chain systems in trying to identify likely candidates to be DIB carriers are discussed.

Carbon clusters as interstellar molecules and grains

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Carbon is the most abundant condensable element in our galaxy. Besides forming a variety of bond types, of which linear sp -C, triangular sp^2 -C, and tetrahedral sp^3 -C are limiting cases, carbon can also polymerize readily. The latter feature leads to the growth of carbon structures into large molecules and grains. The π -electron system of carbon molecules containing sp -C and sp^2 -C bonds is basically determining the optical

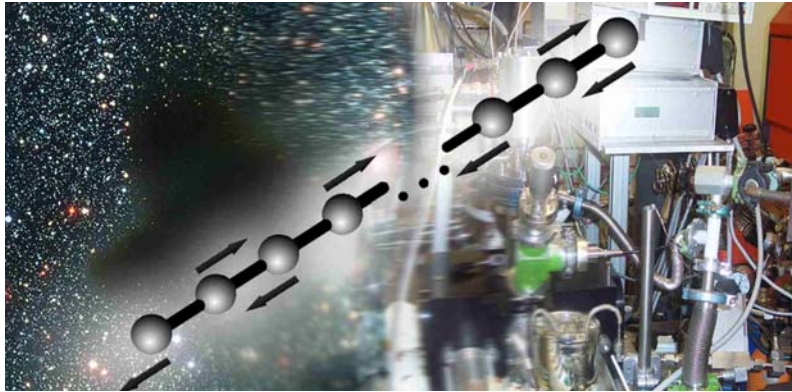


Fig. 1: Linear carbon molecules are connecting our laboratory research with that of interstellar matter. The arrows drawn at the molecule indicate the atomic displacements of the most intense IR absorption of the carbon chain.

absorptions, and also contributes to the inter-atomic force constants responsible for the IR absorptions. For this reason, certain size effects and scaling laws of the energy of spectral transitions are expected.

As an example, we recently measured the IR absorptions of very long linear sp -C chains in matrix-isolated state and found surprising regularities reminiscent to those already known from the UV-VIS absorptions of such species [1,2]. Concerning the UV-VIS absorptions of long carbon chains, we draw attention to the striking similarity with the pattern of DIBs [3]. With regard to the presence of sp^2 -C networks in interstellar

space, we think that transmutations between polycyclic hydrocarbons and partly open sp^2 -C hydrogenated fullerenes play a role, as already suggested by other researchers [4]. The requirement of strong interstellar UV absorbers at around 220 nm wavelength suggests as carriers (almost) spherical graphitic grains in which collective excitations, i.e., surface plasmons can occur. The most likely candidates fulfilling this requirement are fullerene anions. Reported recent laboratory experiments seem to support this view [5].

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Gas phase: reactions of astrochemical importance

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An overview of laboratory reaction studies relevant to the field of astrochemistry will be provided. This will include a brief discussion of current state-of-the-art in laboratory techniques for the study of low temperature collision studies of ions, radicals and molecules in well defined energy states. In this discussion, the importance of astrophysical chemical

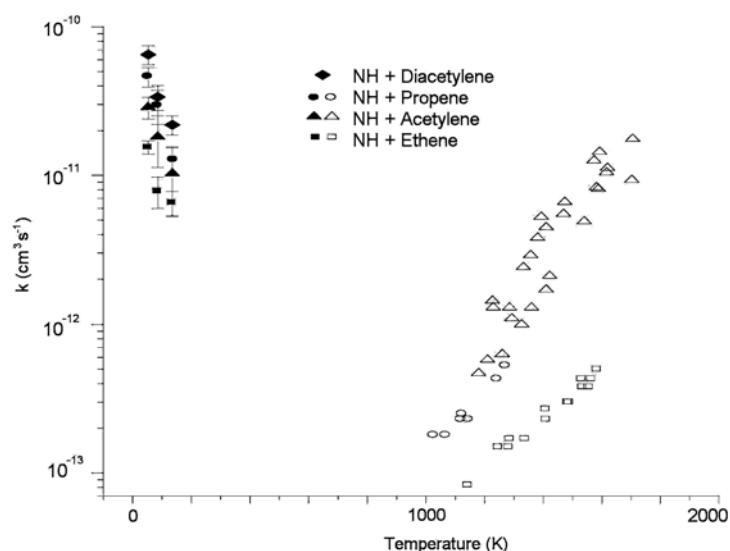


Fig. 1: Temperature dependent rate coefficients for the reaction of NH with unsaturated hydrocarbons.¹

modeling of extraterrestrial molecular environments will be introduced. Of course, owing to the tremendous range of physical conditions, the generality of non-equilibrium conditions and the uncertainties in atomic and chemical composition, comprehensive study of molecular development in extraterrestrial environments remains an elusive goal. However, progress in reaction studies continues to address specific questions that arise as a result of advances made in molecular observations or refinements in modeling.

Finally, parallels between chemical understanding of interstellar composition and dynamics and that of planetary environments within our own solar system will be mentioned. In particular, recent results from the Cassini-Huygens mission and laboratory studies of Titan chemistry will be presented in this context. The non-oxidative Titan atmosphere and the balance between plasma- and photo-chemistry provide intriguing parallels



Fig. 2: An example of laboratory plasma produced “tholin” aerosol.^{2,3}

between classes of molecules present in the ISM, wholly absent in natural Earth environments and yet believed to play key roles in the atmospheric and surface chemical dynamics of this moon of Saturn. Some advancements in the study of nitrogen fixation in planetary atmospheres, the formation and understanding of $C_xH_yN_z$ “tholin” aerosols and the prebiologic potential of these aerosol feedstocks in the presence of water will be mentioned.

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Experimental investigation of neutral-neutral reactions and energy transfer at low temperatures

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Chemistry at extremely low temperatures – and, in particular, the study of collisional processes in the gas phase – is a fascinating area of research. It provides a unique opportunity for a stringent comparison of experimental data with theoretical models of gas phase kinetics and energy transfer. It is also of direct application to the chemistry of such diverse environments as the atmospheres of Earth and other planets, and the synthesis of a wide range of molecular species within dense interstellar clouds (ISCs).

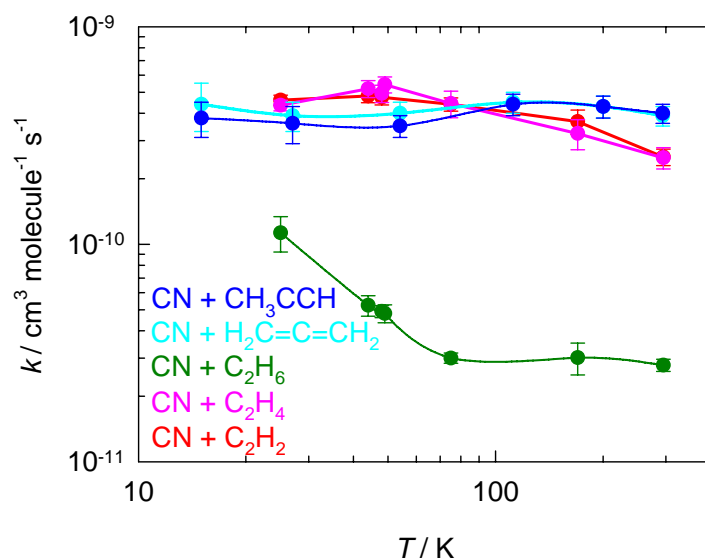


Fig. 1: Rate constants as a function of temperature for reactions of the CN radical with various hydrocarbons measured in the CRESU apparatus. All of these reactions are found to be rapid at low temperatures, contrary to the accepted view prior to these studies.

Over the last few years, we have applied the CRESU (Reaction Kinetics in Uniform Supersonic Flow) technique to the study of neutral-

neutral reactions and energy transfer processes in the gas phase. This has enabled the rates of a wide range of reactions between electrically neutral species to be measured down to temperatures as low as ~ 10 K. These results have generated significant interest amongst theoretical chemists, and especially amongst astrochemists. Our measurements of low temperature rate coefficients have had a significant impact on the models used to simulate the chemistry of dense ISCs.

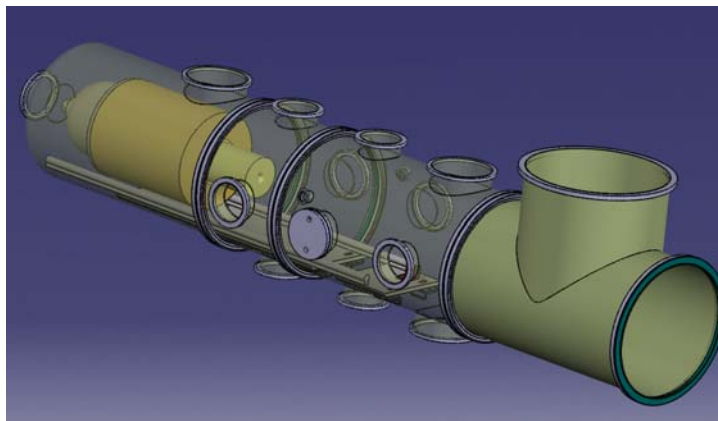


Fig. 2: The heart of the CRESU apparatus is a Laval nozzle, seen here mounted on the moveable double jacketed reservoir within the CRESU main chamber.

In this lecture I will review the experimental techniques available for obtaining rate coefficients and absolute cross sections for gas phase reactive and inelastic collisional processes at very low temperatures, and give a detailed description of the CRESU technique. I will then give an overview of the results obtained in Rennes and Birmingham, and attempt to highlight some general trends in reactivity at low temperatures. I will then focus on the results of some recent studies, including rotational and spin-orbit energy transfer in collisions of CO and $C(^3P_J)$ with He and H_2 , as well as a number of reactive processes of interstellar interest, including reactions of carbon containing radicals such as C_2 .

Modeling: the budget of hydrocarbons and deuterated variants

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We present new developments in interstellar chemistry, with particular emphasis on the carbon and deuterium chemistry.

Carbon chemistry will be discussed at the light of recent observations performed at high spatial resolution in the Horsehead nebula [1, 2], which is a nearby Photon-Dominated Region (PDR) where the density and radiation fields are relatively well constrained.

Deuterium chemistry will be related regarding the multiply deuterated molecules detected in the B1 cold dark interstellar cloud [3, 4, 5].

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Astrochemistry in ICR traps

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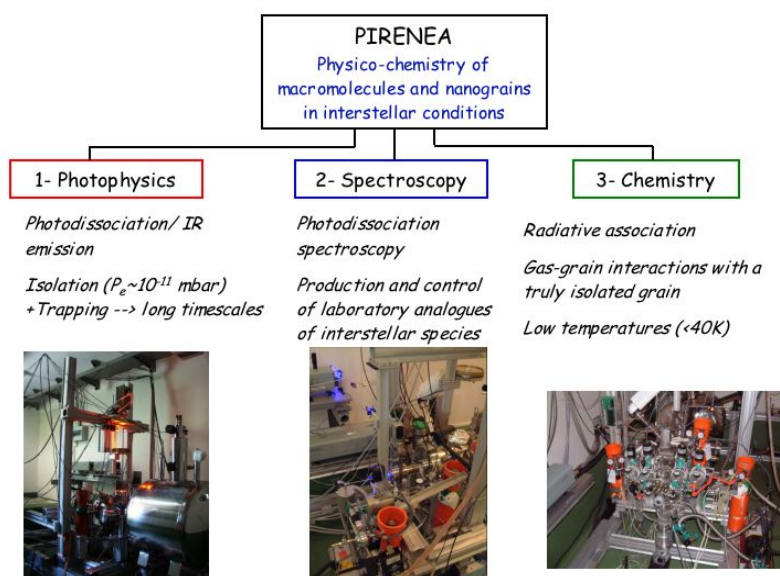


Fig.1: Typical experiments which can be conducted with a cold ICR trap to study processes of interstellar relevance involving macromolecules and nanograins. Pictures are from the PIRENEA set-up at CESR (CNRS-UPS) in Toulouse.

One of the challenges for laboratory astrochemistry is to approach the physical conditions that prevail in interstellar space: a cold environment (10-50 K), absence of collisions on long timescales and presence of stellar UV photons ($h\nu < 13.6$ eV) at the surface of clouds. Using the trapping, and the mass spectrometry analysis of an ion cyclotron resonance (ICR) cell that is connected to cryogenic shields, novel studies can be performed on processes which occur on long timescales and which are of interstellar relevance: IR radiative cooling, photodissociation in low energy channels, radiative association. The technique can also be coupled to (photodissociation) spectroscopy with the advantage of an easy mass selection of the studied species. Infrared spectroscopy in particular can

provide structural information but is also a direct way for comparison with astronomical observations.

I will illustrate these different aspects by the results obtained by several groups. I will describe in more details the PIRENEA set-up which has been developped specifically to study large molecules and nano-objects of astrophysical interest.

Reaction Dynamics of Radicals of Astrochemical Interest

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A detailed knowledge of the reactivity of carbon-bearing radicals in interstellar ices and in the gas phase of the interstellar medium is of paramount interest to understand the astrochemical evolution of cold molecular clouds, circumstellar envelopes, and of star-forming regions. Since the present composition of each interstellar environment reflects the matter from which it was formed and the processes which have changed the chemical nature since the origin (cosmic ray exposure, photolysis,

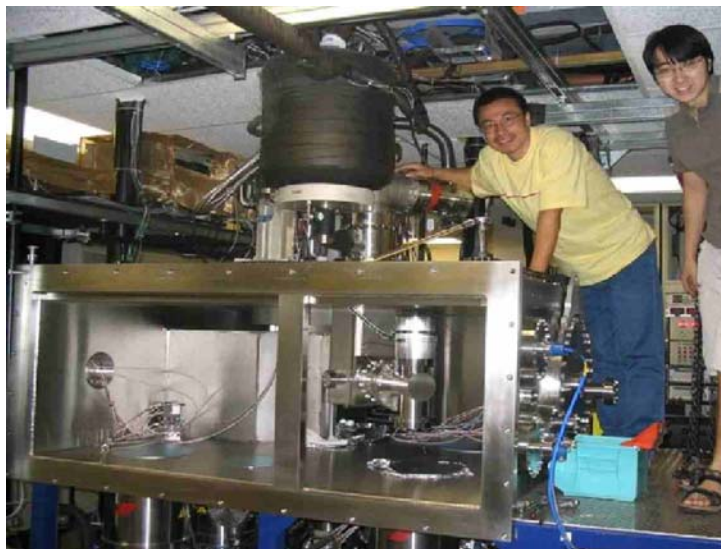


Fig. 1: Crossed beams machine

chemical reactions), a detailed investigation of the physicochemical mechanisms altering the pristine environment is of vital importance to understand the contemporary composition. Once these underlying processes have been unraveled, we can identify those molecules, which belonged to the nascent setting, distinguish molecular species synthesized in

a later stage, and predict the imminent chemical evolution of, for instance, molecular clouds.

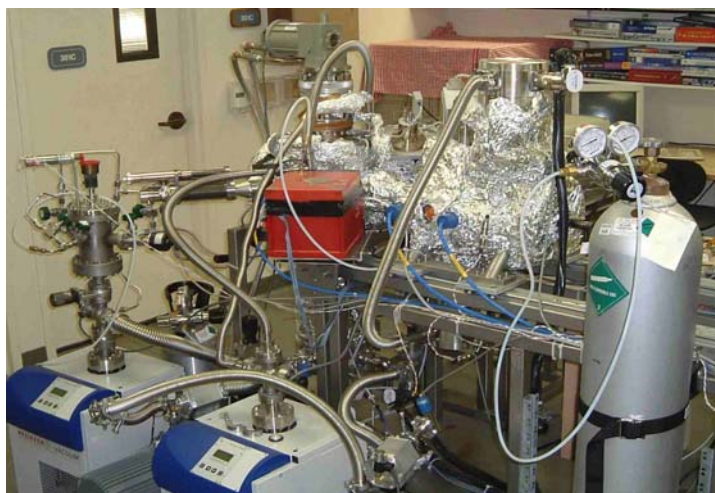


Fig. 2: Surface scattering machine

This talk overviews the experimental setups utilized in the current experiments (surface scattering machine, crossed beams machine) and portrays then typical results of each setup (formation of aminoacids, aldehydes, alcohols, epoxides; synthesis of hydrogen terminated carbon chains as precursors to complex PAHs and to carbonaceous dust grains in general). These laboratory results can predict then where in the interstellar medium complex, carbon bearing molecules can be formed on interstellar grains and in the gas phase.

Forming interstellar molecules: the need to know

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Molecules are found in a wide assortment of astronomical environments, from stellar atmospheres to interstellar clouds of gas and dust in our galaxy, and from nearby external galaxies to the most distant and early regions of the universe. Molecules yield unparalleled information concerning physical conditions in the regions where they are located through detailed interpretation of both gas-phase and condensed-phase spectra, mainly via rotational and vibrational transitions. In addition, an understanding of the chemistry of molecules can tell us about the lifetime and history of the sources. Such an understanding, however, requires detailed chemical knowledge of gas-phase and grain-surface chemical processes under often exotic (typically low-temperature) conditions; this knowledge is often unavailable and requires new laboratory and theoretical chemical studies. Indeed, the needs of molecular astronomy have prompted and continue to stimulate new work in a variety of fields of chemistry.

In my review talk, I will go over the state of interstellar chemical models, which contain thousands of reactions, many of which have not been studied theoretically or in the laboratory. How can these networks be made more secure so that predictions of interest to astronomers can themselves be treated with more seriousness? What reactions are most poorly understood? Some emphasis will be placed on the process of deuterium fractionation, which, if understood correctly, should help to tell us much about the early stages of star formation.



Fig. 1: A young
astro-chemist

We will consider two classes of models: those constructed out of only gas-phase reactions, and those that contain both gas-phase chemistry and chemistry occurring on the surfaces of tiny dust particles. Although there are serious problems remaining to be solved in gas-phase chemistry, the problems of understanding surface chemistry at low temperatures on poorly known and irregular surfaces are particularly daunting. Nevertheless, progress is certainly being made.



Fig. 2: An interstellar region in which star formation is advanced.

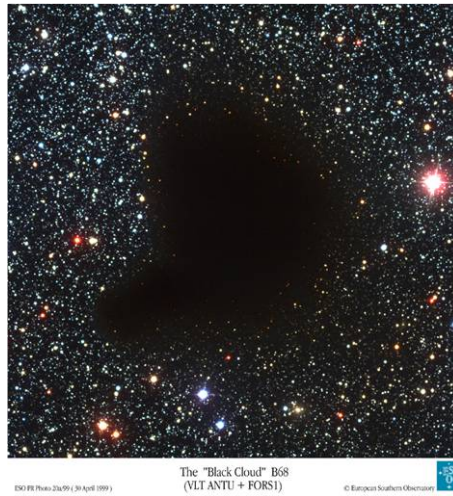


Fig. 3: A region in which star formation is about to start

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Molecules of astrobiological relevance

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In the last decade astronomical observations, laboratory simulation and analysis of extraterrestrial material have enhanced our knowledge regarding the inventory of organic matter in the interstellar medium (ISM), and on small bodies and planetary surfaces (Ehrenfreund & Charnley 2000, Ehrenfreund et al. 2002). Data from those investigations document the complexity of organic chemistry in space. Comets, asteroids and their fragments, meteorites, and interplanetary dust particles (IDPs) contributed significant amounts of extraterrestrial organic matter, predominantly in the form of aromatic macromolecules, to our Solar System during its formation. This material degraded and reacted on catalytic surfaces to form organic structures that may have served as building blocks for life on the early Earth.

Molecules of astrobiological relevance include the building blocks of our genetic material nucleic acids, composed of subunits such as N-heterocycles (purines and pyrimidines) and sugars. Another crucial component of life as we know it are proteins, 3-dimensional assemblies of amino acids. N-heterocycles, amino acids and pre-sugars have all been identified in extracts of carbonaceous meteorites (Ehrenfreund et al. 2002). However, only a few of those compounds are identified as “truly extraterrestrial”. The lack of isotopic data for many of those trace compounds found in carbonaceous meteorites prevents a definitive answer on their extraterrestrial identity.

Recently the simplest amino acid glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) was detected in three star-forming regions (Kuan et al. 2003). This molecule, which is described as the “Holy Grail” of interstellar chemistry, has evaded detection for over 20 years. Glycine is difficult to detect because its transitions are intrinsically weak, which requires long signal-integration times, and the spectral lines can be easily confused with transitions of other molecules that can contaminate the spectral region. Identifying glycine took a careful analysis of data that was collected over several years. Theoretical studies argue against the formation of nucleobases such as adenine in interstellar and circumstellar environments (Smith et

al. 2001). Small N-heterocycles with a limited amount of N-atoms in the ring may be present in trace abundances (Peeters et al. 2005) in circumstellar regions. We have conducted extensive astronomical searches for the N-bearing ring molecules pyridine, quinoline and isoquinoline towards the circumstellar envelopes of carbon-rich stars, and for interstellar pyrimidine in hot molecular cores. Here we report the derived upper limits on the column densities of these molecules and summarize the current status of these observations.

We also present laboratory measurements on the photostability of prebiotic molecules and show that amino acids and N-heterocycles can barely survive in regions with elevated UV radiation. These results also provide important evidence that those prebiotic compounds are not formed by UV radiation on interstellar grain mantles in star-forming regions. All material in the protosolar nebula was once interstellar matter. Even heavily processed nebular organic material has an origin in the interstellar medium, where several distinct chemical processes are responsible for their formation (Ehrenfreund & Charnley 2000). We present recent observations, laboratory data and related theoretical models in order to critically investigate the role of interstellar prebiotic molecules in the context of the origin of life.

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Theoretical analysis of capture-controlled bimolecular reactions of ions and radicals under low-temperature conditions

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Bimolecular reactions of ions and radicals at low temperatures occur with non-negligible rates only if the potential is essentially barrierless. The reactions are initiated by capture which is followed by a series of branching processes into various product channels. This talk presents the state-of-the-art of the understanding of the capture processes. The method of choice is the SACM/CT approach [1] (statistical adiabatic channel model combined with classical trajectory calculations) which supersedes earlier less appropriate methods like ADO, AQO, ACCSA, VTST etc.

For ultralow temperatures (below 1 K) hybrid SACM / CT / wavepacket codes are used [2]. It is shown that the capture dynamics in general is adiabatic in conserved modes but non-adiabatic in transitional modes. The capture rates depend crucially on the properties of the interaction potential. The SACM/CT approach has led to compact analytical and easy-to-use expressions for various types of potentials. Their use is demonstrated.

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PAH's in the lab and in space

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This session will cover several aspects of the on-going work on PAH's. Two major directions will be discussed : i) the electronic absorption and emission properties of neutral and cationic PAH's in relation to the observations of diffuse interstellar bands and extended red emission; ii) the chemical processes governing the formation and the growth of PAH's.

Photoinduced chemistry within cold coronene clusters in the gas phase [1]

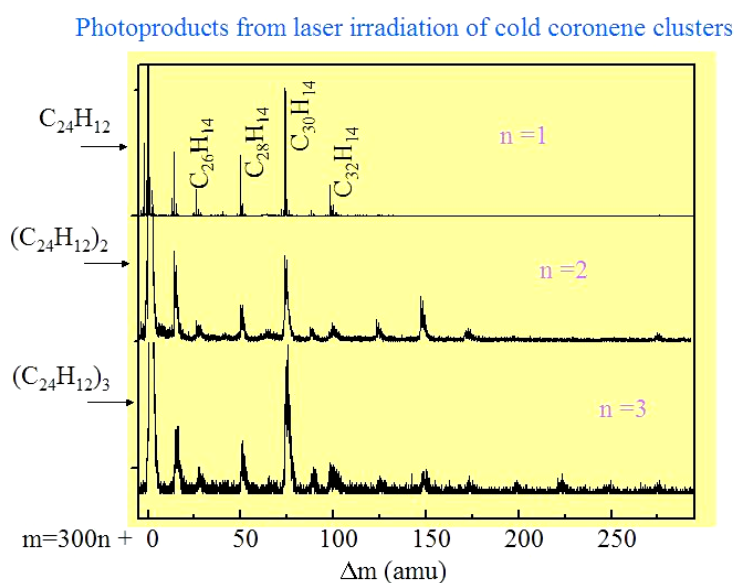


Fig.1: RETOF analysis showing the products formed from excimer laser irradiation of free cold coronene clusters. The mass spectrum is displayed in 3 successive panels of 300 amu width. The newly formed products extend over 100 amu mass range up from the coronene monomer in the top panel, then over 200 amu up from the coronene dimer in the middle panel, and over 300 amu up from the coronene trimer in the bottom panel.

Free cold pure coronene clusters containing up to 13 coronene molecules, *i.e.* 312 carbon atoms, have been formed in a gas aggregation source. When these clusters were irradiated with excimer laser pulses at $h\nu = 4$ eV, a rich photo-induced chemistry was observed. It leads to the formation of new covalently bound species, whose size is larger than the initial coronene units, thus contributing to the PAH growth.

The analysis of the photoproducts thanks to a reflectron time-of-flight mass spectrometer (Fig.1) has shown that photo-initiated intracluster reactions take place, leading to ionic species which may include PAH's larger than coronene, PAH-coronene clusters, as well as coronene clusters branched with unsaturated aliphatic chains. The relevance of these results in the context of the interstellar medium chemistry, and in particular the carriers of the aromatic infrared emission bands (AIBs) will be discussed.

Such photoinduced chemistry taking place at the boundaries of molecular clouds [2] may provide a route to the *hydrocarbonated nanograins* which are thought to be responsible for these bands.

Probing the carbonaceous particles within an acetylene-rich flame

Recent results from a low-pressure flame are presented on a poster.

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PAHs and the Diffuse Interstellar Bands. What have we Learned from the New Generation of Laboratory and Observational Studies?

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Polycyclic Aromatic Hydrocarbons (PAHs) are an important and ubiquitous component of carbon-bearing materials in space. PAHs are the best-known candidates to account for the IR emission bands (UIR). PAHs are also thought to be among the carriers of the diffuse interstellar absorption bands (DIBs). In the model dealing with the interstellar spectral features, PAHs are present as a mixture of radicals, ions and neutral species. PAH ionization states reflect the ionization balance of the medium while PAH size, composition, and structure reflect the energetic and chemical history of the medium. A major challenge for laboratory astrophysics is to reproduce (in a realistic way) the physical conditions that exist in the emission and/or absorption interstellar zones.

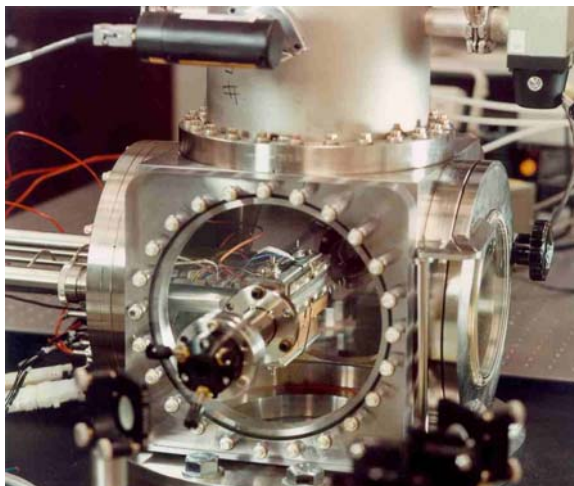


Fig. 1: An Interstellar Simulation Chamber (ISC) was developed at NASA Ames to measure jet-cooled molecular ions and neutral molecules under conditions that are relevant for comparison with astronomical data. The chamber combines a cavity ringdown spectroscopy system with a pulsed discharge nozzle (CRDS-PDN).

An extensive laboratory program has been developed at NASA Ames to characterize the physical and chemical properties of PAHs in astrophysical environments and to describe how they influence the radiation and energy balance in space and the interstellar chemistry. Laboratory experiments provide measurements of the spectral characteristics of interstellar PAH analogues from the UV and visible range to the IR range for comparison with astronomical data.

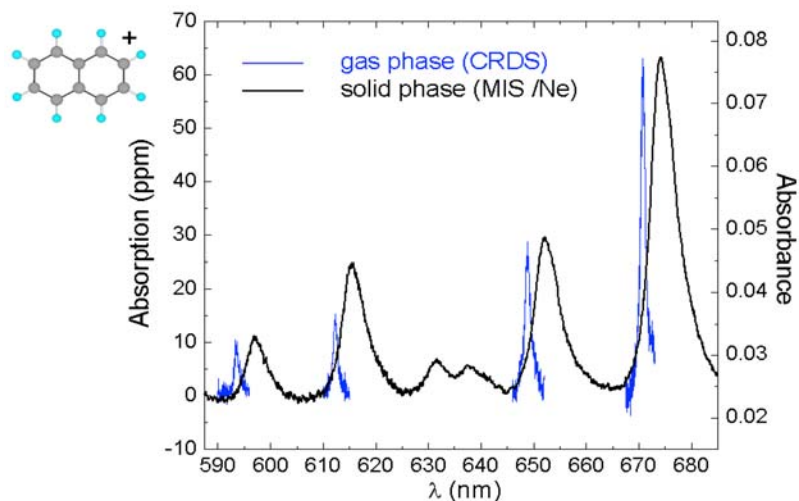


Fig. 2: The electronic absorption spectrum of the naphthalene cation measured in the gas phase with ISC is superposed on the same spectrum measured in a solid neon matrix with MIS. This comparison illustrates the solid phase effect on band peak positions and band profiles, two key elements for comparison with astronomical data .

This paper will focus on the recent progress made in this laboratory and others to measure the direct absorption spectra of cold, neutral and ionized PAHs in the gas phase in astrophysically relevant environments. These measurements provide data on PAHs and nanometer-sized particles that can now be directly compared to astronomical observations. The laboratory data are discussed and compared with recent astronomical spectra of DIBs and with the spectra of circumstellar environments of selected carbon stars and the implications for the interstellar PAH population are derived.

This work is supported by the NASA Astronomy and Physics Research and Analysis (APRA) Program of the Science Mission Directorate and NASA Ames DDF program.

Observations of neutral and ionized PAH's in the red rectangle

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The post-AGB, proto-planetary nebula known as the Red Rectangle (HD 44179) is the brightest source of the mid-IR aromatic hydrocarbon emission features (AEF) at 3.3, 6.2, 7.7, 8.6, 11.2, and 12.4 micron, which have been widely attributed to vibrational and bending modes in polycyclic aromatic hydrocarbon (PAH) molecules and/or ions. HD 44179 is a C-rich object and carbonaceous molecules and clusters are thought to be forming currently in the stellar outflow. As a result of an extremely favorable geometry, which greatly suppresses direct and scattered radiation from the central stellar source, the Red Rectangle offers an exceptional opportunity for observing absorptions and emissions at UV/optical wavelengths arising from the molecules present in the nebula. UV-spectra of the central source show the signature of PAH ionization. Nebular spectra in the near-UV/blue spectral range show evidence of emission that can be attributed to fluorescence by three-to-four ringed neutral PAH molecules. We have obtained for the first time fully resolved fluorescence spectra of the outer regions of the Red Rectangle, which represent an identification challenge to laboratory spectroscopy.^{1,2}

The energetics and morphology of the extended red emission (ERE), which gives the Red Rectangle its distinctive color, are consistent with fluorescence by PAH di-cations. Nano-sized clusters, stochastically heated to near 1400 K, are observed near the central source as well as at an offset of 5 arcsec, corresponding to 3500 AU at the distance of the Red Rectangle. Equally noteworthy as these positive detections is the total absence in the spectrum of HD 44179 of two phenomena often thought to be associated with carbonaceous nanoparticles or molecules, the 217.5 nm absorption feature and the diffuse interstellar bands (DIBs). This represents a major difficulty to models which attribute these features to PAH molecules and/or ions and carbonaceous nanoparticles.

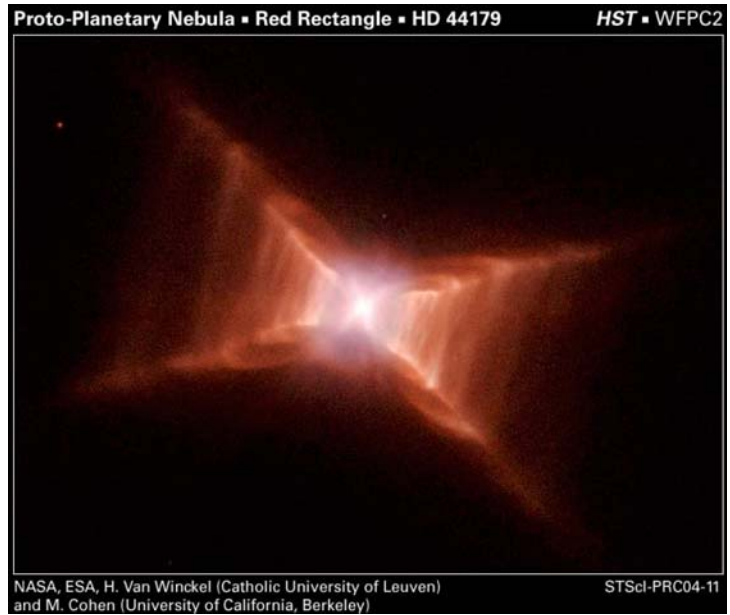


Fig. 1: This HST image of the Red Rectangle nebula illustrates the highly structured morphology as it appears in the light of the extended red emission (ERE). Superimposed upon the center is the disk-bifurcated image of the scattered-light halo of the central star, HD 44179. The heavy dust obscuration (factor ~ 40) of the central source makes this an ideal object for observing dust and molecule emissions excited by short-wavelength stellar photons.

Acknowledgements

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The flame chemistry preceding PAH formation: quantitative detection of intermediate species

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Understanding the formation of soot remains one of the challenges in combustion chemistry. The emission of potentially hazardous particulate matter from practical combustion systems receives increasing public attention because of health considerations. After several decades of research, many features of the pathways from fuel decomposition towards polycyclic aromatic hydrocarbons (PAH), via carbonaceous clusters to soot particles have been revealed, but in spite of long-standing intense collaborative research between engineers, chemists and physicists, important aspects remain unsolved or must be addressed in more detail. This is not as astonishing as it seems – soot particles with millions of carbon atoms form from organic fuels with only a few carbon atoms per molecule in some milliseconds, and in this rapid assembly process, an enormous variety of potential isomeric structures of possible intermediates is encountered.

It is accepted today that the first aromatic building blocks are of special importance in this vast reaction network, and most models of the soot formation process distinguish a molecular reaction domain – fuel decomposition, hydrocarbon oxidation, formation of PAH structures with three or four rings – from a further build-up regime where soot nuclei are formed from these templates. Thus, many recent studies have addressed the detailed reaction sequences from different fuel molecules (alkanes, alkenes, cyclic alkanes, etc.) towards benzene, naphthalene, and small PAH, and the results of these studies provide a crucial test of combustion models which attempt to simulate these reactions and the further process of particulate formation. In the past few years, we have used a combination of techniques to investigate fuel-rich laboratory flames to provide insight into the pathways of the formation of benzene and several larger aromatic molecules with molecular mass of up to 200 amu. The laminar, premixed flames of aliphatic fuels with two to five carbon atoms have been burned under reduced pressure to facilitate detailed studies of the reaction zone. Flame temperature as well as the concentrations of several small reactive intermediates has been measured with spectroscopic techniques such as laser-induced fluorescence (LIF) and cavity ring-down spectroscopy (CRDS). In situ mass spectrometric techniques have been used to determine the concentrations of larger molecular intermediates; in

particular, different ionization schemes have been applied, including electron impact, resonant multi-photon ionization (REMPI) and, most recently in a multi-laboratory collaboration, photo-ionization with synchrotron radiation. Comparison with the predictions of combustion models is underway.

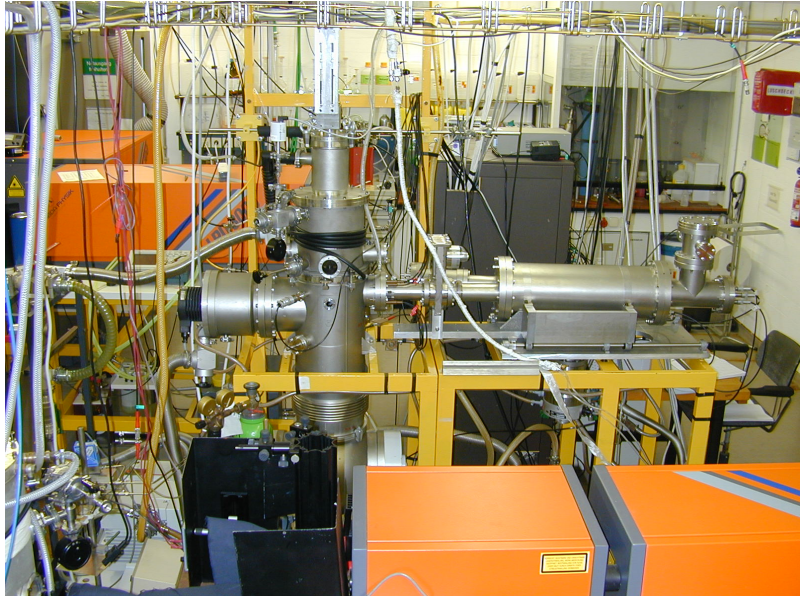


Fig. 1: REMPI experiment for combustion studies

The talk will present an overview of these studies and will highlight some examples to discuss the potential of this approach and the related problems to be solved.

Cosmic dust formation: problems - questions - desiderata

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By spotlighting basic problems of astronomical dust condensation in viewing the impressive diagnostical, theoretical, and laboratory progress in the last decades, the present status of cosmic dust formation will be addressed, essentially focusing on still open important questions and

Fig. 1: Textfeld, Formatierung: Breite 9,5 cm, Abstand vom Rand 0,5 cm
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on urgent future desiderata.

Dust formation in circumstellar environments

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Dust is formed by nearly all stellar types in their late evolutionary phases either in massive stellar outflows or following explosive mass ejections resp. stellar explosions. In most cases the ejected material is enriched with the ashes of nuclear burning processes brought to the surface by deep mixing processes or by exposing former burning zones after massive mass-loss. Cosmic dust formation therefore occurs in stellar ejecta with widely different element mixtures and very different mineral mixtures condense in the cooling flows. The most efficient dust factories in space are outflows from low and intermediate mass stars which account for most of the dust input into the interstellar medium of galaxies.

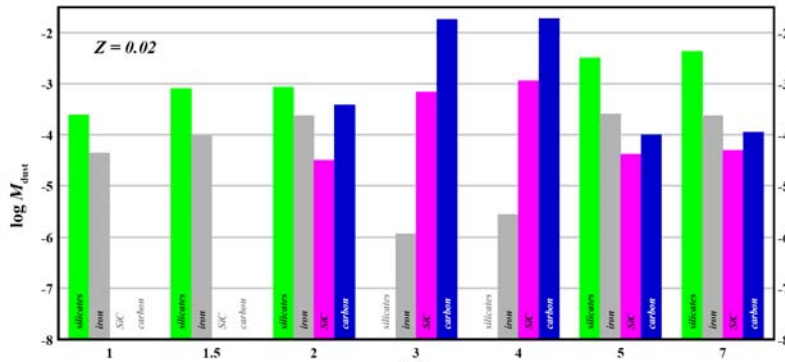


Fig. 1: Dust production (in solar masses) on the AGB by stars of different initial masses and a metallicity of $Z=0.02$. This is calculated by models for synthetic AGB evolution combined with models for the mass-loss by AGB stars and model calculations for dust formation the stellar wind. The dust formation model considers olivine, pyroxene, quartz, metallic iron, silicon carbide, and solid carbon. The mass return rate for silicates is the total production for ol+py+qu.

The talk gives an overview over the physics and chemistry of dust formation in these objects. The compositions of the mineral mixtures expected to be formed by stars of different initial masses and metallicities and results for their efficiency of dust production are discussed. Some

results for the role played by of dust of circumstellar origin for the evolution of interstellar dust and on the input of presolar dust grains into the solar system are presented.

The formation of circumstellar silicates based on new vapor pressure data for SiO

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We have measured the vapor pressure of solid SiO as a function of temperature over the range from 1200K up to 1950K in vacuo using a modified Thermo-Cahn Thermogravimetric system. Although the vapor pressure measured near 2000K is close to that predicted from the work of Schick¹ under reducing conditions, the vapor pressures measured at successively lower temperatures diverge significantly from such predictions and are several orders of magnitude lower than predicted at 1200K. We will explain the data reduction methods used to obtain the new vapor pressure data and show calibration measurements made using Palladium metal vapor in order to validate our experimental technique.

This new vapor pressure data has been inserted into a simple model for the gas expanding from a late stage star. Using the new vapor pressure curve makes a significant difference in the temperature and stellar radius at which SiO gas becomes supersaturated, although SiO still becomes supersaturated at temperatures that are too low to be consistent with observations. We have therefore also explored including the effects of vibrational disequilibrium² of SiO in the expanding shell on the conditions under which nucleation occurs. These calculations are much more interesting in that supersaturation now occurs at much higher temperatures. We note however, that both vibrational disequilibrium and the new vapor pressure are required to induce SiO supersaturation in stellar outflows at temperatures above 1000K. These new calculations represent a work in progress that will be presented to attendees to stimulate discussion of the more important variables that are likely to control grain formation in a circumstellar environment.

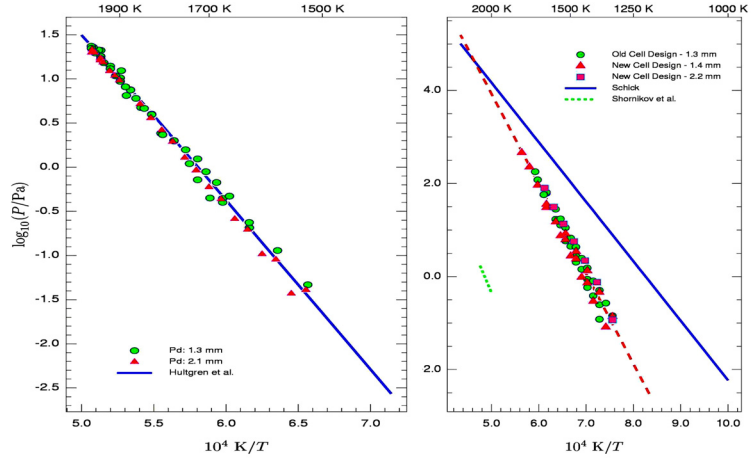


Fig. 1: Left: Vapor pressure measurements of palladium metal are presented as a function of temperature over the range from 1500K to 2000K. The symbols represent individual measurements under different experimental conditions, while the solid blue line represents the best available vapor pressure estimate for palladium metal. These data are presented to validate our experimental technique.

Right: Vapor pressure measurements of SiO are presented as a function of temperature over the range from 1300K to 1800K. The individual symbols represent measurements obtained under a wide variety of experimental conditions. The broken red line is a least squares fit through our data points. The solid blue line is the thermodynamic vapor pressure curve predicted by Schick¹. The dotted green points represent a vapor pressure measurement by Shornikov.

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Molecular clusters in astrophysical dust formation processes as link between gas phase and solid state

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The transition from a gas to solid particles, i.e. the transformation of one phase into another under non-equilibrium conditions, takes place via the formation and growth of small clusters in the gas phase. The required kinetic and thermodynamic data of such microphysical processes are in many cases rarely available. Theoretical computation is therefore often the only means to obtain at least some information about the desired quantities. Consequently, the nature and physical properties of molecular clusters possibly involved in dust formation processes from the gas phase have been studied theoretically employing computational electronic structure techniques. The properties, thus obtained, are necessary prerequisites for the study of such phase transitions in astrophysical environments such as e.g. circumstellar surroundings of cool, late-type stars, nova and supernova ejecta, or substellar atmospheres.

Implications regarding the formation of dust particles under astrophysical conditions are discussed.

Carbynoid species in large free and supported carbon clusters

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I will report about the experimental and theoretical investigation of the growth and of the structure of large isolated carbon clusters produced in a supersonic expansion by a pulsed microplasma cluster source. The absence of a significant thermal annealing during the cluster growth causes the formation of disordered structures where sp^2 and sp hybridizations can coexist for particles larger than roughly 90 atoms. Among different structures we recognize sp^2 closed networks encaging sp chains. This “nutshell” configuration can prevent the fragmentation of sp species upon deposition of the clusters thus allowing the formation of nanostructured films containing carbynoid species, as shown by Raman spectroscopy. The long-term stability and the behavior of carbyne-rich films under different gas exposure have been characterized showing different evolution for different sp configurations. Endohedral sp chains in sp^2 cages represent a novel way in which carbon nanostructures may be organized with possible implications for the behaviour of carbonaceous interstellar matter.

Formation of solids from impact-produced vapors

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Hypervelocity collisions are fundamental processes which affect the evolution of solid material in the universe. Solid material during an impact is subjected to high-temperature flash heating during its compression in a shock wave. After the release of the pressure the temperature can remain rather high to cause partial or complete vaporization of colliding material. Subsequent expansion and cooling of impact-generated vapor plumes produce condensed particles with nanometer to micron sizes. The main reason of chemical differentiation here is the selective character of volatility of rock forming elements, which can result in sufficiently different compositions of impact products (melted residua, vaporized / condensed stuff, etc.).

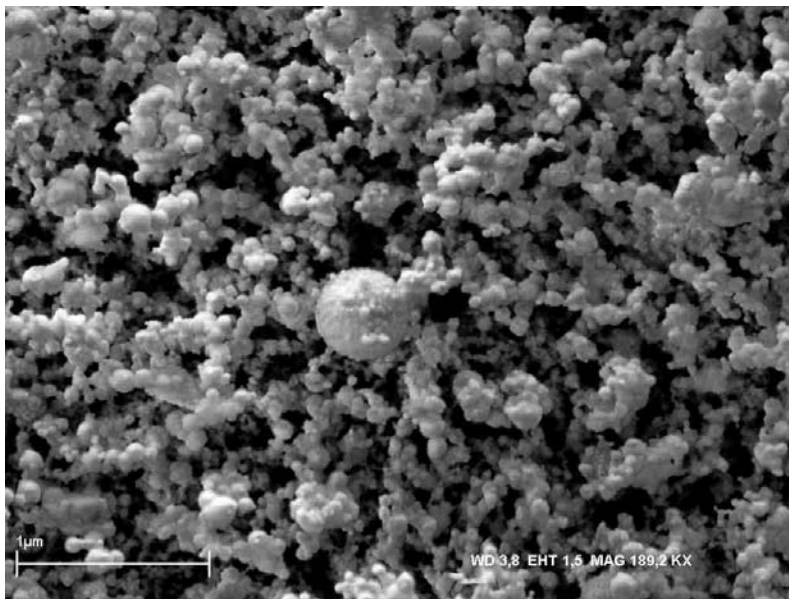


Fig. 1: A typical SEM picture of condensed particles produced in a laser pulse experiment

Behavior of siliceous systems at temperatures 3000 to 5000 K have some peculiarities, among which the most pronounced are the volatilization of elements as complex molecular clusters, which can join elements with different individual volatility, and sufficient temperature driven reduction of iron and of other siderophile elements. Siderophile elements have a noticeable trend of enrichment in the forming metallic particles. The density of impact produced vapors is high enough to provide close to equilibrium gas-solid exchange during a wide period of the vapor expansion. Surfaces of forming condensed nanoparticles provide conditions for polymerization of complex hydrocarbons from simple hydrogen- and carbon-containing gases (H_2 , H_2O , CO , CO_2 , CH_4 , etc.) inside an expanding vapor. Some organics are polymerized into a complex kerogen-like material. The process of star bursts also has some similarity to the evolution of initially high temperature and high-pressure impact-produced plumes.

Acknowledgment

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Synthesis of nanoparticles by laser pyrolysis

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Laser pyrolysis in the gas phase is a versatile and efficient method for the synthesis of nanoparticles [1]. From the interaction of the infrared radiation emitted by a CO₂ laser with a flow of molecular precursors, ultra fine particles are obtained, with sizes typically in the 10-60 nm range and a narrow size distribution. Chemical composition, structure and size of the nanoparticles are sensitive to the precursor mixture, the laser power and the gas flow. In this paper, the versatility of the process will be addressed in the case of carbon and silicon-based nanoparticles [2-10]. I will try to show how this technique is suitable to form nanoparticles model of the interstellar dust.

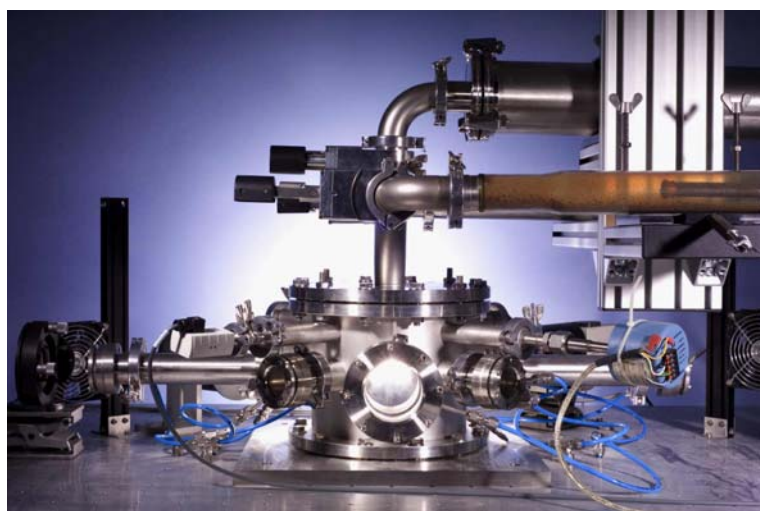


Fig. 1: Photo of the laser pyrolysis reactor

With a pure hydrocarbon precursor, aromatic nanoparticles are obtained with a structure very sensitive to the synthesis parameters. As the flame temperature in the interaction zone increases, the nanoparticles evolve drastically from poorly organized, highly hydrogenated samples toward turbostratic concentric particles of carbon. The multi-scale organi-

zation of the samples and its evolution with the synthesis parameters are quantitatively determined and correlated to infrared spectroscopy through HRTEM image analysis [2-3].

Fullerene-rich soot can be obtained when an oxygen-rich precursor mixture is pyrolysed. The production yield of fullerene is very sensitive to the C/O ratio as observed in combustion. The C₆₀ yield is comparable to the best yields found in the literature. The residence time of the reactants in the pyrolysis flame influences also dramatically the fullerene formation [4].

In addition, precursor mixtures including hetero-atoms such as nitrogen [5] or iron are shown to influence noticeably the growth of carbon nanoparticles. Nanocrystals of metallic carbide such as TiC can be formed also from the synthesis of mixed TiOC nanoparticles with very well controlled chemical composition [6]. Finally, silicon-based nanoparticles synthesis and properties will be discussed [7-10] and some perspectives traced.

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Manipulation of interstellar molecules with electric fields: the OH radical

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Getting full control over both the internal and external degrees of freedom of molecules has been an important goal in molecular physics during the last decades. Trapped samples of neutral molecules have been created by means of buffer gas cooling in a magnetic trap, by using deceleration of a molecular beam in combination with an electrostatic trap, and by pairing cold atoms to form molecules in optical or magnetic traps.

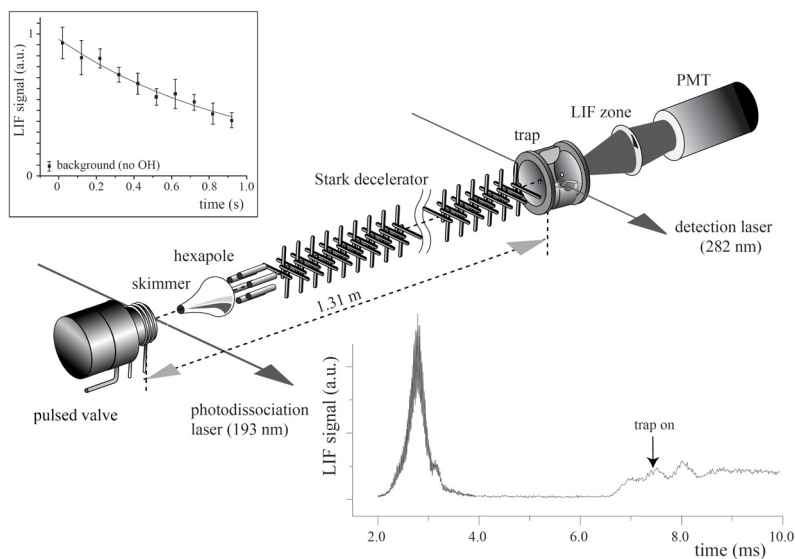


Fig. 1: Scheme of the experimental set-up. OH radicals are produced by photodissociation of HNO_3 and are cooled by collisions in the expansion region. OH radicals in the low-field seeking component of the $J = 3/2$ level are decelerated and loaded into an electrostatic trap. The depth of the trap is about 500 mK and the temperature of the trapped sample is almost an order of magnitude less. The insets show the laser induced fluorescence (LIF) intensity of the OH ($J = 3/2$) radicals at the center of the trap as a function of time after their production.

Recently, spectacular progress has been made with association of ultra-cold atoms assisted by magnetically induced Feshbach resonances, resulting in the first molecular Bose-Einstein condensates.

In this presentation I will give an overview of the various experiments that we have performed during the last few years to explore the possibilities of manipulating neutral polar molecules with electric fields. Arrays of time-varying, inhomogeneous electric fields have been used to reduce in a stepwise fashion the forward velocity of molecules in a beam [1]. With this so-called 'Stark decelerator', the equivalent of a LINear ACcelerator (LINAC) for charged particles, one can transfer the high phase-space density that is present in the moving frame of a pulsed molecular beam to a reference frame at any desired velocity; molecular beams with a computer-controlled (calibrated) velocity and with a narrow velocity distribution, corresponding to sub-mK longitudinal temperatures, can be produced. These decelerated beams offer new possibilities for collision studies, for instance, and enable spectroscopic studies with an improved spectral resolution; first proof-of-principle high-resolution spectroscopic studies have been performed [2].

These decelerated beams have also been used to load OH radicals in an electrostatic trap at a density of (better than) 10^7 mol/cm³ and at temperatures of around 50 mK [3]. Trapping of vibrationally excited OH ($v=1$) radicals has enabled a direct measurement of the infrared radiative lifetime, benchmarking the Einstein A-coefficient in the Meinel system of OH. Ground-state molecules have been trapped in a novel AC electric field trap [4], decelerated molecular beams have been injected in an electrostatic storage ring, and, using micro-structured electrode arrays, a switchable mirror for neutral molecules has been constructed and tested.

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Kinetic models applied to the chemistry of protoplanetary discs

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I will present a brief review of basic concepts in chemical modeling, and the importance of chemistry in protoplanetary disc models. I will describe the content and results of a specific kinetic model used for the primary purpose of calculating the ionization degree in a protoplanetary disc. I will discuss the implications of these results for the existence of MHD turbulence in such discs.

Detailed experimental studies of the desorption of molecules from surfaces

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For the understanding of catalytically activated reactions at surfaces the investigation of the dynamical processes are of general interest. These processes govern the associative desorption and its counterpart, the dissociative adsorption of molecules at surfaces. In recent years a joint effort of several experimental and theoretical groups has led to a detailed understanding of such reactions of hydrogen on noble and transition metals and on silicon [1,2].

For a diatomic molecule the reaction on a surface is described by at least a six-dimensional potential: the distance from the surface, the separation of the two atoms, the two rotational degrees of freedom parallel and perpendicular to the surface normal, and the x- and y- positions within the surface unit cell. Thereby the creation of electron-hole pairs and phonons in the surface is neglected. The ab initio calculation of this six-dimensional potential poses a great challenge to the theory. In addition a dynamical calculation of the motion of the atoms on this potential has to be performed before a comparison with experimental data can be made. Therefore, only in the last decade detailed theoretical investigations could be performed due to the increased computing power available.

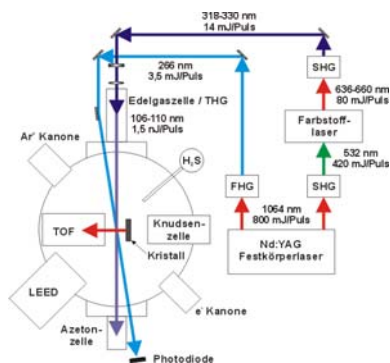


Fig. 1. Experimental set up for state-specific determination of the velocity and angular distributions.

Experimentally, we can address the problem only after the fact, i.e. after the molecule has been formed and is detected in the gas phase or a dissociative adsorption has occurred. Conclusions can be drawn from the detailed comparison with theoretical calculations. Therefore, the study of all molecular degrees of freedom accessible is necessary for both theory and experiment. Specifically, the rotational and vibrational state populations, internal state-specific velocity and angular distributions, and the influence of the spatial alignment of the rotational angular momentum yield dynamical information about the reaction.

Experimental and theoretical results are reported for the thermal desorption of H_2 and D_2 from Cu, Pd, and sulphur-covered palladium surfaces. Further, first results for laser-induced desorption of D_2 from atomically adsorbed D on Ru(0001) will be shown. Copper surfaces generally pose large barriers between 0.5 and about 1 eV for the dissociative adsorption of hydrogen molecules. In desorption this results in a high translational energy, as well as a strong population of high rotational and vibrational states. Palladium surfaces show a very different behavior, depending on the adsorption site within the surface unit cell. At bridge sites there exist no barrier at all, while at on top sites a barrier of only about 100 meV has to be overcome. On this surface a significant steering effect of slow molecules to adsorption pathways which have no barrier can be observed. Also, the potential acts on the spatial alignment of the molecules [3]. Pre-adsorption of sulphur onto a Pd surface causes a general barrier between 250 meV and more than 2.5 eV, depending upon the sulphur coverage, which dramatically changes the dynamic reaction behaviour [4,5].

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Hydrogen recombination on astrophysically relevant surfaces

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While most chemical reactions in the interstellar medium take place in the gas phase, those occurring on the surfaces of dust grains are of fundamental importance. In particular, the formation of molecular hydrogen, which is the most abundant molecule in the Universe, takes

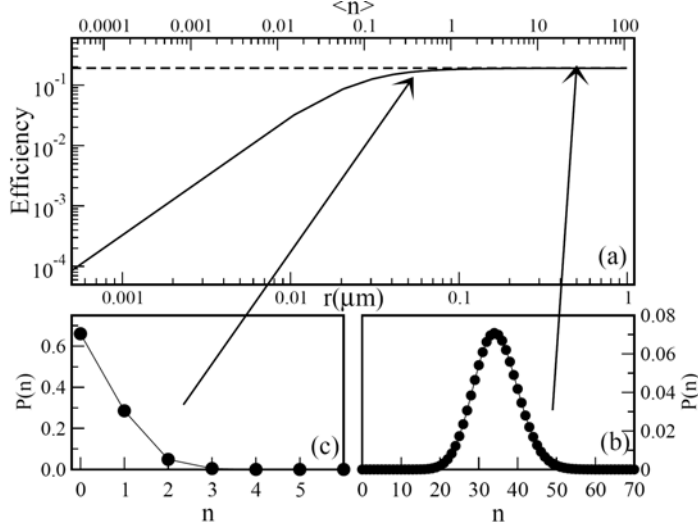


Fig. 1: (a) The production efficiency of H_2 molecules, obtained from the master equation (solid line) and from the rate equation (dashed line) vs. the grain radius for olivine grains at 10 K. Below $0.1 \mu m$, the average number $\langle n \rangle$ of atoms on a grain (upper scale) becomes smaller than 1 and the production efficiency starts to deviate from the rate equation results. The distribution $P(n)$ of the number of atoms on a grain is shown for a large grain (b) and a small grain (c). For more details see Ref. 7.

place on dust grains. Molecular hydrogen plays a crucial role in the cooling processes that enable gravitational collapse and star formation. It is also a necessary component in the reaction networks that give rise to the chemical complexity observed in interstellar clouds.

In this talk I will describe the analysis and interpretation of laboratory experiments on molecular hydrogen formation on astrophysically

relevant surfaces such as olivine, amorphous carbon [1] and amorphous ice [2], done by Vidali, Pirronello and collaborators. The analysis is based on rate equations that are appropriate for macroscopic surfaces such as those used experimentally. The implications to the interstellar medium will then be considered. The results indicate that hydrogen recombination is efficient only within a narrow temperature range between 10 and 20 K. Observations show that molecular hydrogen is abundant also in warmer environments such as photon-dominated regions, where grain temperatures may reach 45 K. Possible explanations of this apparent discrepancy will be discussed, particularly the role of chemisorption sites, porosity and temperature fluctuations.

Due to the microscopic size of the dust grains in the interstellar medium, the mean-field approximation on which the rate equations are based may not apply. In this case, one should take into account the discrete nature of the population of atomic and molecular species on the grain. I will present an approach based on the master equation, that provides correct results for recombination rates even on small grains [3,4]. Using these results, the calculation of the recombination rate constant will be presented, taking into account the size distribution of grains. The generalization to deuteration processes [5] as well as to complex reaction networks of multiple species [6] on grain surfaces will also be discussed.

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Stochastic simulation of surface reactions

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In this talk the stochastic approach to interstellar grain-surface reactions will be described. The different methods for solving the chemical master equation will be presented and various algorithms compared. Applications to interstellar chemistry problems and future directions will be discussed.

