Abstracts
Contributed papers

Isotopic segregation of molecular hydrogen on water ice surface at low temperature: importance for interstellar grain chemistry

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A first step, before studying the formation of molecules on surfaces at low temperature by recombination of atoms, is a good understanding of the adsorption / desorption mechanisms of the molecules themselves and a correct interpretation of the results of TPD (Thermally Programmed Desorption) experiments.

Experimental studies (performed on our new experimental setup "FORMOLISM") of adsorption and desorption of molecular hydrogen and deuterium on an amorphous porous solid water ice surface between 10 and 35 K reveal a very efficient isotopic segregation process. The slight difference of about 2 K in the maximum desorption temperature between the two isotopes leads to a preferential coverage of the more bounding sites of the ice surface by D2, independent of the gas deposition process history.

A statistical model which takes into account thermodynamic aspects of adsorption sites as well as isotopic competition, is proposed to understand the enhancement of deuterium fractionation. Model results are in very good agreement with the experimental ones.

This mechanism could play a key role in chemistry at the surface of interstellar dust grains. It could in particular explain the isotopic enrichment observed in some dark clouds.

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State specific probing of H_3^+ using overtone excitation

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H_3^+ and its isotopomers can be considered as the simplest polyatomic ions, the differences between individual rotational energy levels are relatively large and at cryogenic temperatures just a few states are populated. Because of that they are obvious candidates to study the influence of internal excitation on their reactions with electrons and neutrals. The dependence of the electron recombination rate of H_3^+ on rotational excitation has already been subject to theoretical calculations [1]. Prior to experimental studies the problem of "in situ" identification of ions in particular rotational states has to be solved. We are using near IR diode lasers (~1.4 μm) to measure absorption spectra and to monitor the internal state distribution and the kinetic energy of ions stored in a low temperature 22-pole RF ion trap [2]. In addition we are using the CRDS technique to measure absorption spectra and the recombination rate of H_3^+ ions in afterglow experiments. In the 22-pole RF trap, where we are dealing with just a few thousand trapped ions, standard absorption techniques are not sensitive enough. Therefore to obtain absorption spectra laser-excited ions are detected by a proton transfer reaction with a monitor gas added to the ion trap. The product ions are then detected with a mass spectrometer. This way nearly all absorption events are recorded (Laser induced reaction - LIR). Using LIR we have studied stored H_3^+ ions and we have found that the absorption of D_3^+ is too low to be studied by this method. Investigation of DH_2^+ and HD_2^+ using H_2 as a monitor will be discussed also.

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Supersonic Plasma Expansions and Molecular Laboratory Astrophysics

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Recent progress with sensitive optical spectroscopic techniques and state-of-the-art supersonic plasma expansions allows the detection of electronic gas-phase spectra of molecules that play a role as reactive intermediates in interstellar chemistry. A large number of species has been identified meanwhile in the laboratory and the quality of the spectra is such that a direct comparison with astronomical data becomes possible [1-3].

In this presentation we discuss the potential of supersonic plasma expansions into new directions. A time-of-flight experiment has been performed to study mass spectrometrically the variety and the conditions under which molecular radicals, anions and cations are formed in high energetic and non-thermal plasma [4]. In addition, it is shown that plasma expansions give direct access to vibrationally and electronically excited states without a serious loss in rotational cooling [4,5]. This is of particular importance in view of recent interest to use excited states for astronomical mapping.

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One- and two-photon processes in the OH radical

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The OH radical has been of theoretical and experimental interest for more than five decades now, mainly because of it's importance in astronomy, atmospheric chemistry, and combustion processes. We present results of two combined experimental and theoretical studies.

The first study was done in collaboration with the groups of D. Parker (dpt. of Molecular and Laser Physics, University of Nijmegen) and M. Lester (dpt. of Chemistry, University of Pennsylvania). In this project we studied (2+1) REMPI $(D,3)^2\Sigma^- \leftarrow X^2\Pi$ of rotationally cold, state-selected, aligned OH molecules and we were able to model the (2+1) REMPI spectrum.

We also studied the lifetimes of the Rydberg $^2\Sigma^-$ states, including the effect of spin-orbit, gyroscopic, and spin-electronic coupling [1][2]. We show that (homogeneous) predissociation processes determine the lifetime of the rotationally cold Rydberg $^2\Sigma^-$ states of OH and OD.

The second study was done in collaboration with the group of Gerard Meijer (Molecular Physics Department, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin), and involves the calculation and measurement of the liftime of vibrationally excited $OH(X^2\Pi)$ states [3]. We get a good agreement between experimental and theoretical radiative lifetimes.

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Dissociative recombination sulfur-containing interstellar ions

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Branching ratios and absolute cross sections have been measured for the dissociative recombination of three important interstellar sulfur-containing ions, namely HCS^+, COS^+ and SO_2^+. The CRYRING ion storage ring located at the Manne Siegbahn Laboratory in Stockholm has been used for these investigations. In the case of HCS^+, fracture of the C-S bond is predominant (81 %), with the production of H + CS accounting for the remainder (19 %). With SO_2 the branching ratio of the $SO_2^+ + e^- \rightarrow SO + O$ channel amounts to 61%, whilst the three body break-up $SO_2^+ + e^- \rightarrow S + 2\ O$ accounts for the remaining 39 % of the total reaction. Concerning COS^+, the channel leading to CO + S (83 %) dominates, whereas the other exoergic pathways leading to CS + O (14 %) and C + SO (3 %) are of lesser importance.

The cross section of the reactions could be fitted by the expressions $\sigma = 1.2 \times 10^{-15}\ E^{-0.96\pm0.02}\ cm^2$, $\sigma = 4.47 \times 10^{-16}\ E(eV)^{-1.14}\ cm^2$ and $\sigma = 1.41 \times 10^{-15}\ E(eV)^{-1.11}\ cm^2$ for HCS^+, COS^+, and SO_2^+, respectively. These lead to thermal reaction rates of $k(T) = 9.7 \times 10^{-7}\ (T/300)^{-0.57}\ cm^3\ s^{-1}$, $3.5 \times 10^{-7}\ (T/300)^{-0.62}\ cm^3\ s^{-1}$, and $4.6 \times 10^{-7}\ (T/300)^{-0.52\pm0.02}\ cm^3\ s^{-1}$ for HCS^+, COS^+ and SO_2^+, respectively.

The impact of the newly found – and often counter-intuitive – branching ratios on the predictions of models of different astronomical environments are discussed. For example, we use these data to investigate the HCS^+/CS abundance ratio in dark clouds and obtain that the models using the UMIST and Ohio State University databases have even more difficulty in accounting for the large observed ratio. The rate and branching ratio found for the dissociative recombination of SO_2^+ is found to be in line with theories that hold this process responsible for the disappearance of this ion in the ionosphere of Jupiter's satellite Io during eclipses.

Nano-diamonds in the Universe

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The first direct evidence for nano-diamonds in space came from meteorites. Laboratory analyses on fine-grained diamond residues from primitive meteorites have shown that nano-diamonds represent the most abundant form of stardust preserved in meteoritic samples. The meteoritic nano-diamonds carry isotopic anomalies, which indicate the presents of several groups of diamonds possible with an origin in different types of stellar environments. In order to identify the sites of formation observationally, we have measured the optical properties of the meteoritic nano-diamonds [1]. Based on these observations [2] have shown that nano-diamond dust is successful in reproducing the 1000 Å break as well as the far-UV rise seen at shorter wavelengths in distant quasars. We are also currently using the optical properties of nano-diamonds in our models of the wind properties of late-type stars [3].

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Molecular hydrogen formation under interstellar conditions - from PDRs to dense clouds.

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The most abundant molecule in the interstellar medium, molecular hydrogen, is believed to be formed on the surface of interstellar dust grains. Observations indicate that molecular hydrogen formation takes place under a wide range of interstellar conditions, e.g. in the cold interior of dense interstellar dust and molecular clouds, in diffuse interstellar clouds and in the warmer and more hostile environment of photo dissociation regions (PDRs). The relatively broad range of gas and dust grain temperatures found in these different regions imply that a number of different surface chemical processes must contribute to molecular hydrogen formation. Recent laboratory experiments simulating molecular hydrogen formation under varying interstellar conditions and on dust grain surface analogues indicate what these different processes are. The experiments show that under the conditions prevailing in dense clouds, recombination of weakly bound, physisorbed hydrogen atoms on ice covered dust grain surfaces should be efficient [1,2], in diffuse cloud regions recombination of more strongly bound physisorbed atoms on silicate and carbon surfaces, maybe involving atoms bound at surface defects is believed to be relevant [3] and in PDRs, recombination of atoms bound at defects and in chemisorbed states is suggested as the prevailing mechanism [4, 5].

We present results from recent experiments on molecular hydrogen formation on interstellar dust grain analogues under conditions relevant to both dense interstellar clouds and PDRs. Specifically, we present results on molecular hydrogen formation on amorphous ice surfaces and from chemisorbed states on graphite surfaces. We address the issues of recombination efficiency, the influence of surface morphology [1,6] and the distribution of the 4.5 eV of recombination energy liberated in the formation process between the various degrees of freedom, i.e. between translational and internal energy of the formed molecule and heating of the grain surface.

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Evaporation and aggregation of clusters of polycyclic aromatic hydrocarbons of astrophysical interest

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Polycyclic Aromatic Hydrocarbons (PAHs) have been proposed as the carriers of the aromatic infrared bands observed in many places of the interstellar medium. In order to better characterize the chemical nature of these species, we have analyzed spectro-imagery data obtained with the camera CAM on board of the Infrared Space Observatory, applying the singular value decomposition method. This work [1] strongly suggests that PAHs are produced by photoevaporation of very small carbonaceous grains which could be PAH clusters. This model is at the origin of the following theoretical work.

We have performed a parallel tempering Monte Carlo search of the structures with lowest energy of PAHs clusters ranging from two to thirty molecules [2]. We found evidence that stacking the PAH molecules generally yields the most stable structures. After some critical size, one-dimensional pattern is replaced by two and three-dimensional growth, again with small stacks as the building block.

Concerning the formation of these clusters, we have studied the collision of a PAH molecule with a PAH cluster. The resulting excited cluster can then loose one or more molecules. The emission of infrared photons is another channel for relaxation. The comparison of the evaporation rate of these clusters obtained with a statistical method with the infrared emission rate of PAH molecules allows to characterize the environments favourable to the PAH clusters growth.

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The role of dust in the deuteration and depletion of molecules in pre-stellar cores

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We present the results of model calculations of the chemistry in collapsing prestellar cores. We take account of both depletion on to dust grain surfaces and grain coagulation, with the associated reduction in grain surface area. We consider the ortho/para abundance ratio of molecular hydrogen and related species and of their deuterated counterparts. The calculations show that extreme assumptions concerning the rate of grain coagulation are required to significantly influence the rate of depletion of species containing heavy elements, given that current observations indicate that CO depletes rapidly, on the order of the free-fall time.

We find that, under conditions of high heavy element depletion, the major ion is either H^+ or H_3^+ (or, equivalently, one of its deuterated isotopes), depending on the grain size distribution. Present observations of H_2D^+ suggest that grain dimensions in observed prestellar cores, such as L1544, remain below 0.1 μm. However, only ortho- H_2D^+ is observed currently, and so the ortho/para ratio for this species must be calculated. We address also one of the puzzles posed by the nitrogen chemistry in such cores: the observation of nitrogen-containing species in high density cores in which compounds containing other heavy elements have already depleted on to grains. We consider the possibility that the sticking coefficient (adsorption probability) of atomic nitrogen may be lower than for other species. If the sticking coefficient for atomic oxygen is also low, NO is predicted to have a high abundance simultaneously with ammonia.

Emission Bands of the Red Rectangle Nebula

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The Red Rectangle is a remarkable object comprising a binary star, an oxygen-rich circumbinary disk and an extended bipolar carbon-rich nebula. It displays a very wide range of spectroscopic features including infrared (UIR/PAH and silicate) emission bands, unidentified optical (electronic) emission bands that may originate in PAH-based molecules, and a broad 'extended red emission' (ERE) feature. It is a superb astronomical 'laboratory' which holds the potential for revealing the exact chemical nature of the carriers of the 'unidentified' IR (UIR) emission bands, ERE and, possibly, some of the optical diffuse interstellar absorption bands. These spectroscopic signatures are seen in many astrophysical sources, but widely-accepted precise assignments at a ‘molecular’ level have proved elusive. Assignments would undoubtedly provide new probes of astrophysical conditions and processes.

We review here recent results and challenges presented by these observations, particularly in the context of laboratory experiments that could usefully be conducted.

Discovery of Small-Scale-Structure in the Large Molecule/Dust Distribution in the Diffuse ISM

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There is mounting evidence that far from being homogeneously distributed, interstellar matter can have a clumpy or filamentary structure on the scale of 10s to a few 1000s of AU and which is commonly described as small scale structure (SSS). Initially confined to VLBI H I observations and H I observations of high-velocity pulsars, evidence for SSS has also come indirectly from molecular radio studies of e.g. HCO^+ and infrared absorption by H_3^+. Much of the recent data on SSS has been obtained through optical/UV detection of atomic and diatomic molecular lines.

Is there small scale structure in the large molecule/dust distribution? While this question could in principle be explored by measuring differences in the interstellar extinction towards the components of binary stars, in practice this would be difficult. Rather we chose to investigate this by recording very high signal-to-noise spectra of diffuse interstellar absorption bands. Although the carriers remain unidentified, the diffuse bands are generally considered to be tracers of the large molecule/dust distribution and scale well with reddening.

Using the Anglo-Australian Telescope we have made UCLES observations of pairs of stars with separations ranging between 500 and 30,000 AU. The signal-to-noise achieved was up to 2000, thus allowing variations in central depth of less than a few tenths of a percent to be discernible. Striking differences in diffuse band strengths for closely spaced lines of sight are found showing clearly that there exists small-scale-structure in the large molecule/dust distribution. This opens a new avenue of diffuse band research in its own right and provides a rigorous test for models and theories of diffuse band carrier structure and behaviour.

High-resolution Spectroscopy of Emission Bands of PAHs and Nanodiamonds in Extended Objects

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The UIR bands are found in a wide variety of sources including H II regions, PNe, post-AGB stars, YSOs, the diffuse ISM, external galaxies and active galactic nuclei, and are normally attributed to polycyclic aromatic hydrocarbons (PAHs). Apart from the intrinsic importance in determining the chemical form of interstellar matter and its role in astrophysical processes, there are much wider astronomical implications; *e.g.* the use of the UIR features as a probe of external galaxies. A few objects have recently been shown to exhibit IR emission from nanodiamonds.

A high-resolution study has been undertaken of near-infrared emission (3.0 - 3.6 μm) from a variety of objects (Elias 1, the Orion Bar and the CS region of HD 44179), and additionally of the 11.3 μm emission feature in the Red Rectangle nebula. The aim has been to investigate the spatial intensity variations of the bands within these objects and to map the evolution of their spectral profiles. This provides insight into the nature of the carriers and is a probe of the physical and chemical properties of the circumstellar and nebular environments.

The Herbig Ae/Be star Elias 1 is an interesting case as it exhibits the rare nanodiamond emission at 3.4/3.5 μm in addition to 3.3 μm PAH emission which is found to be more extended. The Red Rectangle is also unusual in that the UIR emission is very strong in the carbon-rich nebula whereas the silicate emission appears to be confined largely to the circumbinary disk. This chemical spatial separation must reflect different epochs of mass-loss. The 11.3 μm emission feature develops substructure as a function of offset in a manner analogous to the development of the 3.3 μm band.

A Computational Study of Small Iron Containing Aromatic Hydrocarbons

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Polycyclic aromatic hydrocarbons (PAHs) are an abundant component of interstellar matter. Recent observations show that PAHs exist as free molecules in FUV-irradiated regions and are in a more condensed form inside molecular clouds. One possibility is that they are included in organometallic grains of the Fe-PAH-type. The presence of such species has been proposed at the beginning of the 90's but little is still known on their physical and chemical properties.

We present here the first results of a theoretical study on small charged and neutral Fen-benzene and Fen-coronene systems using a density functional approach (B3LYP/6-31G(d)). We discuss structural and energetic properties as well as vibrational frequencies.

Dynamics of hydrogen molecule formation on graphite surfaces

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The understanding of hydrogen molecule formation on bare carbonaceous grain surfaces at the temperatures found in the photodissociation regions (PDR) of interstellar molecular clouds has been boosted by the discovery that hydrogen atoms with high translational energies (>2000 K) can bind to graphite surfaces in the chemisorption state [1]. In the same study it was found that this state is stable at room temperature on a laboratory time scale, and that hydrogen molecules desorb recombinatively with a first order kinetics mechanism when the surface is heated.

We have performed laboratory studies on the dynamics and kinetics of hydrogen molecule formation on graphite surfaces in the chemisorption regime. In our laser assisted associative desorption (LAAD) experiments [2] we find a high translational energy distribution for the desorbing molecules, as a result of the strong exothermicity of the recombination reaction. We will also present angular distribution measurements, including desorption from defect sites. Isotope effects have also been studied. All results will be discussed in terms of the energy barriers involved and will be compared to recent ab-initio calculations [3], suggesting that the D (H) atoms recombine from next nearest adsorption sites on top of carbon atoms, which pucker out of the surface plane by several tenths of an Ångstrom [1].

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Reactions of aromatic hydrocarbon ions with H2 and N2 molecules

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The ionic chemistry of benzene and polycyclic aromatic hydrocarbons has attracted great interest from research aimed at understanding reaction mechanisms in various ionized environments (e.g. laboratory and industrial plasmas, combustion systems, interstellar medium). An example, in the field of planetary ionospheres, is given by the recent discovery of benzene in the upper atmosphere of Titan by the Cassini probe. In the recent past we have studied the reactions of phenylium $C_6H_5^+$ and naphthylium $C_{10}H_7^+$ ions with H_2 and D_2 [1,2]. Cross sections as a function of collision energy have been measured for several reaction channels in a tandem mass spectrometer equipped with a RF octopole scattering cell. Experimental results, supported by DFT calculations, have shown that for both ionic systems, the reaction pathway proceeds via the formation of a stable intermediate complex of σ type geometry, with a significant mobility of hydrogen atoms along the rings.

Recently we have studied the plasma chemistry of benzene-N_2 mixtures. The mass spectra from an atmospheric pressure corona discharge plasma fed with a benzene-N_2 mixture show the presence, besides the expected main peak due to the benzene radical cation, of other abundant peaks attributable to reactions between benzene and air molecules (e.g. oxygenated species $C_6H_6O^+$ at m/z=94, nitrogen containing species at m/z=105, benzene dimer at m/z=156, and benzene-oxidized benzene adduct at m/z 171). We have focused our attention on the production of the ion at m/z=105 with molecular formula $C_6H_5N_2^{+.}$ The identification of such ion as benzenediazonium ion is supported by measurements carried out using isotopically labelled reactants, and by MS-MS experiments performed in an ion-trap analyzer. To elucidate the mechanism whereby $C_6H_5N_2^+$ can be produced in the plasma, we have investigated a series of possible ion-molecule reactions in the tandem mass spectrometer. We have found that, in analogy with the H_2 case, the addition reaction of the $C_6H_5^+$ ion with N_2 is responsible for the production of $C_6H_5N_2^+$.

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In situ NEXAFS characterization of sp-rich cluster assembled carbon film

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Linear carbon chains with sp coordination (also known as carbynoid structures) represent an elusive form of carbon interesting for both nanoscience and astrophysics. Although many physical and chemical routes have been proposed to synthesize carbynoid structures both in the solid state and in the gas phase, stabilizing molecular groups have always been used to avoid interchain crosslinking.

Recently we have demonstrated that it is possible to synthesize by supersonic cluster beam deposition an sp-rich pure carbon system. This has been shown by Raman spectroscopy characterization, which is a very sensitive technique to detect sp-chains presence in a carbon system, but that unfortunately does not allow to determine the fraction of the film consisting in sp carbon.

For this reason we have developed a versatile apparatus CESYRA (Cluster Experiments with Synchrotron Radiation) that can be used for in situ inner-shell X-ray absorption spectroscopy of cluster assembled films. As well as Raman spectroscopy, Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy is an effective technique for identifying sp-hybridised carbon atoms. NEXAFS has the further advantage of enabling an evaluation of the sp fraction, even though in an amorphous system the sp contribution could be partially concealed by the prominent sp^2 peak.

Combining Raman and NEXAFS characterization we have thus been able to estimate the content of sp species in the in situ grown nanostructured carbon films. This result opens new perspectives in the understanding of the structure of nanostructured carbon films deposited by supersonic cluster beam deposition, and sheds new light on the nature of the precursor carbon clusters.

In this poster we also present the configuration of CESYRA for performing NEXAFS measurements on free clusters.

Probing the potential energy surface of OH radical reactions by photoelectron photofragment coincidence (PPC) spectroscopy

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Reactions of the hydroxyl radical (OH) play a central role in combustion chemistry, atmospheric chemistry and other reactive environments like the inner magnetosphere of Saturn.[1] For a detailed understanding of the reactions involved in these complex environments, the potential energy surfaces which govern the kinetics and dynamics of the competing reactions have to be known. Photodetachment from hydrogen bonded anions of the type AHB^- provides a route to the exploration of the transition state region for the corresponding neutral bimolecular reactions.[2] Photoelectron-photofragment coincidence (PPC) spectroscopy can extend the knowledge about the dynamics in the transition state significantly by allowing characterization of the entire dissociative photodetachment (DPD) event. In this poster we present a photoelectron photofragment coincidence study of the three following reactions:

$$\begin{array}{rcccl} OH + F & \leftarrow & O\text{-}H\text{-}F & \rightarrow & O(^3P) + HF \\ OH + OH & \leftarrow & HO\text{-}H\text{-}O & \rightarrow & H_2O + O\ (^3P) \\ OH + H_2O & \leftarrow & HO\text{-}H\text{-}OH & \rightarrow & H_2O + OH \end{array}$$

Comparison of the PPC spectra shows an adiabatic separation of the neutral fragments subsequent to photodetachment for all three systems and in the case of OHF^- an additional non adiabatic dissociation.[3] The data reveal vibrationally resolved product translational energy distributions. Examination of the translational energy release between the neutral products reveals a dependence on the product vibrational state. For the interpretation of the obtained observables, detailed quantum dynamics calculations are needed which include all product energies of the DPD event.

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Probing the carbonaceous particles within an acetylene-rich flame

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The mid-infrared emission bands ubiquitously observed in interstellar space have since long been recognized to involve hydrocarbonated aromatic material. It is now widely accepted that these interstellar "nanograins" should have sizes intermediate between those of the PAHs easily accessible to laboratory studies and of the "standard" interstellar grains (ca 50 nm). The nanometer size is related to their capability of being transiently heated upon absorption of UV starlight.

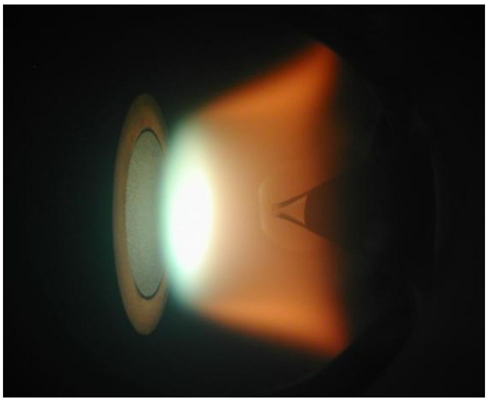

Fig. 1: View of a premixed acetylene-rich low-pressure laminar flame from a flat burner (left). The flame is sampled at a given location with the quartz cone seen on the right hand side.

We will describe the preliminary results obtained with a new experimental set-up aimed at the formation of carbonaceous nanoparticles. The strategy consists to use reactive media to prepare a whole ensemble of chemically related compounds and to control their chemical composition and the growth of the particles. We have used in particular as reactor the flame shown in Fig. 1. When operated under low-pressure conditions, the spatial development of the flame allows us to sample its content at various stages of the particles growth. Analysis has so far been made by transmission spectroscopy of thin film deposits using an infrared microscope.

The excitation of extended red emission in interstellar dust

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The carrier of the dust-associated photoluminescence process causing the extended red emission (ERE) in many dusty interstellar environments remains unidentified. Several competing models are more or less able to match the observed broad, unstructured ERE band. We constrained the character of the ERE carrier further by determining the wavelengths of the radiation that initiates the ERE. Using the imaging capabilities of the Hubble Space Telescope, we have resolved the width of narrow ERE filaments appearing on the surfaces of externally illuminated molecular clouds and compared them with the depth of penetration of radiation of known wavelengths into the same cloud surfaces. We identified photons with wavelengths shortward of 118~nm as the source of ERE initiation, not to be confused with ERE excitation, however. There are strong indications from the well-studied ERE in the Red Rectangle nebula and in the high-$|b|$ Galactic cirrus that the photon flux with wavelengths shortward of 118 nm is too small to actually excite the observed ERE, even with 100\% quantum efficiency. We conclude, therefore, that ERE excitation results from a two-step process. The first step , involving far-UV photons with E > ~10.5 eV, leads to the creation of the ERE carrier, most likely through photo-ionization or photo-dissociation of an existing precursor. The second step, involving more abundant near-UV/optical photons, consists of the optical pumping of the previously created carrier, followed by subsequent de-excitation via photoluminescence. The latter process can occur many times for a single particle, depending upon the lifetime of the ERE carrier in its active state. While none of the previously proposed ERE models can match these new constraints, we note that under interstellar conditions most polycyclic aromatic hydrocarbon (PAH) molecules are ionized to the di-cation stage by photons with E >$ 10.5 eV and that the electronic energy level structure of PAH di-cations is consistent with fluorescence in the wavelength band of the ERE. Therefore, PAH di-cations deserve further study as potential carriers of the ERE.

Based on observations made with the NASA/ESA Hubble Space Telescope, obtained at the Space Telescope Science Institute, which is operated by the Association of Universities for Research in Astronomy, Inc., under NASA contract NAS 5-26555. These observations are associated with program #9471.

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H_3^+ studies using near IR lasers

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We report application of near infrared diode laser for H_3^+ studies. Two different setups were used: The first experiment is using a near infrared continuous wave cavity ring-down absorption spectrometer (cw-CRDS). The spectrometer works on the second overtone transitions of H_3^+. Measured absorption lines broadening and population of states allow us to determine ion number density and ion temperature [1]. In this set-up the H_3^+ ions are formed in plasma generated by microwave pulses. From measured H_3^+ absolute number density the recombination rate coefficient in H_3^+ dominated plasma was determined. We have used several absorption lines for these measurements and varied temperature and pressure of a buffer gas and H_2. Present measurements of recombination rate coefficient are in agreement with our previous data obtained in SA and FALP experiments [2].

The second experiment the details of which are described in a separate poster, probes cold trapped ions using Laser Induced Reactions (LIR) [3].

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State specific laser probing of stored ions by combining a 4K-22PT with a molecular beam

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Since the first development of low temperature ion traps, a variety of methods have been developed to characterize in detail the stored ions.[1] Chemical reactions such as clustering or near thermo-neutral processes such as isotope exchange can be used as a "thermometer", provided that the specific rate coefficients $k_i(T)$ are known. More detailed information can be obtained if one uses laser based methods. Some aspects of the laser-trap combination have been summarized recently.[2] A recent application [3], the characterization of H_3^+ via proton transfer to Ar, is described in a separate contribution. In general the spectral resolution is sufficient to record ion velocity distribution via the Doppler profile while the determination of the actual population of low lying states is not straight forward.

All systems studied so far (N_2^+, $C_2H_2^+$, H_3^+, CH_5^+) suffered from the fact that the gas used for chemical probing (Ar, CO_2) was condensing on the walls restricting the temperature range. In this contribution an experimental setup is described in which a well-skimmed effusive or supersonic molecular beam passes axially through a low temperature (5 K) multi-electrode rf trap. In this way the neutrals interact only with the trapped ions but not with the cold walls. This will allow us, for example, to follow the thermalization of H_3^+ or H_2D^+ in n-H_2 or p-H_2 down to a few K. A special aspect of the new arrangement is the dedicated use of scattering dynamics some aspects of which have been described in Ref. 4. The potential of the method will be illustrated with chemical probing of cold CH_5^+ ions via resonant proton transfer to a fast CH_4 beam.

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Dust production by AGB stars

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There is a well known 30 micron feature in spectra of many C-stars, post AGB stars and PNs. This strong emission is most likely caused by MgS dust grains. However, modelling of condensation of MgS in sufficient quantities is difficult because of its low temperature of condensation. The posibility is investigated that MgS condenses on some kind of precursor dust, which condenses at significant higher temperatures.

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Asymptotic calculation of outer portion of the potential energy surfaces for the reaction $O(^3P_j)+OH(^2\Pi_\Omega) \rightarrow O_2 + H$

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For low collision energies, the reaction $O(^3P_j) + OH(X^2\Pi_\Omega) \rightarrow O_2 + H$ proceeds via a long-lived complex. Cross section and rate coefficient for the complex formation are determined by the outer part of the potential energy surfaces that correlate with the fine-structure components of the reagents.

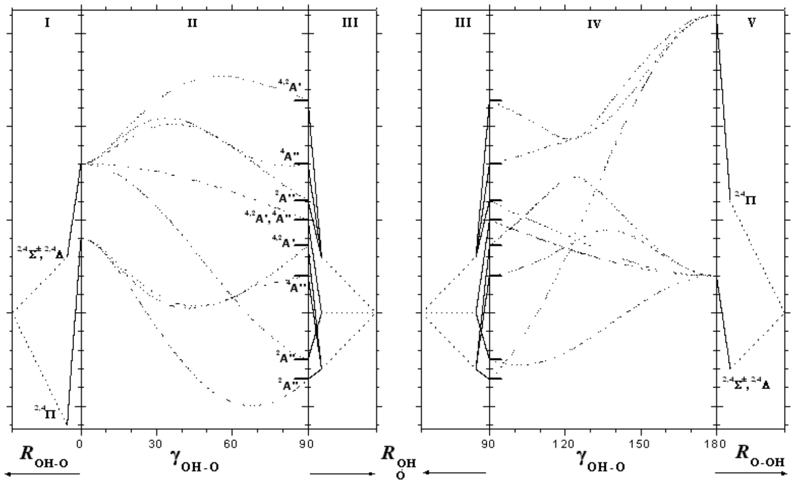

Fig. 1: Correlation diagram/pilot asymptotic calculations of electronic PES of O-OH system for linear and perpendicular approaches (distance R) joint by a circular path (angle γ). Spin-orbit coupling is ignored (hence 12 electronic states), and only the leading terms of interaction are taken into account (dipole-quadrupole, dashed lines, and dipole-quadrupole plus exchange of the σ-σ type, full lines). The degeneracy of some PES in the bent configuration is due to the neglect of other interaction terms

We have calculated 18 PES (each corresponding to a Kramers doublet) taking into account the following interaction terms: electrostatic interaction via quadrupole of O atom with dipole, quadrupole and octupole of OH (R^{-4}, R^{-5}, R^{-6} dependence), dispersion interaction (R^{-6}) and asymptotic exchange interaction (roughly exponential in R). The spin-orbit coupling is assumed to be unaffected by the interfragment interaction. If the spin-orbit coupling is ignored, the minimum energy path for the complex formation corresponds to mutual dipole-quadrupole attraction in the linear O + HO arrangement until the partners begin to feel the exchange repulsion due to the overlap of doubly-filled *p*-orbital of O with doubly-filled 3σ orbital of OH (panel I, Fig.1). This repulsion is then lowered by the rotation of OH and can be made even insignificant if OH begins to rotate earlier than shown in Fig.1. In addition, rotation of OH increases the attractive exchange interaction between an electron from the triplet pair of oxygen in the ^3P state and the unpaired electron of OH that occupies the outer 1π orbital of OH (panel II). On the other hand, in perpendicular approach the fragments encounter no barrier though the dipole-quadrupole attraction is weaker (panel III). We associate a minimum in the lowest $^2A''$ state, (panels II, III and IV) with the entrance to the potential well in the ground electronic state of the O_2H complex. Along these paths, there are several regions of substantial non-adiabatic coupling between the states of the same multiplicity and reflection symmetry. If the spin-orbit interaction is included, the situation becomes more complicated. Along the minimum energy path the spin-orbit coupling in O and OH will be partly destroyed due to the coupling of the orbital angular momenta to the collision axis. This recoupling results in the appearance of additional regions of non-adiabatic interaction. The results reported here provide the input data for the dynamical/statistical calculations of the kinetic attributes of the title reaction.

Infrared Bands of $CaCO_3$ and $CaMg[CO_3]_2$ at Low Temperatures

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Carbonates, especially calcite ($CaCO_3$) and dolomite ($CaMg[CO_3]_2$) have repeatedly been suggested as carriers of stardust emission and absorption bands. However, the band assignments proposed so far were mainly based on room temperature powder transmission spectra of the respective minerals. We have derived the IR optical constants of calcite and dolomite from polarized reflectance spectra -- measured both at room temperature and at cryogenic temperatures (200K, 100K and 10K) -- and calculated small particle spectra from them.

We have studied the following changes in the properties of calcite and dolomite bands with decreasing temperature: (1) band shift towards smaller wavelengths; (2) increase of the band strengths; (3) decrease of the bandwidths.

Our work may serve as a basis for finding out for which grain shapes and temperatures - if at all - the current astronomical band assignments to carbonates can be maintained.