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Abstracts

Formation of the acenaphthylene cation as a common C2H2-loss fragment in dissociative ionization of the PAH isomers anthracene and phenanthrene

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Polycyclic aromatic hydrocarbons (PAHs) are thought to be a major constituent of astrophysical environments, being the carriers of the ubiquitous aromatic infrared bands (AIBs) observed in the spectra of galactic and extra-galactic sources that are irradiated by ultraviolet (UV) photons. Small (2-cycles) PAHs were unambiguously detected in the TMC-1 dark cloud, showing that PAH growth pathways exist even at low temperatures. The processing of PAHs by UV photons also leads to their fragmentation, which has been recognized in recent years as an alternative route to the generally accepted bottom-up chemical pathways for the formation of complex hydrocarbons in UV-rich interstellar regions. Here we consider the C12H8+ ion that is formed in our experiments from the dissociative ionization of the anthracene and phenanthrene (C14H10) molecules. By employing the sensitive action spectroscopic scheme of infrared pre-dissociation (IRPD) in a cryogenic ion trap instrument coupled to the free-electron lasers at the FELIX Laboratory, we have recorded the broadband and narrow line-width gas-phase IR spectra of the fragment ions (C12H8+) and also the reference spectra of three low energy isomers of C12H8+. By comparing the experimental spectra to those obtained from quantum chemical calculations we have identified the dominant structure of the fragment ion formed in the dissociation process to be the acenaphthylene cation for both isomeric precursors. Ab initio molecular dynamics simulations are presented to elucidate the fragmentation process. This result reinforces the dominant role of species containing a pentagonal ring in the photochemistry of small PAHs.

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Discovery of interstellar NC4NH+: dicyanopolyynes are indeed abundant in space

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The previous detection of two species related to the non polar molecule cyanogen (NCCN), its protonated form (NCCNH+) and one metastable isomer (CNCN), in cold dense clouds supported the hypothesis that dicyanopolyynes are abundant in space. Here we report the first identification in space of NC4NH+, which is the protonated form of NC4N, the second member of the series of dicyanopolyynes after NCCN. The detection was based on the observation of six harmonically related lines within the Yebes 40m line survey of TMC-1 QUIJOTE. The six lines can be fitted to a rotational constant B = 1293.90840 +/- 0.00060 MHz and a centrifugal distortion constant D = 28.59 +/- 1.21 Hz. We confidently assign this series of lines to NC4NH+ based on high-level ab initio calculations, which supports the previous identification of HC5NH+ by Marcelino et al. (2020) from the observation of a series of lines with a rotational constant 2 MHz lower than that derived here. The column density of NC4NH+ in TMC-1 is (1.1 +1.4 -0.6)e10 cm-2, which implies that NC4NH+ is eight times less abundant than NCCNH+. The species CNCN, previously reported toward L483 and tentatively in TMC-1, is confirmed in this latter source. We estimate that NCCN and NC4N are present in TMC-1 with abundances a few times to one order of magnitude lower than HC3N and HC5N, respectively. This means that dicyanopolyynes NC-(CC)n-CN are present at a lower level than the corresponding monocyanopolyynes HCC-(CC)n-CN. The reactions of the radicals CN and C3N with HNC arise as the most likely formation pathways to NCCN and NC4N in cold dense clouds.

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Meteorite Parent Body Aqueous Alteration Simulations of Interstellar Residue Analogs

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Some families of carbonaceous chondrites are rich in prebiotic organics that may have contributed to the origin of life on Earth and elsewhere. However, the formation and chemical evolution of complex soluble organic molecules from interstellar precursors under relevant parent body conditions has not been thoroughly investigated. In this study, we approach this topic by simulating meteorite parent body aqueous alteration of interstellar residue analogs. The distributions of amines and amino acids are qualitatively and quantitatively investigated and linked to closing the gap between interstellar and meteoritic prebiotic organic abundances. We find that the abundance trend of methylamine > ethylamine> glycine > serine > alanine > β-alanine does not change from pre- to post-aqueous alteration, suggesting that certain parental cloud conditions have an influential role on the distributions of interstellar-inherited meteoritic organics. However, the abundances for most of the amines and amino acids studied here varied by about 2-fold when aqueously processed for 7 days at 125 °C, and the changes in the α- to β-alanine ratio were consistent with those of aqueously altered carbonaceous chondrites, pointing to an influential role of meteorite parent body processing on the distributions of interstellar-inherited meteoritic organics. We detected higher abundances of α- over β-alanine, which is opposite to what is typically observed in aqueously altered carbonaceous chondrites; these results may be explained by at least the lack of minerals, inorganic species, and insoluble organic matter-relevant materials in the experiments. The high abundance of volatile amines in the non-aqueously altered samples suggests that these types of interstellar volatiles can be efficiently transferred to asteroids and comets, supporting the idea of the presence of interstellar organics in solar system objects.

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Coincidence study of core-ionized adamantane: site-sensitivity within a carbon cage?

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We investigate the fragmentation dynamics of adamantane dications produced after core-ionization at the carbon edge followed by Auger decay. The combination of high-resolution electron spectroscopy, energy-resolved electron-ion multi-coincidence spectroscopy and different theoretical models allows us to give a complete characterization of the processes involved after ionization. We show that energy- and site-sensitivity is observed even for a highly-symmetric molecule that lacks any unique atomic site.

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Laboratory and Astronomical Detection of the SiP Radical (X2Πi): More Circumstellar Phosphorus

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The millimeter-wave spectrum of the SiP radical (X 2Πi) has been measured in the laboratory for the first time using direct-absorption methods. SiP was created by the reaction of phosphorus vapor and SiH4 in argon in an AC discharge. Fifteen rotational transitions ($J + 1 \leftarrow J$) were measured for SiP in the $\Omega = 3/2$ ladder in the frequency range 151–533 GHz, and rotational, lambda-doubling, and phosphorus hyperfine constants determined. Based on the laboratory measurements, SiP was detected in the circumstellar shell of IRC+10216, using the Submillimeter Telescope (SMT) and the 12 m antenna of the Arizona Radio Observatory at 1 mm and 2 mm, respectively. Eight transitions of SiP were searched: four were completely obscured by stronger features, two were uncontaminated ($J = 13.5 \rightarrow 12.5$ and $16.5 \rightarrow 15.5$) and two were partially blended with other lines ($J = 8.5 \rightarrow 7.5$ and $17.5 \rightarrow 16.5$). The SiP line profiles were broader than expected for IRC+10216, consistent with the hyperfine splitting. From non-LTE radiative transfer modeling, SiP was found to have a shell distribution with a radius ~ 300 R*, and an abundance, relative to H2, of f ~ 2e-9. From additional modeling, abundances of 7e-9 and 9e-10 were determined for CP and PN, respectively, both located in shells at 550-650 R*. SiP appears to be formed from grain destruction, which liberates both phosphorus and silicon into the gas phase, and then is channeled into other P-bearing molecules such as PN and CP.

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Red-Shifting the Excitation Energy of Carbonic Acid Clusters Via Nonminimum Structures

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Nonminimum carbonic acid clusters provide excitation energies and oscillator strengths in line with observed ice-phase UV absorptions better than traditional optimized minima. This equation-of-motion coupled cluster quantum chemical analysis on carbonic acid monomers and dimers shows that shifts to the dihedral angle for the internal heavy atoms in the monomer produce UV electronic excitations close to 200 nm with oscillator strengths that would produce observable features. This t(OCOO) dihedral is actually a relatively floppy motion unlike what is often expected for sp2 carbons and can be distorted by 30 degrees away from equilibrium for an energy cost of only 11 kcal/mol. As this dihedral decreases beyond 30 degrees, the excitation energies decrease further. The oscillator strengths do, as well, but only to a point. Hence, the lower-energy distortions of t(OCOO) are sufficient to produce structures that exhibit excitation energies and oscillator strengths that would red-shift observed spectra of carbonic acid ices away from the highest UV absorption feature at 139 nm. Such data imply that colder temperatures (20 K) in the experimental treatment of carbonic acid ices are freezing these structures out after annealing, whereas the warmer temperature experiments (80 K) are not.

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Analysis of the first infrared spectrum of quasi-bound H2 line emission in Herbig-Haro 7.

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Context. Highly excited molecular hydrogen (H2) has been observed in many regions of shocked molecular gas. A recently published K-band spectrum of Herbig-Haro 7 (HH7) contains several vibration-rotation lines of H2 from highly excited energy levels that have not been detected elsewhere, including a line at 2.179 μm identified as arising from the v = 2, J = 29 level, which lies above the dissociation limit of H2. One emission line at 2.104 μm in this spectrum was unidentified. Aims: We aim to complete the analysis of the spectrum of HH7 by including previously missing molecular data that have been recently computed. Methods: We re-analysed the K-band spectrum, emphasising the physics of quasi-bound upper levels that can produce infrared emission lines in the K band. Results: We confirm the identification of the 2 − 1 S(27) line at 2.1785 μm and identify the line at 2.1042 μm as due to the 1−0 S(29) transition of H2, whose upper level energy is also higher than the dissociation limit. This latter identification, its column density, and the energy of its upper level further substantiate the existence of a hot thermal component at 5000 K in the HH7 environment. Conclusions: The presence of the newly identified 1 − 0 S(29) line, whose quasi-bound upper level (v = 1, J = 31) has a significant spontaneous dissociation probability, shows that dissociation of H2 is occurring. The mechanism by which virtually all of the H2 in levels with energies from 20 000 K to 53 000 K is maintained in local thermodynamic equilibrium at a single temperature of ~5000 K remains to be understood.

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Constraints on the non-thermal desorption of methanol in the cold core LDN 429-C

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Cold cores are an early step of star formation, characterized by densities > 10^4 cm^{-3}, low temperatures (< 15 K), and very low external UV radiation. We investigate the physico-chemical processes at play to tracing the origin of molecules that are predominantly formed via reactions on dust grain surfaces. We observed the cold core LDN 429-C with the NOEMA interferometer and the IRAM 30m single dish telescope in order to obtain the gas-phase abundances of key species, including CO and CH_3OH. Comparing the observed gas phase of methanol to its solid phase previously observed with Spitzer allows us to put quantitative constraints on the efficiency of the non-thermal desorption of this species. With physical parameters determined from available Herschel data, we computed abundance maps of 11 detected molecules with a non-local thermal equilibrium radiative transfer model. These observations allowed us to probe the molecular abundances as a function of density and visual extinction, with the variation in temperature being restrained between 12 and 18 K. We then compared the observed abundances to the predictions of the Nautilus astrochemical model. We find that all molecules have lower abundances at high densities and visual extinctions with respect to lower density regions, except for methanol. Comparing these observations with a grid of chemical models based on the local physical conditions, we were able to reproduce these observations, allowing only the parameter time to vary. Comparing the observed gas-phase abundance of methanol with previous measurements of the methanol ice, we estimate a non-thermal desorption efficiency between 0.002% and 0.09%, increasing with density. The apparent increase in the desorption efficiency cannot be reproduced by our model unless the yield of cosmic-ray sputtering is altered due to the ice composition varying as a function of density.

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Molecular-rotation-induced splitting of the binary ridge in the velocity map of sub-eV H^+ ions ejected from H_2 molecules by ion impact

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In studies of ion-induced molecular fragmentation, the challenging measurement of the velocity distribution of fragments emitted below 1-eV kinetic energy is rarely achieved, although most fragments have an energy below this value. Here, we study H^+ fragment emission in collisions of 10-keV O^+ ions with H_2 molecules using a field-free time-of-flight technique developed specifically to detect sub-eV fragments. We find that, in the velocity map, the binary ridge due to direct H^+ knockout is split into two parts arising from the rotational motion of the H_2 molecule, and that this split scales with rotational velocity. The velocity distribution of the nuclei in the original molecule is determined and the thermally populated J=1 rotational level is found to be the dominant contributor, although asymmetry in the split indicates projectile-induced rotational transitions between M sublevels. These rotation effects influence fragment emission probabilities, thus carrying important consequences for the radiation-induced hydrogen loss and H_2 dissociation in the atmospheres or exospheres of planets and moons.

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Proton and electron irradiations of CH4:H2O Mixed Ices

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The organic chemistry occurring in interstellar environments may lead to the production of complex molecules that are relevant to the emergence of life. Therefore, in order to understand the origins of life itself, it is necessary to probe the chemistry of carbon-bearing molecules under conditions that simulate interstellar space. Several of these regions, such as dense molecular cores, are exposed to ionizing radiation in the form of galactic cosmic rays, which may act as an important driver of molecular destruction and synthesis. In this paper, we report the results of a comparative and systematic study of the irradiation of CH4:H2O ice mixtures by 1 MeV protons and 2 keV electrons at 20 K. We demonstrate that our irradiations result in the formation of a number of new products, including both simple and complex daughter molecules such as C2H6, C3H8, C2H2, CH3OH, CO, CO2, and probably also H2CO. A comparison of the different irradiation regimes has also revealed that proton irradiation resulted in a greater abundance of radiolytic daughter molecules compared to electron irradiation, despite a lower radiation dose having been administered. These results are important in the context of the radiation astrochemistry occurring within the molecular cores of dense interstellar clouds, as well as on outer Solar System objects.

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An Ice Age JWST inventory of dense molecular cloud ices

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Icy grain mantles are the main reservoir of the volatile elements that link chemical processes in dark, interstellar clouds with the formation of planets and the composition of their atmospheres. The initial ice composition is set in the cold, dense parts of molecular clouds, before the onset of star formation. With the exquisite sensitivity of the James Webb Space Telescope, this critical stage of ice evolution is now accessible for detailed study. Here we show initial results of the Early Release Science programme Ice Age that reveal the rich composition of these dense cloud ices. Weak ice features, including 13CO2, OCN−, 13CO, OCS and complex organic molecule functional groups, are now detected along two pre-stellar lines of sight. The 12CO2 ice profile indicates modest growth of the icy grains. Column densities of the major and minor ice species indicate that ices contribute between 2% and 19% of the bulk budgets of the key C, O, N and S elements. Our results suggest that the formation of simple and complex molecules could begin early in a water-ice-rich environment.

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Cyanopolyyne chemistry in the L1544 prestellar core: new insights from GBT observations

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We report a comprehensive study of the cyanopolyyne chemistry in the prototypical prestellar core L1544. Using the 100m Robert C. Byrd Green Bank Telescope (GBT) we observe 3 emission lines of HC3N, 9 lines of HC5N, 5 lines of HC7N, and 9 lines of HC9N. HC9N is detected for the first time towards the source. The high spectral resolution (~ 0.05 km s−1) reveals double-peak spectral line profiles with the redshifted peak a factor 3-5 brighter. Resolved maps of the core in other molecular tracers indicates that the southern region is redshifted. Therefore, the bulk of the cyanopolyyne emission is likely associated with the southern region of the core, where free carbon atoms are available to form long chains, thanks to the more efficient illumination of the interstellar field radiation. We perform a simultaneous modelling of the HC5N, HC7N, and HC9N lines, to investigate the origin of the emission. To enable this analysis, we performed new calculation of the collisional coefficients. The simultaneous fitting indicates a gas kinetic temperature of 5--12 K, a source size of 80", and a gas density larger than 100 cm−3. The HC5N:HC7N:HC9N abundance ratios measured in L1544 are about 1:6:4. We compare our observations with those towards the the well-studied starless core TMC-1 and with the available measurements in different star-forming regions. The comparison suggests that a complex carbon chain chemistry is active in other sources and it is related to the presence of free gaseous carbon. Finally, we discuss the possible formation and destruction routes in the light of the new observations.

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