AstroChemical Newsletter #104

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Abstracts

A multi-grain multi-layer astrochemical model with variable desorption energy for surface species

Juris Kalvāns, Aija Kalniņa, Kristaps Veitners

Context. Interstellar surface chemistry is a complex process that occurs in icy layers that have accumulated onto grains of different sizes. The efficiency of the surface processes often depends on the immediate environment of the adsorbed molecules. Aims. We investigated how gas-grain chemistry changes when the surface molecule binding energy is modified, depending on the properties of the surface.} Methods. In a gas-grain astrochemical model, molecular binding energy gradually changes for three different environments - (1) the bare grain surface, (2) polar water-dominated ices, and (3) weakly polar carbon monoxide-dominated ices. In addition to diffusion, evaporation, and chemical desorption, photodesorption was also made binding energy-dependent, in line with experimental results. These phenomena occur in a collapsing prestellar core model that considers five grain sizes with ices arranged into four layers. Results. Variable desorption energy moderately affects gas-grain chemistry. Bare-grain effects slow down ice accumulation, while easier diffusion of molecules on weakly polar ices promotes the production of carbon dioxide. Efficient chemical desorption from bare grains significantly delays the appearance of the first ice monolayer. Conclusions. The combination of multiple aspects of grain surface chemistry creates a gas-ice balance that is different from simpler models. The composition of the interstellar ices is regulated by several binding-energy dependent desorption mechanisms. Their actions overlap in time and space, explaining the similar proportions of major ice components (water and carbon oxides) observed in all directions.

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Unveiling gas phase H2NCO radical: Laboratory rotational spectroscopy and interstellar search toward IRAS 16293-2422

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Context. The carbamoyl radical (H2NCO) is believed to play a central role in the ice-grain chemistry of crucial interstellar complex organic molecules as formamide and acetamide. Yet, little is known about this radical that remains elusive in laboratory gas-phase experiments. Aims. In order to enable interstellar searches of H2NCO, we have undertaken a mandatory laboratory characterisation of its pure rotational spectrum. Methods. We report the gas-phase laboratory detection of H2NCO, produced by H-atom abstraction from formamide, using pure rotational spectroscopy at millimetre and submillimetre wavelengths. Millimetre-wave data were acquired using chirped-pulse Fourier- transform spectroscopy while submillimetre-wave ones were obtained using Zeeman-modulated spectroscopy. Experimental measurements were guided by quantum-chemical calculations at the ωB97X-D/cc-pVQZ level of theory. Interstellar searches for the radical have been undertaken on the Protostellar Interferometric Line Survey (PILS) towards the solar-type protostar IRAS 16293–2422. Results. From the assignment and fit of experimental transitions up to 660 GHz, reliable spectroscopic parameters for H2NCO in its ground vibrational state have been derived, enabling accurate spectral predictions. No transitions of the radical were detected on the PILS survey. The inferred upper limit shows that H2NCO abundance is at least 60 times below that of formamide and 160 times below that of HNCO in this source; a value that is in agreement with predictions from a physico-chemical model of this young protostar.

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Photodesorption efficiency of OH radical on the ice surface in the wavelength range from ultraviolet to visible

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The photodesorption efficiencies of the hydroxyl (OH) radical from the water ice surface were measured in the range of 310–700 nm for the first time. Although isolated H2O molecules and OH radicals do not absorb visible photons, the photodesorption of OH interacting with the ice surface was found to occur by a one-photon process in the entire visible range. The photodesorption efficiency strongly depended on the wavelength, and the analyses of photodesorption cross sections indicated that only strongly bound OH radicals were desorbed at longer wavelengths, whereas both weakly and strongly bound OH radicals were desorbed at shorter wavelengths.

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Enhanced formation of interstellar complex organic molecules on carbon monoxide ice

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We investigate the role of carbon monoxide ice in the chemical evolution of prestellar cores using astrochemical rate equation models. We constrain the ratios of the binding energies on CO ice and H2O ice for a series of adsorbates deemed important in diffusive chemistry on H2O ices. We later include these ratios in our chemical reaction network model, where the binding and diffusion energies of icy species vary as a function of the surface composition. When the surface coverage of CO increases, the model shows an enhancement of O-bearing complex organic molecules, especially those formed from the intermediate products of CO hydrogenation (e.g. HCO) and CH3/CH2. Because the binding energy of CH3/CH2 is in the right range, its diffusion rate increases significantly with CO coverage. At T>14 K and with less influence, enhanced diffusion of HCO also contributes to the increase of the abundances of COM. We find, however, that chemistry is not always enhanced on CO ice and that the temperature and cosmic ray ionization rate of each astronomical object is crucial for this particular chemistry, revealing a highly non-trivial behavior that needs to be addressed on a per-case basis. Our results are highly relevant in the context of interstellar ice observations with JWST.

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Deep Search for Phosphine in a Prestellar Core

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Understanding in which chemical forms phosphorus exists in star- and planet-forming regions and how phosphorus is delivered to planets are of great interest from the viewpoint of the origin of life on Earth. Phosphine (PH3) is thought to be a key species to understanding phosphorus chemistry, but never has been detected in star- and planet-forming regions. We performed sensitive observations of the ortho-PH3 1_0-0_0 transition (266.944 GHz) toward the low-mass prestellar core L1544 with the ACA stand-alone mode of ALMA. The line was not detected down to 3 sigma levels in 0.07 km s-1 channels of 18 mK. The non-detection provides the upper limit to the gas-phase PH3 abundance of 5e-12 with respect to H2 in the central part of the core. Based on the gas-ice astrochemical modeling, we find the scaling relationship between the gas-phase PH3 abundance and the volatile (gas and ice with larger volatility than water) P elemental abundance for given physical conditions. This characteristic and well-constrained physical properties of L1544 allow us to constrain the upper limit to the volatile P elemental abundance of 5e-9, which is a factor of 60 lower than the overall P abundance in the ISM. Then the majority of P should exist in refractory forms. The volatile P elemental abundance of L1544 is smaller than that in the coma of comet 67P/C-G, implying that the conversion of refractory phosphorus to volatile phosphorus could have occurred along the trail from the presolar core to the protosolar disk through e.g., sputtering by accretion/outflow shocks.

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Overtone Transition 2ν1 of HCO+ and HOC+: Origin, Radiative Lifetime, Collisional Quenching

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We present spectra of the first overtone vibration transition of C-H/O-H stretch (2ν1) in HCO+ and HOC+, recorded using a laser induced reaction action scheme inside a cryogenic 22 pole radio frequency trap. Band origins have been located at 6078.68411(19) and 6360.17630(26) cm-1, respectively. We introduce a technique based on mass selective ejection from the ion trap for recording background free action spectra. Varying the number density of the neutral action scheme reactant (CO2 and Ar, respectively) and collisional partner reactant inside the ion trap, permitted us to estimate the radiative lifetime of the state to be 1.53(34) and 1.22(34) ms, respectively, and the collisional quenching rates of HCO+ (2ν1) with He, H2, and N2.

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Rotational spectroscopy of CH3OD with a reanalysis of CH3OD toward IRAS 16293−2422

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We have started a measurement campaign of numerous methanol isotopologs in low-lying torsional states in order to provide extensive line lists for radio astronomical observations from an adequate spectroscopic model and to investigate how the intricate vibrationtorsion-rotation interactions manifest themselves in the spectra of different isotopic species. After CD3OH and CD3OD, we turn our focus to CH3OD, which is an important species for studying deuteration in prestellar cores

and envelopes that enshroud protostars. Notably, deuteration is frequently viewed as a diagnostic tool for star formation. The measurements used in this study were obtained in two spectroscopic laboratories and cover large fractions of the 34 GHz−1.35 THz range. As done in previous studies, we employed a torsion-rotation Hamiltonian model for our analysis that is based on the rho-axis method. The resulting model describes the ground and first excited torsional states of CH3OD well up to quantum numbers J <= 51 and Ka <= 18. We derived a line list for radio astronomical observations from this model that is accurate up to at least 1.35 THz and should be sufficient for all types of radio astronomical searches for this methanol isotopolog in these two lowest torsional states. This line list was applied to a reinvestigation of CH3OD in data from the Protostellar Interferometric Line Survey of IRAS 16293−2422 obtained with the Atacama Large Millimeter/submillimeter Array. The new accurately determined value for the column density of CH3OD implies that the deuteration in methanol differs in its two functional groups by a factor of ∼7.5.

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Identification of hot gas around low-mass protostars

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The low carbon content of Earth and primitive meteorites compared to the Sun and interstellar grains suggests that carbon-rich grains were destroyed in the inner few astronomical units of the young solar system. A promising mechanism to selectively destroy carbonaceous grains is thermal sublimation within the soot line at > ~300 K. To address whether such hot conditions are common amongst low-mass protostars, we observe CH3CN transitions at 1, 2 and 3 mm with the NOrthern Extended Millimeter Array (NOEMA) toward seven low-mass and one intermediate-mass protostar (Lbol ∼ 2-300 Lsun), as CH3CN is an excellent temperature tracer. We find > 300 K gas toward all sources, indicating that hot gas may be prevalent. Moreover, the excitation temperature for CH3OH obtained with the same observations is always lower (~135-250 K), suggesting that CH3CN and CH3OH have a different spatial distribution. A comparison of the column densities at 1 and 3 mm shows a stronger increase at 3 mm for CH3CN than for CH3OH. Since the dust opacity is lower at longer wavelengths, this indicates that CH3CN is enhanced in the hot gas compared to CH3OH. If this CH3CN enhancement is the result of carbon-grain sublimation, these results suggests that Earth's initial formation conditions may not be rare.

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Modelling predicts a molecule-rich disk around the AGB star L2 Puppis

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The nearby oxygen-rich AGB star L2 Pup hosts a well-studied nearly edge-on disk. To date, disks around AGB stars have not been chemically studied in detail. By combining a parameterisation commonly used for protoplanetary disks and archival ALMA observations, we retrieved an updated density and temperature structure of this disk. This physical model was then used as input to the first chemical model of an AGB disk. The model shows that the physical structure of the disk has a large impact on its chemistry, with certain species showing large changes in column density relative to a radial outflow, indicating that chemistry could be used as a tracer of disks that cannot be directly imaged. Despite its oxygen-rich nature, the daughter species formed within the disk are surprisingly carbon-rich. Two chemical regimes can be distinguished: cosmic-ray induced chemistry in the midplane and photochemistry induced by the interstellar radiation field in the outer regions. Certain complex organic molecules are formed in the midplane. This occurs via gas-phase chemistry only, as the disk is too warm for dust-gas chemistry. The photochemistry in the outer regions leads to the efficient formation of (long) carbon-chains. The predictions of the model allow us to tentatively put the disk's age ≲1e5 yr. Additional observations are necessary to better constrain the physical structure of L2 Pup's disk and are essential to test the predictions made by the chemical model. Our exploratory work paves the way for a more general study of the chemistry of AGB disks.

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Binding energies of ethanol and ethylamine on interstellar water ices: synergy between theory and experiments

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Experimental and computational chemistry are two disciplines to conduct research in Astrochemistry, providing essential reference data for both astronomical observations and modeling. These approaches not only mutually support each other, but also serve as complementary tools to overcome their respective limitations. Leveraging on such synergy, we characterized the binding energies (BEs) of ethanol (CH3CH2OH) and ethylamine (CH3CH2NH2), two interstellar complex organic molecules (iCOMs), onto crystalline and amorphous water ices through density functional theory (DFT) calculations and temperature programmed desorption (TPD) experiments. Experimentally, CH3CH2OH and CH3CH2NH2 behave similarly, in which desorption temperatures are higher on the water ices than on a bare gold surface. Computed cohesive energies of pure ethanol and ethylamine bulk structures allow describing the BEs of the pure species deposited on the gold surface, as extracted from the TPD curve analyses. The BEs of submonolayer coverages of CH3CH2OH and CH3CH2NH2 on the water ices cannot be directly extracted from TPD due to their co-desorption with water, but they are computed through DFT calculations, and found to be greater than the cohesive energy of water. The behaviour of CH3CH2OH and CH3CH2NH2 is different when depositing adsorbate multilayers on the amorphous ice, in that, according to their computed cohesive energies, ethylamine layers present weaker interactions compared to ethanol and water. Finally, from the computed BEs of ethanol, ethylamine and water, we can infer that the snow-lines of these three species in protoplanetary disks will be situated at different distances from the central star. It appears that a fraction of ethanol and ethylamine is already frozen on the grains in the water snow-lines, causing their incorporation in water-rich planetesimals.

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OH mid-infrared emission as a diagnostic of H2O UV photodissociation. III. Application to planet-forming disks

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JWST gives a unique access to the physical and chemical structure of inner disks (<10 au), where the majority of the planets are forming. However, the interpretation of mid-infrared (mid-IR) spectra requires detailed thermo-chemical models able to provide synthetic spectra readily comparable to spectroscopic observations. Our goal is to explore the potential of mid-IR emission of OH to probe H2O photodissociation. We include in the DALI disk model prompt emission of OH following photodissociation of H2O in its B̃ electronic state (λ<144 nm). This model allows to compute in a self-consistent manner the thermo-chemical structure of the disk and the resulting mid-IR line intensities of OH and H2O. The OH line intensities in the 9−13 μm range are proportional to the total amount of water photodissociated. As such, these lines are a tracer of the amount of water exposed to the FUV field, which depends on the temperature, density, and strength of the FUV field reaching the upper molecular layers. In particular, the OH line fluxes primarily scale with the FUV field emitted by the star in contrast with H2O lines in the 10-20 μm range which scale with the bolometric luminosity. OH is therefore a key diagnostic to probe the effect of Lyα and constrain the dust FUV opacity in the upper molecular layers. A strong asymmetry between the A' and A'' components of each rotational quadruplet is also predicted. OH mid-IR emission is a powerful tool to probe H2O photodissociation and infer the physical conditions in disk atmospheres. As such, the inclusion of OH mid-IR lines in the analysis of JWST-MIRI spectra will be key for robustly inferring the composition of planet-forming disks. The interpretation of less excited OH lines requires additional quantum calculations of the formation pumping of OH levels by O+H2 and the collisional rate coefficients.

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Flux and fluence effects on the Vacuum-UV photodesorption and photoprocessing from CO2 ices

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CO2 is a major component of the icy mantles surrounding dust grains in planet and star formation regions. Understanding its photodesorption is crucial for explaining gas phase abundances in the coldest environments of the interstellar medium irradiated by vacuum-UV (VUV) photons. Photodesorption yields determined experimentally from CO2 samples grown at low temperatures (T=15 K) have been found to be very sensitive to experimental methods and conditions. Several mechanisms have been suggested for explaining the desorption of CO2, O2 and CO from CO2 ices. In the present study, the cross sections characterizing the dynamics of photodesorption as a function of photon fluence (determined from released molecules in the gas phase) and of ice composition modification (determined in situ in the solid phase) are compared for the first time for different photon flux conditions (from 7.3e12 photon/s to 2.2e14 photon/s) using monochromatic synchrotron radiation in the VUV range (on the DESIRS beamline at SOLEIL). This approach reveals that CO and O2 desorption are decorrelated from that of CO2. CO and O2 photodesorption yields depend on photon flux conditions and can be linked to surface chemistry. By contrast, the phodesorption yield of CO2 is independent of the photon flux conditions and can be linked to bulk ice chemical modification, consistently with an indirect desorption induced by electronic transition (DIET) process.

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Discovery of widespread CO2 and CO in small outer solar system icy bodies

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Trans-Neptunian Objects (TNOs) are small icy bodies of the outer solar system. They are thought to be remnants of planetary formation in the protoplanetary disk. Their chemical composition is key to reconstruct a picture of the early solar system and the processes that shaped it. But until now, their characterization was very limited with only water and methanol ice detections on a few objects. A large observation program of the James Webb Space Telescope has recently provided the first comprehensive view of TNOs. Observations of 59 objects obtained with the NIRSpec instrument reveal the first detections of CO2 and CO ices on small bodies in the outer solar system. Unexpectedly, CO2 is widespread, present on 95% of the objects in varying proportions. While CO is not stable on TNO surfaces, it is detected together with CO2 on 47% of objects. This diversity in composition, reflected in variations in the abundance and physico-chemical state of the ice, will enable us to retrace the history of TNOs and find their formation region in the protoplanetary disk, differentiating its influence from that of later evolutionary processes.

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Chemical Evolution of Complex Organic Molecules in Turbulent Protoplanetary Disks: Effect of stochastic UV irradiation

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We investigate the chemical evolution of complex organic molecules (COMs) in turbulent disks using gas-ice chemical reaction network simulations. We trace trajectories of dust particles considering advection, turbulent diffusion, gas drag, and vertical settling, for 1e6 yrs in a protoplanetary disk. Then, we solve a gas-ice chemical reaction network along the trajectories and obtain the temporal evolution of molecular abundances. We find that the COM abundances in particles can differ by more than two orders of magnitude even when the UV fluence (i.e., the time integral of UV flux) received by the particles are similar, suggesting that not only the UV fluence but also the time variation of the UV flux does matter for the evolution of COMs in disks. The impact of UV fluence on molecular abundances differs between oxygen-bearing and nitrogen-bearing COMs. While higher UV fluence results in oxygen being locked into CO2, leading to reduced abundances of oxygen-bearing COMs such as CH3OCH3, mild UV exposure can promote their formation by supplying the precursor radicals. On the other hand, nitrogen is not locked up into specific molecules, allowing the formation of nitrogen-bearing COMs, particularly CH3NH2, even for the particle that receives the higher UV fluence. We also find that the final COM abundances are mostly determined by the inherited abundances from the protostellar core when the UV fluence received by dust particles is less than a critical value, while they are set by both the inherited abundances and the chemistry inside the disk at higher UV fluence.

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Mind the Trap: Non-negligible effect of volatile trapping in ice on C/O ratios in protoplanetary disks and exoplanetary atmospheres

N.F.W. Ligterink, K.A. Kipfer, S. Gavino

The ability of bulk ices (H2O, CO2) to trap volatiles has been well studied in any experimental sense, but largely ignored in protoplanetary disk and planet formation models as well as the interpretation of their observations. We demonstrate the influence of volatile trapping on C/O ratios in planet-forming environments. We created a simple model of CO, CO2, and H2O snowlines in protoplanetary disks and calculated the C/O ratio at different radii and temperatures. We included a trapping factor, which partially inhibits the release of volatiles (CO, CO2) at their snowline and releases them instead, together with the bulk ice species (H2O, CO2). Our aim has been to assess its influence on trapping solid-state and gas phase C/O ratios throughout planet-forming environments. Volatile trapping significantly affects C/O ratios in protoplanetary disks. Variations in the ratio are reduced and become more homogeneous throughout the disk when compared to models that do not include volatile trapping. Trapping reduces the proportion of volatiles in the gas and, as such, reduces the available carbon- and oxygen-bearing molecules for gaseous accretion to planetary atmospheres. Volatile trapping is expected to also affect the elemental hydrogen and nitrogen budgets. Volatile trapping is an overlooked, but important effect to consider when assessing the C/O ratios in protoplanetary disks and exoplanet atmospheres. Due to volatile trapping, exoplanets with stellar C/O have the possibility to be formed within the CO and CO2 snowline.

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Constraints on the gas-phase C/O ratio of DR Tau's outer disk from CS, SO, and C2H observations

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Millimeter wavelength observations of Class II protoplanetary disks often display strong emission from hydrocarbons and high CS/SO values, providing evidence that the gas-phase C/O ratio commonly exceeds 1 in their outer regions. We present new NOEMA observations of CS 5−4, SO 7_6−6_5 and 5_6−4_5, C2H N=3−2, HCN 3−2, HCO+ 3−2, and H13CO+ 3−2 in the DR Tau protoplanetary disk at a resolution of ∼0.4″ (80 au). Estimates for the disk-averaged CS/SO ratio range from ∼0.4−0.5, the lowest value reported thus far for a T Tauri disk. At a projected separation of ∼180 au northeast of the star, the SO moment maps exhibit a clump that has no counterpart in the other lines, and the CS/SO value decreases to <0.2 at its location. Thermochemical models calculated with DALI indicate that DR Tau's low CS/SO ratio and faint C2H emission can be explained by a gas-phase C/O ratio that is <1 at the disk radii traced by NOEMA. Comparisons of DR Tau's SO emission to maps of extended structures traced by 13CO suggest that late infall may contribute to driving down the gas-phase C/O ratio of its disk.

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Sublimation of volatiles from H2O:CO2 bulk ices in the context of comet 67P/Churyumov–Gerasimenko II. Noble gases

N. F. W. Ligterink, K. A. Kipfer, M. Rubin, K. Altwegg, N. Hänni, D. R. Müller, P. Wurz, A. Galli and S. F. Wampfler

Context. The ROSINA instrument on board the Rosetta spacecraft measured, among others, the outgassing of noble gases from comet 67P/Churyumov–Gerasimenko. The interpretation of this dataset and unravelling underlying desorption mechanisms requires detailed laboratory studies. Aims. We aim to improve our understanding of the desorption patterns, trapping, and fractionation of noble gases released from the H2O:CO2-dominated ice of comet 67P. Methods. In the laboratory, ice films of neon, argon, krypton, or xenon (Ne, Ar, Kr, and Xe) mixed in CO2:H2O were prepared at 15 K. Temperature-programmed desorption mass spectrometry is employed to analyse the desorption behaviour of the noble gases. Mass spectrometric ROSINA data of 67P were analysed to determine the fraction of argon associated with CO2 and H2O, respectively. Results. CO2 has a significant effect on noble gas desorption behaviour, resulting in the co-release of noble gases with CO2, decreasing the amount of noble gas trapped within water, shifting the pure phase noble gas peak desorption temperature to lower temperatures, and prolonging the trapping of neon. These effects are linked to competition for binding sites in the water ice and the formation of crystalline CO2. Desorption energies of the pure phase noble gas release were determined and found to be higher than those previously reported in the literature. Enhancement of the Ar/Kr and Ar/Xe ratios are at best 40% and not significantly influenced by the addition of CO2. Analysis of ROSINA mass spectrometric data shows that the fraction of argon associated with H2O is 0.53 ± 0.30, which cannot be explained by our laboratory results. Conclusions. Multicomponent ice mixtures affect the desorption behaviour of volatiles compared to simple binary mixtures and experiments on realistic cometary ice analogues are vital to understanding comet outgassing.

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In-Depth Exploration of Catalytic Sites on Amorphous Solid Water: I. The Astrosynthesis of Aminomethanol

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Chemical processes taking place on ice-grain mantles are pivotal to the complex chemistry of interstellar environments. In this study, we conducted a comprehensive analysis of the catalytic effects of an amorphous solid water (ASW) surface on the reaction between ammonia (NH3) and formaldehyde (H2CO) to form aminomethanol (NH2CH2OH) using density functional theory. We identified potential catalytic sites based on the binding energy distribution of NH3 and H2CO reactants, on a set-of-clusters surface model composed of 22 water molecules and found a total of 14 reaction paths. Our results indicate that the catalytic sites can be categorized into four groups, depending on the interactions of the carbonyl oxygen and the amino group with the ice surface in the reactant complex. A detailed analysis of the reaction mechanism using Intrinsic Reaction Coordinate and reaction force analysis revealed three distinct chemical events for this reaction: formation of the C–N bond, breaking of the N–H bond, and formation of the O–H hydroxyl bond. Depending on the type of catalytic site, these events can occur within a single, concerted, albeit asynchronous, step, or can be isolated in a step-wise mechanism, with the lowest overall transition state energy observed at 1.3 kcal mol−1. A key requirement for the low-energy mechanism is the presence of a pair of dangling OH bonds on the surface, found at 5% of the potential catalytic sites on an ASW porous surface.

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Investigation of the rotational spectrum of CH3(17O)H and its tentative detection toward Sagittarius B2(N)

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Methanol is an abundant molecule in space. The column density of CH3(18)OH is in some star-forming regions so high that the search for CH3(17)OH is promising. But only very few transition frequencies of CH3(17)OH with a microwave accuracy have been published thus far. We recorded the rotational spectrum of CH3(17)OH between 38 and 1095 GHz employing a methanol sample enriched in 17O to 20%. A torsion-rotation Hamiltonian model based on the rho-axis method was employed to fit the data, as in our previous studies. We searched for rotational transitions of CH3(17)OH in the imaging spectral line survey ReMoCA obtained with the Atacama Large Millimeter/submillimeter Array (ALMA) toward the high-mass star-forming region Sgr B2(N). The observed spectra were modeled under the assumption of local thermodynamic equilibrium (LTE). The assignments cover 0 <= J <= 45, Ka <= 16, and mainly the vt = 0 and 1 torsional states. The Hamiltonian model describes our data well. The model was applied to derive a line list for radio-astronomical observations. We report a tentative detection of CH3(17)OH along with secure detections of the more abundant isotopologs of methanol

toward Sgr B2(N2b). The derived column densities yield isotopic ratios 12C/13C = 25, 16O/18O = 240, and 18O/17O = 3.3, which are consistent with values found earlier for other molecules in Sgr B2. The agreement between the 18O/17O isotopic ratio that we obtained for methanol and the 18O/17O ratios reported in the past for other molecules in Sgr B2(N) strongly supports our tentative interstellar identification of CH3(17)OH. The accuracy of the derived line list is sufficient for further radio astronomical searches for this methanol isotopolog toward other star-forming regions.

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Formation of S-bearing complex organic molecules in interstellar clouds via ice reactions with C2H2, HS, and atomic H

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The chemical network governing interstellar sulfur has been the topic of unrelenting discussion for the past decades due to the conspicuous discrepancy between its expected and observed abundances in different interstellar environments. More recently, the astronomical detections of CH3CH2SH and CH2CS highlighted the importance of interstellar formation routes for sulfur-bearing organic molecules with two carbon atoms. In this work, we perform a laboratory investigation of the solid-state chemistry resulting from the interaction between C2H2 molecules and SH radicals – both thought to be present in interstellar icy mantles – at 10 K. Reflection absorption infrared spectroscopy and quadrupole mass spectrometry combined with temperature-programmed desorption experiments are employed as analytical techniques. We confirm that SH radicals can kick-start a sulfur reaction network under interstellar cloud conditions and identify at least six sulfurated products: CH3CH2SH, CH2CHSH, HSCH2CH2SH, H2S2, and tentatively CH3CHS and CH2CS. Complementarily, we utilize computational calculations to pinpoint the reaction routes that play a role in the chemical network behind our experimental results. The main sulfur-bearing organic molecule formed under our experimental conditions is CH3CH2SH and its formation yield increases with the ratios of H to other reactants. It serves as a sink to the sulfur budget within the network, being formed at the expense of the other unsaturated products. The astrophysical implications of the chemical network proposed here are discussed.

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FAUST XVII: Super deuteration in the planet-forming system IRS 63 where the streamer strikes the disk

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Recent observations suggest that planet formation starts early, in protostellar disks of <=1e5 yrs, which are characterized by strong interactions with the environment, such as through accretion streamers and molecular outflows. To investigate the impact of such phenomena on the physical and chemical properties of a disk, it is key to understand what chemistry planets inherit from their natal environment. In the context of the ALMA large program Fifty AU Study of the chemistry in the disk/envelope system of solar-like protostars (FAUST), we present observations on scales from ∼1500 au to ∼60 au of H2CO, HDCO, and D2CO toward the young planet-forming disk IRS 63. The H2CO probes the gas in the disk as well as in a large scale streamer (∼1500 au) impacting onto the southeast disk side. We detected for the first time deuterated formaldehyde, HDCO and D2CO, in a planet-forming disk and HDCO in the streamer that is feeding it. These detections allowed us to estimate the deuterium fractionation of H2CO in the disk: [HDCO]/[H2CO]∼0.1−0.3 and [D2CO]/[H2CO]∼0.1. Interestingly, while HDCO follows the H2CO distribution in the disk and in the streamer, the distribution of D2CO is highly asymmetric, with a peak of the emission (and [D]/[H] ratio) in the southeast disk side, where the streamer crashes onto the disk. In addition, D2CO was detected in two spots along the blue- and redshifted outflow. This suggests that (i) in the disk, HDCO formation is dominated by gas-phase reactions in a manner similar to H2CO, while (ii) D2CO is mainly formed on the grain mantles during the prestellar phase and/or in the disk itself and is at present released in the gas phase in the shocks driven by the streamer and the outflow. These findings testify to the key role of streamers in the buildup of the disk concerning both the final mass available for planet formation and its chemical composition.

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SO2 and OCS toward high-mass protostars: A comparative study between ice and gas

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We investigate the chemical history of interstellar OCS and SO2 by deriving a statistically-significant sample of gas-phase column densities towards massive protostars and comparing to observations of gas and ices towards other sources spanning from dark clouds to comets. We analyze a subset of 26 line-rich massive protostars observed by ALMA as part of the ALMAGAL survey. Column densities are derived for OCS and SO2 from their rare isotopologues O13CS and 34SO2 towards the compact gas around the hot core. We find that gas-phase column density ratios of OCS and SO2 with respect to methanol remain fairly constant as a function of luminosity between low- and high-mass sources, despite their very different physical conditions. The derived gaseous OCS and SO2 abundances relative to CH3OH are overall similar to protostellar ice values, with a significantly larger scatter for SO2 than for OCS. Cometary and dark-cloud ice values agree well with protostellar gas-phase ratios for OCS, whereas higher abundances of SO2 are generally seen in comets compared to the other sources. Gaseous SO2/OCS ratios are consistent with ices toward dark clouds, protostars, and comets, albeit with some scatter. The constant gas-phase column density ratios throughout low and high-mass sources indicate an early stage formation before intense environmental differentiation begins. Icy protostellar values are similar to the gas phase medians, compatible with an icy origin of these species followed by thermal sublimation. The larger spread in SO2 compared to OCS ratios w.r.t. CH3OH is likely due to a more water-rich chemical environment associated with the former, as opposed to a CO-rich origin of the latter. Post-sublimation gas-phase processing of SO2 can also contribute to the large spread. Comparisons to ices in dark clouds and comets point to a significant inheritance of OCS from earlier to later evolutionary stages.

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Revisiting Jupiter's deuterium fraction in the rotational ground-state line of HD at high spectral resolution

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The cosmic deuterium fraction, set by primordial nucleosynthesis and diminished by subsequent astration, is a valuable diagnostic tool to link the protosolar nebula to the history of star formation. However, in the present-day Solar System, the deuterium fraction in various carriers varies by more than an order of magnitude and reflects environmental conditions rather than the protosolar value. The latter is believed to be preserved in the atmospheres of the gas giant planets, yet determinations inferred from the CH3D/CH4 pair require a larger fractionation correction than those from HD/H2, which are close to unity. The question of whether a stratospheric emission feature contaminates the absorption profile forming in subjacent layers was never addressed, owing to the lack of spectral resolving power. Here we report on the determination of the Jovian deuterium fraction using the rotational ground-state line of HD (J = 1 − 0) at 112 micrometer wavelength. Employing the GREAT heterodyne spectrometer on board SOFIA, we detected the HD absorption and, thanks to the high resolving power, a weak stratospheric emission feature underneath; the former is blue-shifted with respect to the latter. The displacement is attributed to a pressure-induced line shift and reproduced by dedicated radiative-transfer modeling based on recent line-profile parameters. Using atmospheric standard models, we obtained D/H = (19 ± 4) ppm, which agrees with a recent measurement in Saturn’s atmosphere and with the value inferred from solar-wind measurements and meteoritic data. The result suggests that all three measurements represent bona fide protosolar D/H fractions. As a supplement and test for the consistency of the layering assumed in our model, we provide an analysis of the purely rotational J = 6 − 5 line of CH4 (in the vibrational ground state, at 159 micrometer wavelength).

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Pathways to Interstellar Amides via Carbamoyl (NH2CO) Isomers by Radical-Neutral Reactions on Ice Grain Mantles

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Explaining the formation pathways of amides on ice-grain mantels is crucial to understanding the prebiotic chemistry in an interstellar medium. In this computational study, we explore different radical-neutral formation pathways for some of the observed amides (formamide, acetamide, urea, and N-methylformamide) via intermediate carbamoyl (NH2CO) radical precursors and their isomers. We assess the relative energy of four NH2CO isomers in the gas phase and evaluate their binding energy on small water clusters to discern the affinity that the isomers present to an ice model. We consider three possible reaction pathways for the formation of the carbamoyl radicals, namely, the OH + HCN, CN + H2O, and NH2 + CO reaction channels. We computed the binding energy distribution for the HCN and CH3CN precursors on an ice model consisting of a set of clusters of 22 water molecules each to serve as a starting point for the reactivity study on the ice surface. The computations revealed that the lowest barrier to the formation of an NH2CO isomer corresponds to the NH2 + CO reaction (12.6 kJ/mol). The OH + HCN reaction pathway results in the exothermic formation of the N-radical form of carbamoyl HN(C=O)H with a reaction barrier of 26.7 kJ/mol. We found that the CN + H2O reaction displays a high energy barrier of 70.6 kJ/mol. Finally, we also probed the direct formation of the acetamide radical precursor via the OH + CH3CN reaction and found that the most probable outcome on interstellar ices is the H-abstraction reaction to yield CH2CN and H2O. Based on these results, we believe that including alternative reaction pathways, leading to the formation of amides via the N-radical form of carbamoyl, would provide an improvement in the prediction of the amide abundances in astrochemical models, especially regarding the chemistry of star-forming regions.

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Announcements

Special Issue of ACS Earth and Space Chemistry: Chemical Complexity in Planetary Systems

Martin Cordiner (NASA GSFC) and Chris Bennett (UCF) were co-editors of a special issue of the ACS journal Earth and Space Chemistry, entitled “Chemical Complexity in Planetary Systems” (see https://pubs.acs.org/page/aesccq/vi/chemical-complexity-planet). The special issue contains 20 research articles and reviews on subjects ranging from laboratory and theorical astrochemistry to observations, of particular relevance to the origins of chemical complexity in planetary environments, star-forming regions and comets. This special issue arose out of the conference presentations given at the American Chemical Society’s Astrochemistry Symposium, held in Texas in 2021.