AstroChemical Newsletter #91

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Abstracts

Chemical Differentiation around Five Massive Protostars Revealed by ALMA -Carbon-Chain Species, Oxygen-/Nitrogen-Bearing Complex Organic Molecules-

Kotomi Taniguchi, Liton Majumdar, Paola Caselli, Shigehisa Takakuwa, Tien-Hao Hsieh, Masao Saito, Zhi-Yun Li, Kazuhito Dobashi, Tomomi Shimoikura, Fumitaka Nakamura, Jonathan C. Tan, Eric Herbst

We present Atacama Large Millimeter/submillimeter Array Band 3 data toward five massive young stellar objects (MYSOs), and investigate relationships between unsaturated carbon-chain species and saturated complex organic molecules (COMs). An HC5N (J=35-34) line has been detected from three MYSOs, where nitrogen(N)-bearing COMs (CH2CHCN and CH3CH2CN) have been detected. The HC5N spatial distributions show compact features and match with a methanol (CH3OH) line with an upper-state energy around 300 K, which should trace hot cores. The hot regions are more extended around the MYSOs where N-bearing COMs and HC5N have been detected compared to two MYSOs without these molecular lines, while there are no clear differences in the bolometric luminosity and temperature. We run chemical simulations of hot-core models with a warm-up stage, and compare with the observational results. The observed abundances of HC5N and COMs show good agreements with the model at the hot-core stage with temperatures above 160 K. These results indicate that carbon-chain chemistry around the MYSOs cannot be reproduced by warm carbon-chain chemistry, and a new type of carbon-chain chemistry occurs in hot regions around MYSOs.

H2CN/H2NC abundance ratio: a new potential temperature tracer for the interstellar medium

D. San Andrés, L. Colzi, V. M. Rivilla, J. García de la Concepción, M. Melosso, J. Martín-Pintado, I. Jiménez-Serra, S. Zeng, S. Martín, M. A. Requena-Torres

The H2NC radical is the high-energy metastable isomer of H2CN radical, which has been recently detected for the first time in the interstellar medium towards a handful of cold galactic sources, besides a warm galaxy in front of the PKS 1830-211 quasar. These detections have shown that the H2CN/H2NC isomeric ratio, likewise the HCN/HNC ratio, might increase with the kinetic temperature (T_{kin}), but the shortage of them in warm sources still prevents us to confirm this hypothesis and shed light about their chemistry. In this work, we present the first detection of H2CN and H2NC towards a warm galactic source, the G+0.693-0.027 molecular cloud (with $T_{kin}>70K$), using IRAM 30m observations. We have detected multiple hyperfine components of the $N\_KaKc=1\_01-0\_00$ and 2_02-1_01 transitions. We derived molecular abundances with respect to H2 of $(6.8\pm1.3)\times1e{-}11$ for H2CN and of $(3.1\pm0.7)\times1e{-}11$ for H2NC, and a H2CN/H2NC abundance ratio of 2.2±0.5. These detections confirm that the H2CN/H2NC ratio is ≳2 for sources with $T_{kin}>70K$, larger than the ~1 ratios previously found in colder cores ($T_{kin}\sim10K$). This isomeric ratio dependence with temperature cannot be fully explained with the currently proposed gas-phase formation and destruction pathways. Grain surface reactions, including the H2NC→H2CN isomerization, deserve consideration to explain the higher isomeric ratios and H2CN abundances observed in warm sources, where the molecules can be desorbed into the gas phase through thermal and/or shock-induced mechanisms.

Comprehensive Study of the Chemical Composition and Spatial Outgassing Behavior of Hyperactive Comet 46P/Wirtanen Using Near-IR Spectroscopy during its Historic 2018 Apparition

Younas Khan, Erika L. Gibb, Nathan X. Roth, Michael A. DiSanti, Neil Dello Russo, Boncho P. Bonev, Chemeda T. Ejeta, Mohammad Saki, Ronald J. Vervack Jr., Adam J. McKay, Hideyo Kawakita, Michael R. Combi, Danna Qasim, and Yinsi Shou

We present a comprehensive analysis of the chemical composition of the Jupiter-family comet and potential spacecraft target 46P/Wirtanen, in the near-IR wavelength range. We used iSHELL at the NASA Infrared Telescope Facility to observe the comet on 11 pre-, near-, and postperihelion dates in 2018 December and 2019 January and February during its historic apparition. We report rotational temperatures, production rates, and mixing ratios with respect to H2O and C2H6 or 3σ upper limits of the primary volatiles H2O, HCN, CH4, C2H6, CH3OH, H2CO, NH3, CO, C2H2, and HC3N. We also discuss the spatial outgassing of the primary volatiles, to understand their sources and the spatial associations between them. The spatial profiles of H2O in 46P/Wirtanen suggest the presence of extended H2O outgassing sources in the coma, similar to

the EPOXI target comet 103P/Hartley 2. 46P/Wirtanen is among the few known hyperactive comets, and we note that its composition and outgassing behavior are similar to those of other hyperactive comets in many ways. We note that the analyzed parent volatiles showed different variations (relative mixing ratios) during the apparition. We compared the chemical composition of 46P/Wirtanen with the mean abundances in Jupiter-family comets and the comet population as measured with ground-based near-IR facilities to date. The molecular abundances in 46P/Wirtanen suggest that although they were changing, the variations were small compared to the range in the comet population, with CH3OH showing notably more variation as compared to the other molecules.

A 3D physico-chemical model of a pre-stellar core. I. Environmental and structural impact on the distribution of CH3OH and c-C3H2

S. S. Jensen, S. Spezzano, P. Caselli, T. Grassi, T. Haugbølle

Pre-stellar cores represent the earliest stage of the star- and planet-formation process. By characterizing the physical and chemical structure of these cores we can establish the initial conditions for star and planet formation and determine to what degree the chemical composition of pre-stellar cores is inherited to the later stages. A 3D MHD model of a pre-stellar core embedded in a dynamic star-forming cloud is post-processed using sequentially continuum radiative transfer, a gas-grain chemical model, and a line-radiative transfer model. Results are analyzed and compared to observations of CH3OH and c-C3H2 in L1544. Nine different chemical models are compared to the observations to determine which initial conditions are compatible with the observed chemical segregation in the prototypical pre-stellar core L1544. The model is able to reproduce several aspects of the observed chemical differentiation in L1544. Extended methanol emission is shifted towards colder and more shielded regions of the core envelope while c-C3H2 emission overlaps with the dust continuum, consistent with the observed chemical structure. Increasing the strength of the interstellar radiation field or the cosmic-ray ionization rate with respect to the typical values assumed in nearby star-forming regions leads to synthetic maps that are inconsistent with the observed chemical structure. Our model shows that the observed chemical dichotomy in L1544 can arise as a result of uneven illumination due to the asymmetrical structure of the 3D core and the environment within which the core has formed. This highlights the importance of the 3D structure at the core-cloud transition on the chemistry of pre-stellar cores.

Crossroads at the Origin of Prebiotic Chemical Complexity: Hydrogen Cyanide Product Diversification

Hilda Sandström, Martin Rahm

Products of hydrogen cyanide (HCN) reactivity are suspected to play important roles in astrochemistry and, possibly, the origin of life. The composition, chemical structure, and mechanistic details for formation of products from HCN's self-reactions have, however, proven elusive for decades. Here, we elucidate base-catalyzed reaction mechanisms for the formation of diaminomaleonitrile and polyimine in liquid HCN using ab initio molecular dynamics simulations. Both materials are proposed as key intermediates for driving further chemical evolution. The formation of these materials is predicted to proceed at similar rates, thereby offering an explanation of how HCN's self-reactions can diversify quickly under kinetic control. Knowledge of these reaction routes provides a basis for rationalizing subsequent reactivity in astrochemical environments such as on Saturn's moon Titan, in the subsurface of comets, in exoplanet atmospheres, and on the early Earth.

First observations of warm and cold methanol in Class 0/I proto-brown dwarfs

Riaz, B. ; Thi, W. -F. ; Machida, M. N.

We present results from the first molecular line survey to search for the fundamental complex organic molecule, methanol (CH3OH), in 14 Class 0/I proto-brown dwarfs (proto-BDs). IRAM 30-m observations over the frequency range of 92-116 GHz and 213-280 GHz have revealed emission in 14 CH3OH transition lines, at upper state energy level, Eupper ~7-49 K, and critical densities, ncrit of 1e5 to 1e9 cm−3. The most commonly detected lines are at Eupper < 20 K, while 11 proto-BDs also show emission in the higher excitation lines at Eupper ~21-49 K and ncrit ~ 1e5 to 1e8 cm−3. In comparison with the brown dwarf formation models, the high excitation lines likely probe the warm (~25-50 K) corino region at ~10-50 au in the proto-BDs, while the low-excitation lines trace the cold (< 20 K) gas at ~50-150 au. The column density for the cold component is an order of magnitude higher than the warm component. The CH3OH ortho-to-para ratios range between ~0.3-2.3. The volume-averaged CH3OH column densities show a rise with decreasing bolometric luminosity among the proto-BDs, with the median column density higher by a factor of ~3 compared to low-mass protostars. Emission in high-excitation (Eupper > 25 K) CH3OH lines together with the model predictions suggest that a warm corino is present in ~78%

of the proto-BDs in our sample. The remaining show evidence of only the cold component, possibly due to the absence of a strong, high-velocity jet that can stir up the warm gas around it.

A rich hydrocarbon chemistry and high C to O ratio in the inner disk around a very low-mass star

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Carbon is an essential element for life but how much can be delivered to young planets is still an open question. The chemical characterization of planet-forming disks is a crucial step in our understanding of the diversity and habitability of exoplanets. Very low-mass stars (<0.2 Msun) are interesting targets because they host a rich population of terrestrial planets. Here we present the JWST detection of abundant hydrocarbons in the disk of a very low-mass star obtained as part of the MIRI mid-INfrared Disk Survey (MINDS). In addition to very strong and broad emission from C2H2 and its 13C12CH2 isotopologue, C4H2, benzene, and possibly CH4 are identified, but water, PAH and silicate features are weak or absent. The lack of small silicate grains implies that we can look deep down into this disk. These detections testify to an active warm hydrocarbon chemistry with a high C/O ratio in the inner 0.1 au of this disk, perhaps due to destruction of carbonaceous grains. The exceptionally high C2H2/CO2 and C2H2/H2O column density ratios suggest that oxygen is locked up in icy pebbles and planetesimals outside the water iceline. This, in turn, will have significant consequences for the composition of forming exoplanets.

The edge-on protoplanetary disk HH 48 NE I. Modeling the geometry and stellar parameters

J.A. Sturm, M.K. McClure, C.J. Law, D. Harsono, J.B. Bergner, E. Dartois, M.N. Drozdovskaya, S. Ioppolo, K.I. Öberg, M.E. Palumbo, Y.J. Pendleton, W.R.M. Rocha, H. Terada, and R.G. Urso

Context. Observations of edge-on disks are an important tool for constraining general protoplanetary disk properties that cannot be determined in any other way. However, most radiative transfer models cannot simultaneously reproduce the spectral energy distributions (SEDs) and resolved scattered light and submillimeter observations of these systems, due to the differences in geometry and dust properties at different wavelengths. Aims. We simultaneously constrain the geometry of the edge-on protoplanetary disk HH 48 NE and the characteristics of the host star. HH 48 NE is part of the JWST early release science program Ice Age. This work serves as a stepping stone towards a better understanding of the disk physical structure and icy chemistry in this particular source. This kind of modeling lays the groundwork for studying other edge-on sources to be observed with the JWST. Methods. We fit a parameterized dust model to HH 48 NE by coupling the radiative transfer code RADMC-3D and an MCMC framework. The dust structure was fitted independently to a compiled SED, a scattered light image at 0.8 μm and an ALMA dust continuum observation at 890 μm. Results. We find that 90% of the dust mass in HH 48 NE is settled to the disk midplane, less than in average disks, and that the atmospheric layers of the disk contain exclusively large grains (0.3-10 μm). The exclusion of small grains in the upper atmosphere likely has important consequences for the chemistry due to the deep penetration of high-energy photons. The addition of a relatively large cavity (ca. 50 au in radius) is necessary to explain the strong mid-infrared emission, and to fit the scattered light and continuum observations simultaneously.

The edge-on protoplanetary disk HH 48 NE II. Modeling ices and silicates

J.A. Sturm, M.K. McClure, J.B. Bergner, D. Harsono, E. Dartois, M.N. Drozdovskaya, S. Ioppolo, K.I. Öberg, C.J. Law, M.E. Palumbo, Y.J. Pendleton, W.R.M. Rocha, H. Terada, and R.G. Urso

The abundance and distribution of ice in protoplanetary disks (PPD) is critical to understand the linkage between the composition of circumstellar matter and the composition of exoplanets. Edge-on PPDs are a useful tool to constrain such ice composition and its location in the disk, as ice spectral signatures can be observed in absorption against the continuum emission arising from the warmer central disk regions. The aim of this work is to model ice absorption features in PPDs and determine how well the abundance of the main ice species across the disk can be determined within the uncertainty of the physical parameter space. The edge-on PPD around HH 48 NE, a target of the JWST ERS program IceAge, is used as a reference system. We use RADMC-3D to raytrace the mid-infrared continuum. Using a constant parameterized ice abundance, ice opacities are added to the dust opacity in regions wherever the disk is cold enough for the main carbon, oxygen and nitrogen carriers to freeze out. The global abundance of the main ice carriers in HH 48 NE can be determined within a factor of 3, when taking the uncertainty of the physical parameters into account. Ice features in PPDs can be

saturated at an optical depth <1, due to local saturation. Spatially observed ice optical depths cannot be directly related to column densities due to radiative transfer effects. Vertical snowlines will not be a clear transition due to the radially increasing height of the snowsurface, but their location may be constrained from observations using radiative transfer modeling. Radial snowlines are not really accesible. Not only the ice abundance, but also inclination, settling, grain size distribution and disk mass have strong impact on the observed ice absorption features in disks. Relative changes in ice abundance can be inferred from observations only if the source structure is well constrained

First ALMA Maps of Cosmic-Ray Ionization Rate in High-mass Star-forming Regions

G. Sabatini, S. Bovino and E. Redaelli

Low-energy cosmic rays (<1 TeV) are a pivotal source of ionization of the interstellar medium, where they play a central role in determining the gas chemical composition and drastically influence the formation of stars and planets. Over the past few decades, H_3^+ absorption line observations in diffuse clouds have provided reliable estimates of the cosmic-ray ionization rate relative to H_2 (ζ_{ion}). However, in denser clouds, where stars and planets form, this method is often inefficient due to the lack of H_3^+ rotational transitions. The ζ_{ion} estimates are, therefore, still provisional in this context and represent one of the least understood components when it comes to defining general models of star and planet formation. In this Letter, we present the first high-resolution maps of the ζ_{ion} in two high-mass clumps obtained with a new analytical approach recently proposed to estimate the ζ_{ion} in the densest regions of molecular clouds. We obtain $\langle\zeta_{ion}\rangle$ that span from 3e-17 to 1e-16 s-1, depending on the different distribution of the main ion carriers, in excellent agreement with the most recent cosmic-ray propagation models. The cores belonging to the same parental clump show comparable ζ_{ion}, suggesting that the ionization properties of prestellar regions are determined by global rather than local effects. These results provide important information for the chemical and physical modeling of star-forming regions.

Experimental, theoretical and astrochemical modelling investigation of the gas-phase reaction between the amidogen radical (NH2) and acetaldehyde (CH3CHO) at low temperatures

Kevin M. Douglas, Desmond Lok Hin Li, Catherine Walsh, Julia H. Lehman, Mark Blitz, Dwayne E. Heard

The first experimental study of the low-temperature kinetics of the gas-phase reactions of NH_2 with acetaldehyde (CH_3CHO) has been performed. Experiments were carried out using laser-flash photolysis and laser-induced spectroscopy to create and monitor the temporal decay of NH_2 in the presence of CH_3CHO. Low temperatures relevant to the interstellar medium were achieved using a pulsed Laval nozzle expansion. Rate coefficients were measured over the temperature and pressure range of 29 – 107 K and (1.4 – 28.2)e16 molecule cm-3 respectively, with the reaction exhibiting a negative temperature dependence and a positive pressure dependence. The yield of CH_3CO from the reaction has also been determined at 67.1 and 35.0 K, by observing OH produced from the reaction of CH_3CO with added O_2. Ab initio calculations of the potential energy surface (PES) were combined with Rice-Rampsberger-Kessel-Marcus (RRKM) calculations to predict rate coefficients and branching ratios over a broad range of temperatures and pressures. The calculated rate coefficients were shown to be sensitive to the calculated density of states of the stationary points, which in turn are sensitive to the inclusion of hindered rotor potentials for several of the vibrational frequencies. The experimentally determined rate coefficients and yields have been used to fit the calculated PES, from which low-pressure liming rate coefficients relevant to the ISM were determined. These have been included in a single-point dark cloud astrochemical model, in which the reaction is shown to be a potential source of gas-phase CH_3CO radicals under dark cloud conditions.

High-resolution rovibrational and rotational spectroscopy of singly deuterated cyclopropenyl cation, c-C3H2D+

D. Gupta, W. G D P Silva, J. L Domenech, E. Plaar, S. Thorwirth, S. Schlemmer and O. Asvany

Applying a novel action spectroscopic technique in a 4 K cryogenic ion trap instrument, the molecule $C_3H_2D^+$ has been investigated by high-resolution rovibrational and pure rotational spectroscopy for the first time. In total, 126 rovibrational transitions within the fundamental band of the ν_1 symmetric C-H stretch were measured with a band origin centred at 3168.565 cm−1, which were used to predict pure rotational transition frequencies in the ground vibrational state. Based on these predictions, 16 rotational transitions were observed between 90 and 230 GHz. These new measurements will enable the first radio-astronomical search for $C_3H_2D^+$.

Reliable Gas Phase Reaction Rates at Affordable Cost by Means of the Parameter-Free junChS-F12 Model Chemistry

V. Barone, J. Lupi, Z. Salta, N. Tasinato

A recently developed strategy for the computation at affordable cost of reliable barrier heights ruling reactions in the gas-phase (junChS, [Barone et al. J. Chem. Theory Comput. 2021, 17, 4913-4928]) has been extended to the employment of explicitly-correlated (F12) methods. A thorough benchmark based on a wide range of prototypical reactions shows that the new model (referred to as junChS-F12), which employs cost-effective revDSD-PBEP86-D3(BJ) reference geometries, has an improved performance with respect to its conventional counterpart and outperforms the most well-known model chemistries without the need of any empirical parameter and at an affordable computational cost. Several benchmarks show that revDSD-PBEP86- D3(BJ) structures and force fields provide zero point energies and thermal contributions, which can be confidently used, together with junChS-F12 electronic energies, for obtaining accurate reaction rates in the framework of the master equation approach based on the ab initio transition-state theory.

ALMA ACA study of the H2S/OCS ratio in low-mass protostars

Tanya Kushwahaa, Maria N. Drozdovskaya, Lukasz Tychoniec, and Benoît Tabone

Context. The identification of the main sulfur reservoir on its way from the diffuse interstellar medium to the cold dense star-forming cores and eventually to protostars is a long-standing problem. Despite sulfur's astrochemical relevance, the abundance of S-bearing molecules in dense cores and regions around protostars is still insufficiently constrained. Aims. The goal of this investigation is to derive the gas-phase H2S/OCS ratio for several low-mass protostars, which could provide crucial information about the physical and chemical conditions in the birth cloud of Sun-like stars. Methods. Using ALMA ACA Band 6 observations, H2S, OCS, and their isotopologs are searched for in 10 Class 0/I protostars with different source properties such as age, mass, and environmental conditions. An LTE model is used to fit synthetic spectra to the detected lines and to derive the column densities based solely on optically thin lines. Results. The H2S and OCS column densities span four orders of magnitude across the sample. The H2S/OCS ratio is found to be in the range from 0.2 to above 9.7. IRAS 16293-2422 A and Ser-SMM3 have the lowest ratio, while BHR71-IRS1 has the highest. Only the H2S/OCS ratio of BHR71-IRS1 agress within uncertainties with the ratio in comet 67P/Churyumov–Gerasimenko. Conclusions. The determined gas-phase H2S/OCS ratios can be below the upper limits on the solid-state ratios by as much as an order of magnitude. The H2S/OCS ratio depends significantly on the environment of the birth cloud, such as UV-irradiation and heating received prior to the formation of a protostar. The highly isolated birth environment of BHR71-IRS1 is hypothesized to be the reason for its high gaseous H2S/OCS ratio due to lower rates of photoreactions and more efficient hydrogenation reactions under such dark, cold conditions. The gaseous inventory of S-bearing molecules in BHR71-IRS1 appears to be most similar to that of interstellar ices.

Announcements

JWST Observations of Ices During Star Formation
Application closing date:- June 30th 2023
Interviews:- w/c July 17th 2023

Start Date:- available "now" and ideally starting on or before Nov 1st 2023

https://www.open.ac.uk/about/employment/vacancies/post-doctoral-research-associate-jwst-observations-ices-during-star-formation-20928

For further information please email helen.fraser@open.ac.uk

Salary: £36,333 or up to £38,474 (dependent on previous postdoctoral experience)
Location: Milton Keynes, UK
Please quote reference: 20928
Role: Full time, Fixed Term 36 months

We invite applications for a 3-year fixed-term postdoctoral researcher in Observational Astronomy. The postdoctoral research associate (PDRA) will be involved in the preparation, reduction, analysis, exploitation, and dissemination of JWST observational data from a variety of cycle 1 / 2 GT GO and ERS programmes, all of which focus on observing interstellar ices in pre-stellar phases of star-formation. The post is part of the STFC-funded project "The JWST IceAge: Chemical Evolution of Ices During Star Formation" in the OU Astrochemistry Group with Dr Helen Jane Fraser and Dr Hugh Dickinson.

The overarching aim of this work is to unveil the link between solid-state ice chemistry, and the gas and dust tracers of star-formation, by connecting ice formation, ice evolution and ice destruction to the astrophysical environment in pre- and proto-stellar cores.

You will be involved in the reduction, analysis, exploitation, and dissemination of JWST observational data focusing on observing interstellar ices in pre-stellar phases of star-formation. You will be expected to lead the day-to-day data reduction, data analysis and resulting scientific publications. By exploiting existing cycle 1 GT GO and ERS JWST data, you will couple NIRCam-WFSS, NIRSpec-MSA and MIRI-MRS spectroscopic ice observations with laboratory ice spectra, and you will determine ice abundances and map the distribution of H_2O, CO, CO_2, and CH_3OH ices at unprecedented spatial and spectral resolution. You will combine these ice-maps with sub-mm gas-phase and dust observations of the same pre-stellar cores, to gain an astrochemical understanding of the formation, evolution and destruction of ice in these regions.

You will have opportunities to disseminate your work at major national and international conferences, as well as working with international collaborators, particularly in JPL, Leiden Observatory, University of Hawaii, and University of Marseille. You will be expected to develop your JWST observing skills, and submit your own PI-led observing proposals to major facilities (i.e. JWST, VLT, ALMA, IRAM, JCMT) to develop your research independence, alongside delivering the primary goals of this project.

Skills and Experience

You will hold a PhD in Astronomy, Astrochemistry or a closely related field (e.g. Physics or Chemistry)
You will have prior experience working with (at least) one of the following observational techniques: IR astronomy (imaging or spectroscopy); sub-mm astronomy; slit-less spectroscopy; photometry.
You will be able to evidence extensive skills in python programming for scientific data processing and analysis, using local and HPC machines, as well as experience designing and executing astronomical observations on major telescopes.
You will also have excellent communication skills and be able to evidence strong teamwork in scientific or engineering projects, as well as demonstrating an emerging track record of peer-reviewed publications in international scientific journals.

To apply for this role please submit the following;
CV
Personal statement, up to 1,000 words, you should set out in your statement why you're interested in this role and provide examples of where your skills and experience meet the required competencies for this role as detailed in the job and person specification. To ensure your file is uploaded to our system correctly, please make sure your document is saved with the following file name as appropriate to the vacancy you are applying for: reference, surname, first initial.

Remember to attach your CV and Cover Letter as ONE DOCUMENT.

You will receive updates regarding your application from resourcing-applications@open.ac.uk. Please ensure this email address is added to your list of trusted senders. Please also keep an eye on your junk folder to ensure you do not miss any important updates regarding this role.

Closing date: 30th June 2023

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