

# AstroChemical Newsletter #61

December 2020

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## Abstracts

### Detection of infrared fluorescence of carbon dioxide in R Leonis with SOFIA/EXES

J. P. Fonfria, E. J. Montiel, J. Cernicharo, C. N. DeWitt, M. J. Richter

We report on the detection of hot CO<sub>2</sub> in the O-rich AGB star R Leo based on high spectral resolution observations in the range 12.8-14.3  $\mu\text{m}$  carried out with the Echelon-cross-Echelle Spectrograph (EXES) mounted on the Stratospheric Observatory for Infrared Astronomy (SOFIA). We have found  $\sim 240$  CO<sub>2</sub> emission lines in several vibrational bands. These detections were possible thanks to a favorable Doppler shift that allowed us to avoid contamination by telluric CO<sub>2</sub> features. The highest excitation lines involve levels at an energy of  $\sim 7000$  K. The detected lines are narrow (average deconvolved width  $\sim 2.5$  km/s) and weak (usually  $< 10\%$  the continuum). A ro-vibrational diagram shows that there are three different populations, warm, hot, and very hot, with rotational temperatures of  $\sim 550$ , 1150, and 1600 K, respectively. From this diagram, we derive a lower limit for the column density of  $\sim 2.2 \times 10^{16}$  cm<sup>-2</sup>. Further calculations based on a model of the R Leo envelope suggest that the total column density can be as large as  $7 \times 10^{17}$  cm<sup>-2</sup> and the abundance with respect to H<sub>2</sub>  $\sim 2.5 \times 10^{-5}$ . The detected lines are probably formed due to de-excitation of CO<sub>2</sub> molecules from high energy vibrational states, which are essentially populated by the strong R Leo continuum at 2.7 and 4.2  $\mu\text{m}$ .

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### Extending the view of ArH<sup>+</sup> chemistry in diffuse clouds

Arshia M. Jacob, Karl M. Menten, Friedrich Wyrowski, Benjamin Winkel, David A. Neufeld

One of the surprises of the Herschel mission was the detection of ArH<sup>+</sup> towards the Crab Nebula in emission and in absorption towards strong Galactic background sources. Although these detections were limited to the first quadrant of the Galaxy, the existing data suggest that ArH<sup>+</sup> ubiquitously and exclusively probes the diffuse atomic regions of the ISM. In this study, we extend the coverage of ArH<sup>+</sup> to other parts of the Galaxy with new observations of its  $J = 1-0$  transition along seven Galactic sight lines towards bright sub-mm continuum sources. We aim to benchmark its efficiency as a tracer of purely atomic gas by evaluating its correlation (or lack thereof) with other well-known atomic and molecular gas tracers. The observations of ArH<sup>+</sup> near 617.5 GHz were made feasible with the new, sensitive SEPIA660 receiver on the APEX 12 m telescope. The two sidebands of this receiver allowed us to observe p-H<sub>2</sub>O<sup>+</sup> transitions

of at 607.227 GHz simultaneously with the ArH+ line. By analysing the steady state chemistry of OH+ and o-H2O+, we derive on average a cosmic-ray ionisation rate (CRIR), of  $2.3 \times 10^{-16} \text{ s}^{-1}$  towards the sight lines studied in this work. Using the derived values of the CRIR and the observed ArH+ abundances we constrain the molecular fraction of the gas traced by ArH+ to lie below  $2 \times 10^{-2}$  with a median value of  $8.8 \times 10^{-4}$ . Combined, our observations of ArH+, OH+, H2O+, and CH probe different regimes of the ISM, from diffuse atomic to diffuse and translucent molecular clouds. Over Galactic scales, we see that the distribution of  $N(\text{ArH}^+)$  is associated with that of  $N(\text{H})$ , particularly in the inner Galaxy with potentially even contributions from the warm neutral medium phase of atomic gas at larger galactocentric distances. We derive an average o/p-ratio for H2O+ of 2.1, which corresponds to a nuclear spin temperature of 41 K, consistent with the typical gas temperatures of diffuse clouds.

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## Eta Carinae & the Homunculus: Far Infrared/Sub-millimeter Spectral Lines detected with the Herschel Space Observatory

**T. R. Gull, P. W. Morris, J. H. Black, K. E. Nielsen, M. J. Barlow, P. Royer and B. M. Swinyard**

The evolved massive binary star Eta Carinae underwent eruptive mass loss events that formed the complex bi-polar Homunculus nebula harboring tens of solar masses of unusually nitrogen-rich gas and dust. Despite expectations for the presence of a significant molecular component to the gas, detections have been observationally challenged by limited access to the far-infrared and the intense thermal continuum. A spectral survey of the atomic and rotational molecular transitions was carried out with the Herschel Space Observatory, revealing a rich spectrum of broad emission lines originating in the ejecta. Velocity profiles of selected PACS lines correlate well with known substructures: HI in the central core; NH and weak [C II] within the Homunculus; and [NII] emissions in fast-moving structures external to the Homunculus. We have identified transitions from [OI], HI, and 18 separate light C- and O-bearing molecules including CO, CH, CH+, and OH, and a wide set of N-bearing molecules, NH, NH+, N2H+, NH2, NH3, HCN, HNC, CN, and N2H+. Half of these are new detections unprecedented for any early-type massive star environment. A very low ratio  $[^{12}\text{C}/^{13}\text{C}] < 4$  is estimated from five molecules and their isotopologues. We demonstrate that non-LTE effects due to the strong continuum are significant. Abundance patterns are consistent with line formation in regions of carbon and oxygen depletions with nitrogen enhancements, reflecting an evolved state of the erupting star with efficient transport of CNO-processed material to the outer layers. The results offer many opportunities for further observational and theoretical investigations of the molecular chemistry under extreme physical and chemical conditions around massive stars in their final stages of evolution.

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## Herschel spectroscopy of massive young stellar objects in the Magellanic Clouds

**J.M. Oliveira, J.Th. van Loon, M. Sewilo, M.-Y. Lee, V. Lebouteiller, C.-H.R. Chen, D. Cormier, M.D. Filipovic, L.R. Carlson, R. Indebetouw, S. Madden, M.**

## Meixner, B. Sargent, Y. Fukui

We present Herschel Space Observatory Photodetector Array Camera and Spectrometer (PACS) and Spectral and Photometric Imaging Receiver Fourier Transform Spectrometer (SPIRE FTS) spectroscopy of a sample of 20 massive Young Stellar Objects (YSOs) in the Large and Small Magellanic Clouds (LMC and SMC). We analyse the brightest far-infrared (far-IR) emission lines, that diagnose the conditions of the heated gas in the YSO envelope and pinpoint their physical origin. We compare the properties of massive Magellanic and Galactic YSOs. We find that [O I] and [C II] emission, that originates from the photo-dissociation region associated with the YSOs, is enhanced with respect to the dust continuum in the Magellanic sample. Furthermore the photoelectric heating efficiency is systematically higher for Magellanic YSOs, consistent with reduced grain charge in low metallicity environments. The observed CO emission is likely due to multiple shock components. The gas temperatures, derived from the analysis of CO rotational diagrams, are similar to Galactic estimates. This suggests a common origin to the observed CO excitation, from low-luminosity to massive YSOs, both in the Galaxy and the Magellanic Clouds. Bright far-IR line emission provides a mechanism to cool the YSO environment. We find that, even though [O I], CO, and [C II] are the main line coolants, there is an indication that CO becomes less important at low metallicity, especially for the SMC sources. This is consistent with a reduction in CO abundance in environments where the dust is warmer due to reduced ultraviolet-shielding. Weak H<sub>2</sub>O and OH emission is detected, consistent with a modest role in the energy balance of wider massive YSO environments.

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## ROSINA ion zoo at Comet 67P

**A. Beth, K. Altwegg, H. Balsiger, J.-J. Berthelier, M. R. Combi, J. De Keyser, B. Fiethe, S. A. Fuselier, M. Galand, T. I. Gombosi, M. Rubin, T. Sémon**

The Rosetta spacecraft escorted Comet 67P/Churyumov-Gerasimenko for 2 yr along its journey through the Solar System between 3.8 and 1.24 au. Thanks to the high resolution mass spectrometer on board Rosetta, the detailed ion composition within a coma has been accurately assessed in situ for the very first time. Previous cometary missions, such as Giotto, did not have the instrumental capabilities to identify the exact nature of the plasma in a coma because the mass resolution of the spectrometers onboard was too low to separate ion species with similar masses. In contrast, the Double Focusing Mass Spectrometer (DFMS), part of the Rosetta Orbiter Spectrometer for Ion and Neutral Analysis on board Rosetta (ROSINA), with its high mass resolution mode, outperformed all of them, revealing the diversity of cometary ions. We calibrated and analysed the set of spectra acquired by DFMS in ion mode from October 2014 to April 2016. In particular, we focused on the range from 13–39 u q<sup>-1</sup>. The high mass resolution of DFMS allows for accurate identifications of ions with quasi-similar masses, separating <sup>13</sup>C<sup>+</sup> from CH<sup>+</sup>, for instance. We confirm the presence in situ of predicted cations at comets, such as CH<sub>m</sub><sup>+</sup> (m = 1–4), H<sub>n</sub>O<sup>+</sup> (n = 1–3), O<sup>+</sup>, Na<sup>+</sup>, and several ionised and protonated molecules. Prior to Rosetta, only a fraction of them had been confirmed from Earth-based observations. In addition, we report for the first time the unambiguous presence of a molecular dication in the gas envelope of a Solar System body, namely CO<sub>2</sub><sup>++</sup>.

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## **Influence of galactic arm scale dynamics on the molecular composition of the cold and dense ISM III. Elemental depletion and shortcomings of the current physico-chemical models**

**Wakelam, V.; Iqbal, W.; Melisse, J. -P.; Gratier, P.; Ruaud, M.; Bonnell, I.**

We present a study of the elemental depletion in the interstellar medium. We combined the results of a Galactic model describing the gas physical conditions during the formation of dense cores with a full-gas-grain chemical model. During the transition between diffuse and dense medium, the reservoirs of elements, initially atomic in the gas, are gradually depleted on dust grains (with a phase of neutralization for those which are ions). This process becomes efficient when the density is larger than  $100 \text{ cm}^{-3}$ . If the dense material goes back into diffuse conditions, these elements are brought back in the gas phase because of photo-dissociations of the molecules on the ices, followed by thermal desorption from the grains. Nothing remains on the grains for densities below  $10 \text{ cm}^{-3}$  or in the gas phase in a molecular form. One exception is chlorine, which is efficiently converted at low density. Our current gas-grain chemical model is not able to reproduce the depletion of atoms observed in the diffuse medium except for Cl, which gas abundance follows the observed one in medium with densities smaller than  $10 \text{ cm}^{-3}$ . This is an indication that crucial processes (involving maybe chemisorption and/or ice irradiation profoundly modifying the nature of the ices) are missing.

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## **A non-energetic mechanism for glycine formation in the interstellar medium**

**S. Ioppolo, G. Fedoseev, K.-J. Chuang, H. M. Cuppen, A. R. Clements, M. Jin, R. T. Garrod, D. Qasim, V. Kofman, E. F. van Dishoeck, H. Linnartz**

The detection of the amino acid glycine and its amine precursor methylamine on the comet 67P/Churyumov-Gerasimenko by the Rosetta mission provides strong evidence for a cosmic origin of amino acids on Earth. How and when such molecules form along the process of star formation remains debated. Here we report the laboratory detection of glycine formed in the solid phase through atom and radical-radical addition surface reactions under dark interstellar cloud conditions. Our experiments, supported by astrochemical models, suggest that glycine forms without the need for 'energetic' irradiation (such as ultraviolet photons and cosmic rays) in interstellar water-rich ices, where it remains preserved, during a much earlier star-formation stage than previously assumed. We also confirm that solid methylamine is an important side-reaction product. A prestellar formation of glycine on ice grains provides the basis for a complex and ubiquitous prebiotic chemistry in space enriching the chemical content of planet-forming material.

Nature Astronomy (2020)

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## Methanimine as a Key Precursor of Imines in the Interstellar Medium: The Case of Propargylimine

J. Lupi, C. Pizzarini, and V. Barone

A gas-phase formation route is proposed for the recently detected propargylimine molecule. In analogy to other imines, such as cyanomethanimine, the addition of a reactive radical (C<sub>2</sub>H in the present case) to methanimine (CH<sub>2</sub>NH) leads to reaction channels open also in the harsh conditions of the interstellar medium. Three possible isomers can be formed in the CH<sub>2</sub>NH + C<sub>2</sub>H reaction: Z- and E-propargylimine (Z-,E-PGIM) as well as N-ethynyl-methanimine (N-EMIM). For both PGIM species, the computed global rate coefficient is nearly constant in the 20–300 K temperature range, and of the order of  $2\text{--}3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , while that for N-EMIM is about two orders of magnitude smaller. Assuming equal destruction rates for the two isomers, these results imply an abundance ratio for PGIM of  $[Z]/[E] \sim 1.5$ , which is only slightly underestimated with respect to the observational datum.

Astrophys. J. Lett., vol. 903, no. 2, p. L35, 2020

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## Irradiation dose affects the composition of organic refractory materials in space: results from laboratory analogues

R. G. Urso, V. Vuitton, G. Danger, L. Le Sergeant dHendecourt, L. Flandinet, Z. Djouadi, O. Mivumbi, F. R. Orthous-Daunay, A. Ruf, V. Vinogradoff, C. Wolters, R. Brunetto

Context. Near- and mid-infrared observations have revealed the presence of organic refractory materials in the Solar System, in cometary nuclei and on the surface of centaurs, Kuiper-belt and trans-neptunian objects. In these astrophysical environments, organic materials can be formed because of the interaction of frozen volatile compounds with cosmic rays and solar particles, and favoured by thermal processing. The analysis of laboratory analogues of such materials gives information on their properties, complementary to observations. Aims. We present new experiments to contribute to the understanding of the chemical composition of organic refractory materials in space. Methods. We bombard frozen water, methanol and ammonia mixtures with 40 keV H<sup>+</sup> and we warmed the by-products up to 300 K. The experiments enabled the production of organic residues that we analysed by means of infrared spectroscopy and by very high resolution mass spectrometry to study their chemical composition and their high molecular diversity, including the presence of hexamethylenetetramine and its derivatives. Results. We find that the accumulated irradiation dose plays a role in determining the composition of the residue. Conclusions. Based on the laboratory doses, we estimate the astrophysical timescales to be short enough to induce an efficient formation of organic refractory materials at the surface of icy bodies in the outer Solar System.

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## The TW Hya Rosetta Stone Project II: Spatially resolved emission of formaldehyde hints at low-temperature gas-phase formation

**Jeroen Terwisscha van Scheltinga, Michiel R. Hogerheijde, L. Ilsedore Cleeves, Ryan A. Loomis, Catherine Walsh, Karin I. Öberg, Edwin A. Bergin, Jennifer B. Bergner, Geoffrey A. Blake, Jenny K. Calahan, Paolo Cazzoletti, Ewine F. van Dishoeck, Viviana V. Guzmán, Jane Huang, Mihkel Kama, Chunhua Qi, Richard Teague, David J. Wilner**

Formaldehyde (H<sub>2</sub>CO) is an important precursor to organics like methanol (CH<sub>3</sub>OH). It is important to understand the conditions that produce H<sub>2</sub>CO and prebiotic molecules during star and planet formation. H<sub>2</sub>CO possesses both gas-phase and solid-state formation pathways, involving either UV-produced radical precursors or CO ice and cold ( $\leq 20$  K) dust grains. To understand which pathway dominates, gaseous H<sub>2</sub>CO's ortho-to-para ratio (OPR) has been used as a probe, with a value of 3 indicating "warm" conditions and  $< 3$  linked to cold formation in the solid-state. We present spatially resolved ALMA observations of multiple ortho- and para-H<sub>2</sub>CO transitions in the TW Hya protoplanetary disk to test H<sub>2</sub>CO formation theories during planet formation. We find disk-averaged rotational temperatures and column densities of  $33 \pm 2$  K,  $(1.1 \pm 0.1) \times 10^{12}$  cm<sup>-2</sup> and  $25 \pm 2$  K,  $(4.4 \pm 0.3) \times 10^{11}$  cm<sup>-2</sup> for ortho- and para-H<sub>2</sub>CO, respectively, and an OPR of  $2.49 \pm 0.23$ . A radially resolved analysis shows that the observed H<sub>2</sub>CO emits mostly at rotational temperatures of 30-40 K, corresponding to a layer with  $z/R \geq 0.25$ . The OPR is consistent with 3 within 60 au, the extent of the pebble disk, and decreases beyond 60 au to  $2.0 \pm 0.5$ . The latter corresponds to a spin temperature of 12 K, well below the rotational temperature. The combination of relatively uniform emitting conditions, a radial gradient in the OPR, and recent laboratory experiments and theory on OPR ratios after sublimation, lead us to speculate that gas-phase formation is responsible for the observed H<sub>2</sub>CO across the TW Hya disk.

ApJ, accepted

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## **High level ab initio binding energy distribution of molecules on interstellar ices: Hydrogen fluoride**

**G. Bovolenta, S. Bovino, E. Vöhringer-Martinez, D. A. Saez, T. Grassi, S. Vogt-Geisse**

The knowledge of the binding energy of molecules on astrophysically relevant ices can help to obtain an estimate of the desorption rate, i.e. the molecules residence time on the surface. This represents an important parameter for astrochemical models, crucial to determine the chemical fate of complex organic molecules formed on dust grains and observed in the densest regions of the interstellar medium. In this work, we propose a new robust procedure to study the interaction of atoms and molecules with interstellar ices, based on ab initio molecular dynamics and density functional theory, validated by high-level ab initio methods at a CCSD(T)/CBS level. We have applied this procedure to hydrogen fluoride (HF), a promising tracer of the molecular content of galaxies. In total we found 13 unique equilibrium structures of HF binding to small water clusters of up to 4 molecules, with binding energies ranging from 1208 to 7162 K. We computed a 22-molecules model of amorphous solid water (ASW) surface using ab initio molecular dynamics simulations and carried out a systematic analysis of the binding sites of HF, in terms of binding modes and binding energies. Considering 10 different water clusters, we found a binding energy distribution with an average value of  $5313 \pm 74$  K, and a dispersion of  $921 \pm 115$  K. Finally, the effect of the electrostatic field of the 22 water molecules on the binding energies was investigated incrementally by symmetry adapted perturbation theory, in order to gauge the effect of the water

environment. The results indicate that the extent of the electrostatic interaction of HF with ASW depends strongly on the properties of the binding site. We expect that this work will provide a solid foundation for a systematic development of a binding energy distribution database of molecules on interstellar surfaces.

In press Mol. Astrophys

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## Sustained Oscillations in interstellar chemistry models

**E. Roueff, J. Le Bourlot**

Non-linear behavior in interstellar chemical models has been recognized for 25 years now. Different mechanisms account for the possibility of multiple fixed-points at steady state, characterized by the ionization degree of the gas. Chemical oscillations are also a natural behaviour of non-linear chemical models. We study under which conditions spontaneous sustained chemical oscillations are possible, and what kind of bifurcations lead to, or quench, the occurrence of such oscillations. The well known Ordinary Differential Equations (ODE) integrator VODE is used to explore initial conditions and parameter space in a gas phase chemical model of a dark interstellar cloud. We recall that the time evolution of the various chemical abundances under fixed temperature conditions depends on the density over cosmic ionization rate  $n_{\text{H}} / \zeta$  ratio. We also report the occurrence of naturally sustained oscillations for a limited but well defined range of control parameters. The period of oscillations is within the range of characteristic time scales of interstellar processes and could lead to spectacular resonances in time dependent models. The amplitude of oscillations can reach several orders of magnitudes for low abundances species. The mechanism responsible for oscillations is tightly linked to the chemistry of nitrogen, and requires long chains of reactions such as found in multi-deuteration processes.

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## Chemical modelling of dust-gas chemistry within AGB outflows III. Photoprocessing of the ice and return to the ISM

**M. Van de Sande, C. Walsh, T.J. Millar**

To explain the properties of dust in the interstellar medium (ISM), the presence of a refractory organic mantle is necessary. The outflows of AGB stars are among the main contributors of stellar dust to the ISM. We present the first study of the refractory organic contribution of AGB stars to the ISM. Based on laboratory experiments, we included a new reaction in our extended chemical kinetics model: the photoprocessing of volatile complex ices into inert refractory organic material. The refractory organic feedback of AGB outflows to the ISM is estimated using observationally motivated parent species and grids of models of C-rich and O-rich outflows. Refractory organic material is mainly inherited from the gas phase through accretion onto the dust and subsequent photoprocessing. Grain-surface chemistry, initiated by photodissociation of ices, produces only a minor part and takes place in a sub-monolayer regime in almost all outflows. The formation of refractory organic material increases with outflow density and depends on the initial gas-phase composition. While O-rich dust is negligibly covered by refractory organics, C-rich dust has an average coverage of 3–9%, but can be as high as 8–22%. Although C-rich dust does not enter the ISM bare, its average

coverage is too low to influence its evolution in the ISM or significantly contribute to the coverage of interstellar dust. This study opens up questions on the coverage of other dust-producing environments. It highlights the need for an improved understanding of dust formation and for models specific to density structures within the outflow.

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## Announcements

### **Release of the IAU Proceedings: Laboratory Astrophysics: from Observations to Interpretation**

The proceedings of the first topical symposium on Laboratory Astrophysics sponsored by the International Astronomical Union, "Laboratory Astrophysics: from Observations to Interpretation", have been released.

This volume of Proceedings devoted to Laboratory Astrophysics and Astrochemistry is a collection of over 500 pages of science articles with contributions from leading scientists in the field describing the current state-of-the-art in this vibrant multidisciplinary field (see the links below for more details).

This volume constitutes an invaluable reference for the community at large and will, hopefully, be a first in a long series of IAU Proceedings devoted to Laboratory Astrophysics.

Laboratory Astrophysics: from Observations to Interpretation

Proceedings IAU Symposium No. 350, 2019

F. Salama & H. Linnartz, eds.

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### **PhD student position in Astrochemistry at Onsala Space Observatory**

We are looking for a motivated and analytical PhD candidate who wants to investigate outstanding questions in astrochemistry. You will have the opportunity to work on theoretical and observational investigations of chemical evolution in star-forming environments under the supervision of associate professor Eva Wirström, in connection to the Chalmers Initiative on Cosmic Origins as well as international collaborators. The position is a full-time temporary employment at Chalmers University of Technology, Sweden. Starting date is expected in mid-2021, but no later than 1 September 2021. The starting salary for PhD positions at Chalmers is approximately 31,000 SEK per month. Expected position duration is 4 years which include course work corresponding to 1 year. Application deadline 28 February 2021. To learn more and apply, see: <http://www.chalmers.se/en/about-chalmers/Working-at-Chalmers/Vacancies/?rmpage=job&rmjob=9038>