# AstroChemical Newsletter #66

## May 2021

You can access the full abstracts by clicking the paper titles. Submit your abstracts before the 25th of each month for inclusion in the following newsletter.

# Abstracts

### Interaction of Aromatic Molecules with Forsterite: Accuracy of the Periodic DFT-D4 Method

**Dario Campisi, Thanja Lamberts, Nelson Y. Dzade, Rocco Martinazzo, Inge Loes ten Kate, and Alexander G. G. M. Tielens**

Density functional theory (DFT) has provided deep atomic-level insights into the adsorption behavior of aromatic molecules on solid surfaces. However, modeling the surface phenomena of large molecules on mineral surfaces with accurate plane wave methods (PW) can be orders of magnitude more computationally expensive than localized atomic orbitals (LCAO) methods. In the present work, we propose a less costly approach based on the DFT-D4 method (PBE-D4), using LCAO, to study the interactions of aromatic molecules with the {010} forsterite ($Mg_2SiO_4$) surface for their relevance in astrochemistry. We studied the interaction of benzene with the pristine {010} forsterite surface and with transition-metal cations ($Fe^{2+}$ and $Ni^{2+}$) using PBE-D4 and a vdW-inclusive density functional (Dion, Rydberg, Schröder, Langreth, and Lundqvist (DRSLL)) with LCAO methods. PBE-D4 shows good agreement with coupled-cluster methods (CCSD(T)) for the binding energy trend of cation complexes and with PW methods for the binding energy of benzene on the forsterite surface with a difference of about 0.03 eV. The basis set superposition error (BSSE) correction is shown to be essential to ensure a correct estimation of the binding energies even when large basis sets are employed for single-point calculations of the optimized structures with smaller basis sets. We also studied the interaction of naphthalene and benzocoronene on pristine and transition-metal-doped {010} forsterite surfaces as a test case for PBE-D4. Yielding results that are in good agreement with the plane wave methods with a difference of about 0.02–0.17 eV, the PBE-D4 method is demonstrated to be effective in unraveling the binding structures and the energetic trends of aromatic molecules on pristine and transition-metal-doped forsterite mineral surfaces. Furthermore, PBE-D4 results are in good agreement with its predecessor PBE-D3(BJM) and with the vdW-inclusive density functionals, as long as transition metals are not involved. Hence, PBE-D4/CP-DZP has been proven to be a robust theory level to study the interaction of aromatic molecules on mineral surfaces.

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### Mechanism of Indirect Photon-induced Desorption at the Water Ice Surface

**R. Dupuy, M. Bertin, G. Féraud, X. Michaut, P. Marie-Jeanne, P. Jeseck, L. Philippe, V. Baglin, R. Cimino, C. Romanzin, and J.-H. Fillion**

Electronic excitations near the surface of water ice lead to the desorption of adsorbed molecules, through a so far debated mechanism. A systematic study of photon-induced indirect desorption, revealed by the spectral dependence of the desorption (7–13 eV), is conducted for Ar, Kr, $N_2$, and CO adsorbed on $H_2O$ or $D_2O$ amorphous ices. The mass and isotopic dependence and the increase of intrinsic desorption efficiency with photon energy all point to a mechanism of desorption induced by collisions between adsorbates and energetic H/D atoms, produced by photodissociation of water. This constitutes a direct and unambiguous experimental demonstration of the mechanism of indirect desorption of weakly adsorbed species on water ice, and sheds new light on the possibility of this mechanism in other systems. It also has implications for the description of photon-induced desorption in astrochemical models.

Phys. Rev. Lett. 126, 156001
DOI: 10.1103/PhysRevLett.126.156001
Full-text URL: https://arxiv.org/abs/2104.05567

### Submillimeter imaging of the Galactic Center starburst Sgr B2. Warm molecular, atomic, and ionized gas far from massive star-forming cores

**M. G. Santa-Maria, J. R. Goicoechea, M. Etxaluze, J. Cernicharo, S. Cuadrado**

We present 168 arcmin^2 spectral images of the Sgr B2 complex taken with Herschel/SPIRE-FTS. We detect ubiquitous emission from CO (up to J=12-11), $H_2O$, [CI]492, 809GHz, and [NII] 205um lines. We also present maps of the SiO, $N_2H^+$, HCN, and $HCO^+$ emission obtained with the IRAM30m telescope. The cloud environment dominates the emitted FIR (80%), $H_2O$ 752 GHz (60%) mid-J CO (91%), and [CI] (93%) luminosity. The region shows very extended [NII] emission (spatially correlated with the 24 and 70 um dust emission). The observed FIR luminosities imply G_0~1e3. The extended [CI] emission arises from a pervasive component of neutral gas with n_H~1e3 cm-3. The high ionization rates, produced by enhanced cosmic-ray (CR) fluxes, drive the gas heating to Tk~40-60 K. The mid-J CO emission arises from a similarly extended but more pressurized gas component (Pth~1e7 K cm-3). Specific regions of enhanced SiO emission and high CO-

to-FIR intensity ratios (>1e-3) show mid-J CO emission compatible with shock models. A major difference compared to more quiescent star-forming clouds in the disk of our Galaxy is the extended nature of the SiO and N2H+ emission in Sgr B2. This can be explained by the presence of cloud-scale shocks, induced by cloud-cloud collisions and stellar feedback, and the much higher CR ionization rate (>1e-15 s-1) leading to overabundant H3+ and N2H+. Hence, Sgr B2 hosts a more extreme environment than star-forming regions in the disk of the Galaxy. As a usual template for extragalactic comparisons, Sgr B2 shows more similarities to ultra luminous infrared galaxies such as Arp 220, including a "deficit" in the [CI]/FIR and [NII]/FIR intensity ratios, than to pure starburst galaxies such as M82. However, it is the extended cloud environment, rather than the cores, that serves as a useful template when telescopes do not resolve such extended regions in galaxies.

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## Thiols is the ISM: first detection of HC(O)SH and confirmation of C2H5SH

**Lucas F. Rodríguez-Almeida, Izaskun Jiménez-Serra, Víctor M. Rivilla, Jesús Martín-Pintado, Shaoshan Zeng, Belén Tercero, Pablo de Vicente, Laura Colzi, Fernando Rico-Villas, Sergio Martín and Miguel A. Requena-Torres**

The chemical compounds carrying the thiol group (-SH) have been considered essential in recent prebiotic studies regarding the polymerization of amino acids. We have searched for this kind of compounds toward the Galactic Centre quiescent cloud G+0.693-0.027. We report the first detection in the interstellar space of the trans-isomer of monothioformic acid (t-HC(O)SH) with an abundance of ~1e-10. Additionally, we provide a solid confirmation of the gauche isomer of ethyl mercaptan (g-C2H5SH) with an abundance of ~3e-10, and we also detect methyl mercaptan (CH3SH) with an abundance of ~5e-9. Abundance ratios were calculated for the three SH-bearing species and their OH-analogues, revealing similar trends between alcohols and thiols with increasing complexity. Possible chemical routes for the interstellar synthesis of t-HC(O)SH, CH3SH and C2H5SH are discussed, as well as the relevance of these compounds in the synthesis of prebiotic proteins in the primitive Earth.

Accepted in Astrophysical Journal Letters
Full-text URL: https://arxiv.org/abs/2104.08036

## Molecular Astrophysics

**A.G.G.M. Tielens**

Focusing on the organic inventory of regions of star and planet formation in the interstellar medium of galaxies, this comprehensive overview of the molecular universe is an invaluable reference source for advanced undergraduates through to entry-level researchers. It includes an extensive discussion of microscopic physical and chemical processes in the universe; these play a role in the excitation, spectral characteristics, formation, and evolution of molecules in the gas phase and on grain surfaces. In addition, the latest developments in this area of molecular astrophysics provide a firm foundation for an in-depth understanding of the molecular phases of the interstellar medium. The physical and chemical properties of gaseous molecules, mixed molecular ices, and large polycyclic aromatic hydrocarbon molecules and fullerenes and their role in the interstellar medium are highlighted. For those with an interest in the molecular universe, this advanced textbook bridges the gap between molecular physics, astronomy, and physical chemistry.

Cambridge University Press
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Full-text URL: https://doi.org/10.1017/9781316718490

## How Does Temperature Affect the Infrared Vibrational Spectra of Nanosized Silicate Dust?

**Joan Mariñoso Guiu, Antoni Macià Escatllar, Stefan T. Bromley**

Magnesium-rich silicates are pervasive throughout the universe and are found in many astronomical environments as small dust grains. Most of the information we have about such silicate dust comes from infrared (IR) observations, whereby the prominent ∼9.7 μm Si-O stretching and 18–20 μm O–Si–O bending vibrational bands are used as identifying signatures. During the initial stages of silicate dust nucleation around aging stars, the nascent grains are nanosized and heated to 800–1000 K. Later, the larger fully formed grains are ejected into the cold interstellar medium and are subsequently heavily processed (e.g., by shattering and sputtering), likely leading to an abundant population of nanosilicate grains. Such ultrasmall grains can eventually form a dust component of protoplanetary disks, where they can be again heated to a few hundred degrees. Although nanosilicate grains are astrochemically important and are likely carriers of the ubiquitous anomalous microwave emission, they have yet to be unambiguously identified through observation. The advent of the James Webb Space Telescope, with IR instruments of unrivalled sensitivity covering the 5-28 μm wavelength range, promises to open a window on these elusive, but presumably abundant, species. Here, we examine Mg-rich ultrasmall silicate clusters with both olivinic ($Mg_2SiO_4$) and pyroxenic ($MgSiO_3$) stoichiometries and accurately calculate their IR spectra at temperatures between 0 and 800 K. Although this temperature range is below that required to anneal bulk magnesium silicates (∼1000 K), we show that nanosized grains can exhibit significant anharmonic motions and premelted structural conformational fluxionality even at 400 K. As a result, we demonstrate that the IR spectra of nanosilicates are highly sensitive to temperature, which should thus be considered when attempting to identify these species.

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Full-text URL: https://pubs.acs.org/doi/abs/10.1021/acsearthspacechem.0c00341

## Identification of prestellar cores in high-mass star forming clumps via H2D+ observations with ALMA

**E. Redaelli, S. Bovino, A. Giannetti, G. Sabatini, P. Caselli, F. Wyrowski, D. R. G. Schleicher, and D. Colombo**

Context. The different theoretical models concerning the formation of high-mass stars make distinct predictions regarding their progenitors, i.e. the high-mass prestellar cores. However, so far no conclusive observation of such objects has been made. Aims. We aim to study the very early stages of high-mass star formation in two infrared-dark, massive clumps. Our goal is to identify the core population that they harbour and to investigate their physical and chemical properties at high spatial resolution. Methods. We obtained ALMA Cycle 6 observations of continuum emission at 0.8 mm and of the ortho-H2D+ transition at 372 GHz towards the two clumps. We use the SCIMES algorithm to identify substructures (i.e. cores) in the position-position-velocity space, finding 16 cores. We model their observed spectra using a Bayesian fitting approach in the approximation of local thermodynamic equilibrium. We derive the centroid velocity, the linewidth, and the molecular column density maps. We also study the correlation between the continuum and molecular data, which in general do not present the same structure. Results. We report for the first time the detection of ortho-H2D+ in high-mass star-forming regions performed with an interferometer. The molecular emission shows narrow and subsonic lines, suggesting that locally the temperature of the gas is less than 10K. From the continuum emission we estimate the cores' total masses, and compare them with the respective virial masses. We also compute the volume density values, which are found to be higher than 1e6 cm−3. Conclusions. Our data confirm that ortho-H2D+ is an ideal tracer of cold and dense gas. Interestingly, almost all the H2D+-identified cores are less massive than ≈ 13 Msun, with the exception of one core in AG354, which could be as massive as 39 Msun in the assumption of low dust temperature (5 K). Furthermore, most of them are subvirial and larger than their Jeans masses. These results are hence difficult to explain in the context of the turbulent accretion models, which predict massive and virialised prestellar cores. We however cannot exclude that the cores are still in the process of accreting mass, and that magnetic fields are providing enough support for the virialisation. ALMA could also be seeing only the innermost parts of the cores, and hence the total cores' masses could be higher than inferred in this work. Furthermore, we note that the total masses of the investigated clumps are below the average for typical high-mass clumps, and thus studies of more massive sources are needed.

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Full-text URL: https://arxiv.org/abs/2104.06431

## Formation of Interstellar Silicate Dust via Nanocluster Aggregation: Insights From Quantum Chemistry Simulations

**Albert Rimola, Stefan T. Bromley**

The issue of formation of dust grains in the interstellar medium is still a matter of debate. One of the most developed proposals suggests that atomic and heteromolecular seeds bind together to initiate a nucleation process leading to the formation of nanostructures resembling very small grain components. In the case of silicates, nucleated systems can result in molecular nanoclusters with diameters ≤ 2 nm. A reasonable path to further increase the size of these proto-silicate nanoclusters is by mutual aggregation. The present work deals with modeling this proto-silicate nanocluster aggregation process by means of quantum chemical density functional theory calculations. We simulate nanocluster aggregation by progressively reducing the size of a periodic array of initially well-separated nanoclusters. The resulting aggregation leads to a set of silicate bulk structures with gradually increasing density which we analyze with respect to structure, energetics and spectroscopic properties. Our results indicate that aggregation is a highly energetically favorable process, in which the infrared spectra of the finally formed amorphous silicates match well with astronomical observations.

Frontiers in Astronomy and Space Sciences| 8, 659494 (2021).
DOI: 10.3389/fspas.2021.659494
Full-text URL: https://www.frontiersin.org/articles/10.3389/fspas.2021.659494/full

## Modeling chemistry during star formation: Water deuteration in dynamic star-forming regions

**S. S. Jensen, J. K. Jørgensen, K. Furuya, T. Haugbølle, Y. Aikawa**

Recent observations of the HDO/H2O ratio toward protostars in isolated and clustered environments show an apparent dichotomy, where isolated sources show higher D/H ratios than clustered counterparts. Establishing which physical and chemical processes create this differentiation can provide insights into the chemical evolution of water during star formation and the chemical diversity during the star formation process and in young planetary systems. Methods: The evolution of water is modeled using 3D physicochemical models of a dynamic star-forming environment. The physical evolution during the protostellar collapse is described by tracer particles from a 3D MHD simulation of a molecular cloud region. Each particle trajectory is post-processed using RADMC-3D to calculate the temperature and radiation field. The chemical evolution is simulated using a three-phase grain-surface chemistry model and the results are compared with interferometric observations of H2O, HDO, and D2O in hot corinos toward low-mass protostars. Results: The physicochemical model reproduces the observed HDO/H2O and D2O/HDO ratios in hot corinos, but shows no correlation with cloud environment for similar identical conditions. The observed dichotomy in water D/H ratios requires variation in the initial conditions (e.g., the duration and temperature of the prestellar phase). Reproducing the observed D/H ratios in hot corinos requires a prestellar

phase duration t~1-3 Myr and temperatures in the range T~ 10-20 K prior to collapse. This work demonstrates that the observed differentiation between clustered and isolated protostars stems from differences in the molecular cloud or prestellar core conditions and does not arise during the protostellar collapse itself.

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# Announcements

### Special Research topic on Astrochemistry in "Frontiers in Astronomy and Space Sciences"

The submission deadline to the article collection on "RNA World Hypothesis and the Origin of Life: Astrochemistry Perspective" in "Frontiers in Astronomy and Space Sciences" has been extended up until July 31st 2021.
More scientific details and information about the submission process can be found at the following webpage:
https://www.frontiersin.org/research-topics/16120/rna-world-hypothesis-and-the-origin-of-life-astrochemistry-perspective?utm_source=F-RTM&utm_medium=TED1&utm_campaign=PRD_TED1_T1_RT-TITLE
or by contacting the topic editors:
Ashraf Ali: ashrali100@gmail.com
David Leisawitz: david.t.leisawitz@nasa.gov
André Canosa: andre.canosa@univ-rennes1.fr

### CONFERENCE "CHEMICAL PROCESSES IN SOLAR-TYPE STAR FORMING REGIONS",

"CHEMICAL PROCESSES IN SOLAR-TYPE STAR FORMING REGIONS" (https://sites.google.com/inaf.it/aco-conference/) jointly organised by the Department of Chemistry of the University of Torino, INAF Astrophysical Observatory of Arcetri and IPAG University of Grenoble Alpes.

VENUE
The conference will take place the 13-17 September 2021 in the Department of Chemistry, University of Torino, Italy. The meeting will be held physically, respecting the distancing rules, unless there is a new outbreak of COVID-19. As a consequence the limit for the number of attending participants is 80. To date, only 20 free seats remain, so hurry up!

KEY DATES
May 28: Deadline for registration and abstract submission. We have postponed it to allow a better understanding of the COVID-19 pandemic evolution and the clarification on the travelling rules linked to the vaccination process. We still have about 20 free seats, so hurry up!
15 June: Announcement of the selected oral contributions.
15 July: Deadline for payment of the registration fee

RATIONAL & FORMAT
How the chemical complexity evolves during the process leading to the formation of a Sun and its planetary system? Is the chemical richness of a Solar-like planetary system, at least partially, inherited from the earliest stages or is there a complete chemical reset? A powerful way to answering these questions is by comparing the chemical content in young protostars and primitive bodies of the Solar System, using astrochemistry as a tool. Yet, to do so, we need to fully understand the processes that govern the chemical evolution of a molecular cloud into a young planetary system. The goal of the conference is to gather together the actors of this intrinsically interdisciplinary endeavor: astronomers, chemists and modellers. The recent huge progresses in the three areas make the time ripe for these communities to join and ride this scientific wave. With the above goal, the conference aims at stimulating the interest and discussion on:
*) The new results from the powerful observing facilities, such as the IRAM-NOEMA, ALMA and VLA interferometers, and the chemical composition during the youngest phases of Solar-like planetary systems, from prestellar cores to protoplanetary disks, with particular emphasis on the interstellar complex organic molecules;
*) The recent progresses due to the enhancement of high-performance computing facilities combined with efficient quantum chemistry algorithms, which allow for the in-silico simulation of many chemical processes occurring both in gas-phase and at grain surfaces;
*) The latest laboratory experiments which have provided new insights on the possible processes occurring in the interstellar conditions;
*) The new generation astrochemical models as well as the innovative tools to interpret the astronomical observations that have seen the light in the last few years;
*) The most recent results on the chemical composition of the small bodies of the Solar System.

CONTENT & FORMAT
The conference will consist of four sessions, where astronomical observations and modelling as well as laboratory experiments and theoretical computations will be reviewed and discussed:
1. Interstellar Ices
2. Molecular Complexity
3. Molecular Fractionation
4. Cometary Ices
Two invited speakers will introduce each session.

In addition to the invited speakers, the conference will consist of several contributed talks, where a particular attention will be given to young researchers contributions. Ample time will be reserved to poster sessions, to allow for the discussions that we have been missing for more than one year now.
Support for PhD and young students is planned.

CONFIRMED INVITED SPEAKERS
N. Balucani (University of Perugia, Italy), D. Bockelée-Morvan (Observatoire de Paris, France), A. Boogert (University of Hawaii, USA), P. Caselli (MPE, Garching, Germany), J. Cernicharo (Instituto de Física Fundamental, CSIC, Madrid, Spain), R. Martín-Domenech (CfA, Cambridge, USA), M. McCoustra (Heriot-Watt University, United Kingdom), S. Tachibana (University of Tokyo, Japan)

SCIENTIFIC COMMITTEE
P. Ugliengo (co-chair), C. Codella (co-chair), A. Barucci, C. Ceccarelli, L. Piccirillo, A. Rimola, C. Vastel, S. Viti, S. Yamamoto SPONSORS & CONTACTS The conference is organised in the context of the EC H2020 projects ITN AstroChemical Origins (ACO) ad ERC Dawn of Organic Chemistry (DOC). For more informations and questions, please contact aco.itn@inaf.it or look at https://sites.google.com/inaf.it/aco-conference/