

AstroChemical Newsletter #63

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Abstracts

A New Method for Simulating Photoprocesses in Astrochemical Models

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We propose a new model for treating solid-phase photoprocesses in interstellar ice analogues. In this approach, photoionization and photoexcitation are included in more detail, and the production of electronically-excited (suprathermal) species is explicitly considered. In addition, we have included non-thermal, non-diffusive chemistry to account for the low-temperature characteristic of cold cores. As an initial test of our method, we have simulated two previous experimental studies involving the UV irradiation of pure solid O₂. In contrast to previous solid-state astrochemical model calculations which have used gas-phase photoabsorption cross-sections, we have employed solid-state cross-sections in our calculations. This method allows the model to be tested using well-constrained experiments rather than poorly constrained gas-phase abundances in ISM regions. Our results indicate that inclusion of non-thermal reactions and suprathermal species allows for reproduction of low-temperature solid-phase photoprocessing that simulate interstellar ices within cold (~ 10 K) dense cores such as TMC-1.

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Quantitative inference of the H₂ column densities from 3 mm molecular emission: case study towards Orion B

Pierre Gratier, Jérôme Pety, Emeric Bron, Antoine Roueff, Jan H. Orkisz, Maryvonne Gerin, Victor de Souza Magalhaes, Mathilde Gaudel, Maxime Vono, Sébastien Bardeau, Jocelyn Chanut, Pierre Chainais, Javier R. Goicoechea, Viviana V. Guzmán, Annie Hughes, Jouni Kainulainen, David Languignon, Jacques Le Boulot, Franck Le Petit, François Levrier, Harvey Liszt, Nicolas Peretto, Evelyne Roueff and Albrecht Sievers

Context. Based on the finding that molecular hydrogen is unobservable in cold molecular clouds, the column density measurements of molecular gas currently rely either on dust emission observation in the far-infrared, which requires space telescopes, or on star counting, which is limited in angular resolution by the stellar density. The (sub)millimeter observations of numerous trace molecules can be effective using ground-based telescopes, but the relationship between the emission of one molecular line and the H₂ column density is non-linear and sensitive to excitation

conditions, optical depths, and abundance variations due to the underlying physico-chemistry. **Aims.** We aim to use multi-molecule line emission to infer the H₂ molecular column density from radio observations. **Methods.** We propose a data-driven approach to determine the H₂ gas column densities from radio molecular line observations. We use supervised machine-learning methods (random forest) on wide-field hyperspectral IRAM-30m observations of the Orion B molecular cloud to train a predictor of the H₂ column density, using a limited set of molecular lines between 72 and 116 GHz as input, and the Herschel-based dust-derived column densities as “ground truth” output. **Results.** For conditions similar to those of the Orion B molecular cloud, we obtained predictions of the H₂ column density within a typical factor of 1.2 from the Herschel-based column density estimates. A global analysis of the contributions of the different lines to the predictions show that the most important lines are 13CO(1-0), 12CO(1-0), C18O(1-0), and HCO+(1-0). A detailed analysis distinguishing between diffuse, translucent, filamentary, and dense core conditions show that the importance of these four lines depends on the regime, and that it is recommended that the N₂H+(1-0) and CH₃OH(20-10) lines be added for the prediction of the H₂ column density in dense core conditions. **Conclusions.** This article opens a promising avenue for advancing direct inferencing of important physical parameters from the molecular line emission in the millimeter domain. The next step will be to attempt to infer several parameters simultaneously (e.g., the column density and far-UV illumination field) to further test the method.

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C18O, 13CO, and 12CO abundances and excitation temperatures in the Orion B molecular cloud - Analysis of the achievable precision in modeling spectral lines within the approximation of the local thermodynamic equilibrium

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Context. CO isotopologue transitions are routinely observed in molecular clouds for the purpose of probing the column density of the gas and the elemental ratios of carbon and oxygen, in addition to tracing the kinematics of the environment. **Aims.** Our study is aimed at estimating the abundances, excitation temperatures, velocity field, and velocity dispersions of the three main CO isotopologues towards a subset of the Orion B molecular cloud, which includes IC 434, NGC 2023, and the Horsehead pillar. **Methods.** We used the Cramer Rao bound (CRB) technique to analyze and estimate the precision of the physical parameters in the framework of local-thermodynamic-equilibrium (LTE) excitation and radiative transfer with added white Gaussian noise. We propose a maximum likelihood estimator to infer the physical conditions from the 1-0 and 2-1 transitions of CO isotopologues. Simulations show that this estimator is unbiased and proves efficient for a common range of excitation temperatures and column densities ($T_{\text{ex}} > 6$ K, $N > 1e14-1e15$ cm⁻²). **Results.** Contrary to general assumptions, the various CO isotopologues have distinct excitation temperatures and the line intensity ratios between different isotopologues do not accurately reflect the

column density ratios. We find mean fractional abundances that are consistent with previous determinations towards other molecular clouds. However, significant local deviations are inferred, not only in regions exposed to the UV radiation field, but also in shielded regions. These deviations result from the competition between selective photodissociation, chemical fractionation, and depletion on grain surfaces. We observe that the velocity dispersion of the C18O emission is 10% smaller than that of 13CO. The substantial gain resulting from the simultaneous analysis of two different rotational transitions of the same species is rigorously quantified. Conclusions. The CRB technique is a promising avenue for analyzing the estimation of physical parameters from the fit of spectral lines. Future works will generalize its application to non-LTE excitation and radiative transfer methods.

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Tracers of the ionization fraction in dense and translucent gas I. Automated exploitation of massive astrochemical model grids

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Context. The ionization fraction in the neutral interstellar medium (ISM) plays a key role in the physics and chemistry of the ISM, from controlling the coupling of the gas to the magnetic field to allowing fast ion-neutral reactions that drive interstellar chemistry. Most estimations of the ionization fraction have relied on deuterated species such as DCO⁺, whose detection is limited to dense cores representing an extremely small fraction of the volume of the giant molecular clouds that they are part of. As large field-of-view hyperspectral maps become available, new tracers may be found. The growth of observational datasets is paralleled by the growth of massive modeling datasets and new methods need to be devised to exploit the wealth of information they contain. **Aims.** We search for the best observable tracers of the ionization fraction based on a grid of astrochemical models, with the broader aim of finding a general automated method applicable to searching for tracers of any unobservable quantity based on grids of models. **Methods.** We built grids of models that randomly sample a large range of physical conditions (unobservable quantities such as gas density, temperature, elemental abundances, etc.) and computed the corresponding observables (line intensities, column densities) and the ionization fraction. We estimated the predictive power of each potential tracer by training a random forest model to predict the ionization fraction from that tracer, based on these model grids. **Results.** In both translucent medium and cold dense medium conditions, we found several observable tracers with very good predictive power for the ionization fraction. Many tracers in cold dense medium conditions are found to be better and more widely applicable than the traditional DCO⁺/HCO⁺ ratio. We also provide simpler analytical fits for estimating the ionization fraction from the best tracers, and for estimating the associated uncertainties. We discuss the limitations of the present study and select a few recommended tracers in both types of conditions. **Conclusions.** The method presented here is very general and can be applied to the measurement of any other quantity of interest (cosmic ray flux, elemental abundances, etc.) from any type of model (PDR

models, time-dependent chemical models, etc.).

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Bottlenecks to interstellar sulfur chemistry. Sulfur-bearing hydrides in UV-illuminated gas and grains

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Hydride molecules lie at the base of interstellar chemistry, but the synthesis of sulfuretted hydrides is poorly understood. Motivated by new observations of the Orion Bar PDR - 1" resolution ALMA images of SH⁺; IRAM 30m detections of H₂S, H₂S₃, and H₂S₃₃; H₃S⁺ (upper limits); and SOFIA observations of SH - we perform a systematic study of the chemistry of S-bearing hydrides. We determine their column densities using coupled excitation, radiative transfer as well as chemical formation and destruction models. We revise some of the key gas-phase reactions that lead to their chemical synthesis. This includes ab initio quantum calculations of the vibrational-state-dependent reactions SH⁺ + H₂ <-> H₂S⁺ + H and S + H₂ <-> SH + H. We find that reactions of UV-pumped H₂ (v>1) with S⁺ explain the presence of SH⁺ in a high thermal-pressure gas component, P_{th}~1e8 cm⁻³ K, close to the H₂ dissociation front. However, subsequent hydrogen abstraction reactions of SH⁺, H₂S⁺, and S with vibrationally excited H₂, fail to ultimately explain the observed H₂S column density (~2.5x1e14 cm⁻², with an ortho-to-para ratio of 2.9+/-0.3). To overcome these bottlenecks, we build PDR models that include a simple network of grain surface reactions leading to the formation of solid H₂S (s-H₂S). The higher adsorption binding energies of S and SH suggested by recent studies imply that S atoms adsorb on grains (and form s-H₂S) at warmer dust temperatures and closer to the UV-illuminated edges of molecular clouds. Photodesorption and, to a lesser extent, chemical desorption, produce roughly the same H₂S column density (a few 1e14 cm⁻²) and abundance peak (a few 1e-8) nearly independently of n_H and G₀. This agrees with the observed H₂S column density in the Orion Bar as well as at the edges of dark clouds without invoking substantial depletion of elemental sulfur abundances.

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The CALYPSO IRAM-PdBI survey of jets from Class 0 protostars. Are jets ubiquitous in young stars ?

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As a part of the CALYPSO large programme, we constrain the properties of protostellar jets and outflows in a sample of 21 Class 0 protostars with internal luminosities, L_{int}, from 0.035 to 47 L_{sun}. We analyse high angular resolution (~0.5"-1") IRAM PdBI observations in CO (2-1), SO (5₆-4₅), and SiO (5-4). CO (2-1), which probes outflowing gas, is detected in all the sources (for the first time in SerpS-MM22 and SerpS-MM18b). Collimated high-velocity jets in SiO (5-4) are detected in 67% of the sources (for the first time in IRAS4B2, IRAS4B1, L1448-NB, SerpS-MM18a), and 77% of these also show jet/outflow emission in SO (5₆-4₅). In 5 sources (24% of the sample) SO (5₆-4₅) probes the inner envelope and/or the disk. The CALYPSO survey

shows that the outflow phenomenon is ubiquitous and that the detection rate of high-velocity jets increases with protostellar accretion, with at least 80% of the sources with $L_{\text{int}} > 1 L_{\text{sun}}$ driving a jet. The protostellar flows exhibit an onion-like structure, where the SiO jet (opening angle ~ 10 degree) is nested into a wider angle SO (~ 15 degree) and CO (~ 25 degree) outflow. On scales > 300 au the SiO jets are less collimated than atomic jets from Class II sources (~ 3 degree). Velocity asymmetry between the two jet lobes are detected in one third of the sources, similarly to Class II atomic jets, suggesting that the same launching mechanism is at work. Most of the jets are SiO rich (SiO/H₂ from $> 2.4 \times 10^{-7}$ to $> 5 \times 10^{-6}$), which indicates efficient release of $> 1\%$ - 10% of silicon in gas phase likely in dust-free winds, launched from inside the dust sublimation radius. The mass-loss rates (from $\sim 7 \times 10^{-8}$ to $\sim 3 \times 10^{-6}$ M_{sun}/yr) are larger than what was measured for Class II jets. Similarly to Class II sources, the mass-loss rates are $\sim 1\%$ - 50% of the mass accretion rates suggesting that the correlation between ejection and accretion in young stars holds from 1×10^4 yr up to a few Myr.

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ALMA chemical survey of disk-outflow sources in Taurus (ALMA-DOT) III. The interplay between gas and dust in the protoplanetary disk of DG Tau

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Planets form in protoplanetary disks and inherit their chemical composition. It is therefore crucial to understand the disks molecular content. We aim to characterize the distribution and abundance of molecules in the disk of DG Tau. In the context of the ALMA chemical survey of Disk-Outflow sources in Taurus (ALMA-DOT) we analyse ALMA observations of the disk of DG Tau in H₂CO 3(1,2)-2(1,1), CS 5-4, and CN 2-1 at $\sim 0.15''$, i.e. ~ 18 au at 121 pc. H₂CO and CS originate from a disk ring at the edge of the 1.3mm dust continuum, with CS probing an outer disk region with respect to H₂CO (peaking at ~ 70 and ~ 60 au, respectively). CN originates from an outermost disk/envelope region peaking at ~ 80 au. H₂CO is dominated by disk emission, while CS probes also two streams of material possibly accreting onto the disk with a peak of emission where the stream connects to the disk. The ring- and disk-height- averaged column densities are ~ 2.4 - 8.6×10^{13} cm⁻² (H₂CO), ~ 1.7 - 2.5×10^{13} cm⁻² (CS), and ~ 1.9 - 4.7×10^{13} cm⁻² (CN). Unsharp masking reveals a ring of enhanced dust emission at ~ 40 au, i.e. just outside the CO snowline (~ 30 au). CS and H₂CO emissions are co-spatial suggesting that they are chemically linked. The observed rings of molecular emission at the edge of the 1.3mm continuum may be due to dust opacity effects and/or continuum over-subtraction in the inner disk; as well as to increased UV penetration and/or temperature inversion at the edge of the mm-dust which would cause an enhanced gas-phase formation and desorption of these molecules. Moreover, H₂CO and CS originate from outside the ring of enhanced dust emission, which also coincides with a change of the linear polarization at 0.87mm. This suggests that outside the CO snowline there could be a change of the dust properties which would reflect in the increase of the intensity (and change of polarization) of continuum, and of molecular emission.

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The prebiotic molecular inventory of Serpens SMM1 I. An investigation of the isomers CH₃NCO and HOCH₂CN

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Methyl isocyanate (CH₃NCO) and glycolonitrile (HOCH₂CN) are isomers and prebiotic molecules that are involved in the formation of peptide structures and the nucleobase adenine, respectively. ALMA observations of the intermediate-mass Class 0 protostar Serpens SMM1-a and ALMA-PILS data of the low-mass Class 0 protostar IRAS16293B are used. Spectra are analysed with the CASSIS line analysis software package in order to identify and characterise molecules. CH₃NCO, HOCH₂CN, and various other molecules are detected towards SMM1-a. HOCH₂CN is identified in the PILS data towards IRAS16293B in a spectrum extracted at a half-beam offset position from the peak continuum. CH₃NCO and HOCH₂CN are equally abundant in SMM1-a at $[X]/[CH_3OH]$ of $5.3e-4$ and $6.2e-4$, respectively. A comparison between SMM1-a and IRAS16293B shows that HOCH₂CN and HNCO are more abundant in the former source, but CH₃NCO abundances do not differ significantly. Data from other sources are used to show that the $[CH_3NCO]/[HNCO]$ ratio is similar in all these sources within $\sim 10\%$. The new detections of CH₃NCO and HOCH₂CN are additional evidence for a large interstellar reservoir of prebiotic molecules that can contribute to the formation of biomolecules on terrestrial planets. A plausible formation pathway for HOCH₂CN is the thermal Strecker-like reaction of CN⁻ with H₂CO. The similar $[CH_3NCO]/[HNCO]$ ratios indicate that these two species either are chemically related or their formation is affected by physical conditions in the same way. The relatively high abundances of HOCH₂CN and HNCO in SMM1-a may be explained by a prolonged stage of relatively warm ice mantles, where thermal and energetic processing of HCN in the ice results in the efficient formation of both species.

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Hunting for the elusive methylene radical

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CH₂ transitions between 68 and 71 GHz were first detected toward the Orion-KL and W51 Main SFRs. Given their upper level energies of 225 K, they were thought to arise in dense, hot molecular cores near newly formed stars. However, this has not been confirmed by further observations of these lines and their origin has remained unclear. Generally, there is a scarcity of observational data for CH₂ and, while it is an important compound in the astrochemical context, its actual occurrence in astronomical sources is poorly constrained. The present study, along with other recent observations of the Orion region we report, rule out the possibility of an association with gas that is both hot and dense. We find that the distribution of the CH₂ emission closely follows that of the [CII] 158 μ m emission, while CH₂ is undetected toward the hot core itself. The observations suggest, rather, that its extended emission arises from hot but dilute layers of PDRs and not from the denser parts of such regions as in the case of the Orion Bar. This hypothesis was corroborated by comparisons of the observed CH₂ line profiles with those of CRRLs, well-known PDR tracers. In addition, we report the detection of the 70 GHz fine- and hfs lines of o-CH₂ toward the W51E, W51M, W51N, W49N, W43, W75N, DR21, and S140 SFRs, and three of the fine- and hfs lines

between 68-71 GHz toward W3 IRS5. Furthermore, using a non-LTE radiative transfer analysis, we can constrain the gas temperatures and H₂ density to 163 K and 3.4e3 cm⁻³, respectively. This analysis confirms our hypothesis that CH₂ originates in warm and dilute PDR layers. Our analysis suggests that for the excitation conditions under the physical conditions that prevail in such regions, these lines are masering, with weak level inversion. The resulting amplification of the lines' spontaneous emission greatly aids in their detection.

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ALMA chemical survey of disk-outflow sources in Taurus (ALMA-DOT) IV. Thioformaldehyde (H₂CS) in protoplanetary disks: spatial distributions and binding energies

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Context. Planet formation starts around Sun-like protostars with ages ≤ 1 Myr, but the chemical compositions of the surrounding discs remains unknown. **Aims:** We aim to trace the radial and vertical spatial distribution of a key species of S-bearing chemistry, namely H₂CS, in protoplanetary discs. We also aim to analyse the observed distributions in light of the H₂CS binding energy in order to discuss the role of thermal desorption in enriching the gas disc component. **Methods:** In the context of the ALMA chemical survey of disk-outflow sources in the Taurus star forming region (ALMA-DOT), we observed five Class I or early Class II sources with the o-H₂CS(71,6-61,5) line. ALMA-Band 6 was used, reaching spatial resolutions ≈ 40 au, that is, Solar System spatial scales. We also estimated the binding energy of H₂CS using quantum mechanical calculations, for the first time, for an extended, periodic, crystalline ice. **Results:** We imaged H₂CS emission in two rotating molecular rings in the HL Tau and IRAS 04302+2247 discs, the outer radii of which are ~ 140 au (HL Tau) and 115 au (IRAS 04302+2247). The edge-on geometry of IRAS 04302+2247 allows us to reveal that H₂CS emission peaks at radii of 60-115 au, at $z = \pm 50$ au from the equatorial plane. Assuming LTE conditions, the column densities are $\sim 1e14$ cm⁻². We estimate upper limits of a few $1e13$ cm⁻² for the H₂CS column densities in DG Tau, DG Tau B, and Haro 6-13 discs. For HL Tau, we derive, for the first time, the [H₂CS]/[H] abundance in a protoplanetary disc ($\approx 1e-14$). The binding energy of H₂CS computed for extended crystalline ice and amorphous ices is 4258 and 3000-4600 K, respectively, implying thermal evaporation where dust temperatures are $\geq 50-80$ K. **Conclusions:** H₂CS traces the so-called warm molecular layer, a region previously sampled using CS and H₂CO. Thioformaldehyde peaks closer to the protostar than H₂CO and CS, plausibly because of the relatively high excitation level of the observed 71,6-61,5 line (60 K). The H₂CS binding energy implies that thermal desorption dominates in thin, au-sized, inner and/or upper disc layers, indicating that the observed H₂CS emitting up to radii larger than 100 au is likely injected in the gas phase due to non-thermal processes.

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ALMA chemical survey of disk-outflow sources in Taurus (ALMA-DOT) V: Sample, overview, and demography of disk

molecular emission

Antonio Garufi, Linda Podio, Claudio Codella, Davide Fedele, Eleonora Bianchi, Cecile Favre, Francesca Bacciotti, Cecilia Ceccarelli, Seyma Mercimek, Kazi Rygl, Richard Teague, Leonardo Testi

We present an overview of the ALMA chemical survey of disk-outflow sources in Taurus (ALMA-DOT), a campaign devoted to the characterization of the molecular emission from partly embedded, young stars. The project aims at better understanding the gaseous products that are delivered to planets by means of high-resolution maps of assorted lines probing disks at the time of the planet formation (less than 1 Myr). Nine different molecules are surveyed by our observations of six Class I/flat-spectrum sources. A series of accompanying articles analyze specific targets and molecules. Here we describe the sample and provide a general overview of the results, focusing on the spatial distribution, column densities, and abundance ratios of H₂CO, CS, and CN. The results of this work are a first step toward the characterization of the disk chemical evolution that need to be complemented by further observations of less exceptional disks and customized thermo-chemical modeling.

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Chemically tracing the water snowline in protoplanetary disks with HCO⁺

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[Abridged] Planet formation is expected to be enhanced around snowlines in protoplanetary disks, in particular around the water snowline. However, the close proximity of the water snowline to the host star and water in the Earth's atmosphere makes a direct detection of the water snowline in protoplanetary disks challenging. Following earlier work on protostellar envelopes, the aim of this research is to investigate the validity of HCO⁺ and H₁₃CO⁺, as tracers of the water snowline in protoplanetary disks, as HCO⁺ is destroyed by gas-phase water. Two small chemical networks are used to predict the HCO⁺ abundance in a typical Herbig Ae disk. Subsequently, the corresponding emission profiles are modelled for H₁₃CO⁺ and HCO⁺ J=2-1, which provides the best balance between brightness and optical depth effects of the continuum emission. The HCO⁺ abundance jumps by two orders of magnitude just outside the water snowline at 4.5 AU. We find that the emission of H₁₃CO⁺ and HCO⁺ is ring-shaped due to three effects: destruction of HCO⁺ by gas-phase water, continuum optical depth, and molecular excitation effects. The presence of gas-phase water causes an additional drop of only ~13% and 24% in the center of the disk, for H₁₃CO⁺ and HCO⁺, respectively. For the much more luminous outbursting source V883 Ori, our models predict that the effect of dust and excitation are not limiting if the snowline is located outside ~40 AU. Our analysis of ALMA observations of HCO⁺ J=3-2 is consistent with the water snowline located around 100 AU. The HCO⁺ abundance drops steeply around the water snowline, but dust and excitation can conceal the drop in HCO⁺ emission due to the water snowline. Therefore, locating the water snowline with HCO⁺ in Herbig disks is very difficult, but it is possible for outbursting sources like V883 Ori.

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Rapid ortho-to-para nuclear spin conversion of H₂ on a silicate dust surface

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The H₂ molecule has two nuclear spin isomers, the so-called ortho and para isomers. Nuclear spin conversion (NSC) between these states is forbidden in the gas phase. The energy difference between the lowest ortho and para states is as large as 14.7 meV, corresponding to ~170 K. Therefore, each state of H₂ differently affects not only the chemistry but also the macroscopic gas dynamics in space, and thus, the ortho-to-para abundance ratio (OPR) of H₂ has significant impacts on various astronomical phenomena. For a long time, the OPR of nascent H₂ upon formation on dust grains has been assumed to have a statistical value of three and to gradually equilibrate in the gas phase at the temperature of the circumstances. Recently, NSC of H₂ was experimentally revealed to occur on water ice at very low temperatures and thus incorporated into gas-dust chemical models. However, H₂ molecules should form well before dust grains are coated by water ice. Information about how the OPR of H₂ behaves on bare silicate dust before ice-mantle formation is lacking. Knowing the influence of the OPR of H₂ if the OPR changes even on a bare silicate surface within an astronomically meaningful time scale is desirable. We report the first laboratory measurements of NSC of H₂ physisorbed on amorphous silicate (Mg₂SiO₄) at temperatures up to 18 K. The conversion was found to occur very rapidly.

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Sulfur Ice Astrochemistry: A Review of Laboratory Studies

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Sulfur is the tenth most abundant element in the universe and is known to play a significant role in biological systems. Accordingly, in recent years there has been increased interest in the role of sulfur in astrochemical reactions and planetary geology and geochemistry. Among the many avenues of research currently being explored is the laboratory processing of astrophysical ice analogues. Such research involves the synthesis of an ice of specific morphology and chemical composition at temperatures and pressures relevant to a selected astrophysical setting (such as the interstellar medium or the surfaces of icy moons). Subsequent processing of the ice under conditions that simulate the selected astrophysical setting commonly involves radiolysis, photolysis, thermal processing, neutral-neutral fragment chemistry, or any combination of these, and has been the subject of several studies. The in-situ changes in ice morphology and chemistry occurring during such processing has been monitored via spectroscopic or spectrometric techniques. In this paper, we have reviewed the results of laboratory investigations concerned with sulfur chemistry in several astrophysical ice analogues. Specifically, we review (i) the spectroscopy of sulfur-containing astrochemical molecules in the condensed phase, (ii) atom and radical addition reactions, (iii) the thermal processing of sulfur-bearing ices, (iv) photochemical experiments, (v) the non-reactive charged particle radiolysis of sulfur-bearing ices, and (vi) sulfur ion bombardment of and implantation in ice analogues. Potential future studies in the field of solid phase sulfur astrochemistry are also discussed in the context of forthcoming space missions, such as the NASA James Webb Space

Telescope and the ESA Jupiter Icy Moons Explorer mission.

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Vacuum ultraviolet photoabsorption spectroscopy of space-related ices: Formation and destruction of solid carbonic acid upon 1~keV electron irradiation

S. Ioppolo, Z. Kaňuchová, R. L. James, A. Dawes, A. Ryabov, J. Dezalay, N. C. Jones, S. V. Hoffmann, N. J. Mason and G. Strazzulla

Carbonic acid (H_2CO_3) is a weak acid relevant to astrobiology which, to date, remains undetected in space. Experimental work has shown that the beta-polymorph of H_2CO_3 forms under space relevant conditions through energetic (UV photon, electron, and cosmic ray) processing of CO_2 - and H_2O -rich ices. We present a systematic set of VUV photoabsorption spectra of pure and mixed CO_2 and H_2O ices exposed to 1 keV electrons at 20 and 80 K to simulate different interstellar and Solar System environments. Ices were then annealed to obtain a layer of pure H_2CO_3 which was further exposed to 1 keV electrons at 20 and 80 K to monitor its destruction pathway. Fourier-transform infrared (FT-IR) spectroscopy was used as a secondary probe providing complementary information on the physicochemical changes within an ice. Our laboratory work shows that the formation of solid H_2CO_3 , CO, and O_3 upon the energetic processing of CO_2 : H_2O ice mixtures is temperature-dependent in the range between 20 and 80 K. The amorphous to crystalline phase transition of H_2CO_3 ice is investigated for the first time in the VUV spectral range by annealing the ice at 200 and 225 K. We have detected two photoabsorption bands at 139 and 200 nm, and we assigned them to beta- H_2CO_3 and gamma- H_2CO_3 , respectively. We present VUV spectra of the electron irradiation of annealed H_2CO_3 ice at different temperatures leading to its decomposition into CO_2 , H_2O , and CO ice. Laboratory results are compared to Cassini UltraViolet Imaging Spectrograph observations of the 70-90 K ice surface of Saturn's satellites Enceladus, Dione, and Rhea.

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Ubiquitous aromatic carbon chemistry at the earliest stages of star formation

Andrew M. Burkhardt, Ryan A. Loomis, Christopher N. Shingledecker, Kin Long Kelvin Lee, Anthony J. Remijan, Michael C. McCarthy & Brett A. McGuire

Benzonitrile ($c\text{-C}_6\text{H}_5\text{CN}$, where 'c' indicates a cyclic structure), a polar proxy for benzene ($c\text{-C}_6\text{H}_6$), has the potential to serve as a highly convenient radio probe for aromatic chemistry, provided that this ring can be found in other astronomical sources beyond the molecule-rich prestellar cloud TMC-1. Here we present radio astronomical evidence of benzonitrile in four other prestellar, and possibly protostellar, sources: Serpens 1A, Serpens 1B, Serpens 2 and MC27/L1521F. These detections establish that benzonitrile is not unique to TMC-1; rather, aromatic chemistry appears to be widespread throughout the earliest stages of star formation, probably persisting at least until the initial formation of a protostar. The abundance of benzonitrile far exceeds predictions from models that well reproduce the abundances of carbon chains such as

HC7N, a cyanopolyne with the same heavy atoms, indicating that the chemistry responsible for planar carbon structures (as opposed to linear ones) in primordial sources is favourable but not well understood. The abundance of benzonitrile relative to carbon chain molecules displays sizable variations between sources within the Taurus and Serpens clouds, implying the importance of physical conditions and initial elemental reservoirs of the clouds themselves.

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Vacuum ultraviolet photoabsorption spectroscopy of space-related ices: 1 keV electron irradiation of nitrogen- and oxygen-rich ices

S. Ioppolo, Z. Kaňuchová, R. L. James, A. Dawes, N. C. Jones, S. V. Hoffmann, N. J. Mason and G. Strazzulla

Context: Molecular oxygen, nitrogen, and ozone have been detected on some satellites of Saturn and Jupiter, as well as on comets. They are also expected to be present in ice-grain mantles within star-forming regions. The continuous energetic processing of icy objects in the Solar System induces physical and chemical changes within the ice. Laboratory experiments that simulate energetic processing (ions, photons, and electrons) of ices are therefore essential for interpreting and directing future astronomical observations. Aims: We provide vacuum ultraviolet (VUV) photoabsorption spectroscopic data of energetically processed nitrogen- and oxygen-rich ices that will help to identify absorption bands and/or spectral slopes observed on icy objects in the Solar System and on ice-grain mantles of the interstellar medium. Methods: We present VUV photoabsorption spectra of frozen O₂ and N₂, a 1:1 mixture of both, and a new systematic set of pure and mixed nitrogen oxide ices. Spectra were obtained at 22 K before and after 1 keV electron bombardment of the ice sample. Ices were then annealed to higher temperatures to study their thermal evolution. In addition, Fourier-transform infrared spectroscopy was used as a secondary probe of molecular synthesis to better identify the physical and chemical processes at play. Results: Our VUV data show that ozone and the azide radical (N₃) are observed in our experiments after electron irradiation of pure O₂ and N₂ ices, respectively. Energetic processing of an O₂:N₂ = 1:1 ice mixture leads to the formation of ozone along with a series of nitrogen oxides. The electron irradiation of solid nitrogen oxides, pure and in mixtures, induces the formation of new species such as O₂, N₂, and other nitrogen oxides not present in the initial ice. Results are discussed here in light of their relevance to various astrophysical environments. Finally, we show that VUV spectra of solid NO₂ and water can reproduce the observational VUV profile of the cold surface of Enceladus, Dione, and Rhea, strongly suggesting the presence of nitrogen oxides on the surface of the icy Saturn moons.

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Highly-accurate quartic force fields for the prediction of anharmonic rotational constants and fundamental vibrational frequencies

Mason B. Gardner, Brent R. Westbrook, Ryan C. Fortenberry, and Timothy J. Lee

The CcCR quartic force field (QFF) methodology is capable of computing B0 and C0 rotational constants to within 35 MHz (0.14%) of experiment for triatomic and larger molecules with at least two heavy atoms. Additionally, the same constants for molecules with four or more atoms agree to within 20 MHz (0.12%) of experiment for the current test set. This work also supports previous claims that the same QFF methodology can produce fundamental vibrational frequencies with a deviation less than 5.7 cm⁻¹ from experiment. Consequently, this approach of augmenting complete basis set extrapolated energies with treatments of core electron correlation and scalar relativity produces some of the most accurate rovibrational spectroscopic data available.

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<https://www.sciencedirect.com/science/article/abs/pii/S138614252031163X>

Anharmonic Vibrational Frequencies and Spectroscopic Constants for the Detection of Ethynol in Space

Jax D. Dallas, Brent R. Westbrook, and Ryan C. Fortenberry

The ethynol (HCCOH) molecule has recently been shown to be present in simulated astrochemical ices possibly linking it to molecular building blocks for interstellar complex organic molecules like amino acids. The proposed reaction mechanism suggests the simultaneous formation of both ketene and ethynol from mixed carbon monoxide/water ice in simulated interstellar conditions. Rigorous anharmonic spectral data within both the IR and microwave regions are needed for possible detection of ethynol in the interstellar medium. This study provides the first such data for this molecule from high-level quantum chemical computations where experiment is currently lacking. Ethynol has a B_{eff} comparable to, but distinct from acetonitrile at 9,652.1 MHz and three notable infrared features with two in the hydride stretching-regions and the C-C stretch at 2,212.8 cm⁻¹. The ketene isomer has already been detected in the interstellar medium, and the possible detection of ethynol made possible by this work may lead to a deeper understanding of the proposed ice formation mechanism involving both species and how this relates to the molecular origins of life.

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An investigation of spectral line stacking techniques and application to the detection of HC11N

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As the inventory of interstellar molecules continues to grow, the gulf between small species, whose individual rotational lines can be observed with radio telescopes, and large ones, such as polycyclic aromatic hydrocarbons best studied in bulk via infrared and optical observations, is slowly being bridged. Understanding the connection between these two molecular reservoirs is critical to understanding the interstellar carbon cycle, but will require pushing the boundaries of how far we can probe

molecular complexity while still retaining observational specificity. Towards this end, we present a method for detecting and characterizing new molecular species in single-dish observations towards sources with sparse line spectra. We have applied this method to data from the ongoing GOTHAM (GBT Observations of TMC-1: Hunting Aromatic Molecules) Green Bank Telescope large programme, discovering six new interstellar species. Here we highlight the detection of HC₁₁N, the largest cyanopolyne in the interstellar medium.

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Behavior of Hydroxyl Radicals on Water Ice at Low Temperatures

Masashi Tsuge, Naoki Watanabe

Because chemical reactions on/in cosmic ice dust grains covered by amorphous solid water (ASW) play important roles in generating a variety of molecules, many experimental and theoretical studies have focused on the chemical processes occurring on the ASW surface. In laboratory experiments, conventional spectroscopic and mass-spectrometric detection of stable products is generally employed to deduce reaction channels and mechanisms. However, despite their importance, the details of chemical reactions involving reactive species (i.e., free radicals) have not been clarified because of the absence of experimental methods for in situ detection of radicals. Because OH radicals can be easily produced in interstellar conditions by not only the photolysis and/or ion bombardments of H₂O but also the reaction of H and O atoms, they are thought to be one of the most abundant radicals on ice dust. In this context, the development of a close monitoring method of OH radicals on the ASW surface may help to elucidate the chemical reactions occurring on the ASW surface.

Acc. Chem. Res. in press

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Characterizing the line emission from molecular clouds. Stratified random sampling of the Perseus cloud

M. Tafalla, A. Usero, A. Hacar

Context. The traditional approach to characterize the structure of molecular clouds is to map their line emission. Aims. We aim to test and apply a stratified random sampling technique that can characterize the line emission from molecular clouds more efficiently than mapping. Methods. We sampled the molecular emission from the Perseus cloud using the H₂ column density as a proxy. We divided the cloud into ten logarithmically spaced column density bins, and we randomly selected ten positions from each bin. The resulting 100 cloud positions were observed with the IRAM 30m telescope, covering the 3mm-wavelength band and parts of the 2 and 1mm bands. Results. We focus our analysis on 11 molecular species detected toward most column density bins. In all cases, the line intensity is tightly correlated with the H₂ column density. For the CO isotopologs, the trend is relatively flat, while for high-dipole moment species such as HCN, CS, and HCO⁺ the trend is approximately linear. We reproduce this behavior with a cloud model in which the gas density increases with column density, and where most species have abundance profiles characterized by an outer photodissociation edge and an inner freeze-out drop. The intensity behavior of the high-dipole moment species

arises from a combination of excitation effects and molecular freeze out, with some modulation from optical depth. This quasi-linear dependence with the H₂ column density makes the gas at low column densities dominate the cloud-integrated emission. It also makes the emission from most high-dipole moment species proportional to the cloud mass inside the photodissociation edge. Conclusions. Stratified random sampling is an efficient technique for characterizing the emission from whole molecular clouds. It shows that despite the complex appearance of Perseus, its molecular emission follows a relatively simple pattern.

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Announcements

PhD student position in Quantum Chemistry and Computational Astrobiology

Would you like to help seek evidence for the structure, function and formation mechanisms of prebiotically relevant polymers from simple building blocks!?

The host research group (www.rahmlab.com) is part of the Department of Chemistry and Chemical Engineering at Chalmers University of Technology in Gothenburg, Sweden. The research team is also a part of Chalmers Initiative for Cosmic Origins (<http://cosmicorigins.space>) an interdisciplinary research collaboration that address fundamental questions about the formation of galaxies, stars, planets and life in the Universe.

More details and application form can be found here:

[https://www.chalmers.se/en/about-chalmers/Working-at-](https://www.chalmers.se/en/about-chalmers/Working-at-Chalmers/Vacancies/Pages/default.aspx?rmpage=job&rmjob=9196&rmlang=UK)

[Chalmers/Vacancies/Pages/default.aspx?rmpage=job&rmjob=9196&rmlang=UK](https://www.chalmers.se/en/about-chalmers/Working-at-Chalmers/Vacancies/Pages/default.aspx?rmpage=job&rmjob=9196&rmlang=UK)

Deadline 28th of February, 2021.

Postdoctoral Position in Merged-Fast-Beams Astrochemical Studies

The Columbia Astrophysics Laboratory (CAL) invites applications for a Postdoctoral Research Scientist (PdRS) in the group of Dr. Daniel Wolf Savin. The main goal of the project is to perform merged-fast-beams studies of deuterating reactions that form key molecules used to probe the properties of prestellar cores and protoplanetary disks. The successful candidate will be appointed and based at Columbia. Appointments are for one year, with the possibility of renewal for up to two additional years contingent on the availability of funds and mutual satisfaction.

The successful candidate will have a Ph.D. or the equivalent degree in Physics, Chemistry, Astrophysics, or a related field, with an emphasis in molecular physics. Desired laboratory skills include experience with ion sources, fast ion beams, ion optics, ultra-high vacuum techniques, infrared lasers, apparatus design and construction, single particle detectors and associated electronics, analog and digital signal processing, data reduction, and statistical and systematic error propagation. Desired computer skills include programming, multidimensional data analysis, LabView, 3D CAD, SIMION, Mathematica, or similar, Linux OS, and Windows OS.

The successful candidate will have a strong background in at least some of the areas listed above, a proven research ability, and evidence of future research potential. The candidate is expected to be able to work well independently and cooperatively with a team and to communicate the results of his/her research both orally and in writing. Demonstrated written and oral communication skills are highly desirable. Questions

regarding this position can be addressed to Dr. Savin at dws26@columbia.edu. Applicants should submit a cover letter, curriculum vitae (including a list of publications) and statement of past research. In addition, they should arrange to have three letters of reference sent directly by the writers to Dr. Savin. Applications will be considered only after all of the requested material has been received. Applications and letters should be submitted by email to dws26@columbia.edu. Screening of applicants will begin immediately and will continue until the position has been filled.

Columbia is an Equal Opportunity Employer/Disability/Veteran Employer. CAL values a diverse workforce and culture of inclusion, which are keys to attracting and engaging the brightest minds to further our record of scientific excellence and groundbreaking innovations. Applications from women, minorities, and other underrepresented groups are strongly encouraged.

PhD student position in Astrochemistry at Onsala Space Observatory, Chalmers

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>

Conference announcement: DELVE: Death-throes of Evolved stars, a Virtual Encounter

The chairs, on behalf of the SOC, would like to announce an upcoming online conference on the topic of evolved stars. DELVE: Death-throes of Evolved stars, a Virtual Encounter will run April 12-16 with different time slots on different days to accommodate people working in different time zones across the world.

The scientific focus of the conference will be on the chemistry and physics of evolved stars, particularly AGB and RSG stars. We welcome contributions delving into any topic related to AGB or RSG stars, including observations, modelling and theory of the chemical or physical states of these stars and their circumstellar environments.

We will have talks over Zoom (uploaded to YouTube for asynchronous viewing) with coffee breaks and poster sessions taking place in the virtual space of Gather Town. Registration is open now and abstract submissions will close on 1 March. For more details visit our website: <https://fys.kuleuven.be/ster/events/conferences/2021/delve>

Funding Available for SOFIA Archival Research

SOFIA is pleased to invite proposals for the SOFIA Archival Research Program (SARP), aimed at encouraging the use of SOFIA archival observations for impactful science. This program funds archival research projects primarily using SOFIA data in the Infrared Science Archive (IRSA) and is open to all astronomers affiliated with a U.S. institution.

Two distinct types of proposals for the archival research program are solicited:

Regular Proposals - Large programs requesting up to \$150,000 per year, or more in exceptional cases, and lasting up to two years

Small Proposals - Targeted programs requesting up to \$50,000 and lasting for one year
This call is open to all U.S. institutions.

Proposals are due February 12, 2021. Learn more here:

<https://www.sofia.usra.edu/science/proposing-and-observing/proposal-calls/sofia-archival-research-program>

This program complements the Astrophysics Data Analysis Program (ADAP) under the NASA Research Opportunities in Space and Earth Sciences (ROSES) solicitation.

1 year position at LERMA in Numerical analysis and HPC

A 1 year position (that may be extended) is currently open at LERMA, Paris Observatory in the field of numerical analysis and HPC. Details can be found at: "<https://lerma.obspm.fr/spip.php?article436>" (in french)

(Google automatic translation:) "The agent will participate, in collaboration with LERMA researchers, in the development, optimization and porting to HPC architectures of new generations of digital codes essential to meet the major challenges of the discipline in the priority themes of LERMA (galaxies and large structures, interstellar medium and astrophysical plasmas, quantum physics calculations). He will typically devote half of his time to activities related to SKA preparation. Through his expertise, he will help bring the code prototypes developed in this context to a level of maturity allowing for service mode production in SKA data processing centers (SDP and SKA regional centers). He will also participate in the development of astrophysical modeling codes at LERMA."

CASSUM Undergraduate Research Fellowships

The Chalmers Astrophysics and Space Science Summer (CASSUM) Research Fellowship program for undergraduate students is now accepting applications for summer 2021.

Like last year, we expect most/all projects will be carried out by remote supervision.

The website listing various projects is here: <http://cosmicorigins.space/cassum>

If you advise undergraduate students who may be looking for such research opportunities, please encourage them to apply to the program.

The application deadline is 19th Feb. 2021.

Molecules in starless and pre-stellar cores: tools to understand low- and high-mass star-formation EAS 2021 Special Session -SS15- July 1st, 2021

Starless and pre-stellar cores are the earliest stages in the formation of stars and planetary systems. Molecules are an essential tool to understand the chemistry and physics at the dawn of star formation. Several studies showed that a memory of chemical processes that happen in this early stage is kept after the ignition of the protostar and also during the process of planet formation, as witnessed by the cometary ice composition. Furthermore, molecular tracers are used to study the kinematics and physical properties of the gas in the process of star-formation. In this special session we will focus on the use of molecules as tools to understand the physics and chemistry at the onset of star formation. We aim at bringing together observers and modellers working on high- and low-mass star-formation to discuss the future challenges and derive strategies to exploit the current (e.g. IRAM, ALMA, APEX, JCMT, JVLA, SOFIA) and upcoming facilities (e.g. JWST).

Program: Chemical complexity before star-formation Isotopic fractionation Cores and their surrounding: from cores to filaments

Invited speakers: Laura Colzi (Centro de Astrobiología, Spain), Asunción Fuente (Observatorio Astronómico Nacional, Spain), Mika Juvela (University of Helsinki, Finland), Fabien Louvet (CEA, France), Elena Redaelli (MPE, Germany), Samantha Scibelli (University of Arizona, USA).

Abstract submission is now open! Submitters can select oral or e-poster presentations.

Abstract portal: <https://kuonicongress.eventsair.com/eas-2021/abstractsubmission>

More information can be found on the website:

https://eas.unige.ch/EAS_meeting/session.jsp?id=SS15 Please, feel free to share this announcement with your colleagues. We hope to see all of you in July. Best regards,
SOC: Paola Caselli (MPE, Germany), Peter Schilke (University of Cologne, Germany),
Silvia Spezzano (Chair, MPE, Germany), Mario Tafalla (Observatorio Astronómico
Nacional, Spain), Jonathan Tan (Chalmers University, Sweden), Charlotte Vastel (IRAP,
France), Eva Wirström (Chalmers University, Sweden)