

# AstroChemical Newsletter #71

October 2021

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## Abstracts

### Chemical compositions in the vicinity of protostars in Ophiuchus

**Kotomi Taniguchi, Liton Majumdar, Adele Plunkett, Shigehisa Takakuwa, Dariusz C. Lis, Paul F. Goldsmith, Fumitaka Nakamura, Masao Saito, Eric Herbst**

We have analyzed Atacama Large Millimeter/submillimeter Array (ALMA) Cycle 4 Band 6 data toward two young stellar objects (YSOs), Oph-emb5 and Oph-emb9, in the Ophiuchus star-forming region. The YSO Oph-emb5 is located in a relatively quiescent region, whereas Oph-emb9 is irradiated by a nearby bright Herbig Be star. Molecular lines from cyclic-C<sub>3</sub>H<sub>2</sub> (c-C<sub>3</sub>H<sub>2</sub>), H<sub>2</sub>CO, CH<sub>3</sub>OH, <sup>13</sup>CO, C<sub>18</sub>O, and DCO<sup>+</sup> have been detected from both sources, while DCN is detected only in Oph-emb9. Around Oph-emb5, c-C<sub>3</sub>H<sub>2</sub> is enhanced at the west side, relative to the IR source, whereas H<sub>2</sub>CO and CH<sub>3</sub>OH are abundant at the east side. In the field of Oph-emb9, moment 0 maps of the c-C<sub>3</sub>H<sub>2</sub> lines show a peak at the eastern edge of the field of view, which is irradiated by the Herbig Be star. Moment 0 maps of CH<sub>3</sub>OH and H<sub>2</sub>CO show peaks farther from the bright star. We derive the N(c-C<sub>3</sub>H<sub>2</sub>)/N(CH<sub>3</sub>OH) column density ratios at the peak positions of c-C<sub>3</sub>H<sub>2</sub> and CH<sub>3</sub>OH near each YSO, which are identified based on their moment 0 maps. The N(c-C<sub>3</sub>H<sub>2</sub>)/N(CH<sub>3</sub>OH) ratio at the c-C<sub>3</sub>H<sub>2</sub> peak is significantly higher than at the CH<sub>3</sub>OH peak by a factor of ~19 in Oph-emb9, while the difference in this column density ratio between these two positions is a factor of ~2.6 in Oph-emb5. These differences are attributed to the efficiency of the photon-dominated region (PDR) chemistry in Oph-emb9. The higher DCO<sup>+</sup> column density and the detection of DCN in Oph-emb9 are also discussed in the context of UV irradiation flux.

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### Interstellar Catalysts and the PAH Universe

**D. Campisi**

Organic molecules in interstellar space are important as they influence the structure of galaxies and star formations. Studying catalytic processes in space allows us to understand how molecular species are formed and chemically evolved in the interstellar medium and solar system objects. Quantum chemical methods, such as “Density Functional Theory” (DFT), can be employed to study the chemical pathways for the formation of molecular species, which is challenging with only observations and experiments. This thesis studies, with DFT methods, how polycyclic aromatic hydrocarbons (PAHs), the most abundant organic species in space, catalyze the formation of molecular hydrogen in the interstellar medium. Specifically, how linear

PAHs become superhydrogenated and how the presence of Stone Wales defect in PAHs contributes to their catalytic activity for molecular hydrogen formation. In addition, this thesis reports the study of the catalytic activity of forsterite, a silicate mineral abundant in grains, asteroids, and meteorites. Specifically, the presence of Schottky MgO vacancy in forsterite can catalyze the C-H activation of PAHs as the first step to study the breakdown reaction of PAHs in asteroidal settings. The latter is indispensable to understand the formation of the so-called organic inventory of solar system objects.

PhD thesis, Leiden University Scholarly Publications

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## **The impact of water vapor on the OH reactivity toward CH<sub>3</sub>CHO at ultra-low temperatures (21.7–135.0 K): Experiments and theory**

**E. M. Neeman, D. González, S. Blázquez, B. Ballesteros, A. Canosa, M. Antiñolo, L. Vereecken, J. Albaladejo, and E. Jiménez**

The role of water vapor (H<sub>2</sub>O) and its hydrogen-bonded complexes in the gas-phase reactivity of organic compounds with hydroxyl (OH) radicals has been the subject of many recent studies. Contradictory effects have been reported at temperatures between 200 and 400 K. For the OH + acetaldehyde reaction, a slight catalytic effect of H<sub>2</sub>O was previously reported at temperatures between 60 and 118 K. In this work, we used Laval nozzle expansions to reinvestigate the impact of H<sub>2</sub>O on the OH-reactivity with acetaldehyde between 21.7 and 135.0 K. The results of this comprehensive study demonstrate that water, instead, slows down the reaction by factors of ~3 (21.7 K) and ~2 (36.2–89.5 K), and almost no effect of added H<sub>2</sub>O was observed at 135.0 K.

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## **Theoretical computations on the efficiency of acetaldehyde formation on interstellar icy grains**

**Joan Enrique-Romero, Cecilia Ceccarelli, Albert Rimola, Dimitrios Skouteris, Nadia Balucani and Piero Ugliengo**

Interstellar grains are known to be important actors in the formation of interstellar molecules such as H<sub>2</sub>, water, ammonia, and methanol. It has been suggested that the so-called interstellar complex organic molecules (iCOMs) are also formed on the interstellar grain icy surfaces by the combination of radicals via reactions assumed to have an efficiency equal to unity. In this work, we aim to investigate the robustness or weakness of this assumption by considering the case of acetaldehyde (CH<sub>3</sub>CHO) as a starting study case. In the literature, it has been postulated that acetaldehyde is formed on the icy surfaces via the combination of HCO and CH<sub>3</sub>. Here we report new theoretical computations on the efficiency of its formation. To this end, we coupled quantum chemical calculations of the energetics and kinetics of the reaction CH<sub>3</sub> + HCO, which can lead to the formation of CH<sub>3</sub>CHO or CO + CH<sub>4</sub>. Specifically, we combined reaction kinetics computed with the Rice-Ramsperger-Kassel-Marcus (RRKM) theory (tunneling included) method with diffusion and desorption competitive channels. We provide the results of our computations in the format used by astrochemical models to facilitate their exploitation. Our new computations indicate that the efficiency

of acetaldehyde formation on the icy surfaces is a complex function of the temperature and, more importantly, of the assumed diffusion over binding energy ratio  $f$  of the  $\text{CH}_3$  radical. If the ratio  $f$  is  $\geq 0.4$ , the efficiency is equal to unity in the range where the reaction can occur, namely between 12 and 30 K. However, if  $f$  is smaller, the efficiency dramatically crashes: with  $f=0.3$ , it is at most 0.01. In addition, the formation of acetaldehyde is always in competition with that of  $\text{CO} + \text{CH}_4$ .

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## **An unbiased NOEMA 2.6 to 4 mm survey of the GG Tau ring: First detection of CCS in a protoplanetary disk**

**N.T. Phuong, A. Dutrey, E. Chapillon, S. Guilloteau, J. Bary, T. L. Beck, A. Coutens, O. Denis-Alpizar, E. Di Folco, P.N. Diep, L. Majumdar, J-P. Melisse, C-W. Lee, V. Pietu, T. Stoecklin, Y-W. Tang**

Molecular line surveys are among the main tools to probe the structure and physical conditions in protoplanetary disks (PPDs), the birthplace of planets. The large radial and vertical temperature as well as density gradients in these PPDs lead to a complex chemical composition, making chemistry an important step to understand the variety of planetary systems. We aimed to study the chemical content of the protoplanetary disk surrounding GG Tau A, a well-known triple T Tauri system. We used NOEMA with the new correlator PolyFix to observe rotational lines at 2.6 to 4 mm from a few dozen molecules. We analysed the data with a radiative transfer code to derive molecular densities and the abundance relative to  $^{13}\text{CO}$ , which we compare to those of the TMC1 cloud and LkCa15 disk. We report the first detection of CCS in PPDs. We also marginally detect OCS and find 16 other molecules in the GG Tauri outer disk. Ten of them had been found previously, while seven others ( $^{13}\text{CN}$ ,  $\text{N}_2\text{H}^+$ , HNC, DNC,  $\text{HC}_3\text{N}$ , CCS, and  $\text{C}_3\text{H}_4\text{S}$ ) are new detections in this disk. The analysis confirms that sulphur chemistry is not yet properly understood. The D/H ratio, derived from  $\text{DCO}^+/\text{HCO}^+$ ,  $\text{DCN}/\text{HCN}$ , and  $\text{DNC}/\text{HNC}$  ratios, points towards a low temperature chemistry. The detection of the rare species CCS confirms that GG Tau is a good laboratory to study the protoplanetary disk chemistry, thanks to its large disk size and mass

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## **The SVS13-A Class I chemical complexity as revealed by S-bearing species. SOLIS XIII**

**C. Codella, E. Bianchi, L. Podio, S. Mercimek, C. Ceccarelli, A. Lopez-Sepulcre, R. Bachiller, P. Caselli, N. Sakai, R. Neri, F. Fontani, C. Favre, N. Balucani, B. Lefloch, S. Viti, S. Yamamoto**

**Aims:** The goal is to obtain a census of S-bearing species using interferometric images, towards SVS13-A, a Class I object associated with a hot corino rich in interstellar complex organic molecules. **Methods:** We used data at 3mm and 1.4mm obtained with IRAM-NOEMA in the framework of the Large Program SOLIS. **Results:** We imaged the spatial distribution of the line emission of  $^{32}\text{SO}$ ,  $^{34}\text{SO}$ ,  $\text{C}_3\text{H}_4\text{S}$ ,  $\text{C}_3\text{H}_3\text{S}$ , OCS,  $\text{H}_2\text{C}_3\text{H}_2\text{S}$ ,  $\text{H}_2\text{C}_3\text{H}_4\text{S}$ , and NS. The low excitation (9 K)  $^{32}\text{SO}$  line is tracing the fast collimated jet driven by the nearby SVS13-B. Conversely, the rest of the lines are confined in the inner SVS13-A region, where complex organics have been previously

imaged. The non-LTE LVG analysis of SO, SO<sub>2</sub>, and H<sub>2</sub>CS indicates a hot corino origin (60-120 au). Temperatures between 50 K and 300 K, and volume densities larger than 1e5 cm<sup>-3</sup> have been derived. The abundances are in the following ranges: 0.3-6 1e-6 (CS), 7 1e-9 - 1 1e-7 (SO), 1-10 1e-7 (SO<sub>2</sub>), a few 1e-10 (H<sub>2</sub>CS and OCS), and 1e-10 - 10e-9 (NS). The N(NS)/N(NS+) ratio is larger than 10, supporting that the NS+ ion is mainly formed in the extended envelope. Conclusions: The [H<sub>2</sub>CS]/[H<sub>2</sub>CO] ratio increases with time (from Class 0 to Class II objects) by more than one order of magnitude. This suggests that [S]/[O] changes along the Sun-like star forming process. The estimate of the [S]/[H] budget in SVS13-A is 2%-17% of the Solar System value (1.8 10<sup>-5</sup>), being consistent with what was previously measured towards Class 0 objects (1%-8%). This supports that the enrichment of the sulphuretted species with respect to dark clouds keeps constant from the Class 0 to the Class I stages of low-mass star formation. The present findings stress the importance of investigating the chemistry of star forming regions using large observational surveys as well as sampling regions on a Solar System scale.

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## Establishing the evolutionary timescales of the massive star formation process through chemistry

**G. Sabatini, S. Bovino, A. Giannetti, T. Grassi, J. Brand, E. Schisano, F. Wyrowski, S. Leurini, K. M. Menten**

(Abridged) Understanding the details of the formation process of massive (i.e.  $M < 8-10 M_{\odot}$ ) stars is a long-standing problem in astrophysics. [...] We present a method to derive accurate timescales of the different evolutionary phases of the high-mass star formation process. We model a representative number of massive clumps of the ATLASGAL-TOP100 sample which cover all the evolutionary stages. The models describe an isothermal collapse and the subsequent warm-up phase, for which we follow their chemical evolution. The timescale of each phase is derived by comparing the results of the models with the properties of the sources of the ATLASGAL-TOP100 sample, taking into account the mass and luminosity of the clumps, and the column densities of methyl acetylene (CH<sub>3</sub>CCH), acetonitrile (CH<sub>3</sub>CN), formaldehyde (H<sub>2</sub>CO) and methanol (CH<sub>3</sub>OH). We find that the chosen molecular tracers are affected by the thermal evolution of the clumps, showing steep ice evaporation gradients from 103 to 105 AU during the warm-up phase. We succeed in reproducing the observed column densities of CH<sub>3</sub>CCH and CH<sub>3</sub>CN, while H<sub>2</sub>CO and CH<sub>3</sub>OH show a poorer agreement with the observed values. The total (massive) star formation time is found to be  $\sim 5.2 \times 10^5$  yr, which is defined by the timescales of the individual evolutionary phases of the ATLASGAL-TOP100 sample:  $\sim 5 \times 10^4$  yr for 70- $\mu$ m weak,  $\sim 1.2 \times 10^5$  yr for mid-IR weak,  $\sim 2.4 \times 10^5$  yr for mid-IR bright and  $\sim 1.1 \times 10^5$  yr for HII-regions phases. Our models, with an appropriate selection of molecular tracers that can act as chemical clocks, allow to get robust estimates of the duration of the individual phases of the high-mass star formation process, with the advantage of being capable to include additional tracers aimed at increasing the accuracy of the estimated timescales.

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## Transmission Electron Microscopy Study of the Morphology of

## **Ices Composed of H<sub>2</sub>O, CO<sub>2</sub>, and CO on Refractory Grains**

**Akira Kouchi, Masashi Tsuge, Tetsuya Hama, Yasuhiro Oba, Satoshi Okuzumi, Sin-iti Sirono, Munetake Momose, Naoki Nakatani, Kenji Furuya, Takashi Shimonishi, Tomoya Yamazaki, Hiroshi Hidaka, Yuki Kimura, Ken-ichiro Murata, Kazuyuki Fujita, Shunichi Nakatsubo, Shogo Tachibana, Naoki Watanabe**

It has been implicitly assumed that ices on grains in molecular clouds and protoplanetary disks are formed by homogeneous layers regardless of their composition or crystallinity. To verify this assumption, we observed the H<sub>2</sub>O deposition onto refractory substrates and the crystallization of amorphous ices (H<sub>2</sub>O, CO<sub>2</sub>, and CO) using an ultra-high-vacuum transmission electron microscope. In the H<sub>2</sub>O-deposition experiments, we found that three-dimensional islands of crystalline ice (Ic) were formed at temperatures above 130 K. The crystallization experiments showed that uniform thin films of amorphous CO and H<sub>2</sub>O became three-dimensional islands of polyhedral crystals; amorphous CO<sub>2</sub>, on the other hand, became a thin film of nano-crystalline CO<sub>2</sub> covering the amorphous H<sub>2</sub>O. Our observations show that crystal morphologies strongly depend not only on the ice composition but also on the substrate. Using experimental data concerning the crystallinity of deposited ices and the crystallization timescale of amorphous ices, we illustrated the criteria for ice crystallinity in space and outlined the macroscopic morphology of icy grains in molecular clouds as follows: amorphous H<sub>2</sub>O covered the refractory grain uniformly, CO<sub>2</sub> nano-crystals were embedded in the amorphous H<sub>2</sub>O, and a polyhedral CO crystal was attached to the amorphous H<sub>2</sub>O. Furthermore, a change in the grain morphology in a protoplanetary disk is shown. These results have important implications for the chemical evolution of molecules, nonthermal desorption, collision of icy grains, and sintering.

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## **Vibrational excitation and dissociation of deuterium molecule by electron impact**

**V Laporta, R Agnello, G Fubiani, I Furno, C Hill, D Reiter and F Taccogna**

A theoretical investigation of electron-D<sub>2</sub> resonant collisions—via the low-lying and the Rydberg states of D—2—is presented for vibrational excitation, dissociative electron attachment and dissociative excitation processes by using the local-complex-potential approach. Full sets of vibrationally resolved cross sections, involving the ground electronic state—X 1 $\Sigma$ +g—and the first two electronic excited states—b 3 $\Sigma$ +u and B 1 $\Sigma$ +u—of the D<sub>2</sub> molecule, are given for fusion plasma applications in their technologically relevant partially dissociated, detached divertor regimes. In particular, transitions between electronic excited states are also considered. Comparisons are made with cross sections present in the literature, where available.

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## **Protostellar Interferometric Line Survey of the Cygnus X region (PILS-Cygnus) - First results: observations of CygX-N30**

**S. J. van der Walt, L. E. Kristensen, J. K. Jørgensen, H. Calcutt, S. Manigand,**



(Abridged) Complex organic molecules (COMs) are commonly detected in and near star-forming regions. However, the dominant process in the release of these COMs from the icy grains - where they predominately form - to the gas phase is still an open question. We investigate the origin of COM emission in a protostellar source, CygX-N30, through high-angular-resolution interferometric observations over a continuous broad frequency range. We used 32 GHz Submillimeter Array observations with continuous frequency coverage from 329 to 361 GHz at an angular resolution of  $\sim 1''$  to do a line survey and obtain a chemical inventory of the source. The line emission was used to determine column densities and excitation temperatures for the COMs. We mapped out the intensity distribution of the different species and identified approximately 400 lines that can be attributed to 29 different molecular species and their isotopologues. We find that the molecular peak emission is along a linear gradient, coinciding with the axis of red- and blueshifted H<sub>2</sub>CO and CS emission. Chemical differentiation is detected along this gradient, with the O-bearing molecular species peaking towards one component of the system and the N- and S-bearing species peaking towards the other. The inferred column densities and excitation temperatures are compared to other sources where COMs are abundant. The origin of the observed COM emission is probably a combination of the young stellar sources along with accretion of infalling material onto a disc-like structure surrounding a young protostar. The low D/H ratio observed ( $< 0.1\%$ ) likely reflects a pre-stellar phase where COMs formed on the ices at warm temperatures ( $\sim 30$  K), with inefficient deuterium fractionation. The observations and results presented here demonstrate the importance of good frequency coverage and high angular resolution when disentangling the origin of COM emission.

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## **ATOMIUM: Halide molecules around the S-type AGB star W Aquilae**

**T. Danilovich, M. Van de Sande, J. M. C. Plane, T. J. Millar, P. Royer, M. A. Amor, K. Hammami, L. Decock, C. A. Gottlieb, L. Decin, A. M. S. Richards, E. De Beck, A. Baudry, J. Bolte, E. Cannon, F. De Ceuster, A. de Koter, S. Etoka, D. Gobrecht, M. Gray, F. Herpin, W. Homan, M. Jeste, P. Kervella, T. Khouri, E. Lagadec, S. Maes, J. Malfait, I. McDonald, K. M. Menten, M. Montargès, H. S. P. Müller, B. Pimpanuwat, R. Sahai, S. H. J. Wallström, L. B. F. M. Waters, K. T. Wong, J. Yates, A. Zijlstra**

S-type asymptotic giant branch (AGB) stars are thought to be intermediates in the evolution of oxygen- to carbon-rich AGB stars. The chemical compositions of their circumstellar envelopes are also intermediate, but have not been studied in as much detail as their carbon- and oxygen-rich counterparts. We aim to determine the abundances of AlCl and AlF from rotational lines, which have been observed for the first time towards an S-type AGB star, W Aql. In combination with models based on PACS observations, we aim to update our chemical kinetics network based on these results. We analyse ALMA observations towards W Aql of AlCl in the ground and first two vibrationally excited states and AlF in the ground vibrational state. Using radiative transfer models, we determine the abundances and spatial abundance distributions of Al<sup>35</sup>Cl, Al<sup>37</sup>Cl, and AlF. We also model HCl and HF emission and compare these models to PACS spectra to constrain the abundances of these species. AlCl is found in clumps very close to the star, with emission confined within  $0.1''$  of the star. AlF emission is

more extended, with faint emission extending 0.2'' to 0.6'' from the continuum peak. We find peak abundances, relative to H<sub>2</sub>, of  $1.7 \times 10^{-7}$  for Al<sup>35</sup>Cl,  $7 \times 10^{-8}$  for Al<sup>37</sup>Cl and  $1 \times 10^{-7}$  for AlF. From the PACS spectra, we find abundances of  $9.7 \times 10^{-8}$  and  $\leq 10^{-8}$ , relative to H<sub>2</sub>, for HCl and HF, respectively. The AlF abundance exceeds the solar F abundance, indicating that fluorine synthesised in the AGB star has already been dredged up to the surface of the star and ejected into the circumstellar envelope. From our analysis of chemical reactions in the wind, we conclude that AlF may participate in the dust formation process, but we cannot fully explain the rapid depletion of AlCl seen in the wind.

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## Clump-scale chemistry in the NGC2264-D cluster-forming region

**Kotomi Taniguchi, Adele Plunkett, Tomomi Shimoikura, Kazuhito Dobashi, Masao Saito, Fumitaka Nakamura, Eric Herbst**

We have conducted mapping observations toward the n3 and n5 positions in the NGC2264-D cluster-forming region with the Atacama Compact Array (ACA) of the Atacama Large Millimeter/submillimeter Array (ALMA) in Band 3. Observations with 10000 au scale beam reveal the chemical composition at the clump scale. The spatial distributions of the observed low upper-state-energy lines of CH<sub>3</sub>OH are similar to those of CS and SO, and the HC<sub>3</sub>N emission seems to be predominantly associated with clumps containing young stellar objects. The turbulent gas induced by the star formation activities produces large-scale shock regions in NGC2264-D, which are traced by the CH<sub>3</sub>OH, CS and SO emissions. We derive the HC<sub>3</sub>N, CH<sub>3</sub>CN, and CH<sub>3</sub>CHO abundances with respect to CH<sub>3</sub>OH. Compared to the n5 field, the n3 field is farther (in projected apparent distance) from the neighboring NGC2264-C, yet the chemical composition in the n3 field tends to be similar to that of the protostellar candidate CMM3 in NGC2264-C. The HC<sub>3</sub>N/CH<sub>3</sub>OH ratios in the n3 field are higher than those in the n5 field. We find an anti-correlation between the HC<sub>3</sub>N/CH<sub>3</sub>OH ratio and their excitation temperatures. The low HC<sub>3</sub>N/CH<sub>3</sub>OH abundance ratio at the n5 field implies that the n5 field is an environment with more active star formation compared with the n3 field.

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## Anharmonic Fundamental Vibrational Frequencies and Spectroscopic Constants of the Surprisingly Abundant HSO<sub>2</sub> Radical

**R. C. Fortenberry and J. S. Francisco**

The recent report that HSO<sub>2</sub> is likely kinetically favored over the HOSO thermodynamic product in hydrogen addition to sulfur dioxide in simulated Venusian atmospheric conditions has led to the need for reference rotational, vibrational, and rovibrational spectral data for this molecule. While matrix-isolation spectroscopy has been able to produce vibrational frequencies for some of the vibrational modes, the full infrared to microwave spectrum of 1 2A' HSO<sub>2</sub> is yet to be generated. High-level quantum chemical computations show in this work that the >2.5 D dipole moment of this radical makes it a notable target for possible radioastronomical observation. Additionally, the

high intensity antisymmetric S–O stretch is computed here to be 1298.3 cm<sup>–1</sup>, a 13.9 cm<sup>–1</sup> blueshift up from H<sub>2</sub> matrix analysis. In any case, the full set of rotational and spectroscopic constants and anharmonic fundamental vibrational frequencies is provided in this work in order to help characterize HSO<sub>2</sub> and probe its kinetic favorability.

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## Linear and Helical Carbonic Acid Clusters

**A. Wallace, R. Fortenberry**

Crystallization of carbonic acid likely begins with a linear or ribbon-esque oligomerization, but a helical spiral is shown here to be a new, competing motif for this process. The present combined density functional theory and coupled-cluster theory work examines both the ribbon and the new helical spiral motifs in terms of relative energies, sequential binding energies, and electronic spectra which could potentially aid in distinguishing between the two forms. The helix diverges in energy from the ribbon by roughly 0.2 eV (~4 kcal/mol) per dimer addition, but the largest intensity absorption features at 9.16 eV (135 nm) and 7.11 eV (175 nm), respective of the ribbon and spiral, will allow these to be separately observed and classified via electronic spectroscopy to determine more conclusively which motif holds in the earliest formation stages of solid carbonic acid.

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## Dynamical effects of the radiative stellar feedback on the H I-to-H<sub>2</sub> transition

**V. Maillard, E. Bron, F. Le Petit**

The atomic-to-molecular hydrogen (H/H<sub>2</sub>) transition has been extensively studied as it controls the fraction of gas in a molecular state in an interstellar cloud. This fraction is linked to star-formation by the Schmidt-Kennicutt law. While theoretical estimates of the column density of the H I layer have been proposed for static photodissociation regions (PDRs), Herschel and well-resolved ALMA (Atacama Large Millimeter Array) observations have revealed dynamical effects in star forming regions, caused by the process of photoevaporation. We extend the analytic study of the H/H<sub>2</sub> transition to include the effects of the propagation of the ionization front, in particular in the presence of photoevaporation at the walls of blister H II regions, and we find its consequences on the total atomic hydrogen column density at the surface of clouds in the presence of an ultraviolet field, and on the properties of the H/H<sub>2</sub> transition. We solved semi-analytically the differential equation giving the H<sub>2</sub> column density profile by taking into account H<sub>2</sub> formation on grains, H<sub>2</sub> photodissociation, and the ionization front propagation dynamics modeled as advection of the gas through the ionization front. Taking this advection into account reduces the width of the atomic region compared to static models. The atomic region may disappear if the ionization front velocity exceeds a certain value, leading the H/H<sub>2</sub> transition and the ionization front to merge. For both dissociated and merged configurations, we provide analytical expressions to determine the total H I column density. Our results take the metallicity into account. Finally, we compared our results to observations of PDRs illuminated by O-stars, for which we



conclude that the dynamical effects are strong, especially for low-excitation PDRs.

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## Knowledge Gaps in the Emission Spectra of Oxygen-Bearing Molecular Cations.

**R. C. Fortenberry, D. Bodewits, and D. M. Pierce**

Molecular cations are present in various astronomical environments, most notably in cometary atmospheres and tails where sunlight produces exceptionally bright near-UV to visible transitions. Such cations typically have longer-wavelength and brighter electronic emission than their corresponding neutrals. A robust understanding of their near-UV to visible properties would allow these cations to be used as tools for probing the local plasma environments or as tracers of neutral gas in cometary environments. However, full spectral models are not possible for characterization of small, oxygen-containing molecular cations given the body of molecular data currently available. The five simplest such species ( $\text{H}_2\text{O}^+$ ,  $\text{CO}_2^+$ ,  $\text{CO}^+$ ,  $\text{OH}^+$ , and  $\text{O}_2^+$ ) are well characterized in some spectral regions but are lacking robust reference data in others. Such knowledge gaps hinder fully quantitative models of cometary spectra, specifically hindering accurate estimates of physical-chemical processes originating with the most common molecules in comets. Herein, the existing spectral data are collected for these molecules, and the places where future work is needed are highlighted, specifically where the lack of such data would greatly enhance the understanding of cometary evolution.

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## Further Astrochemical Insights From Bond Strengths of Small Molecules Containing Atoms From the First Three Rows of the Periodic Table

**E. S. Doerksen and R. C. Fortenberry**

The atoms contributing to the strongest “single bonds” on the periodic table do not continue to produce the strongest “double bonds” or “triple bonds.” In fact, the opposite appears to be the case. This quantum chemical examination of nominal  $\text{X} = \text{Y}$  and  $\text{X} \equiv \text{Y}$  bonds in model molecules of atoms from the first three rows of the periodic table shows that the strongest “double bond” is in formaldehyde once the astrophysically-depleted Be and B atoms are removed from consideration. The strongest “triple bond” is a close match between acetylene and  $\text{N}_2$ . However, these results indicate that astrophysical regions containing a high abundance of hydride species will likely be areas where inorganic oxide formation is favored. Those where  $\text{H}_2$  molecules have already been dissociated will favor organic/volatile astrochemistry.

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## Quantification of $\text{O}_2$ formation during UV photolysis of water

## ice - H<sub>2</sub>O and H<sub>2</sub>O:CO<sub>2</sub> ices

**M. Bulak, D.M. Paardekooper, G. Fedoseev, K.-J. Chuang, J. Terwisscha van Scheltinga, C. Eistrup, and H. Linnartz**

Context. The Rosetta and Giotto missions investigated the composition of the cometary comae of 67P/Churyumov-Gerasimenko and 1P/Halley, respectively. In both cases, a surprisingly large amount of molecular oxygen (O<sub>2</sub>) was detected and was well correlated with the observed abundances of H<sub>2</sub>O. Laboratory experiments simulating chemical processing for various astronomical environments already showed that formation of solid state O<sub>2</sub> is linked to water. However, a quantitative study of O<sub>2</sub> formation upon UV photolysis of pure H<sub>2</sub>O and H<sub>2</sub>O dominated interstellar ice analogues is still missing. Aims. The goal of this work is to investigate whether the UV irradiation of H<sub>2</sub>O-rich ice produced at the earliest stages of star formation is efficient enough to explain the observed abundance of cometary O<sub>2</sub>. Methods. The photochemistry of pure H<sub>2</sub><sup>16</sup>O (H<sub>2</sub><sup>18</sup>O) as well as mixed H<sub>2</sub>O:CO<sub>2</sub> (ratio of 100:11, 100:22, 100:44) and H<sub>2</sub>O:CO<sub>2</sub>:O<sub>2</sub> (100:22:2) ices was quantified during UV photolysis. Laser desorption post-ionisation time of flight mass spectrometry (LDPI TOF MS) was used to probe molecular abundances in the ice as a function of UV fluence. Results. Upon UV photolysis of pure amorphous H<sub>2</sub>O ice, deposited at 20 K, formation of O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> is observed at abundances of, respectively, (0.9 +/- 0.2)% (O<sub>2</sub>/H<sub>2</sub>O) and (1.3 +/- 0.3)% (H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O). To the best of our knowledge, this is the first quantitative characterisation of the kinetics of this process. During the UV photolysis of mixed H<sub>2</sub>O:CO<sub>2</sub> ices, the formation of the relative amount of O<sub>2</sub> compared to H<sub>2</sub>O increases to a level of (1.6 +/- 0.4)% (for H<sub>2</sub>O:CO<sub>2</sub> ratio of 100:22), while the (H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O) yield remains similar to experiments with pure water. In an ice enriched with O<sub>2</sub> (2%), the O<sub>2</sub> level increases up to 7% with regard to H<sub>2</sub>O, at low UV fluence, which is higher than expected on the basis of the enrichment alone. The resulting O<sub>2</sub>/H<sub>2</sub>O values derived for the H<sub>2</sub>O and H<sub>2</sub>O:CO<sub>2</sub> ices may account for a (substantial) part of the high oxygen amounts found in the comae of 67P and 1P.

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## The vibrational properties of benzene on an ordered water ice surface

**Victoria H J Clark, David M Benoit**

We present a hybrid CCSD(T)+PBE-D3 approach to calculating the vibrational signatures for gas phase benzene and benzene adsorbed on an ordered water-ice surface. We compare the results of our method against experimentally recorded spectra and calculations performed using PBE-D3-only approaches (harmonic and anharmonic). Calculations use a proton ordered XIh water-ice surface consisting of 288 water molecules, and results are compared against experimental spectra recorded for an ASW ice surface. We show the importance of including a water ice surface into spectroscopic calculations, owing to the resulting differences in vibrational modes, frequencies and intensities of transitions seen in the IR spectrum. The overall intensity pattern shifts from a dominating  $\nu_{11}$  band in the gas-phase to several high-intensity carriers for an IR spectrum of adsorbed benzene. When used for adsorbed benzene, the hybrid approach presented here achieves an RMSD for IR active modes of 21 cm<sup>-1</sup>, compared to 72 cm<sup>-1</sup> and 49 cm<sup>-1</sup> for the anharmonic and harmonic PBE-D3 approaches, respectively. Our hybrid model for gaseous benzene also achieves the

best results when compared to experiment, with an RMSD for IR active modes of 24 cm<sup>-1</sup>, compared to 55 cm<sup>-1</sup> and 31 cm<sup>-1</sup> for the anharmonic and harmonic PBE-D3 approaches, respectively. To facilitate assignment, we generate and provide a correspondence graph between the normal modes of the gaseous and adsorbed benzene molecules. Finally, we calculate the frequency shifts,  $\Delta\nu$ , of adsorbed benzene relative to its gas phase to highlight the effects of surface interactions on vibrational bands and evaluate the suitability of our chosen dispersion-corrected density functional theory.

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## First detection of C<sub>2</sub>H<sub>5</sub>NCO in the ISM and search of other isocyanates towards the G+0.693-0.027 molecular cloud

**L. F. Rodríguez-Almeida, V. M. Rivilla, , I. Jiménez-Serra, M. Melosso, L. Colzi, S. Zeng, B. Tercero, P. de Vicente, S. Martín, M. A. Requena-Torres, F. Rico-Villas, and J. Martín-Pintado**

**Context.** Little is known about the chemistry of isocyanates (compounds with the functional group R-N=C=O) in the interstellar medium (ISM), as only four of them have been detected so far: isocyanate radical (NCO), isocyanic acid (HNCO), N-protonated isocyanic acid (H<sub>2</sub>NCO<sup>+</sup>), and methyl isocyanate (CH<sub>3</sub>NCO). The molecular cloud G+0.693-0.027, located in the Galactic Centre, represents an excellent candidate to search for new isocyanates since it exhibits high abundances of the simplest ones, HNCO and CH<sub>3</sub>NCO. **Aims.** After CH<sub>3</sub>NCO, the next most complex isocyanates are ethyl isocyanate (C<sub>2</sub>H<sub>5</sub>NCO) and vinyl isocyanate (C<sub>2</sub>H<sub>3</sub>NCO). Their detection in the ISM would enhance our understanding of the formation of these compounds in space. **Methods.** We have searched for C<sub>2</sub>H<sub>5</sub>NCO, H<sub>2</sub>NCO<sup>+</sup>, C<sub>2</sub>H<sub>3</sub>NCO, and cyanogen isocyanate (NCNCO) in a sensitive unbiased spectral survey carried out in the 2 mm and 7 mm radio windows using the IRAM 30m and Yebes 40m radio telescopes, respectively. **Results.** We have detected C<sub>2</sub>H<sub>5</sub>NCO and H<sub>2</sub>NCO<sup>+</sup> towards G+0.693-0.027 (the former for the first time in the ISM) with molecular abundances of (4.7-7.3)×10<sup>-11</sup> and (1.0-1.5)×10<sup>-11</sup>, respectively. A ratio of CH<sub>3</sub>NCO / C<sub>2</sub>H<sub>5</sub>NCO = 8 ± 1 is obtained; therefore, the relative abundance determined for HNCO:CH<sub>3</sub>NCO:C<sub>2</sub>H<sub>5</sub>NCO is 1:1/55:1/447, which implies a decrease by more than one order of magnitude, going progressively from HNCO to CH<sub>3</sub>NCO and to C<sub>2</sub>H<sub>5</sub>NCO. This is similar to what has been found for alcohols and thiols, for example, and suggests that C<sub>2</sub>H<sub>5</sub>NCO is likely formed on the surface of dust grains. In addition, we have obtained column density ratios of HNCO / NCO > 269, HNCO / H<sub>2</sub>NCO<sup>+</sup> = 2100, and C<sub>2</sub>H<sub>3</sub>NCO / C<sub>2</sub>H<sub>5</sub>NCO < 4. A comparison of the methyl/ethyl ratios for isocyanates (-NCO), alcohols (-OH), formates (HCOO<sup>-</sup>), nitriles (-CN), and thiols (-SH) is performed and shows that ethyl derivatives may be formed more efficiently for the N-bearing molecules than for the O- and S-bearing molecules.

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## Sulfur ion irradiation experiments simulating space weathering of Solar System body surfaces - Organosulfur compound formation

**Alexander Ruf , Alexis Bouquet , Philippe Schmitt-Kopplin , Philippe Boduch ,**

**Context.** Sulfur (S) is of prime interest in the context of (astro)chemical evolution and habitability. However, the origin of S-bearing organic compounds in the Solar System is still not well constrained. **Aims.** We carried out laboratory experiments to test whether complex organosulfur compounds can be formed when surfaces of icy Solar System bodies are subject to high-energy S ions. **Methods.** Non-S-bearing organic residues, formed during the processing of astrophysical H<sub>2</sub>O:CH<sub>3</sub>OH:NH<sub>3</sub> -bearing ice analogs, were irradiated with 105 keV-S 7+ ions at 10 K and analyzed by high-resolving FT-ICR-MS. The resulting data were comprehensively analyzed, including network analysis tools. **Results.** Out of several thousands of detected compounds, 16% contain at least one sulfur atom (organosulfur (CHNOS) compounds), as verified via isotopic fine structures. These residue-related organosulfur compounds are different from those formed during the S ion irradiation of ices at 10 K. Furthermore, insoluble, apolar material was formed during the sulfur irradiation of residues. Potential organosulfur precursors (CHNO molecules) were identified by means of molecular networks. **Conclusions.** This evidence of organosulfur compounds formed by sulfur irradiation of organic residues sheds new light onto the rich and complex scope of pristine organosulfur chemistry in the Solar System, presented in the context of current and future space missions. These results indicate that the space weathering of Solar System bodies may lead to the formation of organosulfur compounds.

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## **Ice Inheritance in Dynamical Disk Models**

**J. Bergner, F. Ciesla**

The compositions of planet-forming disks are set by a combination of material inherited from the interstellar medium and material reprocessed during disk formation and evolution. Indeed, comets and primitive meteorites exhibit interstellar-like isotopic ratios and/or volatile compositions, supporting that some pristine material was incorporated intact into icy planetesimals in the solar nebula. To date, the survival of volatile interstellar material in the disk stage has not been modeled using realistic disk physics. Here, we present a modeling framework to track the destruction of interstellar ices on dust grains undergoing transport processes within a disk, with a particular focus on explaining the incorporation of pristine material into icy planetesimals. We find that it is difficult to explain inheritance through the local assembly of comets, as ice destruction is rapid for small (<10  $\mu$ m) grains in the inner few tens of au. Instead, a plausible pathway to inheritance is to form pebbles at larger disk radii, which then drift inward to the comet-forming zone with their ices mostly preserved. Small grains beyond  $\sim$ 100 au can experience ice photodissociation at the tens of percent level; however, little of the ice is actually lost from the grain, likely making this a robust site for in situ ice chemistry. Our models also indicate that many complex organic species should survive passage through the disk intact. This raises the possibility that organics synthesized in the interstellar medium can be delivered to terrestrial planets by icy-body impact and thus potentially participate in origins of life chemistry.

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# Announcements

## **Postdoctoral Fellowships in Star- and Planet Formation, Astrochemistry**

Two postdoctoral positions of 3-4 years each will be available within the Molecular Astrophysics group of Prof. dr. Ewine van Dishoeck located at Leiden Observatory, the Netherlands. The positions are centered around JWST-MIRI and NIRSPEC (guaranteed and open time) spectroscopic observations of protostars and planet-forming disks to trace - in concert with ALMA data - the journey of molecules from clouds to disks and the inventory of the material that will form planets.

One position will be observationally oriented by working directly with the JWST observations: the Leiden group has access to several hundred hours of guaranteed and open time data that target a variety of lines of molecules and ices in a wide range of sources. The second position focuses on physico-chemical models of the excitation, chemistry and evolution of molecules in the planet-forming zones of disks.

The postdocs will be part of a diverse international team studying the physical and chemical structure and evolution of protostars and disks. They are expected to support and co-supervise PhD or MSc students, and are encouraged to also pursue a personal research program. The positions can start anytime in summer 2022 or later.

Candidates with an observational or theoretical background in astrochemistry, star- and planet formation, planet-forming disks, and/or familiarity with infrared or submillimeter spectroscopy, are encouraged to apply. Applications should include a curriculum vitae, publication list, and a brief statement of research experience and interests, and arrange for at least three letters of reference to be uploaded on the relevant website. Review of applications will start on November 1 2021.

Please submit your applications to <http://jobs.strw.leidenuniv.nl/2021/dishoeckPD/>

## **Evolved Stars and their Circumstellar Environments', Dec 14-17, 2021, virtual**

The online workshop 'Evolved Stars and their Circumstellar Environments' will happen on December 14-17, 2021: <https://sofia-science-series.constantcontactsites.com>

The event will be an exciting platform for discussions about the current main questions in the field of evolved stars, and the next observational opportunities. Several invited speakers have already confirmed attendance, and we strongly encourage you to submit an abstract for a contributed talk - before November 22d.

There is no registration deadline or fee, and we strongly support participation from all interested scientists, in particular early-career.