

# AstroChemical Newsletter #79

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## Abstracts

### Siloxyl radical initiated HCN polymerization: computation of N-heterocycles formation and surface passivation

Marco Fioroni, Nathan J DeYonker

In this work, by means of quantum chemistry (Density Functional Theory (DFT), PW6B95/def2-TZVPP; DLPNO-CCSD(T)/CBS), HCN polymerization [(HCN)<sub>1–4</sub>] initiated and catalysed by a siloxyl radical (Si-O•) on a model silica surface is analysed. Linear HCN polymers (pHCN) are obtained by a radical initiated mechanism at a SiO• site and are characterized by a -(HC-N)- skeleton due to radical localization on the terminal N atom and radical attack on the C centre. NC heterocycles are formed by cyclization of the linear SiO-(HCN)<sub>3–4</sub> and are always thermodynamically preferred over their linear counterparts, acting as thermodynamic sinks. Of particular interest to the astrochemistry community is the formation of the N-heterocycle 1,3,5-triazine that can be released into the gas phase at relatively low T ( $\Delta G^\ddagger = 23.3$  kcal/mol). Full hydrogenation of SiO-(HCN•) follows two reaction channels with products: (a) SiO-CH<sub>3</sub> + •NH<sub>2</sub> or (b) amino-methanol + Si•, though characterized by slow kinetics. Nucleophilic addition of H<sub>2</sub>O to the electron-rich SiO-(HCN•) shows an unfavourable thermodynamics as well as a high-activation energy. The cleavage of the linear (HCN)<sub>1–4</sub> from the SiO• site also shows a high thermodynamic energy penalty ( $\Delta G \geq 82.0$  kcal/mol). As a consequence, the silicate surface will be passivated by a chemically active 'pHCN brush' modifying the surface physico-chemical properties. The prospect of surface-catalysed HCN polymers exhibiting a high degree of chemical reactivity and proposed avenues for the formation of 1,3,5-triazine and amino-methanol opens exciting new chemical pathways to Complex Organic Matter formation in astrochemistry.

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### Comets in context: Comparing comet compositions with protostellar nebula models

Karen Willacy, Neal Turner, Boncho Bonev, Erika Gibb, Neil Dello Russo, Michael DiSanti, Ronald J. Vervack, Nathan X.Roth

Comets provide a valuable window into the chemical and physical conditions at the time of their formation in the young solar system. We seek insights into where and when these objects formed by comparing the range of abundances observed for nine molecules and their average values across a sample of 29 comets to the predicted midplane ice abundances from models of the protosolar nebula. Our fiducial model,

where ices are inherited from the interstellar medium, can account for the observed mixing ratio ranges of each molecule considered, but no single location or time reproduces the abundances of all molecules simultaneously. This suggests that each comet consists of material processed under a range of conditions. In contrast, a model where the initial composition of disk material is 'reset', wiping out any previous chemical history, cannot account for the complete range of abundances observed in comets. Using toy models that combine material processed under different thermal conditions we find that a combination of warm (CO-poor) and cold (CO-rich) material is required to account for both the average properties of the Jupiter-family and Oort cloud comets, and the individual comets we consider. This could occur by the transport (either radial or vertical) of ice-coated dust grains in the early solar system. Comparison of the models to the average Jupiter-family and Oort cloud comet compositions suggest the two families formed in overlapping regions of the disk, in agreement with the findings of A'Hearn et al. (2012) and with the predictions of the Nice model (Gomes et al. 2005; Tsiganis et al. 2005).

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## Comparative Electron Irradiations of Amorphous and Crystalline Astrophysical Ice Analogues

**Duncan V. Mifsud, Perry A. Hailey, Péter Herczku, Béla Sulik, Zoltán Juhász, Sándor T. S. Kovács, Zuzana Kanuchová, Sergio Ioppolo, Robert W. McCullough, Béla Paripás, Nigel J. Mason**

Laboratory studies of the radiation chemistry occurring in astrophysical ices have demonstrated the dependence of this chemistry on a number of experimental parameters. One experimental parameter which has received significantly less attention is that of the phase of the solid ice under investigation. In this present study, we have performed systematic 2 keV electron irradiations of the amorphous and crystalline phases of pure CH<sub>3</sub>OH and N<sub>2</sub>O astrophysical ice analogues. Radiation-induced decay of these ices and the concomitant formation of products were monitored in situ using FT-IR spectroscopy. A direct comparison between the irradiated amorphous and crystalline CH<sub>3</sub>OH ices revealed a more rapid decay of the former compared to the latter. Interestingly, a significantly lesser difference was observed when comparing the decay rates of the amorphous and crystalline N<sub>2</sub>O ices. These observations have been rationalised in terms of the strength and extent of the intermolecular forces present in each ice. The strong and extensive hydrogen-bonding network that exists in crystalline CH<sub>3</sub>OH (but not in the amorphous phase) is suggested to significantly stabilise this phase against radiation-induced decay. Conversely, although alignment of the dipole moment of N<sub>2</sub>O is anticipated to be more extensive in the crystalline structure, its weak attractive potential does not significantly stabilise the crystalline phase against radiation-induced decay, hence explaining the smaller difference in decay rates between the amorphous and crystalline phases of N<sub>2</sub>O compared to those of CH<sub>3</sub>OH. Our results are relevant to the astrochemistry of interstellar ices and icy Solar System objects, which may experience phase changes due to thermally-induced crystallisation or space radiation-induced amorphisation.

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## Radiation-induced D/H Exchange Rate Constants in Aliphatics

## Embedded in Water Ice

**Danna Qasim, Reggie L. Hudson, Christopher K. Materese**

Gas-phase and solid-state chemistry in low-temperature interstellar clouds and cores leads to a D/H enhancement in interstellar ices, which is eventually inherited by comets, meteorites, and even planetary satellites. Hence, the D/H ratio has been widely used as a tracer for the origins of extraterrestrial chemistry. However, the D/H ratio can also be influenced by cosmic rays, which are ubiquitous and can penetrate even dense interstellar molecular cores. The effects of such high-energy radiation on deuterium fractionation have not been studied in a quantitative manner. In this study, we present rate constants for radiation-induced D-to-H exchange for fully deuterated small (1–2 C) hydrocarbons embedded in H<sub>2</sub>O ice at 20 K and H-to-D exchange for the protiated forms of these molecules in D<sub>2</sub>O ice at 20 K. We observed larger rate constants for H-to-D exchange in the D<sub>2</sub>O ice versus D-to-H exchange in H<sub>2</sub>O ice, which we have attributed to the greater bond strength of C–D versus C–H. We find that the H-to-D exchange rate constants are smaller for protiated methane than ethane, in agreement with bond energies from the literature. We are unable to obtain rate constants for the unsaturated and reactive hydrocarbons ethylene and acetylene. Interpretation of the rate constants suggest that D/H exchange products are formed in abundance alongside radiolysis products. We discuss how our quantitative and qualitative data can be used to interpret the D/H ratios of aliphatic compounds observed throughout space.

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## Infrared spectroscopy of the benzylium-like (and tropylium-like) isomers formed in the –H dissociative ionization of methylated PAHs

**Gabi Wenzel, Aude Simon, Shreyak Banhatti, Pavol Jusko, Stephan Schlemmer, Sandra Brünken, Christine Joblin**

Cationic benzylium and tropylium are known to be two competitive isomers for the –H fragment of the methylbenzene (toluene) cation. Methylated polycyclic aromatic hydrocarbon (PAH) cations are expected to be abundant in space and their dehydrogenation could lead to the formation of both the benzylium- and tropylium-like cations, which are expected to be the two lowest-energy isomers. Here, we considered 1-methylpyrene and two less compact acene-substituted species, namely 2-methylnaphthalene and 2-methylantracene, as precursors. The cationic –H fragments, C<sub>17</sub>H<sub>11</sub><sup>+</sup>, C<sub>11</sub>H<sub>9</sub><sup>+</sup>, and C<sub>15</sub>H<sub>11</sub><sup>+</sup>, were produced by dissociative ionization, and their neon tagged complexes were formed in the 22-pole cryogenic ion trap instrument FELion that is coupled to the FELIX free electron laser. Infrared (IR) predissociation spectroscopy was performed showing that the strongest depletion band is located at about 1620 cm<sup>-1</sup>, which reveals the predominance of the benzylium-like, XCH<sub>2</sub><sup>+</sup>, isomers, where X = Pyr, Nap, or Ant. Saturation depletion measurements showed that only this isomer is present in the case of C<sub>17</sub>H<sub>11</sub><sup>+</sup>, whereas for the acene-derived species at least two are present with a large abundance. Synthetic spectra were generated from the theoretical anharmonic IR spectra of the two lowest-energy isomers, namely XCH<sub>2</sub><sup>+</sup> and the tropylium-like isomers, XC<sub>7</sub><sup>+</sup>. Spectral comparison led us to conclude that there is no evidence for PyrC<sub>7</sub><sup>+</sup> but clear evidence for NapC<sub>7</sub><sup>+</sup>. No specific spectral features could be identified for AntC<sub>7</sub><sup>+</sup> due to a high spectral congestion. These results support the important role of PAH compactness in

preventing the formation of XC7+ species. They also reveal the potential of XCH2+ species to account for the aromatic infrared band observed in emission at 6.2  $\mu\text{m}$  in astrophysical environments.

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## **Infrared action spectroscopy of fundamental nitrilium ions: Protonated vinyl- and ethyl cyanide**

**Sven Thorwirth, Oskar Asvany, Michael E. Harding, Pavol Jusko, Michael C. McCarthy, Sandra Brünken, Stephan Schlemmer**

Infrared action spectra of the protonated forms of two fundamental organic nitriles, vinyl cyanide, C<sub>2</sub>H<sub>3</sub>CN, and ethyl cyanide, C<sub>2</sub>H<sub>5</sub>CN, have been observed using the FELion 22-pole ion trap apparatus and the Free Electron Laser for Infrared eXperiments (FELIX) at Radboud University, Nijmegen (The Netherlands). Vibrational bands of both ions were observed in the wavenumber regime between 300 and 2500 cm<sup>-1</sup> and spectroscopically assigned based on results from anharmonic force field calculations performed here at the coupled cluster level of theory. As the action spectroscopy scheme used in the present study probes the Ne-tagged weakly bound complexes, C<sub>2</sub>H<sub>3</sub>CNH<sup>+</sup>- Ne and C<sub>2</sub>H<sub>5</sub>CNH<sup>+</sup>- Ne, corresponding quantum-chemical calculations of these systems were also performed. Significant blueshifts observed for the strong -CNH<sup>+</sup> bending modes indicate that the neon atom is attached to the proton bound to the nitrile group in both molecular ions.

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## **Precursors of fatty alcohols in the ISM: Discovery of n-propanol**

**I. Jimenez-Serra, L. F. Rodriguez-Almeida, J. Martin-Pintado, V. M. Rivilla, M. Melosso, S. Zeng, L. Colzi, Y. Kawashima, E. Hirota, C. Puzzarini, B. Tercero, P. de Vicente, F. Rico-Villas, M. A. Requena-Torres, S. Martin**

Theories on the origins of life propose that early cell membranes were synthesized from amphiphilic molecules simpler than phospholipids such as fatty alcohols. The discovery in the interstellar medium (ISM) of ethanolamine, the simplest phospholipid head group, raises the question whether simple amphiphilic molecules are also synthesized in space. We investigate whether precursors of fatty alcohols are present in the ISM. For this, we have carried out a spectral survey at 7, 3, 2 and 1 mm toward the Giant Molecular Cloud G+0.693-0.027 located in the Galactic Center using the IRAM 30m and Yebes 40m telescopes. Here, we report the detection in the ISM of the primary alcohol n-propanol (in both conformers Ga-n-C<sub>3</sub>H<sub>7</sub>OH and Aa-n-C<sub>3</sub>H<sub>7</sub>OH), a precursor of fatty alcohols. The derived column densities of n-propanol are  $(5.5 \pm 0.4) \times 10^{13} \text{ cm}^{-2}$  for the Ga conformer and  $(3.4 \pm 0.3) \times 10^{13} \text{ cm}^{-2}$  for the Aa conformer, which imply molecular abundances of  $(4.1 \pm 0.3) \times 10^{-10}$  for Ga-n-C<sub>3</sub>H<sub>7</sub>OH and of  $(2.5 \pm 0.2) \times 10^{-10}$  for Aa-n-C<sub>3</sub>H<sub>7</sub>OH. We also searched for the AGa conformer of n-butanol (AGa-n-C<sub>4</sub>H<sub>9</sub>OH) without success yielding an upper limit to its abundance of  $< 4.1 \times 10^{-11}$ . The inferred CH<sub>3</sub>OH:C<sub>2</sub>H<sub>5</sub>OH:C<sub>3</sub>H<sub>7</sub>OH:C<sub>4</sub>H<sub>9</sub>OH abundance ratios go as 1:0.04:0.006:<0.0004 toward G+0.693-0.027, i.e. they decrease roughly by one order of magnitude for increasing complexity. We also report the detection of both syn and

anti conformers of vinyl alcohol, with column densities of  $(1.11 \pm 0.08) \times 10^{14} \text{ cm}^{-2}$  and  $(1.3 \pm 0.4) \times 10^{13} \text{ cm}^{-2}$ , and abundances of  $(8.2 \pm 0.6) \times 10^{-10}$  and  $(9.6 \pm 3.0) \times 10^{-11}$ , respectively. The detection of n-propanol, together with the recent discovery of ethanolamine in the ISM, opens the possibility that precursors of lipids according to theories of the origin of life, could have been brought to Earth from outer space.

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## **An Interferometric View of H-MM1. I. Direct Observation of NH<sub>3</sub> Depletion**

**Jaime E. Pineda, Jorma Harju, Paola Caselli, Olli Sipilä, Mika Juvela, Charlotte Vastel, Erik Rosolowsky, Andreas Burkert, Rachel K. Friesen, Yancy Shirley, María José Maureira, Spandan Choudhury, Dominique M. Segura-Cox, Rolf Güsten, Anna Punanova, Luca Bizzocchi, Alyssa A. Goodman**

Spectral lines of ammonia, NH<sub>3</sub>, are useful probes of the physical conditions in dense molecular cloud cores. In addition to advantages in spectroscopy, ammonia has also been suggested to be resistant to freezing onto grain surfaces, which should make it a superior tool for studying the interior parts of cold, dense cores. Here we present high-resolution NH<sub>3</sub> observations with the Very Large Array (VLA) and Green Bank Telescope (GBT) towards a prestellar core. These observations show an outer region with a fractional NH<sub>3</sub> abundance of  $X(\text{NH}_3) = (1.975 \pm 0.005) \times 10^{-8}$  ( $\pm 10\%$  systematic), but it also reveals that after all, the  $X(\text{NH}_3)$  starts to decrease above a H<sub>2</sub> column density of  $\approx 2.6 \times 10^{22} \text{ cm}^{-2}$ . We derive a density model for the core and find that the break-point in the fractional abundance occurs at the density  $n(\text{H}_2) \sim 2 \times 10^5 \text{ cm}^{-3}$ , and beyond this point the fractional abundance decreases with increasing density, following the power law  $n^{-1.1}$ . This power-law behavior is well reproduced by chemical models where adsorption onto grains dominates the removal of ammonia and related species from the gas at high densities. We suggest that the break-point density changes from core to core depending on the temperature and the grain properties, but that the depletion power law is anyway likely to be close to  $n^{-1}$  owing to the dominance of accretion in the central parts of starless cores.

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## **Collisional excitation of HNC by He found to be stronger than for structural isomer HCN in experiments at the low temperatures of interstellar space**

**B. M. Hays, D. Gupta, T. Guillaume, O. Abdelkader Khedaoui, I. R. Cooke, F. Thibault, F. Lique and I. R. Sims**

HCN and its unstable isomer HNC are widely observed throughout the interstellar medium, with the HNC/HCN abundance ratio correlating strongly with temperature. In very cold environments HNC can even appear more abundant than HCN. Here we use a chirped pulse Fourier transform spectrometer to measure the pressure broadening of HCN and HNC, simultaneously formed in situ by laser photolysis and cooled to low temperatures in uniform supersonic flows of helium. Despite the apparent similarity of these systems, we find the HNC-He cross section to be more than twice as big as the

HCN-He cross section at 10 K, confirming earlier quantum calculations. Our experimental results are supported by high-level scattering calculations and are also expected to apply with para-H<sub>2</sub>, demonstrating that HCN and HNC have different collisional excitation properties that strongly influence the derived interstellar abundances.

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## The KOSMA- $\tau$ PDR Model -- I. Recent updates to the numerical model of photo-dissociated regions

**M. Röllig, V. Ossenkopf-Okada**

Numerical models of Photodissociation Regions (PDRs) are an essential tool to quantitatively understand observations of massive star forming regions through simulations. Few mature PDR models are available and the Cologne KOSMA- $\tau$  PDR model is the only sophisticated model that uses a spherical cloud geometry thereby allowing us to simulate clumpy PDRs. We present the current status of the code as reference for modelers and for observers that plan to apply KOSMA- $\tau$  to interpret their data. For the numerical solution of the chemical problem we present a superior Newton-Raphson stepping algorithm and discuss strategies to numerically stabilize the problem and speed up the iterations. The chemistry in KOSMA- $\tau$  is upgraded to include the full surface chemistry in an up-to-date formulation and we discuss a novel computation of branching ratios in chemical desorption reactions. The high dust temperature in PDRs leads to a selective freeze-out of oxygen-bearing ice species due to their higher condensation temperatures and we study changes in the ice mantle structures depending on the PDR parameters, in particular the impinging UV field. Selective freeze-out can produce enhanced C abundances and higher gas temperatures resulting in a fine-structure line emission of atomic carbon [C] enhanced by up to 50% if surface reactions are considered. We show how recent ALMA observations of HCO<sup>+</sup> emission in the Orion Bar with high spatial resolution on the scale of individual clumps can be interpreted in the context of non-stationary, clumpy PDR ensembles. Additionally, we introduce WL-PDR, a simple plane-parallel PDR model written in Mathematica to act as numerical testing environment of PDR modeling aspects.

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## Computer Generated Realistic Interstellar Icy Grain Models: Physicochemical Properties and Interaction with NH<sub>3</sub>

**A. Germain, L. Tinacci, S. Pantaleone, C. Ceccarelli, P. Ugliengo**

Interstellar grains are composed by a rocky core (usually amorphous silicates) covered by an icy mantle, the most abundant molecule being H<sub>2</sub>O followed by CO, CO<sub>2</sub>, NH<sub>3</sub>, and also radicals in minor quantities. In dense molecular clouds, gas-phase chemical species freeze onto the grain surface, making it an important reservoir of molecular diversity/complexity whose evolution leads to interstellar complex organic molecules (iCOMs). Many different models of water clusters have appeared in the literature, but without a systematic study on the properties of the grain (such as the H-bonds features, the oxygen radial distribution function, the dangling species present on the

mantle surface, the surface electrostatic potential, etc.). In this work, we present a computer procedure (ACO-FROST) grounded on the newly developed semiempirical GFN2 tight-binding quantum mechanical method and the GFN-FF force field method to build-up structures of amorphous ice of large size. These methods show a very favorable accuracy/cost ratio as they are ideally designed to take noncovalent interactions into account. ACO-FROST program can be tuned to build grains of different composition mimicking dirty icy grains. These icy grain models allow studying the adsorption features (structure, binding energy, vibrational frequencies, etc.) of relevant species on a large variety of adsorption sites so to obtain a statistically meaningful distribution of the physicochemical properties of interest to be transferred in numerical models. As a test case, we computed the binding energy of ammonia adsorbed at the different sites of the icy grain surface, showing a broad distribution not easily accounted for by other more size limited icy grain models. Our method is also the base for further refinements, adopting the present grain in a more rigorous QM:MM treatment, capable of giving binding energies within the chemical accuracy.

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## Hydroaluminum Isocyanide Isomers: Prediction of Spectroscopic Properties

**P. Redondo, M. Sanz-Novo, C. Barrientos**

Metal cyanides and isocyanides play a relevant role in the metal chemistry of the carbon-rich circumstellar envelope IRC+10216. It is thought that hydrometal cyanides/isocyanides could also be present in these environments; in fact, HMgNC has been detected in the same source that MgCN, MgNC, and AlNC. The aim of this work is to provide information about hydroaluminum cyanide/isocyanide. For this goal, a comprehensive analysis of the doublet and quartet potential energy surfaces of the [Al, C, H, N] system has been carried out. Different quantum chemistry methodologies from density functional theory to ab initio have been employed. For the [Al, C, H, N] isomers the stability against dissociation and their interconversion processes have been analyzed. Our results show that the most relevant isomers from an experimental point of view are HAICN and HAINC. HAINC has been found to be the most stable isomer followed by HAICN which is located at 1.59 kcal/mol (0.0689 eV) at the composite level. The interconversion process between HAICN and HAINC presents an energy barrier of 10.0 kcal/mol (5032 K) that makes this process not viable in the interstellar medium. We provide a complete set of relevant spectroscopic parameters for rotational spectroscopy for both HAICN and HAINC isomers using state-of-the-art quantum chemical computations, mandatory to guide an eventual laboratory or interstellar detection. Moreover, both isomers present sizable  $\mu_a$  dipole moment components (3.7 and 3.3 D respectively), which are large enough to enable a characterization by means of rotational spectroscopy, further increasing their interest as interstellar candidates.

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## Spectroscopic Detection of Cyano-Cyclopentadiene Ions as Dissociation Products upon Ionization of Aniline

**D.B. Rap, T.J.H.H. van Boxtel, B. Redlich, S. Brünken**

The H-loss products ( $C_6H_6N^+$ ) from the dissociative ionization of aniline ( $C_6H_7N$ ) have been studied by infrared predissociation spectroscopy in a cryogenic ion trap instrument at the free electron laser for infrared experiments (FELIX) laboratory. Broadband and narrow line width vibrational spectra in the spectral fingerprint region of  $550\text{--}1800\text{ cm}^{-1}$  have been recorded. The comparison to calculated spectra of the potential isomeric structures of the fragment ions reveals that the dominant fragments are five-membered cyano-cyclopentadiene ions. Computed  $C_6H_7N^{\bullet+}$  potential energy surfaces suggest that the dissociation path leading to H loss starts with an isomerization process, following a similar trajectory as the one leading to HNC loss. The possible presence of cyano-cyclopentadiene ions and related five-membered ring species in Titan's atmosphere and the interstellar medium are discussed.

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## The Zeeman effect in $CO^+$ observed with rotational action spectroscopy

**A.N. Marimuthu, K. Steenbakkers, B. Redlich, S. Brünken**

We discuss newly measured rotational transitions of  $CO^+$  ( $X^2\Sigma^+$ ) in its vibrational ground state  $v = 0$ , in particular the fine-structure components of the  $N = 0\text{--}1$  and  $N = 1\text{--}2$  transitions. We employed a rotational action spectroscopic technique in a cryogenic ion trap for the measurements. The recorded low-temperature and high-resolution spectra of  $CO^+$  show resolved Zeeman splittings caused by the Earth's magnetic field. The highly accurate experimental transition frequencies and derived molecular constants agree with previous measurements and improve the spectroscopic parameters for this known interstellar molecular ion.

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## Spectral Signatures of Hydrogen Thioperoxide (HOSH) and Hydrogen Persulfide (HSSH): Possible Molecular Sulfur Sinks in the Dense ISM

**Charles Z. Palmer, Ryan C. Fortenberry, Joseph S. Francisco**

For decades, sulfur has remained underdetected in molecular form within the dense interstellar medium (ISM), and somewhere a molecular sulfur sink exists where it may be hiding. With the discovery of hydrogen peroxide ( $HOOH$ ) in the ISM in 2011, a natural starting point may be found in sulfur-bearing analogs that are chemically similar to  $HOOH$ : hydrogen thioperoxide ( $HOSH$ ) and hydrogen persulfide ( $HSSH$ ). The present theoretical study couples the accuracy in the anharmonic fundamental vibrational frequencies from the explicitly correlated coupled cluster theory with the accurate rotational constants provided by canonical high-level coupled cluster theory to produce rovibrational spectra for use in the potential observation of  $HOSH$  and  $HSSH$ . The  $\nu_6$  mode for  $HSSH$  at  $886.1\text{ cm}^{-1}$  is within  $0.2\text{ cm}^{-1}$  of the gas-phase experiment, and the  $B_0$  rotational constant for  $HSSH$  of  $6979.5\text{ MHz}$  is within  $9.0\text{ MHz}$  of the experimental benchmarks, implying that the unknown spectral features (such as the first overtones and combination bands) provided herein are similarly accurate. Notably, a previous experimentally-attributed  $2\nu_1$  mode, at  $7041.8\text{ cm}^{-1}$ , has been reassigned to the  $\nu_1 + \nu_5$  combination band based on the present work's  $\nu_1 + \nu_5$  value at  $7034.3$



cm<sup>-1</sup>. The most intense vibrational transitions for each molecule are the torsions, with HOSH having a more intense transition of 72 km/mol compared to HSSH's intensity of 14 km/mol. Furthermore, HOSH has a larger net dipole moment of 1.60 D compared to HSSH's 1.15 D. While HOSH may be the more likely candidate of the two for possible astronomical observation via vibrational spectroscopy due to the notable difference in their intensities, both HSSH and HOSH have large enough net dipole moments to be detectable by rotational spectroscopy to discover the role these molecules may have as possible molecular sulfur sinks in the dense ISM.

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## First experimental confirmation of the CH<sub>3</sub>O + H<sub>2</sub>CO -> CH<sub>3</sub>OH + HCO reaction: expanding the CH<sub>3</sub>OH formation mechanism in interstellar ices

**J. C. Santos, K.-J. Chuang, T. Lamberts, G. Fedoseev, S. Ioppolo, H. Linnartz**

The successive addition of H atoms to CO in the solid phase has been hitherto regarded as the primary route to form methanol in dark molecular clouds. However, recent Monte Carlo simulations of interstellar ices alternatively suggested the radical-molecule H-atom abstraction reaction CH<sub>3</sub>O + H<sub>2</sub>CO -> CH<sub>3</sub>OH + HCO, in addition to CH<sub>3</sub>O + H -> CH<sub>3</sub>OH, as a very promising and possibly dominating (70 - 90 %) final step to form CH<sub>3</sub>OH in those environments. Here, we compare the contributions of these two steps leading to methanol by experimentally investigating hydrogenation reactions on H<sub>2</sub>CO and D<sub>2</sub>CO ices, which ensures comparable starting points between the two scenarios. The experiments are performed under ultrahigh vacuum conditions and astronomically relevant temperatures, with H:H<sub>2</sub>CO (or D<sub>2</sub>CO) flux ratios of 10:1 and 30:1. The radical-molecule route in the partially deuterated scenario, CHD<sub>2</sub>O + D<sub>2</sub>CO -> CHD<sub>2</sub>OD + DCO, is significantly hampered by the isotope effect in the D-abstraction process, and can thus be used as an artifice to probe the efficiency of this step. We observe a significantly smaller yield of D<sub>2</sub>CO + H products in comparison to H<sub>2</sub>CO + H, implying that the CH<sub>3</sub>O-induced abstraction route must play an important role in the formation of methanol in interstellar ices. Reflection-Absorption InfraRed Spectroscopy (RAIRS) and Temperature Programmed Desorption-Quadrupole Mass Spectrometry (TPD-QMS) analyses are used to quantify the species in the ice. Both analytical techniques indicate constant contributions of ~80 % for the abstraction route in the 10 - 16 K interval, which agrees well with the Monte Carlo conclusions. Additional H<sub>2</sub>CO + D experiments confirm these conclusions.

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Full-text URL: <https://arxiv.org/abs/2205.12284>

## Polycyclic Aliphatic Hydrocarbons: Is Tetrahedrane Present in UIR Spectra?

**Brent R. Westbrook, Griffin M. Beasley and Ryan C. Fortenberry**

The smallest Platonic hydrocarbon, tetrahedrane, has been subject to frequent theoretical and experimental study for 50 years, but its infrared spectrum and synthetic pathway remain a mystery. The recent partial attribution of the ultraviolet extinction bump observed in the interstellar medium (ISM) of the Milky Way galaxy to

hydrogenated T-carbon, a larger tetrahedral cluster formed from tetrahedrane and C<sub>4</sub> monomers, has brought renewed interest to the molecule. Similarly, as a polycyclic hydrocarbon, tetrahedrane is similar in structure to the molecules proposed to be responsible for the so-called unidentified infrared bands (UIRs) observed in all kinds of astronomical environments. Furthermore, tetrahedrane's  $\nu_2$  and  $\nu_7$  fundamental vibrational frequencies, with values of 3210.6 cm<sup>-1</sup> (3.11  $\mu$ m) and 752.5 cm<sup>-1</sup> (13.29  $\mu$ m) as computed in the present quantum chemical study, have substantial intensities of 59 and 183 km mol<sup>-1</sup>, respectively. These come tantalizingly close to, but potentially distinct from, the 3.3 and 13.2  $\mu$ m regions of the infrared spectrum typically included in the UIRs. As such, tetrahedrane or related clusters of these polycyclic aliphatic hydrocarbons may have a role to play in both of these sets of observations and could even help to explain the relation between them. Regardless, if tetrahedrane is present in the ISM, the highly-accurate theoretical data reported herein should help to aid in its identification and may assist in guiding future synthetic experiments as well.

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## Announcements

### AstroChemical Origins conference

Toulouse, France, 5-9th of June 2023

In the context of the [AstroChemical Origin ITN H2020 project](#), the [DOC ERC](#), the [SIRC ANR](#) and the [ERC project QuantumGrain](#), we are organizing a conference entitled "Chemical Processes in Solar-type Star-Forming Regions", in Toulouse, France, 5-9th of June 2023.

The aim is to gather together the actors of the intrinsically interdisciplinary topics present in ACO: instrumentalists, astronomers, chemists, and modelers. The goal of the conference is to review and discuss the recent huge progress in the four areas and, hopefully, open new future avenues.

The meeting will consist of invited reviews, invited and contributed talks, and posters, in 4 sessions which will cover the astronomical observations and modeling, as well as laboratory experiments and theoretical computations:

- I. Interstellar ices,
- II. Molecular complexity,
- III. Molecular fractionation,
- IV. Cometary ices.

Confirmed invited speakers: Alexander Tielens (NL), Piero Ugliengo (IT), Eleonora Bianchi (DE), Fabrice Duvernay (FR), Eva Wirström (SE), Oba Yashiro (JP), Stephanie Cazaux (NL).

The website <https://aco-conference2023.sciencesconf.org/> will be opened for registration on September 1st, 2022.

The Scientific Organising Committee:

Charlotte Vastel (chair)

François Dulieu (co-chair)

Nadia Balucani

Claudio Codella

Cecilia Ceccarelli  
Albert Rimola  
Patrice Theulé  
Serena Viti

## **PhD position in astrochemistry in Cergy and Garching**

Title: Detailed study of the formation of methanol and its return to the gas phase: coupled experimental, modelling and observational approach.

Thesis supervisors: Francois Dulieu and Emanuele Congiu (LERMA CY, FR) and Paola Caselli (MPE-Garching, DE)

Starting date: September-November 2022

Each phase of the formation of stars and planets is accompanied by a particular combination of molecular signatures, which indicates the physical conditions, but also the chemical evolution of the astrophysical environments (Caselli and Ceccarelli 2012). Methanol (CH<sub>3</sub>OH) is the emblematic Complex Organic Molecule (COMs). It is an easily detectable molecule with a rich spectrum. It is relatively abundant so that it is the only COM detected in the ice (Boogert, Gerakines, and Whittet 2015). In radio-millimetric observations of molecular clouds and star-forming regions, the abundances of other COMs are often compared to methanol. In the pre-stellar phase, the conditions of high density ( $>10^4 \text{ cm}^{-3}$ ) and low temperature ( $<12\text{K}$ ) mean that methanol should accrete completely onto the grains, especially since it is likely to be formed directly on their surface. In the Center for Astrochemical Studies (MPE Garching), observations and modelling of methanol have been performed (Punanova et al. 2018, Harju et al. 2020, Vasyunin et al. 2017). In Cergy, the formation (Minissale, Moudens, et al. 2016), sticking (Gadallah et al. 2020) and the return to the gas phase by chemical desorption have been measured (Minissale, Dulieu, et al. 2016). Nevertheless, there is still progress to be made because not all the experimental conditions have been studied, and not all the observational constraints are perfectly reproduced by the models. Among the possible developments we can note the following question: what fraction of atomic oxygen still available reduces the formation of methanol (CO would be transformed into CO<sub>2</sub>)? Can this explain the CH<sub>3</sub>OH/CO<sub>2</sub> abundance ratios measured in the ice? How can we evaluate the impact of environmental dynamics (e.g. slow shocks due to accreting material onto molecular cloud cores) in the desorption of methanol? Is the visual extinction range in which methanol is observed in the gas phase (away from a young stellar object) significant for the role of UV, or are there other explanations?

More information : <https://cyclerma.cyu.fr/version-francaise/thesis-proposal>