

# AstroChemical Newsletter #29

March 2018

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## Abstracts

### **ALMA spectral line and imaging survey of a low and a high mass-loss rate AGB star between 335 and 362 GHz**

**L. Decin, A.M.S. Richards, T. Danilovich, W. Homan, J.A. Nuth**

A spectral line and imaging survey of the low mass-loss rate AGB star R Dor ( $\dot{M} \sim 1e-7$  Msun/yr) and the high mass-loss rate AGB star IK Tau ( $\dot{M} \sim 5e-6$  Msun/yr) was made with ALMA between 335 and 362 GHz at a spatial resolution of  $\sim 150$  mas, corresponding to the locus of the main dust formation region of both targets. Some 200 spectral features from 15 molecules (and their isotopologues) were observed, including rotational lines in both the ground and vibrationally excited states. Detected species include the gaseous precursors of dust grains such as SiO, AlO, AlOH, TiO, and TiO<sub>2</sub>. We present a spectral atlas for both stars and the parameters of all detected spectral features. A clear dichotomy for the sulphur chemistry is seen: while CS, SiS, SO, and SO<sub>2</sub> are abundantly present in IK Tau, only SO and SO<sub>2</sub> are detected in R Dor. Also other species such as NaCl, NS, AlO, and AlOH display a completely different behaviour. From some selected species, the minor isotopologues can be used to assess the isotopic ratios. The channel maps of many species prove that both large and small-scale inhomogeneities persist in the inner wind of both stars in the form of blobs, arcs, and/or a disk. The high sensitivity of ALMA allows us to spot the impact of these correlated density structures in the spectral line profiles. The spectral lines often display a half width at zero intensity much larger than expected from the terminal velocity,  $v_{\infty}$ , previously derived for both objects (36 km/s versus  $v_{\infty} \sim 17.7$  km/s for IK Tau and 23 km/s versus  $v_{\infty} \sim 5.5$  km/s for R Dor). Both a more complex 3D morphology and a more forceful wind acceleration of the (underlying) isotropic wind can explain this trend. The formation of fractal grains in the region beyond  $\sim 400$  mas can potentially account for the latter scenario. From the continuum map, we deduce a dust mass of  $\sim 3.7e-7$  Msun for IK Tau and  $\sim 2e-8$  Msun for R Dor.

Astronomy & Astrophysics, in press

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### **Kinetic Monte Carlo simulations of water ice porosity: extrapolations of deposition parameters from the laboratory to interstellar space**

**Aspen R. Clements, Brandon Berk, Ilsa R. Cooke, Robin T. Garrod**

Dust grains in cold, dense interstellar clouds build up appreciable ice mantles through the accretion and subsequent surface chemistry of atoms and molecules from the gas. These mantles, of thicknesses on the order of 100 monolayers, are primarily composed

of H<sub>2</sub>O, CO, and CO<sub>2</sub>. Laboratory experiments using interstellar ice analogues have shown that porosity could be present and can facilitate diffusion of molecules along the inner pore surfaces. However, the movement of molecules within and upon the ice is poorly described by current chemical kinetics models, making it difficult either to reproduce the formation of experimental porous ice structures or to extrapolate generalized laboratory results to interstellar conditions. Here we use the off-lattice Monte Carlo kinetics model MIMICK to investigate the effects that various deposition parameters have on laboratory ice structures. The model treats molecules as isotropic spheres of a uniform size, using a Lennard-Jones potential. We reproduce experimental trends in the density of amorphous solid water (ASW) for varied deposition angle, rate and surface temperature; ice density decreases when the incident angle or deposition rate is increased, while increasing temperature results in a more-compact water ice. The models indicate that the density behaviour at higher temperatures ( $\geq 80$  K) is dependent on molecular rearrangement resulting from thermal diffusion. To reproduce trends at lower temperatures, it is necessary to take account of non-thermal diffusion by newly-adsorbed molecules, which bring kinetic energy both from the gas phase and from their acceleration into a surface binding site. Extrapolation of the model to conditions appropriate to protoplanetary disks, in which direct accretion of water from the gas-phase may be the dominant ice formation mechanism, indicate that these ices may be less porous than laboratory ices.

Physical Chemistry Chemical Physics

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## Nitrogen and hydrogen fractionation in high-mass star-forming cores from observations of HCN and HNC

L. Colzi, F. Fontani, P. Caselli, C. Ceccarelli, P. Hily-Blant, L. Bizzocchi

The ratio between the two stable isotopes of nitrogen, <sup>14</sup>N and <sup>15</sup>N, is well measured in the terrestrial atmosphere (272), and for the pre-Solar nebula (441, deduced from the solar wind). Interestingly, some pristine Solar system materials show enrichments in <sup>15</sup>N with respect to the pre-Solar nebula value. However, it is not yet clear if and how these enrichments are linked to the past chemical history because we have only a limited number of measurements in dense star-forming regions. In this respect, dense cores, which are believed to be the precursors of clusters and also contain intermediate- and high-mass stars, are important targets because the Solar system was probably born within a rich stellar cluster, and such clusters are formed in high-mass star-forming regions. The number of observations in such high-mass dense cores has remained limited so far. In this work, we show the results of IRAM-30 m observations of the J = 1-0 rotational transition of the molecules HCN and HNC and their <sup>15</sup>N-bearing counterparts towards 27 intermediate and high-mass dense cores that are divided almost equally into three evolutionary categories: high-mass starless cores, high-mass protostellar objects, and ultra-compact HII regions. We have also observed the DNC(2-1) rotational transition in order to search for a relation between the isotopic ratios D/H and <sup>14</sup>N/<sup>15</sup>N. We derive average <sup>14</sup>N/<sup>15</sup>N ratios of 359  $\pm$  16 in HCN and of 438  $\pm$  21 in HNC, with a dispersion of about 150-200. We find no trend of the <sup>14</sup>N/<sup>15</sup>N ratio with evolutionary stage. This result agrees with what has been found for N<sub>2</sub>H<sup>+</sup> and its isotopologues in the same sources, although the <sup>14</sup>N/<sup>15</sup>N ratios from N<sub>2</sub>H<sup>+</sup> show a higher dispersion than in HCN/HNC, and on average, their uncertainties are larger as well. Moreover, we have found no correlation between D/H and <sup>14</sup>N/<sup>15</sup>N in HNC. These findings indicate that (1) the chemical evolution does not seem to play a role in the fractionation of nitrogen, and that (2) the fractionation of hydrogen and

nitrogen in these objects is not related.

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## Constraints on metal oxide and metal hydroxide abundances in the winds of AGB stars - Potential detection of FeO in R Dor

**L. Decin, T. Danilovich, D. Gobrecht, J.M.C Plane, A.M.S. Richards, C.A. Gottlieb, K.L.K. Lee**

Using ALMA, we observed the stellar wind of two oxygen-rich Asymptotic Giant Branch (AGB) stars, IK Tau and R Dor, between 335 and 362 GHz. One aim was to detect metal oxides and metal hydroxides (AlO, AlOH, FeO, MgO, MgOH), some of which are thought to be direct precursors of dust nucleation and growth. We report on the potential first detection of FeO ( $v=0$ ,  $\Omega=4$ ,  $J=11-10$ ) in R Dor (mass-loss rate,  $\dot{M}$ ,  $\sim 1e-7$   $M_{\text{sun}}/\text{yr}$ ). The presence of FeO in IK Tau ( $\dot{M} \sim 5e-6$   $M_{\text{sun}}/\text{yr}$ ) cannot be confirmed due to a blend with  $^{29}\text{SiS}$ , a molecule that is absent in R Dor. The detection of AlO in R Dor and of AlOH in IK Tau was reported earlier by Decin et al. (2017). All other metal oxides and hydroxides, as well as MgS, remain undetected. We derive a column density  $N(\text{FeO})$  of  $1.1 \pm 0.9e15 \text{ cm}^{-2}$  in R Dor, or a fractional abundance  $[\text{FeO}/\text{H}] \sim 1.5e-8$  accounting for non-LTE effects. The derived fractional abundance  $[\text{FeO}/\text{H}]$  is a factor  $\sim 20$  larger than conventional gas-phase chemical kinetic predictions. This discrepancy may be partly accounted for by the role of vibrationally excited OH in oxidizing Fe, or may be evidence for other currently unrecognised chemical pathways producing FeO. Assuming a constant fractional abundance w.r.t.  $\text{H}_2$ , the upper limits for the other metals are  $[\text{MgO}/\text{H}_2] < 5.5e-10$  (R Dor) and  $< 7e-11$  (IK Tau),  $[\text{MgOH}/\text{H}_2] < 9e-9$  (R Dor) and  $< 1e-9$  (IK Tau),  $[\text{CaO}/\text{H}_2] < 2.5e-9$  (R Dor) and  $< 1e-10$  (IK Tau),  $[\text{CaOH}/\text{H}_2] < 6.5e-9$  (R Dor) and  $< 9e-10$  (IK Tau), and  $[\text{MgS}/\text{H}_2] < 4.5e-10$  (R Dor) and  $< 6e-11$  (IK Tau). The retrieved upper limit abundances for these latter molecules are in accord with the chemical model predictions.

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## Seeds of Life in Space (SOLIS). III. Zooming into the methanol peak of the pre-stellar core L1544

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Towards the pre-stellar core L1544, the methanol ( $\text{CH}_3\text{OH}$ ) emission forms an asymmetric ring around the core centre, where  $\text{CH}_3\text{OH}$  is mostly in solid form, with a clear peak 4000 au to the north-east of the dust continuum peak. As part of the NOEMA Large Project SOLIS (Seeds of Life in Space), the  $\text{CH}_3\text{OH}$  peak has been spatially resolved to study its kinematics and physical structure and to investigate the cause behind the local enhancement. We find that methanol emission is distributed in a ridge parallel to the main axis of the dense core. The centroid velocity increases by

about 0.2 km/s and the velocity dispersion increases from subsonic to transonic towards the central zone of the core, where the velocity field also shows complex structure. This could be indication of gentle accretion of material onto the core or interaction of two filaments, producing a slow shock. We measure the rotational temperature and show that methanol is in local thermodynamic equilibrium (LTE) only close to the dust peak, where it is significantly depleted. The CH<sub>3</sub>OH column density,  $N_{\text{tot}}(\text{CH}_3\text{OH})$ , profile has been derived with non-LTE radiative transfer modelling and compared with chemical models of a static core. The measured  $N_{\text{tot}}(\text{CH}_3\text{OH})$  profile is consistent with model predictions, but the total column densities are one order of magnitude lower than those predicted by models, suggesting that the efficiency of reactive desorption or atomic hydrogen tunnelling adopted in the model may be overestimated; or that an evolutionary model is needed to better reproduce methanol abundance.

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## Deuterium 15N fractionation in N<sub>2</sub>H<sup>+</sup> during the formation of a Sun-like star

**M. De Simone, F. Fontani, C. Codella, C. Ceccarelli, B. Lefloch, R. Bachiller, A. López-Sepulcre, E. Caux, C. Vastel, J. Soldateschi**

Although chemical models predict that the deuterium fractionation in N<sub>2</sub>H<sup>+</sup> is a good evolutionary tracer in the star formation process, the fractionation of nitrogen is still a poorly understood process. Recent models have questioned the similar evolutionary trend expected for the two fractionation mechanisms in N<sub>2</sub>H<sup>+</sup>, based on a classical scenario in which ion-neutral reactions occurring in cold gas should have caused an enhancement of the abundance of N<sub>2</sub>D<sup>+</sup>, <sup>15</sup>NNH<sup>+</sup>, and N<sup>15</sup>NH<sup>+</sup>. In the framework of the ASAI IRAM-30m large program, we have investigated the fractionation of deuterium and <sup>15</sup>N in N<sub>2</sub>H<sup>+</sup> in the best known representatives of the different evolutionary stages of the Sun-like star formation process. The goal is to ultimately confirm (or deny) the classical "ion-neutral reactions" scenario that predicts a similar trend for D and <sup>15</sup>N fractionation. We do not find any evolutionary trend of the <sup>14</sup>N/<sup>15</sup>N ratio from both the <sup>15</sup>NNH<sup>+</sup> and N<sup>15</sup>NH<sup>+</sup> isotopologues. Therefore, our findings confirm that, during the formation of a Sun-like star, the core evolution is irrelevant in the fractionation of <sup>15</sup>N. The independence of the <sup>14</sup>N/<sup>15</sup>N ratio with time, found also in high-mass star-forming cores, indicates that the enrichment in <sup>15</sup>N revealed in comets and protoplanetary disks is unlikely to happen at core scales. Nevertheless, we have firmly confirmed the evolutionary trend expected for the H/D ratio, with the N<sub>2</sub>H<sup>+</sup>/N<sub>2</sub>D<sup>+</sup> ratio decreasing before the pre-stellar core phase, and increasing monotonically during the protostellar phase. We have also confirmed clearly that the two fractionation mechanisms are not related.

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## XUV photodesorption of carbon clusters ions and ionic photofragments from a mixed methane-water ice

**Tushar Suhasaria, John Throver, Robert Frigge, Sebastian Roling, Mathieu Bertin, Xavier Michaut, Jean-Hugues FILLION and Helmut Zacharias**

The photochemical processing of a CH<sub>4</sub>:D<sub>2</sub>O 1:3.3 ice mixture adsorbed on a HOPG

surface in the XUV regime has been investigated using pulses obtained from the Free-electron LASer in Hamburg (FLASH) facility. The ice films were exposed to femtosecond pulses with a photon energy of  $h\nu = 40.8$  eV, consistent with the HeII resonance line. Cationic species desorbing directly from the ice film were detected using time-of-flight (ToF) mass spectrometry. Simple ions formed through the fragmentation of the parent molecules and subsequent recombination reactions were detected and are consistent with efficient  $D^+$  and  $H^+$  ejection from the parent species, similar to the case for low energy electron irradiation. The FEL fluence dependencies of these ions are linear or exhibit a non-linear order of up to 3. In addition, a series of  $C_n^+$  cluster ions (with  $n$  up to 12) were also identified. These ions display a highly non-linear desorption yield with respect to the FEL fluence, having an order of 6-10, suggesting a complex multi-step process involving the primary products of  $CH_4$  fragmentation. Two-pulse correlation measurements were performed to gain further insight into the underlying reaction dynamics of the photo-chemical reactions. The yield of the  $D_2O$  derived products displayed a different temporal behaviour with respect to the  $C_n^+$  ions, indicating the presence of very different reaction pathways to the two families of ionic products.

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## Reactive Desorption of CO Hydrogenation Products under Cold Pre-stellar Core Conditions

**K-J Chuang, G Fedoseev, D Qasim, S Ioppolo, EF van Dishoeck, H Linnartz**

The astronomical gas-phase detection of simple species and small organic molecules in cold pre-stellar cores, with abundances as high as  $\sim 1e-8$ – $1e-9$  nH, contradicts the generally accepted idea that at 10 K, such species should be fully frozen out on grain surfaces. A physical or chemical mechanism that results in a net transfer from solid-state species into the gas phase offers a possible explanation. Reactive desorption, i.e., desorption following the exothermic formation of a species, is one of the options that has been proposed. In astronomical models, the fraction of molecules desorbed through this process is handled as a free parameter, as experimental studies quantifying the impact of exothermicity on desorption efficiencies are largely lacking. In this work, we present a detailed laboratory study with the goal of deriving an upper limit for the reactive desorption efficiency of species involved in the  $CO$ – $H_2CO$ – $CH_3OH$  solid-state hydrogenation reaction chain. The limit for the overall reactive desorption fraction is derived by precisely investigating the solid-state elemental carbon budget, using reflection absorption infrared spectroscopy and the calibrated solid-state band-strength values for  $CO$ ,  $H_2CO$  and  $CH_3OH$ . We find that for temperatures in the range of 10 to 14 K, an upper limit of  $0.24 \pm 0.02$  for the overall elemental carbon loss upon  $CO$  conversion into  $CH_3OH$ . This corresponds with an effective reaction desorption fraction of 0.07 per hydrogenation step, or 0.02 per H-atom induced reaction, assuming that H-atom addition and abstraction reactions equally contribute to the overall reactive desorption fraction along the hydrogenation sequence. The astronomical relevance of this finding is discussed.

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## The NASA Ames PAH IR Spectroscopic Database:

## Computational Version 3.00 with Updated Content and the Introduction of Multiple Scaling Factors

C.W. Bauschlicher Jr., A. Ricca, C. Boersma, L. J. Allamandola

Version 3.00 of the library of computed spectra in the NASA Ames PAH IR Spectroscopic Database (PAHdb) is described. Version 3.00 introduces the use of multiple scale factors, instead of the single scaling factor used previously, to align the theoretical harmonic frequencies with the experimental fundamentals. The use of multiple scale factors permits the use of a variety of basis sets; this allows new PAH species to be included in the database, such as those containing oxygen, and yields an improved treatment of strained species and those containing nitrogen. In addition, the computed spectra of 2439 new PAH species have been added. The impact of these changes on the analysis of an astronomical spectrum through database-fitting is considered and compared with a fit using Version 2.00 of the library of computed spectra. Finally, astronomical constraints are defined for the PAH spectral libraries in PAHdb.

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## Nautilus multi-grain model: Importance of cosmic-ray-induced desorption in determining the chemical abundances in the ISM

W. Iqbal, and V. Wakelam

Species abundances in the interstellar medium (ISM) strongly depend on the chemistry occurring at the surfaces of the dust grains. To describe the complexity of the chemistry, various numerical models have been constructed. In most of these models, the grains are described by a single size of 0.1micron. We study the impact on the abundances of many species observed in the cold cores by considering several grain sizes in the Nautilus multi-grain model. We used grain sizes with radii in the range of 0.005micron to 0.25micron. We sampled this range in many bins. We used the previously published, MRN and WD grain size distributions to calculate the number density of grains in each bin. Other parameters such as the grain surface temperature or the cosmic-ray-induced desorption rates also vary with grain sizes. We present the abundances of various molecules in the gas phase and also on the dust surface at different time intervals during the simulation. We present a comparative study of results obtained using the single grain and the multi-grain models. We also compare our results with the observed abundances in TMC-1 and L134N clouds. We show that the grain size, the grain size dependent surface temperature and the peak surface temperature induced by cosmic ray collisions, play key roles in determining the ice and the gas phase abundances of various molecules. We also show that the differences between the MRN and the WD models are crucial for better fitting the observed abundances in different regions in the ISM. We show that the small grains play a very important role in the enrichment of the gas phase with the species which are mainly formed on the grain surface, as non-thermal desorption induced by collisions of cosmic ray particles is very efficient on the small grains.

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# Hydrodynamics with gas-grain chemistry and radiative transfer: comparing dynamical and static models

O. Sipilä, P. Caselli

We study the chemical abundance gradients given by a dynamical model of core collapse including time-dependent changes in density and temperature and find out if they differ greatly from the abundances derived from static models, where the density and temperature structures of the core are kept fixed as the chemistry evolves. For this study we developed a new one-dimensional spherically symmetric hydrodynamics code that couples the hydrodynamics equations with a comprehensive time-dependent gas-grain chemical model, including deuterium and spin-state chemistry, and radiative transfer calculations to derive self-consistent time-dependent chemical abundance gradients. We applied the code to model the collapse of a starless core up to the point when the infall flow becomes supersonic. The abundances predicted by the dynamical and static models are almost identical during the quiescent phase of core evolution, but the results start to diverge after the onset of core collapse, where the static model underestimates abundances at high medium density (inner core) and underestimates them at low density (outer core), and this is clearly reflected in simulated lines. The static model generally overestimates deuteration, which is increasingly evident the more D atoms are substituted in the molecule. We also find that using a limited chemical network, or a limited set of cooling molecules, may lead to an overestimate of the collapse timescale, and in some cases may prevent the collapse altogether. In our model, most of the line cooling near the center of the core is due to HCN, CO, and NO. In conclusion, the use of a static physical model is not a reliable method of simulating chemical abundances in starless cores after the onset of gravitational collapse. The adoption of complex chemistry and a comprehensive set of cooling molecules is necessary to model the collapse adequately.

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## Announcements

### **“New Spectroscopic Techniques for Astrochemistry.”**

Dr. Michael C. McCarthy and Dr. Kyle Crabtree organise a symposium at the 2018 ACS Fall National Meeting in Boston, MA, August 19-23, titled “New Spectroscopic Techniques for Astrochemistry.” This symposium will focus on the role that laboratory spectroscopy plays in addressing current challenges in the field of astrochemistry, with a particular emphasis on new and innovative approaches and techniques. The program will cover all areas of molecular spectroscopy from the microwave to the UV and beyond, both in the gas phase and condensed phase. While the primary focus of the symposium is laboratory spectroscopy, we also welcome talks from astronomers, modelers, and theoreticians working in the field of astrochemistry to highlight current needs that spectroscopy can address. Abstract submission is currently open for contributed talks at <https://acsnm256.abstractcentral.com>, and the deadline is March 12.

### **Cosmic Cycle of Dust and Gas in the Galaxy: from Old to Young Stars**

The registration for the conference Cosmic Cycle of Dust and Gas in the Galaxy: from Old to Young Stars -July 9th to July 13th, 2018- is now open. The conference will take

place at the International Center for Interdisciplinary Science and Education (ICISE) which is located in the beautiful coastal city of Quy Nhon, Vietnam. You are invited to register and submit contributed talks and posters.

<https://cosmiccycle2018.sciencesconf.org/> Organized in the framework of the "Rencontres du Vietnam", the conference focuses on the evolution of dust and gas from evolved to young stars. The aim of the conference is to bring astronomers working on the circumstellar environment of evolved stars and star forming regions and planetologists working on the origin of the solar system together to discuss about science in a friendly and relaxed environment at ICISE. In July 2016, in the same cycle of conferences, "Blowing In the Wind" addressed issues of dynamics of gas and dust in the Galaxy. In July 2017, another conference "Star Formation in Different Environments" focused on how stars form. This year's conference will be dedicated to the physico-chemistry and evolution of gas and dust. It will review state-of-the-art knowledge of the molecular and dust components of envelopes and shells surrounding AGB stars, planetary nebulae, diffuse giant molecular clouds as well as Supernovae. Special sessions will be dedicated to the origin and evolution of matter in the solar system: meteorites, comets, etc. Recent observations, in particular with ALMA, are the source of major progress in the study of the cosmic cycle of gas and dust in the Galaxy making such a conference very timely. The list of invited speakers can be found at: <https://cosmiccycle2018.sciencesconf.org/resource/page/id/6> There is some funding from the Rencontres du Vietnam to pay the hotel for a few participants. Grants will be given in priority to those giving a talk at the conference. If you need support, please fill in a form in the following link (Financial Support section):

<https://cosmiccycle2018.sciencesconf.org/resource/page/id/2> Bootcamp: During the weekend before the conference, we organize a series of tutorials and lectures introducing the topics of the conference to senior undergraduates, PhD students and young postdocs. If you are interested in attending it, please contact Tuan-Anh Pham (ptanh@vnsc.org.vn). Anne Dutrey & Diep Ngoc Pham on behalf of the SOC