AstroChemical Newsletter #37

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Abstracts

Chemical tracers in proto-brown dwarfs: CN, HCN, and HNC observations

B. Riaz, W.-F. Thi, P. Caselli

We present results from a study of nitrogen chemistry in Class 0/I proto-brown dwarfs (proto-BDs). We have used the IRAM 30 m telescope to observe the CN (2-1), HCN (3-2), and HNC (3-2) lines in 7 proto-BDs. All proto-BDs show a large CN/HCN abundance ratio of >20, and a HNC/HCN abundance ratio close to or larger than unity. The enhanced CN/HCN ratios can be explained by high UV flux originating from an active accretion zone in the proto-BDs. The larger than unity HNC/HCN ratio for the proto-BDs is likely caused by a combination of low temperature and high density. Both CN and HNC show a flat distribution with CO, indicating that these species can survive in regions where CO is depleted. We have investigated the correlations in the molecular abundances of these species for the proto-BDs with Class 0/I protostars. We find tentative trends of CN (HCN) abundances being about an order of magnitude higher (lower) in the proto-BDs compared to protostars. HNC for the proto-BDs shows a nearly constant abundance unlike the large spread of ~2 orders of magnitude seen for the protostars. Also notable is a rise in the HNC/HCN abundance ratio for the lowest luminosity objects, suggesting that this ratio is higher under low-temperature environments. None of the relatively evolved Class Flat/Class II brown dwarfs in our sample show emission in HNC. The HNC molecule can be considered as an efficient tracer to search and identify early stage sub-stellar mass objects.

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Can Formamide Be Formed on Interstellar Ice? An Atomistic Perspective

Albert Rimola, Dimitrios Skouteris, Nadia Balucani, Cecilia Ceccarelli, Joan Enrique-Romero, Vianney Taquet, Piero Ugliengo

Interstellar formamide (NH2CHO) has recently attracted significant attention due to its potential role as a molecular building block in the formation of precursor biomolecules relevant for the origin of life. Its formation, whether on the surfaces of the interstellar grains or in the gas phase, is currently debated. The present article presents new theoretical computations based on quantum chemical and kinetic calculations on possible NH2CHO formation routes in water-rich amorphous ices, simulated by a 33 H2O molecule cluster. We have considered three possible routes. The first one refers to a scenario used in several current astrochemical models, that is, the radical−radical association reaction between NH2 and HCO. Our calculations show that formamide can indeed be formed, but in competition with formation of NH3 and CO through a direct H transfer process. The final outcome of the NH2 + HCO reactivity depends on the relative orientation of the two radicals on the ice surface. We also analyzed two other possibilities, suggested here for the first time: reaction of either HCN or CN with water molecules of the ice mantle. The reaction with HCN has been found to be characterized by large energy barriers and, therefore, cannot occur under the interstellar ice conditions. On the contrary, the reaction with the CN radical can occur, possibly leading through multiple steps to the formation of NH2CHO. For this reaction, water molecules of the ice act as catalytic active sites since they help the H transfers involved in the process, thus reducing the energy barriers (compared to the gas-phase analogous reaction). Additionally, we apply a statistical model to estimate the reaction rate coefficient when considering the cluster of 33 H2O molecules as an isolated moiety with respect to the surrounding environment (i.e., the rest of the ice). Our conclusion is that CN quickly reacts with a molecule of amorphous ice and that it can synthesize formamide, even though the efficiency of the NH2CHO formation is difficult to estimate as it depends on the unknown number of ice water active sites and the fine details of energy transfer through the ice body itself. Our results have two important consequences on the modeling of interstellar surfacechemistry. First, the H2O molecules of the ice, usually considered as an inert support in astrochemical models, can instead react with active radicals, like CN, forming more complex species, and can also act as catalysts by helping H transfer processes. Second, most of the involved intermediate steps toward formamide formation on the 33-H2O molecule cluster are so fast that it is unlikely that the energy released in each of them can be dispersed in the entire ice body of the grain. In other words, the system cannot be fully equilibrated at the grain temperature in each intermediate step, as assumed in all current models, because the localized energy can promote endothermic or high barrier processes in small portions of the ice before complete equilibration. The time scale of energy redistribution within the ice molecules, a poorly characterized process, should be explicitly accounted for if a realistic model of grain surface chemistry is pursued.

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Detection of Prebiotic Molecules in Plasma and Photochemical Aerosol Analogs Using GC/MS/MS Techniques

Joshua A. Sebree, Madeline C. Roach, Emma R. Shipley, Chao He, and Sarah M. Hörst

The formation and identification of prebiotic compounds in the organically rich atmospheres of Titan and Pluto are of great interest due to the potential implications such discoveries may have on theories of the origins of life on the early Earth. In past work, hindrances in detecting prebiotic molecules in lab-generated aerosol analogs have been the large number of products formed, often compounded by limited sample amounts. In this work, we detail a GC/MS/MS protocol that is highly selective (>30 simultaneously detectable compounds) and highly sensitive (limits of detection ~1 picomole). Using this method to analyze aerosol analogs (tholins) generated by either cold plasma or photochemical irradiation of 1:1 mixtures of methane and carbon monoxide in nitrogen, this work has expanded the number of identifiable compounds in Titan/Pluto analog aerosols to include the nonbiological nucleobases xanthine and hypoxanthine in plasma aerosols and the first identification of glycine as a product in photochemical aerosols produced under reducing atmospheric conditions. Several species (glycine, guanidine, urea, and glycolic acid) were found to be present in both plasma and photochemical aerosols. Such parallel product pathways bring new understanding to the nature of plasma and photochemical aerosols and allow for new insights into the prebiotic chemistry of organically rich atmospheres including Pluto, Titan, and the early Earth.

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A global optimisation study of the low-lying isomers of the alumina octomer (Al2O3)8

David Gobrecht, Leen Decin, Sergio Cristallo, Stefan T. Bromley

We employ the Monte-Carlo Basin-Hopping (MC-BH) global optimisation technique with inter- atomic pair potentials to generate low-energy candidates of stoichiometric alumina octomers ((Al2O3)8). The candidate structures are subsequently refined with density functional theory calculations employing hybrid functionals (B3LYP and PBE0) and a large basis set (6-311+G(d)) including a vibrational analysis. We report the discovery of a set of energetically low-lying alumina octomer clusters, including a new global minimum candidate, with shapes that are elongated rather than spherical. We find a stability limit for these and smaller-sized clusters at a temperature of T≃1300−1450 K corresponding to a phase transition in liquid alumina.

Chemical Physics Letters (cplett), Vol. 711, pp. 138 (2018)
DOI: 10.1016/j.cplett.2018.09.018
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H2CO Ortho-to-para Ratio in the Protoplanetary Disk HD 163296

V. V. Guzmán, K. I. Öberg, J. Carpenter, R. Le Gal, C. Qi, and J. Pegues

Ortho-to-para (o/p) ratios of species like water, ammonia, and formaldehyde (H2CO) are believed to encode information about the formation history of the molecule. Measurements of o/p ratios in protoplanetary disks could thus be used to constrain their physical and chemical histories. We present the first measurement of the H2CO o/p ratio in a protoplanetary disk, using three ortho and two para lines observed with the Submillimeter Array (SMA) combined with one highly resolved measurement of a single H2CO line with the Atacama Large Millimeter/submillimeter Array (ALMA) toward the disk around Herbig Ae star HD 163296. We find a disk-average H2CO o/p ratio of 1.8–2.8 (depending on the assumed disk structure), corresponding to a spin temperature of 11–22 K. We also derive a rotational temperature of 24 K from the flux ratio of the three ortho lines. The observed spatial distribution, as seen by ALMA, as well as the rotational temperature and the o/p ratio, at the large scales the SMA is most sensitive to, are consistent with a low-temperature formation pathway, most likely grain surface chemistry, of H2CO in this disk.

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Temperature spectra of interstellar dust grains heated by cosmic-rays II: dark cloud cores

Kalvans, J.

Cosmic-ray (CR) induced heating of whole interstellar grains is an important desorption mechanism for grain surface molecules in interstellar molecular clouds. This study aims to provide a detailed temperature spectra for such CR-induced heating. For this, olivine grains with radius of 0.05, 0.1 and 0.2 microns shielded by interstellar gas with isotropic column densities characteristic to dark cores were considered. The accumulation of an ice mantle of increasing thickness was taken into account. The CR energy spectra was obtained for these column densities for 32 cosmic-ray constituents. We calculated the frequencies with which a CR nucleus with a known energy hits a grain, depositing a certain amount of energy. As a result, we obtain the energy and temperature spectra for grains affected by CR hits. This allows to improve the existing approaches on CR-induced whole-grain heating in astrochemical modeling.

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On the gas-phase formation of the HCO- anion: accurate quantum study of the H- +CO radiative association and HCO radiative electron attachment

Thierry Stoecklin, Philippe Halvick, Miguel Lara-Moreno, Tarek Trabelsi and Majdi Hochlaf

The hydrogen anion has never been observed in the interstellar medium, but it is most likely present in some interstellar regions. Since direct detection appears especially difficult, improving the knowledge of the astrochemical processes involving this anion should be valuable in defining a way of indirect detection. We present the first study of the radiative association of H and CO to form the HCO anion within a quantum time-independent approach. We use a state-of-the-art potential energy surface which has been calculated for the present study. The calculated radiative association rate coefficient is monotonically decreasing from 6x1e16 to 5x1e19 cm3 per molecule per s across the 0.01–1000 K temperature range. At the typical temperature of the cold interstellar medium, 10 K, the radiative association rate is 2x1e17 cm3 per molecule per s. On the other hand, the plane wave approximation is used to calculate the HCO radiative electron attachment rate coefficient. It is found to be almost constant and also equal to 2x1e17 cm3 per molecule per s. Setting aside the question of the abundances of the reactants of both processes, these results demonstrate that among the two gas-phase modes of production of the HCO anion in cold interstellar medium considered in this study, the H + CO radiative association is dominating below 10 K while the radiative electron attachment rate is larger above 10 K.

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Gas Phase Reactivity of the CN Radical with Methyl Amines at Low Temperatures (23−297 K): A Combined Experimental and Theoretical Investigation

C. Sleiman, G. El Dib, D. Talbi and A. Canosa

The gas phase reactivity of the CN radical in the presence of dimethylamine (CH3)2NH and trimethylamine (CH3)3N has been investigated experimentally using a uniform supersonic expansion CRESU reactor coupled to the pulsed laser photolysis/laser-induced fluorescence technique. Rate constants have been obtained in the temperature range 23−297 K and were found to be independent of temperature for both reactants. A typical rate constant of 5 × 10−10 cm3 molecule−1 s−1 is representative of the full set of experiments. Additionally, ab initio calculations at the ROCCSD(T)/6-311++G(3df,2pd)//M062X/6-311++G(d,p) level of theory have been carried out in order to determine the energy profiles along the reaction pathways. The paths corresponding to the hydrogen abstraction with the formation of HCN were found to be barrierless and very exothermic for the two studied reactions. Results are compared to previous works concerning the reactivity of CN with ammonia NH3 and methylamine CH3NH2. The energy profile for the reaction with methylamine has been revisited using the level of theory mentioned above. Calculations indicate that hydrogen abstraction is the major reaction pathway as well, in contradiction with a previous investigation claiming that the CN/CH3 substitution is the dominant exit channel.

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A theoretical investigation of the reaction between the amidogen, NH, and the ethyl, C2H5, radicals: a possible gas-phase formation route of interstellar and planetary ethanimine

Nadia Balucani, Dimitrios Skouteris, Cecilia Ceccarelli, Claudio Codella, Stefano Falcinelli, Marzio Rosi

The reaction between the amidogen, NH, radical and the ethyl, C2H5, radical has been investigated by performing electronic structure calculations of the underlying doublet potential energy surface. Rate coefficients and product branching ratios have also been estimated by combining capture and RRKM calculations. According to our results, the reaction is very fast, close to the gas-kinetics limit. However, the main product channel, with a yield of ca. 86–88% in the range of temperatures investigated, is the one leading to methanimine and the methyl radical. The channels leading to the two E-, Z-stereoisomers of ethanimine account only for ca. 5–7% each. The resulting ratio [E-CH3CHNH]/[Z-CH3CHNH] is ca. 1.2, that is a value rather lower than that determined in the Green Bank Telescope PRIMOS radio astronomy survey spectra of Sagittarius B2 North (ca. 3). Considering that ice chemistry would produce essentially only the most stable isomer, a possible conclusion is that the observed [E-CH3CHNH]/[Z-CH3CHNH] ratio is compatible with a combination of gas-phase and grain chemistry. More observational and laboratory data are needed to definitely address this issue.

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The 12CO2 and 13CO2 Absorption Bands as Tracers of the Thermal History of Interstellar Icy Grain Mantles

J. He, S. Emtiaz, A. Boogert, and G. Vidali

Analyses of infrared signatures of CO2 in water dominated ices in the ISM can give information on the physical state of CO2 in icy grains and on the thermal history of the ices themselves. In many sources, CO2 was found in the "pure" crystalline form, as signatured by the splitting in the bending mode absorption profile. To a large extent, pure CO2 is likely to have formed from segregation of CO2 from a CO2:H2O mixture during thermal processing. Previous laboratory studies quantified the temperature dependence of segregation, but no systematic measurement of the concentration dependence of segregation is available. In this study, we measured both the temperature dependence and concentration dependence of CO2 segregation in CO2:H2O mixtures, and found that no pure crystalline CO2 forms if the CO2:H2O ratio is less than 23%. Therefore the segregation of CO2 is not always a good thermal tracer of the ice mantle. We found that the position and width of the broad component of the asymmetric stretching vibrational mode of 13CO2 change linearly with the temperature of CO2:H2O mixtures, but are insensitive to the concentration of CO2. We recommend using this mode, which will be observable towards low mass protostellar envelopes and dense clouds with the James Webb Space Telescope, to trace the thermal history of the ice mantle, especially when segregated CO2 is unavailable. We used the laboratory measured 13CO2 profile to analyze the ISO-SWS observations of ice mantles towards Young Stellar Objects, and the astrophysical implications are discussed.

ApJ accepted
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HSCO+ and DSCO+: a multi-technique approach in the laboratory for the spectroscopy of interstellar ions

V. Lattanzi, S. Spezzano, J. C. Laas, J. Chantzos, L. Bizzocchi, K. L. K. Lee, M. C. McCarthy, P. Caselli

Protonated molecular species have been proven to be abundant in the interstellar gas. This class of molecules is also pivotal for the determination of important physical parameters for the ISM evolution (e.g. gas ionisation fraction) or as tracers of non-polar, hence not directly observable, species. The identification of these molecular species through radioastronomical observations is directly linked to a precise laboratory spectral characterisation. The goal of the present work is to extend the laboratory measurements of the pure rotational spectrum of the ground electronic state of protonated carbonyl sulfide (HSCO+) and its deuterium substituted isotopomer (DSCO+). At the same time, we show how implementing different laboratory techniques allows the determination of different spectroscopical properties of asymmetric-top protonated species. Three different high-resolution experiments were involved to detected for the first time the b−type rotational spectrum of HSCO+, and to extend, well into the sub-millimeter region, the a−type spectrum of the same molecular species and DSCO+. The electronic ground-state of both ions have been investigated in the 273-405 GHz frequency range, allowing the detection of 60 and 50 new rotational transitions for HSCO+ and DSCO+, respectively. The combination of our new measurements with the three rotational transitions previously observed in the microwave region permits the rest frequencies of the astronomically most relevant transitions to be predicted to better than 100 kHz for both HSCO+ and DSCO+ up to 500 GHz, equivalent to better than 60 m/s in terms of equivalent radial velocity. The present work illustrates the importance of using different laboratory techniques to spectroscopically characterise a protonated species at high frequency, and how a similar approach can be adopted when dealing with reactive species.

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Astrochemical Kinetic Grid Models of Groups of Observed Molecular Abundances: Taurus Molecular Cloud 1 (TMC-1)

Dominique M. Maffucci, Trey V. Wenger, Romane Le Gal, Eric Herbst

The emission line spectra of cyanoacetylene and methanol reveal chemical and physical heterogeneity on very small (< 0.1 pc) scales toward the peak in cyanopolyyne emission in the Taurus Molecular Cloud, TMC-1 (CP). We generate grids of homogeneous chemical models using a three-phase rate equation approach to obtain all time-dependent abundances spanning the physical conditions determined from molecular tracers of compact and extended regions of emission along this line of sight. Each time-dependent abundance is characterized by one of four features: a maximum/minimum, a monotonic increase/decrease, oscillatory behavior, or inertness. We similarly classify the time-dependent agreement between modeled and observed abundances by calculating both the root-mean-square logarithm difference and root-mean-square deviation between the modeled and observed abundances at every point in our grid models for three groups of molecules: (i) a composite group of all species present in both the observations and our chemical network G, (ii) the cyanopolyynes C = {HC3N, HC5N, HC7N, HC9N}, and (iii) the oxygen-containing organic species methanol and acetaldehyde S = {CH3OH, CH3CHO}. We discuss how the Bayesian uncertainties in the observed abundances constrain solutions within the grids of chemical models. The calculated best fit times at each grid point for each group are tabulated to reveal the minimum solution space of the grid models and the effects the Bayesian uncertainties have on the grid model solutions. The results of this approach separate the effect different physical conditions and model-free parameters have on reproducing accurately the abundances of different groups of observed molecular species.

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Announcements

Virginia Cosmic Origins Postdoctoral Research Associates

The University of Virginia (UVA) invites applications for Postdoctoral Research Associate positions as part of the interdisciplinary Virginia Initiative on Cosmic Origins (VICO). The incumbents will lead an ambitious, independent research programs related to Cosmic Origins science, expected to align with the wide range of research at UVA, as well as at the National Radio Astronomy Observatory (NRAO) on the grounds of the University. The relevant themes include star formation, planet formation and evolution, planetary science, astrochemistry and astrobiology, from both theoretical and observational perspectives. See www.cosmicorigins.space for more information. The Postdoctoral Research Associates will participate in departmental activities and promote collaboration both within VICO and with its partner institutes, Chalmers University of Technology, Gothenburg, Sweden and the Center for Astrochemical Studies at the Max Planck Institute for Extraterrestrial Physics (MPE), Garching, Germany. There are three types of research programs: 1) Virginia Cosmic Origins Program; (2) Virginia-Chalmers Cosmic Origins Program; (3) Virginia-MPE Cosmic Origins Program (funding pending for this cycle). Applicants should indicate in their cover letter if they have preferences among these research programs. All positions will start at UVA and are initially a one-year appointment, with renewal for an additional two one-year increments for the Virginia position, contingent upon satisfactory performance and available funding, and an additional three one-year increments for the Virginia-Chalmers and Virginia-MPE positions, contingent upon satisfactory performance and available funding (Years 3 and 4 would be at Chalmers or MPE). Applicants are required to have a Ph.D. in astrophysics, astrochemistry, astrobiology or related disciplines by the appointment start date. To apply, visit http://jobs.virginia.edu and search on Posting Number 0624333. Complete a Candidate Profile online and electronically attach as a single PDF document as "Other 1": cover letter; curriculum vitae; list of publications; summary of previous and current research (limited to 3 pages, including references); research proposal (limited to 3 pages text plus up to 2 pages of references/figures). Applicants should also arrange for 3 letters of recommendation to be submitted to vico-postdoc@virginia.edu. Review of applications will begin on December 15, 2018; however, the position will remain open until filled. A competitive salary and benefits package is offered at University of Virginia. The positions also include travel funds and opportunities for dissemination, networking, and international collaboration. Questions regarding the position should be directed to: Eric Herbst (eh2ef@virginia.edu), Jonathan Tan (jct6e@virginia.edu) or Ilse Cleeves (lic3f@virginia.edu). Additional information on the research can be found at http://cosmicorigins.space/ Questions regarding the application process in Jobs@UVA should be directed to: Richard Haverstrom, (rkh6j@Virginia.EDU). The University of Virginia is fundamentally committed to increasing the diversity of its faculty and staff. UVA is an affirmative action and equal opportunity employer. We welcome nominations of and applications from women, members of minority groups, veterans and individuals with disabilities. We also welcome others who would bring additional dimensions of diversity to the university's research and teaching mission. We believe diversity is excellence expressing itself through every person's perspectives and lived experiences.