

AstroChemical Newsletter #44

July 2019

You can access the full abstracts by clicking the paper titles. Submit your abstracts before the 25th of each month for inclusion in the following newsletter.

Abstracts

Standing in the shadow of dark gas : ALMA observations of absorption from dark CO in the molecular DNM of Chamaeleon

H. Liszt, M. Gerin, I Grenier

We had detected J=1-0 HCO⁺ absorption in 12 directions lacking detected CO emission in the outskirts of the Chamaeleon complex and on 1 sightline with integrated CO emission 2.4 K-km/s. 8 sightlines had a much larger mean column density of dark neutral medium (DNM)-gas not represented in H I or CO emission-and were found to have much higher mean molecular column density. The 5 other sightlines had little or no DNM and were found to have much smaller but still detectable N(HCO⁺). To determine N(CO) along previously-observed Chamaeleon sightlines and to determine why CO emission was not detected in directions where molecular gas is present. We took 12CO J=1-0 absorption profiles on 5 sightlines having higher DNM and HCO⁺ column densities and 1 sightline with smaller N(DNM) and N(HCO⁺). We converted the integrated HCO⁺ optical depths to N(H₂) in the weak-excitation limit using N(HCO⁺)/N(H₂)=3×10⁻⁹ and converted the integrated CO optical depths WCO to CO column density N(CO) =1.861×10¹⁵cm⁻² WCO^{1.131} as found along comparable lines of sight previously studied in J=1-0 and J=2-1 CO absorption & emission. CO absorption was detected along the 5 sightlines in the higher-DNM group, with CO column densities 4×10¹³ cm⁻² < N(CO) <10¹⁵ cm⁻² that are generally below the detectability limit of CO emission surveys. In the outskirts of the Chamaeleon complex, the presence of molecular DNM resulted primarily from small CO column densities at the onset of CO formation around the H I/H₂ transition in diffuse molecular gas. CO relative abundances N(CO)/N(H₂) <2×10⁻⁶ in the outskirts of Chamaeleon are comparable to those seen in UV absorption toward early-type stars, including in Chamaeleon.

Astronomy and Astrophysics, In press

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Molecular oxygen generation from the reaction of water cations with oxygen atoms

R. C. Fortenberry, Tarek Trabelsi, B. R. Westbrook, W. A. Del Rio, and J. S. Francisco

The oxywater cation (H₂OO⁺), previously shown to form barrierlessly in the gas phase from water cations and atomic oxygen, is proposed here potentially to possess a 2A'' ← 4A'' excitation leading to the H₂...O₂⁺ complex. This complex could then easily decompose into molecular hydrogen and the molecular oxygen cation. The present quantum chemical study shows that the necessary electronic transition takes place in the range of 1.92 eV (645 nm), in the orange-red range of the visible and solar spectrum, and dissociation of the complex only requires 5.8 kcal/mol (0.25 eV). Such a process for the abiotic, gas phase formation of O₂ would only need to be photocatalyzed by visible wavelength photons. Hence, such a process could produce O₂ at the mesosphere/stratosphere boundary as climate change is driving more water into the upper atmosphere, in the comet 67P/Churyumov-Gerasimenko where surprisingly high levels of O₂ have been observed, or at gas-surface (ice) interfaces.

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Rotational spectroscopy of isotopic species of methyl mercaptan at millimeter and submillimeter wavelengths: CH₃(34)SH

Olena Zakharenko, Frank Lewen, Vadim V. Ilyushin, Holger S. P. Müller, Stephan Schlemmer, Eugene A. Alekseev, Igor Krapivin, Li-Hong Xu, Ronald M. Lees, Robin Garrod, Arnaud Belloche, Karl M. Menten

Methyl mercaptan (CH₃SH) is an important sulfur-bearing species in the interstellar medium, terrestrial environment, and potentially in planetary atmospheres. The aim of the present study is to provide accurate spectroscopic parameters for the most abundant minor isotopolog CH₃(34)SH to support radio astronomical observations at millimeter and submillimeter wavelengths. The rotational spectrum of CH₃(34)SH, which is complicated by the large-amplitude internal rotation of the CH₃ group versus the (34)SH frame, was investigated in the 49–510 GHz and 1.1–1.5 THz frequency ranges in natural isotopic abundance. The analysis of the spectrum was performed up to the second excited torsional state, and the obtained data were modeled with the RAM36 program. A fit within experimental accuracy was obtained with a RAM Hamiltonian model that uses 72 parameters. Predictions based on this fit are used to search for CH₃(34)SH with the Atacama Large Millimeter/submillimeter Array (ALMA) toward the hot molecular core Sgr B2(N₂), but blends with emission lines of other species prevent its firm identification in this source.

Impact of nonconvergence and various approximations of the partition function on the molecular column densities in the interstellar medium

M. Carvajal, C. Favre, I. Kleiner, C. Ceccarelli, E. Bergin, D. Fedele

We emphasize that the completeness of the partition function, that is, the use of a converged partition function at the typical temperature range of the survey, is very important to decrease the uncertainty on this quantity and thus to derive reliable interstellar molecular densities. In that context, we show how the use of different approximations for the rovibrational partition function together with some interpolation and/or extrapolation procedures may affect the estimate of the interstellar molecular column density. For that purpose, we apply the partition function calculations to astronomical observations performed with the IRAM-30m telescope towards the NGC7538-IRS1 source of two N-bearing molecules: isocyanic acid (HNCO, a quasilinear molecule) and methyl cyanide (CH₃CN, a symmetric top molecule). The case of methyl formate (HCOOCH₃), which is an asymmetric top O-bearing molecule containing an internal rotor is also discussed. Our analysis shows that the use of different partition function approximations leads to relative differences in the resulting column densities in the range 9 to 43%. Thus, we expect this work to be relevant for surveys of sources with temperatures higher than 300K and to observations in the infrared.

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Interactions of Atomic and Molecular Hydrogen with a Diamond-like Carbon Surface: H₂ Formation and Desorption

M. Tsuge, T. Hama, Y. Kimura, A. Kouchi, N. Watanabe

The interactions of atomic and molecular hydrogen with bare interstellar dust grain surfaces are important for understanding H₂ formation at relatively high temperatures (>20 K). We investigate the diffusion of physisorbed H atoms and the desorption energetics of H₂ molecules on an amorphous diamond-like carbon (DLC) surface. From temperature-programmed desorption experiments with a resonance-enhanced multiphoton ionization (REMPI) method for H₂ detection, the H₂ coverage-dependent activation energies for H₂ desorption are determined. The activation energies decrease with increasing H₂ coverage and are centered at 30 meV with a narrow distribution. Using a combination of photostimulated desorption and REMPI methods, the time variations of the surface number density of H₂ following atomic and molecular hydrogen depositions are studied. From these measurements, we show that H₂ formation on a DLC surface is quite efficient, even at 20 K. A significant kinetic isotope effect for H₂ and D₂ recombination reactions suggests that H-atom diffusion on a DLC surface is mediated by quantum mechanical tunneling. In astrophysically relevant conditions, H₂ recombination due to physisorbed H-atoms is unlikely to occur at 20 K, suggesting that chemisorbed H atoms might play a role in H₂ formation at relatively high temperatures.

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Re-exploring Molecular Complexity with ALMA (ReMoCA): Interstellar detection of urea

A. Belloche, R. T. Garrod, H. S. P. Müller, K. M. Menten, I. Medvedev, J. Thomas, Z. Kisiel

Urea, NH₂C(O)NH₂, is a molecule of great importance in organic chemistry and biology. Two searches for urea in the interstellar medium were reported in the past, but neither were conclusive. We want to take advantage of the increased sensitivity and angular resolution provided by ALMA to search for urea toward the hot cores embedded in the high-mass star forming region Sgr B2(N). We use the new spectral line survey ReMoCA performed toward Sgr B2(N) with ALMA in its observing cycle 4. The spectra are analyzed under the LTE approximation. We construct a full synthetic spectrum that includes all the molecules identified so far. We use new spectroscopic predictions for urea in its vibrational ground state and first vibrationally excited state to search for this complex organic molecule in the ReMoCA data set. We employ the gas-grain chemical kinetics model MAGICKAL to interpret the astronomical observations. We report the secure detection of urea toward the hot core Sgr B2(N1) at a position called N1S slightly offset from the continuum peak, which avoids obscuration by the dust. We derive a column density of 2.7×10^{16} cm⁻² for urea, two orders of magnitude lower than formamide, and one order of magnitude below methyl isocyanate, acetamide, and N-methylformamide. The latter molecule is reliably identified toward N1S with 60 clearly detected lines, confirming an earlier claim of its tentative interstellar detection. We report the first interstellar detections of NH₂CH₁₈O and 15NH₂CHO. We also report the nondetection of urea toward the secondary hot core Sgr B2(N2) with an abundance relative to the other four species at least one order of magnitude lower than toward the main hot core. Our chemical model roughly reproduces the relative abundances of formamide, methyl isocyanate, acetamide, and N-methylformamide, but it overproduces urea by at least one order of magnitude.

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Quantum Roaming in the Complex-Forming Mechanism of the Reactions of OH with Formaldehyde and Methanol at Low Temperature and Zero Pressure: A Ring Polymer Molecular Dynamics Approach

Pablo del Mazo-Sevillano, Alfredo Aguado, Elena Jiménez, Yury V. Suleimanov, and Octavio Roncero

The quantum dynamics of the title reactions are studied using the ring polymer molecular dynamics (RPMD) method from 20 to 1200 K using recently proposed full dimensional potential energy surfaces which include long range dipole–dipole interactions. A V-shaped dependence of the reaction rate constants is found with a minimum at 200–300 K, in rather good agreement with the current experimental data. For temperatures above 300 K the reaction proceeds following a direct H-abstraction mechanism. However, below 100 K the reaction proceeds via organic molecule...OH collision complexes, with very long lifetimes, longer than 10⁻⁷ s, associated with quantum roaming arising from the inclusion of quantum effects by the use of RPMD. The long lifetimes of these complexes are comparable to the time scale of the tunnelling to form reaction products. These complexes are formed at zero pressure because of quantum effects and not only at high pressure as suggested by transition state theory (TST) calculations for OH + methanol and other OH reactions. The zero-pressure rate constants reproduce quite well measured ones below 200 K, and this agreement opens the question of how important the pressure effects on the reaction rate constants are, as implied in TST-like formalism. The zero pressure mechanism is applicable only to very low gas density environments, such as the interstellar medium, which are not repeatable by experiments.

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Molecular complexity on disk-scales uncovered by ALMA: The chemical composition of the high-mass protostar AFGL 4176

Eva G. Bøgelund, Andrew G. Barr, Vianney Taquet, Niels F. W. Ligterink, Magnus V. Persson, Michiel R. Hogerheijde, Ewine F. van Dishoeck

The chemical composition of high-mass protostars reflects the physical evolution associated with different stages of star formation. In this study, the molecular inventory of the forming high-mass star AFGL 4176 is studied in detail at high angular resolution (~0.35 arcsec) using ALMA. This high resolution makes it possible to separate the emission associated with the inner hot envelope and disk around the forming star from that of its cool outer envelope. In addition, the high sensitivity of ALMA makes it possible to identify weak and optically thin lines and allows for many isotopologues to be detected, providing a more complete and accurate inventory of the source. A total of 23 different molecular species and their isotopologues are detected in the spectrum towards AFGL 4176. The most abundant species is methanol (CH₃OH), remaining species are present at levels between 0.003 % and 15 % with respect to CH₃OH. Hints that N-bearing species peak slightly closer to the location of the peak continuum emission than the O-bearing species are seen. AFGL 4176 comprises a rich chemical inventory including many complex species present on disk-scales. On average, the derived column density ratios with respect to methanol of O-bearing species are higher than those derived for N-bearing species by a factor of three. This may indicate that AFGL 4176 is a relatively young source since nitrogen chemistry generally takes longer to evolve in the gas-phase. Taking methanol as a reference, the composition of AFGL 4176 more closely resembles that of the low-mass protostar IRAS 16293-2422B than that of high-mass star-forming regions located near the Galactic centre. This similarity hints that the chemical composition of complex species is already set in the cold cloud stage and implies that AFGL 4176 is a young source whose chemical composition has not yet been strongly processed by the central protostar.

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The complex chemistry of hot cores in Sagittarius B2(N): Influence of cosmic-ray ionization and thermal history

M. Bonfand, A. Belloche, R. T. Garrod, K. M. Menten, E. Willis, G. Stéphan, H. S. P. Müller

As the number of complex organic molecules (COMs) detected in the interstellar medium increases, it becomes important to place meaningful constraints on the formation pathways of these species. The molecular cloud SgrB2(N) is host to several hot molecular cores in the early stage of star formation, where a great variety of COMs are detected in the gas phase. Because of its exposure to the extreme conditions of the Galactic center region, SgrB2(N) is one of the best targets to study the impact of environmental conditions on the production of COMs. Our main goal is to characterize the physico-chemical evolution of SgrB2(N)'s sources in order to explain their chemical differences and constrain their environmental conditions. The chemical composition of SgrB2(N)'s hot cores, N2, N3, N4, and N5 is derived by modeling their 3mm emission spectra extracted from the EMOCA imaging spectral line survey performed with ALMA. We derive the density distribution in the envelope of the sources based on the masses computed from the ALMA dust continuum emission maps. We use the radiative transfer code RADMC-3D to compute temperature profiles based on the COM rotational temperatures derived from population diagrams. We use published results of 3D RMHD simulations of high-mass star formation to estimate the time evolution of the sources properties. We employ the chemical code MAGICKAL to compute time-dependent chemical

abundances in the sources and investigate how physical properties and environmental conditions influence the production of COMs. We find that chemical models with a cosmic-ray ionization rate of $7\text{e-}16\text{ s}^{-1}$ best reproduce the abundances with respect to methanol of ten COMs observed toward SgrB2(N2-N5). We also show that COMs still form efficiently on dust grains with minimum dust temperatures in the prestellar phase as high as 15K, but that minimum temperatures higher than 25K are excluded.

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Modeling C-Shock Chemistry in Isolated Molecular Outflows

A. M. Burkhardt, C. N. Shingledecker, R. Le Gal, B. A. McGuire, A. J. Remijan, and E. Herbst

Shocks are a crucial probe for understanding the ongoing chemistry within ices on interstellar dust grains where many complex organic molecules (COMs) are believed to be formed. However, previous work has been limited to the initial liberation into the gas phase through non-thermal desorption processes such as sputtering. Here, we present results from the adapted three-phase gas-grain chemical network code NAUTILUS, with the inclusion of additional high-temperature reactions, non-thermal desorption, collisional dust heating, and shock-physics parameters. This enhanced model is capable of reproducing many of the molecular distributions and abundance ratios seen in our prior observations of the prototypical shocked-outflow L1157. In addition, we find that, among others, NH_2CHO , HCOOCH_3 , and CH_3CHO have significant post-shock chemistry formation routes that differ from those of many other COMs observed in shocks. Finally, a number of selected species and phenomena are studied here with respect to their usefulness as shock tracers in various astrophysical sources.

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Dissociative recombination of CH_2NH_2^+ : a crucial link with interstellar methanimine and Titan ammonia.

C. H. Yuen, M. A. Ayouz, N. Balucani, C. Ceccarelli, I. F. Schneider and V. Kokoouline.

Cross-sections for dissociative recombination (DR) and vibrational excitation of the CH_2NH_2^+ ion in collisions with electrons are determined theoretically. The corresponding thermally averaged rate coefficients are computed and fitted to analytical formulas. The obtained DR rate coefficient is significantly smaller than the values recently employed in the photochemical models of the upper atmosphere of Titan, which has an important impact on the models that aim to reproduce the Titan ammonia abundance. On the other hand, the present results support the astrophysical models reproducing the abundance of the methanimine (CH_2NH) detected in massive star formation regions. In these models, the CH_2NH_2^+ DR is a major route of formation of this molecule with a high prebiotic potential.

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Full-text URL: <https://academic.oup.com/mnras/article-abstract/484/1/659/5270737?redirectedFrom=fulltext>

The role of atom tunneling in gas-phase reactions in planet-forming disks

J. Meisner, I. Kamp, W.-F. Thi, J. Kästner

Context: Gas-phase chemical reactions of simple molecules have been recently revised to include atom tunneling at very low temperatures. This paper investigates the impact of the increased reaction rate constant due to tunneling effects on planet-forming disks. Aims: Our aim is to quantify the astrophysical implications of atom tunneling for simple molecules that are frequently used to infer disk structure information or to define the initial conditions for planet (atmosphere) formation. Methods: We quantify the tunneling effect on reaction rate constants by using $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$ as a scholarly example in comparison to previous UMIST2012 rate constants. In a chemical network with 1299 reactions, we identify all chemical reactions that could show tunneling effects. We devise a simple formulation of reaction rate constants that overestimates tunneling and screen a standard T Tauri disk model for changes in species abundances. For those reactions found to be relevant, we find values of the most recent literature for the rate constants including tunneling and compare the resulting disk chemistry to the standard disk model, a T Tauri and a Herbig disk. Results: The rate constants in the UMIST2012 database in many cases already capture tunneling effects implicitly, as seen in the curvature of the Arrhenius plots of some reactions at low temperature. A rigorous screening procedure identified three neutral-neutral reactions where atom tunneling could change simple molecule abundances. However, by adopting recent values of the rate constants of these reactions and due to the layered structure of planet-forming disks, the effects are limited to a small region between the ion-molecule dominated regime and the ice reservoirs where cold ($< 250\text{ K}$) neutral-neutral chemistry dominates. Abundances of water close to the midplane snowline can increase by a factor of two at most compared to previous results with UMIST2012 rates. Observables from the disk surface, such as high excitation ($> 500\text{ K}$) water line fluxes, decrease by 60% at most when tunneling effects are explicitly excluded. On the other hand, disk midplane quantities relevant for planet formation such as the C-to-O ratio and also the ice-to-rock ratio are clearly affected by these gas-phase tunneling effects.

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Announcements

SAVE THE DATE Everything You Always Wanted to Know About Interstellar Shocks* (*But Were Afraid to Ask)

We will organize a session in the Physics School of Les Houches in France on the topic of interstellar shocks in March, 22-27, 2020.

The session will give a comprehensive view of the role and impacts of shocks, that are ubiquitous in galaxies and their close environments. The session will include lectures on physical and chemical processes in interstellar shocks, observations, models, experiments, as well as hands-on sessions. The speakers are confirmed but the program may still be subject to minor changes.

GENERAL INTRODUCTION: SHOCK PHYSICS

Pierre Lesaffre, LPENS, ENS, LERMA, Paris Observatory, CNRS, France

Glenn E. Ciolek, New York Center for Astrobiology & Rensselaer Polytechnic Institute, New York USA

John Raymond, Smithsonian Astrophysical Observatory & Harvard University, Cambridge, USA

SHOCK MODELS

Andrew Lehmann, LPENS, ENS, Paris, France

Brent Groves, Australian National University, Canberra, Australia

SHOCK CHEMISTRY Michael Kaufman, San Jose State University, San Jose, USA

Vincent Guillet, LUPM, Montpellier, IAS, Paris Sud University, France

SHOCK OBSERVATIONS

David Neufeld, Johns Hopkins University, Baltimore, USA

Sylvie Cabrit, LERMA, Paris Observatory, Paris, France

Pierre Guillard, IAP, Sorbonne University, Paris, France

SHOCK EXPERIMENTS

Andrea Ciardi, LERMA, Sorbonne University, Paris Observatory, Paris, France

COLLISIONLESS AND PARTICLE ACCELERATION

Martin Lemoine, IAP, CNRS, Paris, France

Alexandre Marcowith, LUPM, CNRS, Montpellier, France

HANDS-ON SESSION SHOCK MODELS

Brent Groves, Australian National University, Canberra, Australia

Benjamin Godard, LERMA, Paris Observatory, LPENS, ENS Paris, France

Pierre Guillard, IAP & Sorbonne University, Paris, France

Antoine Gusdorf, LPENS, ENS, LERMA, Paris Observatory, CNRS, France

Pierre Lesaffre, LPENS, ENS, LERMA, Paris Observatory, CNRS, France

BROADENING THE SUBJECT

Edith Falgarone, LPENS, ENS, LERMA, Paris Observatory, CNRS, France

Julien Devriendt, Oxford University, Oxford, UK

Martin Houde, University of Western Ontario, Canada

Postdoctoral position in electron/molecule collisions at Le Havre University, France

An 18 months postdoctoral position on electron/molecule collisions in carbonated cold plasmas at Normandie Université/Le Havre, LOMC-UMR-6294, Reactive Processes group, is open.

Expected date of employment: September 1st 2019 Closing date for the applications: August 1st 2019 Salary ~ 2500 €/month according to experience The position is financed by the FEDER and the French ANR.

The postdoctoral work aims to study reactive collisions playing a major role in the kinetics of cold ionized gases, mainly those involved in the removal/conversion of the carbon dioxide, in the hydrocarbon-based nanoparticle-containing/dusty plasmas and in astrochemistry.

The processes to be explored are electron/molecule (positively ionized or neutral) reactive collisions - dissociative recombination, dissociative attachment, ro-vibrational and dissociative excitation. All these processes involve super-excited molecular states, inducing often spectacular resonances in the shape of the cross sections, which have to be included in the dynamics treatment in order to allow the production of accurate rate coefficients.

The project consists in two complementary and interconnected parts:

(1) the production of cross sections and rate coefficients for carbon- containing targets - CO, CO₂, C_xH_y, etc. and their cations - and other species populating the carbonated plasmas (containing H, N, O, Ar, etc.) for the modelling of the kinetics and of the energetic transfers,

(2) the development of theoretical tools (methods, computing programs) in order to increase their performance in accuracy, account of major reaction mechanisms and capability to address complex species. The methods used will be mainly time-independent - Multichannel Quantum Defect Theory (MQDT), Configuration Interaction method (CI), etc. - and will rely on

the use of modern tools in the study of the molecular structure and collision theory - MOLPRO and QUANTEMOL packages, R-matrix method, etc. Openings to close-coupling and time-dependent methods are also welcome.

The required qualification includes a PhD in Physics or Chemistry, solid background in Quantum Mechanics, in particular in Collision Theory, facility in using numerical methods, FORTRAN programming skills, ability for interactive working within a team and with other teams, good knowledge of English (spoken, written). Experience in Quantum Chemistry, analytic calculation skills, capacity of understanding experiments and their link with theoretical models and/or elementary knowledge on Plasma Physics are very welcome.

The project relies on strong collaborations with other Normand laboratories - CORIA and LSPC in Rouen, LCS in Caen - with other laboratories in France - GREMI in Orléans, LSPM, ITODYS, LGPM, Aimé-Cotton, LPGP in Paris, LUPM in Montpellier, IPAG in Grenoble - and abroad - University of Central Florida - Orlando, University College London, Forschungszentrum Jülich, Nanotec in Bari, ATOMKI in Debrecen, Calcutta University, Politehnica and West Universities in Timisoara, etc. For the first six months of the project, the candidate will often visit the CORIA laboratory in the framework of the collaboration.

The interested candidates are strongly encouraged to apply by sending a cover letter, a CV, a full publications list, and contact details of two references to Ioan Schneider, ioan.schneider@univ-lehavre.fr, or Arnaud Bultel, arnaud.bultel@coria.fr.

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