

AstroChemical Newsletter #15

January 2017

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Abstracts

Quantum tunneling during interstellar surface-catalyzed formation of water: the reaction $\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{OH}$

Thanja Lamberts, Pradipta Kumar Samanta, Andreas Köhn, Johannes Kästner

The final step of the water formation network on interstellar grain surfaces starting from the $\text{H} + \text{O}_2$ route is the reaction between H and H_2O_2 . This reaction is known to have a high activation energy and therefore at low temperatures it can only proceed via tunneling. To date, however, no rate constants are available at temperatures below 200 K. In this work, we use instanton theory to compute rate constants for the title reaction with and without isotopic substitutions down to temperatures of 50 K. The calculations are based on density functional theory, with additional benchmarks for the activation energy using unrestricted single-reference and multireference coupled-cluster single-point energies. Gas-phase bimolecular rate constants are calculated and compared with available experimental data not only for $\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{OH}$, but also for $\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2 + \text{HO}_2$. We find a branching ratio where the title reaction is favored by at least two orders of magnitude at 114 K. In the interstellar medium this reaction predominantly occurs on water surfaces, which increases the probability that the two reactants meet. To mimic this one, two, or three spectator H_2O molecules are added to the system. Eley-Rideal bimolecular and Langmuir-Hinshelwood unimolecular rate constants are presented here. The kinetic isotope effects for the various cases are compared to experimental data as well as to expressions commonly used in astrochemical models. Both the rectangular barrier and the Eckart approximations lead to errors of about an order of magnitude. Finally, fits of the rate constants are provided as input for astrochemical models.

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Suggestion for search of cyclopropenone ($\text{c-C}_3\text{H}_2\text{O}$) in a cosmic object

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Following Minimum Energy Principle, out of the three isomers of chemical formula $\text{C}_3\text{H}_2\text{O}$, the cyclopropenone ($\text{c-C}_3\text{H}_2\text{O}$) is the most stable and therefore may be the most abundant and easily detectable in a cosmic object. The cyclopropenone is detected in Sgr B2(N). Owing to half-spin of each of two hydrogen atoms, the $\text{c-C}_3\text{H}_2\text{O}$ has two distinct ortho and para species. Using the rotational and centrifugal distortion constants along with the electric dipole moment, we have calculated energies of 100 rotational levels of each of the ortho and para species of $\text{c-C}_3\text{H}_2\text{O}$ and the Einstein A-

coefficients for radiative transitions between the levels. The values of Einstein A-coefficients along with the scaled values for collisional rate coefficients are used for solving a set of statistical equilibrium equations coupled with the equations of radiative transfer. Brightness temperatures of seven rotational transitions of each of the ortho and para species of c-C₃H₂O are investigated. Out of fourteen transitions, seven are found to show anomalous absorption and rest seven are found to show emission feature. We find that the transitions 110–111 (1.544 GHz) may play important role in identification of cyclopropenone in a cosmic object.

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Chemistry of TMC-1 with multiply deuterated species and spin chemistry of H₂, H₂⁺, H₃⁺ and their isotopologues

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Deuterated species are unique and powerful tools in astronomy since they can probe the physical conditions, chemistry, and ionization level of various astrophysical media. Recent observations of several deuterated species along with some of their spin isomeric forms have rekindled the interest for more accurate studies on deuterium fractionation. This paper presents the first publicly available chemical network of multiply deuterated species along with spin chemistry implemented on the latest state-of-the-art gas-grain chemical code 'NAUTILUS'. D/H ratios for all deuterated species observed at different positions of TMC-1 are compared with the results of our model, which considers multiply deuterated species along with the spin chemistry of light hydrogen bearing species H₂, H₂⁺, H₃⁺ and their isotopologues. We also show the differences in the modeled abundances of non-deuterated species after the inclusion of deuteration and spin chemistry in the model. Finally, we present a list of potentially observable deuterated species in TMC-1 awaiting detection.

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Systematic Theoretical Study on the Interstellar Carbon Chain Molecules

Etim, Emmanuel E.; Gorai, Prasanta; Das, Ankan; Chakrabarti, Sandip K.; Arunan, Elangannan

In an effort to further our interest in understanding the basic chemistry of interstellar molecules, here we carry out an extensive investigation of the stabilities of interstellar carbon chains; C_n, H₂C_n, HC_nN and C_nX (X = N, O, Si, S, H, P, H–, N–). These sets of molecules account for about 20% of all the known interstellar and circumstellar molecules. Their high abundances, therefore, demand serious attention. High-level ab initio quantum chemical calculations are employed to accurately estimate the enthalpy of formation, chemical reactivity indices, global hardness and softness, and other chemical parameters of these molecules. Chemical modeling of the abundances of these molecular species has also been performed. Of the 89 molecules considered from these groups, 47 have been astronomically observed, and these observed molecules are found to be more stable with respect to other members of the group. Of the 47 observed molecules, 60% are odd-numbered carbon chains. Interstellar

chemistry is not actually driven by thermodynamics, but it is primarily dependent on various kinetic parameters. However, we found that the detectability of the odd-numbered carbon chains could be correlated due to the fact that they are more stable than the corresponding even-numbered carbon chains. Based on this aspect, the next possible carbon chain molecule for astronomical observation in each group is proposed. The effect of kinetics in the formation of some of these carbon chain molecules is also discussed.

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Accurate rotational constants for linear interstellar carbon chains: achieving experimental accuracy

Emmanuel E. Etim, Elangannan Arunan

Linear carbon chain molecular species remain the dominant theme in interstellar chemistry. Their continuous astronomical observation depends on the availability of accurate spectroscopic parameters. Accurate rotational constants are reported for hundreds of molecular species of astrophysical, spectroscopy and chemical interests from the different linear carbon chains; C_nH , C_nH- , C_nN , C_nN- , C_nO , C_nS , HC_nS , C_nSi , $CH_3(CC)_nH$, HC_nN , $DC_{2n+1}N$, $HC_{2n}NC$, and $CH_3(C\equiv C)_nCN$ using three to four moments of inertia calculated from the experimental rotational constants coupled with those obtained from the optimized geometries at the Hartree Fock level. The calculated rotational constants are obtained from the corrected moments of inertia at the Hartree Fock geometries. The calculated rotational constants show accuracy of few kHz below irrespective of the chain length and terminating groups. The obtained accuracy of few kHz places these rotational constants as excellent tools for both astronomical and laboratory detection of these molecular species of astrophysical interest. From the numerous unidentified lines from different astronomical surveys, transitions corresponding to known and new linear carbon chains could be found using these rotational constants. The astrophysical, spectroscopic and chemical implications of these results are discussed.

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Search for Interstellar monohydric Thiols

Prasanta Gorai, Ankan Das, Amaresh Das, Bhalamurugan Sivaraman, Emmanuel E. Etim, Sandip K. Chakrabarti

It has been pointed out by various astronomers that very interesting relationship exists between interstellar alcohols and the corresponding thiols (sulfur analogue of alcohols) as far as the spectroscopic properties and chemical abundances are concerned. Monohydric alcohols such as methanol and ethanol are widely observed and 1-propanol is recently claimed to have been seen in Orion KL. Among the monohydric thiols, methanethiol (chemical analogue of methanol), has been firmly detected in Orion KL and Sgr B2(N2) and ethanethiol (chemical analogue of ethanol) has been claimed to be observed in Sgr B2(N2) though the confirmation of this detection is yet to come. It is very likely that higher order thiols could be observed in these regions. In this paper, we study the formation of monohydric alcohols and their thiol analogues. Based on our quantum chemical calculation and chemical modeling, we find that Tg conformer of 1-

propanethiol is a good candidate of astronomical interest. We present various spectroscopically relevant parameters of this molecule to assist its future detection in the Interstellar medium (ISM).

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Reactions of Atomic Carbon with Butene Isomers: Implications for Molecular Growth in Carbon-Rich Environments

J. Bourgalais, M. Spencer, D. L. Osborn, F. Goulay and S. D. Le Picard

Product detection studies of C(3P) atom reactions with butene (C₄H₈) isomers (but-1-ene, cis-but-2-ene, trans-but-2-ene) are carried out in a flow tube reactor at 353 K and 4 Torr under multiple collision conditions. Ground state carbon atoms are generated by 248 nm laser photolysis of tetrabromomethane, CBr₄, in a buffer of helium. Thermalized reaction products are detected using synchrotron tunable VUV photoionization and time-of-flight mass spectrometry. The temporal profiles of the detected ions are used to discriminate products from side or secondary reactions. For the C(3P) + trans-but-2-ene and C(3P) + cis-but-2-ene reactions, various isomers of C₄H₅ and C₅H₇ are identified as reaction products formed via CH₃ and H elimination. Assuming equal ionization cross sections for all C₄H₅ and C₅H₇ isomers, C₄H₅:C₅H₇ branching ratios of 0.63:1 and 0.60:1 are derived for the C(3P) + trans-but-2-ene and the C(3P) + cis-but-2-ene reactions, respectively. For the C(3P) + but-1-ene reaction, two reaction channels are observed: the H-elimination channel, leading to the formation of the ethylpropargyl isomer, and the C₃H₃ + C₂H₅ channel. Assuming equal ionization cross sections for ethylpropargyl and C₃H₃ radicals, a branching ratio of 1:0.95 for the C₃H₃ + C₂H₅ and H + ethylpropargyl channels is derived. The experimental results are compared to previous H atom branching ratios and used to propose the most likely mechanisms for the reaction of ground state carbon atoms with butene isomers.

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Announcements

International Journal of Quantum Chemistry "Computational Astrochemistry" Special Issue

A complete special issue of IJQC (Volume 117, Issue 2) has been dedicated to the use of quantum chemical computation with application to astrochemistry. Reviews, perspectives, software updates, and full papers are available describing the state-of-the-art in this field. The special issue is available at <http://onlinelibrary.wiley.com/doi/10.1002/qua.v117.2/issuetoc?platform=hootsuite>.

2017 Astrobiology Graduate Conference - Applications Open

Applications for the 2017 Astrobiology Graduate Conference (AbGradCon) are now open. Key Details: Host: National Radio Astronomy Observatory When: June 5-9, 2017 Where: Charlottesville, VA Website: www.abgradcon.org Application Deadline: February 6th AbGradCon provides a unique setting for astrobologically-inclined graduate students and early career researchers to come together to share their research, collaborate, and network, without the presence of senior researchers and PIs. AbGradCon 2017 marks the thirteenth year of this conference. This year, the

conference will be held at the National Radio Astronomy Observatory in Charlottesville, VA from June 5 – June 9. AbGradCon is truly a unique and rewarding experience. It is a rare opportunity to learn how your own work fits into the hugely interdisciplinary big picture that is Astrobiology. The presentations and discussion at AbGradCon have the same level of scientific rigor found at more traditional meetings, but with the added benefit of the more fluid interaction one expects from one's peers. Conference attendees will share their research over a period of two days. Attendees have the option of presenting a 15-minute talk or presenting a poster. Topics to be covered include astronomy, astrochemistry, exoplanet research, planetary science, geology, atmospheric chemistry, geobiology, computer science, origins of life research, and aerospace engineering, and everything in between. The conference culminates on the third day with attendees participating in an educational field trip. Applications from exceptional senior undergraduates who will be attending a graduate program in Fall 2017 are welcome to apply. In addition, a virtual Undergraduate Poster Competition will be held for other all other interested undergraduates, with at least one winner chosen to attend the conference as a fully-funded participant. Lastly, an optional Proposal Writing Retreat (PWR) will be held from June 2 – June 5 at the Green Bank Observatory, 2.5 hours away from Charlottesville. Participants in the PWR will work in teams to conceive and write a NASA research proposal which the entire workshop will peer-review. Past years' participants have lauded the PWR as one of the best (and perhaps most challenging) professional development experiences they have participated in. In addition, participants can expect to enjoy hiking on the numerous on-site trails in their free time while writing research proposals in teams. The winning team will present in the conference later in the week. We strive to keep attendance costs as low as possible to support as many participants as possible. In addition, we have secured significant funds to support travel and participation in the conference for many applicants, with funding levels based on demonstrated need. Please see our website, www.abgradcon.org, for additional details and to apply. Applications will be due February 6th.

Symposium: Molecules in space: Linking the interstellar medium to (exo)planets

Fall National Meeting of the American Chemical Society 20-24th August, 2017, Washington DC, USA Organizers: Prof. Alexander Tielens (Leiden University) and Dr. Partha P. Bera (NASA Ames Research Center) Molecules from simple to as complex as fullerenes have been identified in various astrophysical environments such as the interstellar media, dark clouds, hot cores, outflows of carbon stars, protoplanetary disks, and in the atmospheres of (exo)planets. We are only beginning to understand by sustained laboratory experimental, spectroscopic, computational, modeling, and observational efforts how these molecules are synthesized in the gas phase and on grain surfaces, evolve in those exotic conditions, and become incorporated in to planetary bodies. With the advent of new and upcoming capabilities such as the Atacama Large Millimeter Array (ALMA) and the James Webb Space Telescope (JWST), the scope of molecular exploration will increase many folds over the next decade. We are organizing a five-day symposium “Molecules in Space: Linking the Interstellar Medium to (exo)planets” at the American Chemical Society’s Fall National Meeting to be held in Washington DC from 20-24th August, 2017 to address the exploration of the molecular universe. The symposium will cover a wide breadth of subjects that will include organic inventory of the gas phase, the chemistry of the dark clouds, interplay of gas and dust, hot-cores and corinos, organic inventory of proto-planetary disks, high-resolution spectroscopy, the diffuse interstellar bands, the chemistry of atmospheres of stars and planets, and present and future opportunities such as ALMA, SOFIA, and JWST. Each session will begin with an overview talk by an eminent scholar in

the field, followed by talks on astronomical observation, laboratory experiment, quantum chemistry calculations, and modeling. The sessions will be introduced by overview talks followed by invited talks on specific aspects of the session and contributed papers. In addition, there are poster sessions. Abstracts can be submitted for consideration for contributed talks and posters through the ACS Fall 2017 National Meeting webpage between the following dates. Abstract submission window opens on 23rd January, 2017 (tentatively). Abstract submission window closes on 20th March, 2017 (tentatively). Session Titles Session I: Organic inventory of the gas phase: from small molecules to PAHs Session II: Chemistry of dark clouds: the interplay of gas and dust Session III: Hot cores and corinos: Observations, theory and experiments Session IV: Organic inventory of protoplanetary disks Session V: Spectroscopy: Meeting the needs of astronomers with experiments and theory Session VI: The DIBs: solving a century old problem Session VII: Chemistry of atmospheres of stars and planets