Laboratory astrophysics : tracking the evolution of cosmic matter towards molecular complexity

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Ice inventory in the highly extincted star forming region Chameleon I: First results from the Ice Age JWST program

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Icy grain mantles are the main reservoir for volatile elements in star-forming regions, as well as the formation site of molecules of increasing complexity up to prebiotic complex organic molecules (COMs). The IceAge Early Release Science program on the James Webb Space Telescope proposes to trace the evolution of pristine and complex ice chemistry in Chameleon I – a representative low-mass star-forming region – through observations of: the dense cloud, the pre-stellar core, a Class 0 protostar, a Class I protostar, and a protoplanetary disk. Here we present the first results of the IceAge program.

Observations for the IceAge Early Release Science program on the James Webb Space Telescope [1] were made in summer 2022 using the NIRCam, NIRSpec and MIRI instruments. These observations have allowed us to obtain high spectral resolution (R~1500-3000), high sensitivity (S/N>100) spectra from 2.5 to 13 µm of two highly extincted background stars (Av < 100) towards the densest region of the cloud.

Here, we present the very first results of this program: a complete ice inventory towards these lines of sight, including derived column densities for expected ice species as well as the first detection of several species along lines of sight in a quiescent cold core [2].

References

[1] M. McClure, J. Bailey, T. Beck, A. C. A. Boogert, W. Brown, P. Caselli., J. Chiar, E. Egami, H. J. Fraser, R. Garrod, K. D. Gordon, S. Ioppolo, I. Jimenez-Serra, J. Jorgensen, L. E. Kristensen, H. Linnartz, M. McCoustra, N. Murillo, J. A. Noble, K. Oberg, M. E. Palumbo, Y. J. Pendleton, K. M. Pontoppidan, E. F. van Dishoeck. & S. Viti "IceAge: Chemical Evolution of Ices during Star Formation" 2017, *JWST cycle 0 ERS Accepted Proposal 1309*, arxiv: 2017jwst.prop.1309M

[2] M. K. McClure, W. R. M. Rocha, K. M. Pontoppidan, N. Crouzet, L. E. U. Chu, E. Dartois, T. Lamberts, J. A. Noble, Y. J. Pendleton, G. Perotti, D. Qasim, M. G. Rachid, Z. L. Smith, F. Sun, T. L. Beck, A. C. A. Boogert, W. A. Brown, P. Caselli, S. B. Charnley, H. M. Cuppen, H. Dickinson, M. N. Drozdovskaya, E. Egami, J. Erkal, H. Fraser, R. T. Garrod, D. Harsono, S. Ioppolo, I. Jiménez-Serra, M. Jin, J. K. Jørgensen, L. E. Kristensen, D. C. Lis, M. R. S. McCoustra, B. A. McGuire, G. J. Melnick, K. I. Öberg, M. E. Palumbo, T. Shimonishi, J. A. Sturm, E. F. van Dishoeck & H. Linnartz "An IceAge JWST inventory of dense molecular cloud ices" 2023, *Nature Astronomy*, doi: 10.1038/s41550-022-01875-w

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Conformationally selected ions for reactions with conformationally selected neutral molecules

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The different effective dipole moment of conformational isomers allows for their spatial separation by means of electrostatic deflection, enabling their individual reactivity to be investigated [1]. Recently, the conformer-specific polar cycloaddition of dibromobutadiene (DBB) with trapped propene ions has shown that both *gauche* and *s-trans* DBB conformers display capture-limited reaction rates [2]. The reaction was found to occur through both a concerted and a stepwise reaction mechanism, despite the spatial rearrangement of atoms necessary in *s-trans* DBB for the latter to take place. These results were obtained by selectively aiming the molecular beam containing either one of the two conformers at a static target of propene ions embedded within a laser-cooled Coulomb crystal of calcium ions.

In order to gain further control over the reaction partners, we now wish to also select the conformational isomer of the ionic reactant. Here, we discuss the generation of conformationally selected ionic targets of *meta*-aminostyrene to enable the study of fully conformationally selected ion–molecule reactions. Following the successful isomer-selective ionisation and loading of the two *m*-aminostyrene conformers into a Coulomb crystal, we aim to selectively detect them to determine their stability to such environment before investigating their isomer-specific reactivity.

References

[1] Y.-P. Chang, K. Długołęcki, J. Küpper, D. Rösch, D. Wild and S. Willitsch, *Science*, **342**, 98 (2013)

[2] A. Kilaj, J. Wang, P. Straňák, M. Schwilk, U. Rivero, L. Xu, O. A. von Lilienfeld, J. Küpper and S. Willitsch, *Nat. Commun.*, **12**, 6047 (2021)

The excitation of ethynyl in the interstellar medium : A key to understand isotopic fractionation

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Since the discovery of the ethynyl CCH radical in the interstellar medium [1], it has been detected in a wide range of astrophysical environments. It is one of the most abundant hydrocarbon in space and together with its detected isotopologues (CCD, ^{13}CCH and C^{13}CH), they are useful tracers of physical conditions. Indeed, as abundances strongly depend on the formation pathways, the measurment for the ratio [CCD]/[CCH] may constrain the age of molecular clouds in astrophysical models [2]. However, hyperfine resolved ^{13}C-based spectra show a higher intensity in favor of C^{13}CH lines than ^{13}CCH ones [3, 4] whereas their formation path is supposed to be the same. It is then of high interest to investigate this apparent different abundance of the two isotopologues.
An accurate interpretation of these observations requires to determine precise rate coefficients. Such quantities are necessary for non local thermodynamic equilibrium modeling which takes into account competition between radiative and collisional processes.

Non zero nuclear spins from ^{13}C, D and H atoms lead to a resolved hyperfine structure for these species. Such complex energetic structure is a real theoretical challenge as exact scattering calculations are not feasible in a reasonable time. Then, it is necessary to develop numerical and methodological tools in order to determine accurate collisional data for astrophysical applications. I will present calculations of new accurate collisional data for all the CCH isotopologues.
Scattering calculations have been performed using a recoupling technique in order to determine accurate hyperfine resolved rate coefficients of CCH and its isotopologues in collision with H2. These data were derived for a large range of temperature and are expected to improve abundance ratio calculations and better understand the evolution of the isotopic fraction in astrochemical models.

References

[1] K. D. Tucker, M. L. Kutner, and P. Thaddeus, The Astrophysical Journal 193, 115 (1974).
[2] S. P. Trevi~no-Morales, P. Pilleri, A. Fuente, C. Kramer, E. Roueff, M. González-García, J. Cernicharo, M.
Gerin, J. R. Goicoechea, J. Pety, O. Berné, V. Ossenkopf, D. Ginard, S. García-Burillo, J. R. Rizzo, and S. Viti, A&A 569 (2014), 10.1051/0004-6361/201423407.
[3] S. Cuadrado, J. R. Goicoechea, P. Pilleri, J. Cernicharo, A. Fuente, and C. Joblin, A&A 575 (2015), 10.1051/0004-6361/201424568.
[4] N. Sakai, O. Saruwatari, T. Sakai, S. Takano, and S. Yamamoto, A&A 512 (2010), 10.1051/0004-6361/200913098.

Measurement of low temperature product branching fraction for the reaction of CN radical and propene

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In order to improve current astrochemical models, reaction kinetic parameters are needed. This includes both rate constants and product channel branching ratios. The latter is more challenging to determine since it requires the detection of multiple products at the same time. This work will present an implementation of the Skimmed uniform supersonic flow (SKISURF) technique, designed for branching ratio measurements. It combines the CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) technique to reach low temperatures, with molecular beam sampling into an E-band chirped pulse Fourier transform millimeter wave spectrometer to detect reaction products (figure 1). The rate constants of many reactions involving hydrocarbons and different radicals are well known to have negative temperature dependences [2][3]. In this work we observed the products of CN and propene reaction relevant to interstellar medium and planetary atmospheres. The branching fraction determination of the vinyl cyanide channel will be given at 35 and 50 K. The limitation and impact of vibrational relaxation will be discussed in relation to these values. Preliminary results on the potential energy surface will be presented along with future directions for calculating the branching fractions using master equation models.

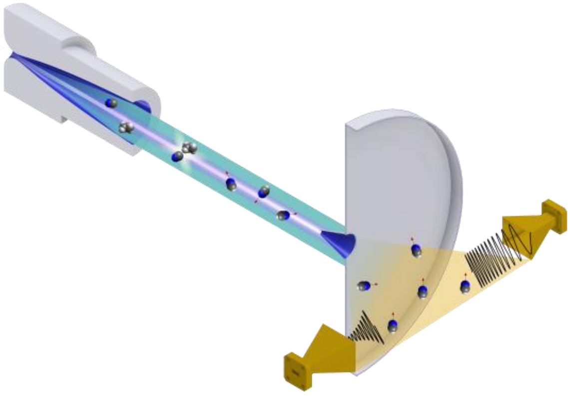

Figure 1: SKISURF experimental schematic

References

[1] C. Abeysekera, B. Joalland, N. Ariyasingha, L. N. Zack, I. R. Sims, R. W. Field, and A. G. Suits, J. Phys. Chem. Lett., Product branching in the low temperature reaction of CN with propyne by chirped-pulse microwave spectroscopy in a uniform supersonic flow, 6, 1599-1604, 2015

[2] I.R. Sims, J.L. Queffelec, D. Travers, B.R. Rowe, L.B. Herbert, J. Karthäuser & I.W.M. Smith,1993, Chem. Phys. Lett., Rate constants for the reactions of CN with hydrocarbons at low and ultra-temperatures, 211(4-5):461-468

[3] H. Sabbah, L. Biennier, I. R. Sims, Y. Georgievskii, S. J. Klippenstein, & I. W. Smith, Science, Understanding reactivity at very low temperatures: The reactions of oxygen atoms with alkenes, 317(5834):102–105, 2007.

Laboratory Spectroscopy of (*Z*)-1,2-Ethenediol and its First Detection Towards the Galactic Centre

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Prebiotic sugars could have formed on primitive Earth by the formose reaction. However, the mechanism of this process is not fully understood and it is conceivable that key intermediates could have formed in extraterrestrial environments and then delivered on early Earth by cometary bodies. 1,2-Ethenediol (HO-CH=CH-OH), the enol form of glycolaldehyde, represents a key, highly reactive intermediate of the formose reaction and is likely detectable in the interstellar space [1].

Here, the first characterization of (*Z*)-1,2-ethenediol by means of rotational spectroscopy is reported. This compound has been produced in the gas phase through flash vacuum pyrolysis of bis-*exo*-5-norbornene-2,3-diol at 750°C, via a retro-Diels-Alder reaction. The spectral analysis was aided by high-level quantum-chemical calculations, which predicted spectroscopic parameters in excellent agreement with the experiment [2].

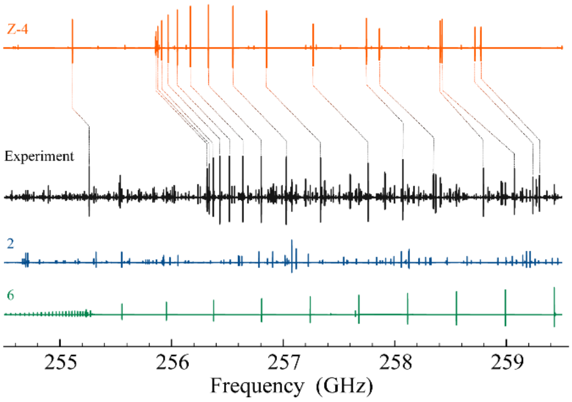

Figure 1: Experimental spectrum compared with simulations of (*Z*)-1,2-ethenediol and some by-products.

The accurate spectral data obtained were then used to search for (*Z*)-1,2-ethenediol emission in the interstellar medium. We have unambiguously observed 18 clean rotational transitions belonging to this species towards the G+0.693-0.027 molecular cloud located in the Galactic Center. The emission from (*Z*)-1,2-ethenediol was modeled under LTE conditions and led to a column density estimate of $(1.7\pm0.1)\times10^{13}$ cm^{-2}. The abundance of ethenediol is finally compared with that of related species, such as glycolaldehyde, and its importance as possible precursor in the formation of glyceraldehyde in the interstellar medium is discussed [3].

References

[1] N. F. Kleimeier, A. K. Eckhardt and R. I. Kaiser, *J. Am. Chem. Soc.*, **2021**, 143, 14009-14018.
[2] M. Melosso, L. Bizzocchi, H. Gazzeh, et al., *ChemComm*, **2022**, 58, 2750-2753.
[3] V.M. Rivilla, L. Colzi, I. Jiménez-Serra, et al., *ApJL*, **2022**, 929:L11.

Near-infrared spectroscopy of dissociated naphthalene in a radiofrequency plasma

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Polycyclic aromatic hydrocarbons (PAHs) are abundant organic molecules detected in several objects in the universe, such as molecular clouds in the interstellar medium (ISM) [1], asteroids [2], or planetary atmospheres [3]. These molecules play a key role in space, whether for the formation of stars [4] or the origin of absorption features known as diffuse interstellar bands [5]. The present study focuses on the plasma-driven processes in the ISM which is of high interest in modern astrophysics. As a prototypal PAH molecule, naphthalene ($C_{10}H_8$) is fragmented in a radiofrequency (RF) plasma and probed using cavity ringdown spectroscopy (CRDS) in the near infrared.

Our low-power RF plasma source, called Platypus, is adapted from a small plasma thruster ("Pocket Rocket") designed by the Space Plasma Power and Propulsion laboratory of the ANU [6]. Namely, Platypus is based on an electro-thermal capacitively-coupled RF plasma operating at 13.56 MHz. The continuous RF source delivers a transmitted power between 5 and 30 W and is fed with argon and gaseous $C_{10}H_8$. A stable supersonic jet plasma is generated by expanding the mixture of argon and dissociated $C_{10}H_8$ into a vacuum chamber through a 20 mm long, 4 mm wide slit nozzle (Fig. 1A, 1B) [7]. The jet-cooled fragmented $C_{10}H_8$ is probed with the ultra-sensitive CRDS technique to achieve an important signal-to-noise ratio.

We recorded a spectrum from 5950 to 6120 cm^{-1} composed of several hundred transitions (Fig. 1C). These transitions are linked to a huge number of neutrals and ionized, stables, and radical species [8] which we are going to investigate in an upcoming mass spectrometry study.

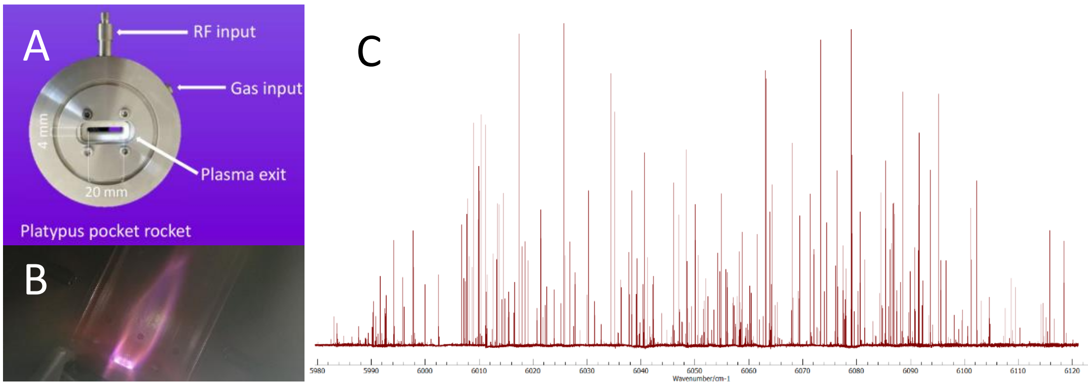

Fig. 1. A) Platypus plasma source [7]. B) Jet-plasma expansion of argon and gaseous naphthalene. C) CRD spectrum from 5950 to 6120 cm^{-1}.

References

[1] L.J. Allamandola *et al.*, *The Astrophysical Journal* **290,** L25-L28 (1985).
[2] M.A. Sephton *et al.*, *Geochimica et Cosmochimica Acta* **62.10**, 1821-1828 (1998).
[3] C. Sagan *et al.*, *The Astrophysical Journal* **414**, 399-405 (1993).
[4] E. Peeters *et al.*, *The Astrophysical Journal* **613.2**, 986 (2004).
[5] F. Salama, *et al.*, *The Astrophysical Journal* **728.2**, 154 (2011).
[6] C. Charles and R. W. Boswell. *Plasma Sources Science and Technology* **21.2**, 022002 (2012).
[7] E. Dudás, *Ph.D Thesis*, 149-162 (2021).
[8] M. Alliati *et al.*, *The Journal of Physical Chemistry A* **123.10,** 2107-2113 (2019).

Formation of covalently-linked PAHs in interstellar space

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Carbonaceous compounds and especially polycyclic aromatic hydrocarbons (PAHs) are abundant in many regions in space. Their exact chemical composition and structure as well as the formation pathways in different astronomical environments are still under debate. To date, only fused PAHs such as indene and two cyano-naphthalene isomers have been detected using radio-astronomical searches. [1-3] Using a combination of infrared spectroscopy and ion-molecule kinetics, we have studied the reactivity of the benzonitrile$^+$ and ortho-benzyne$^+$ cations with acetylene molecules. Using the FELIX free-electron laser [4], the chemical structures of the ion-molecule reaction products have been determined by infrared action spectroscopy and quantum-chemical calculations. This reveals a new set of exothermic ion-molecule reactions that show the formation of non-fused, but linked, dumbbell-shaped (nitrogen-containing)-PAHs such as 2-phenyl-pyridine$^+$ and phenyl-cyclobutadiene$^+$. These linked PAHs can play an important role in the carbon chemistry in cold molecular clouds such as TMC-1 and are therefore of interest for further radio-astronomical investigations.

References

[1] Burkhardt, A. M., Long Kelvin Lee, K., Bryan Changala, P., Shingledecker, C. N., Cooke, I. R., Loomis, R. A., Wei, H., Charnley, S. B., Herbst, E., McCarthy, M. C. & McGuire, B. A. Discovery of the Pure Polycyclic Aromatic Hydrocarbon Indene (c-C9H8) with GOTHAM Observations of TMC-1. *Astrophys J Lett* **913**, L18 (2021).

[2] Cernicharo, J., Agúndez, M., Cabezas, C., Tercero, B., Marcelino, N., Pardo, J. R. & de Vicente, P. Pure hydrocarbon cycles in TMC-1: Discovery of ethynyl cyclopropenylidene, cyclopentadiene, and indene. *Astron Astrophys* **649**, L15 (2021).

[3] McGuire, B. A., Loomis, R. A., Burkhardt, A. M., Lee, K. L. K., Shingledecker, C. N., Charnley, S. B., Cooke, I. R., Cordiner, M. A., Herbst, E., Kalenskii, S., Siebert, M. A., Willis, E. R., Xue, C., Remijan, A. J. & McCarthy, M. C. Detection of two interstellar polycyclic aromatic hydrocarbons via spectral matched filtering. *Science (1979)* **371**, 1265–1269 (2021).

[4] Jusko, P., Brünken, S., Asvany, O., Thorwirth, S., Stoffels, A., Van Der Meer, L., Berden, G., Redlich, B., Oomens, J. & Schlemmer, S. The FELion cryogenic ion trap beam line at the FELIX free-electron laser laboratory: Infrared signatures of primary alcohol cations. *Faraday Discuss* **217**, 172–202 (2019).

Infrared Spectrum of Ions of Interstellar Interest

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We are using helium droplets to make molecular ions tagged with helium atoms. Infrared (IR) spectra of these bare and helium-tagged ions can then be recorded using photo-dissociation spectroscopy. Protonated formaldehyde was an ion of potential astrochemical interest targeted in this.[1, 2]

Isolation of single molecules in Helium droplets and then ionising them with high-energy electrons allows us to isolate ions and selectively tune to them with quadrupole mass spectrometry. We use this to create protonated formaldehyde *in situ* by ionising a methanol precursor, which we can then create an IR induced photo-dissociation. We are able to see in Figure 1 that we were able to find the OH stretch at 3417 cm^{-1}, but the a/symmetric CH stretches at 2976 cm^{-1} and 3111 cm^{-1}, respectively, would have been lost amongst the noise, we may be able to find them by taking multiple scans and averaging them to eliminate as much noise as possible.

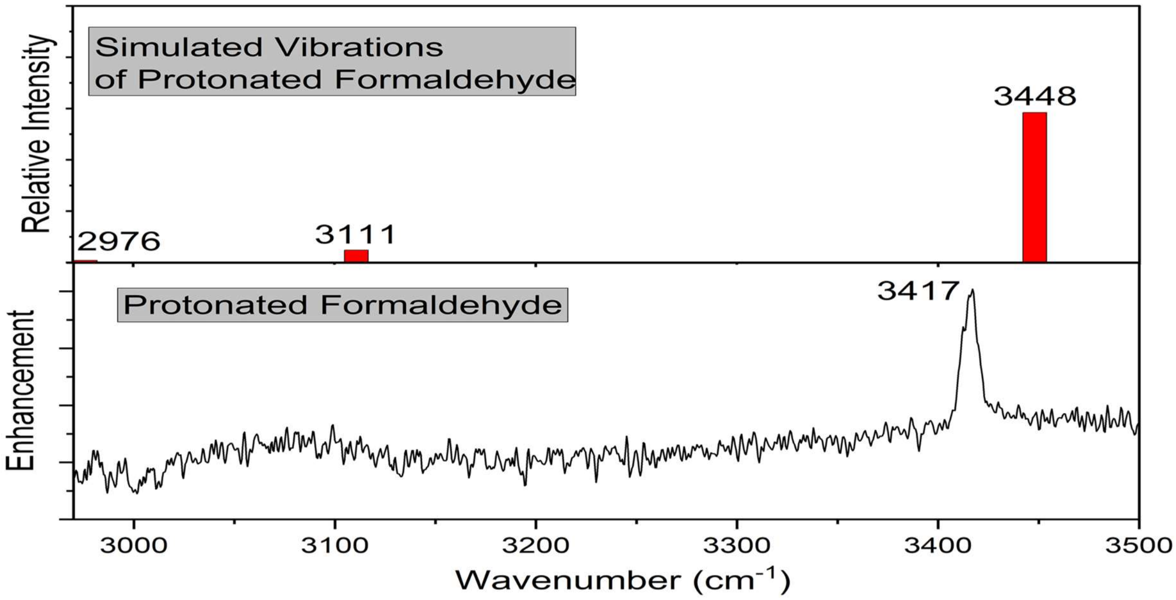

Figure 1: Top: Infrared spectrum of protonated formaldehyde Bottom: Computationally predicated IR spectrum of protonated formaldehyde calculated in Gaussian 16 at the B3LYP/aug-cc-pVTZ level of theory/basis-set (scaled: 0.968).[3, 4]

References

1. R. Martinez, A. N. Agnihotri, P. Boduch, A. Domaracka, D. Fulvio, G. Muniz, M. E. Palumbo, H. Rothard and G. Strazzulla, *The Journal of Physical Chemistry A*, 2019, **123**, 8001-8008.
2. A. G. G. M. Tielens, *The Physics and Chemistry of the Interstellar Medium*, Cambridge University Press, Cambridge, 2005.
3. M. J. Frisch et al., Gaussian 16, 2016.
4. J. P. Merrick, D. Moran and L. Radom, *The Journal of Physical Chemistry A*, 2007, **111**, 11683-11700.

Interaction of CH_3CN and CH_3NC with He : temperature dependence of the collisional rate coefficients

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Several nitrogen-bearing molecules, such as methyl cyanide (or acetonitrile, CH_3CN) and methyl isocyanide (CH_3NC), have been observed in various astrophysical environments. In order to get access to their absolute and relative abundances, it is essential to understand their collisional/quenching schemes. This work deals with the calculation of rate coefficients for the rotational excitation of both para- and ortho- symmetries of CH_3CN and CH_3NC molecules in collision with He atoms from low (7K) to moderate kinetic temperature (100K).

We compute the rotationally inelastic cross sections for all levels up to 268 cm^{-1} of collision energy, employing at low energy exact Coupled Channels methods [1], and at higher energies, approximate Coupled States methods [2]. Rates of quenching are computed and most are found to differ from those reported earlier by Green [3] (up to a factor of a thousand), calling for a possible reexamination of the temperatures assigned to low density gases.

CH_3CN-He rate coefficients were compared to CH_3NC-He ones. As expected, differences were found. Such a comparison confirms the importance of having specific collisional date of each isomer and show that the use of CH_3CN rate coefficients in order to interpret CH_3NC observations may be dangerous for astrophysical applications, since the use of CH_3CN collisional rate coefficients will probably significantly modify the excitation of the CH_3NC molecule.

References

[1] Arthurs A. M., Dalgarno A., 1960, Proceedings of the Royal Society ofLondon. Series A. Mathematical and Physical Sciences, 256, 540
[2] McGuire P., Kouri D. J., 1974, The Journal of Chemical Physics, 60, 2488
[3] Green S., 1986, The Astrophysical Journal, 309, 331

The spectroscopy and analysis of Renner-Teller affected radical cations

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In this study we have measured and analyzed the vibrational spectra of several astrochemically relevant reactive intermediates, with a particular focus on linear open-shell radical cations such as CCH^+ ($^3\Pi$), $HCCH^+$ ($^2\Pi$) and $HCCCN^+$ ($^2\Pi$). These cations are subjected to Renner-Teller (RT) and spin-orbit coupling effects making them not only interesting from an astrochemical perspective, but also from a fundamental spectroscopic one. Using the cryogenic ion trap instrument FELion interfaced with FELIX [1] we can produce, trap, and cool these ions after which we can apply several action spectroscopic techniques to obtain their vibrational spectra. The most widespread technique to target these reactive species is infrared pre-dissociation (IRPD) spectroscopy, which uses a messenger rare-gas atom to obtain the vibrational spectrum. The downside of this technique is that the tag may induce some structural changes to the ion. Leak-out spectroscopy (LOS), recently developed by P. Schmid *et al.* [2], overcomes this problem and allows to target the bare-ion spectrum. Both techniques were applied to record the spectra of several RT active species. We found that IRPD generally gives a better signal-to-noise ratio than LOS and allows to target the full range of the RT split bending modes, but the tag induces a clear distortion in the vibrational spectrum of the complex and cannot be taken as a proxy for the bare ion spectrum. Analysis of the Renner-Teller splitting was done on the basis of *ab initio* calculations at CCSD(T) level of theory combined with an effective Hamiltonian approach [3].

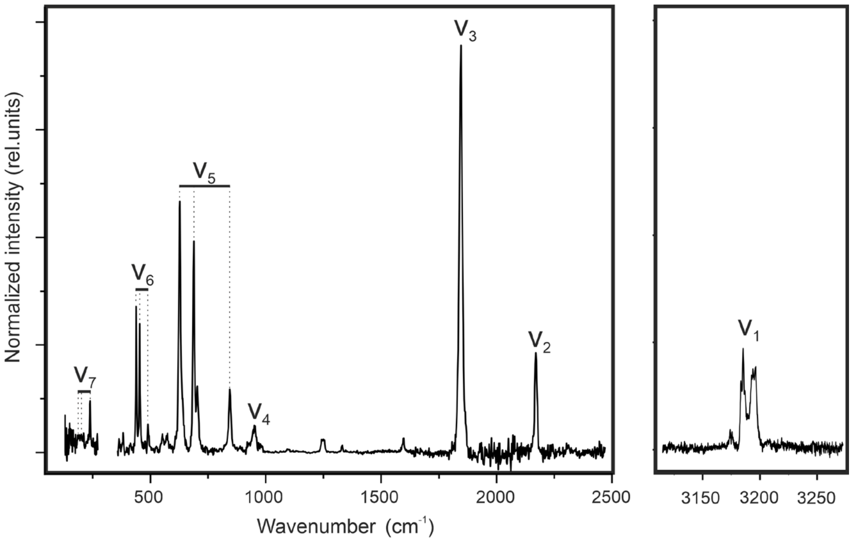

Figure 1: Measured IRPD spectrum of the HC_3N^+ ion in the wavenumber ranges 130-270 cm^{-1} (FEL1), 310-2500 cm^{-1} (FEL2), and 3110-3270 cm^{-1} (OPO) using Ne as a messenger atom. The v_1-v_4 labels represent the four stretching modes of HC_3N^+ and v_5-v_7 the RT affected bending modes [3].

References

[1] P. Jusko *et al.*, Faraday Discuss., 217, 172, **2019**.
[2] P. C. Schmid *et al.*, J. Phys. Chem. A., 126(43), **2022**
[3] K. Steenbakkers *et al.*, J. Chem. Phys, **2022**, submitted

Low-Energy Dissociative Recombination of CH^+

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Modelling the dissociative recombination (DR) of molecular ions becomes complicated when the direct and indirect DR mechanisms compete with each other. This typically occurs in ions with low-energy electronic resonances, e.g., open-shell molecular ions. We present a theoretical approach to model this process, which combines three methods: (i) fixed-nuclei electron-ion scattering with the UK R-matrix method (ii) rovibronic frame transformation with dissociative wave functions obtained with a complex absorbing potential (iii) molecular quantum-defect theory. We apply this approach to the CH^+ ion. Past studies [1–7] of the DR of CH^+ have shown that the Rydberg series belonging to the two lowest excited states of the ion, $a^3\Pi$ and $A^1\Pi$, and d-type partial waves of the incident electron have a significant impact on the DR cross-section. We improve on our recent study of CH^+ [7], of which the results were only vibronically resolved, by performing a rovibronic frame transformation and present our rotationally resolved results compared against recent experimental data.

References

[1] L Carata et al. In: *Phys. Rev. A* 62.5 (2000), p. 052711.

[2] J Zs Mezei et al. In: *Plasma Sources Sci. Technol.* 24.3 (2015), p. 035005.

[3] J Zs Mezei et al. In: *Plasma Sources Sci. Technol.* 25.5 (2016), p. 055022.

[4] K Chakrabarti et al. In: *J. Phys. B* 51.10 (2018), p. 104002.

[5] Zsolt J Mezei et al. In: *Atoms* 7.3 (2019), p. 82.

[6] K Chakrabarti, R Ghosh, and BS Choudhury. In: *J. Phys. B* 52.10 (2019), p. 105205.

[7] Xianwu Jiang et al. In: *Physical Review A* 100.6 (2019), p. 062711.

Fine excitation of CCS by He: Potential energy surface and scattering calculations

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The CCS($3\Sigma^-$) radical have been detected in several dark molecular clouds, including TMC-1 and in the circumstellar enveloppe IRC+10216. [1, 2] The CCS radical presents large fine structure splitting, which makes the estimation of the rate coefficients incorrect and the line modeling difficult.[1] Therefore, the CCS rate coefficients must be accurately determined.

The fine structure excitation of the interstellar CCS radical induced by collisions with He is investigated. The first potential energy surface (PES) for the CCS-He van der Waals complex is presented. It was obtained from a highly correlated spin unrestricted coupled cluster approach with single double and perturbative triple excitations. [3] The PES presents two shallow minima of 31.85 and 37.12 cm^{-1} for the linear (He facing S) and the nearly T-shaped geometries, respectively.

Inelastic scattering calculations were performed using the close-coupling approach. Cross sections for transitions between the 61 first fine structure levels of CCS were obtained for energy up to 600 cm^{-1} and rate coefficients for the 5 - 50 K temperature range were derived. [3] These rates were compared to the ones of Wolkovitch *et al.* [4] and a difference of a factor of 2-10 is globally observed. This new set of collisional data can be used to model CCS emission spectra in dark molecular interstellar clouds and circumstellar enveloppes and enable an accurate determination of CCS abundance in these astrophysical media.

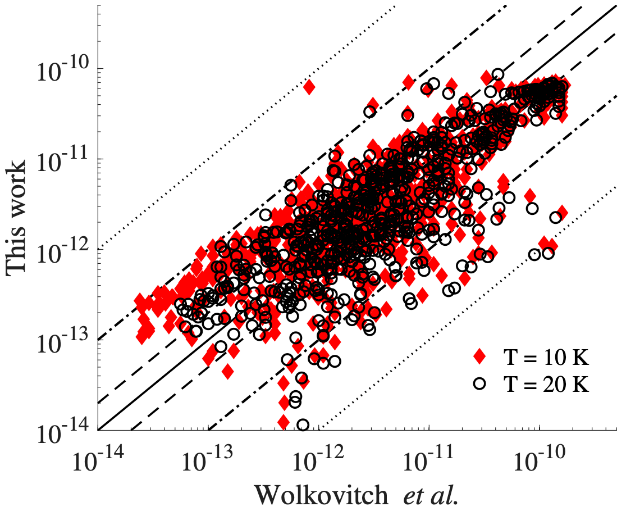

Figure 1: Direct comparison of Wolkovitch *et al.* [4] rate coefficients and the one provided in this work [3] at 10 K and 20 K. The solid line represent a perfect agreement; dashed, dashed-dotted and dotted lines delimit the regions where the rate coefficients differ by less than a factor 2, 10 and 100, respectively.

References

[1] S. Saito, K. Kawaguchi, S. Yamamoto, M. Ohishi, H. Suzuki, N. Kaifu, ApJ **317**, L115-L119 (1987).
[2] H. Suzuki, S. Yamamoto, M. Ohishi, N. Kaifu, S. Ishikawa, Y. Hirahara, S. Takano, *ApJ.,* **392**, 551 (1992).
[3] A. Godard Palluet and F. Lique, J. Chem. Phys., **158** (2023).
[4] D. Wolkovitch, W. D. Langer, T. Velusamy, T. B. H. Kuiper, and S. Levin, ApJ **477**, 241 (1997)

Towards the first stages in nucleation: low temperature reaction kinetics of heterogeneous complex formation

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Nucleation is a process consisting of a succession of unions of small gas-phase molecules leading to the formation and growth of droplets and particles. Consequently, it is a crucial process in the formation of clouds and dust particles in a range of systems including planetary atmospheres and circumstellar shells. Under certain conditions, low temperatures and/or high degrees of supersaturation, nucleation can become a barrierless process, and dimerization, the complexation of the two smallest molecular species involved, becomes the rate-limiting step of nucleation.

Previous investigations of the kinetics of formation of homogeneous dimers using the CRESU (a French acronym standing for reaction kinetics in uniform supersonic flow) technique have mainly used mass spectrometric detection. However, in this research we have employed a completely new detection scheme, chirped-pulse Fourier transform mm-wave spectroscopy, to study for the first time the kinetics of formation of a heterogeneous dimer. This innovative technique combines the ability to generate continuous cold uniform supersonic flows with the high selectivity and general applicability of rotational spectroscopy, allowing us to follow both reactant and product concentrations simultaneously. Furthermore, the high sensitivity achieved has allowed us to employ pseudo-first-order conditions to obtain absolute rate constants.

We will report the first measurements of rate constants for the formation of formic acid – CO2 heterodimers at temperatures down to 35 K or below. Both molecules are present in a wide range of interstellar ices, dense molecular clouds, star-forming regions, cometary comae and planetary atmospheres, where the formation of the heterodimer may be key in the nucleation and condensation processes taking place at these environments.

Collisional excitation of interstellar water molecules

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Water is among the most ubiquitous and abundant molecules in space and was recently observed in highly excited rovibrational states close to more than a dozens of oxygen-rich evolved stars [1]. They are continuously expelling their mass through pulsations to form a circumstellar envelope and enrich the interstellar medium with matter. Accurate determination of the physical conditions around these stars relies on knowing accurate collisional cross sections of water with the most abundant collider, H_2.

The Crossed Molecular Beam (CMB) approach allows to measure experimentally the integral cross sections of collision induced transitions at low collision energies by varying the angle at which two molecular beams collide. The first rotational excitations of H_2O and D_2O, have been previously studied in the COMEX group [2-4].

In this poster, the CMB setup (Figure 1) is presented along with its application to study the rotational excitation of another isotopologue of water, HDO ($0_{00} \rightarrow 1_{11}$), by inelastic collisions with H_2 in the range of 10-100 cm^{-1}. The experimental cross sections are compared to theoretical computations performed at the quantum close-coupling level by Alexandre Faure and Laurent Wiesenfeld.

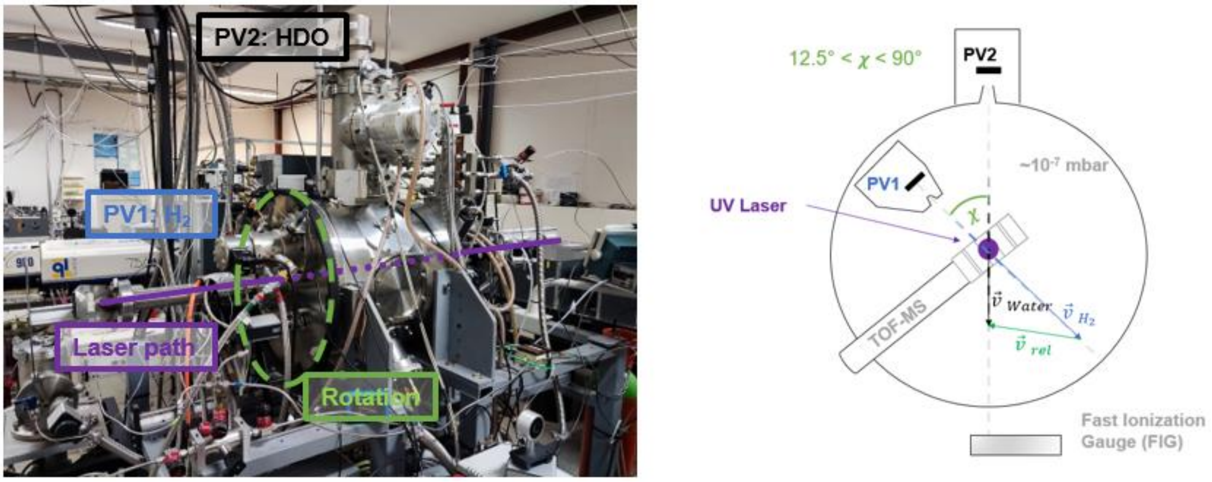

Figure 1. Scheme of the CMB experimental setup at COMEX.

References

[1] Etoka, S., Baudry, A., Richards, A., Gray, M., & Decin, L. "Tracing the inner regions of circumstellar envelopes via high-excitation water transitions". Proceedings of the International Astronomical Union, 2020, 16(S366), 199-203.

[2] Bergeat A., Faure A., Wiesenfeld L., Miossec C., Morales S.B., Naulin C. "Near-Threshold and Resonance Effects in Rotationally Inelastic Scattering of D_2O with Normal-H_2". Molecules, 2022, 27(21):7535.

[3] Bergeat A., Morales S.B., Naulin C, Faure A., Wiesenfeld L.,. "Probing low-energy resonances in water-hydrogen inelastic collisions". Phys. Rev. let., 2020, 125, 143402.

[4] Bergeat A., Faure A., Morales S.B., Moudens A., Naulin C. "Low-Energy Water–Hydrogen Inelastic Collisions". The Journal of Physical Chemistry A, 2020, 124 (2), 259-264.

Hydrocarbon chemistry in the inner regions of planet forming disk

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The analysis of the mid-infrared spectra helps understanding the composition of the gas in the inner, dense and warm regions of the disk where terrestrial planets form. ALMA has detected hydrocarbons in the outer regions of the planet forming disk and Spitzer detected C_2H_2 in the inner regions. JWST- MIRI will provide high spectral resolution observations of C_2H_2 and potentially CH_4. Interpreting the fluxes observed in the spectra is challenging and radiation thermo-chemical codes should be used to properly take into account the disk structure, radiative transfer, chemistry and thermal balance. Various disk physical parameters like the gas-dust ratio, dust evolution including radial drift, dust growth and settling can affect the fluxes observed in the mid-IR. Thermo-chemical disk models have been studied in the past but were not always successful in matching all observed molecular emission bands. The goal of project is two fold. We analyse the warm carbon chemistry in the inner regions of the disk, i.e. within 10 au to find pathways forming C_2H_2 missing from the existing chemical networks. Second, we analyse the effect of the new chemistry on the line fluxes of acetylene. We use radiative thermo-chemical disk code to expand the hydrocarbon chemistry that occurs in a typical standard TTauri disks. We used the UMIST and KIDA rate databases for collecting reactions for the species. We included isotopomers for the species that we found in the databases. The chemistry is then analysed in the regions that produces observable features in the mid-infrared spectra. The effect of addition of the new hydrocarbons on the mid-infrared spectra is studied.

Acetylene is formed via two pathways in the surface layers: neutral-neutral and ion-neutral. The neutral-neutral pathway proceeds via the hydrogenation of C and the ion neutral pathway proceeds via addition of H to C^+. Thus, the abundances of C, C^+, H and H_2 affect the formation of C_2H_2. The formation of H_2 hence indirectly affects the abundance of acetylene. Chemisorbed H is more efficient in forming H_2 compared to physisorbed H at warm temperatures and hence increases the abundance of C_2H_2. We provide a new extended warm chemical network that considers 8 carbon atom long species and takes into account different isotopomers and can build the simplest form of PAH: C_6H_6. For a standard TTauri disk with a canonical value of gas mass, the line fluxes increase only a factor of less than 2. With the advent of JWST, we are hopeful to detect hydrocarbons like methane, acetylene and C_4H_2 etc. in disks having high C/O ratio. We conclude that using the new extended warm hydrocarbon network while invoking physical processes like drift, mixing is key for interpreting the observed mid-infrared fluxes.

Simulating exoplanetary atmospheres in the laboratory: understanding the chemical stability and evolution of potential biosignatures

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Since the first discovery of an exoplanet, several thousand more, including some rocky planets, have been discovered [1]. As the new generation of telescopes (e.g. James Webb Space Telescope, Extremely Large Telescope) are capable of recording spectroscopic data of exoplanet atmospheres [1], [3], the search for extraterrestrial life has been significantly advanced. Spectroscopically detectable atmospheric biosignatures on Earth-like exoplanets are of particular interest [4], [5]. Given the large variety of exoplanets, the correct interpretation of these measurements requires a profound understanding of complex atmospheric processes, both from atmospheric models and complementary lab work [6].

With the newly build planetary simulation chamber at Freie Universitaet Berlin, we can simulate a large set of atmospheric parameters in the laboratory, including pressure, temperature and various gas compositions for Earth-like objects. To trigger complex photochemical processes (either in the gas or solid phase), samples can be exposed to electromagnetic and particle radiation. Such incoming spectra can be varied to simulate the photochemical and climate effects of rocky planets orbiting different stars.

Many telescopes operate in the VIS/NIR range that corresponds to the fingerprint regions of organic molecules of interest. Our facility allows continuous, real-time spectroscopic monitoring of samples in the VUV, UV/VIS and NIR regions, as well as simultaneous mass spectrometric analysis. This simulation facility will provide valuable insights into complex chemical pathways across a range of atmospheric compositions, which will not only complement current atmospheric models but will also improve our ability to assess and interpret atmospheric biosignature signals.

References

[1] George R. Ricker , “The Transiting Exoplanet Survey Satellite (TESS): Discovering New Earths and Super-Earths in the Solar Neighborhood ”, American Astronomical Society, Volume 47, November 2015

[2] G. H. Rieke, G. S.Wright, T. Böker, et all, “The Mid-Infrared Instrument for the James Webb Space Telescope”, The Astronomical Society of the Pacific, 127:584–594, July 2015

[3] D. Deming, S. Seager, J. Winn, et all, “Discovery and Characterization of Transiting Super Earths Using an All-Sky Transit Survey and Follow-up by the James Webb Space Telescope”, The Astronomical Society of the Pacific, 121:952–967, 2009 September

[4] David J. des Marais, Martin O. Harwit, Kenneth W. Jucks, et all, “Remote Sensing of Planetary Properties and Biosignatures on Extrasolar Terrestrial Planets”, ASTROBIOLOGY, Volume 2, Number 2, 2002

[5] S. Seager, W. Bainsand, J.J. Petkowski, “Toward a List of Molecules as Potential Biosignature Gases for the Search for Life on Exoplanets and Applications to Terrestrial Biochemistry”, ASTROBIOLOGY, Volume 16, Number 6, 2016[6] Jonathan J. Fortney, Tyler D. Robinson, Shawn Domagal-Goldman, et all, “The Need for Laboratory Work to Aid in The Understanding of Exoplanetary Atmospheres”, NExSS, 2016

Ion-molecule reactions as a function of photon and collision energy for astrochemistry

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HCO^+ and HOC^+ are two isomeric cations detected in Photon Dominated Regions [1], diffuse clouds [2], and Mars atmosphere [3,4]. They correspond to the protonation of carbon monoxide on either the carbon or oxygen atom and are important intermediates in the formation of complex molecules as HCO^+ is the most abundant ion in molecular clouds. There is a difference in reactivity between the two isomers and isomerization occurs when energy is provided and is possible through collision. The isomers have a difference of energy of 1.7 eV (HCO^+ being the more stable) and are separated by an isomerization barrier of 1.5 eV [5] (from HOC^+). Previous studies of their reactivity have mostly been obtained by electron ionization [6,7] which does not allow the formation of pure HOC^+ nor precise internal energy determination.

The CERISES [8] instrument, connected on the DESIRS beamline at SOLEIL Synchrotron, was used to produce (i) HCO^+ from formaldehyde (H_2CO) and (ii) HOC^+ from deuterated methanol (CD_3OH). We have studied the reactivity of the two isomers with a series of neutral targets to (i) characterize the ionic purity and internal energy content of the two isomers and (ii) study complex reactivity (with a potential increase in chemical complexity). From this extensive data set, we have determined isomeric purity, the evolution of internal energy as a function of photon energy, and that the reactivity of both isomers with methanol is dominated by Proton Transfer (PT) and dissociative PT. Attempts to evaluate the collision-mediated isomerization are also being performed through an innovative method that combines time-of-flight spectrometry with SIMION simulation.

The reactivity of **molecular anions** is also of major interest since they are detected in Titan's ionosphere [9] and are present (sometimes in large abundance) in various interstellar environments [10]. In order to study these species, we are currently developing, in parallel to our activity at SOLEIL, a new anion source for the CERISES instruments. We aim at generating anions by dissociative electron attachment on precursors, using secondary electrons produced by electron impact on an aluminium target. Results will illustrate the current development through the reactivity of CN^- anions produced from cyanogen bromide (BrCN) with a series of oxygenated organic targets.

References

[1] A. Fuente, et al., A&A. 406 (2003) 899–913. https://doi.org/10.1051/0004-6361:20030712.
[2] H. Liszt, et al., A&A. 428 (2004) 117–120. https://doi.org/10.1051/0004-6361:20041649.
[3] J.L. Fox, Icarus. 252 (2015) 366–392. https://doi.org/10.1016/j.icarus.2015.01.010.
[4] M. Matta, et al., J. Geophys. Res. Space Physics. 118 (2013) 2681–2693. https://doi.org/10.1002/jgra.50104.
[5] A.J. Chalk, L. Radom, J. Am. Chem. Soc. 119 (1997) 7573–7578. https://doi.org/10.1021/ja971055c.
[6] A.J. Illies, et al., J. Am. Chem. Soc. 105 (1983) 2562–2565. https://doi.org/10.1021/ja00347a008.
[7] W. Wagner-Redeker, et al., J. Chem. Phys. 83 (1985) 1121–1131. https://doi.org/10.1063/1.449474.
[8] B. Cunha de Miranda, et al., J. Phys. Chem. A. 119 (2015) 6082–6098. https://doi.org/10.1021/jp512846v.
[9] A.J. Coates, et al., Geophys. Res. Lett. 34 (2007) L22103. https://doi.org/10.1029/2007GL030978.
[10] T.J. Millar, et al., Chem. Rev. 117 (2017) 1765–1795. https://doi.org/10.1021/acs.chemrev.6b00480.

Hyperfine excitation of $HC^{17}O^+$ with p-H2 collisions

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The formyl ion (HCO^+) plays a major role both in interstellar chemistry and dynamics of the interstellar gas, being one of the most abundant ions in molecular clouds. Moreover, the HCO^+ chemistry is straightforward and well understood [1], thus making it an excellent candidate as a tracer of molecular ionized gas through the evolutionary stages of the interstellar medium (ISM) [2,3].
For this reason, the accurate rotational rate coefficients of HCO^+ and its isotopes with the most abundant perturbing species in the ISM are crucial in non-local thermal equilibrium (LTE) models and deserve special attention. To this end, many efforts have been made in order to retrieve accurate collisional parameters of HCO^+ interacting with the He and H_2 colliders [4,5,6] as well as for some of its isotopologues (see for example [7] and references therein).
However, in spite of several spectroscopic studies and astrophysical detections carried out on $HC^{17}O^+$ [8,9], to the best of our knowledge, an accurate characterization of its collisional parameters has not been carried out yet. Although rarer, the $HC^{17}O^+$ isotope assumes a prominent role when looking to solve non-LTE radiative transfer problem to deduce molecular densities. Indeed, both the presence of an hyperfine structure (nuclear spin of 5/2) and its optical thinness with respect to the HCO^+ ion, which renders its transitions intensities proportional to the molecule column density, are able to furnish a direct measure of the optical depth.
With the aim of filling this lack, this work reports the first determination of hyperfine resolved rate coefficients for the excitation of $HC^{17}O^+$ by para-H_2 (J=0).

The characterization of the potential energy surface of the HCO^+ and H_2 collisional system exploited the accuracy of explicitly correlated coupled-cluster methods by means of the CCSD(T)-F12a/aug-cc-pVQZ level of theory. The computed interaction energies have been averaged over five H_2 rotation and then fitted by means of the procedure described by Werner et al. (1989) [11].
Before moving on with the scattering calculations, the entity of the coupling involved between the different rotational states of H_2 (J=0,1,2) on the computation of the inelastic cross sections has been assessed. This allowed us to neglect in a good approximation the influence of $J(H_2)>0$, thus simplifying the problem in the assumption of a spherical average potential with respect to the orientations of H_2.
To conclude, state-to-state rate coefficients between the lower hyperfine levels have been computed using recoupling techniques for temperatures ranging from 5 to 100 K.

References

[1] Herbst E., Klemperer W., 1973, *The Astrophysical Journal*, **185**, 505.
[2] Jørgensen J. K., Schöier F. L., and Van Dishoeck. E. F., 2004, *Astronomy & Astrophysics*, **416.2**, 603.
[3] Guélin M., Langer W., Wilson R., 1982a, *Astronomy and Astrophysics*, **107**, 107.
[4] Tonolo F., Bizzocchi L., Melosso M., Lique F., Dore L., Barone V., Puzzarini C., 2021, *The Journal of Chemical Physics*, **155**, 234306.
[5] Massó H., Wiesenfeld L., 2014, *The Journal of Chemical Physics*, **141**, 184301.
[6] Yazidi O., Ben Abdallah D., Lique F., 2014, *Monthly Notices of the Royal Astronomical Society*, **441**, 664.
[7] Denis-Alpizar O., Stoecklin T., Dutrey A., Guilloteau S., 2020, *Monthly Notices of the Royal Astronomical Society*, **497**, 4276.
[8] Plummer G., Herbst E., De Lucia F., 1983, *The Astrophysical Journal*, **270**, L99.
[9] Dore L., Cazzoli G., Caselli P., 2001, *Astronomy & Astrophysics*, **368**, 712.
[10] Werner H. J., Follmeg B., Alexander M. H., Lemoine D., 1989, *The Journal of Chemical Physics*, **91**, 5425.

The CP+CH_2NH and *c*-C_2H_4O+CN reactions as test case for ab initio gas-phase interstellar reactivity

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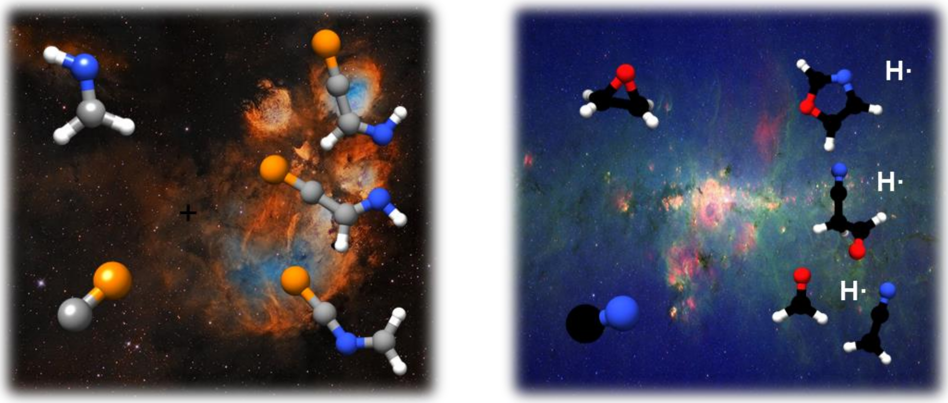
The increasing molecular complexity of the interstellar medium (ISM) is testified by the substantial number of new detections made in 2021 [1]. These new observations claim for innovative formation routes which can be explored effectively via *ab initio* methodologies that analyze both the thermodynamic and kinetic aspects of one reaction. Computer-aided studies of gas-phase routes are of particular importance since they can reproduce the cold environments of the ISM, discriminating between different paths and retaining only those open in the ISM conditions (i.e. exothermic routes with only submerged barriers). Once the reactive channels are characterized, they can be employed to compute rate constants for appropriate sets of temperature and pressures.

In this context, two reaction mechanisms that can occur in the gas phase will be described: (*i*) the mechanism between the CP radical and CH_2NH and (*ii*) the reaction between oxirane (*c*-C_2H_4O) and the CN radical, schematically represented with their products in Fig. 1. The former, has a reaction mechanism consistent with those of the reactions CH_2NH+CN· or +CCH·. Indeed, in analogy to these reactions that produce of cyanomethanimine (*E*-/*Z*-HN=CHCN) and propargylimine (*E*-/*Z*-HNCHCCH) respectively, the results of the reaction with the CP radical produce *E*- and *Z*-HN=CHCP together with H_2C=NCP [2]

The second path, c-C_2H_4O+CN is of interest since its potential products belong to the C_3H_3NO family of isomers. The latter contains several prebiotic species like propiolamide, cyanooxirane or vinyl isocyanate, but all of them seem to be elusive in the ISM. The thermodynamically allowed channels were employed to run kinetic simulations at a temperature of 60 K, pointing out to the H-abstraction as preferred pathway, while the second-most probable mechanism is the dissociation into H_2CO+H_2CCN.

Figure 1: Schematic representation of the reactions with their possible products.



References

[1] CDMS database, *https://cdms.astro.uni-koeln.de/classic/molecules*
[2] S. Alessandrini, F. Tonolo, C. Puzzarini, *J. Chem. Phys*. 2021, 154, 054306
[3] S. Alessandrini, M. Melosso, *Front. Astron. Space Sci.* 2021, 8, 159

Rapid molecular growth induced by low-temperature ion-molecule reactions of CH_3^+ and $C_2H_5^+$ with a selection of hydrocarbons: applications to the chemistry of the interstellar medium

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The aim of this upcoming work is identifying key ionic processes leading to the molecular growth of small organic molecules in astrophysical environments. We will start with small ions such as CH_3^+ and $C_2H_5^+$. Preliminary results obtained for those two ions show that collisions with neutral hydrocarbons tend to lead to dominant products conserving all carbon atoms.

To do so we will use the CRESU method (French acronym for "Cinétique de Réaction en Ecoulement Supersonique Uniforme"). This method initially invented in Meudon and transferred to Rennes was recently updated to study the reactivity of selective ions. The new experimental scheme, shown below, combines a mass-selective ion source with a CRESU reactor.

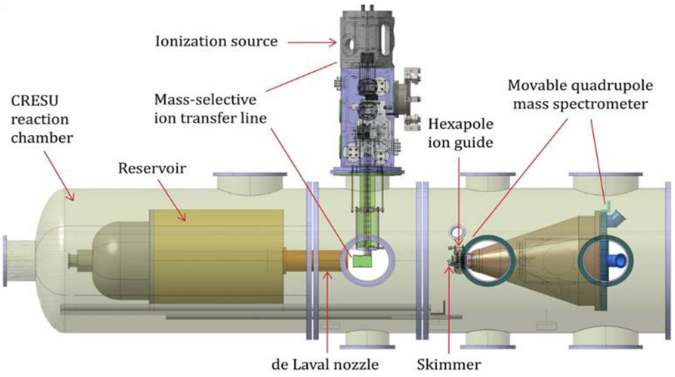

Figure 1: The CRESU reaction chamber [1]

The ions are created in the ionization source, filtered, guided down, and finally injected into the supersonic, adiabatic expansion. The cold flow emerging from the Laval nozzle and characterized by a temperature that can go down to 10 K is probed with the help of a quadrupole mass spectrometer. The apparatus is employed to measure the kinetics and branching ratio of low-temperature ion-molecule reactions.

This study aims to contribute to assess the role of ion-molecule reactions in the growth of complexity in astrophysical environments such as interstellar clouds.

References

[1] Joalland, B., Jamal-Eddine, N., Papanastasiou, D., Lekkas, A., Carles, S., & Biennier, L. *The Journal of chemical physics*, *150*(16), 164201. 2019

CH_3OH formation from H_2CO + CH_3O: a dominant route under dense-molecular-cloud conditions

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The successive addition of H atoms to CO in the solid phase has been hitherto regarded as the primary route to form methanol in dark molecular clouds. However, recent Monte Carlo simulations of interstellar ices alternatively suggested the radical-molecule reaction CH_3O + $H_2CO \rightarrow CH_3OH$ + HCO, in addition to CH_3O + H → CH_3OH, as a very promising and possibly dominating (70—90\%) final step to form CH_3OH in those environments [1]. Here, we compare the contributions of these two steps leading to methanol by experimentally investigating hydrogenation reactions on H_2CO and D_2CO ices, which ensures comparable starting points between the two scenarios. The experiments are performed under ultrahigh vacuum conditions and astronomically relevant temperatures, with H:H_2CO (or D_2CO) flux ratios of 10:1 and 30:1. The radical-molecule route in the partially deuterated scenario, $CHD_2O + D_2CO \rightarrow CHD_2OD$ + DCO, is significantly hampered by the isotope effect in the D-abstraction process, and can thus be used as an artifice to probe the efficiency of this step. We observed a significantly smaller yield of D_2CO + H products in comparison to H_2CO + H, implying that the CH_3O-induced abstraction route must play an important role in the formation of methanol in interstellar ices. Reflection-Absorption InfraRed Spectroscopy (RAIRS) and Temperature Programmed Desorption-Quadrupole Mass Spectrometry (TPD-QMS) analyses are used to quantify the species in the ice. Both analytical techniques indicate constant contributions of ~80% for the abstraction route in the 10-16 K interval, which agrees well with the Monte Carlo conclusions.

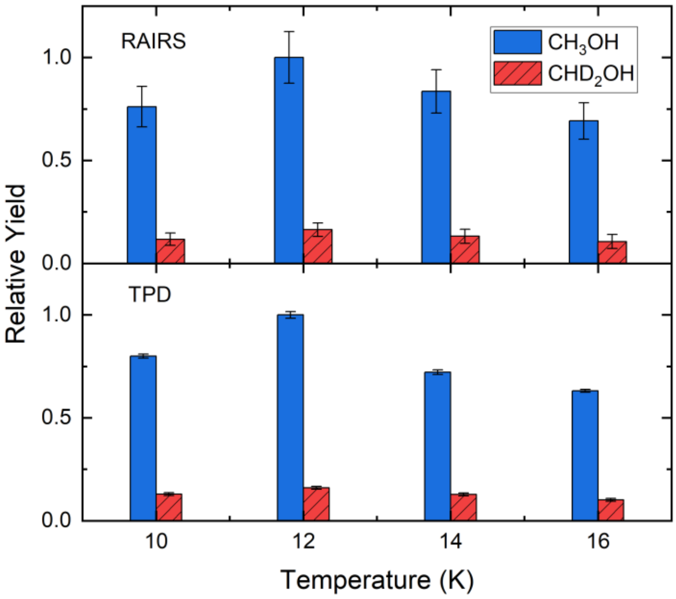

Figure 1: Upper panel: Yields of CH_3OH and CHD_2OH relative to the column density of CH_3OH after 360 minutes of H_2CO+H codeposition at 10, 12, 14, and 16 K, as derived from the RAIRS data. Lower panel: Same as the upper panel, but for the TPD-QMS data.

References

[1] M. A. J. Simons, T. Lamberts & H. M. Cuppen, 2020, A&A 634, A52.

On-resonance infrared irradiation of interstellar ice analogues: mixtures of H_2O and CO_2

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The icy mantles on interstellar dust grains are postulated to play a major role in the formation of numerous simple and complex organic species. Only 6 molecular species have so far been detected in the solid state - H_2O, CO, CO_2, CH_3OH, NH_3 and CH_4, in order of abundance [1,2]. However, it is suggested that there are many more species present in these icy mantles, such as complex organic molecules (COMs). The recent launch of the James Webb Space Telescope (JWST) targets the detection of these species and the high sensitivity and resolution of the infrared instruments aboard JWST will enable the observation of spectral changes associated with different ice morphologies, thermal histories, and mixing environments in star-forming regions. In order to corroborate the interpretation of these novel JWST results, laboratory experiments are required to study these ice morphologies and how they change as a result of environmental influences, such as the presence of other molecular species or radiation.

The Laboratory Ice Surface Astrophysics (LISA) end station at the free electron laser (FEL) facility FELIX in Nijmegen, the Netherlands, has been designed to study the effect of the release of vibrational energy in the bonding network of ices of interstellar relevance [3,4]. By employing the wide tunability and high intensity of the FELs at FELIX, interstellar ice analogues grown in the ultra-high vacuum chamber of LISA are selectively irradiated on resonance in the mid-infrared range. Previous studies of the resonant MIR irradiation of porous amorphous solid water (pASW) showed a restructuring of the ice. The modification of the IR absorption band profile indicated a growing crystalline-like contribution and a decreasing amorphous one [4]. Restructuring after resonant IR excitation was also observed in other ices, such as pure CO_2 and mixtures of H_2O and CO_2 [3].

Our latest experiments covered mixtures of CO_2 and H_2O in different ratios. We observed clear irreversible structural changes upon on-resonance irradiation of the different ice samples. From our set of observations, it appears that H_2O and CO_2 restructure together, i.e. when irradiating CO_2 changes are observed in H_2O and vice versa which implies an energy exchange mechanism between the species. To explain these results on a microscopic level, we will employ molecular dynamics simulations [5,6]. In future experiments we aim expand our studies to layered ices, as well as mixtures of other molecular species.

References

[1] Herbst, E. and E.F. van Dishoeck, Annu Rev Astron Astr, 2009. **47**: p. 427.
[2] Boogert, A.C.A. *et al.* Annu Rev Astron Astr, 2015. **53**(1): p. 541-581.
[3] Ioppolo, S. *et al.*, J. Mol. Spectrosc., 2022. **385**: p. 111601
[4] Noble, J.A. *et al.*, J Phys Chem C, 2020. **124**(38): p. 20864-20873.
[5] Cuppen, H.M. and E. Herbst, Astrophys J, 2007. **668**(1): p. 294-309.
[6] Cuppen, H.M. and R.T. Garrod, A&A, 2011. **529**.

Quantifying non-thermal desorption from NH_3 ices - Comparative study of photon and electron irradiation in the valence- and core –shell energy ranges.

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In the interstellar medium, the relative abundances of gaseous and solid nitrogen remain controversial [1]. Besides the difficulty in observing atomic N and N_2, the quantities of nitrogen returning to the gas phase from the ices by photo-processing of the ice mantles are not well constrained. In particular, in star-forming regions, NH_3 containing ices are exposed to UV and X-Ray photons [2]. This leads to a non-thermal photodesorption, induced by the primary radiation or by the exothermic photochemistry (recombination of the secondary species created in the ice mantles, i.e. the chemical radicals and the electrons).

In order to quantify the non-thermal desorption of N containing molecules and to have a deeper understanding of the complex surface chemistry in ice mantles, we have conducted comparative measurements of photo- and electron-induced desorption (PSD and ESD) in condensed NH_3. Two setups were used for these experiments, the SPICES setup of the LERMA group, and the E/SOLID setup housed at ISMO. In both systems, NH_3 ices are formed by cryogenic deposition (50-100 molecular layers), and the desorption of neutral species is measured by mass spectrometry. Thermal desorption experiments (TPD) were used to calibrate the desorption signal, the ice thickness and for the analysis the processed ice layers. The SPICES setup was coupled to two SOLEIL synchrotron beamlines: (i) DESIRS, valence-shell range (6-12 eV) and (ii) SEXTANTS, core-shell range (395-420 eV, N-K edge) at the SEXTANTS beamline. The twin electron irradiation experiments were performed using the E/SOLID setup, in the low-energy range as well as at 385 eV, in order to mimic the secondary Auger electrons known to be major vectors of chemical changes in X-ray irradiations at the N-K edge.[3,4]

Desorption yields per incident particles are compared for photon and electron irradiation either as a function of the incident energy in the low-dose regime (spectroscopic study), or as a function of the cumulated dose at a fixed irradiation energy (kinetic study).

- In the valence shell range, NH_3 and N_2 are the major desorbing species, with an apparent energy threshold at ~6 e□V, showing that both direct and indirect desorption occurs, involving the chemistry in the ice. Different mechanisms at play will be discussed.
- In the core-shell range, again NH_3 and N_2 are the major desorption products, keeping in mind that N_2 is also remains trapped in the ice. The remarkable matching between the photo-desorption yields in the ionization continuum and the ESD at 385 eV confirms the key role of the Auger electrons in the photodesorption process.[3,4]

References

[1] R. Le Gal, et al. *Astron. Astrophys.*, vol. 562, p. A83, févr. 2014, doi: 10.1051/0004-6361/201322386.
Sipilä et al, *MNRAS*, vol. 487, n°1, p1269-1282, doi : 10.1093/mnras/stz1344
[2] M. Bertin *et al.*, *Astrophys. J.*, vol. 817, n° 2, p. L12, janv. 2016, doi: 10.3847/2041-8205/817/2/L12. ;
R. Dupuy *et al.*, *Nat. Astron.*, vol. 2, n° 10, p. 796‑801, oct. 2018, doi: 10.1038/s41550-018-0532-y.
[3] R. Basalgète *et al.*, *J. Chem. Phys.*, vol. 157, n° 8, p. 084308, août 2022, doi: 10.1063/5.0100014.
[4] Daniela Torres-Díaz et al., Cryogenic Chemistry and Quantitative Non-Thermal Desorption from Pure Methanol Ices: High-Energy Electron versus X-Ray Induced Processes. *Chem.Phys.Chem, under revision*

VUV photodesorption from interstellar ices analogues: Energy, flux and fluence effects on the photodesorption yields from CO_2 ices

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Detection of several molecules in the gas phase in the coldest regions of the interstellar medium, ISM (molecular clouds, protoplanetary disks…), has motivated intense laboratory experiments with the purpose of quantification and a better understanding of indirect desorption processes[1]. Condensation of gas-phase atoms and molecules on the surface of cold dust grains in these regions are known to form an icy mantle rich in molecular compounds which are trapped in the solid phase. The thermal desorption being negligible in these regions, there must be non-thermal desorption processes at play to explain actual gas phase abundances. Despite its potential central role in the gas-to-ice abundance ratio, some aspects of the photodesorption are still poorly understood or constrained. Here we have investigated the photodesorption from solid CO_2 at 15K under different flux, energy and fluence conditions in order to get more insights on its photodesorption mechanism, which was before only partially understood[2].

Experiments were carried out in the UHV chamber SPICES coupled to the beamline DESIRS in the VUV range (7-14eV) at the synchrotron facility SOLEIL. Molecular ices of thickness of 50 ML of CO_2, grown on Au substrate at 15K, were irradiated, and the amount of desorbed neutral species were measured using a quadrupole mass spectrometer. The flux conditions were varied either by selecting zero (10^{14-15} $s^{-1}cm^{-2}$) or first order (10^{12-13} $s^{-1}cm-^{2}$) of the grating of the DESIRS beamline. The study was performed at different photon energies, in order to selectively excite the studied molecules or any expected photoproduct.

We present the outcomes of these experiments performed to investigate the flux and fluence dependent photodesorption yields of CO_2, and discuss the relevance of such experimental measurements to the astrophysical conditions of the interstellar medium.

References

[1] Oberg et al. A&A 496 281 (2009) ; Martin-Domenech et al. A&A 584 A14 (2015)
[2] Fillion et al. Faraday discuss 168 533 (2014)

Quantifying the contribution of Auger electrons in XESD: Pure methanol ice

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X-Ray irradiation of interstellar ices analogues has been shown to produce non-thermal desorption of intact molecules and their fragments (e.g. H_2O [1] and CH_3OH [2]), as well as contributing to the chemical enrichment of the gas phase [2], [3]. The proposed desorption mechanism is X-ray induced electron stimulated desorption (XESD), which involves the Auger decay of the excited/ionised molecules following X-ray photon absorption, and the subsequent thermalization of the Auger electron in the ice [1], [2].

With the aim of quantifying the role of the released electrons in the desorption process and of comparing it to the global X-ray desorption yields [2], we have irradiated pure methanol ices deposited at 23 K with 505 eV electrons under UHV conditions, to simulate the Auger electron originating from a O 1s core absorption in the ice, as illustrated in Figure 1. The effects of the irradiation flux and the ice thickness on desorption were studied in the range of $0.8 – 7.0\times10^{13}$ $s^{-1}cm^{-2}$ and in the multilayer regime, respectively. Desorption of neutral fragments was probed with a quadrupole mass spectrometer (QMS) during irradiation. Several m/z were recorded. After calibrating the QMS signal using temperature programmed desorption experiments (TPD) we derived desorption yields in molecules per incident electron.

Desorption of the parent molecule (CH_3OH) was observed, and the corresponding yield is consistent, in order of magnitude, with the yield derived in X-Ray irradiation experiments [2]. Electron irradiation was observed to lead to the synthesis and desorption of stable products [4], mainly CO, CO_2, CH_4/O, H_2O formaldehyde (H_2CO) and ethane (C_2H_6), as well as other minor products. Qualitative data from post-irradiation TPD spectra corroborates the presence of irradiation products and supports the interpretation of the mass spectra recorded during electron irradiation.

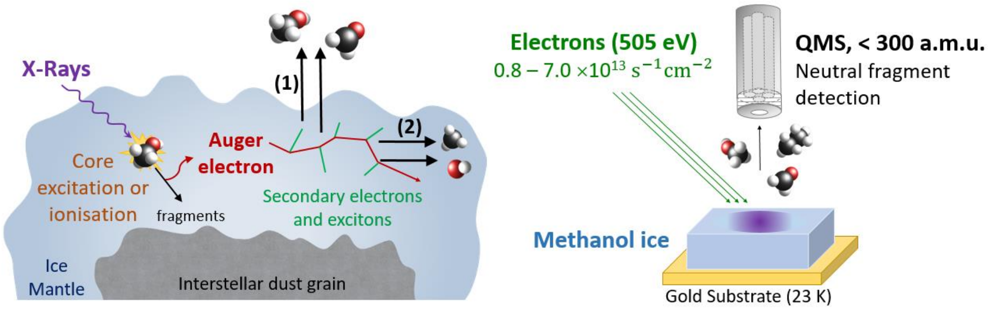

Figure 1: (Left) Simplified diagram of the thermalization path of an Auger electron in the ice mantle of an interstellar grain, which can lead to desorption (1) and fragmentation (2). Reactive fragments created in the ice can react to form new products, which can subsequently desorb. (Right) Scheme of the electron irradiation experiments done.

References

[1] R. Dupuy *et al.*, 2018, Nat Astron 2, 796
[2] R. Basalgète *et al.*, 2021, A&A 647, A35
[3] A. Jiménez-Escobar *et al.*, 2018, ApJ 868, 73
[4] D. Torres-Díaz *et al.*, *under revision*

Influence of nuclear spin conversion of H_2 molecules on the chemistry of the interstellar medium - Experiment and modelling

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Hydrogenated molecules like H_2 and H_2O exist in several nuclear spin configurations due to the Pauli exclusion principle. These configurations are called ortho (parallel proton spins) and para (antiparallel proton spins). The ortho and para populations have been regularly determined by observations in different regions of space in far UV absorption (Copernicus, FUSE) and in IR and sub-mm emission (ISO, Spitzer, Herschel). The ortho/para ratio (OPR) depends on physico-chemical processes in these environments such as chemical formation, reactive collisions, adsorption and desorption effects of molecules on ice grains and could be a tracer of the history of molecules. In order to interpret the astronomical observations, it is important to confront the observations with the outputs of the more complete astrochemical model. H_2 is the most abundant molecule in the interstellar medium and is known to be the main reactant involved in the reaction chain to form hydrogenated molecules (Van Dishoeck *et al.* 2013), the ortho/para ratio of H_2 then plays a role in the chemical evolution of molecules like water (Bron *et al*. 2016, Dislaire *et al*. 2012).

For this purpose, we update the Meudon PDR code to take into account selective ortho/para chemistry in the gas and on grains. A gas-phase chemical network which takes into account the ortho/para aspect of the species (like the UGAN network developed by IPAG-Grenoble) is implemented to compare the models in PDRs with and without ortho/para species. Moreover, the ortho/para ratio of H_2 in gas phase could be affected by desorption processes on interstellar grains in cold regions and has to be implemented in the PDR Code. It is then necessary to know the characteristic time for the equilibration of the nuclear spin states of H_2 on solid water at low temperature and the relative abundances of the nuclear spin states during desorption. To address these questions, we are currently developing a new laboratory experiment (COSPINU 2) in an ultra-high vacuum chamber to perform in situ measurements of the nuclear spin conversion of H_2 deposited on H_2O ices using Fourier transform infrared spectroscopy.

First results obtained with the new version of the Meudon PDR code using a chemical network restricted to a few ortho/para species will be presented ($H_2^+ + H_2 \longrightarrow H_3^+ + \mathrm{H}$). Measurements reported in the literature on the characteristic time of the nuclear spin conversion of H_2 on solid water have shown large discrepancies - ranging from minutes to hours - (Ueta *et al.* 2016, Chehrouri *et al*. 2011, Sugimoto and Fukutani. 2011). We will present how the recent results obtained with COSPINU 2 fit into this context.

Difficult ice chemistry: Identifying complex molecules in electron irradiated ice using probabilistic detection methods

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Ices play an important role in the overall chemistry of space. Ice layers are present on interstellar dust grains, icy moons, and Kuiper belt objects. The pristine ices consist mainly of simple molecules, for example H_2O, N_2, and CH_4 [1, 2]. These ice layers are of special interest as thermal processing and irradiation of the ices can lead to the formation of more complex molecules, including prebiotic molecules [3, 4, 5].

We simulate ice chemistry with laboratory experiments using the ICEBEAR setup. Briefly, a copper sample holder is placed in a high vacuum chamber (P<1E-8 mbar) and cooled down to temperatures as low as 4 K using a cryostat. Gas can be injected into the chamber via a leak valve, where it condenses onto the sample holder due to the low temperatures, forming a layer of ice. The temperature of the sample holder is monitored by a diode, attached to a temperature controller, with which the sample holder can be heated via resistive heating. The setup is equipped with an electron gun to process the ice.

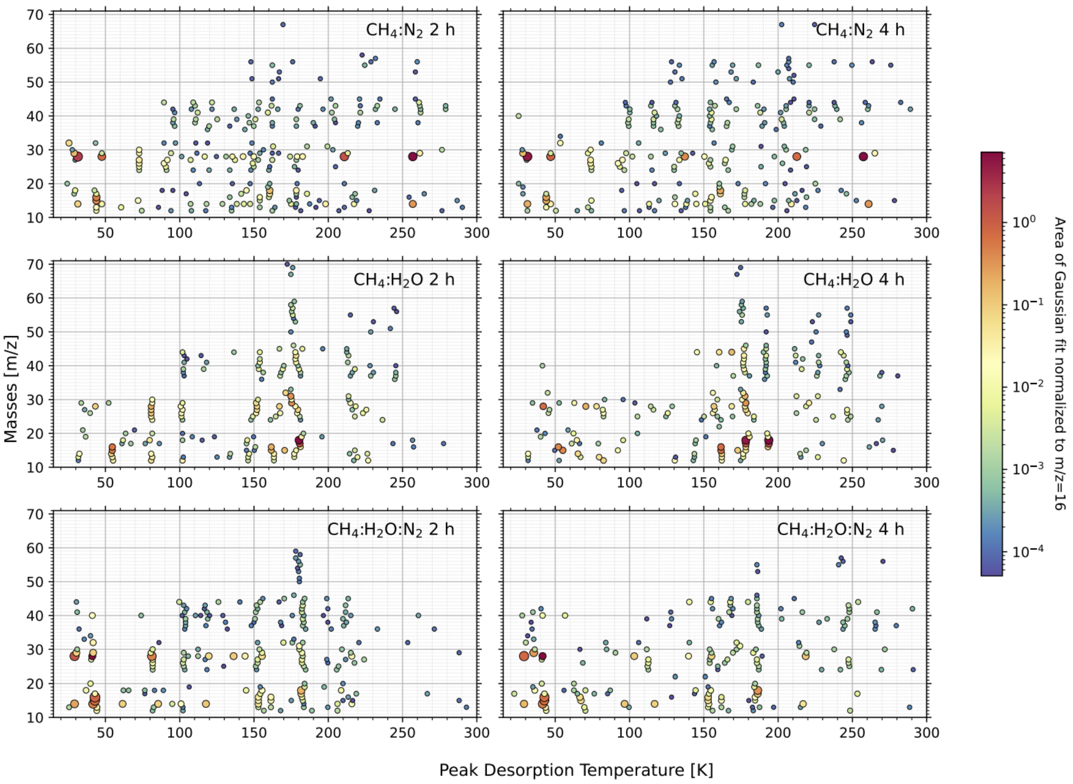

Figure 1: The location of desorption peaks as a function of the temperature for the different ice mixtures, irradiated for 2 or 4 hours.

In this contribution, the results of temperature programmed desorption – mass spectrometry (TPD-MS) measurements of electron irradiated ice mixtures (CH_4, H_2O, N_2) are analyzed and the influence of the different components on the formation of volatile irradiation products studied.

The gas mixtures are deposited at 20 K and subsequently irradiated with 5 keV electrons. During the irradiation, a change in color of the irradiated spot is observed, suggesting processing of the ice. After the irradiation, a TPD-MS measurement is performed, during which the sample holder is heated from 20 to 300 K with a heating ramp of 2 K/min and the desorption products monitored using a QMS. The TPD-MS results provide information about the desorption temperatures and mass spectrometric “fingerprints” of the molecules that are desorbing.

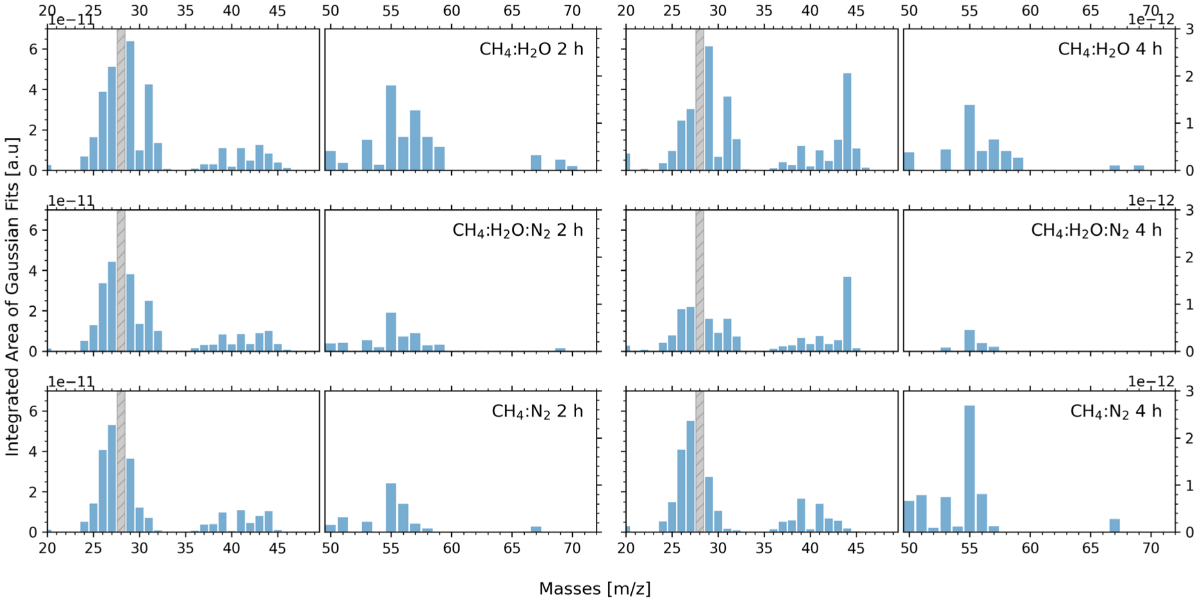

Figure 2: Integrated areas of the TPD signals for each m/z over the temperature range 60 K to 300 K. Differences in the presence and abundance of signal can be seen as a function of irradiation duration as well as ice composition. M/z=28 has been included due to the strong influence of N_2 on the signal.

Our studies show that a variety of molecules form in these irradiation experiments. The starting composition and irradiation duration does influence which molecules form, but we also find significant changes in desorption temperatures and abundances when the same molecules are formed in different mixtures. These differences are signposts of how reaction pathways and desorption temperatures are affected by the chemical environment of the ice.

References

[1] Boogert, A.C. Adwin, Perry A. Gerakines, and Douglas C.B. Whittet (2015). “Observations of the Icy Universe”. Annual Review of Astronomy and Astrophysics 53.1, pp. 541–581

[2] Öberg, Karin & Bergin, Edwin. (2020). Astrochemistry and compositions of planetary systems.

[3] Abou Mrad, Ninette et al. (May 2016). “Methanol ice VUV photoprocessing: GC-MS analysis of volatile organic compounds”. MNRAS 458.2, pp. 1234–1241

[4] Allamandola, L. J. et al. (1999). “Evolution of interstellar ices.” In: Space science reviews 90 1-2, pp. 219–32

[5] Herbst, Eric and Ewine F. van Dishoeck (Sept. 2009). “Complex Organic Interstellar Molecules”. In: Annual Review of Astronomy and Astrophysics 47.1, pp. 427–480

[6] Padovani, M., D. Galli, and A. E. Glassgold (July 2009). “Cosmic-ray ionization of molecular clouds”. In: AAP 501.2, pp. 619–631

[7] Oba, Y., Takano, Y., Naraoka, H. et al. Nucleobase synthesis in interstellar ices. Nature Communications 10, 4413 (2019). https://doi.org/10.1038/s41467-019-12404-1

A systematic FTIR and VUV investigation of ion, electron, and thermal processing of ethanolamine ice

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Ethanolamine (EtA) is one of the key components of the building blocks of cell membranes, i.e., phospholipids. Its recent detection in the interstellar medium (ISM) by Revilla et al. [1], could support an exogenous origin of life-relevant biomolecules. The survivability and stability of EtA under ISM conditions, have not yet been demonstrated. Hence, we have systematically exposed pure EtA and H_2O:EtA mixed ices to some of the main energetic mechanisms that are known to induce changes within the ice material, i.e., ion, electron, and thermal processing of the ice under controlled laboratory conditions (assuming EtA mainly forms in interstellar ice grains).

FTIR and VUV spectra of EtA-rich ices are collected during 1 keV electron and 1 MeV He^+ ion irradiation at different doses at 20 K. Products like H_2O, CO, CO_2, OCN^-, HNCO, NH_3, C_2H_5OH, and CH_3CHO have been identified.

Electron irradiation destroys 29.3% of the pure EtA ice and 7.98% of the EtA in the H_2O:EtA mixed ice, while He^+ ion irradiation destroys almost all the EtA (99.6%) in a water environment. Such remarkable differences correlate with the different penetration depth of ions versus electrons in thicker ices.

We have thus observed that, EtA mixed in water ice is more stable than when in its pure form. Furthermore, if H_2O:EtA mixed ice is present in Kuyper Belt Objects (KBOs), it would only have a half-life of 910 years, showing that it is efficiently destroyed. Whereas EtA diluted in water ice in cold dense clouds would have a half-life of 1.7×10^7 years, suggesting that it is more stable under ISM conditions.

References

[1] Rivilla V. M., et al., 2021, Proc. Natl. Acad. Sci., 118

Amorphous and crystalline pyridine ices irradiated by MeV ions

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Pyridine (C_5H_5N) is an important complex organic molecule (COM). It is heterocyclic and appears in compounds such as vitamins and pharmaceuticals [1]. Although pyridine has not yet been directly observed in space, Parker et al. (2015)[2] have revealed a potential pathway to a facile pyridine synthesis in the gas phase via the reaction of the cyano vinyl (C_2H_2CN) radical with vinyl cyanide (C_2H_3CN) in high temperature environments simulating conditions in carbon-rich circumstellar envelopes.

Pyridine ices, in amorphous and crystalline phases, have been irradiated with 396 MeV Ar^{17+} and 61 MeV Kr^{15+} at 10, 15 and 130 K in the SME and IRRSUD beam lines of the GANIL heavy ion accelerator facility. Infrared spectroscopy was employed to follow the structural and chemical evolution of the samples as a function of projectile fluence. The apparent destruction cross sections, σ_d^{ap}, which includes the dissociation effects of radiolysis and also ejection of particles by sputtering, were measured for all samples. The local doses needed to complete amorphization of the crystalline samples were calculated as well, see Fig. 1.

Pyridine ices that were initially crystalline present apparent destruction cross sections approximately three times higher than amorphous ones. However, after amorphization is completed, originally crystalline samples have the same σ_d^{ap} as ices that were initially amorphous. Targets irradiated at 130 K are more radioresistant than the ones at 10 K, they have smaller destruction cross sections σ_d^{ap}.

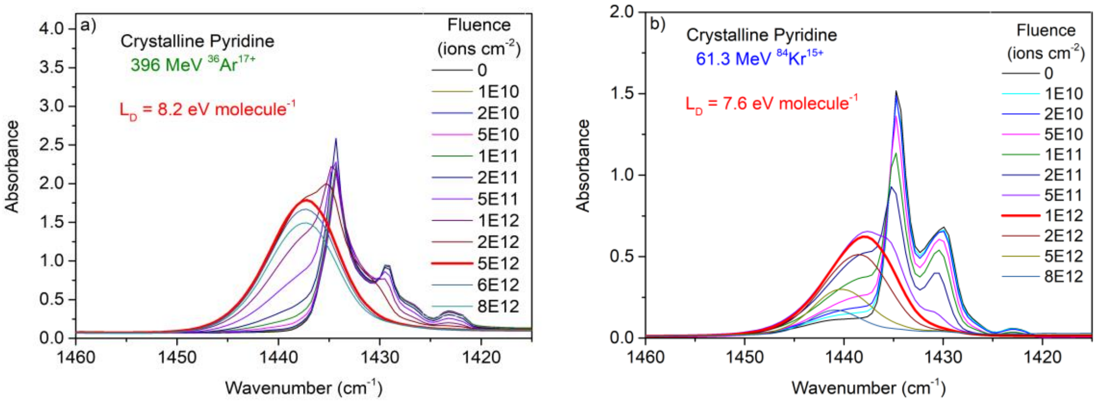

Figure 1: Evolution of infrared spectra of crystalline pyridine with projectile fluence of (a) 396 MeV Ar17+ and (b) 61.3 MeV Kr15+ ion beams irradiated at 15 K. Thicker red curves indicate the transition fluence value to complete amorphization. Obtained local doses are 8.2 and 7.6 eV/molecule, respectively.

References

[1] E. F. Scriven, & R. Murugan, 2000, Kirk-Othmer Encyclopedia of Chemical Technology.
[2] D. S. Parker, R. I. Kaiser, O. Kostko, et al. 2015, Physical Chemistry Chemical Physics, 17, 32000.

Constraints on the composition of methanol-bearing Trans-Neptunian Objects and Centaurs from NIR spectroscopy of irradiated ices

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Methanol has been detected at the surface of the Centaur Pholus [1], the Trans-Neptunian Object (TNO) 2002 VE$_{95}$ [2] and the cold classical Kuiper Belt Object Arrokoth [3]. Methanol is often found alongside water, the most widespread ice of the outer solar system [4]. Thermodynamical studies predict that water and methanol ices should be ubiquitous on small bodies like Arrokoth as they are the two most refractory ices [5]. Methanol is detected in the coma of comets where its relative abundance to water ranges from <0.2% to 4.8% [6]. Methanol is also omnipresent in interstellar ices where its abundance can be higher, in the <0.2% to 31 % range [7]. The methanol detected on TNOs could be directly inherited from the protostellar cloud as these objects are thought to be remnants of the building blocks of the outer solar system. But even if they stayed dynamically stable, like Arrokoth over 4.5 Gyrs [8], their surfaces have undergone physico-chemical changes as they were subjected to different weathering events, particularly solar wind and cosmic ion irradiation [9]. The surfaces of Pholus, 2002 VE$_{95}$ and Arrokoth also present red slopes in the visible and near-infrared (Vis-NIR) range (the reflectance increases with wavelength). This effect is commonly associated to complex organic molecules similar to laboratory produced "tholins" [1,2,3]. Such red slopes can be reproduced in the laboratory upon irradiation of methanol [10]. Moreover, the ratio of the NIR bands of methanol used for its detection depends on the irradiation dose and the original composition of the ice [11]. Methanol can then be used as a proxy to constrain the origin and history of the objects that bear it. Until now, TNOs surfaces were observed in the Vis-NIR, while laboratory experiments of complex ices were mostly probed in the mid infrared (MIR) range where chemical information is easier to derive [12,13,14]. We aim at measuring and providing Vis-NIR spectra of irradiated methanol ices, pure and mixed with water, which were previously well characterized in the MIR, in support of past New Horizons and future JWST observations.

We use the INGMAR experimental setup to simulate the effects of ion irradiation at the surface of icy bodies [11]. INGMAR is a high-vacuum chamber connected to the SIDONIE ion accelerator, separator and implanter (part of the JANNuS-SCALP platform of IJCLab) [15]. The ices are formed by condensation of a gaseous mixture on a substrate cooled down to 60 K by a He-cryocooler. We use 30 keV H^+ ions to irradiate the ices, H^+ being the most abundant component of the solar wind and producing physico-chemical modifications mainly via inelastic energy loss. We monitor the physico-chemical changes upon irradiation of the ices by Vis-NIR-MIR spectroscopy. Transmittance spectra cover the 0.4 to 5 µm range while the reflectance spectra cover the 0.6 to 2.5 µm range. We investigate pure methanol ice and water-methanol ice mixtures of different proportions.

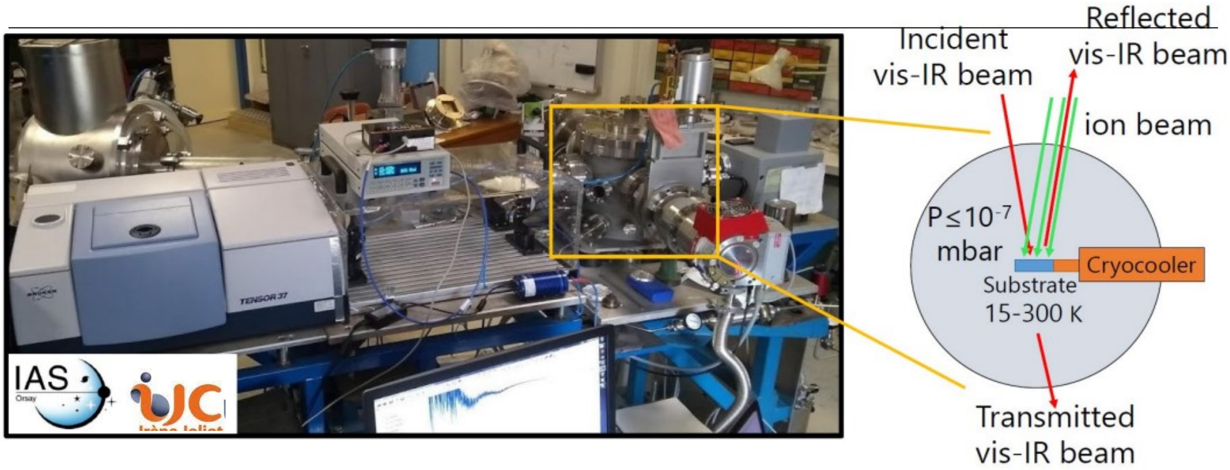

Figure 1: Schematic representation of the INGMAR experimental setup

The major irradiation products of CH_3OH are CO_2, CO, CH_4, H_2CO and H_2O, whose production yields depend on the dose and the relative abundances of water and methanol in the initial mixture [12,13]. To characterize the evolution of the irradiated ices, we focus specifically on three parameters. The first one being the CO/CO_2 ratio which varies as a function of irradiation dose and initial composition of the ices. The second one is the CH_3OH/H_2O as a function of irradiation. And finally, the Vis-NIR slope, defined by the normalized reflectivity gradient [16] between the J and R bands, at 1.25 and 0.68 μm respectively. The JR slope here characterizes the complex organic molecules produced by irradiation and was found to depend on the original water content of the ice mixture as increasing it produces less red spectra. We will see how combining the CH_3OH/H_2O ratio and the Vis-NIR slopes help constrain the irradiation history of the surfaces of TNOs and Centaurs. We will also show how the CO/CO_2 ratio derived from future JWST spectra of methanol-rich surfaces might shed further light on the evolution of these icy small bodies.

References

[1] Cruikshank et al. (1998) Icarus, 135.2, 389–407.
[2] Merlin et al. (2012) A&A, 544, A20.
[3] Grundy et al. (2020) Science, 367, 6481.
[4] Barucci and Merlin. (2020) The Trans-Neptunian Solar System, 109-126.
[5] Lisse et al. (2021) Icarus, 356, 114072.
[6] Dello Russo (2016) Icarus, 278, 301–332.
[7] Boogert et al. (2015) Annu. Rev. Astron. Astrophys, 53, 541-581.
[8] Stern et al. (2019) Science 364, 649.
[9] Strazzulla et al. (2003) C. R. Physique, 4, 791–801.
[10] Brunetto et al. (2006) ApJ, 644, 646.
[11] Urso et al. (2020) ApJ, 894, L3.
[12] Palumbo et al. (1999) A&A, 342, 551-562.
[13] Moore et al. (1996) Planet. Space Sci., 44, 927-935.
[14] Baratta et al. Planetary & Space Sci., 42.9, 759-766.
[15] Chauvin et al. (2004) Nucl. instrum. methods phys. res., Sect. A, Accel., spectrom. detect. assoc. equip., 521, 149-155
[16] Jewitt (2002) The Astronomical Journal, 123.2, 1039.

Oxygen ion irradiation of Titan aerosol analogs

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In its 13 years of operation, the Cassini-Huygens mission has revealed a complex chemical diversity of Saturn's moons Titan and Enceladus. Heavy molecules reaching several thousand atomic mass units [1, 2] and O+ ions [3] have been detected in Titan's atmosphere and magnetosphere, respectively. The heavy molecules are attributed to potentially nitrogenous polycyclic aromatic hydrocarbons [4, 5]. The energetic O+ ions deposit in Titan’s atmosphere [6] and are believed to alter the structure and chemical composition of these macromolecules by implantation. The products of this process, namely oxygenated organic molecules (prebiotics such as amino acids and nucleic bases), could have strong astrobiological implications.

The aim of this PhD project is therefore to study this process by irradiating organic materials (titan aerosol analogs or tholins, polycyclic aromatic hydrocarbons, pure organics). In addition to the possible oxygenation of these molecules, other processes like sample destruction rates (by e.g. sputtering) and the overall impact of irradiation on the chemical complexity will be investigated.

The irradiation experiments are performed at the Institut d'Astrophysique Spatiale / Irène Joliot Curie Lab and at the Grand Accélérateur National d'Ions Lourds (GANIL). In situ measurements with spectroscopy in the mid-infrared are executed during irradiation to determine the composition and spectral properties of the samples. Ex situ high resolution mass spectrometry (HRMS) experiments will reveal the chemical evolution, in particular the degree of oxygenation, of the samples.

By now, we have acquired 11 adenine and 9 tholin samples which were irradiated with O+ and Ne+-ions at varying energies (30, 50, 60, 70keV), temperatures (150, 300 K), and sample thicknesses (230, 350, 500 nm). We present preliminary result showing IR- and mass spectra of some irradiated samples. The question if implantation of oxygen takes place or how high the grade of oxygenation is, has yet to be determined. In the future, more samples will be prepared, irradiated and analyzed with possibly other methods like: i) structural analysis by attenuated reflectance micro-FTIR spectroscopy, ii) UV-visible spectroscopy in liquid phase, and iii) Raman spectroscopy.

References

[1] Waite, J.H., M.R. Combi, W.-H. Ip, T.E. Cravens, R.L. McNutt, W.T. Kasprzak, R.V. Yelle, et al. "Cassini Ion and Neutral Mass Spectrometer: Enceladus plume composition and structure". Science 311 (2006): 1419- 22.

[2] Crary, F.J., B.A. Magee, K. Mandt, J.H. Waite Jr., J. Westlake, and D.T. Young. "Heavy ions, temperatures and winds in Titan's ionosphere: Combined Cassini CAPS and INMS observations". Planet. Space Sci. 57 (2009): 1847- 56.

[3] Cravens, T.E., I.P. Robertson, S.A. Ledvina, D. Mitchell, S.M. Krimigis, and J.H. Waite Jr. "Energetic ion precipitation at Titan." Geophys. Res. Lett. 35 (2008): ♯L03103.

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[4] López-Puertas, M., B.M. Dinelli, A. Adriani, B. Funke, M. García-Comas, M.L. Moriconi, E. D'Aversa, et al. " Large abundances of polycyclic aromatic hydrocarbons in Titan's upper atmosphere". Astrophys. J. 770 (2013): #132.

[5] Haythornthwaite, R. P., A.J. Coates, G.H. Jones, A. Wellbrock, J.H. Waite, V. Vuitton, and P. Lavvas. "Heavy positive ion groups in Titan's ionosphere from Cassini Plasma Spectrometer IBS observations," Planet. Sci. J. 2, (2021): #26.

[6] Hörst, S. M., Vuitton, V., & Yelle, R. V. (2008). Origin of oxygen species in Titan's atmosphere. Journal of Geophysical Research: Planets, 113(E10).

Modelling prebiotic molecules trapped in interstellar ice.

New DFTB/MM (QM/MM) Hybrid Method and Real Time – TD-DFTB in deMonNano : implementation and first applications.

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Formation, distribution and behaviour of complex organic molecules (COM's) in space is an important subject of research to the better understanding of the initial condition for the appearance of life on Earth. Furthermore, the study of high energy chemical processes in the interstellar medium (cosmic radiation's effect) and in solar system (solar wind's effect), is been of high interest [1].

The aim of this work is to study astrophysical molecules trapped in interstellar ice systems under the effect of high energy radiation. These ices are characterised by being large systems, with large number of atoms.

QM/MM hybrid method has become a very popular tool for molecular systems' simulations with a large number of atoms, appearing as a good compromise between accuracy and computational costs. We report the implementation of QM/MM hybrid method [2] in the deMonNano software, using the Density Functional based Tight Binding (DFTB) [3,4], an approximated DFT scheme, combined with Molecular Mechanic (MM) approach, namely Force Fields (FF) of class 1, such as OPLS-AA and AMBER-families of FFs. A complete implementation was performed using the QM/MM additive coupling scheme [5].

In addition, the investigation of high energy chemical processes requires the explicit simulation of the electronic dynamics beyond the Born Oppenheimer approximation [6].
As first step towards such dynamics, we will report the implementation of Real Time TD-DFTB in deMonNano, consisting in solving the Time-Dependent Schrödinger equation within the DFTB [7], where the electronic density matrix is propagated along time.

We report a brief introduction to new DFTB/MM and RT-TD-DFTB implementations as well as the first applications on glycine prebiotic molecule trapped in an interstellar ice. PAH and pyridine interstellar systems will be a matter of future studies.

References

[1] Ioppolo, S., et al. *Nature Astronomy* 5.2 (2021): 197-205.
[2] Groenhof, G. *Biomolecular Simulations* (2013): 43-66.
[3] Elstner, M., et al. *Physical Review B* 58.11 (1998): 7260.
[4] Spiegelman, F., et al. *Advances in physics: X* 5.1 (2020): 1710252.
[5] Yusef Buey, M., Mineva, T., and Rapacioli, M. *Theoretical Chemistry Accounts* 141.3 (2022): 1-10.
[6] Alvarez-Ibarra, A., et al. *Royal Society of Chemistry*, 2021. 117-143.
[7] Niehaus, T. A., et al. *The European Physical Journal D-Atomic, Molecular, Optical and Plasma Physics* 35.3 (2005): 467-477

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Meteorites, Organic Astrochemistry, Origins of Life, and Sample-Return Missions

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Carbonaceous chondrites (carbon-rich meteorites) represent some the oldest and most primitive pieces of material formed in the Solar System; indeed, they could even be older than the Sun itself. These carbon-rich meteorites may have delivered an important concentration of organic compounds and water to the primitive Earth. Multiple organic classes, including those required for life (e.g., amino acids, carboxylic acids, nucleobases, and polyols) have been identified from carbonaceous chondrites, providing valuable insights into the chemical inventory of the early Solar System, the primordial synthesis of organic matter, and the question of how life appeared on Earth [1].

Amino acids constitute the basic building blocks of all protein-based living organisms on Earth and thus, they are among the most intriguing and studied organic compounds found in carbonaceous chondrites. Homochirality (predominance of the L-enantiomer) in terrestrial biological proteins is a fundamental feature of life as we know it. L-enantiomeric excesses have been observed in some meteoritic amino acids, raising interesting questions about a potential link between meteorites and terrestrial homochirality [2]. In addition, the stable isotopic compositions (D, ^{13}C, ^{15}N) of meteoritic organic compounds provide information on their formation mechanisms and histories [3]. Contrasting the molecular distribution, chirality, and isotopic values of meteoritic organic compounds in a wide range of carbonaceous chondrites provide is key to fully understand the ubiquitous environments and universality of their occurrence, and to solve current challenges related to the synthesis and destruction (and new formation) or overall fractionation processes faced by meteoritic organic compounds [4].

Our extensive investigation on the abundance and molecular distribution of amino acids, and other biologically relevant molecules extracted from meteorites provide important insights on the composition and environments of the protosolar nebula, the meteorite parent bodies, and thus, the chemical inventory at the formation of the solar system and the potential link between extraterrestrial organic compounds and the emergence of life on Earth. Finally, the collective analyses of meteoritic organic compounds have been pivotal to the asteroid sample return missions Hayabusa2 (JAXA, December 6, 2020) and OSIRIS REx (NASA, September 24, 2023).

References

[1] D. P. Glavin et al. “Primitive Meteorites and Asteroid”, ed. Elsevier: Amsterdam, Netherlands, 2018, p. 205-271.
[2] J. E. Elsila et al. 2016, ACS Cent. Sci. 2, 370.
[3] L. Chimiak et al. 2021, Geochim. Cosmochim. Acta 292, 188.
[4] J. C. Aponte et al. 2017, ACS Earth Space Chem. 1, 3.

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The remarkable discovery by the Cassini spacecraft of exospheric plumes emanating from Enceladus into space [1] revolutionised our understanding of ocean-bearing icy moons in the Solar System. The on-board magnetometer showed a disturbance in Saturn's magnetosphere due to plumes outgassing [2], whereupon closer flybys of the icy moon were planned. The observation of the plumes' composition further revealed the presence of complex organic molecules [3], hereby raising the question of their origin. A study by Nölle et al. [4] evidenced how on their outward journey to Saturn's E-ring from 4 to 8 Saturn radii, the organic portion in icy grains diminishes owing to the energetic bombardment by photons, plasma particles or cosmic rays.

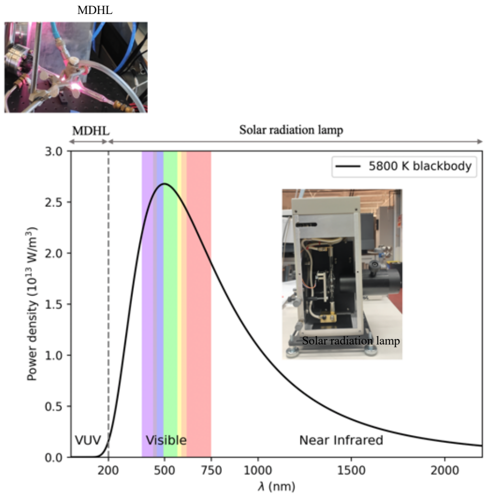

Figure 1. The solar SED following a blackbody radiation at 5800K. A microwave discharge hydrogen-flow lamp or MDHL (left), simulates radiation in the VUV, while the solar radiation lamp covers emissions above 200nm (right).

Our objective is to better understand what role photolysis plays in the solid state chemistry of Enceladus ices and whether it can potentially explain the observed chemical complexity of the plumes. In this regard, we conducted an experimental study which aims at comparing irradiation-induced effects in analogue ices and their chemical evolution from the UV to a solar radiation lamp representing the solar spectral energy distribution (SED), particularly in the VIS and near-IR regime (Fig. 1). Past studies have extensively investigated the VUV irradiation of icy grains in the interstellar medium [5, 6], whereas little is known about photon irradiation of ices under environmental conditions characteristic for those found on ocean-bearing moons such as Enceladus.

By using an UHV chamber at the LfA, thin ices can be grown on a cryogenically cooled substrate. Hereby, infrared and mass spectroscopic techniques facilitate the monitoring of changes in the solid state as well as the detection of desorbing species from ice processes. With the aforementioned suite of laboratory tools, we expect to draw comparative conclusions between the photolysis effects in ices due to the emission, on one hand, in the VUV and, on the other hand, in the VIS and near-IR regime, while taking into consideration typical environmental conditions at Enceladus. This will clarify how the solar radiation affects the formation and evolution of C and O-bearing photoproducts on the surface of Enceladus.

References

[1] Porco, C. C., Helfenstein, P., & Thomas, P. C. et al. 2006, Sci, 311, 1393.
[2] Dougherty, M., Khurana, K., Neubauer, F., et al. 2006, Science, 311, 1406.
[3] Waite, J. H. et al., 2017 Science 356, 155–159.
[4] Nölle, L., et al., 2019, EPSC, 2019, EPSC-DPS2019-468.
[5] Linnartz, H. et al. 2015, Int. Rev. Phys. Chem., 34, 205.
[6] Muñoz Caro, G. M., et al. 2002 Nature 416, 403.

Pyrene dimer in interaction with water molecules: theoretical structures and energetics

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Polycyclic aromatic hydrocarbons (PAHs) are a family of molecules that have multiple research interests, especially in atmospheric science and in astrophysics/astrochemistry. Forty years ago, PAHs were proposed as the carriers of the aromatic infrared bands (AIBs), observed in many regions of the interstellar medium (ISM) [1]. Moreover, it is believed that in the colder and denser regions of the ISM, PAHs could freeze upon the icy mantle of interstellar dust grains and interact with other molecules like water [2]. Therefore, it is relevant to study theoretically and experimentally the field of PAH-water interactions (at the molecular and cluster size).

We present here a theoretical study of the interactions of the dimer of pyrene (Py), $C_{16}H_{10}$, with water clusters. Previous works focused on pyrene clusters on one hand [3], and on the interactions of a single PAH with water clusters on the other hand [4,5]. Combining this two approaches, we report the investigation of $(Py)_2(H_2O)_n$ (n=1,10) systems [6].

We used the following strategy to search for the most stable structures. First, Parallel-Tempering Monte-Carlo (PTMC) simulations were done to explore the potential energy surfaces of these clusters, using the DFTB potential (density-functional based tight-binding). Optimisations were then done, with the DFTB potential as well, and the lowest-energy structures were refined with DFT (density functional theory). For the lowest stoichiometries (n=1,5), it was found that the structures where the water cluster is on the side of the pyrene molecules (σ interactions) are almost always the most stable ones (except for n=3). Competition arises for the highest stoichiometries (n=6,10), and we notice a beginning of a solvation cage with the largest water clusters. Several dissociation channels were explored (evaporation of one water or pyrene molecule, separation into two homogenous subclusters, complete separation of the molecules) and "magic numbers" were determined. Thanks to this study of energetics, peculiar behaviours for n=4 and n=5 (in contrast with other stoichiometries) were unveiled and explained with their structural arrangement.

References

[1] Léger, A.; Puget, J. L. *Astron. Astrophys.* **1984,** *137,* L5-L8.
[2] Burke, D. J.; Brown, W. A. *Phys. Chem. Chem. Phys.* **2010,** *12,* 5947-5969.
[3] Dontot, L.; Spielgelman, F.; Rapacioli, M. *J. Phys. Chem. A* **2019,** *123,* 9531.
[4] Simon, A.; Noble, J. A.; Rouaut, G.; Moudens, A.; Aupetit, C.; Iftner, C.; Mascetti, J. *Phys. Chem. Chem. Phys.* **2017,** *19,* 8516-8529.
[5] Michoulier, E.; Armor, N. B.; Rapacioli, M.; Noble, J. A.; Mascetti, J.; Toubin, C.; Simon, A. *Phys. Chem. Chem. Phys.* **2018,** *20,* 11941.
[6] Leboucher, H.; Simon, A.; Rapacioli, M. submitted to *J. Chem. Phys.* (**2022**)

Effect of swift ion irradiation on pyrene and pyrene-water mixtures

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Polycyclic Aromatic Hydrocarbons (PAHs) represent significant amount of carbon in space both in gas and in solid phases [1]. Usually these PAHs molecules contain 50-100 C-atoms and representing clusters containing tens of PAH molecules. In dense clouds this very small grains can freeze out on cosmic dust. Individual PAHs can also condense onto dust grains as “guest molecules” in icy grain mantles [2]. When PAHs are exposed to ionizing radiation, they can be destroyed. It is therefore important to study the radioresistance of PAHs to ionizing radiation according to the environmental conditions (temperature, surrounding molecules, etc.) to predict their lifetime in space.

We report the results of an experimental study of irradiation the complex organic molecule pyrene and mixtures of pyrene and water in the solid phase at 20 K. The experiments were performed at a beam line of the ATOMKI ICA facility (Debrecen, Hungary) by C2+ (2 MeV) and H+ (2 MeV and 200 keV) projectiles (see. Fig. 1). The destruction of the initial molecules were followed by in-situ infrared absorption spectroscopy as a function of projectile fluence.

References

[1] Tielens A., Rev. Mod. Phys., A 85, 1021 (2013).
[2] Sandford S. A., ApJ, A 417, 815 (1993).

Molecular content in Si + C dust growth processes for laboratory astrophysics

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The outflows of C-rich AGB stars produce a rich, dusty chemistry in which silicon is of major importance. Our view of the molecular species involved in hydrocarbon growth and dust formation in these environments is still very limited. We study the chemistry of different forms of carbon in reaction with silicon using two dust reactors. By focusing on the hydrocarbon content formed in both reactors, we aim to learn more about the role of silicon in hydrocarbon formation under different temperature and pressure conditions.

In the Stardust setup [1], Si and C are sputtered with Ar, and aggregate in the presence of a lateral H_2 flow. Reaction temperatures are estimated at 500 – 1000 K. In PIRENEA 2 [2], one or two solid rods (Si and/or C) are laser vaporized in the presence of a He pulse which can be seeded with H_2 or C_2H_2. Temperatures are estimated at $\lesssim$4000 K in the plasma plume. For both setups, dust (analog) deposits were prepared for *ex-situ* analysis with the high-resolution laser desorption/ionization molecular analyzer AROMA [3].

The AROMA analyses of both dusty samples reveal a large variety of hydrocarbons, in particular of polycyclic aromatic hydrocarbons (PAHs) whose detection is optimized by the used laser scheme. The most abundant PAH in the mass spectra is found to be $C_{16}H_{10}^+$, which mimics findings in meteoritic materials [4]. The Stardust experiment clearly shows that Si can promote the formation of PAHs under circumstellar envelope conditions. In PIRENEA 2, the addition of Si in a C_2H_2 plasma leads to the growth of methyl-substituted PAHs. From the combined results, we conclude that Si does not inhibit PAH formation under higher temperature and pressure conditions. Future research will consider the role of iron in hydrocarbon formation and growth.

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References:

[1] L. Martínez *et al.* (2020). Nat. Astron., **4**(1), 97–105.
[2] A. Bonnamy *et al.*, (2018), 22nd Int. Mass Spectrom. Conf., Florence link to poster
[3] H. Sabbah *et al.*, (2017), Astrophys. J., **843**(34), pp. 1–8
[4] H. Sabbah *et al.* (2022) Astrophys. J. **931**(2), 91.

Providing essential laboratory data to detect complex organic molecules in JWST observations of interstellar ices

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The detections of gas-phase molecules considered building blocks of life toward protostars (e.g., ALMA-PILS, [1]) and in comets (Comet 67P/Churyumov-Gerasimenko, [2]) indicate that complex organic molecules (COMs) can be formed in space conditions. Nevertheless, the exact formation pathways of these COMs in the interstellar medium (ISM) are still an open question. The upcoming James Webb Space Telescope (JWST) observations will bring a new dimension to this scenario by looking at interstellar ices in dark clouds and objects in the early stages of star formation. Several hours of JWST observations have been granted to look at interstellar ices in a variety of astrophysical conditions (e.g. ERS Ice Age, GTO/1290, GO/1959). A positive detection of COMs in ices will put constraints on the formation pathways of these species in space environments. To interpret these observations, a large collection of mid-infrared spectra of frozen molecules in conditions that simulate interstellar environments is essential. Here, it is presented an overview of the laboratory ice spectroscopy work carried out in the Laboratory for Astrophysics at the Leiden Observatory (e.g.,[3,4]) and the updated version of the Leiden Ice Database for Astrochemistry (LIDA, [5]).

References

[1] J. K. Jørgensen, M.H.D. van der Wiel, A., Coutens, J.M. Lykke, H.S.P. Müller., E.F. van Dishoeck, H. Calcutt, P. Bjerkeli, T.L. Bourke, M.N. Drozdovskaya & C. Favre, 2016, A&A 595, A117.

[2] K. Altwegg, H. Balsiger, J.J. Berthelier, A. Bieler, U. Calmonte, S.A. Fuselier, F. Goesmann, S. Gasc, T.I. Gombosi, L. Le Roy & J. de Keyser, 2017, MNRAS, 469, (Suppl_2) S130-S141.

[3] M. G. Rachid, N. Brunken, D. de Boe, G. Fedoseev, A.C.A. Boogert, & H. Linnartz, 2021, A&A, 653, A116.

[4] M.G. Rachid, W. R. M Rocha, & H. Linnartz, H., 2022, A&A, 665, A89.

[5] W. R. M. Rocha, M. G. Rachid, B. Olsthoorn, E. F. van Dishoeck, M. K. McClure & H. Linnartz, 2022, A&A, 668, A63.

Isomer discrimination of trapped pyrene related cations using visible MPD spectroscopy

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Isomerism finds its importance and challenges in many research fields, as isomers differ in their structural and chemical properties. Polycyclic aromatic hydrocarbons (PAHs), which are key species in combustion but also in astrochemistry comprise many isomers, which can be involved selectively in different chemical processes.

In this work, we focus on the characterization of PAH cations at two different m/z, namely the pyrene cation isomers (m/z=202.078) and the isomers of the –H fragment of the methyl pyrene cation (m/z=215.086) by using multiple photon dissociation (MPD) spectroscopy in the PIRENEA experimental setup [1]. To differentiate the isomers, action spectra and fragmentation patterns are used, which are recorded as a function of wavelength and time of irradiation time (number of laser pulses).

For m/z=202.078, pyrene (Pyr^+), fluoranthene (Flu^+), and 9-ethynylphenanthrene (EtP^+) were characterized individually. We could differentiate the parent ions from their breakdown curves at 436 nm (Fig.1(a) and 455 nm.

The species at m/z=215.086 ($C_{17}H_{11}^+$) could contain a mixture of two isomers, the methylene pyrene cation ($PyCH_2^+$) and the tropylium-like cation (PyC_7^+) [2]. We expect to modify the isomer ratio by using different methods to activate the methyl pyrene cation and produce the –H fragment of interest. Both low-energy collision induced dissociation (CID) and photon induced dissociation (PID) were used. We found evidence for change in the isomer ratio from the recorded breakdown curves at 587 nm for both parents and fragments (Fig.1(b)). This work can be applied to discriminate isomers, in complex samples like meteorites [3] and cosmic dust analogues.

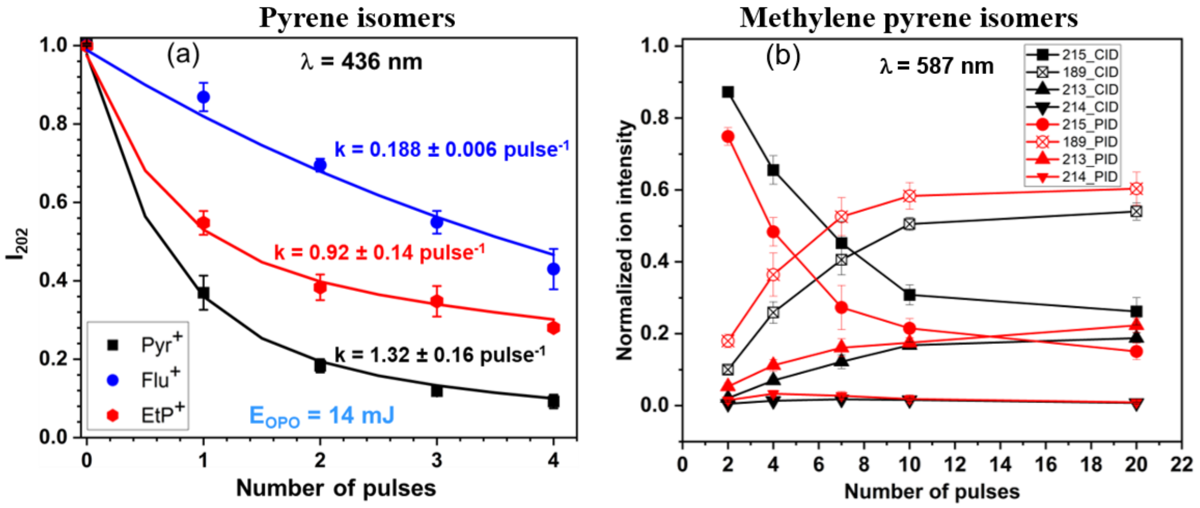

Figure 1: (a) Parent breakdown curve of pyrene cation isomers as a function of number of laser pulses at 436 nm (b) Breakdown curves of $C_{17}H_{11}^+$ (CID and PID production) and its major fragments as a function of the number of OPO laser pulses at 587 nm. In both cases, there is a 2 second delay between pulses.

References

[1] F. Useli-Bacchitta, A. Bonnamy, G. Mulas, G. Malloci, D. Toublanc, C. Joblin, *Chemical Physics*, 371 **(2010)**, 16-23.
[2] M. Rapacioli, A. Simon, C.C.M. Marshall, J. Cuny, D. Kokkin, F. Spiegelman, C. Joblin, *The Journal of Physical Chemistry A*, 119 **(2015)**, 12845-12854.
[3] H. Sabbah, A. Bonnamy, D. Papanastasiou, J. Cernicharo, J.-A. Martín-Gago, C. Joblin, *The Astrophysical Journal*, 843 **(2017)**, 34.

Ab initio molecular dynamics study of vibrational energy redistribution in CO aggregates: towards a new understanding of the (photo)desorption mechanism

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In the coldest regions (~ 10 K) of the interstellar medium (ISM), most molecular species apart from H_2 accrete on dust grains to form ice mantles, acting as particularly rich molecular reservoirs. Nevertheless, large amounts of gas phase species are also detected in these regions and their existence can be explained by desorption processes at the ice surface. Among these processes, the desorption induced by UV radiations, known as UV photodesorption, has been the subject of several experimental and theoretical studies on different compounds, such as CO[1-3], the second most abundant species in the interstellar medium. It has been shown that the UV photodesorption in pure CO ices may follow an indirect "Desorption Induced by Electronic Transition" (DIET) mechanism.[4] In this astrochemical context, the theoretical work presented here aims to understand at the molecular level, the vibrational energy redistribution mechanism in pure CO ices that could lead to the desorption of molecular CO. The chosen approach is the *ab initio* molecular dynamics one (AIMD) based on Density Functional Theory (DFT) as implemented in the VASP package. In particular, the focus is on the end of the DIET mechanism where the electronic energy of the excited molecule, redistributed on a high vibrational state of its electronic ground state, is transferred to neighbouring molecules inducing or not a desorption. To do this, an aggregate approach is used to model the amorphous structure of the simulated ice. These aggregates, initially created, optimised, and then thermalised at 10K, are then used in molecular dynamics simulations in which a single CO molecule is excited at the vibrational level v = 40. The vibrational energy redistribution in translational, rotational, and vibrational modes in the aggregate after this excitation as well as the desorption mechanism are analysed. The results show efficient energy transfers between the excited molecule and neighbouring ones leading to the desorption of CO molecules in almost all the trajectories, which is in very good agreement with the experimental results and in disagreement with previous theoretical studies.[3]

Références

[1] M. Bertin, E.C. Fayolle, C. Romanzin, K.I. Öberg, X. Michaut, A. Moudens, L. Philippe, P. Jeseck, H. Linnartz, and J.-H. Fillion, Phys. Chem. Chem. Phys. **14**, 9929 (2012).

[2] E.C. Fayolle, M. Bertin, C. Romanzin, X. Michaut, K.I. Öberg, H. Linnartz, and J.-H. Fillion, Astrophys. J. **739**, L36 (2011).

[3] M.C. van Hemert, J. Takahashi, and E.F. van Dishoeck, J. Phys. Chem. A 119, 6354 (2015).

[4] M. Bertin, E.C. Fayolle, C. Romanzin, H.A.M. Poderoso, X. Michaut, L. Philippe, P. Jeseck, K.I. Öberg, H. Linnartz, and J.-H. Fillion, Astrophys. J. **779**, 120 (2013).

Efficient formation of pentagonal rings in VUV photoexcited PAH-water complexes

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Polycyclic aromatic hydrocarbons (PAHs) and water molecules are ubiquitous in different astrophysical environments. These species could form complexes which, by photoprocessing, could lead to the incorporation of oxygen into PAHs, thus forming enols, ketones or quinones [1, 2], which are species of potential prebiotic interest. In particular, cationic complexes such as $[(\mathrm{PAH\text{-}H})(\mathrm{H_2O})]^+$ and $[\mathrm{PAH}(\mathrm{H_2O})]^+$ have been proposed as intermediates in this photoreaction pathway [1]. In these complexes, the water molecule can be either physisorbed or chemisorbed which involves different binding energies. Hence, their VUV photoexcitation could lead to several processes in competition such as (i) fragmentation (e.g. H_2O-loss), (ii) ionization or (iii) photoreactivity.

We have investigated these mechanisms during a SOLEIL beamtime on the SMRS2 LTQ ion trap coupled to the DESIRS VUV beamline [3]. In these conditions, only chemisorbed complexes could survive and their fragment channel yields as a function of the VUV photon energy could be measured. We have identified three main fragment families: the CO+*n*H, O+*n*H and *n*H -loss fragments. The CO-loss fragment channel appears to be very efficient at low energy (around 6 eV), reaching more than the percent level for coronene-water complexes. To better understand these results, we have computed the photoabsorption cross section, at the TD-DFT level of theory, of several PAH-water complex isomers. The comparison between the theoretical photo-absorption spectra and the experimental fragmentation yields suggests that the CO-loss fragment is isomer dependent. This sheds light on specific enol and ketone structures which could play a major role in astrochemistry.

References

[1] Z. Guennoun, C. Aupetit, and J. Mascetti, "Photochemistry of pyrene with water at low temperature: Study of atmospherical and astrochemical interest," J. Phys. Chem. A, 2011, 115:10, p. 1844–1852.

[2] J. A. Noble, C. Jouvet, C. Aupetit, A. Moudens, and J. Mascetti, "Efficient photochemistry of coronene:water complexes," A&A, 2017, 599, p. A124.

[3] A. Giuliani, J.-L. Giorgetta, J.-P. Ricaud, F. Jamme, V. Rouam, F. Wien, O. Laprévote, and M. Réfrégiers, "Atmospheric pressure photoionization using tunable VUV synchrotron radiation," Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 2012, 279, p. 114-117.

Tracing shock-induced fragmentation of fullerenes in the interstellar medium

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Shock waves are produced in the interstellar medium (ISM) in various ways like cloud-cloud collisions, supersonic outflows from newly formed stars, supernovae explosion of dying stars, etc. They play a crucial role to alter the chemical constituents of the ISM. Dust grains in the warm neutral/ionized medium of the ISM are destroyed by shocks and form new molecular species [1] . Unfortunately, the evolution of the interstellar dust analogues by shock wave is not very well characterized in the laboratory.

We have investigated the processing of the C_{60} fullerene powder using pressure driven shock wave. A new light detection module was installed on a shock tube to study the *in situ* shock processing of C_{60}. The distinctive emission spectrum of C_2 Swan bands superposed to a broad emission continuum was observed. We anticipate that this broad continuum is likely due to the recurrent fluorescence of small carbon clusters which were formed during the shock processing of C60. We note that the spectrum is also affected by self-absorption. Detailed theoretical analysis was performed for the spectral interpretation and the dynamics of the destruction of the clusters was investigated using molecular dynamics simulations.

Acknowledgement

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References

[1] Jones, A. P., Tielens, A. G. G. M., & Hollenbach, D. J. 1996, ApJ, 469, 740.

Collision Induced Dissociation of Water Pyrene Molecular Clusters

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In photodissociation regions (PDRs) associated with star formation, the matter composed of gas and tiny dust particles is in strong interaction with the ultraviolet (UV) radiation from young stars. From previous infrared space missions such as the Spitzer telescope, we have observed the destruction of very small carbonaceous grains and the production of isolated polycyclic aromatic hydrocarbons (PAHs) at the edge of these PDRs [1]. Clusters of PAHs have been proposed as models for these carbonaceous nanograins [2]. Furthermore, carbonaceous nanograins come from the inner part of interstellar clouds where models predict a transition from gaseous to icy water [3]. In order to get insight into the interaction of water with the carbonaceous nanograins we are performing experiments on water-PAH molecular clusters.

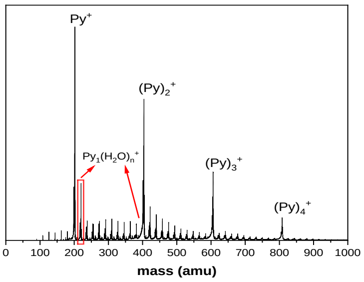

Figure 1. Mass spectrum of water pyrene clusters

Mixed water pyrene ($C_{16}H_{10}$, Py) cluster cations are produced in a gas aggregation source [4] prior to thermalization at 25K (see example in Figure 1). In the present conditions, clusters with up to 28 water molecules and 4 pyrene molecules can be observed. Protonated species dominate the mass spectrum. In order to study the energetics of these species and to get insights into their structure, we recorded absolute fragmentation cross sections using collision induced dissociation (CID). The species of interest are mass selected and undergo collisions with inert gases (helium, neon, argon, krypton, xenon) at varying kinetic energy of the ions. The products are analysed by time-of-fight mass spectrometry.

CID experiments were performed on $(Py)_m(H_2O)_nH^+$ (m= 1 to 3, n= 1 to 10) at 7.5 eV centre-of-mass collision energy. Both water loss and pyrene loss channels are observed. Structural and energetic calculations of these species were performed to support the analysis of the experimental results in terms of proton localization and dissociation energies. The proton localization in these fragments are investigated and will be presented.

References

[1] P. Pilleri, J. Montillaud, O. Berné, and C. Joblin, Astron. & Astrophys. 542, A69 (2012).
[2] M. Rapacioli, C. Joblin, and P. Boissel, Astron. Astrophys. 429, 193–204 (2005).
[3] D. Hollenbach, M. J. Kaufman, E. A. Bergin, G. J. Melnick, Astrophys. J. 690, 1497 (2009).
[4] I. Braud, S. Zamith, and J.-M. L'Hermite, Rev. Sci. Instrum. 88, 043102 (2017).

A system-bath approach for the quantum vibrational dynamics of large molecules

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Addressing the relaxation dynamics and spectral properties of large molecules is of interest for different scientific communities and in particular in astrophysics, owing to the increasingly large number of complex molecules that have been detected in the interstellar medium (ISM). For example, fullerene C_{60} [1,2], indene [3] and cyanonaphthalenes [4] have been identified from their vibrational or rotational signature.

In this context, we are developing a new theoretical model for the simulation of the quantum vibrational dynamics of relatively large molecules (> 20 atoms) that takes into account their vibrational anharmonicity and allows for an explicit coupling to the electromagnetic field. Our approach is based on a system-bath model in which one particular vibrational mode of interest, for which we want to obtain the spectral or dynamical information, is in contact with a bath formed by the remaining vibrational modes of the molecule. The mode of interest and its couplings to the other modes are treated as exactly as possible but the bath part of the Hamiltonian is simplified with its modes being replaced by a ladder of energy-dependent effective quantum states that describe the energy stored in those modes. Such an approach scales very mildly with the number of degrees of freedom, allowing for large systems to be considered. In particular, it will be possible to analyze the response of the bath to the excitation of the mode of interest [5] and to study the infrared spectra at finite temperature and the relaxation dynamics of astrophysically relevant molecules such as PAH.

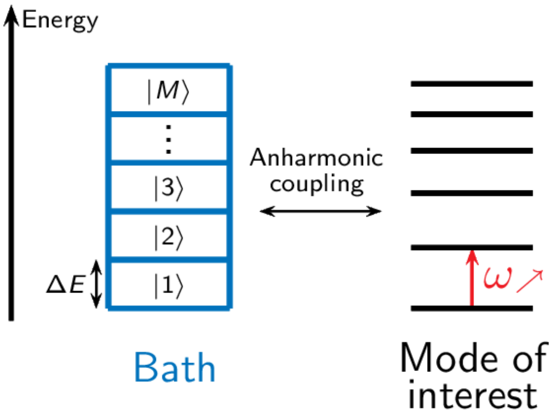

Figure 1: Schematic view of our model with the vibrational levels of the selected mode (in black) and the bath (in blue) which is described by its total energy. In our model the electromagnetic field is only coupled to the mode of interest.

References

[1] J. Cami, J. Bernard-Salas, E. Peeters, and S. E. Malek, Science, 2010, 329.
[2] K. Sellgren, M. W. Werner, J. G. Ingalls, J. D. T. Smith *et al.*, ApJ, 2010, 722.
[3] J. Cernicharo, M. Agúndez,C. Cabezas, B. Tercero *et al.*, A&A, 2021, 649.
[4] B. McGuire, R. Loomis, A. Burkhardt, K. Lee *et al.*, Science, 2021, 371.
[5] F. Bouakline, F. Lüder, R. Martinazzo and P. Saalfrank, J. Phys. Chem. *A*, 2012, 116.

Electronic Spectroscopy of Helium Tagged Ionic Pentacene

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Messenger spectroscopy is a powerful tool used for the search for carriers of diffuse interstellar bands (DIBs). The attachment of weakly interacting messengers, like helium (He) atoms, to the molecule of interest ensures that the induced spectral shift is small. In our experimental setup we obtain He tagged ions by doping multiply charged helium nanodroplets (HNDs) with polycyclic aromatic hydrocarbons (PAHs) and subsequently colliding the HNDs with a stainless-steel surface. The ionic species are detected with a time-of-flight mass spectrometer (TOF-MS). Absorption spectra of PAH ions, in this case pentacene, are obtained by tracing the increase of the bare ion yield and the decrease of the He tagged PAH ion yield after interaction with a tunable pulsed laser (tunable from 210 nm to 2600 nm). Mass spectra that were recorded after laser illumination are compared to mass spectra without laser illumination at the different wavelengths for background correction and the compensation of ion signal fluctuations. A spectral shift for different numbers of attached helium atoms can be observed. Our laboratory absorption spectra can be compared to astronomical observations. [1,2,3]

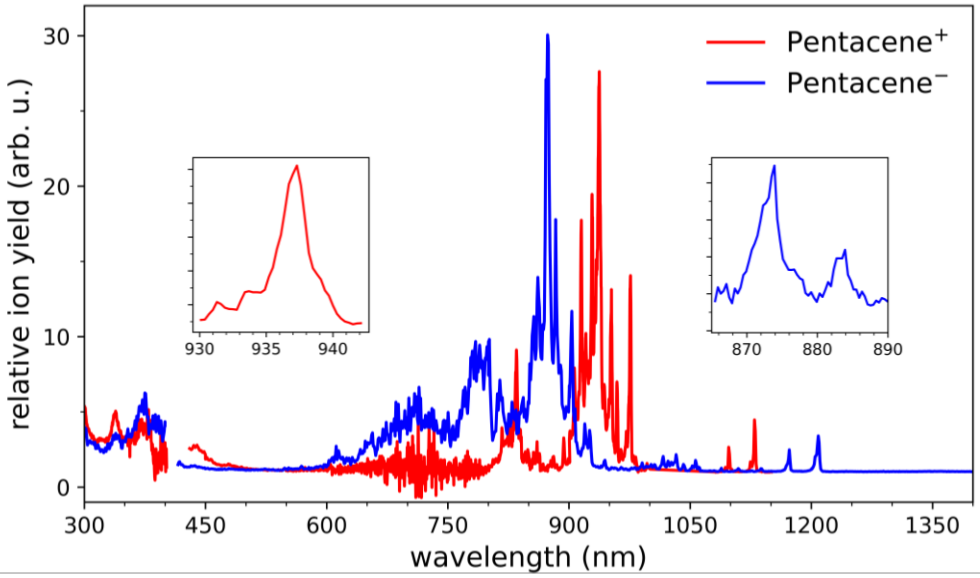

Figure 1: Absorption spectra of pentacene cations and anions. Shown in the insets are the most intense absorption bands.

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References

[1] M. Meyer, P. Martini, A. Schiller, F. Zappa, S. A. Krasnokutski, P. Scheier, 2021, ApJ 913(2), 136.
[2] M. Kappe, A. Schiller, F. Zappa, S. A. Krasnokutski, M. S. Sättele, H. F. Bettinger, P. Scheier, 2022, A&A, accepted.
[3] M. Kappe, B. Rasul, M. Mahmoodi-Darian, A. Schiller, S. A. Krasnokutski, P. Scheier, 2022, Mol. Phys., submitted.

DESIRS : a state-of-the-art VUV beamline featuring high flux, high resolution and variable polarization opening scientific opportunities for laboratory astrophysics experiments

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Open to users in 2008, DESIRS is a high resolution variable polarization VUV beamline [1] at Synchrotron SOLEIL devoted to the study, on dilute (cold molecules, radicals, ions, clusters and nanoparticles) and condensed (thin films, ices) matter, of molecular and electronic structures, reactivity and polarization-dependant photodynamics involving valence-shell excitations. See also https://www.synchrotron-soleil.fr/fr/lignes-de-lumiere/desirs

This program is carried out via mainly 3 endstations: (i) a VUV Fourier-Transform Spectrometer (FTS), based upon a wavefront-division interferometer, for ultra-high resolution absorption spectroscopy with unprecedented resolving power up to 10^6 [2]; (ii) a versatile electron/ion double imaging electron/ion coincidence spectrometer coupled to the molecular beam chamber SAPHIRS [3,4]; (iii) an ion trap enabling the performance of VUV action spectroscopy on large molecular cations/anions including PAH-related species.[5]

The photon source is a 10 m-long electromagnetic variable polarization undulator producing light from a few eVs (300 nm) up to 40 eV (30 nm) with tailored elliptical polarization providing at the sample location fully calibrated quasi-perfect linear and circular polarizations as measured with an *in situ* VUV polarimeter. Gas-filtered harmonic-free photons are feeding a 6.65 m Normal Incidence Monochromator equipped with four gratings, allowing to adjust smoothly the flux-to-resolution compromise. Measured ultimate instrumental resolving powers reach 250000, while the typical measured flux are up to 10^{13} ph/sec in a 1/1000 bandwidth, and 10^{15} ph/sec in a 7% bandwidth (with zeroth order radiation). The monochromator feeds two branches: one on which is sitting our molecular beam set-up, and the other one which can host the ion trap, the CERISES ion-molecule reactivity associated experiment, or any other set-up brought by users.

All these features make DESIRS a unique tool for studying astrophysical objects and simulating the VUV radiation encountered in the ISM and planetary ionosphere. As such, ~30 % of the delivered beamtime is used by a broad community linked to Sciences of the Universe (from astrophysics to astrobiology). A few examples of astro-related studies will be presented.

References

[1] L. Nahon, N. de Oliveira, G. Garcia, J. F. Gil, B. Pilette, O. Marcouille, B. Lagarde and F. Polack J. Synchrotron Rad. **19**, 508 (2012).

[2] N. de Oliveira, M. Roudjane, D. Joyeux, D. Phalippou, J. C. Rodier and L. Nahon, Nature Photonics **5**, 149 (2011).

[3] G. Garcia, B. Cunha de Miranda, M. Tia, S. Daly and L. Nahon, Review of Scientific Instruments **84**, 053112 (2013).

[4] X. Tang, G. Garcia, J.-F. Gil and L. Nahon, Review of Scientific Instruments **86**, 123108 (2015).

[5] A. R. Milosavljevic, C. Nicolas, J. F. Gil, F. Canon, M. Refregiers, L. Nahon and A. Giuliani, J. Synchrot. Radiat. **19**, 174 (2012).

Molecular physics of closed and open shell aromatics of astrophysical interest

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Polycyclic Aromatic Hydrocarbons (PAHs) have long been predicted to be the main carriers of two sets of interstellar spectral features: the diffuse interstellar bands, a series of absorption bands in the near-UV to visible domain, and the MIR emission features known as the aromatic infrared bands. After decades of searching, the N-bearing aromatic benzonitrile was the first interstellar aromatic molecule detected via rotational spectroscopy [1]. Recently, the second and third, 1- and 2-cyanonaphthalene, were detected in the same starless cloud core TMC-1 [2]. These studies suggest that PAHs can form at much lower temperatures than previously assumed. The N- bearing family of PANHs are thus expected to be an important component of the interstellar PAHs, present in neutral, radical and protonated forms in interstellar environments. It is predicted that the hydrogenated forms of PAHs and PANHs are involved in the formation of molecular H2, while PA(N)Hs will also interact with photons, protons and small molecules such as water. In their radical or aggregate forms, the photophysics of the PA(N)Hs is likely to be fundamentally altered, as the structure (and thus spectroscopy) might shift, and additional energy dissipation pathways open up.

We will present several recent results obtained using experimental setups in the PIIM laboratory allowing us to study the photophysics of interstellar-relevant aromatics in various charge and hydration states. A study of neutral xylene isomers interacting with water molecules has recently been performed [3], confirming the role of an aggregate's structure in its photoreactivity. The protonated benzonitrile species was studied in collaboration with the national SOLEIL synchrotron facility [4], and the results have shown that these molecules are highly UV sensitive and unlikely to be photostable in interstellar environments with high UV flux, such as photon-dominated regions or planetary atmospheres. Interestingly, the photodegradation product of benzonitrile are key intermediates in the formation of larger PAHs, so far undetected. We are now extending our study to other N- bearing aromatics in various charge states including molecules with N heteroatoms in the aromatic skeleton or N-bearing functional groups such as -CN, species with multiple rings (including cyanonaphthalene), and open shell radicals with one H atom removed or added from the neutral molecule (i.e. (de)-hydrogenated species).

References

[1] B. A. McGuire, A. M. Burkhardt, S. Kalenskii et al., 2018, Science doi: 10.1126/science.aao4890
[2] B. A. McGuire, R. A. Loomis, A. M. Burkhardt et al., 2021 Science doi: 10.1126/science.abb7535
[3] J. E. Fulker, A. Gutierrez-Quintanilla, W. A. Brown et al. 2023 Submitted to J. Mol. Spec.
[4] U. Jacovella, J. A. Noble, A. Guliani et al. 2022 Astron. Astrophys. doi: 10.1051/0004-6361/202142206

Jet-cooled ethylene spectroscopy in the 1.6 µm spectral region for the atmosphere of the hot Jupiter exoplanets

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The hot Jupiter exoplanets are giant gas planets orbiting very closely to their star, leading to external temperatures up to 3000K. Methane [1] and acetylene [2] were already detected in such environments, and the presence of other small hydrocarbons is expected. The recent launch of the James Webb space telescope (JWST) and the upcoming Ariel mission will allow a better understanding of their atmospheric composition using infrared spectrometry [3,4]. Interpretation of these observations will require accurate knowledge of the absorption fingerprint of the expected species. In the case of ethylene (C_2H_4), unambiguous spectral assignment in the near infrared is not available beyond 3500 cm^{-1} [5], partly due to its highly congested absorption spectrum at higher wavenumbers.

We first focus on providing accurate assignments of the ethylene cold transitions. To do so, the jet-cooled gas is probed in the 1.65-1.68 nm spectral range using a cavity ring-down spectrometer. The low temperature is obtained by expanding the gas contained in a high-pressure reservoir into a low-pressure chamber through an 8,5 cm long slit, with a tunable opening width ranging from 0 to 350 µm. This cooling process enables a simplification of the absorption spectrum by narrowing the linewidths and by reducing the number of excited ro-vibrational transitions. Two spectra were recorded with a vibrational temperature of about 220K but different rotational temperatures: 5K and 15K. The latter is shown in Fig. 1(a). Unambiguous assignment of the observed lines was performed using the TheoReTS *ab initio* line list [6]. Up to now, 95 lines were assigned to the $\nu_5+\nu_{11}$ band, 63 to the $\nu_9+2\nu_{12}$ band, 12 to the $\nu_3+\nu_{11}$ and 6 the $\nu_1+\nu_2+\nu_{12}$ band. These assignments are presented in Fig. 1(b) for the spectrum with T_{rot} = 15K. Further assignment is ongoing, which will be later used to extend the TheoReTS *ab initio* line list of ethylene towards temperatures relevant to hot Jupiters

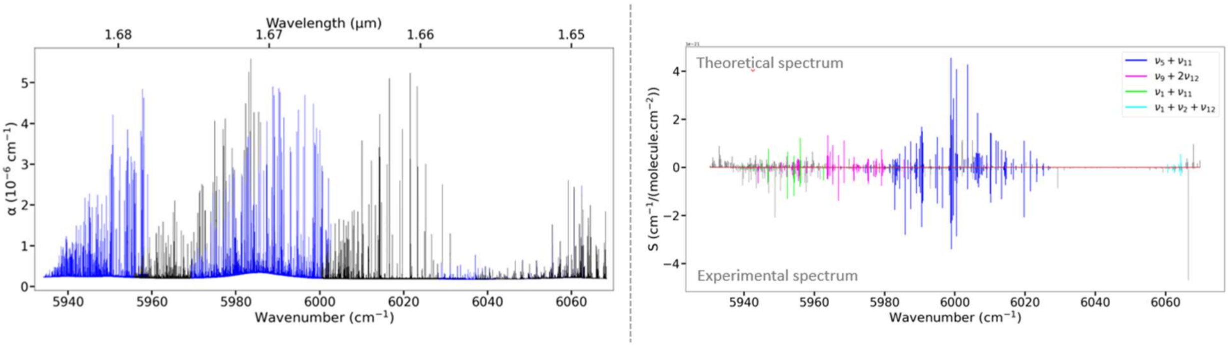

Figure 1: a) Experimental spectrum of C_2H_4 with T_{rot} = 15K. b) Comparison between the experimental and simulated spectra of C_2H_4 with T_{rot} = 15K and vibrational band assignment of observed lines.

References

[1] M. R. Swain, G. Vasisht, G. Tinetti, Nature, **463** (7281), 637-639 (2008)
[2] P. Giacobbe, *et al.*, Nature, **592** (7853), 205-208 (2021)
[3] see https://wwww.jwst.nasa.gouv/ and https://arielmission.space/
[4] B.E. Miles, *et al.*, arXiv : 2209.00620 (2023)
[5] I.E. Gordon, *et al.*, J. Quant. Spectrosc. Radiat. Transfer, **277**, 107949 (2022)
[6] M. Rey, A. V. Nikitin, Y. L. Babikov, and V. G. Tyuterev, J. Mol. Spectrosc., **327**, 138–158 (2016)

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