

# AstroChemical Newsletter #31

May 2018

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## Abstracts

### The pure rotational spectrum of the T-shaped AlC<sub>2</sub> radical (X<sup>2</sup>A<sub>1</sub>)

D. T. Halfen and L. M. Ziurys

The pure rotational spectrum of the AlC<sub>2</sub> radical (X<sup>2</sup>A<sub>1</sub>) has been measured using Fourier transform microwave/millimeter-wave (FTMmmW) techniques in the frequency range 21–65 GHz. This study is the first high-resolution spectroscopic investigation of this molecule. AlC<sub>2</sub> was created in a supersonic jet from the reaction of aluminum, generated by laser ablation, with a mixture of CH<sub>4</sub> or HCCH, diluted in argon, in the presence of a DC discharge. Three transitions (N<sub>Ka</sub>,K<sub>c</sub> = 101 - 000, 202 - 101, and 303 - 202) were measured, each consisting of multiple fine/hyperfine components, resulting from the unpaired electron in the species and the aluminum-27 nuclear spin (I = 5/2). The data were analyzed using an asymmetric top Hamiltonian and rotational, fine structure, and hyperfine constants determined. These parameters agree well with those derived from previous theoretical calculations and optical spectra. An r<sub>0</sub> structure of AlC<sub>2</sub> was determined with r(Al-C) = 1.924 Å, r(C-C) = 1.260 Å, and γ(C-Al-C) = 38.21°. The Al-C bond was found to be significantly shorter than in other small, Al-bearing species. The Fermi contact term established in this work indicates that the unpaired electron in the valence orbital has considerable 3p<sub>z</sub> character, suggesting polarization towards the C<sub>2</sub> moiety. A high degree of ionic character in the molecule is also evident from the quadrupole coupling constant. These results are consistent with a T-shaped geometry and an Al<sup>+</sup>C<sub>2</sub><sup>-</sup> bonding scheme. AlC<sub>2</sub> is a possible interstellar molecule that may be present in the circumstellar envelopes of carbon-rich AGB stars.

2018, PCCP, DOI: 10.1039/c7cp08613j

DOI: [10.1039/c7cp08613j](https://doi.org/10.1039/c7cp08613j)

Full-text URL:

<http://pubs.rsc.org/en/content/articlelanding/2018/cp/c7cp08613j#!divAbstract>

### Comment on "Methanol dimer formation drastically enhances hydrogen abstraction from methanol by OH at low temperature" by W. Siebrand, Z. Smedarchina, E. Martínez-Núñez and A. Fernández-Ramos, *Phys. Chem. Chem. Phys.*, 2016, 18, 22712

Shannon, R.J.; Gómez-Martín, J.C.; Caravan, R.L.; Blitz, M.A.; Plane, J.M.C.; Heard, D.E.; Antiñolo, M.; Agúndez, M.; Jiménez, E.; Ballesteros, B.; Canosa, André; El Dib, Gisèle; Albaladejo, J.; Cernicharo, J.

The article "Methanol dimer formation drastically enhances hydrogen abstraction from methanol by OH at low temperature" proposes a dimer mediated mechanism in order

to explain the large low temperature rate coefficients for the OH + methanol reaction measured by several groups. It is demonstrated here theoretically that under the conditions of these low temperature experiments, there are insufficient dimers formed for the proposed new mechanism to apply. Experimental evidence is also presented to show that dimerization of the methanol reagent does not influence the rate coefficients reported under the conditions of methanol concentration used for the kinetics studies. It is also emphasised that the low temperature experiments have been performed using both the Laval nozzle expansion and flow-tube methods, with good agreement found for the rate coefficients measured using these two distinct techniques.

Phys. Chem. Chem. Phys., 20[12], 8349-8354 (2018).

DOI: [10.1039/C7CP04561A](https://doi.org/10.1039/C7CP04561A)

Full-text URL:

<http://pubs.rsc.org/en/content/articlelanding/2018/cp/c7cp04561a#!divAbstract>

## Depletion of heavy nitrogen in the cold gas of star-forming regions

**K. Furuya, Y. Aikawa**

We investigate nitrogen isotope fractionation in forming and evolving molecular clouds using gas-ice astrochemical simulations. We find that the bulk gas can become depleted in heavy nitrogen ( $^{15}\text{N}$ ) due to the formation of  $^{15}\text{N}$ -enriched ices. Around the chemical transition from atomic nitrogen to  $\text{N}_2$ ,  $\text{N}^{15}\text{N}$  is selectively photodissociated, which results in the enrichment of  $^{15}\text{N}$  in atomic nitrogen. As  $^{15}\text{N}$ -enriched atomic nitrogen is converted to ammonia ice via grain surface reactions, the bulk gas is depleted in  $^{15}\text{N}$ . The level of  $^{15}\text{N}$  depletion in the bulk gas can be up to a factor of two compared to the elemental nitrogen isotope ratio, depending on the photodesorption yield of ammonia ice. Once the nitrogen isotopes are differentially partitioned between gas and solids in a molecular cloud, it should remain in the later stages of star formation (e.g., prestellar core) as long as the sublimation of ammonia ice is inefficient. Our model suggests that all the N-bearing molecules in the cold gas of star-forming regions can be depleted in  $^{15}\text{N}$ , which is at least qualitatively consistent with the observations toward prestellar core L1544. In our models, icy species show both  $^{15}\text{N}$  and deuterium fractionation. The fractionation pattern within ice mantles is different between  $^{15}\text{N}$  and deuterium, reflecting their fractionation mechanisms; while the concentration of deuterium almost monotonically increases from the lower layers of the ice mantles to the upper layers, the concentration of  $^{15}\text{N}$  reaches the maximum at a certain depth and declines towards the surface.

Accepted for publication in ApJ

DOI: [10.3847/1538-4357/aab768](https://doi.org/10.3847/1538-4357/aab768)

Full-text URL: <https://arxiv.org/abs/1803.06787>

## A survey of $\text{CH}_3\text{CN}$ and $\text{HC}_3\text{N}$ in protoplanetary disks

**J. Bergner, V. Guzman, K. Oberg, R. Loomis, J. Pegues**

The organic content of protoplanetary disks sets the initial compositions of planets and comets, thereby influencing subsequent chemistry that is possible in nascent planetary systems. We present observations of the complex nitrile-bearing species  $\text{CH}_3\text{CN}$  and  $\text{HC}_3\text{N}$  toward the disks around the T Tauri stars AS 209, IM Lup, LkCa 15, and V4046 Sgr as well as the Herbig Ae stars MWC 480 and HD 163296.  $\text{HC}_3\text{N}$  is detected toward all disks except IM Lup, and  $\text{CH}_3\text{CN}$  is detected toward V4046 Sgr, MWC 480, and HD 163296. Rotational temperatures derived for disks with multiple detected lines range

from 29 to 73 K, indicating emission from the temperate molecular layer of the disk. V4046 Sgr and MWC 480 radial abundance profiles are constrained using a parametric model; the gas-phase CH<sub>3</sub>CN and HC<sub>3</sub>N abundances with respect to HCN are a few to tens of percent in the inner 100 au of the disk, signifying a rich nitrile chemistry at planet- and comet-forming disk radii. We find consistent relative abundances of CH<sub>3</sub>CN, HC<sub>3</sub>N, and HCN between our disk sample, protostellar envelopes, and solar system comets; this is suggestive of a robust nitrile chemistry with similar outcomes under a wide range of physical conditions.

ApJ 857:69

DOI: [10.3847/1538-4357/aab664](https://doi.org/10.3847/1538-4357/aab664)

Full-text URL: <https://arxiv.org/abs/1803.04986>

## Variation in photon flux during extended photochemical aerosol experiments: Implications for atmospheric laboratory simulation

**J. Sebree, J. Wayson, J. Lopez**

In order to simulate the interaction of sunlight with planetary atmospheres, including Pluto, Titan and the early Earth, many laboratory studies have used high-power broadband lamps with spectral features that extend into the vacuum-ultraviolet (VUV, <200 nm) to initiate photochemistry relevant to the atmosphere of interest. In many cases, experiments are run on the order of hundreds of hours with no accounting for how the photon flux within the system may be evolving with lamp age or a possible buildup of films over optical surfaces when working with high-yield photochemical systems. Given that the nature of photochemistry depends on the ratio of photons to reactants, variations in flux must be taken into account if the system is to be fully understood. In this study, standard N<sub>2</sub>O actinometry was used to measure the VUV flux of high-intensity deuterium lamps before, during, and after the photochemical synthesis of Titan analog aerosols made from methane or benzene precursors. It was found that VUV photon flux can be decreased by over 50% in under 10 h at higher number densities, with recorded flux losses of over 75% during extended (>60 h) photochemical experiments. While this is only one model system, it is apparent that changes in photon flux during simulations must be taken into account if adequate comparisons of the photochemical kinetics to their respective planetary environments are to be made.

2018 Journal of Photochemistry and Photobiology A: Chemistry, 360, 1-5

DOI: [10.1016/j.jphotochem.2018.04.023](https://doi.org/10.1016/j.jphotochem.2018.04.023)

Full-text URL: <https://www.sciencedirect.com/science/article/pii/S1010603017312157>

## A ring polymer molecular dynamics approach to study the transition between statistical and direct mechanism in the H<sub>2</sub> + H<sub>3</sub><sup>+</sup> → H<sub>3</sub><sup>+</sup> + H<sub>2</sub> reaction

**Y. V. Suleimanov, A. Aguado, S. Gómez-Carrasco and O. Roncero**

Because of its fundamental importance in astrochemistry, the H<sub>2</sub> + H<sub>3</sub><sup>+</sup> → H<sub>3</sub><sup>+</sup> + H<sub>2</sub> reaction has been studied experimentally in a wide temperature range. Theoretical studies of the title reaction significantly lag primarily because of the challenges associated with the proper treatment of the zero-point energy (ZPE). As a result, all previous theoretical estimates for the ratio between a direct proton-hop and indirect exchange (via the H<sub>5</sub><sup>+</sup> complex) channels deviate from the experiment, in particular, at lower temperatures where the quantum effects dominate. In this work, the ring

polymer molecular dynamics (RPMD) method is applied to study this reaction, providing very good agreement with the experiment. RPMD is immune to the shortcomings associated with the ZPE leakage and is able to describe the transition from direct to indirect mechanisms below room temperature. We argue that RPMD represents a useful tool for further studies of numerous ZPE-sensitive chemical reactions that are of high interest in astrochemistry.

J. Phys. Chem. Lett. 2018, 9, 2133–2137

DOI: [10.1021/acs.jpcllett.8b00783](https://doi.org/10.1021/acs.jpcllett.8b00783)

Full-text URL: <https://pubs.acs.org/doi/pdf/10.1021/acs.jpcllett.8b00783>

## NeON<sup>+</sup>: An Atom and a Molecule

**Ryan C. Fortenberry & Steven R. Gwaltney**

The NeON<sup>+</sup> molecule is stable with a Ne + NO<sup>+</sup> dissociation energy of 0.90 kcal/mol. While this is small, the two vibrational modes that include the neon atom are less than this barrier at 57.9 and 45.0 cm<sup>-1</sup>. Hence, this “L”-shaped molecule will not readily vibrate itself apart in cold environments, such as the interstellar medium, where the nitrosylium cation is believed to exist. While the 2359.2 cm<sup>-1</sup> N≡O vibrational frequency is only slightly perturbed (but perturbed nonetheless) by the presence of the Ne atom, the other two fundamental vibrational frequencies will be observable in the terahertz region, where future space telescopes may operate. Furthermore, the curiosity of a stable molecule whose constituent atomic symbols spell the name of one such atom give this structure a unique place in the chemical imagination. Hence, “neon” is both a molecule and an atom.

ACS Earth Space Chem., 2018, (in press)

DOI: [10.1021/acsearthspacechem.8b00019](https://doi.org/10.1021/acsearthspacechem.8b00019)

Full-text URL: <https://pubs.acs.org/doi/10.1021/acsearthspacechem.8b00019>

## Understanding the quantum nature of low-energy C(3P<sub>j</sub>) + He inelastic collisions

**Astrid Bergeat, Simon Chefdeville, Michel Costes, Sébastien B. Morales, Christian Naulin, Uzi Even, Jacek Kłos and François Lique**

Inelastic collisions that occur between open-shell atoms and other atoms or molecules, and that promote a spin-orbit transition, involve multiple interaction potentials. They are non-adiabatic by nature and cannot be described within the Born-Oppenheimer approximation; in particular, their theoretical modelling becomes very challenging when the collision energies have values comparable to the spin-orbit splitting. Here we study inelastic collisions between carbon in its ground state C(3P<sub>j</sub>=0) and helium atoms—at collision energies in the vicinity of spin-orbit excitation thresholds (~0.2 and 0.5 kJ mol<sup>-1</sup>)—that result in spin-orbit excitation to C(3P<sub>j</sub>=1) and C(3P<sub>j</sub>=2). State-to-state integral cross-sections are obtained from crossed-beam experiments with a beam source that provides an almost pure beam of C(3P<sub>j</sub>=0). We observe very good agreement between experimental and theoretical results (acquired using newly calculated potential energy curves), which validates our characterization of the quantum dynamical resonances that are observed. Rate coefficients at very low temperatures suitable for chemical modelling of the interstellar medium are also calculated.

Nature Chemistry

DOI: [10.1038/s41557-018-0030-y](https://doi.org/10.1038/s41557-018-0030-y)

## **SOLIS IV. Hydrocarbons in the OMC-2 FIR4 Region, a Probe of Energetic Particle Irradiation of the Region**

**C. Favre, C. Ceccarelli, A. López-Sepulcre, F. Fontani, R. Neri, S. Manigand, M. Kama, P. Caselli, A. Jaber Al-Edhari, C. Kahane, F. Alves, N. Balucani, E. Bianchi, E. Caux, C. Codella, F. Dulieu, J. E. Pineda, R. Sims, P. Theulé**

We report new interferometric images of cyclopropenylidene,  $c\text{-C}_3\text{H}_2$ , towards the young protocluster OMC-2 FIR 4. The observations were performed at 82 and 85 GHz with the NOEMA as part of the project Seeds Of Life In Space (SOLIS). In addition, IRAM-30m data observations were used to investigate the physical structure of OMC-2 FIR4. We find that the  $c\text{-C}_3\text{H}_2$  gas emits from the same region where previous SOLIS observations showed bright HC5N emission. From a non-LTE analysis of the IRAM-30m data, the  $c\text{-C}_3\text{H}_2$  gas has an average temperature of  $\sim 40$  K, a  $\text{H}_2$  density of  $\sim 3 \times 10^5 \text{ cm}^{-3}$ , and a  $c\text{-C}_3\text{H}_2$  abundance relative to  $\text{H}_2$  of  $(7 \pm 1) \times 10^{-12}$ . In addition, the NOEMA observations provide no sign of significant  $c\text{-C}_3\text{H}_2$  excitation temperature gradients across the region (about 3-4 beams), with  $T_{\text{ex}}$  in the range  $8 \pm 3$  up to  $16 \pm 7$  K. We thus infer that our observations are inconsistent with a physical interaction of the OMC-2 FIR4 envelope with the outflow arising from OMC-2 FIR3, as claimed by previous studies. The comparison of the measured  $c\text{-C}_3\text{H}_2$  abundance with the predictions from an astrochemical PDR model indicates that OMC-2 FIR4 is irradiated by a FUV field  $\sim 1000$  times larger than the interstellar one, and by a flux of ionising particles  $\sim 4000$  times larger than the canonical value of  $10^{-17} \text{ s}^{-1}$  from the Galaxy cosmic rays, which is consistent with our previous HC5N observations. This provides an important and independent confirmation of other studies that one or more sources inside the OMC-2 FIR4 region emit energetic ( $\geq 10$  MeV) particles.

Accepted for publication in ApJ

Full-text URL: <https://arxiv.org/abs/1804.07825>

## **Discovery of the elusive radical NCO and confirmation of $\text{H}_2\text{NCO}^+$ in space**

**N. Marcelino, M. Agundez, J. Cernicharo, E. Roueff, M. Tafalla**

The isocyanate radical (NCO) is the simplest molecule containing the backbone of the peptide bond,  $\text{C}(=\text{O})\text{-N}$ . This bond has a prebiotic interest since is the one linking two amino acids to form large chains of proteins. It is also present in some organic molecules observed in space such as HNCO,  $\text{NH}_2\text{CHO}$  and  $\text{CH}_3\text{NCO}$ . In this letter we report the first detection in space of NCO towards the dense core L483. We also report the identification of the ion  $\text{H}_2\text{NCO}^+$ , definitively confirming its presence in space, and observations of HNCO, HOCN, and HCNO in the same source. For NCO, we derive a column density of  $2.2 \times 10^{12} \text{ cm}^{-2}$ , which means that it is only about 5 times less abundant than HNCO. We find that  $\text{H}_2\text{NCO}^+$ , HOCN and HCNO have abundances relative to HNCO of 1/400, 1/80, and 1/160, respectively. Both NCO and  $\text{H}_2\text{NCO}^+$  are involved in the production of HNCO and several of its isomers. We have updated our previous chemical models involving NCO and the production of the CHNO isomers. Taking into account the uncertainties in the model, the observed abundances are reproduced relatively well. Indeed, the detection of NCO and  $\text{H}_2\text{NCO}^+$  in L483 supports the chemical pathways to the formation of the detected CHNO isomers. Sensitive observations of NCO in sources where other molecules containing the  $\text{C}(=\text{O})\text{-N}$  subunit have been detected could help in elucidating its role in prebiotic chemistry in space.



# Announcements

## Open source code to discover reaction mechanisms

A new code is available to discover reaction mechanisms, including those relevant in astrochemistry: <http://forge.cesga.es/wiki/g/tsscads/HomePage>

## EPSC 2018 Session: Organic Matter in Space- Call for abstract

Call for abstract for the European Planetary Science Congress 2018, EPSC 2018

Session: Organic Matter in Space 16–21 September 2018, Berlin, Germany

<https://meetingorganizer.copernicus.org/EPSC2018/session/29897> Abstract deadline:

16 May 2018, 13:00 CEST. Dear colleagues, We would like to invite the world-wide community of planetary scientists working on the organic matter to submit an abstract to the session "Organic Matter in Space" that is co-organized between the Small Bodies (SB) and Astrobiology (AB) programme groups. Resume: Organic matter was abundant in the protosolar nebula, as attested by the wide range of organic compounds in the primitive bodies of our solar system, such as comets and carbonaceous chondrites.

These organic compounds were delivered to the early Earth and may have played a role in the emergence of life. However, the origin of this organic matter remains debated. Is it synthesized in the protosolar nebula and/or inherited from the interstellar medium?

This session focuses on the organic matter origin and evolution in astrophysical environments and on the connection that could exist between the organic matter of the interstellar medium and the compounds detected in primitive bodies of the solar system. This session invites communications on experimental, theoretical and observational studies related to the origin of organic matter in the primitive bodies, such as: a) detection and evolution of organic compounds in the interstellar medium, b) characterization and evolution of the organic matter in primitive bodies, c) distribution of organic matter in the protosolar disk, d) observation of organic matter in planetary surfaces. The session will consist of Oral and Poster contributions. You may see all deadlines & milestones of the conference at the following website:

[https://www.epsc2018.eu/information/deadlines\\_and\\_milestones.html](https://www.epsc2018.eu/information/deadlines_and_milestones.html) Please forward this message to colleagues who may be interested. We look forward to seeing you in Berlin. With best wishes, Conveners : Vassilissa Vinogradoff, Grégoire Danger, Laurent Remusat.

## Oxygen in Space

Oxygen in Space October 16-17, 2018 Maison Internationale de la Recherche, Neuville

sur Oise, France After hydrogen, oxygen is the second most abundant reactive element. The reduction-oxidation reaction is one of the pillars of chemistry, on Earth and in space. The present workshop focuses on the role and form of oxygen in astrophysical environments. During two days, the elusive presence of molecular oxygen in the Interstellar Medium and its unexpectedly high abundance in comets will be discussed. A session devoted to proxy molecules such as NO, SO and sulfur-substituted molecules will take place. The last part of the workshop will be devoted to the hydrogenated forms of oxygen (such as water and methanol), with a special attention to their deuterated isotopologues. Observational, modelling, and laboratory aspects will be included in the discussion. The workshop will be located at the Maison Internationale de la Recherche in Neuville-sur-Oise, 45 minutes by train from the center

of Paris (France). The participation is free of fees and is limited to 60 participants, by order of registration which is open. About half of the time will be devoted to contributions and posters. <http://laboratoires.u-cergy.fr/~lerma/OxygenInSpace/index.html> First announcement: 15th of April. ; Second announcement: 1st of June. Submission deadline : 28th of August Final program: 5th of September. Symposium: The workshop will be followed by the Symposium honoring Paul F. Goldsmith: "Velocity-Resolved Far-Infrared Imaging Spectroscopy of the Future", which will take place at the Paris Observatory on October 18-19. Confirmed speakers :Aurore Bacmann (IPAG, France), Dominique Bockelée-Morvan (Observatoire de Paris, France), Claudio Codella (Osservatorio di Arcetri, Italy), Ewine van Dishoeck (Leiden Observatory, NL), Kostas Giapis (California Institute of Technology, USA), Paul F. Goldsmith (NASA JPL, Pasadena, USA), Marco Minissale (Aix-Marseille Université, France), Vianney Taquet (Osservatorio di Arcetri, Italy),Valentine Wakelam (Laboratoire d'astrophysique de Bordeaux, France), Naoki Watababe (Hokkaido University, Japan)