

Laser Ablation

An Innovative Approach for the Generation of Species of the Interstellar Medium

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Abstract: The large amount of unstable species in the realm of interstellar chemistry drives an urgent need to develop efficient methods for the *in situ* generations of molecules that enable their spectroscopic characterizations. Such laboratory experiments are fundamental to decode the molecular universe by matching the interstellar and terrestrial spectra. We propose an approach based on laser ablation of nonvolatile solid organic precursors. The generated chemical species are cooled in a supersonic expansion and probed by high-resolution microwave spectroscopy. We present a proof of concept through a simultaneous formation of interstellar compounds and the first generation of aminocynoacetylene using diaminomaleonitrile as a prototypical precursor. With this micro-laboratory, we open the door to generation of unsuspected species using precursors not typically accessible to traditional techniques such as electric discharge and pyrolysis.

Interstellar space hosts exceptionally complex chemical reactions that proceed in multiple steps with a correspondingly large number of intermediate compounds. The compounds may include molecular ions, radicals, carbenes, metastable isomers, molecular adducts, and other transient

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species.^[1,2] The remote spectroscopic detection of these short-lived species is often the only way to disentangle the chemical puzzle of the environments where they reside and to elucidate the reaction mechanisms involved. This spectroscopic diagnostic primarily relies on laboratory experiments, which provide reference data as a guide to interpret those from remote observations. Thus, a delicate interplay between laboratory rotational spectroscopy and astronomical observations became particularly important for the chemical mapping of interstellar clouds.^[3–6] However, creating the short-lived species in laboratories by contemporary chemistry is arduous, if not impossible, and their nature precludes storage. Therefore, dedicated laboratory experiments are needed to enable *in situ* generations. The most common methods are electric discharge, pyrolysis, and photolysis, used in many spectroscopic laboratories.^[7–20] Nonetheless, these generation procedures typically require gaseous precursors prepared by mixing different gases or easily vaporizable liquids and solids. From this, solid organic compounds with high melting points and low vapor pressures are rarely utilized as potential precursors. New experimental approaches that would enable participation of these organic solids as precursors for the generation of new chemical species have to be developed to bridge this critical gap in current experimental procedures.

Laser ablation is an efficient tool for the fast desorption of solid samples and has been applied in a wide range of experiments.^[21–27] We have combined laser ablation with the latest Fourier transform microwave instrumentation^[28,29] to generate neutral forms of proteogenic amino acids in a supersonic expansion by laser ablation of their zwitterionic forms,^[30,31] allowing their first structural investigation. These experimental approaches have also been applied successfully to many other relevant building blocks of life,^[32–36] synthesizing metal-containing species^[37–40] and molecular complexes.^[41–44] Significant photo-fragmentation effects were revealed; unwanted lines of decomposition products appeared in crowded rotational spectra. Consequently, we improved our laser ablation experiments to minimize the photo-fragmentation.^[45,46] Despite this, in the recent study of laser-ablated hydantoic acid, an acyclic compound, we discovered the formation of two cyclic molecules among other species.^[47] Some of them are also present in the harsh environment of the interstellar medium (ISM). These findings indicate that the organic plasma plume produced by the laser ablation may contain a rich assortment of fragments that may be actively involved in a series of reactions leading to the formation of entirely new chemical compounds. With these unexpected but inspiring results in hands, a fundamental question arises: Could laser ablation of solid organic pre-

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cursors constitute a novel tool for the laboratory in situ generations of new species of astrophysical relevance?

To shed light on this potential laser application not explored to date, we have carried out a series of experiments based on our laser ablation chirped-pulse Fourier transform microwave (LA-CP-FTMW) instrumentation^[32] but working in the opposite direction trying to maximize the photo-fragmentation effects. Diaminomaleonitrile (DAMN), a compound believed to be a key player in the emergence of life-giving nucleobases,^[48] is chosen as a precursor. It contains two pairs of -NH₂ and -CN functional groups (see Figure 1), very appealing from the astrochemical point of view. They might be a source of N-bearing compounds that constitute about 40% of the ISM species.^[4] We used the picosecond pulse from an Nd:YAG laser to efficiently remove a matter from the solid DAMN rod and drag it into the plasma plume. As Figure 1 shows, the plasma plume is perpendicularly crossed with a pulse of neon carrier gas. In this way, all chemical species populating the plasma are picked up and flushed into the homemade nozzle's exit channel, situated behind the sample rod. The confinement of the gas mixture in this channel stimulates collisions and molecular reactions. The generated species are immediately expanded into the vacuum chamber and monitored by a broadband CP-FTMW spectroscopy^[28,29] in different frequency ranges.

Guided by the theoretical predictions, we assigned the precursor's rotational spectrum (see the Supplementary Information for details). DAMN possesses four ¹⁴N nuclei with non-zero nuclear quadrupole moments; its rotational lines displayed an extremely complex hyperfine structure

arising from nuclear quadrupole coupling interactions^[49] (see the upper inset of Figure 2A). The analysis of central frequencies of the hyperfine multiplets conducted to the rotational constants in Table S1. The list of the observed transitions can be found in Table S2.

Once the precursor's rotational spectrum was characterized, we focused on tuning up our experiment to achieve the experimental conditions that maximize the photo-fragmentation. With this aim, the laser fluence, stagnation pressure, and time delays between the gas, laser and microwave pulses were interactively modified until the intensity of the DAMN lines was minimized as a sign of the maximum photo-fragmentation. Figure 2A shows the congested rotational spectrum we obtained. Notice that rotational signatures of the precursor could not be wholly suppressed. We also tested in the spectrum the lines observed when the laser ablation was turned off. They were identified as instrumental spurious and water complexes^[50,51] formed from residual water. In the next step, we proceeded to eliminate them and those of the precursor, which leads us to the spectrum in Figure 2B. It should be considered as a photo-fragmentation spectrum in which only the signals attributable to the effects of laser ablation photo-fragmentation remain. This spectrum became the real target of our research.

The high number of lines in the photo-fragmentation spectrum points to the existence of a mixture of species. Most of these lines present the hyperfine structure emerging from ¹⁴N nuclear quadrupole coupling interactions, as anticipated according to the precursor's nature. Although this phenomenon significantly increases the spectral complexity, it is of

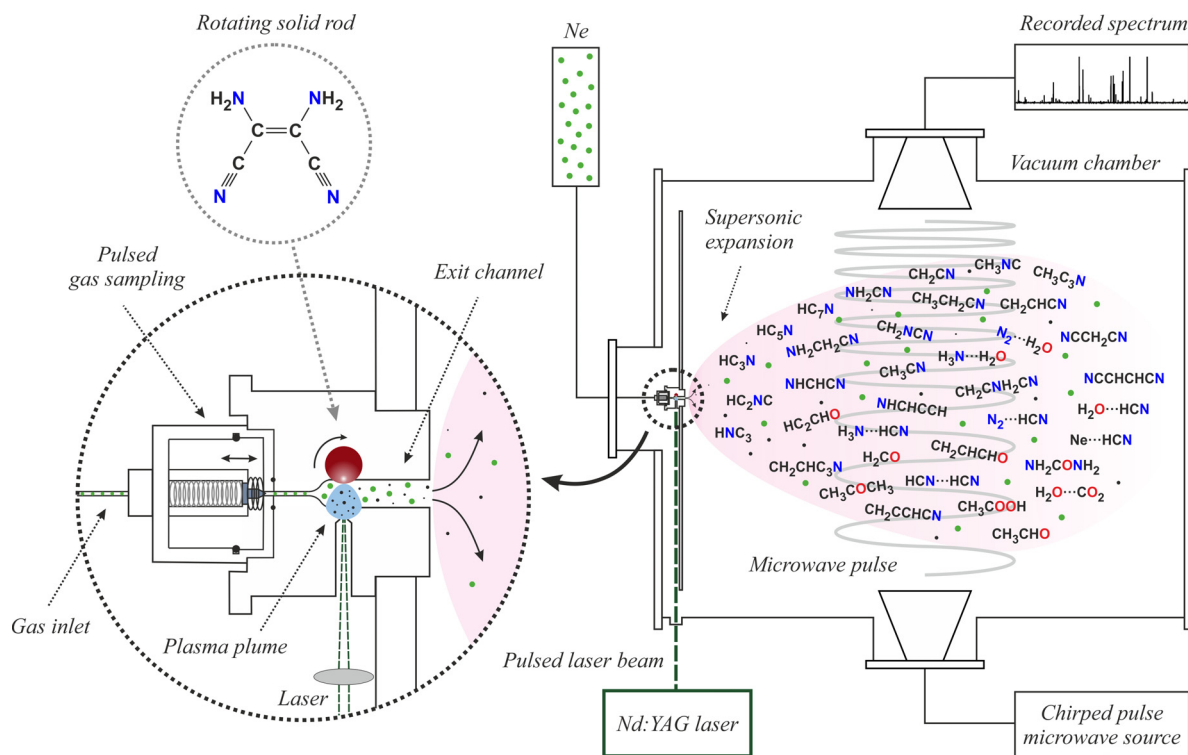


Figure 1. The experimental layout. A micro-laboratory for the generation of chemical species, consisting of a laser ablation nozzle, is coupled to the vacuum chamber of the Fourier transform microwave spectrometer to monitor the produced species.

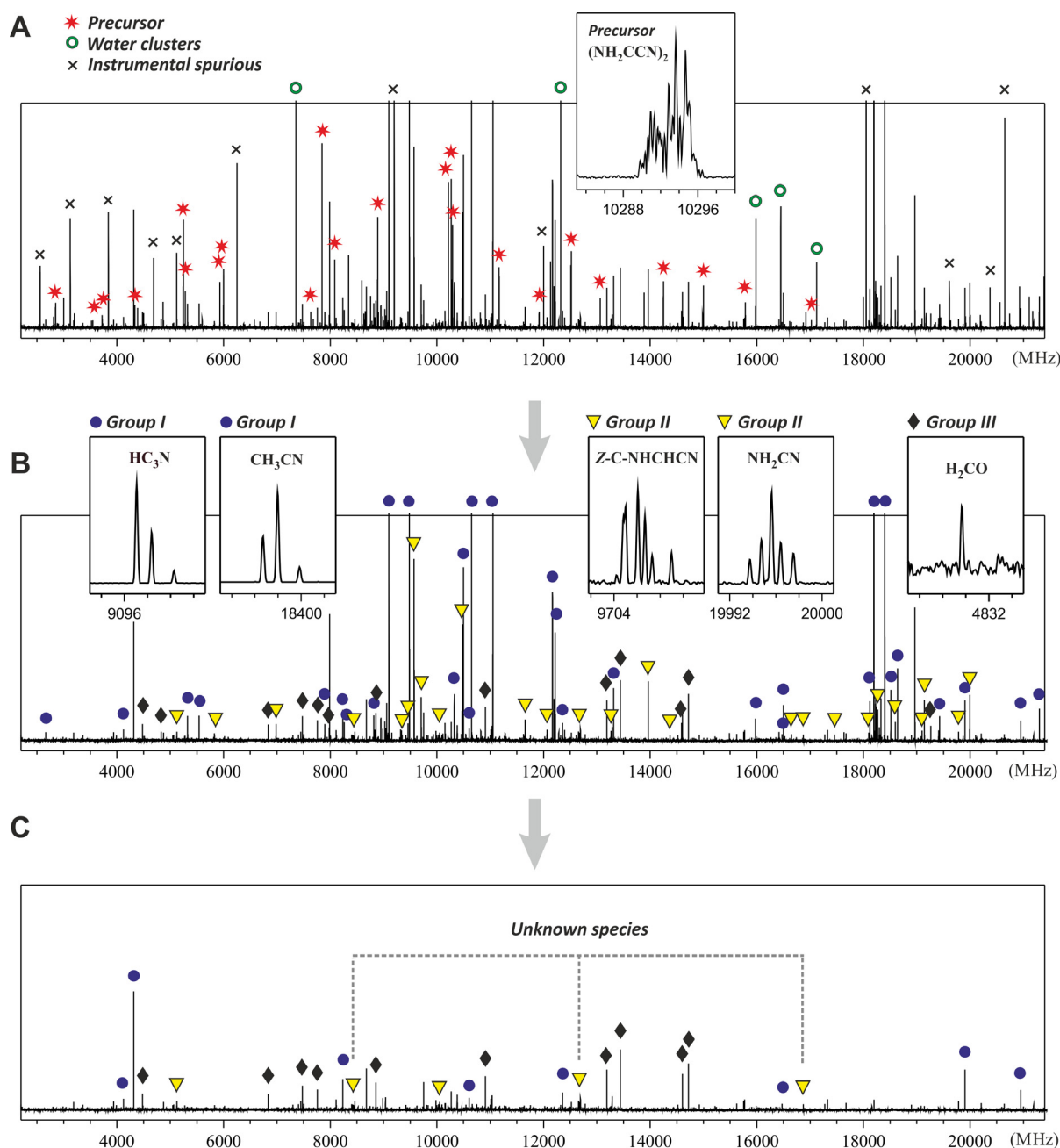


Figure 2. Strategy to track multiple species generated by the laser ablation of diaminomaleonitrile. A) Broadband spectrum between 2 and 21.4 GHz. The upper inset shows the complex hyperfine structure arising from nuclear quadrupole coupling interactions of four ^{14}N nuclei in diaminomaleonitrile precursor. B) Photo-fragmentation spectrum results from subtracting the lines belonging to the precursor and laser-independent features (water complexes, instrumental spurious). Lines are categorized into three groups according to the existence and complexity of the nuclear quadrupole hyperfine structure. C) The remaining spectrum after removing the lines from the 36 species shown in Figure 3. A line progression corresponding to the unknown species is highlighted.

fundamental importance since it hides the first clues on the chemical nature of molecular carriers responsible for the lines in Figure 2B. The hyperfine structure of the rotational lines is highly specific; it strongly depends on the number of ^{14}N nuclei in the molecule and their chemical environments. We, therefore, systematically classified the lines according to the ^{14}N nuclear quadrupole hyperfine structure (see the insets in Figure 2B). The lines with relatively simple hyperfine patterns, likely belonging to species bearing a single ^{14}N nucleus,

were allocated in Group I. We filled Group II with the lines that present more complex hyperfine structures possibly originating from species containing two or more ^{14}N nuclei. Finally, all the lines without hyperfine structures were gathered in Group III. This kind of taxonomy^[52] allowed us to examine the above lines by spectral databases exhaustively.^[53–55] We also used microwave literature to capture molecules that do not appear in the databases. In this way, we can confirm the identity of 36 distinct chemical species

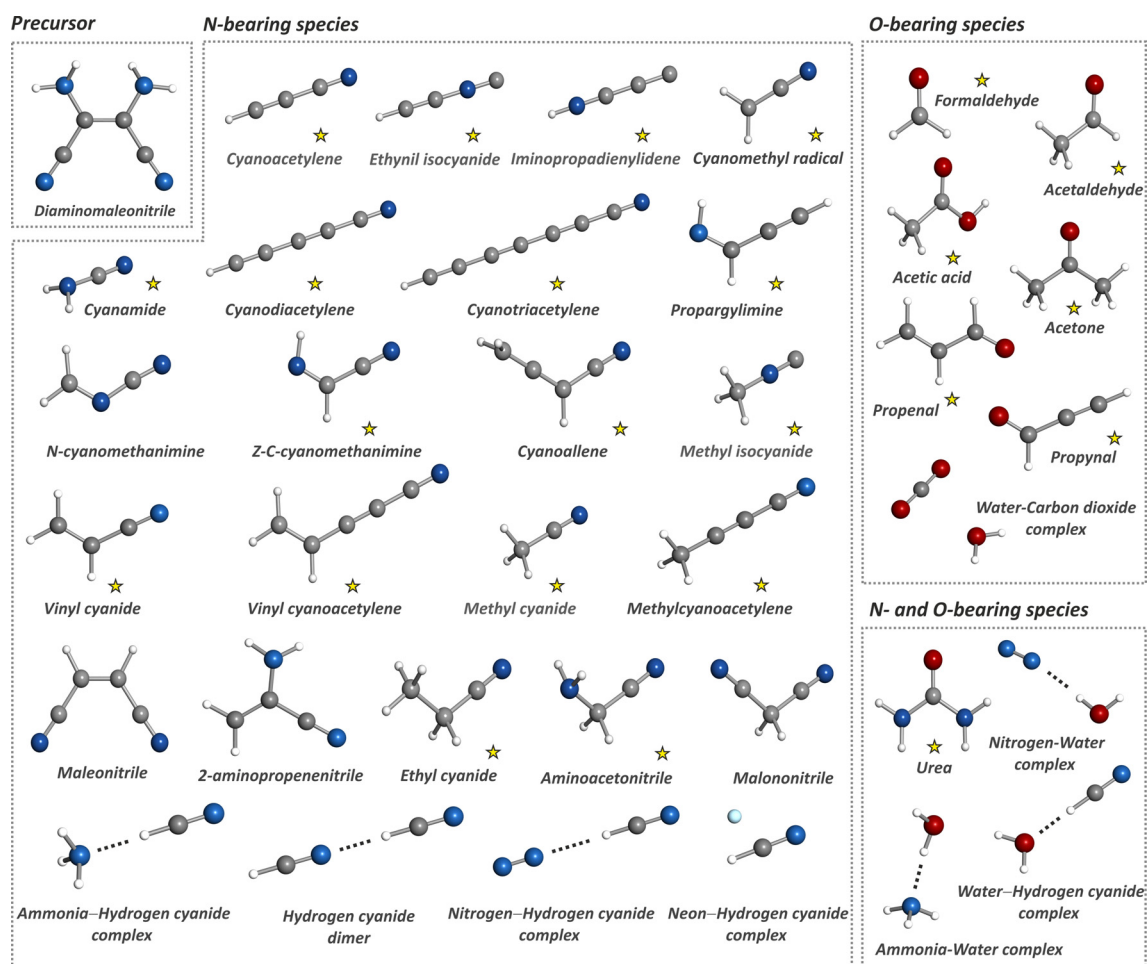


Figure 3. Known chemical species detected in the rotational spectra of laser-ablated diaminomaleonitrile precursor. Of these molecules, C-cyanomethanimine was observed through its two most stable Z- and E-isomers and only the most stable Z-form is shown in the Figure. The star shows that a given species has been detected in space.

summarized in Figure 3. We identified 28 monomers and 8 molecular complexes. The latter gives evidence about the presence in the mixture of light molecules (HCN, NH₃) whose rotational spectra lie out of the range of our experiment and non-polar molecules (N₂, CO₂).

We then removed from the spectrum all signatures of the above 36 species (see Table S3 for details). This stepwise line elimination brought us to the spectrum in Figure 2C. It might contain the rotational signatures of unknown species generated in the laser ablation processes. We soon discovered a progression among the remaining lines from Group II (see Figure 2C). It consisted of closely spaced triplets, a characteristic feature for *a*-type transitions of a nearly-prolate asymmetric top.

In a first attempt, we limited the search on this unknown species to candidates related to the precursor, bearing -CN, -NH₂ functional groups. Among them, aminocyanoacetylene (H₂NCCCN) shown in Figure 4 is an up-and-coming candidate. It is a nearly-prolate asymmetric rotor containing two ¹⁴N nuclei in agreement with the observed nuclear quadrupole hyperfine structure and, above all, its rotational constants are in perfect agreement with those predicted theoretically (see Table 1). The observation and analysis of the nuclear quadru-

pole hyperfine structure of the rotational transitions constitute the definitive factor in identifying this N-bearing species. Figure 4 shows 1₀₁ ← 0₀₀ transition for the unknown species under the scrutiny of our narrowband cavity-based FTMW spectrometer.^[56] The number and distribution of the hyperfine components perfectly match with the predicted pattern for H₂NCCCN. Table 1 shows the close agreement between the experimentally determined nuclear quadrupole coupling constants with their theoretical counterparts. More details concerning the analysis can be found in the Supplementary Information, along with the list of line transitions (Table S4). We emphasize that H₂NCCCN has never been generated in the laboratory. Many other unassigned lines in Figure 2C belonging to other new chemical species are presently under investigation.

We experimentally demonstrate that the laser ablation of DAMN produces very rich chemistry, which results in an impressive number and variety of species as recognized by eyes of high-resolution microwave spectroscopy. By detecting linear homologous series HC₃N, HC₅N, and HC₇N, we provide pieces of evidence about the capability of this experimental approach to generating carbon chain species of different lengths. The carbon chain growth trend is further seen from

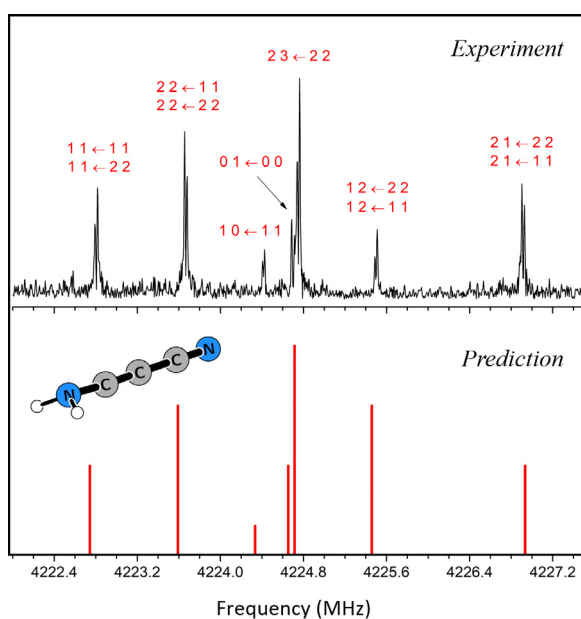


Figure 4. Comparison of the experimentally measured hyperfine structure for $1_{01} \leftarrow 0_{00}$ rotational transition of the unknown species with the predicted pattern for H_2NCCCNC . The hyperfine components are labeled using the l and F quantum numbers according to the notation $l' F' \leftarrow l'' F''$. All the hyperfine components are observed as Doppler doublets due to the coaxial configuration of the supersonic jet and the microwave radiation. The resonance frequencies are determined as the arithmetic means of the two Doppler components. The predictions are made using the experimental rotational constants obtained from the initial fit of the unknown species and the predicted nuclear quadrupole coupling constants for H_2NCCCNC from Table 1.

Table 1: Spectroscopic parameters for the unknown species in comparison with those for aminocynoacetylene.

Parameter ^[a]	Unknown species	H_2NCCCNC ^[b]
A [MHz]	— ^[c]	317955
B [MHz]	2118.5520 (28) ^[d]	2121
C [MHz]	2106.1450 (28)	2110
Δ_{JK} [kHz]	26.3 (16)	36.40
$\chi_{aa}(\text{N}_c)$ [MHz]	−4.068 (10)	−4.20
$\chi_{bb}(\text{N}_c)$ [MHz]	2.690 (50)	2.61
$\chi_{cc}(\text{N}_c)$ [MHz]	1.379 (48)	1.59
$\chi_{aa}(\text{N}_a)$ [MHz]	2.954 (11)	2.94
$\chi_{bb}(\text{N}_a)$ [MHz]	1.857 (65)	1.83
$\chi_{cc}(\text{N}_a)$ [MHz]	−4.812 (62)	−4.76
$ \mu_a $ [D]	yes ^[e]	6.3
$ \mu_b $ [D]	— ^[f]	0.0
$ \mu_c $ [D]	— ^[f]	0.9
$N_{\text{rot}}/N_{\text{hfs}}$	5/17	—
σ_{fit} [kHz]	8.5	—

[a] A , B , and C are the rotational constants; Δ_{JK} is the quartic centrifugal distortion constant; χ_{aa} , χ_{bb} , and χ_{cc} are the diagonal nuclear quadrupole coupling constants for ^{14}N nucleus in the cyano (N_c) and amino (N_a) groups; $|\mu_a|$, $|\mu_b|$ and $|\mu_c|$ are the absolute values of the electric dipole moment components along the inertial axis a , b , c ; N_{rot} and N_{hfs} represent the number of fitted rotational transitions and hyperfine components, respectively; σ_{fit} is the root mean square deviation of the fit. [b] Equilibrium parameters at the B2PLYPD3/aug-cc-pvtz level of the theory. [c] Undeterminable constant from the present data set. [d] The numbers in parentheses are 1σ uncertainties in units of the last decimal digit. [e] Observation of a given type of transition. [f] Favorable transitions not available in the studied frequency range.

$\text{CH}_3\text{CN}/\text{CH}_3\text{C}_3\text{N}$ and $\text{CH}_2\text{CHCN}/\text{CH}_2\text{CHC}_3\text{N}$ pairs of molecules. We can also notice a simultaneous formation of members of different isomeric families (C_3HN , $\text{C}_2\text{H}_3\text{N}$, $\text{C}_2\text{H}_2\text{N}_2$, $\text{C}_3\text{H}_3\text{N}$, and $\text{C}_4\text{H}_2\text{N}$) and a potential of this technique for the generation of open-shell species through the detection of CH_2CN radical. Although some of the molecules can be related to parts of the DAMN backbone (e.g. the new molecule H_2NCCCNC), our experiment indicates that processes leading to the observed species are more complex than the precursor's cracking and the recombination of the fragments. The residual water and other impurities participating in the chemistry triggered by the laser ablation process, is shown by detecting O-bearing and both N- and O-bearing species in Figure 3. These observations lead us to envisage that adding oxygen or other chemicals into the carrier gas would immensely increase the produced mixture's chemical complexity. Finally, as an actual result of this work, we consider that although our experimental conditions do not mimic those in the ISM, they produce astrophysically relevant species; more than 60% of the species in Figure 3 are molecules discovered in the ISM.

By piecing together all these results, we can affirm that we have created a micro-laboratory for the generation of interstellar species using laser ablation of solid organic precursors. We present a proof of concept by the first generation and identification of H_2NCCCNC in the terrestrial laboratory. It is a larger variant of interstellar cyanamide ($\text{H}_2\text{N}_2\text{CN}$) and a candidate for detection by radio-astronomy. Rigorous fields of investigation, such as molecular astrophysics, may thus enormously benefit from this work's results. H_2NCCCNC can be taken as the first example from a large variety of molecules of astrophysical interest that could be generated by this innovative approach employing nonvolatile solid organic precursors with different structures and functional groups. A direct comparison of our broadband records to interstellar surveys supports a hunt for new interstellar molecules and provide new pieces into the chemical puzzle of interstellar space.

The next generation of our experimental approach is under development in our laboratory to enhance the molecular production efficiency. The choice of ablation laser, its wavelength, pulse energy, and the nozzle's exit channel dimensions are considered parameters of paramount importance.

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Conflict of Interest

The authors declare no conflict of interest.

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