On the Synthesis of Chocolate Flavonoids (Propanols, Butanals) in the Interstellar Medium

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Complex organic molecules are ubiquitous in star- and planet-forming regions as well as on comets such as on 67P/Churyumov-Gerasimenko, but their origins have remained largely unexplained until now. Here, we report the first laboratory detection of distinct C_3H_8O (propanol, methyl ethyl ether) and C_4H_8O (n-butanal, i-butanal) isomers formed within interstellar analog ices through interaction with ionizing radiation. This study reveals that complex organics with propyl (C_3H_7) and butyl (C_4H_9) groups can be synthesized easily in deep space and may act as key evolutionary tracers of a cosmic ray driven non-equilibrium chemistry in low temperature interstellar ices at 10 K. These processes are of vital importance in initiating a chain of chemical reactions leading to complex organics—some of which are responsible for the flavors of chocolate—not only in the interstellar medium, but also on comet 67P/Churyumov-Gerasimenko.

Complex organic molecules (COMs)—molecules containing six or more atoms of hydrogen, carbon, nitrogen, and oxygen among them vital precursors to molecular building blocks of life such as the sugar-related glycolaldehyde ($HCOCH_2OH$) and formamide ($HCONH_2$)—account for one third of all detected molecules in the interstellar medium (ISM), although these are relatively simple molecules in terrestrial terms.[1] The elucidation of their formation routes is critical not only to understand the cosmic carbon budget and the most fundamental processes that drive the hitherto poorly characterized organic chemistry in the ISM, but also to define the level of molecular complexity of organic molecules, which can be synthesized in our galaxy.[2] Modern astrochemical models propose that COMs are formed in cold molecular clouds on interstellar dust grains—silicate-based and/or carbonaceous nanoparticles coated with a few tens of nanometers of ices of water (H_2O), methanol (CH_3OH), carbon monoxide (CO), carbon dioxide (CO_2), ammonia (NH_3), formaldehyde (H_2CO), and methane (CH_4)[3]—through processing by galactic cosmic rays (GCRs) and the internal ultraviolet (UV) field at temperatures as low as 10 K.[1a, 4] Once the molecular cloud gravitationally collapses, the newly formed molecules may sublime from the ices as the temperature of the grains rises due to the non-isothermal phase of collapse and later due to heating from the hot core.[1a] Eventually, the processed matter—including COMs—enters the circumstellar disk and is incorporated at least partially into planetary bodies (planets, moons, comets) thus providing the raw material for Solar Systems including our own.[5] A recent analysis of *Rosetta* data obtained from comet 67P/Churyumov-Gerasimenko connected with the detection of organic molecules was portrayed as *an inventory of organics, which is much more diverse and complex than anticipated based on currently accepted chemistry models.*[6] Therefore, a fundamental understanding of the level of molecular complexity of COMs, which can be reached in deep space, along with the knowledge of the underlying formation pathways of COMs is still lacking.

In this Communication, we reveal that key COMs of unprecedented complexity—n- and/or i-propanol (n-C_3H_8O, $CH_3CH_2CH_2OH$; i-C_3H_8O, $(CH_3)_2CHOH$), along with n-butanal (n-C_4H_8O; $CH_3CH_2CH_2CHO$) and i-butanal (i-C_4H_8O; $(CH_3)_2CHCHO$), of which three species are flavor molecules responsible for the taste and smell of chocolate (n-C_3H_8O, i-C_3H_8O, i-C_4H_8O)[7]—are synthesized within interstellar analog ices exposed to ionizing radiation via non-equilibrium chemistry (Figure 1). The detection of COMs with chemically complex propyl (C_3H_7) and butyl (C_4H_9) groups provides compelling evidence that organics carrying (branched) alkyl groups beyond methyl (CH_3) and ethyl (C_2H_5) can be produced easily within interstellar ices at temperatures as low as 10 K in molecular clouds and are predicted to be ubiquitous in space. Since branched propyl and butyl
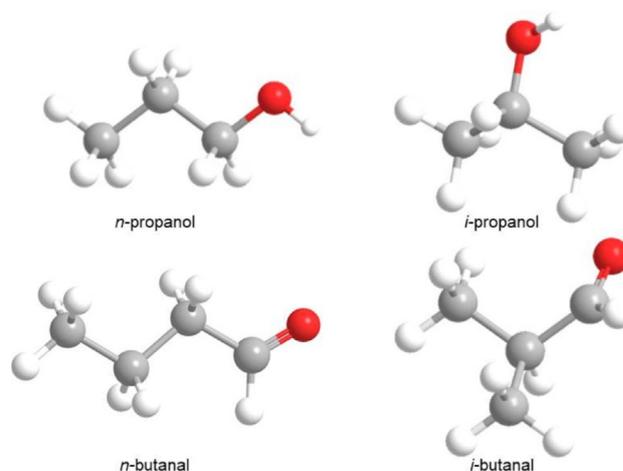
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Figure 1. Selected complex organic molecules in chocolate.

groups are also prevailing in amino acids valine (*iso*-propyl), leucine (*iso*-butyl), and isoleucine (*sec*-butyl) as detected in Murchison,[8] our studies assist the elucidation of the level of molecular complexity of organic molecules—including precursors to the origins of life—which can be synthesized in the universe.[9]

The experiments were carried out in an ultrahigh-vacuum (UHV) surface-science chamber at pressures of a few 10^{-11} torr[10] by exposing ices of carbon monoxide (^{13}CO) and methane ($^{13}CD_4$) to energetic electrons at 5 K. This simulates the energy absorbed by pristine apolar, anhydrous interstellar ices via secondary electrons that are generated by GCRs over a few 10^6 years, which represents the typical lifetime of interstellar ices in cold molecular clouds (Supporting Information; Tables S1 and S2).[11] The use of isotopically labeled reactants allows unique mass-to-charge ratios that do not overlap with other COMs to be correlated with the isomers of interest in this study. After the irradiation, a controlled heating of the ice to 300 K (temperature programmed desorption; TPD) sublimates the reactants and newly formed molecules into the gas phase. The chemical modifications of the ice were probed on line and in situ via Fourier Transform Infrared spectroscopy (FTIR) before, during, and after irradiation (Figures S1 and S2; Tables S1 and S3). During the TPD phase, the subliming molecules were also ionized via tunable vacuum ultraviolet (VUV) photoionization (PI) and mass resolved in a reflectron time-of-flight mass spectrometer (PI-ReTOF-MS) (Figure 2). By systematically tuning the PI energy, we selectively ionize *specific* structural isomers based on their ionization energy (IE) and determine which isomer(s) is(are) produced in the interstellar analog ices (Supporting Information). It is critical to point out that these apolar interstellar model ices containing carbon monoxide and methane were chosen to explore the proof of concept that COMs carrying propyl and butyl groups can be synthe-

sized via interaction with ionizing radiation. Considering observations from the Spitzer space telescope, ices containing carbon monoxide (CO) at levels of up to 85 % were observed toward low-mass star-forming regions; apolar mixtures with methane (CH_4) at levels of up to 11 % were also detected.[3] Ehrenfreund et al. verified that the exploitation of interstellar analog ices offers a corroborated procedure and the very first step in understanding ISM ices.[12]

During the energetic processing of the ices, several new infrared features emerged (Figure S1, Table S3). These absorptions could be associated with carbon dioxide ($^{13}CO_2$, ν_3, 2276 cm^{-1}), ethane ($^{13}C_2D_6$, ν_{10}, 2214 cm^{-1}), ethylene ($^{13}C_2D_4$, ν_{11}, 2177 cm^{-1}), ketene ($^{13}CD_2^{13}CO$, ν_2, 2051 cm^{-1}), and the formyl radical (D^{13}CO, ν_2, 1774 cm^{-1}). Besides these individual molecules, an intense absorption in the range of 1663 to 1682 cm^{-1} could be linked to the carbonyl functional group ($^{13}C{=}O$). A deconvolution of this feature exposed that at least five carbonyl-bearing molecules can be associated with this absorption (Figures S2 and S3). One of the isomers of interest for this study, *i*-butanal ($^{13}C_4D_8O$; ($^{13}CD_3)_2^{13}CD^{13}CDO$), belongs to this group and, therefore, might be a contributor to this band. Infrared stretches belonging to *n*-propanol ($^{13}C_3D_7OD$) could not be uniquely confirmed.[13] Unfortunately, the most intense modes, and therefore the most likely to be detected, overlap with the ν_4 fundamental of the methane ($^{13}CD_4$) reactant centered at 985 cm^{-1}. A similar problem exists for *i*-propanol since the most intense mode observed in ($^{13}CD_3)_2^{13}CDOD$ is concealed by the ν_3 fundamental of the methane ($^{13}CD_4$) reactant (2237 cm^{-1}); the ^{13}CO stretching is obscured by the ν_3 fundamental of the ethylene ($^{13}C_2D_4$; 1067 cm^{-1}) product.[14] Therefore, since the fundamentals of functional groups such as of carbonyls in COMs often fall in the same range, infrared spectroscopy rarely allows an identification of individual COMs. Therefore, an alternative analytical technique is imperative to
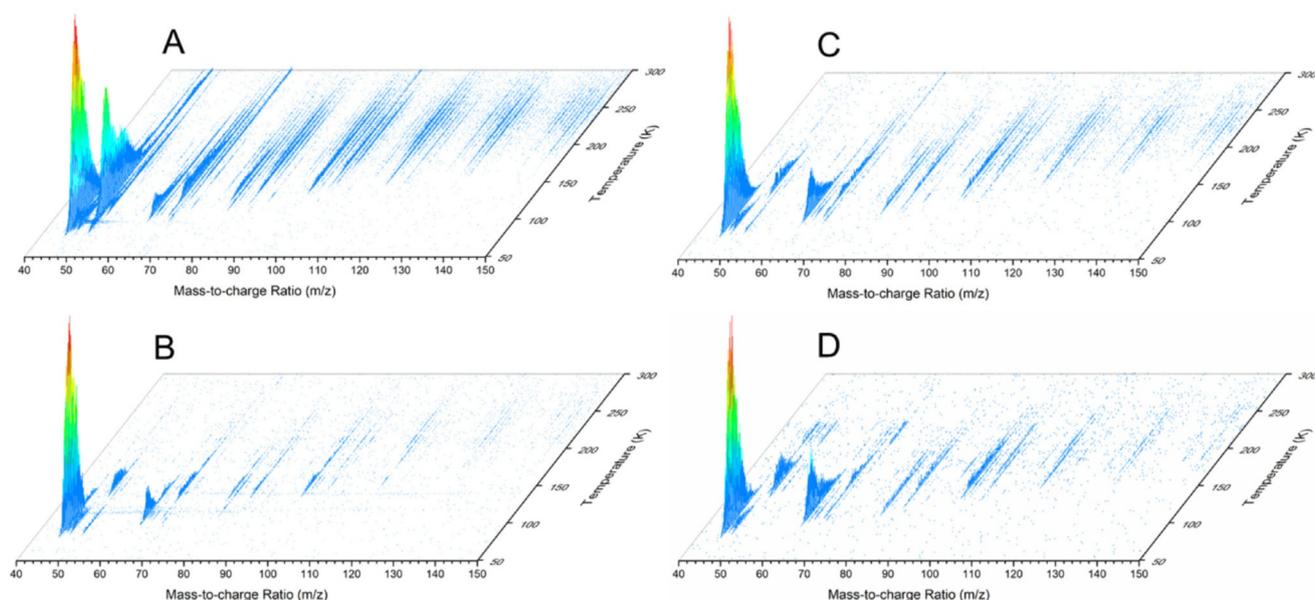

Figure 2. PI-ReTOF-MS data reporting the temperature-dependent mass spectra at photoionization energies of (A) 10.49 eV, (B) 9.93 eV, (C) 9.75 eV, and (D) 9.63 eV for irradiated methane ($^{13}CD_4$) and carbon monoxide (^{13}CO) ices.

probe discrete organics in the irradiated ices. This objective is achieved by exploiting PI-ReTOF-MS (Figures 2 and 3) during the annealing of the irradiated ices.

During the TPD phase, an ion signal corresponding to $^{13}C_3D_8O^+$ (m/z = 71) and $^{13}C_4D_8O^+$ (m/z = 84) was observed at a PI energy of 10.49 eV. Considering the adiabatic ionization energies of the C_3H_8O and C_4H_8O isomers (Supporting Information), multiple species can contribute to signal at m/z = 71 and 84. Therefore, additional experiments with PI energies of 9.63 eV, 9.75 eV, and 9.93 eV were carried out to discriminate which isomers are formed. Considering the molecular formula $^{13}C_3D_8O$,[15] three isomers, that is, n-propanol (IE = 10.22 ± 0.06 eV), i-propanol (IE = 10.17 ± 0.02 eV), and methyl ethyl ether ($^{13}CD_3O^{13}C_2D_5^+$; IE = 9.72 ± 0.07 eV) have to be discriminated. At a PI of 10.49 eV, all three isomers can be ionized. The TPD profile at m/z = 71 has a bimodal structure peaking at 121 K and 162 K (Figure 3B); this might be linked to distinct isomers as the more polar alcohol isomers sublime at a higher temperature compared to the less polar ether isomer.[4] At a PI energy of 9.93 eV, only methyl ethyl ether can be ionized since this PI energy is below the IEs of both alcohol isomers. The TPD data reveal that only the early sublimation peak at 121 K is visible at PI = 9.93 eV thus unambiguously attributing this event to methyl ethyl ether (Figure 3C). For PI = 9.75 eV the lack of signal at m/z = 71 is rationalized by the error associated with the IE of methyl ethyl ether as its upper limit (9.79 eV) lies above this PI (9.75) and would result in the molecule not being ionized and therefore not detected (Figure 3D). Consequently, the late sublimation event has to be associated with the alcohol isomer(s); the ionization energies of n- and i-propanol are too close to be separated (Supporting Information). At a PI energy of 9.63 eV, none of the isomers can be ionized (Figure 3E). Furthermore, we confirmed the aforementioned assignments in separate experiments by doping carbon monoxide-methane ($CO-CH_4$) ices with distinct C_3H_8O isomers, recorded the TPD profiles of these isomers, and compared those calibration data with the TPD profile of the irradiated sample recorded at m/z = 71 (Supporting Information; Figures S3 to S5; Tables S1 and S4). The onset of the sublimation of n- and i-propanol in the doped samples agrees nicely with the sublimation events in the irradiation experiments. The yields of n-propanol, i-propanol, and methyl ethyl ether were determined to be 2.2 ± 0.9 × 10^{-4} molecules eV^{-1}, 1.2 ± 0.5 × 10^{-3} molecules eV^{-1}, and 2.1 ± 0.9 × 10^{-5} molecules eV^{-1}, respectively, with the yields for n- and i-propanol representing upper limits as these isomers cannot be discriminated (Supporting Information).

Further, the molecular formula $^{13}C_4D_8O^+$ matches more than 30 isomers including n-butanal (IE = 9.82 ± 0.04 eV) and i-butanal (IE = 9.71 ± 0.02 eV).[15] Although multiple isomers exist, none has overlapping ionization energy ranges with n- or i-butanal. At PI = 10.49 eV, the ion signal of m/z = 84 is very broad from 100 K to 180 K (Figure 3G). Switching the PI energy to 9.93 eV allows for n- or i-butanal to be ionized; no isomers with higher IEs contribute to the ion counts (Figure 3H). Further, by tuning the PI to 9.75 eV, n-butanal will no longer be ionized (Figure 3I). The difference of the TPD profiles recorded at 9.93 eV and 9.75 eV allows us to determine the contribution of n-butanal (Supporting Information). Similarly, at PI = 9.75 eV
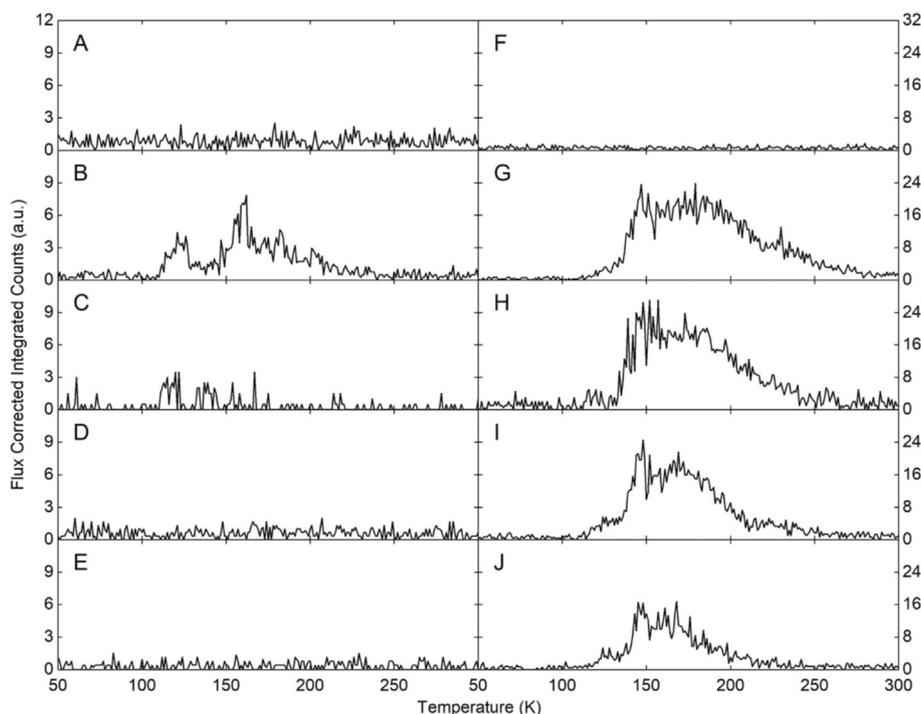

Figure 3. (Left) PI-ReTOF-MS data recorded at m/z = 71 from the $^{13}CO-^{13}CD_4$ system at photoionization energies of A) 10.49 eV (no irradiation), B) 10.49 eV, C) 9.93 eV, D) 9.75 eV, and E) 9.63 eV after irradiation of the ice during heating. (Right) PI-ReTOF-MS data recorded at m/z = 84 system at photoionization energies of F) 10.49 eV (no irradiation), and G) 10.49 eV, (H) 9.93 eV, (I) 9.75 eV, and J) 9.63 eV after irradiation of the ice during TPD. The molecules of interest that were detected in chocolate analysis are depicted in the top panels.

(Figure 3 I), *i*-butanal is still ionized, but when the PI is changed to 9.63 eV (Figure 3 J) it cannot be ionized; therefore, a change in both TPD profiles allows us to extract the contribution of the *i*-butanal isomer. Calibration experiments with *n*-/*i*-butanal doped ices confirm these assignments (Figures S3 to S5) with yields determined for *n*-butanal and *i*-butanal to be $2.0 \pm 0.8 \times 10^{-4}$ molecules eV^{-1} and $1.3 \pm 0.5 \times 10^{-4}$ molecules eV^{-1}, respectively (Table S4; Supporting Information).

Also, ion signals corresponding to $^{13}C_4D_{10}O^+$ ($m/z = 88$) and $^{13}C_5D_{10}O^+$ ($m/z = 101$) were detected; both of these molecular formulae contain isomers that are correlated with the taste and smell of chocolate[7b, 16] along with possible molecules detected on comet 67P/Churyumov-Gerasimenko, that is, *i*-butanol ($C_4H_{10}O$; $(CH_3)_2CHCH_2OH$) and 3-pentanone ($C_5H_{10}O$; $(C_2H_5)_2CO$) (Figures S6 to S7)[6b] However, overlapping IEs of these isomers do not allow specific identifications. The $^{13}C_4D_{10}O^+$ ion signal was narrowed to possibly contain *i*-butanol (IE = 10.02 ± 0.02 eV) and one or more of the following isomers: diethyl ether (IE = 9.51 ± 0.03 eV), *n*-propyl methyl ether (IE = 9.41 ± 0.07 eV), *iso*-propyl methyl ether (IE = 9.45 ± 0.04 eV) (Figure S6). The *i*-butanol isomer could not be uniquely identified as another isomer, *n*-butanol ($^{13}C_4D_9OD$; IE = 9.99 ± 0.05 eV), has an overlapping IE. The ion signal corresponding to $^{13}C_5D_{10}O^+$ remained even at a PI energy of 9.63 eV and therefore could be due to the isomer proposed to be part of the COMs on 67P/Churyumov-Gerasimenko: 3-pentanone (IE = 9.31 ± 0.02 eV) and/or the chocolate-related molecule 2-methyl butanal ($^{13}CD_3^{13}CD_2(^{13}CD_3)^{13}CD^{13}CDO$; IE = 9.59 ± 0.01 eV) (Figure S7).[6b, 7b, 15] However, multiple isomers with overlapping IEs exist making it impossible to uniquely identify either of those isomers (Supporting Information).[15]

In conclusion, by exposing carbon monoxide–methane interstellar analog ices to ionization radiation and exploiting an array of complementary in situ analytical tools, the present study offers compelling evidence on a facile formation of distinct COMs carrying propyl (C_3H_7) and butyl (C_4H_9) groups—*n*-(C_3H_8O; $CH_3CH_2CH_2OH$) and/or *i*-propanol (C_3H_8O; $(CH_3)_2CHOH$) along with *n*- (C_4H_8O; $CH_3CH_2CH_2CHO$) and *i*-butanal (C_4H_8O; $(CH_3)_2CHCHO$)—of which three are flavor molecules defining the taste and smell of chocolate. Considering the branching ratios of the structural isomers along with the distinct energetics, these organics are synthesized *within* the ices via an exotic non-equilibrium chemistry, but not through thermal processes (Table S6; Supporting Information). Although future experiments have to be carried out to constrain the formation mechanisms of these COMs on the molecular level (Supporting Information), the present study embodies a significant first step toward elucidating possible abiotic pathways toward COMs carrying propyl (C_3H_7) and butyl (C_4H_9) groups with alcohol and aldehydes representing important redox systems in contemporary biochemistry on Earth. The identification of at least two C_3H_8O isomers (propanol, methyl ethyl ether) is fascinating as propanol has been detected on comet 67P/Churyumov-Gerasimenko and tentatively identified toward Orion KL;[6b, 17] methyl ethyl ether has also been detected, tentatively toward Orion KL[17b, 18] with our experiments demonstrating that these isomers should be synthesized via a GCR mediated chemistry in

the ISM as well. It is important to note that no simulation experiment worldwide can mimic the chemical complexity and diverse radiation environment of the ISM simultaneously; real interstellar grains are not only exposed to a range of energetic GCRs but also to UV photons. UV photons only penetrate the first few icy layers of the grains, but energetic GCRs might pass through the icy mantle. Therefore, simulation experiments must be carried out with well-defined model ices and irradiation sources first to gain a systematic understanding of the fundamental processes leading to COMs in the processed ices.

Therefore, COMs with propyl (C_3H_7) and (branched) butyl (C_4H_9) side groups as detected in the present study such as in propanol and butanal isomers are expected to be formed deep within interstellar ices and hence should be detectable in the gas phase upon sublimation in star forming regions. With the commission of the Atacama Large Millimeter/Submillimeter Array (ALMA), the detection of heavier molecular weight organics with complex alkyl chains will continue to grow beyond *n*-propyl cyanide (*n*-C_3H_7CN)[19] and *iso*-propyl cyanide (*i*-C_3H_7CN)[2] as detected toward the star forming region Sagittarius B2(N). An understanding of these data will rely on critical advances in experimental laboratory astrophysics as exposed here, not only eliminating the gap between observational and laboratory data that existed for decades, but also providing further insight into the link between the origin and evolution of comets and the interstellar material that created them. This brings us closer to eventually predicting where in the Galaxy molecular precursors linked to the *Origins of Life* might have been synthesized.

Acknowledgements

[1] a) E. Herbst, *Int. Rev. Phys. Chem.* **2017**, *36*, 287–331; b) J. M. Hollis, F. J. Lovas, P. R. Jewell, *Astrophys. J.* **2000**, *540*, L107–L110.

[2] A. Belloche, R. T. Garrod, H. S. Müller, K. M. Menten, *Science* **2014**, *345*, 1584–1587.

[3] A. C. A. Boogert, P. A. Gerakines, D. C. B. Whittet, *Annu. Rev. Astron. Astrophys.* **2015**, *53*, 541–581.

[4] M. J. Abplanalp, S. Gozem, A. I. Krylov, C. N. Shingledecker, E. Herbst, R. I. Kaiser, *Proc. Natl. Acad. Sci. USA* **2016**, *113*, 7727–7732

[5] A. G. G. M. Tielens, *Rev. Mod. Phys.* **2013**, *85*, 1021–1081.

[6] a) M. J. Mumma, S. B. Charnley, *Annu. Rev. Astron. Astrophys.* **2011**, *49*, 471–524; b) 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, A. Morse, M. Rubin, M. Schuhmann, M. G. G. T. Taylor, C. Y. Tzou, I. Wright, *Mon. Not. R. Astron. Soc.* **2017**, *469*, S130–S141.

[7] a) A. C. Aprotosoaie, S. V. Luca, A. Miron, *Compr. Rev. Food Sci. Food Saf.* **2016**, *15*, 73–91; b) C. Counet, D. Callemien, C. Ouwerx, S. Collin, *J. Agric. Food Chem.* **2002**, *50*, 2385–2391.

[8] T. Koga, H. Naraoka, *Sci. Rep.* **2017**, *7*, 636.

[9] The processed material of molecular clouds eventually enters circumstellar disks and is at least partially incorporated into planetesimals.

[10] M. J. Abplanalp, M. Förstel, R. I. Kaiser, *Chem. Phys. Lett.* **2016**, *644*, 79–98.

[11] C. J. Bennett, C. S. Jamieson, Y. Osamura, R. I. Kaiser, *Astrophys. J.* **2005**, *624*, 1097–1115.

[12] P. Ehrenfreund, D. P. Glavin, O. Botta, G. Cooper, J. L. Bada, *Proc. Natl. Acad. Sci. USA* **2001**, *98*, 2138–2141.

[13] J. A. Noble, S. Coussan, *J. Phys. Chem. A* **2015**, *119*, 11371145.

[14] J. C. Dobrowolski, S. Ostrowski, R. Kołos, M. H. Jamróz, *Vib. Spectrosc.* **2008**, *48*, 82–91.

[15] S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, W. G. Mallard, S. A. Kafafi, in *NIST Chemistry WebBook, NIST Standard Reference Database Number 69* (Eds.: P. J. Linstrom, W. G. Mallard), National Institute of Standards and Technology, Gaithersburg MD, 20899, DOI:10.18434/T4D303, (retrieved February 1, 2017).

[16] D. Kadow, J. Bohlmann, W. Phillips, R. Lieberei, *J. Appl. Bot. Food Qual.* **2013**, *86*, 90–98.

[17] a) H. S. P. Müller, A. Belloche, L.-H. Xu, R. M. Lees, R. T. Garrod, A. Walters, J. van Wijngaarden, F. Lewen, S. Schlemmer, K. M. Menten, *Astron. Astrophys.* **2016**, *587*, A91; b) B. Tercero, J. Cernicharo, A. López, N. Brouillet, L. Kolesniková, R. Motiyenko, L. Margulès, J. Alonso, J.-C. Guillemin, *Astron. Astrophys.* **2015**, *582*, L1.

[18] G. W. Fuchs, U. Fuchs, T. F. Giesen, F. Wyrowski, *Astron. Astrophys.* **2005**, *444*, 521–530.

[19] A. Belloche, R. T. Garrod, H. S. P. Müller, K. M. Menten, C. Comito, P. Schilke, *Astron. Astrophys.* **2009**, *499*, 215–232.