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Exploiting Photoionization Reflectron Time-of-Flight Mass Spectrometry to Explore Molecular Mass Growth Processes to Complex Organic Molecules in Interstellar and Solar System Ice Analogs

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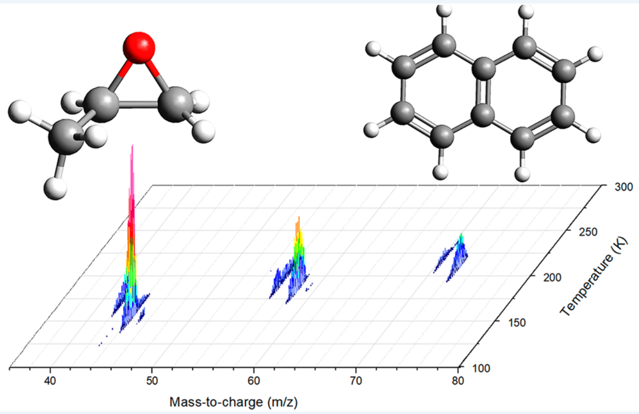

CONSPECTUS: This Account presents recent advances in our understanding on the formation pathways of complex organic molecules (COMs) within interstellar analog ices on ice-coated interstellar nanoparticles upon interaction with ionizing radiation exploiting reflectron time-of-flight mass spectrometry (ReTOF-MS) coupled with tunable vacuum ultraviolet (VUV) single photon ionization (PI) and resonance enhanced multiphoton ionization (REMPI) of the subliming molecules during the temperature-programmed desorption (TPD) phase. Laboratory simulation experiments provided compelling evidence that key classes of complex organics (aromatic hydrocarbons, alcohols, ethers, aldehydes, enols, ketones, and carboxylic acids) can be synthesized upon exposure of astrophysically relevant model ices to ionizing radiation *within* and *throughout* the ices at temperatures as low as 5 K.

Molecular mass growth processes can be initiated by suprathermal or electronically excited reactants along with barrierless radical−radical recombination if both radicals hold a proper recombination geometry. Methyl (CH_3), amino (NH_2), hydroxyl (OH), ethyl (C_2H_5), vinyl (C_2H_3), ethynyl (C_2H), formyl (HCO), hydroxycarbonyl (HOCO), hydroxymethyl (CH_2OH), methoxy (CH_3O), and acetyl (CH_3CO) represent readily available reactants for *radical−radical recombination within* the ices. Reactive singlet species were found to *insert* without barrier into carbon−hydrogen and carbon−carbon single bonds (carbene) leading to an extension of the carbon chain and may *add* to carbon−carbon double bonds (carbene, atomic oxygen) forming cyclic reaction products. These galactic cosmic ray-triggered nonequilibrium pathways overcome previous obstacles of hypothesized thermal grain-surface processes and operate *throughout the ice* at 5 K. Our investigations discriminate between multiple structural isomers such as alcohols/ethers, aldehydes/enols, and cyclic/acyclic carbonyls. These data provide quantitative, *isomer selective* input parameters for a cosmic ray-dictated formation of complex organics in interstellar ices and are fully able to replicate the astronomical observations of complex organics over typical lifetimes of molecular clouds of a few 10^6 to 10^7 years. Overall, PI-ReTOF-MS revealed that the processing of astrophysically relevant ices can lead to multifaceted mixtures of organics reaching molecular weights of up to 200 amu. Further advances in laboratory techniques beyond the FTIR-QMS limit are clearly desired not only to confidently assign detection in laboratory ice analog experiments of increasingly more complex molecules of interest but also from the viewpoint of future astronomical searches in the age of the Atacama Large Millimeter/submillimeter Array (ALMA).

KEY REFERENCES

- Abplanalp, M. J.; Gozem, S.; Krylov, A. I.; Shingledecker, C. N.; Herbst, E.; Kaiser, R. I. A study of interstellar aldehydes and enols as tracers of a cosmic ray-driven nonequilibrium synthesis of complex organic molecules. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113*, 7727−7732.[1] *This combined experimental, computational, and astrochemical*

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modeling study reveals that interstellar enols like vinyl alcohol (C_2H_3OH) may act as tracers of a cosmic-ray-driven nonequilibrium chemistry leading to complex organics within low-temperature interstellar ices at 10 K.

- Bergantini, A.; Abplanalp, M. J.; Pokhilko, P.; Krylov, A. I.; Shingledecker, C. N.; Herbst, E.; Kaiser, R. I. A Combined Experimental and Theoretical Study on the Formation of Interstellar Propylene Oxide (CH_3CHCH_2O)—A Chiral Molecule. *Astrophysical Journal* **2018**, *860*, 108.[2] *This work discloses that racemic propylene oxide (c-C_3H_6O) detected toward the high-mass star-forming region Sagittarius B2(N) can be synthesized by nonequilibrium reactions initiated by galactic cosmic rays on ice-coated interstellar nanoparticles through excited-state, spin-forbidden pathways operating at 10 K.*
- Abplanalp, M. J.; Frigge, R.; Kaiser, R. I. Low-temperature synthesis of polycyclic aromatic hydrocarbons in Titan's surface ices and on airless bodies. *Science Advances* **2019**, *5*, eaaw5841.[3] *Aromatic molecules such as benzene, naphthalene, and phenanthrene can be efficiently formed via galactic cosmic ray processing of low-temperature acetylene ices (of airless bodies) throughout our Solar System thus challenging conventional wisdom that aromatic hydrocarbons are formed solely via gas phase reactions in hydrocarbon-rich atmospheres of planets and their moons.*
- Kleimeier, N. F.; Turner, A. M.; Fortenberry, R. C.; Kaiser, R. I. On the Formation of the Popcorn Flavorant 2,3-Butanedione ($CH_3COCOCH_3$) in Acetaldehyde-Containing Interstellar Ices. *ChemPhysChem* **2020**, *21*, 1531−1540.[4] *We reveal the laboratory detection of 2,3-butanedione (diacetyl, $CH_3COCOCH_3$), a butter and popcorn flavorant, synthesized within acetaldehyde-based interstellar analog ices exposed to ionizing radiation exploiting isotopic substitution experiments combined with isomer-selective, tunable vacuum ultraviolet (VUV) photoionization of the subliming molecules, thus constraining the molecular complexity of molecules forming in extraterrestrial ices.*

1. INTRODUCTION

For the last decades, cold molecular clouds, such as the Taurus Molecular Cloud (TMC-1) and Bernard 68 (Figure 1), have emerged as *molecular factories* and *natural laboratories* on a macroscopic scale and aided our understanding of the fundamental processes leading to the synthesis of complex organic molecules (COMs) in the interstellar medium (ISM), the space between the stars, through astronomical observations combined with astrochemical modeling and laboratory experiments (Table 1).[1−4] Molecular clouds are characterized by number densities of 10^2 to 10^4 molecules cm^{-3} and kinetic gas temperatures of 10−15 K with interstellar dust particles, nanometer-sized siliceous and carbonaceous grain nuclei, shielding COMs from the destructive photon field.[5] Due to the efficient extinction of ultraviolet (UV) and visible (vis) photons, dense clouds entirely block the light of stars lying behind them. Considering that COMs comprise close to 80% of the 206 detected interstellar and circumstellar molecules, among them essential precursors to molecular building blocks of life such as the sugar-related glycolaldehyde ($HCOCH_2OH$), the processes that drive low-temperature organic chemistry in deep space represent a fundamental chemistry problem. These pathways define the molecular complexity that can be reached in our universe and advance our perception of where in our Galaxy molecular precursors to the *origins of life* might be synthesized.

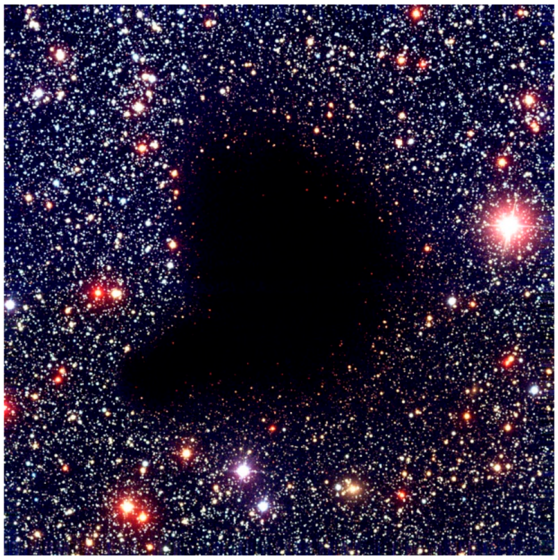
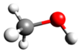
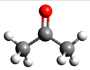
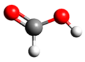
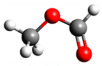
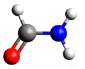
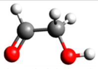
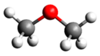
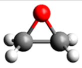
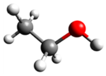
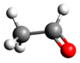
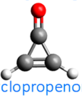
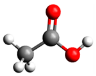
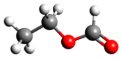
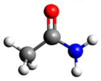
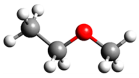
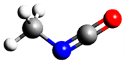
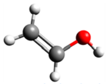
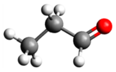
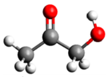
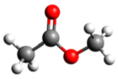
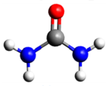
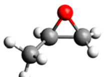
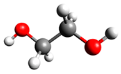
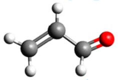
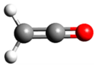
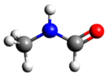
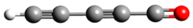
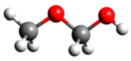
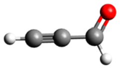
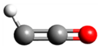
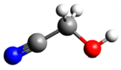
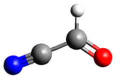
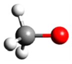


Figure 1. Image of the cold molecular cloud Bernard 68. This cloud is on the brink of gravitational collapse within the next 200 000 years leading to the formation of stars and conceivably solar systems (Credit: ESO).

Whereas sophisticated gas phase reaction networks coupling barrierless, bimolecular ion−molecule[6] and neutral−neutral reactions[5] account for the formation of hydrogen-deficient organics like cyanopolyynes ($H(C{\equiv}C)_nCN$; n = 1−4),[7,8] pathways leading to COMs have remained elusive, with gas phase models predicting fractional abundances orders of magnitude lower than observed.[1] Mehringer et al. proposed that the synthesis of complex organics is linked to the processing of low temperature (10 K) ice-coated nanoparticles (interstellar grains) by ionizing radiation such as galactic cosmic rays (GCRs) and the internal ultraviolet photon field in cold molecular clouds and in star forming regions.[9] Interstellar ices consist of, for example, water (H_2O), methanol (CH_3OH), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), and ammonia (NH_3) a few hundred nanometers thick (Table 2). Exposure of these ices to ionizing radiation (photons, GCRs) may trigger the formation of COMs by reactions of atoms with excess kinetic energy[10] and vibrationally excited radicals,[1] which are not in thermal equilibrium with the surrounding ice. Along with reactions of electronically excited atoms and molecules,[11] these species can easily overcome reaction barriers[5] that lead to complex organics, some of which can be ejected from the grains via grain explosions,[12] grain−grain collisions,[13] photodesorption,[14] or reactive desorption,[15] which enriches the gas phase even at 10 K. Eventually, the densest parts of these molecular clouds undergo gravitational collapse and ultimately develop into star forming regions. There, heating from the central star raises temperatures up to 300 K and leads to partial sublimation of the molecules formed on the grains into the gas phase, and these molecules can be detected by radio telescopes. In this hot core stage, the molecular synthesis may also advance thermally through radical−radical recombination when the radicals diffuse within the ices as well as on the grain surface.[16] The relative role of nonthermal (molecular cloud stage) versus thermal (hot core stage) molecular synthesis

Table 1. Key Classes of Ubiquitous Complex Organic Molecules (COMs)[a] identified in the Gas Phase of the Interstellar Medium (ISM)[b]

Alcohol	Aldehyde	Ketone	Acid	Ester	Amide	Sugar-Related	Ether	Other
 **Methanol** **CH_3OH**	 **Formaldehyde** **H_2CO**	 **Acetone** **CH_3COCH_3**	 **Formic Acid** **HCOOH**	 Methyl formate $HCOOCH_3$	 **Formamide** **$HCONH_2$**	 Glycolaldehyde $HCOCH_2OH$	 Dimethyl ether CH_3OCH_3	 Ethylene oxide $c\text{-}C_2H_4O$
 **Ethanol** **CH_3CH_2OH**	 **Acetaldehyde** **$HCOCH_3$**	 Cyclopropenone $c\text{-}C_3H_2O$	 **Acetic Acid** **CH_3COOH**	 Ethyl formate $HCOOCH_2CH_3$	 **Acetamide** **CH_3CONH_2**		 Ethyl methyl ether $CH_3CH_2OCH_3$	 **Methyl isocyanate** **CH_3NCO**
 Vinyl alcohol H_2CCHOH	 **Propanal** **$HCOCH_3CH_2$**	 Hydroxyacetone CH_3COCH_2OH		 **Methyl acetate** **CH_3COOCH_3**	 Urea $(NH_2)_2CO$			 Propylene oxide CH_3CHCH_2O
 **Ethylene glycol** **$HOCH_2CH_2OH$**	 Propenal $HCOC_2H_3$	 Ketene H_2CCO			 N-Methylformamide $HCONHCH_3$			 1-oxo-2,4-pentadiynyl HC_5O
 Methoxymethanol CH_3OCH_2OH	 Propynal HCOCCH	 Ketenyl HCCO						 1-oxo-2,4,6-hexatriynyl HC_7O
 Glycolonitrile $HOCH_2CN$	 Cyanoformaldehyde HCOCN							 Methoxy CH_3O

[a]COMs are per astronomical definition organic molecules containing six or more atoms of carbon, hydrogen, oxygen, and nitrogen. [b]Molecular hydrogen represents the dominant molecule followed by carbon monoxide (CO) with fractional abundances relative to molecular hydrogen of about 8×10^{-5} with COMs detected at levels of up to some 10^{-8}. Molecules in bold were confirmed in comet 67P/Churyumov−Gerasimenko; molecules whose formation pathways have been untangled in our laboratory are color coded in blue.

Table 2. Molecules Identified on Interstellar Grains toward Massive Young Stellar Objects (MYSO) and in Cometary Ices along with Their Abundances Relative to Water[a]

molecule	abundance toward molecular clouds[b]	abundance in comets[b]
H_2O	100	100
CH_3OH	3−31	0.2−7
CO	3−26	0.4−30
CO_2	11−27	4−30
CH_4	1−3	0.4−1.6
H_2CO	2−7	0.11−1.0
NH_3	7	0.2−1.4
OCS	0.03−0.16	0.1−0.4
OCN^-	0.1−1.9	

[a]These molecules represent the molecular building blocks and precursors to complex organic molecules (COMs) synthesized in low temperature extraterrestrial ices by ionizing radiation in the form of photons and galactic cosmic rays. Tenuous detections, such as for HCOOH, are not included. Data from ref 26. [b]Relative to the water ice.

is essentially unknown, but growing numbers of observations suggest that the nonthermal formation mechanisms can be more efficient at low temperatures than previously thought.[17−19]

Traditionally, Fourier-transform infrared spectrometry (FTIR) has been implemented to elucidate the effects of the interaction of ionizing radiation with astrophysical analog ices.[20,21] Although FTIR represents a facile approach to unravel the destruction kinetics of small molecules such as water (H_2O), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), and methanol (CH_3OH), along with the formation rates of new radicals within the ices like formyl (HCO), hydroxycarbonyl (HOCO), hydroxymethyl (CH_2OH), and methyl (CH_3), the capability of FTIR to detect COMs synthesized within the ices is often restricted.[22] Since *functional groups* of organics such as of carbonyl groups of, for example, aldehydes and ketones portray comparable group frequencies in the range of 1850 to 1600 cm^{-1}, FTIR rarely permits an assignment of newly synthesized individual molecules in complex mixtures within the ices.[23] Complementary to FTIR in the condensed phase, quadrupole mass spectrometry (QMS) coupled with electron impact (EI) ionization of the subliming molecules during the temperature-programmed desorption (TPD) of the irradiated ices has been widely explored to identify molecules after their sublimation into the gas phase.[20] EI sources operating at typical electron energies up to 90 eV lead to extensive fragmentation and, in the most unfavorable situation, elimination of the molecular parent ion. Considering that ion fragments of structural isomers frequently overlap, isomers can hardly be discriminated. Soft ionization with low-energy electrons of a few electronvolts has only a limited advantage considering the extensive voltage drop of 1−2 eV across the filament, and even structural isomers such as acetaldehyde ($HCOCH_3$; IE = 10.23 eV) and ethylene oxide ($c\text{-}C_2H_4O$; IE = 10.56 eV) cannot be discriminated since their ionization energies (IE) fall within the energy spread of the electrons.

These considerations make it clear that a high-level innovative experimental investigation of the formation and isomer-selective detection of complex organics is imperative to deliver much

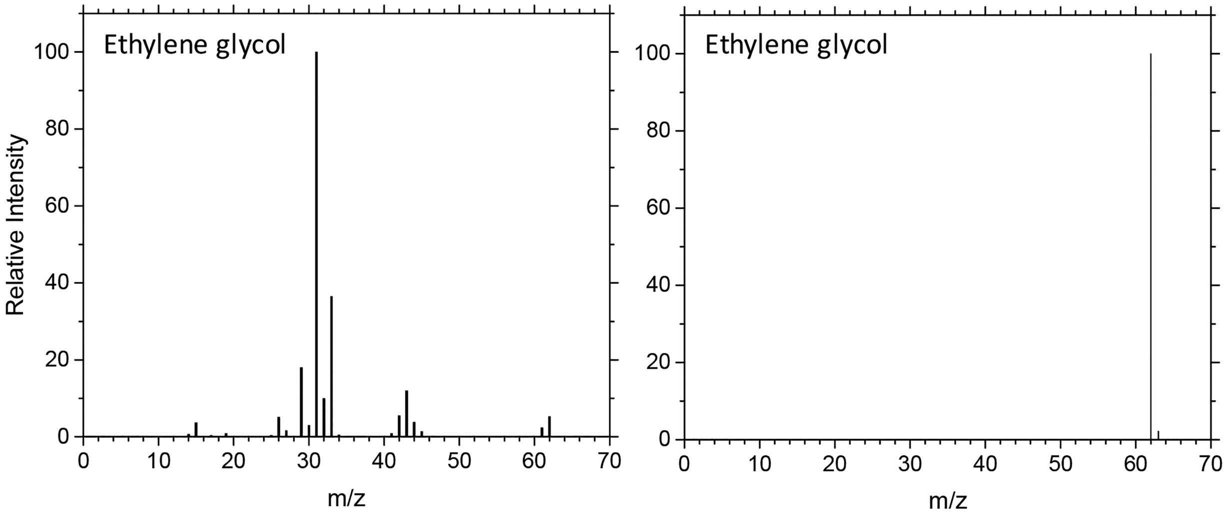


Figure 2. Benefits of fragment free single photon ionization. (left) Extensive fragmentation by electron impact ionization (70 eV) of ethylene glycol ($HOCH_2CH_2OH$); (right) single photon fragment-free ionization (10.6 eV) resulting in an intense molecular ion peak.

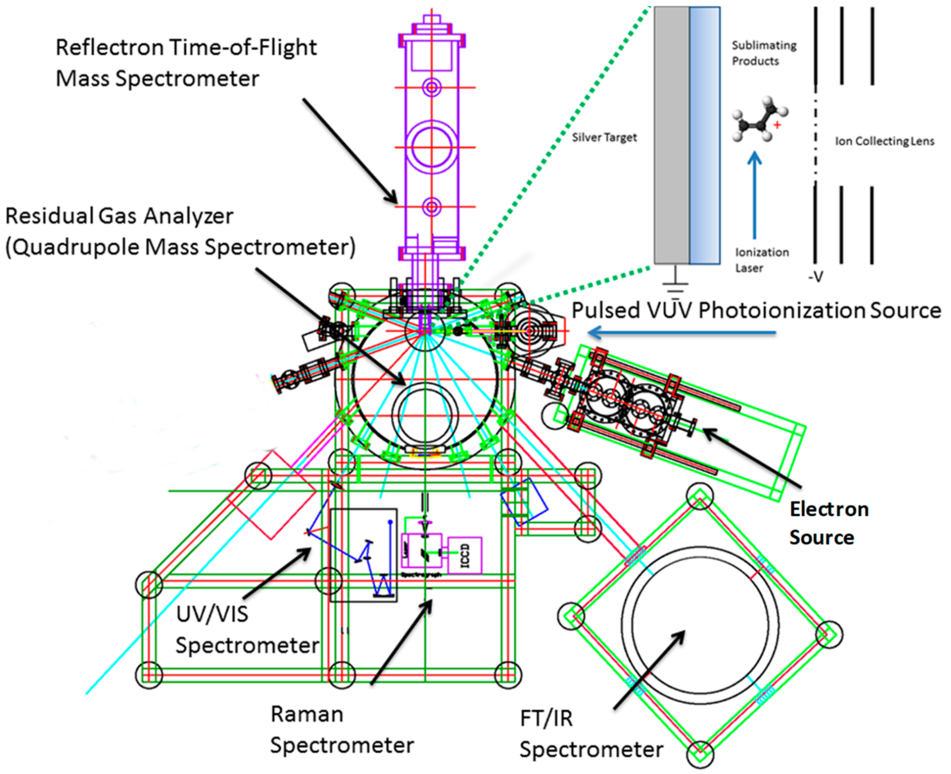


Figure 3. Top view of the main chamber including the cryogenic target (point of converging lines), analytical instruments, and electron source. The particle source is aligned with respect to the low temperature target to allow for the simultaneous in situ monitoring of FTIR, Raman, and UV−vis spectroscopies. After exposing the sample to ionizing radiation, the cold head is heated allowing the newly formed products to sublime and become photoionized and mass analyzed. The inset (top right) shows the geometry of the ReTOF ion source with respect to the target and ionization laser.

needed identification of the synthesized COMs along with the underlying synthetic pathways. This requires new expertise exploring transformative concepts in laboratory astrophysics and exploiting previously unavailable detection techniques interfaced to space simulation chambers. These studies yield a better understanding of the formation of key classes of complex organics and constrain the molecular complexity that can be synthesized in deep space. In this Account, recent advances on the formation pathways of four key classes of complex organics in interstellar ices are examined: (i) aromatic hydrocarbons, (ii) alcohols and ethers, (iii) aldehydes and enols, and (iv) carboxylic acids. By implementation of these findings into astrochemical models incorporating previously discounted nonequilibrium chemistry throughout the interstellar ices, exciting reaction mechanisms for key classes of ubiquitous COMs are revealed and presented in astrochemical context. This Account concludes with implications of our work and comments on future research directions in this field.

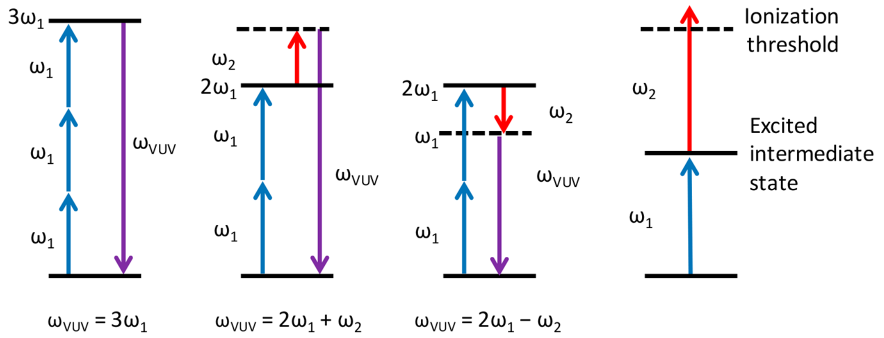


Figure 4. Schematics of distinct photoionization schemes. (left) Nonresonant four-wave mixing in a rare gas (nonlinear medium) from one frequency (ω_1) to generate vacuum-ultraviolet light (VUV), $\omega_{VUV} = 3\omega_1$. (center) Resonant four-wave mixing to produce VUV light in a rare gas (nonlinear medium). The blue arrows represent the first frequency (ω_1), red arrows correspond to the second frequency used (ω_2), and purple arrows designate the VUV photon that is produced (ω_{VUV}). Typically, ω_1 is a UV photon and ω_2 is a photon in the visible region. Four-wave sum mixing is shown on the center left. Here, two photons of ω_1 ($2\omega_1$) are added to ω_2 producing ω_{VUV}($\omega_{VUV} = 2\omega_1 + \omega_2$). Four-wave difference mixing is depicted on the center right. Here, the difference of ω_1 ($2\omega_1$) and ω_2 produces ω_{VUV} ($\omega_{VUV} = 2\omega_1 - \omega_2$). (right) Schematic representation of a [1 + 1′] resonance enhanced multiphoton ionization scheme (REMPI) exploiting ω_1 and ω_2.

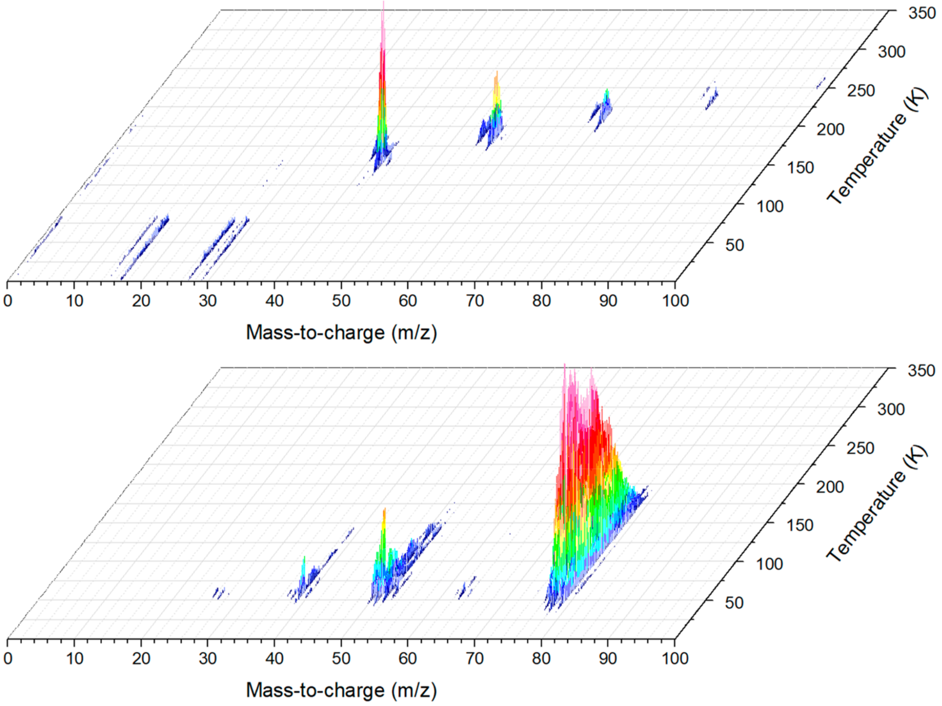


Figure 5. Temperature dependent PI-ReTOF-MS data for distinct ice systems exposed to energetic electrons. (top) Subliming products of irradiated methane ices photoionized at 10.49 eV. (bottom) Subliming products of irradiated acetylene ices photoionized with REMPI by first accessing an excited intermediate state using 4.787 eV photons followed by ionization with a second photon.

2. METHODOLOGY

Reflecting on the limitations of traditional analytical techniques (FTIR, QMS) in space simulation chambers, a different approach is required. Surface experiments, in which *monochromatic* photons or *monoenergetic* charged particles interact with interstellar ice analogs (typically 3 eV molecule^{-1}) up to 1 μm thick under clean conditions present in ultrahigh vacuum (UHV) systems, are geared to provide this understanding. Further, these simulation experiments should also identify individual newly formed molecules in the *gas phase* during sublimation of the ice samples via warm up (TPD) *online* and *in situ* at 0.5 K min^{-1} to resolve distinct isomers while maintaining adequate signal. *Individual COMs* subliming into the gas phase are identified exploiting a reflectron time-of-flight mass spectrometer (ReTOF-MS) coupled with *soft photoionization* and monitoring the decay signal of relevant *functional groups* in the condensed phase via FTIR. By softly ionizing the subliming molecules in the gas phase via single photon ionization (PI) and detection of the photoionized molecules via a reflectron time-of-flight mass spectrometer (PI-ReTOF-MS), we monitor the complete product spectrum based on distinct mass-to-charge ratios of the ionized molecules. The relevant organics have ionization energies between 8 and 11 eV; therefore, vacuum ultraviolet (VUV) light is necessary for the photoionization process. Further, since the energy of the photon can be tuned within a resolution of typically 0.001 eV, the subliming molecules can be photoionized according to their *known* ionization energies. Distinct organics have discrete ionization

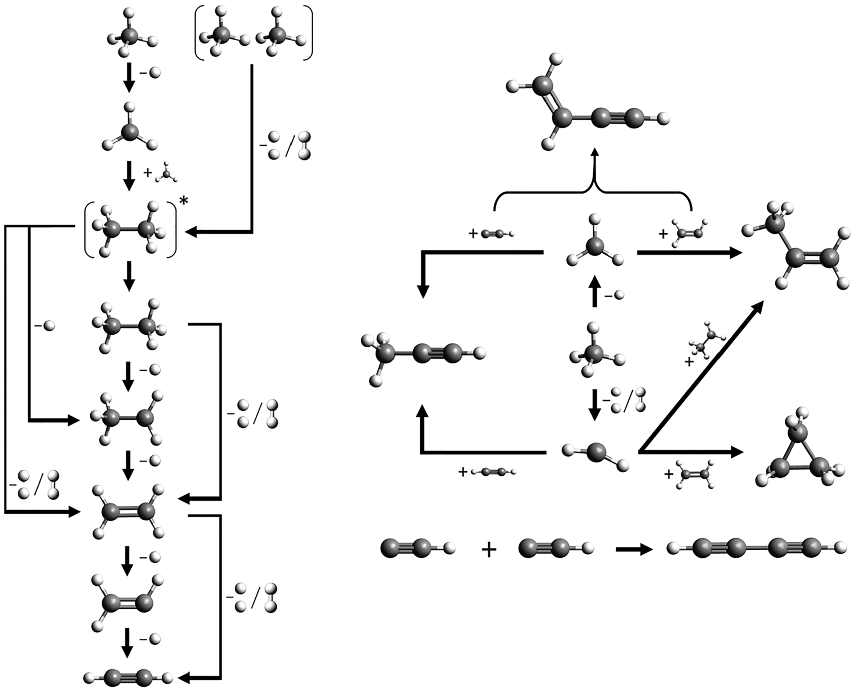


Figure 6. (left) Dominating formation pathways to C1 and C2 hydrocarbons and their radicals derived from FTIR spectroscopy Beginning with methane (CH_4), radiation-generated methyl radicals (CH_3) recombine to ethane (C_2H), which undergoes successive radiation-induced hydrogen-loss to ethylene (C_2H_4) then acetylene (C_2H_2). (right) Dominating formation pathways to C3 and C4 hydrocarbons elucidated via PI-ReTOF-MS depicted through radical−radical recombination of methyl (CH_3), ethynyl (C_2H), and vinyl (C_2H_3) radicals or through carbene (CH_2) insertion into bonds of ethane (C_2H_6), ethylene (C_2H_4), and acetylene (C_2H_2).

energies; hence a correlation of the ionization energy with the mass-to-charge of the product helps to uniquely identify *individual complex organic molecules* and in particular *their isomers*. Near the ionization threshold, this isomer-specific ionization method is ideally fragment-free, which is a critical advantage of single photon VUV photoionization compared to electron impact ionization (Figure 2). The subliming structural isomers might also be separated via fractionated sublimation; thus this sublimation sequence along with the correlation of the ionization energy with the mass-to-charge of the product offers a powerful methodology to identify complex organics synthesized in these ices.

The incorporation of *single photon soft photoionization* coupled to a ReTOF-MS interfaced to the space simulation chamber (Figure 3) requires the generation of VUV light from 8 to 11 eV. Here, pulsed VUV light at fluxes of 10^{13}−10^{15} photons pulse^{-1} is generated by resonance-enhanced sum ($2\omega_1 + \omega_2$) and difference ($2\omega_1 - \omega_2$) frequency nonlinear mixing, referred to as *resonance-enhanced four-wave mixing*, by accessing distinct resonance lines of krypton and xenon (Figure 4).[22,24] Pulsed VUV light (ω_{vuv}) is generated by two dye lasers (each pumped by a Nd:YAG laser, which generates the UV (ω_1) output for the resonant line ($2\omega_1$) in the gas medium and tunable photon frequencies in the visible range (ω_2). The VUV light is thus generated, including the sum ($2\omega_1 + \omega_2$) and difference frequency ($2\omega_1 - \omega_2$), along with the fundamental ω_1 and ω_2 beams and a minor fraction of the tripled frequency ($3\omega_1$). Sometimes, the ionization energies of two molecules are, within the error limits, too close to be discriminated. In this case, the isomers might be discriminated be selectively photolyzing the isomer(s) at distinct wavelengths in the ices.[25] Alternatively, resonance-enhanced multiphoton ionization (REMPI) followed by a mass-resolved detection in a ReTOF-MS often selectively ionizes individual isomers of, for example, polycyclic aromatic molecules upon their sublimation (Figure 4).[3]

3. RESULTS AND DISCUSSION

3.1. Hydrocarbons

Methane (CH_4) represents the simplest saturated hydrocarbon and has been detected on interstellar grains at fractions of a few percent (Table 2).[26] Methane ices are also abundant in the outer solar system on trans-Neptunian objects (TNOs) such as Pluto and Makemake.[27] Comets like Hyakutake are important repositories of methane as well since comets are contemplated to carry the material that was present during our solar system's formation.[28] Exposure of methane ices[29−31] along with ethane (C_2H_6),[32] ethylene (C_2H_4),[33] and acetylene (C_2H_2)[3,34] as the dominant radiolysis products lead up to C18 hydrocarbons with key products like C3−C4 hydrocarbons[35] and polycyclic aromatic hydrocarbons (PAHs)[3,36] detectable via PI and REMPI schemes coupled with ReTOF-MS (Figures 5a,b). Recall that FTIR spectroscopy can be exploited to identify small C1 to C2 hydrocarbons.[37] Kinetic fitting of the temporal profiles allowed the extraction of fundamental reaction mechanisms (Figure 6). However, after the sublimation of these hydrocarbons, multiple infrared absorptions remained, which revealed that multiple complex hydrocarbons beyond C2 species were synthesized as well.

3.1.1. C_3H_4. The ion signal detected at $m/z = 40$ during the TPD phase using 10.49 eV photons can be linked to the molecular formula C_3H_4, which has three possible isomers, methylacetylene (CH_3CCH; IE = 10.36 eV), allene (H_2CCCH_2; IE = 9.69 eV), and cyclopropene (c-C_3H_4; IE = 9.67 eV) (Figure 7a). In order to identify the isomer(s)

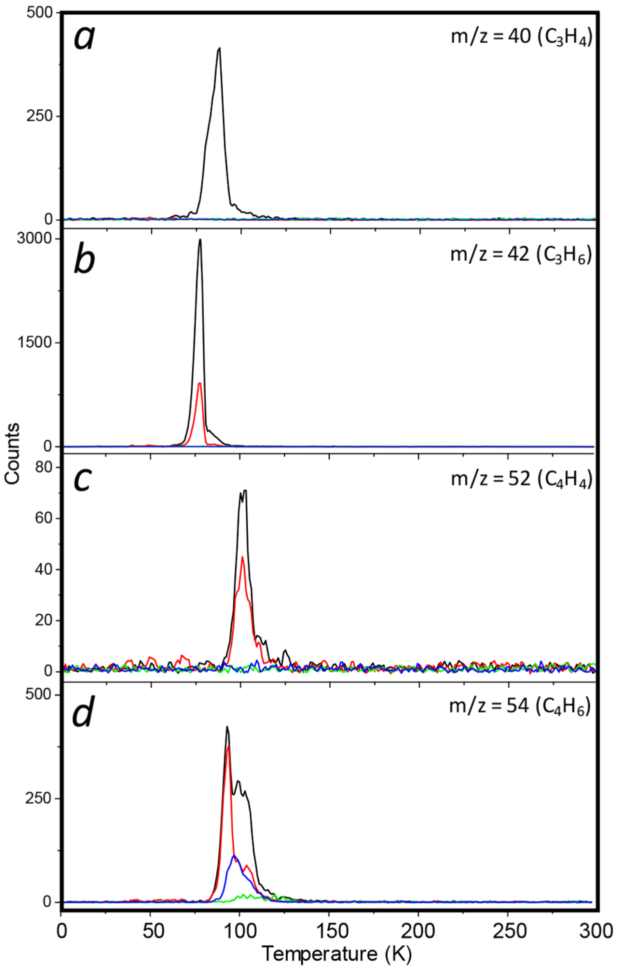


Figure 7. TPD sublimation profiles of (a) $m/z = 40$ ($C_3H_4^+$), (b) $m/z = 42$ ($C_3H_6^+$), (c) $m/z = 52$ ($C_4H_4^+$), and (d) $m/z = 54$ ($C_4H_6^+$) in electron irradiated methane ices at photoionization energies of 10.49 eV (black), 9.77 eV (red), 9.45 eV (blue), and 9.15 eV (green).

contributing to the signal, the photon energy was tuned to 9.77 eV. At this energy, no signal was detected at $m/z = 40$ suggesting that the signal at $m/z = 40$ only originated from the methylacetylene isomer. Detailed isotopic substitution experiments were conducted to elucidate the underlying formation mechanism of methylacetylene via insertion of carbene (CH_2) into an acetylene carbon—hydrogen bond versus recombination of a methyl radical (CH_3) with an ethynyl radical (CCH). Both carbene and methyl can be formed via decomposition of methane by energetic electrons.[37] In the D4-methane (CD_4)—acetylene (C_2H_2) system, the detection of $m/z = 42$ ($C_3H_2D_2$) would reveal that methylacetylene was formed via insertion of D2-carbene (16 amu) into the carbon—hydrogen bond of acetylene (C_2H_2; 26 amu), whereas signal at $m/z = 43$ (C_3HD_3) would provide evidence of the radical (CD_3; 18 amu)—radical (C_2H; 25 amu) recombination. Signal was detected at $m/z = 42$ and 43. Supported by tunable photoionization experiments at 10.49 and 9.93 eV, methylacetylene was revealed to be formed via radical—radical recombination and carbene insertion in a ratio of (2.0 ± 0.4):1.0 (Figure 6).[35]

3.1.2. C_3H_6. The ion signal monitored at $m/z = 42$ using 10.49 eV photons can be linked to a hydrocarbon with the molecular formula C_3H_6, which can be due to cyclopropane (c-C_3H_6; IE = 9.86 eV) or propene (CH_3CHCH_2; IE = 9.73 eV) (Figure 7b). Exploiting tunable VUV light, propene and cyclopropane were identified with a branching ratio of (30 ± 22):(1 ± 0.75). The reaction mechanisms were explored in methane (CH_4) and D4-ethylene (C_2D_4) ices. In combination with experiments at distinct photon energies of 10.49, 9.86, 9.77, and 9.73 eV, the detection of $m/z = 45$ indicates that propene is produced via radical recombination of the methyl radical (CH_3; 15 amu) with the D3-vinyl radical (C_2D_3; 30 amu). Ion counts at $m/z = 46$ combined with experiments at tunable photon energies revealed two pathways: an insertion of carbene (CH_2; 14 amu) into the carbon—deuterium bond of D4-ethylene (C_2D_4; 32 amu) to D4-propylene and an addition of carbene (CH_2; 14 amu) to the carbon—carbon double bond of D4-ethylene (C_2D_4; 32 amu) forming D4-cyclopropane. Propene is formed via radical—radical recombination and carbene insertion with a ratio of (1.5 ± 0.4):1, while propene and cyclopropane were prepared via carbene insertion at a ratio of (2.3 ± 0.2):(1.0 ± 0.3).[35]

3.1.3. C_4H_2 (Diacetylene, HCCCCH). Ion counts at $m/z = 50$ in electron-exposed acetylene ices are associated with the molecular formula C_4H_2, which includes diacetylene (HCCCCH; IE = 10.0 eV) and the carbene butatrienylidene (H_2CCCC; IE = 9.8 eV). Experiments exploiting tunable photons and $^{13}C_2H_2$—C_2H_2 ices suggest that diacetylene is formed via recombination of ethynyl radicals.

3.1.4. C_4H_4 and C_4H_6. Signal detected at $m/z = 52$ at a photon energy of 10.49 eV corresponds to the molecular formula C_4H_4 and could be due to vinylacetylene (CH_2CHCCH; IE = 9.58 eV), 1,2,3-butatriene (H_2CCCCH_2; IE = 9.16 eV), cyclobutadiene (c-C_4H_4; IE = 8.16 eV), or methylenecyclopropene (CH_2(c-C_3H_2); IE = 8.15 eV) (Figure 7c). Tuning the photon energy to 9.45 eV produced no signal at $m/z = 42$ indicating that only the vinylacetylene isomer is formed. Exploiting tunable photon energies in D2-acetylene (C_2D_2)—$^{13}C_2$-ethylene ($^{13}C_2H_4$) ices, vinylacetylene was found to be formed predominantly via recombination of the ethynyl radical (C_2D; 26 amu) with a vinyl radical ($^{13}C_2H_3$; 29 amu).[35] Exploiting this strategy for signal at $m/z = 54$, 1,3-butadiene, 1,2-butadiene, 2-butyne, and 1-butyne were assigned with ratios of (3.5 ± 2.5):(4.9 ± 3.4):(1 ± 0.7):(3.2 ± 2.3) (Figure 7d).[35]

3.1.5. Polycyclic Aromatic Hydrocarbons. Experiments exploring the interaction of acetylene ices, the dominant alkyne formed in the radiolysis of methane, with energetic electrons mimic the exposure of acetylene ices to secondary electrons released by GCRs penetrating these ices.[3] Although ultraviolet—visible (UV—vis) and FTIR spectroscopy revealed the formation of *functional groups* associated with aromatic systems such as $\pi \rightarrow \pi^*$ transitions and absorptions at, for example, 890—1100 cm^{-1} (out-of-plane C—H deformation modes in substituted benzenes/aromatics) and 3030 cm^{-1} (aromatic CH stretching modes), individual molecules could not be detected considering the aforementioned problems associated with overlapping absorption bands. At a photon energy of 10.49 eV, the entire array of subliming products was monitored since aromatics hold IEs below 10.49 eV (Figures 5 and 8). Ion signals that can be linked to at least to $m/z = 78$ ($C_6H_6^+$), 102 ($C_8H_6^+$), 104 ($C_8H_8^+$), 128 ($C_{10}H_8^+$), and 178 ($C_{14}H_{10}^+$) were detected. These ion counts might be associated with benzene (IE = 9.244 eV), phenylacetylene (IE = 8.825 eV), styrene (IE = 8.464 eV), naphthalene (IE = 8.144 eV), phenanthrene (IE = 7.891 eV), and anthracene (IE = 7.439 eV), respectively. Each of these molecules has multiple isomers that can be all ionized at 10.49 eV as well. Therefore, the overlap of distinct IEs of multiple

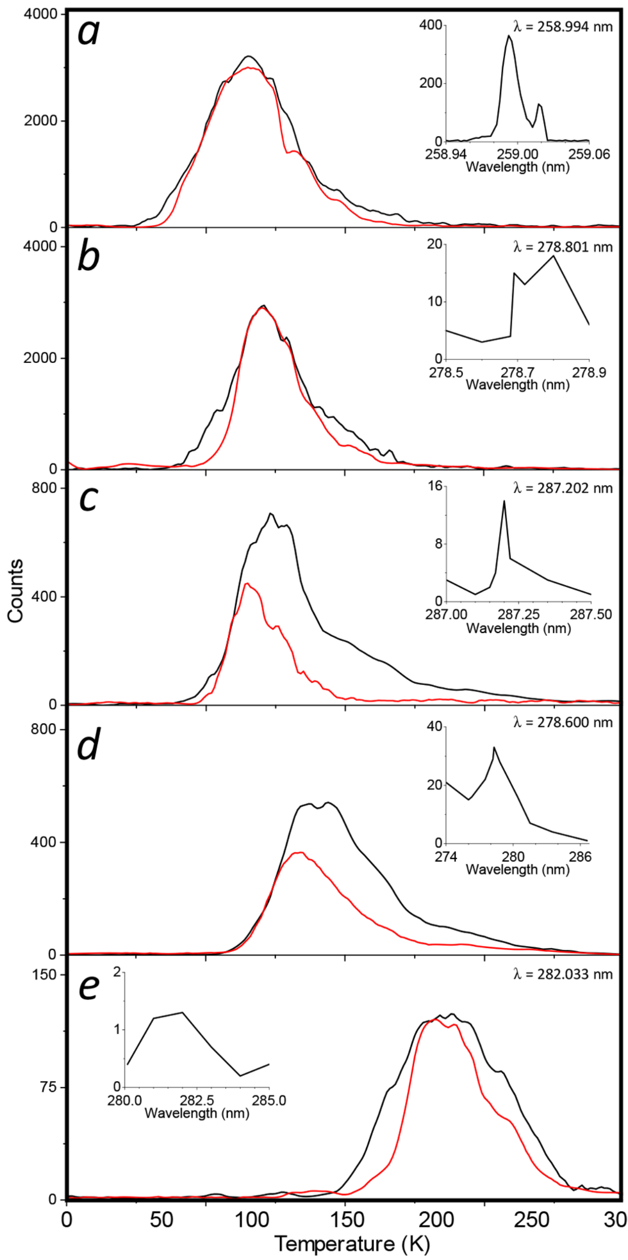


Figure 8. TPD sublimation profiles obtained via 10.49 eV photoionization (black) and REMPI (red) for benzene (a, m/z = 78), phenylacetylene (b, m/z = 102), styrene (c, m/z = 104), naphthalene (d, m/z = 128), and phenanthrene (e, m/z = 178). The insets display the REMPI wavelength dependence.

isomers complicates the assignment of individual isomers of aromatic molecules exploiting single photon ionization.

REMPI represents an ideal tool to overcome the aforementioned difficulties. This technique first accesses an excited intermediate state, which is distinct for the individual isomer to be probed, via a resonant photon absorption followed by a second photon that ionizes the molecule. Figure 8 compares the REMPI data with those obtained at 10.49 eV. One-color [1 + 1] REMPI schemes are exploited, which are isomer specific for benzene (4.787 eV), phenylacetylene (4.447 eV), styrene (4.317 eV), and naphthalene (4.450 eV). A comparison of the data at 10.49 eV and those obtained from REMPI recorded at m/z = 78 ($C_6H_6^+$) and m/z = 102 ($C_8H_6^+$) shows that benzene and phenylacetylene are the dominating contributors. Here, the differences between the single photon ionization and REMPI sublimation profiles can be rationalized with the ionization of additional C_6H_6 and C_8H_6 isomers that cannot be ionized with the [1 + 1] REMPI scheme. REMPI also delivers evidence for the synthesis of styrene (C_8H_8) and naphthalene ($C_{10}H_8$). Two-color REMPI (3.635 eV, 4.317 eV) is isomer specific for phenanthrene, while the one-color process (4.396 eV) can ionize anthracene and phenanthrene. This procedure identified at least the phenanthrene isomer ($C_{14}H_{10}$). Finally, more complex PAHs up to 260 amu were also ionized exploiting the [1 + 1] REMPI (4.787 eV), and their identification is in progress. Our experiments also provided yields and branching ratios calculated to be (314 ± 110):(39 ± 14):(23 ± 8):(13 ± 5):(1 ± 0.4) for benzene, phenylacetylene, styrene, naphthalene, and phenanthrene, respectively. The decrease of the molecular complexity with increasing ring size suggests stepwise molecular mass growth processes in the radiolyzed ices.

3.2. Alcohols and Ethers

The underlying formation pathways toward structural isomers of COMs such as C2 and C3 alcohols and ethers is of particular importance since these molecules represent key tracers to determine the physical and chemical conditions of interstellar environments and to test chemical models of molecular clouds and star-forming regions such as of Sgr B2 (Table 1). First, combining photoionization studies of the subliming molecules at distinct photon energies with directed isotopic labeling of the reactants in CD_3OD/CH_4 and CH_3OH/CD_4 ices elucidates discrete reaction pathways to ethanol (C_2H_5OH) and the dimethyl ether (CH_3OCH_3) isomers (Figure 9).[38,39] The interaction of methane with energetic electrons leads to the formation of methyl radicals (CH_3) plus atomic hydrogen (H) as well as carbene (CH_2) plus two hydrogen atoms/molecular hydrogen,[40] while methanol decomposes via atomic hydrogen loss from the methyl group or hydroxyl group resulting in the formation of the hydroxymethyl (CH_2OH) and methoxy (CH_3O) radicals, respectively. Carbene can insert into single bonds, whereas the doublet radicals methyl, methoxy, and hydroxymethyl can undergo radical—radical reactions. Radical—radical recombination of methyl (CH_3) with hydroxymethyl (CH_2OH) and methoxy (CH_3O) lead to ethanol and dimethyl ether, respectively, with branching ratios ranging from 1.0 to 1.4. Stereospecific insertions of carbene into the carbon—hydrogen and carbon—oxygen bonds formed ethanol, whereas insertion into the oxygen—hydrogen bond resulted in dimethyl ether. Branching ratios of ethanol to dimethyl ether were derived to be 1.9:4.5. Second, this principle of stepwise molecular mass growth processes via radical—radical reactions was also transferred in pure methanol ices to synthesize the isomer triplet ethylene glycol ($HOCH_2CH_2OH$), methoxymethanol (CH_3OCH_2OH), and *dimethyl peroxide* (CH_3OOCH_3) via recombination of hydroxymethyl (CH_2OH)—hydroxymethyl (CH_2OH), methoxy (CH_3O)—hydroxymethyl (CH_2OH), and methoxy (CH_3O)—methoxy (CH_3O), respectively; molecules in italics have not been detected in interstellar environments to date.[41] Third, our studies were also able to detect the more complex C3 alcohols (*n-/i-propanol* (C_3H_7OH) and the ethyl methyl ether isomer ($CH_3OC_2H_5$).[42,43] The trialcohol *glycerol* ($HOCH_2CH(OH)CH_2OH$), a fundamental building block of glycerol phosphates in cell membranes, could also be detected in electron-exposed methanol ices.[44] The identification of glycerol and ethylene glycol in irradiated methanol ices exploiting PI-

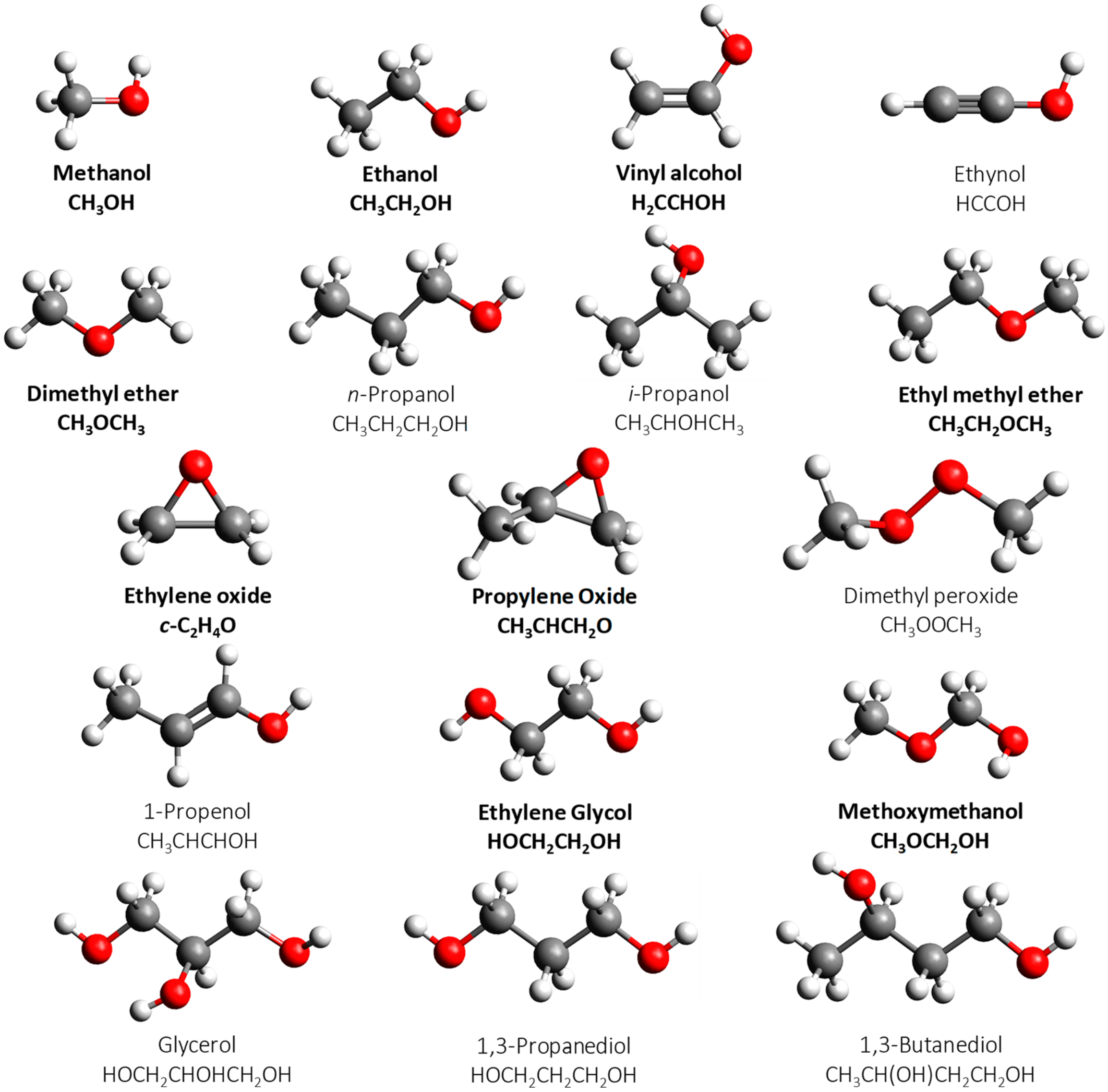


Figure 9. Alcohols and ethers identified in the present studies with molecules detected in the interstellar medium in bold.

ReTOF-MS represents a particular success since both molecules have essentially indistinguishable infrared spectra, and classical FTIR cannot be utilized in their identification in complex mixtures.[44] Fourth, our studies also revealed the mechanisms leading to the formation of the epoxides (cyclic ethers) ethylene oxide ($c\text{-}C_2H_4O$)[45] and propylene oxide ($c\text{-}C_3H_6O$)[2] via addition of suprathermal ground state oxygen ($O(^3P)$) or electronically excited oxygen ($O(^1D)$) to carbon−carbon double bonds[46] of ethylene and propylene, respectively. Racemic propylene oxide represents the first chiral molecule detected in the interstellar medium.[47] Finally, our studies unraveled the homologous series of the C2 alcohols ethanol (C_2H_5OH), vinyl alcohol (C_2H_3OH),[1] and *ethynol* (C_2HOH), an isomer of ketene (H_2CCO), involving keto−enol tautomerization (ethanol; 3.3) and hydrogenation of triplet dicarbon monoxide (CCO).[48]

3.3. Aldehydes and Enols

Aldehydes carry the carbonyl moiety (C═O), hold crucial functions in contemporary biochemistry (redox systems), and are considered as precursors to form carbon hydrates (condensation reactions), proteins (amino acids), and lipids (esters). First, PI-ReTOF-MS has been applied successfully to detect the C1−C4 homologue series acetaldehyde ($HCOCH_3$),[1] propanal ($HCOCH_2CH_3$),[1,23] and *n- and i-butanal* ($HCOCH_2CH_2CH_3$, $HCOCH(CH_3)_2$),[43] which were formed at 5 K in electron irradiated ices containing carbon monoxide and alkanes (CH_4, C_2H_6) (Figure 10). Detailed isotopic substitution experiments revealed that the radical−radical recombination of the formyl radical (HCO), formed via addition of suprathermal atomic hydrogen to carbon monoxide, with methyl (CH_3) and ethyl (C_2H_5) form acetaldehyde and propanal. The pathways to *n*- and *i*-butanal are still under investigation and could involve recombination of formyl and 1- or 2-propyl or carbene insertion into a carbon−hydrogen bond of the ethyl group of propanal. Keto−enol tautomerization within the ices at 5 K was found to be the driving force to synthesize vinyl alcohol from acetaldehyde and cis/trans *1-propen-1-ol* ($CH_3CHCHOH$) from propanal. Second, radical−radical recombination involving the formyl radical plus a hydrocarbon radical (vinyl, ethynyl) was also the driving force to synthesize the hydrogen-deficient counterparts of propanal:[1,23] propenal (C_2H_3CHO)[49] and propynal (HCCCHO)

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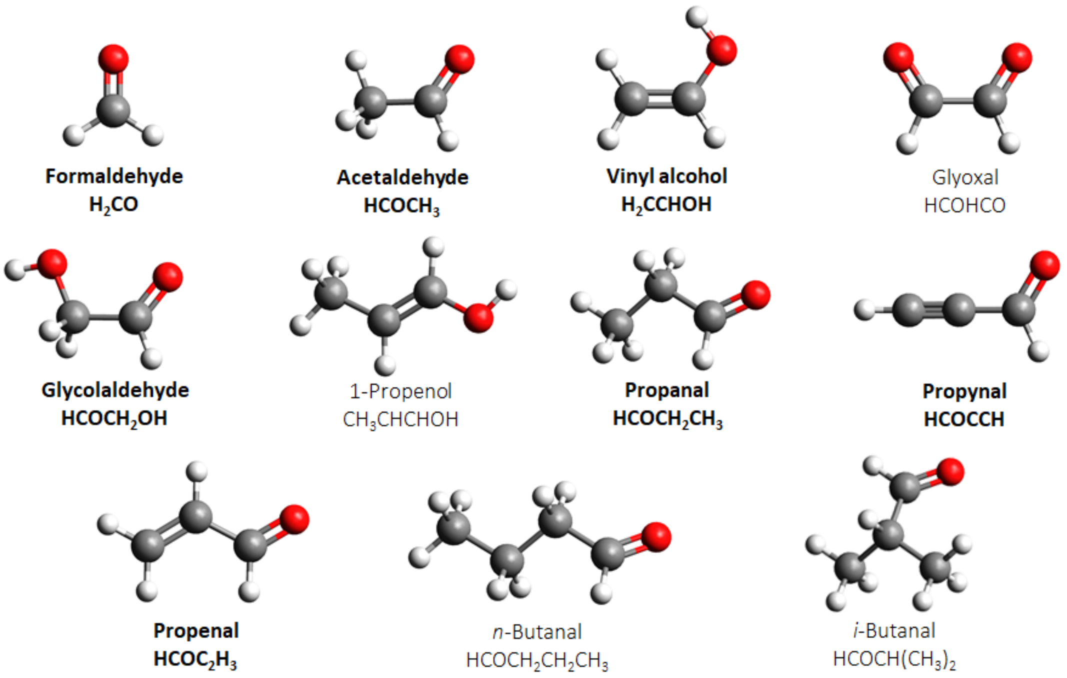

Figure 10. Aldehydes and enols identified in the present studies with molecules detected in the interstellar medium in bold.

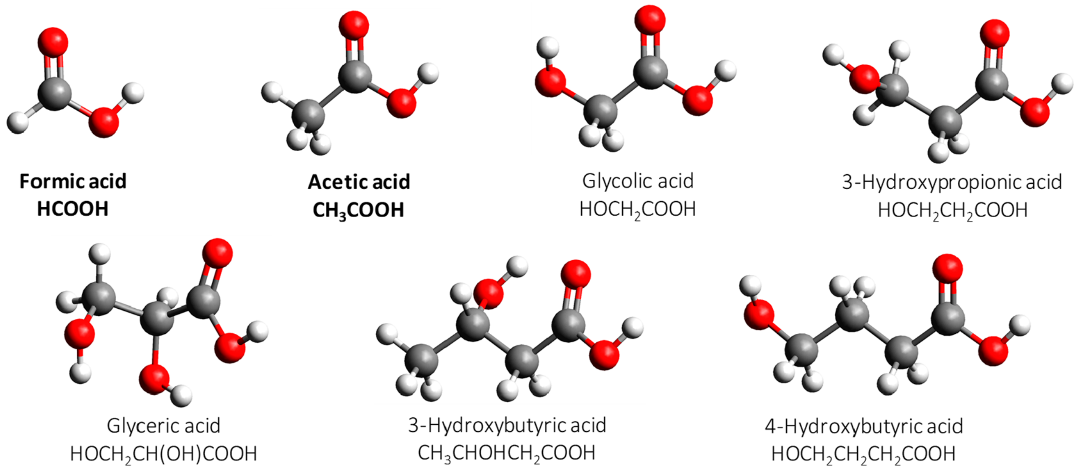

Figure 11. Carboxylic acids identified in the present studies with molecules detected in the interstellar medium in bold.

(Figure 10).[50] Third, more exotic cyclic carbonyls, cyclopropanone (c-C_3H_4O)[49] and *cyclopropenone* (c-C_3H_2O),[50] which are isomers of propenal and propynal, were formed via unimolecular reaction of complexes of carbon monoxide with ethylene and acetylene, respectively. Finally, the elucidated mechanism of barrierless radical−radical recombination pathways involving the formyl (HCO) species to complex organics can be also exported to truly biorelevant organics as evidenced from the preparation and detection of the sugar-related glycolaldehyde ($HCOCH_2OH$),[51,52] which forms via the recombination of a formyl radical (HCO) with a hydroxymethyl radical (CH_2OH), and of *glyoxal* (HCOCHO)[23] through recombination of two formyl radicals. The recombination of two acetyl (CH_3CO) radicals in acetone-doped water ices led to the popcorn flavorant *2,3-butanedione* ($CH_3COCOCH_3$).[4] These studies reveal that complex organics carrying more than one functional group can form easily in astrophysical model ices exposed to ionizing radiation. It should be noted that the explicit identification of the aforementioned molecules represents only a small fraction of nearly 300 molecular formulas of newly formed complex organics, including molecular formulas that could be connected to the formation of C4 to C5 sugars synthesized in astrophysical analog ices upon interaction with ionizing radiation (4).[52]

3.4. Carboxylic Acids

Carboxylic acids are considered crucial biomarkers and reaction intermediates in the formation of amino acids and proteins with long chain carboxylic acids acting as backbones of lipids, which perform critical biological functions including storing energy, signaling, and cell membranes.[53] Only two carboxylic acids, formic acid (HCOOH) and acetic acid (CH_3COOH), have been identified in the interstellar medium toward Sgr B2 (Table 1; Figure 11). The successful identification of formic acid in water−carbon monoxide ices exposed to ionizing radiation via the recombination of the hydroxycarbonyl (HOCO) radical with a hydroxyl (OH) radical[54] fueled the identification of

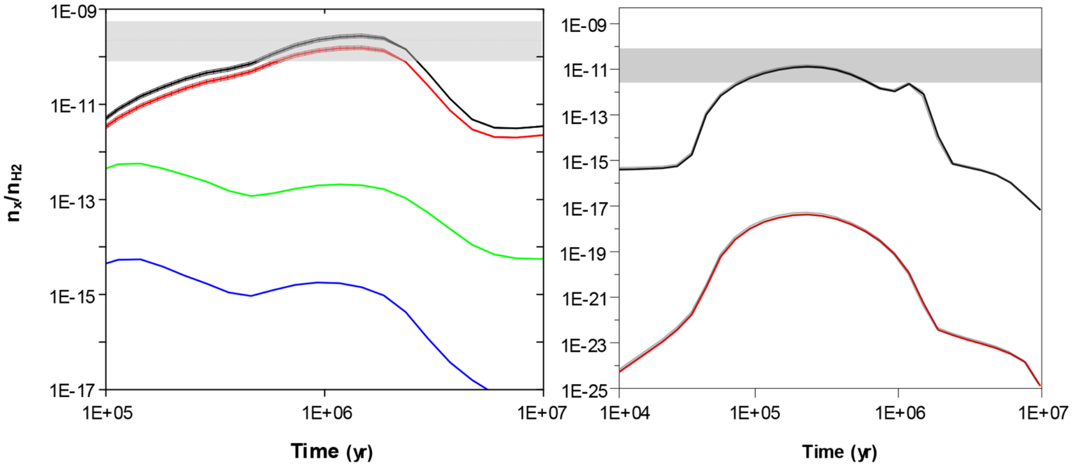

Figure 12. (left) Astrochemical models predicting the fractional abundances of acetaldehyde and vinyl alcohol in Sgr B2(N) operated with (black and red, respectively) and without (green and blue, respectively) a cosmic-ray-triggered chemistry. These results provide compelling evidence of the essential role of a cosmic-ray-driven formation of acetaldehyde and vinyl alcohol. (right) Astrochemical models predicting the fractional abundances of propylene oxide in cold material in front of Sgr B2(N) revealing that solely gas-phase reactions (red) cannot reproduce the relative abundance of astronomically detected propylene oxide. Models including a cosmic-ray-triggered chemistry (black) provide compelling evidence of the critical role of a cosmic-ray-driven formation of propylene oxide within interstellar ices. In both graphs, gray bars define the observed astronomical abundances along with the error limits revealing a remarkable match to the predicted data.

distinct formation pathways of acetic acid. Isotopic labeling experiments combined with PI-ReTOF-MS revealed that in *apolar* methane−carbon dioxide ices, acetic acid can be synthesized easily via the recombination of a methyl radical (CH_3) with the hydroxycarbonyl (HOCO) radical;[55] however, in *polar* acetaldehyde-doped water ices, acetic acid was formed through the radical−radical reaction of the acetyl radical (CH_3CO) with a hydroxyl radical (OH).[56] These investigations demonstrate that the polarity of the ice matrix can dramatically alter the underlying formation mechanisms to even simple complex organics. Further, *glycolic acid* (HCOCOOH),[57] a biorelevant molecule of the Krebs cycle carrying two functional groups prepared via recombination of a formyl radical (HCO) with a hydroxycarbonyl radical (HOCO), was detected exploiting PI-ReTOF-MS.

4. SUMMARY AND OUTLOOK

In this Account, reflectron time-of-flight mass spectrometry coupled with tunable vacuum ultraviolet (VUV) single photon ionization (PI-ReTOF-MS) and resonance enhanced multiphoton ionization (REMPI) of the subliming molecules during the temperature-programmed desorption (TPD) phase has been established as a versatile approach to explore the formation pathways of complex organic molecules in interstellar analog ices upon interaction with ionizing radiation. These experiments have been conducted under ultrahigh vacuum conditions (UHV) at temperatures as low as 5 K and have identified key classes of complex organics, in particular thermally unstable molecules like enols and cyclic carbonyls, which are difficult to probe by traditional analytical tools (FTIR, QMS).

First, the laboratory simulation experiments provided compelling evidence that key classes of complex organics can be formed upon exposure of astrophysically relevant model ices *within* the ices at temperatures as low as 5 K.[1] At low temperatures, the reaction mechanisms are dictated by suprathermal (H(^{2}S), O(^{3}P)) and electronically excited reactants (CH_2, NH, O(^{1}D))[2,22] along with barrierless radical−radical recombination if both radicals hold a proper recombination geometry.[1] Our experiments revealed that doublet radicals methyl (CH_3), amino (NH_2), hydroxyl (OH), ethyl (C_2H_5), vinyl (C_2H_3), ethynyl (C_2H), formyl (HCO), hydroxycarbonyl (HOCO), hydroxymethyl (CH_2OH), methoxy (CH_3O), and acetyl (CH_3CO) represent readily available reactants for barrierless *radical−radical recombination within* the ices at 5 K (Figure 6). These radicals are formed from the closed-shell simple precursors. Further, the reactive singlet species *insert* without barrier into carbon−hydrogen and carbon−carbon single bonds (carbene) leading to molecular mass growth by expansion of the carbon chain and also *add* to carbon−carbon double bonds (carbene, atomic oxygen) forming cyclic products. Suprathermal atoms holding excess kinetic energies of a few electronvolts react under nonthermal (non-Arrhenius) and hence nonequilibrium conditions.[10] This excess energy may be imparted in the transition state of a chemical reaction thus opening up classically (thermally) closed reactions under nonequilibrium conditions. Exploiting an inverse Laplace transformation, these processes have been shown to have suprathermal rate constants close to gas kinetics limits ($\sim 10^{-10}$ cm^3 s^{-1}), which are orders of magnitude faster than the corresponding thermal reactions at 5 K (10^{-13} to 10^{-70} cm^3 s^{-1}).[22] Most important, suprathermal pathways and radical−radical recombination at 5 K throughout the ices bypass previous obstacles of hypothesized thermal grain surface scenarios leading to complex organics, which only consider the first few monolayers of reactants and thus less than 1% of the mass of the icy layers. Our studies also reveal that the low temperature ices store reactive radicals such as formyl (HCO) and hydroxymethyl (CH_2OH). Upon annealing of the ices, these radicals may diffuse and recombine. Based on our results, however, this thermal route represents less prominent pathways leading to complex organics within the processed ices at a level of a few percent compared to a formation of these organics at 5 K.

Second, PI-ReTOF-MS is able to discriminate between structural isomers. Further, distinctly polar and apolar ices were found to have diverse reaction pathways to complex organics such as to acetic acid. Astronomical models excluding suprathermal chemistry do not fully replicate the astronomical observations of complex organics *isomer-selectively* such as acetaldehyde ($HCOCH_3$) versus vinyl alcohol (C_2H_3OH) and propylene oxide (c-C_3H_6O). Although suprathermal reactions triggered by GCRs have been predicted to advance the chemistry on interstellar grains for decades,[36,37,58] previous computational difficulties have been overcome only recently. An incorporation of *isomer selective production rates* of organics via a GCR mediated suprathermal chemistry using formation rates determined in the present studies can fully replicate the astronomical observations of complex organics over typical life times of molecular clouds (Figure 12), thus revealing the unprecedented potential of combining formation rates of complex organics obtained from PI-ReTOF-MS studies with astrochemical models to rationalize astronomical observations quantitatively.

Third, although focusing on the formation of complex organics in the interstellar medium, organics were also identified in carbonaceous chondrites,[59] which are considered *the most primitive* remnants from the formation of the solar system.[59,60] Further, comets such as 67P/Churyumov−Gerasimenko are regarded as leftover debris from gas, ice, rocks, and dust that formed the solar system from interstellar matter. Hence, a comparison of the organic inventory from comets with results from our studies could be crucial in constraining fundamental reaction mechanisms that might have led to the formation of organics detected on comets. Once formed abiotically, these organics might have been delivered to early Earth, thus providing the feedstock of organic molecules for the earliest stages of biochemical evolution. Since disk debris have also been observed in extrasolar systems such as toward Formalhaut, our studies also define an inventory of organics that are available to seed the evolution of life in extrasolar systems.

Finally, PI-ReTOF-MS can be expanded beyond astrochemical questions to explore fundamental problems of chemical bonding through the preparation of novel molecules relevant to astrobiology and inorganic chemistry. This has been accomplished via the detection of organics carrying the peptide bond (formamide, $HCONH_2$;[61] urea, H_2NCONH_2;[62] *N*-methylformamide, $HCONHCH_3$)[63] and of phosphorus-containing species like phosphorus oxoacids[64,65] along with their alkyl-substituted counterparts like alkylphosphoric and alkylphosphonic acids.[66] Recently identified exotic phosphorus-carrying molecules like formylphosphine ($HCOPH_2$) and phosphino formic acid (PH_2COOH)[40,67−69] along with two P_3N_3 isomers, cyclotriphosphazene and 1,3,5-triphosha-2,4,6-triazabicyclo[2.2.0]hexa-2,5-diene, the inorganic analogs of benzene and Dewar-benzene,[25] highlight the potential of PI-ReTOF-MS.

Overall, PI-ReTOF-MS reveals that the processing of astrophysically relevant ices leads to multifaceted mixtures of organics in terms of hydrocarbons, alcohols, aldehydes, and carboxylic acids that reach molecular weights of up to 200 amu. Advances in laboratory techniques are clearly desired not only to confidently assign detection of molecules in laboratory experiments as the molecules of interest become more complex but also from the viewpoint of future astronomical searches in the age of the Atacama Large Millimeter/submillimeter Array (ALMA). This should be combined with advanced astrochemical modeling to account for the actual findings in the laboratory and literature. Structural isomers serve as key tracers to a better understanding of nonequilibrium versus thermal reaction pathways and constrain not only the molecular complexity, but also the fundamental chemical pathways leading to complex organics based on cutting edge physical chemistry experiments coupled with novel astrochemical models and astronomical observations. However, these techniques and the detection of more complex organic molecules in space, in particular biorelevant molecules relevant to the *origins of life* theme, have just scratched the surface. Future experimental advances should couple PI-ReTOF-MS to synchrotron facilities to take advantage of beamlines operating with tunable VUV light. Further, although pump−probe experiments are widely used in the gas phase to explore, for instance, the photodissociation dynamics of organics,[70] they have not been exploited extensively in low-temperature targets to elucidate, in particular, the formation of molecules in astrophysically relevant ices. This requires the development of ultrashort electron pulses to initiate chemical bond cleavages, whereas a laser pulse investigates the progress of, for example, the initial bond rupture. Finally, exploiting radio frequency trapping of nanoparticles has been achieved,[71,72] but this technique could be expanded by cooling single nanoparticles to 10 K, condensing ices onto their surfaces, chemically processing these ices, and probing the newly formed molecules.

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Notes

The authors declare no competing financial interest.

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Ralf I. Kaiser received his Ph.D. in Chemistry from the University of Münster (Germany) in 1994 and conducted postdoctoral work at UC Berkeley (Department of Chemistry). During 1997−2000, he received a fellowship from the German Research Council (DFG) to perform his Habilitation at the Department of Physics (University Chemnitz, Germany) and Institute of Atomic and Molecular Sciences (Academia Sinica, Taiwan). He joined the Department of Chemistry at the University of Hawai'i at Mānoa in 2002, where he is currently Professor of Chemistry and Director of the W. M. Keck Research Laboratory in Astrochemistry. He was elected Fellow of the Royal Astronomical Society (UK), the Royal Society of Chemistry (UK), the American Physical Society (APS), the American Association for the Advancement of Science (AAAS), the Institute of Physics (UK), and the American Chemical Society (ACS).

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