Formation of Paraldehyde (C$_6$H$_{12}$O$_3$) in Interstellar Analog Ices of Acetaldehyde Exposed to Ionizing Radiation

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Acetaldehyde (CH$_3$CHO) plays a crucial role in the synthesis of prebiotic molecules such as amino acids, sugars, and sugar-related compounds, and in the progress of chain reaction polymerization in deep space. Here, we report the first formation of the cyclic acetaldehyde trimer – paraldehyde (C$_6$H$_{12}$O$_3$) – in low-temperature interstellar analog ices exposed to energetic irradiation as proxies of galactic cosmic rays (GCRs). Utilizing vacuum ultraviolet photoionization reflectron time-of-flight mass spectrometry and isotopic substitution experiments, paraldehyde was identified in the gas phase during the temperature-programmed desorption of the irradiated acetaldehyde ices based on the calculated adiabatic ionization energies and isomer-specific dissociative fragmentation patterns upon photo-ionization. As acetaldehyde is ubiquitous throughout the interstellar medium and has been tentatively identified in interstellar ices, paraldehyde could have formed in acetaldehyde-containing ices in a cold molecular cloud and is an excellent candidate for gas-phase observation in star-forming regions via radio telescopes. The identification of paraldehyde in the gas phase from the processed acetaldehyde ices advances our understanding of how complex organic molecules can be synthesized through polymerization reactions in extraterrestrial ices exposed to GCRs.

Introduction

Since the first identification of acetaldehyde (CH$_3$CHO, **1**) – the simplest methyl-bearing aldehyde – in the interstellar medium (ISM) half a century ago,[1,2] it has received considerable attention from the astronomy,[3–5] astrobiology,[6–8] astrochemistry[9–12] and physical organic chemistry communities[13–17] due to its role as a crucial precursor to interstellar complex organic molecules, which in the astronomical context are defined as organic molecules containing six or more atoms.[18,19] Acetaldehyde has been identified toward star-forming regions[20–23] and the low-mass protostar IRAS 16293−2422,[24,25] and has been tentatively detected in interstellar ices at levels of up to a few percent relative to water toward the protostar W33 A.[26] Ices observed in the ISM consist of simple molecules such as water (H$_2$O), carbon monoxide (CO), carbon dioxide (CO$_2$), methanol (CH$_3$OH), ammonia (NH$_3$), and methane (CH$_4$) condensed on interstellar nanoparticle-sized carbonaceous or siliceous grains.[27] Through thermal reactions, **1** can react with ammonia and methanol to form 1-aminoethanol (NH$_2$CH(OH)CH$_3$) and 1-methoxyethanol (CH$_3$OCH(OH)CH$_3$) at low temperatures via quantum tunneling, contributing to the formation of chelating agents and interstellar sugar-related molecules.[8,28] Upon exposure to ionizing radiation in the form of galactic cosmic rays (GCRs) or the shower of secondary particles they produce, vinyl alcohol (CH$_2$CHOH) or the popcorn flavorant 2,3-butanedione (CH$_3$COCOCH$_3$) can be formed via enolization or a barrierless radical-radical recombination of two acetyl radicals (CH$_3$ĊO), respectively, in processed acetaldehyde–water and pure acetaldehyde ices.[29–31] Triggered by energetic radiation, **1** reacts with water and carbon dioxide to form acetic acid (CH$_3$COOH)[31] and pyruvic acid (CH$_3$COCOOH),[7] which are considered key molecules in the synthesis of amino acids and metabolism processes. Once produced within interstellar ices in cold molecular clouds, these molecules can be incorporated into planetesimals and ultimately delivered to planets such as early Earth via carbonaceous asteroids and comets.[32,33] Therefore, **1** serves as a key precursor in the synthesis of astrobiologically relevant molecules linked to the *Origins of Life*.[34–36] In addition, **1** has played a crucial role in the progress of chain reaction polymerization,[37] which may significantly enhance our understanding of polymer science in deep space. However, the fundamental understanding of the formation mechanisms of complex organic molecules starting from **1** under astrophysical conditions has just scratched the surface, and experimental evidence on the interstellar polymerization processes leading to the formation of its cyclic trimer paraldehyde (C$_6$H$_{12}$O$_3$, **2**; Figure 1) is still lacking.

Paraldehyde (**2**) exists as two diastereomers, and each diastereomer has two chair conformers with different orientations of the methyl (CH$_3$) groups relative to the six-membered ring structure (Figure 2).[38] The methyl groups can be either in

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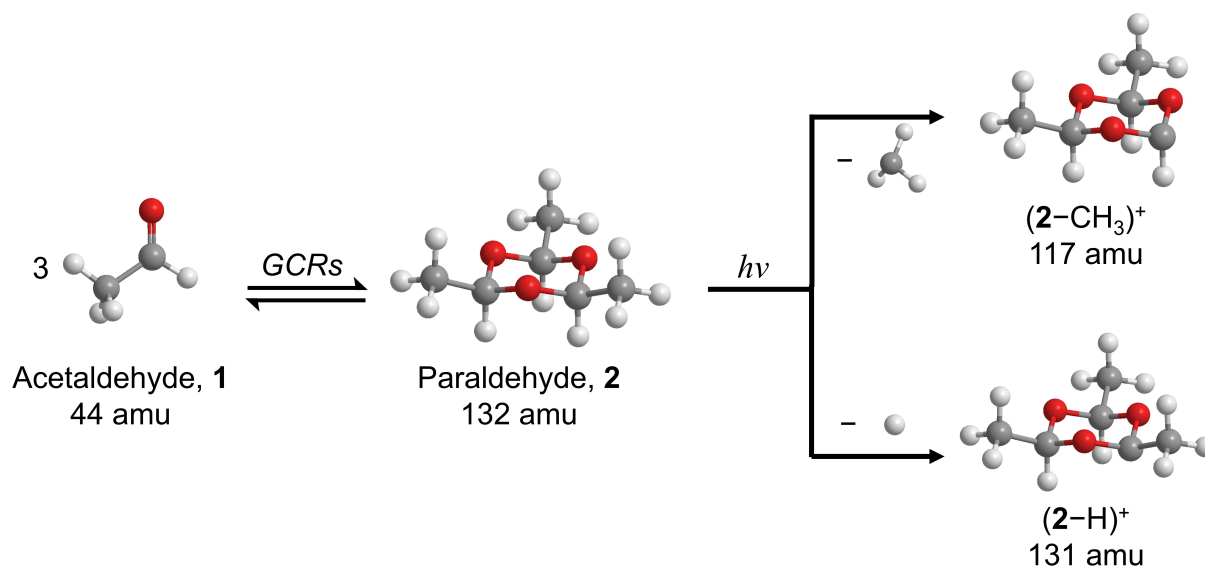📖 *Supporting information for this article is available on the WWW under https://doi.org/10.1002/cphc.202400837*

Figure 1. Trimerization reaction of acetaldehyde (CH$_3$CHO, **1**) leading to the formation of paraldehyde (C$_6$H$_{12}$O$_3$, **2**) triggered by galactic cosmic rays (GCRs) and the potential fragmentation of **2** upon gas phase photoionization.

axial (a) or in equatorial (e) orientation, producing structures **2a** (eee), **2b** (aee), **2c** (aae), and **2d** (aaa).[39] The polymerization of acetaldehyde has been studied for decades. In the 1930s, Hatcher et al. investigated the polymerization of **1** to **2** using phosphoric acid (H$_3$PO$_4$) as a catalyst.[40] On metal surfaces, **1** can polymerize to **2** with very low efficiency,[39,41] while in the presence of acid catalysts such as sulfuric acid (H$_2$SO$_4$), **2** is produced from **1** with a conversion fraction greater than 90%.[42] Among the approximately 300 molecules identified in the ISM, **2** has not yet been identified;[43] however, it may be formed in acetaldehyde-containing ices via a trimerization reaction triggered by GCRs (Figure 1). Once synthesized, **2** can act as a molecular reservoir of **1** within astrophysical ices during the formation of stars and planets due to its low volatility and high stability. Hence, unraveling the formation pathways of **2** can advance our knowledge of the molecular mass-growth processes of large complex organic molecules in deep space.

Here, we present the first formation of paraldehyde (**2**) in low-temperature interstellar ice analogs upon exposure to energetic irradiation as proxies for GCRs. This was accomplished in irradiated acetaldehyde ices through the cyclotrimerization reaction. Utilizing vacuum ultraviolet (VUV) photoionization reflectron time-of-flight mass spectrometry (PI-ReToF-MS) and isotopic substitution, **2** was identified in the gas phase during temperature-programmed desorption (TPD) of radiation-processed ices based on the calculated adiabatic ionization energies (IEs) and fragmentation pathways upon photoionization (Figure 1). Acetaldehyde has been tentatively identified in interstellar ices,[26] therefore, the astronomically unobserved **2** could be formed in acetaldehyde-containing ices. Considering the dipole moment of **2** (1.43 ± 0.02 D),[44] along with its measured infrared[45,46] and microwave spectra,[38] it is a suitable candidate for gas-phase searches in star-forming regions via radio telescopes such as the Green Bank Observatory (GBT) and the Yebes Observatory.

Experimental Section

All experiments were conducted at the W. M. Keck Research Laboratory in Astrochemistry at the University of Hawaii at Manoa. Hydrocarbon-free magnetically-levitated turbo molecular pumps (Osaka Vacuum, TG1300MUCWB and TG420MCAB) and a scroll pump (Edwards Vacuum, GVSP30) were used to maintain ultrahigh vacuum in the main chamber at base pressures of a few 10^{-11} Torr.[47] A polished silver substrate was cooled to 5 K by mounting it onto an oxygen-free high thermal conductivity copper target, which is interfaced to a closed-cycle helium compressor (Sumitomo Heavy Industries, RDK-415E). The silver substrate can rotate freely and move vertically through a rotary feedthrough and a bellows. Acetaldehyde (CH$_3$CHO, Sigma Aldrich, anhydrous, ≥ 99.5% purity; CD$_3$CHO, CDN isotopes, ≥ 98 atom % D; CD$_3$CDO, Sigma Aldrich, ≥ 99 atom % D) was stored in a borosilicate vial, and several freeze-thaw cycles were performed to remove residual atmospheric gases. After the substrate was cooled to 5 K, acetaldehyde vapor was deposited onto the substrate surface via a glass capillary array at a pressure of 3×10^{-8} Torr. In the experiment with the ice mixture of acetaldehyde (CH$_3$CHO) and acetaldehyde-d$_4$ (CD$_3$CDO), both vapors were deposited simultaneously via separate glass capillary arrays.[29] Although the abundance of acetaldehyde in interstellar ices is low, the pure acetaldehyde ice used in the experiments ensures the highest possible yield of paraldehyde and thus facilitates its detection. Laser interferometry was exploited to monitor the ice thickness during the deposition, and the oscillating reflected power due to the interference pattern was recorded using a helium-neon laser (632.8 nm) and a photodiode.[48] The ice thickness was determined to be 490 ± 50 nm (Table S1) using the refractive index of acetaldehyde (n = 1.303) at 15 K.[49] A Fourier transform infrared (FTIR) spectrometer (Thermo Electron, Nicolet 6700) was used to measure the infrared spectra of acetaldehyde ices in the range of 500–6000 cm^{-1}. In mixed ice, the ratio of CH$_3$CHO to CD$_3$CDO was determined to be (1.1 ± 0.1):1 using infrared absorptions of the pure CH$_3$CHO ice and CD$_3$CDO ice. After deposition, the ices were irradiated with 5 keV electrons at a current of 15 ± 2 nA for 5 minutes. Based on the Monte Carlo simulations in the CASINO software suite,[50] this results in irradiation doses of 0.28 ± 0.06 eV molecule^{-1} (Table S1) using its density of 0.787 g cm^{-3} for CH$_3$CHO.[49] These doses simulate those
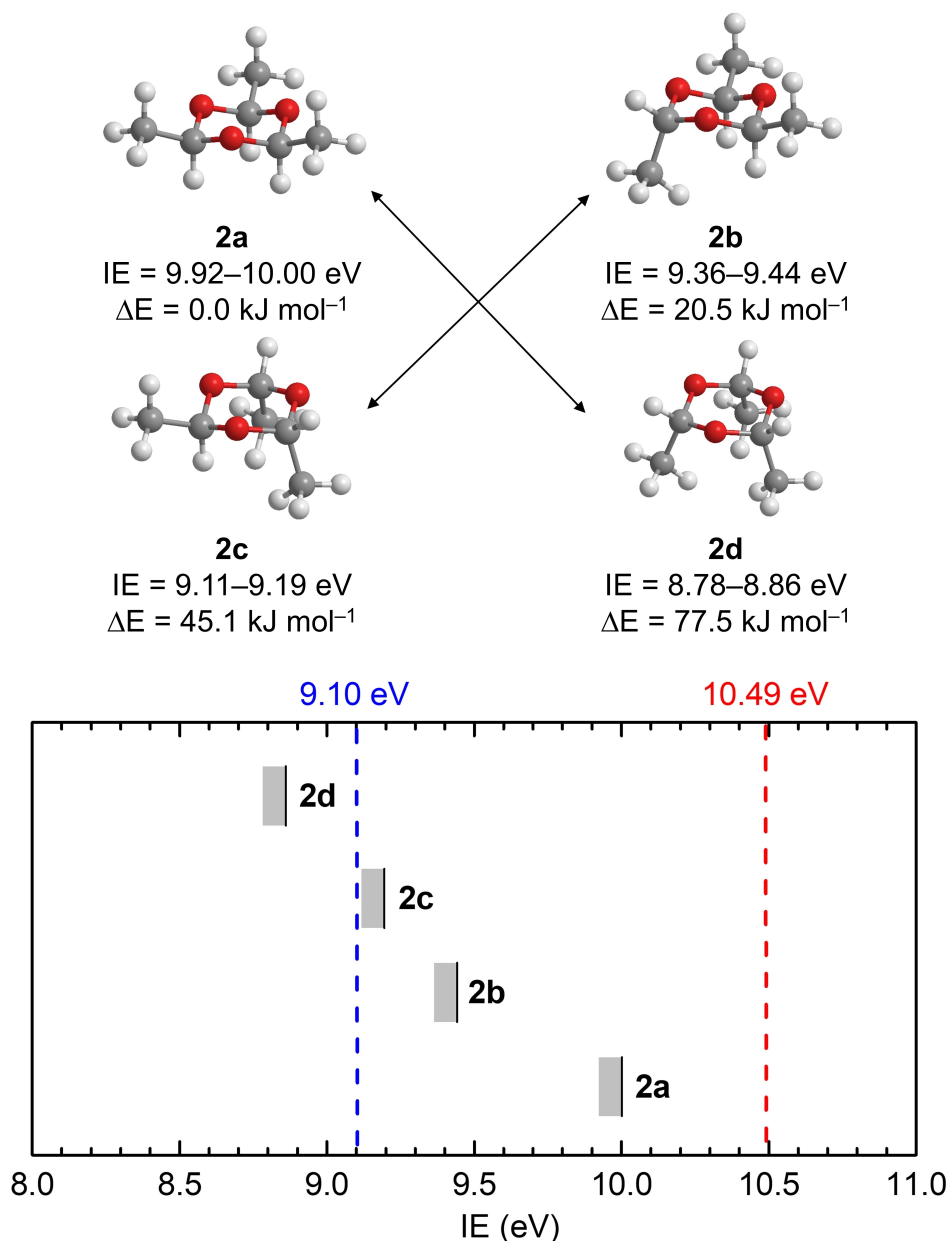
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Figure 2. Molecular structures of distinct conformers of paraldehyde (**2**). Paraldehyde exists as two diastereomers (black arrows), and each diastereomer has two chair conformers (**2a** and **2d**; **2b** and **2c**). The adiabatic ionization energies (IEs) are computed at the CCSD(T)-F12b/cc-pVTZ//B3LYP/aug-cc-pVTZ level of theory including the zero-point vibrational energy (ZPVE) corrections. The bottom figure compiles the calculated IEs (black solid line) and IE ranges of the conformers (grey area) after error analysis (Table S6). VUV photon energies at 10.49 eV and 9.10 eV were used during TPD.

received by astrophysical ices from secondary electrons generated in the track of GCRs in cold molecular clouds aged about $(6 \pm 1) \times 10^5$ years.[51] The average penetration depth of the electrons was determined to be 340 ± 50 nm, which is less than the thickness of deposited ices, preventing electrons from reaching the substrate. Infrared spectra of ices were collected before, during, and after irradiation.

After the irradiation, temperature-programmed desorption (TPD) was conducted by heating the ice from 5 K–320 K at a rate of 0.5 K min^{-1} by a programmable temperature controller (Lakeshore, Model 336). The subliming molecules were photoionized in the gas phase by vacuum ultraviolet (VUV) photons at 10.49 eV and 9.10 eV. The resulting ions were detected by a dual microchannel plate (MCP) utilizing reflectron time-of-flight mass spectrometry (ReToF-

MS). VUV photons were generated by a non-resonant or two-photon resonance four-wave mixing method using xenon as a nonlinear medium (Table S2). The 10.49 eV photons were generated by frequency tripling of the third harmonic (355 nm) of the fundamental of a Nd:YAG laser (Spectra Physics, Quanta Ray Pro-250-30) via non-resonant four-wave mixing.[52] The 9.10 eV photons were generated by resonant four-wave mixing using two dye lasers (Sirah, Cobra-Stretch) and two Nd:YAG lasers (Spectra Physics, Quanta Ray Pro-250-30 and Pro-270-30). The VUV light was spatially separated from other laser beams through a biconvex lithium fluoride lens (ISP Optics) in an off-axis geometry and passed 2.0 ± 0.5 mm above the substrate surface to photoionize subliming molecules during TPD. The MCP signal was amplified with a preamplifier (Ortec 9305) and analyzed by a multichannel scaler

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(FAST ComTec, P788-1 E, 30 Hz) based on arrival times in 4 ns bin widths.[30] Each mass spectrum was integrated for 3600 sweeps with an accumulation time of 2 minutes. Additional blank experiments using CH_3CHO ice, CD_3CHO ice, and CD_3CDO ice were carried out without irradiation at 10.49 eV.

Computational Details

The geometries are optimized and harmonic frequencies are computed with the B3LYP density functional and the aug-cc-pVTZ basis set within the Gaussian16 quantum chemistry program.[53–57] From these geometries CCSD(T)-F12b/cc-pVTZ–F12 single point energies are computed within the MOLPRO 2022.1 quantum chemistry program.[58–61] These energies are then paired with the B3LYP/aug-cc-pVTZ zero-point energies to provide the energies for each structure. These energies are, then, used to compute the adiabatic ionization energies as the difference between the optimized neutral and corresponding radical cation geometries. This approach has demonstrated a good correlation with previous experiments, yielding combined error limits of $-0.05/+0.03$ eV for the calculated IEs.[62] The relative energies are also computed as the difference between the optimized neutrals and the lowest energy conformer. The calculated Cartesian coordinates and harmonic vibrational frequencies of neutral paraldehyde structures, as well as their respective cations resulting from adiabatic ionization, are provided in the supporting information.

Results and Discussion

Infrared Spectroscopy

The infrared spectra of acetaldehyde (**1**), acetaldehyde-d_3 (**1**-d_3), and acetaldehyde-d_4 (**1**-d_4) ices were collected before and after irradiation (Figures S1–S3). Before the irradiation, all features can be linked to the infrared active modes of reactants including the dominant absorptions of the C=O stretching mode (ν_4) at 1719 cm^{-1} in CH_3CHO ice, 1721 cm^{-1} in **1**-d_3 ice, and 1704 cm^{-1} in **1**-d_4 ice (Tables S3–S5). After the irradiation at a dose of 0.28 ± 0.06 eV molecule^{-1}, several new infrared features emerge. Carbon monoxide can be identified via its stretch at 2130 cm^{-1}, 2137 cm^{-1}, and 2136 cm^{-1} in irradiated **1**, **1**-d_3, and **1**-d_4 ices, respectively.[63] In CH_3CHO ice, an absorption at 3386 cm^{-1} can be linked to the OH stretching modes of the formed products.[30] Additionally, absorption at 1841 cm^{-1} can be linked to acetyl radical ($CH_3\dot{C}O$, ν_3); this assignment is confirmed by the detection of acetyl-d_3 radical ($CD_3\dot{C}O$) via absorptions at 1849 cm^{-1} (ν_3) in CD_3CHO ice and 1853 cm^{-1} (ν_3) in CD_3CDO ice.[64,65] Since the infrared modes of paraldehyde (**2**) overlap with the absorptions of **1**,[46] it is challenging to detect **2** utilizing FTIR alone. Therefore, another, isomer-selective and more sensitive technique is needed to identify complex organic molecules such as **2**.

Photoionization Reflectron Time-of-Flight Mass Spectrometry

PI-ReToF-MS represents an isomer-selective method to identify individual molecules in the gas phase during TPD based on their mass-to-charge ratios (m/z) and distinct IEs.[19,66] Figure 3a compiles the PI-ReTOF-MS data collected during TPD for the unirradiated (blank) **1** ice and irradiated (15 nA, 5 minutes) **1**, **1**-d_3, and **1**-d_4 ices. Focusing on the $C_6H_{12}O_3$ isomers, the TPD profile of the ion signal at $m/z=132$ for the irradiated CH_3CHO ice at 10.49 eV (Figure 3b) reveals sublimation events peaking at 252 K (Peak I) and 312 K (Peak II). The signal at $m/z=132$ can be assigned to multiple molecular formulae, hence it is necessary to use isotopically labeled reactants to determine the molecular formula(e). The replacement of the CH_3CHO ice by CD_3CDO ice shifts the m/z from $m/z=132$ to $m/z=144$ (Figure 3d). This finding confirms the presence of twelve hydrogen atoms, indicating the possible molecular formula $C_6H_{12}O_3$. The signal at $m/z=141$ ($C_6H_3D_9O_3^+$) in irradiated CD_3CHO ice only shows the existence of Peak I (Figure 3c). Therefore, Peak I can be assigned to a molecule of the formula $C_6H_{12}O_3$. It is worth noting that Peak II is likely due to the cosublimation of isomers with large clusters of acetaldehyde such as its tetramers ($C_8H_{16}O_4$), pentamers ($C_{10}H_{20}O_5$), and/or hexamers ($C_{12}H_{24}O_6$) (Figure S4). Additional experiments of unirradiated CH_3CHO, CD_3CHO, and CD_3CDO ices were conducted without irradiation under otherwise identical conditions; these experiments did not observe any ion signals after 200 K, confirming that Peak I in Figures 3b–3d is the result of the irradiation of the acetaldehyde ices. Note that the signals around 150 K in the blank experiment (Figure 4) are likely due to contamination in the acetaldehyde samples.

The TPD profile of $m/z=132$ ($C_6H_{12}O_3^+$) in the irradiated CH_3CHO ice at 10.49 eV reveals Peak I with a sublimation from 230 K–270 K (Figure 3b). Peak I can be likely linked to the cyclic acetaldehyde trimer, paraldehyde (**2**). At 10.49 eV, all four conformers **2a** (IE=9.92–10.00 eV), **2b** (IE=9.36–9.44 eV), **2c** (IE=9.11–9.19 eV), and **2d** (IE=8.78–8.86 eV) can be ionized (Figure 2 and Table S6). Importantly, the TPD profile of $m/z=132$ ($C_6H_{12}O_3^+$) is in good agreement with the TPD profiles recorded for $m/z=117$ ($C_5H_9O_3^+$) and $m/z=131$ ($C_6H_{11}O_3^+$) in irradiated CH_3CHO ice (Figure 4a); these ion signals of $m/z=117$ and $m/z=131$ can be assigned to the fragment cations of the parent cation of **2** ($m/z=132$) due to dissociative photoionization.

Intramolecular vibrational energy redistribution can occur after photoionization by photons with excess energy relative to the threshold ionization energy.[28] In addition, the charge delocalization of the radical cation can lead to the formation of a stable fragment ion due to hyperconjugation.[67,68] Here, the radical cation of **2** dissociates to a fragment ion (**2** − CH_3)$^+$ plus a methyl radical ($\dot{C}H_3$) or a fragment ion (**2** − H)$^+$ plus a hydrogen atom (H$^-$) (Figure 1). This mechanism was further confirmed through the detections of fragment ions at $m/z=123$ for (**2**-d_9 − CD_3)$^+$ and $m/z=140$ for (**2**-d_9 − H)$^+$ in irradiated CD_3CHO ice (Figure 4b) and at $m/z=126$ for (**2**-d_{12} − CD_3)$^+$ and $m/z=142$ for (**2**-d_{12} − D)$^+$ in irradiated CD_3CDO ice (Figure 4c). These results suggest that Peak I is linked to **2**. Upon reducing the photon energy to 9.10 eV, at which conformers **2a**–**2c** cannot be ionized, Peak I disappears, and no sublimation event was observed at $m/z=141$ ($C_6H_3D_9O_3^+$) in irradiated CD_3CHO ice (Figure 3c), indicating that Peak I recorded at 10.49 eV can be assigned to conformers **2a**–**2c**.
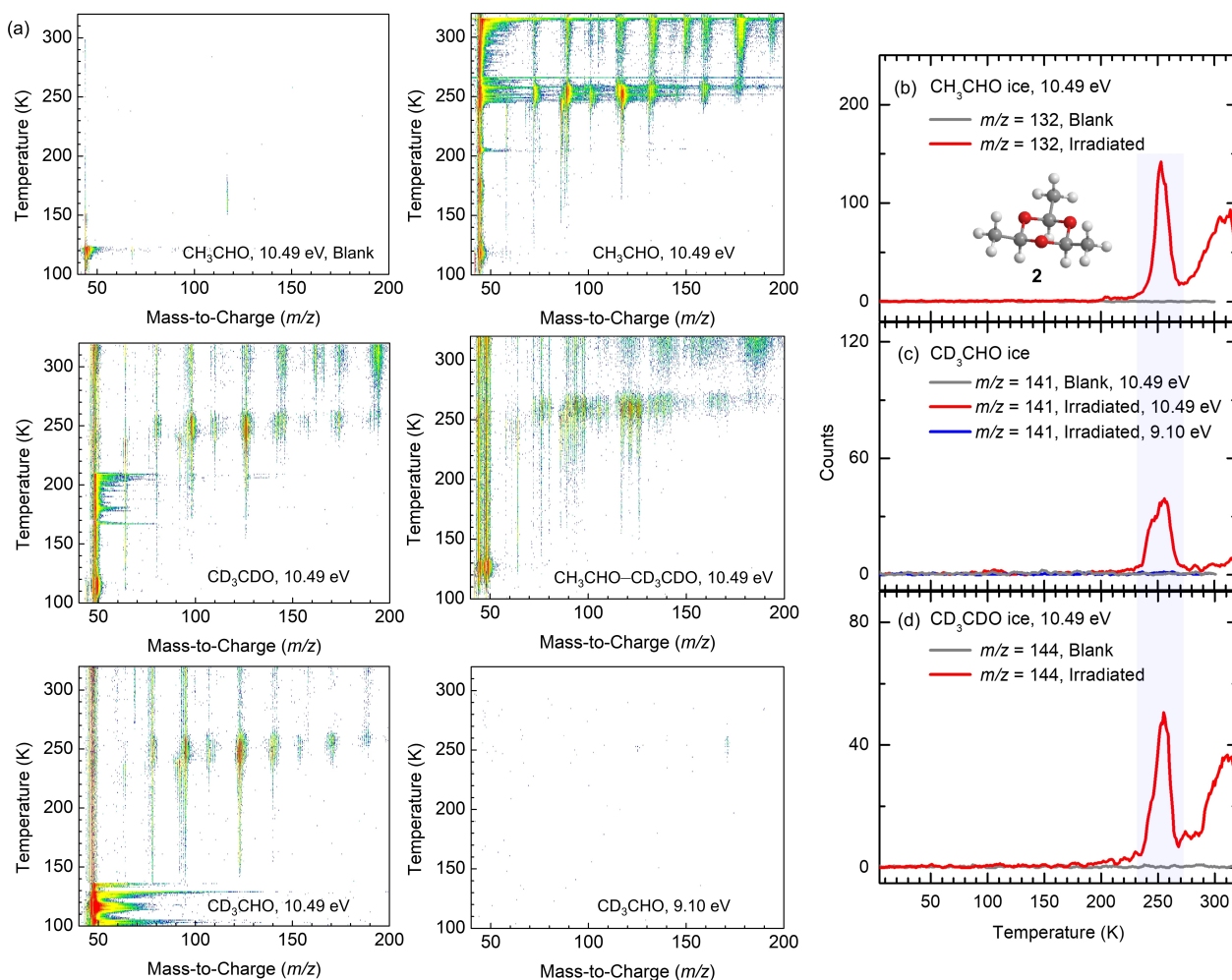
Figure 3. PI-ReToF-MS data during TPD of acetaldehyde ices. Data were recorded for the unirradiated (blank) CH_3CHO ice at 10.49 eV, and irradiated (15 nA, 5 minutes) CH_3CHO ice, CD_3CDO ice, and CH_3CHO–CD_3CDO ice at 10.49 eV, and irradiated (15 nA, 5 minutes) CD_3CHO ice at 10.49 eV and 9.10 eV (a). TPD profiles of $m/z = 132$ in CH_3CHO ice (b), $m/z = 141$ in CD_3CHO ice (c), and $m/z = 144$ in CD_3CDO ice (d) were shown. The blue-shaded region indicates the sublimation region corresponding to **2**.
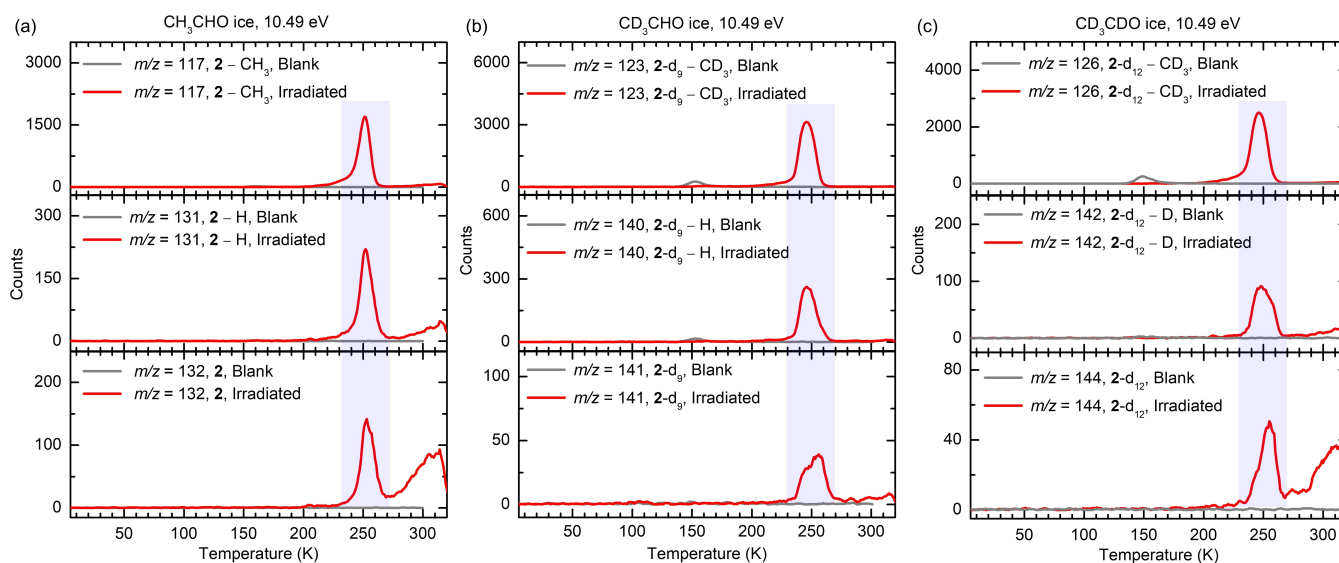

Figure 4. PI-ReToF-MS data of isotopically labeled acetaldehyde ices recorded at 10.49 eV. TPD profiles of $m/z = 117$, 131, and 132 collected for the CH_3CHO ice (a), $m/z = 123$, 140, and 141 collected for the CD_3CHO ice (b), and $m/z = 126$, 142, and 144 collected for the CD_3CDO ice (c) are shown. The blue-shaded regions indicate sublimation temperatures of **2**.

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An additional experiment with a CH$_3$CHO—CD$_3$CDO ice mixture was performed at 10.49 eV to detect the distinct levels of deuteration of paraldehyde for **2** at $m/z = 132$ (C$_6$H$_{12}$O$_3^+$), **2**-d$_4$ at $m/z = 136$ (C$_6$H$_8$D$_4$O$_3^+$), **2**-d$_8$ at $m/z = 140$ (C$_6$H$_4$D$_8$O$_3^+$), and **2**-d$_{12}$ at $m/z = 144$ (C$_6$D$_{12}$O$_3^+$) (Figure 5). Ions of possible fragments upon photoionization for isotopologues of **2** were detected (Table S7). Considering the parent ions and their fragments, the integrated ion signals of **2**, **2**-d$_4$, **2**-d$_8$, and **2**-d$_{12}$ are 5857 ± 265, 14317 ± 491, 17253 ± 546, and 9288 ± 442 counts, respectively. The ratio of the integrated counts of **2**-d$_{12}$ to **2** is determined to be (1.59 ± 0.10):1. Paraldehyde-d$_8$ (**2**-d$_8$), which requires the reaction of one acetaldehyde with two acetaldehyde-d$_4$ molecules, forms at slightly higher abundances compared to **2**-d$_4$.

Having provided evidence on the formation of paraldehyde (**2**) in irradiated acetaldehyde (**1**) ices, we now focus on its potential formation mechanisms. In the experiments, ices were exposed to energetic electrons at a current of 15 ± 2 nA for 5 minutes, which corresponds to a low dose of 0.28 ± 0.06 eV molecule^{-1}. This low dose irradiation was designed to minimize sequential reactions. The overall pathway involves three acetaldehyde molecules. Upon irradiation at 5 K, **1** can react with two nearby acetaldehyde molecules to form **2** via C—O bond formation if they have a favorable recombination geometry. This reaction is exoergic by 113 kJ mol^{-1} in the gas phase.[42] Note that the FTIR spectra of processed acetaldehyde ices provide no evidence for the formation of ionic species in the ices after irradiation (Figures S1–S3); the role of ions in the formation of **2** has not been considered. Notably, **2** is a particularly stable acetaldehyde oligomer with two diastereomers, each having different orientations of the methyl groups relative to the six-membered ring structure (Figure 2).[37,38] Among all the conformers, **2a** is the most stable with the lowest relative energy. Recall that **2d** was not detected in our experiments. Due to the repulsion caused by the axial methyl group, **2d** is not expected to be energetically favorable;[38] it has the highest relative energy, 77.5 kJ mol^{-1} relative to **2a**, calculated at the CCSD(T)-F12b/cc-pVTZ//B3LYP/aug-cc-pVTZ level of theory (Table S6).

Conclusions

Overall, our combined experimental and computational investigation revealed the first formation of paraldehyde (**2**) through trimerization reaction in low-temperature interstellar analog ices exposed to energetic electrons as proxies of GCRs. Acetaldehyde (**1**) ices were irradiated with doses of 0.28 ± 0.06 eV molecule^{-1}, simulating secondary electrons generated in the track of GCRs in a cold molecular cloud aged about (6 ± 1)×10^5 years.[51] Paraldehyde was identified in the gas phase during the TPD of processed ices utilizing vacuum ultraviolet photoionization reflectron time-of-flight mass spectrometry (PI-ReToF-MS) and isotopic substitution studies. Since **1** is ubiquitous in the interstellar medium and has been tentatively identified in interstellar ices,[26] our findings suggest that the astronomically unobserved **2** can form in acetaldehyde-containing ices in a cold molecular cloud. Considering **2** has a dipole moment of 1.43 ± 0.02 D,[44] the warming of these ices during star formation allows paraldehyde molecules to sublime into the gas phase and are viable targets for radio telescopic searches with instruments such as the Green Bank Observatory (GBT) and the Yebes Observatory. A firm detection of paraldehyde in the ISM would enhance our understanding of the polymerization reactions in ices upon ionizing radiation in deep space. It is worth noting that previous experiment on irradiated **1**—water-d$_2$ (CH$_3$CHO—D$_2$O) ice was conducted with an acetaldehyde to water-d$_2$ ratio of 1:10;[31] however, no evidence for the formation of **2** was found. Future laboratory experiments to identify **2** under different conditions such as varying ice compositions and irradiation doses can be carried out.

Acknowledgements

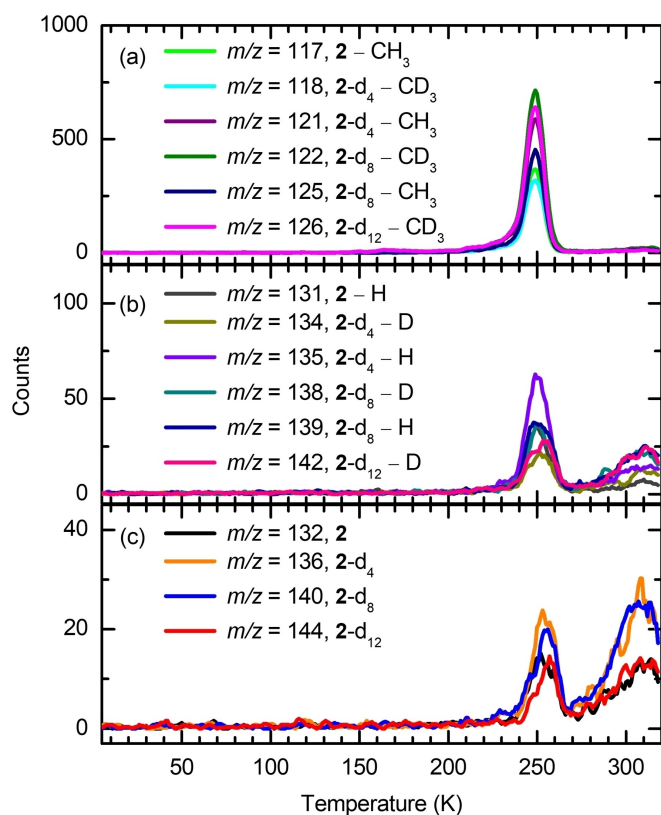**Figure 5.** TPD profiles with different levels of deuteration in the irradiated CH$_3$CHO—CD$_3$CDO ice recorded at 10.49 eV.

In figure:
(a) $m/z = 117$, **2** – CH$_3$; $m/z = 118$, **2**-d$_4$ – CD$_3$; $m/z = 121$, **2**-d$_4$ – CH$_3$; $m/z = 122$, **2**-d$_8$ – CD$_3$; $m/z = 125$, **2**-d$_8$ – CH$_3$; $m/z = 126$, **2**-d$_{12}$ – CD$_3$
(b) $m/z = 131$, **2** – H; $m/z = 134$, **2**-d$_4$ – D; $m/z = 135$, **2**-d$_4$ – H; $m/z = 138$, **2**-d$_8$ – D; $m/z = 139$, **2**-d$_8$ – H; $m/z = 142$, **2**-d$_{12}$ – D
(c) $m/z = 132$, **2**; $m/z = 136$, **2**-d$_4$; $m/z = 140$, **2**-d$_8$; $m/z = 144$, **2**-d$_{12}$

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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