**Preparation of Acetylenediol (HOCCOH) and Glyoxal (HCOCHO) in Interstellar Analog Ices of Carbon Monoxide and Water**

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**Abstract**

Enols — tautomers of ketones or aldehydes — are considered key intermediates in the formation of prebiotic sugars and sugar acids. Although laboratory simulation experiments suggest that enols should be ubiquitous in the interstellar medium, the underlying formation mechanisms of enols in interstellar environments are largely elusive. Here, we present the laboratory experiments on the formation of glyoxal (HCOCHO) along with its ynol tautomer acetylenediol (HOCCOH) in interstellar ice analogs composed of carbon monoxide (CO) and water (H2O) upon exposure to energetic electrons as a proxy for secondary electrons generated from Galactic cosmic rays. Utilizing tunable vacuum ultraviolet photoionization reflectron time-of-flight mass spectrometry, glyoxal and acetylenediol were detected in the gas phase during temperature-programmed desorption. Our results reveal the formation pathways of glyoxal via radical-radical recombination of two formyl (HĊO) radicals, and that of acetylenediol via keto-enol-ynol tautomerization. Due to the abundance of carbon monoxide and water in interstellar ices, glyoxal and acetylenediol are suitable candidates for future astronomical searches. Furthermore, the detection of acetylenediol in astrophysically relevant ices advances our understanding for the formation pathways of high-energy tautomers such as enols in deep space.

**Unified Astronomy Thesaurus (UAT) Concepts:** Laboratory astrophysics (2004); Astrochemistry (75); Radical-radical recombination (1071); Complex organic molecules (2256); Interstellar molecules (849)

**1. Introduction**

Since the first identification of vinyl alcohol (CH2CHOH) in the interstellar medium (ISM) by Turner et al. ([Turner & Apponi 2001](#_ENREF_86)) two decades ago toward the dense molecular cloud Sagittarius B2(N), enols — alkenes carrying a hydroxyl group at a carbon-carbon double bond — have received considerable attention from the astroche­mistry ([Abplanalp et al. 2016b](#_ENREF_2); [Kleimeier, Eckhardt, & Kaiser 2021](#_ENREF_41); [Kleimeier & Kaiser 2022](#_ENREF_44)), synthetic organic chemistry ([Mardyukov, Keul, & Schreiner 2021](#_ENREF_55); [Mardyukov, Wende, & Schreiner 2023](#_ENREF_56)), physical chemistry ([Melosso et al. 2022](#_ENREF_60); [Rösch et al. 2021](#_ENREF_71); [Taatjes et al. 2005](#_ENREF_77)), and theoretical chemistry ([Ballotta et al. 2023](#_ENREF_6); [Elango et al. 2010](#_ENREF_26); [Mó et al. 2023](#_ENREF_64); [Würmel & Simmie 2024](#_ENREF_96)) communities. This interest is mainly due to their key role as reactive intermediates in the synthesis of biorelevant molecules related to the *Origins of Life*. 1,2-ethenediol (HOCHCHOH) and 1,1,2-ethenetriol (HOCHC(OH)2), the enol forms of glycolaldehyde (HCOCH2OH) and glycolic acid (HOCH2COOH), respectively, have been proposed as key intermediates leading to the prebiotic formation of three- to five-carbon sugars ([Coggins & Powner 2017](#_ENREF_18); [Kim et al. 2011](#_ENREF_40); [Ricardo et al. 2004](#_ENREF_68)) and sugar acids ([Mardyukov, et al. 2021](#_ENREF_55)). Gas-phase enols in the ISM exhibit significantly greater stability ([Abplanalp, et al. 2016b](#_ENREF_2); [Taatjes, et al. 2005](#_ENREF_77)) because they cannot overcome the high keto-enol tautomerization barriers (230–290 kJ mol–1) at low temperatures and pressures ([da Silva 2010](#_ENREF_21); [Kleimeier & Kaiser 2021](#_ENREF_43); [Schreiner et al. 2011](#_ENREF_74); [Wang et al. 2023c](#_ENREF_93)).

Among the nearly 300 molecules identified in deep space ([McGuire 2022](#_ENREF_59)); however, only few enols have been detected. Besides vinyl alcohol, 1,2-ethenediol (HOCHCHOH) has been identified toward the G+0.693−0.027 molecular cloud located in the Galactic Center with a molecular abundance of 1.3 × 10–10 with respect to molecular hydrogen ([Rivilla et al. 2022](#_ENREF_70)). In addition, 3-hydroxypropenal (HOCHCHCHO), the enol tautomer of malonaldehyde (HCOCH2CHO),has been tentatively detected in the ISM toward the solar-type protostar IRAS 16293–2422 ([Coutens et al. 2022](#_ENREF_20)). On the other hand, laboratory studies on interstellar analog ices revealed a facile formation of enols (Figure 1, Table 1). These results suggest that enols should be ubiquitous in hot cores and star-forming regions and readily available for an abiotic synthesis of complex organic molecules (COMs) — organic molecules containing six or more atoms of carbon, hydrogen, oxygen, or nitrogen ([Herbst & Dishoeck 2009](#_ENREF_33)) — in interstellar environment ([Kleimeier, et al. 2021](#_ENREF_41); [Kleimeier et al. 2020](#_ENREF_42); [Kleimeier & Kaiser 2022](#_ENREF_44); [Wang et al. 2008](#_ENREF_89); [Wang et al. 2023b](#_ENREF_92); [Wang, et al. 2023c](#_ENREF_93)). Once formed in molecular clouds, these molecules can sublime into the gas phase in the star-forming region and be incorporated into asteroids and comets ([Cooper et al. 2011](#_ENREF_19); [Kleimeier, et al. 2020](#_ENREF_42)). Eventually, parts of enols may survive entry into the atmosphere of other planets such as the early Earth, serving as crucial intermediates in the formation of prebiotic molecules linked to the *Origin of Life* ([Benner et al. 2010](#_ENREF_7)). Furthermore, a fundamental understanding of the formation of enols and their keto tautomers such as the vinyl alcohol – acetaldehyde pair is of crucial importance as these molecules are considered key tracers of non-equilibrium chemistry driven by cosmic rays leading to COMs ([Abplanalp, et al. 2016b](#_ENREF_2); [Kleimeier, et al. 2021](#_ENREF_41)). However, despite the efforts of laboratory simulations, unraveling the formation mechanism of enols within icy grains has just scratched the surface.

In particular, this is true for the C2H2O2 isomers including glyoxal (HCOCHO, **1**) as well as its enol tautomer hydroxyketene (HOCHCO, **2**) and ynol tautomer acetylenediol (HOCCOH, **3**) as potential reactive precursors to larger COMs both in laboratories and the ISM. Glyoxal (**1**), the simplest α-dicarbonyl, is a key molecule in atmospheric chemistry ([Fu et al. 2008](#_ENREF_29)) and serves as a model for investigating the photophysics and photochemistry of small organics ([Mielke et al. 2008](#_ENREF_61)). Astrophysical models suggest that glyoxal (**1**) could be formed through recombination of two formyl (HĊO) radicals ([Butscher et al. 2017](#_ENREF_12); [Chuang et al. 2017](#_ENREF_16); [Enrique-Romero et al. 2022](#_ENREF_27); [Fedoseev et al. 2015](#_ENREF_28); [Woods et al. 2013](#_ENREF_95)). Laboratory experiments on carbon monoxide−methane (CO–CH4) ices exposed to energetic electrons at 5 K revealed the identification of glyoxal (**1**) during temperature-programmed desorption (TPD) ([Abplanalp & Kaiser 2019](#_ENREF_3)). Glyoxal (**1**) has also been detected in the organic residue resulting from a vacuum ultraviolet-irradiated ice mixture composed of water (H2O), methanol (CH3OH), and ammonia (NH3) ([de Marcellus et al. 2015](#_ENREF_22)). Therefore, glyoxal (**1**) is a potential candidate to be searched for in the ISM. Based on Fourier transform infrared (FTIR) spectroscopy and *ab initio* calculations, Mielke et al. revealed that the irradiation (λ > 370 nm) of the glyoxal (**1**)–methanol complex in solid argon leads to its photo-conversion into the hydroxyketene (**2**)–methanol complex ([Mielke, et al. 2008](#_ENREF_61)), confirming the formation of hydroxyketene (**2**). Acetylenediol (**3**), a metastable tautomer of glyoxal (**1**), is predicted to be 196 kJ mol−1 less stable at the CCSD(T)/cc-pVTZ level of theory ([Vijay & Sastry 2005](#_ENREF_88)). It has been prepared and identified in the gas phase by neutralization-reionization mass spectrometry ([Terlouw et al. 1986](#_ENREF_78)) and detected directly in an argon matrix at 10 K upon irradiation (λ = 254 nm) of squaric acid (C4H2O4)([Maier & Rohr 1996](#_ENREF_53)). The detection of interstellar 1,2-ethenediol (HOCHCHOH) ([Rivilla, et al. 2022](#_ENREF_70)) suggests the possible existence of the analogous acetylenediol (**3**,HOCCOH) derivative in the ISM, in which the carbon-carbon double bond is replaced by a carbon-carbon triple bond ([Mó, et al. 2023](#_ENREF_64)). Acetylenediol (**3**) is predicted to be formed from glyoxal (**1**) through keto-enol-ynol tautomerization involving the hydroxyketene (**2**) as an intermediate (Figure 2) ([Maier & Rohr 1996](#_ENREF_53)). Although this enolization process leading to acetylenediol (**3**) from glyoxal (**1**) is unique and interesting in organic chemistry ([Maier & Rohr 1996](#_ENREF_53)), no experimental evidence has been reported as of now.

Here, we present laboratory experiments on the formation of glyoxal (**1**) along with its ynol tautomer acetylenediol (**3**) in low-temperature interstellar model ices comprised of carbon monoxide and water (CO−H2O). The ice mixtures were irradiated with energetic electrons, simulating the secondary electrons generated in the track of Galactic cosmic rays (GCRs) ([Bennett et al. 2011](#_ENREF_8)) over lifetimes of molecular clouds of up to 50 million years ([Yeghikyan 2011](#_ENREF_98)). Utilizing vacuum ultraviolet (VUV) photoionization reflectron time-of-flight mass spectrometry (PI-ReTOF-MS), both glyoxal (**1**) and acetylenediol (**3**) were detected in the gas phase via *isomer-specific* photoionization during TPD based on their adiabatic ionization energies (IEs) of C2H2O2 isomers (Table 2). These results reveal the formation pathways of glyoxal (**1**) through radical-radical recombination of formyl radicals and its ynol tautomer acetylenediol (**3**) via the keto-enol- ynol tautomerization mechanism, advancing the fundamental knowledge of the formation of key reactive organics such as enols in deep space. Water is the most abundant molecule in interstellar ices ([Öberg et al. 2011](#_ENREF_65); [Tielens 2013](#_ENREF_80)) and carbon monoxide is one of the most commonly detected molecules in interstellar ices with a fractional abundance of up to 55% with respect to water toward IRAS 08375–4109 ([Thi et al. 2006](#_ENREF_79)). Therefore, carbon monoxide and water are suitable choices for simple astrophysical ice analogs. Our results suggest that the hitherto astronomically unobserved glyoxal (**1**) and acetylenediol (**3**) represent promising candidates for future astronomical searches via telescopes such as the Atacama Large Millimeter/submillimeter Array (ALMA) and the James Webb Space Telescope (JWST).

**2. Experimental**

All experiments were carried out in a hydrocarbon-free stainless steel chamber capable of reaching ultrahigh vacuum pressures of a few 10−11 Torr by magnetically levitated turbomolecular pumps ([Jones & Kaiser 2013](#_ENREF_39)). A polished silver wafer was mounted on an oxygen-free high-conductivity copper head cooled to 5 K using a closed-cycle helium cryostat (Sumitomo Heavy Industries, RDK-415E). The cold head assembly can rotate within the horizontal plane through a rotatable flange (Thermionics Vacuum Products, RNN-600/FA/MCO) and translate vertically via an adjustable bellows (McAllister, BLT106). The carbon monoxide (CO, 99.99%, Sigma Aldrich) and water (H2O, HPLC, Fisher Scientific) vapor were premixed with a ratio of carbon monoxide to water of 1:2. After the silver substrate was cooled to 5 K, the premixed samples were introduced via a glass capillary array to the substrate. Water samples were stored in glass vials and subjected to several freeze-thaw cycles to remove residual atmospheric gases. The ice thickness was monitored via laser interferometry using a helium-neon laser (632.8 nm) during the deposition ([Turner et al. 2015](#_ENREF_82)). A photodiode was used to record the interference fringes between the reflections of the ice surface and the substrate. Considering the average refractive index (n) of 1.26 ± 0.04 between the refractive indices of carbon monoxide ice (n = 1.25 ± 0.03) ([Bouilloud et al. 2015](#_ENREF_11); [Pipes et al. 1978](#_ENREF_67); [Roux et al. 1980](#_ENREF_72)) and water ice (n = 1.27 ± 0.02) ([Bouilloud, et al. 2015](#_ENREF_11)), the thickness of the ice mixture was determined to be 1,000 ± 200 nm. Fourier transform infrared (FTIR) spectra (Thermo Electron, Nicolet 6700) were collected with a resolution of 4 cm−1 after ice deposition at 5 K. The relative concentration of CO and H2O in the ices was determined to be (1.4 ± 0.4) utilizing integrated infrared absorptions for *ν*1 (2139 cm−1, CO, 1.12 × 10−17 cm molecule−1), *ν*1 (2091 cm−1, 13CO, 1.32 × 10−17 cm molecule−1), 2*ν*1 (4251 cm−1, CO, 1.04 × 10−19 cm molecule−1) for carbon monoxide, and *ν*2 (1645 cm−1 , H2O, 9.0 × 10−18 cm molecule−1), *v*1/*v*3 (3700–3000 cm−1, H2O, 3.8 × 10−16 cm molecule−1) for water ([Bouilloud, et al. 2015](#_ENREF_11); [Turner et al. 2018](#_ENREF_81)). The ices were then irradiated with 5 keV electrons (SPECS, EQ PU-22) at a current of 50 nA for 120 minutes, resulting in a dose of up to 15 ± 3 eV per molecule of carbon monoxide and 10 ± 2 eV per molecule of water, respectively ([Turner et al. 2020](#_ENREF_85)). For an interstellar ice grain, these doses correspond to around 50 million years of exposure to GCRs within a molecular cloud ([Yeghikyan 2011](#_ENREF_98)). Utilizing Monte Carlo simulations carried out in the CASINO program ([Drouin et al. 2007](#_ENREF_24)), the average penetration depth of the electrons was 360 ± 60 nm; 99 % of the electron energy was deposited in the top 600 ± 50 nm sample layers, which is less than the ice thickness, to prevent the interaction between the electrons and the substrate ([Turner et al. 2021](#_ENREF_83)).

After the irradiation, the ices were heated to 300 K at 1 K min−1 using a temperature-programmed desorption (TPD) scheme. During TPD, subliming molecules were photoionized in the gas phase by pulsed 30 Hz coherent VUV light at photon energies of 10.82 eV, 9.75 eV, 9.10 eV, 8.81 eV, and 8.20 eV. VUV light was generated via a two-photon resonant difference four-wave mixing (ωvuv = 2ω1−ω2) scheme using krypton or xenon gases as a nonlinear medium. Detailed parameters for VUV generation are listed in Table 3. The VUV photons were separated from other energy photons via a lithium fluoride biconvex lens (Korth Kristalle, R1 = R2 = 131 mm) in an off-axis geometry and passed 2 ± 0.5 mm above the ice surface to ionize subliming species in the gas phase. The resulting ions were detected via a reflectron time-of-flight mass spectrometer (ReToF-MS, Jordan TOF Products, Inc.). Ion signals were amplified by a preamplifier (Ortec 9305) and recorded by a multichannel scaler (FAST ComTec, MCS6A). The accumulation time for each recorded mass spectra during TPD was 2 minutes (3600 sweeps). To confirm the mass assignments, isotopically labeled experiments were performed using 13CO (99 atom% 13C, Sigma Aldrich), 13C18O (95 atom % 18O, 99 atom % 13C, Sigma Aldrich), D2O (99.9 atom% D, Sigma Aldrich) and H218O (99% 18O, Sigma Aldrich). An additional blank experiment was performed without electron irradiation, verifying that the observed ion signals at *m/z* = 58 were caused by an external energy source.

**3. Theoretical**

All computations make use of coupled cluster singles, doubles, and perturbative triples within the explicitly correlated formalism [CCSD(T)-F12b] with the cc-pVTZ-F12 basis set as available in MOLPRO 2022.3 ([Adler, Knizia, & Werner 2007](#_ENREF_4); [H.-J. Werner 2021](#_ENREF_31); [Knizia, Adler, & Werner 2009](#_ENREF_45); [Peterson, Adler, & Werner 2008](#_ENREF_66); [Yousaf & Peterson 2008](#_ENREF_99)). Harmonic frequencies confirm the structures as minima and produce the zero-point vibrational energies (ZPVEs), which are added to the total electronic energies. Differences in the electronic plus ZPVE energies between conformers produce the relative energies, and differences between these energies for the neutral and radical-cation produce the ionization energies. The same procedure is utilized to compute degradation products where the final energies are simple Hess’s Law reaction energetics based upon the computed electronic plus ZPVE energies. Electronic energies, optimized Cartesian coordinates, and harmonic frequencies are provided in the Appendix, Table A1.

**4. Results and Discussion**

***4.1. Infrared Spectroscopy***

FTIR spectra of carbon monoxide−water (CO−H2O) ices were collected before, during, and after the irradiation with energetic electrons (Figure 3). Before the irradiation, the CO−H2O ice spectra are dominated by the CO stretching (CO, 2139 cm−1; 13CO, 2092 cm−1) and overtone (4251 cm−1) modes of carbon monoxide, OH dangling (3630 cm−1), OH stretching (*v*1/*v*3, 3000−3610 cm−1) and H-O-H bending (*v*2, 1644 cm−1) modes for water ([Bouilloud, et al. 2015](#_ENREF_11)). Processing of the CO−H2O ice resulted in several new absorptions. The absorptions at 2345 cm−1 and 2279 cm−1 were assigned to C=O stretching (ν3) of carbon dioxide ([Bouilloud, et al. 2015](#_ENREF_11)), which is the dominant product in processed CO-containing ices ([Abplanalp & Kaiser 2019](#_ENREF_3); [Schmidt, Swiderek, & Bredehöft 2019](#_ENREF_73)). Formaldehyde (H2CO) was identified with the C=O stretching (ν2,1716 cm−1) and CH2 scissoring (ν3, 1499 cm−1) modes ([Bouilloud, et al. 2015](#_ENREF_11)). The absorption at 1849 cm−1 can be linked to the ν3 fundamental (CO stretch) of the formyl radical (HĊO) ([Milligan & Jacox 1964](#_ENREF_62)), which has been identified previously in CO-containing interstellar analog ices such as CO−H2S (1840 cm−1) ([Wang et al. 2022](#_ENREF_90)), CO−C2H2 ice (1853 cm−1) ([Abplanalp & Kaiser 2019](#_ENREF_3)), CO−CH4 ice (1853 cm−1) ([Bennett et al. 2005](#_ENREF_9)), and CO−CH3OH ice (1843 cm−1) ([Bennett & Kaiser 2007](#_ENREF_10)). The absorptions of carbon dioxide, formaldehyde, and formyl have been shifted in isotopically labeled systems (13CO−H2O ice, CO−D2O ice, and 13C18O−H218O ice), as shown in Figure A1. It is worth noting that the absorption at 1716 cm−1 may also be linked to the C=O stretching of glyoxal (**1**) ([Hudson, Moore, & Cook 2005](#_ENREF_37); [Verderame, Catellucci, & Califano 1970](#_ENREF_87)). The OH stretching (3586 cm−1) and OH bending (1212 cm−1) modes of acetylenediol (**3**) have been observed in an argon matrix at 10 K previously ([Maier & Rohr 1996](#_ENREF_53)), however, they were not detected in the irradiated H2O–CO ice due to the overlap of functional groups such as hydroxyl group (−OH) or the low sensitivity of our FTIR setup. Therefore, an isomer-selective identification of the target isomers **1**–**3** cannot be accomplished by infrared spectroscopy; an alternative, more sensitive approach is required to identify individual C2H2O2 isomers formed in these ices.

***4.2. PI-ReTOF-MS***

Photoionization reflectron time-of-flight mass spectrometry (PI-ReTOF-MS) was utilized to identify individual C2H2O2 isomers during the heating of the irradiated ices. This technique allows for the identification of specific structural isomers based on their distinct desorption temperatures and adiabatic ionization energies ([Turner & Kaiser 2020](#_ENREF_84)). Here, the subliming products were photoionized in separate experiments with photon energies of 10.82 eV, 9.75 eV, 9.10 eV, 8.81 eV, and 8.20 eV to determine which C2H2O2 isomers were formed (Figure 2). Photons with energies of 10.82 eV can ionize all isomers glyoxal (**1**), hydroxyketene (**2**), acetylenediol (**3**), and ethynyl hydroperoxide (**4**). 9.75 eV and 9.10 eV photons can ionize hydroxyketene (**2**, IE = 8.66 – 8.74 eV) and acetylenediol (**3**, IE = 8.97 – 9.05 eV), whereas 8.81 eV photons can only ionize hydroxyketene (**2**). 8.20 eV photons cannot ionize either C2H2O2 isomer. At a photon energy of 10.82 eV, the TPD profile of *m/z* = 58 in the irradiated CO−H2O ice shows a broad sublimation event that starts at 140 K and ends at 185 K (Figure 4) ([Turner, et al. 2021](#_ENREF_83)). After the early sublimation event, a shoulder peaking at around 170 K is found with varying intensity in isotopically labeled ices. This is attributed to the sublimation of molecules trapped within the water-ice matrix that comprises the bulk of the ice until its sublimation. Since the ion signal of *m/z* = 58 can be associated with C2H2O2, C3H6O, and/or C4H10, it is imperative to confirm the assignment of the molecular formula using isotopically labeled precursors. In particular, this TPD profile shifts by 2 amu from *m/z* = 58 to *m/z* = 60 in both 13CO–H2O and CO−D2O ices indicating the presence of two carbon atoms and two deuterium atoms, respectively. Furthermore, the replacement of the CO−H2O ice by 13C18O–H218O ice shifts the *m/z* by 6 amu from *m/z* = 58 (C2H2O2+) to *m/z* = 64 (13C2H218O2+), indicating the presence of two carbon atoms and two oxygen atoms. In addition, the formation of C3H6O isomers can be ruled out from the TPD profiles of isotopically labeled ice mixtures (Figure A2). Hence, the ion signal of *m/z* = 58, at least in the range from 140 K to 170 K, can be clearly linked to a molecule of the formula C2H2O2.

Since the 10.82 eV photons are capable of ionizing all C2H2O2 isomers, the TPD profile of *m/z* = 58 can be linked to isomers **1−4**. This profile is deconvoluted with three Gaussian fits peaking at 156 K (peak 1), 161 K (peak 2), and 169 K (peak 3), respectively (Figure 5a). It should be noted that these peaks are not present in the blank experiment conducted under the same conditions but without exposing the ices to ionizing radiation, confirming that the sublimation event of *m/z* = 58 (C2H2O2+) is the result of the irradiation exposure of the ices. Utilizing a photon energy of 9.75 eV and 9.10 eV, at which glyoxal (**1**, IE = 9.93 – 10.12 eV) and ethynyl hydroperoxide (**4**, IE = 9.82 – 9.90 eV) cannot be ionized, the early sublimation event (peak 1) vanishes (Figure 5b), indicating that peak 1 is associated with glyoxal (**1**) and/or ethynyl hydroperoxide (**4**). We calculated the dissociation pathways for the cation of ethynyl hydroperoxide (**4**) at the CCSD(T)-F12b/cc-pVTZ-F12 level of theory (Figure 6); cleaving the O-O bond in the cation is strictly Morse-like behavior and only requires 20 kJ mol–1 (pathway a). After the photoionization at 10.82 eV, the excess energy in the cation is at least 89 kJ mol−1, which is notable larger than the energy needed to open the dissociation pathway in which the cation (HCCOOH+) leads to fragment ion HCCO+ plus hydroxyl radical (ȮH) (Figure 6). One would expect to observe an ion signal of HCCO+ (*m/z* = 41) at 10.82 eV if ethynyl hydroperoxide (**4**) was formed; however, no ion signal was detected at *m/z* = 41, ruling out the formation of ethynyl hydroperoxide (**4**) under current experimental conditions. Therefore, peak 1 is assigned to glyoxal (**1**). It is worth noting that glyoxal (**1**) is known to desorb near 160 K ([Butscher, et al. 2017](#_ENREF_12)), which agrees well with our results.

Additionally, the TPD profile of *m/z* = 58 recorded at both 9.75 eV and 9.10 eV exhibits a sublimation event corresponding to peaks 2 and 3, which can be linked to hydroxyketene (**2**, IE = 8.66 – 8.74 eV) and/or acetylenediol (**3**, IE = 8.97 – 9.05 eV). We then lowered the photon energy to 8.81 eV, at which only hydroxyketene (**2**) can be ionized. In contrast to the results at 9.75 eV, peak 2 vanishes at 8.81 eV (Figure 5b), suggesting that this event can be linked to acetylenediol (**3**). At 8.81 eV, a sublimation event (peak 3) remains. Previous work revealed that water has a sublimation event peaking at 170 K ([Zheng, Jewitt, & Kaiser 2006](#_ENREF_100)) and 165 K ([Bennett, et al. 2011](#_ENREF_8)) in electron-irradiated H2O ice and CO–H2O ice, respectively. The coincidence of peak 3 at 169 K can be due to the co-sublimation of a compound with water molecules. In addition, the sublimation event of *m/z* = 72 that can be assigned to C3H4O2 isomers ([Turner, et al. 2021](#_ENREF_83)) partially matches the TPD profile of *m/z* = 58 (Figure A3), indicating that peak 3 may origin from the fragment of the dissociative photoionization of C3H4O2 species. Therefore, peak 3 cannot be uniquely assigned to hydroxyketene (**2**). Further lowering the photon energy to 8.20 eV eliminates peak 3, and no ion signal of *m/z* = 58 was observed. Overall, the PI-ReTOF-MS studies demonstrate the gas-phase detection of glyoxal (**1**) and acetylenediol (**3**), and a tentative identification of hydroxyketene (**2**). The detected counts of glyoxal (**1**) and acetylenediol (**3**) in the irradiated CO–H2O ices were 1800 ± 200 and 880 ± 100 counts, respectively.

Having provided evidence for the formation of glyoxal (**1**) and acetylenediol (**3**) in carbon monoxide−water ices under astrophysical conditions, we shift our attention to their potential formation pathways. *First*, upon interaction of energetic electrons, water molecule undergoes unimolecular decomposition to form a hydroxyl radical (ȮH) and a suprathermal hydrogen atom (Ḣ) with excess kinetic energy of up to a few eV (reaction [1]) ([Zheng, et al. 2006](#_ENREF_100)). Since reaction [1] is strongly endoergic by 466 kJ mol−1 ([Bennett, et al. 2011](#_ENREF_8)), the input of energy originating from GCRs is necessary. *Second*, the addition of the hydrogen atom to a carbon monoxide molecule leads to the formation of the formyl radical (HĊO) via reaction [2] ([Wang, et al. 2022](#_ENREF_90)). This reaction is exoergic by 60 kJ mol−1 with an entrance barrier of 11 kJ mol−1 ([Bennett, et al. 2005](#_ENREF_9)), which can be overcome by the excess kinetic energy of the suprathermal hydrogen atom. Extensive studies have demonstrated the formation of the formyl radical (HĊO) in CO−H2O ice analogs under simulated astrophysical conditions, which involve reactions initiated by energetic heavy ions (46 MeV 58Ni11+) ([de Barros et al. 2022](#_ENREF_23)), protons (0.8 MeV) ([Hudson & Moore 1999](#_ENREF_36)), electrons (5 keV) ([Bennett, et al. 2011](#_ENREF_8); [Eckhardt et al. 2019](#_ENREF_25); [Turner, et al. 2021](#_ENREF_83); [Turner, et al. 2020](#_ENREF_85)), X-rays ([Jiménez-Escobar et al. 2016](#_ENREF_38)), and VUV photolysis ([Milligan & Jacox 1971](#_ENREF_63)). This is also confirmed by our FTIR results that the CO stretch (1849 cm−1) of formyl radical was observed in irradiated CO−H2O ice. *Third*, if the formyl radical has a favorable recombination geometry with another nearby formyl radical, the barrierless radical-radical recombination of two formyl radicals can proceed to form glyoxal (**1**) via reaction [3]. It is worth noting that reaction [3] has a diffusion barrier of around 4 kJ mol−1 on water ice surface calculated at the BHLYP-D3(BJ)/6-311++G(2df,2pd) level of theory ([Enrique-Romero, et al. 2022](#_ENREF_27)). The origin of the barrier is that formyl radicals need to overcome partly the intermolecular forces with the surfaces to orient and react ([Enrique-Romero, et al. 2022](#_ENREF_27)). This small barrier can be easily overcome by the energy contributed by energetic electrons. Glyoxal (**1**) exists in stable planar *syn* and *anti*-conformations that refer to the relative positions of the two oxygen atoms with respect to the carbon-carbon single bond. The *anti*-glyoxal is more stable than the *syn* form by 19 kJ mol−1 (Table 2), indicating that *anti* conformation is predominantly at 300 K equilibrium ([Mielke, et al. 2008](#_ENREF_61)). The isomerization barrier from *anti*-to *syn*-glyoxalis 23 kJ mol−1 ([Koch, Khieu, & Peslherbe 2001](#_ENREF_46); [Xiong et al. 2014](#_ENREF_97)). The formation of *anti*-glyoxal via reaction [3] is exoergic by 293 kJ mol–1 calculated at the M06-2X-D3/aug-cc-pVTZ level of theory ([Butscher, et al. 2017](#_ENREF_12)). Previous studies on the dimerization of formyl radical in the gas phase ([Clark, Moore, & Nogar 1978](#_ENREF_17)) and rare gas matrix ([Butscher, et al. 2017](#_ENREF_12)) indicate that the production of formaldehyde is the favored pathway. This route may contribute to the formation of formaldehyde in the irradiated ices ([Butscher et al. 2015](#_ENREF_13)) as formaldehyde was observed in our FTIR spectra. However, the presence of neighboring molecules with similar vibrational structures in the ices may aid intermolecular energy transfer ([Wang et al. 2023a](#_ENREF_91)), and effectively stabilize glyoxal (**1**) formed via highly exoergic recombination. Furthermore, cage effects can impose a significant barrier to dissociative reaction pathways such as that which produces formaldehyde.

H2O → ȮH + Ḣ ΔRG = + 466 kJ mol−1 [1]

Ḣ + CO → HĊO ΔRG = − 60 kJ mol−1 [2]

HĊO + HĊO → HCOCHO (**1**) ΔRG = − 293 kJ mol−1 [3]

*Finally*, glyoxal (**1**) likely undergoes subsequent keto-enol-ynol tautomerization to form hydroxyketene (**2**) and acetylenediol (**3**). Glyoxal (**1**) has a pair of conjugated carbon-oxygen double bonds; it can first tautomerize to hydroxyketene (**2**) through reaction [4] ([Mielke, et al. 2008](#_ENREF_61)), which can further tautomerize to acetylenediol (**3**) via reaction [5] ([Maier & Rohr 1996](#_ENREF_53)). The reactions [4] and [5] are endoergic by 65 kJ mol−1 and128 kJ mol−1, respectively. Reaction [4] involves a four-member-ring transition state with a reaction barrier of 318 kJ mol−1 calculated at the W1U level of theory ([Xiong, et al. 2014](#_ENREF_97)). The barrier of reaction [5] was predicted to be 373 kJ mol−1 at the MP2/6-31G\*\*//HF/6-31G\*\*level of theory ([Lewars & Bonnycastle 1997](#_ENREF_51)). These tautomerization barriers can be overcome by the energy contributed by GCRs ([Wang, et al. 2022](#_ENREF_90)).

HCOCHO (**1**) ⇋ HOCHCO (**2**) ΔRG = + 65 kJ mol−1 [4]

HOCHCO (**2**) ⇋ HOCCOH (**3**) ΔRG = + 128 kJ mol−1 [5]

**5. Astrophysical Implications**

This work presents laboratory experiments on the formation of hitherto astronomically unobserved glyoxal (**1**) along with its enol tautomer acetylenediol (**3**) in interstellar model ices composed of carbon monoxide and water. Prior studies on chemical modeling of interstellar ices suggest that glyoxal (**1**) could be formed through radical-radical recombination of formyl radicals (HĊO) ([Abplanalp, Forstel, & Kaiser 2016a](#_ENREF_1); [Abplanalp & Kaiser 2019](#_ENREF_3); [Butscher, et al. 2017](#_ENREF_12); [Chuang, et al. 2017](#_ENREF_16); [de Marcellus, et al. 2015](#_ENREF_22); [Fedoseev, et al. 2015](#_ENREF_28); [Kleimeier, et al. 2021](#_ENREF_41); [Maity, Kaiser, & Jones 2015](#_ENREF_54); [Turner, et al. 2021](#_ENREF_83); [Woods, et al. 2013](#_ENREF_95)). The formyl radical is one of the most well-known astrophysically relevant radical species ([Butscher, et al. 2017](#_ENREF_12)) and has been detected in the Galactic molecular clouds W3, NGC 2024, W51, and K3-50 ([Snyder, Hollis, & Ulich 1976](#_ENREF_76)), the cold and dense core B1-b ([Cernicharo et al. 2012](#_ENREF_14)), the Blazars BL Lac and 3C 111 ([Liszt et al. 2014](#_ENREF_52)), prestellar cores ([Bacmann & Faure 2016](#_ENREF_5)), and the solar-type protostellar binary IRAS 16 293−2422 ([Rivilla et al. 2018](#_ENREF_69)). Although *syn*-glyoxal (**1**) may be detected in the ISM due to its large dipole moment (4.3 D) ([Leroux, Guillemin, & Krim 2019](#_ENREF_49)), glyoxal (**1**) would be in its preferred *anti*-configuration with zero dipole moment by symmetry, which makes its astronomical detection difficult ([Leroux, Guillemin, & Krim 2021](#_ENREF_50)). Once formed in the ices, glyoxal (**1**) may further lead to the formation of formaldehyde and carbon monoxide ([Butscher, et al. 2017](#_ENREF_12)). Further, glyoxal (**1**) and acetylenediol (**3**) may be found with low concentrations in the ISM due to their high reactivity.

As of now, the enols vinyl alcohol (CH2CHOH), 1,2-ethenediol (HOCHCHOH) and 3-hydroxypropenal (HOCHCHCHO; tentative) have been detected toward the dense molecular cloud Sagittarius B2(N) ([Turner & Apponi 2001](#_ENREF_86)), the G+0.693−0.027 molecular cloud ([Rivilla, et al. 2022](#_ENREF_70)), and the solar-type protostar IRAS 16293–2422 ([Coutens, et al. 2022](#_ENREF_20)), respectively. Laboratory simulations suggested that both vinyl alcohol and 1,2-ethenediol can be formed through the enolization of their aldehydes ([Abplanalp, et al. 2016b](#_ENREF_2); [Kleimeier, et al. 2021](#_ENREF_41); [Kleimeier & Kaiser 2021](#_ENREF_43); [Zhu et al. 2022b](#_ENREF_102)). Our findings reveal the formation route of ynol acetylenediol (**3**) via keto-enol-ynol tautomerization of glyoxal (**1**) with enol hydroxyketene (**2**) as an intermediate, which was tentatively identified in our experiments. These pathways may occur via GCR-induced keto-enol tautomerization reactions in carbon monoxide-rich and water-rich interstellar ices. Although acetylenediol (**3**) has been detected in argon matrix isolation ([Maier & Rohr 1996](#_ENREF_53)), we present its first identification in interstellar ice analogs. The observation of acetylenediol (**3**) reveals that keto-enol-ynol tautomerization can proceed in interstellar ices composed of simple, abundant precursors such as carbon monoxide and water, advancing our fundamental knowledge of the formation mechanisms of key reactive COMs such as enols in deep space.

Water is the most abundant molecule in interstellar ices ([Öberg, et al. 2011](#_ENREF_65); [Tielens 2013](#_ENREF_80)) and carbon monoxide has been detected at levels up to 55% with relative to water toward IRAS 08375–4109 ([Thi, et al. 2006](#_ENREF_79)). Considering the abundance of carbon monoxide and water in the interstellar ices, both glyoxal (**1**) and acetylenediol (**3**) are promising candidates to search for towards background stars such as Taurus field star Elias 16 ([Chiar et al. 1995](#_ENREF_15)), NIR38 and J110621 ([McClure et al. 2023](#_ENREF_58)), and young stellar objects such as IRAS 08375–4109 ([Thi, et al. 2006](#_ENREF_79)), NGC 7538 IRS 9 ([Whittet 1997](#_ENREF_94)), GL 7009S and W33A ([Gibb et al. 2000](#_ENREF_30)). The high-resolution FTIR spectra of glyoxal (**1**, C2H2O2) ([Larsen et al. 2002](#_ENREF_47)) as well as its isotopomers ([Larsen et al. 2003](#_ENREF_48)) are known. Although the rotational spectrum of acetylenediol (**3**) is lacking, two IR bands at 3586 cm−1 and 1212 cm−1 have been observed in an argon matrix ([Maier & Rohr 1996](#_ENREF_53)). Glyoxal (**1**) and acetylenediol (**3**) may act as reactive precursors to form biorelevant molecules. Through successive hydrogenation, glyoxal (**1**) can convert to the sugar-related glycolaldehyde (HOCH2CHO) and ethylene glycol (HOCH2CH2OH), which have been detected toward the Galactic Center source Sagittarius B2(N) ([Hollis, Lovas, & Jewell 2000](#_ENREF_34); [Hollis et al. 2002](#_ENREF_35)). Once formed in interstellar ices, these molecules may eventually be incorporated into comets and delivered to planets like early Earth. In fact, extraterrestrial C2H2O2 species have recently been detected and can likely be assigned to glyoxal (**1**) in comet 67P’s dusty coma ([Hänni et al. 2023](#_ENREF_32)). A firm detection of glyoxal (**1**) and acetylenediol (**3**) in the ISM in conjunction with their reaction pathways leading to other organics could enhance our comprehension of how high-energy tautomers contribute to the formation mechanisms of COMs in deep space ([Kleimeier & Kaiser 2022](#_ENREF_44)).

**Conflicts of interest**

The authors declare no competing financial interests.

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**Appendix**

Magnified view of FTIR spectra for isotopically labeled carbon monoxide–water ices before and after irradiation are presented in Figure A1. TPD profiles recorded at 10.82 eV for isotopically labeled ice mixtures are shown in Figure A2, ruling out the formation of C3H6O isomers. TPD profiles of *m/z* = 58 and *m/z* = 72 in irradiated CO–H2O ices recorded at 8.81 eV are provided in Figure A3. Electronic energies, optimized Cartesian coordinates, and vibrational frequencies of C2H2O2 isomers calculated at the CCSD(T)-F12b/cc-pVTZ-F12 level of theory are shown in Table A1.

A group of molecules with text

Description automatically generated with medium confidence

**Figure 1**. Enol tautomers prepared and detected in distinct interstellar analog ices subjected to ionizing radiation. Isomers in bold indicate astronomical detections.

A graph of a chemistry experiment

Description automatically generated with medium confidence

**Figure 2**. Reaction scheme leading to C2H2O2 (*m/z* = 58) isomers (**1**−**3**) in irradiated carbon monoxide–water ices (top). Barrierless reactions of two formyl radicals (HĊO, **A**)produce **1**; tautomerization of **1** leads to isomers **2** and **3**. The adiabatic ionization energies (IEs) are corrected for computational accuracy at the CCSD(T)-F12b/cc-pVTZ-F12 level of theory (Table 2). The bottom figure compiles the computed IEs of C2H2O2 isomers (black solid lines) and IE ranges (gray area) after error analysis. Five VUV photon energies (dashed lines) were selected to photoionize subliming molecules during TPD.

A graph of a red line

Description automatically generated

**Figure 3.** FTIR spectra of CO–H2O ice at 5 K before (black line) and after (red line) irradiation. A magnified view of the region between 2300 and 1400 cm−1 shows new peaks after irradiation.

A graph of a graph of a temperature

Description automatically generated with medium confidence

**Figure 4.** TPD profiles recorded at 10.82 eV for isotopically labeled carbon monoxide–water ice mixtures: *m/z* = 58 in irradiated CO−H2O ice, *m/z* = 60 in irradiated 13CO−H2O ice, *m/z* = 60 in irradiated CO−D2O ice, and *m/z* = 64 in irradiated 13C18O−H218O ice.

A diagram of a graph showing different types of signal

Description automatically generated

**Figure 5.** TPD profiles for *m/z* = 58 (C2H2O2+) in irradiated CO–H2O ice recorded at 10.82 eV, 9.75 eV, 9.10 eV, 8.81 eV, and 8.20 eV, as well as in the blank (unirradiated) experiment recorded at 10.82 eV. The solid red lines indicate the total fits of the spectra.

A diagram of energy and energy

Description automatically generated with medium confidence

**Figure 6**. Calculated dissociation pathways of the ethynyl hydroperoxide radical cation (**4∙**+). The energies (kJ mol−1) computed at the CCSD(T)-F12b/cc-pVTZ-F12 level are relative to the cation **4∙**+. The dashed gray line indicates the excess internal energy (89 kJ mol−1) in the cation after photoionization at 10.82 eV.

**Table 1.** The enols and ynols formed in interstellar analog ices subjected to ionizing radiation. The relative energies (ΔE) are relative to their aldehyde or ketone tautomers.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| No. | Aldehydes or ketones | Enols or ynols | ΔE  (kJ mol−1) | Reference |
| 1 | ketene  (H2CCO) | ethynol  (HCCOH) | 140 | ([Turner, et al. 2020](#_ENREF_85)) |
| 2 | acetaldehyde  (CH3CHO) | vinyl alcohol (CH2CHOH) | 41 | ([Abplanalp, et al. 2016b](#_ENREF_2); [Zhu, et al. 2022b](#_ENREF_102)) |
| 3 | acetic acid  (CH3COOH) | 1,1-ethenediol (H2CC(OH)2) | 112 | ([Kleimeier & Kaiser 2022](#_ENREF_44)) |
| 4 | glycolaldehyde (HCOCH2OH) | 1,2-ethenediol (HOCHCHOH) | 34 | ([Kleimeier, et al. 2021](#_ENREF_41)), |
| 5 | glycinal  (NH2CH2CHO) | 2-aminoethenol (NH2CHCHOH) | 24 | ([Marks et al. 2023](#_ENREF_57)) |
| 6 | propanal  (CH3CH2CHO) | 1-propenol (CH3CHCHOH) | 42 | ([Singh et al. 2022](#_ENREF_75)) |
| 7 | acetamide  (NH2COCH3) | 1-aminoethenol (NH2C(OH)CH2) | 101 | ([Marks, et al. 2023](#_ENREF_57)) |
| 8 | acetone  (CH3COCH3) | propen-2-ol (CH3C(OH)CH2) | 61 | ([Wang, et al. 2023c](#_ENREF_93)) |
| 9 | hydroxyacetone (CH3COCH2OH) | prop-1-ene-1,2-diol (CH3C(OH)CHOH) | 62 | ([Wang, et al. 2023b](#_ENREF_92)) |
| prop-2-ene-1,2-diol (CH2C(OH)CH2OH) | 62 | ([Wang, et al. 2023b](#_ENREF_92)) |
| 10 | methyl acetate (CH3COOCH3) | 1-methoxyethen-1-ol (CH2C(OH)OCH3) | 116 | ([Wang, et al. 2023b](#_ENREF_92)) |
| 11 | 3-hydroxypropanal (HCOCH2CH2OH) | prop-1-ene-1,3-diol  (HOCHCHCH2OH) | 49 | ([Wang, et al. 2023b](#_ENREF_92)) |
| 12 | pyruvic acid  (CH3COCOOH) | 2-hydroxyacrylic acid (CH2C(OH)COOH) | 28 | ([Kleimeier, et al. 2020](#_ENREF_42)) |

**Table 2.** Error analysis of adiabatic ionization energies (IEs) and relative energies (ΔE) of distinct C2H2O2 isomers **1**−**4**; IEs and ΔE were computed at the CCSD(T)-F12b/cc-pVTZ-F12 level of theory including the zero-point vibrational energy (ZPVE) corrections. The IE ranges are corrected for the thermal and Stark effect by −0.03 eV and the combined error limits of −0.05/+0.03 eV ([Zhu et al. 2022a](#_ENREF_101)).

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Name | Isomer | | ΔE  (kJ mol−1) | | Computed IE (eV) | | Corrected IE ranges (eV) | |
| Glyoxal | *anti*-**1** | | 0 | | 10.12 | | 10.04–10.12 | |
| *syn*-**1** | | 19 | | 10.01 | | 9.93–10.01 | |
| Hydroxyketene | | **2** | | 65 | | 8.74 | | 8.66–8.74 | |
| Acetylenediol | | **3** | | 193 | | 9.05 | | 8.97–9.05 | |
| Ethynyl hydroperoxide | | **4** | | 407 | | 9.90 | | 9.82–9.90 | |

**Table 3.** Difference four-wave mixing parameters for the generation of VUV light with an uncertainty less than 0.001 eV for photon energies.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| VUV photon energy  (2ω1 − ω2) (eV) | Nonlinear medium | ω1 laser wavelength (nm) | ω1 Dye | ω2 laser wavelength (nm) | ω2 Dye |
| 10.82 | Krypton | 202.316 | Rhodamine 610 and 640 | 863.117 | LDS 867 |
| 9.75 | Krypton | 202.316 | Rhodamine 610 and 640 | 494.657 | Coumarin 503 |
| 9.10 | Xenon | 222.566 | Coumarin 450 | 607.379 | Rhodamine 610 and 640 |
| 8.81 | Xenon | 222.566 | Coumarin 450 | 532 | − |
| 8.20 | Xenon | 249.628 | Coumarin 503 | 715.207 | LDS 722 |

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**Appendix**

A graph of a graph of a chemical reaction

Description automatically generated with medium confidence

**Figure A1.** Magnified view of FTIR spectra of 13CO−H2O ice (a), CO−D2O ice (b), and 13C18O−H218O ice (c) before (black line) and after (red line) irradiation.

A graph of a temperature

Description automatically generated

**Figure A2.** TPD profiles recorded at 10.82 eV for isotopically labeled carbon monoxide–water ice mixtures (*m/z* = 58 in irradiated CO−H2O ice, *m/z* = 61 in irradiated 13CO−H2O ice, *m/z* = 64 in irradiated CO−D2O ice, and *m/z* = 63 in irradiated 13C18O−H218O ice), ruling out the formation of C3H6O isomers.

A graph of a graph of a function

Description automatically generated with medium confidence

**Figure A3**. TPD profiles of *m/z* = 58 (C2H2O2+) and *m/z* = 72 (C3H4O2+) in the irradiated CO–H2O ices recorded at a photon energy of 8.81 eV. The red-shaded region indicates their overlap in sublimation temperatures.

**Table A1.** Electronic energy (Hartree; E at 0 K), optimized Cartesian coordinates (Å), and vibrational frequencies (cm−1) of C2H2O2 isomers computed at the CCSD(T)-F12b/cc-pVTZ-F12 level of theory.

|  |  |  |
| --- | --- | --- |
| **Isomer** | Cartesian coordinates (Å) | Frequency (cm−1) |
| Atom X Y Z |
| *anti*-**1**  E = -227.5816  ZPVE = 0.03697535  E (total) = -227.54462 | C -0.643921 0.402829 0.000000  C 0.643921 -0.402829 0.000000  O -1.721263 -0.141348 0.000000  O 1.721263 0.141348 0.000000  H -0.514710 1.497823 0.000000  H 0.514710 -1.497823 0.000000 | 129.29      333.69  559.48      813.17  1064.79 1095.54  1339.47    1380.36  1760.87    1779.11 2985.56    2988.95 |
| *syn*-**1**  E = -227.57421  ZPVE = 0.03664855  E (total) = -227.53757 | C 0.000000 0.768102 0.525590  C 0.000000 -0.768102 0.525590  O 0.000000 1.411476 -0.490596  O 0.000000 -1.411476 -0.490596  H 0.000000 1.242891 1.524282  H 0.000000 -1.242891 1.524282 | 85.74       280.82  739.65      822.94  848.95 1065.61  1393.09     1399.25  1768.83   1798.88  2927.91   2955.19 |
| **2**  E = -227.55736  ZPVE = 0.03733779  E (total) = -227.52002 | H -1.615801 -0.041735 -0.793397  C -0.555145 0.010865 -0.597670  C -0.132309 0.007089 0.657853  O 0.222525 0.000246 1.767985  O 0.366167 -0.062511 -1.636438  H 0.463248 0.816154 -2.011865 | 224.96       282.68  484.89      574.53  678.98. 1037.08  1181.14   1279.83  1430.27     2181.49 3212.70     3820.86 |
| **3**  E = -227.50819  ZPVE = 0.0369341  E (total) = -227.47126 | C -0.599219 -0.009531 -0.021021  C 0.599219 0.009531 -0.021021  O -1.922920 0.048051 -0.021021  O 1.922920 -0.048051 -0.021021  H -2.258907 -0.619161 0.584157  H 2.258907 0.619161 0.584157 | 223.48      232.67  285.49      346.37  354.97 799.34  1248.46  1284.69  1374.32     2434.65  3818.67    3820.32 |
| **4**  E = -227.42432  ZPVE = 0.03451985  E (total) = -227.3898 | H -0.458615 -0.859946 1.770221  O -0.473515 0.057967 1.465627  O 0.647006 0.001413 0.501961  C 0.136057 0.000603 -0.699389  C -0.275850 -0.007288 -1.832353  H -0.629455 -0.002956 -2.833256 | 179.44      219.68  388.93      520.10  562.92.  660.10  784.87      1048.94  1362.75     2189.77  3473.19     3761.77 |