Supporting Information for

Interstellar Formation of 1,2-Propanediol ($CH_3CH(OH)CH_2OH$) and 1,2-Ethenediol (HOCHCHOH) — Key Precursors to Sugars and Sugar Derivatives

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Methods

Experimental. The experiments were conducted in an ultrahigh vacuum chamber evacuated to a base pressure at a few 10^{-11} Torr using magnetically suspended turbomolecular pumps (Osaka, TG1300MUCWB and TG420MCAB) in combination with an oil-free scroll pump (XDS35i, BOC Edwards).[1] A polished silver substrate was mounted on an oxygen-free high conductivity copper cold head, which was cooled to 5 K using a closed-cycle helium cryostat (Sumitomo Heavy Industries, RDK415E). The cold head was vertically translatable via an adjustable bellows (McAllister, BLT86) and rotatable horizontally using a rotatable flange (Thermionics Vacuum Products, RNN-600/FA/MCO).[2] The samples used in the experiments included methane (CH_4, Specialty Gases of America, 99.999%), methane-^{13}C ($^{13}CH_4$, AirGas, >99.9%), ethylene glycol ($HOCH_2CH_2OH$, Sigma-Aldrich, 99.8%), ethylene glycol–$^{13}C_2$ ($HO^{13}CH_2{}^{13}CH_2OH$, Sigma-Aldrich, 99 atom % ^{13}C), ethylene glycol-d_2 ($DOCH_2CH_2OD$, Cambridge Isotope Laboratories Inc., 98 atom % D), and ethylene glycol-d_4 ($HOCD_2CD_2OH$, CDN isotopes, 98.9 atom % D). Ethylene glycol was transferred into a borosilicate vial connected to an ultrahigh vacuum chamber and degassed through multiple freeze-pump-thaw cycles using liquid nitrogen. After cooling the silver substrate to 5.2 ± 0.1 K, methane and ethylene glycol vapor were indepedently deposited onto the substrate via 10 mm diameter glass capillary arrays at partial pressures of 4×10^{-8} Torr and 4×10^{-9} Torr, respectively. The ice thickness was monitored during deposition via laser interferometry using a helium–neon laser (CVI Melles Griot, 25-LHP-230) operating at 632.8 nm. The resulting interference fringes, formed between reflections from the ice surface and the substrate, were detected with a photodiode.[3] The refractive index (n) of the CH_4–$HOCH_2CH_2OH$ ice was determined to be 1.39 ± 0.06, calculated as the average of the refractive indices of pure methane (n = 1.34 ± 0.03)[4] and ethylene glycol ice (n = 1.43).[5] This yields ice thickness of 730 ± 50 nm. After the deposition, Fourier transform infrared (FTIR) spectra of the ices were measured using a FTIR spectrometer (Thermo Electron, Nicolet 6700) at 4 cm^{-1} resolution (Figure 1, Figures S1−S3, Tables S1−S4). The ice composition of methane to ethylene glycol in CH_4–$HOCH_2CH_2OH$ ice was estimated to be 0.9 ± 0.2:1 (Table S6) based on integration the infrared features of methane at 1300, 3007, 4201, and 4297 cm^{-1} using absorption coefficients of 8.0×10^{-18}, 1.1×10^{-17}, 3.5×10^{-19}, and 5.3×10^{-19} cm $molecule^{-1}$, respectively.[4] Densities of 0.45 ± 0.03 g cm^{-3} and 1.1 g cm^{-3} were used for CH_4 and $HOCH_2CH_2OH$ ices, respectively.[4,6] Variations in density were accounted for based on the molecular masses of the isotopically labeled

methane and ethylene glycol species. Note that the methane to ethylene glycol ratio used in this work may not represent typical abundances in interstellar ices, it was selected to maximize the production of interested isomers and thereby facilitate their detection.

After the deposition, ice mixtures were irradiated with an electron gun (SPECS, EQ PU-22) producing 5 keV electrons rastered over the sample surface at an incidence angle of 70°. These electrons simulate the effects of the secondary electrons generated by galactic cosmic rays (GCRs) penetrating interstellar ices.[2] The CH_4–$HOCH_2CH_2OH$ ice was irradiated with a current of 108 nA for 30 minutes, corresponding to doses of 3.9 ± 0.6 eV per CH_4 molecule and 10.9 ± 1.8 eV per $HOCH_2CH_2OH$ molecule (Table S6), as dertermnied through Monte Carlo simulations using the CASINO software suite.[7] The simulations indicated an average electron penetration depth of 460 ± 20 nm, which is much less than the 730 ± 50 nm thickness of the deposited ices, thereby minimizing electron-substrate interactions. FTIR spectra of the ices were collected *in situ* before, during, and after irradiation. Following irradiation, ice mixtures were heated from 5 K to 320 K at a rate of 0.5 K min^{-1} (temperature-programmed desorption; TPD). Subliming species were detected in the gas phase via vacuum ultraviolet (VUV) photoionization reflectron time-of-flight mass spectrometry (PI-ReToF-MS). VUV photons were generated by resonant four-wave mixing in a pulsed noble gas jet. The 9.60 eV and 9.10 eV photons were produced via difference frequency generation ($2\omega_1 - \omega_2$) using two synchronized, pulsed (30 Hz) laser beams (ω_1, ω_2) from two dye lasers (Sirah, Cobra-Stretch) and two Nd: YAG lasers (Spectra-Physics, Quanta Ray Pro 250-30 and 270-30) (Table S7). To produce 9.60 eV light, an Nd: YAG laser pumped the dye laser with stilbene 420 dye to produce 425.112 nm, which underwent second harmonic generation to yield 212.556 nm (ω_1). A second Nd: YAG laser pumped a rhodamine 610/rhodamine 640 dye mixture to obtain 600.108 nm (ω_2), generating 9.60 eV light using krypton gas as a nonlinear medium. Similarly, 9.10 eV light was produced in xenon gas with 222.566 nm (ω_1) and 607.379 nm (ω_2) laser beams; the 222.566 nm was produced through frequency doubling 445.132 nm light, which was obtained from a dye laser using coumarin 450 dye. A biconvex lithium fluoride lens (Korth Kristalle, R = 131 mm) in an off-axis geometry was used to spatially separate the VUV light from the fundamental laser beams. The VUV beam was then directed 2.0 ± 0.5 mm above the ice surface to ionize the subliming molecules during TPD. The resulting ions were extracted into the ReToF-MS (Jordan TOF Products) and detected with a dual multichannel plate detector. Ion signals were amplified, discriminated, and measured by a multichannel scaler (FAST ComTec, MCS6A), which

accumulated signals into 3.2 ns bins and for 2 minute intervals (3600 sweeps). To assist in the identification of 1,2-propanediol and 2-methoxyethanol, blank experiments were conducted at 9.60 eV by introducing less than 1% 1,2-propanediol ($CH_3CH(OH)CH_2OH$, Sigma-Aldrich, ACS reagent, ≥99.5%) or 1% 2-methoxyethanol ($CH_3OCH_2CH_2OH$, Sigma-Aldrich, for HPLC, ≥99.9%) in the CH_4−$HOCH_2CH_2OH$ ice mixture.

Computational

All initial conformers were generated with CREST.[8] All quantum chemical calculations were carried out with Gaussian 16, Revision C.01.[9] For geometry optimizations and frequency computations, the density functional theory (DFT) B3LYP functional[10-12] was employed utilizing the Dunning correlation consistent split valence basis set cc-pVTZ.[13] Based on these geometries, the corresponding frozen-core coupled cluster[14-17] CCSD(T)/cc-pVTZ and CCSD(T)/cc-pVQZ single point energies were computed utilizing the built-in extrapolation routine in ORCA 5.0.3[18] and extrapolated to complete basis set limit[19-22] CCSD(T)/CBS with B3LYP/cc-pVTZ zero-point vibrational energy (ZPVE) corrections. The adiabatic ionization energies were computed by taking the ZPVE corrected energy difference between the neutral and ionic species that correspond to similar conformations. The accuracy of our CCSD(T)/CBS computed energies is estimated to be within 8 kJ mol^{-1}.[23,24] The calculated IEs were compared with experimental measurements, yielding combined error bounds of −0.03/+0.06 eV (Table S8). A correction of −0.03 eV, accounting for thermal and Stark effects, was applied to the calculated IEs. The optimized Cartesian coordinates, harmonic frequencies, and infrared intensities of the computed structures are provided in Table S9.

Identification of vinyl alcohol (CH_2CHOH) and possible formation pathways

The TPD profile of ion signal of *m/z* = 44 recorded at 9.60 eV for the irradiated CH_4–$HOCH_2CH_2OH$ ice reveals a sublimation event peaking at 182 K (Figure S6a). Upon replacing the CH_4–$HOCH_2CH_2OH$ ice with fully ^{13}C-labeled $^{13}CH_4$–$HO^{13}CH_2{}^{13}CH_2OH$ ice, the ion signal shifts by 2 amu from *m/z* = 44 to *m/z* = 46, indicating the incorporation of exactly two carbon atoms and assigning the reaction products a molecular formula of C_2H_4O. The C_2H_4O family includes vinyl alcohol (**7**), acetaldehyde (CH_3CHO), and ethylene oxide (*c*-C_2H_4O). However, at 9.60 eV, only **7** (IE = 9.30 ± 0.05 eV (*syn*-**7**); IE = 9.17 ± 0.05 eV (*anti*-**7**))[25] can be photoionized , whereas acetaldehyde (IE = 10.2290 ± 0.0007 eV) and ethylene oxide (IE = 10.56 ± 0.01 eV) remain inaccessible.[26] Therefore, the observed sublimation event at *m/z* = 44 ($C_2H_4O^+$) can be assigned to **7**. Lowering the photon energy to 9.10 eV, at which **7** cannot be ionized, results in the disappearance of the sublimation event, providing further evidence for this assignment. Previous studies of electron-irradiated acetaldehyde ice revealed that a broad sublimation event peaking at 193 K for **7**,[27] which is close to our observed peak at 182 K. Notably, replacing CH_4–$HOCH_2CH_2OH$ ice with CH_4–$DOCH_2CH_2OD$ ice shifts the *m/z* by 1 amu from *m/z* = 44 (CH_2CHOH^+) to *m/z* = 45 (CH_2CHOD^+) (Figure S6b). Similarly, substituting $HOCH_2CH_2OH$ with $HOCD_2CD_2OH$ results in products with three deuterium (D) atoms detected at *m/z* = 47 (CD_2CDOH^+) in the irradiated CH_4–$HOCD_2CD_2OH$ ice (Figure S6c). These isotopic substitution experiments suggest that **7** forms via a dehydration mechanism from ethylene glycol, involving the loss of a hydrogen atom from one carbon atom and a hydroxyl group (ȮH) from the neighboring carbon atom.

Molecule **7** can form from the decomposition of radical **18** by losing a hydroxyl (ȮH) radical through reaction (S1), which proceeds with an endoergicity of 122 kJ mol^{-1}. Alternatively, **3** can first lose a hydroxyl (ȮH) radical to generate the 2-hydroxyethyl ($ĊH_2CH_2OH$, **21**) radical via reaction (S2), followed by the loss of a hydrogen atom to yield **7** through reaction (S3). Reactions (S2) and (S3) are endoergic by 394 and 116 kJ mol^{-1}, respectively.[28] In a third pathway, **7** can also be produced from **3** through the elimination of a water molecule via reaction (S4) with a reaction energy of 23 kJ mol^{-1}.[28] The energy transferred from the impinging energetic electrons can overcome the endoergicity of these reactions leading to the formation of **7**, which was identified via FTIR spectroscopy at 1654 cm^{-1} (ν_5) in irradiated CH_4–$HOCH_2CH_2OH$ ice and the corresponding isotopic shifts observed in isotopically labeled ices.

$$HO\dot{C}HCH_2OH\ (\mathbf{18}) \rightarrow CH_2CHOH\ (\mathbf{7}) + \dot{O}H \quad (S1)$$

$$HOCH_2CH_2OH\ (\mathbf{3}) \rightarrow \dot{C}H_2CH_2OH\ (\mathbf{21}) + \dot{O}H \quad (S2)$$

$$\dot{C}H_2CH_2OH\ (\mathbf{21}) \rightarrow CH_2CHOH\ (\mathbf{7}) + \dot{H} \quad (S3)$$

$$HOCH_2CH_2OH\ (\mathbf{3}) \rightarrow CH_2CHOH\ (\mathbf{7}) + H_2O \quad (S4)$$

In addition, other ion signal up to *m/z* = 134 ($C_5H_{10}O_4^+$) was detected at 9.60 eV from irradiated methane−ethylene glycol ices (Figures S7−S12). Detailed molecular formula assignments are provided in Table S5.

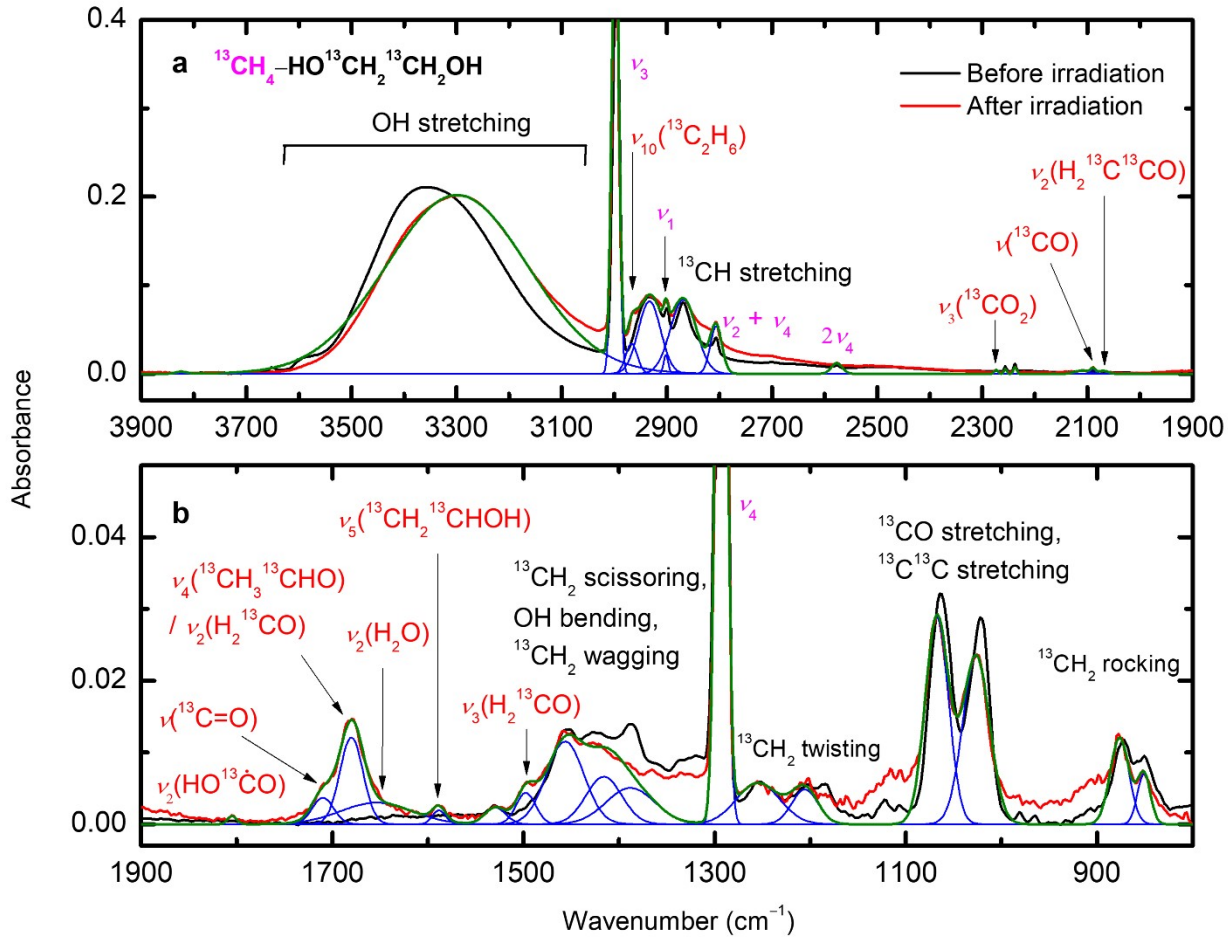


Figure S1. Infrared spectra (baseline corrected) of $^{13}CH_4$–HO$^{13}CH_2$$^{13}CH_2$OH ice before (black) and after (red) irradiation with deconvolution of the regions: 3900–1900 cm^{-1} (a) and 1900–800 cm^{-1} (b). The green lines indicate the total fit of the spectra. Detailed assignments are provided in Table S2.

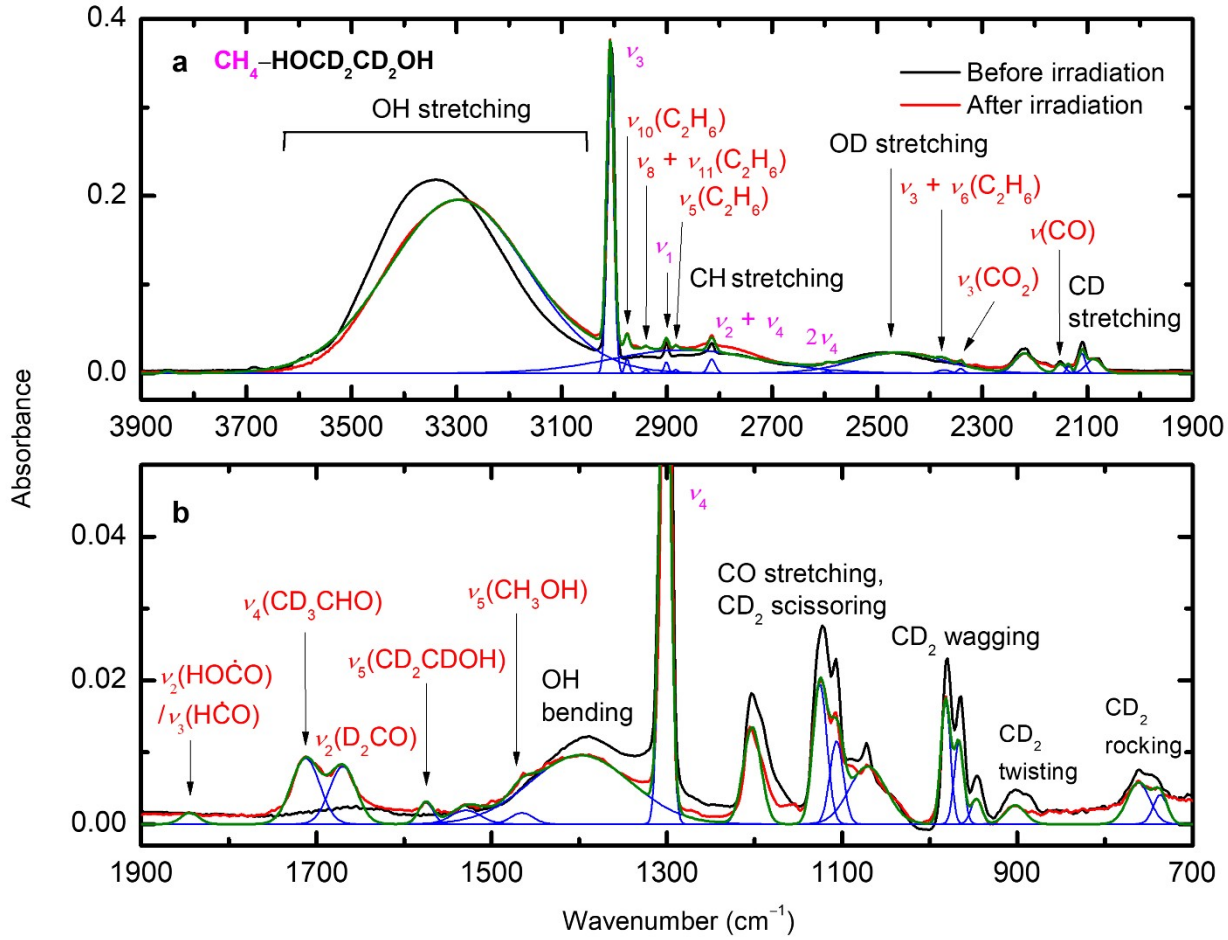


Figure S2. Infrared spectra (baseline corrected) of CH_4–$HOCD_2CD_2OH$ ice before (black) and after (red) irradiation with deconvolution of the regions: 3900–1900 cm^{-1} (a) and 1900–700 cm^{-1} (b). The green lines indicate the total fit of the spectra. Detailed assignments are provided in Table S3.

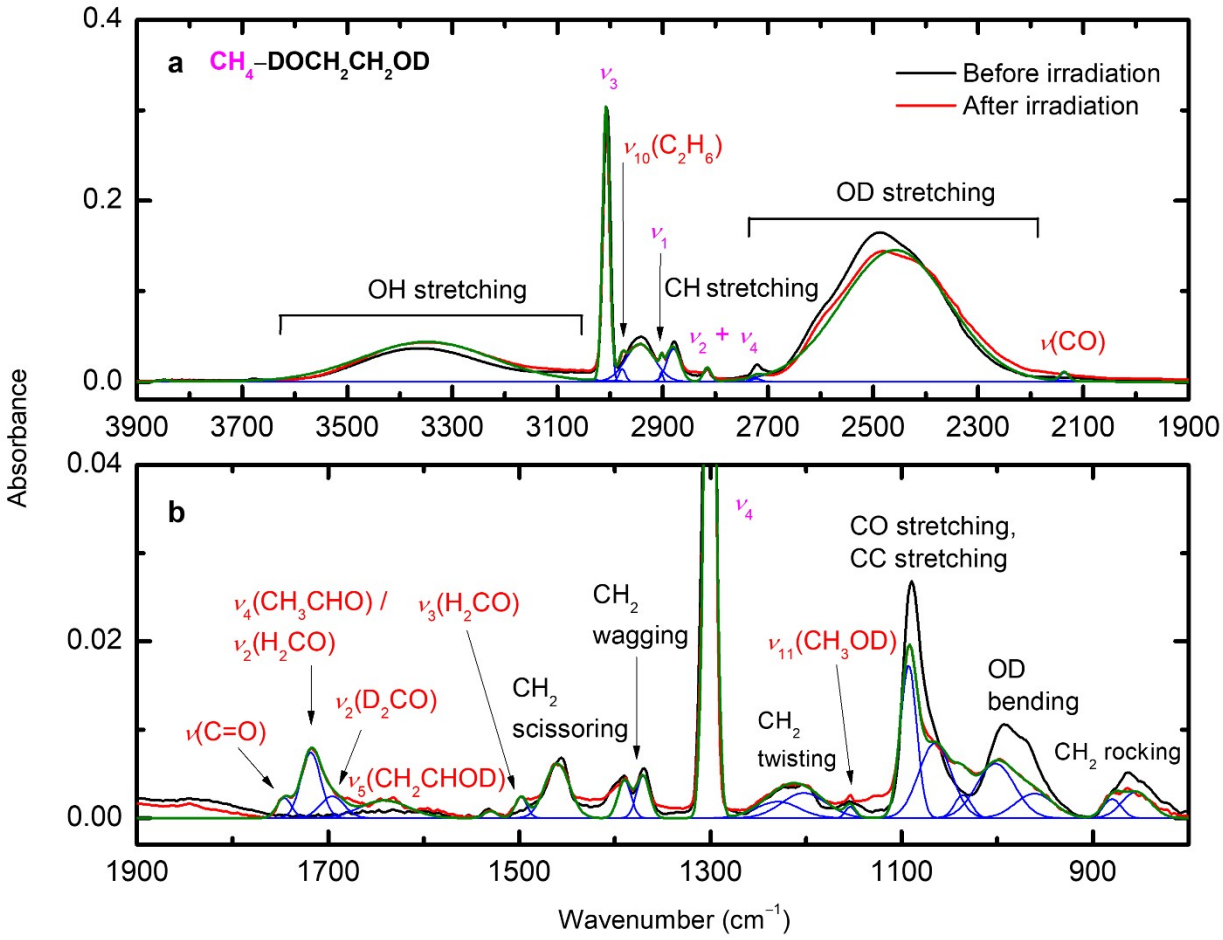


Figure S3. Infrared spectra (baseline corrected) of CH_4–$DOCH_2CH_2OD$ ice before (black) and after (red) irradiation with deconvolution of the regions: 3900–1900 cm^{-1} (a) and 1900–800 cm^{-1} (b). The green lines indicate the total fit of the spectra. Detailed assignments are provided in Table S4.

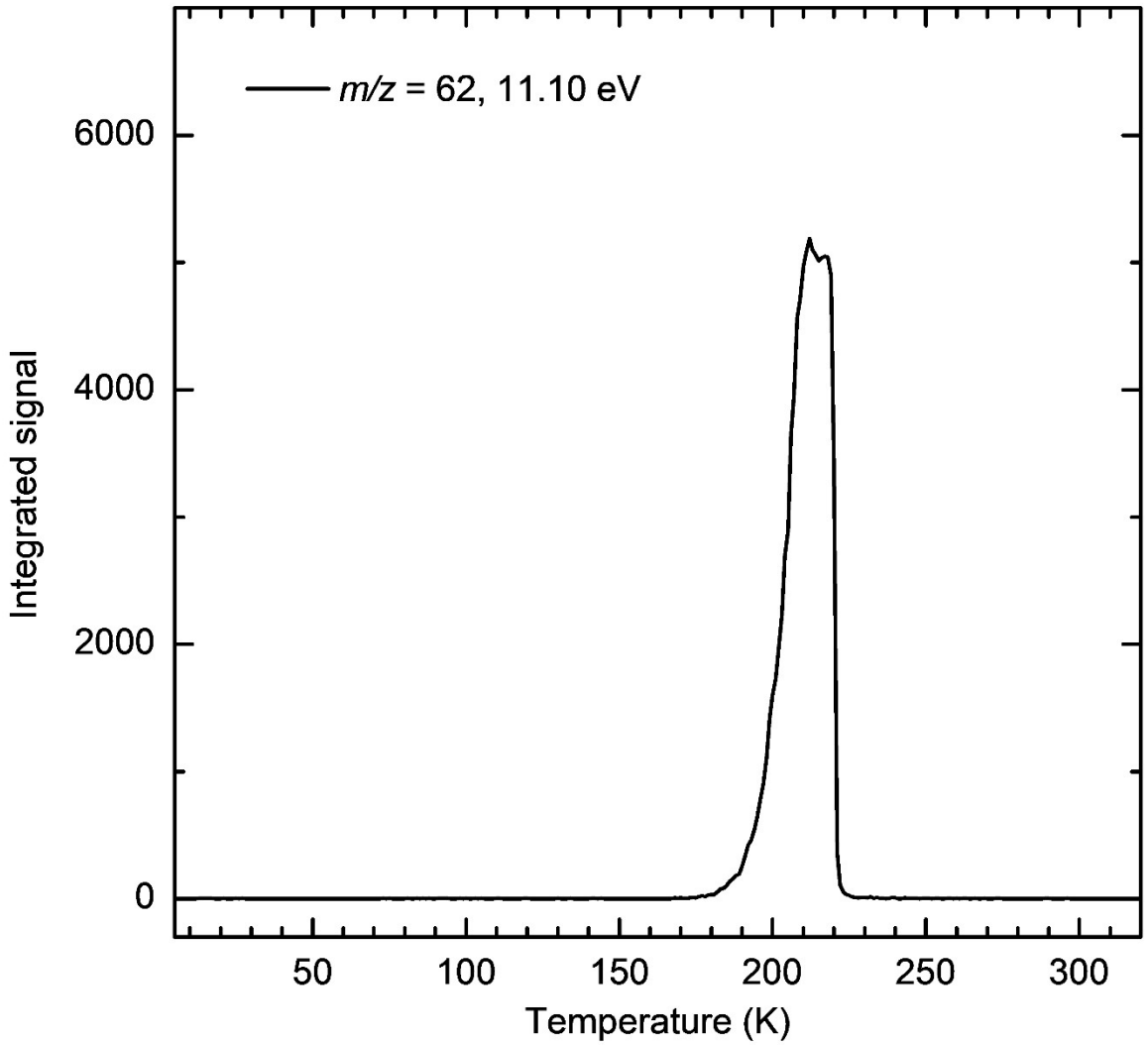


Figure S4. TPD profiles of ethylene glycol ($HOCH_2CH_2OH$, *m/z* = 62) in unirradiated (Blank) CO_2–$HOCH_2CH_2OH$ ice recorded at 11.10 eV. The ion signal of ethylene glycol (IE = 9.68−9.81 eV)[29] exhibits a sublimation event peaking at 214 K.

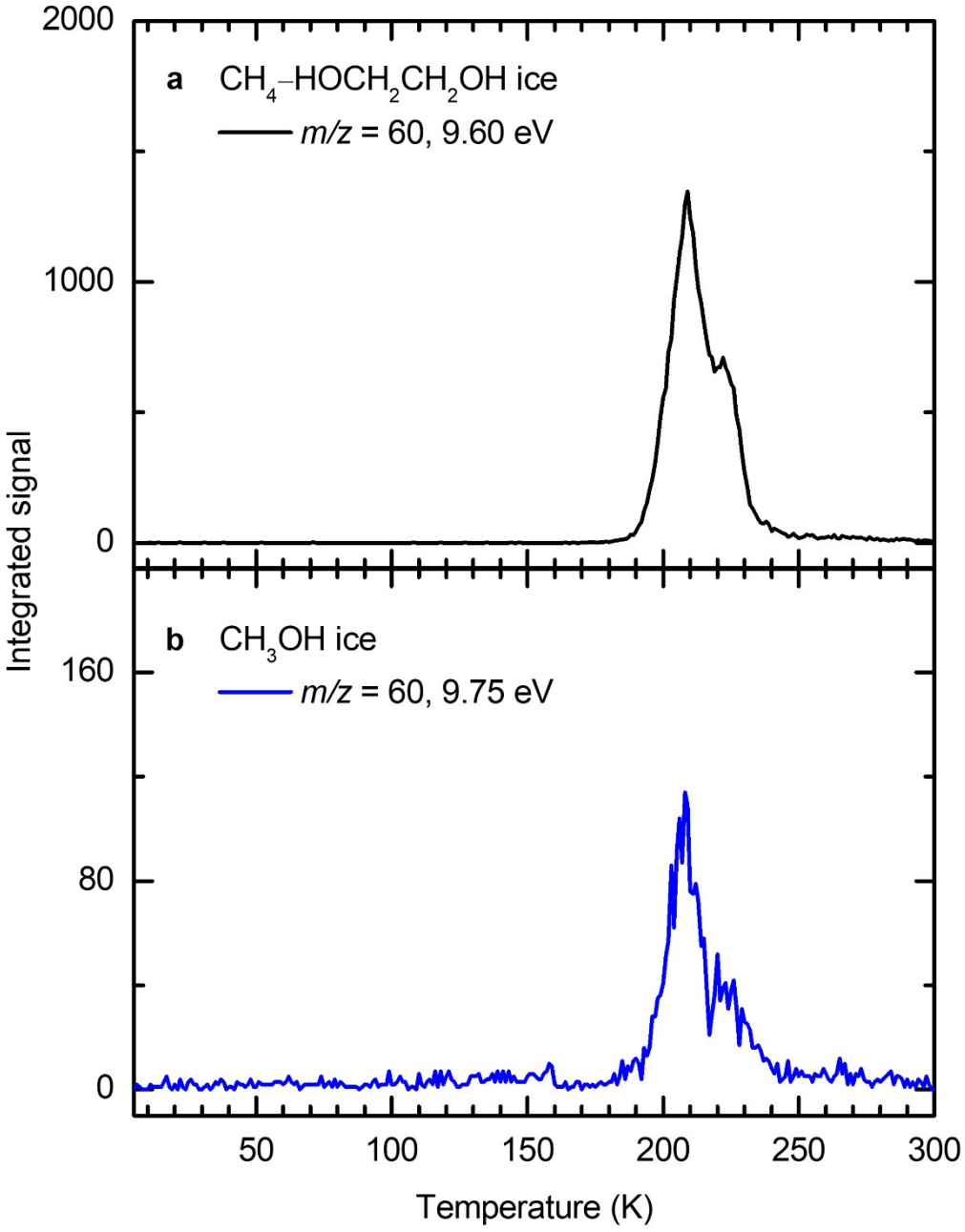


Figure S5. TPD profiles of *m/z* = 60 ($C_2H_4O_2^+$) in irradiated CH_4–$HOCH_2CH_2OH$ ice measured at 9.60 eV (a). TPD profiles of 1,2-ethenediol (**6**; *m/z* = 60, $C_2H_4O_2^+$) from irradiated CH_3OH ice measured at 9.75 eV (b).[30]

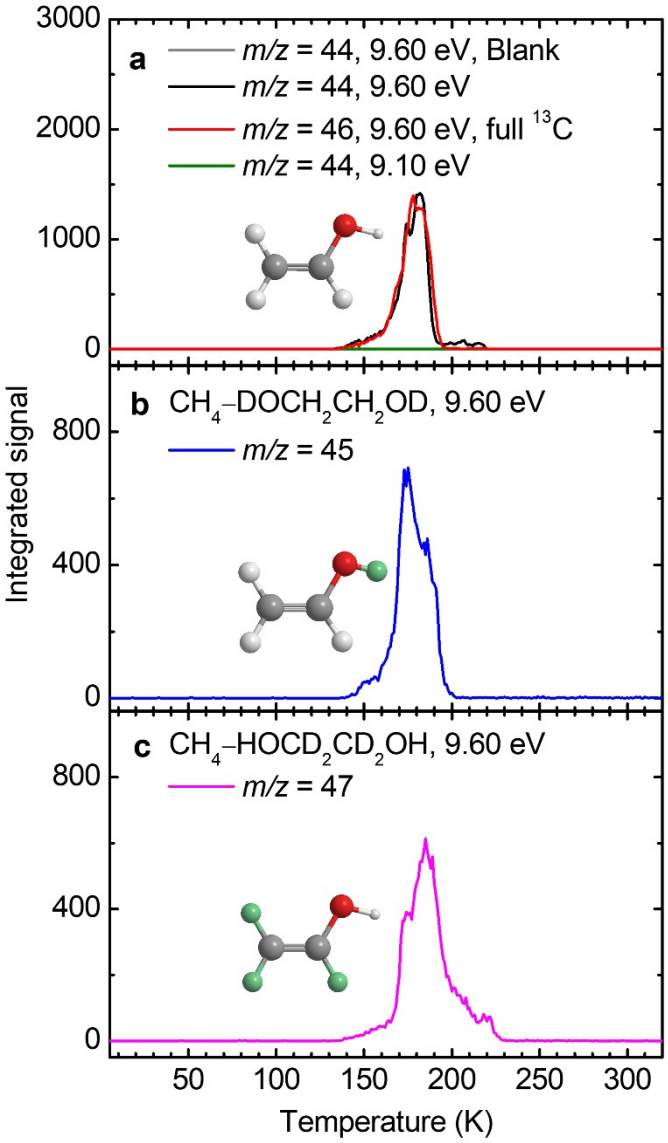


Figure S6. TPD profiles of *m/z* = 44 from irradiated CH_4–$HOCH_2CH_2OH$ ice at 9.60 eV and 9.10 eV (a), *m/z* = 46 from irradiated $^{13}CH_4$–$HO^{13}CH_2{}^{13}CH_2OH$ ice at 9.60 eV (a), *m/z* = 45 from irradiated CH_4–$DOCH_2CH_2OD$ ice at 9.60 eV (b), *m/z* = 47 from CH_4–$HOCD_2CD_2OH$ ice at 9.60 eV (c).

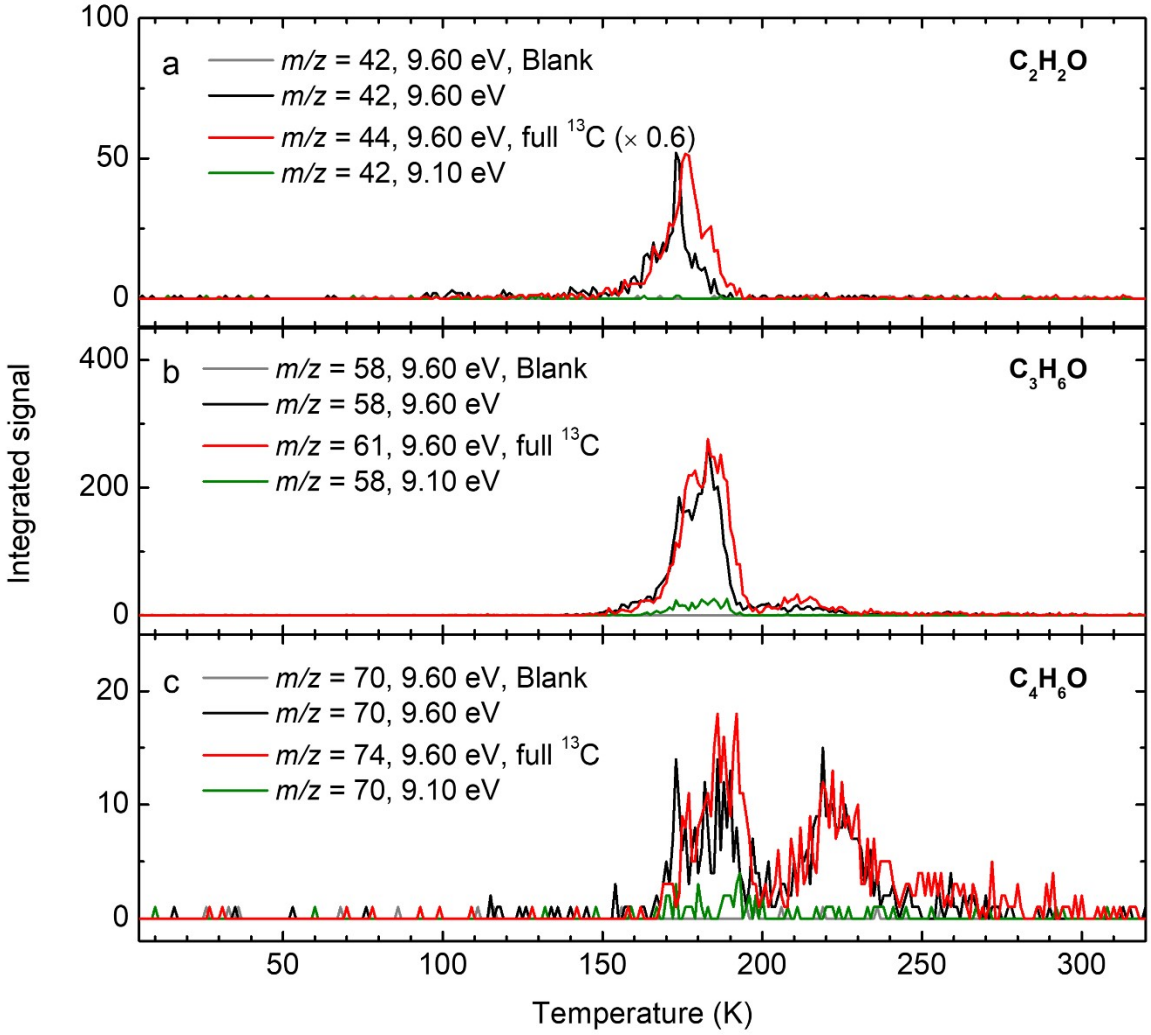


Figure S7. PI-ReToF-MS ion signals for C_2H_2O (a), C_3H_6O (b), and C_4H_6O (c) versus temperature subliming from irradiated CH_4–$HOCH_2CH_2OH$ ice and fully ^{13}C labeled ice ($^{13}CH_4$–$HO^{13}CH_2{}^{13}CH_2OH$).

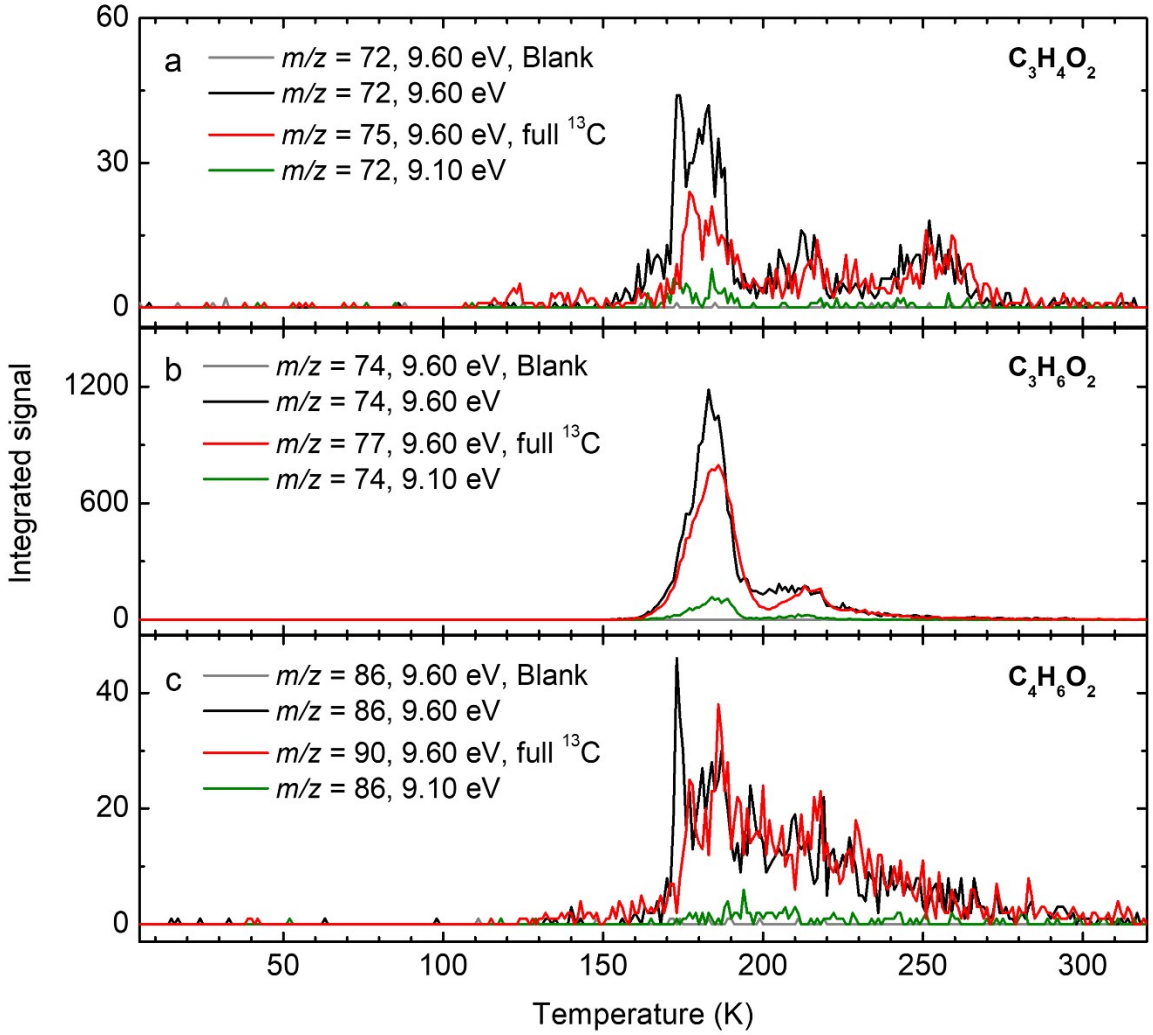


Figure S8. PI-ReToF-MS ion signals for $C_3H_4O_2$ (a), $C_3H_6O_2$ (b), and $C_4H_6O_2$ (c) versus temperature subliming from irradiated CH_4–$HOCH_2CH_2OH$ ice and fully ^{13}C labeled ice ($^{13}CH_4$–$HO^{13}CH_2{}^{13}CH_2OH$).

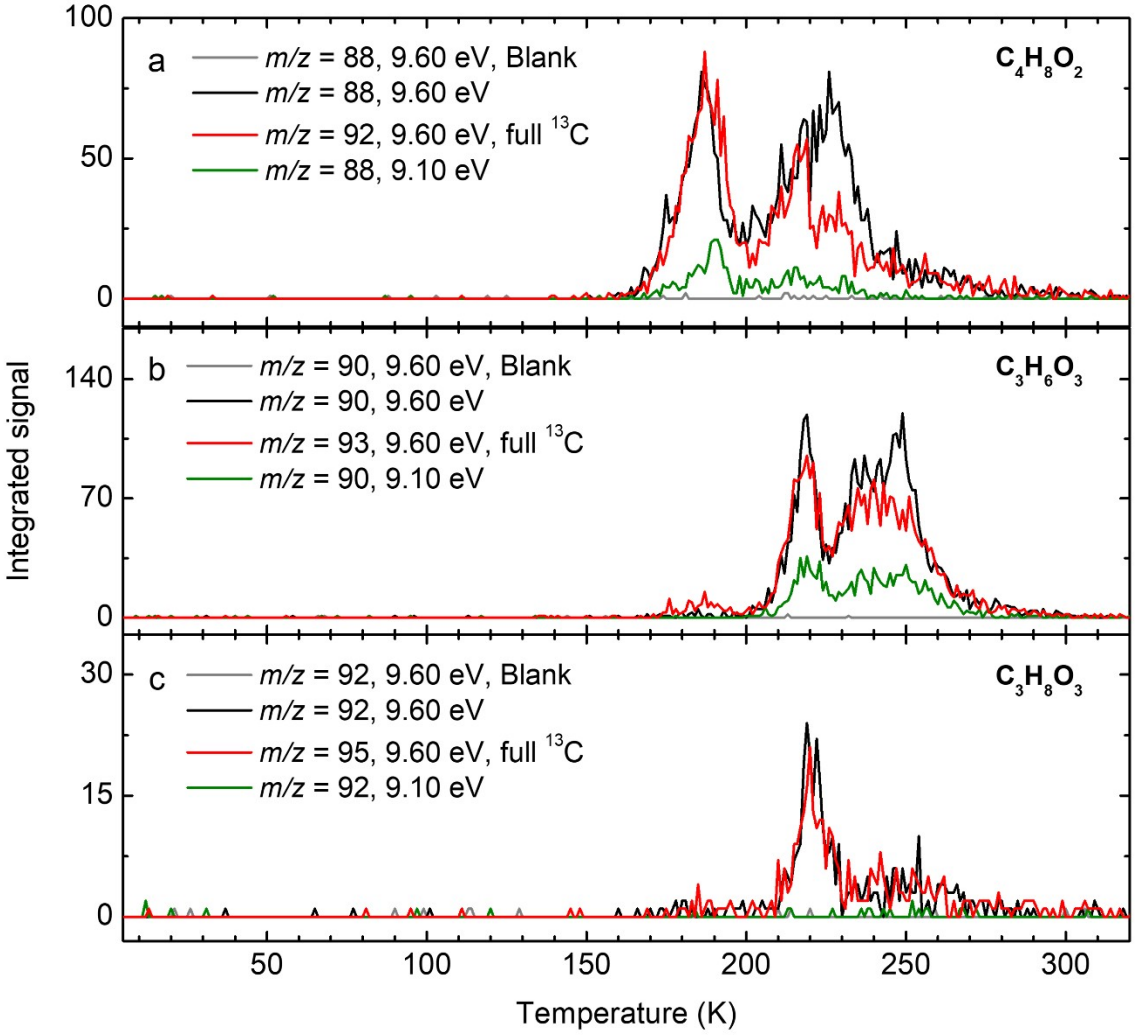


Figure S9. PI-ReToF-MS ion signals for $C_4H_8O_2$ (a), $C_3H_6O_3$ (b), and $C_3H_8O_3$ (c) versus temperature subliming from irradiated CH_4–$HOCH_2CH_2OH$ ice and fully ^{13}C labeled ice ($^{13}CH_4$–$HO^{13}CH_2{}^{13}CH_2OH$).

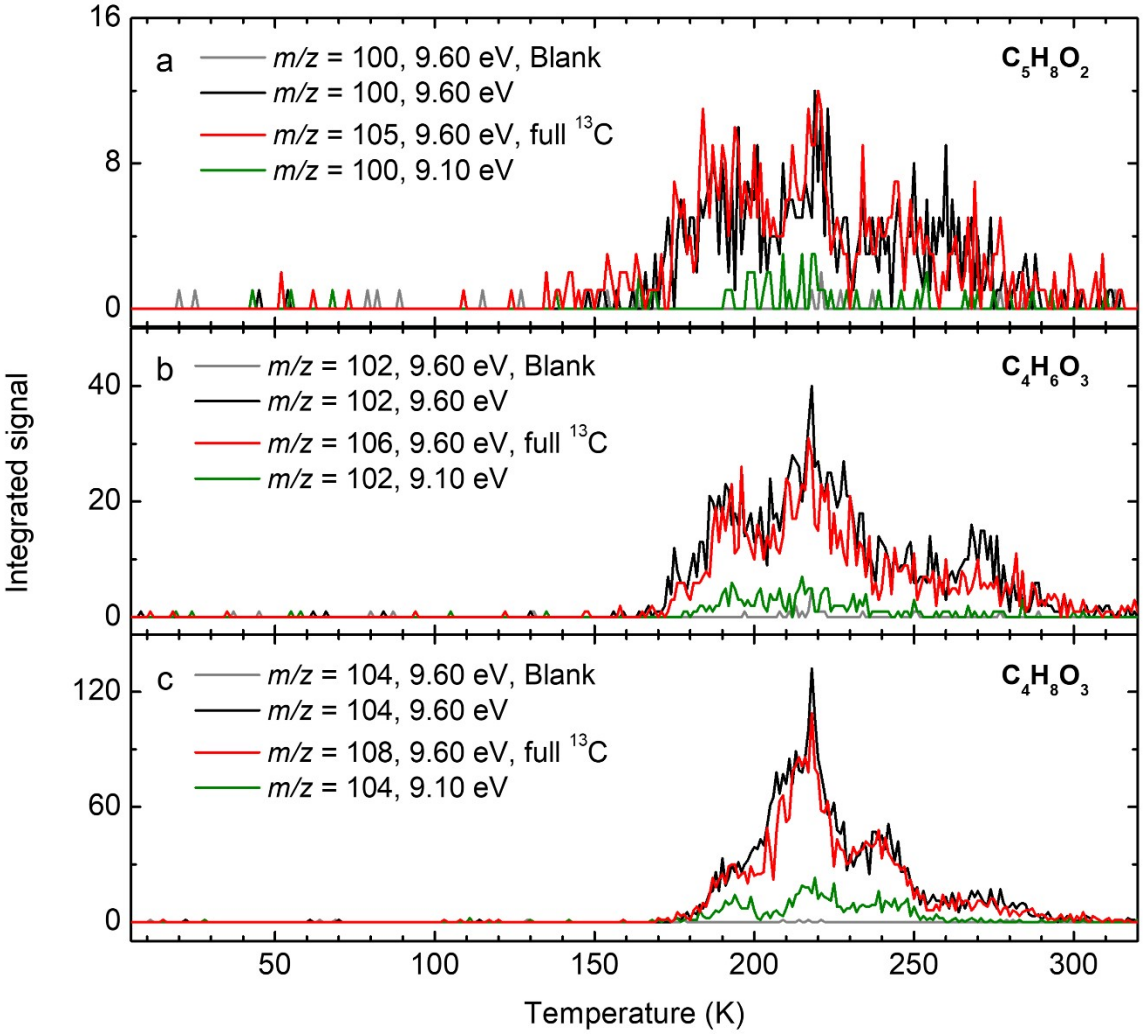


Figure S10. PI-ReToF-MS ion signals for $C_5H_8O_2$ (a), $C_4H_6O_3$ (b), and $C_4H_8O_3$ (c) versus temperature subliming from irradiated CH_4–$HOCH_2CH_2OH$ ice and fully ^{13}C labeled ice ($^{13}CH_4$–$HO^{13}CH_2{}^{13}CH_2OH$).

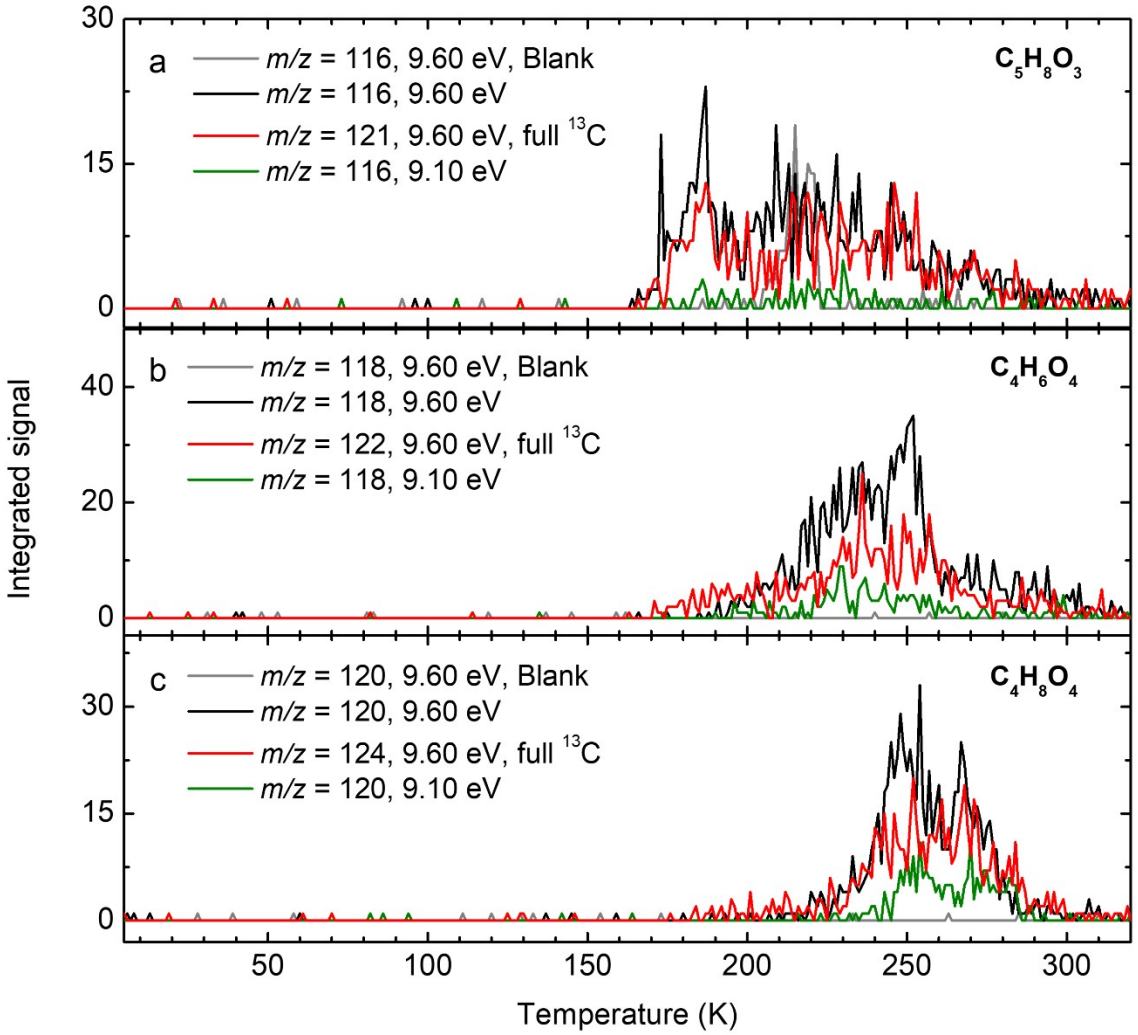


Figure S11. PI-ReToF-MS ion signals for $C_5H_8O_3$ (a), $C_4H_6O_4$ (b), and $C_4H_8O_4$ (c) versus temperature subliming from irradiated CH_4–$HOCH_2CH_2OH$ ice and fully ^{13}C labeled ice ($^{13}CH_4$–$HO^{13}CH_2{}^{13}CH_2OH$).

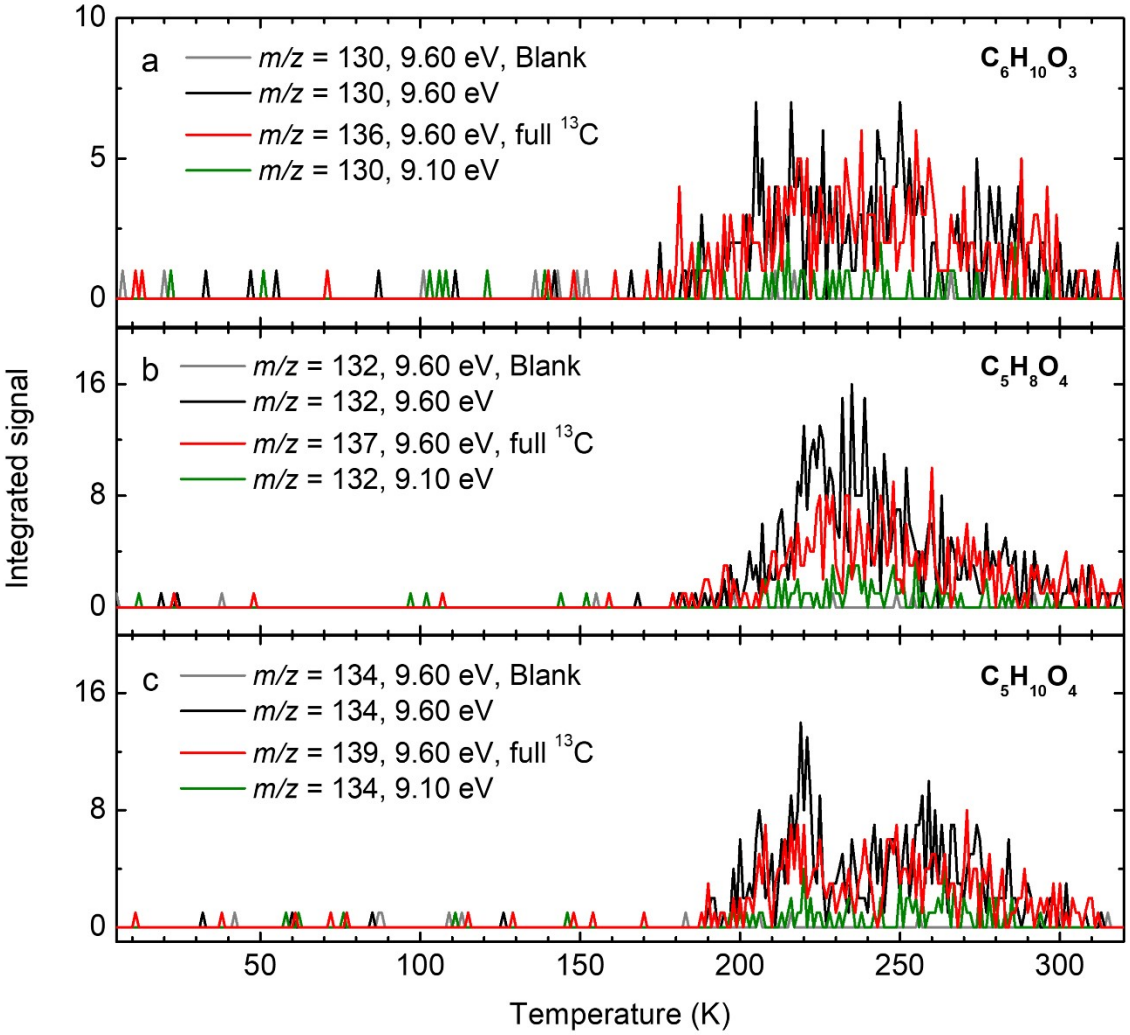


Figure S12. PI-ReToF-MS ion signals for $C_6H_{10}O_3$ (a), $C_5H_8O_4$ (b), and $C_5H_{10}O_4$ (c) versus temperature subliming from irradiated CH_4–$HOCH_2CH_2OH$ ice and fully ^{13}C labeled ice ($^{13}CH_4$–$HO^{13}CH_2{}^{13}CH_2OH$).

Table S1. Infrared absorption features observed in CH_4–$HOCH_2CH_2OH$ ice before and after electron irradiation at 5 K.

Absorptions before irradiation (cm^{-1})	
CH_4	Assignment[4,31]
5984, 5800, 5562, 4528, 4297, 4201, 3848	overtones/combinations ($2\nu_3$, $\nu_1 + \nu_3$, $\nu_3 + 2\nu_4$, $\nu_2 + \nu_3$, $\nu_3 + \nu_4$, $\nu_1 + \nu_4$, $3\nu_4$)
3007	degenerate stretching (ν_3)
2899	symmetric stretching (ν_1)
2814	combination ($\nu_2 + \nu_4$)
2593	overtone ($2\nu_4$)
1300	degenerate deformation (ν_4)
$HOCH_2CH_2OH$	Assignment[6,32]
3337	OH stretching
2943, 2868	CH stretching
1530	combination
1456	CH_2 scissoring
1402, 1344	OH bending and CH_2 wagging
1260, 1211	CH_2 twisting
1092, 1048	CO stretching and CC stretching
887, 864	CH_2 rocking
New absorptions after irradiation (cm^{-1})	Assignment[4,33-36]
2976	$\nu_{10}(C_2H_6)$
2339	$\nu_3(CO_2)$
2135	$\nu(CO)$
1845	$\nu_2(HO\dot{C}O)$ / $\nu_3(H\dot{C}O)$
1748	C=O stretch
1718	$\nu_4(CH_3CHO)$ / $\nu_2(H_2CO)$
1654	$\nu_2(H_2O)$/ $\nu_5(CH_2CHOH)$
1499	$\nu_3(H_2CO)$
1136	$\nu_{11}(CH_3OH)$
956	$\nu_7(C_2H_4)$
822	$\nu_{12}(C_2H_6)$

Table S2. Infrared absorption features observed in $^{13}CH_4$–$HO^{13}CH_2{}^{13}CH_2OH$ ice before and after electron irradiation at 5 K.

Absorptions before irradiation (cm^{-1})	
$^{13}CH_4$	Assignment[37]
5967, 5780, 5539, 4519, 4281, 4191, 3824	overtones/combinations ($2\nu_3$, $\nu_1 + \nu_3$, $\nu_3 + 2\nu_4$, $\nu_2 + \nu_3$, $\nu_3 + \nu_4$, $\nu_1 + \nu_4$, $3\nu_4$)
2998	degenerate stretching (ν_3)
2902	symmetric stretching (ν_1)
2807	combination ($\nu_2 + \nu_4$)
2577	overtone ($2\nu_4$)
1293	degenerate deformation (ν_4)
$HO^{13}CH_2{}^{13}CH_2OH$	Assignment[32,38]
3359	OH stretching
2933, 2869	^{13}CH stretching
2111	combination
1530, 1498	combinations
1456	$^{13}CH_2$ scissoring
1416, 1388	OH bending and $^{13}CH_2$ wagging
1255, 1206	$^{13}CH_2$ twisting
1068, 1027	^{13}CO stretching and $^{13}C^{13}C$ stretching
876, 851	$^{13}CH_2$ rocking
New absorptions after irradiation (cm^{-1})	Assignment[33,36,39-43]
2967	$\nu_{10}(^{13}C_2H_6)$
2274	$\nu_3(^{13}CO_2)$
2090	$\nu(^{13}CO)$
2070	$\nu_2(H_2{}^{13}C{}^{13}CO)$
1805	$\nu_2(HO^{13}\dot{C}O)$
1710	$^{13}C{=}O$ stretching
1680	$\nu_4(^{13}CH_3{}^{13}CHO)$ / $\nu_2(H_2{}^{13}CO)$
1654	$\nu_2(H_2O)$
1588	$\nu_5(^{13}CH_2{}^{13}CHOH)$
1498	$\nu_3(H_2{}^{13}CO)$

Table S3. Infrared absorption features observed in CH_4–$HOCD_2CD_2OH$ ice before and after electron irradiation at 5 K.

Absorptions before irradiation (cm^{-1})	
CH_4	Assignment[4,31]
5984, 5798, 5562, 4529, 4298, 4202, 3849	overtones/combinations ($2\nu_3$, $\nu_1 + \nu_3$, $\nu_3 + 2\nu_4$, $\nu_2 + \nu_3$, $\nu_3 + \nu_4$, $\nu_1 + \nu_4$, $3\nu_4$)
3008	degenerate stretching (ν_3)
2901	symmetric stretching (ν_1)
2815	combination ($\nu_2 + \nu_4$)
2594	overtone ($2\nu_4$)
1302	degenerate deformation (ν_4)
$HOCD_2CD_2OH$	Assignment[32]
3347	OH stretching
2459	OD stretching
2220, 2151, 2111, 2088	CD stretching
1529	combination
1399	OH bending
1203, 1125, 1106, 1071	CO stretching and CD_2 scissoring
982, 967	CD_2 wagging
947, 902	CD_2 twisting
762, 737	CD_2 rocking
New absorptions after irradiation (cm^{-1})	Assignment[33-36,41]
2976	$\nu_{10}(C_2H_6)$
2940	$\nu_8 + \nu_{11}(C_2H_6)$
2882	$\nu_5(C_2H_6)$
2373	$\nu_3 + \nu_6(C_2H_6)$
2341	$\nu_3(CO_2)$
2135	$\nu(CO)$
1844	$\nu_2(HO\dot{C}O)$ / $\nu_4(H\dot{C}O)$
1712	$\nu_4(CD_3CHO)$
1670	$\nu_2(D_2CO)$
1575	$\nu_5(CD_2CDOH)$
1466	$\nu_5(CH_3OH)$

Table S4. Infrared absorption features observed in CH_4–$DOCH_2CH_2OD$ ice before and after electron irradiation at 5 K.

Absorptions before irradiation (cm^{-1})	
CH_4	Assignment[4,31]
5983, 5800, 5563, 4529, 4299, 4202, 3847	overtones/combinations ($2\nu_3$, $\nu_1 + \nu_3$, $\nu_3 + 2\nu_4$, $\nu_2 + \nu_3$, $\nu_3 + \nu_4$, $\nu_1 + \nu_4$, $3\nu_4$)
3008	degenerate stretching (ν_3)
2903	symmetric stretching (ν_1)
2815	combination ($\nu_2 + \nu_4$)
1302	degenerate deformation (ν_4)
$DOCH_2CH_2OD$	Assignment[6,32]
3373	OH stretching
2943, 2880	CH stretching
2704, 2458	OD stretching
1530	combination
1460	CH_2 scissoring
1390, 1371	CH_2 wagging
1230, 1202	CH_2 twisting
1093, 1065	CO stretching
1036	CC stretching
1002, 961	OD bending
880, 855	CH_2 rocking
New absorptions after irradiation (cm^{-1})	Assignment[30,33,34,36,41]
2977	$\nu_{10}(C_2H_6)$
2136	ν (CO)
1745	C=O stretch
1718	$\nu_4(CH_3CHO)$ / $\nu_2(H_2CO)$
1696	$\nu_2(D_2CO)$
1641	$\nu_5(CH_2CHOD)$
1498	$\nu_3(H_2CO)$
1154	$\nu_{11}(CH_3OD)$

Table S5. Other ions detected subliming from irradiated methane−ethylene glycol ices at 9.60 eV and 9.10 eV.

Formula	CH_4−$HOCH_2CH_2OH$ (*m/z*)		$^{13}CH_4$−$HO^{13}CH_2{}^{13}CH_2OH$ (*m/z*)
	9.60 eV	9.10 eV	9.60 eV
C_2H_2O[a]	42	−	44
C_3H_6O	58	58	61
C_4H_6O	70	−	74
$C_3H_4O_2$	72	72	75
$C_3H_6O_2$	74	74	77
$C_4H_6O_2$	86	86	90
$C_4H_8O_2$	88	88	92
$C_3H_6O_3$	90	90	93
$C_3H_8O_3$	92	−	95
$C_5H_8O_2$	100	−	105
$C_4H_6O_3$	102	102	106
$C_4H_8O_3$	104	104	108
$C_5H_8O_3$	116	116	121
$C_4H_6O_4$	118	118	122
$C_4H_8O_4$	120	120	124
$C_6H_{10}O_3$	130	−	136
$C_5H_8O_4$	132	−	137
$C_5H_{10}O_4$	134	−	139

[a] The ion signal of *m/z* = 42 can be assigned to ketene (CH_2CO).

Table S6. Experimental conditions including ice composition, thickness, irradiation parameters, and VUV photon energies.

Exp.	Ice	Composition of methane to ethylene glycol	Thickness (nm)	Current (nA)	Irradiation time (s)	Dose (eV/ methane)	Dose (eV/ ethylene glycol)	Photon energy (eV)
1	CH_4–$HOCH_2CH_2OH$	0.9 ± 0.2 : 1	730 ± 50	–	–	–	–	9.60
2	CH_4–$HOCH_2CH_2OH$	0.9 ± 0.2 : 1	690 ± 50	108 ± 1	1800 ± 10	3.9 ± 0.6	10.9 ± 1.8	9.60
3	CH_4–$HOCH_2CH_2OH$	0.6 ± 0.2 : 1	730 ± 50	105 ± 3	1800 ± 10	3.8 ± 0.6	10.6 ± 1.7	9.10
4	$^{13}CH_4$–$HO^{13}CH_2{}^{13}CH_2OH$	1.7 ± 0.4 : 1	690 ± 50	111 ± 2	1800 ± 10	4.2 ± 0.7	11.6 ± 1.9	9.60
5	CH_4–$DOCH_2CH_2OD$	0.9 ± 0.2 : 1	710 ± 50	107 ± 1	1800 ± 10	3.8 ± 0.6	11.1 ± 1.8	9.60
6	CH_4–$HOCD_2CD_2OH$	1.2 ± 0.2 : 1	690 ± 50	111 ± 2	1800 ± 10	4.0 ± 0.6	11.9 ± 1.9	9.60
7[a]	CH_4–$HOCH_2CH_2OH$	0.7 ± 0.2 : 1	730 ± 50	–	–	–	–	9.60
8[b]	CH_4–$HOCH_2CH_2OH$	1.1 ± 0.2 : 1	730 ± 50	–	–	–	–	9.60

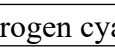
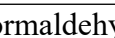
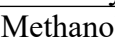
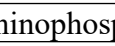
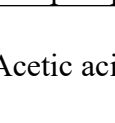
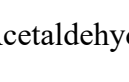
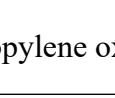
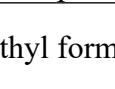
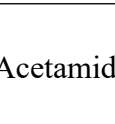
[a] Add 1,2-propanediol into ice mixture.

[b] Add 2-methoxyethanol into ice mixture.

Table S7. Vacuum ultraviolet (VUV) light generation parameters.

VUV photon energy (eV)	Nonlinear medium in four-wave mixing	ω_1 laser wavelength (nm)	ω_1 Dye	ω_2 laser wavelength (nm)	ω_2 Dye
9.60 ($2\omega_1 - \omega_2$)	Krypton	212.556	Stilbene 420	600.108	Rhodamine 610 and Rhodamine 640
9.10 ($2\omega_1 - \omega_2$)	Xenon	222.566	Coumarin 450	607.379	Rhodamine 610 and Rhodamine 640

Table S8. Error analysis of IEs of 19 compounds computed at the CCSD(T)/CBS//B3LYP/cc-pVTZ level of theory including the ZPVE corrections.

Compounds	Structure	Experimental IE (eV)	Computed IE (eV)	Difference to lower bound (eV)	Difference to upper bound (eV)
Hydrogen cyanide		13.60 ± 0.01[44]	13.57	0.01	0.04
Acetonitrile		12.20 ± 0.01[44]	12.20	−0.01	0.01
Formaldehyde		10.88 ± 0.01[44]	10.89	−0.02	0.00
Methanol		10.84 ± 0.01[44]	10.86	−0.03	−0.01
Methinophosphide		10.79 ± 0.01[45]	10.76	0.02	0.04
Acetic acid		10.65 ± 0.02[44]	10.65	−0.02	0.02
Acetaldehyde		10.229 ± 0.0007[44]	10.24	−0.0117	−0.0103
Propylene oxide		10.22 ± 0.02[44]	10.24	−0.04	0.00
Propanal		9.96 ± 0.01[44]	9.97	−0.02	0.00
Phosphine	PH_3	9.869 ± 0.002[44]	9.82	0.047	0.051
N-methyl formamide		9.83 ± 0.04[44]	9.80	−0.01	0.07
Acetamide		9.77 ± 0.02[46]	9.74	0.01	0.05
Acetone		9.703 ± 0.006[44]	9.71	−0.013	−0.001

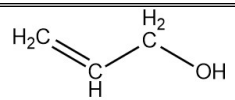
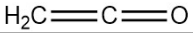
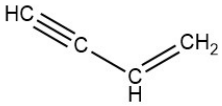
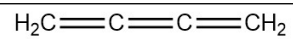
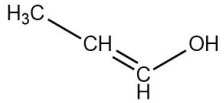
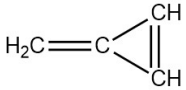
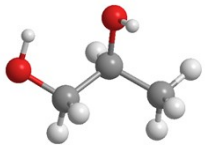
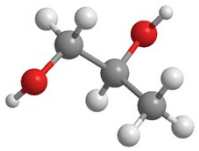
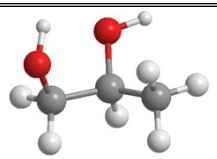
2-Propen-1-ol		9.67 ± 0.03[44]	9.65	−0.01	0.05
Ketene		9.617 ± 0.003[44]	9.58	0.034	0.040
Vinylacetylene		9.58 ± 0.02[44]	9.59	−0.03	0.01
1,2,3-Butatriene		9.15 ± 0.02[47]	9.14	−0.01	0.03
(*E*)-1-Propenol		8.64 ± 0.02[48]	8.64	−0.02	0.02
Methylenecyclopropene		8.15 ± 0.03[49]	8.11	0.01	0.07
				Average −0.01 ± 0.02	Average +0.03 ± 0.03
				Combined error limits −0.03 – +0.06	

Table S9. The B3LYP/cc-pVTZ optimized Cartesian coordinates (distances in Å), vibrational frequencies (cm^{-1}), and intensities (km mol^{-1}) of 1,2-propanediol (**5**) and 2-methoxyethanol (**19**). The electronic energy (Hartree; E at 0 K), zero-point vibrational energies (ZPVE; kcal mol^{-1}), and extrapolated CCSD(T)/CBS energies (in Hartree) were computed at CCSD(T)/CBS//B3LYP/cc-pVTZ level of theory.

Isomer **5**		Cartesian coordinates			Frequency	Intensity	Frequency	Intensity
5_1  E = –269.6830339 E[CCSD(T)/CBS] = –269.3030690 ZPVE = 70.9436	O	–1.933152	–0.059366	–0.117305	144.6721	8.5732	1325.974	1.7578
	C	–0.737331	–0.732922	0.225335	225.9378	0.4701	1379.595	18.631
	C	0.488030	–0.021954	–0.338272	248.3776	1.6916	1407.195	4.6634
	O	0.465559	1.353937	0.077688	306.4468	50.6928	1419.171	44.584
	C	1.794679	–0.704304	0.031245	370.8534	14.5874	1435.669	45.9224
	H	–1.753844	0.882289	–0.003329	462.9782	2.3205	1492.218	5.6627
	H	–0.631498	–0.819310	1.318045	476.1288	118.3901	1496.955	4.8009
	H	–0.809114	–1.744076	–0.179254	530.2872	45.6084	1507.475	2.6538
	H	0.385508	0.028285	–1.423900	826.6265	27.8108	2937.212	64.9358
	H	0.730494	1.394015	1.003604	919.6231	7.2788	3018.965	14.8909
	H	1.914709	–0.757750	1.116880	927.7128	7.6554	3049.823	18.0542
	H	2.640643	–0.154426	–0.379565	1062.199	60.4343	3063.104	18.5434
	H	1.826970	–1.723757	–0.356488	1087.599	120.7864	3084.519	50.6174
					1093.75	11.3792	3105.364	19.5687
					1163.355	21.7161	3763.833	42.4461
					1208.487	33.6605	3785.053	16.0992
					1298.631	14.2734		
5_2 	O	–1.660518	–1.046247	–0.216598	127.8161	8.6243	1356.678	1.3069
	C	–0.969501	0.056504	0.360250	229.1104	8.611	1384.066	9.8121
	C	0.402251	0.306521	–0.273442	256.089	6.7884	1399.431	4.4825
	O	0.962084	1.510127	0.255571	270.4309	4.6162	1408.287	55.7382
	C	1.343836	–0.877779	–0.124171	272.0302	196.6529	1416.573	24.7132
	H	–1.964904	–0.792504	–1.092824	393.788	26.4415	1489.988	5.1887
	H	–1.556646	0.977874	0.302117				

	H	–0.843163	–0.190091	1.417694	442.7138	6.3738	1496.948	5.2014
E = –269.6795567	H	0.253950	0.518398	–1.336775	496.1003	2.2475	1508.426	2.853
E[CCSD(T)/CBS] =	H	1.267759	1.333980	1.151626	837.398	8.3017	3008.735	49.141
–269.2995197	H	0.893873	–1.779759	–0.537869	914.3429	5.3907	3010.71	0.2456
ZPVE = 70.6587	H	1.553783	–1.067079	0.932939	953.0899	8.0667	3019.458	30.7008
	H	2.288098	–0.685095	–0.632507	1046.265	35.3529	3056.543	50.2366
					1070.116	147.382	3085.862	36.4068
					1112.04	58.3422	3113.553	15.08
					1129.125	3.1444	3797.128	19.2803
					1212.724	8.3455	3817.211	25.3719
					1293.726	2.9027		
					142.3535	5.1796	1348.108	15.8943
					221.1753	0.3832	1376.164	18.4983
					241.4652	35.0795	1409.185	20.6158
	O	–1.918749	–0.037565	–0.090904	258.045	63.5868	1411.555	9.1946
5_3	C	–0.722989	–0.700550	0.276206	363.3557	10.4005	1438.773	32.9493
	C	0.503960	–0.035280	–0.328100	438.9439	108.7193	1491.926	3.6727
	O	0.473918	1.314862	0.163410	472.313	12.9938	1496.95	3.554
	C	1.798771	–0.739329	0.049124	515.7199	12.6824	1503.271	3.9075
	H	–1.773590	0.898783	0.088171	835.4232	23.9613	2972.579	24.6071
	H	–0.605241	–0.730284	1.367493	922.6058	25.823	2995.148	67.0015
	H	–0.803813	–1.726570	–0.083910	926.0465	4.456	3025.714	16.8667
	H	0.382805	–0.025448	–1.417375	1070.852	77.0579	3076.981	16.3396
	H	1.095757	1.847023	–0.340130	1075.722	54.2034	3085.642	36.18
	H	1.923228	–0.756348	1.132487	1111.687	65.495	3098.34	34.2941
	H	2.660120	–0.226838	–0.382805	1136.643	12.2881	3783.872	38.0171
	H	1.805677	–1.766895	–0.319530	1197.986	8.4765	3830.337	31.4144
E = –269.6832763					1288.16	41.4387		
E[CCSD(T)/CBS] =								
–269.3036480								
ZPVE = 70.8539								
	O	–1.553778	–0.379662	0.611849	135.6959	6.9806	1361.963	15.9218
5_4	C	–0.863704	–0.450114	–0.624685	229.1166	1.1848	1379.355	6.9845
	C	0.574554	0.043727	–0.512007				

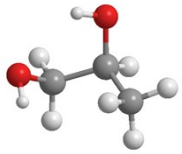


E = –269.6826865
E[CCSD(T)/CBS] = –269.3030953
ZPVE = 70.9393

O	0.462879	1.407934	–0.077983
C	1.419617	–0.780939	0.448487
H	–1.445722	0.523515	0.931752
H	–0.873834	–1.495229	–0.935496
H	–1.376940	0.139256	–1.393029
H	1.020660	0.013973	–1.514526
H	1.330271	1.722459	0.191070
H	2.418659	–0.351498	0.554406
H	1.538443	–1.800589	0.078275
H	0.948826	–0.823048	1.429632

250.3297	63.6916	1404.195	10.757			
274.8602	37.324	1423.473	27.2507			
354.8916	18.2209	1428.272	33.9627			
425.7305	9.0886	1489.35	4.4762			
447.0516	119.2275	1500.53	7.4602			
658.249	15.2752	1504.832	1.8064			
804.9144	10.0478	2970.364	34.5157			
922.7221	18.6783	2996.857	89.3937			
937.4252	28.9851	3024.842	19.0063			
1006.03	35.0678	3076.914	9.4667			
1075.065	62.8514	3082.519	46.8082			
1119.694	57.9525	3112.237	19.0135			
1138.224	14.7511	3786.076	34.6685			
1199.198	22.8699	3826.759	25.1975			
1275	37.3957					

5_5

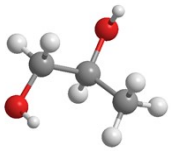
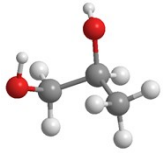


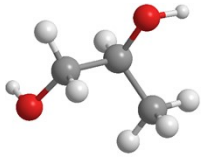
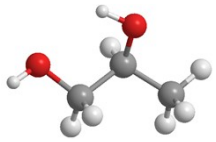
E = –269.6817268
E[CCSD(T)/CBS] = –269.3020015
ZPVE = 70.9787

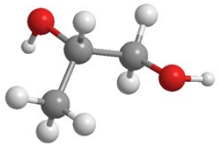
O	–1.573614	–0.302864	0.603731
C	–0.849565	–0.452972	–0.620753
C	0.574743	0.086348	–0.497357
O	0.535419	1.442228	–0.064271
C	1.460211	–0.758047	0.416845
H	–1.302823	–0.995496	1.212828
H	–0.844689	–1.495691	–0.953824
H	–1.393624	0.139935	–1.355010
H	1.013618	0.104293	–1.498648
H	–0.132225	1.487626	0.631726
H	1.569445	–1.775805	0.035457
H	1.048067	–0.808937	1.427450
H	2.449733	–0.309561	0.490301

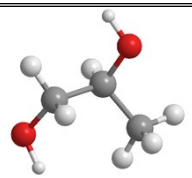
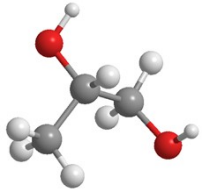
122.4285	2.219	1371.297	2.9241			
240.4543	1.75	1377.499	7.942			
262.9603	2.3737	1396.56	18.0949			
289.1038	71.615	1413.106	13.9122			
367.6332	4.5476	1420.175	59.3491			
425.4498	3.9216	1488.167	6.8962			
453.652	157.5918	1496.497	2.075			
656.7429	8.0769	1504.724	6.5517			
798.7721	13.1234	3008.637	30.9901			
911.799	15.8274	3020.654	23.1219			
932.0863	18.0213	3030.233	33.4762			
1000.957	53.2098	3078.599	49.635			
1069.067	43.0437	3089.602	27.2834			
1089.384	42.6617	3107.038	19.7462			
1138.521	59.356	3761.618	38.7934			
1224.479	30.0189	3824.891	26.1135			

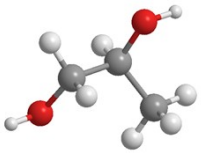
					1277.548	12.361		
					145.3655	3.7878	1352.723	33.1136
					215.8906	0.5291	1380.278	4.7862
					248.3356	3.5229	1392.557	18.4365
5_6	O	–1.911991	–0.015979	–0.040319	307.5699	69.3559	1413.689	25.0525
	C	–0.707912	–0.737356	0.233899	360.5562	13.7427	1437.957	26.2916
	C	0.508998	–0.006731	–0.321329	478.1556	22.4173	1485.787	3.6945
	O	0.527220	1.331071	0.160007	489.8775	88.2671	1495.163	4.2647
	C	1.814953	–0.670596	0.074057	529.4925	43.9311	1503.36	2.0724
	H	–2.128101	–0.121463	–0.972095	845.4244	14.1634	2919.118	70.202
	H	–0.637435	–0.787750	1.321103	919.8628	18.2166	3007.598	43.2669
	H	–0.759028	–1.758304	–0.158144	937.6478	4.1196	3033.935	21.5079
	H	0.429351	0.000040	–1.420593	1036.586	120.0942	3079.312	18.7125
	H	–0.386173	1.642876	0.140943	1074.248	27.6641	3097.954	37.5602
	H	1.871408	–1.687536	–0.317293	1090.22	19.2915	3107.687	20.5091
	H	1.909865	–0.705296	1.160180	1166.988	19.9483	3763.447	45.4409
	H	2.656877	–0.103759	–0.321332	1224.313	16.4658	3809.312	26.6751
					1294.303	50.1265		
E = –269.6833563								
E[CCSD(T)/CBS] = –269.3035673								
ZPVE = 70.9707								
	O	–1.481389	–0.408785	0.626690	129.5256	5.2005	1318.66	19.9106
	C	–0.834010	–0.485815	–0.646789	220.8182	96.7244	1374.125	6.7992
	C	0.570986	0.079078	–0.475360	232.0979	4.1841	1404.677	12.3013
	O	0.495790	1.430441	–0.029520	267.2279	4.928	1421.075	50.3567
5_7	C	1.440467	–0.767635	0.450690	370.2213	0.8405	1439.888	8.2058
	H	–2.425287	–0.536961	0.508431	402.6727	59.8058	1491.119	8.7002
	H	–0.786405	–1.521946	–1.000034	440.7282	60.8269	1501.135	1.0263
	H	–1.369907	0.115269	–1.386817	646.0322	21.6113	1512.342	6.8011
	H	1.033367	0.123123	–1.464325	802.7105	6.6193	2990.74	46.8707
	H	–0.112093	1.436745	0.719629	927.4388	0.3969	3029.971	4.5457
	H	2.414941	–0.296656	0.572038	948.9979	20.0612	3034.178	55.9461
	H	1.588078	–1.769663	0.042288	996.1028	81.1508	3040.918	39.9009
	H	0.976160	–0.865152	1.432150	1072.895	40.0362	3094.193	32.7705
E = –269.6818164								
E[CCSD(T)/CBS] = –269.3023157								
ZPVE = 70.8922								

					1125.681	29.051	3111.577	22.4648
					1145.334	49.6414	3776.474	34.2383
					1207.467	35.7518	3846.823	42.3543
					1265.961	14.0578		
5_8  E = –269.6788536 E[CCSD(T)/CBS] = –269.2990008 ZPVE = 70.6278	O	–1.679323	–1.008146	–0.292908	122.2304	5.0889	1362.996	3.3716
	C	–0.974558	0.057633	0.330962	230.3805	17.3607	1379.086	25.0991
	C	0.401028	0.324272	–0.286015	250.9911	17.9597	1398.52	21.8057
	O	0.948295	1.520063	0.272189	264.4058	19.5811	1402.656	20.76
	C	1.359834	–0.850111	–0.145753	285.6098	163.2975	1418.836	18.5233
	H	–1.291382	–1.842991	–0.017799	396.3232	26.2122	1491.29	2.3276
	H	–1.588755	0.948224	0.205729	435.5052	6.2131	1497.289	4.9917
	H	–0.861373	–0.118061	1.410280	493.9572	3.5022	1506.955	5.7717
	H	0.257673	0.548508	–1.344461	828.0323	1.7633	2958.538	55.8643
	H	1.169302	1.353972	1.194869	913.6333	9.888	3009.622	18.3362
	H	0.977179	–1.737723	–0.652570	947.7898	22.1539	3051.699	11.4995
	H	1.517972	–1.099958	0.908183	1056.831	155.5621	3078.34	43.8688
	H	2.325654	–0.603714	–0.585309	1065.928	50.6522	3091.485	28.5546
					1100.929	18.6009	3103.854	19.7505
					1141.099	1.7851	3793.102	15.5902
					1210.81	14.144	3829.431	23.2225
					1286.682	22.8043		
5_9  E = –269.6821515 E[CCSD(T)/CBS] = –269.3023498	O	–1.551937	–0.421084	0.631974	136.0901	10.082	1333.992	16.0155
	C	–0.859924	–0.510470	–0.600476	216.6282	2.0452	1375.985	2.3259
	C	0.562825	0.039510	–0.499337	261.3129	8.9208	1398.549	5.5469
	O	0.505164	1.395308	–0.018210	302.7623	47.4659	1427.769	43.69
	C	1.439945	–0.734804	0.467920	371.4658	23.8307	1437.018	12.7457
	H	–1.367861	0.458581	0.984003	423.2027	5.6902	1488.317	8.3957
	H	–0.841174	–1.564378	–0.883341	475.5229	152.4915	1500.444	1.9405
	H	–1.398485	0.033834	–1.389915	667.8614	16.1642	1508.996	1.0287
	H	1.014425	0.021092	–1.498430	803.4751	8.7171	2947.527	67.9401
	H	0.150739	1.954996	–0.716325	927.495	8.358	2987.828	71.6712

ZPVE = 70.9851	H	0.982661	–0.763745	1.455888	934.9606	38.5896	3042.509	11.8039
	H	2.418808	–0.264321	0.548305	1007.052	50.7579	3064.711	31.7662
	H	1.573057	–1.760339	0.121768	1081.712	44.9554	3107.262	24.8909
					1085.647	25.7133	3117.767	18.543
					1149.985	24.3757	3766.672	35.6671
					1219.349	38.0885	3808.31	22.4773
					1276.596	49.9417		
5_10  E = –269.6795829 E[CCSD(T)/CBS] = –269.2998161 ZPVE = 70.6319	O	–1.665206	–1.020207	–0.176427	124.5265	6.7165	1355.624	1.3658
	C	–0.944590	0.073697	0.377975	233.125	4.3333	1380.973	26.2102
	C	0.411503	0.281863	–0.293041	246.2419	93.3884	1392.207	13.8395
	O	0.935020	1.482033	0.277895	267.3769	28.2417	1412.666	20.7997
	C	1.346314	–0.901865	–0.099996	276.8605	98.1851	1427.842	11.5479
	H	–1.982403	–0.768447	–1.048559	384.2157	12.1456	1490.832	4.3724
	H	–1.514705	1.005633	0.320792	449.1328	7.8352	1500.318	6.93
	H	–0.793607	–0.160068	1.432395	505.6854	3.407	1512.114	2.0287
	H	0.235970	0.430354	–1.369319	842.499	2.5366	2935.748	66.9715
	H	1.835868	1.604568	–0.034582	917.7456	11.3507	3015.881	53.5069
	H	1.572188	–1.032886	0.959626	950.6598	36.4532	3022.893	13.8969
	H	2.285703	–0.753766	–0.637658	1045.838	129.9258	3078.824	12.4611
	H	0.882587	–1.815212	–0.472165	1090.181	19.2339	3083.599	48.4854
					1103.089	0.9009	3106.648	17.7772
					1122.83	58.2073	3817.615	25.0734
					1211.663	5.26	3822.07	21.5177
					1280.208	36.3353		
5_11 	O	–1.877127	–0.053384	–0.145328	144.7125	3.9924	1290.513	58.4104
	C	–0.700682	–0.764139	0.249627	213.8001	0.4328	1380.114	31.0376
	C	0.484692	–0.021962	–0.346393	239.5134	96.5368	1397.555	5.4843
	O	0.491010	1.327045	0.107582	253.0273	7.8122	1429.815	11.2096
	C	1.810808	–0.650372	0.037912	364.0518	8.9698	1448.811	13.9123
	H	–2.620046	–0.351329	0.384993	449.8134	94.2924	1487.917	5.102
	H	–0.604008	–0.779760	1.340344	482.0185	15.0559	1502.891	3.2258

E = –269.6833528 E[CCSD(T)/CBS] = –269.3039230 ZPVE = 70.8706	H	–0.724992	–1.795436	–0.119568	518.5105	26.2689	1508.365	4.5317
	H	0.373614	–0.041697	–1.439179	839.4488	9.2653	2962.086	34.9089
	H	–0.409277	1.655868	–0.000418	932.1437	11.8386	2987.036	49.4759
	H	2.631023	–0.081039	–0.397161	947.5224	4.3367	3029.773	53.5639
	H	1.876091	–1.677725	–0.323025	1040.956	115.8386	3034.649	20.4701
	H	1.935054	–0.649039	1.121739	1078.595	30.0549	3097.942	33.9374
					1114.163	30.2504	3109.053	20.1584
					1154.263	19.2398	3779.999	41.8524
					1249.638	33.171	3842.421	39.7596
					1263.614	3.9884		
5_12  E = –269.6793177 E[CCSD(T)/CBS] = –269.2996506 ZPVE = 70.5745	O	–1.608163	–1.031594	–0.247740	123.2783	19.3205	1308.913	30.4181
	C	–0.974182	0.070469	0.393877	216.3773	95.0463	1370.47	5.1562
	C	0.373774	0.312112	–0.279222	233.9786	7.4088	1400.803	10.8041
	O	0.954499	1.509278	0.241189	259.7216	27.5657	1414.423	38.8699
	C	1.313863	–0.876890	–0.160766	275.143	74.3956	1447.671	3.9586
	H	–2.487369	–1.143590	0.122037	396.7043	13.8704	1490.599	6.3794
	H	–1.570870	0.983473	0.308511	437.4571	1.4239	1497.785	5.4959
	H	–0.813211	–0.133075	1.462230	497.7949	8.0725	1520.842	3.0887
	H	0.186935	0.523599	–1.333739	832.1661	17.8793	2954.288	59.1504
	H	1.305121	1.319541	1.117671	931.8407	0.6779	3012.496	21.4032
	H	2.248304	–0.676174	–0.684060	954.8852	2.2082	3023.227	36.1533
	H	0.855893	–1.771364	–0.580921	1061.225	52.2716	3052.81	33.7535
	H	1.543691	–1.080596	0.889835	1068.266	173.8134	3087.237	38.0112
					1101.877	6.0335	3116.392	13.4586
					1166.242	8.6593	3797.412	16.3564
					1234.062	14.2687	3837.396	32.748
					1243.793	8.2013		
5_13	O	–1.683431	–1.020948	–0.276092	121.1149	5.3117	1337.504	1.7479
	C	–0.970754	0.040150	0.347286	225.7007	5.268	1378.169	14.3054
	C	0.391940	0.313667	–0.296081	251.3872	26.7289	1399.212	12.1407
	O	0.984509	1.466349	0.307755	273.1559	111.2366	1406.515	5.8878

	C	1.372355	–0.829720	–0.112760	285.2527	103.7219	1441.417	20.1408
	H	–1.301629	–1.856688	0.004898	388.9713	12.7027	1490.641	3.0386
	H	–1.601444	0.925444	0.238861	435.1501	1.4518	1496.902	1.9456
	H	–0.831999	–0.136302	1.419885	502.2879	3.5887	1507.706	4.3749
	H	0.233101	0.482882	–1.367962	843.2335	1.401	2981.14	14.4843
	H	0.441406	2.234807	0.107731	916.6585	10.3528	2998.756	70.4003
	H	2.325757	–0.589142	–0.581270	947.3039	39.36	3030.929	15.7778
	H	0.993218	–1.744045	–0.570832	1055.354	48.6261	3054.779	45.8163
E = –269.6794073	H	1.550216	–1.010187	0.949187	1075.665	75.7768	3095.114	30.1094
E[CCSD(T)/CBS] =					1111.982	44.2317	3107.293	20.6017
–269.2997789					1120.572	0.7853	3812.548	21.7063
ZPVE = 70.6611					1221.655	62.0624	3830.292	25.2574
					1283.818	30.6272		
					133.5892	4.1085	1340.726	1.2784
					220.6446	4.0115	1386.008	31.7857
					259.9854	15.7252	1396.315	6.6647
5_14	O	–1.666460	–1.057234	–0.188476	263.4689	52.448	1406.918	0.8675
	C	–0.967692	0.048986	0.367216	295.9859	154.3361	1437.276	21.9601
	C	0.394163	0.294626	–0.288494	388.0101	15.6488	1489.662	5.3584
	O	1.002198	1.458200	0.274546	447.2232	13.1865	1496.39	1.9616
	C	1.355657	–0.859360	–0.084470	503.7793	4.6169	1508.683	2.1659
	H	–1.904816	–0.847818	–1.096630	851.885	1.8057	2933.375	68.1414
	H	–1.569778	0.965859	0.306109	917.6468	4.1937	2964.699	76.7075
	H	–0.823114	–0.178877	1.423688	953.2531	30.1738	3038.096	13.838
	H	0.233845	0.442354	–1.367473	1051.91	102.2929	3078.258	25.3982
	H	0.438315	2.218960	0.103600	1079.435	69.011	3102.711	29.482
	H	2.288505	–0.680218	–0.617787	1099.491	8.0584	3118.49	14.3982
	H	0.911926	–1.786822	–0.443479	1130.052	27.6977	3807.67	16.5461
E = –269.6793583	H	1.582396	–0.969370	0.977159	1230.417	0.7695	3811.725	22.7561
E[CCSD(T)/CBS] =					1278.115	67.0857		
–269.2995580								
ZPVE = 70.6521								
5_15	O	–1.618448	–1.000610	–0.222003	116.7251	19.2771	1294.72	2.1592

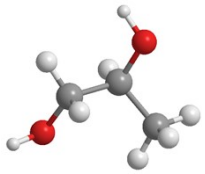


E = –269.6794216
E[CCSD(T)/CBS] = –269.2999986
ZPVE = 70.5442

C	–0.949169	0.089701	0.404071
C	0.384030	0.288069	–0.301249
O	0.929621	1.483480	0.261978
C	1.319122	–0.899900	–0.133133
H	–2.459683	–1.139622	0.219425
H	–1.526812	1.015470	0.322064
H	–0.766196	–0.107433	1.466701
H	0.173819	0.436274	–1.367686
H	1.802446	1.626148	–0.114401
H	1.563871	–1.041185	0.921119
H	2.249273	–0.744294	–0.684539
H	0.849937	–1.808362	–0.509464

210.2035	39.0443	1375.039	1.7535
234.1537	78.5506	1396.036	3.9542
239.6878	92.2859	1416.396	35.2618
270.7283	7.6807	1458.889	0.6938
387.511	8.0296	1490.828	5.3835
442.9955	6.0245	1504.127	5.195
506.985	2.6144	1526.056	3.0459
837.4192	5.6936	2976.57	11.0028
935.3608	2.1923	2989.669	75.8679
953.6481	15.5571	3022.757	22.1615
1055.305	54.3059	3030.432	55.7493
1074.065	112.8817	3081.607	37.0127
1120.593	66.3367	3109.721	16.0502
1161.186	2.2525	3825.947	21.8834
1206.011	58.4263	3841.886	37.7882
1253.159	3.4705		

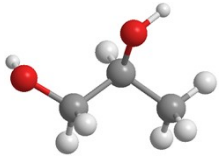
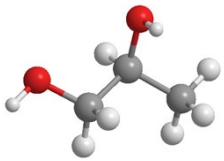
5_16

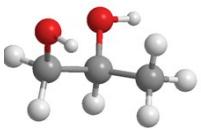
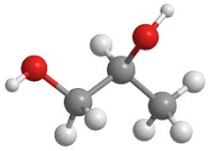


E = –269.6793444
E[CCSD(T)/CBS] = –269.2998481
ZPVE = 70.5795

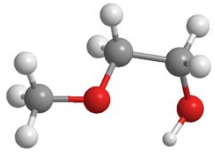
O	–1.624303	–1.024561	–0.246019
C	–0.956862	0.037881	0.426316
C	0.367793	0.300199	–0.285360
O	0.995814	1.453033	0.280829
C	1.340177	–0.855032	–0.150322
H	–2.417270	–1.254892	0.244348
H	–1.561009	0.954745	0.404372
H	–0.755643	–0.208509	1.474950
H	0.150424	0.467881	–1.347112
H	0.465829	2.228175	0.072200
H	0.885728	–1.773281	–0.518679
H	1.612577	–0.992577	0.897636
H	2.248983	–0.655127	–0.716718

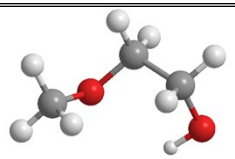
122.4853	17.5996	1288.242	40.5931
216.1166	96.4881	1361.192	4.2318
224.1377	6.9059	1397.598	4.4262
265.0952	6.9135	1434.803	19.3881
282.5126	106.46	1449.705	4.4243
391.4057	5.4099	1491.23	6.5258
436.2499	10.8262	1497.851	2.0491
506.6153	2.1725	1520.203	2.3356
847.7611	7.0697	2962.041	78.3027
935.722	1.2311	2981.609	13.0198
952.2662	13.6237	3012.733	71.3157
1061.893	158.0304	3036.782	21.2942
1065.884	37.5945	3101.016	30.3723
1105.781	9.6823	3121.044	13.5342
1162.819	7.5859	3813.184	18.6526

					1242.294	34.4795	3837.643	33.4113
					1245.168	16.5862		
5_17  E = –269.6772219 E[CCSD(T)/CBS] = –269.2975812 ZPVE = 70.4620	O	–1.958744	–0.070454	–0.095428	105.8218	11.6181	1341.03	3.8707
	C	–0.724198	–0.642447	0.301702	220.3696	30.239	1388.98	10.7777
	C	0.499915	0.022092	–0.314243	232.5781	65.2429	1401.174	20.1988
	O	0.534337	1.366150	0.157507	247.5533	38.9881	1409.301	29.88
	C	1.778641	–0.729867	0.042057	269.5353	74.9974	1435.386	9.4288
	H	–2.030860	–0.126232	–1.052994	370.0476	3.0408	1490.124	0.0922
	H	–0.677026	–0.526781	1.385290	472.3973	26.3776	1494.557	5.4373
	H	–0.692919	–1.715138	0.073183	510.1432	10.1432	1502.47	5.4217
	H	0.374934	0.016731	–1.408396	843.5433	15.3985	2929.35	66.5522
	H	1.290638	1.810996	–0.235909	918.3515	33.5661	2981.426	55.4601
	H	2.650001	–0.233105	–0.388971	931.5557	1.9891	3024.46	20.5267
	H	1.758656	–1.752167	–0.339456	1053.383	50.7666	3076.264	16.5532
	H	1.911169	–0.763346	1.124405	1086.773	82.7582	3083.634	31.9546
					1101.206	2.872	3096.518	34.9907
					1147.141	74.3797	3811.492	18.7799
					1193.613	27.6274	3818.148	20.2252
					1300.56	29.1551		
5_18  E = –269.6768686 E[CCSD(T)/CBS] = –269.2971692 ZPVE = 70.3707	O	–1.920467	–0.070568	–0.129967	105.7464	18.2361	1331.476	8.5129
	C	–0.719819	–0.681351	0.315765	202.3484	61.9224	1342.355	2.7989
	C	0.469037	0.032270	–0.312190	224.2286	85.2137	1406.231	7.2433
	O	0.544012	1.398368	0.086183	230.2206	50.8369	1420.642	41.1308
	C	1.774463	–0.704040	–0.025153	260.5519	3.546	1454.994	0.3003
	H	–2.666266	–0.530169	0.264330	375.3785	2.5972	1492.5	3.5738
	H	–0.629259	–0.628132	1.411119	459.3695	11.0028	1497.449	5.8237
	H	–0.686108	–1.740884	0.033285	515.0977	28.7142	1511.867	4.8691
	H	0.300181	0.073964	–1.390032	829.1008	15.7677	2943.78	56.9626
	H	0.607906	1.434651	1.046517	925.1183	1.1179	2990.18	48.8405
	H	2.609215	–0.153329	–0.455857	941.354	17.3645	3018.513	20.9715
	H	1.769262	–1.710287	–0.447648	1059.223	73.0819	3051.386	13.5035
	H	1.946655	–0.791449	1.051198				

					1084.422	86.8845	3081.921	50.9751
					1106.191	21.7895	3109.338	19.8637
					1139.654	49.0739	3793.413	14.2684
					1234.682	11.3178	3832.782	30.0747
					1253.488	41.1295		
5_19  E = –269.6767967 E[CCSD(T)/CBS] = –269.2971893 ZPVE = 70.6082	O	–1.563496	–0.451182	0.652057	115.8187	5.1568	1370.062	10.866
	C	–0.898079	–0.302754	–0.593318	220.3519	73.6405	1391.901	17.3952
	C	0.566877	0.116706	–0.491860	247.7089	73.436	1399.743	14.7878
	O	0.589295	1.470737	–0.044290	265.4733	21.2232	1416.579	6.6768
	C	1.388379	–0.787180	0.420700	280.4821	54.8076	1423.837	21.8412
	H	–1.263789	–1.262158	1.071078	369.906	12.628	1487.147	5.7346
	H	–0.956996	–1.223833	–1.185547	423.2404	16.0295	1496.104	2.8506
	H	–1.437508	0.476747	–1.130305	643.7112	17.4328	1507.864	4.3523
	H	0.972778	0.057677	–1.512285	800.072	7.5008	2945.935	43.1608
	H	1.503516	1.737490	0.088305	913.5343	33.5202	2990.495	74.8081
	H	1.359113	–1.825343	0.081963	931.9238	25.8015	3022.107	19.052
	H	1.013425	–0.734180	1.443089	1005.227	33.0228	3077.588	31.0291
	H	2.435384	–0.477871	0.430975	1086.802	7.4411	3088.948	23.2585
					1095.531	66.4588	3097.915	23.9734
					1139.241	62.4145	3818.316	18.5519
					1238.489	9.4882	3828.602	20.8528
					1250.503	55.8003		
5_20  E = –269.6773332 E[CCSD(T)/CBS] =	O	–1.937119	–0.082689	–0.162029	122.2232	15.1172	1308.266	24.8594
	C	–0.735413	–0.581256	0.411036	143.0998	104.4737	1356.798	12.3318
	C	0.448537	0.021642	–0.321179	199.7052	110.1812	1406.417	5.9306
	O	0.540885	1.386499	0.091580	223.5881	0.5292	1408.738	10.0863
	C	1.741241	–0.731614	–0.023205	272.3839	1.8603	1460.649	0.6132
	H	–2.662029	–0.245789	0.446119	372.6924	1.492	1494.315	5.0591
	H	–0.654907	–0.312862	1.470007	461.0732	9.9181	1497.718	1.1237
	H	–0.689389	–1.673674	0.327017	511.2132	15.3472	1509.067	6.3858
	H	0.228840	–0.028791	–1.394249				

–269.2978981	H	1.147023	1.845441	–0.496347	842.6791	11.2034	2979.633	48.604
ZPVE = 70.3346	H	1.688608	–1.764711	–0.371262	933.5574	38.7812	2987.586	25.2615
	H	1.945991	–0.733088	1.048614	938.9678	1.9672	3022.396	50.5335
	H	2.584669	–0.253702	–0.524078	1060.153	148.1896	3025.283	22.1788
					1073.997	9.2781	3087.189	32.6006
					1106.274	4.9749	3093.761	34.4584
					1147.195	31.2173	3826.358	23.396
					1206.72	32.7113	3840.535	31.2015
					1279.53	34.8573		

Isomer **19**		Cartesian coordinates			Frequency	Intensity	Frequency	Intensity
					92.3957	1.1607	1381.258	4.8286
					137.5911	6.6384	1402.227	28.1239
					221.0834	4.9094	1433.615	33.9458
	O	–1.844804	–0.707235	0.192401	275.7191	2.7206	1476.518	1.8095
19_1	C	–1.334808	0.544337	–0.237276	365.2905	9.5751	1488.059	6.9243
	C	0.086109	0.767620	0.235580	413.8001	119.9606	1499.226	11.0026
	O	0.888423	–0.252095	–0.337453	545.7634	6.245	1500.835	2.0619
	C	2.226987	–0.233547	0.110723	839.1503	20.2276	1517.079	3.8254
	H	–1.200392	–1.373323	–0.071349	903.104	14.5855	2959.827	38.2237
	H	–1.368020	0.629412	–1.330091	1021.762	14.2359	2975.426	77.3623
	H	–1.985215	1.312725	0.181994	1076.049	117.4801	2982.913	3.2624
E = –269.6666508	H	0.130785	0.710859	1.330810	1123.045	7.483	3004.054	125.399
E[CCSD(T)/CBS] = –269.2823352	H	0.441610	1.759945	–0.074669	1148.535	128.6976	3016.871	41.9351
	H	2.724656	0.707477	–0.152378	1181.77	2.3022	3077.8	33.3965
ZPVE = 71.0235	H	2.746076	–1.055685	–0.378060	1196.094	31.4565	3108.536	26.7996
	H	2.288527	–0.367187	1.197270	1252.604	11.3859	3794.806	33.1015
					1268.856	23.2084		
	O	–1.783304	–0.705749	0.085515	74.4967	0.8105	1369.961	3.7966
19_2	C	–1.147505	0.445845	–0.444003	136.7528	5.1649	1396.203	18.0941
	C	0.038320	0.863469	0.410544	205.8843	6.667	1427.245	45.4172
	O	0.983342	–0.194139	0.543769				

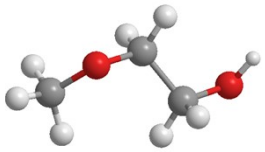


E = –269.6640272
E[CCSD(T)/CBS] = –269.2799805
ZPVE = 71.0546

C	1.896092	–0.303318	–0.533156
H	–1.081467	–1.317977	0.336076
H	–0.831787	0.275655	–1.481350
H	–1.888287	1.247293	–0.456072
H	–0.304155	1.082387	1.422616
H	0.516617	1.761550	0.000335
H	1.400683	–0.529401	–1.483037
H	2.575745	–1.118558	–0.293006
H	2.475529	0.619213	–0.653230

292.6155	6.4706	1473.121	0.2747
415.4923	92.504	1488.392	9.5257
434.3794	1.9535	1490.089	0.1692
534.3275	11.938	1509.285	7.3475
825.2878	27.9903	1512.928	4.6976
884.337	13.0515	2972.938	19.4668
990.0288	4.5288	2980.929	50.3176
1074.426	129.7953	2991.575	88.1318
1095.521	43.1004	3029.767	51.3474
1147.455	54.6176	3062.535	29.2597
1177.6	2.7764	3077.789	43.0104
1216.163	26.6172	3109.146	24.7542
1221.394	29.5968	3777.585	33.8537
1307.763	19.8787		

19_3

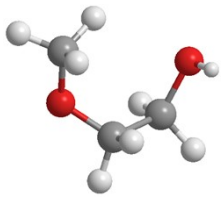


E = –269.6603814
E[CCSD(T)/CBS] = –269.2760175
ZPVE = 70.8048

O	–2.272009	–0.232247	0.319799
C	–1.016599	–0.360703	–0.337733
C	0.027451	0.583467	0.257954
O	1.283767	0.492605	–0.389406
C	2.106124	–0.560353	0.074954
H	–2.640569	0.631760	0.112966
H	–0.717077	–1.399610	–0.201516
H	–1.099178	–0.177863	–1.414263
H	0.121673	0.394358	1.334014
H	–0.307339	1.616532	0.130747
H	2.294664	–0.471881	1.151457
H	3.052760	–0.482857	–0.456389
H	1.676343	–1.548139	–0.122453

78.0864	5.2722	1344.228	0.6946
104.7543	5.1427	1394.401	32.4331
172.7776	1.9129	1426.152	1.3933
270.354	51.2851	1476.481	0.7761
305.4621	84.9654	1492.118	5.4178
381.0726	1.0553	1500.194	0.3655
494.4115	2.5138	1508.06	8.9045
800.9974	2.371	1519.239	1.8803
944.258	24.2212	2976.789	52.0417
1030.423	44.8182	2988.706	28.5732
1059.495	99.0197	3005.853	69.4791
1091.791	21.1139	3023.403	58.7167
1126.491	59.8401	3040.061	24.4209
1174.827	3.9656	3085.772	48.8614
1205.367	89.8121	3107.262	27.7943
1262.972	7.3097	3813.668	24.8828
1322.76	4.6584		

19_4

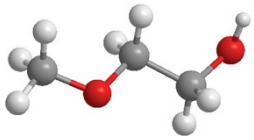


E = –269.6611552
E[CCSD(T)/CBS] = –269.2762780
ZPVE = 70.8257

O	–1.578762	–0.878342	0.174192
C	–1.276888	0.415589	–0.341892
C	0.061613	0.981228	0.113275
O	1.192855	0.352787	–0.452136
C	1.586940	–0.861183	0.165427
H	–1.696025	–0.808813	1.126479
H	–1.265944	0.306008	–1.426385
H	–2.066792	1.133380	–0.084219
H	0.120936	0.962314	1.212612
H	0.111813	2.027506	–0.199733
H	0.854301	–1.656170	0.015747
H	1.741397	–0.721429	1.243096
H	2.534095	–1.149530	–0.287302

87.8028	6.112	1380.143	7.3604
146.0013	0.6661	1401.615	13.3259
198.803	7.1824	1412.184	27.3365
286.5887	105.5699	1471.011	0.4376
326.1586	11.7681	1483.351	8.6741
399.3724	9.6201	1488.74	1.4443
519.8116	21.9293	1491.045	0.7042
819.6791	8.6271	1517.256	8.0623
901.1054	51.2228	2941.676	46.3805
981.8949	17.9001	2973.558	105.5815
1050.223	33.829	2975.882	36.4322
1087.087	37.7261	3045.225	46.0907
1148.51	86.4648	3056.973	36.1292
1179.439	7.0672	3083.811	25.2043
1199.806	68.0455	3106.351	28.6814
1243.641	15.2731	3811.313	21.4456
1327.246	8.7054		

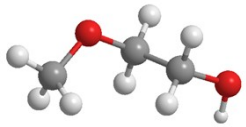
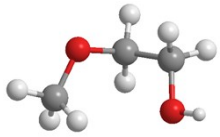
19_5

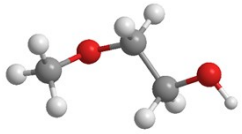
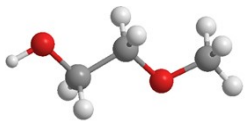


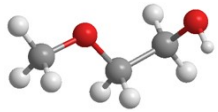
E = –269.6626679
E[CCSD(T)/CBS] = –269.2780676
ZPVE = 70.7578

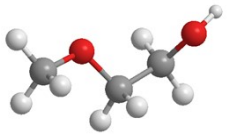
O	–2.354329	–0.139856	0.386965
C	–1.206788	0.066142	–0.427134
C	0.081342	–0.086977	0.367673
O	1.168679	0.112722	–0.510224
C	2.424260	–0.034314	0.116081
H	–2.443155	0.604799	0.988755
H	–1.244166	–0.691834	–1.208639
H	–1.222794	1.046334	–0.914237
H	0.118475	–1.085672	0.821625
H	0.107237	0.648716	1.186727
H	3.187761	0.135412	–0.640551
H	2.551472	–1.041469	0.531373
H	2.557946	0.693538	0.926104

98.799	1.9469	1352.56	4.1552
115.775	6.0578	1389.73	42.1216
194.815	0.4383	1432.77	1.8573
226.52	6.412	1479.44	0.9324
281.707	117.113	1487.71	6.3944
425.326	0.3615	1503.2	8.9028
445.594	12.9996	1514.69	1.1676
819.875	1.9603	1529.08	1.8632
980.826	39.4993	2935.91	61.4671
1042.95	46.3187	2969.38	69.3954
1075.13	66.222	2985.26	32.7086
1097.04	14.841	3010.07	74.3521
1154.36	151.155	3012.33	56.9382

					1175.08	1.8984	3090.31	31.4179
					1216.24	4.8986	3108.02	29.2373
					1223.53	37.1328	3817.8	23.9776
					1303.95	5.2179		
19_6  E = –269.6600339 E[CCSD(T)/CBS] = –269.2756453 ZPVE = 70.7707	O	–2.296369	–0.140480	0.309356	79.4022	0.9123	1345.842	1.8613
	C	–1.031267	–0.360334	–0.304645	105.9865	2.0391	1388.387	44.3244
	C	0.021608	0.615678	0.219273	176.1753	0.598	1424.001	0.7445
	O	1.270608	0.481976	–0.434539	262.1616	65.986	1475.793	0.7155
	C	2.099679	–0.540473	0.080711	300.7011	65.9742	1491.255	5.377
	H	–2.239278	–0.394711	1.235117	381.3113	1.8142	1499.768	0.6241
	H	–0.702785	–1.396865	–0.173397	493.3116	2.3458	1508.135	8.1146
	H	–1.175996	–0.193135	–1.371408	800.2746	2.658	1518.256	2.1247
	H	0.140171	0.491824	1.305714	944.0964	30.2108	2953.27	54.0381
	H	–0.322254	1.634492	0.038164	1026.06	37.5814	2975.215	56.3603
	H	3.039549	–0.494833	–0.466168	1060.166	83.0823	2999.278	37.3407
	H	1.669359	–1.538952	–0.051258	1093.334	6.3559	3022.461	73.9105
	H	2.303204	–0.387110	1.147623	1129.174	117.6997	3070.777	23.4905
					1173.869	2.6136	3091.381	39.0634
					1204.921	46.5342	3106.731	28.2057
					1261.137	9.6768	3814.982	21.999
					1327.238	8.339		
19_7  E = –269.6615741 E[CCSD(T)/CBS] = –269.2770613	O	–1.518969	–0.876506	0.203360	80.8562	4.5193	1340.18	27.9626
	C	–1.285573	0.419869	–0.344806	147.307	7.313	1404.01	10.949
	C	0.044087	0.950363	0.157016	190.41	4.2629	1448.83	2.1649
	O	1.174316	0.345172	–0.439554	236.861	105.7	1471.03	0.3842
	C	1.609856	–0.857367	0.174263	325.409	4.7256	1484.68	9.4002
	H	–2.305042	–1.249144	–0.204619	401.419	3.8591	1488.39	0.3142
	H	–1.260878	0.386529	–1.439176	507.665	19.1865	1505.91	3.4964
	H	–2.074935	1.118940	–0.038480	831.097	12.7807	1516.16	7.4914
	H	0.083628	0.856630	1.249656	906.635	48.4252	2968.37	54.9176
	H	0.100365	2.012272	–0.093496				

ZPVE = 70.7759	H	1.817882	–0.701990	1.239811	976.191	5.8367	2980.23	52.4462
	H	2.533838	–1.145551	–0.324453	1087.48	49.1861	2986.23	46.8263
	H	0.874670	–1.657822	0.075693	1094.56	6.2006	3020.12	65.9466
					1136.75	144.742	3055.8	44.828
					1179.45	2.6515	3059.38	36.7507
					1212.66	32.9747	3105.67	29.7465
					1257.26	30.0332	3829.6	28.7162
					1271.9	4.8567		
19_8  E = –269.6601387 E[CCSD(T)/CBS] = –269.2759310 ZPVE = 70.7325	O	–2.234291	–0.225851	0.344125	77.343	10.5846	1323.888	5.287
	C	–1.015321	0.494004	0.189588	102.5391	2.4845	1380.334	4.7657
	C	–0.001645	–0.476727	–0.402696	174.1568	3.8241	1456.465	3.7346
	O	1.258841	0.130912	–0.621502	230.5832	104.1581	1476.949	0.5398
	C	2.112063	0.133481	0.505395	298.3119	14.5606	1491.225	4.7054
	H	–2.907477	0.370584	0.680857	383.1027	3.3469	1506.192	1.033
	H	–1.131729	1.345122	–0.489500	496.2505	2.5788	1509.404	9.963
	H	–0.658780	0.875314	1.153019	818.2753	0.0902	1529.825	3.3947
	H	–0.362575	–0.817165	–1.373723	945.5672	40.9062	2974.652	35.3423
	H	0.089833	–1.354175	0.248043	1007.782	31.545	2986.479	49.0194
	H	1.706561	0.717095	1.339177	1062.276	74.6412	2994.867	41.7162
	H	3.052021	0.584654	0.192888	1114.445	74.2777	3017.14	86.7562
	H	2.307802	–0.886051	0.858423	1169.993	29.8528	3023.009	41.2481
					1180.129	21.541	3078.184	44.801
					1215.278	61.1793	3105.644	29.1227
					1239.145	21.3161	3836.986	32.7292
					1271.668	5.1194		
19_9 	O	–2.302724	–0.147031	0.406963	97.941	0.8656	1302.239	0.8022
	C	–1.203167	0.153520	–0.445819	107.4826	20.8751	1387.08	12.7122
	C	0.060488	–0.120814	0.345037	199.8467	7.0861	1464.56	3.2547
	O	1.165416	0.171875	–0.485184	219.0208	101.1875	1482.59	0.0637
	C	2.405610	–0.047762	0.149301	228.0847	7.6115	1487.296	6.2079
	H	–3.118222	0.018913	–0.071986				

E = –269.6625717 E[CCSD(T)/CBS] = –269.2782036 ZPVE = 70.6886	H	–1.207510	–0.470728	–1.345503	431.4393	0.3723	1505.586	8.6944
	H	–1.210728	1.202524	–0.759938	443.1257	5.421	1525.57	1.2804
	H	0.076117	–1.171161	0.663657	837.9509	0.7907	1536.257	3.3957
	H	0.072882	0.501685	1.249103	983.3956	53.3757	2963.068	31.1191
	H	3.186515	0.203957	–0.565713	1029.202	29.7154	2973.523	67.7659
	H	2.523700	–1.095723	0.451484	1069.366	57.8695	2992.242	24.5943
	H	2.520458	0.583518	1.039119	1156.041	141.8828	2992.41	68.9579
					1156.642	0.1714	3009.537	62.268
					1184.756	2.0841	3031.867	82.908
					1210.839	83.9679	3106.961	29.8189
					1229.971	6.1344	3840.691	35.2015
					1260.787	12.0172		
19_10  E = –269.6616636 E[CCSD(T)/CBS] = –269.2770301 ZPVE = 70.6255	O	–1.925002	–0.699841	0.178906	89.1302	2.0962	1380.124	7.5423
	C	–1.312809	0.505537	–0.251600	124.9961	6.4832	1407.246	35.1683
	C	0.111107	0.687697	0.235790	219.1598	55.9123	1427.857	17.3669
	O	0.950018	–0.275471	–0.358848	229.1949	21.3008	1477.412	0.6063
	C	2.287652	–0.191152	0.078146	298.6547	46.883	1487.633	6.5933
	H	–1.949843	–0.706501	1.140478	358.0777	2.9022	1494.1	3.9716
	H	–1.314259	0.467076	–1.340893	540.7727	11.9252	1499.29	9.3904
	H	–1.897355	1.382448	0.055256	847.965	14.0232	1516.607	1.9761
	H	0.145563	0.601425	1.334025	898.0271	23.1887	2925.094	45.963
	H	0.448230	1.704474	–0.018245	1043.011	50.9401	2953.087	54.4257
	H	2.731367	0.784069	–0.160314	1059.211	27.1967	2964.513	73.6879
	H	2.847636	–0.969049	–0.436984	1095.963	71.8639	2981.198	94.8958
	H	2.369700	–0.351934	1.160645	1157.122	115.2358	3003.035	62.2607
					1176.887	1.1039	3084.588	24.3593
					1206.165	33.3317	3108.692	27.7115
					1237.792	30.5195	3811.38	18.9839
					1299.275	5.0637		
19_11	O	–1.883826	–0.713513	0.167531	85.4196	5.131	1312.571	22.5182
	C	–1.304765	0.503959	–0.285679	133.4275	3.4027	1410.005	17.231

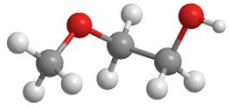


E = –269.6618751
E[CCSD(T)/CBS] = –269.2774806
ZPVE = 70.5862

C	0.083733	0.632896	0.293768
O	0.962924	–0.240533	–0.383190
C	2.261242	–0.249045	0.164879
H	–2.675647	–0.890440	–0.346395
H	–1.232201	0.530029	–1.377869
H	–1.899288	1.366551	0.040631
H	0.050595	0.395097	1.365338
H	0.424010	1.673550	0.189656
H	2.727154	0.744214	0.120438
H	2.858060	–0.944039	–0.422671
H	2.255795	–0.581111	1.210440

175.7209	117.053	1461.057	2.0037
228.0847	2.452	1477.464	1.2185
281.9045	0.6846	1487.343	6.2235
362.0532	3.0003	1497.804	11.6823
527.2864	10.3965	1506.126	5.0194
859.0657	20.3967	1516.354	2.9431
909.2193	30.4358	2949.081	20.1915
1030.098	48.2839	2964.256	77.4844
1092.17	23.2521	2978.66	61.3937
1098.496	34.6977	2988.785	82.0056
1152.567	141.8875	3004.065	52.8287
1178.677	5.4157	3023.873	58.7445
1220.349	23.0181	3106.433	29.3368
1238.122	9.7916	3836.817	30.68
1282.382	35.8855		

19_12



E = –269.6593528
E[CCSD(T)/CBS] = –269.2752364
ZPVE = 70.6611

O	–1.810723	–0.697237	0.010614
C	–1.064858	0.389768	0.540810
C	0.024572	0.761942	–0.449361
O	1.039347	–0.210462	–0.607441
C	1.993392	–0.236326	0.431244
H	–2.443185	–0.991553	0.671021
H	–1.699887	1.273437	0.688749
H	–0.626172	0.133306	1.511820
H	0.460549	1.725244	–0.149227
H	–0.430140	0.884387	–1.433224
H	2.472006	0.743233	0.560025
H	2.751770	–0.964382	0.149527
H	1.563710	–0.540314	1.392369

52.422	2.2223	1339.944	27.8742
139.357	2.1101	1406.654	12.902
205.557	64.4369	1451.603	2.524
227.7097	45.542	1470.678	0.2234
295.6049	5.1238	1483.526	7.9107
433.1656	5.1601	1489.404	0.1374
512.5604	20.7633	1508.607	8.1861
840.9029	13.0824	1513.779	8.5865
888.1678	23.4621	2958.319	14.357
998.203	53.2887	2965.517	35.2357
1078.297	29.409	2977.842	132.0718
1093.153	58.1915	3001.622	35.8881
1151.873	71.5822	3014.772	73.6681
1174.937	4.1376	3075.998	33.7585
1210.283	42.173	3105.185	27.8001
1257.64	37.5082	3833.083	29.8077

		1271.761	11.4934

References

1 B. M. Jones and R. I. Kaiser, *J. Phys. Chem. Lett.*, 2013, **4**, 1965-1971.
2 J. Wang, C. Zhang, J. H. Marks, M. M. Evseev, O. V. Kuznetsov, I. O. Antonov and R. I. Kaiser, *Nat. Commun.*, 2024, **15**, 10189.
3 A. M. Turner, M. J. Abplanalp, S. Y. Chen, Y. T. Chen, A. H. H. Chang and R. I. Kaiser, *Phys. Chem. Chem. Phys.*, 2015, **17**, 27281-27291.
4 M. Bouilloud, N. Fray, Y. Benilan, H. Cottin, M. C. Gazeau and A. Jolly, *Mon. Not. R. Astron. Soc.*, 2015, **451**, 2145-2160.
5 C. Pale-Grosdemange, E. S. Simon, K. L. Prime and G. M. Whitesides, *J. Am. Chem. Soc.*, 1991, **113**, 12-20.
6 R. L. Hudson, M. H. Moore and A. M. Cook, *Adv. Space Res.*, 2005, **36**, 184-189.
7 D. Drouin, A. R. Couture, D. Joly, X. Tastet, V. Aimez and R. Gauvin, *Scanning*, 2007, **29**, 92-101.
8 P. Pracht, F. Bohle and S. Grimme, *Phys. Chem. Chem. Phys.*, 2020, **22**, 7169-7192.
9 M. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, G. Scalmani, V. Barone, B. Mennucci and G. Petersson, *et al., Gaussian 16, Revision C. 01*, Gaussian Inc., Wallingford CT, 2019.
10 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098-3100.
11 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789.
12 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652.
13 T. H. Dunning, *J. Chem. Phys.*, 1989, **90**, 1007-1023.
14 J. Čížek, *J. Chem. Phys.*, 1966, **45**, 4256-4266.
15 R. J. Bartlett, J. D. Watts, S. A. Kucharski and J. Noga, *Chem. Phys. Lett.*, 1990, **165**, 513-522.
16 K. Raghavachari, *Annu. Rev. Phys. Chem.*, 1991, **42**, 615-642.
17 J. F. Stanton, *Chem. Phys. Lett.*, 1997, **281**, 130-134.
18 F. Neese, *WIREs Comput. Mol. Sci.*, 2018, **8**, e1327.
19 K. A. Peterson, D. E. Woon and T. H. D. Jr., *J. Chem. Phys.*, 1994, **100**, 7410-7415.
20 T. Helgaker, W. Klopper, H. Koch and J. Noga, *J. Chem. Phys.*, 1997, **106**, 9639-9646.
21 A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen and A. K. Wilson, *Chem. Phys. Lett.*, 1998, **286**, 243-252.
22 S. Zhong, E. C. Barnes and G. A. Petersson, *J. Chem. Phys.*, 2008, **129**, 184116.
23 J. Zhang and E. F. Valeev, *J. Chem. Theory Comput.*, 2012, **8**, 3175-3186.
24 A. M. Thomas, B. B. Dangi, T. Yang, R. I. Kaiser, L. Lin, T.-J. Chou and A. H. H. Chang, *J. Phys. Chem. Lett.*, 2018, **9**, 3340-3347.
25 G. Y. Matti, O. I. Osman, J. E. Upham, R. J. Suffolk and H. W. Kroto, *J. Electron Spectrosc. Relat. Phenom.*, 1989, **49**, 195-201.
26 P. J. Linstrom, W. G. Mallard, NIST Chemistry webBook, NIST Standard Reference Database Number 69, 2013. http:// webbook.nist.gov/
27 N. F. Kleimeier and R. I. Kaiser, *ChemPhysChem*, 2021, **22**, 1229-1236.
28 B. Ruscic and H. Bross, *Active Thermochemical Tables (ATcT) values based on ver. 1.202 of the Thermochemical Network*, ATcT.anl.gov, 2021.
29 C. Zhu, R. Frigge, A. Bergantini, R. C. Fortenberry and R. I. Kaiser, *Astrophys. J.*, 2019, **881**, 156.

30 N. F. Kleimeier, A. K. Eckhardt and R. I. Kaiser, *J. Am. Chem. Soc.*, 2021, **143**, 14009-14018.
31 C. J. Bennett, C. S. Jamieson, Y. Osamura and R. I. Kaiser, *Astrophys. J.*, 2006, **653**, 792-811.
32 P. Buckley and P. A. Giguère, *Can. J. Chem.*, 1967, **45**, 397-407.
33 M. E. Jacox, *J. Chem. Phys.*, 1988, **88**, 4598-4607.
34 S. Maity, R. I. Kaiser and B. M. Jones, *Phys. Chem. Chem. Phys.*, 2015, **17**, 3081-3114.
35 M. J. Abplanalp and R. I. Kaiser, *Phys. Chem. Chem. Phys.*, 2019, **21**, 16949-16980.
36 J. H. Marks, J. Wang, M. M. Evseev, O. V. Kuznetsov, I. O. Antonov and R. I. Kaiser, *Astrophys. J.*, 2023, **942**, 43.
37 C. Zhang, C. Zhu, A. M. Turner, I. O. Antonov, A. D. Garcia, C. Meinert, L. A. Young, D. C. Jewitt and R. I. Kaiser, *Sci. Adv.*, 2023, **9**, eadg6936.
38 J. Wang, J. H. Marks, R. C. Fortenberry and R. I. Kaiser, *Sci. Adv.*, 2024, **10**, eadl3236.
39 D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, 1971, **54**, 927-942.
40 M. Hawkins and L. Andrews, *J. Am. Chem. Soc.*, 1983, **105**, 2523-2530.
41 M. M. Wohar and P. W. Jagodzinski, *J. Mol. Spectrosc.*, 1991, **148**, 13-19.
42 T. Butscher, F. Duvernay, G. Danger and T. Chiavassa, *Astron. Astrophys.*, 2016, **593**, A60.
43 J. Wang, J. H. Marks, A. M. Turner, A. M. Mebel, A. K. Eckhardt and R. I. Kaiser, *Sci. Adv.*, 2023, **9**, eadg1134.
44 P. J. Linstrom and W. G. Mallard, *NIST Chemistry webBook, NIST Standard Reference Database Number 69*, 2013, http://webbook.nist.gov/.
45 D. C. Frost, S. T. Lee and C. A. McDowell, *Chem. Phys. Lett.*, 1973, **23**, 472-475.
46 K. Watanabe, T. Nakayama and J. Mottl, *J. Quant. Spectrosc. Radiat. Transfer*, 1962, **2**, 369-382.
47 F. Brogli, E. Heilbronner, E. Kloster-Jensen, A. Schmelzer, A. S. Manocha, J. A. Pople and L. Radom, *Chem. Phys.*, 1974, **4**, 107-119.
48 F. Tureček, *J. Chem. Soc., Chem. Commun.*, 1984, DOI: 10.1039/C39840001374, 1374-1375.
49 S. W. Staley and T. D. Norden, *J. Am. Chem. Soc.*, 1989, **111**, 445-449.