Supporting Information for

Formation of Complex Organic Molecules in Methanol and Methanol - Carbon Monoxide Ices Exposed to Ionization Radiation - A Combined FTIR and Reflectron Time-of-Flight Mass Spectroscopic Study

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Table S1. List of oxygen bearing complex organic molecules observed in the selective interstellar sources.

Formula	Name	Sources	Abundances (molecule cm^{-2})
Aldehydes and ketones			
CH_3CHO	Acetaldehyde	Sgr B2(N)[6]	1.4×10^{17}
		TMC-1[7]	6.0×10^{12}
		Galactic Center [8]	8.2×10^{14}
CH_3CH_2CHO	Propanal	Sgr B2 (N)[1]	...
		Galactic Center[3]	1.0×10^{14}
CH_2CHCHO	Propenal	Sgr B2(N)[1]	...
		Galactic Center[3]	2.7×10^{13}
HC_2CHO	Propynal	Sgr B2 (N)[1]	...
		TMC-1[2]	4.0×10^{13}
		Galactic Center[3]	4.1×10^{13}
CH_3COCH_3	Acetone	Sgr B2(N)[16]	2.9×10^{16}
c-H_2C_3O	Cyclopropenone	Sgr B2(N)[5]	1.0×10^{13}
Alcohols			
CH_3CH_2OH	Ethanol	Sgr B2(N)[15]	4.4×10^{15}
		Galactic Center[12]	9.0×10^{14}
H_2CCHOH	Vinyl alcohol	Sgr B2(N)[10]	2.2×10^{14}
$HOCH_2CH_2OH$	Ethylene glycol	Sgr B2(N)[17]	2.3×10^{15}
		Galactic Center[3]	3.3×10^{14}
Acids and Esters			
CH_3COOH	Acetic acid	Sgr B2(N)[13]	7.0×10^{16}
$HCOOCH_3$	Methyl formate	Sgr B2(N)[11]	1.9×10^{17}
		Galactic Center[12]	1.1×10^{15}
$HCOOC_2H_5$	Ethyl formate	Sgr B2(N)[18]	5.4×10^{16}
		Orion KL[19]	9.0×10^{14}
CH_3COOCH_3	Methyl acetate	Orion KL[19]	4.2×10^{15}
Amide			
NH_2CHO	Formamide	Sgr B2(N)[4]	6.2×10^{15}
CH_3CONH_2	Acetamide	Sgr B2(N)[4]	1.6×10^{14}
Ether			
CH_3OCH_3	Dimethyl ether	Sgr B2 (N)[12]	6.7×10^{15}
		Galactic Center[12]	9.0×10^{14}
$C_2H_5OCH_3$	Methylethyl ether	SgrB2 (N)[20]	$1.0 \times 10^{14-15}$
		W51e2[20]	2.0×10^{14}
Others			
c-C_2H_4O	Ethylene oxide	Sgr B2(N)[9]	3.3×10^{14}
		Galactic Center[3]	8.5×10^{13}
$HOCH_2CHO$	Glycolaldehyde	Sgr B2(N)[14]	1.8×10^{15}
		Galactic Center[3]	2.5×10^{14}

Note: The abundance in galactic center is an average of the abundances in MC G-0.11-0.08, MC G-0.02-0.07 and MC G+0.693-0.03

Table S2. List of parameters derived using Monte Carlo simulations (CASINO).

	CH_3OH	CH_3OH+CO
Energy of the Electrons	5.0 keV	5.0 keV
Transmitted Energy	0.008±0.001 keV	0.029±0.008 keV
Backscattered Energy	1.06 ± 0.16 keV	1.10 ± 0.20 keV
Penetration Depth	252 ± 10 nm	265 ± 10 nm
Total energy transferred	4.65 ± 0.32 keV	4.60 ± 0.31 keV
Dose per molecule	6.5 ± 0.8 eV	5.2 ± 0.8 eV

Table S3: List of molecules, mass-to-charge ratios of the molecular ion peaks and % of the premixed vapors are shown for each sample mixture used for the calibration experiments.

Molecules	Mass	Ice: CH_3OH		Ice: CH_3OH-CO (4:5)	
	m/z (amu)	%	sample	Vapor %	sample
Acetaldehyde (CH_3CHO)	44	1.0±0.2	**Sample 1**	0.5±0.1	**Sample 2**
Acetone (CH_3COCH_3)	58	1.2±0.2		0.6±0.1	
1-Propanol ($CH_3CH_2CH_2OH$)	60	1.2±0.2		0.6±0.1	
1-Butanol ($CH_3CH_2CH_2CH_2OH$)	74	1.0±0.2		0.5±0.1	
Ethanol (CH_3CH_2OH)	46	1.1±0.2	**Sample 3**	0.6±0.1	**Sample 4**
Propanal (CH_3CH_2CHO)	58	1.2±0.2		0.6±0.1	
Butanal ($CH_3CH_2CH_2CHO$)	72	1.0±0.2		0.5±0.1	
2-Butanol ($CH_3CH_2CH(OH)CH_3$	74	1.2±0.2		0.6±0.1	
Dimethyl Ether (CH_3OCH_3)	46	1.0±0.2	**Sample 5**	0.5±0.1	**Sample 6**
Allyl Alcohol ($CH_2CHCHOH$)	58	1.0±0.2		0.5±0.1	
2-Propanol ($CH_3CH(OH)CH_3$)	60	1.2±0.2		0.6±0.1	
Butanone ($CH_3CH_2COCH_3$)	72	1.0±0.2		0.5±0.1	
iso-Butanol ($CH_3CH(CH_3)CH_2OH$)	74	2.1±0.2		1.1±0.1	
iso-Butanal ($CH_3CH(CH_3)CHO$)	72	1.9±0.2	**Sample 7**	1.0±0.1	**Sample 8**
tert-Butanol ($(CH_3)_3COH$)	74	1.1±0.2		0.6±0.1	
Propenal (CH_2CHCHO)	56	2.5±0.2	**Sample 9**	6.5±0.5	**Sample 10**
Ethylene Glycol ($HOCH_2CH_2OH$)	62	4.8±0.4	**Sample 11**	4.7±0.4	**Sample 12**

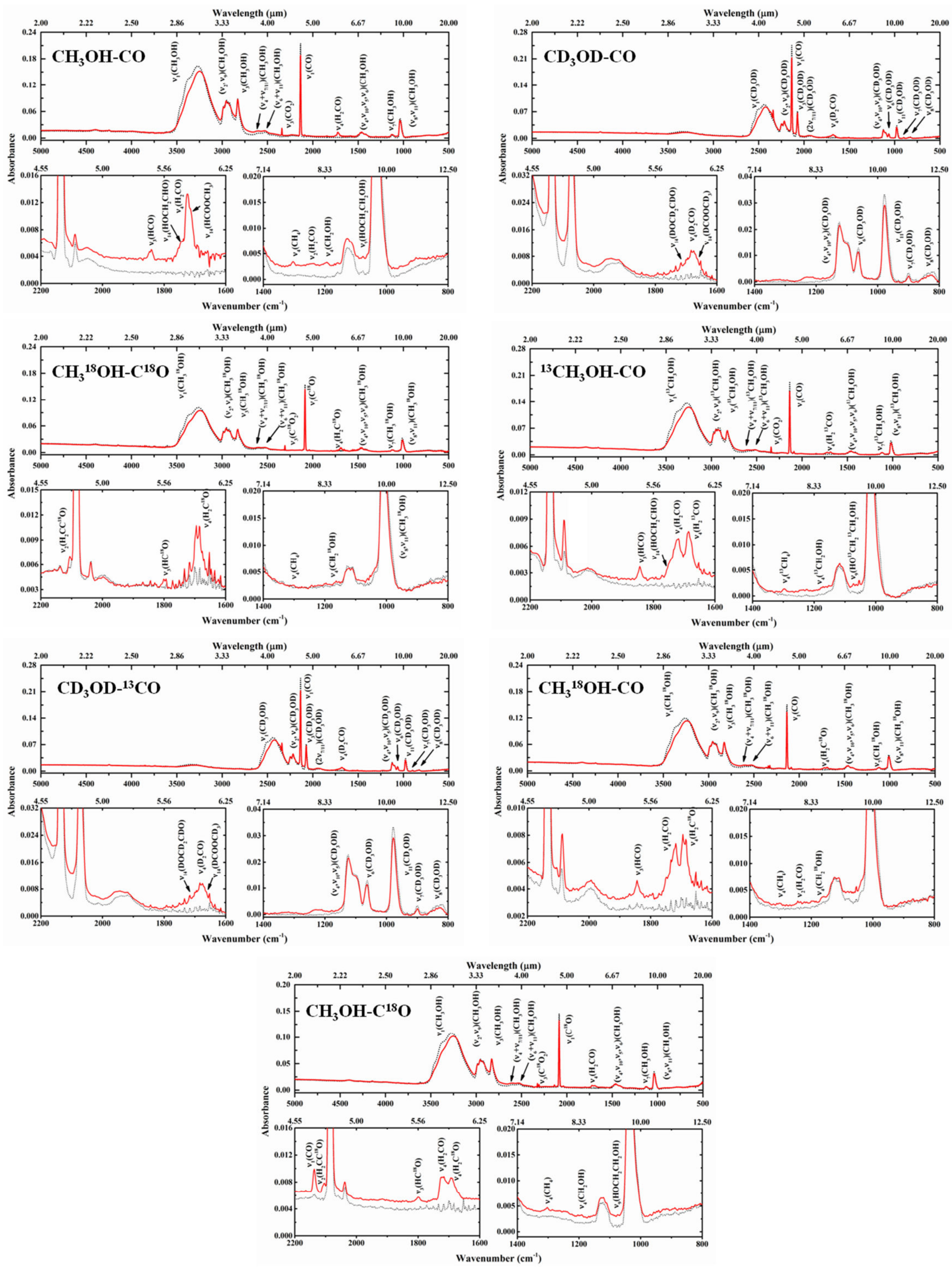


Figure S1. Infrared absorption spectra of methanol - carbon monoxide mixed ices (CH_3OH-CO, CD_3OD-CO, $CH_3{}^{18}OH$-$C^{18}O$, $^{13}CH_3OH$-CO, CD_3OD-^{13}CO, $CH_3{}^{18}OH$-CO and CH_3OH-$C^{18}O$) before (dotted trace) and after (solid trace) irradiation at 5.5 K. Newly emerged absorption features in each ice are shown in 2200 – 1600 cm^{-1} and 1400 – 800 cm^{-1} regions along with the assignments as listed in Table 2.

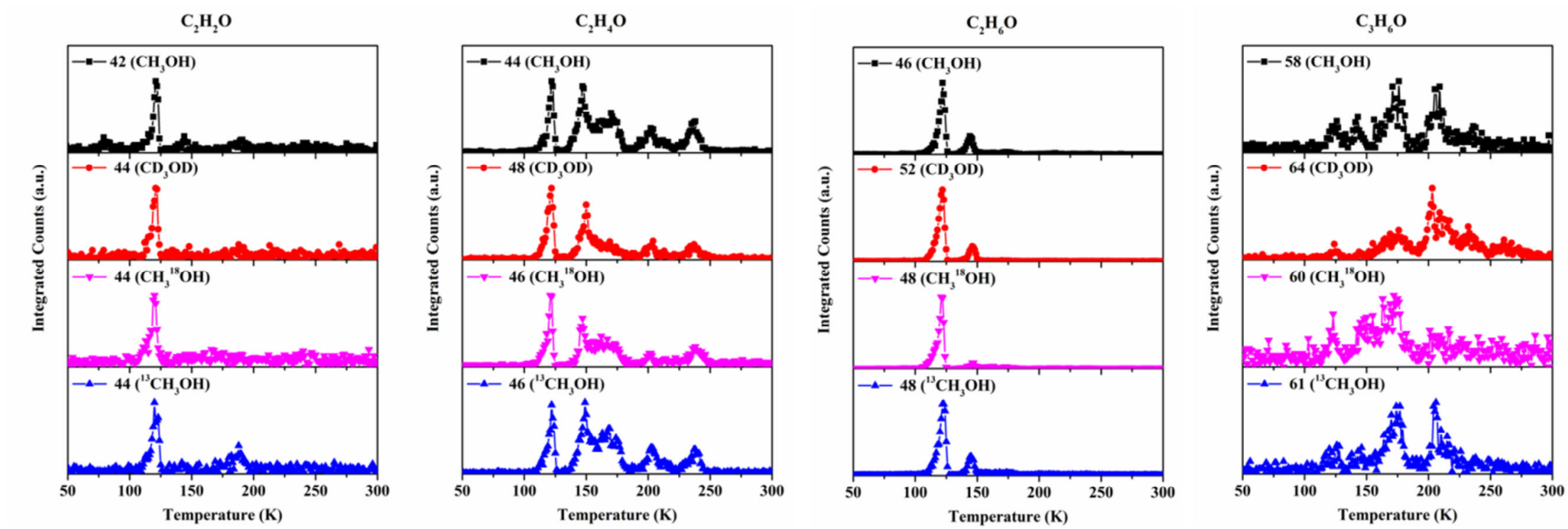


Figure S2. Sublimation profiles recorded using ReTOF mass spectrometer at the mass-to-charge ratios correspond to the isotopomer of the products C_2H_4O, C_2H_4O, C_2H_6O and C_3H_6O observed in irradiated methanol ices (CH_3OH, CD_3OD, $CH_3{}^{18}OH$ and ${}^{13}CH_3OH$).

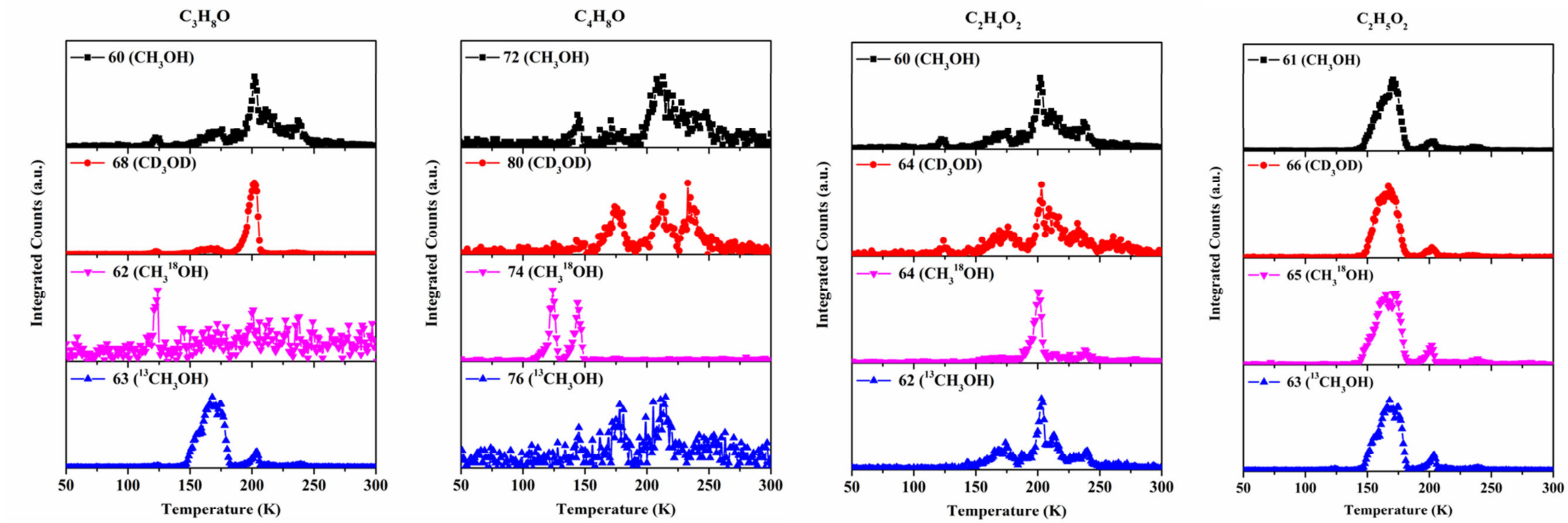


Figure S3. Sublimation profiles recorded using ReTOF mass spectrometer at the mass-to-charge ratios correspond to the isotopomer of the products C_3H_8O, C_4H_8O, $C_2H_4O_2$ and $C_2H_5O_2$ observed in irradiated methanol ices (CH_3OH, CD_3OD, $CH_3{}^{18}OH$ and $^{13}CH_3OH$).

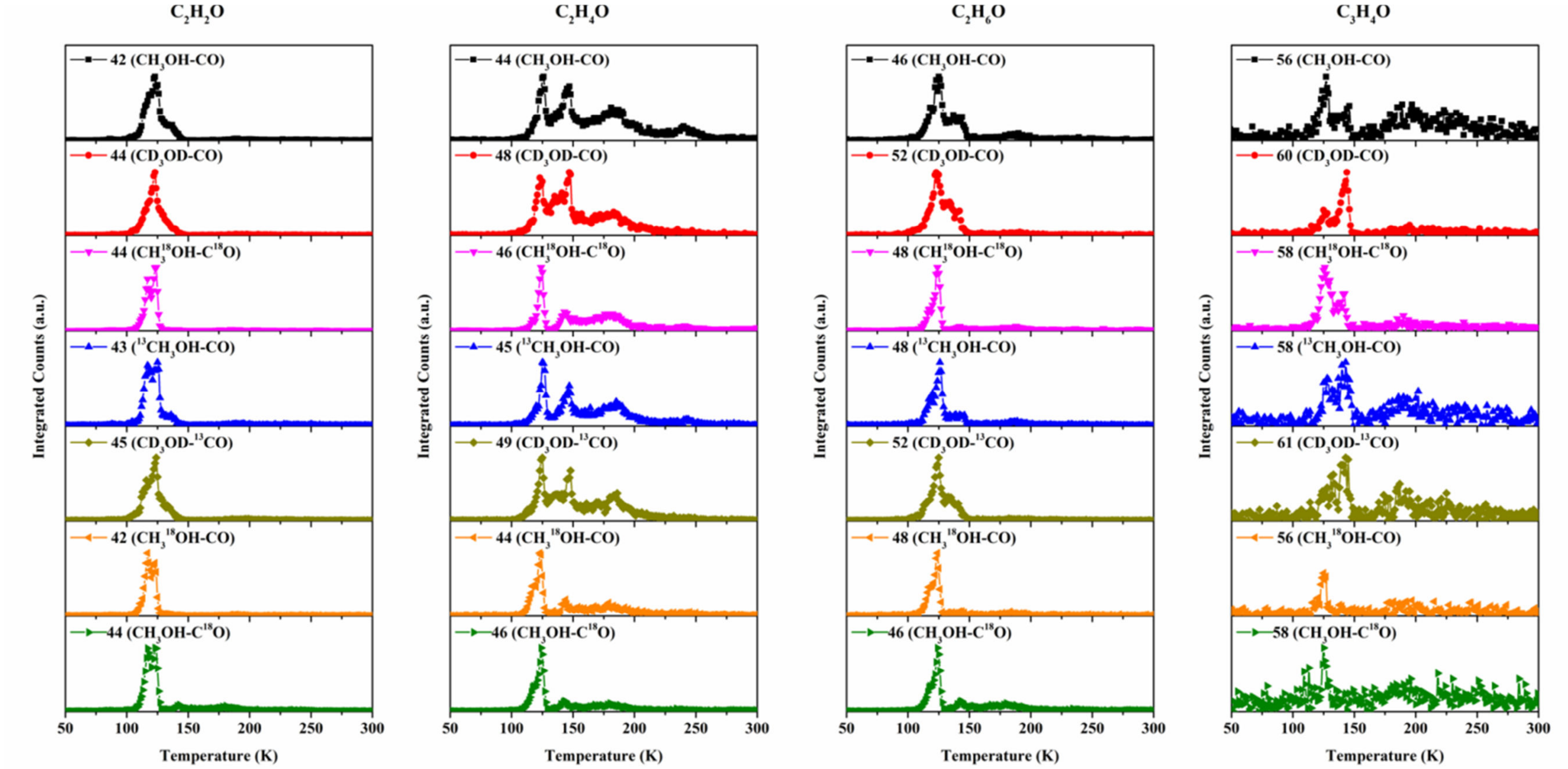


Figure S4. Sublimation profiles recorded using ReTOF mass spectrometer at the mass-to-charge ratios correspond to the isotopomer of the products C_2H_2O, C_2H_4O, C_2H_6O and C_3H_4O observed in irradiated methanol-carbon monoxide ices (CH_3OH-CO, CD_3OD-CO, $CH_3{}^{18}OH$-$C^{18}O$, $^{13}CH_3OH$-CO, CD_3OD-^{13}CO, $CH_3{}^{18}OH$-CO, CH_3OH-$C^{18}O$).

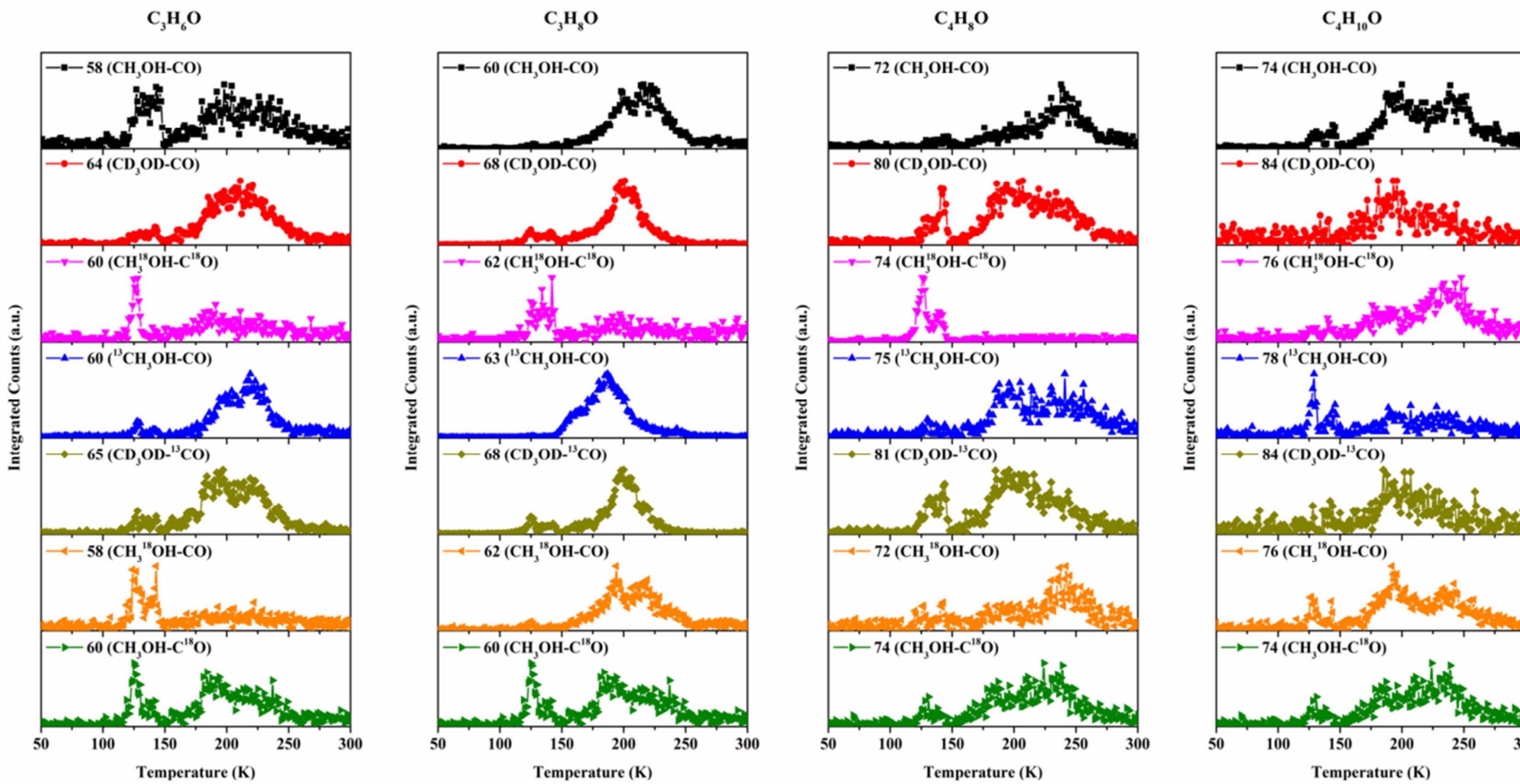


Figure S5. Sublimation profiles recorded using ReTOF mass spectrometer at the mass-to-charge ratios correspond to the isotopomer of the products C_3H_6O, C_3H_8O, C_4H_8O and $C_4H_{10}O$ observed in irradiated methanol-carbon monoxide ices (CH_3OH-CO, CD_3OD-CO, $CH_3{}^{18}OH$-$C^{18}O$, $^{13}CH_3OH$-CO, CD_3OD-^{13}CO, $CH_3{}^{18}OH$-CO, CH_3OH-$C^{18}O$).

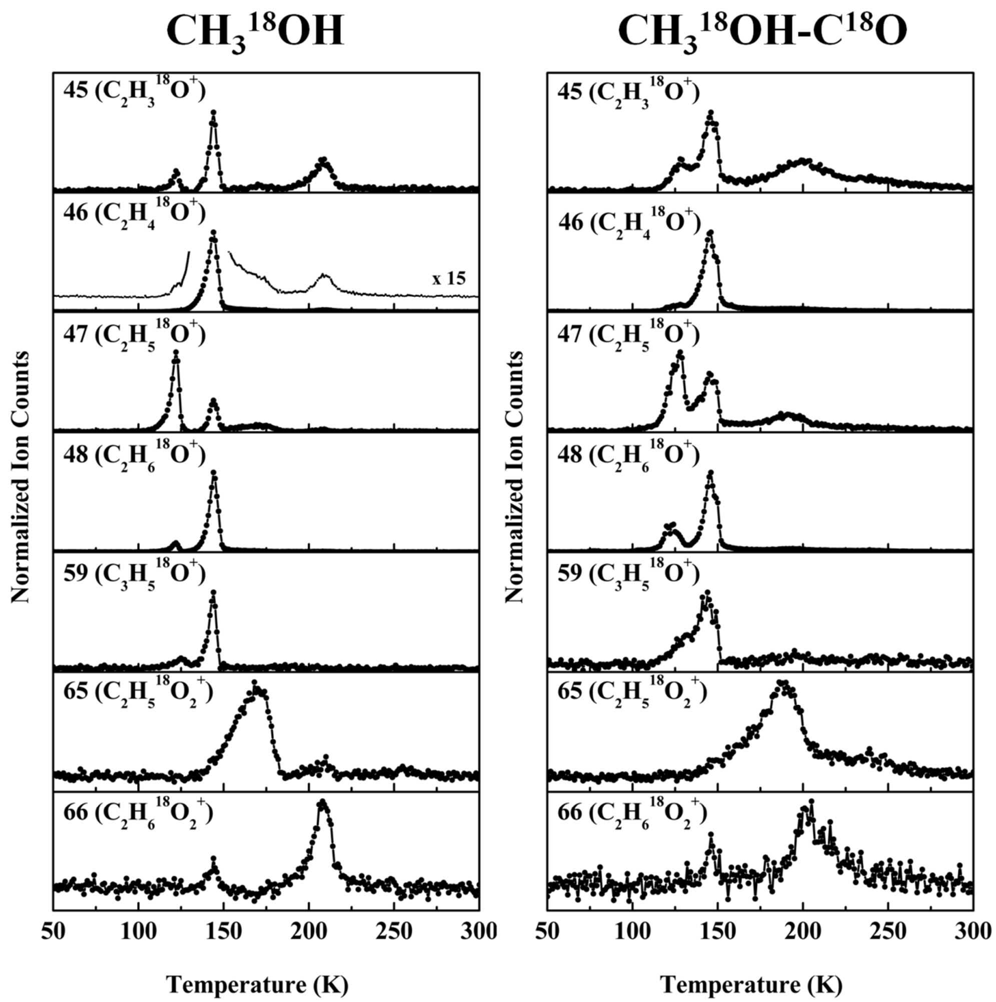


Figure S6. Sublimation profiles recorded using quadrupole mass spectrometer (QMS) at the mass-to-charge ratios correspond to $C_2H_3{}^{18}O^+$, $C_2H_4{}^{18}O^+$, $C_2H_5{}^{18}O^+$, $C_2H_6{}^{18}O^+$, $C_3H_5{}^{18}O^+$, $C_2H_5{}^{18}O_2{}^+$ and $C_2H_6{}^{18}O_2{}^+$ observed in irradiated $CH_3{}^{18}OH$ and $CH_3{}^{18}OH$-$C^{18}O$ ices.

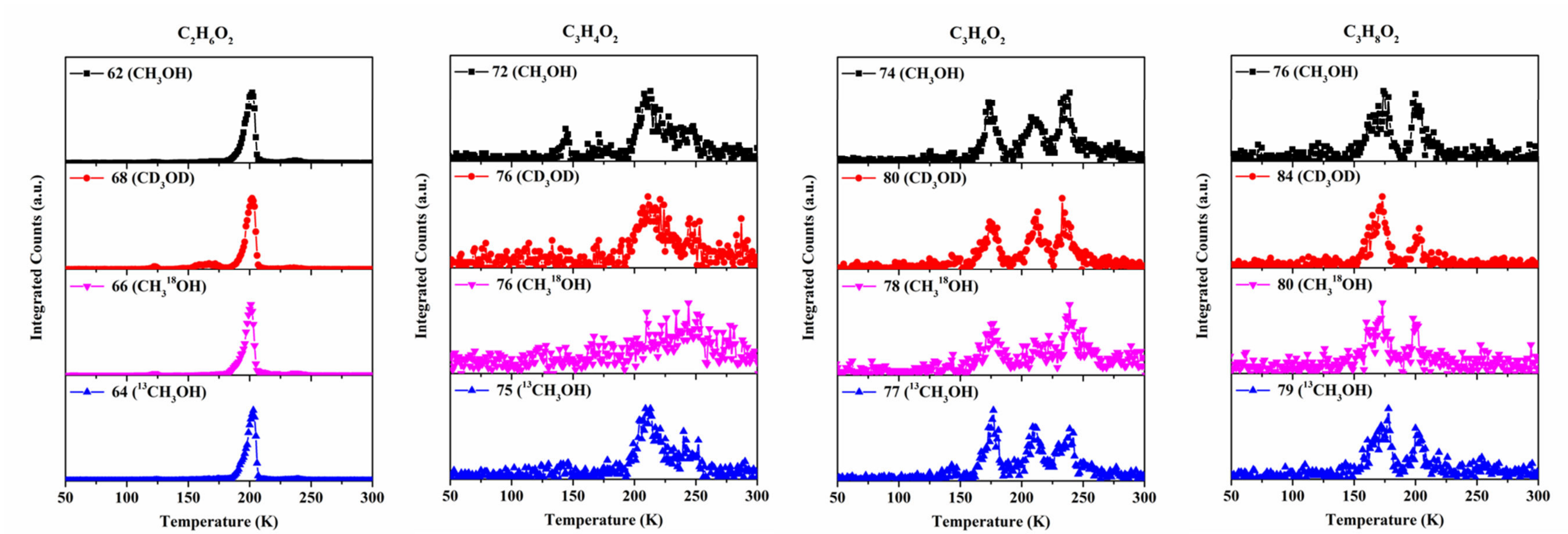


Figure S7. Sublimation profiles recorded using ReTOF mass spectrometer at the mass-to-charge ratios correspond to the isotopomer of the products $C_2H_6O_2$, $C_3H_4O_2$, $C_3H_6O_2$ and $C_3H_8O_2$ observed in irradiated methanol ices (CH_3OH, CD_3OD, $CH_3{}^{18}OH$ and $^{13}CH_3OH$).

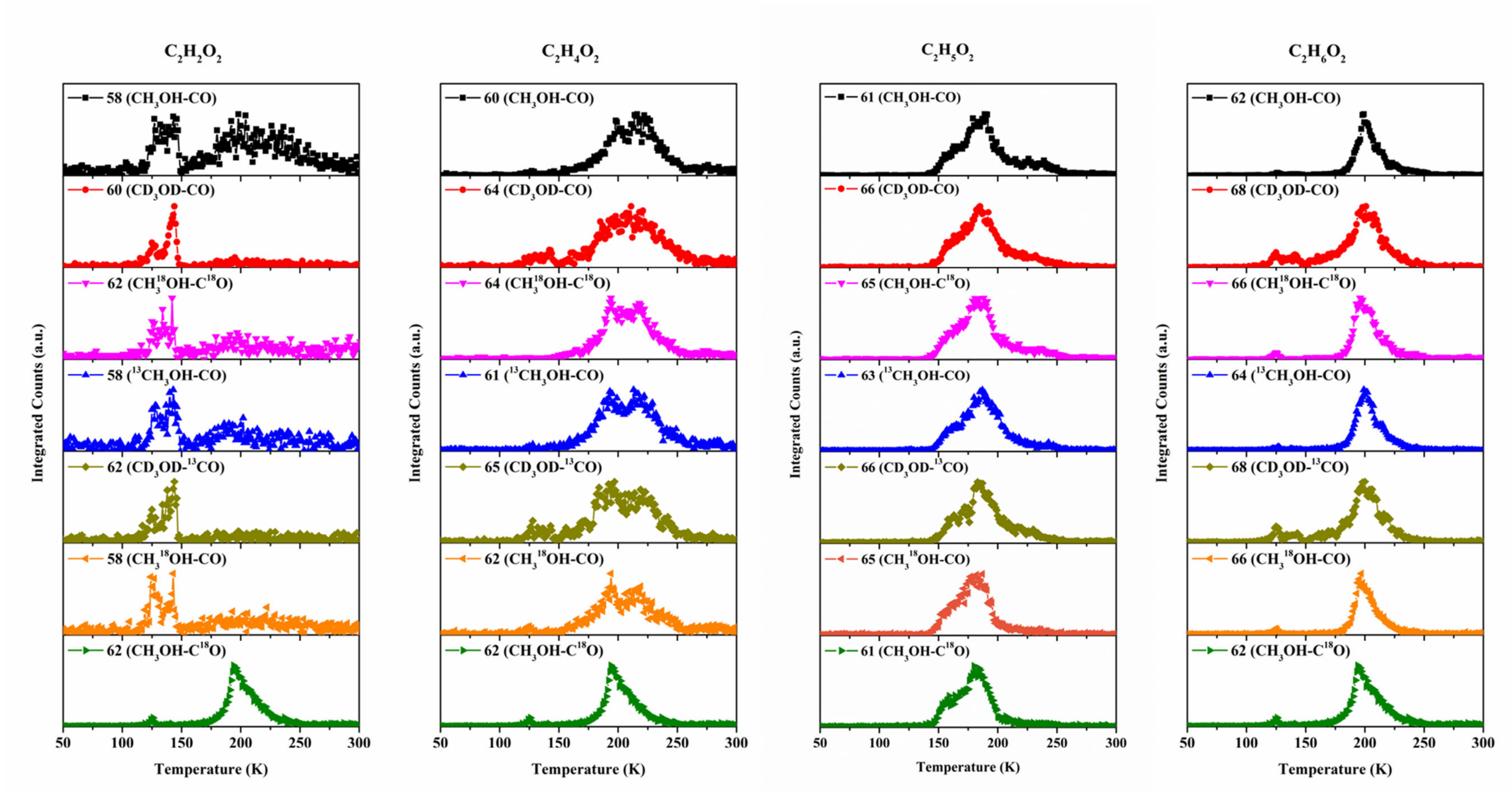


Figure S8. Sublimation profiles recorded using ReTOF mass spectrometer at the mass-to-charge ratios correspond to the isotopomer of the products $C_2H_2O_2$, $C_2H_4O_2$, $C_2H_5O_2$ and $C_2H_6O_2$ observed in irradiated methanol-carbon monoxide ices (CH_3OH-CO, CD_3OD-CO, $CH_3{}^{18}OH$-$C^{18}O$, $^{13}CH_3OH$-CO, CD_3OD-^{13}CO, $CH_3{}^{18}OH$-CO, CH_3OH-$C^{18}O$).

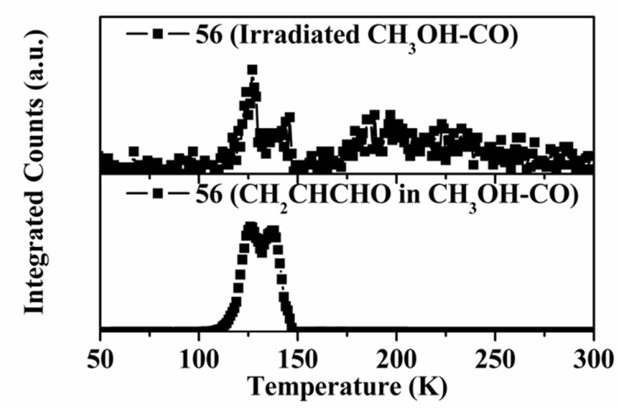


Figure S9. Sublimation profiles of the calibration samples containing C_3H_4O isomer [Propenal; m/z = 56 amu] in CH_3OH-CO (4:5) (Sample 10) ices is compared with the sublimation profiles of m/z = 56 amu recorded in irradiated CH_3OH-CO (4:5) ices.

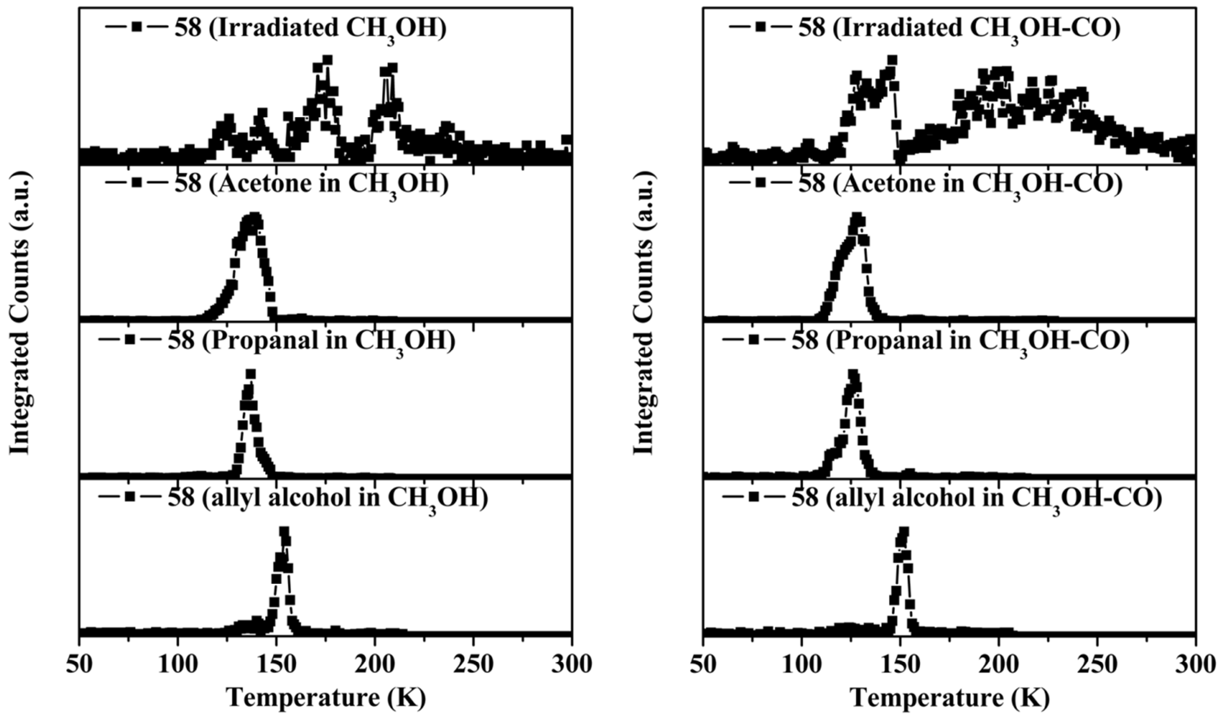


Figure S10. Sublimation profiles of the calibration samples containing C_3H_6O isomers [Acetone (CH_3COCH_3), Propanal (CH_3CH_2CHO) and allyl alcohol (CH_2CHCH_2OH); m/z = 58 amu] in (left) CH_3OH (Samples 1, 3 and 5) and (right) CH_3OH-CO (4:5) (Samples 2, 4 and 6) ices are compared with the sublimation profiles of m/z = 58 amu recorded in irradiated CH_3OH and CH_3OH-CO (4:5) ices.

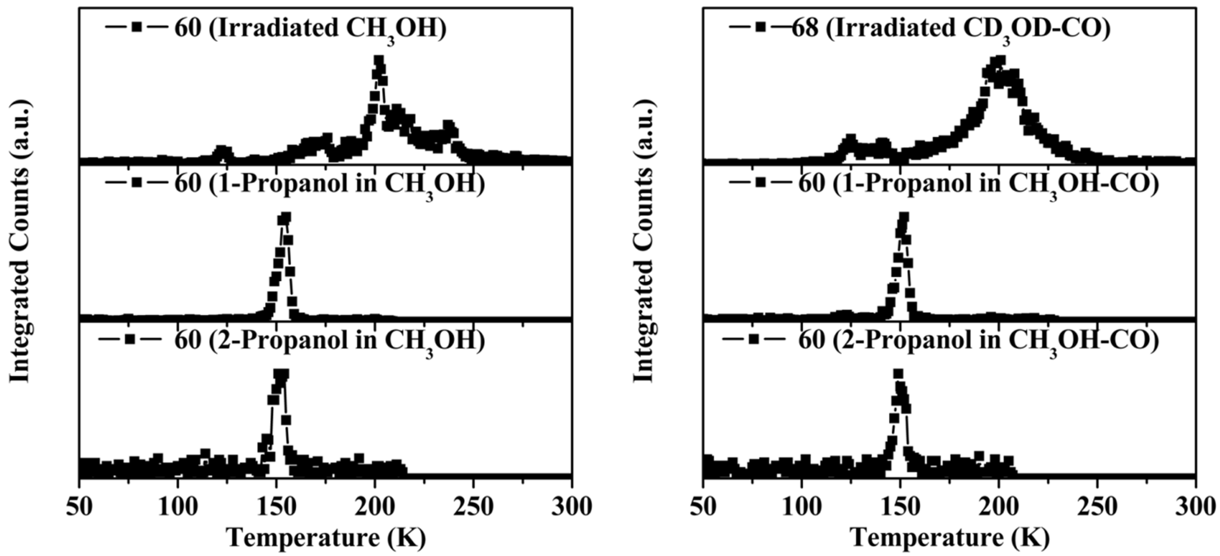


Figure S11. Sublimation profiles of the calibration samples containing C_3H_8O isomers [1-propanol ($CH_3CH_2CH_2OH$) and 2-propanol($CH_3CH(OH)CH_3$); m/z = 60 amu] in (left) CH_3OH (Samples 1 and 5) and (right) CH_3OH-CO (4:5) (Samples 2 and 6) ices are compared with the sublimation profiles of m/z = 60 amu recorded in irradiated CH_3OH and m/z = 68 amu recorded in irradiated CD_3OD-CO (4:5) ices.

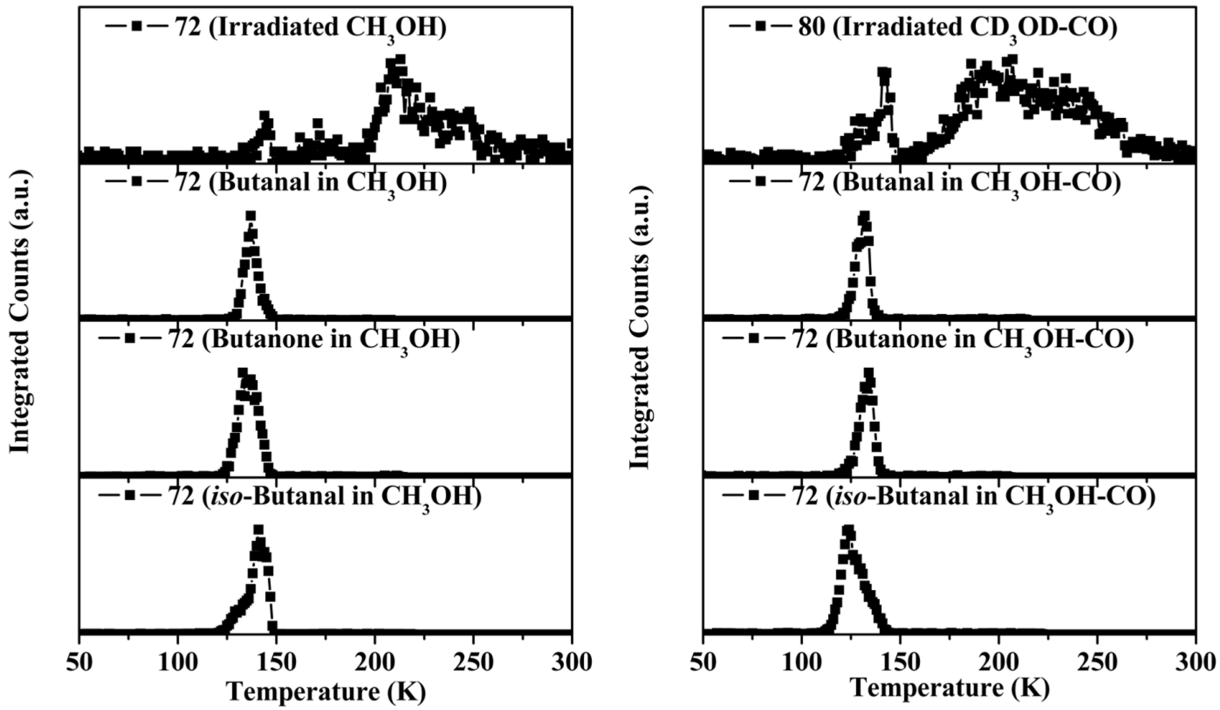


Figure S12. Sublimation profiles of the calibration samples containing C_4H_8O isomers [Butanal ($CH_3CH_2CH_2CHO$), Butanone ($CH_3CH_2COCH_3$) and *iso*-Butanal ($(CH_3)_2CHCHO$); m/z = 72 amu] in (left) CH_3OH (Samples 3, 5 and 7) and (right) CH_3OH-CO (4:5) (Samples 4, 6 and 8) ices are compared with the sublimation profiles of m/z = 72 amu recorded in irradiated CH_3OH and m/z = 80 in CD_3OD-CO (4:5) ices.

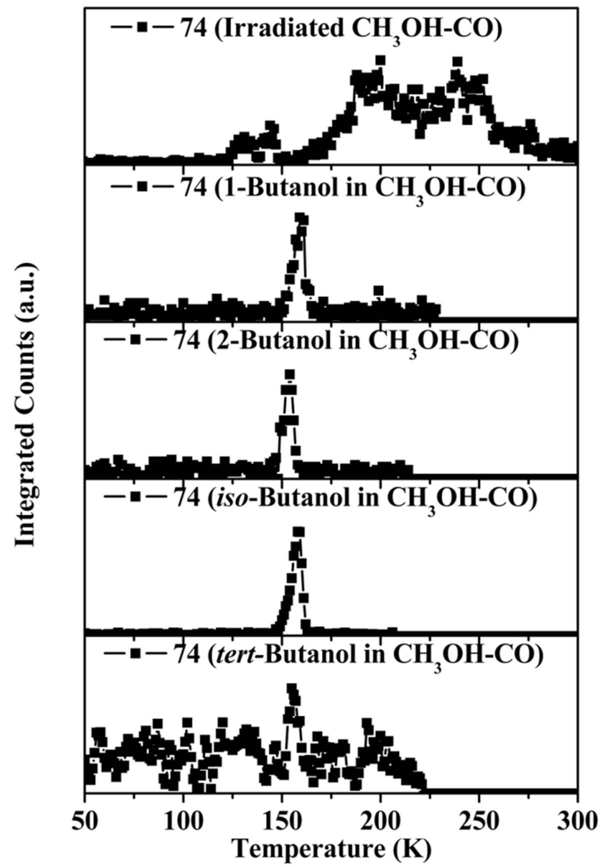


Figure S13. Sublimation profiles of the calibration samples containing $C_4H_{10}O$ isomers [1-Butanol ($CH_3CH_2CH_2CH_2OH$), 2-Butanol($CH_3CH(OH)CH_2CH_3$), *iso*-Butanol ($(CH_3)_2CHCH_2OH$) and *tert*-Butanol ($(CH_3)_3COH$); m/z = 74 amu] in CH_3OH-CO (4:5) (Samples 2, 4, 6 and 8) ices are compared with the sublimation profiles of m/z = 74 amu recorded in irradiated CD_3OD-CO (4:5) ices.

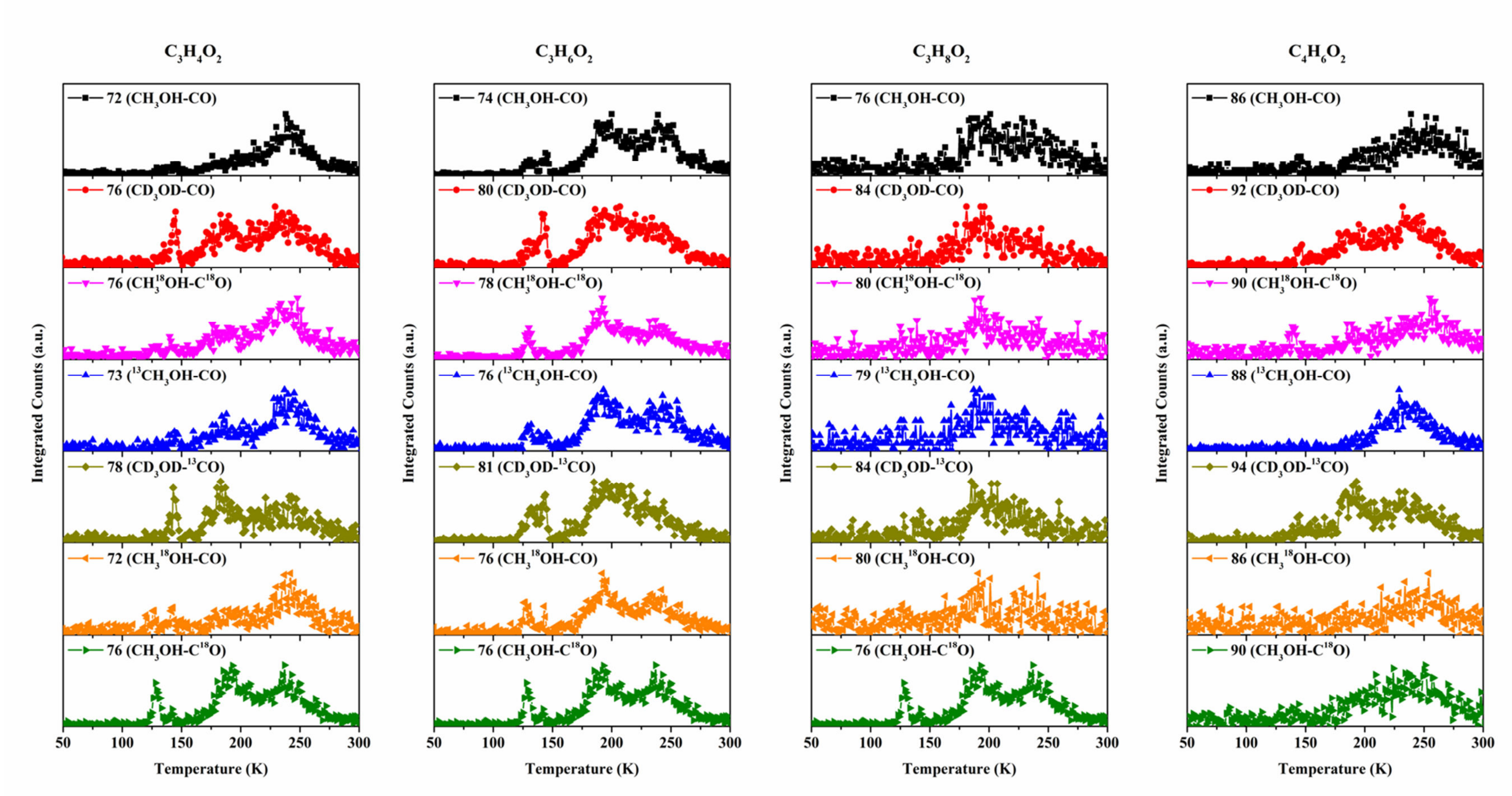


Figure S14. Sublimation profiles recorded using ReTOF mass spectrometer at the mass-to-charge ratios correspond to the isotopomer of the products $C_3H_4O_2$, $C_3H_6O_2$, $C_3H_8O_2$ and $C_4H_6O_2$ observed in irradiated methanol-carbon monoxide ices (CH_3OH-CO, CD_3OD-CO, $CH_3{}^{18}OH$-$C^{18}O$, $^{13}CH_3OH$-CO, CD_3OD-^{13}CO, $CH_3{}^{18}OH$-CO, CH_3OH-$C^{18}O$).

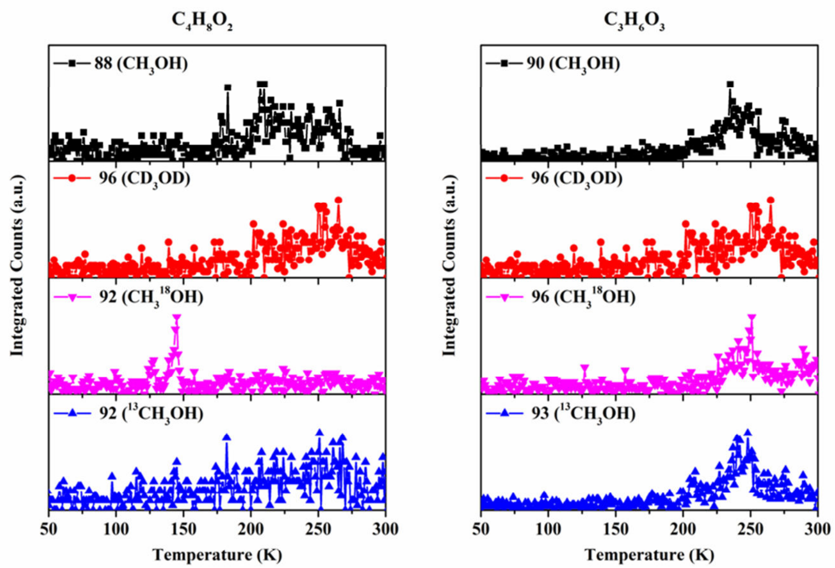


Figure S15. Sublimation profiles recorded using ReTOF mass spectrometer at the mass-to-charge ratios correspond to the isotopomer of the products $C_4H_8O_2$ and $C_3H_6O_3$ observed in irradiated methanol ices (CH_3OH, CD_3OD, $CH_3{}^{18}OH$ and $^{13}CH_3OH$).

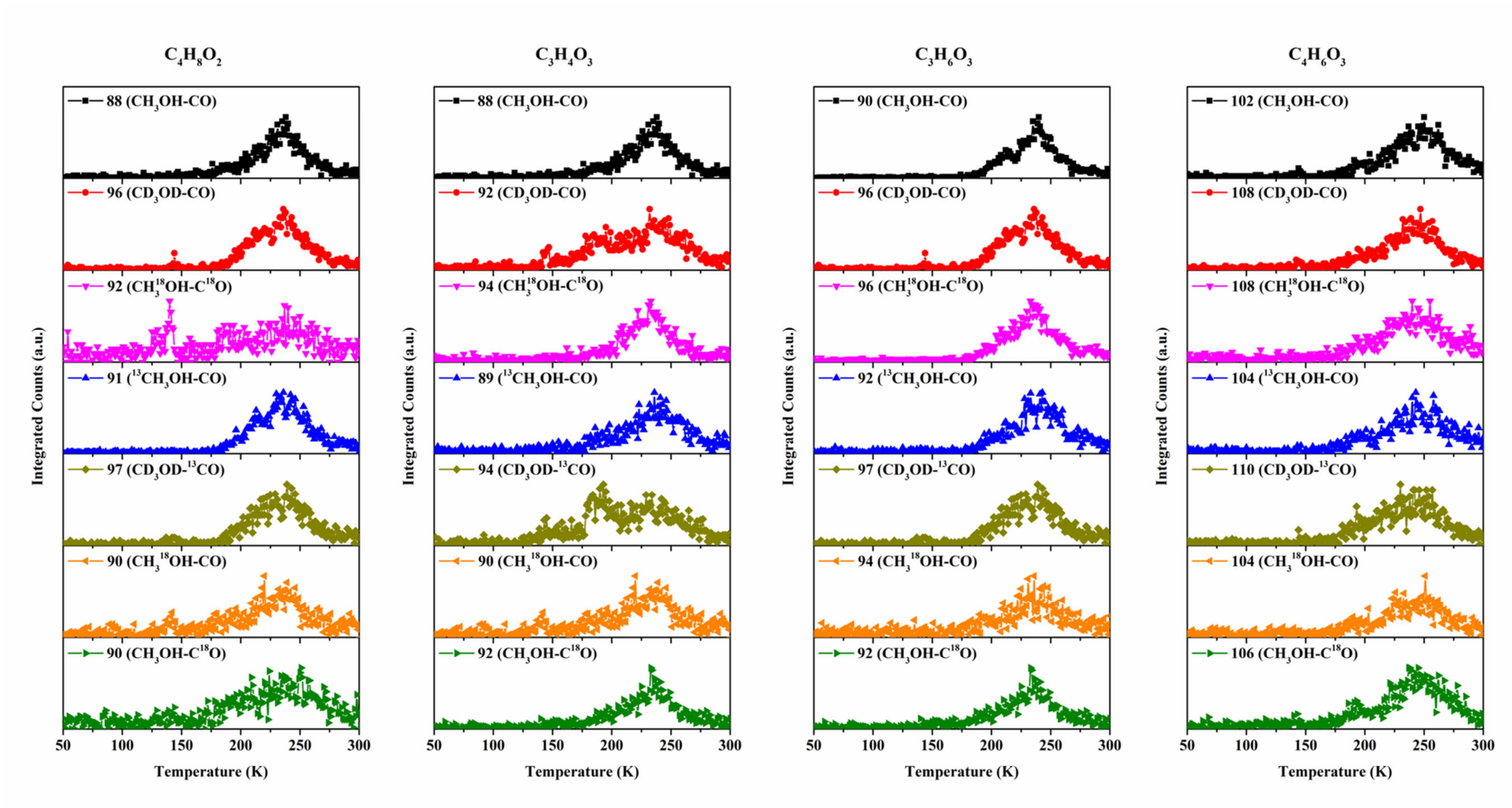


Figure S16. Sublimation profiles recorded using ReTOF mass spectrometer at the mass-to-charge ratios correspond to the isotopomer of the products $C_4H_8O_2$, $C_3H_4O_3$, $C_3H_6O_3$ and $C_4H_6O_3$ observed in irradiated methanol-carbon monoxide ices (CH_3OH-CO, CD_3OD-CO, $CH_3{}^{18}OH$-$C^{18}O$, $^{13}CH_3OH$-CO, CD_3OD-^{13}CO, $CH_3{}^{18}OH$-CO, CH_3OH-$C^{18}O$).

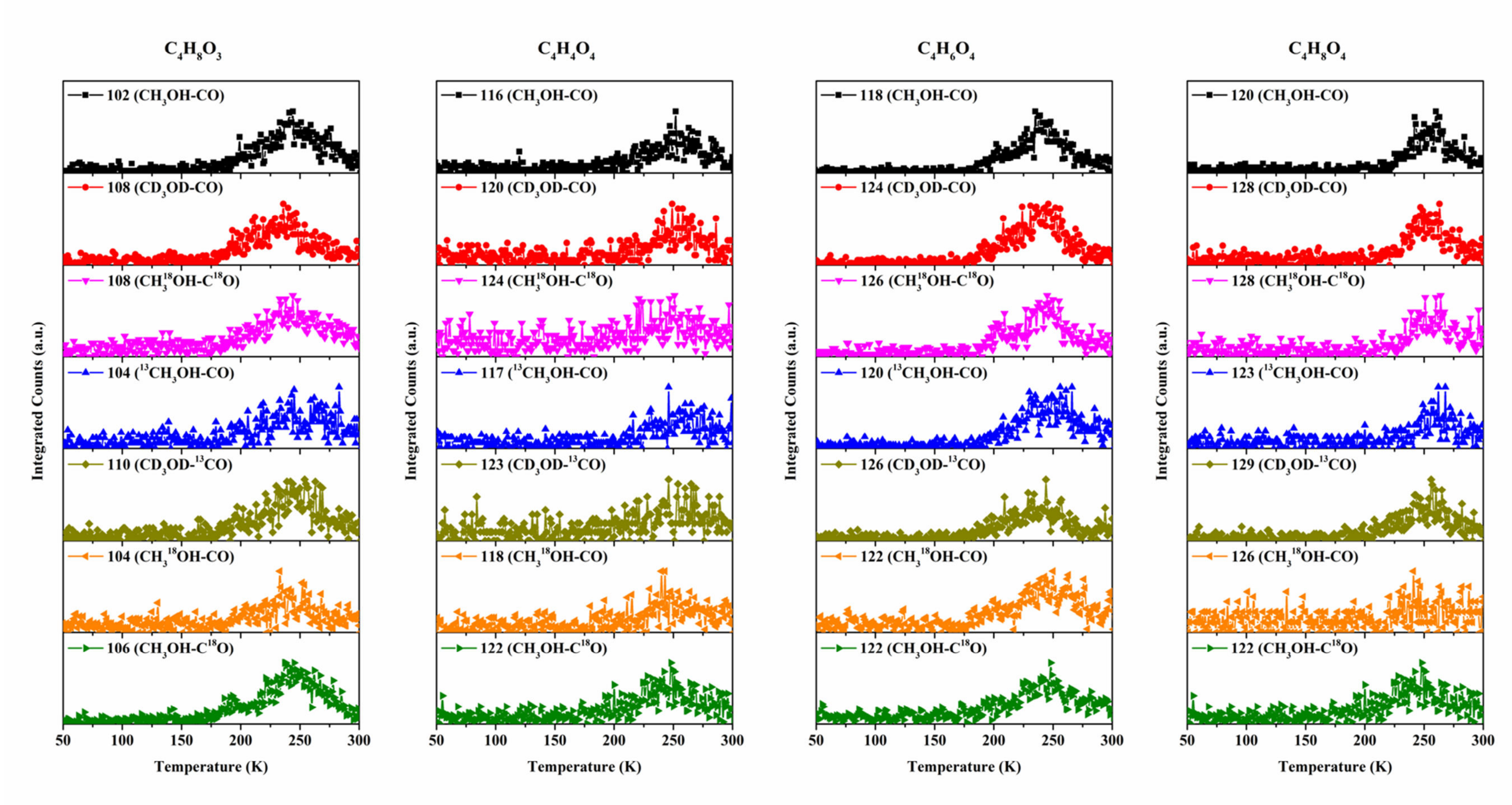


Figure S17. Sublimation profiles recorded using ReTOF mass spectrometer at the mass-to-charge ratios correspond to the isotopomer of the products $C_4H_8O_3$, $C_4H_4O_4$, $C_4H_6O_4$ and $C_4H_8O_4$ observed in irradiated methanol-carbon monoxide ices (CH_3OH-CO, CD_3OD-CO, $CH_3{}^{18}OH$-$C^{18}O$, $^{13}CH_3OH$-CO, CD_3OD-^{13}CO, $CH_3{}^{18}OH$-CO, CH_3OH-$C^{18}O$).

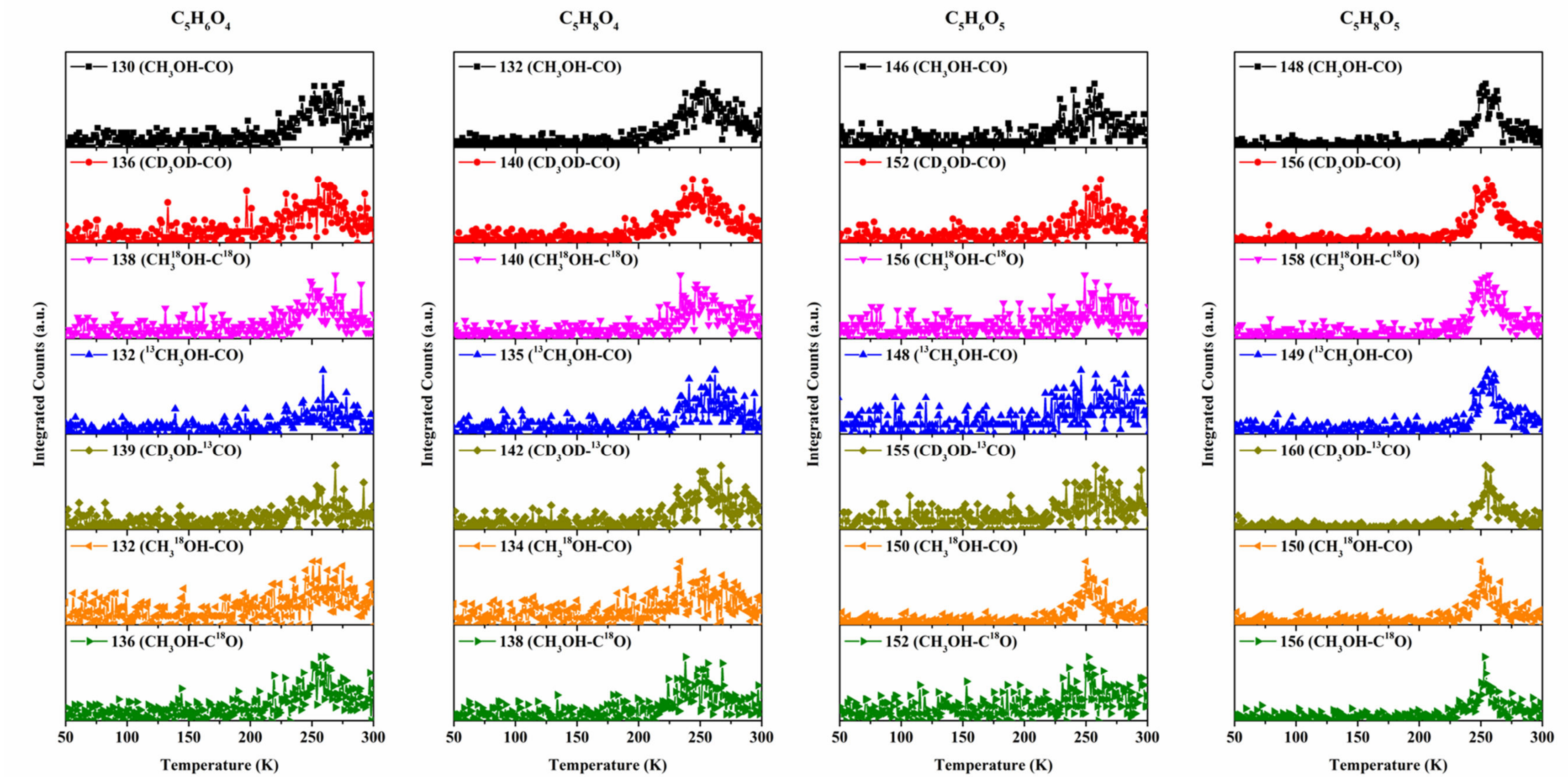
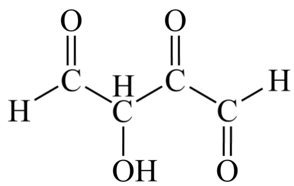
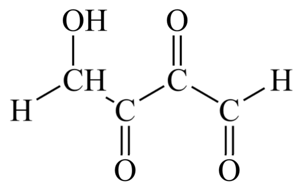


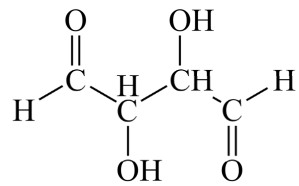
Figure S18. Sublimation profiles recorded using ReTOF mass spectrometer at the mass-to-charge ratios correspond to the isotopomer of the products $C_5H_6O_4$, $C_5H_8O_4$, $C_5H_6O_5$ and $C_5H_8O_5$ observed in irradiated methanol-carbon monoxide ices (CH_3OH-CO, CD_3OD-CO, $CH_3{}^{18}OH$-$C^{18}O$, $^{13}CH_3OH$-CO, CD_3OD-^{13}CO, $CH_3{}^{18}OH$-CO, CH_3OH-$C^{18}O$).



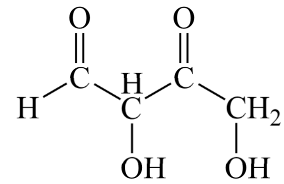
3-Hydroxy-
2-oxosuccinaldehyde



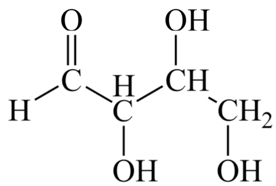
4-Hydroxy-
2,3-dioxobutyraldehyde



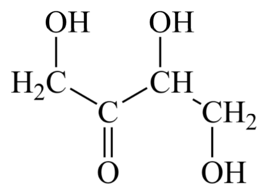
2,3-Dihydroxy
succinaldehyde



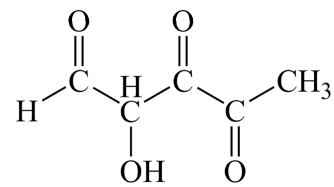
2,4-Dihydroxy-
3-oxobutanal



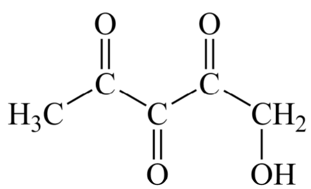
2,3,4-Trihydroxybutanal



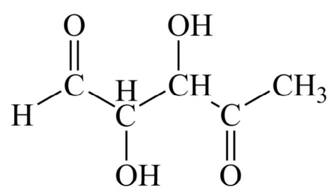
1,3,4-Trihydroxybutan-2-one



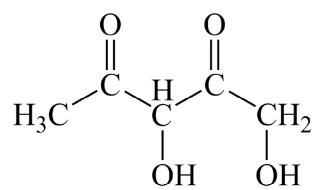
2-Hydroxy-3,4-dioxopentanal



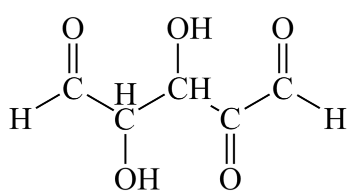
1-Hydroxypentane-2,3,4-trione



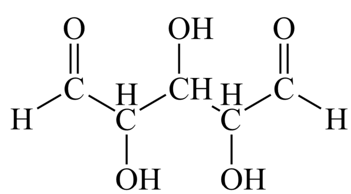
2,3-Dihydroxy-4-oxopentanal



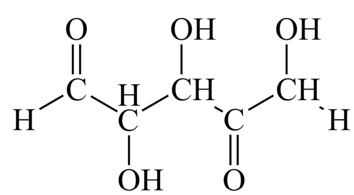
1,3-Dihydroxypentane-2,4-dione



2,3-Dihydroxy-4-oxopentanedial

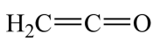


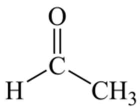
2,3,4-Trihydroxypentanedial

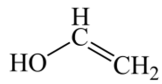


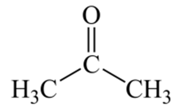
2,3,5-Trihydroxy-4-oxopentanal

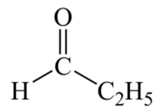
Figure S19. Chemical structures of the selected isomers of products with four and five oxygen atoms.

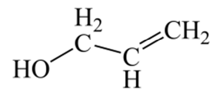

Ketene
9.6 eV

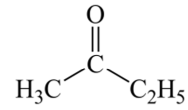

Acetaldehyde
10.2 eV

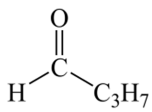

Vinyl Alcohol
9.3 eV

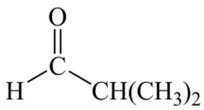

Acetone
9.7 eV

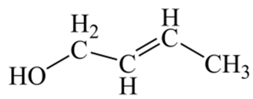

Propanal
10.0 eV

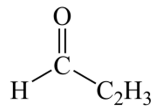

Allyl Alcohol
9.7 eV

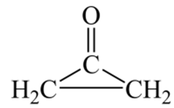

Butanone
9.3 eV

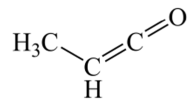

Butanal
9.8 eV

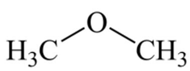

iso-Butanal
9.7 eV

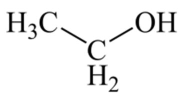

2-Buten-1-ol
9.1 eV

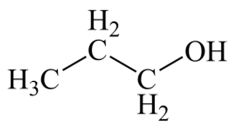

Propenal
10.1 eV

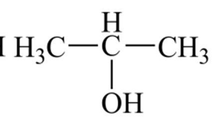

Cyclopropanone
9.1 eV

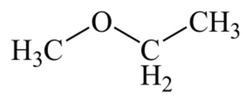

Methyl ketene
8.95 eV

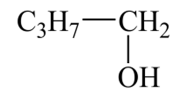

Methoxymethane
10.0 eV

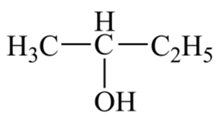

Ethanol
10.48 eV

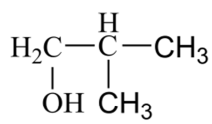

1-Propanol
10.2 eV

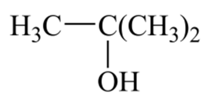

2-Propanol
10.2 eV

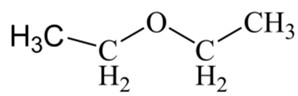

Methoxyethane
9.7 eV

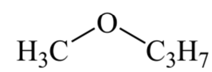

1-Butanol
10.0 eV

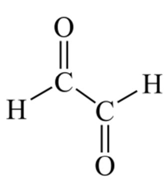

2-Butanol
9.9 eV

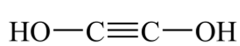

iso-Butanol
10.0 eV

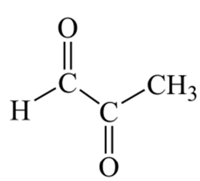

tert-Butanol
9.9 eV

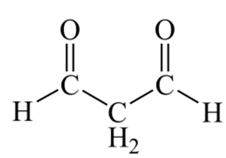

Ethoxyethane

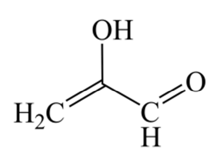

Methoxypropane

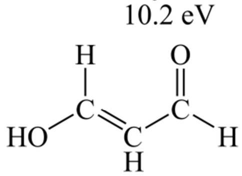

Glyoxal
10.2 eV

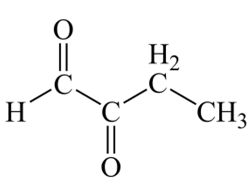

Ethyne-1,2-diol
9.3 eV

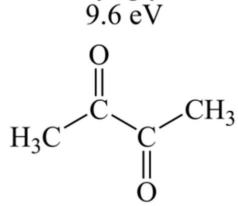

Methyl glyoxal
9.6 eV

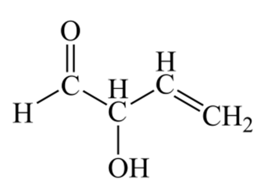

1,3-Propanedial

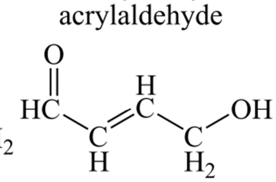

2-Hydroxy
acrylaldehyde


3-Hydroxy
acrylaldehyde


2-oxobutanal


Butane-2,3-dione
9.3 eV


2-hydroxybut-3-enal


4-Hydroxybut-
2-enal

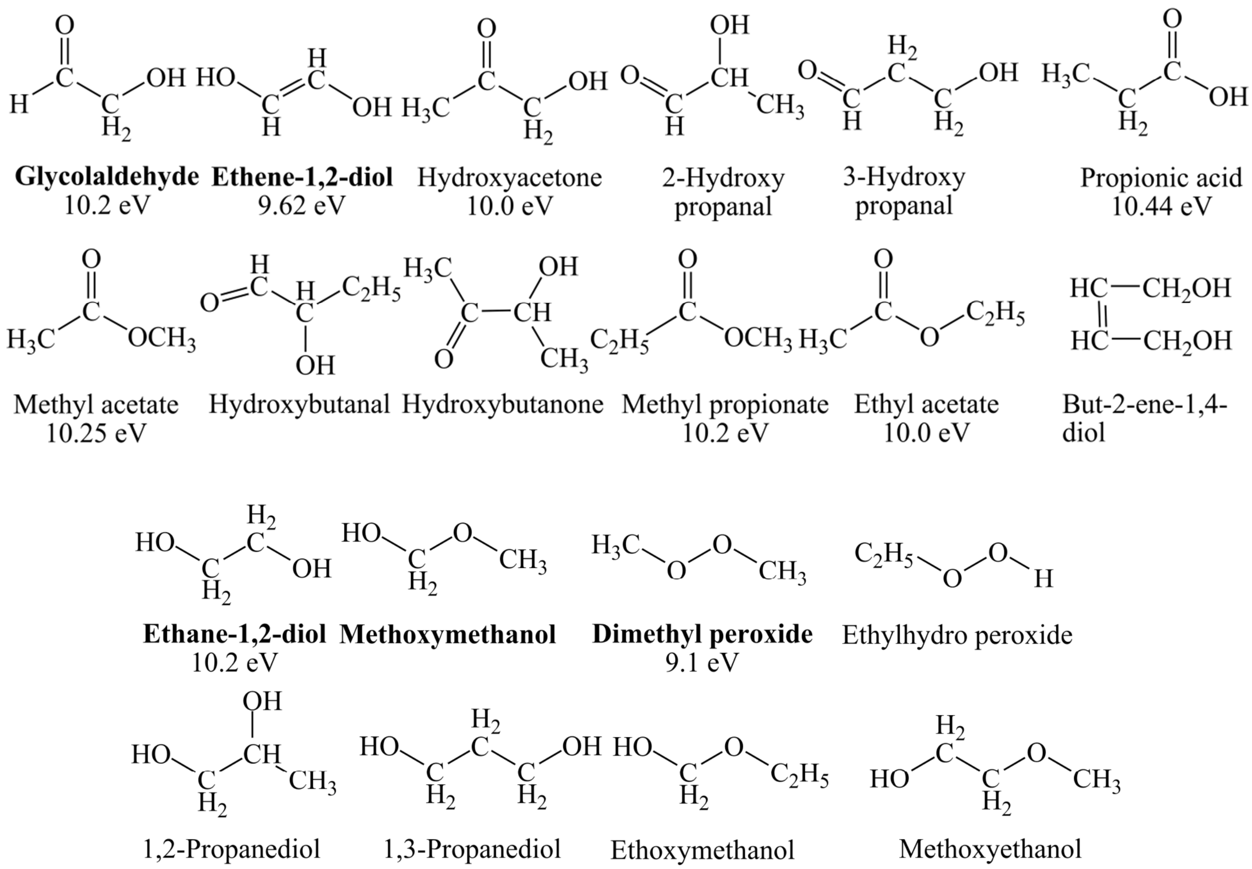


Figure S20. Summary of molecular formula observed in this study and their corresponding chemical structures with identified molecules are marked in bold.

References:

1 J. M. Hollis, P. R. Jewell, F. J. Lovas, A. Remijan and H. Mollendal, *The Astrophysical Journal Letters*, 2004, **610**, L21.
2 W. M. Irvine, *Astrophys. J.*, 1988, **335**, L89-L93.
3 M. A. Requena-Torres, J. Martín-Pintado, S. Martín and M. R. Morris, *Astrophys. J.*, 2008, **672**, 352.
4 J. M. Hollis, F. J. Lovas, A. J. Remijan, P. R. Jewell, V. V. Ilyushin and I. Kleiner, *Astrophys. J.*, 2006, **643**, L25-L28.
5 J. M. Hollis, A. J. Remijan, P. R. Jewell and F. J. Lovas, *Astrophys. J.*, 2006, **642**, 933.
6 A. Belloche, H. S. P. Muller, K. M. Menten, P. Schilke and C. Comito, *Astronomy and Astrophysics*, 2013, **559**, 47.
7 H. E. Matthews, Friberg, P., & Irvine, W. M., *ApJ*, 1985, **290**, 609.
8 J. N. Chengalur and N. Kanekar, *Astronomy and Astrophysics*, 2003, **403**, L43-L46.
9 J. E. Dickens, Irvine, W. M., Ohishi, M., Ikeda, M., Ishikawa, S., Nummelin, A., Hjalmarson, A. , *ApJ*, 1997, **489**, 753.
10 B. E. Turner and A. J. Apponi, *Astrophys. J.*, 2001, **561**, L207-L210.
11 R. D. Brown, J. G. Crofts, P. D. Godfrey, F. F. Gardner, B. J. Robinson and J. B. Whiteoak, *Astrophys. J.*, 1975, **197**, L29-L31.
12 M. A. Requena-Torres, J. Martin-Pintado, A. Rodriguez-Franco, S. Martin, N. J. Rodrmguez-Fernandez and P. De Vicente, *Astronomy and Astrophysics*, 2006, **455**, 971-985.
13 D. M. Mehringer, L. E. Snyder, Y. Miao and F. J. Lovas, *The Astrophysical Journal Letters*, 1997, **480**, L71.
14 D. T. Halfen, A. J. Apponi, N. Woolf, R. Polt and L. M. Ziurys, *Astrophys. J.*, 2006, **639**, 237-245.
15 B. Zuckerman, B. E. Turner, D. R. Johnson, F. J. Lovas, N. Fourikis, P. Palmer, M. Morris, A. E. Lilley, J. A. Ball and F. O. Clark, *Astrophys. J.*, 1975, **196**, L99-L102.
16 L. E. Snyder, F. J. Lovas, D. M. Mehringer, N. Y. Miao, Y.-J. Kuan, J. M. Hollis and P. R. Jewell, *Astrophys. J.*, 2002, **578**, 245.
17 J. M. Hollis, F. J. Lovas, P. R. Jewell and L. H. Coudert, *The Astrophysical Journal Letters*, 2002, **571**, L59-L62.
18 A. Belloche, R. T. Garrod, H. S. P. Muller, K. M. Menten, C. Comito and P. Schilke, *A&A*, 2009, **499**, 215-232.
19 B. Tercero, I. Kleiner, J. Cernicharo, H. V. L. Nguyen, A. Lopez and G. M. M. Caro, *The Astrophysical Journal Letters*, **770**, L13.
20 U. Fuchs, G. Winnewisser, P. Groner, F. C. De Lucia and E. Herbst, *The Astrophysical Journal Supplement Series*, 2003, **144**, 277.