

## Table of Contents

Results and Discussion: TPD measurements of unirradiated ices (pg. 2)

Results and Discussion: Ratio determination for D<sub>2</sub>O + CH<sub>3</sub>CHO ice (pg. 2)

Results and Discussion: Formation of acetaldehyde clusters (pg. 3)

Results and Discussion: Formation of Acetone (pg. 3-4)

Table S1 (pg. 4)

Table S2 (pg. 5)

Table S3 (pg. 6)

Table S4 (pg. 7)

Table S5 (pg. 8)

Table S6 (pg. 9)

Table S7 (pg. 10)

Table S8 (pg. 11)

Table S9 (pg. 11)

Figure S1 (pg. 12)

Figure S2 (pg. 12)

Figure S3 (pg. 13)

Figure S4 (pg. 14)

Figure S5 (pg. 14)

Figure S6 (pg. 15)

Figure S7 (pg. 15)

Figure S8 (pg. 16)

B3LYP/aug-cc-pVTZ Cartesian coordinates (in Å) for the molecules analyzed. (pg. 17-31)

B3LYP/aug-cc-pVTZ harmonic frequencies (in cm<sup>-1</sup>) for the molecules analyzed. (pg. 31-42)

References (pg. 43)

## PI ReToF-MS TPD measurements of unirradiated ices

To elucidate the reaction product(s), the TPD experiments were first conducted with unprocessed acetaldehyde and acetaldehyde-2,2,2-d<sub>3</sub> ices at a photon energy of 10.49 eV (Fig. S3). As acetaldehyde polymerizes at low temperatures, these experiments are necessary to probe potential (protonated) acetaldehyde clusters as well as other impurities of the acetaldehyde. Fig. S3 shows the desorption profiles of mass-to-charge ratios between 40 and 200 for temperatures ranging from 80 K to 320 K for these measurements. While the main impurity of acetaldehyde-d<sub>4</sub> is found at a mass-to-charge ratio of 64, most probably corresponding to a C<sub>2</sub>D<sub>4</sub>O<sub>2</sub> isomer, the only impurity all three samples have in common is found at mass-to-charge ratios of 117, 123, and 126 for CH<sub>3</sub>CHO, CD<sub>3</sub>CHO, and CD<sub>3</sub>CDO ices, respectively. These different masses indicate the empirical formula of the impurity to be C<sub>5</sub>H<sub>9</sub>O<sub>3</sub> (C<sub>5</sub>D<sub>6</sub>H<sub>3</sub>O<sub>3</sub> for acetaldehyde-2,2,2-d<sub>3</sub>), which points to a protonated cluster, e.g. of methylglyoxal (CD<sub>3</sub>COCHO) and acetaldehyde. Otherwise, no notable signals appear in the TPD profiles.

## Ratio determination for D<sub>2</sub>O + CH<sub>3</sub>CHO ice

Deuterium oxide and the acetaldehyde isotopologues were condensed onto the silver substrate through two separate gas deposition arms with partial pressures amounting to  $3 \times 10^{-8}$  Torr and  $3 \times 10^{-9}$  Torr for deuterium oxide and acetaldehyde, respectively. The thickness of the ice was determined to be  $950 \pm 50$  nm by laser interference measurements. To determine the ratio of constituents in the ice, the integrated absorption of each acetaldehyde IR absorption feature shown in Fig. S6 was compared to that of the 500 nm thick neat acetaldehyde ice to determine the column density and corresponding thickness of the acetaldehyde in the ice. In this analysis the absorption peak at  $1720 \text{ cm}^{-1}$  was neglected as it changed drastically in shape in the mixed ice and its evaluation lead to a thickness more than twice of that derived from any other absorption feature. This analysis lead to a thickness of  $220 \pm 30$  nm for acetaldehyde and correspondingly  $730 \pm 60$  nm for deuterium oxide. Assuming densities of  $0.78 \text{ g cm}^{-3}$  and  $1.05 \text{ g cm}^{-3}$  for acetaldehyde and deuterium oxide, respectively, this translates to column densities of  $(2.3 \pm 0.3) \times 10^{17} \text{ molecules cm}^{-1}$  and  $(2.3 \pm 0.2) \times 10^{18} \text{ molecules cm}^{-1}$ , respectively, corresponding to a ratio of  $(10 \pm 1):1$ .

## Formation of acetaldehyde oligomers

Upon irradiation, oligomers of acetaldehyde molecules form. In the experiments reported here they consist of up to four acetaldehyde molecules and are detected at  $m/z = 94$ ,  $m/z = 141$ , and  $m/z = 188$  with decreasing signal strength as molecular mass grows. Additionally, strong signals can be seen at  $m/z = 95$ ,  $m/z = 142$ , and  $m/z = 189$ , corresponding to protonated acetaldehyde oligomers. The abundance of protonated oligomers in electron irradiated acetaldehyde ice also provides evidence of the suppressed formation of the vinoxy radical, which releases deuterium compared to the formation of the acetyl radical, which releases hydrogen. If both radicals formed at roughly equal abundance, this would be reflected in the relative amounts of protonated and deuterated oligomers assuming these radicals to be the main source of hydrogen and deuterium. However, protonated acetaldehyde dimers ( $m/z = 95$ ) are detected at a much higher signal strength than the deuterated dimers ( $m/z = 96$ ), the latter amounting to 9% of the signal at mass 95, as shown in Fig. S7. The deuterium needed to form the deuterated dimers could be provided by release in the formation of ketene- $d_2$  ( $CD_2CO$ ).

## Formation of acetone

Another radical-radical reaction product detected in the TPD experiment is acetone- $d_6$  ( $CD_3COCD_3$ ) at  $m/z = 64$ , as shown at 10.49 eV in Fig. S8. To validate the empirical formula, the desorption profile of  $m/z = 58$  of irradiated acetaldehyde ice is also shown. Acetone can form from the reaction of the acetyl radical ( $CD_3\dot{C}O$ ) with the methyl ( $\dot{C}D_3$ ) radical:



As seen for the diacetyl, the same desorption profile is also detected at  $m/z = 63$  at about 20% signal strength and at  $m/z = 62$  with even lower signal strength, which is another indication of H/D exchange in the sample. Again, no additional desorption event is seen at  $m/z = 63$  for propionaldehyde ( $CD_3CD_2CHO$ ) which forms in the reaction of the methyl and the vinoxy radical.

Similar to the formation of diacetyl, the formation of acetone from acetaldehyde is endoergic, but steps (3b) and (4) are both exoergic.

Even though the formation of the methyl radical should also produce the formyl radical ( $\dot{\text{HCO}}$ , step 3a above), no reaction products involving the formyl radical are detected. As the recombination of the acetyl and the formyl radical is exoergic and proceeds barrierless, this indicates that either the formyl radical exclusively reacts with hydrogen to form carbon monoxide and molecular hydrogen, which is endoergic ( $\Delta_{\text{R}}G = -373 \text{ kJ mol}^{-1}$ ), that the formation of methyl only proceeds from the acetyl radical to directly form methyl and carbon monoxide (step 3b), or that triple fragmentation to methyl, hydrogen and carbon monoxide is the dominating channel as seen in the gas phase photolysis experiments at 248 nm<sup>[1]</sup>.

**Table S1.** Data used to calculate the irradiation dose of acetaldehyde-2,2,2-d<sub>3</sub> (CD<sub>3</sub>CHO)

<b>irradiation current, I (nA)</b>	<b>15 ± 2</b>
<b>initial kinetic energy of the electrons, E<sub>init</sub></b>	<b>5 keV</b>
<b>total number of electrons</b>	<b>(2.8 ± 0.3) × 10<sup>13</sup></b>
<b>average penetration depth, l* (nm)</b>	<b>310 ± 30</b>
<b>density of the ice, ρ (g cm<sup>-3</sup>)</b>	<b>0.87 ± 0.09</b>
<b>average kinetic energy of transmitted electrons, E<sub>trans</sub>* (keV)</b>	<b>1.6 ± 0.2</b>
<b>average kinetic energy of backscattered electrons, E<sub>bs</sub>* (keV)</b>	<b>3.3 ± 0.3</b>
<b>fraction of transmitted electrons, f<sub>trans</sub>*</b>	<b>0.07 ± 0.01</b>
<b>fraction of backscattered electrons, f<sub>bs</sub>*</b>	<b>0.34 ± 0.03</b>
<b>irradiated area, A (cm<sup>2</sup>)</b>	<b>1.0 ± 0.1</b>
<b>dose per acetaldehyde molecule (eV)</b>	<b>0.31 ± 0.06</b>
<b>total # molecules processed</b>	<b>(3.5 ± 0.5) × 10<sup>17</sup></b>

Notes: \*CASINO output values

**Table S2.** Observed infrared absorption features and their assignments before irradiation of acetaldehyde ice ( $\text{CH}_3\text{CHO}$ ) at 5 K.

Absorption $\text{cm}^{-1}$	Assignment <sup>[2]</sup>	Approximate type of mode <sup>[2]</sup>
3417	$2\nu_4$	overtone
3123	$\nu_4 + \nu_6$	combination
3001	$\nu_1$	$\nu_{\text{as}}(\text{CH}_3)$
2964	$\nu_{11}$	$\nu(\text{CH}_3)$
2916	$\nu_2$	$\nu_s(\text{CH}_3)$
2858	$2\nu_6$	overtone
2843	$2\nu_6$	overtone
2759	$\nu_3$	$\nu(\text{CH})$
2736	$\nu_3$	$\nu(\text{CH})$
2598	$\nu_4 + \nu_9$	combination
2466	$\nu_7 + \nu_8$	combination
2234	$\nu_7 + \nu_9$	combination
2003	$\nu_8 + \nu_9$	combination
1769	$2\nu_9$	overtone
1726	$\nu_4$	$\nu(\text{CO})$
1718	$\nu_4$	$\nu(\text{CO})$
1680	$\nu_4 (\text{CH}_3^{13}\text{CHO})$	$\nu(^{13}\text{CO})$
1641	$\nu_8 + \nu_{10}$	combination
1546	$2\nu_{14}$	overtone
1430	$\nu_{12} / \nu_5$	$\delta(\text{CH}_3) / \delta_{\text{as}}(\text{CH}_3)$
1406	$\nu_9 + \nu_{10}$	combination
1392	$\nu_6$	$\delta(\text{CH})$
1347	$\nu_7$	$\delta_s(\text{CH}_3)$
1123	$\nu_8$	$\gamma_r(\text{CH}_3)$
1107	$\nu_8 (^{13}\text{CH}_3\text{CHO})$	$\gamma_r(^{13}\text{CH}_3)$
886	$\nu_{14} + \nu_{15}$	combination
772	$\nu_{14}$	$\gamma(\text{CH})$

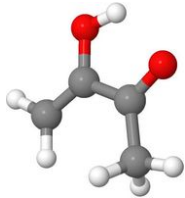
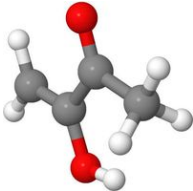
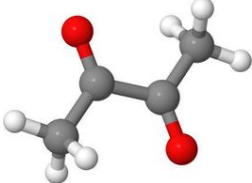
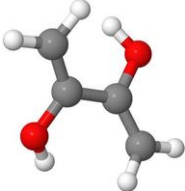
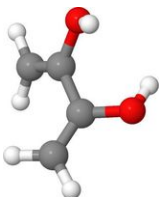
**Table S3.** Observed infrared absorption features and their assignments before irradiation of acetaldehyde-2,2,2-d<sub>3</sub> ice (CD<sub>3</sub>CHO) at 5 K.

Absorption cm <sup>-1</sup>	Assignment <sup>[2]</sup>	Approximate type of mode <sup>[2]</sup>
3405	2ν <sub>4</sub>	overtone
3112	ν <sub>4</sub> + ν <sub>5</sub>	combination
2853	2ν <sub>5</sub>	overtone
2749	ν <sub>1</sub>	ν(CH)
2252	ν <sub>2</sub>	ν <sub>as</sub> (CD <sub>3</sub> )
2228	ν <sub>11</sub>	ν(CD <sub>3</sub> )
2118	ν <sub>3</sub>	ν <sub>s</sub> (CD <sub>3</sub> )
2085	ν <sub>6</sub> + ν <sub>8</sub>	combination
1890	ν <sub>6</sub> + ν <sub>9</sub>	combination
1728	ν <sub>4</sub>	ν(CO)
1711	ν <sub>4</sub>	ν(CO)
1397	ν <sub>5</sub>	δ(CH)
1138	ν <sub>6</sub>	ν(CC)
1029	ν <sub>7</sub>	δ <sub>as</sub> (CD <sub>3</sub> )
963	ν <sub>8</sub>	δ <sub>s</sub> (CD <sub>3</sub> )

**Table S4.** Masses observed in the PI-ReToF-MS data of electron irradiated acetaldehyde and acetaldehyde-2,2,2-d<sub>3</sub>, corresponding empirical formula and tentative assignment based on deuterium and hydrogen content.

CH <sub>3</sub> CHO	CD <sub>3</sub> CHO	Formula	Assignment
42	44	C <sub>2</sub> D <sub>2</sub> O	Ketene (CD <sub>2</sub> CO)
43	46	C <sub>2</sub> D <sub>3</sub> O	Fragment of 62 and 92
44	47	C <sub>2</sub> D <sub>3</sub> HO	Acetaldehyde (CD <sub>3</sub> CHO)
58	62	C <sub>2</sub> D <sub>6</sub> O	Acetone (CD <sub>3</sub> COCOD <sub>3</sub> )
72	78	C <sub>4</sub> D <sub>6</sub> H <sub>2</sub> O	?
86	92	C <sub>4</sub> D <sub>6</sub> O <sub>2</sub>	Diacetyl (CD <sub>3</sub> COCOCOD <sub>3</sub> )
88	94	C <sub>4</sub> D <sub>6</sub> H <sub>2</sub> O <sub>2</sub>	(CD <sub>3</sub> CHO) <sub>2</sub>
89	95	C <sub>4</sub> D <sub>6</sub> H <sub>3</sub> O <sub>2</sub>	(CD <sub>3</sub> CHO) <sub>2</sub> H
101	107	C <sub>5</sub> D <sub>6</sub> H <sub>3</sub> O <sub>2</sub>	(CD <sub>3</sub> CHCO)H(CD <sub>3</sub> CHO)
103	109	C <sub>5</sub> D <sub>6</sub> H <sub>5</sub> O <sub>2</sub>	(CD <sub>3</sub> CH <sub>2</sub> CHO)H(CD <sub>3</sub> CHO)
117	123	C <sub>5</sub> D <sub>6</sub> H <sub>3</sub> O <sub>3</sub>	(CD <sub>3</sub> COCOH)H(CD <sub>3</sub> CHO)
131	140	C <sub>6</sub> D <sub>9</sub> H <sub>2</sub> O <sub>3</sub>	(CD <sub>3</sub> COCOCOD <sub>3</sub> )H(CD <sub>3</sub> CHO)
132	141	C <sub>6</sub> D <sub>9</sub> H <sub>3</sub> O <sub>3</sub>	(CD <sub>3</sub> CHO) <sub>3</sub>
133	142	C <sub>6</sub> D <sub>9</sub> H <sub>4</sub> O <sub>3</sub>	(CD <sub>3</sub> CHO) <sub>3</sub> H
145	154	C <sub>7</sub> D <sub>9</sub> H <sub>4</sub> O <sub>3</sub>	(CD <sub>3</sub> CHCO)H(CD <sub>3</sub> CHO) <sub>2</sub>
149	158	C <sub>6</sub> D <sub>9</sub> H <sub>4</sub> O <sub>4</sub>	(CD <sub>3</sub> CHO) <sub>2</sub> H(CD <sub>3</sub> COOH)
159	171	C <sub>8</sub> D <sub>12</sub> H <sub>3</sub> O <sub>3</sub>	(CD <sub>3</sub> COCOCOD <sub>3</sub> )H(C <sub>4</sub> D <sub>6</sub> H <sub>2</sub> O)
176	188	C <sub>8</sub> D <sub>12</sub> H <sub>4</sub> O <sub>4</sub>	(CD <sub>3</sub> CHO) <sub>4</sub>
177	189	C <sub>8</sub> D <sub>12</sub> H <sub>5</sub> O <sub>4</sub>	(CD <sub>3</sub> CHO) <sub>4</sub> H
203	215	C <sub>8</sub> D <sub>12</sub> H <sub>5</sub> O <sub>5</sub>	(CD <sub>3</sub> CHO) <sub>3</sub> H(CD <sub>3</sub> COOH)

**Table S5.** Calculated ionization energies (IE) and relative energies ( $E_{\text{rel}}$ ) for possible reaction products from reactions of two acetyl- $\text{d}_3$  radicals ( $m/z = 92$ ). Values given in parentheses are experimentally determined ionization energies.

Structure	Name	IE (eV) <sup>a</sup>	$E_{\text{rel}}$ (kJ mol <sup>-1</sup> ) <sup>b</sup>
	<i>cis</i> -3-hydroxybut-3-en-2-one	9.40	16
	<i>trans</i> -3-hydroxybut-3-en-2-one	9.39	47
	<i>trans</i> -diacetyl	9.25 (9.23-9.30) <sup>[3,4]</sup>	0
	<i>trans</i> -buta-1,3-diene-2,3-diol	8.95	83
	<i>cis</i> -buta-1,3-diene-2,3-diol	8.77	90

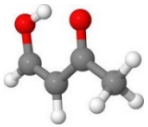
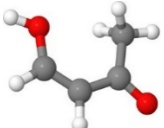
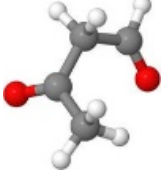
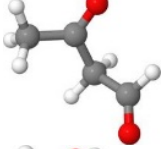
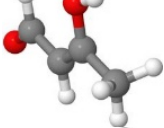
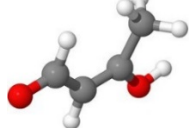
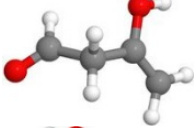
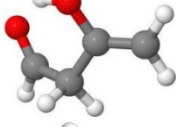
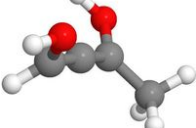
**Notes.**

<sup>a</sup>Relative ionization potential by CCSD(T)/CBS with B3LYP/cc-pVTZ zero-point energy correction in eV.

<sup>b</sup>Relative energy by CCSD(T)/CBS with B3LYP/cc-pVTZ zero-point energy correction in kJ mol<sup>-1</sup>



**Table S6.** Calculated ionization energies (IE) and relative energies ( $E_{\text{rel}}$ ) for possible reaction products from reactions of one acetyl- $\text{d}_3$  radical with one vinoxy-2,2- $\text{d}_2$  radical ( $m/z = 91$ ).

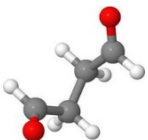
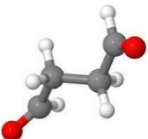
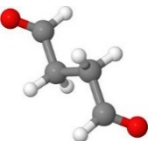
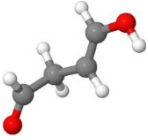
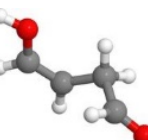
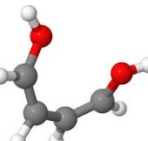
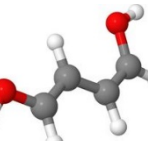
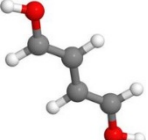
Structure	Name	IE (eV) <sup>a</sup>	$E_{\text{rel}}$ (kJ mol <sup>-1</sup> ) <sup>b</sup>
	( <i>E</i> )-4-hydroxybut-3-en-2-one	10.34	-4
	( <i>Z</i> )-4-hydroxybut-3-en-2-one	9.98	43
	<i>cis</i> -3-oxobutanal	9.96	22
	<i>trans</i> -3-oxobutanal	9.58	22
	( <i>Z</i> )-3-hydroxybut-2-enal	9.34	40
	( <i>E</i> )-3-hydroxybut-2-enal	9.34	43
	<i>trans</i> -3-hydroxybut-3-enal	9.23	63
	<i>cis</i> -3-hydroxybut-3-enal	8.68	61
	<i>cis</i> -buta-1,2-diene-1,3-diol	8.50	156

**Notes.**

<sup>a</sup>Relative ionization potential by CCSD(T)/CBS with B3LYP/cc-pVTZ zero-point energy correction in eV.

<sup>b</sup>Relative energy by CCSD(T)/CBS with B3LYP/cc-pVTZ zero-point energy correction in kJ mol<sup>-1</sup>

**Table S7.** Calculated ionization energies (IE) and relative energies ( $E_{\text{rel}}$ ) for possible reaction products from reactions of two vinoxy-2,2-d<sub>2</sub> radicals ( $m/z = 90$ ).

Structure	Name	IE (eV) <sup>a</sup>	$E_{\text{rel}}$ (kJ mol <sup>-1</sup> ) <sup>b</sup>
	<i>cis</i> -succinaldehyde	10.37	56
	<i>trans</i> -succinaldehyde C <sub>2</sub>	10.22	54
	<i>trans</i> -succinaldehyde C <sub>i</sub>	10.19	54
	( <i>E</i> )-4-hydroxybut-3-enal	9.07	77
	( <i>Z</i> )-4-hydroxybut-3-enal	9.00	76
	(1 <i>Z</i> ,3 <i>Z</i> )-buta-1,3-diene-1,4-diol	7.74	113
	(1 <i>Z</i> ,3 <i>E</i> )-buta-1,3-diene-1,4-diol	7.64	94
	(1 <i>E</i> ,3 <i>E</i> )-buta-1,3-diene-1,4-diol	7.61	96

**Notes.**

<sup>a</sup>Relative ionization potential by CCSD(T)/CBS with B3LYP/cc-pVTZ zero-point energy correction in eV.

<sup>b</sup>Relative energy by CCSD(T)/CBS with B3LYP/cc-pVTZ zero-point energy correction in kJ mol<sup>-1</sup>

**Table S8.** Reaction energies for all reactions considered in this study

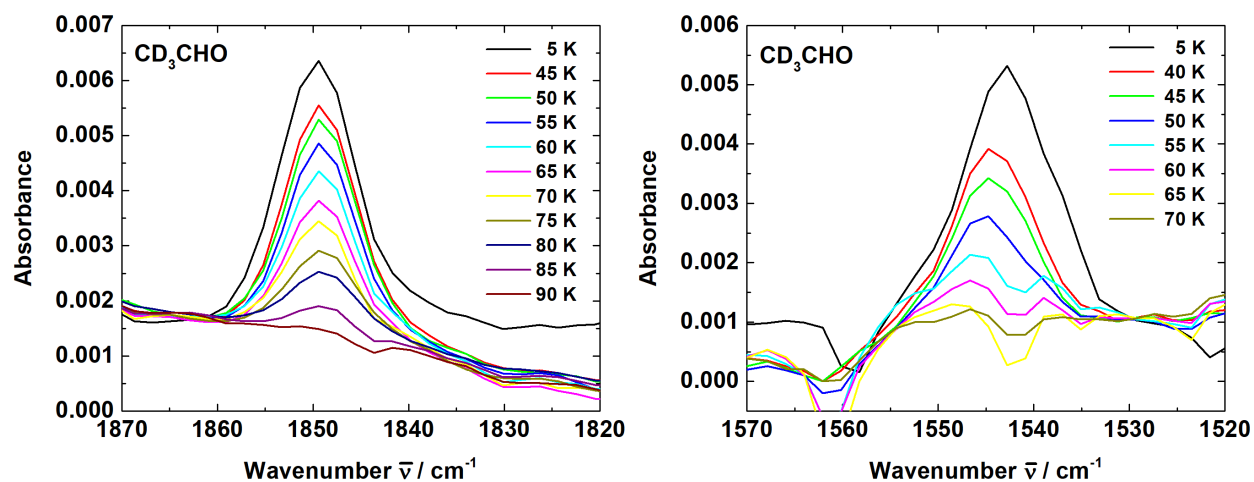
Reaction	$\Delta_R G^a$ kJ mol <sup>-1</sup>
CH <sub>3</sub> CHO → CH <sub>3</sub> CO + H	377
CH <sub>3</sub> CHO + H → CH <sub>3</sub> CO + H <sub>2</sub>	-59
CH <sub>3</sub> CO + CH <sub>3</sub> CO → CH <sub>3</sub> COCOCH <sub>3</sub>	-303
2 CH <sub>3</sub> CHO → CH <sub>3</sub> COCOCH <sub>3</sub> + 2 H	451
2 CH <sub>3</sub> CHO → CH <sub>3</sub> COCOCH <sub>3</sub> + H <sub>2</sub>	15
CH <sub>3</sub> CHO → CH <sub>3</sub> + HCO	359
CH <sub>3</sub> CHO → CH <sub>3</sub> + CO + H	423
2 CH <sub>3</sub> CHO → CH <sub>3</sub> COCH <sub>3</sub> + H + HCO	384
2 CH <sub>3</sub> CHO → CH <sub>3</sub> COCH <sub>3</sub> + CO + H <sub>2</sub>	11
CH <sub>3</sub> CO → CH <sub>3</sub> + CO	45
CH <sub>3</sub> CHO + H → CH <sub>3</sub> + CO + H <sub>2</sub>	-13
CH <sub>3</sub> CO + CH <sub>3</sub> → CH <sub>3</sub> COCH <sub>3</sub>	-352
CH <sub>3</sub> CO + HCO → CH <sub>3</sub> COCHO	-305
CHO + H → CO + H <sub>2</sub>	-373
CHO → H + CO	63
CH <sub>3</sub> CHO → CH <sub>2</sub> CO + 2H	559
CH <sub>3</sub> CHO → CH <sub>2</sub> CO + H <sub>2</sub>	123
CH <sub>3</sub> CO → CH <sub>2</sub> CO + H	182
CH <sub>3</sub> CO + H → CH <sub>2</sub> CO + H <sub>2</sub>	-254
CH <sub>3</sub> CHO + CH <sub>2</sub> CO → CH <sub>3</sub> COCOCH <sub>3</sub>	-107

**Notes:** <sup>a</sup> values taken from <http://webbook.nist.gov/chemistry>

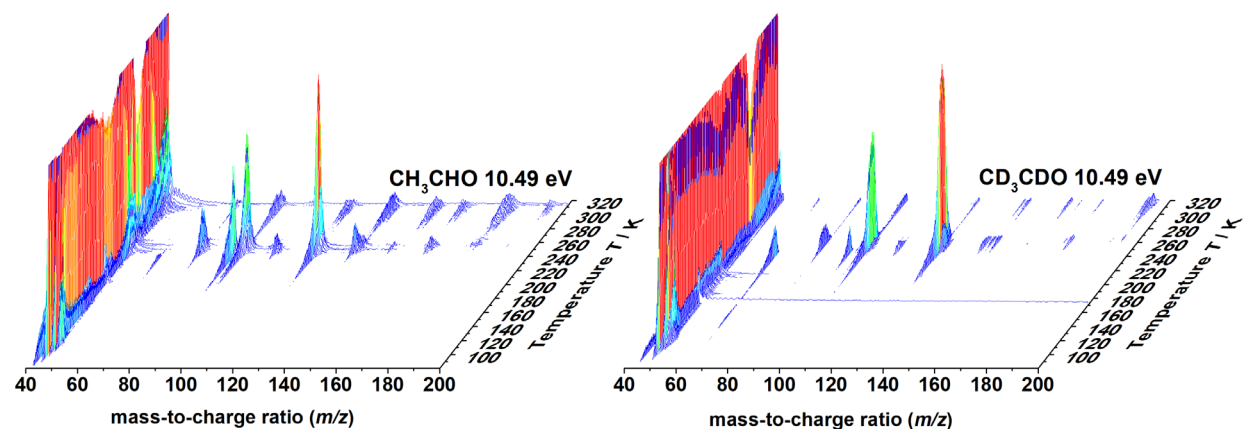
**Table S9.** Wavelengths and nonlinear media used to generate the different photoionization photon energies

Photoionization energy / eV		10.49	10.11	9.50	9.30	9.10
Wavelength / nm		118.2	122.6	130.51	133.3	136.2
$\omega_1$	Wavelength / nm	355	202.316	202.316	222.566	222.566
Nd:YAG ( $\omega_1$ )	Wavelength / nm	355	532	532	355	355
Dye laser ( $\omega_1$ )	Wavelength / nm	-	606.948	606.948	445.132	445.132
Dye ( $\omega_1$ ) <sup>a</sup>			Rh mix	Rh mix	C 450	C 450
$\omega_2$	Wavelength / nm	-	578	450	673	607
Nd:YAG ( $\omega_2$ )	Wavelength / nm	-	532	355	532	532
Dye laser ( $\omega_2$ )	Wavelength / nm	-	578	450	673	607
Dye ( $\omega_2$ ) <sup>a</sup>			P 597	C 450	P 1	Rh mix

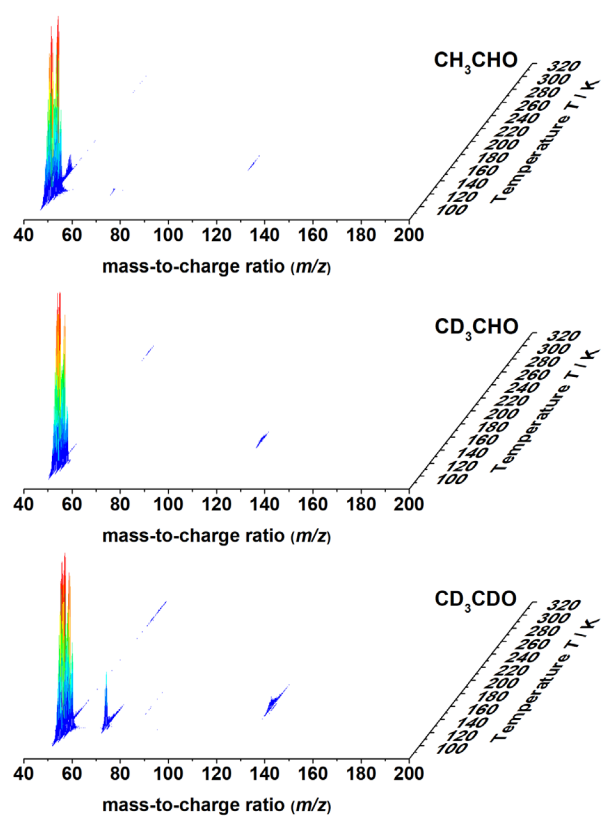
**Notes:** <sup>a</sup> Rh mix: Rhodamine 610 + Rhodamine 640, C 450: Coumarin 450, P 597: Pyrromethene 597, P 1: Pyridine 1



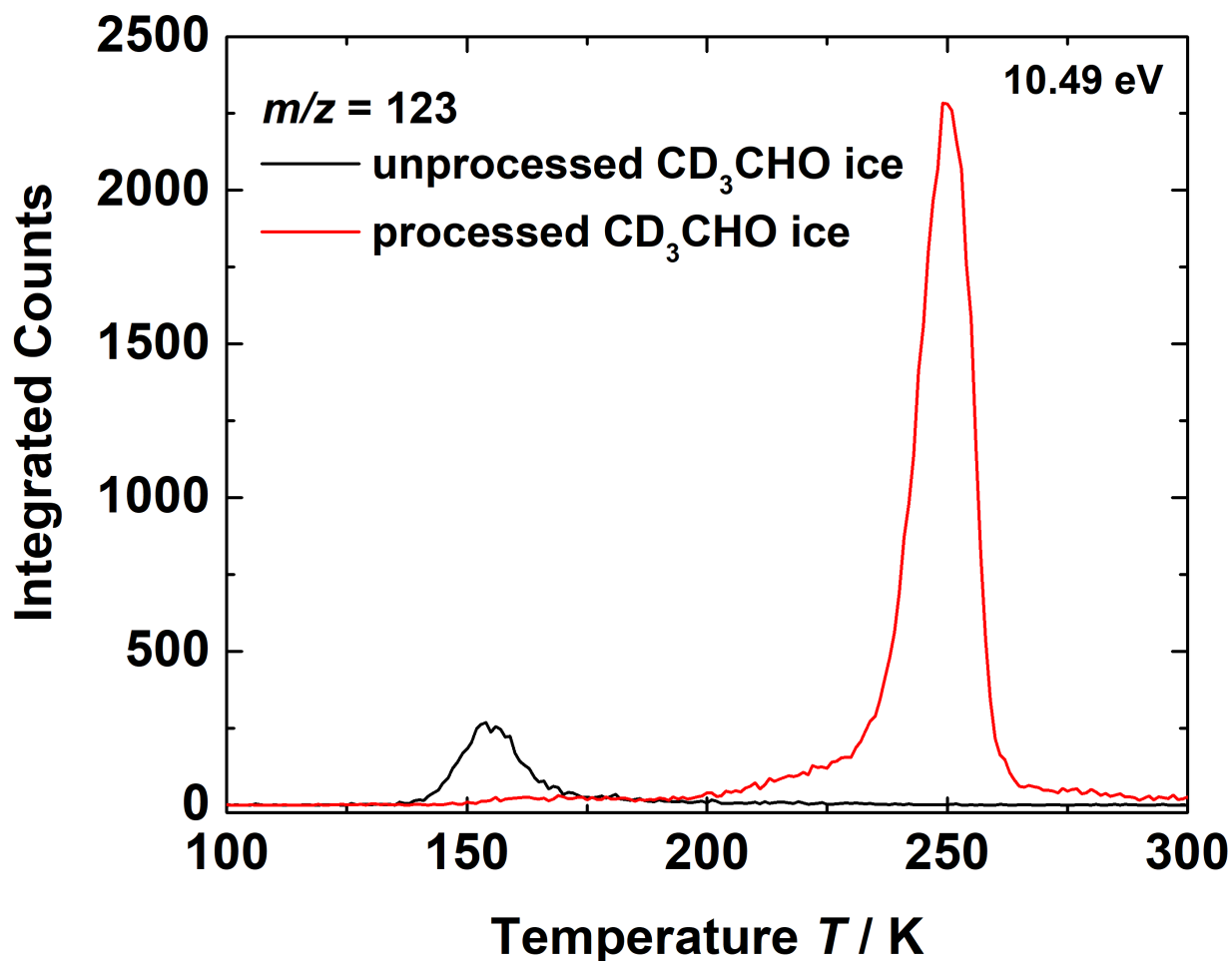
**Figure S1.** Temperature-dependent FTIR spectra of the two radicals found in the experiments.



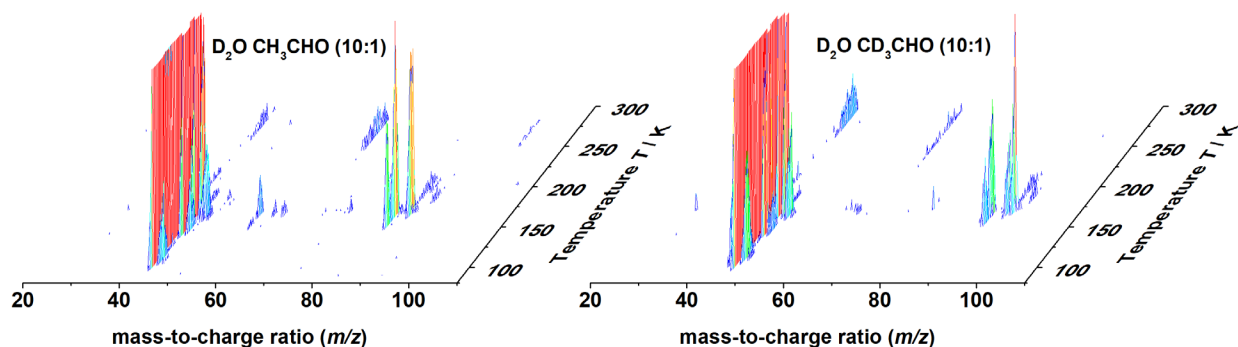
**Figure S2.** Temperature-dependent PI-ReToF mass spectra of acetaldehyde and acetaldehyde- $d_4$  after irradiation with a dose of  $0.31 \text{ eV molecule}^{-1}$ . Spectra were recorded at  $10.49 \text{ eV}$ .



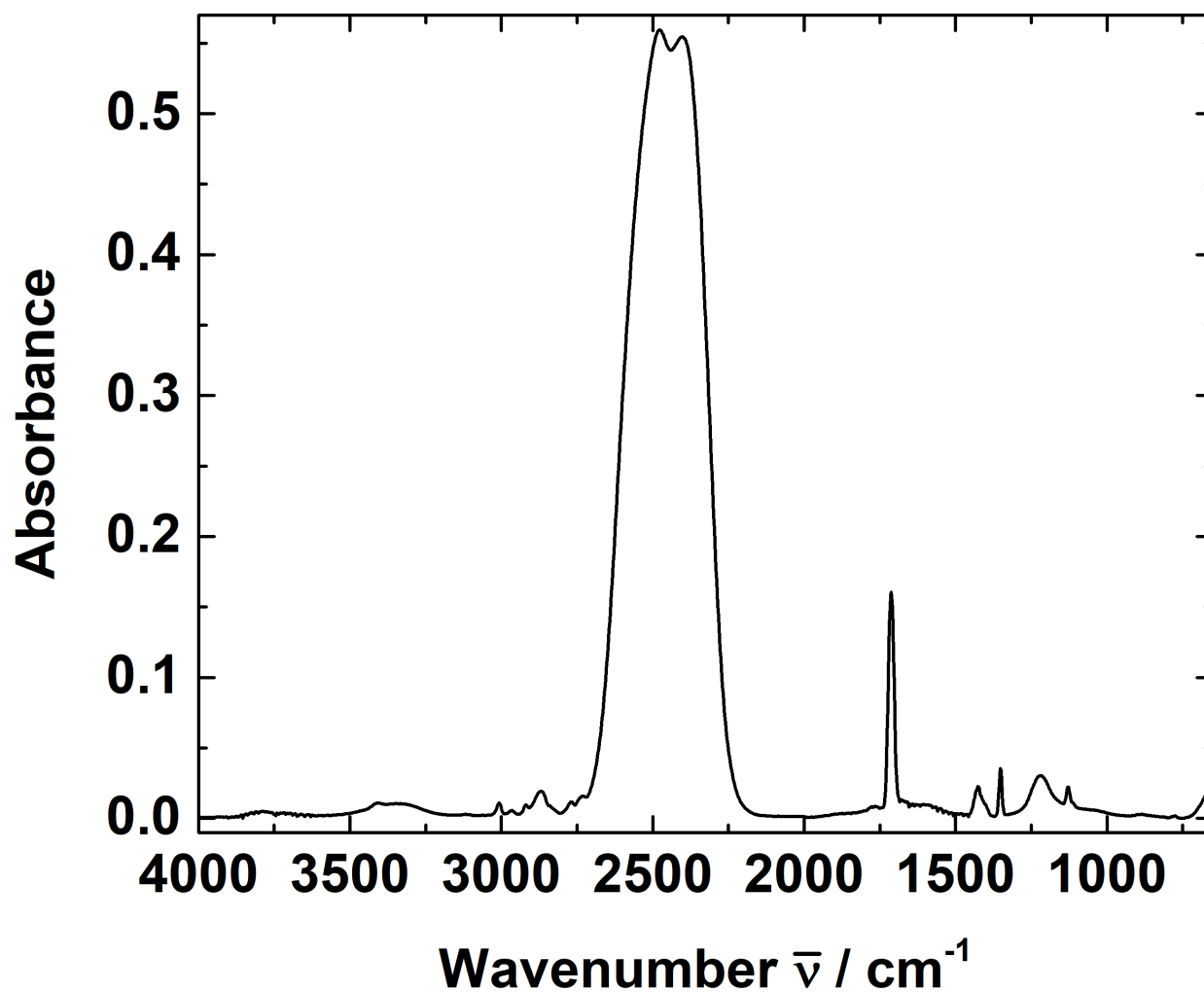
**Figure S3.** Temperature-dependent PI-ReToF mass spectra of acetaldehyde, acetaldehyde- $\text{d}_4$  and acetaldehyde-2,2,2- $\text{d}_3$  recorded at 10.49 eV.



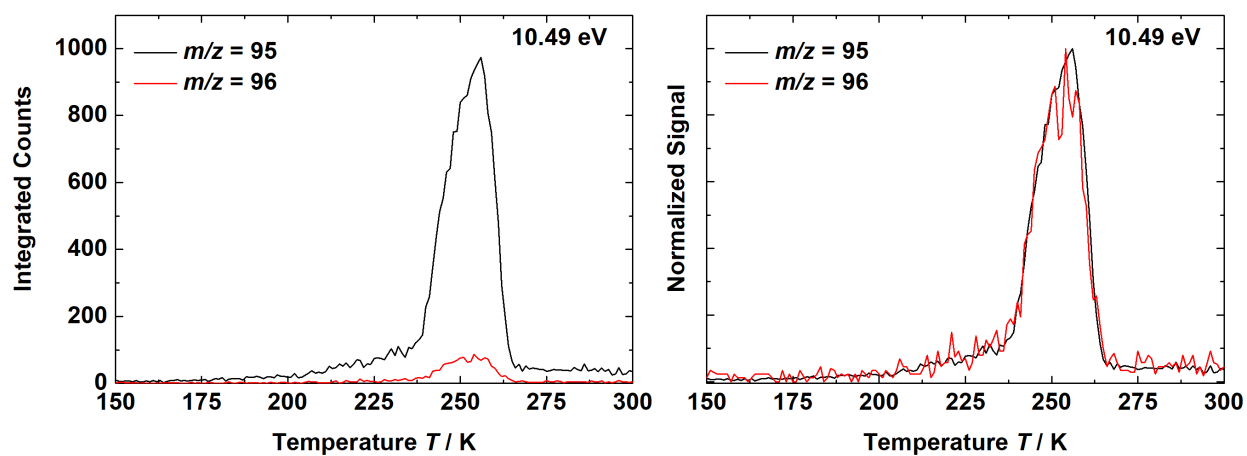
**Figure S4.** ReToF MS Sublimation profile of the main impurity of acetaldehyde-2,2,2-d<sub>3</sub> (C<sub>5</sub>D<sub>6</sub>H<sub>3</sub>O<sub>3</sub>,  $m/z = 123$ ) of unprocessed and processed ices recorded at 10.49 eV.



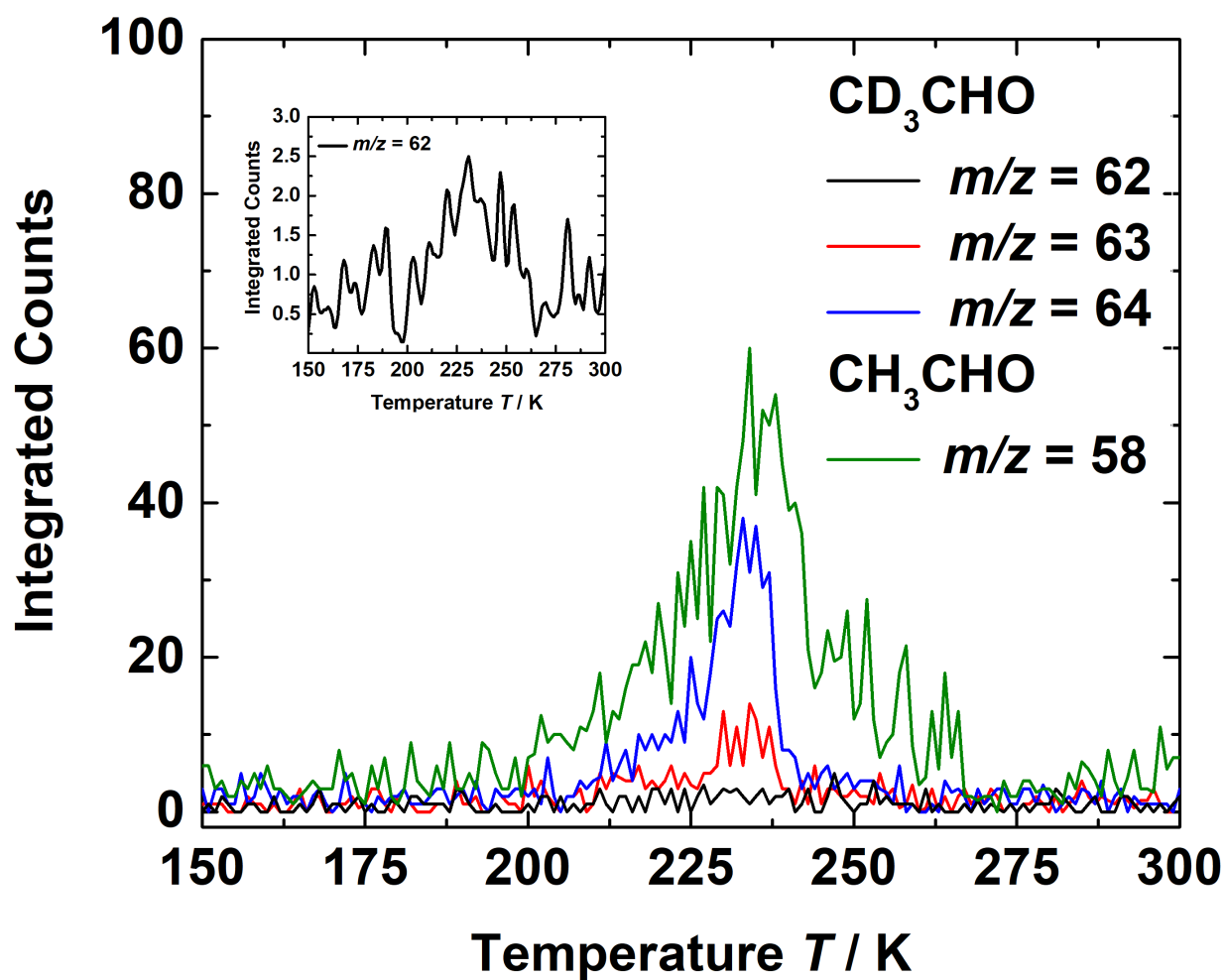
**Figure S5.** Temperature-dependent PI-ReToF mass spectra for 10:1 mixtures of deuterium oxide and acetaldehyde (left), and deuterium oxide and acetaldehyde-d<sub>3</sub> (right).



**Figure S6.** FTIR spectrum of the 10:1 mixture of deuterium oxide and acetaldehyde.



**Figure S7.** Temperature Programmed Desorption profiles of protonated (black lines) and deuterated (red lines) acetaldehyde dimers forming in the irradiated acetaldehyde-2,2,2- $\text{d}_3$  ice.



**Figure S8.** PI-ReToF sublimation profiles of  $m/z = 62$ , 63, and 64 after electron irradiation of acetaldehyde-2,2,2- $d_3$ , and  $m/z = 58$  after electron irradiation of acetaldehyde. The inset shows a zoom into smoothed data of the  $m/z = 62$  TPD profile. Spectra were recorded at a photon energy of 10.49 eV.



**B3LYP/aug-cc-pVTZ Cartesian coordinates (in Å) for the molecules analyzed.**

*cis*-buta-1,3-diene-2,3-diol+

C	-0.172019	1.477384	1.181224
C	0.022473	0.724339	0.047476
C	-0.022473	-0.724339	0.047476
C	0.172019	-1.477384	1.181224
H	0.169833	-2.556112	1.108438
H	0.356815	-1.023496	2.140650
O	-0.172019	-1.380374	-1.102953
H	-0.610782	-0.866994	-1.797666
O	0.172019	1.380374	-1.102953
H	0.610782	0.866994	-1.797666
H	-0.356815	1.023496	2.140650
H	-0.169833	2.556112	1.108438

*cis*-buta-1,3-diene-2,3-diol

C	-0.146945	0.174126	-0.047312
C	-0.022792	-0.032460	1.261292
C	1.256605	0.009167	2.001650
C	2.390212	-0.549776	1.585650
H	3.296876	-0.453679	2.164376
H	2.410160	-1.122015	0.673053
O	1.203968	0.618649	3.237132
H	0.472195	1.245437	3.258871
O	-1.146274	-0.231410	2.035153
H	-0.903382	-0.687551	2.848644
H	0.713569	0.439033	-0.638944
H	-1.110831	0.098002	-0.528279

*cis*-3-hydroxybut-3-en-2-one+

C	1.145824	1.610533	0.000000
C	-0.083714	0.780975	0.000000
C	0.000000	-0.771830	0.000000
C	1.149094	-1.579923	0.000000
H	2.133316	-1.134766	0.000000
H	1.049625	-2.658238	0.000000
O	-1.150694	-1.331924	0.000000
H	-1.828938	-0.591298	0.000000
O	-1.225329	1.170316	0.000000
H	1.755039	1.387926	0.880755
H	1.755039	1.387926	-0.880755
H	0.876879	2.662782	0.000000

*cis*-3-hydroxybut-3-en-2-one

C	1.333250	1.419879	0.000000
C	0.000000	0.721546	0.000000
C	-0.084267	-0.772510	0.000000
C	0.974133	-1.586998	0.000000
H	1.974717	-1.188717	0.000000
H	0.850520	-2.659875	0.000000
O	-1.353046	-1.235963	0.000000
H	-1.925409	-0.447855	0.000000
O	-1.051609	1.339512	0.000000
H	1.915080	1.141490	0.879261
H	1.915080	1.141490	-0.879261
H	1.168547	2.493576	0.000000

*trans*-biacetyl<sup>+</sup>

C	-0.485745	-1.983720	0.000000
C	0.485745	-0.868553	0.000000
C	-0.485745	0.868553	0.000000
C	0.485745	1.983720	0.000000
H	-0.065873	2.922610	0.000000
H	1.122765	1.897377	0.881766
H	1.122765	1.897377	-0.881766
O	-1.632088	0.710735	0.000000
O	1.632088	-0.710735	0.000000
H	0.065873	-2.922610	0.000000
H	-1.122765	-1.897377	0.881766
H	-1.122765	-1.897377	-0.881766

*trans*-biacetyl

C	-0.401030	-1.933684	0.000000
C	0.401030	-0.664746	0.000000
C	-0.401030	0.664746	0.000000
C	0.401030	1.933684	0.000000
H	-0.267951	2.789208	0.000000
H	1.057369	1.960746	0.871316
H	1.057369	1.960746	-0.871316
O	-1.609521	0.625490	0.000000
O	1.609521	-0.625490	0.000000
H	0.267951	-2.789208	0.000000
H	-1.057369	-1.960746	0.871316
H	-1.057369	-1.960746	-0.871316

*trans*-buta-1,3-diene-2,3-diol+

C	-0.017061	0.183712	0.044449
C	-0.013034	-0.152335	1.378788
C	1.222131	-0.155946	2.148357
C	1.250565	0.297410	3.447227
H	2.193837	0.366309	3.971202
H	0.357077	0.652320	3.938296
O	2.376738	-0.495346	1.586740
H	2.280292	-0.963508	0.745722
O	-1.184808	-0.368222	1.965355
H	-1.115080	-0.764202	2.845199
H	0.895243	0.437435	-0.473966
H	-0.955739	0.263411	-0.486202

*trans*-buta-1,3-diene-2,3-diol

C	-0.324944	1.806743	-0.257928
C	0.324944	0.664259	-0.019486
C	-0.324944	-0.664259	-0.019486
C	0.324944	-1.806743	-0.257928
H	-0.192285	-2.752677	-0.209602
H	1.357133	-1.805750	-0.570954
O	-1.666602	-0.685539	0.226809
H	-1.924226	0.151196	0.630569
O	1.666602	0.685539	0.226809
H	1.924226	-0.151196	0.630569
H	-1.357133	1.805750	-0.570954
H	0.192285	2.752677	-0.209602

*trans*-3-hydroxybut-3-en-2-one+

C	1.827286	-0.638391	0.375386
C	0.724589	0.275125	-0.031372
C	-0.743365	-0.138804	0.040810
C	-1.695022	0.800240	0.411466
H	-1.388529	1.806212	0.653772
H	-2.732836	0.508552	0.506386
O	-1.138812	-1.317664	-0.352263
H	-0.424097	-1.962443	-0.488972
O	0.833213	1.378071	-0.505205
H	1.649522	-1.022303	1.382575
H	1.885179	-1.494947	-0.304726
H	2.774615	-0.107349	0.332967

*trans*-3-hydroxybut-3-en-2-one

C	1.448651	1.201892	0.000000
C	0.000000	0.752643	0.000000
C	-0.274256	-0.726110	0.000000
C	-1.520058	-1.196403	0.000000
H	-2.342991	-0.500901	0.000000
H	-1.715047	-2.258287	0.000000
O	0.789276	-1.592671	0.000000
H	1.621700	-1.113777	0.000000
O	-0.904353	1.558317	0.000000
H	1.975936	0.834149	0.884706
H	1.975936	0.834149	-0.884706
H	1.479061	2.287367	0.000000

*cis*-buta-1,2-diene-1,3-diol+

C	0.987434	1.401204	-0.024648
C	0.938166	-0.081723	-0.008317
C	-0.227349	-0.812986	-0.018456
C	-1.569923	-0.682223	-0.025745
O	-2.174774	0.481906	0.038193
H	-3.141165	0.400610	0.020446
H	-2.191723	-1.573412	-0.080243
O	2.104828	-0.662949	0.023647
H	2.048698	-1.633325	0.052960
H	1.275112	1.740371	0.976035
H	1.767048	1.725654	-0.715431
H	0.031624	1.842817	-0.285492

*cis*-buta-1,2-diene-1,3-diol

C	1.848846	1.149864	-0.075328
C	0.960689	-0.050154	0.029877
C	-0.333301	-0.026993	0.222260
C	-1.609821	0.022704	0.476522
O	-2.572836	0.080350	-0.508964
H	-3.442071	0.107449	-0.098545
H	-1.997693	0.020340	1.492124
O	1.686391	-1.214133	-0.109892
H	1.082915	-1.963656	-0.050955
H	2.620081	1.111156	0.696530
H	2.353761	1.156387	-1.043189
H	1.276092	2.066065	0.034899

*cis*-3-hydroxybut-3-enal+

C	0.168277	1.052943	0.000
C	1.597588	0.557803	0.000
O	1.872777	-0.625493	0.000
H	2.389275	1.317138	0.000
C	-0.873713	-0.030533	0.000
C	-2.258726	0.246596	0.000
H	-2.961650	-0.575531	0.000
H	-2.619895	1.264908	0.000
O	-0.518060	-1.260073	0.000
H	0.518922	-1.304048	0.000
H	0.017289	1.711013	0.864419
H	0.017289	1.711013	-0.864419

*cis*-3-hydroxybut-3-enal

C	0.197893	0.952964	0.372642
C	1.575044	0.546269	-0.086785
O	1.912780	-0.587826	-0.337034
H	2.312903	1.367771	-0.152424
C	-0.921403	-0.008548	0.057492
C	-2.119577	0.392114	-0.358848
H	-2.903343	-0.325183	-0.551648
H	-2.335705	1.440649	-0.491364
O	-0.664829	-1.326225	0.297276
H	0.282900	-1.484890	0.156380
H	0.293198	1.069440	1.463285
H	-0.025308	1.947821	-0.013167

*cis*-oxobutanal+

C	0.281880	-0.978098	-0.411026
C	1.643232	-0.349000	-0.065671
O	1.854744	0.689721	0.461444
H	2.467285	-1.025958	-0.381525
C	-0.938239	-0.114721	-0.014698
C	-1.017378	1.356977	-0.305592
H	-0.594170	1.557845	-1.289392
H	-2.052023	1.679285	-0.238202
H	-0.412298	1.887389	0.433522
O	-1.816754	-0.750424	0.498618
H	0.238791	-1.146983	-1.494028
H	0.231524	-1.956906	0.071043

*cis*-oxobutanal

C	0.345498	-0.802922	-0.628223
C	1.657971	-0.267364	-0.096043
O	1.788065	0.689651	0.620908
H	2.542733	-0.846470	-0.427737
C	-0.913599	-0.190209	-0.022019
C	-1.205163	1.252399	-0.339482
H	-1.245611	1.403488	-1.420779
H	-2.148526	1.548926	0.110657
H	-0.394147	1.873894	0.043871
O	-1.632570	-0.864801	0.677548
H	0.364335	-0.647417	-1.713727
H	0.329015	-1.882650	-0.465338

(*E*)-3-hydroxybut-2-enal+

C	1.362720	1.301682	-0.045052
H	1.399406	1.625954	-1.091601
H	2.360295	1.416885	0.378766
H	0.673311	1.965462	0.473458
C	0.917966	-0.109061	0.002098
C	-0.417631	-0.558450	0.068379
C	-1.552803	0.315329	0.132855
O	-2.661272	-0.141682	-0.120118
H	-1.437517	1.393508	0.306420
H	-0.609480	-1.619832	-0.021876
O	1.790988	-1.072171	-0.005768
H	2.714751	-0.768147	0.012235

(*E*)-3-hydroxybut-2-enal

C	1.352451	1.298574	0.000
H	1.968369	1.485531	-0.883753
H	1.968369	1.485531	0.883753
H	0.536907	2.013650	0.000
C	0.876342	-0.118891	0.000
C	-0.395703	-0.561306	0.000
C	-1.571474	0.285802	0.000
O	-2.712214	-0.136030	0.000
H	-1.397624	1.378971	0.000
H	-0.570454	-1.629379	0.000
O	1.861569	-1.054501	0.000
H	2.727952	-0.634328	0.000

*(E)*-4-hydroxybut-3-en-2-one+

C	-2.294185	0.239334	-0.000049
C	-0.796652	-0.067501	0.000013
C	0.178650	0.960474	0.000057
C	1.513419	0.678849	-0.000010
H	2.244570	1.481756	-0.000065
O	1.945319	-0.555840	-0.000002
H	2.911054	-0.634639	-0.000197
H	-0.163878	1.982289	0.000078
O	-0.535389	-1.279753	0.000034
H	-2.496558	0.829023	0.895361
H	-2.496558	0.829023	-0.895361
H	-2.885652	-0.670283	-0.000422

*(E)*-4-hydroxybut-3-en-2-one

C	0.00000000	0.00000000	0.00000000
C	-1.46825796	-0.34072001	0.0000
C	-2.43165494	0.73631399	0.000
C	-3.76182398	0.46185500	0.000
H	-4.51271599	1.24401400	0.000
O	-4.26846000	-0.75614000	0.000
H	-3.48113695	-1.37521201	0.000
H	-2.10383590	1.76423099	0.000
O	-1.83346695	-1.52812701	0.0000
H	0.24978603	0.58423900	-0.88852805
H	0.24978603	0.58423900	0.88852805
H	0.59282784	-0.91028410	0.0000

*trans*-3-hydroxybut-3-enal+

C	0.335974	0.203775	0.778382
C	1.496316	-0.344232	-0.153927
O	2.466066	0.295523	-0.362489
H	1.323656	-1.361235	-0.549442
C	-0.962885	0.042695	0.122896
C	-1.738219	1.118111	-0.296350
H	-2.726601	0.972934	-0.713785
H	-1.372624	2.127923	-0.184451
O	-1.319461	-1.211538	-0.062960
H	-2.150940	-1.319036	-0.553002
H	0.407390	-0.446257	1.656806
H	0.559164	1.231691	1.041457

*trans*-3-hydroxybut-3-enal

C	0.369116	0.164365	0.729844
C	1.467854	-0.300773	-0.209691
O	2.544166	0.231172	-0.287934
H	1.222250	-1.184423	-0.828437
C	-0.992185	0.086482	0.107197
C	-1.714100	1.135307	-0.279718
H	-2.692135	1.020692	-0.728415
H	-1.337385	2.137150	-0.149116
O	-1.385794	-1.218435	-0.032140
H	-2.236605	-1.257552	-0.483045
H	0.394153	-0.502819	1.599273
H	0.598629	1.172763	1.064536

*trans*-oxobutanal+

C	1.019932	-0.363659	0.000000
C	0.280961	-1.672830	0.000000
O	-0.919017	-1.738513	0.000000
H	0.876516	-2.601816	0.000000
C	0.000000	0.768151	0.000000
C	0.481511	2.193835	0.000000
H	-0.361677	2.876346	0.000000
H	1.105590	2.351661	0.882374
H	1.105590	2.351661	-0.882374
O	-1.178588	0.496185	0.000000
H	1.680198	-0.296106	0.871841
H	1.680198	-0.296106	-0.871841

*trans*-oxobutanal

C	0.358935	-0.133652	-0.777325
C	1.520913	0.298386	0.098290
O	2.454320	-0.411331	0.364593
H	1.447269	1.329893	0.487245
C	-0.971029	0.174624	-0.088578
C	-1.852076	-0.999714	0.250020
H	-2.749787	-0.662691	0.760891
H	-2.122325	-1.537013	-0.662024
H	-1.304847	-1.706006	0.878971
O	-1.264342	1.316164	0.181112
H	0.393499	0.480875	-1.681731
H	0.475909	-1.181579	-1.043425



(Z)-3-hydroxybut-2-enal+

C	2.130544	-0.799918	-0.035381
H	2.846916	-0.365588	-0.736189
H	1.929219	-1.830717	-0.311944
H	2.594510	-0.794139	0.958576
C	0.892977	0.009865	0.021339
C	-0.384150	-0.563733	-0.007946
C	-1.571805	0.232291	-0.142393
O	-2.665808	-0.265276	0.087551
H	-1.495800	1.307072	-0.361385
H	-0.500699	-1.627908	0.131688
O	0.960246	1.312951	0.075801
H	1.864964	1.658848	-0.001279

(Z)-3-hydroxybut-2-enal

C	2.213833	-0.525709	0.000000
H	2.580112	-1.056952	0.882995
H	2.638406	0.474277	0.000000
H	2.580112	-1.056952	-0.882995
C	0.720583	-0.479924	0.000000
C	0.000000	0.657418	0.000000
C	-1.453517	0.711456	0.000000
O	-2.087528	1.750190	0.000000
H	-1.976791	-0.260463	0.000000
H	0.522862	1.602883	0.000000
O	0.091796	-1.685462	0.000000
H	0.735758	-2.400068	0.000000

(Z)-4-hydroxybut-3-en-2-one+

C	0.902346	1.376337	0.0000
C	0.923161	-0.149828	0.0000
C	-0.188232	-1.025022	0.0000
C	-1.496609	-0.633701	0.000
H	-2.266351	-1.399395	0.0000
O	-1.885592	0.618010	0.000
H	-2.849748	0.709163	0.000
H	0.017874	-2.084320	0.000
O	2.087027	-0.592473	0.0000
H	0.365937	1.694477	0.894109
H	1.912529	1.774714	0.000
H	0.365937	1.694477	-0.894109

(Z)-4-hydroxybut-3-en-2-one

C	0.00000000	0.00000000	0.00000000
C	0.18244700	-1.50050300	0.000000
C	-0.99316000	-2.39199700	0.0000
C	-2.29597800	-2.08699100	0.0000
H	-3.03679000	-2.87896300	0.0000
O	-2.79583100	-0.82579300	0.0000
H	-3.75651399	-0.85239100	0.0000
H	-0.74771900	-3.44487000	0.0000
O	1.29764600	-1.99453100	0.0000
H	-0.56870200	0.31816300	0.87480560
H	0.97801201	0.47361900	0.0000
H	-0.56870200	0.31816300	-0.87480560

(1E,3E)-buta-1,3-diene-1,4-diol+

C	0.342006	1.814449	0.000000
C	-0.336728	0.608563	0.000000
C	0.336728	-0.608563	0.000000
C	-0.342006	-1.814449	0.000000
O	0.336728	-2.934076	0.000000
H	-0.226747	-3.721946	0.000000
H	-1.426176	-1.864372	0.000000
H	1.419927	-0.642387	0.000000
H	-1.419927	0.642387	0.000000
O	-0.336728	2.934076	0.000000
H	0.226747	3.721946	0.000000
H	1.426176	1.864372	0.000000

(1E,3E)-buta-1,3-diene-1,4-diol

C	0.336460	1.805514	0.000000
C	-0.324032	0.645755	0.000000
C	0.324032	-0.645755	0.000000
C	-0.336460	-1.805514	0.000000
O	0.324032	-3.007655	0.000000
H	-0.310603	-3.727700	0.000000
H	-1.419462	-1.856217	0.000000
H	1.408471	-0.678431	0.000000
H	-1.408471	0.678431	0.000000
O	-0.324032	3.007655	0.000000
H	0.310603	3.727700	0.000000
H	1.419462	1.856217	0.000000

(1Z,3E)-buta-1,3-diene-1,4-diol+

C	0.017752	-2.013904	0.000000
C	-0.646777	-0.795535	0.000000
C	0.000000	0.437138	0.000000
C	-0.715237	1.621106	0.000000
O	-0.074401	2.760984	0.000000
H	-0.662819	3.530573	0.000000
H	-1.800760	1.637973	0.000000
H	1.081019	0.495538	0.000000
H	-1.727639	-0.843064	0.000000
O	1.328444	-2.060991	0.000000
H	1.674476	-2.965219	0.000000
H	-0.531045	-2.948575	0.000000

(1Z,3E)-buta-1,3-diene-1,4-diol

C	-0.050008	0.000000	-0.039159
C	-0.032214	0.000000	1.297380
C	1.157295	0.000000	2.119000
C	1.120110	0.000000	3.453562
O	2.264207	0.000000	4.205622
H	2.041431	0.000000	5.139339
H	0.187604	0.000000	4.007614
H	2.122343	0.000000	1.628053
H	-0.997043	0.000000	1.788767
O	1.102409	0.000000	-0.783713
H	0.886294	0.000000	-1.718697
H	-0.977819	0.000000	-0.596323

(1Z,3Z)-buta-1,3-diene-1,4-diol+

C	0.000000	1.644545	0.158766
C	0.000000	0.700034	1.175945
C	0.000000	-0.700034	1.175945
C	0.000000	-1.644545	0.158766
O	0.000000	-1.352021	-1.115495
H	0.000000	-2.143286	-1.674520
H	0.000000	-2.694523	0.431229
H	0.000000	-1.152270	2.158986
H	0.000000	1.152270	2.158986
O	0.000000	1.352021	-1.115495
H	0.000000	2.143286	-1.674520
H	0.000000	2.694523	0.431229

(1Z,3Z)-buta-1,3-diene-1,4-diol

C	-0.113108	1.603754	0.152698
C	0.113108	0.719695	1.128833
C	-0.113108	-0.719695	1.128833
C	0.113108	-1.603754	0.152698
O	0.652283	-1.276857	-1.056490
H	0.730622	-2.065400	-1.598456
H	-0.104746	-2.654536	0.303383
H	-0.466847	-1.150208	2.057807
H	0.466847	1.150208	2.057807
O	-0.652283	1.276857	-1.056490
H	-0.730622	2.065400	-1.598456
H	0.104746	2.654536	0.303383

*cis*-succinaldehyde+

C	0.245834	0.720157	0.876918
C	-0.039475	1.498730	-0.407968
O	-0.245834	2.658158	-0.518846
H	-0.014982	0.874259	-1.350676
C	-0.245834	-0.720157	0.876918
C	0.039475	-1.498730	-0.407968
O	0.245834	-2.658158	-0.518846
H	0.014982	-0.874259	-1.350676
H	0.206643	-1.284049	1.691822
H	-1.334147	-0.765874	0.995919
H	1.334147	0.765874	0.995919
H	-0.206643	1.284049	1.691822

*cis*-succinaldehyde

C	0.107871	0.761516	0.957861
C	-0.612589	1.459543	-0.171339
O	-0.107871	2.269135	-0.904522
H	-1.681440	1.183380	-0.288623
C	-0.107871	-0.761516	0.957861
C	0.612589	-1.459543	-0.171339
O	0.107871	-2.269135	-0.904522
H	1.681440	-1.183380	-0.288623
H	0.296044	-1.169384	1.890158
H	-1.165566	-1.023383	0.915505
H	1.165566	1.023383	0.915505
H	-0.296044	1.169384	1.890158

(*E*)-4-hydroxybut-3-enal+

C	0.731533	-0.788166	-0.497948
C	1.881261	-0.082738	0.391187
O	2.411478	0.898694	0.010873
H	2.122819	-0.600904	1.332562
C	-0.560193	-0.637880	0.146223
C	-1.503055	0.266690	-0.313051
O	-2.695330	0.434939	0.178728
H	-2.903421	-0.136833	0.937552
H	-1.309470	0.914816	-1.160768
H	-0.790858	-1.233745	1.023906
H	0.793030	-0.329674	-1.480763
H	1.061445	-1.830163	-0.527765

(*E*)-4-hydroxybut-3-enal

C	0.749299	0.742242	0.255340
C	1.785125	-0.127787	-0.428229
O	2.827838	-0.470944	0.065716
H	1.502264	-0.464896	-1.447011
C	-0.539266	-0.010092	0.438337
C	-1.660700	0.278164	-0.217657
O	-2.854308	-0.364884	-0.114314
H	-2.781820	-1.099588	0.505973
H	-1.729072	1.099764	-0.919344
H	-0.526194	-0.841635	1.136754
H	1.161447	1.081788	1.206623
H	0.578378	1.616034	-0.380956

*trans*-succinaldehyde/c<sub>2</sub> cation

C	0.443848	0.614493	-0.199193
C	-0.443848	1.898175	-0.308966
O	-0.527563	2.672519	0.584689
H	-0.963734	2.056874	-1.271200
C	-0.443848	-0.614493	-0.199193
C	0.443848	-1.898175	-0.308966
O	0.527563	-2.672519	0.584689
H	0.963734	-2.056874	-1.271200
H	-1.027327	-0.708084	0.713018
H	-1.102830	-0.661290	-1.070372
H	1.102830	0.661290	-1.070372
H	1.027327	0.708084	0.713018

*trans*-succinaldehyde/c<sub>2</sub> neutral

C	0.417597	0.646082	-0.136721
C	-0.457135	1.866977	-0.275016
O	-0.457135	2.801172	0.481844
H	-1.136042	1.854187	-1.154724
C	-0.417597	-0.646082	-0.136721
C	0.457135	-1.866977	-0.275016
O	0.457135	-2.801172	0.481844
H	1.136042	-1.854187	-1.154724
H	-1.016520	-0.736305	0.768360
H	-1.096640	-0.637408	-0.997965
H	1.096640	0.637408	-0.997965
H	1.016520	0.736305	0.768360

*trans*-succinaldehyde+

C	0.391169	-0.594450	0.259117
C	0.384058	-0.590996	1.821307
O	1.396575	-0.493361	2.431658
H	-0.594171	-0.713286	2.319069
C	-0.391169	0.594450	-0.259117
C	-0.384058	0.590996	-1.821307
O	-1.396575	0.493361	-2.431658
H	0.594171	0.713286	-2.319069
H	-1.431092	0.598385	0.059705
H	0.080047	1.545670	0.005198
H	1.431092	-0.598385	-0.059705
H	-0.080047	-1.545670	-0.005198

*trans*-succinaldehyde

C	0.397194	-0.600519	0.276753
C	0.405270	-0.590045	1.785060
O	1.395680	-0.486166	2.460728
H	-0.593441	-0.675745	2.261201
C	-0.397194	0.600519	-0.276753
C	-0.405270	0.590045	-1.785060
O	-1.395680	0.486166	-2.460728
H	0.593441	0.675745	-2.261201
H	-1.427637	0.595122	0.078280
H	0.082602	1.527778	0.051789
H	1.427637	-0.595122	-0.078280
H	-0.082602	-1.527778	-0.051789

(Z)-4-hydroxybut-3-enal+

C	0.500822	0.399555	0.804974
C	1.498230	-0.547430	-0.048959
O	2.543635	-0.159945	-0.427089
H	1.109158	-1.565348	-0.215514
C	-0.494104	0.955922	-0.094177
C	-1.701555	0.349665	-0.390624
O	-1.990630	-0.820909	0.122001
H	-2.867742	-1.146755	-0.134649
H	-2.429655	0.827352	-1.037119
H	-0.286695	1.890669	-0.597802
H	0.084907	-0.264783	1.561796
H	1.145625	1.159431	1.236719

(Z)-4-hydroxybut-3-enal

C	0.529990	0.104072	0.711862
C	1.579197	-0.382715	-0.266327
O	2.749802	-0.105224	-0.212964
H	1.186564	-1.024802	-1.080826
C	-0.532881	0.893543	0.000313
C	-1.751937	0.447324	-0.286057
O	-2.172914	-0.808085	0.059659
H	-3.095462	-0.923994	-0.179779
H	-2.475321	1.064059	-0.805421
H	-0.286057	1.894307	-0.326099
H	0.082846	-0.775980	1.181434
H	1.026106	0.699531	1.478388

**B3LYP/aug-cc-pVTZ harmonic frequencies (in cm<sup>-1</sup>) for the molecules analyzed.**

*cis*-buta-1,2-diene-1,3-diol+

117.1262	191.6782	266.3152
359.8887	403.1887	464.1305
549.4904	572.1101	608.7702
624.0681	710.6812	791.2714
958.7622	959.3495	986.7263
1006.0761	1139.1263	1213.0739
1297.9229	1409.4750	1433.7361
1469.5966	1516.2366	1592.8455
3171.0923	3177.4014	3282.1574
3289.9661	3723.4508	3729.7955

<i>cis</i> -buta-1,2-diene-1,3-diol		
83.7865	148.3495	254.6449
322.5566	377.4196	494.1598
500.1530	613.3441	706.1363
733.7405	745.3094	774.3202
881.3983	881.8685	960.6687
977.1929	1170.8976	1254.4010
1284.4097	1330.7490	1420.3744
1444.4853	1711.4703	1712.3681
3169.8113	3170.5876	3265.4070
3266.6088	3789.3317	3791.8704

<i>cis</i> -3-hydroxybut-3-en-2-one <sup>+</sup>		
108.9589	147.1491	238.7266
277.6425	390.3993	400.1055
433.2090	598.5523	653.0285
675.3240	912.1201	968.8754
985.5917	1027.6221	1052.1894
1158.6315	1210.6858	1400.7498
1424.0584	1456.8594	1458.8794
1477.6397	1564.4468	1789.1171
3023.0367	3073.8023	3151.9153
3154.8463	3194.5433	3269.3956

<i>cis</i> -3-hydroxybut-3-en-2-one		
95.9580	116.0544	281.2404
368.1144	404.1034	455.1378
602.5676	614.6698	681.4885
734.2355	735.0448	893.9466
981.3498	988.3612	1052.8667
1168.5861	1282.0419	1381.6772
1405.9504	1442.6220	1474.4827
1477.1231	1704.3656	1729.6591
3045.1394	3101.0809	3144.0992
3174.1884	3267.9806	3621.4831

<i>trans</i> -diacetyl <sup>+</sup>		
21.8810	106.6671	111.1047
195.0850	197.0029	302.7265
338.9223	465.3164	478.6802
514.9206	881.5728	896.0003
1008.4694	1029.8679	1043.0503
1045.3164	1367.1885	1371.7712
1427.4145	1432.2727	1440.2327



1440.9482	1997.9101	2005.9756
3038.9604	3039.6572	3112.0320
3112.2461	3142.4244	3143.1776

*trans*-diacetyl

44.1023	101.3832	102.6632
239.2620	350.5575	360.7958
518.5448	546.5309	623.1111
682.9376	910.2076	961.1833
1013.7093	1072.6121	1135.5468
1274.0199	1388.5757	1394.2365
1455.6915	1456.7333	1456.8419
1462.0305	1776.4002	1778.6675
3042.2031	3042.2360	3093.6381
3093.9117	3148.6605	3149.2897

*trans*-buta-1,2-diene-1,3diol+

107.1685	244.0006	327.7298
385.1216	397.7739	490.7103
498.1186	564.4018	573.4094
622.5521	675.0977	797.2529
952.8426	958.2651	988.7085
1005.3223	1151.1669	1205.3019
1305.3931	1326.0881	1444.7003
1473.3198	1492.2207	1620.1408
3163.3741	3164.6499	3269.8489
3269.8510	3747.5047	3756.2312

*trans*-buta-1,2-diene-1,3-diol

107.0779	280.0174	351.1950
394.7832	412.5057	436.2002
515.1917	553.5910	715.9443
720.3943	760.7783	780.5195
862.8483	865.6943	977.7908
983.7140	1180.7133	1248.2196
1290.1234	1382.3291	1437.2142
1446.7517	1674.7811	1717.2469
3169.7331	3169.9686	3256.7859
3257.2118	3778.1026	3779.0541

*trans*-3-hydroxybut-3-en-2-one+

57.5857	110.7616	214.3533
291.9160	353.5383	474.7612
536.7156	561.8946	580.1924
640.7050	702.7805	961.4372
980.8500	1017.8659	1041.9111

1134.8365	1189.7410	1372.3537
1396.9501	1432.1826	1451.2943
1461.9525	1512.1889	1759.5136
3018.0852	3077.2401	3149.1576
3160.6795	3279.4113	3687.8398

*trans*-3-hydroxybut-3-en-2-one

49.5980	167.5817	193.9175
276.2639	393.9310	394.2396
483.7173	551.2673	644.3507
717.1052	741.9656	920.7148
951.2379	979.2777	1038.0627
1150.4019	1227.5425	1330.3879
1381.3348	1419.6397	1474.5821
1484.9397	1683.5513	1769.5144
3015.6168	3067.6415	3142.9681
3173.0546	3273.6259	3840.4576

*cis*-buta-1,2-diene-1,3-diol+

45.7715	55.2100	141.4333
220.5488	363.8873	450.6264
562.1883	595.7622	702.3547
711.9445	791.4838	987.0466
1018.0286	1034.8420	1096.7079
1247.9812	1276.3332	1345.3979
1382.6641	1421.2142	1443.0823
1467.1380	1533.0856	1691.0027
3025.9580	3090.3676	3129.8937
3166.2993	3685.6114	3723.4783

*cis*-buta-1,2-diene-1,3-diol

111.6840	119.1677	175.4997
254.7785	346.3702	382.6080
449.7826	510.7189	575.9528
591.7861	782.6253	864.7655
993.9212	1057.8278	1064.7425
1146.2657	1257.5758	1270.1921
1354.2115	1411.5942	1474.4768
1475.6185	1536.5792	2051.3194
3031.1469	3079.8509	3104.0403
3138.7476	3789.6753	3823.6241

*cis*-3-hydroxybut-3-enal+

70.6726	203.8132	320.7716
390.8365	395.9160	487.4079
501.2001	728.0149	733.5143

848.4694	900.4015	946.2758
1027.7457	1044.1903	1146.2783
1225.2954	1239.6746	1365.7948
1385.5876	1413.5236	1466.0192
1524.2232	1576.1554	1755.1689
2537.7124	3012.4474	3031.7912
3041.7889	3155.2568	3272.1936
<i>cis</i> -3-hydroxybut-3-enal		
81.8382	111.6331	239.6844
374.0372	463.6755	490.5880
618.3915	697.6114	735.7086
759.9309	858.6999	860.6490
965.0952	991.4781	1041.6673
1220.5599	1272.3399	1329.6532
1365.2535	1417.5236	1427.9506
1451.9749	1725.4146	1782.0107
2913.6401	2966.6145	3083.9662
3164.4279	3252.4501	3639.0257
<i>cis</i> -oxobutanal+		
55.9257	105.5096	145.5869
187.2519	319.3889	439.9852
462.4492	657.3773	711.8490
722.0893	805.4831	942.6317
988.0898	1056.1753	1093.9447
1164.2585	1237.9980	1289.8669
1357.9900	1408.2723	1438.9938
1459.5196	1700.3445	1836.1008
2854.7950	3025.9142	3043.8626
3089.8196	3110.1880	3166.9649
<i>cis</i> -oxobutanal		
48.5895	101.2806	131.8353
184.2014	357.4502	480.8323
508.2404	686.9064	723.1063
787.7774	923.5100	938.5379
1045.5345	1082.6774	1189.7595
1250.3977	1311.3180	1387.1857
1417.3030	1435.9273	1469.3279
1476.2703	1781.5609	1804.1378
2888.1944	3011.3096	3031.8548
3071.8004	3089.5840	3142.2364
<i>(E)</i> -3-hydroxybut-2-enal+		
97.6177	131.0342	164.2077

207.7279	395.1279	474.5365
524.5049	566.9223	655.7011
845.5389	868.7081	969.0627
1015.9463	1034.7354	1069.8399
1176.0665	1291.2665	1346.9756
1393.9404	1427.1277	1447.7460
1493.0568	1501.6409	1545.2366
3008.4417	3015.8779	3087.6673
3130.7226	3196.9375	3684.4311

(*E*)-3-hydroxybut-2-enal

129.1273	180.7407	226.6162
227.7954	392.2271	405.5475
496.9020	540.4173	554.7312
868.6555	897.0280	1011.9010
1024.5111	1066.3953	1166.7021
1203.9259	1260.8904	1369.7812
1422.8947	1445.7912	1480.4789
1483.8291	1702.2617	1733.4020
2889.8169	3020.1058	3064.0953
3150.5848	3180.7747	3804.9090

(*E*)-4-hydroxybut-3-en-2-one+

77.3405	124.4966	170.2677
259.4201	328.0988	422.6730
498.7109	640.0039	683.4479
778.4049	872.1473	985.8884
1002.1788	1009.7639	1083.4258
1147.2267	1235.8307	1310.9080
1339.9051	1427.2834	1435.0252
1462.0893	1500.6514	1644.6789
3037.7022	3116.4325	3158.4916
3169.3165	3234.9314	3740.3548

(*E*)-4-hydroxybut-3-en-2-one

33.4620	132.3557	258.0603
374.2927	379.2868	534.9058
626.5903	726.7800	791.9010
921.1625	953.9723	990.0698
1032.0191	1055.6488	1121.5559
1227.8315	1292.1272	1382.5382
1393.0888	1463.5322	1475.7398
1489.5537	1627.7770	1684.5647
3032.6543	3077.6214	3084.8879
3140.9020	3169.0349	3210.0894

<i>trans</i> -3-hydroxybut-3-enal+		
68.9795	115.3746	211.1578
394.0203	435.3903	467.7596
514.0954	615.1661	619.9779
764.3703	858.8185	914.8517
949.4830	990.7743	1021.4143
1153.4035	1180.8329	1236.2930
1306.1305	1415.5057	1447.4186
1482.5814	1515.5578	1857.0213
2939.4226	3035.1032	3151.2064
3166.6229	3262.2695	3705.2907

<i>trans</i> -3-hydroxybut-3-enal		
62.9723	74.9071	208.5085
400.4141	428.3886	441.5477
523.8936	605.4761	726.8446
762.5227	837.3139	894.7210
979.0889	1033.8916	1051.6439
1185.4880	1215.5779	1290.3102
1363.7905	1415.8561	1439.9907
1463.5126	1710.8905	1800.4746
2913.7449	3012.3308	3123.3589
3149.0789	3243.4475	3794.7114

<i>trans</i> -oxobutanal+		
65.5936	117.4892	220.9857
254.1205	361.2980	449.2548
519.8511	689.9392	713.4559
839.4733	905.4719	939.5973
985.2645	1071.0532	1135.4589
1194.9521	1277.2449	1316.8661
1366.0627	1388.7892	1451.0623
1460.5144	1665.1744	1747.4466
2962.0526	3030.0421	3038.4219
3059.0833	3097.9209	3172.0595

<i>trans</i> -oxobutanal		
33.3959	96.8507	147.4209
220.9916	368.8026	465.1026
528.6857	591.5598	752.3438
863.9933	919.5749	966.7532
1070.3533	1085.6987	1158.4470
1218.0987	1296.3477	1387.9347
1404.8419	1452.8645	1463.7189

1472.7911	1766.9899	1807.9422
2933.5229	3027.2058	3035.4538
3078.9913	3120.1737	3141.8564

(Z)-3-hydroxybut-2-enal+

73.0597	126.2925	173.0480
189.2441	373.4878	449.1742
546.3854	577.9700	640.3360
818.9228	929.9677	964.1837
980.2995	1029.3102	1080.3682
1162.9843	1250.9462	1315.4940
1386.8613	1430.9550	1459.4576
1480.4866	1502.6241	1549.0134
2994.3014	3008.2568	3075.0040
3149.5551	3222.2263	3696.7252

(Z)-3-hydroxybut-2-enal

131.8955	179.2283	194.9301
206.1582	361.4942	385.5293
497.7900	567.1036	577.7802
846.6519	917.9360	1021.1085
1025.6851	1066.5434	1117.9843
1188.3726	1284.9329	1359.7055
1415.0304	1432.3977	1480.0852
1482.5381	1705.9424	1733.9417
2934.2442	3015.0597	3059.6243
3134.7931	3196.1578	3818.8491

(Z)-4-hydroxybut-3-ene-2-one+

104.4745	184.4206	212.9230
302.0397	345.0839	396.0023
552.0301	626.3586	710.4873
770.2461	840.1608	991.9487
1012.2090	1015.7998	1060.1258
1216.4181	1273.5409	1327.2456
1352.8678	1423.5705	1463.2338
1472.1692	1486.9304	1660.5324
3042.5573	3124.5998	3159.2105
3160.1949	3218.8070	3745.3453

(Z)-4-hydroxybut-3-ene-2-one

75.0968	168.5875	210.1191
298.3572	356.5073	417.8321
513.4369	620.5957	698.2286
798.6446	814.9694	982.9602
995.2347	1051.0661	1077.6215

1246.1575	1282.2191	1300.3974
1394.5706	1443.7657	1463.4578
1476.4503	1705.4137	1719.5764
3040.6064	3095.8542	3139.7539
3146.8338	3192.3532	3835.9275

(1*E*,3*E*)-buta-1,3-diene-1,4-diol+

117.7831	149.3028	272.5706
319.8078	397.1086	433.9254
569.5167	595.6466	622.7931
898.1030	928.4335	955.3477
1002.2132	1153.8231	1162.1055
1230.6244	1257.3593	1315.4719
1332.0180	1347.4879	1353.0951
1479.6889	1612.6581	1690.4639
3158.2747	3160.2734	3169.6401
3177.6015	3741.0666	3746.7706

(1*E*,3*E*)-buta-1,3-diene-1,4-diol

120.1449	145.0450	204.5756
230.9729	292.9331	378.7888
397.0147	428.0296	613.2618
827.2386	867.8096	910.8910
973.6572	1097.7288	1130.7033
1177.0351	1185.2570	1223.9807
1314.4861	1348.7223	1350.8229
1408.7334	1701.1405	1740.9938
3140.8250	3145.4648	3149.1417
3152.8129	3852.6042	3854.1200

(1*Z*,3*E*)-buta-1,3-diene-1,4-diol+

149.5251	164.8372	202.7499
327.3629	384.3047	520.2866
582.3354	603.3264	702.7143
844.7741	949.8198	956.8148
1001.0627	1077.9842	1162.7593
1217.3414	1261.4859	1310.5543
1330.0003	1337.2546	1362.3658
1532.0652	1598.5151	1679.2882
3156.3501	3173.3789	3186.8666
3195.0865	3741.4243	3751.1760

(1*Z*,3*E*)-buta-1,3-diene-1,4-diol

139.0695	142.8168	196.9558
249.9717	301.9157	312.8836
508.9561	533.8935	695.5267

754.5715	861.7373	918.5108
967.2251	1020.3566	1129.8190
1154.1365	1194.0200	1254.5497
1285.6796	1341.2096	1352.7361
1455.1804	1696.0032	1734.8421
3143.1138	3155.8195	3173.7388
3179.8893	3851.2137	3854.4089

(1Z,3Z)-buta-1,3-diene-1,4-diol+

13.6568	201.0117	244.3899
249.4724	450.2616	596.5033
614.1100	638.1476	760.2100
863.4548	899.4231	924.1560
991.4540	1000.0437	1083.0864
1251.4637	1265.7665	1279.0693
1339.0708	1388.3680	1482.9173
1562.6656	1610.2509	1660.0821
3161.1441	3163.7286	3182.7137
3193.1845	3735.0939	3740.6796

(1Z,3Z)-buta-1,3-diene-1,4-diol

99.4995	155.3122	232.2367
260.2144	285.0810	406.8113
542.6929	647.6126	734.1376
770.4448	857.2569	909.7783
938.6010	939.0269	1049.2778
1120.6936	1243.4401	1268.6448
1292.3175	1318.1823	1423.8423
1471.5891	1717.1537	1720.6857
3141.2142	3144.7314	3162.1691
3168.8393	3847.6486	3848.5320

*cis*-succinaldehyde+

23.7996	90.8532	138.8821
221.2766	412.6279	436.1732
515.2905	679.3803	736.1690
841.8731	893.8929	956.0929
997.4599	1091.3377	1177.1601
1236.7082	1255.1822	1260.6814
1306.8715	1321.7008	1429.0218
1437.8396	1818.3162	1835.6931
2573.2600	2682.2089	3021.7007
3027.7189	3103.8265	3107.5250

*cis*-succinaldehyde

47.0846	69.5865	106.5206
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278.5929	349.1261	482.4423
528.6863	743.6618	769.8312
927.5966	957.6897	1019.1389
1090.8186	1130.5748	1210.1170
1224.2010	1339.6141	1346.9510
1416.8973	1421.0277	1460.5707
1464.2939	1801.6404	1807.8022
2870.4257	2872.1179	3015.6308
3025.0201	3079.1519	3090.6678

*(E)*-4-hydroxybut-3-enal+

51.6738	149.6489	173.6525
291.1533	331.4252	454.3085
551.0351	636.5727	708.2771
864.3164	885.6544	970.3763
1012.5862	1097.1748	1160.8184
1197.5827	1230.9634	1299.9095
1321.9891	1369.6828	1408.1441
1478.7656	1600.5549	1858.8916
2973.3819	3038.5252	3139.8287
3152.4335	3182.9189	3684.6004

*(E)*-4-hydroxybut-3-enal

57.4044	91.7704	211.4769
291.5821	378.2038	456.1028
468.2140	566.6233	834.6086
839.0627	946.6454	975.9664
1059.2007	1096.8102	1136.2911
1204.6355	1269.7872	1299.9915
1342.1443	1400.4182	1409.8289
1461.5765	1712.4030	1798.3506
2873.9658	3019.9317	3077.8512
3128.8363	3180.8714	3786.6703

*trans*-succinaldehyde+

54.5949	90.5231	92.3992
245.8371	312.7840	463.9984
490.1220	767.2305	768.1304
854.6063	897.6111	932.8929
1033.1601	1051.1310	1163.9196
1252.8959	1256.0961	1281.3972
1299.6697	1328.2586	1470.7932
1477.0448	1794.1364	1798.9114
2941.3482	2941.4131	3032.4178
3043.2285	3120.1008	3136.0013

*trans*-succinaldehyde

48.6918	72.8878	77.8346
238.7837	340.4451	480.8055
545.4405	783.7636	799.7109
939.2296	989.3765	991.2859
1103.6239	1138.5882	1206.8326
1268.8382	1301.1959	1352.0109
1416.1439	1422.1713	1466.3530
1483.2603	1800.1186	1805.6467
2875.2118	2875.5981	3015.4674
3025.2989	3084.1816	3099.2923

(*Z*)-4-hydroxy-but-3-enal+

34.7744	82.1282	211.4066
267.4517	385.9443	487.3502
616.1799	656.8351	682.4635
828.4124	920.6930	964.5821
984.6815	1045.7875	1153.3023
1184.2716	1226.4140	1278.8806
1294.2010	1326.4826	1454.1804
1500.2191	1604.0378	1861.1979
2959.7865	3071.7410	3154.1525
3171.8831	3198.7485	3723.2197

(*Z*)-4-hydroxy-but-3-enal

43.8410	68.5839	229.2541
245.5015	304.7799	493.8984
528.4959	647.9100	764.6040
836.4508	933.9483	952.4717
1038.1020	1060.5039	1113.0288
1206.6400	1280.3798	1286.3152
1296.0908	1412.1230	1428.6513
1463.5878	1732.4751	1795.9671
2881.4868	3033.1652	3090.6904
3158.2988	3188.4592	3849.7288

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