Supporting Information for

Identification of Glycolaldehyde Enol (HOHC=CHOH) in Interstellar Analog Ices

N. Fabian Kleimeier1,2\*\*, André K. Eckhardt3\*\*\*, Ralf I. Kaiser1,2\*

1Department of Chemistry, University of Hawaii at Mānoa, Honolulu, HI 96822, USA

2W.M. Keck Laboratory in Astrochemistry, University of Hawaii at Mānoa, Honolulu, HI 96822, USA

3Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

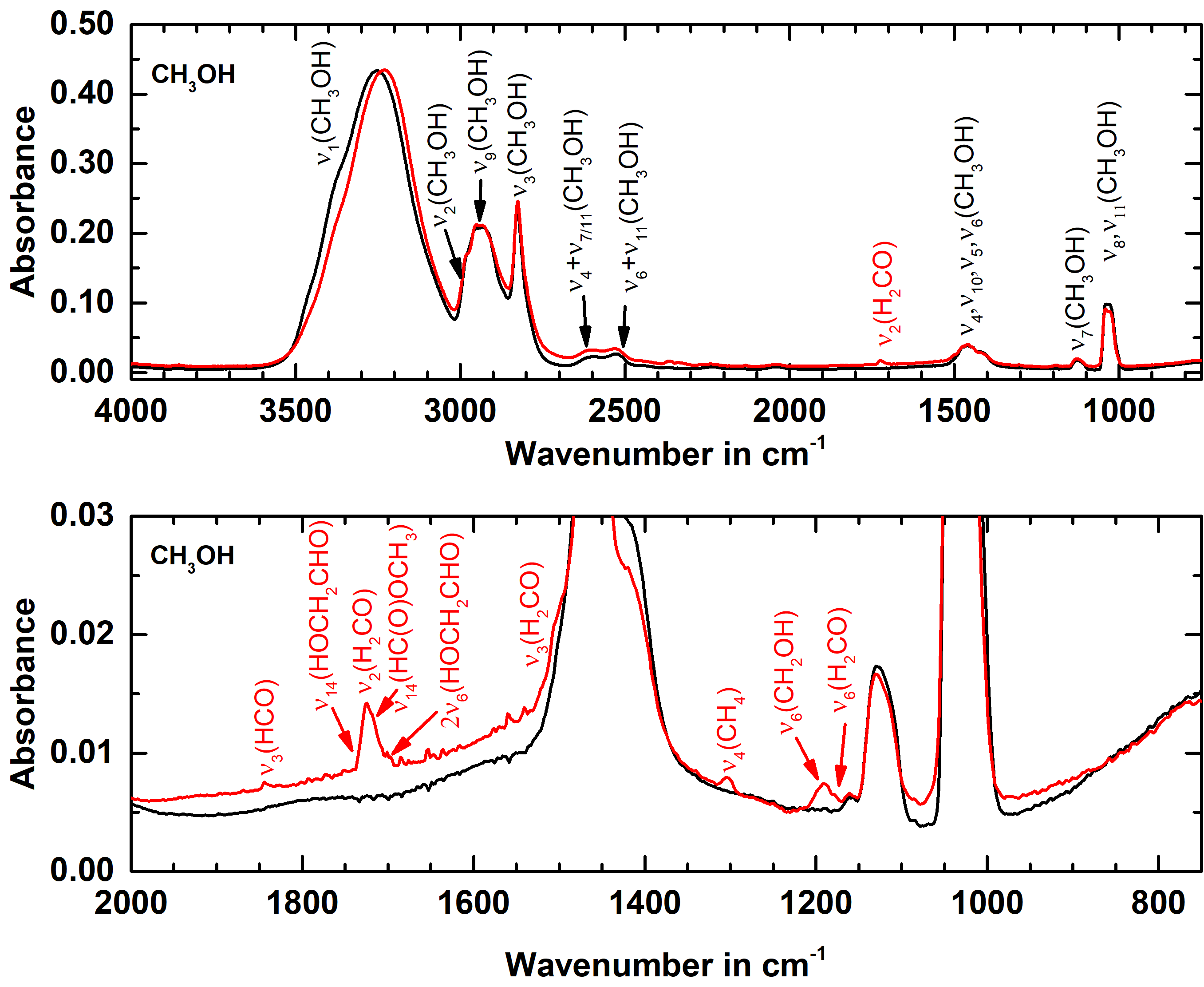
Correspondence: \* ralfk@hawaii.edu  
 \*\* nfk@hawaii.edu  
 \*\*\*ake05@mit.edu

**Error determination of computed ionization energies**

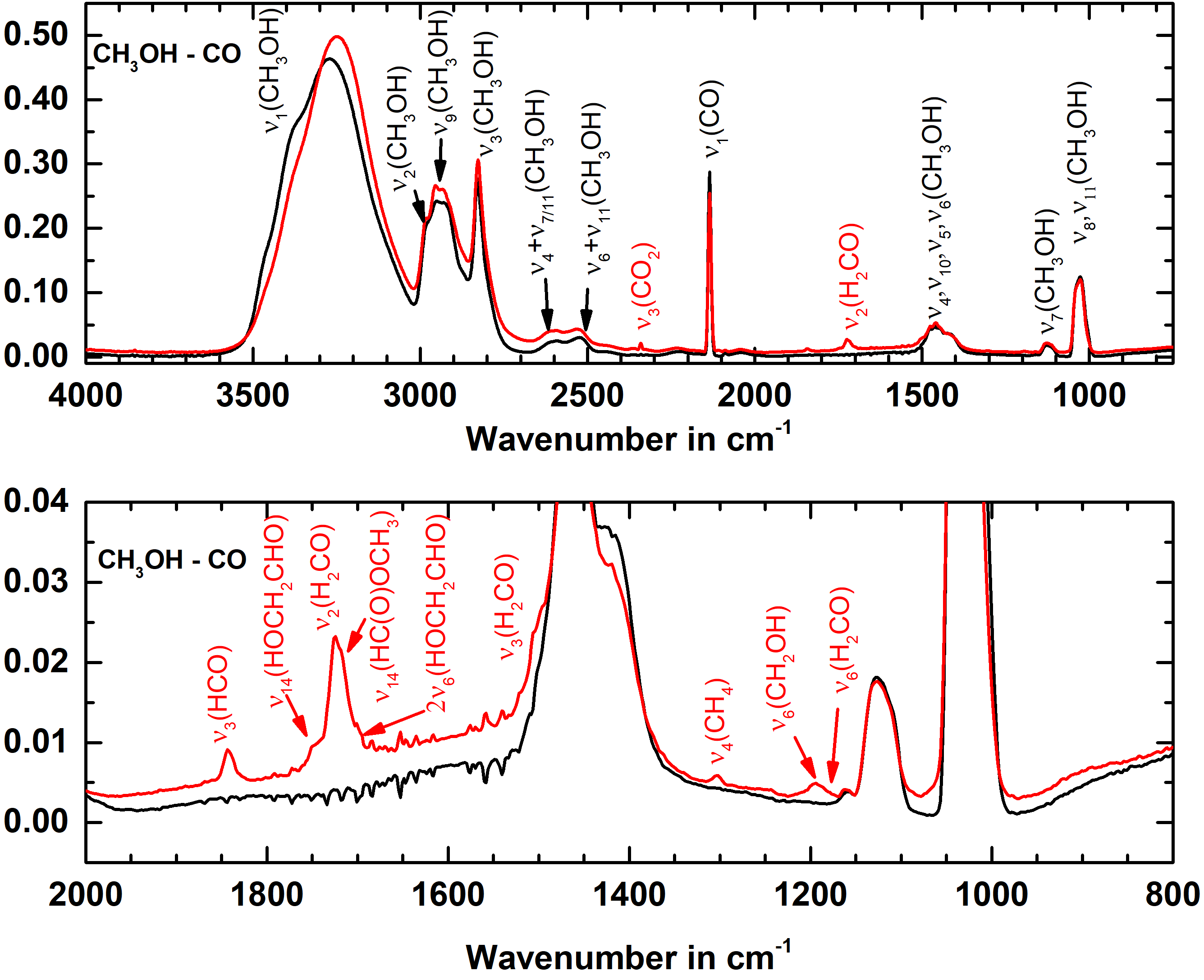
As the identification of different isomers in our studies focusses on the ionization energy of each isomer, we performed additional ionization energy computations at the same level of theory for multiple oxygen-containing complex organic molecules as benchmarks (Table S8). Error bounds were determined by subtracting the calculated ionization energy from the error boundaries of the experimentally determined and hence known values for each molecule. Afterwards, the average difference to the lower and upper boundary as well as their standard deviation were calculated. Finally, the standard deviation was subtracted from or added to the average difference for the lower and upper boundary, respectively. This conservative analysis yielded errors of −0.06/+0.11 eV, which allows us to distinguish all isomers of interest in this study based on their calculated and/or experimentally determined ionization energy.

**CO-CH3OH ratio determination**

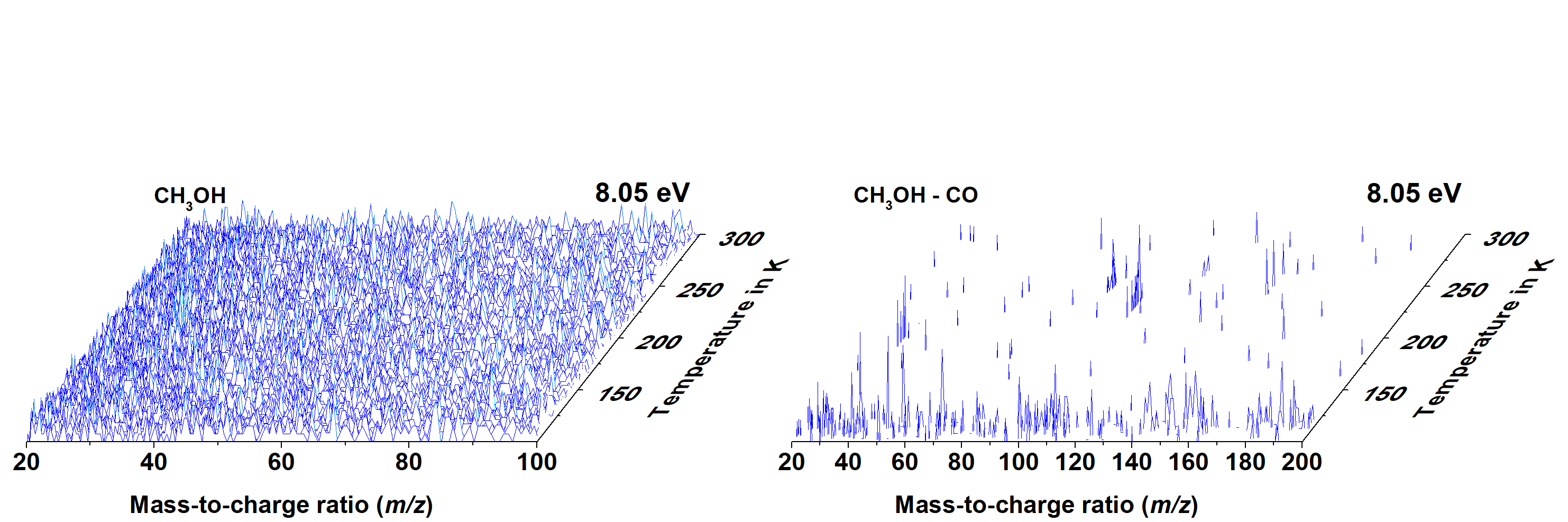
To quantify the ratio of the ice constituents, methanol and carbon monoxide ices of known thicknesses were prepared and IR spectra were taken to determine the absorption coefficient. This absorption coefficient was then used along with a modified Lambert-Beer law to determine the column densities of the ice constituents. The CO stretching and CH3 rocking mode (1040 cm−1; 1027 cm−1, combined absorption coefficient *A* = 1.6 × 10−18 cm molecule−1), the CH3 rocking mode at 1129 cm−1 (*A* = 2.1 × 10−19 cm molecule−1), and the CH deformation and OH bending mode at 1460 cm−1 (*A* = 1.1 × 10−18 cm molecule−1) of methanol were used for the determination of the column density of methanol along with the CO stretching mode of carbon monoxide at 2136 cm−1 (*A* = 1.2 × 10−18 cm molecule−1) to determine its column density. For all binary ices in this study, this analysis yielded a carbon monoxide to methanol ratio of 1:1.2 ± 0.2. The uncertainty was determined by the standard deviation of the column densities determined by individual IR modes and the standard deviation of the ratio across all ices prepared.



**Figure S1:** IR spectra of pure methanol ice before (black lines) and after irradiation (red lines). Spectra are slightly offset to highlight differences. Red labels indicate newly formed molecules.



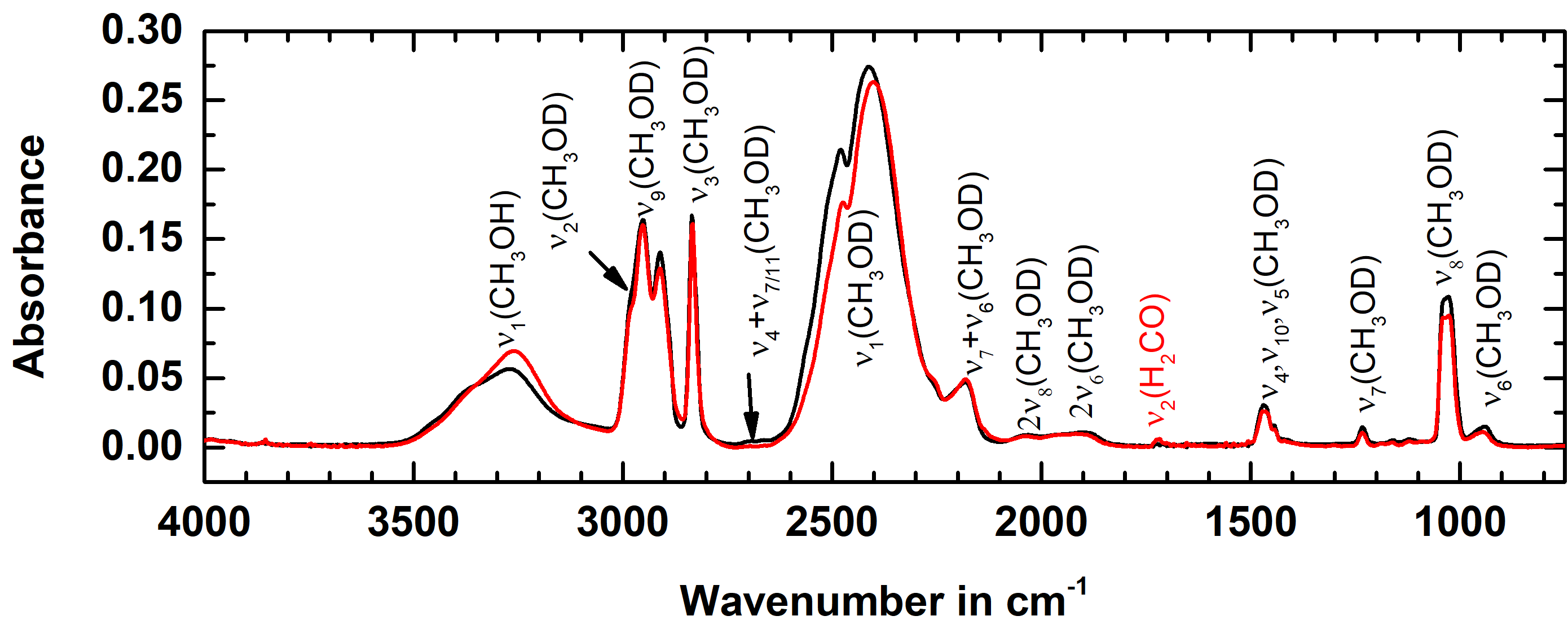
**Figure S2:** IR spectra of methanol-carbon monoxide ice before (black lines) and after irradiation (red lines). Spectra are slightly offset to highlight differences. Red labels indicate newly formed molecules.



**Figure S3:** Temperature-dependent time-of-flight mass spectra of pure methanol ice (left) and methanol – carbon monoxide ice (right) after electron irradiation recorded at 8.05 eV.



**Figure S4:** Reaction pathways inferred from isotopically labelled methanol-OD. Thick arrows designate the pathways considered relevant for the formation of 1,2-ethenediol.



**Figure S5:** IR spectra of methanol-OD before (black lines) and after irradiation (red lines). Red labels indicate newly formed molecules. Modes are numbered according to their order in regular methanol.

****

**Figure S6:** Desorption profile of *m/z* -= 60 (C2H4O2) in irradiated ethylene glycol ((CH2OH)2) recorded at a photon energy of 8.50 eV. The resulting ion signal can only be due to 1,2-ethenediol.

 **Figure S7.** Reaction pathways inferred from isotopically labelled methanol-13C18O. The dashed arrows define the overall process excluding reactive radical intermediates.

|  |
| --- |
| **Table S1:** Computed relative energies and dipole moments for 1,2-ethenediol conformers at B3LYP/cc-pVTZ level of theory. |

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Structure** | **Name** | **Point group** | **Electronic state** | **Rel. energy in kJ mol–1** | **Dipole moment *µ* in Debye** |
|  | *E-anti-anti-*1,2-ethenediol | *C*2 | 1A | 18 | 1.28 |
|  | *E-syn-anti-*1,2-ethenediol | *C*1 | 1A | 17 | 2.36 |
|  | *E-syn-syn-*1,2-ethenediol | *C*2 | 1A | 15 | 0.00 |
|  | *Z-anti-anti-*1,2-ethenediol | *C*2v | 1A1 | 15 | 2.13 |
|  | *Z-syn-anti-*1,2-ethenediol | *C*1 | 1A1 | 0 | 2.25 |

**Table S2:** Data used to calculate irradiation doses.

|  |  |  |  |
| --- | --- | --- | --- |
| Parameter | CH3OH | CH3OH - CO | |
| irradiation current, I (nA) | 30 ± 2 | 30 ± 2 | |
| initial kinetic energy of the electrons, Einit | 5 keV | 5 keV | |
| total number of electrons | (6.7 ± 0.3)×1014 | (6.7 ± 0.3)×1014 | |
| average penetration depth, l\* (nm) | 260 ± 30 | 280 ± 30 | |
| density of the ice, ρ (g cm-3) | 1.020 | 1.023 | |
| average kinetic energy of transmitted electrons, Etrans\* (keV) | 0 | 0 | |
| average kinetic energy of backscattered electrons, Ebs\* (keV) | 3.2 ± 0.3 | 3.3 ± 0.3 | |
| fraction of transmitted electrons, ftrans\* | 0 | 0 | |
| fraction of backscattered electrons, fbs\* | 0.33 ± 0.03 | 0.35 ± 0.03 | |
| irradiated area, A (cm2) | 1.0 ± 0.1 | 1.0 ± 0.1 | |
| molecule | CH3OH | CH3OH | CO |
| total # molecules processed | (5.0± 0.7)×1017 | (3.1 ± 0.5)×1017 | (2.5 ± 0.3)×1017 |
| dose per molecule (eV) | 5.3 ± 0.8 | 4.9 ± 0.8 | 4.2 ± 0.7 |

Notes: \*CASINO output values

**Table S3:**  Wavelengths and dyes used to generate the different photon energies of the photoionization source.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | Photon energy (eV) | 9.75 | 8.82 | 8.50 | 8.05 |
|  | Wavelength (nm) | 127.2 | 140.6 | 145.9 | 154.0 |
| ω1 | Wavelength (nm) | 202.316 | 222.566 | 202.316 | 249.628 |
| Nd:YAG (ω 1) | Wavelength (nm) | 532 | 355 | 532 | 355 |
| Dye laser (ω 1) | Wavelength (nm) | 606.948 | 445.132 | 606.948 | 499.256 |
| Dye (ω 1)*a* |  | Rh mix | C 450 | Rh mix | C 503 |
| ω 2 | Wavelength (nm) | 495 | 534 | 330 | 658 |
| Nd:YAG (ω 2) | Wavelength (nm) | 355 | 355 | 532 | 532 |
| Dye laser (ω 2) | Wavelength (nm) | 495 | 534 | 660 | 658 |
| Dye (ω 2)*a* |  | C 503 | C 540 A | DCM | DCM |

**Notes: *a*** Rh mix: Rhodamine 610 + Rhodamine 640, C 450/503/540 A: Coumarin 450/503/540 A

**Table S4:**  Infrared absorptions in methanol and methanol-OD ices before and after irradiation.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| CH3OH | | CH3OD | | Assignment | Mode |
| Before irradiation  cm−1 | After irradiation cm−1 | Before irradiation cm−1 | After irradiation cm−1 |  |  |
| 4398 |  | 4407 |  | (CH3OH) | Combination |
| 4275 |  | 4276 |  | (CH3OH) | Combination |
| 4020 |  | 4015 |  | (CH3OH) | Combination |
| 3989 |  | 3984 |  | (CH3OH) | Combination |
| 3600-3020 |  | 2600-2100 |  | (CH3OH) | OH Stretching |
|  |  |  | 2253 | unknown |  |
| 2985 |  | 2985 |  | (CH3OH) | CH3 asym. str. |
| 2950 |  | 2950 |  | (CH3OH) | CH3 symm. str. |
| 2925 |  |  |  |  (CH3OH) | Combination/  Overtone |
| 2825 |  | 2825 |  | (CH3OH) | CH3 sym. Str. |
| 2604 |  | 2605 |  |  (CH3OH) | Combination |
| 2526 |  |  |  | (CH3OH) | Combination |
|  | 2340 |  |  | CO2) | C=O stretch |
| 2235 |  |  |  | 2 (CH3OH) | Overtone |
|  |  | 2185 |  |  (CH3OD) | Overtone |
|  | 2134 |  |  | CO) | CO stretch |
| 2040 |  | 2040 |  | 2(CH3OH) | Overtone |
|  |  | 1895 |  | 2(CH3OD) | Overtone |
|  | 1844 |  |  | HCO) | C=O stretch |
|  | 1750 |  |  | (HOCH2CHO) |  |
|  | 1726 |  | 1721 | (H2CO) | C=O stretch |
|  | 1718 |  | 1716 | HC(O)OCH3) | C=O stretch |
|  | 1700 |  |  | (HOCH2CHO) |  |
|  | 1508 |  |  | (H2CO) | CH2 scissor |
|  | 1499 |  |  | (H2CO) | CH2 scissor |
| 1477 |  | 1469 |  | (CH3OH) | CH3 asym. bend |
| 1461 |  | 1461 |  | (CH3OH) | CH3 asym. bend |
| 1445 |  | 1445 |  | (CH3OH) | CH3 symm bend |
| 1420 |  | 940 |  | (CH3OH) | O-H bend |
|  | 1302 |  | 1301 | (CH4) | deformation |
|  |  | 1233 |  |  | CH3 rocking |
|  | 1192 |  | 1190 | (CH2OH) | CO stretch |
|  | 1177 |  |  | (H2CO) | CH2 wagging |
| 1135 |  | 1160 |  | (CH3OH) | CH3 rocking |
| 1123 |  | 1120 |  | (CH3OH) | CH3 rocking |
|  | 1092 |  | 1092 | (HCO) | bending |
| 1040 |  | 1040 |  | (CH3OH) | CH3 rocking |
| 1026 |  | 1027 |  | (CH3OH) | CO stretch |
|  | 667 |  |  | (CO2) | C=O bend |

**Table S5:**  Infrared absorptions in methanol – carbon monoxide and methanol – carbon monoxide-13C18O ices before and after irradiation.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| CH3OH-CO | | CH3OH-13C18O | | Assignment | Mode |
| Before irradiation  cm−1 | After irradiation cm−1 | Before irradiation cm−1 | After irradiation cm−1 |  |  |
| 4400 |  | 4402 |  | (CH3OH) | Combination |
| 4277 |  | 4278 |  | (CH3OH) | Combination |
|  |  | 4049 |  |  |  |
| 4017 |  | 4016 |  | (CH3OH) | Combination |
| 3986 |  | 3984 |  | (CH3OH) | Combination |
| 3600-3020 |  | 3600-3200 |  | (CH3OH) | OH Stretching |
| 2985 |  | 2985 |  | (CH3OH) | CH3 asym. str. |
| 2953 |  | 2954 |  | (CH3OH) | CH3 sym. str. |
| 2925 |  | 2922 |  |  (CH3OH) | Combination/  Overtone |
| 2827 |  | 2829 |  | (CH3OH) | CH3 sym. Str. |
|  |  | 2615 |  |  (CH3OH) | Combination |
| 2604 |  | 2591 |  |  (CH3OH) | Combination |
| 2523 |  | 2522 |  | (CH3OH) | Combination |
|  |  |  | 2361 | CO2) | C=O stretch |
|  | 2340 |  | 2340 | CO2) | C=O stretch |
|  |  |  | 2275 | CO2) | C=O stretch |
|  |  |  | 2258 | C16O18O) | C=O stretch |
|  |  |  | 2239 | C18O2) | C=O stretch |
| 2235 |  |  |  | 2 (CH3OH) | Overtone |
| 2136 |  |  | 2136 | CO) | CO stretch |
|  | 2107 |  |  | unknown |  |
| 2088 |  | 2088 |  | 13CO/C18O) | CO stretch |
|  |  | 2038 |  | 13C18O) | CO stretch |
| 2044 |  |  |  | 2(CH3OH) | Overtone |
|  | 1843 |  |  | HCO) | C=O stretch |
|  | 1750 |  |  | (HOCH2CHO) |  |
|  | 1726 |  | 1721 | H2CO) | C=O stretch |
|  | 1718 |  | 1712 | (HC(O)OCH3) | C=O stretch |
|  | 1700 |  |  | (HOCH2CHO) |  |
|  | 1504 |  | 1507 | (H2CO) | CH2 scissor |
|  | 1499 |  | 1499 | (H2CO) | CH2 scissor |
| 1475 |  | 1475 |  | (CH3OH) | CH3 asym. bend |
| 1461 |  | 1461 |  |  (CH3OH) | CH3 asym. bend |
| 1445 |  | 1445 |  | (CH3OH) | CH3 sym. bend |
| 1421 |  | 1421 |  | (CH3OH) | O-H bend |
|  | 1302 |  | 1304 |  (CH4) | Deg. str. |
|  | 1211 |  |  |  | COH deform. |
|  | 1193 |  | 1192 |  (CH2OH) | CO stretch |
|  | 1177 |  | 1177 |  (H2CO) | CH2 wagging |
| 1158 |  | 1161 |  | (CH3OH) | CH3 rocking |
| 1126 |  | 1125 |  | (CH3OH) | CH3 rocking |
| 1110 |  | 1110 |  | (CH3OH) | CH3 rocking |
|  | 1092 |  |  | (HCO) | bending |
| 1040 |  | 1040 |  | (CH3OH) | CH3 rocking |
| 1027 |  | 1027 |  |  (CH3OH) | CO stretch |
|  | 667 |  | 667 | (CO2) | C=O bend |

**Table S6.** Infrared frequencies and intensities of 1,2-ethenediol conformers at CCSD(T)/cc-pWCVTZ level of theory

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| *E-anti-anti* | | *E-syn-anti* | | *E-syn-syn* | |
| Frequency  in cm−1 | Intensity | Frequency in cm−1 | Intensity | Frequency in cm−1 | Intensity |
| 155.9 | 98.4 | 230.8 | 128.1 | 226.2 | 122.1 |
| 243.3 | 150.6 | 285.4 | 25.8 | 277.4 | 0.0 |
| 326.1 | 15.3 | 321.2 | 17.9 | 315.1 | 34.1 |
| 328.5 | 29.4 | 391.8 | 69.7 | 367.0 | 68.0 |
| 574.0 | 2.2 | 570.1 | 8.0 | 566.7 | 0.0 |
| 801.5 | 3.3 | 787.1 | 11.5 | 784.2 | 0.0 |
| 913.9 | 56.6 | 932.1 | 62.2 | 907.5 | 83.8 |
| 1109.7 | 0.2 | 1102.4 | 92.4 | 1082.9 | 0.0 |
| 1166.9 | 382.1 | 1171.3 | 262.5 | 1152.1 | 368.7 |
| 1216.3 | 71.3 | 1225.2 | 30.6 | 1233.4 | 7.8 |
| 1278.8 | 1.1 | 1316.9 | 3.5 | 1333.2 | 0.0 |
| 1345.8 | 0.0 | 1335.2 | 18.0 | 1366.7 | 0.0 |
| 1400.8 | 13.3 | 1407.7 | 39.7 | 1424.5 | 99.9 |
| 1779.7 | 0.3 | 1753.7 | 11.2 | 1747.7 | 0.0 |
| 3183.2 | 26.4 | 3142.3 | 30.1 | 3203.5 | 27.3 |
| 3187.6 | 0.0 | 3233.6 | 5.3 | 3204.0 | 0.0 |
| 3868.4 | 122.3 | 3830.4 | 34.4 | 3835.4 | 70.3 |
| 3870.0 | 16.3 |  |  |  |  |
|  |  |  |  |  |  |
| *Z-anti-anti* | | *Z-syn-anti* | |
| Frequency in cm−1 | Intensity | Frequency in cm−1 | Intensity |
| 80.9 | 0.0 | 221.1 | 78.4 |
| 93.7 | 196.0 | 257.9 | 60.0 |
| 240.0 | 3.7 | 471.9 | 55.8 |
| 524.4 | 0.0 | 549.0 | 74.5 |
| 713.1 | 78.8 | 725.6 | 37.7 |
| 728.9 | 33.8 | 766.5 | 28.1 |
| 826.2 | 0.0 | 874.4 | 9.1 |
| 1024.5 | 10.1 | 1032.9 | 39.9 |
| 1131.1 | 135.4 | 1122.5 | 146.8 |
| 1230.8 | 127.7 | 1214.2 | 30.7 |
| 1315.9 | 86.2 | 1275.0 | 110.3 |
| 1326.7 | 92.8 | 1380.8 | 2.7 |
| 1454.0 | 28.2 | 1439.6 | 55.2 |
| 1799.6 | 20.5 | 1753.3 | 51.2 |
| 3201.5 | 0.9 | 3218.1 | 4.5 |
| 3225.4 | 18.9 | 3253.8 | 9.9 |
| 3889.6 | 156.6 | 3789.0 | 49.9 |

**Table S7:** Computed adiabatic ionization energies and relative energies for C2H4O2 isomers at CCSD(T)/CBS//B3LYP/cc-pVTZ level of theory + zero-point vibrational energy.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Structure | **Name** | ***IE*calc in eV** | ***IE*exp in eV** | **Electronic state** | **Relative energy in kJ mol–1** |
|  | *anti-*acetic acid | 10.65 | 10.65 ± 0.02[1](#_ENREF_1) | 1A' | 0 |
|  | *syn-*acetic acid | 10.52 | 1A' | 21 |
|  | *syn, syn*-1,1-ethenediol | 8.68 |  | 1A1 | 117 |
|  | *syn, anti-*1,1-ethenediol | 8.58 |  | 1A' | 112 |
|  | *anti, anti-*1,1-ethenediol | 8.59 |  | 1A | 125 |
|  | *anti*-methyl formate | 10.68 | 10.835[1](#_ENREF_1) | 1A' | 93 |
|  | *syn*-methyl formate | 10.83 | 1A' | 73 |
|  | *syn*, *syn*-glycolaldehyde | 10.06 | 9.95 ±0.05[2](#_ENREF_2) | 1A' | 113 |
|  | *syn*, *anti*-glycolaldehyde | 9.84 | 1A' | 134 |
|  | *anti*, *anti*-glycolaldehyde | 9.91 | 1A' | 126 |
|  | *anti*, *gauche*-glycolaldehyde | 9.90 | 1A | 127 |
|  | *E-anti-anti-*1,2-ethenediol | 8.16 |  | 1A | 167 |
|  | *E-syn-anti-*1,2-ethenediol | 8.30 | 1A | 166 |
|  | *E-syn-syn-*1,2-ethenediol | 8.41 | 1A | 165 |
|  | *Z-anti-anti-*1,2-ethenediol | 8.21 | 1A1 | 162 |
|  | *Z-syn-anti-*1,2-ethenediol | 8.37 | 1A | 147 |
|  | *Oxiran-2-ol* | 8.93 |  | 1A | 195 |
|  | *1,3-Dioxetane* | 10.08 |  | 2B1u | 235 |

**Table S8:** Error analysis of computed ionization energies for COMs containing one and two oxygen atoms; adiabatic ionization energies were computed at CCSD(T)/CBS//B3LYP/cc-pVTZ level of theory + zero-point vibrational energy.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Structure** | **Name** | **Experimental adiabatic ionization energy in eV** | **Lowest Computed adiabatic ionization energy**  **in eV** | **Difference to lower bound** | **Difference to upper bound** |
|  | Glycolaldehyde | 9.95 ±0.05 [2](#_ENREF_2) | 9.84 | 0.06 | 0.16 |
|  | Acetic Acid | 10.65 ± 0.02 [1](#_ENREF_1) | 10.52 | 0.11 | 0.15 |
|  | Methyl Formate | 10.835 [1](#_ENREF_1) | 10.68 | 0.155 | 0.155 |
|  | Acetone | 9.703 ± 0.006 [1](#_ENREF_1) | 9.71 | −0.013 | −0.001 |
|  | Propanal | 9.96 ± 0.01 [1](#_ENREF_1) | 9.97 | -0.02 | 0.00 |
|  | Propylene oxide | 10.22 ± 0.02 [3](#_ENREF_3) | 10.24 | −0.04 | 0.00 |
|  | Prop-1-en-2-ol | 8.67 ± 0.05 [4](#_ENREF_4) | 8.71 | −0.09 | 0.01 |
|  | 2-Propen-1-ol | 9.67 ± 0.03 [1](#_ENREF_1) | 9.65 | −0.01 | 0.05 |
|  | (*E*)-1-Propenol | 8.64 ± 0.02 [5](#_ENREF_5) | 8.61 | 0.01 | 0.05 |
|  | (*Z*)-1-Propenol | 8.70 ± 0.03 [5](#_ENREF_5) | 8.63 | 0.04 | 0.10 |
|  | Methanol | 10.84 ± 0.01 | 10.86 | −0.03 | −0.01 |
|  | Propadienone | 9.12 ± 0.05 | 9.15 | −0.08 | 0.02 |
|  | Formaldehyde | 10.88 ± 0.01 | 10.89 | −0.02 | 0.00 |
|  | Ketene | 9.617 ± 0.003 | 9.58 | 0.034 | 0.040 |
|  | Acetaldehyde | 10.229 ± 0.0007 | 10.24 | −0.0117 | −0.0103 |
|  |  |  | Average difference | 0.006 | 0.048 |
|  |  |  | Std. deviation | 0.066 | 0.063 |
|  |  |  | Error bounds | −0.06 | 0.11 |

**Cartesian Coordinates for Selected Structures of C2H4O2**

B3LYP/cc-pVTZ optimized geometry (distances in Å), electronic energies (in hartree), zero-point vibrational energies (ZPVE), extrapolated CCSD(T)/CBS energies (in hartree) and adiabatic ionization energies (IE) at CCSD(T)/CBS//B3LYP/cc-pVTZ level of theory.

*cis* Acetic acid cation (*C*s)

C –1.012317 –0.964938 0.000000

C 0.064451 0.082674 0.000000

H –2.006868 –0.521206 0.000000

H –0.879238 –1.565654 0.905304

H –0.879238 –1.565654 –0.905304

O –0.373776 1.254641 0.000000

O 1.327467 –0.121447 0.000000

H 1.576888 –1.063412 0.000000

E = –228.7951578

E[CCSD(T)/CBS] = –228.4591383

ZPVE = 157.0305 kJ mol–1

*cis* Acetic acid (*C*s)

C 1.384403 –0.444093 0.000000

C –0.020669 0.115577 0.000000

H 2.097845 0.373595 0.000000

H 1.547860 –1.065592 –0.882491

H 1.547860 –1.065592 0.882491

O –0.293502 1.280081 0.000000

O –1.016092 –0.815392 0.000000

H –0.647118 –1.705775 0.000000

E = –229.1725686

E[CCSD(T)/CBS] = –228.8472353

ZPVE = 161.1038 kJ mol–1

*trans* Acetic acid cation (*C*s)

C –1.081166 –0.903862 0.000000

C 0.045594 0.071434 0.000000

H –2.051782 –0.410721 0.000000

H –0.965779 –1.515243 0.901193

H –0.965779 –1.515243 –0.901193

O –0.266434 1.282335 0.000000

O 1.263657 –0.338800 0.000000

H 1.939045 0.369124 0.000000

E = –228.7985722

E[CCSD(T)/CBS] = –228.4616873

ZPVE = 156.0637 kJ mol–1

*trans* Acetic acid (*C*s)

C 1.423315 –0.312362 0.000000

C –0.019649 0.106963 0.000000

H 2.057643 0.567904 0.000000

H 1.631074 –0.924037 –0.877888

H 1.631074 –0.924037 0.877888

O –0.427736 1.238677 0.000000

O –0.850028 –0.965037 0.000000

H –1.753960 –0.617026 0.000000

E = –229.1811770

E[CCSD(T)/CBS] = –228.8554091

ZPVE = 161.7909 kJ mol–1

*cis*, *cis* 1,1-Ethenediol cation (*C*2v)

C 0.000000 0.000000 0.025454

C 0.000000 0.000000 1.443455

H 0.000000 –0.942538 1.969724

H 0.000000 0.942538 1.969724

O 0.000000 1.146808 –0.577470

H 0.000000 1.133094 –1.549871

O 0.000000 –1.146808 –0.577470

H 0.000000 –1.133094 –1.549871

E = –228.8255200

E[CCSD(T)/CBS] = –228.4916277

ZPVE = 159.9339 kJ mol–1

*cis*, *cis* 1,1-Ethenediol (*C*2)

C 0.000000 0.000000 –0.079487

C 0.000000 0.000000 –1.404595

H –0.931416 0.055195 –1.942827

H 0.931416 –0.055195 –1.942827

O 1.128211 –0.212864 0.661238

H 1.132941 0.402815 1.404760

O –1.128211 0.212864 0.661238

H –1.132941 –0.402815 1.404760

E = –229.1326146

E[CCSD(T)/CBS] = –228.8072804

ZPVE = 160.0441 kJ mol–1

*cis*, *trans* 1,1-Ethenediol cation (*C*s)

C –0.014571 0.005326 0.000000

C –0.391208 1.375179 0.000000

H 0.382768 2.128613 0.000000

H –1.432608 1.663026 0.000000

O –0.840287 –0.993688 0.000000

H –1.780303 –0.747631 0.000000

O 1.242361 –0.276385 0.000000

H 1.426254 –1.235319 0.000000

E = –228.8304016

E[CCSD(T)/CBS] = –228.4968440

ZPVE = 160.6893 kJ mol–1

*cis*, *trans* 1,1-Ethenediol (*C*s)

C 0.000000 0.023323 –0.077490

C 0.000000 –0.005160 –1.408088

H 0.000000 0.915395 –1.966530

H 0.000000 –0.942638 –1.940970

O 0.000000 –1.057705 0.752872

H 0.000000 –1.863932 0.227096

O 0.000000 1.165684 0.639497

H 0.000000 0.933426 1.575090

E = –229.1373598

E[CCSD(T)/CBS] = –228.8118010

ZPVE = 159.5802 kJ mol–1

*trans, trans* 1,1-Ethenediol cation (*C*2v)

C 0.000000 0.000000 –0.019064

C 0.000000 0.000000 1.406857

H 0.000000 0.930956 1.956399

H 0.000000 –0.930956 1.956399

O 0.000000 –1.071954 –0.736537

H 0.000000 –1.898631 –0.227486

O 0.000000 1.071954 –0.736537

H 0.000000 1.898631 –0.227486

E = –228.8243955

E[CCSD(T)/CBS] = –228.4913406

ZPVE = 160.4209 kJ mol–1

*trans, trans* 1,1-Ethenediol (*C*2v)

C 0.000000 0.000000 –0.071731

C 0.000000 0.000000 –1.408140

H 0.000000 0.924602 –1.963761

H 0.000000 –0.924602 –1.963761

O 0.000000 –1.089183 0.725564

H 0.000000 –1.876169 0.172050

O 0.000000 1.089183 0.725564

H 0.000000 1.876169 0.172050

E = –229.1356581

E[CCSD(T)/CBS] = –228.8102922

ZPVE = 160.4708 kJ mol–1

Glycolaldehyde #01 cation (*C*1)

O –1.321417 0.597486 0.176457

C –0.059575 0.918359 –0.038775

H –1.812700 0.355296 –0.626507

C 1.038962 –0.495502 0.058623

O 0.634232 –1.577856 0.117324

H 0.362529 1.481896 0.794557

H 0.220975 1.260443 –1.038753

H 2.079147 –0.121421 0.046908

E = –228.7783297

E[CCSD(T)/CBS] = –228.4398472

ZPVE = 153.9289 kJ mol–1

Glycolaldehyde #01 (*C*s)

O –1.347777 0.557051 0.000000

C 0.000000 0.928681 0.000000

H –1.361244 –0.412024 0.000000

C 0.924487 –0.257086 0.000000

O 0.512154 –1.390532 0.000000

H 0.245610 1.542549 0.878739

H 0.245610 1.542549 –0.878739

H 2.008081 –0.034791 0.000000

E = –229.1364389

E[CCSD(T)/CBS] = –228.8117491

ZPVE = 160.0387 kJ mol–1

Glycolaldehyde #02 cation (*C*1)

O –1.293701 0.875070 –0.318733

C –0.004669 1.079178 –0.123125

H –1.818781 0.835904 0.498367

C 0.916406 –0.448994 0.059514

O 0.384232 –1.469662 0.177093

H 0.304852 1.555993 0.810961

H 0.490839 1.434410 –1.027793

H 1.994100 –0.203714 0.037714

E = –228.7783296

E[CCSD(T)/CBS] = –228.4398495

ZPVE = 153.9255 kJ mol–1

Glycolaldehyde #02 (*C*s)

O 1.302044 –0.690422 0.000000

C 0.770533 0.608140 0.000000

H 2.260995 –0.632407 0.000000

C –0.737108 0.581953 0.000000

O –1.420138 –0.402999 0.000000

H 1.072266 1.196088 –0.881008

H 1.072266 1.196088 0.881008

H –1.182560 1.601071 0.000000

E = –229.1279011

E[CCSD(T)/CBS] = –228.8033010

ZPVE = 158.4770 kJ mol–1

Glycolaldehyde #03 cation (*C*1)

O –1.285865 1.187448 –0.069553

C 0.010770 0.894365 –0.159239

H –1.545293 1.528885 0.802634

C 0.201593 –0.844154 0.038605

O 1.118210 –1.232569 0.635639

H 0.680692 1.312135 0.588772

H 0.367322 0.942560 –1.192128

H –0.606998 –1.397301 –0.468937

E = –228.7795703

E[CCSD(T)/CBS] = –228.4407168

ZPVE = 154.8563 kJ mol–1

Glycolaldehyde #03 (*C*s)

O 1.266366 1.879953 0.000000

C 0.780852 0.549904 0.000000

H 2.226566 1.866725 0.000000

C –0.732015 0.603212 0.000000

O –1.429426 –0.375206 0.000000

H 1.097250 –0.014804 0.885128

H 1.097250 –0.014804 –0.885128

H –1.149033 1.630316 0.000000

E = –229.1305150

E[CCSD(T)/CBS] = –228.8061648

ZPVE = 158.0194 kJ mol–1

Glycolaldehyde #04 cation (*C*1)

O –1.655967 –0.296531 0.091481

C –0.632308 0.541599 –0.065199

H –1.957754 –0.369893 1.012429

C 0.849516 –0.404311 –0.165399

O 1.804924 0.014665 0.343493

H –0.428314 1.251992 0.732655

H –0.590662 0.946389 –1.080413

H 0.696324 –1.329874 –0.746137

E = –228.7795703

E[CCSD(T)/CBS] = –228.4407254

ZPVE = 154.8491 kJ mol–1

Glycolaldehyde #04 (*C*1)

O 1.711792 0.231131 –0.003969

C 0.516542 –0.524498 –0.070449

H 1.807441 0.591696 0.882358

C –0.727479 0.344174 –0.124089

O –1.834586 –0.051751 0.125366

H 0.414279 –1.246715 0.745132

H 0.557408 –1.092706 –1.003885

H –0.531156 1.394632 –0.427554

E = –229.1306407

E[CCSD(T)/CBS] = –228.8058664

ZPVE = 158.7039 kJ mol–1

(*E*)-*trans, trans* Ethene-1,2-diol cation (*C*2h)

C 0.565043 –0.411377 0.000000

C –0.565043 0.411377 0.000000

O –1.728648 –0.167757 0.000000

H –2.474330 0.455484 0.000000

H –0.474010 1.492952 0.000000

O 1.728648 0.167757 0.000000

H 2.474330 –0.455484 0.000000

H 0.474010 –1.492952 0.000000

E = –228.8308768

E[CCSD(T)/CBS] = –228.4927525

ZPVE = 164.3151 kJ mol–1

(*E*)-*trans, trans* Ethene-1,2-diol (*C*2)

C 0.546618 0.375520 –0.072170

C –0.546618 –0.375520 –0.072170

O –1.795742 0.198153 0.014140

H –2.440056 –0.395353 –0.379217

H –0.486695 –1.457749 –0.069631

O 1.795742 –0.198153 0.014140

H 2.440056 0.395353 –0.379217

H 0.486695 1.457749 –0.069631

E = –229.1164359

E[CCSD(T)/CBS] = –228.7906112

ZPVE = 158.9087 kJ mol–1

(*E*)-*cis, trans* Ethene-1,2-diol cation (*C*s)

C 0.562695 –0.386979 0.000000

C –0.575731 0.426942 0.000000

O –1.730729 –0.173486 0.000000

H –2.490323 0.432925 0.000000

H –0.521130 1.511932 0.000000

O 1.782069 0.049292 0.000000

H 1.882148 1.017626 0.000000

H 0.469731 –1.467265 0.000000

E = –228.8258146

E[CCSD(T)/CBS] = –228.4878997

ZPVE = 164.1639 kJ mol–1

(*E*)-*cis, trans* Ethene-1,2-diol (*C*1)

C 0.536830 –0.375622 0.035089

C –0.537963 0.404615 0.015759

O –1.805363 –0.140589 –0.053859

H –2.377261 0.305180 0.577977

H –0.464535 1.488776 –0.026431

O 1.837491 0.041868 –0.013468

H 1.867842 1.003075 –0.071255

H 0.452875 –1.452261 0.071581

E = –229.1171363

E[CCSD(T)/CBS] = –228.7913099

ZPVE = 159.8009 kJ mol–1

(*E*)-*cis, cis* Ethene-1,2-diol cation (*C*2)

C 0.565367 0.412826 0.000000

C –0.565367 –0.412826 0.000000

O –0.524446 –1.709114 0.000000

H 0.367752 –2.099730 0.000000

H –1.573260 –0.010024 0.000000

O 0.524446 1.709114 0.000000

H –0.367752 2.099730 0.000000

H 1.573260 0.010024 0.000000

E = –228.8220855

E[CCSD(T)/CBS] = –228.4842479

ZPVE = 164.2288 kJ mol–1

(*E*)-*cis, cis* Ethene-1,2-diol (*C*2)

C 0.535588 –0.393538 0.000000

C –0.535588 0.393538 0.000000

O –0.531842 1.767126 0.000000

H 0.376318 2.087396 –0.000001

H –1.544782 0.001982 0.000000

O 0.531842 –1.767126 0.000000

H –0.376318 –2.087396 –0.000001

H 1.544782 –0.001982 0.000000

E = –229.1179891

E[CCSD(T)/CBS] = –228.7918952

ZPVE = 160.0722 kJ mol–1

(*Z*)-*trans, trans* Ethene-1,2-diol cation (*C*2v)

C 0.000000 0.701558 0.598805

C 0.000000 –0.701558 0.598805

O 0.000000 –1.332423 –0.533871

H 0.000000 –2.299833 –0.440901

H 0.000000 –1.241982 1.538413

O 0.000000 1.332423 –0.533871

H 0.000000 2.299833 –0.440901

H 0.000000 1.241982 1.538413

E = –228.8302182

E[CCSD(T)/CBS] = –228.4928958

ZPVE = 165.1683 kJ mol–1

(*Z*)-*trans, trans* Ethene-1,2-diol (*C*2v)

C 0.000000 0.664463 0.621475

C 0.000000 –0.664463 0.621475

O 0.000000 –1.402610 –0.534851

H 0.000000 –2.335599 –0.311700

H 0.000000 –1.196227 1.562811

O 0.000000 1.402610 –0.534851

H 0.000000 2.335599 –0.311700

H 0.000000 1.196227 1.562811

E = –229.1175585

E[CCSD(T)/CBS] = –228.7924957

ZPVE = 159.4846 kJ mol–1

(*Z*)-*cis, trans* Ethene-1,2-diol cation (*C*s)

C –0.702451 0.603136 0.000000

C 0.700873 0.624098 0.000000

O 1.320059 –0.524193 0.000000

H 2.289374 –0.455608 0.000000

H 1.249525 1.558079 0.000000

O –1.406398 –0.480047 0.000000

H –0.876304 –1.299567 0.000000

H –1.273536 1.522636 0.000000

E = –228.8297013

E[CCSD(T)/CBS] = –228.4931010

ZPVE = 165.1353 kJ mol–1

(*Z*)-*cis, trans* Ethene-1,2-diol (*C*1)

C –0.677832 0.628855 –0.006113

C 0.650200 0.655746 0.024604

O 1.350196 –0.541555 –0.008760

H 2.136784 –0.472167 0.538569

H 1.212465 1.578185 0.006253

O –1.425013 –0.509633 –0.006957

H –0.814926 –1.257861 0.033254

H –1.268115 1.530816 –0.049918

E = –229.1242472

E[CCSD(T)/CBS] = –228.7993516

ZPVE = 161.5028 kJ mol–1

Methyl formate #01 cation (*C*s)

C –0.322049 –0.641116 0.000000

O 0.023000 0.561966 0.000000

C 1.463697 0.969181 0.000000

H 1.582746 1.563796 0.898772

H 1.582746 1.563796 –0.898772

H 2.091024 0.082431 0.000000

O –1.520570 –1.027292 0.000000

H 0.385178 –1.493543 0.000000

E = –228.7632192

E[CCSD(T)/CBS] = –228.4253033

ZPVE = 156.7613 kJ mol–1

Methyl formate #01 (*C*s)

C –0.357854 –0.676644 0.000000

O 0.000000 0.620530 0.000000

C 1.393737 0.939881 0.000000

H 1.613905 1.526903 0.889587

H 1.613905 1.526903 –0.889587

H 2.008234 0.037411 0.000000

O –1.495027 –1.034159 0.000000

H 0.508874 –1.361607 0.000000

E = –229.1489027

E[CCSD(T)/CBS] = –228.8193960

ZPVE = 160.5394 kJ mol–1

Methyl formate #02 cation (*C*s)

C –0.726324 0.499868 0.000000

O 0.517087 0.671541 0.000000

C 1.461909 –0.498483 0.000000

H 1.279460 –1.069809 0.905805

H 2.438191 –0.031936 0.000000

H 1.279460 –1.069809 –0.905805

O –1.329742 –0.607297 0.000000

H –1.391519 1.380858 0.000000

E = –228.7649376

E[CCSD(T)/CBS] = –228.4277752

ZPVE = 156.8178 kJ mol–1

Methyl formate #02 (*C*s)

C –0.763903 0.440753 0.000000

O 0.548851 0.702755 0.000000

C 1.416163 –0.447709 0.000000

H 1.241385 –1.054217 0.886666

H 2.426459 –0.051730 0.000000

H 1.241385 –1.054217 –0.886666

O –1.264527 –0.648895 0.000000

H –1.317291 1.388190 0.000000

E = –229.1561630

E[CCSD(T)/CBS] = –228.8279453

ZPVE = 162.2987 kJ mol–1

1,3-Dioxetane cation (*D*2h)

O –0.000000 1.027455 –0.000000

C –0.959569 –0.000000 –0.000000

C 0.959569 0.000000 –0.000000

O 0.000000 –1.027455 –0.000000

H 1.601708 0.000000 0.901513

H 1.601708 0.000000 –0.901513

H –1.601708 –0.000000 –0.901513

H –1.601708 –0.000000 0.901513

E = –228.7351245

E[CCSD(T)/CBS] = –228.3940852

ZPVE = 154.0980 kJ mol–1

1,3-Dioxetane (*D*2h)

O 0.000000 0.000000 –1.035573

C 0.000000 –0.983257 –0.000000

C –0.000000 0.983257 0.000000

O 0.000000 –0.000000 1.035573

H –0.901963 1.605219 0.000000

H 0.901963 1.605219 0.000000

H 0.901963 –1.605219 –0.000000

H –0.901963 –1.605219 –0.000000

E = –229.0928022

E[CCSD(T)/CBS] = –228.7688123

ZPVE = 164.9067 kJ mol–1

Oxiran-2-ol cation (*C*s)

O 0.527608 0.342942 –0.000000

C –0.498017 –0.418009 0.000000

C 1.818337 –0.083049 –0.000000

H 2.532888 0.720249 –0.000000

H 2.021937 –1.143049 0.000000

O –1.629146 0.180763 0.000000

H –2.393248 –0.420867 0.000000

H –0.400214 –1.501904 0.000000

E = –228.7891396

E[CCSD(T)/CBS] = –228.4507662

ZPVE = 156.2551 kJ mol–1

Oxiran-2-ol (*C*1)

O 0.761180 –0.801134 –0.253427

C –0.212023 –0.048313 0.449567

C 0.993220 0.605920 –0.031809

H 0.913143 1.224709 –0.918238

H 1.803114 0.843711 0.649107

O –1.397976 0.230345 –0.200034

H –1.992184 –0.521689 –0.105163

H –0.316887 –0.326062 1.495432

E = –229.1048487

E[CCSD(T)/CBS] = –228.7812503

ZPVE = 162.5001 kJ mol–1

**Notes and References**

1 Lias, S. G. *"Ionization Energy Evaluation" in NIST Chemistry Webbook, NIST Standard Reference Database Number 69*. (National Institute of Standards and Technology).

2 Porterfield, J. P. *et al.* Pyrolysis of the Simplest Carbohydrate, Glycolaldehyde (CHO−CH2OH), and Glyoxal in a Heated Microreactor. *JPCA* **120**, 2161-2172, doi:10.1021/acs.jpca.6b00652 (2016).

3 Watanabe, K., Nakayama, T. & Mottl, J. Ionization potentials of some molecules. *JQSRT* **2**, 369-382, doi:https://doi.org/10.1016/0022-4073(62)90023-7 (1962).

4 Iraqi, M., Pri-Bar, I. & Lifshitz, C. Electron impact ionization of unstable enols: H2C=CHOH, H2C=C(OH)-CH3 and H2C=C(OH)-C2H5. *Org. Mass Spectrom.* **21**, 661-664, doi:10.1002/oms.1210211010 (1986).

5 Tureček, F. (E)- and (Z)-prop-1-en-1-ol: gas-phase generation and determination of heats of formation by mass spectrometry. *J. Chem. Soc., Chem. Commun.*, 1374-1375, doi:10.1039/C39840001374 (1984).