Supporting Information for

**Formation of Methylglyoxal (****CH3C(O)CHO) in Interstellar Analog Ices – A Key Intermediate in Cellular Metabolism**

Jia Wang,1,2 Joshua H. Marks,1,2 Evgenia A. Batrakova,3 Sergey O. Tuchin,3 Ivan O. Antonov,3\* Ralf I. Kaiser1,2\*

1 W. M. Keck Research Laboratory in Astrochemistry, University of Hawaii at Manoa, Honolulu, HI 96822, USA

2 Department of Chemistry, University of Hawaii at Manoa, Honolulu, HI 96822, USA

3 Samara National Research University, Samara 443086, Russia

\*Corresponding Authors:

Ivan Antonov, [pfizeke@gmail.com](mailto:pfizeke@gmail.com)

Ralf I. Kaiser, [ralfk@hawaii.edu](mailto:ralfk@hawaii.edu)

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Figures S1 to S10

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Supplementary Source code

Supplementary References

A graph of a graph of a substance

Description automatically generated with medium confidence

**Figure S1.** Infrared spectra of (a) CO–CH3CHO ice before (black) and after (red) low dose irradiation (24 nA, 5 minutes) at 5 K with (b) a magnified view and deconvolution of the region 2400–1400 cm−1. The Gaussian fits (blue) and sum of fits (green) are presented. The assignments of the absorptions of CO, CH3CHO, and new absorptions after irradiation are labeled in magenta, black, and red, respectively. Detailed assignments are compiled in Table S9.

A graph of a graph of a number of different colored lines

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**Figure S2.** Infrared spectra of (a) CO–CH3CHOice before (black) and after (red) high dose irradiation (37 nA, 30 minutes) at 5 K with (b) a magnified view and deconvolution of the region 2400–1400 cm−1. The Gaussian fits (blue) and sum of fits (green) are presented. The assignments of the absorptions of CO, CH3CHO, and new absorptions after irradiation are labeled in magenta, black, and red, respectively. Detailed assignments are compiled in Table S10.

A graph of a diagram

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**Figure S3.** Infrared spectra of (a) CO–CD3CDO ice before (black) and after (red) low dose irradiation (23 nA, 5 minutes) at 5 K with (b) a magnified view and deconvolution of the region 2400–1400 cm−1. The Gaussian fits (blue) and sum of fits (green) are presented. The assignments of the absorptions of CO, CD3CDO, and new absorptions after irradiation are labeled in magenta, black, and red, respectively. Detailed assignments are compiled in Table S11.

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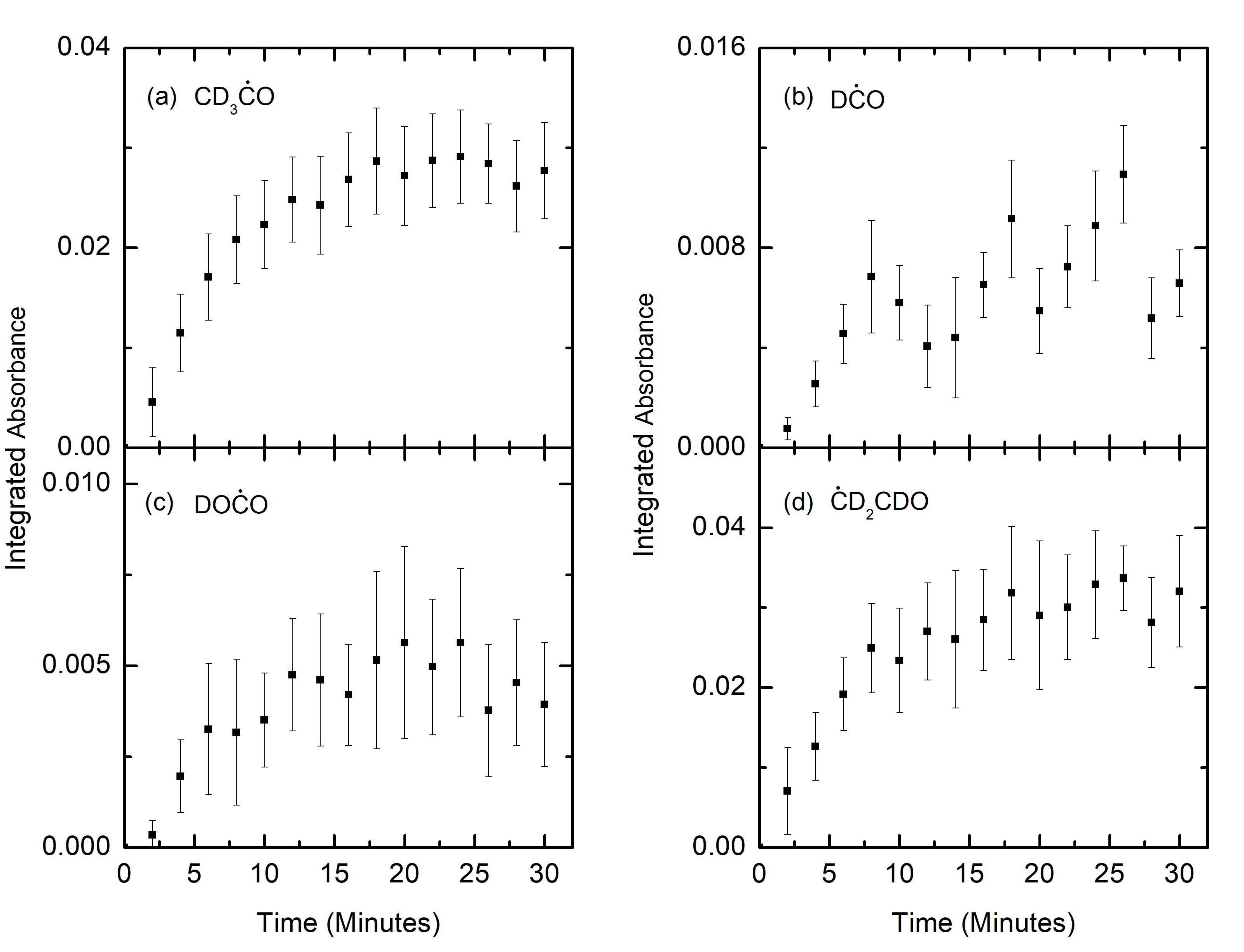
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**Figure S4.** Infrared spectra of (a) CO–CD3CDO ice before (black) and after (red) high dose irradiation (37 nA, 30 minutes) at 5 K with (b) a magnified view and deconvolution of the region 2400–1400 cm−1. The Gaussian fits (blue) and sum of fits (green) are presented. The assignments of the absorptions of CO, CD3CDO, and new absorptions after irradiation are labeled in magenta, black, and red, respectively. Detailed assignments are compiled in Table S12.

A graph of a graph of a substance

Description automatically generated with medium confidence

**Figure S5.** Infrared spectra of (a) C18O–CH3CHO ice before (black) and after (red) low dose irradiation (22 nA, 5 minutes) at 5 K with (b) a magnified view and deconvolution of the region 2300–1500 cm−1. The Gaussian fits (blue) and sum of fits (green) are presented. The assignments of the absorptions of C18O, CH3CHO, and new absorptions after irradiation are labeled in magenta, black, and red, respectively. Detailed assignments are compiled in Table S13.



**Figure S6.** Temporal evolution of three radicals formed during irradiation of CO–CD3CDO ice at 5 K: (a) **14**-d3 (CD3ĊO, 1851 cm–1), (b) **13**-d1 (DĊO, 1794 cm–1), (c) hydroxycarbonyl-d1 (DOĊO, 1786 cm–1), and **17-**d3 (ĊD2CDO, 1513 cm–1).

A graph of a temperature

Description automatically generated **Figure S7.** TPD profiles of *m/z* = 72 in low dose irradiated CO–CH3CHO ice recorded at 11.10 eV and 9.87 eV match well, ruling out the formation of **18**.

A graph of different types of temperature

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**Figure S8.** TPD profiles recorded at 11.10 eV with irradiated CO–CH3CHO ice (*m/z* = 132 and 176) and CO–CD3CDO ice (*m/z* = 144 and 192), confirming the formulae C6H12O3 ((a)and (b)) and C8H16O4 ((c)and (d)). The blue shaded regions indicate the sublimation temperatures of Peaks I and II.

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**Figure S9.** TPD profiles recorded at 11.10 eV with irradiated CO–CH3CHO ice (*m/z* = 72) and CO–CD3CDO ice (*m/z* = 80), indicating that C4H8O isomers contribute to Peaks I and II.

A diagram of a molecule

Description automatically generated with medium confidence

**Figure S10**.Potential energy surfaces of isomerization of methylglyoxal (**1**) leading to the formation of 2-hydroxypropenal (**19**) and 2-hydroxypropenone (**16**). Energies (kJ mol−1) were computed using the CBS–QB3 composite approach and are relative to methylglyoxal (**1**).

**Table S1.** Experimental conditions of carbon monoxide–acetaldehyde ices including ice composition and thickness, irradiation parameters, and VUV photon energies.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Exp. | Ice | Composition of carbon monoxide to acetaldehyde | Thickness (nm) | Current  (nA) | Irradiation  time (s) | Dose (eV/ carbon monoxide) | Dose (eV/ acetaldehyde) | Photon energy (eV) |
| 1 | CO−CH3CHO | 1.3 ± 0.4 : 1 | 750 ± 30 | – | – | – | – | 11.10 |
| 2 | CO−CH3CHO | 1.2 ± 0.4 : 1 | 750 ± 30 | 25 ± 2 | 300 ± 10 | 0.15 ± 0.03 | 0.30 ± 0.05 | 11.10 |
| 3 | CO−CD3CDO | 1.9 ± 0.5 : 1 | 750 ± 30 | 23 ± 6 | 300 ± 10 | 0.14 ± 0.04 | 0.27 ± 0.08 | 11.10 |
| 4 | C18O−CH3CHO | 1.6 ± 0.5 : 1 | 750 ± 30 | 22 ± 1 | 300 ± 10 | 0.13 ± 0.02 | 0.26 ± 0.04 | 11.10 |
| 5 | CO−CH3CHO | 1.2 ± 0.5 : 1 | 750 ± 30 | 24 ± 1 | 300 ± 10 | 0.15 ± 0.03 | 0.29 ± 0.04 | 9.87 |
| 6 | CO−CH3CHO | 1.3 ± 0.6 : 1 | 770 ± 30 | 23 ± 1 | 300 ± 10 | 0.14 ± 0.03 | 0.27 ± 0.04 | 9.39 |
| 7 | CO−CH3CHO | 1.3 ± 0.6 : 1 | 750 ± 30 | 22 ± 1 | 300 ± 10 | 0.13 ± 0.02 | 0.26 ± 0.04 | 8.77 |
| 8 | CO−CH3CHO | 1.3 ± 0.5 : 1 | 750 ± 30 | 37 ± 1 | 1800 ± 10 | 1.35 ± 0.19 | 2.65 ± 0.37 | 8.77 |
| 9 | CO−CD3CDO | 2.0 ± 0.4 : 1 | 750 ± 30 | 37 ± 1 | 1800 ± 10 | 1.35 ± 0.19 | 2.65 ± 0.37 | 8.77 |
| 10 | CO−CH3CHO | 1.2 ± 0.5 : 1 | 750 ± 30 | 40 ± 5 | 1800 ± 10 | 1.46 ± 0.27 | 2.86 ± 0.52 | 7.60 |

**Table S2.** Vacuum ultraviolet (VUV) light generation parameters with an uncertainty of photon energies of less than 0.001 eV.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| VUV photon energy (eV) | Nonlinear medium in four-wave mixing | ω1 laser wavelength (nm) | ω1 Dye | ω2 laser wavelength (nm) | ω2 Dye |
| 11.10  (2ω1 + ω2) | Xenon | 249.628 | Coumarin 503 | 1064 | − |
| 9.87  (2ω1 – ω2) | Krypton | 212.556 | Stilbene 420 | 690.323 | LDS 698 |
| 9.39  (2ω1 – ω2) | Xenon | 222.566 | Coumarin 450 | 707.956 | LDS 698 |
| 8.77  (2ω1 – ω2) | Xenon | 249.628 | Coumarin 503 | 1064 | − |
| 7.60  (2ω1 – ω2) | Xenon | 249.628 | Coumarin 503 | 532 | − |

**Table S3.** Cartesian coordinates (Å), harmonic frequencies (cm1), infrared (IR) intensities (km mol1), and dipole moment (Debye) for methylglyoxal (**1**).

|  |  |  |  |
| --- | --- | --- | --- |
| Structure | Geometry | Frequency | IR intensity |
| A molecule model of a chemical compound  Description automatically generated  **1a**  Dipole moment (Debye)  X: -0.3194  Y: 0.9648  Z: 0.0034  Total: 1.0163 | |  | | --- | | C -1.3485666413 -0.0865833859 -0.1387568206 | | C -0.2020053727 -0.8117634665 0.5875264819 | | C 1.1128971011 -0.0884710095 0.6895557506 | | O -1.2407178033 1.011307249 -0.6167669781 | | H -2.2831390077 -0.6831702047 -0.1741067494 | | O -0.4261236507 -1.9144390498 1.0298508391 | | H 0.9744606318 0.8703282326 1.1973571327 | | H 1.4879337211 0.1474148351 -0.3106112943 | | H 1.8316910217 -0.7034132001 1.2282616381 | | 73.6844  134.3589  247.5145  470.1703  482.9286  570.7444  775.7253  906.4094  1007.7517  1077.8641  1237.8913  1353.6507  1390.9208  1457.9117  1461.0255  1796.0035  1808.8035  2921.4344  3039.8422  3094.5589  3151.0982 | 5.9247  15.1708  15.9045  0.2564  25.0205  13.8849  14.4266  0.5899  2.73  2.8809  23.1416  1.9827  39.7178  16.1981  11.5253  105.8722  117.1068  96.88  0.1128  3.8097  6.2718 |
| A molecule model of a chemical compound  Description automatically generated with medium confidence  **1b**  Dipole moment (Debye)  X: 2.9920  Y: -4.0393  Z: 0.0019  Total: 5.0267 | |  | | --- | | C -1.3563457277 -0.0904932032 -0.1275090571 | | C -0.1958976206 -0.8078549864 0.6186189426 | | C 0.7001626138 -1.6691801622 -0.2388519645 | | O -2.1367423593 0.6219939773 0.4368904658 | | H -1.4172783994 -0.2804699189 -1.2225179526 | | O -0.0636425059 -0.6539831553 1.8048256573 | | H 1.1557836551 -1.0703302086 -1.0351117859 | | H 0.115109424 -2.4536573181 -0.731498522 | | H 1.4786409199 -2.1209250246 0.3732742164 | | 77.5352  126.9107  261.5062  401.0387  464.9074  636.2775  799.5861  877.0806  966.7175  1074.342  1175.1998  1385.0301  1402.4241  1459.5821  1468.2848  1803.406  1835.6309  2866.4125  3023.0739  3074.7805  3147.2186 | 6.3843  0.3912  2.0017  3.202  0.8182  18.786  27.5862  0.5883  32.0158  2.4631  56.8531  39.4458  4.1224  16.3435  11.9457  182.6718  34.4782  117.4244  1.5264  7.3408  5.9417 |

**Table S4.** Cartesian coordinates (Å), harmonic frequencies (cm1), infrared (IR) intensities (km mol1), and dipole moment (Debye) for propanedial (**18**).

|  |  |  |  |
| --- | --- | --- | --- |
| Structure | Geometry | Frequency | IR intensity |
| A molecule model of a chemical compound  Description automatically generated with medium confidence  **18a**  Dipole moment (Debye)  X: 0.0000  Y: 3.3573  Z: 1.2152  Total: 3.5705 | |  | | --- | | C -1.2984418333 -0.167478195 -0.153283553 | | C -0.163143146 -0.9833710855 0.4399534217 | | C 0.369554994 -2.0366277642 -0.5157632531 | | O -2.35028177 0.0174428789 0.3964644604 | | O 0.5148074447 -3.1932814206 -0.2262110041 | | H -1.0919624814 0.2693379669 -1.1551770321 | | H -0.4713055483 -1.4405984487 1.3796373185 | | H 0.6640515491 -0.2812212163 0.6257154305 | | H 0.6327107913 -1.6633527156 -1.5299857887 | | 63.4257  117.5762  282.748  452.1445  549.3128  733.1112  870.0173  954.7325  1089.4891  1112.3929  1190.3469  1254.2659  1421.3375  1431.4666  1435.0912  1807.0583  1837.5543  2859.2571  2879.5205  2997.1427  3129.0232 | 9.7117  1.6301  9.5357  3.1478  29.1182  2.3155  19.3537  75.9626  1.4543  31.1248  35.0134  7.3357  6.9328  6.117  16.6722  321.117  102.0926  11.8485  208.9849  1.623  2.8236 |
| A molecule model of a chemical compound  Description automatically generated  **18b**  Dipole moment (Debye)  X: 1.6835  Y: 3.1146  Z: 1.2840  Total: 3.7661 | |  | | --- | | C -1.3144382211 -1.4789376217 -0.4252812173 | | C -0.1510509949 -0.912653016 0.3668664151 | | C 1.14065341 -0.7965624217 -0.4189443227 | | O -2.4198761764 -1.0048603916 -0.4010096601 | | O 1.2936728784 -1.2003182329 -1.5421523379 | | H -1.0830204255 -2.3776031996 -1.0285546152 | | H 0.0499145192 -1.5772000643 1.2212837932 | | H -0.4275469502 0.0580571768 0.7904949859 | | H 1.9704419605 -0.2990622289 0.1278369591 | | 40.2195  108.3346  229.7122  462.8054  639.3883  697.4472  857.7984  914.6311  1061.3582  1091.9962  1214.9935  1307.3679  1411.2453  1415.9712  1432.0593  1809.8922  1823.9981  2882.52  2934.1665  2998.8611  3072.2047 | 12.0726  0.7678  11.6198  12.5021  5.0189  5.9348  6.2403  9.5936  58.7593  12.8524  7.5318  36.9695  19.4173  14.5308  11.1684  203.9804  128.5002  131.9529  70.4563  2.0832  4.6324 |

**Table S5.** Cartesian coordinates (Å), harmonic frequencies (cm1), infrared (IR) intensities (km mol1), and dipole moment (Debye) for 2-hydroxypropenone (**16**).

|  |  |  |  |
| --- | --- | --- | --- |
| Structure | Geometry | Frequency | IR intensity |
| A molecule model of a chemical compound  Description automatically generated  Dipole moment (Debye)  X: 2.2821  Y: -0.8236  Z: 1.4500  Total: 2.8265 | |  | | --- | | O 0.3103291869 -0.5432242651 -1.9553186994 | | C 0.1630202061 -0.2218488461 -0.8428299774 | | C 0.0049482677 0.1252435796 0.4207175729 | | O 0.4359744058 1.4023976391 0.7972909485 | | C -0.5061980935 -0.8163602942 1.4699341621 | | H -0.3434507905 1.960871279 0.9046852914 | | H -0.7195412064 -1.803851527 1.0537501402 | | H -1.4310334153 -0.439634701 1.9236293903 | | H 0.2364814392 -0.9328428644 2.2661011714 | | 181.9091  187.7001  277.0078  295.3076  363.3187  512.4422  691.5249  765.2709  996.5632  1043.0043  1198.1139  1275.0583  1410.4861  1416.5385  1468.0557  1507.3983  2210.7729  3002.0864  3052.9164  3097.4575  3765.7384 | 1.3263  0.0515  96.0453  17.8531  8.689  21.8917  1.907  8.4858  6.8124  4.7179  110.6414  27.1237  29.9699  4.7732  9.0596  12.4262  525.24  38.2593  26.237  16.5393  29.4633 |

**Table S6.** Cartesian coordinates (Å), harmonic frequencies (cm1), infrared (IR) intensities (km mol1), and dipole moment (Debye) for 2-hydroxypropenal (**19**).

|  |  |  |  |
| --- | --- | --- | --- |
| Structure | Geometry | Frequency | IR intensity |
| A molecule model of a chemical compound  Description automatically generated with medium confidence  **19a**  Dipole moment (Debye)  X: 1.4612  Y: -1.6479  Z: -0.0035  Total: 2.2024 | |  | | --- | | C -1.3257324546 -0.0474302748 -0.0077925995 | | C -0.2032685759 -0.7507325909 0.6746357479 | | C 0.9493497327 -0.1293781276 0.9377294296 | | O -1.3134598894 1.0985641682 -0.377542114 | | H -2.2292266143 -0.6893182681 -0.1620261533 | | O -0.4163902717 -2.0560311392 1.0155415045 | | H 1.0581026227 0.905105663 0.6445526415 | | H 1.76571659 -0.6370542142 1.4334215493 | | H -1.3016411395 -2.3220952164 0.741299994 | | 158.5643  247.004  286.0181  432.5565  469.3063  603.492  737.4448  899.008  903.1035  979.099  1011.7238  1215.4258  1335.6847  1413.3089  1426.9986  1692.6066  1808.1063  2803.1146  3168.3921  3269.5002  3799.3483 | 6.7495  109.5079  9.4267  9.2891  6.4079  10.3984  3.4833  60.4998  53.9914  50.7624  0.5729  40.6783  231.7812  33.3666  6.723  82.3906  99.9871  172.461  2.3965  0.0953  51.8364 |
| A molecule model of a chemical compound  Description automatically generated  **19b**  Dipole moment (Debye)  X: -1.5354  Y: -1.9639  Z: 0.0003  Total: 2.4928 | |  | | --- | | C -1.2965728332 -0.063922938 -0.0152919337 | | C -0.2106035558 -0.772380307 0.6959297224 | | C -0.132113346 -0.7560125419 2.032672035 | | O -1.360403123 -0.083709883 -1.2271672313 | | H -2.032663418 0.4742544171 0.6075976557 | | O 0.6618404112 -1.4139362843 -0.108849827 | | H -0.8748061217 -0.2158747421 2.604339911 | | H 0.6572996782 -1.2702680967 2.5642364058 | | H 0.3542723085 -1.250509624 -1.0174467379 | | 205.3749  291.1645  409.284  532.2568  581.9783  683.8242  738.1645  881.0345  898.6639  984.7133  1007.395  1266.4532  1371.14  1409.7075  1448.7836  1717.1801  1756.0365  2967.5354  3164.0893  3257.4972  3664.436 | 4.0187  23.546  2.0394  0.0128  98.0849  2.1752  13.9714  63.3021  52.5974  37.8731  0.0521  63.4805  18.0169  232.6025  36.5058  14.9187  259.674  64.0139  0.0142  1.7513  102.821 |
| A molecule model of a chemical compound  Description automatically generated  **19c**  Dipole moment (Debye)  X: -4.2780  Y: -1.6331  Z: 0.0000  Total: 4.5791 | |  | | --- | | C -1.3971024091 -1.4950276051 1.1076985536 | | C -0.1926135668 -0.7339602269 0.6739764024 | | C -0.0565504781 0.5492209881 1.0347318379 | | O -1.6090532983 -2.6481774907 0.835177467 | | H -2.1010147145 -0.8931275502 1.7193905887 | | O 0.6685886086 -1.4639424989 -0.0722120627 | | H -0.8204921932 1.0222584618 1.6369264638 | | H 0.7974287956 1.1528006649 0.749123518 | | H 1.4215392557 -0.915084743 -0.3183027686 | | 164.6382  273.5106  423.0266  430.6895  522.9738  659.1123  726.6233  865.6826  877.7793  981.6836  1016.7923  1199.8171  1388.923  1419.8639  1458.807  1686.4367  1802.1916  2899.6575  3150.5067  3239.2684  3819.7464 | 1.2857  4.1576  125.0331  8.2425  0.4342  27.6319  1.3647  64.2762  63.491  20.7059  0.006  147.8404  3.2494  24.7226  13.2616  101.5033  235.4222  92.8123  2.7786  4.1331  43.9889 |
| **19d**  Dipole moment (Debye)  X: 3.4795  Y: 0.2231  Z: 0.0000  Total: 3.4867 | |  | | --- | | C -1.4064892456 -1.4833003505 1.1215849359 | | C -0.2158253259 -0.7321982596 0.6201598443 | | C -0.2315872261 -0.0768327732 -0.5431574961 | | O -2.4570193316 -1.5609908655 0.5351702226 | | H -1.2381153251 -1.9744399986 2.1012570808 | | O 0.8232459675 -0.8258604485 1.4999460067 | | H -1.1372942407 -0.0957722076 -1.1331628642 | | H 0.6235986188 0.4721581067 -0.9200297471 | | H 1.5804861087 -0.3365532033 1.1605820172 | | 159.9836  284.1328  392.4444  441.6726  486.3537  603.5144  727.7701  876.9063  901.0149  973.1587  1031.1843  1167.3377  1346.7241  1425.8323  1431.9774  1684.1637  1808.0803  2921.0295  3151.3636  3250.7445  3826.9428 | 7.721  4.4523  122.019  12.0009  3.0718  13.7543  2.8393  55.298  46.8113  43.2255  0.2679  191.9868  0.5759  24.3833  24.7373  147.173  89.6747  104.6566  7.9936  0.5513  44.539 |

**Table S7.** Cartesian coordinates (Å), harmonic frequencies (cm1), infrared (IR) intensities (km mol1), and dipole moment (Debye) for 3-hydroxypropenal (**20**).

|  |  |  |  |
| --- | --- | --- | --- |
| Structure | Geometry | Frequency | IR intensity |
| A molecule model of a chemical compound  Description automatically generated with medium confidence  **20a**  Dipole moment (Debye)  X: -4.0262  Y: 2.9393  Z: 0.0000  Total: 4.9849 | |  | | --- | | C 0. -0.3105118433 1.334912086 | | C 0. -1.0239181309 0.0544823451 | | C 0. -0.460769553 -1.1683382615 | | O 0. 0.8920051039 1.4882918356 | | H 0. -0.9888237734 2.2176717607 | | O 0. 0.8639794144 -1.3871868197 | | H 0. -1.0928662305 -2.0545569012 | | H 0. -2.1072553423 0.0937434622 | | H 0. 1.0345003552 -2.3338595072 | | 159.8987  190.0585  325.6807  458.7611  495.9448  787.1323  878.3505  922.6683  974.9  1031.5775  1116.5034  1274.4851  1315.9093  1432.1376  1470.4759  1682.1779  1785.2423  2854.7557  3126.2387  3182.113  3844.652 | 2.5035  3.89  115.5542  18.0309  23.582  30.2507  19.6953  71.7678  0.6691  5.4472  16.3774  81.7729  205.0192  3.7016  22.0192  303.6493  146.3769  196.4424  15.6588  9.9996  124.2114 |
| A molecule model of a chemical compound  Description automatically generated with medium confidence  **20b**  Dipole moment (Debye)  X: -0.6282  Y: 3.1283  Z: 0.0000  Total: 3.1907 | |  | | --- | | C 0. 0.329485714 -1.2357997769 | | C 0. 1.0986072054 -0.0200895247 | | C 0. 0.4513111528 1.1804756372 | | O 0. -0.9072844693 -1.262426978 | | H 0. 0.8860694873 -2.1891226658 | | O 0. -0.8600193448 1.3174995882 | | H 0. 0.9826999082 2.1283995412 | | H 0. 2.1790679656 -0.0550585652 | | H 0. -1.2343076192 0.3925027441 | | 278.4153  293.9169  395.8439  521.2067  788.2107  896.9044  929.6361  1001.0524  1012.4617  1043.0019  1115.9373  1291.9089  1400.7859  1407.0405  1475.5736  1634.1752  1704.2931  2963.143  3140.8929  3189.8537  3215.0294 | 7.9795  4.3255  6.142  18.26  35.1881  6.9645  71.1421  44.5141  20.4751  18.3627  11.2576  155.7593  51.4475  63.0864  52.846  267.6262  204.5528  121.7864  154.2756  76.3697  2.4332 |
| A molecule model of a chemical compound  Description automatically generated  **20c**  Dipole moment (Debye)  X: 2.9616  Y: 0.1992  Z: 0.0000  Total: 2.9683 | |  | | --- | | C 0. -0.4396051577 -1.4475765735 | | C 0. -0.7240237335 -0.0104454632 | | C 0. 0.2892149324 0.8695179335 | | O 0. 0.6700914628 -1.9448801872 | | H 0. -1.3412805521 -2.0954291609 | | O 0. 0.0958511506 2.201299217 | | H 0. 1.3151911021 0.5097884279 | | H 0. -1.7536889618 0.328446852 | | H 0. 0.9442197571 2.6551489545 | | 210.5211  215.7994  263.6568  444.5599  447.8478  753.6584  847.5965  992.5887  998.5713  1033.8961  1175.6222  1260.0647  1345.6419  1369.4857  1430.9827  1679.3859  1775.9985  2890.1746  3156.5837  3184.7179  3842.9363 | 12.4721  49.7608  3.3245  105.682  5.3998  92.1523  17.2491  26.1592  27.0044  0.5903  7.5389  198.3248  6.5224  179.9842  10.9735  437.1256  111.0015  168.2566  2.7136  5.2775  123.7711 |
| A molecule model of a chemical element  Description automatically generated with medium confidence  **20d**  Dipole moment (Debye)  X: 2.6471  Y: 3.2182  Z: 0.0000  Total: 4.1670 | |  | | --- | | C 0. -0.4338862553 -1.4399627031 | | C 0. -0.6968234103 0.0023408984 | | C 0. 0.3233521095 0.8789415734 | | O 0. 0.6664149204 -1.9535058859 | | H 0. -1.347624289 -2.0719337583 | | O 0. 0.2433697116 2.2172587632 | | H 0. 1.3506077511 0.5331725783 | | H 0. -1.731049304 0.336548967 | | H 0. -0.682841234 2.491219567 | | 209.7618  210.8385  263.6413  449.261  572.4657  751.1318  827.5731  999.767  1018.8366  1035.9132  1162.265  1299.5918  1323.9714  1400.8063  1433.7671  1653.4555  1776.3593  2882.3347  3148.6409  3202.6158  3787.2677 | 3.0483  0.3837  5.8202  7.5241  93.0732  71.8291  39.0187  99.596  38.1564  6.8044  146.155  8.5605  52.691  0.223  4.0478  596.5689  118.5084  167.5456  14.636  0.176  61.2518 |
| A molecule model of a chemical compound  Description automatically generated  **20e**  Dipole moment (Debye)  X: -6.0057  Y: 0.1586  Z: 0.0000  Total: 6.0078 | |  | | --- | | C 0. 0.3648054847 -1.0779509272 | | C 0. -0.729387609 -0.1071163015 | | C 0. -0.5596408953 1.2247831825 | | O 0. 0.1944460305 -2.280117577 | | H 0. 1.3857972295 -0.6483647262 | | O 0. 0.6607594807 1.8110990691 | | H 0. -1.4131216637 1.8984201939 | | H 0. -1.7376768203 -0.5030183139 | | H 0. 0.564998763 2.7671554004 | | 162.3813  204.6846  279.8592  451.6196  476.0536  692.6553  810.1836  980.6541  1020.994  1033.9043  1148.3736  1249.3361  1298.2161  1393.2811  1465.2152  1708.8881  1761.0895  2920.2493  3142.7136  3195.4977  3863.1498 | 3.1374  0.847  127.9658  11.1902  16.2279  13.9568  45.4142  0.6803  116.2571  1.877  33.6588  18.3138  267.2602  6.7297  16.286  143.7531  281.2062  79.5013  13.4044  3.6016  138.4099 |
| A molecule model of a chemical compound  Description automatically generated  **20f**  Dipole moment (Debye)  X: -3.1854  Y: -0.6304  Z: 0.0000  Total: 3.2472 | |  | | --- | | C 0. 0.3152303772 -1.0850709784 | | C 0. -0.7443680147 -0.089408155 | | C 0. -0.5516707225 1.245641156 | | O 0. 0.1408221884 -2.2847829634 | | H 0. 1.3611816459 -0.6877048591 | | O 0. 0.6097372469 1.9231768388 | | H 0. -1.3890186171 1.934922206 | | H 0. -1.7618356436 -0.4607042559 | | H 0. 1.3594615394 1.315471011 | | 167.742  216.4288  314.5744  476.8064  573.0876  698.5511  821.8712  991.9663  1013.6442  1025.7649  1151.0359  1237.7738  1363.8141  1404.3481  1473.2109  1673.5908  1767.5016  2779.7369  3181.2251  3200.1243  3795.4202 | 7.599  13.5399  8.3495  8.5071  107.5598  7.7633  42.7736  0.0323  85.4221  7.5172  103.7279  168.6832  6.2237  14.4096  19.768  238.5524  300.9672  161.7348  3.485  4.5389  35.6446 |
| A molecule model of a chemical compound  Description automatically generated with medium confidence  **20g**  Dipole moment (Debye)  X: 4.4373  Y: -3.6445  Z: 0.0000  Total: 5.7421 | |  | | --- | | C 0. -0.3407154593 -1.3339997538 | | C 0. 0.3595304365 -0.055302885 | | C 0. -0.3413919876 1.0877190567 | | O 0. 0.1946269039 -2.4213919364 | | H 0. -1.453070294 -1.2509024753 | | O 0. 0.244765388 2.3014571791 | | H 0. -1.4302380185 1.0731879495 | | H 0. 1.4434159538 -0.0538370509 | | H 0. -0.4242629228 2.9925199162 | | 151.853  222.1789  322.4901  423.1217  493.6045  565.956  858.4186  970.6923  1024.4799  1141.5686  1166.1719  1217.5643  1335.9267  1356.6834  1440.4173  1720.1445  1772.5058  2830.7036  3129.2715  3191.007  3846.2099 | 0.1462  4.0125  27.3819  99.569  9.7135  35.7823  10.5887  41.7144  1.3294  79.5854  17.3571  184.5488  211.0437  8.2269  4.797  221.9424  313.3378  133.7324  14.7561  1.4896  129.2742 |
| A molecule model of a chemical compound  Description automatically generated  **20h**  Dipole moment (Debye)  X: 3.6208  Y: -0.6969  Z: 0.0000  Total: 3.6873 | |  | | --- | | C 0. -0.3613032576 1.3360939883 | | C 0. 0.3328034219 0.0533123401 | | C 0. -0.3635160757 -1.095717293 | | O 0. 0.1846416543 2.4183017769 | | H 0. -1.4726820394 1.2595426034 | | O 0. 0.1262700704 -2.3458074551 | | H 0. -1.4491267859 -1.1045896671 | | H 0. 1.419174958 0.0722678344 | | H 0. 1.0917780539 -2.3189141279 | | 153.7181  219.0258  328.4563  491.6946  556.5436  571.7957  849.6213  988.8478  1029.6191  1137.2908  1161.6961  1241.3101  1337.2375  1381.9607  1441.0921  1689.4385  1771.3154  2848.2047  3157.4805  3177.2999  3790.1275 | 4.838  18.8104  21.3251  0.4915  84.5556  3.8835  26.9024  47.6585  10.6349  334.3373  17.528  61.8383  17.4665  7.8929  5.9683  349.5535  284.9879  126.252  6.8307  6.1571  62.9968 |

**Table S8.** Cartesian coordinates (Å) for transitions states of **TS1-19**, and **TS19-16**.

|  |  |
| --- | --- |
| Structure | Geometry |
| A molecule model of a molecule  Description automatically generated  **TS1-19** | |  | | --- | | C -1.533221 0.022278 -0.169685 | | C -0.208303 -0.430615 0.370671 | | C 1.003961 0.273540 0.532689 | | O -1.873335 1.176864 -0.185197 | | H -2.176248 -0.807219 -0.525399 | | O -0.107566 -1.626863 0.826121 | | H 1.035441 1.351880 0.641986 | | H 1.816421 -0.142767 -0.064321 | | H 0.985050 -1.041247 1.244874 | |
| **A molecule model of a chemical compound  Description automatically generated with medium confidenceTS19-16** | O 0.262221 -0.802240 -1.590891  C -0.131275 -0.444574 -0.525166  C 0.041305 0.368513 0.594446  O 0.469841 1.646756 0.639275  C -0.397899 -0.487221 1.661613  H -0.027320 2.138382 1.303435  H -0.643765 -1.340061 0.453599  H -1.449747 -0.691391 1.853394  H 0.205988 -0.523166 2.576735 |

**Table S9.** Absorption peaks observed in CO–CH3CHO ice before and after low dose irradiation (24 nA, 5 minutes) at 5 K. Vibration mode: stretching (*ν*), bending in plane (*δ*), and out of plane (γ). Indication: asymmetric (*a*) and symmetric (*s*).

|  |  |  |
| --- | --- | --- |
| Absorptions of pristine ice (cm−1) |  |  |
| **CO** | Assignment[1](#_ENREF_1) | |
| 4249 | 2*ν*(13CO) | overtone |
| 2136 | *ν*(CO) | *ν*(CO) |
| 2090 | *ν*(13CO) | *ν*(13CO) |
| **CH3CHO** | Assignment[2](#_ENREF_2) | |
| 3425 | 2*ν*4 | overtone |
| 3123 | *ν*4 + *ν*6 | combination |
| 3007 | *ν*1 | *νa*(CH3) |
| 2967 | *ν*11 | *ν*(CH3) |
| 2918 | *ν*2 | *νs*(CH3) |
| 2856, 2830 | 2*ν*6 | overtone |
| 2759, 2737 | *ν*3 | *ν*(CH) |
| 2596 | *ν*4 + *ν*9 | combination |
| 2465 | *ν*7 + *ν*8 | combination |
| 2234 | *ν*7 + *ν*9 | combination |
| 2191 | 2*ν*8 | overtone |
| 2158 | *ν*6 + *ν*14 | combination |
| 1999 | *ν*8 + *ν*9 | combination |
| 1768 | 2*ν*9 | overtone |
| 1722 | *ν*4 | *ν*(CO) |
| 1685 | *ν*4 (CH313CHO) | *ν*(13CO) |
| 1635 | ν8 + *ν*10 | combination |
| 1543 | 2*ν*14 | overtone |
| 1430 | *ν*5 / *ν*12 | *δ*(CH3) / *δa*(CH3) |
| 1405 | *ν*9 + *ν*10 | combination |
| 1389 | *ν*6 | *δ*(CH) |
| 1349 | *ν*7 | *δs*(CH3) |
| 1122 | *ν*8 | *γ*(CH3) |
| 1107 | *ν*8 (13CH3CHO) | *γ*(13CH3) |
| 885 | *ν*14 + *ν*15 | combination |
| 772 | *ν*14 | *γ*(CH) |
| New absorptions after irradiation (cm−1) | Assignment[1](#_ENREF_1), [3-5](#_ENREF_3) | |
| 2343 | *ν*3(CO2) |  |
| 1852 | *ν*3(HĊO) |  |
| 1841 | *ν*3(CH3ĊO) / *ν*2(HOĊO) |  |
| 1571 | *ν*4(ĊH2CHO) |  |

**Table S10.** Absorption peaks observed in CO–CH3CHO ice before and after high dose irradiation (37 nA, 30 minutes) at 5 K. Vibration mode: stretching (*ν*), bending in plane (*δ*), and out of plane (γ). Indication: asymmetric (*a*) and symmetric (*s*).

|  |  |  |
| --- | --- | --- |
| Absorptions of pristine ice (cm−1) |  |  |
| **CO** | Assignment[1](#_ENREF_1) | |
| 4249 | 2*ν*(13CO) | overtone |
| 2137 | *ν*(CO) | *ν*(CO) |
| 2091 | *ν*(13CO) | *ν*(13CO) |
| **CH3CHO** | Assignment[2](#_ENREF_2) | |
| 3425 | 2*ν*4 | overtone |
| 3008 | *ν*1 | *νa*(CH3) |
| 2975 | *ν*11 | *ν*(CH3) |
| 2918 | *ν*2 | *νs*(CH3) |
| 2856, 2824 | 2*ν*6 | overtone |
| 2761, 2738 | *ν*3 | *ν*(CH) |
| 2597 | *ν*4 + *ν*9 | combination |
| 2465 | *ν*7 + *ν*8 | combination |
| 2228 | *ν*7 + *ν*9 | combination |
| 2184 | 2*ν*8 | overtone |
| 2154 | *ν*6 + *ν*14 | combination |
| 2001 | *ν*8 + *ν*9 | combination |
| 1768 | 2*ν*9 | overtone |
| 1721 | *ν*4 | *ν*(CO) |
| 1683 | *ν*4 (CH313CHO) | *ν*(13CO) |
| 1635 | ν8 + *ν*10 | combination |
| 1541 | 2*ν*14 | overtone |
| 1430 | *ν*5 / *ν*12 | *δ*(CH3) / *δa*(CH3) |
| 1405 | *ν*9 + *ν*10 | combination |
| 1389 | *ν*6 | *δ*(CH) |
| 1350 | *ν*7 | *δs*(CH3) |
| 1122 | *ν*8 | *γ*(CH3) |
| 1107 | *ν*8 (13CH3CHO) | *γ*(13CH3) |
| 885 | *ν*14 + *ν*15 | combination |
| 772 | *ν*14 | *γ*(CH) |
| New absorptions after irradiation (cm−1) | Assignment[1](#_ENREF_1), [3-5](#_ENREF_3) | |
| 3343 | *ν*(OH) |  |
| 2941 | *ν*(CH) |  |
| 2343 | *ν*3(CO2) |  |
| 1304 | *ν*4(CH4) |  |
| 1852 | *ν*3(HĊO) |  |
| 1841 | *ν*3(CH3ĊO) / *ν*2(HOĊO) |  |
| 1571 | *ν*4(ĊH2CHO) |  |

**Table S11.** Absorption peaks observed in CO–CD3CDO ice before and after low dose irradiation (23 nA, 5 minutes) at 5 K. Vibration mode: stretching (*ν*), bending in plane (*δ*), and out of plane (γ). Indication: asymmetric (*a*) and symmetric (*s*).

|  |  |  |
| --- | --- | --- |
| Absorptions of pristine ice (cm−1) |  |  |
| **CO** | Assignment[1](#_ENREF_1) | |
| 4250 | 2*ν*(13CO) | overtone |
| 2136 | *ν*(CO) | *ν*(CO) |
| 2088 | *ν*(13CO) | *ν*(13CO) |
| **CD3CDO** | Assignment[2](#_ENREF_2) | |
| 3397 | 2*ν*4 | overtone |
| 2472 | *ν*4 + *ν*9 | combination |
| 2312 | 2*ν*5 | overtone |
| 2258 | *ν*1 | *νa*(CD3) |
| 2222 | *ν*11 | *ν*(CD3) |
| 2183 | *ν*5 + *ν*7 | combination |
| 2104, 2066 | *ν*2 | *νs*(CD3) |
| 1991 | *ν*6 + *ν*13 | combination |
| 1906 | *ν*5 + *ν*9 | combination |
| 1714 | *ν*4 | *ν*(CO) |
| 1696 | *ν*8 + *ν*9 | overtone |
| 1669 | *ν*4 (CD313CDO) | *ν*(13CO) |
| 1521 | 2*ν*14 | overtone |
| 1157 | *ν*5 | *ν*(CC) |
| 1043 | *ν*12 | *δ*(CD3) |
| 1023 | *ν*6 | *δa*(CD3) |
| 953 | *ν*13 | *γ*(CD) |
| 941 | *ν*8 | *δs*(CD3) |
| New absorptions after irradiation (cm−1) | Assignment[1](#_ENREF_1), [3](#_ENREF_3), [4](#_ENREF_4) | |
| 2343 | *ν*3(CO2) |  |
| 1851 | *ν*3(CD3ĊO) |  |
| 1797 | *ν*3(DĊO) |  |
| 1787 | *ν*2(DOĊO) |  |
| 1513 | *ν*4(ĊD2CDO) |  |

**Table S12.** Absorption peaks observed in CO–CD3CDO ice before and after high dose irradiation (37 nA, 30 minutes) at 5 K. Vibration mode: stretching (*ν*), bending in plane (*δ*), and out of plane (γ). Indication: asymmetric (*a*) and symmetric (*s*).

|  |  |  |
| --- | --- | --- |
| Absorptions of pristine ice (cm−1) |  |  |
| **CO** | Assignment[1](#_ENREF_1) | |
| 4250 | 2*ν*(CO) | overtone |
| 2136 | *ν*(CO) | *ν*(CO) |
| 2087 | *ν*(13CO) | *ν*(13CO) |
| **CD3CDO** | Assignment[2](#_ENREF_2) | |
| 3394 | 2*ν*4 | overtone |
| 2462 | *ν*4 + *ν*9 | combination |
| 2253 | *ν*1 | *νa*(CD3) |
| 2226 | *ν*11 | *ν*(CD3) |
| 2187 | *ν*5 + *ν*7 | combination |
| 2103, 2067 | *ν*2 | *νs*(CD3) |
| 1906 | *ν*5 + *ν*9 | combination |
| 1714 | *ν*4 | *ν*(CO) |
| 1695 | *ν*8 + *ν*9 | overtone |
| 1521 | 2*ν*14 | overtone |
| 1158 | *ν*5 | *ν*(CC) |
| 1043 | *ν*12 | *δ*(CD3) |
| 1022 | *ν*6 | *δa*(CD3) |
| 953 | *ν*13 | *γ*(CD) |
| 941 | *ν*8 | *δs*(CD3) |
| New absorptions after irradiation (cm−1) | Assignment[1](#_ENREF_1), [3](#_ENREF_3), [4](#_ENREF_4), [6](#_ENREF_6) | |
| 2498 | *ν*(OD) |  |
| 2342 | *ν*3(CO2) |  |
| 1851 | *ν*3(CD3ĊO) |  |
| 1794 | *ν*3(DĊO) |  |
| 1786 | *ν*2(DOĊO) |  |
| 1578 | *ν*(C=C) / *ν*(C=O) |  |
| 1513 | *ν*4(ĊD2CDO) |  |

**Table S13.** Absorption peaks observed in C18O–CH3CHO ice before and after low dose irradiation (22 nA, 5 minutes) at 5 K. Vibration mode: stretching (*ν*), bending in plane (*δ*), and out of plane (γ). Indication: asymmetric (*a*) and symmetric (*s*).

|  |  |  |
| --- | --- | --- |
| Absorptions of pristine ice (cm−1) |  |  |
| **C**18**O** | Assignment[7](#_ENREF_7) | |
| 4148 | 2*ν*(C18O) | overtone |
| 2136 | *ν*(CO) | *ν*(CO) |
| 2086 | *ν*(C18O) | *ν*(C18O) |
| **CH3CHO** | Assignment[2](#_ENREF_2) | |
| 3426 | 2*ν*4 | overtone |
| 3124 | *ν*4 + *ν*6 | combination |
| 3007 | *ν*1 | *νa*(CH3) |
| 2966 | *ν*11 | *ν*(CH3) |
| 2918 | *ν*2 | *νs*(CH3) |
| 2855, 2836 | 2*ν*6 | overtone |
| 2760, 2737 | *ν*3 | *ν*(CH) |
| 2597 | *ν*4 + *ν*9 | combination |
| 2464 | *ν*7 + *ν*8 | combination |
| 2235 | *ν*7 + *ν*9 | combination |
| 2191 | 2*ν*8 | overtone |
| 2154 | *ν*6 + *ν*14 | combination |
| 2002 | *ν*8 + *ν*9 | combination |
| 1766 | 2*ν*9 | overtone |
| 1723 | *ν*4 | *ν*(CO) |
| 1684 | *ν*4 (CH313CHO) | *ν*(13CO) |
| 1637 | ν8 + *ν*10 | combination |
| 1541 | 2*ν*14 | overtone |
| 1430 | *ν*5 / *ν*12 | *δ*(CH3) / *δa*(CH3) |
| 1405 | *ν*9 + *ν*10 | combination |
| 1389 | *ν*6 | *δ*(CH) |
| 1349 | *ν*7 | *δs*(CH3) |
| 1121 | *ν*8 | *γ*(CH3) |
| 1109 | *ν*8 (13CH3CHO) | *γ*(13CH3) |
| 884 | *ν*14 + *ν*15 | combination |
| 772 | *ν*14 | *γ*(CH) |
| New absorptions after irradiation (cm−1) | Assignment[4](#_ENREF_4), [5](#_ENREF_5) | |
| 1843 | *ν*3(CH3ĊO) / *ν*2(HOĊO) |  |
| 1570 | *ν*4(ĊH2CHO) |  |

**Table S14.** Error analysis of adiabatic ionization energies (IEs) and relative energies (ΔE) of methylglyoxal (**1**) and its enol tautomers (**16** and **19**); IEs and ΔE were computed at CBS–QB3 level of theory including the zero-point vibrational energy (ZPVE) corrections. The IE ranges are corrected for the thermal and Stark effect by –0.03 eV and the combined error limits of –0.05/+0.03 eV.[8](#_ENREF_8)

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Name | Isomer | | Structure | ΔE  (kJ mol−1) | Computed IE (eV) | Corrected IE ranges (eV) |
| Methylglyoxal | **1a** | A molecule model of a chemical compound  Description automatically generated | | 0.0 | 9.60 | 9.52 – 9.60 |
| **1b** | A molecule model of a chemical compound  Description automatically generated with medium confidence | | 21.9 | 9.37 | 9.29 – 9.37 |
| 2-Hydroxypropenone | **16** |  | | 85.7 | 8.17 | 8.09 – 8.17 |
| 2-Hydroxypropenal | **19a** | A molecule model of a chemical compound  Description automatically generated with medium confidence | | 45.4 | 9.53 | 9.45 – 9.53 |
| **19b** | A molecule model of a chemical compound  Description automatically generated | | 15.2 | 9.64 | 9.56 – 9.64 |
| **19c** | A molecule model of a chemical compound  Description automatically generated | | 39.4 | 9.78 | 9.70 – 9.78 |
| **19d** | A molecule model of a molecule  Description automatically generated | | 38.9 | 9.60 | 9.52 – 9.60 |

**Table S15.** Error analysis of IEs and relative energies (ΔE) of propanedial (**18**) and its enol tautomer 3-hydroxypropenal (**20**); IEs and ΔE were computed at CBS–QB3 level of theory including the ZPVE corrections. The IE ranges are corrected for the thermal and Stark effect by –0.03 eV and the combined error limits of –0.05/+0.03 eV.[8](#_ENREF_8)

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Name | Isomer | Structure | ΔE  (kJ mol−1) | Computed IE (eV) | Corrected IE ranges (eV) |
| Propanedial | **18a** | A molecule model of a chemical compound  Description automatically generated with medium confidence | 23.8 | 10.21 | 10.13 – 10.21 |
| **18b** | A molecule model of a chemical compound  Description automatically generated | 18.9 | 10.08 | 10.00 – 10.08 |
| 3-Hydroxypropenal | **20a** | A molecule model of a chemical compound  Description automatically generated with medium confidence | 50.7 | 9.48 | 9.40 – 9.48 |
| **20b** | A molecule model of a chemical compound  Description automatically generated with medium confidence | 1.7 | 9.55 | 9.47 – 9.55 |
| **20c** | A molecule model of a chemical compound  Description automatically generated | 35.9 | 9.49 | 9.41 – 9.49 |
| **20d** | A molecule model of a chemical element  Description automatically generated with medium confidence | 34.3 | 9.60 | 9.52 – 9.60 |
| **20e** | A molecule model of a chemical compound  Description automatically generated | 37.8 | 9.63 | 9.57 – 9.63 |
| **20f** | A molecule model of a chemical compound  Description automatically generated | 38.1 | 9.79 | 9.71 – 9.79 |
| **20g** | A molecule model of a chemical compound  Description automatically generated with medium confidence | 30.9 | 9.67 | 9.59 – 9.67 |
| **20h** | A molecule model of a chemical compound  Description automatically generated | 26.5 | 9.78 | 9.70 – 9.78 |

**Supplementary Source code.** The source code of the program for conformer sorting.

def generate\_input(filename):

with open(filename + '.gjf','r') as file:

data = file.read()

data = data.split('\n\n')[:-1]

del(file)

from re import search, MULTILINE

variables = ['']

old\_variables = []

for line in data[4].split('\n'):

match = search(r'^\s\*(?P<variable\_name>\w\d+)\s+(?P<variable\_value>-?\d+\.\d+)\s\*(?P<number\_of\_scan\_steps>(?:\d+)?)\s\*(?P<scan\_step\_size>(?:-?\d+\.\d+)?)$', line, flags = MULTILINE)

if match['number\_of\_scan\_steps'] == '' and match['scan\_step\_size'] == '':

for index, item in enumerate(variables):

variables[index] = item + line + '\n'

else:

old\_variables = variables[:]

variables = []

pattern = (' ' \* 3) + '{var\_name}' + (' ' \* 13) + '{var\_value}'

name = match['variable\_name']

initial\_value = float(match['variable\_value'])

number\_of\_scan\_steps = int(match['number\_of\_scan\_steps'])

scan\_step\_size = float(match['scan\_step\_size'])

for scan\_step in range(number\_of\_scan\_steps):

value = (initial\_value + scan\_step\_size \* scan\_step)

if value > 180:

value = value - 360

if value <= -180:

value = value + 360

tmp = pattern.format(var\_name = name, var\_value = value)

for item in old\_variables:

variables.append(item + tmp + '\n')

del(old\_variables, line, match, index, item, pattern, name, initial\_value, number\_of\_scan\_steps, scan\_step\_size, scan\_step, value, tmp)

pattern\_neutral\_cbs = '''%nprocshared={nproc}

%Chk={chk\_name}\_neutral\_{conformer}.chk

# cbs-qb3 int(grid=ultrafine)

{title}\t|\tneutral {conformer}

{molecule\_specification}

{variables\_data}'''

pattern\_ion\_cbs = '''%nprocshared={nproc}

%Chk={chk\_name}\_ion\_{conformer}.chk

%OldChk={chk\_name}\_neutral\_{conformer}.chk

# cbs-qb3 int(grid=ultrafine) Geom=Check

{title}\t|\tion {conformer}

1 2

'''

number\_of\_processors\_per\_node = 16

initial\_chk\_name = search(r'^%[Cc]hk=(?P<initial\_chk\_name>.+?)\.chk$', data[0], flags = MULTILINE)['initial\_chk\_name']

neutral\_conformers\_preopt = variables[:]

ion\_conformers\_preopt = []

cbs = []

for index, item in enumerate(neutral\_conformers\_preopt):

neutral\_conformers\_preopt[index] = pattern\_neutral\_cbs.format(nproc = number\_of\_processors\_per\_node,

chk\_name = initial\_chk\_name,

conformer = index + 1,

title = data[2],

molecule\_specification = data[3],

variables\_data = item)

ion\_conformers\_preopt.append(pattern\_ion\_cbs.format(nproc = number\_of\_processors\_per\_node,

chk\_name = initial\_chk\_name,

conformer = index + 1,

title = data[2]))

neutral\_conformers\_preopt = '\n--Link1--\n'.join(neutral\_conformers\_preopt)

ion\_conformers\_preopt = '\n--Link1--\n'.join(ion\_conformers\_preopt)

gjf\_content = '\n--Link1--\n'.join((neutral\_conformers\_preopt, ion\_conformers\_preopt))

gjf\_content = gjf\_content + '\n' \* 5

del(pattern\_neutral\_cbs, pattern\_ion\_cbs, number\_of\_processors\_per\_node, initial\_chk\_name, neutral\_conformers\_preopt, ion\_conformers\_preopt, cbs, index, item)

with open(filename + '.txt','w') as file:

file.write(gjf\_content)

del(file)

#%% Generating inputs

generate\_input('C:\IP calculation\IP\H\_CO\_CHOH\_CH3\_enol\_tautomer\H\_CO\_CHOH\_CH3\_enol\_conformers\_initial')

**Supplementary References**

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