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Supporting Information

Formation of Paraldehyde ($C_6H_{12}O_3$) in Interstellar Analog Ices of Acetaldehyde Exposed to Ionizing Radiation

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Supporting Information for

Formation of Paraldehyde ($C_6H_{12}O_3$) in Interstellar Analog Ices of Acetaldehyde Exposed to Ionizing Radiation

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Figures S1 to S4

Tables S1 to S8

Supplementary References

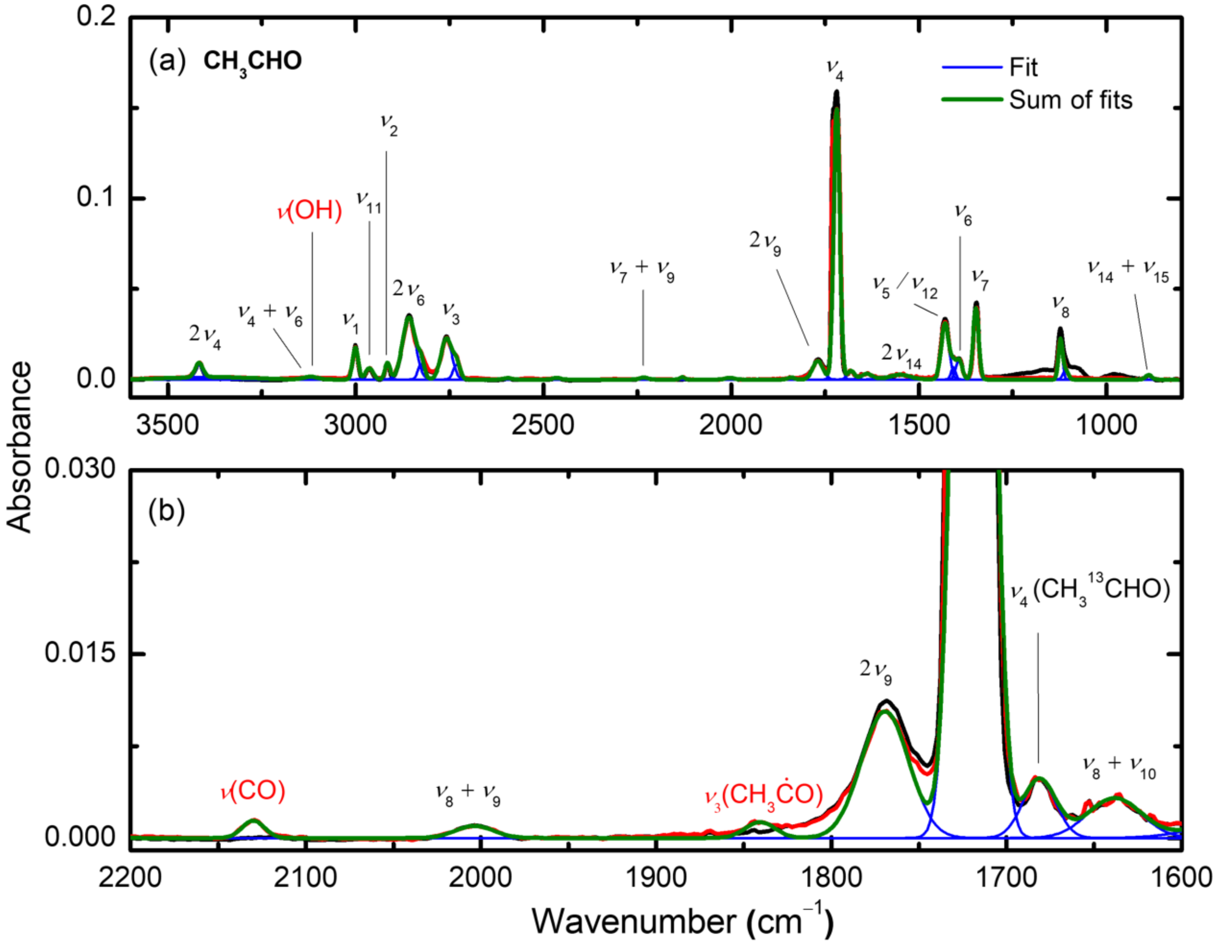


Figure S1. Infrared spectra of (a) CH_3CHO ice before (black) and after (red) irradiation at 5 K with (b) a magnified view and deconvolution (Gaussian) of the region 2200–1600 cm^{-1}. The assignments of the absorptions of CH_3CHO and new absorptions after irradiation are labeled in black and red, respectively. Detailed assignments are compiled in Table S3.

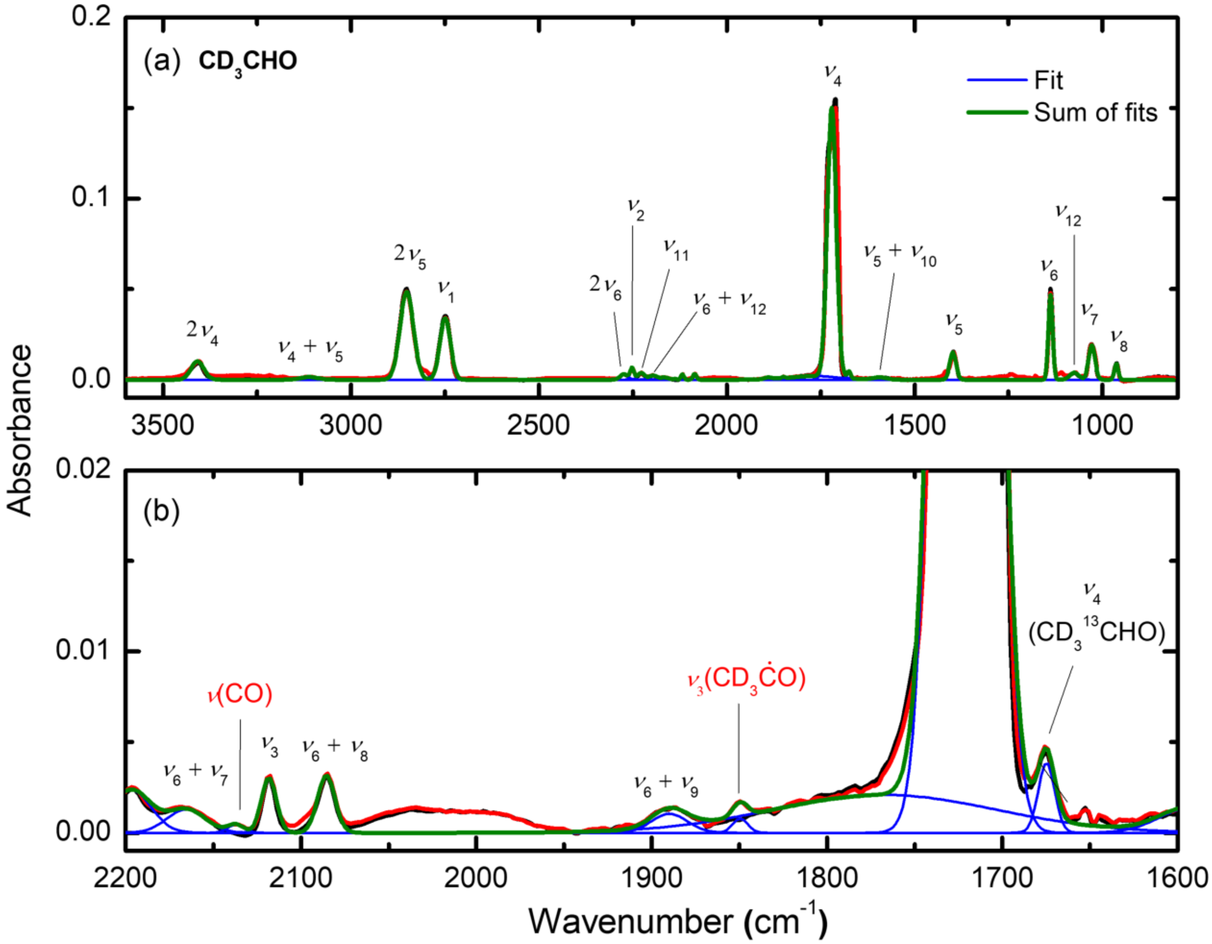


Figure S2. Infrared spectra of (a) CD_3CHO ice before (black) and after (red) irradiation at 5 K with (b) a magnified view and deconvolution (Gaussian) of the region 2200−1600 cm^{-1}. The assignments of the absorptions of CD_3CHO and new absorptions after irradiation are labeled in black and red, respectively. Detailed assignments are compiled in Table S4.

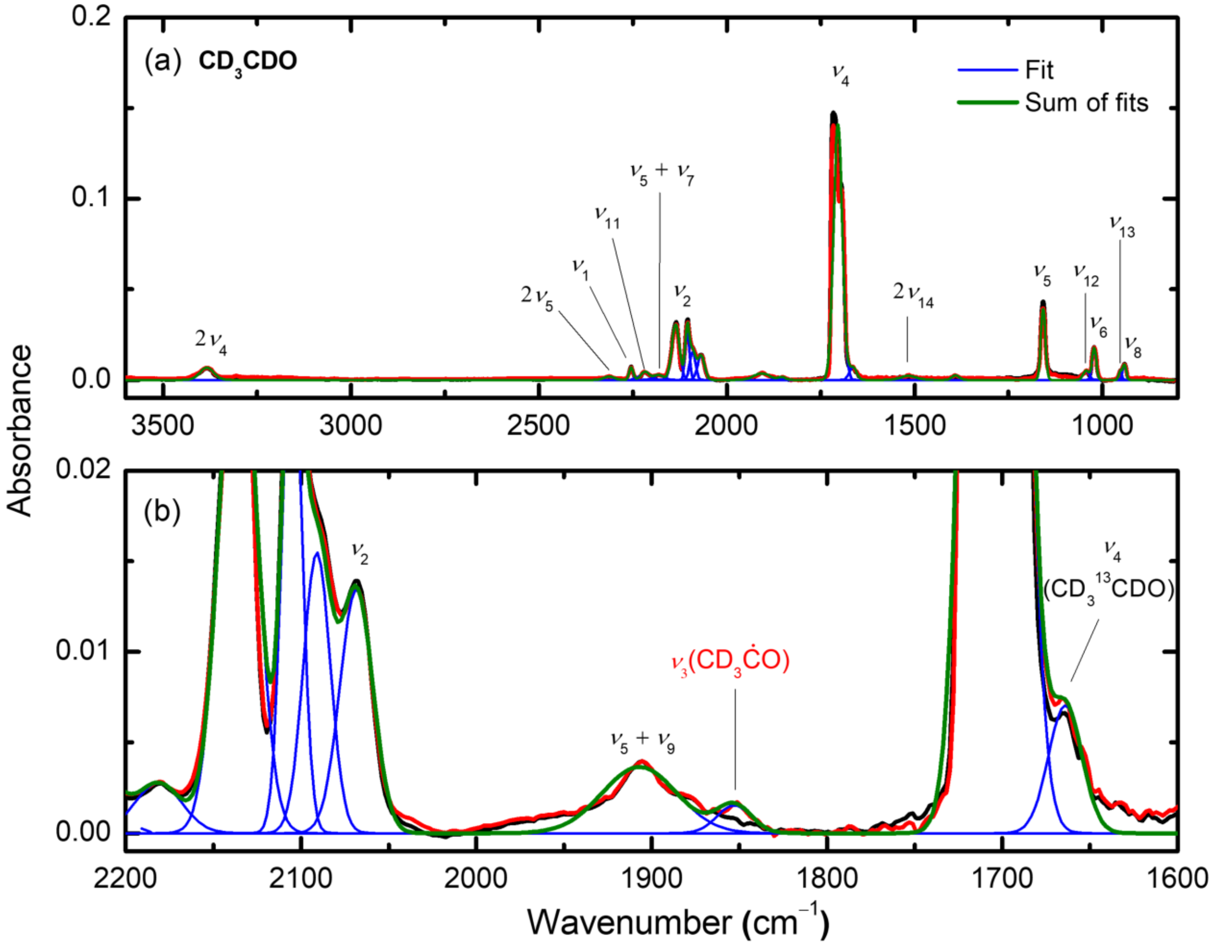


Figure S3. Infrared spectra of (a) CD_3CDO ice before (black) and after (red) irradiation at 5 K with (b) a magnified view and deconvolution (Gaussian) of the region 2200–1600 cm^{-1}. The assignments of the absorptions of CD_3CDO and new absorptions after irradiation are labeled in black and red, respectively. Detailed assignments are compiled in Table S5.

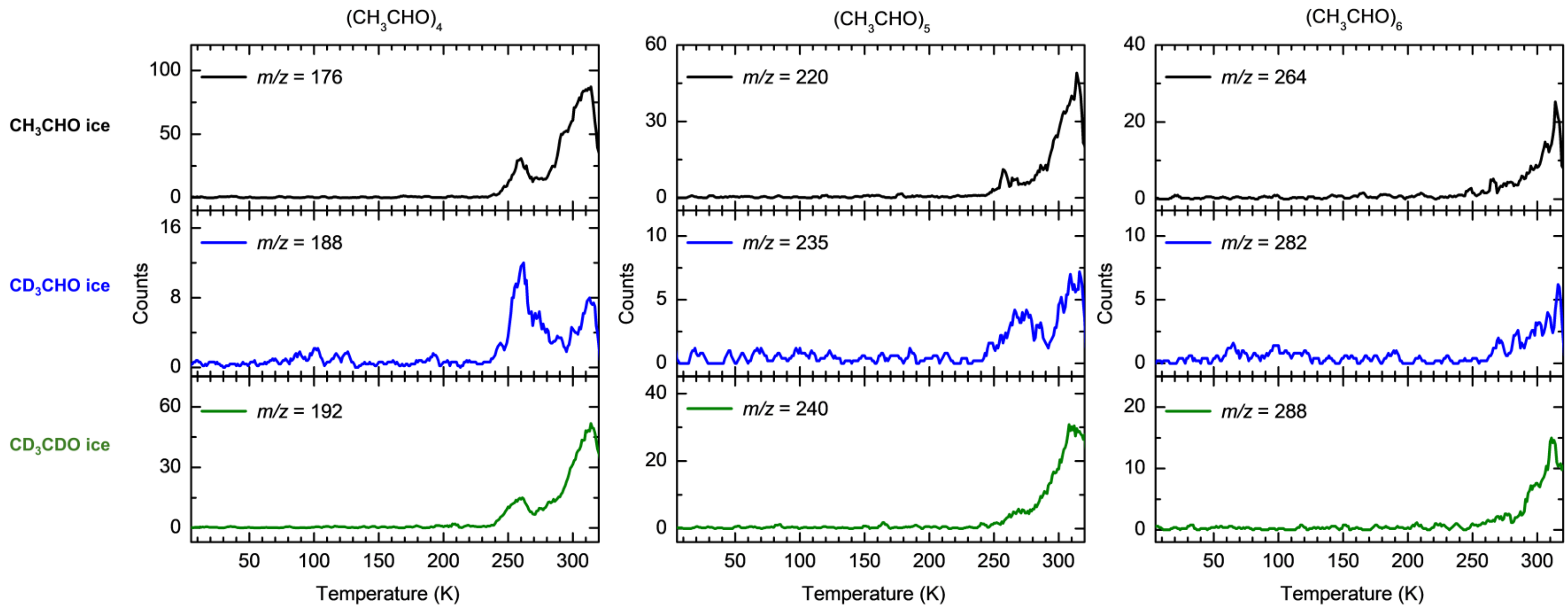


Figure S4. TPD profiles of the irradiated (15 nA, 5 minutes) CH_3CHO ice (black, *m/z* = 176, 220, and 264), CD_3CHO ice (blue, *m/z* = 188, 235, and 282), and CD_3CDO ice (green, *m/z* = 192, 240, and 288) recorded at 10.49 eV, indicating the formula $C_8H_{16}O_4$ (left), $C_{10}H_{20}O_5$ (middle), and $C_{12}H_{24}O_6$ (right).

Table S1. Experimental conditions of acetaldehyde ices including ice thickness, irradiation parameters, and VUV photon energies.

Exp.	Ice	Thickness (nm)	Current (nA)	Irradiation time (s)	Dose (eV acetaldehyde^{-1})	Photon energy (eV)
1	CH_3CHO	550 ± 50	–	–	–	10.49
2	CH_3CHO	490 ± 50	15 ± 2	300 ± 10	0.28 ± 0.06	10.49
3	CD_3CHO	490 ± 50	–	–	–	10.49
4	CD_3CHO	490 ± 50	15 ± 2	300 ± 10	0.30 ± 0.06	10.49
5	CD_3CDO	490 ± 50	–	–	–	10.49
6	CD_3CDO	490 ± 50	15 ± 2	300 ± 10	0.28 ± 0.06	10.49
7[a]	CH_3CHO–CD_3CDO	490 ± 50	15 ± 2	300 ± 10	0.28 ± 0.06 for CH_3CHO / 0.31 ± 0.06 for CD_3CDO	10.49
8	CD_3CHO	490 ± 50	15 ± 2	300 ± 10	0.30 ± 0.06	9.10

[a] The ratio of CH_3CHO to CD_3CDO in the deposited mixture was determined to be (1.1 ± 0.1):1 by comparing the infrared absorptions of the pure CH_3CHO ice and CD_3CDO ice.

Table S2. Vacuum ultraviolet (VUV) light generation parameters.

VUV photon energy (eV)	Nonlinear medium in four-wave mixing	ω_1 laser wavelength (nm)	ω_1 Dye	ω_2 laser wavelength (nm)	ω_2 Dye
10.49 ($3\omega_1$)	Xenon	355	–	–	–
9.10 ($2\omega_1 - \omega_2$)	Xenon	222.566	Coumarin 450	607.379	Rhodamine 610/640

Table S3. Absorption peaks observed in CH_3CHO ice before and after irradiation 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})		
CH_3CHO	Assignment[1,2]	
3418	$2\nu_4$	overtone
3120	$\nu_4 + \nu_6$	combination
3001	ν_1	$\nu_a(CH_3)$
2964	ν_{11}	$\nu(CH_3)$
2916	ν_2	$\nu_s(CH_3)$
2858, 2826	$2\nu_6$	overtone
2758, 2731	ν_3	$\nu(CH)$
2595	$\nu_4 + \nu_9$	combination
2465	$\nu_7 + \nu_8$	combination
2233	$\nu_7 + \nu_9$	combination
2004	$\nu_8 + \nu_9$	combination
1769	$2\nu_9$	overtone
1719	ν_4	$\nu(CO)$
1681	ν_4 ($CH_3{}^{13}CHO$)	$\nu(^{13}CO)$
1638	$\nu_8 + \nu_{10}$	combination
1550	$2\nu_{14}$	overtone
1430	ν_5 / ν_{12}	$\delta(CH_3)$ / $\delta_a(CH_3)$
1408	$\nu_9 + \nu_{10}$	combination
1393	ν_6	$\delta(CH)$
1349	ν_7	$\delta_s(CH_3)$
1123	ν_8	$\gamma(CH_3)$
1109	ν_8 ($^{13}CH_3CHO$)	$\gamma(^{13}CH_3)$
888	$\nu_{14} + \nu_{15}$	combination
773	ν_{14}	$\gamma(CH)$
New absorptions after irradiation (cm^{-1})	Assignment[3-6]	
3386	$\nu(OH)$	
2130	$\nu(CO)$	
1841	$\nu_3(CH_3\dot{C}O)$	

Table S4. Absorption peaks observed in CD_3CHO ice before and after irradiation 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})		
CD_3CHO	Assignment[7,8]	
3408	$2\nu_4$	overtone
3111	$\nu_4 + \nu_5$	combination
2852	$2\nu_5$	overtone
2750	ν_1	ν(CH)
2274	$2\nu_6$	overtone
2252	ν_2	$\nu_a(CD_3)$
2228	ν_{11}	$\nu(CD_3)$
2196	$\nu_6 + \nu_{12}$	combination
2166	$\nu_6 + \nu_7$	combination
2118	ν_3	$\nu_s(CD_3)$
2086	$\nu_6 + \nu_8$	combination
1890	$\nu_6 + \nu_9$	combination
1721	ν_4	ν(CO)
1675	ν_4 ($CD_3{}^{13}CHO$)	$\nu(^{13}CO)$
1593	$\nu_6 + \nu_{10}$	combination
1389	ν_5	δ(CD)
1138	ν_6	ν(CC)
1075	ν_{12}	$\gamma(CD_3)$
1028	ν_7	$\delta_a(CD_3)$
963	ν_8	$\delta_s(CD_3)$
New absorptions after irradiation (cm^{-1})	Assignment[3-5]	
2137	ν(CO)	
1849	$\nu_3(CD_3\dot{C}O)$	

Table S5. Absorption peaks observed in CD_3CDO ice before and after irradiation at 5 K. Vibration mode: stretching (v), bending in plane (δ), and out of plane (γ). Indication: asymmetric (a) and symmetric (s).

Absorptions of pristine ice (cm^{-1})		
CD_3CDO	Assignment[1,8]	
3384	$2v_4$	overtone
2313	$2v_5$	overtone
2254	v_1	$v_a(CD_3)$
2218	v_{11}	$v(CD_3)$
2181	$v_5 + v_7$	combination
2134	v_2	$v_s(CD_3)$
2105, 2068	v_2	$v_s(CD_3)$
1907	$v_5 + v_9$	combination
1704	v_4	$v(CO)$
1664	v_4 ($CD_3{}^{13}CDO$)	$v(^{13}CO)$
1516	$2v_{14}$	overtone
1158	v_5	$v(CC)$
1043	v_{12}	$\delta(CD_3)$
1022	v_6	$\delta_a(CD_3)$
953	v_{13}	$\gamma(CD)$
942	v_8	$\delta_s(CD_3)$
New absorptions after irradiation (cm^{-1})	Assignment[3-5]	
2136	$v(CO)$	
1853	$v_3(CD_3\dot{C}O)$	

Table S6. Error analysis of adiabatic ionization energies (IEs) and relative energies (ΔE) of paraldehyde conformers **2a-2d**. IEs were computed at the CCSD(T)-F12b/cc-pVTZ//B3LYP/aug-cc-pVTZ level of theory including the zero-point vibrational energy (ZPVE) corrections. The IE ranges were corrected for the combined error limits determined to be −0.05/+0.03 eV[9] and the thermal and Stark effect by −0.03 eV. The computed Cartesian coordinates and vibrational frequencies are shown in Table S8.

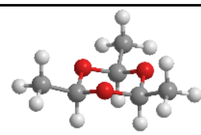
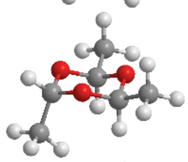
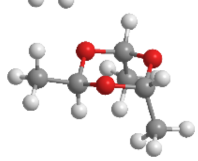
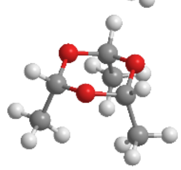
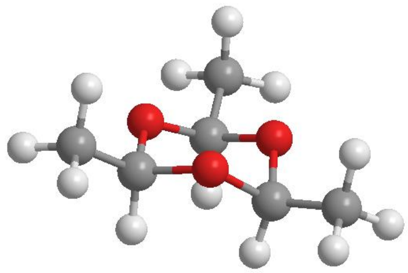
Conformers	Structure	ΔE (kJ mol^{-1})	Computed IE (eV)	IE range after error analysis (eV)	Corrected IE with electric field effect (eV)
2a		0.0	10.00	9.95 – 10.03	9.92 – 10.00
2b		20.5	9.44	9.39 – 9.47	9.36 – 9.44
2c		45.1	9.19	9.14 – 9.22	9.11 – 9.19
2d		77.5	8.86	8.81 – 8.89	8.78 – 8.86

Table S7. Integrated ion signals associated with different isotopologues of paraldehyde (**2**) in $CH_3CHO–CD_3CDO$ ice.

m/z	Assignment	Ion Counts
117	**2** − CH_3	4997 ± 260
118	**2-**d_4 − CD_3	4499 ± 224
121	**2-**d_4 − CH_3	8037 ± 429
122	**2-**d_8 − CD_3	9752 ± 466
125	**2-**d_8 − CH_3	5806 ± 274
126	**2-**d_{12} − CD_3	8545 ± 439
131	**2** − H	590 ± 45
132	**2**	270 ± 27
134	**2-**d_4 − D	382 ± 33
135	**2-**d_4 − H	1002 ± 63
136	**2-**d_4	396 ± 39
138	**2-**d_8 − D	640 ± 48
139	**2-**d_8 − H	698 ± 43
140	**2-**d_8	359 ± 44
142	**2-**d_{12} − D	529 ± 48
144	**2-**d_{12}	215 ± 27

Table S8. Cartesian coordinates (Å) and harmonic frequencies (cm^{-1}) of paraldehyde conformers **2a-2d** and their respective cations computed at the B3LYP/aug-cc-pVTZ level of theory.

Geometries
2a/cation



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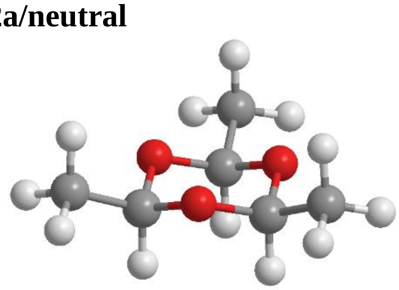
2a/neutral



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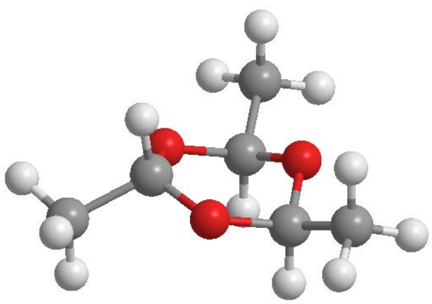
2b/cation



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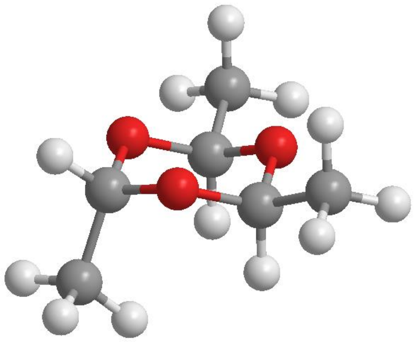

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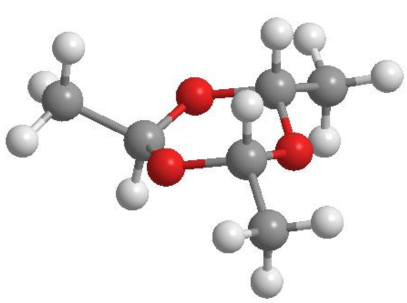
2c/cation



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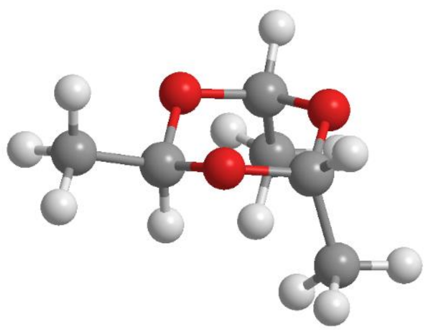
2c/neutral



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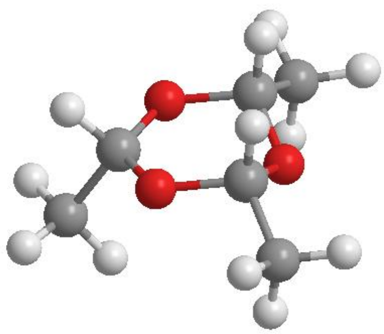
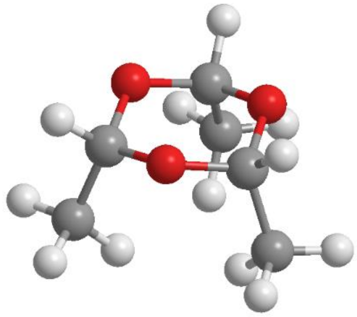
H,0,-2.0680887438,0.6310682927,0.035346058

2d/cation



C,0,0.0155596039,0.0251907384,-0.028401867
O,0,-0.0320877298,0.0657777735,1.434076551
C,0,1.1247727666,0.0670463232,2.1497807648
O,0,2.3192506632,0.0784381595,1.4986673082
C,0,2.352805458,0.037741572,0.0363415827
O,0,1.199262712,-0.5915479492,-0.4262621925
C,0,3.5858487613,-0.7100093935,-0.3907361743
H,0,3.6533885177,-0.677470018,-1.4766175854
H,0,4.4682927063,-0.2364104127,0.0337476944
H,0,3.5324527378,-1.7468199773,-0.0655398522
H,0,2.3768355751,1.0912470235,-0.2676020706
C,0,1.1014294773,-1.1048453179,3.2296349812
H,0,1.1214539183,-2.043257528,2.6821275218
H,0,1.9810977729,-0.9889291038,3.8546390059
H,0,0.1876231721,-0.9985479964,3.8054338668
H,0,1.1018362669,0.970811457,2.8083481077
C,0,-1.1841752695,-0.7353007989,-0.5223752095
H,0,-1.1923735949,-0.7028562647,-1.6103466102
H,0,-1.1377596531,-1.7716914103,-0.1947888878
H,0,-2.0935548892,-0.2712745479,-0.1470227867
H,0,-0.0029822027,1.0786310604,-0.3329512588

2d/neutral



C,0,-0.0452989853,-0.0436875376,-0.0659711205
O,0,0.1456309866,-0.2312713958,1.3257595402
C,0,1.4487789176,-0.0436875298,1.8503297958
O,0,2.075340636,1.1074157214,1.3103985169
C,0,1.9510501082,1.3418552892,-0.0818674168
O,0,0.631131531,1.1074157138,-0.5419407927
C,0,3.0289143525,0.6621458597,-0.9222433362
H,0,2.9196188283,0.9787586077,-1.9594908715
H,0,4.0081903741,0.9787586134,-0.5632914855
H,0,2.985678533,-0.4221731287,-0.8885337604
H,0,2.0775370494,2.4200342939,-0.180485202
C,0,2.3184943553,-1.2975430139,1.8108079555
H,0,2.5454423751,-1.6373404132,0.804915642
H,0,3.2574268446,-1.0915988269,2.3247022925
H,0,1.8031931387,-2.101152454,2.3370098042
H,0,1.2781884667,0.214153226,2.8955899709
C,0,0.2051293566,-1.2975430249,-0.8997891797
H,0,-0.0642692001,-1.0915988443,-1.935697491
H,0,1.2359974472,-1.63734042,-0.8745754409
H,0,-0.4308528714,-2.1011524656,-0.5283725216
H,0,-1.1006022471,0.2141532136,-0.1554415823

Harmonic Frequencies

2a/cation

151.5471	157.9071	186.5078
203.4913	216.2038	219.9357
224.1222	264.6354	395.1871
421.6194	435.1085	499.7569
517.9867	552.7835	635.3076
695.1201	699.2486	743.4903
873.4831	901.7947	940.5660
1040.1022	1045.8464	1063.5026
1113.7207	1119.3833	1133.3498
1144.1698	1168.7636	1213.0408
1288.8092	1316.2883	1346.5686
1379.3959	1398.6722	1415.4692
1422.7002	1429.6105	1450.3716
1475.3236	1477.9620	1478.8370

1480.3121	1482.0586	1486.0564
3013.4401	3016.6831	3054.0134
3057.9273	3057.9696	3077.0507
3124.5071	3131.1203	3131.1484
3144.7642	3146.8715	3146.9128

2a/neutral

161.0969	161.0975	170.2378
206.5185	219.2541	219.2542
266.6112	266.6113	424.3205
469.8187	469.8188	519.6490
575.7429	575.7458	756.4496
838.4964	859.0624	859.0640
889.4401	952.4882	952.4885
1072.3982	1107.3662	1121.0002
1121.0012	1135.4938	1135.4939
1192.9186	1192.9197	1210.4727
1337.9299	1371.8969	1371.8972
1401.5775	1401.5775	1401.8846
1423.9713	1423.9714	1465.0384
1483.0034	1483.0034	1486.0461
1488.6950	1492.3765	1492.3765
2917.5312	2917.5319	2935.4237
3050.3809	3050.3809	3050.7344
3122.4956	3122.8813	3122.8813
3125.3569	3125.3570	3125.5753

2b/cation

58.5289	63.6802	154.7404
222.9080	228.3036	238.0859
247.5045	259.5055	397.8549
426.5650	433.3687	448.9495
582.6943	585.2525	633.7002
738.1397	764.5319	854.8832
886.3711	918.1791	923.0921
986.4561	1015.7853	1043.6244
1062.1422	1074.2891	1116.9803
1124.5249	1127.6178	1157.4887
1191.9254	1232.5326	1309.8622
1331.1625	1342.3740	1380.5939
1395.5006	1416.3531	1421.4853
1461.7629	1473.3251	1479.2844
1480.1377	1481.4143	1484.9291
2668.7332	2979.4146	2993.2406
3060.6597	3060.8240	3064.8395
3140.0930	3140.1012	3145.4752
3145.5605	3163.1296	3176.8100

2b/neutral

140.2045	156.0489	175.1467
207.8190	209.5199	219.2529
265.8208	317.1185	410.8228
447.1265	483.9489	495.0789
569.7939	624.2473	780.1857
799.9277	844.5648	854.2763
899.0404	925.9104	952.3831
1067.4340	1089.3717	1103.4298
1107.1393	1128.4589	1136.2499
1173.3329	1196.8035	1208.3424
1353.9643	1383.2009	1386.6346
1391.9633	1400.0365	1402.4137
1407.6384	1419.8179	1450.6670
1482.4130	1484.0252	1489.4884
1491.4538	1492.4197	1496.4824
2941.1678	2949.3145	3046.0568
3050.3078	3050.5469	3081.4919
3111.5981	3119.6053	3122.7817
3123.0365	3125.7797	3125.9845

2c/cation

58.7169	63.6482	154.5832
222.6130	227.9933	238.3518
247.4979	259.5078	397.8937
426.5500	433.3335	448.9439
582.7104	585.2976	633.7301
737.8405	764.3593	854.8846
886.2804	918.4376	923.0830
986.5406	1015.8217	1043.5052
1062.1357	1074.1731	1116.7892
1124.5339	1127.4740	1157.3649
1191.8789	1232.6489	1309.8240
1331.0758	1342.3386	1380.7026
1395.4142	1416.3049	1421.4334
1461.8340	1473.3722	1479.2550
1480.0980	1481.3865	1484.9104
2667.0280	2979.6823	2993.4695
3060.8096	3060.9737	3064.6484
3140.1752	3140.1837	3145.7131
3145.7985	3162.8756	3176.5422

2c/neutral

128.1337	141.8322	179.9801
200.8609	212.7436	252.9032
283.7365	373.9428	378.7059
418.0404	463.4851	506.9521
604.0878	611.3455	757.7626

806.1598	826.4675	845.1779
900.4837	921.2879	940.1442
1061.6419	1083.5077	1096.0034
1104.3724	1115.7647	1118.6755
1176.6904	1198.8140	1201.3283
1372.1051	1387.1705	1393.6226
1398.1387	1398.3991	1404.5541
1408.7849	1409.7004	1433.5030
1483.0623	1484.3357	1486.1857
1491.6284	1497.5610	1502.5336
2970.8922	3044.8581	3047.3682
3049.9860	3069.2391	3072.3365
3109.0510	3110.1219	3121.4672
3122.5075	3125.6717	3132.6160

2d/cation

50.5726	58.8657	156.0540
219.3410	225.9688	241.7385
264.2470	312.9788	389.7306
410.5649	433.9131	481.0080
506.8863	567.3530	696.7262
723.6540	748.1649	828.7038
882.6132	896.2678	920.3513
976.5067	999.9114	1056.2062
1058.3364	1082.0421	1126.8577
1147.3301	1160.2181	1169.1389
1193.0558	1245.6536	1311.2497
1338.7916	1341.1156	1368.9634
1401.5640	1418.0615	1424.6394
1459.5487	1469.5985	1479.9685
1480.9810	1482.5312	1485.9639
2733.8572	2988.2082	3002.5095
3061.0950	3061.2339	3068.3912
3139.6955	3139.8253	3145.4480
3145.5479	3173.9218	3182.7394

2d/neutral

116.9229	116.9808	178.9103
204.1851	253.8606	255.9481
329.2739	355.3453	355.4097
427.8163	427.8294	547.3258
589.8122	590.1249	728.0816
803.2053	803.4570	834.0471
910.7543	920.7805	920.8068
1059.4776	1086.3908	1096.5667
1096.6680	1104.1919	1104.2462
1178.0980	1204.5114	1204.5411
1386.5602	1397.1083	1397.2544

1405.4393	1405.4770	1409.9085
1411.8058	1414.2600	1414.2990
1473.9598	1485.6133	1485.6344
1501.4790	1501.7961	1503.4428
3045.3688	3045.5221	3048.0849
3057.3317	3057.5449	3062.2695
3105.7482	3106.7731	3107.0420
3137.0934	3137.1496	3156.8959

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